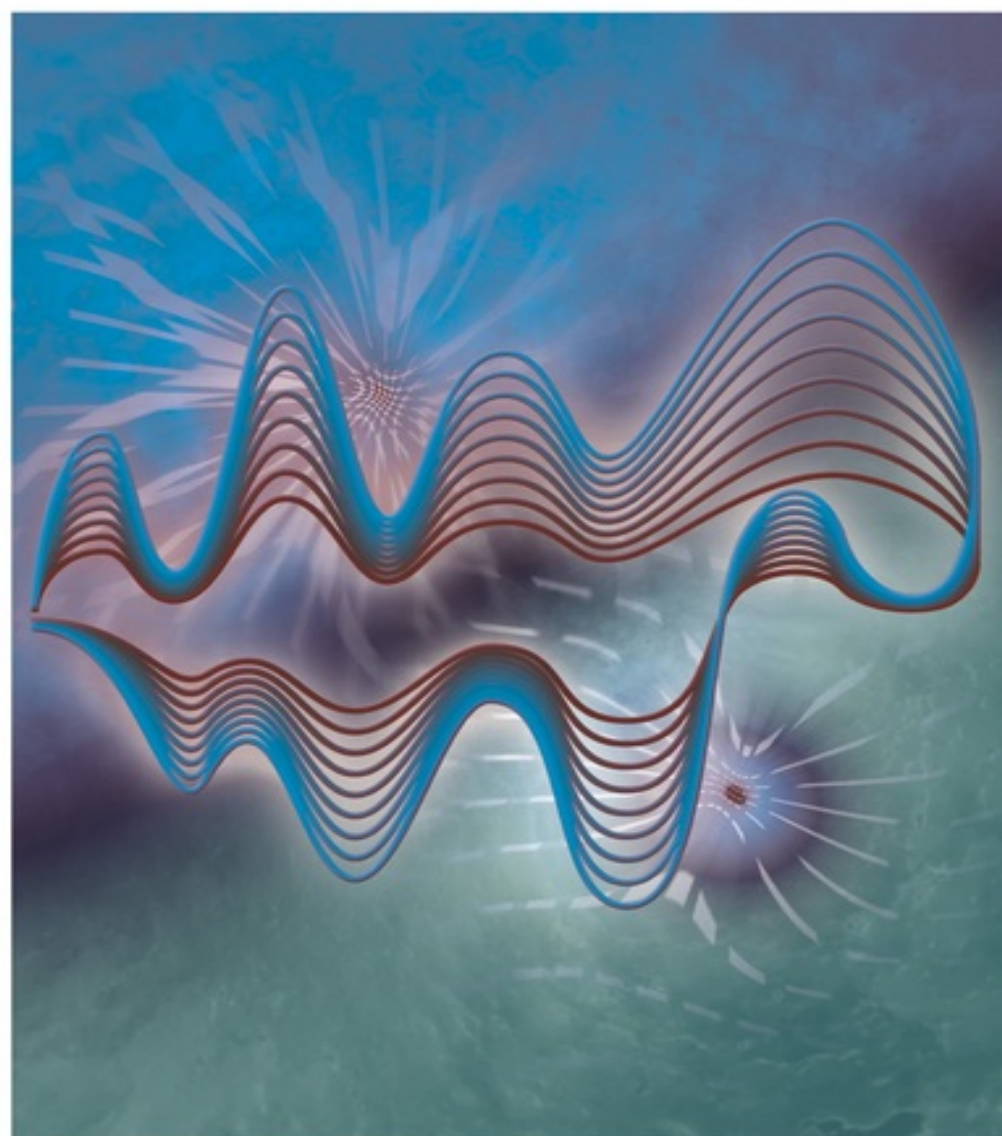


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Electrochemistry of Carbon Electrodes



Volume 16



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Chapter 3: Electrochemistry in One Dimension: Applications of Carbon Nanotubes

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Figure 4.19 (a,b) Scanning electron micrographs, (c) transmission electron micrograph, and (d) electron diffraction pattern of the “3D graphene” catalyst. Panels (e) and (f) show the photovoltaic and voltammetric characterization of the material prepared using three different reaction times.

Chapter 5: The Use of Conducting Diamond in Electrochemistry

Figure 5.1 (a) Room temperature resistivity as a function of boron doping concentration. (Taken with permission from [14]). (b) p-type low-doped BDD at (i) absolute 0 K, no carriers are thermally excited from the valence band to acceptor states; the diamond is an insulator and the Fermi level, E_F , is mid-gap and (ii) nonzero temperature; the number of free carriers in the valence band will depend on the concentration and the ionization energy of the boron acceptors (E_A) and the temperature, yielding an activated electrical resistivity intermediate between that of an insulator and that of a metal; the Fermi level will move downward toward the top of the valence band. (iii) p-type heavily doped BDD ($\sim 10^{20}$ B atoms cm^{-3}), when the impurities are close enough, quantum overlapping of their wave functions results in delocalization leading to metallic behavior at zero temperature with a Fermi level pinned inside the impurity band; the metal–insulator transition takes place. (iv) Very high doping levels $> 10^{20}$ B atoms cm^{-3} ; screening of the impurities modifies the acceptor activation energy and the intrinsic band gap energy will reduce.

Figure 5.2 (a) Schematic showing grain structure of a thick polycrystalline diamond film. Differential boron uptake in different grains indicated by dark and light regions. (b) Processing of sample to remove growth and nucleation surfaces. (c) Resultant sample for investigation. Note the complex interconnection of grains with different dopant densities.

Figure 5.3 Different experimental arrangements used by researchers when working with BDD electrodes. (a) For thin-film BDD still attached to the growth substrate an glass electrochemical cell can be used. (Adapted from Ref. [35].) (i) Cu or Al metal current-collecting plate; (ii) the diamond film electrode; (iii) the Viton O-ring seal; (iv) the input for nitrogen purge gas; (v) carbon rod or Pt counterelectrode; and (vi) reference electrode. (b) Preparation of BDD free-standing electrodes. (Adapted from Ref. [36] with permission.) (i) Laser micro machining is used to cut the required BDD electrode geometry from a BDD free-standing wafer; (ii) here a cylinder is revealed. The electrode is ohmically contacted, sealed in glass, and polished flat to reveal the electrode structure in the left of (iii). Also shown are conventional polymer-sealed Pt, Au, and glassy carbon electrodes. (c) Scanning electron microscopy (SEM) images of a nanoelectrode array. (Adapted from Ref. [37].) (i) Overview of the design with distances of 10 μm between neighboring electrodes with hexagonal order (indicated in red) and (ii) recessed diamond electrode, the insulating diamond layer is clearly visible. (d) Schematic views of a top contacted BDD multiply addressable band electrode device, where the BDD band electrodes lie on insulating silicon oxide.

Figure 5.4 All-diamond coplanar micro- and macroelectrodes. (a) Multiple microelectrode array formed from machining pillar structures in free-standing BDD, overgrowing with insulating diamond, and then polishing flat to reveal a coplanar structure. SEM side on view of cross-sectioned microelectrode array. (Taken from Ref. [50] with permission.) (b) Atomic Force Microscopy (AFM) topography image of one of the electrodes in the array; the location of the BDD microdisk ultramicroelectrode is clearly visible. (Taken from Ref. [28] with permission.) (c) Top: multiple individually addressable microband array electrodes, of width 200 μm , formed by growing BDD into trench structures in insulating diamond. The NDC back contact to each electrode is visible. Bottom: top contacted BDD ring-disk electrode formed using the same procedure. The diameter of the disk electrode is 3 mm.

Figure 5.5 (a) SEM of an as-grown MC BDD electrode. (Taken from Ref. [62] with permission.); (b) Left: SEM of lapped surface of MC BDD; Right: corresponding Raman map of the same area. For both, zones of darker intensity correspond to more heavily boron-doped regions of the surface. (Taken from Ref. [18] with permission.) (c) SEM of thin-film BDD NC and (d) SEM of thin-film BDD UNC.

Figure 5.6 CVs recorded in 0.1 M KNO_3 at a scan rate of 0.1 V s^{-1} for highly doped NDC-free free-standing, microcrystalline BDD (top), NDC-containing free-standing, microcrystalline BDD (second down), glassy carbon (third down), and platinum (bottom). The CVs have been plotted on different scales and vertically offset for clarity.

Figure 5.7 Cyclic voltammetric curves for a lower quality, NDC-containing thin film diamond film electrode in 0.1 M H_2SO_4 before and after acid washing and rehydrogenation. Scan rate, 0.1 V s^{-1} .

Figure 5.8 (a) Raman spectra of the [100] facet of B-doped individual diamond crystals recorded with a single-mode 514.5 nm line of an Ar-ion laser at low power (about 5 mW). “B/C” refers to B/C in the gas phase. (Taken from Ref. [73] with permission.) At low B, a NDC G peak is evident at $\sim 1500 \text{ cm}^{-1}$; as the B concentration increases, the diamond phonon peak becomes more asymmetric and reduces in size. (b) Visible Raman spectrum for a boron-doped NC diamond thin film at laser wavelength = 532 nm and power = 50 mW. Integration time = 5 s.

Figure 5.9 (a) Schematic representation showing the position of the $\text{Ru}(\text{NH}_3)_6^{3+}$ and FcTMA^+ couples with respect to valence (E_{VB}) and conduction (E_{CB}) bands for both O- and H-terminated semiconducting BDD. H-termination (O-termination) is known to induce a negative (positive) electron affinity, with a value of -1.3 eV ($+1.7 \text{ eV}$) measured in vacuum [84]. The presence of water molecules screening the C-H (C-O) surface dipole is expected to reduce the value of the electron affinity (χ) toward less-negative (positive) values. We have chosen a value of approximately $\chi = -1.0 \text{ eV}$ and $\chi = +1.3 \text{ eV}$ for H- and O-terminated surfaces, respectively. In the electrolyte region, the level of the Ag/AgCl reference electrode (E_{ref}) is shown, and all applied voltages are referred to its energy. (b) CVs performed with a 1 mm diameter disk electrode of freestanding polished microcrystalline BDD electrode of dopant density 9.2×10^{16} (black line), 2×10^{18} (red line), mid- 10^{19} (blue line), 1.9×10^{20} (pink line), and 3.2×10^{20} (green line) at a scan rate of 0.1 V s^{-1} for (i) the oxidation of 1 mM FcTMA^+ and (ii) the reduction of 1 mM $\text{Ru}(\text{NH}_3)_6^{3+}$ in 0.1 M KNO_3 . (Taken from Ref. [17] with permission.) The resulting peak-to-peak (ΔE_p) separations are given for the differently doped electrodes in the two different redox mediator solutions.

Figure 5.10 Schematic illustration of (a) outer-sphere and (b) inner-sphere redox process. OHP is the outer Helmholtz plane and IHP is the inner Helmholtz plane.

Figure 5.11 (a) Schematic of the hydrogenated diamond surface in contact with a water layer as it forms in air. (b) Evolution of band bending during the electron transfer process at the interface between diamond and the water layer. VBM = valence band maximum, CBM = conduction band maximum, E_F = Fermi level, μ_c = chemical potential of the liquid phase.

Figure 5.12 (a) Contact angles for H- and O-terminated BDD [102] (b) XPS C1s spectra of semiconducting H-plasma-treated BDD (i) before and (ii) after electrochemical oxidation at 1.5 V for 10 min in 0.1 M KH_2PO_4 [108].

Figure 5.13 CV curves. (a) H-terminated low-doped ($\sim 10^{18}$) BDD electrode in 10 mM $\text{Fe}(\text{CN})_6^{3-/4-}$ with 1 M KCl, scan rate = 25 mV s^{-1} . (b) O-terminated low-doped ($\sim 10^{18}$) BDD electrode in 10 mM $\text{Fe}(\text{CN})_6^{3-/4-}$ with 1 M KCl, scan rate = 25 mV s^{-1} . (c) O-terminated high-doped ($\sim 10^{20}$) BDD electrode in 3 mM $\text{Fe}(\text{CN})_6^{3-/4-}$ with 1 M KCl, scan rate = 20 mV s^{-1} .

Figure 5.14 (a) Schematic illustrating SECM SG-TC mode. The heterogeneously active BDD electrode is biased at a potential to electrolyze the redox couple (Ox to Red or Red to Ox). The tip is biased at a suitable potential to convert the electro-generated species back to its original form at a diffusion-controlled rate. Variations in tip current reflect variations in the underlying ET capabilities of the surface. In feedback, the tip is biased to electrolyze the redox couple and the substrate left unbiased or biased to turn over the electro-generated form of the redox couple at a diffusion limited rate. (b) SECM SG-TC image of polished free-standing MC BDD, $500\mu\text{m} \times 500\mu\text{m}$, for substrate generation of $\text{Ru}(\text{NH}_3)_6^{2+}$ from $\text{Ru}(\text{NH}_3)_6^{3+}$ at a $25\text{-}\mu\text{m}$ -diameter imaging tip. (Taken from Ref. [28] with permission.) (c) SECM feedback image of polished free-standing MC BDD, $100\mu\text{m} \times 100\mu\text{m}$, recorded with a $2\mu\text{m}$ tip electrode biased at a potential to convert $\text{Ru}(\text{NH}_3)_6^{3+}$ to $\text{Ru}(\text{NH}_3)_6^{2+}$. (Taken with permission from Ref. [121].) (d) Scanning Raman image (left) and intermittent contact SG-TC SECM image (right) of the surface of polished free-standing MC BDD, $70\mu\text{m} \times 70\mu\text{m}$, with a $2\mu\text{m}$ tip electrode, biased at a potential to convert FcTMA^{2+} to FcTMA^+ .

Figure 5.15 (a) Boron-doped film with its HPHT substrate before cutting and polishing. (b) Freestanding boron-doped diamond film.

Figure 5.16 SEM and AFM images of different metal NPs deposited under different conditions on BDD. (a) SEM images of flower-like (left) and spherical gold NPs electrodeposited on MC BDD by varying the electrodeposition conditions. (Taken from Ref. [143] with permission.) (b) SEM of citrate-capped gold NPs formed on as-grown BDD by the layer-by-layer assembly procedure. (Taken from Ref. [154] with permission.) (c) SEM of platinum nanoparticles electrodeposited on BDD microelectrodes after two deposition cycles. (Taken from Ref. [149] with permission.) (d) AFM image of nickel hydroxide nanoparticles deposited on free-standing polished MC BDD by electrochemically generating OH^- in the presence of Ni^{2+} .

Figure 5.17 CV responses of 0.1 M phosphate buffer solution pH4 at a scan rate of 50 mV s^{-1} in the absence and presence of 1 mM arsenic(III) at (a) BDD electrode, (b) Ir-wire electrode, and (c) Ir-BDD electrode.

Figure 5.18 (a) Description of the successive diamond surface functionalization steps: first, amination with rf plasma, then aminolysis with 4-pentynoic acid, yne coupling using a thiolated oligonucleotide. (Modified from Ref. [180] with permission.) (b) Illustration of the multistep functionalization of BDD electrodes: first, diazotization, then electroreduction of the diazonium salt for electrografting of phenylazide molecules and finally click cycloaddition between the immobilized phenylazide molecules and ss-DNA (fluorescently labeled).

Chapter 6: Modification of Carbon Electrode Surface

Scheme 6.1 Reductive electrografting of aryl diazonium on a carbon surface.

Figure 6.1 Cyclic voltammograms recorded at a GC electrode without DPPH (left) and

with 1 mM of DPPH (right) in a solution of CH₃CN containing 0.1 M tetrabutylammonium hexafluorophosphate and 1 mM of 4-nitrobenzenediazonium at a scan rate of 50 mV s⁻¹.

Figure 6.2 Mass versus time response of a carbon coated quartz crystal microbalance for the electrochemical grafting of 4-nitrobenzenediazonium (1 mM) at a fixed potential of -0.5 V versus Ag/AgNO₃. Data are fitted using the Langmuir model (solid lines).

Scheme 6.2 Reaction to attach silyl groups at the para position of aryl diazonium.

Scheme 6.3 Modification process to get monolayer surface coverage on carbon using different protecting groups. TMS, TES, TIPS, and TBAF represent trimethylsilyl, triethylsilyl, tri(isopropyl)silyl, and tetrabutylammonium fluoride, respectively.

Figure 6.3 Comparison of bias stability of molecular junctions with Cu and e-C as top contacts. Cu junction breaks down at approximately -1.86 V, due to electrochemical oxidation of Cu, while e-C is stable up to a bias of 3.5 V.

Scheme 6.4 Oxidative electrografting of amine on carbon surface.

Figure 6.4 CVs obtained at GC in a solution of ethanol containing 0.1 M LiClO₄ and 1 mM (a) butylamine, (b) N-methylbutylamine, (c) N-ethylbutylamine, (d) N,N-dimethylbutylamine, and (e) triethylamine. The scan rate was 10 mV s⁻¹.

Figure 6.5 XPS spectra in the N(1 s) region for GC electrode modified by cycling the potential once between 0.0 and 1.4 V versus Ag/AgCl in ethanolic solutions of 1 mM (a) butylamine, (b) N-methylbutylamine, (c) N-ethylbutylamine, and (d) N,N-dimethylbutylamine. Scan rate was 10 mV s⁻¹

Figure 6.6 CVs measured at GC (a,c) and pyrolyzed photoresist films (b,d). (a,b) First scan (—) and second scan (- - -) (0.2 V s⁻¹) with stirring between scans in a solution of 5.2 mM 1-naphthylmethylcarboxylate and 0.1 M tetrabutylammonium tetrafluoroborate in acetonitrile. (c,d) Scans of 3.1 mM [Fe(CN)₆]^{3-/4-} in aqueous 0.2 M KCl at bare (- - -) and 1-naphthylmethylcarboxylate modified (—) surfaces.

Scheme 6.5 Mechanism of grafting by using a redox mediator.

Scheme 6.6 Oxidative electrografting of alcohol on carbon surface.

Scheme 6.7 Various surface construction strategies on iodinated PPF. Firstly, PPF surface is iodinated by exposing it to iodine plasma. Iodinated surface can then be reacted with different alkene and alkyne compounds in the presence of appropriate light (A, B, and C). Further surface modification can then be achieved via “click” reaction (B) or attachment of nanoparticle (C).

Scheme 6.8 Modification of graphene with (a) monoaryldiazonium salt, (b) biaryldiazonium salt, and (c) bipylene-terminated molecular wire.

Scheme 6.9 Reversible interaction of charged pyrene derivatives on graphite surface.

[Scheme 6.10 Water contact angle \(a\) and water absorption \(b\) images of untreated and CTAB-treated carbon felts.](#)

[Scheme 6.11 Electrodeposition of MWCNTs using CTAB surfactant. \(a\), \(b\) and \(c\) show the possible arrangements of CTAB on MWCNTs.](#)

Chapter 7: Carbon Materials in Low-Temperature Polymer Electrolyte Membrane Fuel Cells

[Figure 7.1 Schematic illustration to categorize the most prominent carbon materials.](#)

[Figure 7.2 The three characteristics of carbon black determining its rich properties: particle size, aggregate structure, and surface chemistry.](#)

[Figure 7.3 Templating strategy for obtaining CMK-3 carbon from SBA-15 silica \[10\].](#)

[Figure 7.4 Images of the most prominent carbonaceous support materials: \(a\) graphite and \(b\) Vulcan carbon. \(Taken from Ref. \[14\]. Copyright \(2014\), with permission from Elsevier Limited\).](#)

[Figure 7.5 Comparison of Raman spectra of different carbon materials \[16\].](#)

[Figure 7.6 C K-edge NEXAFS spectra of different carbon materials \(J. Melke, unpublished results\).](#)

[Figure 7.7 Schematic illustration of the three-phase boundary in fuel cell electrodes.](#)

[Figure 7.8 False-color image of an ultrathin section of a fuel cell electrode; the inset shows a typical carbon agglomerate.](#)

[Figure 7.9 \(a\) Current-voltage characteristics of the three morphologically different support materials with the long fibers displaying the highest power output. \(b\) The chord length distributions for the long and short fibers are compared.](#)

[Figure 7.10 Comparison of 3D-reconstructed volumes of \(a\) an airbrushed electrode and \(b\) an LbL-prepared electrode \(b\). \[131\] \(](#)

[Figure 7.11 Electron micrographs of a cross section of a multilayer electrode composed of bilayers of Pt on Sb-doped tin oxide and multiwalled carbon nanotubes in different magnifications \[147\].](#)

[Figure 7.12 Electrospun and carbonized PAN fibers decorated with Pt \(a; bright spots attributed to Pt particles\) and an overview of the final freestanding porous electrode structure \(b\).](#)

[Figure 7.13 \(a\) Schematic illustration of a Pickering emulsion and \(b\) SEM picture of the respective Pt/SnO₂ shell around a polyaniline \(PANI\) core sample.](#)

[Figure 7.14 \(a\) Cross section through a catalytic layer formed by “self-assembly” of the Pickering emulsion and \(b\) the corresponding fuel cell polarization curve.](#)

Chapter 8: Electrochemical Capacitors Based on Carbon Electrodes in Aqueous

Electrolytes

[Figure 8.1 Schematic representation of the charged state of a symmetric electrical double-layer capacitor using porous electrodes and its simplified equivalent circuit.](#)

[Figure 8.2 Ragone plot of various electrochemical energy storage systems.](#)

[Figure 8.3 Gravimetric capacitance versus \(a\) BET and \(b\) DFT specific surface area.](#)

[Figure 8.4 Molar proportions of \$\text{TEA}^+\$ and \$\text{BF}_4^-\$ calculated from the NMR spectra, and relative amount of AN versus the total amount of electrolyte species, after polarization at various cell potentials for 30 min in the \(a\) positive and \(b\) negative electrodes of AC/AC electrochemical capacitor.](#)

[Figure 8.5 Volumetric capacitance of microporous carbons in \$\text{TEABF}_4/\text{AN}\$ electrolyte vs average width \(\$L_0\$ \) of pores accessible to \$\text{CCl}_4\$ \[57\].](#)

[Figure 8.6 Nitrogen adsorption/desorption isotherms obtained at 77 K \(a\) and quenched solid density functional theory \(QSDFT\) pore size distribution \(b\) of AC, AC-PTFE, and AC-PVDF electrodes. For the electrodes, the amount of nitrogen adsorbed is referred to the mass of AC \[60\].](#)

[Figure 8.7 Ragone plots of AC/AC capacitors in \$1 \text{ mol l}^{-1} \text{Li}_2\text{SO}_4\$ and \$6 \text{ mol l}^{-1} \text{KOH}\$ aqueous solutions with cell operating potential windows 0–1.6 and 0–1.0 V, respectively. Values calculated for the total mass of active materials.](#)

[Figure 8.8 Three-electrode cyclic voltammograms \(\$2 \text{ mV s}^{-1}\$ \) showing the potential stability window of AC in \$6 \text{ mol l}^{-1} \text{KOH}\$, \$1 \text{ mol l}^{-1} \text{H}_2\text{SO}_4\$, and \$0.5 \text{ mol l}^{-1} \text{Na}_2\text{SO}_4\$ \[17\].](#)

[Figure 8.9 Three-electrode cyclic voltammograms of AC in \$2 \text{ mol l}^{-1} \text{Li}_2\text{SO}_4\$. The various loops are obtained by stepwise shifting of the negative potential limit. The vertical dashed line at \$-0.35 \text{ V}\$ versus NHE corresponds to the thermodynamic potential for water reduction.](#)

[Figure 8.10 Variation of pH value after cathodic charging \(\$-500 \text{ mA g}^{-1}\$ for 12 h\) of AC electrodes in \$0.5 \text{ mol l}^{-1} \text{Na}_2\text{SO}_4\$ solutions where the initial pH was adjusted by addition of \$1 \text{ mol l}^{-1} \text{H}_2\text{SO}_4\$ or \$1 \text{ mol l}^{-1} \text{NaOH}\$.](#)

[Figure 8.11 Scheme of the accelerated aging protocol \(a\) and magnification of the fifth galvanostatic cycle \(b\). The fifth discharge cycle of each series is considered to estimate the capacitance and ESR values.](#)

[Figure 8.12 Effect of floating cell potential at \$24^\circ\text{C}\$ on the \(a\) relative capacitance and \(b\) relative resistance of an AC/AC capacitor in \$1 \text{ mol l}^{-1} \text{Li}_2\text{SO}_4\$ \[98\].](#)

[Figure 8.13 Pore size distribution \(PSD\) of a fresh electrode \(full dark gray line\) and of aged positive \(dashed light grey line\) and negative \(dotted light grey line\) electrodes](#)

after 120 h of floating at 1.7 V in 1 mol l⁻¹ Li₂SO₄. The Quenched Solid Density Functional Theory (QSDFT) was used to determine the PSD [98].

Figure 8.14 TPD on pristine ACC (full dark grey line) and on aged positive (dashed light grey line) and negative (dotted light grey line) carbon electrodes after 120 h of floating at 1.7 V in 1 mol l⁻¹ Li₂SO₄: (a) mass loss and CO₂ evolution; (b) mass loss and CO evolution; (c) deconvolution of CO₂; and (d) CO patterns (full light grey line: TPD experimental data; dashed lines: individual peaks; thick dashed line: sum of the individual peaks).

Figure 8.15 Nyquist plots of AC/AC capacitors at 0 V before and after floating at 1.6 V for 120 h in (a) 1 mol l⁻¹ Li₂SO₄ and (b) 1 mol l⁻¹ Li₂SO₄ + 0.1 mol l⁻¹ Na₂MoO₄ [106].

Figure 8.16 Voltammetry characteristics of an AC/AC cell in 1 mol l⁻¹ KI solution: (a) AC/AC cell with SCE reference at 5 mV s⁻¹; (b) two-electrode system at 1, 10, and 100 mV s⁻¹ potential scan rate.

Figure 8.17 Cyclic voltammograms (at 1 mV s⁻¹) of two-electrode cells operating with activated carbons AAC 1 or AAC 2 in iodide/vanadium conjugated redox couples as electrolyte solutions [112].

Chapter 10: Carbon Electrodes in Molecular Electronics

Figure 10.1 Generalized schematic of a generic molecular junction, consisting of a molecule (can be one or many) placed between two conductors (examples for each contact are for illustrative purposes). As shown, a wide variety of materials can be used, and the choice of molecules and contacts can impact the specific electronic interactions at the interface – chemisorption (C–C, Si–SiOx) or physisorption (π–π, S–Au, etc.), which can exert a controlling influence on junction behavior. Upon application of voltage across the junction, current flows across the molecular layer. However, the system should be treated as whole, as the thickness and electronic properties of the molecule are not the only factors that will dictate conductivity.

Figure 10.2 Scheme showing chemically modified electrodes that are used to study various electrochemical processes, including electron transfer rates across molecules.

Figure 10.3 Various structures of molecular junctions commonly used in molecular electronics: (a) Cross junction formed by perpendicularly oriented bottom and top contacts with a molecular layer sandwiched between the conductors. Typical junction sizes range from several square microns to a square millimeter. (b) An all-carbon molecular junction formed using pyrolyzed photoresist film (PPF) (on SiO₂ support) as a bottom contact, an evaporated carbon (eC) top contact, and a molecular layer consisting of a multilayer of biphenyl grafted using diazonium chemistry. (c) Molecular junction made by contacting a thiols-based self-assembled molecular layer on Ag with a liquid–metal (in this case, a eutectic alloy of Ga and In). ((c) Reproduced from Ref.

[36].) (d) A mechanically controlled break junction formed using *retractable* electrodes controlled with an STM, where molecules in solution bridge the gap to result in a junction [37]. (e) Other experimental geometries for studying electronic properties of single carbon nanotubes or a graphene nanoribbon can be made through forming contacts with lithographic methods.

Figure 10.4 Fabrication and measurements of molecular junction formed on PPF using diazonium chemistry. (a) Cyclic voltammogram measured at a PPF electrode featuring an irreversible reduction peak at approximately -0.8 V that corresponds to the reduction of diazonium ions with subsequent formation of a C–C with PPF. Growth of the molecular layer results in the increased blocking of electron transfer from the electrode and gradual decrease of the peak intensity (see also Chapter 6 on carbon electrode modification). (b) AFM image of the molecular layer obtained in (a), showing that film is homogeneous, and that the thickness can be measured using AFM. (c) Overlay of the current density–voltage characteristics (semilogarithmic scale) of eight junctions showing good reproducibility. (d) Raman spectra (measured with a 514 nm probe through an optically transparent quartz/PPF substrate made by diluting the photoresist) of a Q/PPF/NAB/Cu junction with and without a Cu top contact showing no changes in the structure of a nitroazobenzene molecular layer. (c) (Reprinted with permission from Ref. [72]. Copyright (2010) American Chemical Society). (d)

Figure 10.5 Bias and temperature stability of all-carbon MJs: (a) Comparison of Cu and e-C as top contacts, showing that the use of Cu leads to breakdown at approximately -1.86 V (due to electrochemical reactions of Cu), while e-C shows stability to ± 3.5 V (with current densities up to ~ 1500 A cm $^{-2}$), junction area: $15\mu\text{m} \times 15\mu\text{m} = 225\mu\text{m}^2$). (b) Overlay of J – V curves for PPF/NAB(4.1)/Au and PPF/NAB(4.1)/eC(10)/Au junctions showing that 10 nm of e-C prevents penetration of Au. (c) J – V curves of PPF/NAB(4.5)/e-C junction after heating in vacuum ($2-4 \times 10^{-6}$ Torr) for 30 min at each temperature. (d) J – V curves of a PPF/NAB(4.5)/e-C junction before and after 1.2×10^9 cycles at 100 °C in lab ambient (air) over the course of ~ 68 h. (Adapted with permission from Ref. [82].) (e) J – V curves of a PPF/BrP(3)/e-C/Au junction before and after the application of ± 0.8 V DC bias for 1–4 h at room temperature. Insets display the same data plotted in a semilog scale.

Figure 10.6 (a,b) Electronic band structure of graphene showing valence and conduction bands touching at the Dirac points and having a linear dispersion relation around the Fermi level. Comparison of (c) zero-band gap graphene, (e) band gap-opened graphene, and (d) a semiconductor, suggesting the possible use of zero-band gap graphene as a conductor for MJs and with a band gap as a molecular layer.

Figure 10.7 Reversible switching of conductance in a junction consisting of graphene functionalized with spiropyran. Spiropyran, a photochromic switch attached to G noncovalently, is able to change states between the ring closed (small dipole moment) and ring open (larger dipole moment) upon irradiation with UV and visible light. (a) Changes in the electronic configuration of spiropyran are translated into changes of the

position of Dirac point of graphene (b), resulting in changes in the applied gate voltage (c) and conductance (d).

Figure 10.8 Graphene functioning as top and bottom electrodes for MJs. (a) Similarly to eC, the presence of graphene between molecular layer and Au top contact protects the junction from short circuits between electrodes. (Reproduced from Ref. [106].) (b) Using diazonium chemistry, an azobenzene layer was grown covalently on a graphene bottom contact, while a top graphene electrode was contacted physically. The mechanical and optical properties of graphene electrodes allowed testing of electronic properties under mechanical stress, and (c) photochemical switching of azobenzene between cis- and trans-isomers induced by multicycle switching (d) of the conductance of the junction, which was reversible (e).

Figure 10.9 Formation of a carbon nanotube by rolling up a graphene sheet. Depending on the chiral vector along which the nanotube is rolled, zigzag, armchair, and other chiral options are possible resulting in metallic or semiconducting CNTs.

Figure 10.10 Construction of FETs with individual (a and b) and collective (c) nanotubes. (a) AFM image of an FET composed of gold source and drain electrodes and an individual carbon nanotube as a channel. A heavily doped wafer served as a back gate electrode. Alternatively, an individual top gate electrode made of Ti can be employed (b). (a,b) (Reprinted with permission from Ref. [132], Copyright (2002) American Chemical Society.) (c) FET composed of an array of CNTs, with an individual gate Ti/Au electrode, separated with an $\text{Al}_2\text{O}_3/\text{SiO}_2$ insulating layer and Ti/Pd source and drain electrodes.

Figure 10.11 (a) A gap in a nanotube is created using an oxygen plasma to yield a space of few nanometers, which is suitable for the formation of a molecular junction. The ends of carbon nanotubes terminated with carboxylic groups and serving as a point of contact for further functionalization. (b) Oligoaniline placed between CNT contacts allows (c) reversible switching of the conductance in the junction by changes in the pH due to protonation/deprotonation.

Figure 10.12 A generic energy level diagram of a molecular junction showing the Fermi level of the contacts offset from molecular HOMO and LUMO levels to define interfacial barriers (here, a barrier to hole transport mediated by the HOMO is shown, (ϕ)). Filled states in the conductors are shaded. A parallel situation can be drawn for electron tunneling (using the LUMO).

Figure 10.13 (a) Attenuation plot for an electrochemical experiment shown in (c). Here, the $\ln$ of the electrochemical rate constant is plotted against thickness to yield a slope of $0.22 \text{ \AA}^{-1}$ (or 2.2 nm^{-1}). (b) Attention plot for a series of aromatic molecules and an aliphatic species by molecular junctions of different thickness of each (a corresponding diagram of the molecular junction is illustrated in (d)). See original text for structures and abbreviations. Here, the aromatic molecules give similar behavior due to the interactions between the molecular layers and the substrate, as discussed in

the text. (a) (Reprinted with permission from Ref. [166]. Copyright (1999) American Chemical Society.) (b), (d)

Chapter 11: Carbon Paste Electrodes

Figure 11.1 Typical microstructures of two related graphite powders and four different carbon paste mixtures made of these carbons. Abbreviations and symbols used: C_{spe} , spectroscopic (or spectral) graphite; C_{nat} , refined natural graphite; SO, silicone oil; TCP, tricresyl phosphate; and IL, ionic liquid (BMImPF6); the individual carbon pastes denoted accordingly above the respective images (a–f). Experimental conditions: scanning electron microscopy, magnification: 1 : 1000 (a–e); scale: the actual size of photos corresponds really to (25 μm $\times$ 35 μm), 1 : 500 (f; $s = 50 \mu\text{m}$). Hitherto unpublished photos from authors' archives, except “(e)” being the alternate view of an image published in [37]. For other specification and details, see [35, 37, 58, 60].

Figure 11.2 Typical microstructures of two new forms of carbon and four carbon paste mixtures, made of traditional oil binders and ionic liquid. Abbreviations and symbols used: C_{spe} , spectroscopic graphite powder; GC, glassy carbon powder (“Sigradur®”); CNTs, carbon nanotubes (“SW-” type); MO, mineral oil; SO, silicone oil (highly viscous type); and IL, ionic liquid (BMImPF6); the individual carbon paste mixtures denoted accordingly above the respective images (a–f). Experimental conditions: scanning electron microscopy, magnification: 1 : 1000, scale as in Figure 11.1. Hitherto unpublished photos from authors' archives, except “(a)” being the alternate view of an image published in [37]. For other specification and details, see [35, 37, 58–60].

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Series Editors Preface

The series *Advances in Electrochemistry and Electrochemical Engineering* was initiated in 1961 by Paul Delahay and Charles Tobias with the purpose to make available authoritative reviews in the area of electrochemical phenomena, and to bridge the gap between electrochemistry as a part of physical chemistry and electrochemical engineering. In 1976, Heinz Gerischer took up the coeditorial role upon the resignation of Paul Delahay. Their efforts led in 1987 to the transfer of the series publication to VCH with a new title: *Advances in Electrochemical Science and Engineering*. Upon the passing of Gerischer and Tobias in the mid-1990s, their editorial tasks were taken up by Richard Alkire and Dieter Kolb. In 2006, the series was merged with the series “Frontiers in Electrochemistry,” established in 1992 by Jacek Lipkowski and Philip Ross. The merged series continued with the legacy title: *Advances in Electrochemical Science and Engineering*. Following the resignation of Philip Ross 2010, and the passing of Dieter Kolb in 2011, the addition of Philip Bartlett as coeditor in 2015 brings the series to its present configuration.

The favorable reception of these volumes and the steady increase of interest in electrochemical science and engineering provide good reasons for the continuation of these editions. We expect to maintain the high standards set in the past and plan no departure from the purpose stated in Introduction to the Series in 1991.

Urbana, IL, USA

June, 2015

Richard C. Alkire
Philip N. Bartlett
Jacek Lipkowski

Preface

Carbon electrodes have been, and continue to be, widely used in electrochemistry across a wide range of applications from energy conversion to electroanalysis, and over a wide range of electrode sizes from micron and submicron scale to electrodes with areas of square meters. Carbon comes in many conducting forms, and electrochemists have been quick to explore the properties and possibilities of these different forms to make electrodes and to exploit the various properties of these different carbon electrode materials. Over recent years, the more traditional forms of carbon – graphite, carbon black, glassy carbon, screen-printed carbon – have been added to by new forms of carbon with new properties – carbon nanotubes, both single wall and multiwall; graphene; boron-doped diamond. The purpose of this volume is to bring together up-to-date accounts of recent developments in the electrochemistry of carbon electrodes of different types, and for different applications.

The chapters cover the fundamental properties of the different carbon materials, their fabrication into electrodes, and their applications across a wide range of areas. Each chapter provides sufficient background material so that it can be of use to nonspecialists and specialists alike. Thus, this volume should be of interest to students and researchers working in many diverse fields of electrochemistry whether they already make frequent use of carbon electrodes in one form or another or whether they are looking for electrodes for new applications.

March 2015

Southampton, UK

Phil Bartlett

Chapter 1

Properties of Carbon: An Overview

Shengxi Huang, Johan Ek Weis, Sara Costa, Martin Kalbac and Mildred S. Dresselhaus

1.1 Overview of Properties

Carbon (element No. 6 in the periodic table) forms a variety of materials, including graphite, diamond, carbon fibers, charcoal, as well as newly discovered nanocarbon materials, such as fullerene, graphene, carbon nanotube, and graphene nanoribbon (GNR). Even though all are composed of the same atoms, different carbon materials can show very different physical and chemical properties, including electrical transport, optical and thermal properties, and chemical reactivity, depending on their structures.

Electrochemistry has been connected to carbon materials since the early days of electrochemistry research [1], and the discoveries of new carbon materials in the past decades have been accompanied by research advances concerning the doping of these materials using electrochemical techniques, with an emphasis on materials preparation, characterization, and applications.

Among the electrochemical techniques and characterization tools, vibrational and optical spectroscopies have been important. Electrochemical charge transfer, an important process in electrochemistry, influences not only the electronic structure of the materials but also their vibrational and optical properties, which are all dependent on the concentration of electrons and holes found in the solid. Therefore, valuable data can be obtained when electrochemistry and *in situ* Raman spectroscopy are applied simultaneously under the heading of spectroelectrochemistry. Such investigations have been carried out extensively on carbon nanomaterials in order to investigate the effects of electron and hole doping.

One advantage of electrochemistry over other experimental techniques is its ability to introduce higher levels of dopants and to make quantitative, reproducible measurements [2, 3]. The electrochemical setup including the choice of the particular electrolyte is an important factor that influences the doping efficiency in spectroelectrochemical experiments. Different electrolytes can thereby require larger electrode potentials than others to achieve the same doping levels, so that attention needs to be given to the choice of the electrolyte for studying a given material system. Failures to pay attention to such issues have, in the past, led to apparent inconsistencies between different sets of published data.

The basic carbon material introduced in this chapter is graphene, which is a single layer of crystalline graphite, because it is the basic building block behind sp^2 carbon materials. Graphite, which represents nature's way to build up stacks of graphene layers into a bulk crystal, is then introduced briefly, together with the synthetic commercial product, highly oriented pyrolytic graphite (HOPG), which closely resembles graphite. Another commonly

used nanocarbon material, carbon nanotube, is also discussed, which has deep scientific interest, and is also interesting along with its related carbon fiber analog for electrochemical commercial applications. Porous carbon is an sp^2 carbon material useful for applications requiring a huge surface area, and is also discussed briefly. Diamond, which is commonly a symbol of societal wealth and prestige, is gaining more and more scientific attention recently due to its extraordinary properties in electrochemistry, quantum physics, and biology, and has promising applications in all of these fields. Finally, brief mention is made of other sp^2 nanocarbon materials with significant current scientific interest, carbon nanoribbons and porous carbon, and these materials may someday find interest for electrochemical science and applications.

In this chapter, we will introduce some typical carbon materials that are widely studied in electrochemistry. Their properties, not restricted to their electrochemical properties, will be briefly described. Some characterization techniques, including spectroelectrochemistry, will be described when applied to selected carbon materials. A brief overview of the application of various carbon materials to electrochemistry will be included in this chapter, which will be concluded by an outlook to the future.

1.2 Different Forms of Carbon

1.2.1 Graphene

1.2.1.1 Optical Properties

It is widely established that graphene has numerous fascinating properties [4–9]. Though considered as a semimetal, graphene has unique electromagnetic/plasmonic effects compared to conventional noble metals [10, 11]. First, its plasma frequency in the long-wavelength limit is expressed as [12–15]

$$\omega_{p,G} = \sqrt{\frac{8E_F\sigma_{\text{uni}}q}{\hbar\epsilon}},$$

where E_F is the Fermi energy of graphene, σ_{uni} is the universal optical conductivity of graphene and is independent of any material parameters: $\sigma_{\text{uni}} = \pi e^2/(2h)$ [16, 17], q is the unit charge, and ϵ is the permittivity. Note that the expression of plasma frequency for graphene is very different from that for metals which is [18]

$$\omega_{p,M} = \sqrt{\frac{2\pi ne^2q}{\epsilon m}},$$

where n is the carrier density in graphene and m is the carrier effective mass. We can see that $\omega_{p,G} \propto E_F^{1/2} \propto n^{1/4}$ and $\omega_{p,M} \propto n^{1/2}$. Such a difference in the plasma frequencies between graphene and metals is due to the Dirac fermions in graphene, rather than to ordinary Schrödinger fermions in normal metals. The plasma frequency of graphene is in the terahertz range, which is 10^3 times lower than ω_p in metals, and which can be tuned through gating or doping [11, 19,

20], or by fabricating graphene ribbons with micron widths (see [Figure 1.1](#)), where ω_p is in the terahertz range. Here, ω_p differs with the ribbon widths and with the Fermi energy E_F , as shown in [Figure 1.1](#). Second, single-layer graphene has a linear dispersion relation and a uniform 2.293% light absorption across a wide frequency range [11, 21–23], resulting from its Dirac-cone band structure and linear energy–momentum relation $E(k)$, as seen in [Figure 1.2](#). Many works have studied the surface plasmonic properties of graphene or graphene ribbons, with different experimental techniques, including optical measurements, electron energy loss spectroscopy, angle-resolved photoemission spectroscopy, and surface tunneling spectroscopy [19, 20, 24–26], as further discussed in the cited references.

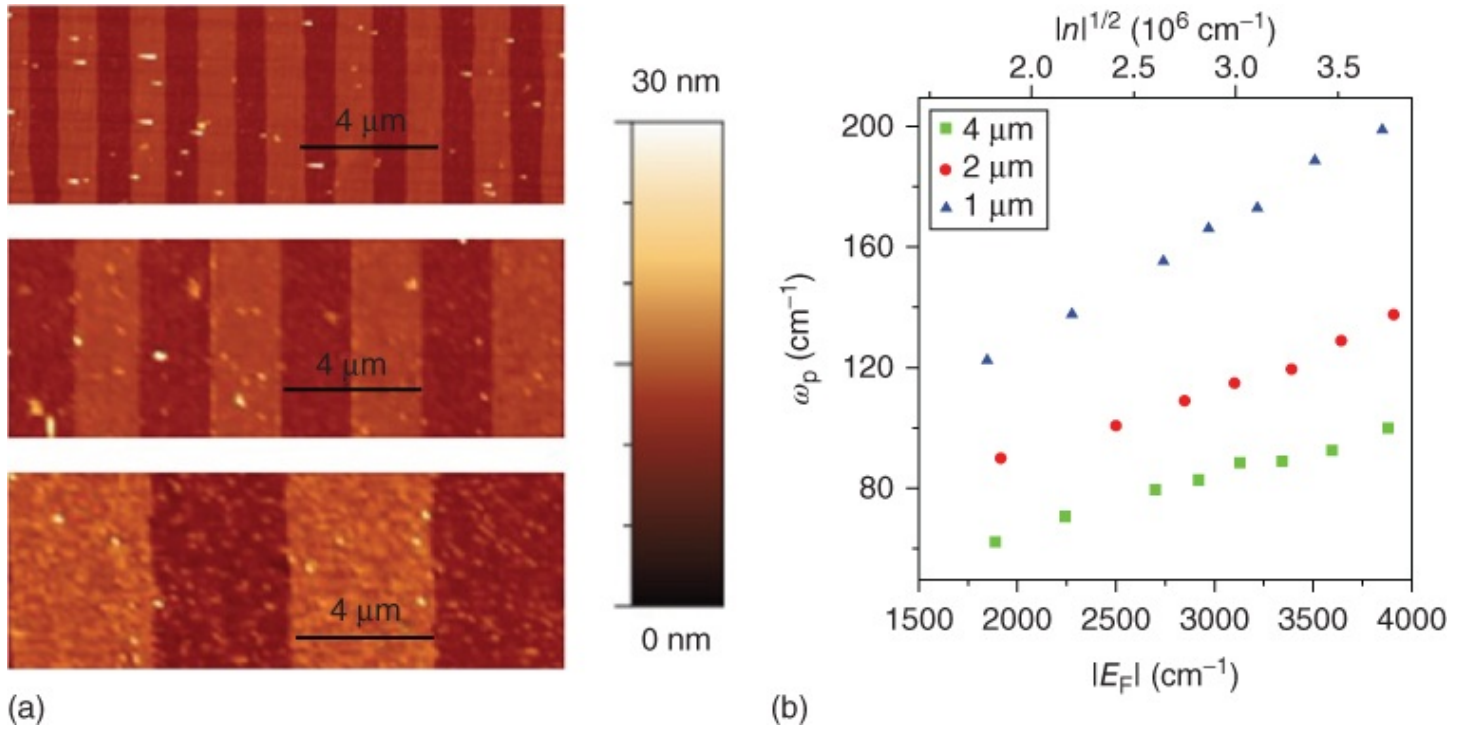


Figure 1.1 Control of the graphene plasmon resonance frequency by electrical gating and microribbon widths. (a) AFM (atomic force microscopy) images of graphene microribbons with widths of 1, 2, and 4 μm. Color bar of the height is shown on the right. (b) Fermi energy (E_F) dependence of the graphene plasmon frequency ω_p (top axis gives related dependence on charge density $|n|^{1/2}$) of ribbons with three different widths.

(Figure adapted from Ref. [20].)

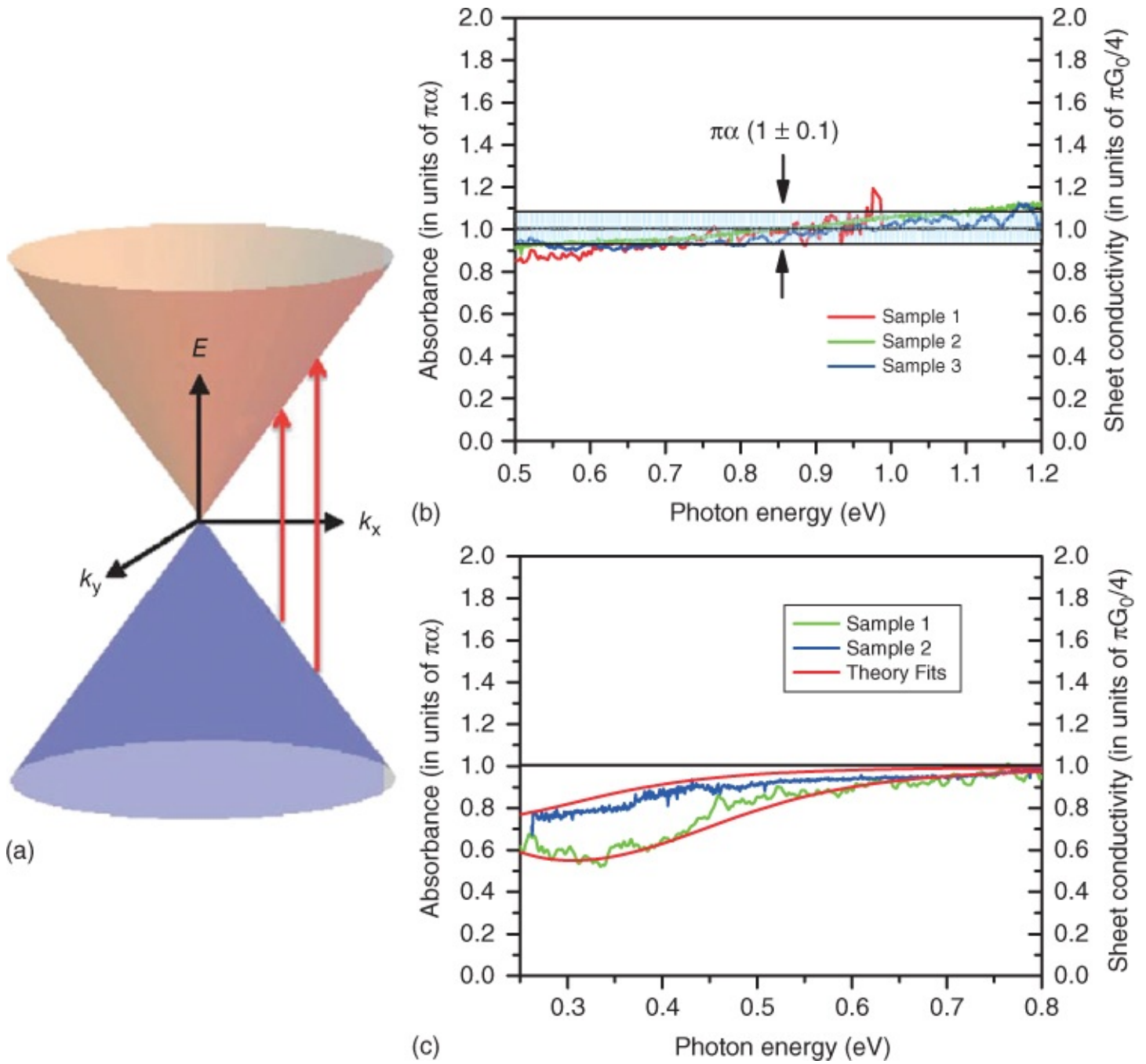


Figure 1.2 Universal light absorbance and optical conductivity of graphene. (a) Schematic of Dirac-cone and interband optical transitions in graphene. (b) Optical absorbance (left axis) and optical sheet conductivity (right axis) of three graphene samples. The spectral range is from 0.5 to 1.2 eV. The black horizontal line shows the universal absorbance value of 2.293% per layer, with the variation within 10%. (c) The optical absorbance of graphene Sample 1 and Sample 2 over a smaller spectral range from 0.25 to 0.8 eV.

(Figure from Refs [22, 23].)

1.2.1.2 Electrical Properties and Tunability

One of the greatest advantages of studying graphene is that its transport and optical properties can be sensitively and controllably tuned by doping. The Fermi level can easily be shifted by introducing either electrons (n-doping) or holes (p-doping). Numerous ways of establishing a

desired doping level have been investigated, for instance, by chemical doping [27, 28], electrochemical doping [29–33], electrostatically by top or back gating [34–36], and by the direct introduction of heteroatoms into the lattice [37].

One of the most studied and widely used techniques is to introduce the charge by top or back gating [34–36]. This technique is appealing due to its similarity to present use in gating field-effect transistors, which allows the knowledge and know-how learned from standard microelectronics to be used more widely in graphene electronics. However, one drawback of this approach is the extremely high gating potential (~ 100 V) that is required, because the present gate dielectrics have a relatively large thickness that restricts the gate capacitance value. For example, bias voltages as high as 80 V had to be used to achieve a carrier density of $\sim 5 \times 10^{12} \text{ cm}^{-2}$ [36], and such a high bias voltage could cause charge trapping from the substrate, thereby altering the properties of both the substrate and the graphene.

Electrochemical doping, on the other hand, is significantly more efficient, insofar as voltages as small as 1.5 V are sufficient to reach charge carrier concentrations of $5 \times 10^{13} \text{ cm}^{-2}$. Higher doping levels can also be achieved by using a combination of a protecting layer and a liquid electrolyte [3] or using ferroelectric polymers [38]. Electrochemical doping is thus especially appealing when higher doping levels are desired, and these high doping levels are achieved by the electrical double layer (EDL) formed at the interface between the electrolyte solution and the graphene surface. The ions in the liquid are attracted by the graphene, which is charged by an opposite sign. These ions migrate to the surface, thus forming a very thin layer that performs as a capacitor with an extremely high capacitance value. Therefore, effective control of carrier densities in the graphene can be implemented through electrochemistry, which furthermore provides a fast response by electrochemical doping.

1.2.1.3 Spectroscopic Properties

Spectroelectrochemical studies are most commonly carried out by using Raman spectroscopy, because this technique is readily available and does not normally perturb the material under investigation, thereby allowing repeated and systematic measurements. The commonly studied features in the Raman spectra of graphene are the G, D, and G' bands (the G' band is also called the **2D band**), see [Figure 1.3](#). The shapes of the electronic bands can be probed by varying the laser excitation energy, which shifts the peak position of the D and G' bands and thus provides additional important information. [Figure 1.4](#) shows the scattering processes that generate these vibrational bands or features [35]. From [Figure 1.4](#), we can see that the G band comes from a first-order one-phonon scattering process, while other bands come from second-order scattering processes. The D band is a symmetry-breaking band, which thus requires the presence of defects in the sample, although boundaries (edges) of the sample also produce D band intensity. Since the D band is not allowed by the crystal symmetry of the graphene lattice, it is commonly used to evaluate the quality of a particular graphene sample. The G and G' bands are present in all sp^2 carbon and graphene-related materials, and are symmetry-allowed. The intensity, frequency, and linewidth of these bands are dependent on several factors, such as strain and doping, the number of graphene layers, and the laser excitation energy. For example, the shape of the G' band of graphene is related to the number of graphene layers and how the

layers are stacked with respect to one another. As shown in [Figure 1.5](#) [35], the shape of the G' band is dramatically different from single layer to four layers and to bulk HOPG (highly oriented pyrolytic graphite, discussed later). The G' band is generated from the second-order two-phonon intervalley scattering process ([Figure 1.4](#)), and the G' band can be fitted with multiple Lorentzian lineshapes, depending upon the structure of the sample.

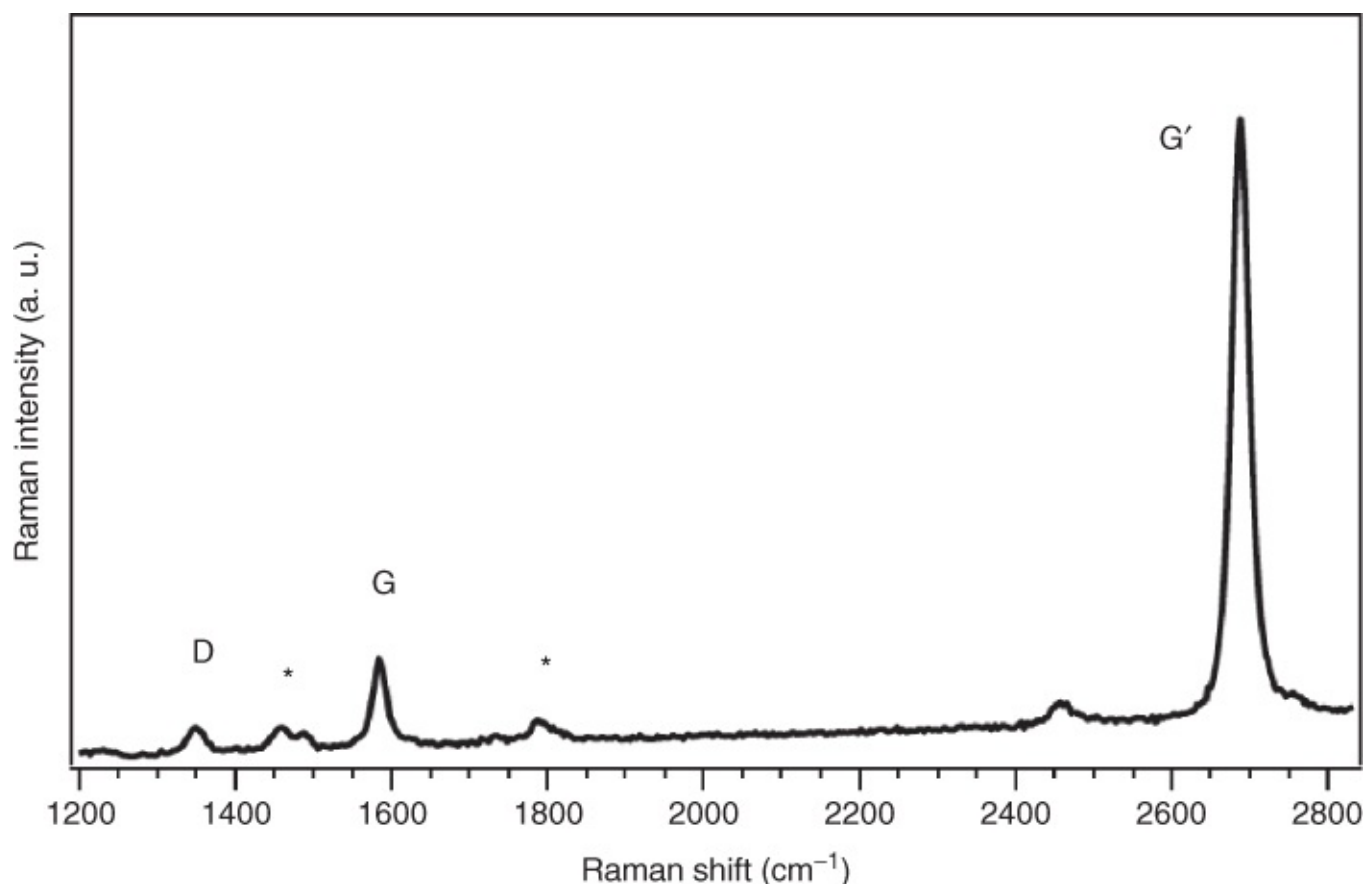


Figure 1.3 Raman spectrum of graphene at 0 V (applied bias voltage), excited by a 2.33 eV laser radiation, in an electrochemical environment. The asterisks (*) indicate Raman bands of the electrolyte.

(From Ref. [33].)

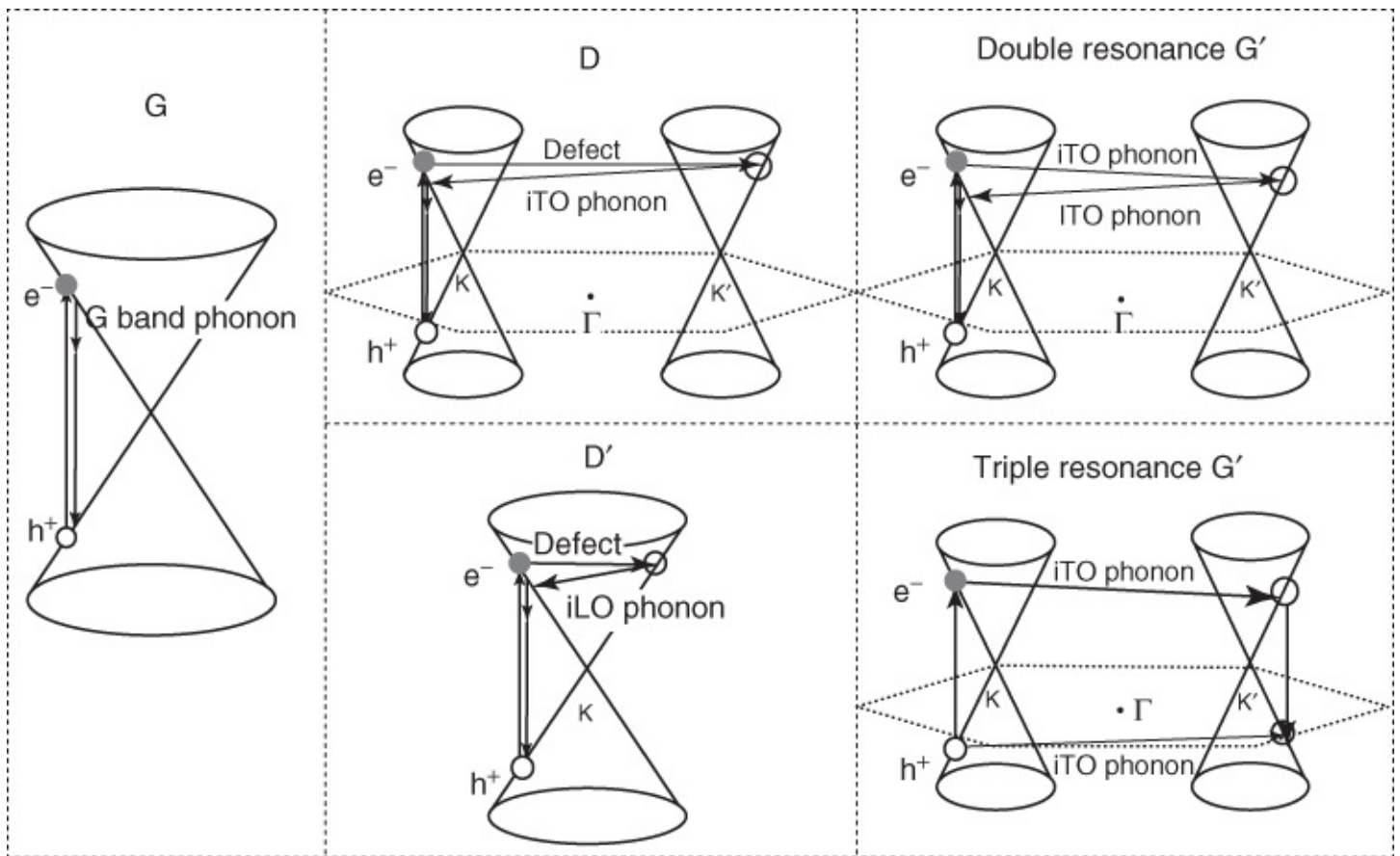


Figure 1.4 The Raman scattering processes of the G, D, D', and G' bands of graphene.

(Figure is from Ref. [35].)

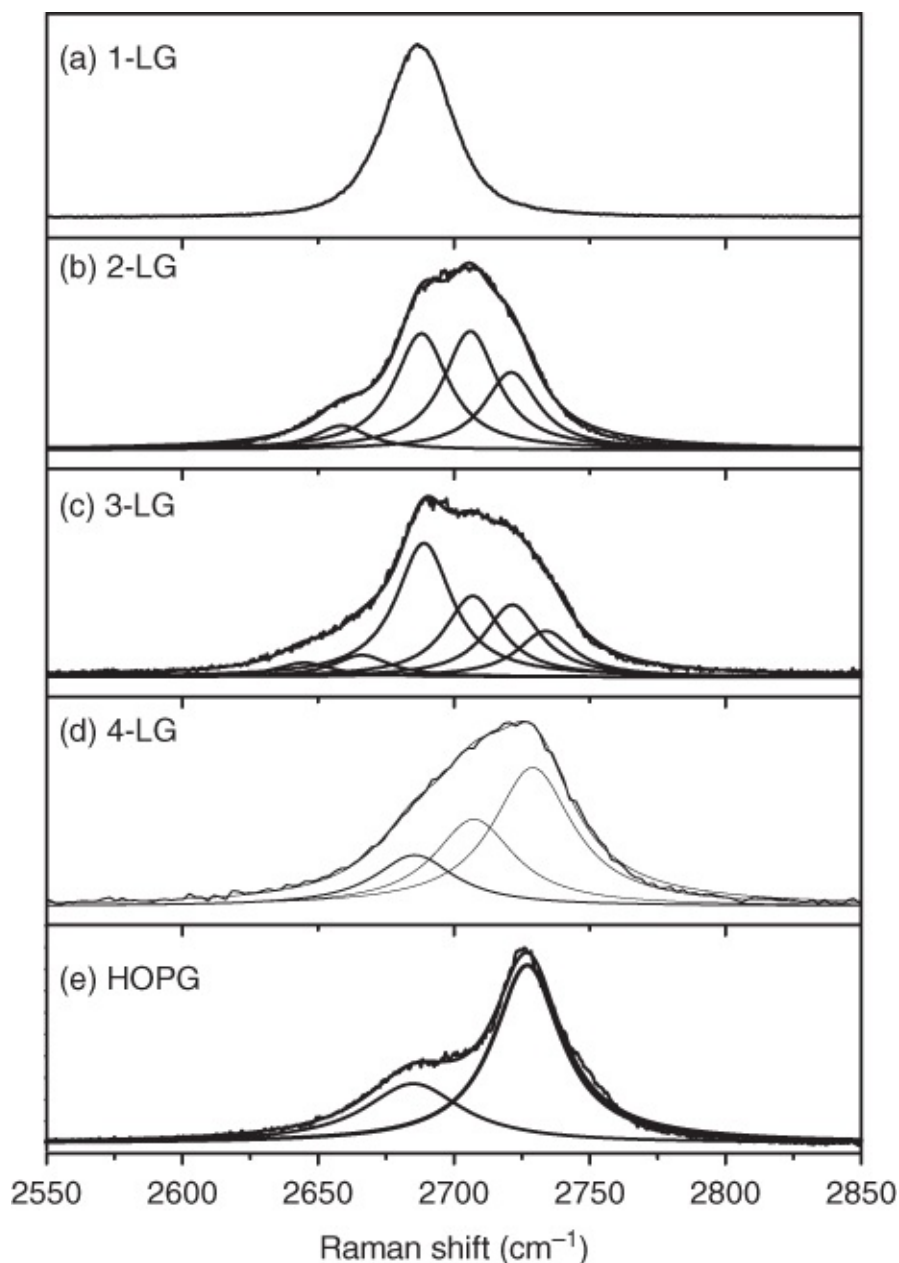


Figure 1.5 Raman spectra of the G' band of graphene with different numbers of layers. The excitation laser wavelength is 514 nm.

(Figure is from Ref. [35].)

The experimental setup of *in situ* Raman spectroelectrochemistry is shown in [Figure 1.6](#) [39]. In the setup, the sample on the substrate serves as a working electrode and is surrounded by electrolyte solution (light grey cylinders). Note that the electrochemical setup requires a high-purity electrolyte, because the contaminants reduce the range of potential that can be applied. The sample is usually contacted by an Au metal (working electrode). The electrochemical cell is completed by an Ag pseudo-reference electrode and a Pt counterelectrode. The three-electrode system and potentiostatic control of the applied voltage assure precise control of the doping level of graphene. The electrochemical cell is placed under the Raman spectrometer to achieve *in situ* spectral acquisition. In [Figure 1.6](#), the sample is a $^{12}\text{C}/^{13}\text{C}$ graphene bilayer, but only the ^{12}C part of the samples is contacted, which enables one to study the charge transfer

between individual graphene layers in this system.

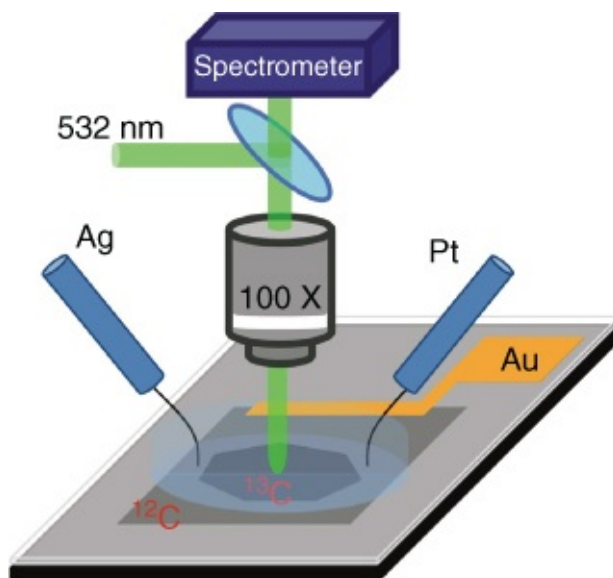


Figure 1.6 The schematic illustration of an experimental setup of *in situ* Raman spectroelectrochemistry. The sample ($^{12}\text{C}/^{13}\text{C}$ bilayer graphene in this sketch) is on the substrate with ionic gating (light grey cylinders), with two electrode probes made of Ag and Pt. The back gating is through the Au metal electrode. The setup is placed under the Raman spectrometer to achieve *in situ* Raman spectroscopy.

(Figure is from Ref. [39].)

The doping of graphene results in changes in all Raman spectral features. These changes reflect variations in the electronic structure of graphene and the stress in the formation of defects. Hence, spectroelectrochemistry is a powerful tool to study charged graphene.

Using spectroelectrochemistry to accurately control and shift the Fermi level, it has, for example, been found that the intensity of the D peak decreases with increasing doping [40], as seen in [Figure 1.7](#). Such an effect was attributed to the fact that the strength of the electron scattering is doping dependent, such that the total scattering rate of the photoexcited electrons and holes increases with doping. It is consequently important to know the doping level of the graphene when estimating the amount and type of defects from the intensity of the D peak.

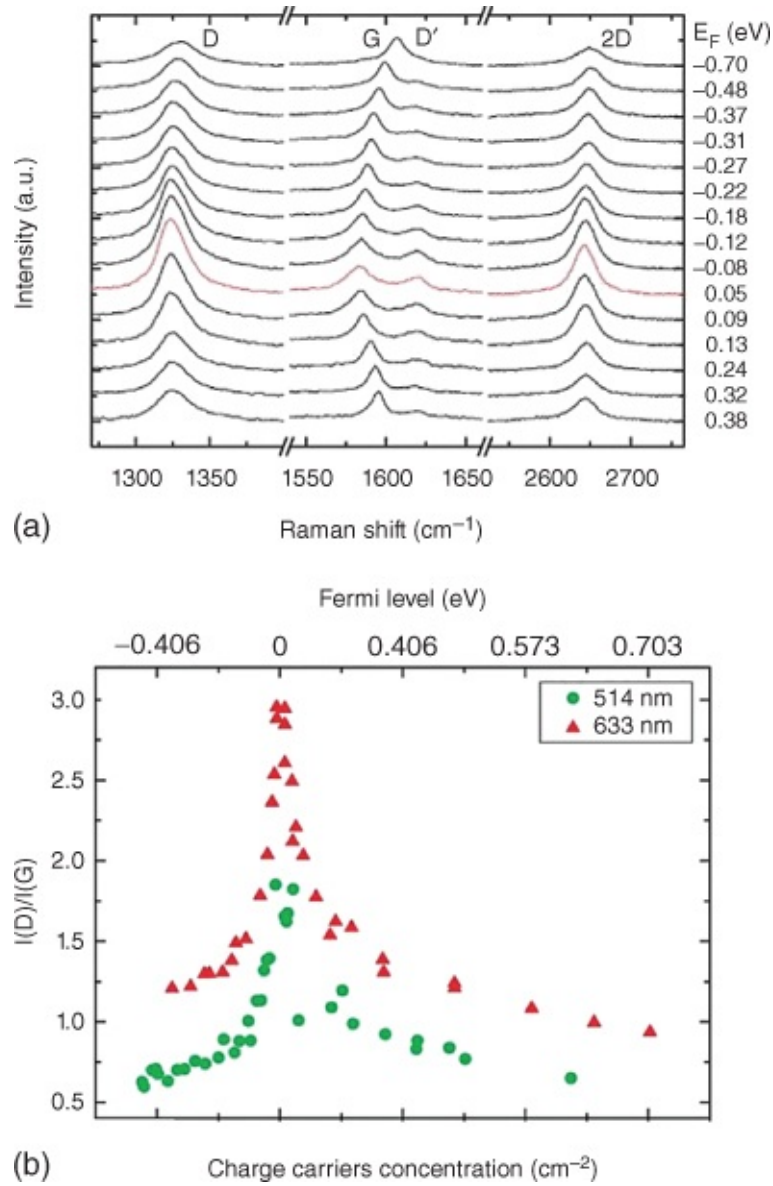


Figure 1.7 The change of D band with electrochemical doping. (a) Raman spectra of defective graphene at different Fermi energies (E_F), measured under 633 nm laser excitation. (b) The normalized intensity of the D band as a function of Fermi level, or charge carrier concentration at 514 and 633 nm laser excitations.

(Figure is adapted from Ref. [40].)

The G band in [Figure 1.3](#) is observed to be due to the optical phonon of graphene, which occurs at a high frequency of $\sim 1580 \text{ cm}^{-1}$, because the carbon atoms are very light, having atomic number 6. From a many-body point of view, the origin of the G band can be explained as that of an electron that is excited from the valence band into a conduction band by absorbing a phonon. An electron–hole pair is thus created. When the electron and the hole then recombine, a phonon is emitted, which has a slightly shifted frequency and a lifetime connected to its bandwidth. The energy of the phonon and the charge carriers will thus be renormalized by the various interactions. Since the band structure of graphene is conical with a linear $E(k)$ relation (see [Figure 1.2a](#)), and thereby symmetric for electrons and holes with respect to the Dirac point, the frequency shift of the G band upon doping can be expected to be equal for

positive and negative doping. However, the C–C bond strength is also changed somewhat when the graphene is doped [36]. Positive (negative) charge doping removes (adds) electrons from (to) antibonding orbitals which increases (decreases) the bond strength. This phenomenon has an opposite effect on positive doping relative to negative doping, as seen in the electrochemical data shown in [Figure 1.8](#). Both the renormalization and the bond strength change lead to an upshift of the phonon frequency for positive doping [29, 33]. For negative doping, on the other hand, the two effects work against each other [29, 33]. This results in a monotonic upshift of the G band frequency for positive doping and a nonmonotonic upshift for negative doping, whereby the shift is always greater for positive doping [33], as seen in [Figure 1.8](#).

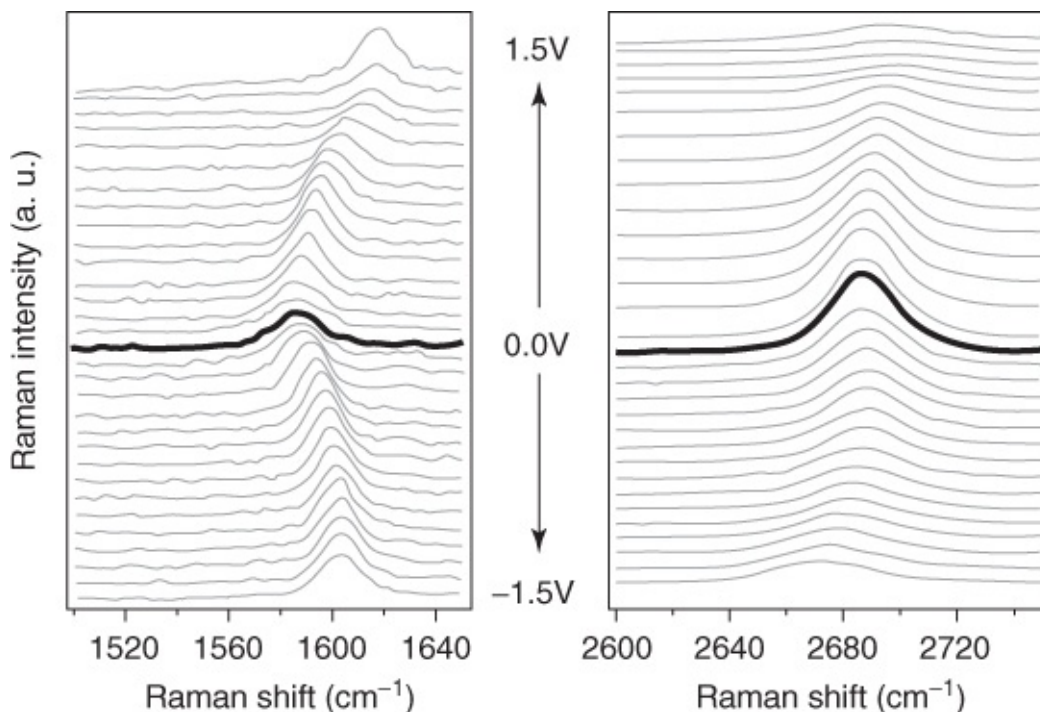


Figure 1.8 *In situ* Raman spectroelectrochemistry data for the G and G' bands of graphene excited by 2.33 eV laser irradiation. The heavy black trace is for $V = 0$ applied voltage.

(Adapted from Ref. [33].)

Another important effect that was observed in doped graphene samples was an anomalous increase of the intensity of the G mode at high electrode potentials [[3, 33, 41]]. This effect was explained by canceling part of possible optical transitions due to quantum interference effects [42].

The G' or 2D band in [Figure 1.3](#) is also sensitive to doping, although to a lesser extent than the G band, as is seen in [Figure 1.8](#). Doping induces changes in the frequency of the G' band due to changes in the C–C bond strength, the electron–phonon coupling, and electron–electron interactions. The frequency of the G' band increases for positive doping, whereas it first increases for negative doping followed by a relatively large decrease at higher negative potentials. It has been found both experimentally [33] and theoretically [43] that the G band frequency shifts by ~ 0.5 times as much as the G' band per volt in the range from 0 to 1 V. Strain can also influence the frequency of the G and G' band. The two effects can be disentangled

from one another by correlating the peak positions in the Raman spectra [33, 44].

The effect of doping on bi- [30] and trilayers [32] has been investigated by a combination of isotopic labeling with *in situ* Raman spectroelectrochemistry. The isotopic labeling allows separate investigation of the individual layers in the multilayered graphene, since the different masses of ^{12}C and ^{13}C result in a large difference of ω_{G} and $\omega_{\text{G'}}$ in the Raman spectra. A typical isotopically labeled turbostatic bilayer graphene sample has the Raman spectra shown in [Figure 1.9](#). The isotope labeling also enables one to study the role of the stacking order of graphene layers on the changes in electronic structure of graphene induced by doping [39]. A more complete review of the combination of isotopic labeling with *in situ* Raman spectroelectrochemistry is found in the review article by Frank *et al.* [31].

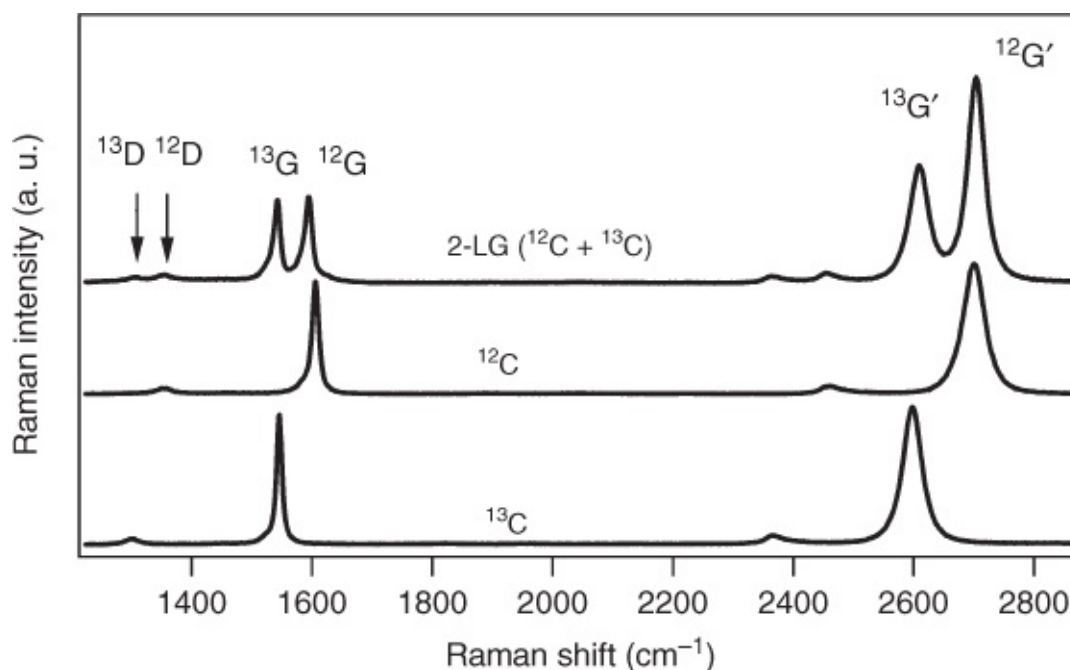


Figure 1.9 The Raman spectra of bilayer graphene with the two layers of: $^{13}\text{C}/^{12}\text{C}$, both ^{13}C , and both ^{12}C . The graphene with the ^{13}C isotope has red-shifted G and G' peaks, compared to ^{12}C graphene.

(Figure from Ref. [30].)

1.2.2 HOPG

Highly oriented pyrolytic graphite (HOPG) is a commonly used synthetic type of graphite with high purity and has an angular spread in the stacking of its graphite sheets of less than 1° [45]. The level of angular spread and perfection of HOPG can be characterized by the full-width half-maximum (FWHM) of the Cu-K α rocking curve measured using X-ray diffraction (XRD). HOPG exhibits an anisotropy similar to graphite and is cleavable. Because of the anisotropy, many of its physical properties, including thermal, electrical, and optical properties [46], are different in different directions, as for example, along and perpendicular to the basal plane ([Table 1.1](#)). HOPG normally shows weak ferromagnetism due to the presence of magnetic impurities associated with the HOPG synthesis process. The observed magnetism is attributed

to the unpaired electron spins at the grain boundaries and to the sample edges, and such effects have been characterized using magnetic force microscopy [48]. HOPG is a highly stable material and it remains stable at high temperatures (3000 °C under vacuum and 500 °C in atmosphere), and exhibits high chemical inertness to almost every chemical. Because of its atomically flat surface, HOPG is usually used as a calibration standard for scanning probe microscopy [49].

Table 1.1 Physical properties of HOPG at 300 K [47].

	Along layer plane (002)	Along (0001) principal axis <i>c</i>
Electrical resistivity (Ω cm)	$3.5\text{--}5.0 \times 10^{-5}$	0.15–0.25
Thermal conductivity ($\text{W m}^{-1} \text{K}^{-1}$)	1700 ± 100	8 ± 1
Thermal expansion (K^{-1})	-1×10^{-6}	20×10^{-6}

HOPG has also been widely used in the field of electrochemistry. The basal plane of HOPG has been used as electrodes for many studies, such as for the creation of nanoscale interfaces for sensing and for biological applications [50, 51], as well as model system for nanoparticle electrocatalysis [52, 53], heterogeneous metal deposition, and nucleation studies [51, 54]. Besides, HOPG is commonly used to study the electrochemistry of sp^2 carbon materials used for improving our understanding of electrochemical processes, such as electrocatalysis [55] and carbon surface functionalization [56].

1.2.3 Carbon Nanotube

1.2.3.1 Structure and Electronic Properties

A carbon nanotube is a seamless 1D structure of rolled-up graphene [57]. Because of the dimensional constraints, the energy bands of a carbon nanotube become discrete [58–60], as shown in [Figure 1.10](#). Moreover, the nanotube axis orientation relative to the six-member ring honeycomb lattice can vary from 0° to 30° (see [Figure 1.11](#)), rendering the classification of carbon nanotubes into zigzag ($\theta = 0^\circ$), armchair ($\theta = 30^\circ$), and chiral nanotubes, which are defined according to the nanotube profile along the diameter (perpendicular to nanotube axis). Sketches of these three types of carbon nanotubes are shown in [Figure 1.12](#). Different types of carbon nanotubes have different electrical properties [57]. As shown in [Figure 1.11](#) [60], the chirality of a carbon nanotube can be defined by the chiral vector $\vec{C}_h$, which can be written as [59]

$$\vec{C}_h = n\vec{a}_1 + m\vec{a}_2 \triangleq (n, m),$$

where $\vec{a}_1$ and $\vec{a}_2$ are the unit vectors of graphene. Different chiralities denoted by the indices (n, m) of carbon nanotubes (the orientation of the hexagons in [Figure 1.11](#) relative to nanotube axis) distinguish between metallic and semiconducting types. Briefly, the condition for a metallic carbon nanotube is [59]

$$2n + m = 3j,$$

where j is an integer. This is also shown in [Figure 1.11](#).

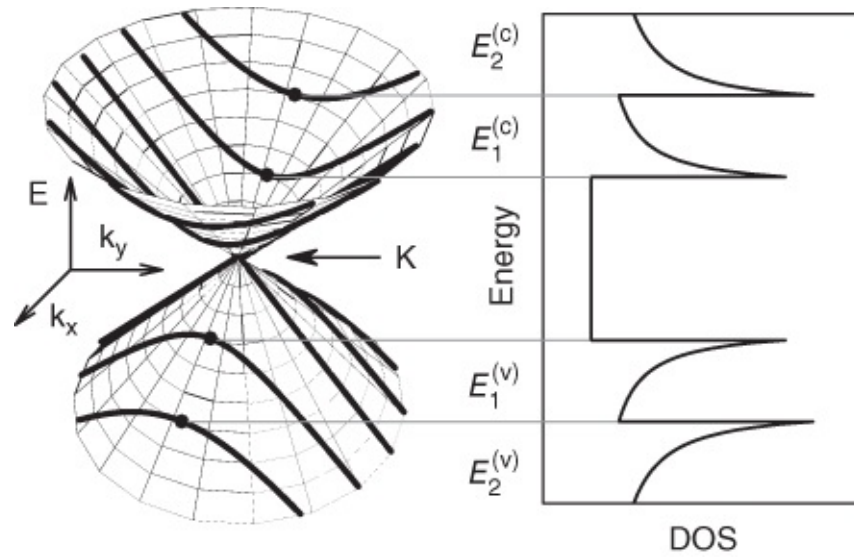


Figure 1.10 Energy band diagram and density of states (DOS) of a carbon nanotube. The 1D van Hove singularities give a high DOS at well-defined energies.

(Figure adapted from Ref. [82].)

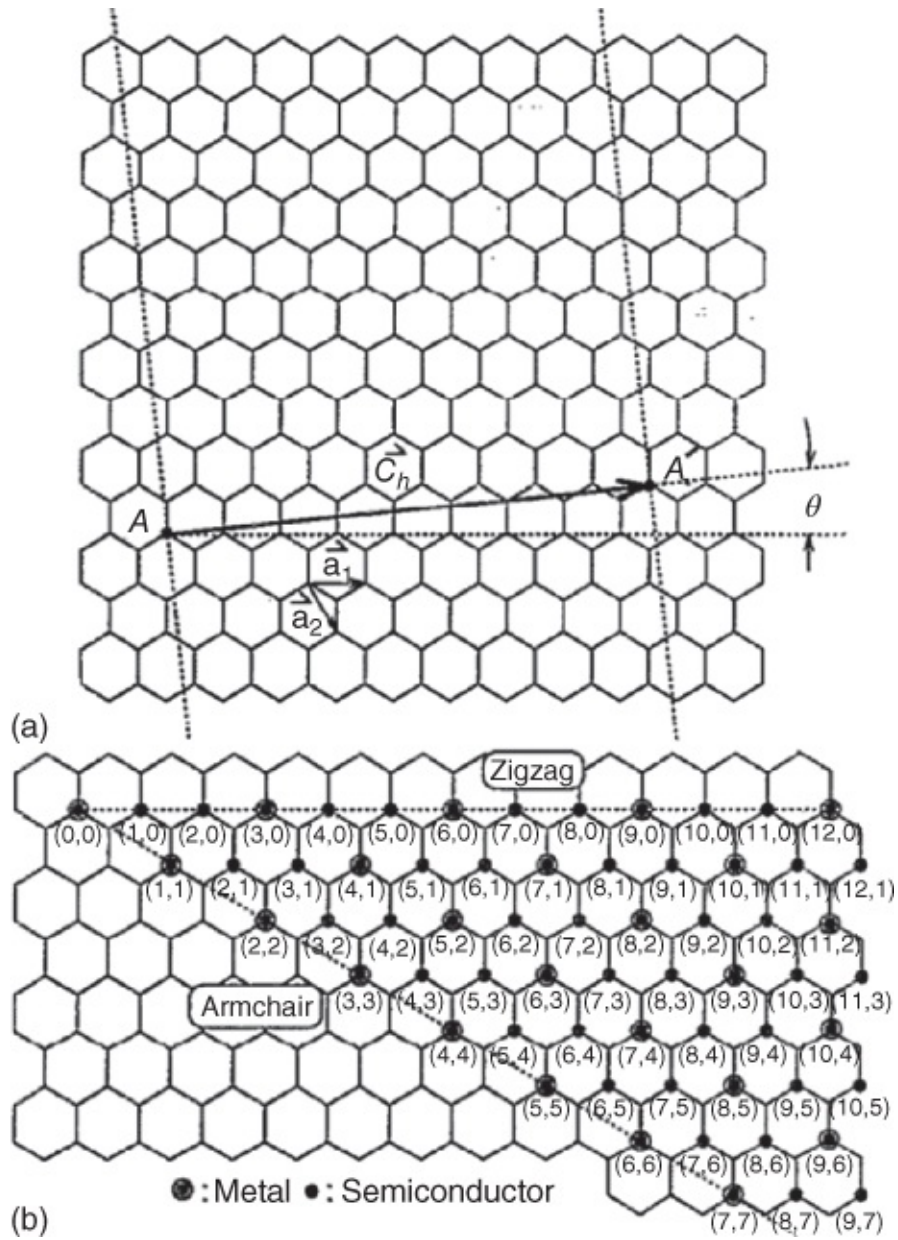


Figure 1.11 (a) A carbon nanotube defined by the chiral vector $\vec{C}_h$, which is perpendicular to the nanotube axis. Here, θ is the chiral angle, and $\vec{a}_1$ and $\vec{a}_2$ are the unit vectors of graphene. (b) Possible chiral vectors (n, m) of carbon nanotubes (see text). Different (n, m) chiralities result in different physical properties, including metallic (large dots) and semiconducting (small dots) nanotubes.

(Figure adapted from Ref. [59].)

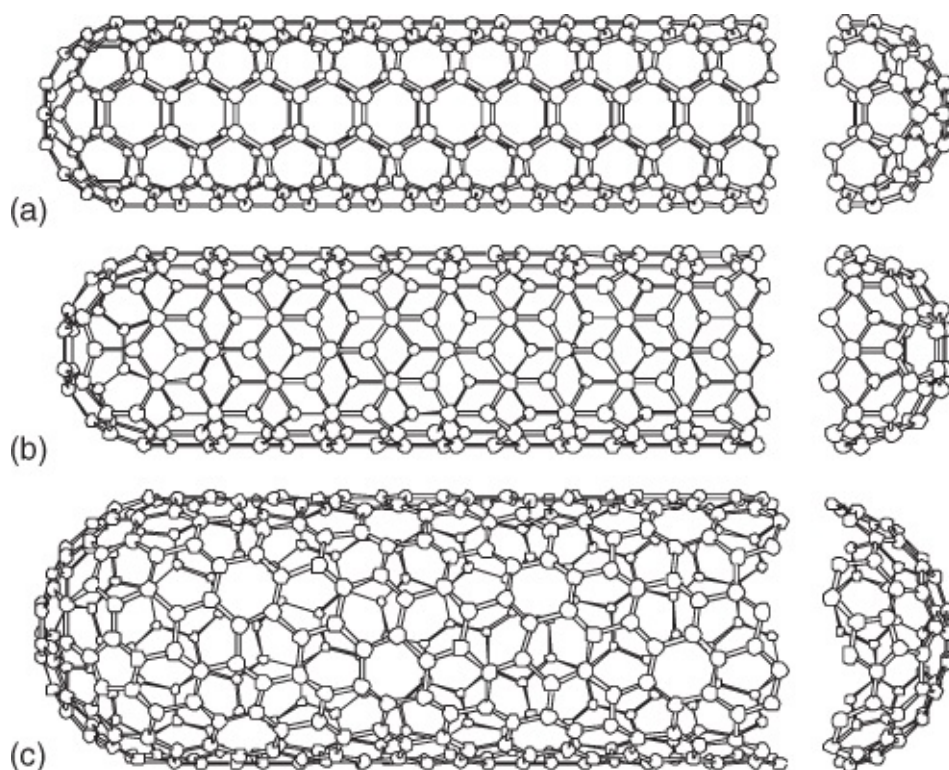


Figure 1.12 Three types of carbon nanotubes: (a) armchair, (b) zigzag, and (c) chiral. The definition of nanotube types is according to the orientation perpendicular to the nanotube axis.

(Figure from Ref. [82].)

1.2.3.2 Spectroscopy and Spectroelectrochemistry of Carbon Nanotubes

The investigation of doped single-wall carbon nanotubes (SWCNTs) by Raman spectroscopy was first reported in 1997 by Rao *et al.* [61]. Even though this first report did not employ electrochemistry, it showed evidence of doping in the Raman spectra, which contributed to the observed frequency shifts of the G band. Electrochemistry connected with Raman spectroscopy has also been used to study the electron–phonon coupling and the charge states of nanotubes in solution or on substrates. The first study employing both electrochemistry and Raman spectroscopy on SWCNTs was published in 1999, by Eklund *et al.* [62]. The experiment also combined chemical and electrochemical doping, since the doping medium that was used, H_2SO_4 , caused parallel chemical and electrochemical doping. Afterward, many other studies, employing numerous aqueous [63–68], and aprotic media (a solution that does not donate H^+ protons) [58, 69–79] followed.

Because a SWCNT is a graphene sheet rolled up seamlessly to form a tube, the Raman signature of carbon nanotubes also contains the D, G, and 2D bands, similar to the Raman spectrum of graphene, although with some differences. For instance, the curvature of the nanotube leads to a G band with two clear components, G^+ and G^- , assigned to transverse (TO) and longitudinal (LO) modes, vibrating along directions perpendicular (TO) or parallel (LO) to the nanotube axis, respectively. This situation is in contrast to graphene where these two modes are degenerate, since graphene is a quasi-2D material. This is shown in [Figure 1.13](#). The G band lineshape, namely its LO component, is sensitive to the Fermi energy, and

can be changed by applying a gate voltage. The LO mode exhibits different lineshapes depending upon whether the probed nanotube is metallic or semiconducting. For metallic nanotubes, the LO component exhibits a Kohn anomaly, which leads to a larger downshift of the peak frequency compared with semiconducting tubes [43].

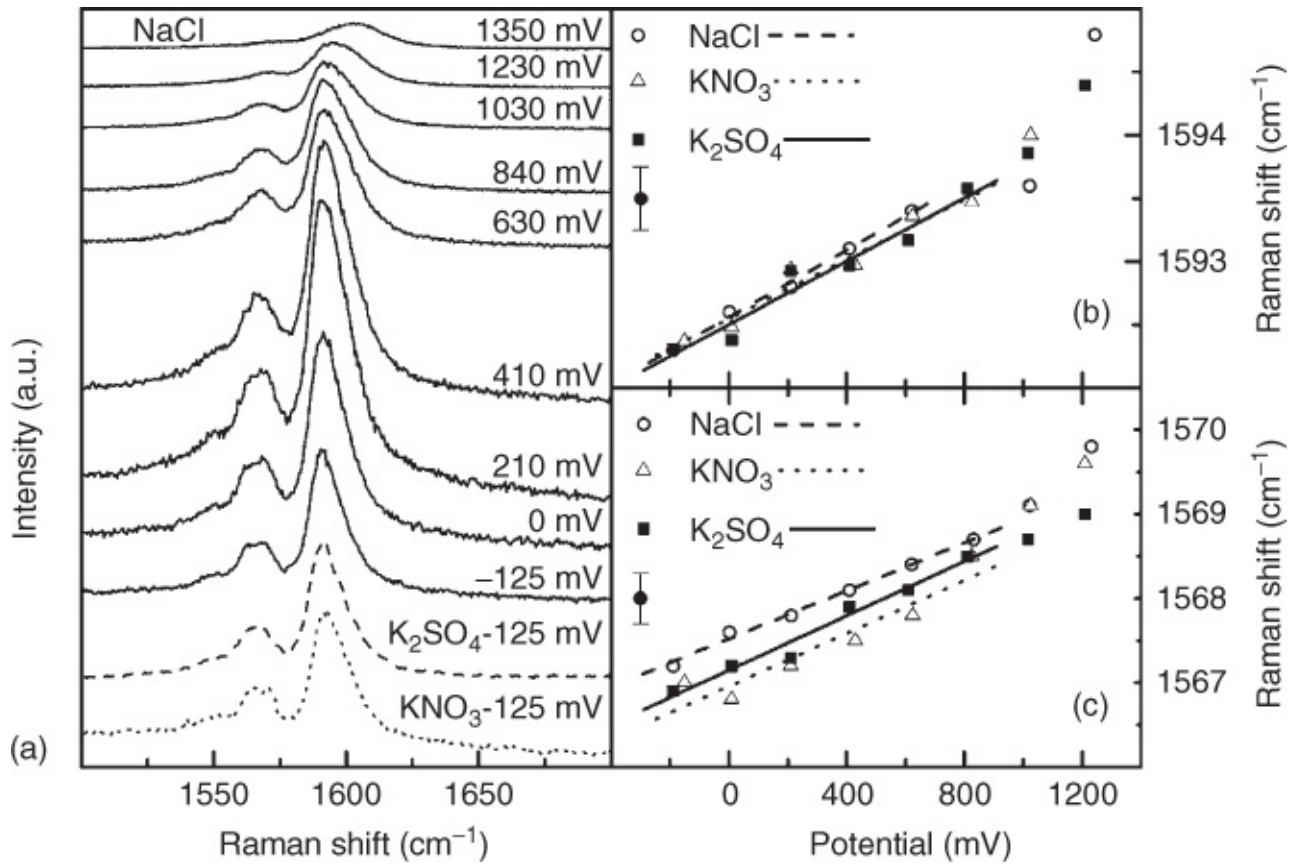


Figure 1.13 (a) Raman spectra of the G band at several potentials applied to a SWCNT bundle. (b,c) Variation of the G⁺ band and G⁻ band frequency, respectively, with the applied potential for three different electrolyte solutions.

(Adapted from Ref. [80].)

In addition, the Raman spectrum of nanotubes shows a feature called the radial breathing mode (RBM) with a frequency ω_{RBM} between 100 and 350 cm⁻¹. The RBM mode is one of the most important features observed in the Raman spectrum of nanotubes, since it provides information regarding the nanotube diameter and the nanotube chirality, through the Kataura plot [81]. The Kataura plot shown in Figure 1.14 is a plot of the relationship between the electronic transition energies and the SWCNT diameters. Each point in the Kataura plot shows an optically allowed electronic transition energy, which is the energy separation between van Hove singularities in the conduction and valence bands. In Figure 1.14 [81–83], crosses represent semiconducting SWCNTs (labeled “S”) and circles represent metallic SWCNTs (labeled “M”). For Raman spectroscopy, this plot gives information about the (n, m) SWCNT chiralities that can be excited for a certain laser excitation energy.

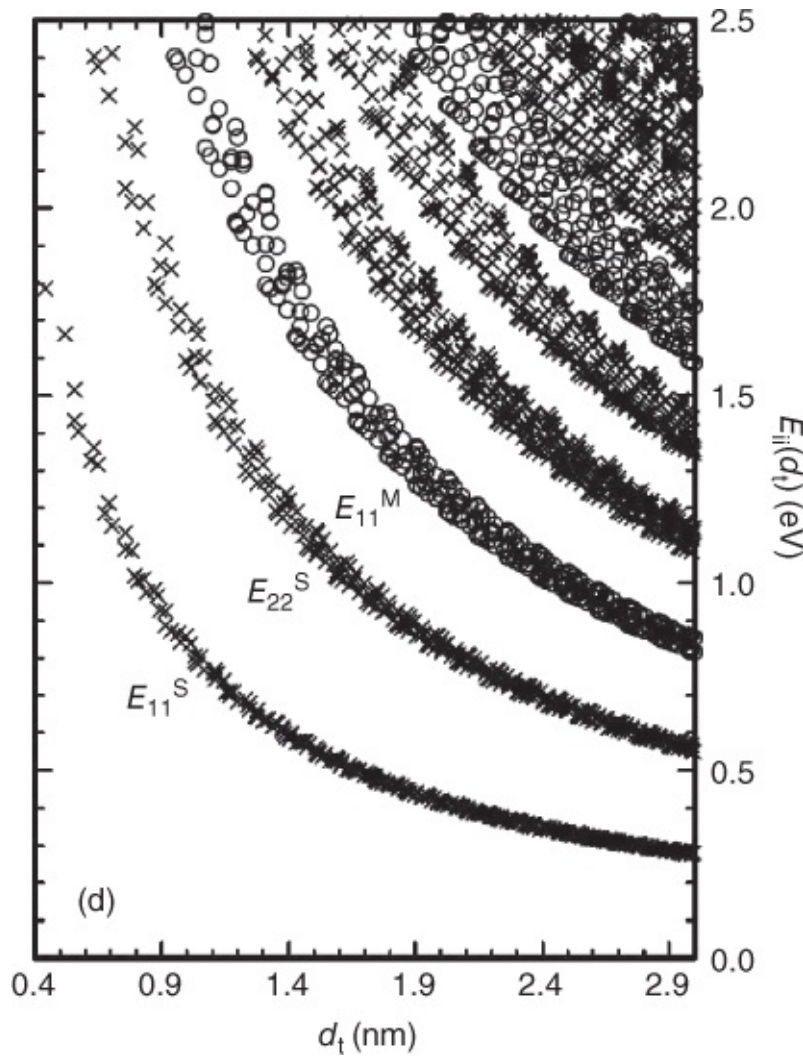


Figure 1.14 Kataura plot [81–83], showing the relationship between electronic transition energies and the SWCNT diameters. Each point on the plot shows an optically allowed electronic transition energy E_{ij} , which is the energy separation between van Hove singularities in the conduction band to the valence band. Crosses represent semiconducting SWCNTs (labeled “S”) and circles represent metallic SWCNTs (labeled “M”).

Raman spectroscopy can detect changes in the C–C bond length, since the RBM varies with diameter and the G band varies with the axial C–C bond length. Moreover, the band intensity also varies as charge transfer occurs, either to or from the nanotubes. Gupta *et al.* [84] monitored the dependence of the C–C bond length in an SWCNT material on charge transfer, for several alkali, halide, and sulfate electrolyte solutions (see [Figure 1.15](#)), and observed a softening of the C–C bond with increasing charge transfer to the nanotubes.

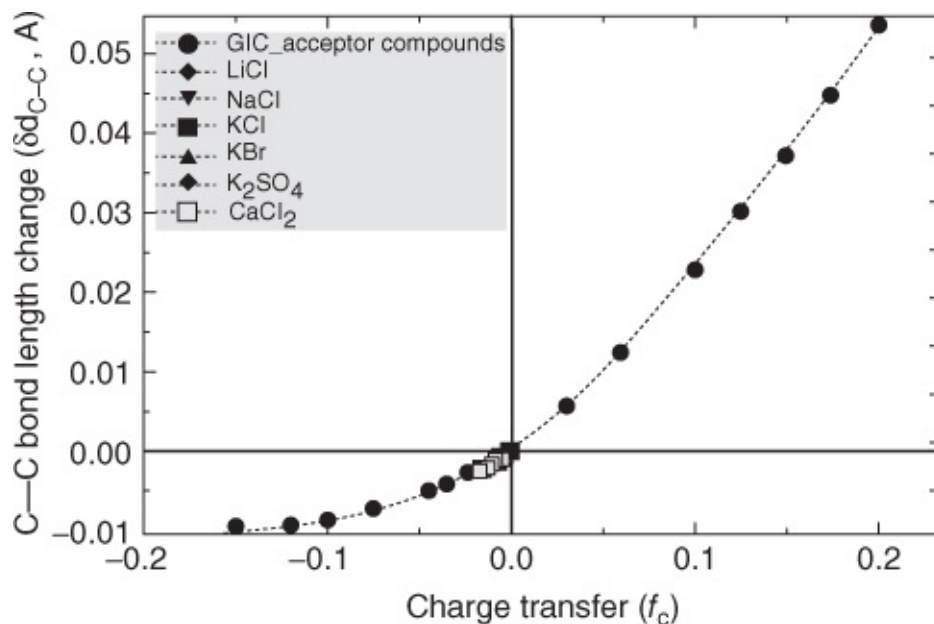


Figure 1.15 Variation of the C–C bond length (estimated from G band variation) with electrochemical charge transfer (f_c) induced on the nanotubes.

(Adapted from Ref. [84].)

SWCNT bundles containing nanotubes with different diameters are easy to obtain experimentally, but such samples may lead to overlapping RBM modes and complex Raman spectra that are difficult to interpret. In contrast, SWCNTs synthesized via the HiPCO method are favored for spectroelectrochemical studies due to their small diameters, which lead to well-separated RBM peaks, thereby simplifying nanotube chirality assignments significantly [58, 72].

The doping of SWCNT leads to changes in all Raman features. The most obvious effect is an overall bleaching of the Raman signal of carbon nanotubes. The shift of the Fermi level cancels the effect of the optical transitions between the van Hove singularities. If these transitions are employed in resonance effects, the Raman signal is dramatically reduced. The doping level, where the Raman signal starts to bleach, should therefore depend on the electronic structure of a particular carbon nanotube. It was indeed observed that the Raman signal of metallic tubes starts to bleach at a lower electrode potential than that of semiconducting tubes [70].

Moreover, a detailed spectroelectrochemical study of an individual SWCNT showed that the “speed” of bleaching of the Raman signal also depends on the match of the nanotube resonance window and laser excitation energy [77]. It was also observed that bleaching of the Raman signal occurs already when the Fermi level crosses any van Hove singularity, even though this singularity is not employed in the resonance enhancement of the Raman signal [85].

The doping-induced changes in the intensity of the Raman signal of carbon nanotubes also have important consequences, that is, they can complicate the quantification of the amount of the particular SWCNT or the quantification of the defect density in SWCNTs, since the D mode intensity is also strongly affected by doping [86, 87].

The doping of carbon nanotubes also causes variations of the frequencies of the Raman

features. These doping-induced changes are only subtle in SWCNTs in the case of RBM bands [74], but they are significant for the G and G' modes [69, 73, 88]. The frequency variation of the G mode is rationalized by changes of the C–C bond strength and also changes in the phonon renormalization energy [71]. In the case of nanotube bundles, the changes in the G mode frequency of individual nanotubes contribute to the change of the G band lineshape of nanotube bundles [69, 89]. Nevertheless, the change in the G mode lineshape can be used to estimate the doping level of carbon nanotubes [69]. The changes in the G' mode frequencies are quite complex even in the case of individual carbon nanotubes, and more detailed studies are needed to understand these phenomena [73].

The spectroelectrochemistry of double-wall carbon nanotubes (DWCNTs) has also been investigated [2, 90–97]. Nevertheless, the understanding of the effect of the doping is more difficult in DWCNTs. In general, the charge is located mostly on the outer tubes; hence, there is a difference between the doping level of the inner and outer tubes. The distinct doping effects for inner and outer tubes are observed in the RBM modes and in the D and G' bands as well. For doped DWCNTs, both the D and G' bands split into two components upon electrochemical charging, in which case the mode at higher frequency is assigned to the outer tubes, since they bleach more rapidly [90, 91, 98]. These differences in the doping behavior can be used to distinguish between the Raman features of inner and outer tubes [94, 95] and even to quantify the amount of DWCNTs in their mixture with SWCNTs [2] in a given sample. Nevertheless, it should be noted that the charge distribution between the inner and outer tubes also strongly depends on their electronic structures, as shown in a recent study on sorted DWCNTs [96, 97].

Fullerene peapods represent another class of nanotube-based materials, which have been widely studied by spectroelectrochemistry [99–102]. The doping behavior of these materials is in general somewhat analogous to DWCNTs, but there are still some unexplained phenomena, such as the anomalous enhancement of the $A_g(2)$ mode of $C_{60}@SWCNT$ at high anodic potentials [103]. Hence, further investigation of these materials is needed.

Spectroelectrochemistry has proven to provide a versatile technique in the field of nanocarbons. It allows the monitoring of the charge transfer to and from carbon nanotubes and graphene, inducing doping in a controlled and easy manner. In fact, spectroelectrochemistry also allows exploration of the possibility of unzipping SWCNTs of different chiralities to obtain GNRs [104]. Metallic nanotubes with smaller diameters were found to unzip at lower potentials (0.36 eV) than other SWCNTs, followed by metallic tubes with larger diameters (at 1.16 eV), while semiconducting nanotubes required even higher potentials (1.66 eV) to unzip [104].

1.2.4 Graphene Nanoribbon

A GNR is a quasi-1D nanomaterial derived from graphene. Like carbon nanotubes, GNRs also show distinct differences in physical properties between their armchair, zigzag, or chiral categories ([Figure 1.16](#)) [105], because GNRs have edges and are not rolled up seamlessly, as are carbon nanotubes. GNRs also have the distinctions of metallic or semiconducting types, due to the different axial or chiral orientations of their edges. Also, the band gaps of GNRs are

decreased with increased ribbon width [106].

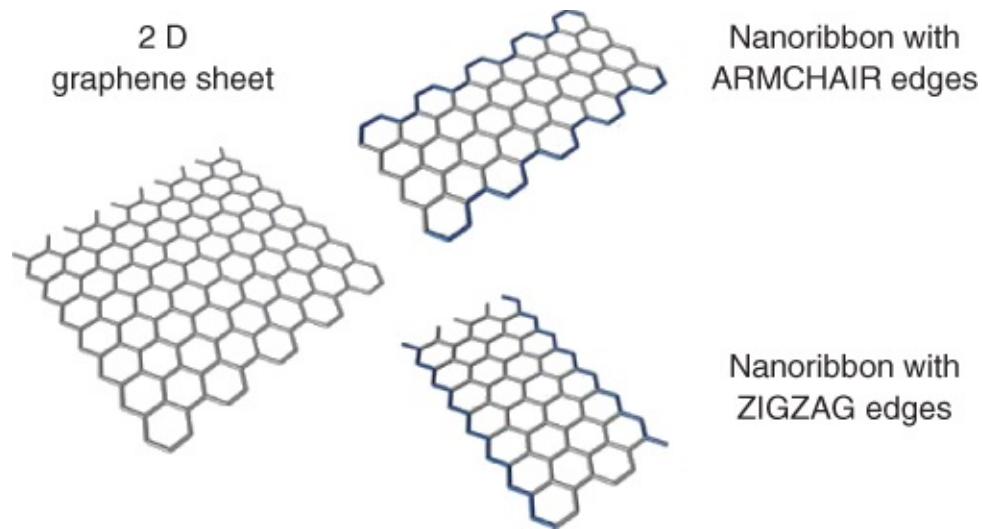


Figure 1.16 GNRs with different chiral orientations: zigzag and armchair.

(Figure is from Ref. [105].)

GNRs have high electron mobility, and small-width semiconducting GNRs have shown interesting band gaps, thus attracting the attention of electrical engineers for potential application in high-speed digital circuits. Because the electronic and magnetic properties of GNRs strongly depend on their edges [107, 108], the synthesis and precise control of GNR edge morphology have remained hot topics over the years. Potential precise synthesis techniques include *in situ* Joule heating inside a TEM (transmission electron microscope) [109] ([Figure 1.17](#)) and unzipping carbon nanotubes [110] ([Figure 1.18](#)), but practical large-scale applications of these scientific demonstrations appear challenging at the present time. Moreover, due to their small width, GNRs have many dangling bonds on their edges, which influence their chemical properties. This characteristic of GNRs triggers scientific study of their electrochemical reactivity [111] and offers an attractive system to study electrochemical applications, such as for electrode materials in Li-ion batteries [112] and for molecule sensing [113].

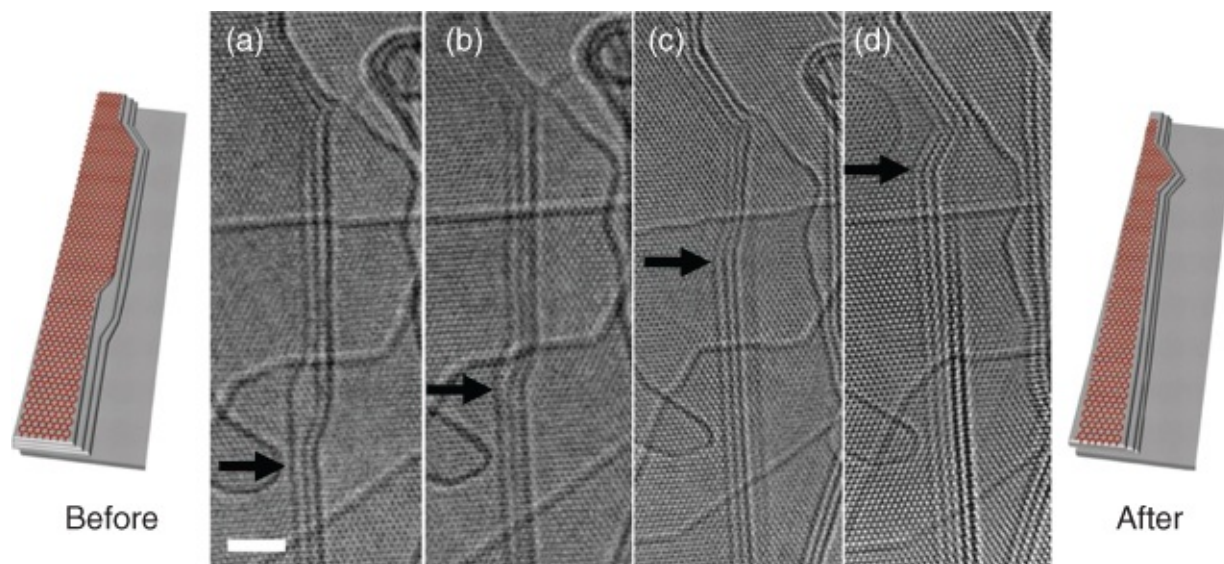


Figure 1.17 Development of edge structures in graphene nanoribbons using Joule heating inside a TEM (transmission electron microscope). (a) Graphene nanoribbon with zigzag–armchair edges. The black arrows indicate the junction between zigzag and armchair edges. With the increased time of Joule heating (a–d), the zigzag–armchair junction position moves. The sketches on the left and right of the TEM images (a–d) indicate the graphene nanoribbon structures before and after Joule heating, respectively. Scale bar in (a): 2 nm.

(Figure from Ref. [109].)

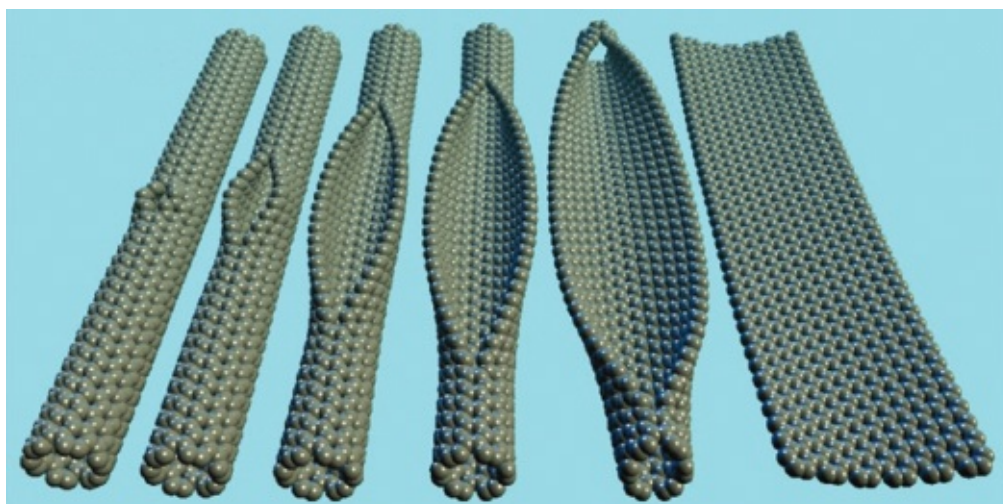


Figure 1.18 Unzipping a carbon nanotube to form a graphene nanoribbon.

Figure from Ref. [110].

1.2.5 Diamond

The electrochemistry of diamond is currently a rapidly growing field, because of the special properties of diamond, such as (i) extreme mechanical hardness, thereby providing an ideal material for ultrasound technology [114, 115], (ii) transparency over a wide spectral range, allowing optical applications [116, 117], (iii) biological compatibility, enabling its use in biological studies and medical applications [118, 119], (iv) apability to be doped to provide

electrical conduction with tunable transport properties [120, 121], (v) very high thermal conductivity, allowing its use as a heat sink for electronic applications [122, 123], (vi) chemical inertness, making it ideal for application in harsh and corrosive environments [124, 125], as well as at high temperature and pressure, (vii) negative electron affinity making it a promising material for active devices, such as field-effect transistors [126, 127], and (viii) the quantum singlet–triplet spin states and N-V defect centers existing in nanodiamond, which open up chances to explore quantum information and quantum physics [128–132].

Highly boron-doped diamond films, which have been widely studied in electrochemistry, can be grown by chemical vapor deposition (CVD) and are electrically conductive. Different electrochemical properties of boron-doped diamond films have been studied, such as reactivity [133] and electronic structure [134]. Different characterization techniques have been used to study the electrochemistry of diamond, such as scanning electron microscopy [123, 135] and Raman spectroscopy [125, 136].

1.2.6 Porous Carbon

Porous carbons constitute a family of lightweight carbon materials with special properties. Porous carbon materials can be made through pyrolysis and by activation of carbonaceous precursors, showing adsorption volumes of $0.5\text{--}0.8\text{ cm}^3\text{ g}^{-1}$ and surface areas of $700\text{--}1800\text{ m}^2\text{ g}^{-1}$, depending upon the activation conditions and activation mechanisms [137]. These materials possess many micropores of varying sizes and thus can adsorb a large variety of molecules in large amounts. In fact, the application of porous carbon dates back to 2000 BCE in Egypt, when charcoals were used to purify water. Nowadays, porous carbons with more controllable micropore sizes and densities, also called **activated carbon**, have been made [138, 139], and well-developed internal surface area and porosity have been achieved [140–142]. Nanocarbon materials, such as graphene, carbon nanotubes, and carbon nanofibers, have also been used as porous aerogels, because of their large surface areas [143–145], and have proven to be useful for applications as composites in supercapacitors, polymers, and energy storage.

1.3 Outlook

Different forms of carbons have different physical and chemical properties, but these different carbon forms are of interest in electrochemical studies and for many applications. Sufficient electrochemical research has already been done on carbon materials to demonstrate their importance in electrochemical energy storage, which is of societal importance. Various experimental techniques have been employed in conjunction with electrochemical methods to characterize carbon-based materials, such as Raman spectroscopy, scanning probe microscopy, electron microscopy, photoelectron spectroscopy, and others. Various manufacturing techniques have also been developed, for commercializing electrochemical carbon-based materials, especially in batteries for energy storage. In particular, nanocarbons, which have unique electrical, mechanical, optical, and chemical properties, have attracted the attention of electrochemists for both fundamental studies of their electrochemical properties and their

exploration for future applications in batteries, electrodes, energy storage, environmental monitoring, and biological and medical science. The nanostructures developed in the last 30 years (carbon nanotubes and graphene) provide a great opportunity for both fundamental research and applications. The morphology of these materials strongly affects their electronic properties, and the recent experimental techniques allow one to monitor and control the nanostructure morphology to constantly increasing degrees, thereby providing a great potential for further research and applications.

In the following chapters of this textbook, different aspects of electrochemical research on carbon materials will be discussed in detail, including carbon electrodes in different applications (fuel cells, molecular electronics, sensing, etc.) using various methods (surface modification, carbon paste, carbon fiber, etc.), and electrochemistry of different carbon materials (graphene, HOPG, carbon nanotube, diamond, etc.).

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Chapter 2

Electrochemistry at Highly Oriented Pyrolytic Graphite (HOPG): Toward a New Perspective

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2.1 Introduction

This chapter is concerned with electrochemistry at, and of, highly oriented pyrolytic graphite (HOPG), a material that has been studied intermittently for several decades, but which is of enduring interest particularly as a comparison to other types of carbon electrodes. Our aim is to give an overview of the field, with a particular focus on recent work that allows key models of the HOPG electrochemistry to be assessed.

Early seminal contributions from the groups of Yeager and Krouse [1] and Gerischer and coworkers [2, 3] primarily considered the capacitive properties of pyrolytic graphite (PG). These studies introduced concepts pertaining to the strong potential dependence of the capacitance of graphite, from which information on the density of electronic states (DOS) was deduced [3]. Even though some voltammetric measurements were made at this time, it was not until the late 1980s to early 1990s that systematic measurements of redox reactions at HOPG were carried out, with extensive studies of HOPG of different grades (bulk and surface quality) reported [4, 5].

A major outcome of these initial studies was that the basal surface of HOPG was characterized by extremely slow kinetics compared to step edges, so that step edges were responsible for most, if not all, of the activity [4]. This view has become ingrained in the electrochemistry community, in textbooks [4, 6] and key reviews [5]. With this *status quo*, a period followed in which there was relatively little work on HOPG electrochemistry *per se*, although HOPG was used prominently as a platform for the deposition of other materials, particularly nanostructures [7–10], as it provided an exemplary flat and well-defined surface (characterized by low background currents) on which complementary microscopy measurements could be carried out alongside electrochemistry.

With the advent of new sp^2 carbon materials, namely carbon nanotubes [11, 12] and then graphene [13–15], HOPG reemerged as an important reference material for electrochemical studies. Prominent work in the early 2000s drew strong comparisons between the electrochemistry of HOPG and multi-walled carbon nanotubes (MWNT), for example, and a popular view emerged that the basal plane of sp^2 carbon was inert for electron transfer (ET), even for classical outer-sphere redox couples [16, 17]. This view of an inert basal surface for outer-sphere ET was extended to single-walled carbon nanotubes (SWNT) for which open oxygenated ends were considered to be the active sites for electrochemistry [18–20]. By contrast, other studies showed that the side wall of SWNTs was highly active for

electrochemistry [21–23]. This difference in the apparent behavior of MWNTs and SWNTs, in different experimental formats, naturally raised questions as to the true behavior of HOPG, because macroscopic measurements may have significant limitations for providing definitive (unambiguous) models for microscopic spatially heterogeneous reactivity, as we show herein.

The emergence of graphene as an electrode material made studies of HOPG even more significant, since some initial reports on graphene (formed by chemical vapor deposition (CVD) [24, 25] and exfoliation [26]) found that graphene displayed higher ET kinetics for various outer-sphere redox couples than in earlier work on HOPG [27–30]. Yet, graphene has a lower DOS than graphite [31]. Within a framework of nonadiabatic ET, one might thus expect graphene to have slower ET kinetics than graphite [32] (and the same kinetics for adiabatic ET) [33–35]. On the other hand, substrate effects (e.g., doping, and changes in morphology, such as wrinkles and ripples [35–37]) may be important in graphene studies, as well as the source of the graphene (e.g., synthesized by CVD vs exfoliated). Other factors such as time from exfoliation/synthesis and surface contamination [38, 39] also require consideration. These issues make a clear understanding of the electrochemical properties of graphite, and particularly the basal plane of HOPG, imperative.

Recent developments in scanning probe microscopy have provided new opportunities to determine the electrical and electrochemical characteristics of graphite (and other sp^2 carbon materials) with unprecedented detail and spatial resolution. These developments receive major attention in this chapter. We begin by providing an overview of the structure and electronic properties of graphite ([Section 2.2](#)). In this light, we assess early electrochemical measurements at HOPG, which tended to rely on macroscopic measurements and correlations between different macroscopic quantities ([Section 2.3](#)). Since many of these measurements have been reviewed extensively [4, 5], most of this chapter discusses more recent electrochemical studies that are able to target particular features of graphite surfaces at high spatial resolution (especially the basal surface in isolation from step edges) and probe the associated electrochemistry ([Section 2.4](#)). This enables microscopic models to be tested rigorously and predictions to be made about the behavior of macroscopic electrodes. These studies highlight new features in the behavior of freshly cleaved HOPG, and also time-dependent (and electrochemical flux) effects that complicate the electrochemical response and analysis of HOPG, with implications for related materials, such as graphene. These recent studies provide new opportunities for understanding fundamental electrochemical processes at graphite, and for the design of optimal graphite-based electrodes, particularly for sensing and energy-related applications. More generally (as highlighted in the [Section 2.5](#)), the new understanding of HOPG electrodes has implications for wider electrochemistry.

2.2 Structure and Electronic Properties of HOPG

2.2.1 Structure and Formation

PG is formed by pyrolysis, whereby a carbonaceous gas, for example, a hydrocarbon such as acetylene, is cracked, generally on a graphite substrate, above 2000 °C. This process results in

a material with a high degree of preferred crystallographic orientation of the c -axis of the microcrystallites (perpendicular to the graphene layer) with respect to the surface of the substrate [40, 41]. To improve the crystallite alignment, stress recrystallization is used. This involves hot pressing with uniaxial pressures of 300–500 kg cm⁻² at 2800–3000 °C and produces specimens more than 10 mm thick along the c -axis, with a density of 2.265 g cm⁻³, >99.95% of the theoretical density of pure single-crystal graphite [5, 40]. Subsequent annealing of such material at 3400–3500 °C under a light load yields HOPG, a polycrystalline material, with multiple layers or graphene sheets stacked on top of each other, and held together by weak attractive intermolecular forces, to make a three-dimensional structure [41–44].

Graphene is a one-atom-thick planar sheet of sp²-bonded carbon atoms that are arranged in a two-dimensional honeycomb crystal lattice, with two crystallographically equivalent atoms in the unit cell, designated A and B ([Figure 2.1a](#)). Each carbon atom in graphene is bonded to each of its three nearest neighbors by a strong planar σ -bond from sp²-hybridized orbitals. At equilibrium, the C–C σ -bonds are 0.142 nm long and are at an angle of 120° to each other [42]. These bonds are responsible for the planar structure of graphene and its exceptional mechanical [47] and thermal properties [48]. The fourth valence electron of carbon, in the half-filled 2p_z orbital, orthogonal to the graphene plane, forms a weak π -bond by overlapping with other 2p_z orbitals [49]. This layered structure results in significant anisotropy in the properties of HOPG. Thus, there is a substantial difference in strengths between planes (easy exfoliable [49], and so used as lubricant) and within the plane (Young's modulus of 1 TPa [47, 50]). Similarly, the conductivity, at room temperature, is of the order of 2×10^4 and $6 \Omega^{-1} \text{ cm}^{-1}$ along and perpendicular to the plane, respectively, with an anisotropy ratio in single-crystal graphite of 10^2 – 10^4 reported [5, 51, 52]. The electrical properties of graphene itself depend on the substrate on which it is supported, defect density and type, and other factors, as described in considerable detail elsewhere [51, 52].

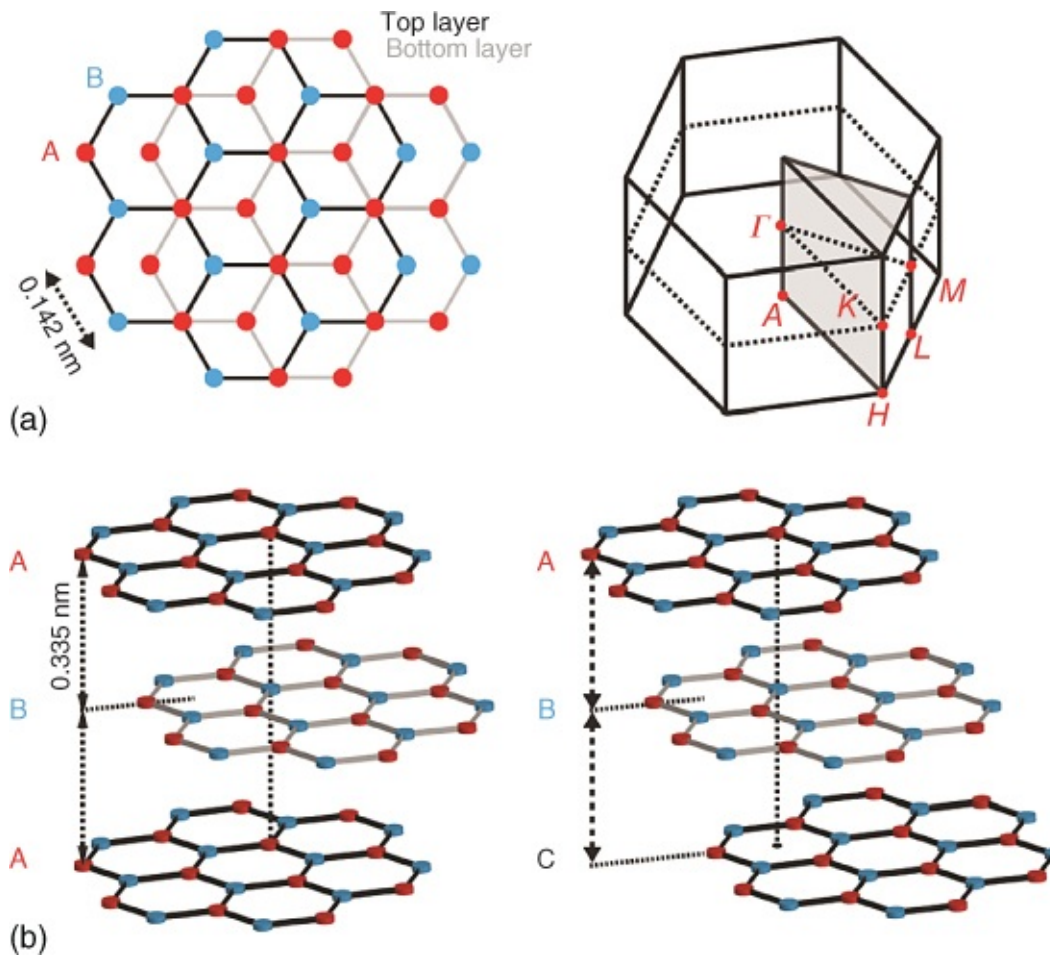


Figure 2.1 (a) Schematics of the graphite crystal structure of AB-stacked graphite and the corresponding Brillouin zone of bulk graphite, together with the labels for special symmetry points. (b) Side views for Bernal (ABA) stacking (left) and rhombohedral (ABC) stacking (right).

(Figure adapted with permission from Refs. [45, 46].)

The graphene sheets in HOPG can adopt two possible arrangements or stacking order: hexagonal and rhombohedral [43], with the type of stacking having important implications for the electronic structure [53, 54], even though the interplane spacing or stacking distance between the layers in both arrangements is 0.3354 nm [42]. Hexagonal or Bernal stacking is the most stable arrangement and the one most observed in HOPG [42]. In the simple case of a graphene bilayer, the A atom of one hexagonal layer is situated directly above the B atom of the other, and is known as **AB stacking**. When a third layer is introduced so that it mirrors the first layer, the resulting arrangement is Bernal, or ABA, stacking (Figure 2.1b). Rhombohedral, or ABC, stacking involves displacing the third graphene layer with respect to the second layer with the same vector as the second layer with respect to the first, such that the A atom in the third layer is directly above the B atom in the second layer (Figure 2.1b). Rhombohedral or ABC stacking is less stable and is found in HOPG or natural crystal graphite in a proportion less than 10% [55].

As a layered polycrystal, HOPG is formed by many graphene monocrystals and graphite flakes or grains of different sizes. The degree of crystallographic orientation of the *c*-axes of these

monocrystals is obtained by X-ray crystallography [56, 57]. A slight misorientation of the graphene layers with respect to each other results in a broadening of the (002) diffraction peak with Cu-K α radiation [56, 57]. Thus, it is common to provide the full-width at half-maximum of the rocking curve, also known as the *mosaic spread*, as a parameter to quantify the degree of perfection of HOPG (or any PG); the lower the angle, the higher the quality of HOPG. For example, pyrolytic carbons have mosaic spread values ranging from 40° to 50°, while HOPG possesses mosaic spreads below 2°. HOPG quality is categorized with a grade terminology that depends on the supplier, with the main ones being GE Advanced Ceramics (GEAC) and SPI Supplies. The highest quality is termed **ZYA** (GEAC) or SPI-1 with mosaic spread of $0.4 \pm 0.1^\circ$. HOPG grades of lower quality are ZYB or SPI-2 (mosaic spread $0.8 \pm 0.2^\circ$), ZYD ($1.2 \pm 0.2^\circ$), and ZYH or SPI-3 grades ($3.5 \pm 1.5^\circ$) (data obtained from SPI supplies and GEAC Web pages). Even though there should be no difference in HOPG between suppliers, it has been reported that ZY crystals (in contrast to the SPI brand) contain sparsely distributed micron-sized particles (e.g., Fe), with typical in-plane separation of 100–200 μm [58, 59]. An exceptional high-quality but ungraded HOPG sample, originating from Dr A. Moore, Union Carbide (now GEAC), termed **AM grade** [38, 60] in this chapter, exhibits a low density of step edges and large basal plane areas, and has been used extensively in some studies (*vide infra*).

HOPG is particularly suitable for providing considerable large areas of pristine, clean atomically flat surfaces by simple exfoliation. The use of Scotch tape to peel off the top layers of HOPG and reveal a fresh surface is the most common procedure [61], but alternative mechanical cleavage procedures are also available [62]. Because of this simplicity in sample preparation, HOPG surfaces have been widely characterized at the atomic level with scanning probe techniques, such as scanning tunneling microscopy (STM) [61, 63] and atomic force microscopy (AFM) [64]. Indeed, HOPG and its monoatomic steps are used as a common material to calibrate such equipment [65].

Atomic resolution images of the graphite basal plane highlight particular technique-dependent features that provide considerable information on the local structure. For STM imaging, for example, basal plane surfaces exhibit a triangular lattice instead of the honeycomb structure that might be expected for the hexagonal crystal lattice of graphite ([Figure 2.1](#)). This is because STM creates images of the local density of electronic states (LDOS) at the Fermi level [66] rather than of the atomic arrangement, thereby revealing the nonequivalence of the carbon atoms on the surface as shown in [Figure 2.2](#), as a consequence of the influence of the underlying layer of graphite structure. With AB stacking, the A atoms in the top layer are stacked above B atoms in the second layer, while B atoms in the top layer are above the hollow sites of the carbon hexagons of the second layer. This asymmetry in the interlayer coupling [61, 67] leads to a strong asymmetry in the LDOS at the Fermi level, yielding STM images where the B atoms on the graphite surface appear more prominent than the A atoms (leading to a triangular lattice [67, 68] or a threefold symmetry “three-for-six” pattern). This behavior is also observed in graphene flakes with two or more atomic-thick layers [31]. In the absence of this interlayer coupling (or for monolayer graphene), all surface carbon atoms are identical, and a symmetrical honeycomb structure is seen in the STM image. For AFM, which

often provides images of true topography [64], all surface atoms can be imaged (under special conditions), leading to images with the expected topography of a honeycomb lattice [69].

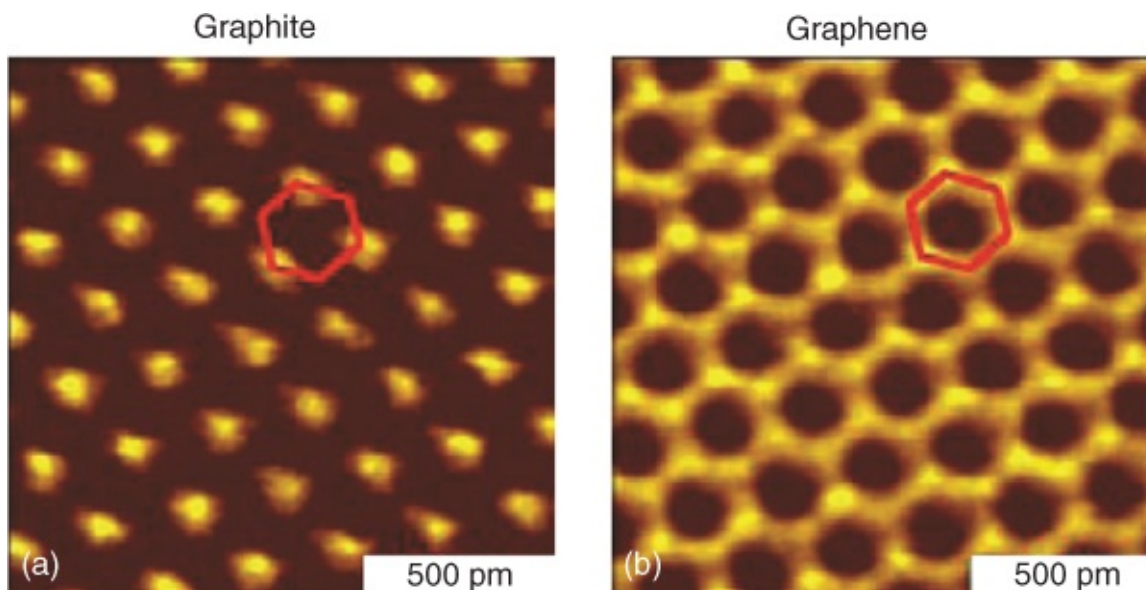


Figure 2.2 Atomic resolution STM images of the surface of (a) graphite and (b) graphene. While the graphite surface shows a triangular structure, the graphene surface exhibits the honeycomb structure with all six atoms in the hexagon vertices visible.

(Figure adapted with permission from Ref. [31].)

When an HOPG surface is examined with AFM on a larger scale, one can discern step edges ranging from single atomic step (well-defined height of 0.335 nm) to several atomic layers [38]. Depending on the HOPG sample quality, that is, the mosaic spread angle and crystallite size, the number of step edges per unit area varies significantly, and this is an important factor of which to take account when considering electrochemistry at HOPG, as we discuss later. Evidently, surface structure in general, and step-edge density in particular, have been considered to play a key role in HOPG electroactivity, even for simple outer-sphere processes [4, 5, 70]. Thus, a deep and precise characterization of the surface structure and properties is essential to establish unequivocal structure–function correlations. This is particularly relevant in studies of the electrochemical activity of HOPG, where the overwhelming majority of previous (early) studies has suggested that HOPG electroactivity is dominated, or controlled entirely, by step edges (edge planes) with the basal plane providing little or no contribution [5, 16, 71–78].

In [Figure 2.3](#), typical tapping-mode AFM images of the surface topography for six different grades of HOPG are presented [38, 60], namely AM, ZYA, ZYH, SPI-1, SPI-2, and SPI-3, mechanically cleaved for AM grade and Scotch tape cleaved for the rest. These images clearly show that on HOPG surfaces, both basal and edge-plane sites can be found, with a very wide range of step-edge densities evident across these different samples. Mechanically cleaved AM-grade HOPG provides by far the most superior surface in terms of low step density, a surface quality that is also obtained when Scotch tape cleavage is employed [38, 79]. The other grades of HOPG show increasing step densities in the order: ZYA, ZYH, SPI-1, SPI-2, and SPI-3. This variety of surface has enabled any significance of step edges on the HOPG

electrode response to be explored and identified as discussed herein ([Section 2.4](#)). Interestingly, SPI-1 grade, used for some cyclic voltammetry (CV) measurements [16, 17], shows a much higher step density than ZYA grade, highlighting the need for AFM topographic analysis, rather than relying only on the values of mosaic spread (which are very similar for these two grades; see above).

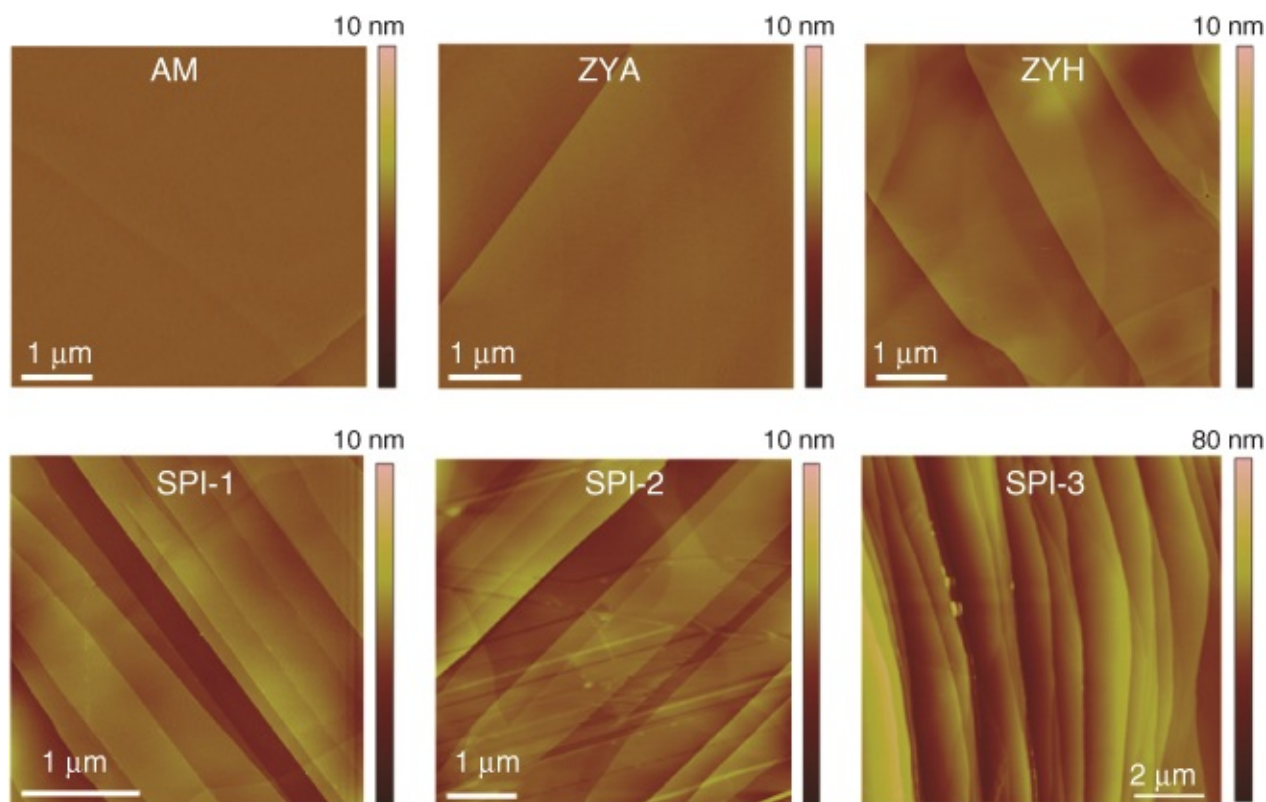


Figure 2.3 AFM images of freshly cleaved HOPG surfaces of different grades, highlighting the significant differences in topographical structure. Note the differences in scale bars (lateral and height).

(Figure adapted with permission from Refs. [38, 60].)

A quantitative analysis of step-edge coverage [38, 60] on these different HOPG grades is summarized in [Table 2.1](#). Step-edge character is defined in two ways: (i) as the step-edge length (μm) in unit area of the surface (μm^2), not taking account of the step height (monolayer, bilayer, etc.) and (ii) as the total step-edge area per unit geometric area of the surface, which takes account of different step-edge heights. These measures highlight the fact that the average step-edge coverage varies significantly across the different grades by more than 2 orders of magnitude, and also that within a grade the range can vary by about an order of magnitude from one area (image) to another.

Table 2.1 Summary of some key properties of different grades of HOPG

	AM	ZYA	ZYH	SPI-1	SPI-2	SPI-3	BPPG
Step-edge density range ($\mu\text{m } \mu\text{m}^{-2}$) from AFM	0.003–0.12	0.1–0.7	0.5–2.3	0.3–3.6	1–3.5	2.5–21.9	—
Mean step-edge density ($\mu\text{m } \mu\text{m}^{-2}$) from AFM	0.02 ± 0.02	0.5 ± 0.1	1.2 ± 0.6	1.5 ± 0.2	2.1 ± 0.9	8.0 ± 5.8	—
Average step-edge coverage on basal plane (%)	0.09 ± 0.09	0.3 ± 0.25	0.8 ± 0.4	1.7 ± 1.6	2.2	30 ± 24	110 ± 5
Step-edge coverage range (%)	0.09–0.48	0.03–1	0.2–2.1	0.5–3.4	0.6–6.7	10.1–78.0	105–120
Capacitance ($\mu\text{F cm}^{-2}$)	2.4 ± 1.5	2.0 ± 0.3	—	2.9 ± 1.2	—	—	—

Data from Refs. [38, 60].

AFM studies [38, 60] have shown that most of the HOPG grades exhibit predominantly monolayer and bilayer steps, with multilayer steps found extensively on the cleaved surface of SPI-3-grade HOPG.

It is also useful to comment on *basal plane pyrolytic graphite* (BPPG), which sometimes appears to be considered as an equivalent substrate to HOPG since the basal graphite plane is exposed [4, 16, 76, 80–84]. However, this form of PG is formed with much smaller crystallite size, as shown in [Figure 2.4a](#) [60]. Thus, although the BPPG surface shows oval basal domains up to 20 nm in height, the sides of these features consist of an abundance of step edges. Interestingly, while *edge plane pyrolytic graphite* (EPPG) has substantial edge character, it has a considerable proportion of basal plane exposed as well, as shown in [Figure 2.4b](#). Thus, there is little difference in the quantity of edge-plane defects between BPPG and EPPG, as judged by Raman spectroscopy [45], with typical spectra also shown in [Figure 2.5c,d](#) [60], despite these materials often being used to compare basal-plane graphite and edge-plane graphite [76, 80–83]. By contrast, under Raman spectroscopy, HOPG is less defective and dominated by the basal surface ([Figure 2.5a,b](#)).

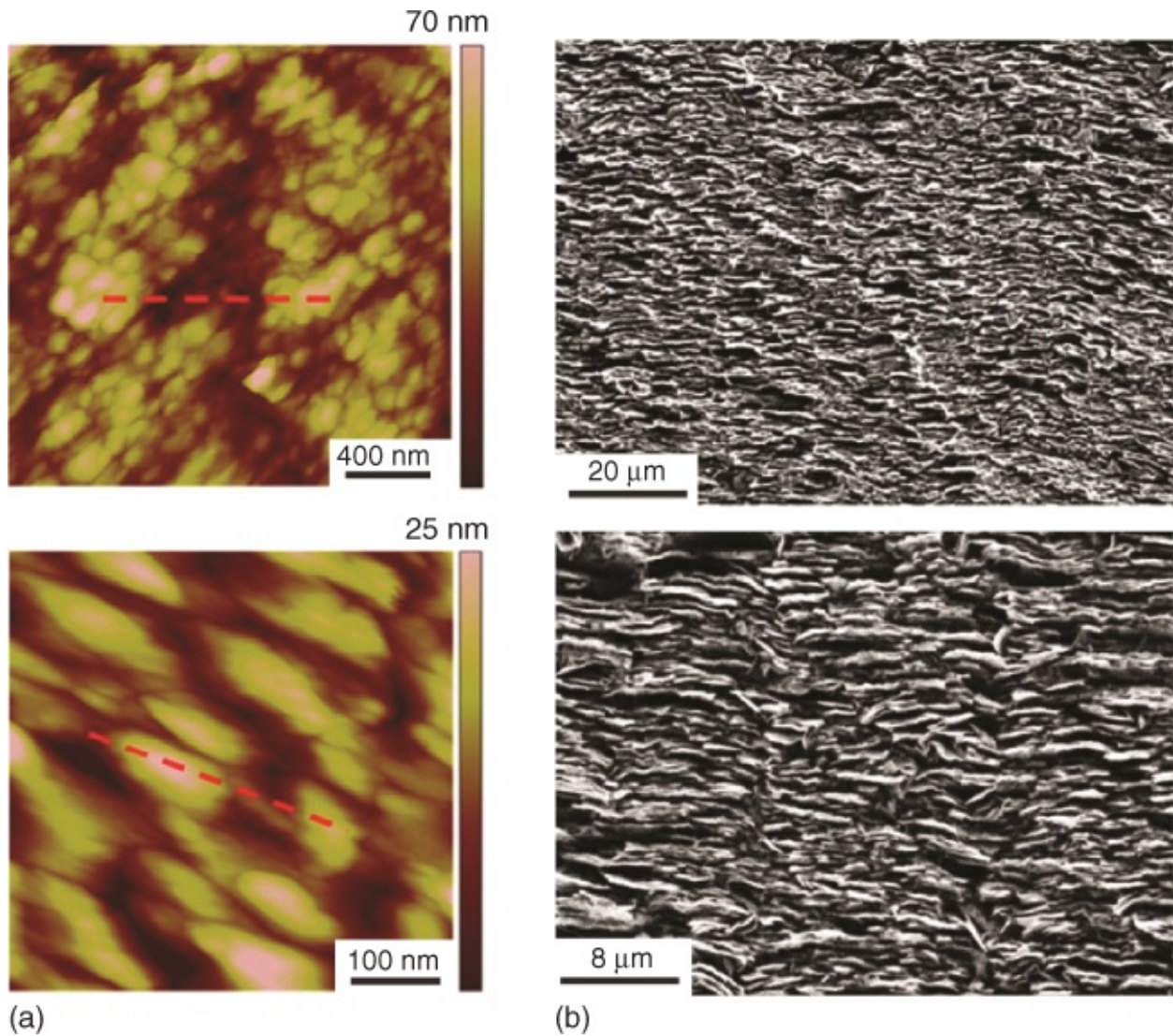


Figure 2.4 (a) AFM images of BPPG and (b) Scanning electron microscopy images of EPPG at different magnifications.

(Figure adapted with permission from Ref. [60].)

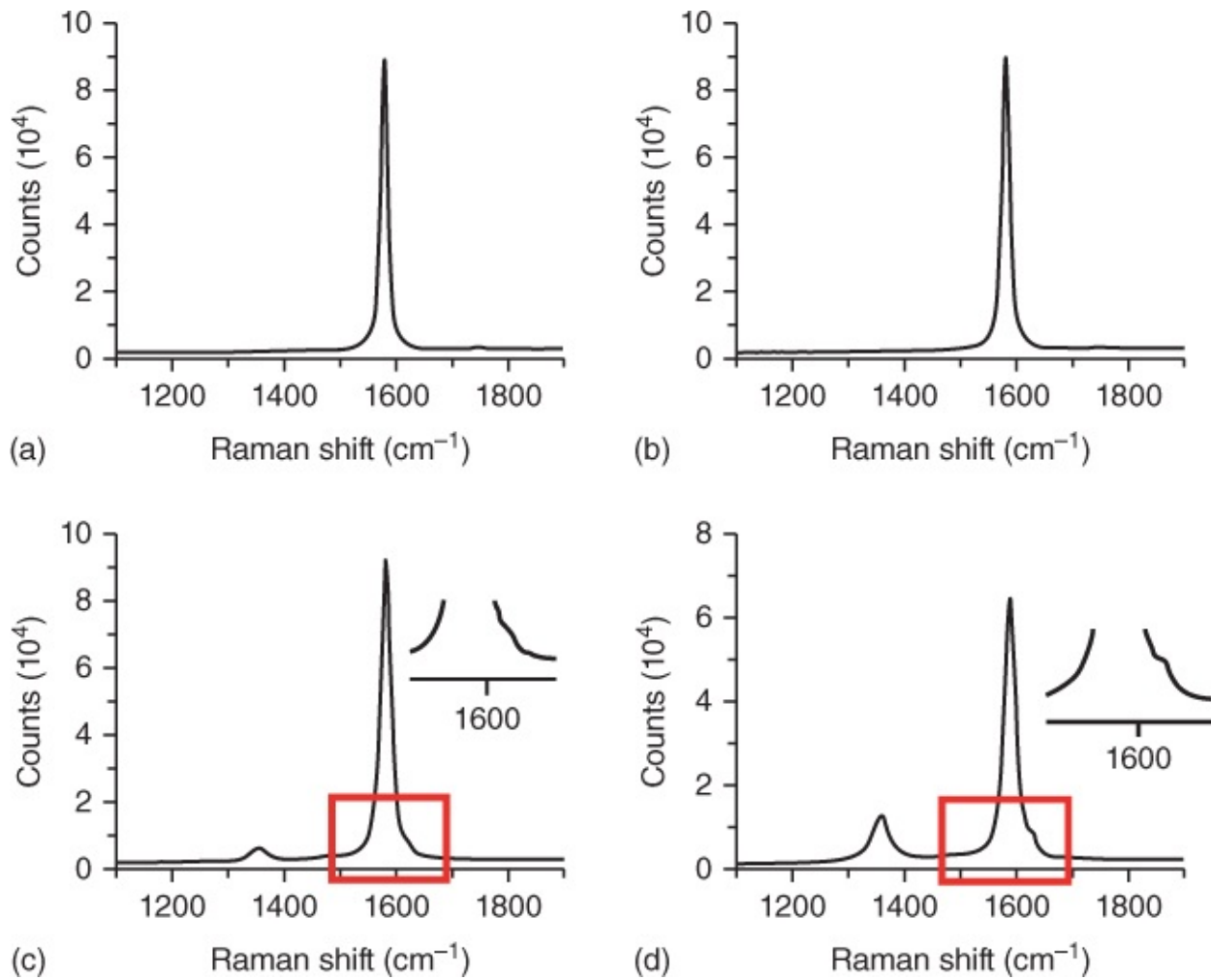


Figure 2.5 Raman spectra acquired on different HOPG grades ((a) AM and (b) SPI-3, (c) BPPG, and (d) EPPG).

(Figure adapted with permission from Ref. [60].)

HOPG crystallite dimensions are usually determined from X-ray diffraction and Raman spectroscopy [4, 40, 41, 51, 85], from which the parameters, L_a and L_c , which correspond to the crystallite dimensions in-plane and perpendicular to the graphene planes, respectively, can be defined. While materials such as carbon black have values down to 10 nm, polycrystalline graphite can have crystallites up to 100 nm, with HOPG exhibiting the largest values, beyond 1 μm . With so much research focused on graphene, it should also be mentioned that multilayered graphene (ultrathin graphite) can be obtained at the wafer scale [86, 87].

2.2.2 Electronic Properties

Each carbon atom in the graphite structure contributes 4 valence electrons, resulting in 16 energy bands, 4 of them π -bands (two bonding and two antibonding) on either side of the Fermi level. In AB-stacked graphite, the separation between the π -bands and σ -bands near the Fermi energy is very large, and the π -electrons thus play a dominant role in the electronic properties of graphite [88]. In simple models of electronic structure to determine the physical properties of graphite, it is often sufficient to consider uniquely the hexagonal planes of carbon atoms

with a weak interaction between the layers. This is reflected in the band structure models for graphite, first developed by Wallace [89] in 1947, and subsequently modified by Slonczewski, Weiss, and McClure [90, 91]. The SWMcC model considers graphite as stacked layers of graphene linked by weak forces [51, 92]. In a given plane, the π -orbitals in the electron network are responsible for the electronic high mobility of graphite [52, 93, 94].

The model for graphite band structure was developed, and complemented, by Johnson and Dresselhaus (JD) [95] and unified by Tatar and Rabii [96]. Recently, new terms have been introduced [97] to provide a better description of the interaction between layers (stacking order), since these are crucial to the electron properties [53, 54, 88, 98]. In the case of single-layer graphene, the valence and conduction bands just touch at the K point of the Brillouin zone, leading to a zero-gap semiconductor. By contrast, for bilayer graphene, the interaction between the B carbon atoms of next nearest neighbor planes [88, 91] yields an overlap between the bands of about 0.16 meV. With an increasing number of graphene layers, the band structure is more complex [46] (Figure 2.6a) and at the K point the overlap reaches about 41 meV for graphite [88], conferring the semimetallic behavior that has been observed experimentally [88, 99].

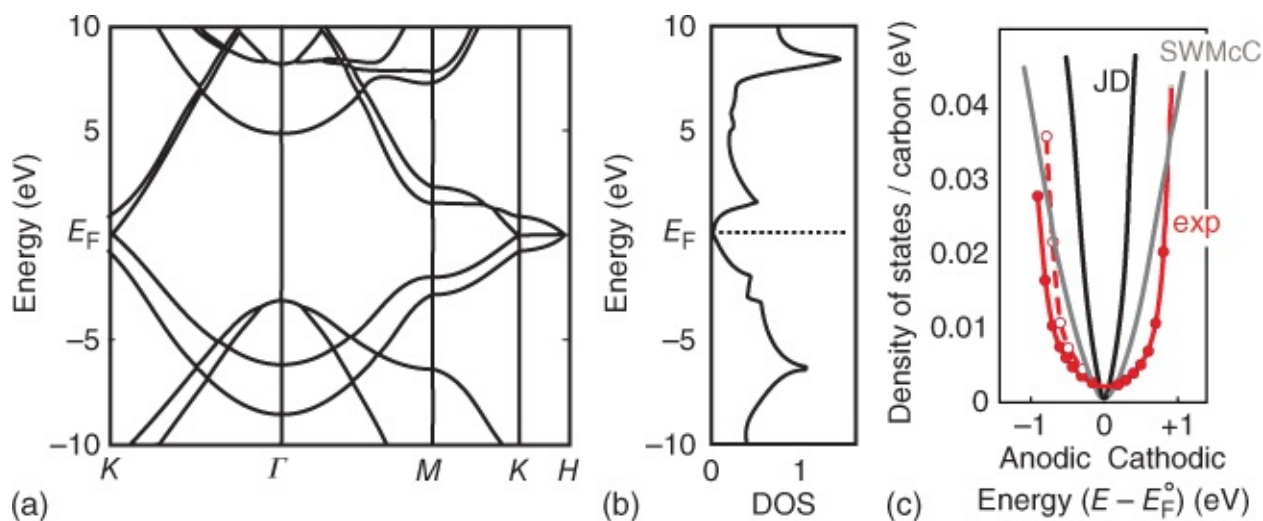


Figure 2.6 (a) Graphite electronic band structure along high-symmetry lines in the Brillouin zone. (b) Electronic DOS of graphite. (c) Curves representing the DOS for pyrolytic graphite determined by Gerischer using capacitance measurements, compared with the curves obtained by the SWMcC and JD models for energy bands near the H - K axis.

(Figure adapted with permission from Refs. [[3, 46]].)

A particular feature of the band structure of HOPG is that around the intrinsic Fermi level, the DOS is low (Figure 2.6b) [88], about $0.0022 \text{ states atom}^{-1} \text{ eV}^{-1}$ [2, 3]. This contrasts with metals such as Au, for which the DOS is around $0.28 \text{ states atom}^{-1} \text{ eV}^{-1}$ and more or less constant for a wide range of energies [100]. An important – and still open – general question in electrochemistry is whether (and when) the DOS of metal (and metal-like) electrodes is important in determining ET kinetics [34, 101–106] and whether the low DOS of graphite has a particularly significant effect [5].

The low DOS of graphite, near the intrinsic Fermi level, leads to a low interfacial capacitance

between a graphite electrode and an aqueous solution, of the order of a few $\mu\text{F cm}^{-2}$ [38, 60, 74, 107–109], compared with metal electrodes that exhibit values of at least 1 order of magnitude larger, for example, Hg $27 \mu\text{F cm}^{-2}$ [110]. Randin and Yeager [107–109] obtained capacitance–potential curves for PG, which showed a parabolic character around a minimum located at the point of zero charge (PZC). Subsequently, Gerischer and coworkers [2, 3] demonstrated a relationship between the interfacial capacitance and the DOS, using as an analogy to the space-charge capacitance model for a semiconductor/electrolyte contact, and calculated values for the DOS as a function of potential around the intrinsic Fermi level of similar order as for the SWMcC model ([Figure 2.6c](#)). Graphite was treated as a solid semiconductor with a limited density of mobile charge carriers, and the capacitance was represented as two capacitors in series: the space-charge capacitance inside the solid and the electrolyte capacitance (that was split into the Helmholtz double layer and the diffuse double layer). However, despite the reasonable comparable trends of experimental data and theory, the question naturally arises as to whether it is reasonable to treat graphite as a semiconductor when it possesses a finite DOS at the Fermi level.

The use of quantum capacitance [111, 112] serves to provide a quantitative explanation of the interfacial capacitance–potential characteristics of graphite and other carbon electrodes, with the charge carrier concentration playing an important role. The capacitance exhibits a symmetric linear dependence on potential with respect to the Dirac point (DP), where there is a minimum, as evident from experiments performed on single-layer graphene [112, 113]. Alternative approaches have used density functional theory to simulate the response of the basal plane of graphite toward an external field [114], avoiding the need to treat graphite as a semiconductor. The study of the field penetration into the surface, combined with a hard-sphere electrolyte model [115], allows the experimental capacitances to be explained quantitatively, without any adjustable parameter. The model is also applicable to metal electrodes.

The DOS at graphitic materials can be modified due to disorder in the crystal structure, and by the presence of step edges [116], local defects [117, 118], dangling bonds [119], or rotation/detachment of the graphene planes due to the turbostratic nature of HOPG [120, 121]. These surface modifications result in defect states with energies between the conduction and valence bands, modifying the DOS near the intrinsic Fermi level. However, most of these modifications (step edges, local defects) are very much localized and are only detectable if high-resolution techniques, such as STM/scanning tunneling spectroscopy (STS), are employed. For these defects to have an effect on the overall DOS of macroscopic HOPG samples, they must be found in relatively large quantity. This is not usually the case; for example, the point defect density for cleaved HOPG is estimated to be in the range $0.1\text{--}10 \mu\text{m}^{-2}$ [122–127].

The nature of defects on HOPG can be studied particularly well by STM, especially as a means of highlighting any differences in the LDOS. As mentioned earlier, STM produces images that are influenced by the electronic states of the surface being studied. Most significantly, STS [128] can be used to obtain a spectrum of the DOS as a function of the electron energy by measuring the electron tunneling current (I) while the voltage (V) between

an STM tip and HOPG sample is swept. The slope of the resulting I – V curve (dI/dV) at a particular potential is proportional to the LDOS [128].

Niimi *et al.* [116] determined the LDOS on graphite step edges of different chirality (zigzag or armchair) and confirmed the existence of a “graphite edge state” predicted by Fujita *et al.* [129]. In [Figure 2.7a](#), the bias dependence of the tunneling conductance (dI/dV) shows a clear enhancement in the LDOS at zigzag edges, compared to the basal surface, but not at the armchair edges. In view of this information, for this step-edge enhancement to noticeably affect the overall DOS of HOPG (by 20%), the step spacing of zigzag edges needs to be less than 4 nm [116]. Thus, one would not expect significant differences in the overall DOS of different HOPGs, since such a high step density is not found on any grade of HOPG, except perhaps for SPI-3 grade, and even here the armchair edge most likely dominates.

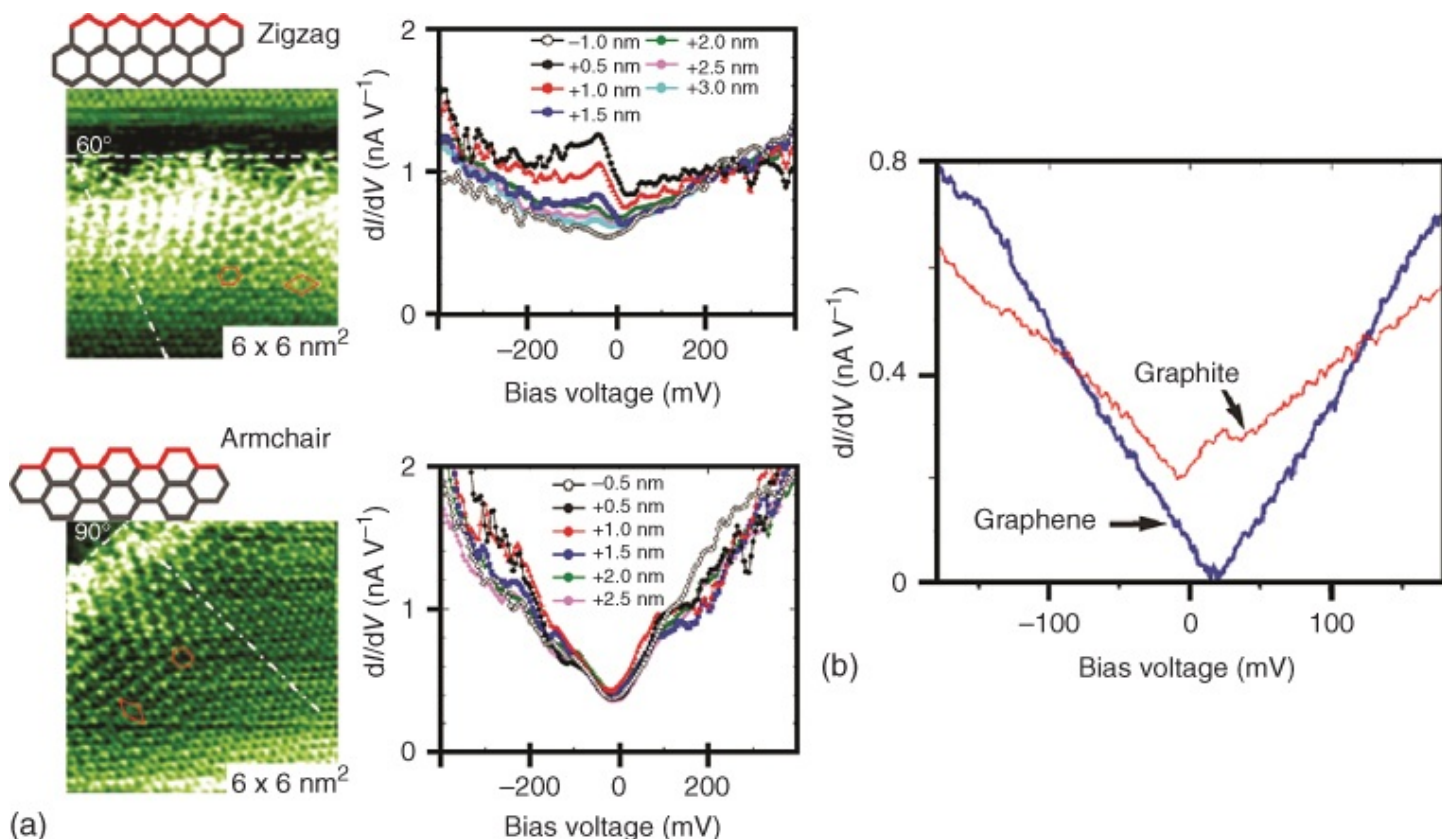


Figure 2.7 (a) STM images and STS spectra near monoatomic steps of an HOPG sample with zigzag edge (top) and armchair edge (bottom). The color key on the spectra assigns the lateral distance of the tip from the step edge. (b) STS spectra of graphene and graphite, showing a finite differential conductance at the neutrality point for graphite, consistent with the finite DOS.

(Figure adapted with permission from Refs. [116, 130].)

While basal plane HOPG presents capacitance values of $>2 \mu\text{F cm}^{-2}$ in aqueous electrolytes [38, 60, 112, 113], other graphite-like materials have much higher values, such as EPPG ($60 \mu\text{F cm}^{-2}$ [75]) and glassy carbon (GC) ($24\text{--}36 \mu\text{F cm}^{-2}$ [131]). In these cases, most of the measured capacitance values can be assigned to the high concentration (density) of oxygen-containing surface functionalities on such materials and the relatively high specific surface

area of such electrodes (even when finely polished), with geometric area usually used to define the capacitance per unit area. Thus, although it has been proposed that capacitance measurements can be used to characterize HOPG quality [38, 60], as shown in [Table 2.1](#), such measurements are not definitive. As shown in this section, techniques such as AFM, STM, and Raman spectroscopy are needed to complement the categorization of HOPG quality.

HOPG can also exhibit macroscopic defects. As a layered material, there is a possibility of decoupling of the graphene layers, which affects the electronic structure, in general, but especially at the intrinsic Fermi level, leading to a decrease (or lack) of DOS. This is exemplified in [Figure 2.7b](#), where STS spectra for graphite and a single layer of graphene (graphite sample with the top layer decoupled) are shown [31, 130]. For graphene, the DOS has a V-shape and vanishes at the DP, while for two or more graphene layers the coupling produces additional states at the DP leading to a finite DOS [132], as discussed earlier in this section.

Other common defects or “faults” in HOPG are related to the stacking order. Rhombohedral (or ABC) stacking can strongly modify the band structure [54], as can the rotation of graphene layers relative to each other. This last fault is usually observed by STM as a superstructure or Moire pattern [67, 133] ([Figure 2.8](#)). The twisting away from Bernal stacking yields a wide range of rotation angles, which results in a rather complex electronic band structure [120, 121, 134].

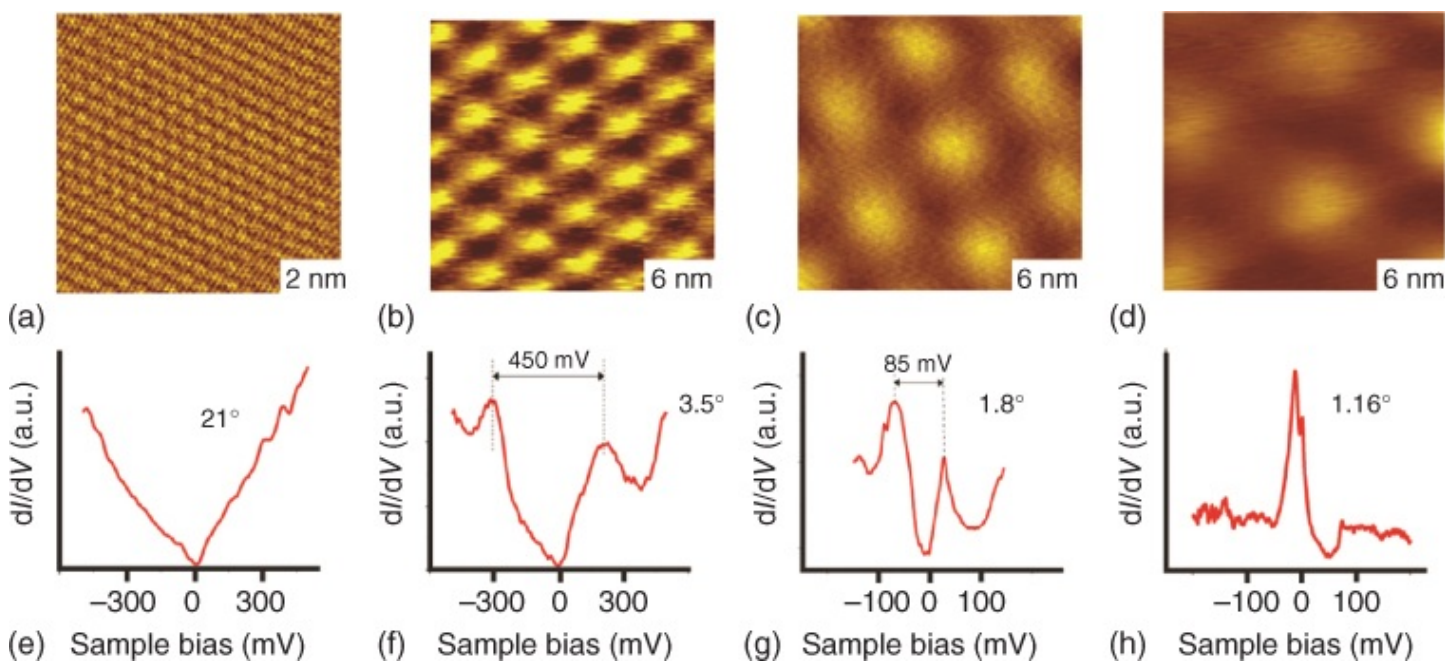


Figure 2.8 (a–d) Set of STM images and (e–h) the corresponding STS spectra of HOPG samples that exhibit Moire patterns due to the existence of a twist angle (indicated) between the top graphene layer and the layer immediately underneath.

(Figure adapted with permission from Ref. [134].)

2.2.3 Implications for Electrochemical Studies

It is evident from the foregoing that cleaved HOPG, although dominated by the basal plane, has

microstructure (and associated disturbances of electron density) that may (or may not) be important for electrochemistry and particular electrochemical reactions. Understanding the impact of this structure on electrochemistry requires that measurements can be made in small regions where the electronic structure being probed is well defined. This demands the use of microscale/nanoscale techniques on known regions of the surface. Alternatively (and with complementarity), macroscopic measurements may be valuable, but need to be carried out across different grades of HOPG and under conditions where the measurement timescale is varied over a wide dynamic range to tune in/out sites with potentially different reactivity. Even so, the analysis of macroscopic measurements will be complicated by the fact that step-edge density (for example) will typically vary locally by up to an order of magnitude on a particular cleaved surface ([Table 2.1](#)). Thus, if the activity is structure dependent, and the reaction involves a diffusional component, the activity will vary spatially in a nontrivial way that will be difficult to model, even with partially active electrode schemes that presently tend to adopt rather idealized views of heterogeneous activity [16, 135–137]. Interestingly, for nanotube network electrochemistry, random array models have been developed that could be applied more widely [138].

A further issue that we discuss herein, and which has been touched on in several studies [38, 139–141] is that the electronic properties (and hence structure) of HOPG surfaces, as well as the electrochemistry, should be viewed as *dynamic* (time dependent), following HOPG cleavage. This arises for several reasons. First, planar sp^2 carbon (graphene, graphite, etc.) is notorious for the adventitious adsorption of atmospheric contaminants, which impacts various properties from wetting [39, 142] to electrochemistry [38, 60]. Second, after cleavage, the exposed surface layers undergo other changes, such as oxidation at reactive dangling bonds [122, 143] and there is also the possibility of delamination and detachment of some flakes, as viewed in conductive AFM [38] or STM [31]. These factors mean that electrochemical measurements of HOPG should be made immediately after cleavage (on a freshly cleaved surface), but also that the time evolution of activity is of interest to truly understand this material and its activity. On the other hand, the time evolution of behavior could well be influenced by the HOPG grade, method of cleavage, and environment (solution and chemical purity) in which measurements are made.

A significant issue for HOPG (and other sp^2 carbon materials) is that it is difficult to assess the cleanliness of the surface, compared to other (metal) electrodes, such as platinum, where the structure and cleanliness of the surface can be identified to a high level via voltammetry [144]. As such, measurements on freshly cleaved surfaces, for the present, provide the best insight into the baseline activity for HOPG.

2.3 Formative Studies of HOPG Electrochemistry

2.3.1 Early Macroscopic Voltammetric Measurements and Correlations

Some of the earliest electrochemical studies of redox reactions at graphite found that the

apparent standard rate constant, k^0 , for several redox processes, especially the ferri/ferrocyanide redox couple, $\text{Fe}(\text{CN})_6^{3-/4-}$ in aqueous solution, were extremely variable (by many orders of magnitude) even on the same grade of HOPG [71]. It was therefore postulated that the reactions could be driven by surface defects [4, 5] and so surface modification procedures were introduced, sometimes accompanied by Raman spectroscopy, to determine the relationship between carbon microstructure and heterogeneous ET [71, 145, 146]. Increased edge-plane density (as revealed by Raman spectroscopy ($\sim 1360 \text{ cm}^{-1}$ band or D band)) appeared to correlate with increased ET rate ([Figure 2.9](#)), from which it was concluded that the basal surface of HOPG was essentially inactive or of very low activity, with edge-plane defects providing essentially all of the activity. Indeed, it was proposed that $\text{Fe}(\text{CN})_6^{3-/4-}$ could be used to probe the step-edge density of graphite surfaces and this has become a popular method [4, 5, 16, 17, 70, 77, 78] to assess the quality of HOPG (*vide infra*) between different experiments. However, it is important to comment on the usefulness of Raman analysis for HOPG samples, as Raman spectra can only highlight relatively high-defect samples. Many different grades of HOPG yield the same defect-free spectra (see [Section 2.2.1](#)) [60].

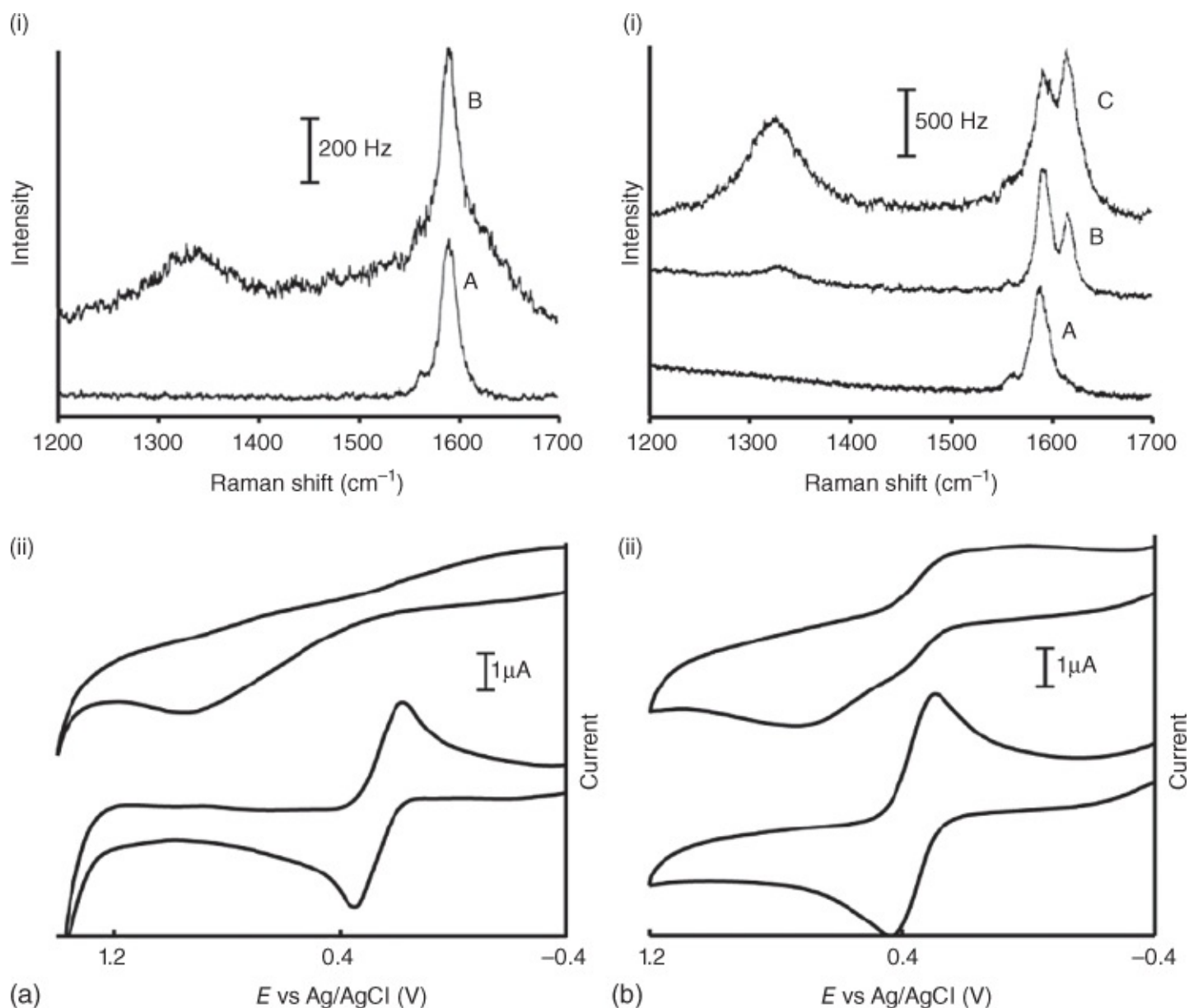


Figure 2.9 (a)(i) Raman spectra of laser-treated HOPG (three pulses, 50 MW cm⁻²): (A) off the laser and (B) on the laser spot. (a)(ii) Corresponding CVs of Fe(CN)₆^{3-/4-} (1 M KCl), 200 mV s⁻¹, on untreated (upper curve) and laser-treated (lower curve) AM-grade HOPG. (b)(i) Raman spectra obtained in air after electrochemically pretreating HOPG for 2 min in 0.1 M KNO₃ solution at different potentials, 1565 cm⁻¹ peak is dioxxygen: (A) 1.6 V; (B) 1.85 V; and (C) 1.95 V vs Ag/AgCl. (b)(ii) Corresponding CVs of Fe(CN)₆^{3-/4-} (1 M KCl), 200 mV s⁻¹ on AM-grade HOPG after 1.85 V electrochemical pretreatment (ECP) (upper curve) and 1.95 V ECP (lower curve). The intensity of the Raman D band, which indicates edge and defect sites, yields comparable results for the two surface activation procedures, laser activation and ECP, with ECP generating more surface oxides than laser activation.

(Figure adapted with permission from Ref. [71, 146].)

The early apparent correlation between step-edge density and k^0 for the Fe(CN)₆^{3-/4-} redox couple led to the use of this couple as an electrochemical “validation” standard to identify low

surface-defect density of HOPG electrode surfaces [73]. Thus, before many electrochemical measurements on HOPG, voltammetry for this couple was run first, followed by the investigation of interest. Typically, this involved taking a freshly cleaved piece of HOPG that was placed onto a conductive metal plate with powdered graphite/Nujol paste serving to ensure good electrical conductivity [74]. A drop of solution was placed onto a reference electrode/counter electrode assembly, which was then lowered onto the HOPG electrode surface. The effective electrode area was determined by $\text{Fe}(\text{CN})_6^{3-/4-}$ chronoamperometry. The experimental setup is known as the ***inverted droplet cell*** [72–74]. This type of cell is considered to be essential for studies of HOPG, to avoid mechanical stress that could induce defects. We note that some studies have used cells where the HOPG sample can be subjected to considerable pressure [16, 77, 78, 147], and this can easily result in surface damage and sample deformation.

CVs of 1 mM $\text{K}_4\text{Fe}(\text{CN})_6$ in 1 M KCl solution resulted in a mean peak-to-peak separation, ΔE_p , of 459 ± 331 mV and a voltage range of 58–1200 mV, even on the same grade of HOPG which corresponds to the standard rate constant (for the entire surface) changing by at least 6 orders of magnitude [72–74]. This immediately raises questions as to the validity of this couple as a measure of step density because as shown earlier ([Section 2.2.1](#)), the step-edge density within a particular grade of HOPG only varies by 1 order of magnitude at most. Nonetheless, it was concluded that the different ΔE_p reflected the amount of surface (edge) defects present, with large ΔE_p corresponding to low defect density. In order to “validate” an HOPG surface as being low in defects, a voltammogram of $\text{Fe}(\text{CN})_6^{3-/4-}$ with $\Delta E_p > 700$ mV at 0.2 V s^{-1} was regarded as mandatory, before the drop of $\text{Fe}(\text{CN})_6^{3-/4-}$ solution was replaced with one of the redox systems of interest. Surfaces that resulted in $\Delta E_p < 700$ mV were discarded and considered to be highly defective [75, 148]. It is important to note that even though $\text{Fe}(\text{CN})_6^{3-/4-}$ is often used as a benchmark, it is notorious for various surface interactions and nonideality [5, 149, 150], notable degradation with time and exposure to light. It is by no means a “simple” or well-behaved redox couple [5, 151].

In the significant body of work from McCreery *et al.* [152, 153], comparisons were often made between the electrochemical activities of the highest quality (low step-edge density) AM-grade HOPG and laser-activated GC. For eight quasi-reversible one-electron redox systems, the GC rates were 1–5 orders of magnitude higher than those measured for $\text{Fe}(\text{CN})_6^{3-/4-}$ “validated” AM-grade HOPG samples and this effect was attributed to the high density of edge sites on GC and the low DOS of HOPG [73]. [Figure 2.10](#) summarizes k^0 values for the eight redox systems on GC and HOPG, correlated with their self-exchange rates, k_{exc} , in homogeneous solutions [73]. Marcus theory, the simplest form of the relationship between $\log k^0$ and $\log k_{\text{exc}}$, predicts a linear relationship with a slope of 0.5 [73] ([Figure 2.10](#)). Most of the GC values are diffusion limited (reversible) and therefore this correlation could not be observed. By contrast, consistently lower values were observed for HOPG, but the correlation of $\log k^0$ with $\log k_{\text{exc}}$ was weak, with a slope of 0.29 rather than 0.5.

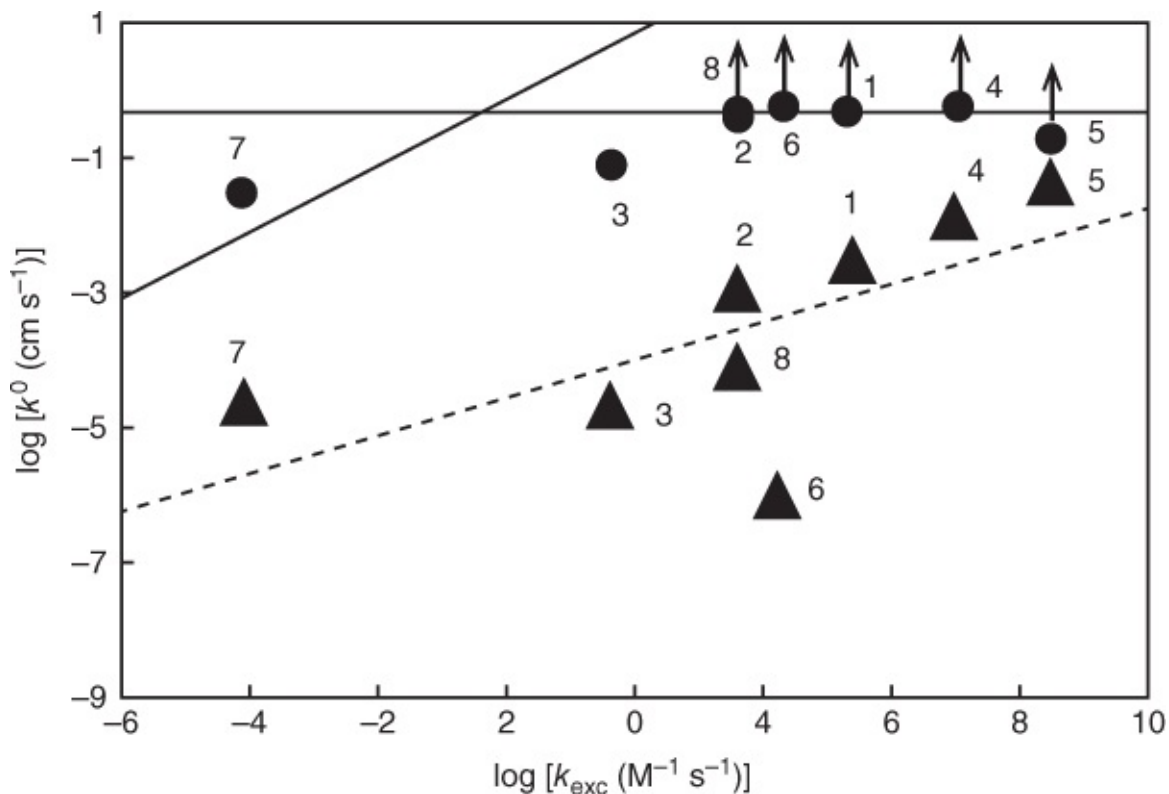


Figure 2.10 Log-log plot of k^0 for “validated” AM-grade HOPG (triangle) and laser-activated GC (circles) versus k_{exc} for eight redox couples. The horizontal line indicates the instrumental limit for k^0 determination, the dashed line is the least-square fit for the HOPG data, with slope = 0.29 and the solid line is from the proposed simple form of the relationship between k^0 and k_{exc} predicted by Marcus theory. Redox systems are (1) $\text{IrCl}_6^{2-/3-}$, (2) $\text{Ru}(\text{NH}_3)_6^{3+/2+}$, (3) $\text{Co}(\text{phen})_3^{3+/2+}$, (4) methyl viologen, (5) $\text{Fe}(\text{phen})_3^{3+/2+}$, (6) $\text{Fe}(\text{CN})_6^{3-/4-}$, (7) $\text{Co}(\text{en})_3^{3+/2+}$, and (8) $\text{Ru}(\text{en})_3^{3+/2+}$, where phen is phenanthroline and en is ethylenediamine.

(Figure adapted with permission from Ref. [73].)

Rice *et al.* [75, 131] investigated the impact of laser ablation of HOPG on the resulting capacitance, C^0 , and k^0 for $\text{Fe}(\text{CN})_6^{3-/4-}$. Over a power density range of 0–130 MW cm^{-2} (three 9 ns pulses from an Nd:YAG laser operating at 1064 nm), k^0 increased by more than 5 orders of magnitude while C^0 increased by a factor of 8 [75, 154, 155] (Figure 2.11). However, capacitance values $>3 \mu\text{F cm}^{-2}$ have been considered to indicate rather defective surfaces [4, 5, 75]. Moreover, the ablation treatment, while creating defects, could easily clean the surface or remove poorly attached (resistive) flakes on the HOPG surface. In this work, it was concluded that the apparent correlation of k^0 and C^0 , by inference, indicated a correlation of k^0 and step-edge density. However, more recent studies on the double-layer capacitance of graphite suggest that capacitance is a weak indicator of surface quality [114, 156].

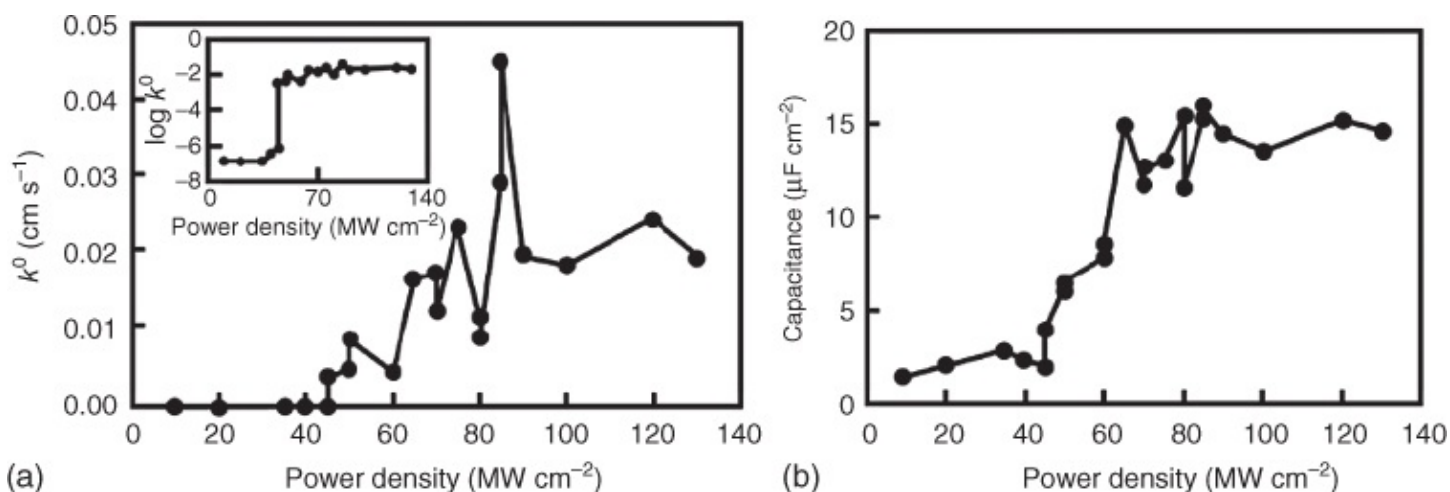


Figure 2.11 (a) Observed k^0 for $\text{Fe}(\text{CN})_6^{3-/4-}$, calculated from CV measurements with the Nicholson method [155] (inset shows same data with a logarithmic ordinate). (b) Observed capacitance, C^0 , for laser-modified HOPG/aqueous electrolytes, determined from semi-integral voltammetry [154], as a function of laser activation power density. Each voltammogram was taken after cleavage of the HOPG surface and three 9 ns laser pulses in air.

(Figure adapted with permission from Ref. [75].)

Other macroscopic correlations have been proposed between the surface coverage, Γ_{ads} , of electroactive adsorbates with k^0 for $\text{Fe}(\text{CN})_6^{3-/4-}$, C^0 , and, by inference, the step-edge density. However, the only attempt to correlate step-edge density measured directly (by STM) and Γ_{ads} of electroactive adsorbed AQDS (anthraquinone-2,6-disulfonate) focused on a very narrow range of step densities on cleaved HOPG samples (mean values from 0.7% to 1.6%), and there was a relatively high uncertainty in the absolute step-edge density such that the errors associated covered the entire range studied [123]. Moreover, it is important to point out that the apparent correlation between the measured step-edge coverage and the AQDS adsorption required 30 times the step-edge area than could be accounted for by the steps alone, and it was proposed that there was a pronounced electronic disturbance extending 5 nm from the step edges, where electrochemistry could occur, with no electrochemistry on any other part of the basal surface [70]. To support this, a constant-height STM image was reported, which showed higher current at the edge over such a distance. However, this measurement is ambiguous because the higher current could come from an edge that was slightly detached from the surface. Moreover, this result is not in accord with what is now known about the LDOS at HOPG step edges, where only zigzag edges have a higher LDOS, and only over a distance of about 1 nm, with little change in the LDOS at armchair edges (see [Section 2.2.2](#)).

It was later shown by AFM imaging [148, 157] that the adsorption of AQDS showed full coverage across the entire HOPG surface, but this did not correlate with the surface coverage calculated from voltammograms that measured the amount of adsorbed AQDS. It was therefore suggested that AQDS adsorption occurred indiscriminately on the basal plane and step edges, but only adsorbate present at step edges was electrochemically active [148, 157]. We discuss more recent studies of this system in [Section 2.4.3](#).

2.3.2 Macroscopic Voltammetry and Modeling

In later work it was proposed that HOPG is a “unique” electrode material given that even though the basal surface conducts electricity easily, it is an electrochemically inert material [16, 17]. The CV response was analyzed numerically with linear diffusion simulations (DigiSim[®]), along with finite-difference simulations on a heterogeneous HOPG electrode with some spatial zones (edges) being more active than others (basal surface), resulting in an “array of microelectrodes” [16, 17, 158], with the basal to edge-plane ratio depending on HOPG quality. This “partially blocked” electrode model was used to analyze the CV response, as a means of deducing the fractional coverage of step edges on HOPG electrode surfaces [16].

Figure 2.12a shows a CV for the oxidation of $\text{Fe}(\text{CN})_6^{4-}$ recorded on EPPG and another at a cleaved surface of HOPG [16]. The best result of fitting the experimental HOPG voltammogram to the linear diffusion simulation (DigiSim[®]) is shown in Figure 2.12b. Both the experimental forward and back peaks are wider than predicted theoretically and the experimental back peak is significantly smaller than predicted. This poor experimental fit was previously observed by McCreery *et al.* [74] who, at the time, attributed the voltammetric behavior to a potential-dependent transfer coefficient on a homogeneous surface. Even though this resulted in a better fit between simulation and experiment, there is no obvious theoretical basis for a potential-dependent transfer coefficient.

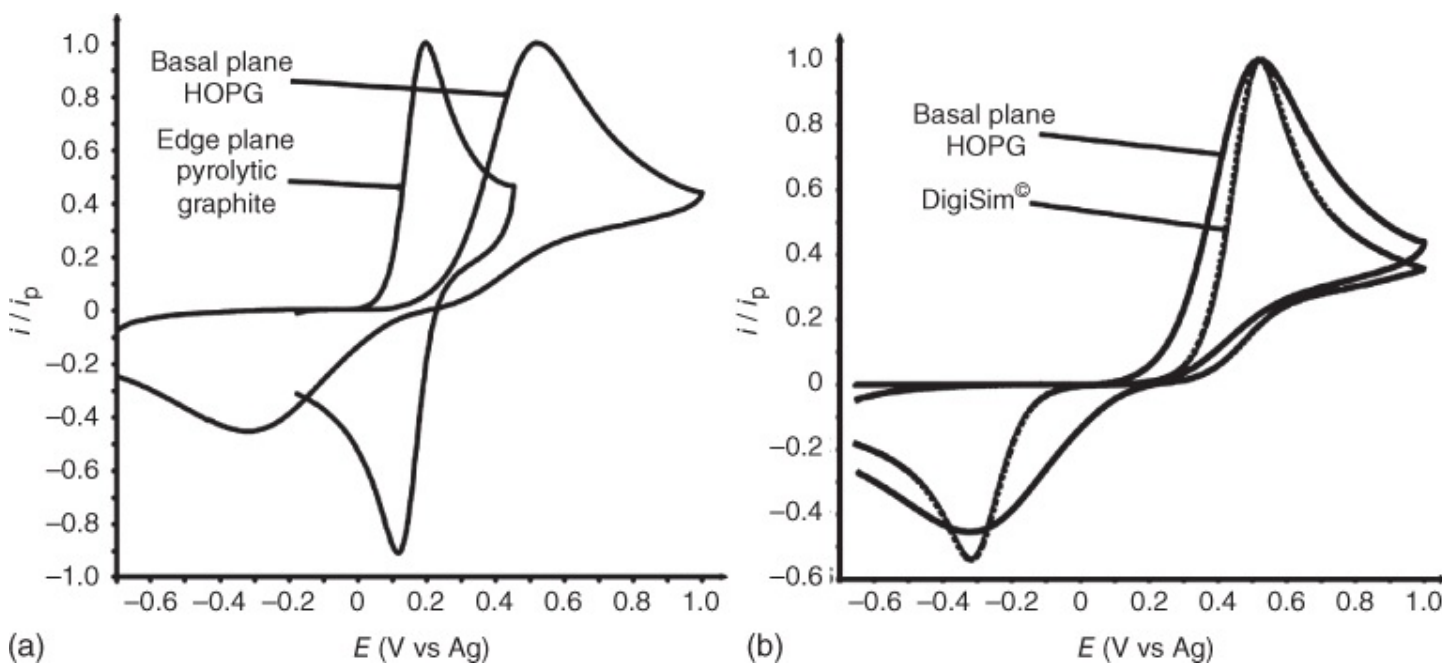


Figure 2.12 (a) CVs recorded at EPPG and basal plane HOPG. (b) Comparison of the basal plane HOPG voltammograms with the best fit to linear diffusion CV simulations for the oxidation of 1 mM $\text{Fe}(\text{CN})_6^{4-}$ (1 M KCl) at 1 V s^{-1} .

(Figure adapted with permission from Ref. [16].)

Compton *et al.* [16, 17, 82] reconsidered this problem by attributing the voltammetric wave shape to the structural heterogeneity of HOPG. This work concluded that the oxidation of

$\text{Fe}(\text{CN})_6^{4-}$ only occurs at HOPG step edges, with the k^0 for the basal plane $<10^{-9} \text{ cm s}^{-1}$, at least 10^7 times lower than at the edge planes, such that the basal plane had essentially no influence on voltammetry. However, this model could not be used quantitatively to determine the edge-plane coverage of cleaved HOPG surfaces, because in order to model the data, the edge-plane coverage applied theoretically had to be 100 times smaller than the actual step-edge coverage value (from AFM). It is important to point out that these conclusions, while widely adopted, seem to have been reached using just one voltammogram [16, 17, 82].

2.3.3 Alternating Current (AC) Voltammetric Methods

Bond *et al.* studied the $\text{Fe}(\text{CN})_6^{3-/4-}$ couple at ZYH-grade HOPG electrodes. Great irreversibility was found, with extreme $\Delta E_p > 1 \text{ V}$ in CV measurements ([Figure 2.13a](#)). When the surface was maltreated by hand polishing or by cleaving with a glass pipette tip to introduce defect sites onto the HOPG surface, a “mini cyclic voltammogram” appeared in the voltammogram ([Figure 2.13b](#)) and this was attributed to fast $\text{Fe}(\text{CN})_6^{3-/4-}$ electrochemistry at the edge-plane defects in this region [78].

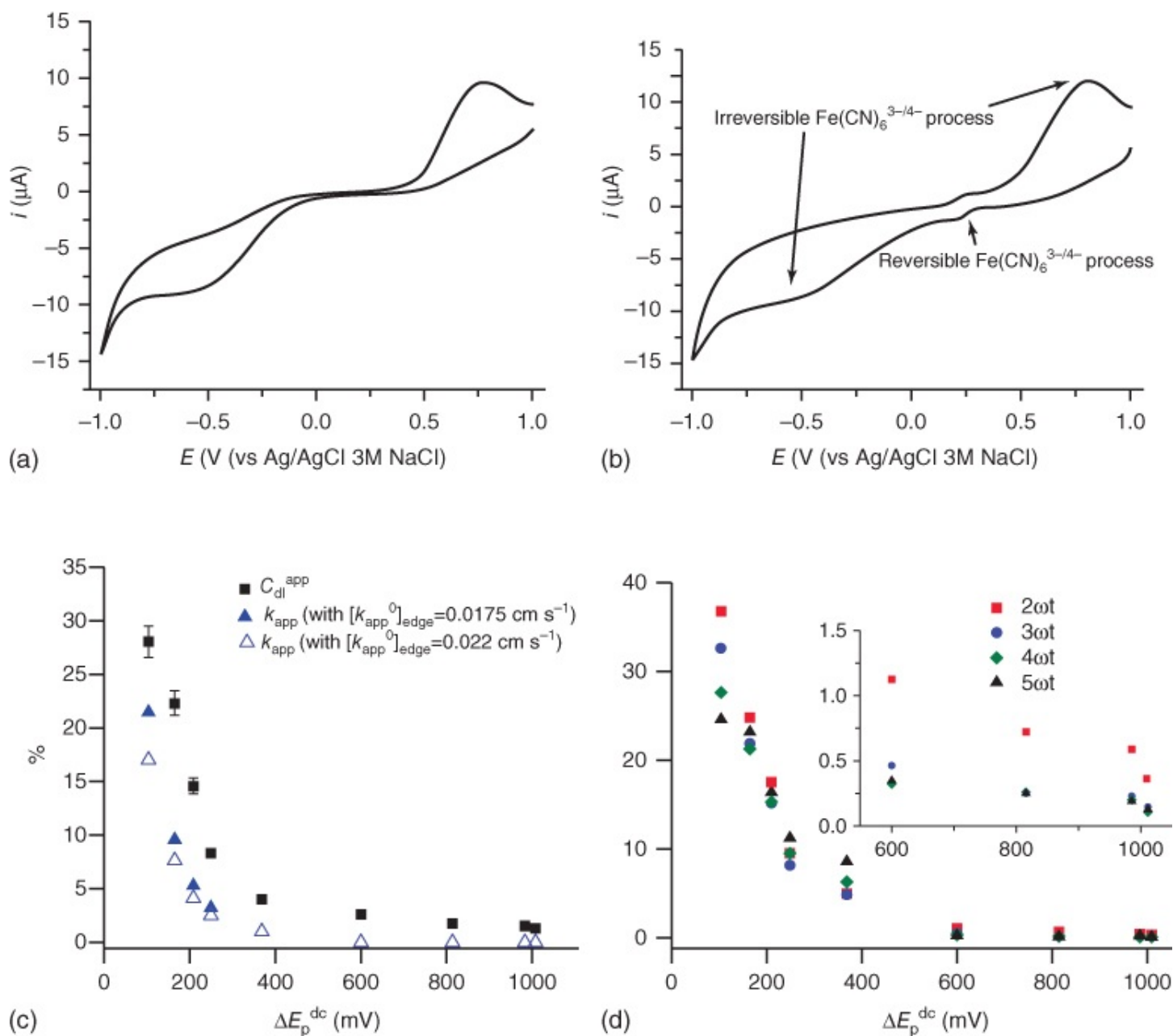


Figure 2.13 CV for the reduction of 1 mM Fe(CN)_6^{3-} in aqueous 0.1 M KCl solution at a scan rate of 75 mV s^{-1} : (a) ZYH-grade HOPG electrode shows a highly irreversible process and (b) ZYH-grade HOPG electrode, which was hand-polished to create edge-plane defect sites, displays both a reversible and irreversible process. (c) Relationship of ΔE_p from CVs to the percentage of edge plane calculated from k^0 (with two values indicated by $\blacktriangle$ and $\triangle$) and C^0 ($\blacksquare$). (d) The individual second to fifth harmonic peak currents ($2-5 \omega t$) from AC voltammetry, with inset showing the closer view for the low-level edge-plane defect regions.

(Figure adapted with permission from Ref. [78].)

Using the higher harmonics of the wide-amplitude AC voltammetry technique [159, 160], it was proposed that the percentage of edge-plane defect coverage could be estimated based on k^0 for $\text{Fe(CN)}_6^{3-/4-}$, C^0 , and AC harmonic peak current data obtained on ZYH-grade HOPG after both hand polishing and electrochemical pretreatment methods (Figure 2.13c,d).

However, as we discuss later, intrinsic ZYH-grade HOPG is characterized by quite high-defect (step-edge) density itself, and based on the capacitance measured by Lee and Bond [77] ($3.4\text{--}76.5\ \mu\text{F cm}^{-2}$), one would have expected a close-to-reversible process for all the surfaces within the defect model of McCreery [5].

2.3.4 Critical Comparison of Macroscopic Data

It is interesting to compare CV data for the approaches outlined earlier, particularly as they reach similar conclusions about the electroactivity of cleaved HOPG, namely that the behavior is dominated by step edges. [Figure 2.14](#) shows the typical CVs reported by the three different groups who worked on different grades of HOPG. A typical CV for $\text{Fe}(\text{CN})_6^{3-/4-}$ on AM-grade HOPG gives a $\Delta E_p \sim 700\ \text{mV}$ ([Figure 2.14a](#)), although this can be larger or smaller, SPI-1 ([Figure 2.14b](#))- and ZYH ([Figure 2.14c](#))-grade HOPG, which have 10–100 times higher density of steps, give a slower response (larger ΔE_p). Yet, these works come to the same conclusion that step edges are responsible for the activity of HOPG, which is counterintuitive based on these data. Given the discrepancies in the literature, it is evident that further scrutiny of the HOPG ET model is required, particularly at the microscopic level, as considered in the next section.

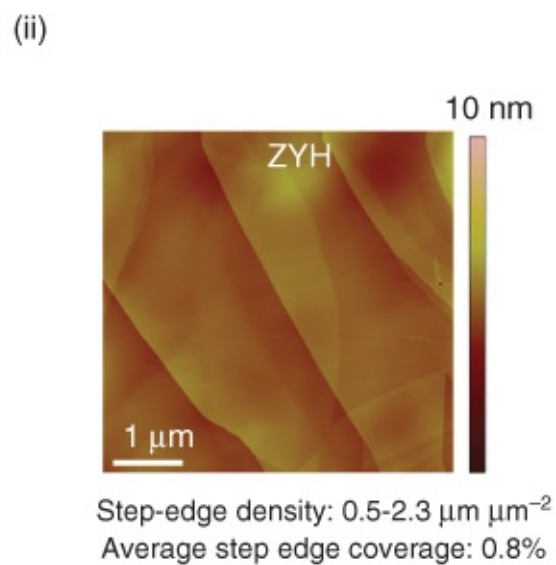
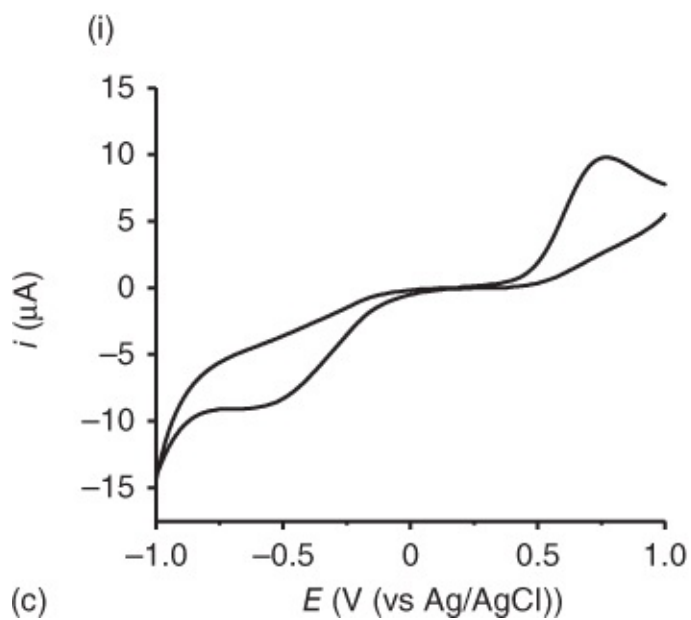
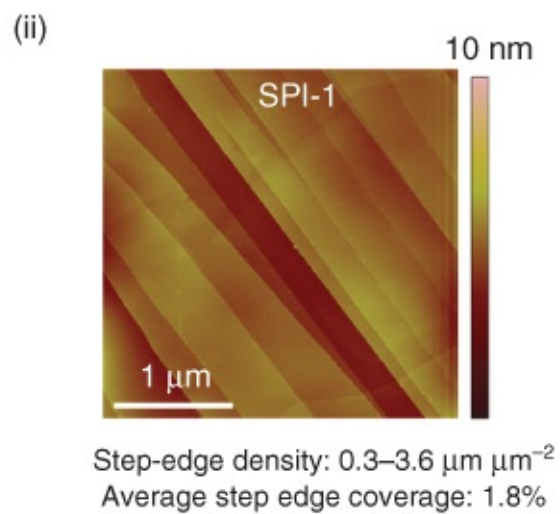
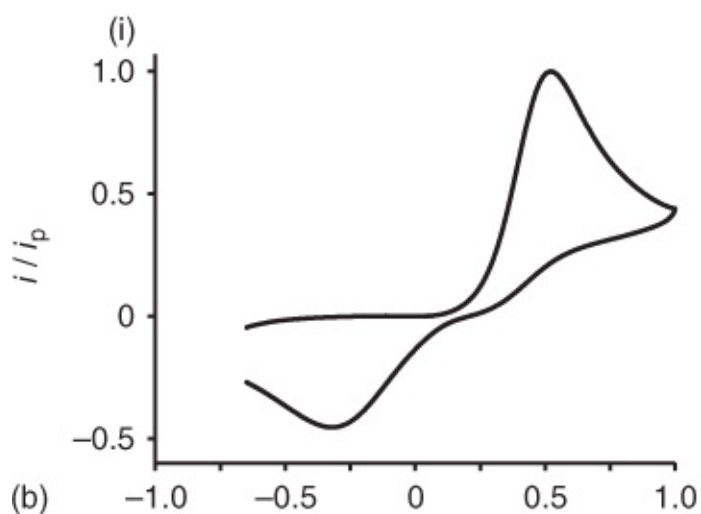
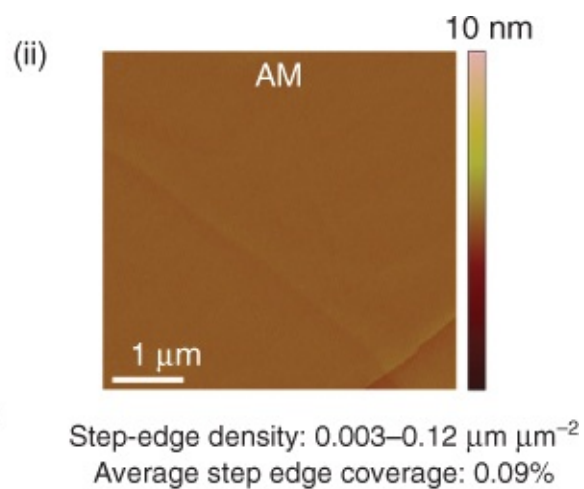
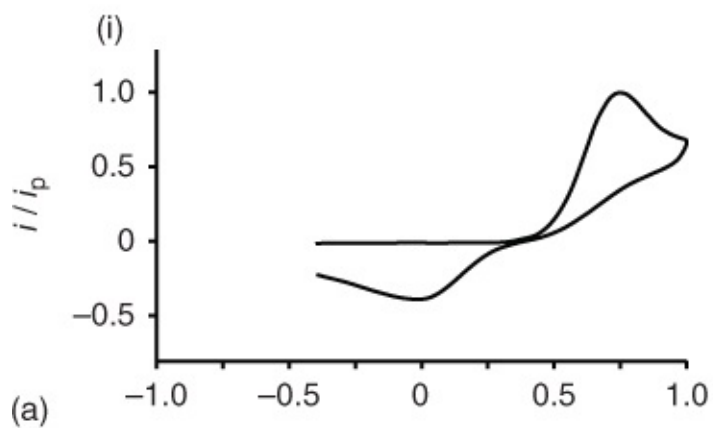


Figure 2.14 CVs for 1 mM $\text{Fe}(\text{CN})_6^{3-/4-}$ redox couple: (a)(i) oxidation in 1 M KCl solution at 1.0 V s^{-1} on AM-grade HOPG; (b)(i) oxidation in 1 M KCl solution at 1.0 V s^{-1} on SPI-1-grade HOPG; and (c)(i) reduction in 0.1 M KCl solution at 75 mV s^{-1} on ZYH-grade HOPG. (a)(ii)–(c)(ii) Corresponding AFM images of the HOPG surface showing typical step-edge densities and coverage for different grades of HOPG samples.

(Figure adapted with permission from Refs. [16, 74, 78].)

2.4 Microscopic Views of Electrochemistry at HOPG

In this section, we highlight how microscopic techniques are able to test the models derived from earlier measurements, producing results that lead to a new perspective on HOPG electrochemistry for a range of reactions, including classical outer-sphere couples, multistep electron–proton coupled reactions, and processes leading to adsorption and the modification of the HOPG surface. Furthermore, the insights obtained with a range of microscopic probes and techniques allow predictions and testing of the macroscopic response of HOPG under CV conditions.

2.4.1 Outer-Sphere Redox Systems

2.4.1.1 Scanning Micropipette Contact Method

As a scanning droplet-based technique [161, 162], SMCM was established as the first means of probing the electroactivity of tiny regions of an HOPG surface, defined by a small area of meniscus contact between an electrolyte solution in a micropipette or nanopipette and a surface (electrode) of interest ([Figure 2.15a](#)) [140]. Meniscus contact was achieved, without the pipette itself contacting the surface, by monitoring the current in the electrochemical cell, as the pipette was translated toward the surface, which was closed on meniscus contact. A key feature of this technique is that the electrochemical cell, defined by the footprint of the meniscus and largely governed by the pipette size, is well defined and so experimental data can be complemented by simulation, which faithfully models the experimental geometry [163]. Simulations have been reported for surfaces of uniform activity and for step-edge (ring geometry) activity. On a surface with uniform activity, the simulation results in [Figure 2.15b](#) show that the transition of the voltammetric response from Nernstian to finite kinetics (Butler–Volmer model, with transfer coefficient, α , of 0.5) occurs for $k^0 < 0.1 \text{ cm s}^{-1}$, with the half-wave potential shifting to higher overpotential and the voltammogram shape becoming broadened as the ET kinetics slow down. The simulations are for a typical tip of $2 \text{ }\mu\text{m}$ diameter with a redox species of diffusion coefficient $1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ and a pipette of 7.5° semiangle. Obviously, the precise kinetics that can be determined depends on the tip geometry and the diffusion coefficient of the redox species, but these simulations provide a guide as to the kinetics that can be measured, with $k^0 > 0.1 \text{ cm s}^{-1}$ indistinguishable from the reversible (Nernstian) case and defining the upper kinetic limit with this technique. Note, however, that with this limit, the technique delivers sufficiently high mass transport rates to test microscopic models derived from microscopic voltammetry, given that macroscopic CV measurements

([Section 2.3](#)) have typically been made at scan rates that have lower associated mass transport rates.

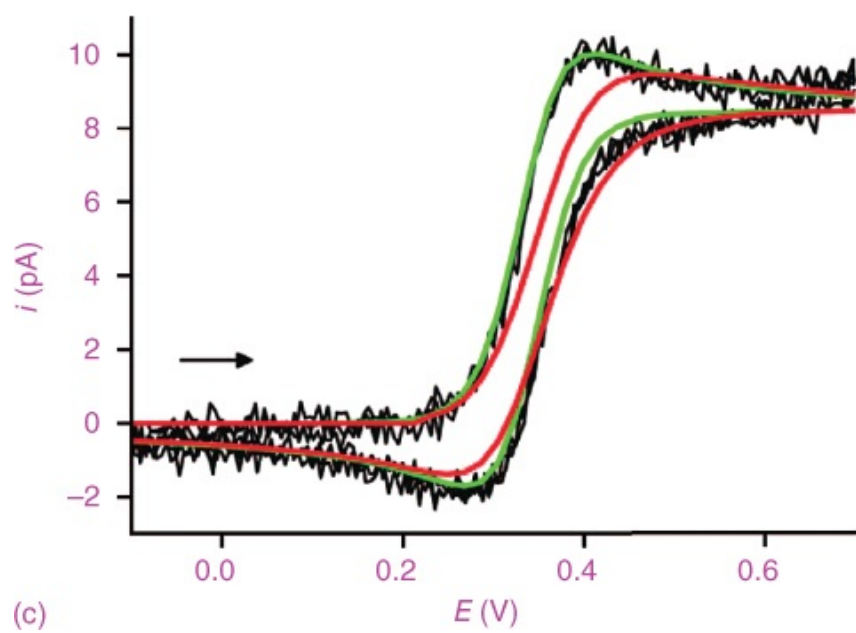
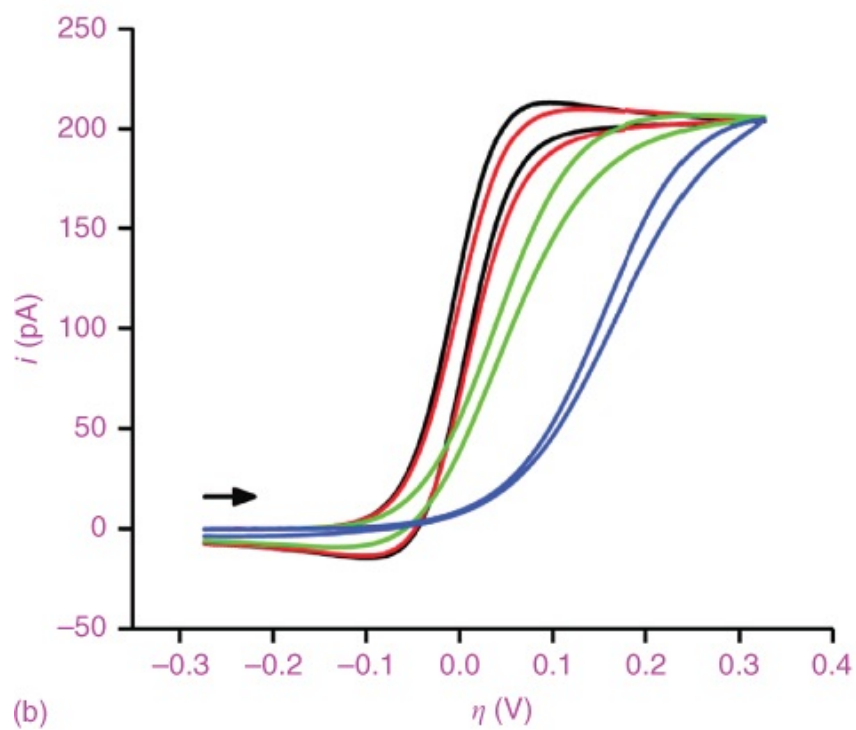
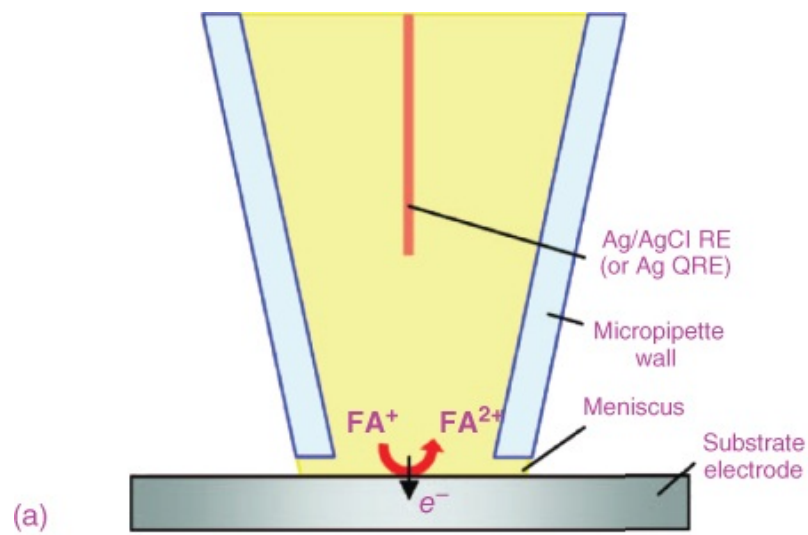


Figure 2.15 (a) Schematic of the SMCM setup, showing the one-electron oxidation of FA^+ to FA^{2+} at a substrate electrode. (b) Simulations showing the influence of kinetics on SMCM CVs, for a pipette of 2 μm diameter and 7.5° taper angle. Black: Nernstian response. Kinetic cases use Butler–Volmer equations ($\alpha = 0.5$). Red: $k^0 = 0.1 \text{ cm s}^{-1}$, Green: $k^0 = 0.01 \text{ cm s}^{-1}$, Blue: $k^0 = 0.001 \text{ cm s}^{-1}$ (5 mM redox species, $D = 1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$), η is the overpotential. (c) Experimental (black) and simulated (Nernstian, green; $k^0 = 0.01 \text{ cm s}^{-1}$, $\alpha = 0.5$, red) CVs for a pipette of 580 nm diameter with a solution of 2 mM FA^+ ($D = 6 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$).

(Figure adapted with permission from Ref. [140].)

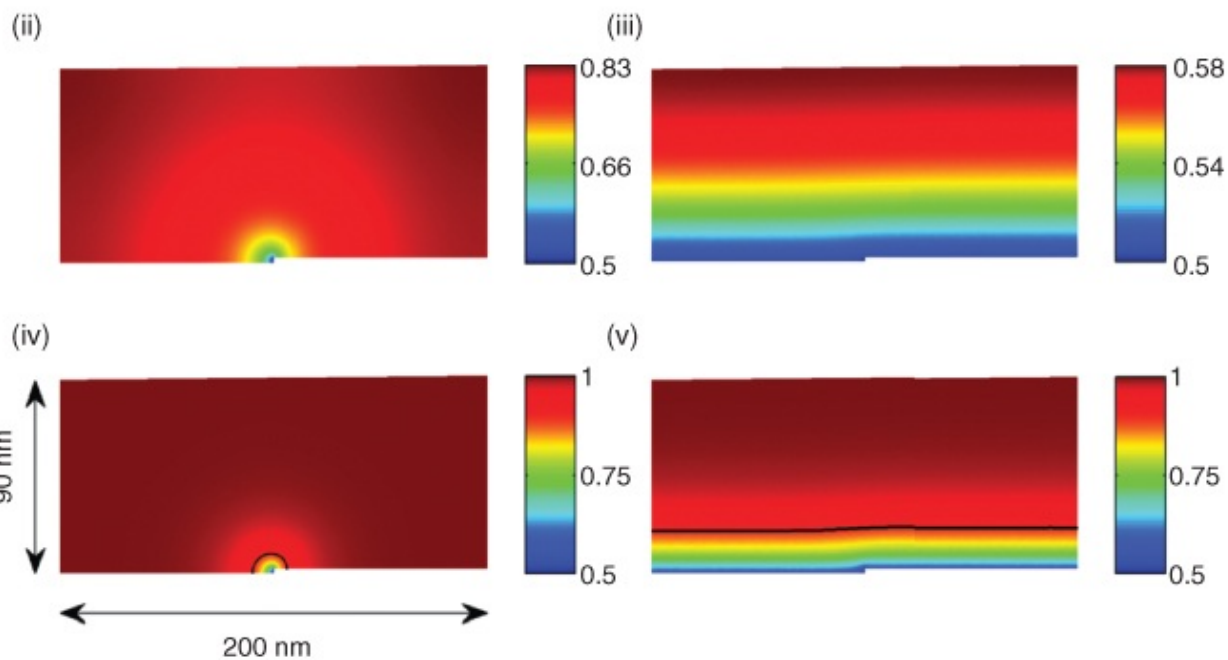
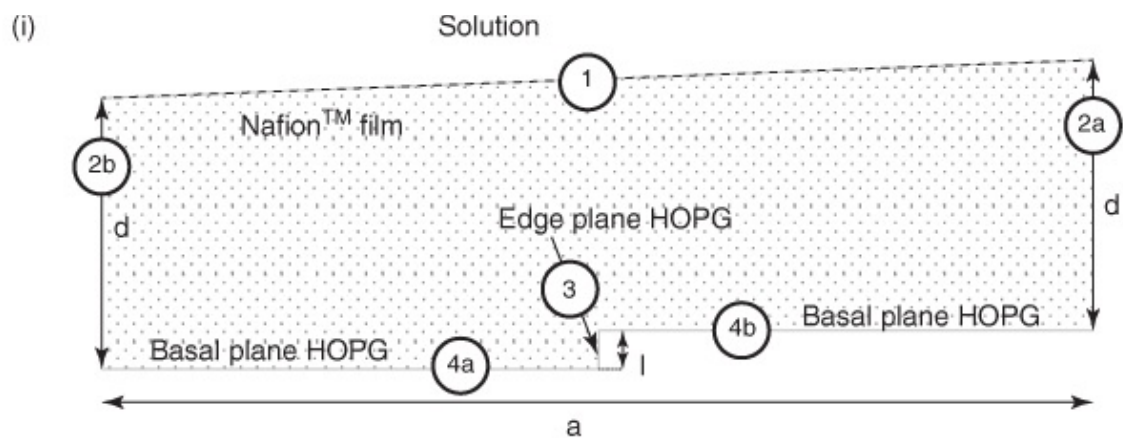
In the case of the oxidation of trimethylammoniomethylferrocene, FA^+ , on HOPG (ZYA grade), experimental data revealed Nernstian ET behavior ([Figure 2.15c](#)), indicating fast kinetics ($k^0 > 0.1 \text{ cm s}^{-1}$) at the area probed. In this case, the micropipette size (580 nm diameter) was smaller than the inter-step spacing on the basal surface (typically 2 μm for ZYA grade; see [Figure 2.3](#) and [Table 2.1](#)), leading to at most one step encapsulated by the meniscus, and most likely no steps. From the fast voltammetric response, it was concluded that the basal surface must have high activity [140].

Line scan profiles, in a hopping mode, where the pipette meniscus was brought into contact with the HOPG surface at a series of discrete points across the surface, were also carried out with one of two different redox couples, that is, $\text{FA}^{+/2+}$ and $\text{Fe}(\text{CN})_6^{4-/3-}$, with the HOPG surface biased at the reversible half-wave potential. No noticeable variation in current was observed for either mediator, with the current magnitude found to be as expected for a reversible process. This indicated the high activity of the basal surface on these low step density samples, even for the $\text{Fe}(\text{CN})_6^{4-/3-}$ couple, in contrast to the prevailing view from macroscopic voltammetry ([Section 2.3](#)). Multiple CV measurements for $\text{FA}^{+/2+}$ at fresh, randomly selected sites on HOPG reached the same conclusion: uniform, fast responses were seen. These studies thus suggested that freshly cleaved HOPG surfaces and the basal plane, in particular, support fast ET kinetics. It was also found, however, that for the $\text{Fe}(\text{CN})_6^{4-/3-}$ couple, the response quickly became less reversible with time after cleavage of the HOPG [140], an important issue which is considered later. Finally, in terms of methodological development, it should be noted that this technique can now be used with pipettes of 100 nm diameter, and on rather rough samples [164], making it a particularly valuable nanoscale visualization method.

2.4.1.2 Nafion Film-Covered HOPG

One of the issues in macroscopic measurements of HOPG electrochemistry is that sites with substantially different electrochemical activity are diffusionally coupled, making it difficult to draw conclusions about the activity of different types of sites, particularly as most CV studies have used only one scan rate [16, 71, 72, 74, 78, 82], and the local step density on the same cleaved surface can vary significantly across the surface ([Section 2.2.1](#)). By slowing down diffusion on the CV timescale, one can distinguish between different cases of electroactivity, as

different sites on the electrode will tend to become diffusionally decoupled as a consequence of greatly shortened diffusion lengths. This is the case when redox mediators are trapped in thin films of Nafion on electrodes [165, 166]. Studies on ruthenium(II) bipyridyl, $\text{Ru}(\text{bpy})_3^{2+}$, or ruthenium(III) hexaamine, $\text{Ru}(\text{NH}_3)_6^{3+}$, in ultrathin Nafion films on HOPG allowed the basal plane to be accessed as the dominant site for electrochemistry. The systems were simulated in the model illustrated in [Figure 2.16a\(i\)](#). When the HOPG surface is coated by a thin Nafion film loaded with redox-active species (e.g., $\text{Ru}(\text{bpy})_3^{2+}$), a difference can be readily seen between the simulated concentration profiles at the half-wave potential for the situations where the basal plane is inert ($k^0 = 0 \text{ cm s}^{-1}$) and only the step edge active ($k^0 = 1 \times 10^{-4} \text{ cm s}^{-1}$, $\alpha = 0.5$), [Figure 2.16a\(ii\)](#) and (iv), and when the basal plane is active with the same kinetics at the edge ($k^0 = 1 \times 10^{-4} \text{ cm s}^{-1}$, [Figure 2.16a\(iii\)](#) and (v)). The distinction is further stressed with increased scan rates, for example, compare [Figure 2.16a\(ii\)](#) and (iv). Moreover, if only the step edge is active, the current density of the simulated CV is much lower (by 1–2 orders of magnitude) than for the case where the basal surface is active, and the wave shape is very different ([Figure 2.16b,c](#)).



(a)

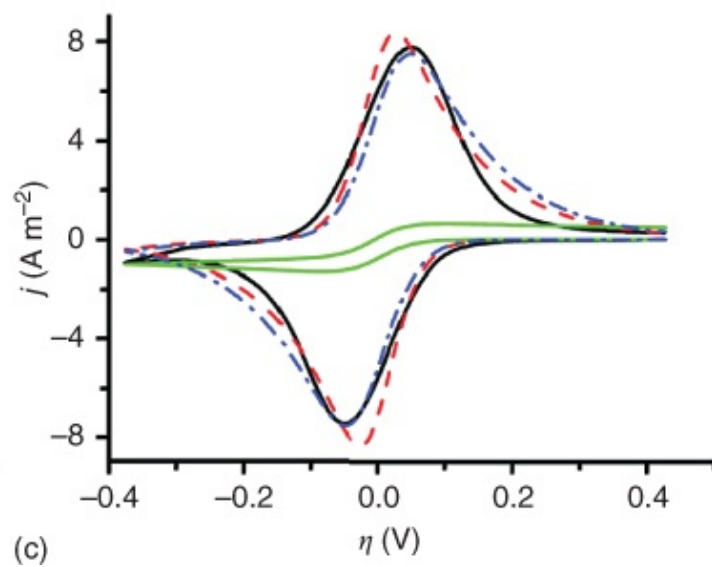
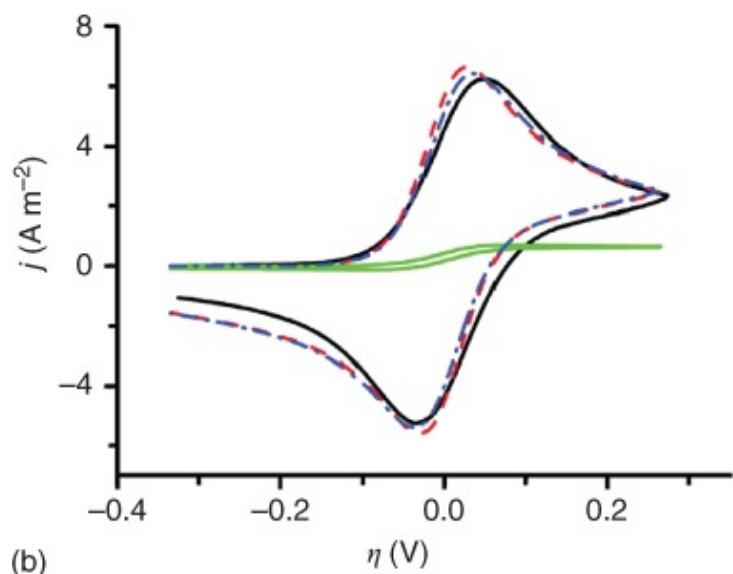


Figure 2.16 (a) Schematic of the simulation geometry model for a Nafion-coated HOPG surface (i), where the numbers are indicative of the film–solution interface (1), periodic boundaries from which the step array response can be determined (2a, 2b), step-edge plane (3), and basal plane (4a, 4b), respectively, and simulated concentration profiles for a Nafion-Ru(bpy)₃²⁺ ($D = 4.7 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$) film at the half-wave potential from a CV at a scan rate of 10 mV s^{-1} (ii, iii) and 1 V s^{-1} (iv, v). The basal plane was assumed to be inert ($k^0 = 0 \text{ cm s}^{-1}$; ii, iv) and active ($k^0 = 1 \times 10^{-4} \text{ cm s}^{-1}$; iii, v), with the step-edge activity at $k^0 = 1 \times 10^{-4} \text{ cm s}^{-1}$. CVs recorded at a scan rate of 0.5 V s^{-1} on an SPI-1-grade HOPG surface, with a deposited thin Nafion film incorporating (b) Ru(bpy)₃²⁺ and (c) Ru(NH₃)₆³⁺, where the experimental data are shown in black, together with simulations with basal plane kinetics either reversible (red), inert ($k^0 = 0 \text{ cm s}^{-1}$, green), or active with a rate constant of $k^0 = 1 \times 10^{-4} \text{ cm s}^{-1}$ for Ru(bpy)₃²⁺ and $k^0 = 4.5 \times 10^{-5} \text{ cm s}^{-1}$ for Ru(NH₃)₆³⁺ (blue).

(Figure adapted with permission from Ref. [166].)

Experimental measurements were found to be in close agreement with a fully active basal surface (close-to-reversible ET). However, the lower bound on rate constant was low, $1 \times 10^{-4} \text{ cm s}^{-1}$ for Ru(bpy)₃²⁺ and $4.5 \times 10^{-5} \text{ cm s}^{-1}$ for Ru(NH₃)₆³⁺ [166], considering the low diffusion rate (charge transfer rate) in the Nafion film and the impact of film resistance. These studies, nonetheless, highlight that the basal plane of HOPG dominates the macroscopic activity on this timescale.

2.4.1.3 Scanning Electrochemical Cell Microscopy (SECCM)

Scanning electrochemical cell microscopy (SECCM) is a recent innovation [161, 167] in electrochemical scanning probe microscopy [168] that has been proven particularly powerful for visualizing electroactivity. In the case of HOPG, the SECCM response also informs on the location of the measurement, that is, basal surface only or basal surface intersected by step edge(s) [139]. SECCM is an advance of SMCM ([Section 2.4.1.1](#)): the probe is a dual-barrel pipette, pulled to a taper before filling with the solution of interest. The meniscus formed across the two barrels at the sharp pipette point acts as the electrochemical cell upon coming into contact with the substrate of interest. A bias is applied (typically +0.1 to +0.5 V) between two quasi-reference counter electrodes (QRCEs) placed in the barrels of the theta pipette, resulting in a conductance (ion migration) current across the meniscus. This has several important consequences, including that it provides a means of controlling and varying the mass transport of charged analytes that can be enhanced several-fold due to migration in the electric field between the QRCEs [139]. A sinusoidal oscillation is also imposed on the tip position (in the direction of the pipette length) to create an AC component at the frequency of the oscillation, due to the periodic motion of the meniscus. This is used as a feedback parameter to maintain a stable and user-defined tip–substrate separation while the meniscus is in contact with the surface [161, 167].

SECCM measurements can be performed on both conducting and nonconducting substrates and the technique is better suited than SMCM for long-duration and large-scale high-resolution

imaging due to the more general feedback control mechanism. With precise position control of the probe and sample, through the use of xyz piezoelectric positioners, high-resolution imaging on various substrates of interest can readily be achieved [21, 23, 28, 38, 139, 161, 167, 169–175]. The SECCM technique is particularly powerful when complemented by other forms of microscopy applied to the same areas as the electrochemical imaging, in a methodology we call “**multimicroscopy**” [169] but the ion current component (e.g., AC amplitude) can also provide information on the location of the measurement, as for HOPG studies where the basal plane and step edges can often be identified (*vide infra*).

Importantly, for HOPG, the response of the basal plane can be isolated from step edges and probed separately by using a small-sized tip, typically with a diameter in the range of several hundred nanometers, which is much smaller than the step-edge spacing on ZYA- or AM-grade HOPG. SECCM imaging/mapping was carried out by Lai *et al.* [139] with two of the most studied redox couples, $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ and $\text{Fe}(\text{CN})_6^{4-/3-}$, on freshly cleaved ZYA-grade HOPG. [Figure 2.17a](#) shows the SECCM setup, together with a typical tip of 300–400 nm in diameter. Sets of images were obtained simultaneously during imaging with each mediator (see [Figure 2.17b–d](#)), including electrochemical activity, for example, [Figure 2.17b\(iii\)](#), (c), and (d), the AC bias current amplitude (e.g., [Figure 2.17b\(ii\)](#)), the DC conductance current (e.g., [Figure 2.17c](#), line profile), and topography (e.g., [Figure 2.17b\(i\)](#)). High surface electroactivity current across the whole area studied was demonstrated for both $\text{Ru}(\text{NH}_3)_6^{3+}$ reduction and $\text{Fe}(\text{CN})_6^{4-}$ oxidation. However, some clear lines were observed corresponding to the step edges (see [Figure 2.17b,c](#), in particular). These were attributed to the transient disturbance in meniscus wettability on the freshly cleaved surface as seen in the ion conductance current image ([Figure 2.17c](#), line profile). Importantly, the redox current at the half-wave potential is more or less uniform (e.g., [Figure 2.17b\(iv\)](#)) and within experimental uncertainty at a value close to that expected for a reversible process. Given that the tip is smaller than the step spacing by 1 order of magnitude [140], a large area of pristine basal surface was accessed in these studies and thus it was concluded that the basal plane unequivocally showed high activity (see, for example, redox current histogram in [Figure 2.17b\(iv\)](#)). Standard ET rate constants of >0.5 and $>1 \text{ cm s}^{-1}$ were estimated for $\text{Ru}(\text{NH}_3)_6^{3+}$ and $\text{Fe}(\text{CN})_6^{4-}$, respectively [139].

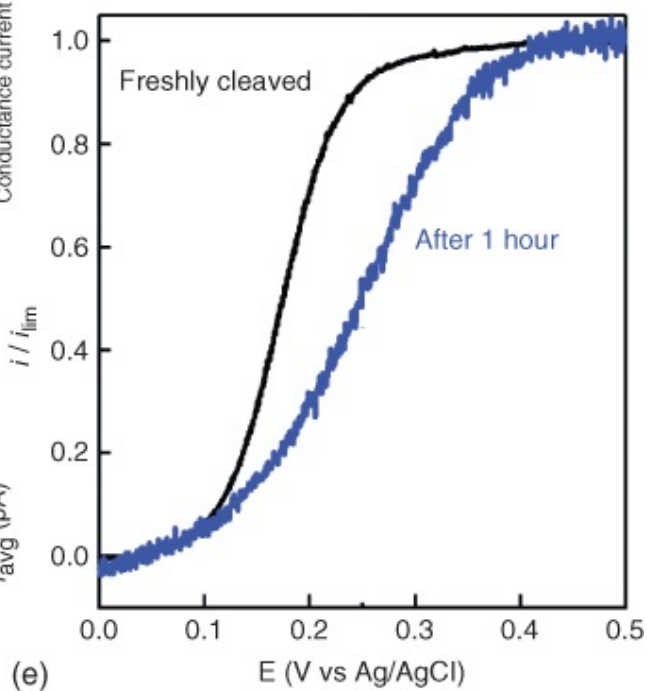
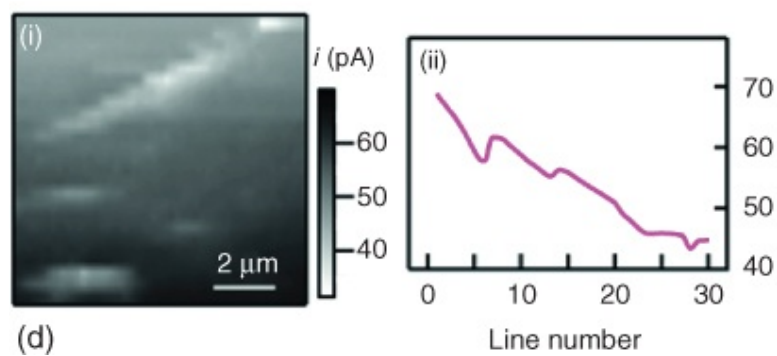
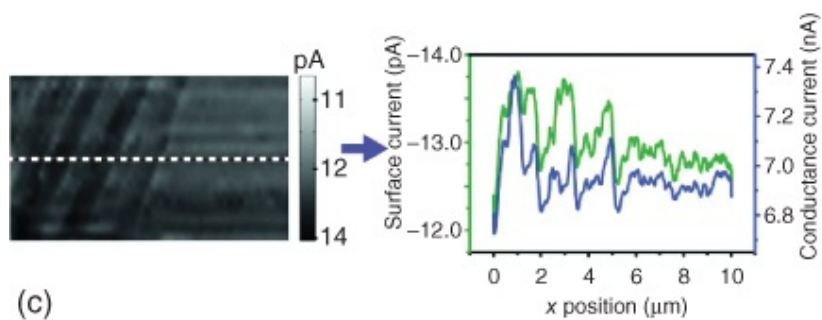
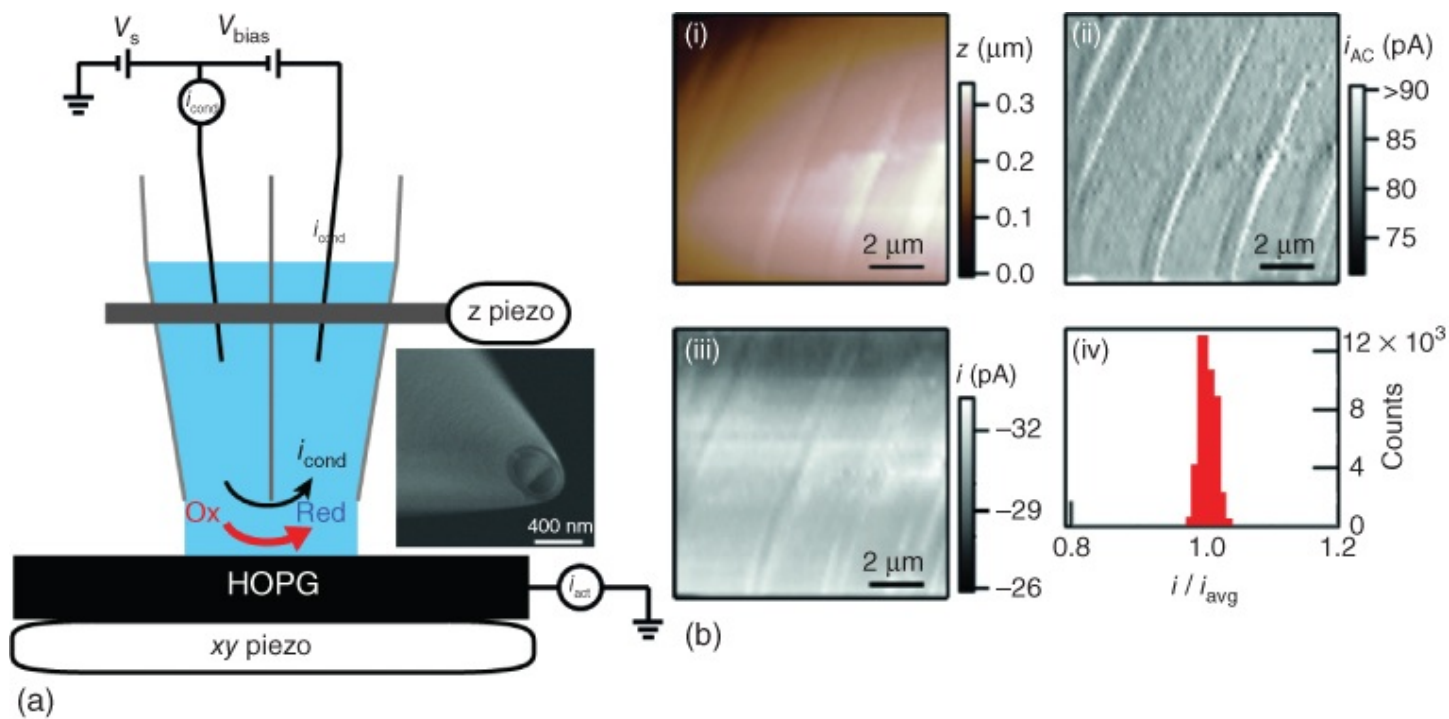


Figure 2.17 (a) Schematic of the SECCM setup and an scanning electron microscopy image of a typical tip employed. (b) SECCM maps for the electro-reduction of 2 mM $\text{Ru}(\text{NH}_3)_6^{3+}$ on ZYA-grade HOPG, showing (i) topography, (ii) AC component of the conductance current, (iii) surface electroactivity, and (iv) a histogram of all the electroactivity (redox current) pixels with respect to the average activity. (c) SECCM surface electroactivity map (left) for 1 mM $\text{Ru}(\text{NH}_3)_6^{3+}$ reduction at AM-grade HOPG, with both surface current (green) and barrel current (blue) shown for a typical line across several steps. (d) Surface electroactivity map for the oxidation of 2 mM $\text{Fe}(\text{CN})_6^{4-}$ (i), with the average current of each line in the image shown in (ii). (e) Normalized linear sweep voltammograms for the oxidation of 2 mM $\text{Fe}(\text{CN})_6^{4-}$ on fresh HOPG (black) and aged HOPG after 1 h exposure in air (blue), with a scan rate of 100 mV s^{-1} .

(Figure reproduced and adapted with permission from Refs. [38, 139].)

It should be noted that, studies of $\text{Fe}(\text{CN})_6^{4-/3-}$ were more difficult, because it was found that the electroactive current on HOPG deteriorated [38] during the timescale of the imaging, as seen by the drop of average current at each line ([Figure 2.17d\(ii\)](#)), and the change of CV shape with time in [Figure 2.17e](#). As a consequence, this time-dependent deactivation should be taken into consideration for the characterization of the intrinsic electrochemical properties of the HOPG surface and related surfaces.

2.4.1.4 Scanning Electrochemical Microscopy (SECM)

SECM has been proven a powerful multipurpose technique for the investigation of a variety of surfaces, interfaces, and processes [176, 177]. Hapiot *et al.* studied the electrochemistry of the $\text{Fe}(\text{CN})_6^{3-/4-}$ redox couple on HOPG using feedback mode of SECM ([Figure 2.18a](#)), in which $\text{Fe}(\text{CN})_6^{3-}$ (Ox) in bulk solution was reduced to $\text{Fe}(\text{CN})_6^{4-}$ (Red) at the tip and this could undergo conversion back to Ox at the carbon sample, depending on the surface ET kinetics. There was no electrical connection on the sample (unbiased conditions), and a gold ultramicroelectrode tip was employed [178]. Approach curves displayed positive feedback on HOPG ([Figure 2.18b](#)), and a high dimensionless ET rate constant was extracted by fitting the experimental data, indicating fast ET of the $\text{Fe}(\text{CN})_6^{3-/4-}$ couple at the HOPG sample.

Surprisingly, while similar behavior was seen sometimes on GC, negative-feedback approach curves were also obtained ([Figure 2.18c](#)). Yet, GC is rich in defects and has been considered to exhibit ET rates much higher than those for the basal plane of HOPG [5, 73, 152, 153]. Along with other studies described in this section, these results thus raise significant questions as to the validity of a defect-driven activity model for graphite electrodes and outer-sphere redox couples. It is further important to note that the authors experienced large reproducibility difficulties with the $\text{Fe}(\text{CN})_6^{3-/4-}$ couple with data showing high dependence on the polishing for GC and the cleavage of HOPG [178].

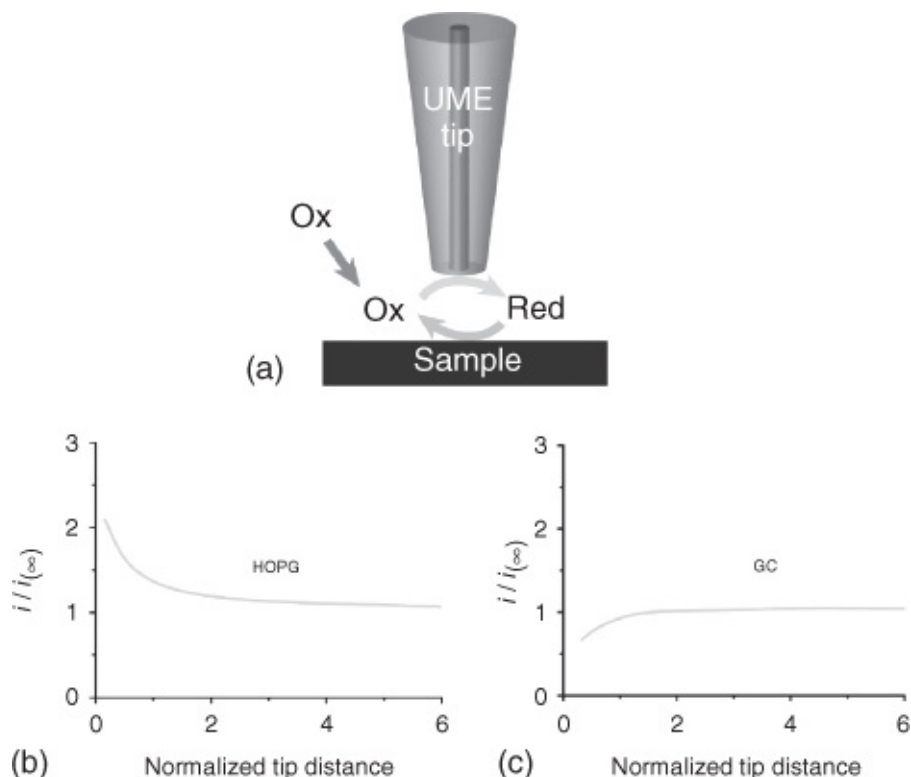


Figure 2.18 (a) Schematic for feedback mode of SECM. SECM steady-state normalized current–distance approach curves with a gold disc ultramicroelectrode (UME) tip (radius 6 μm) for $\text{Fe}(\text{CN})_6^{4-}$ reduction toward (b) HOPG and (c) glassy carbon, where i is the current and $i_{(\infty)}$ is the bulk current. The normalized distance is the absolute tip–substrate distance divided by the tip radius.

(Figure adapted with permission from Ref. [178].)

2.4.1.5 SECM–AFM Studies

SECM–AFM combines the merits of SECM and AFM [179–182], enabling electroactivity to be directly and simultaneously related to the topography on a small length scale, as exemplified by a variety of studies [183–185]. In an investigation of several materials as supports for biological membranes, Frederix *et al.* [141] found that the basal surface of freshly cleaved ZYB-grade HOPG was “as active as template-stripped gold,” as a positive-feedback approach curve of $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ was observed on biased HOPG, with 9.4 cm s^{-1} measured as the lower limit of k^0 . Over time, however, there was a decrease in the kinetics, with k^0 diminishing to $1.9 \times 10^{-2} \text{ cm s}^{-1}$. On maps obtained with the SECM–AFM setup, high current density was observed at the basal surface. Even though there was an increase in the current at some steps (Figure 2.19, steps 1 and 2), the enhancement was not significant and also not all step edges showed an increased current (Figure 2.19). Moreover, when the ET driving force (HOPG potential) was driven more, the topographical effects on the current were further reduced (Figure 2.19e,f). Even with an enhancement of 100 times in ET rate at the step, the increase in surface current compared to the basal surface was minimal, indicating that the basal plane dominates the electroactivity of the HOPG surface (Figure 2.19g).

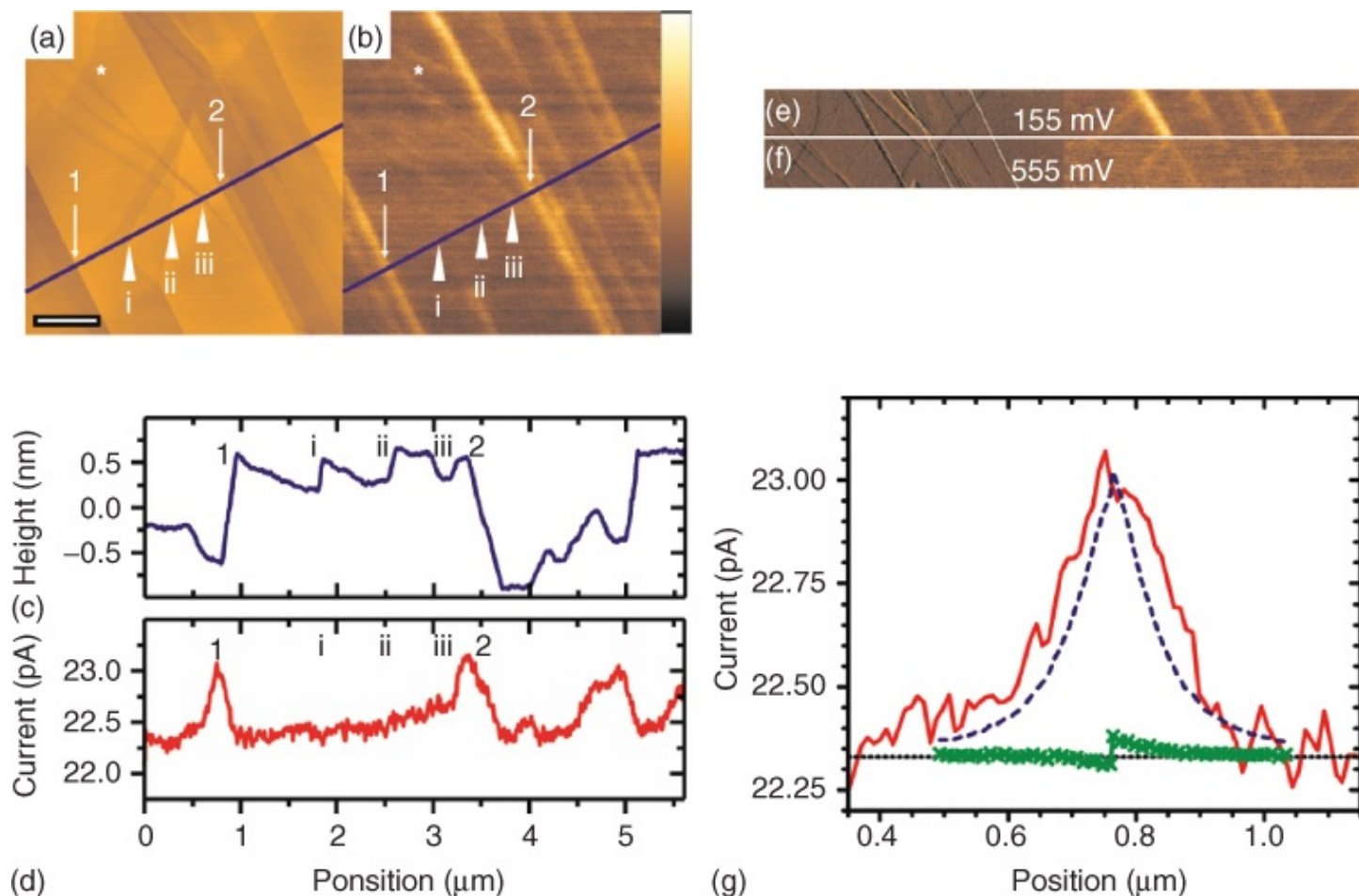


Figure 2.19 (a) Topographical and (b) current features on the surface of HOPG obtained from SECM–AFM, with the corresponding cross-sectional profile (c) and (d) along the line marked in (a) and (b), respectively. (e) Vertical deflection and (f) current response of the upper area of (a) and (b), and the numbers indicated are different support potentials, changing from the white line. (g) Simulation of SECM with a conical electrode, showing the current profiles across step 1 in (a). The experimental response (red line), the current response with a 100 times enhanced reaction rate at the step edge (blue line) and without enhanced reaction rate (green line). Note the small change in absolute current on the y-coordinate.

(Figure adapted with permission from Ref. [141].)

Wain *et al.* [186] investigated graphene/ultrathin graphite, but there was no indication of the period after cleavage before measurements were made. The basal surface was found to be highly active for ferrocenemethanol, FcMeOH, oxidation based on redox current maps, but there were patches of low current on some features that could be due to adsorbed impurities. As we pointed out in [Section 2.1](#), it is important that measurements of HOPG/exfoliated graphite are made as soon as possible after cleavage, or at least an indication of time is given [38].

Demaille *et al.* [187] have also carried out SECM–AFM measurements on HOPG. With the probe functionalized with a tagged ferrocene-based redox mediator, it was found that the basal surface of HOPG displayed a high electrochemical activity. There were some visible lines corresponding to step edges on the redox current maps, but not all step edges were observed to

have enhanced currents, in line with the results of Frederix *et al.* [141]. In a further study [188], Nernstian ET was observed on areas of HOPG, where the basal surface was accessed, indicative of the high electroactivity of the basal plane.

2.4.1.6 Recent Macroscopic Studies

Given the striking disparity between the kinetic results for the basal surface from a variety of microscale/nanoscale studies discussed in this section, which indicate reasonably high activity of the basal surface, and the earlier macroscale measurements ([Section 2.3](#)) which deduced that the basal surface was (largely) inert for outer-sphere ET, recent macroscopic studies have been carried out on well-defined HOPG samples with different (known) step density, on both commercial (ZYA, ZYH, SPI-1, and SPI-2) and unclassified high-quality (AM-grade) HOPG under well-defined conditions (e.g., time after cleavage and cleavage method), to thoroughly investigate the electrochemical behavior of two of the most studied redox couples, $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ and $\text{Fe}(\text{CN})_6^{4-/3-}$ [38].

The $\text{Fe}(\text{CN})_6^{4-/3-}$ couple showed near-reversible electrochemical response on freshly cleaved HOPG surfaces of two grades of HOPG, SPI-1 and ZYA (>400 measurements) [38], with ΔE_p (about 59 mV at 0.1 V s^{-1}) expected of a reversible system, in spite of the low step-edge density on the ZYA surface ([Table 2.1](#)) and the difference in step-edge density between SPI-1 and ZYA grades. As mentioned earlier ([Section 2.3.1](#)), although similar values of ΔE_p were also obtained on some surfaces of HOPG in earlier studies [73, 148], these samples were usually considered to be defective. However, the good quality of the samples employed herein as evident by AFM imaging ([Figure 2.3](#)) and capacitance measurements ([Table 2.1](#)) shows that this is not a reasonable deduction. At the same time, $\text{Ru}(\text{NH}_3)_6^{3+}$ also shows reversible electrochemical behavior on SPI-1-grade HOPG. The responses of the two couples reflect the active nature of the basal plane and are in agreement with microscopic measurements ([Sections 2.4.1.1–2.4.1.5](#)).

It should be noted that in the case of $\text{Fe}(\text{CN})_6^{4-}$ oxidation, in particular, on a freshly cleaved HOPG sample where repetitive scans were performed, a surface-blocking effect was observed in buffered and nonbuffered aqueous solution, which was enhanced at increasing concentration of $\text{Fe}(\text{CN})_6^{4-}$, indicating a flux (concentration)-dependent deactivation process, and ascribed to the formation of Prussian blue-like side products [151, 189]. The small-volume (droplet) electrochemical cells that have necessarily been employed to study HOPG, as it cannot be encapsulated, could play a role in this time-dependent response, that is, over time, counter electrode products may contaminate the solution. Moreover, there is also the possibility of ion intercalation and subsurface processes [190–192] and delamination. Similarly, it is important to note that time-dependent surface passivation was observed on samples left in contact with either solution or air for defined times before running voltammetric experiments of $\text{Fe}(\text{CN})_6^{4-}$ oxidation. Dramatic changes of the CV shape and deterioration of the current were seen ([Figure 2.20a,b](#)), consistent with the microscale measurements [139].

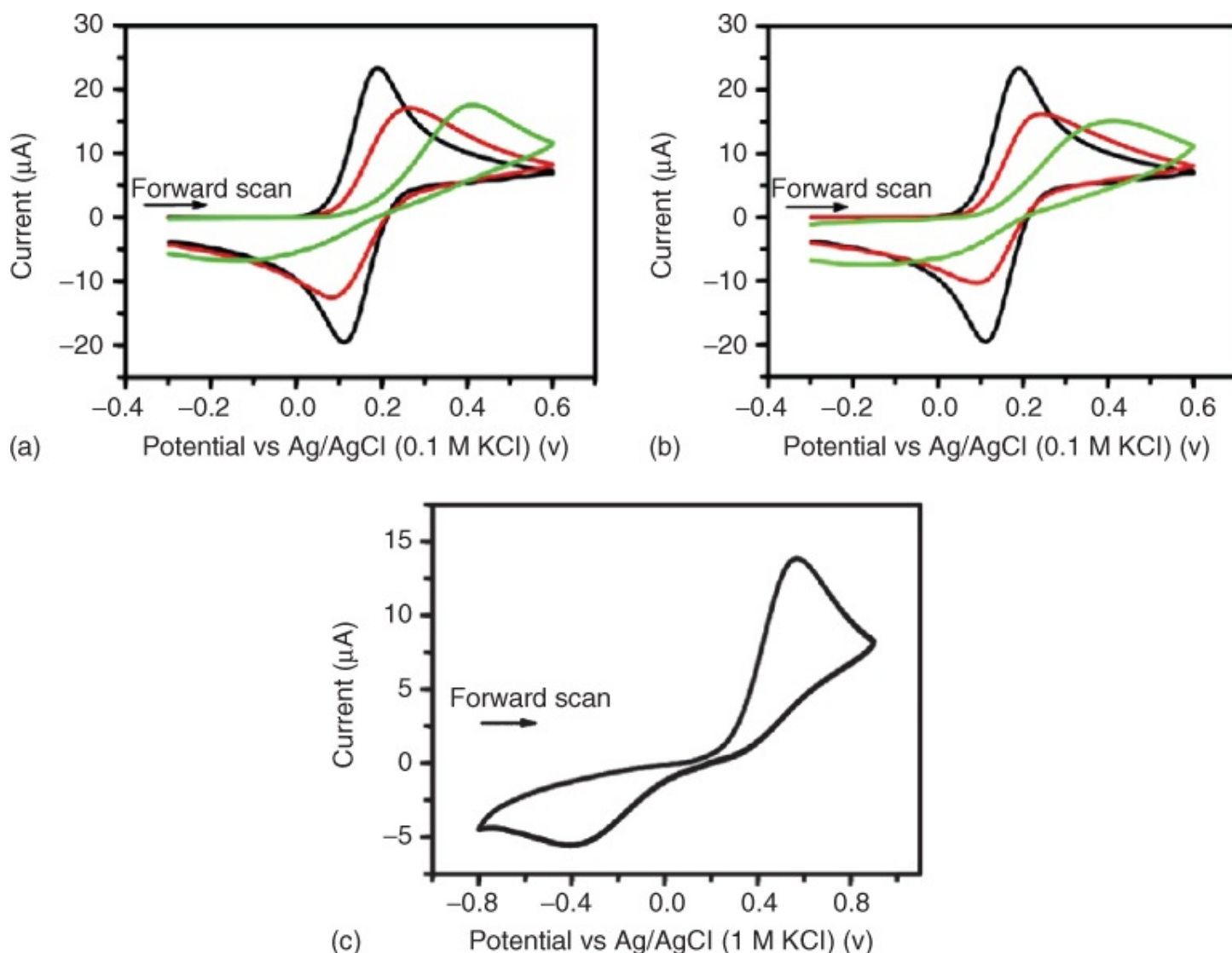


Figure 2.20 CVs for the oxidation of 1 mM $\text{Fe}(\text{CN})_6^{4-}$ in 0.1 M KCl solution, at 0.1 V s^{-1} , after a freshly cleaved HOPG (SPI-1) surface was left (a) in contact with solution or (b) in air, after cleavage for 0 min (black), 1 h (red), and 3 h (green), and (c) after leaving a sample in air for 24 h after cleavage.

(Figure adapted with permission from Ref. [38].)

For the HOPG sample exposed to air, conductive AFM measurements highlighted that the resistance increased substantially compared to a freshly cleaved surface, as illustrated in [Figure 2.21](#). This can be attributed to contamination of the surface and/or delamination of the top layer(s) from the main body of the HOPG [38]. On such surfaces, $\text{Fe}(\text{CN})_6^{4-/3-}$ CVs (0.1 V s^{-1}) can show a response with a huge ΔE_p of $\sim 1000 \text{ mV}$ ([Figure 2.20c](#)), which is rather similar to those seen previously on the basal surface of HOPG (e.g., [Figure 2.14](#), [Section 2.3](#)) [16, 74, 78]. This plethora of possible underlying explanations for macroscopic voltammetric wave shapes – intrinsically inert basal surface [82, 158], time-dependent adventitious contamination [38, 39], surface delamination [38], electrochemical deactivation [151] – highlights the difficulty of understanding HOPG electrochemistry from macroscopic measurements. Importantly, the recent macroscopic measurements on freshly cleaved surfaces discussed in

this section highlight the intrinsic high activity of the basal surface ($k^0 > 0.1 \text{ cm s}^{-1}$ for $\text{Fe}(\text{CN})_6^{4-/3-}$ and $\text{Ru}(\text{NH}_3)_6^{3+/2+}$), with significant important implications for fundamental electrochemistry. Thus, given the low DOS of HOPG, these results of fast kinetics tend to suggest that such processes are essentially adiabatic [34], although further quantitative studies are required to prove this.

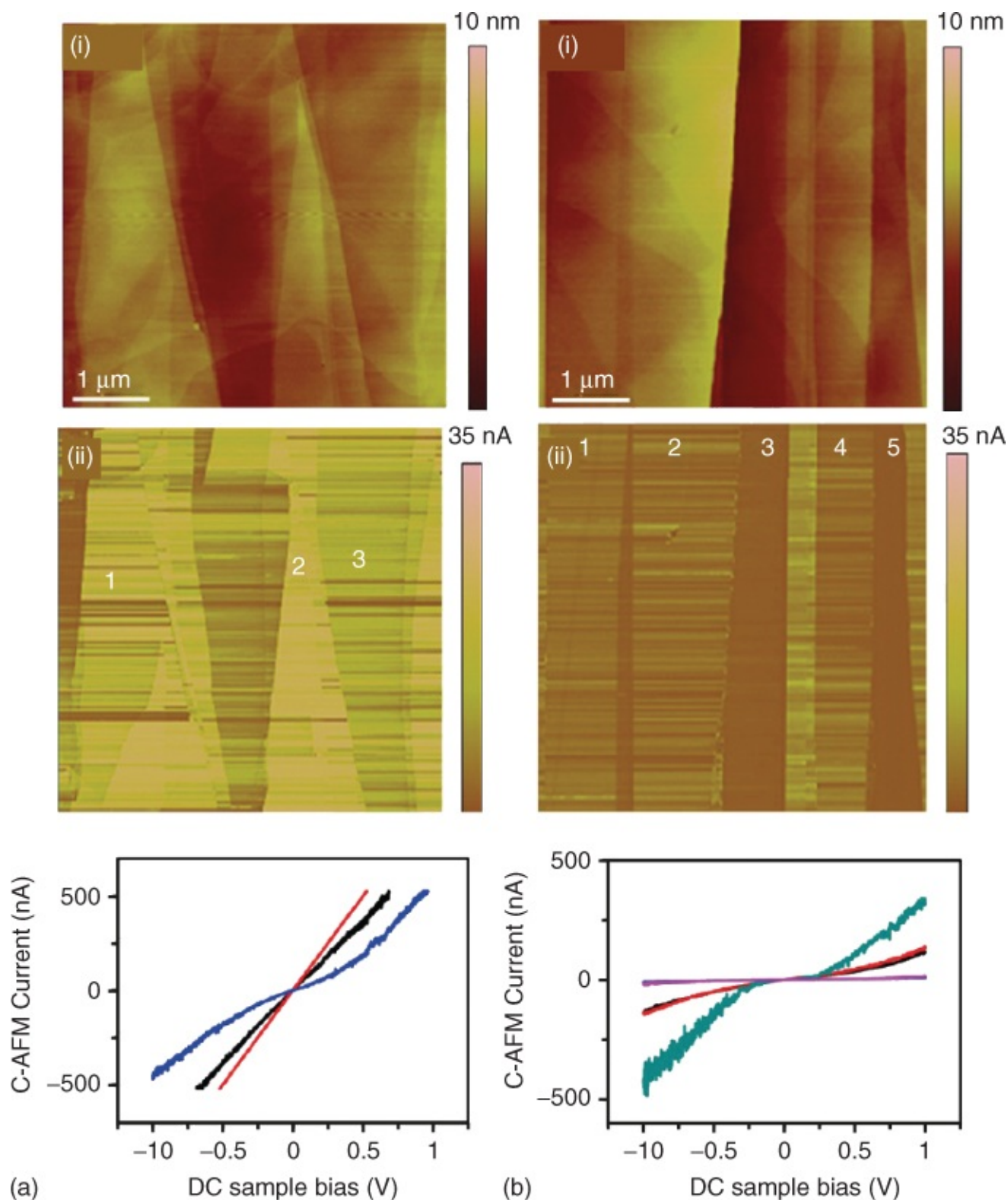


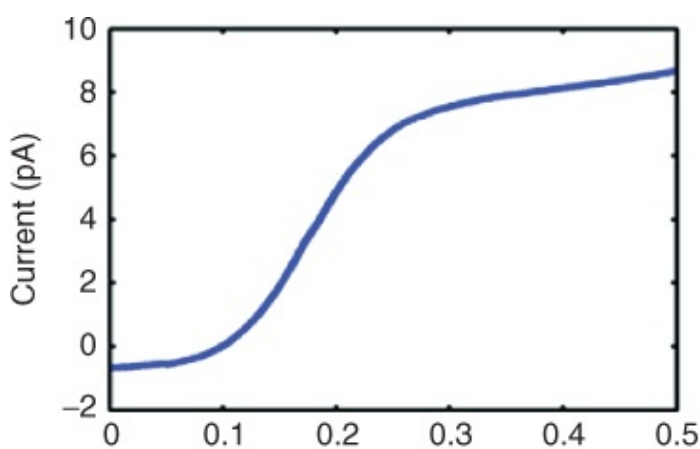
Figure 2.21 Conductive AFM images ($5 \times 5 \mu\text{m}$) of an HOPG (SPI-1) surface showing the (i) height and (ii) conductivity (a) immediately after cleavage and (b) 24 h after cleavage. The conductive AFM i - V curves shown were recorded on the terrace locations marked in (a)(ii) and (b)(ii).

(Figure adapted with permission from Ref. [38].)

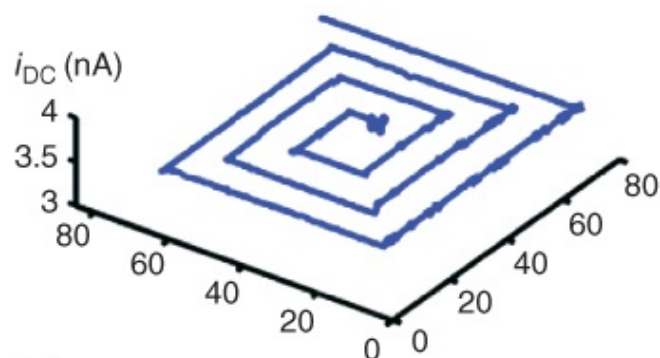
2.4.2 Complex Multistep Reactions: Neurotransmitter Oxidation

Neurotransmitters, such as dopamine (DA) and epinephrine (EP), are catecholamines that undergo complex multistep oxidation processes in aqueous solution via coupled ET, proton transfer ($2e^-$, $2H^+$ at physiological pH), but with the complication of side reactions to form melanin-like compounds that can block electrode surfaces [193]. Such processes are expected to follow a classical scheme of squares [194], and are of considerable interest for the practical detection of neurotransmitters, as carbon electrodes have become the electroanalytical platform of choice [5, 60, 195]. This is due to a desirable range of properties including biocompatibility, chemical inertness, and low background current that are responsible for lower detection limits, wide potential windows, and low cost. Understanding the electrochemical activity of neurotransmitters on carbon electrodes is thus of considerable importance in the design of optimal biosensor platforms.

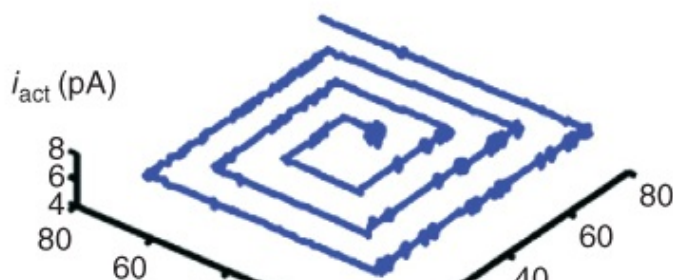
Recent reappraisals of the electrochemical oxidation of DA and EP on HOPG using macroscale CV, SECCM, and SECM have demonstrated that the long-standing view that graphite edges are solely responsible for catalyzing the electro-oxidation of neurotransmitters [16, 71, 83] is incorrect [60, 178, 196, 197]. Rather, the electrochemical response of catecholamines has been shown to be rapid on the basal surface of HOPG, but with surface fouling occurring readily due to oligomeric side products. SECCM studies were designed to take advantage of this by moving the liquid meniscus across the surface at a rate such that the electrode reaction was measured on the basal surface at high resolution, but polymeric products were left behind on the surface that acted as a surface marker (“reactive patterning”) (Figure 2.22). This allowed the electrochemical activity (e.g., Figure 2.22b), complemented by the DC (Figure 2.22c) and AC (Figure 2.22d) conductance current maps, to be related directly to the local surface character by the use of complementary microscopy techniques, namely AFM (Figure 2.22e) and SEM, applied to the same area [60, 197].



(a) Potential vs Ag/AgCl (0.15 M NaCl) (V)



(c)



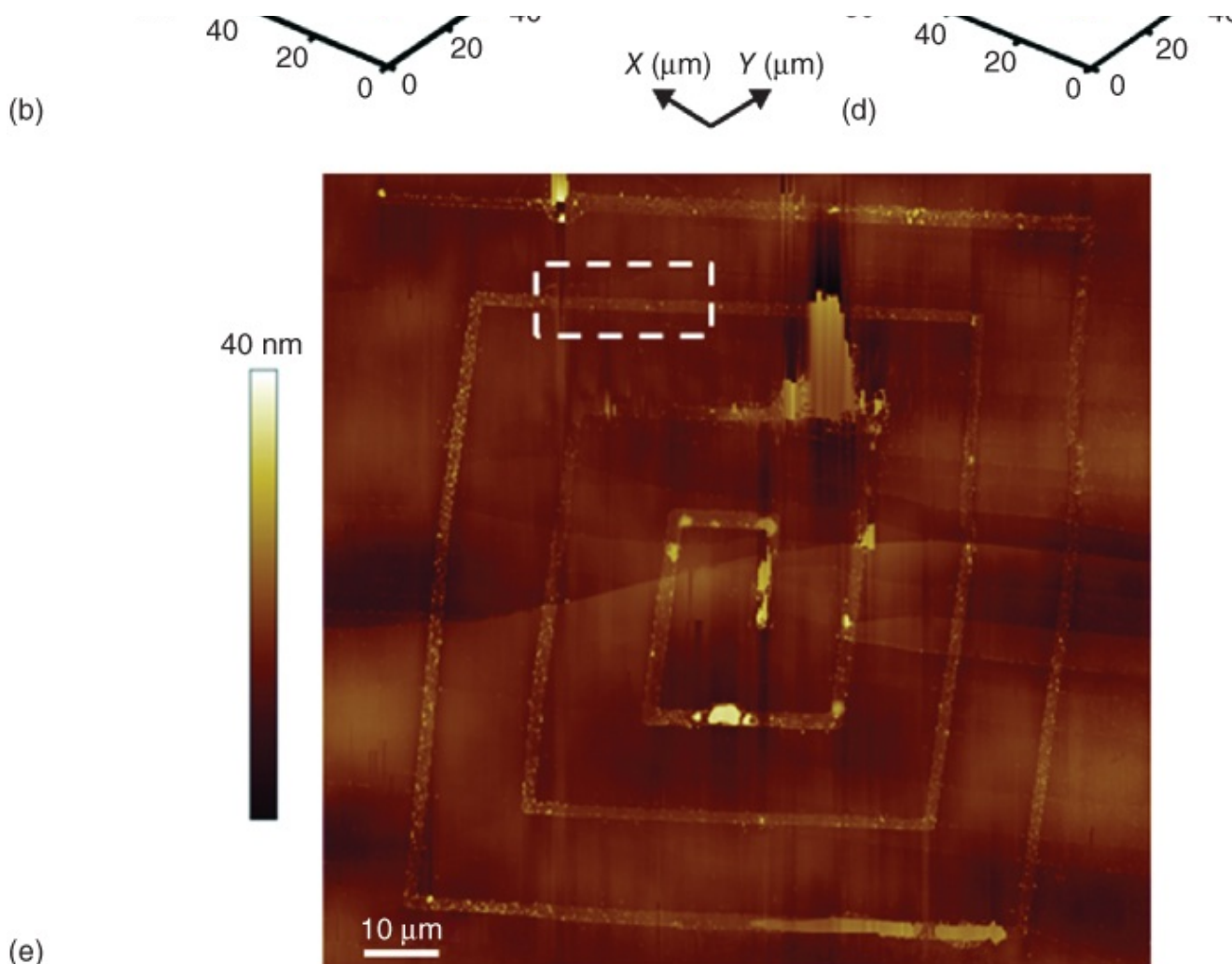


Figure 2.22 (a) SECCM linear sweep voltammogram of the electro-oxidation of 100 μM DA (0.15 M phosphate buffered saline containing 150 mM NaCl (pH 7.2)). Maps of (b) surface activity, (c) DC conductance current, and (d) AC component of the conductance current obtained with SECCM setup, together with (e) an AFM image in the same area.

(Figure adapted with permission from Ref. [197].)

The responses for DA and EP electro-oxidation on different grades of HOPG were studied by recording consecutive CVs ([Figure 2.23](#)) [196, 197]. In this figure, the data are for ZYA- and SPI-3-grade HOPG. In both cases, the recorded CVs are near-identical in terms of both the initial response and the subsequent deterioration pattern on successive potential cycling. Given that the two surfaces differ dramatically in step-edge coverage ([Figure 2.3](#)), a reasonable deduction would be that the reaction is dominated by the basal surface. In fact for DA electro-oxidation, many different grades of HOPG were investigated and the CV responses (10 cycles) were essentially similar across all grades [60].

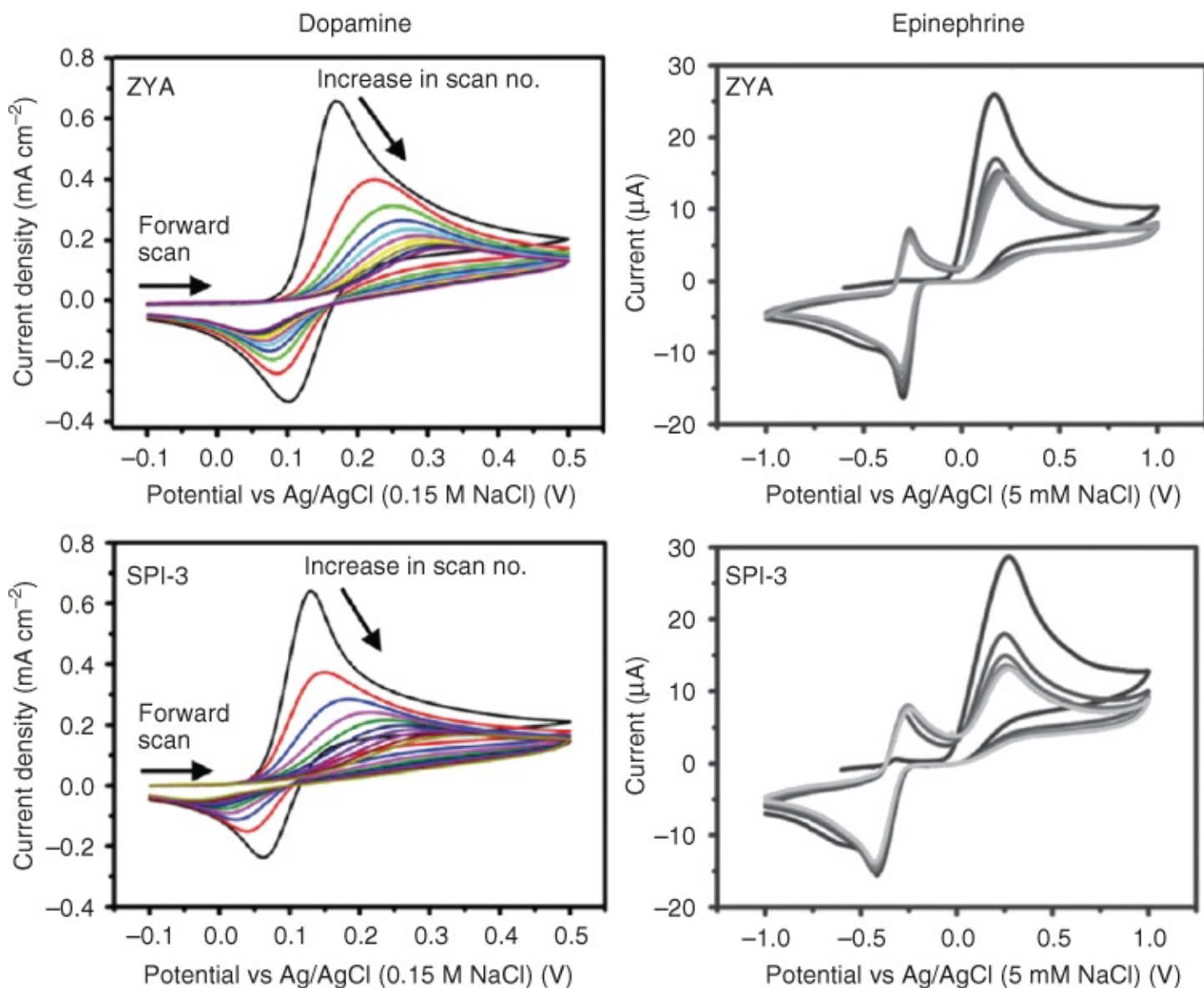


Figure 2.23 Macroscopic CVs for the oxidation of 1 mM DA (a)(i), (b)(i) and 1 mM EP (a) (ii), (b)(ii) on freshly cleaved surfaces of ZYA- and SPI-3-grade HOPG, at a scan rate of 0.1 V s^{-1} .

(Figure adapted with permission from Refs. [[196, 197]].)

A consequence of this work is that the basal surface of HOPG, rather than being inert, and a poor electrode for DA detection, is actually rather good. This is consistent with a related SECM study on the redox behavior of DA/dopamine quinone on HOPG, where fast ET behavior was seen [178]. The low capacitance of HOPG (as for pristine SWNTs [198]) is beneficial in voltammetric studies of DA at sub-micrometer concentrations, where the background response of the low-defect electrode material becomes particularly important to the sensitivity of detection. Thus, HOPG can be used to achieve lower detection limits with voltammetry than other electrodes, such as EPPG, BPPG, and GC [60].

Ascorbic acid (AA) is an antioxidant, which often coexists with DA under physiological conditions at levels ranging from 200 to 400 μM [199, 200]. The oxidation of AA is irreversible and occurs at potentials close to that of DA and norepinephrine on conventional

electrodes, such as Au, Pt, and GC [200–202]. Thus, the development of electrodes that allow the simple and rapid determination of DA with high selectivity and sensitivity is highly desirable for biological diagnostic applications.

Voltammetric studies on HOPG, of solutions containing both AA and DA, resulted in voltammograms showing two distinct peaks that could be assigned to AA and DA oxidation [60]. Continuous potential cycling showed the formation of a film across both the basal surface and edge-plane sites on the HOPG surface, which eliminated the oxidation signal from AA while allowing the DA signal to stay relatively constant with continuous potential cycling [60], illustrating the possibility of detecting DA in complex mixtures.

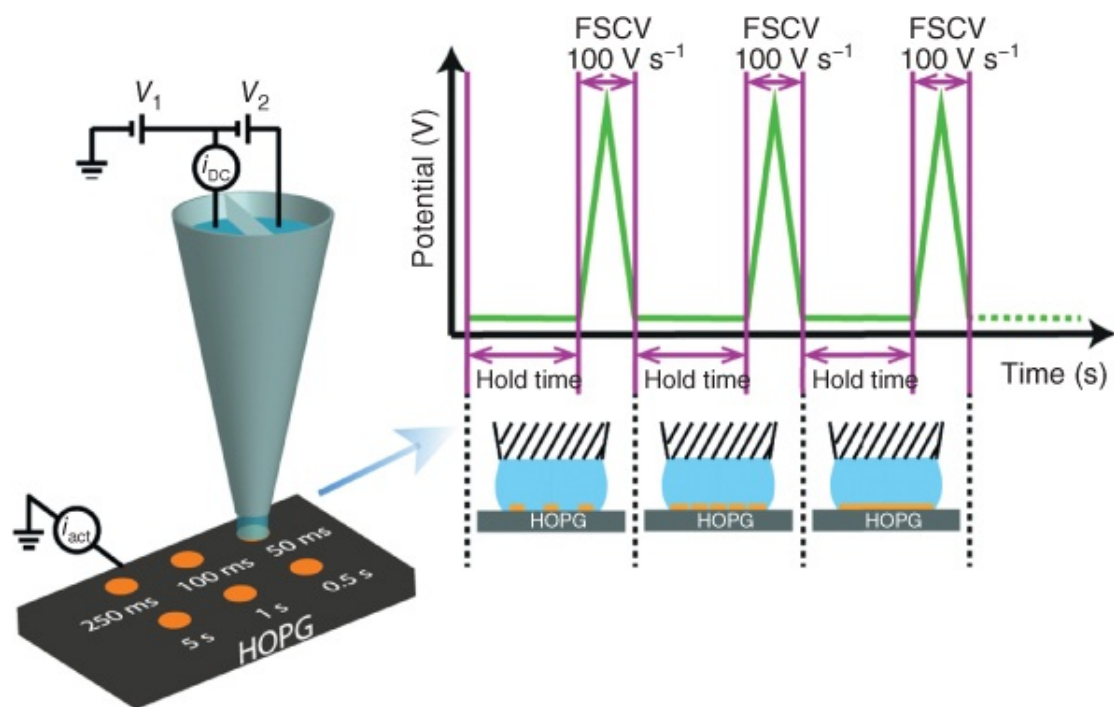
2.4.3 Adsorbed Systems

As discussed in [Section 2.3.1](#), the electrochemistry of adsorbed organic molecules has also been proposed as a means of characterizing the activity of surface structures on HOPG. In the case of quinones, it had been widely assumed that adsorbed AQDS was only electroactive at step edges and adsorbed electroactive AQDS was thus regarded as a key marker of step edges, and used as a means of measuring the quality of HOPG samples [74, 123, 157]. However, as summarized in [Section 2.3.1](#), the only correlation made between step-edge density and surface coverage was based on samples with a narrow window of step-edge densities, that is, 0.7–1.6% coverage, with high uncertainty (standard deviation) in the absolute values [74].

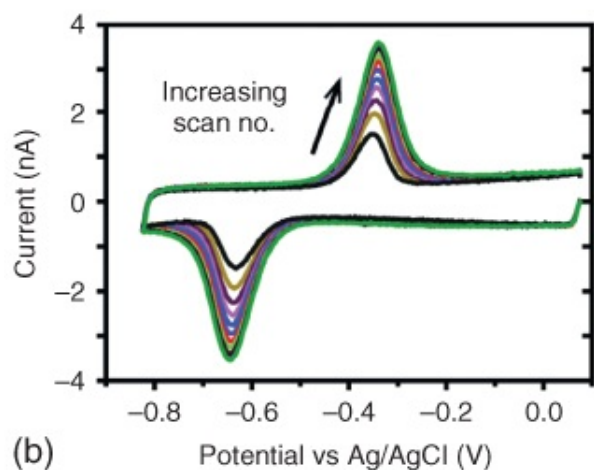
We have investigated the electrochemistry of adsorbed AQDS on HOPG surfaces at three different length scales, spanning the macroscale to nanoscale [79]. In the macroscopic measurements, four different grades of HOPG, specifically AM, ZYA, SPI-1, and SPI-3, with step-edge density varying by 2 orders of magnitude from the highest quality grade (AM) to the lowest quality grade (SPI-3) ([Table 2.1](#)) [38, 196], were employed. However, near-identical fractional surface coverage values from a solution (10 μM AQDS) were obtained: $29.7 \pm 1.6\%$ for Scotch tape-cleaved AM; $29.6 \pm 2.4\%$ for mechanically cleaved AM; $29.4 \pm 1.2\%$ for ZYA; $27.5 \pm 1.4\%$ for SPI-1; $28.0 \pm 0.6\%$ for SPI-3. This indicates that there is no correlation between the electroactive surface coverage of AQDS and step-edge density of HOPG surface.

Further microscale measurements were performed with an innovative fast-scan cyclic voltammetry–scanning electrochemical cell microscopy (FSCV–SECCM) platform, as illustrated in [Figure 2.24a](#). This revealed the evolution of adsorbed electroactive AQDS on HOPG on a rapid timescale ([Figure 2.24b,c](#)). The SECCM meniscus was brought into contact for a defined period, comprising a sequence of hold time (defined in [Figure 2.24a](#)), where the HOPG substrate potential was fixed, and analysis time, where the potential was scanned at 100 V s^{-1} to record a CV for AQDS reduction and reoxidation ([Figure 2.24b](#)). Interestingly, although the measurements were carried out on regions covered by different quantities of steps on the HOPG surface, this appeared to have little influence on the evolution of adsorbed AQDS. Adsorption built up rapidly over the first 6 s, and reached an equilibrium value at about 10 s, with the process controlled entirely by diffusion of AQDS to the HOPG surface (simulation for this model in [Figure 2.24c](#)). AFM imaging on the same areas, as probed

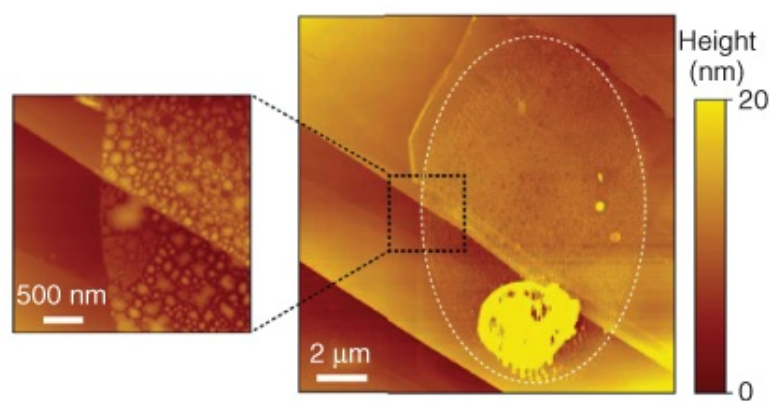
electrochemically by SECCM (e.g., [Figure 2.24d](#)), revealed that the fractional coverage of adsorbed AQDS had no link to the step-edge density on any of the areas investigated, with amounts of AQDS adsorption at least 2 orders of magnitude higher than could be accounted for if only step edges were assumed to be the adsorption sites. Moreover, no link between surface coverage and step-edge density was observed ([Figure 2.24e](#)). For example, in the case of 50 s adsorption time, the step-edge density of the spot in [Figure 2.24](#) is 0.021%, and even taking into account an electronic disturbance area generously extending 5 nm away from the steps on the top terrace [123] to make 0.11%, this is still much smaller than the measured fractional electroactive surface coverage (about 20%). Thus, the electrochemistry of adsorbed AQDS on HOPG is dominated by the basal plane and the basal plane shows high electroactivity.



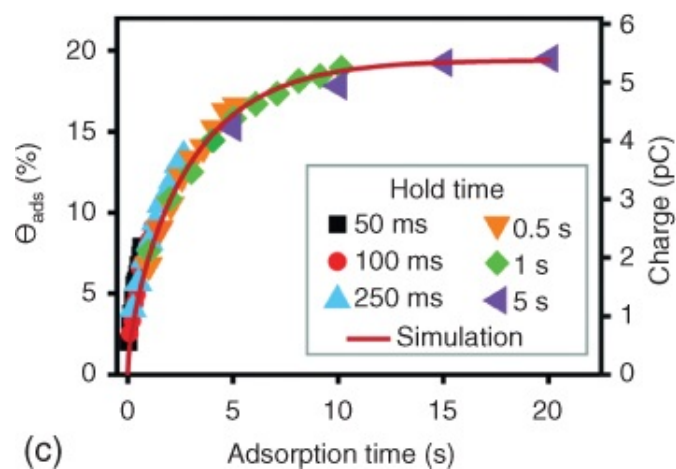
(a)



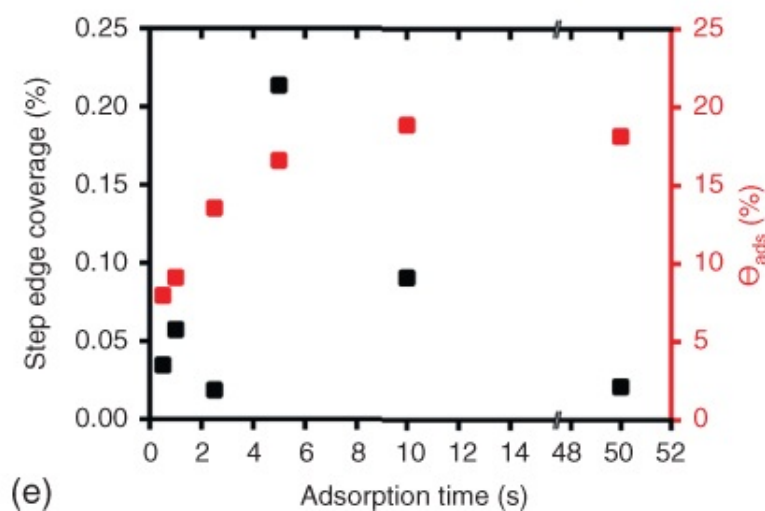
(b)



(d)



(c)



(e)

Figure 2.24 (a) Schematic of the FSCV–SECCM setup where 10 sequential CV scans were carried out in each of a series of spots on an HOPG surface, with hold times of 50 ms, 100 ms, 250 ms, 0.5 s, 1 s, and 5 s between each CV. (b) FSCVs for the adsorption of 1 μM AQDS in 0.05 M HClO_4 solution, recorded at 250 ms intervals (hold time) with a scan rate of 100 V s^{-1} , at AM-grade HOPG. (c) The fractional coverage of AQDS and corresponding charge in different parts of an AM-grade HOPG surface as a function of time, with respect to the different hold times. Solid line is the simulated behavior for diffusion-controlled adsorption. (d) Typical AFM image (*ex situ*) for an adsorption spot on an AM-grade HOPG surface taken after about 10 s, along with a $3 \times 3 \mu\text{m}$ higher resolution image, with the approximate droplet footprint outlined in white. (e) Percentage of step edges found within six adsorption spots, where FSCV measurements were made (at different total adsorption time) and the observed fractional coverage of electroactive AQDS.

(Figure adapted with permission from Ref. [79].)

Finally, SECCM line patterning, carried out to study the diffusional electroactivity of AQDS, was found to lead to uniform substrate current pattern on the whole HOPG surface, highlighting the high activity of the basal plane surface. In a sentence, all the measurements in this study revealed that the basal plane is highly electrochemically active, in contrast to earlier work that claimed the activity of the basal plane was (nearly) zero [72–74, 82, 158].

Note that although the electro-reduction of adsorbed AQDS is a complex 2e^- , 2H^+ process, analogous fractional coverage of AQDS and similar ΔE_p values were obtained on AM- and SPI-3-grade HOPG, under FSCV–SECCM conditions, where kinetics are evident [79]. This is despite the fact that the much higher step-edge density of SPI-3-grade HOPG might be considered to give rise to a higher DOS compared to AM grade. This means that step edges have little effect on the ET kinetics of AQDS on HOPG, and thus the electrochemical reduction of AQDS on HOPG appears to be in an adiabatic regime, which is again consistent with recent views of other fast ET processes [34].

2.4.4 Diazonium Functionalization of HOPG

The electrochemical reduction of diazonium salts is widely used for surface modification [203–206]. This reaction involves the electrochemical generation of a radical that, in the particular case of sp^2 carbon materials such as HOPG, carbon nanotubes, or graphene, bonds to the surface producing a rehybridization of the sp^2 carbons into sp^3 centers. This is particularly attractive in graphene technology, since the introduction of sp^3 centers is a potential route for the generation of band gap in graphene [207].

As highlighted in [Figure 2.25a](#), the electrochemical modification of HOPG with diazonium functionalities passes through two steps: ET for radical generation, followed by radical attachment at the surface (and some radical–radical coupling and radical attack at adsorbed moieties) [203, 209]. As a surface modification reaction, consecutive CVs for the reduction of carboxybenzenediazonium tetrafluoroborate in aqueous solution, as shown in [Figure 2.25](#), exhibit an irreversible reduction wave on the initial potential sweep, corresponding to the

reduction of the diazonium molecule. Further cycles display a diminished current magnitude, since the aryl radicals produced are covalently attached to the surface and partially block further ET [210]. It should be noted again that the grade of HOPG has no influence on the electrochemistry of diazonium (Figure 2.25c,d).

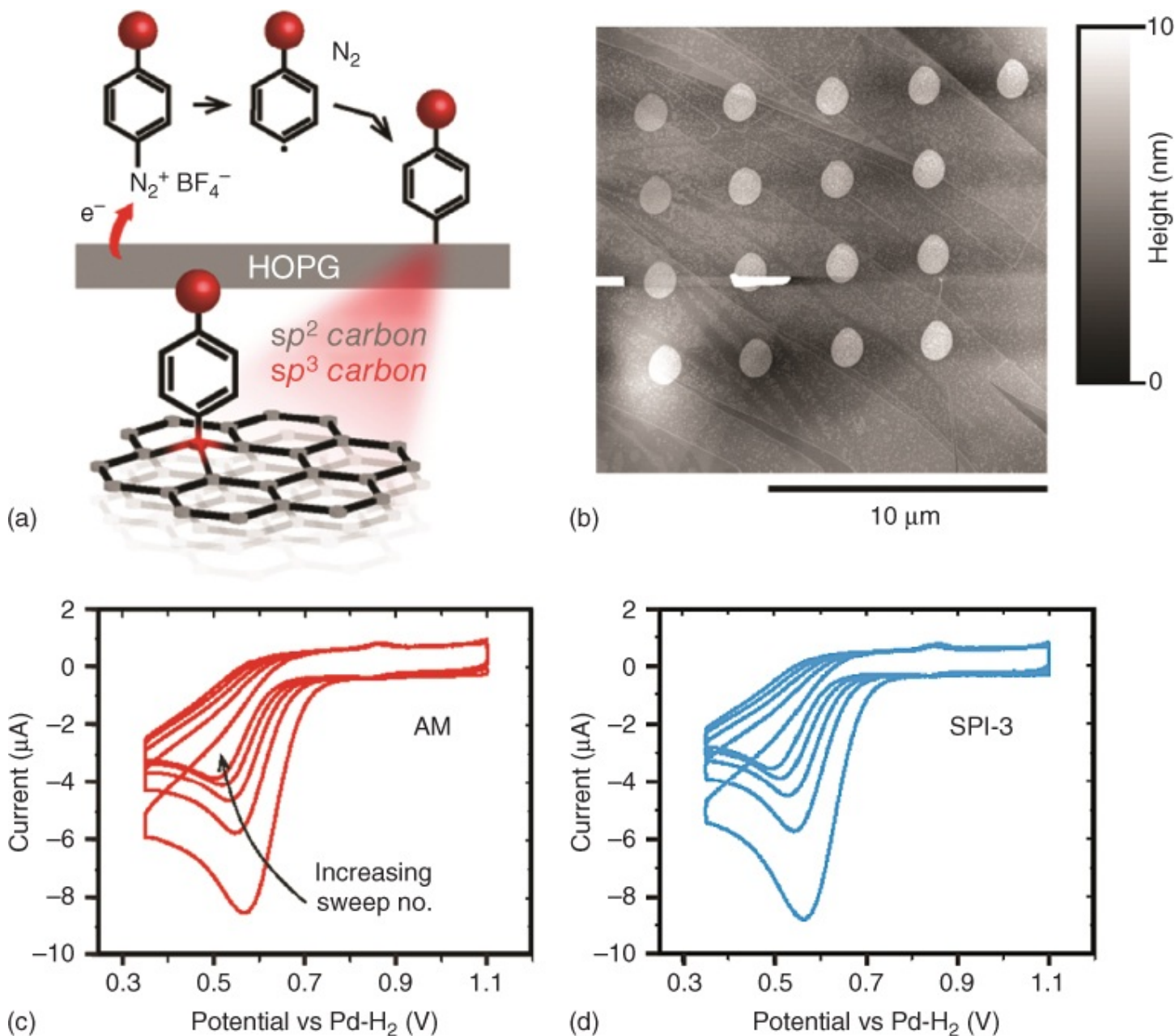


Figure 2.25 (a) Schematic showing the modification of an HOPG surface with an electrogenerated diazonium radical. (b) AFM image of the deposition array on HOPG. CVs of 0.1 mM diazonium in 50 mM H_2SO_4 at the surface of (c) AM-grade and (d) SPI-3-grade HOPG at a scan rate of 0.2 V s^{-1} .

(Figure adapted with permission from Ref. [208].)

The microelectrochemical cell created by SECCM allows the confinement of the modification of areas of HOPG (and, by inference, graphene) down to the microscale, leaving unmodified areas nearby that could be used as a reference, either to determine film thickness or changes in

Raman spectra. This confinement allowed only the basal plane of HOPG to be accessed (if HOPG with large step spacing was used, such as AM or ZYA grade), isolating the contribution of basal plane and step edges toward the electrochemical reduction of diazonium salts. [Figure 2.25b](#) shows an AFM image of an array of 17 well-defined discrete spots of surface modification, each employing a different grafting condition (time). The array reaction approach allowed multiple experimental conditions to be assessed on the same sample and on a very short timescale, minimizing variations in sample preparation (and minimizing contamination) [208].

Precise AFM analysis of spot thickness and the roughness within each spot demonstrated a high homogeneity of the deposited diazonium layers. Importantly, the confined electrochemical cell allowed a wide variety of HOPG surface characteristics to be accessed, such as purely the basal plane to basal surface with intersecting edge-plane areas. In all the cases, a homogeneous compact film was obtained, with no obvious material buildup around step edges, confirming that the basal surface supported the electrogeneration of the radical and the subsequent grafting. This is in agreement with a recent STM study, where it was found that there is no preferential attachment of arylidonium salts at defect sites in graphene, rather the basal surface was modified [211]. In addition, the low density of point defects on HOPG (reported to be between 0.1 and 10 μm^{-2} , as highlighted earlier) [122–126] makes it unlikely that all the radical generation and modification originate on these points.

Further surface characterization with Raman spectroscopy was used to confirm the modification of the surface with diazonium molecules, since the generated sp^3 centers result in an increase of the D band in the Raman spectrum of graphite [206, 212]. It is important to highlight that SECCM allows the electrochemical cell to be formed and dismantled at will (by just retracting the SECCM pipette), thus controlling precisely the time of the reaction and thereby minimizing sample manipulation and spontaneous unwanted processes (not driven electrochemically). This is therefore a potentially powerful platform for modifying and writing devices on graphene.

2.5 Conclusions

This chapter has highlighted HOPG as an important material for electrochemistry in its own right, and as a reference material for studies of novel sp^2 carbons (nanotubes and graphene) [12, 14]. It is important to recognize that HOPG comes in different grades (based on the mosaic angle), which impact the structure (step-edge density). These different grades are now beginning to be well understood in terms of structure and electronic properties, and this provides a tremendous opportunity to investigate structure–activity effects, either by executing measurements on HOPG of very different quality or by using high-resolution electrochemical techniques that can target particular features on the HOPG surface.

An important consideration is that after cleavage, the HOPG surface may undergo changes from both the adsorption of adventitious material [39] and other processes such as delamination, as inferred from time-dependent conductive AFM measurements [38]. Evidently, these processes

may depend on the cleavage method and the environment in which measurements are made. These issues may, in some part, explain some of the differences seen in HOPG electrochemistry in earlier work and more recent macroscopic and microscopic studies discussed in this chapter. For the moment, measurements need to be made as soon as possible after cleavage. In our macroscopic studies [38, 60], for example, solution was brought into contact (to cover) with freshly cleaved HOPG for a few seconds and the electrochemical measurement itself made within 1 min. Future studies to further elucidate the importance of time-dependent processes could investigate environment effects, for example, by making measurements in a glove box or returning to ultra high vacuum–electrochemical setups popular in the 1970s and 1980s [213] for single-crystal metal electrodes, although such measurements are nontrivial.

A major outcome of this overview has been to show the ambiguity that may result in the analysis of macroscopic CVs, without recourse to other information. During a CV measurement, the driving force changes, as does the mass transport rate. If, additionally, the surface is heterogeneously active, and susceptible to time-dependent side reactions, deriving unique microscopic models from a CV measurement alone becomes extremely difficult, particularly if such a measurement only employs one scan rate. Thus, we showed that rather similar (distorted) CVs can be found on HOPG of very different surface quality (step-edge density, capacitance), which mitigates against a step-driven model of activity. Moreover, we showed that this similar distorted CV (sluggish kinetics) can be obtained simply by carrying out multiple potential cycling in a small liquid volume cell or by leaving a cleaved surface for periods of time before making a measurement. This highlights the need for microscopic measurements and/or macroscopic measurements that address well-defined (known step-edge density) samples, of known history.

Microscopic and nanoscopic measurements discussed in [Section 2.4](#) allow the basal surface of HOPG to be targeted without any influence of step edges. The basal surface itself contains point defects, but evidence hitherto indicates the concentration is rather low and in a narrow range [122–126]. Thus, the relatively high activity seen for a wide range of reactions suggests that the basal surface is, itself, intrinsically active, and will dominate macroscopic electrochemistry even if some edges have higher activity. This represents a radical new view of the electrochemistry of graphite materials, with implications for related materials such as carbon nanotubes and graphene. Even though these different graphitic materials have distinct characteristic electronic structures, the DOS values are broadly similar within a potential region on either side of the DP, albeit that graphene has a lower DOS than graphite. Thus, recent studies highlighting the high electrochemical activity of the basal side wall of SWNTs [21, 22, 170, 171, 214, 215] are particularly pertinent to the HOPG studies discussed herein. Indeed, for many electrochemical reactions, the basal surface of HOPG and metallic SWNTs appear to have similar behavior (kinetics) to metallic electrodes [21, 22, 38, 60, 170, 171, 214–216]. Of course, some electrocatalytic reactions involving dissociation, for example, as in the oxygen reduction reaction may be catalyzed by defect sites as seen at SWNTs [171], and further studies of such processes at HOPG could be interesting. Moreover, redox processes whose potential is close to the intrinsic Fermi level of graphene and graphite may reveal

interesting LDOS effects [217].

Given the comparatively low DOS of graphite surfaces, a major view developing is that many fast ET reactions thus appear to be in an adiabatic region. This has been an open question in electrochemistry for a long time, and the low activity seen on HOPG in earlier studies ([Section 2.3](#)) pointed to the opposite conclusion. Recent studies highlighted in this chapter are thus not only important for understanding the electrochemistry of graphitic materials, but are also of huge significance for fundamental electrochemistry generally [218].

Acknowledgments

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Chapter 3

Electrochemistry in One Dimension: Applications of Carbon Nanotubes

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3.1 Carbon Nanotubes: General Considerations

Carbon nanotubes (CNTs) were discovered in 1991 by Iijima [1]. The widespread research on CNTs started in 1990s, but was preceded in 1980 by the first industrial synthesis of some products today known as **CNTs** as well as documented observations of hollow carbon nanofibers as early as 1950s [2].

CNTs are promising materials, with tensile strength significantly higher than that of steel, thermal conductivity better than all but purest diamond, and electrical conductivity similar to copper with the ability to carry higher currents. They represent an important group of nanoscale materials with properties very different from those of conventional materials. At such small scales, materials present unique optical, electrical, chemical, and mechanical characteristics [3–7]. Therefore, CNTs present exceptional properties that make them interesting candidates for applications in different fields mainly due to their unique structure and chemistry. They have been used for a large number of applications in very different fields: scanning probe microscopy, field emission, nanoelectronics, and solar cell technology.

The one-dimensional nature of the basic CNT structure allows them to have a huge surface area, the feasibility to act as a semiconductor or metal, the existence of multiple direct band gaps, and the possibility of attachment of a diversity of functional groups and nanoparticles (NPs) [8]. Since 2006 the capacity of production, one of the first limitations of CNT synthesis, largely increased all over the world and the number of patents and journal publications grew dramatically. Today, CNTs are found everywhere: as composite bicycle frames, antifouling coatings, and printed electronic and electrostatic discharge shielding, among others [8].

CNTs have also received enormous attention as analytical tools in the construction of (bio)sensors to either support the biorecognition element or improve the transduction event, as has been extensively reviewed [9–15].

3.2 Structure and Synthesis of CNTs

CNTs can be thought of as graphitic sheets built from sp^2 carbon units with a hexagonal lattice wrapped into a seamless cylinder being several nanometers in diameter and many microns, and

even millimeters, in length [16–18]. The structure of a CNT can be described using two parameters, the chiral vector (C_h), which goes from the origin atom toward the other with its length equal to the circumference of the nanotube and the chiral angle (θ), which is the angle between C_h and a_1 . $C_h = n\bar{a}_1 + m\bar{a}_2$, where a_1 and a_2 are unit vectors in the two-dimensional hexagonal lattice, and n and m are integers as shown in [Figure 3.1a](#). The integers (n,m) of the nanotubes can alternatively be presented in terms of the diameter (d_t). Therefore, a nanotube can be specified by either its (n,m) indices or, equivalently, d_t and θ . Depending upon how the two-dimensional graphene sheet is rolled up, there are three types of CNTs ([Figure 3.1b](#)): armchair, zigzag, and chiral. Armchair nanotubes are formed when $n = m$ and θ is 30° , zigzag nanotubes when either n or m are 0, and θ is 0° . All other nanotubes are known as **chiral nanotubes** and present θ values between 0° and 30° . The helicity and the diameter introduce important changes in the electronic density of states, conferring to CNTs unique electronic characteristics [19–21].

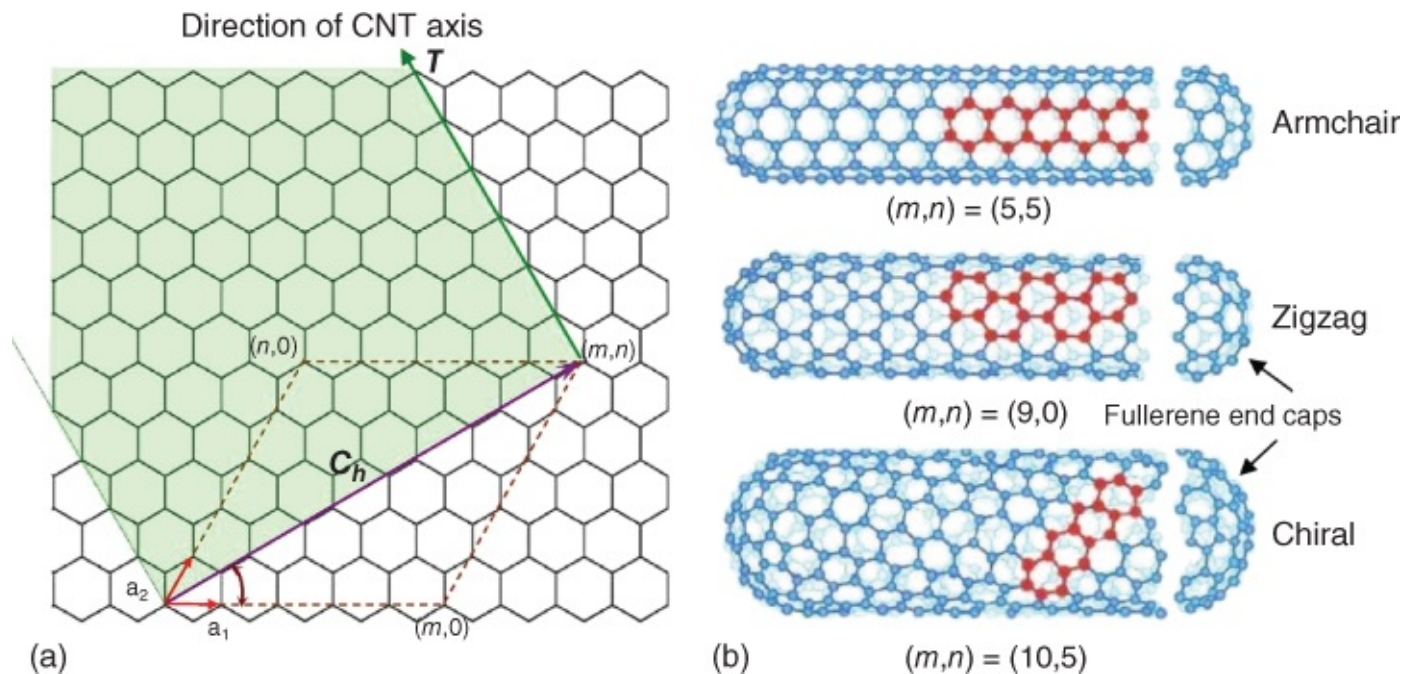


Figure 3.1 (a) Schematic representation of the roll-up vector over the graphene surface, which defines the different CNT structures. (b) SWCNT armchair, zigzag, and chiral.

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On the basis of the number of concentric walls, CNTs can be divided into single-walled carbon nanotubes (SWCNTs) and multiwalled carbon nanotubes (MWCNTs) [22]. SWCNTs consist of a single rolled graphite sheet defining a cylinder of 0.4–2 nm of diameter and up to several microns long. MWCNTs can be visualized as concentric and closed graphite tubules with two (double-walled carbon nanotubes, DWCNTs) or several layers of graphite sheet that define a diameter typically of 2–100 nm separated by an interlayer space of approximately 0.34 nm [23]. [Figures 3.2a,b](#) display transmission electron microscopy (TEM) images of SWCNTs and MWCNTs, respectively. MWCNTs are metallic conductors, whereas SWCNTs can be metallic or semiconducting, depending on their diameter and chirality. For small-

diameter SWCNTs, approximately two-thirds are semiconducting and one-third are metallic. For semiconducting nanotubes, the band gap also depends on the tube diameter [19, 20].

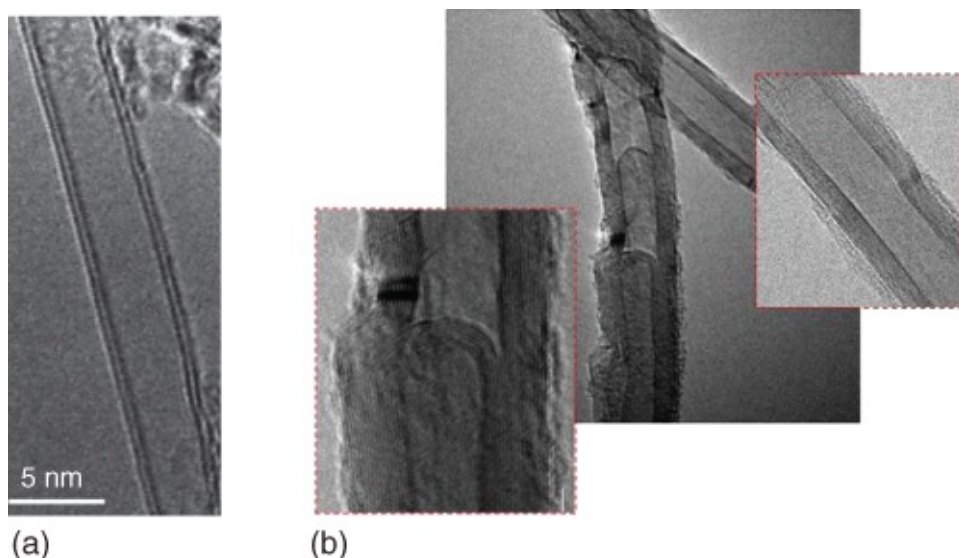


Figure 3.2 (a) TEM micrograph of as-synthesized SWCNT. (b) TEM micrograph of a sample containing both MWCNT and bCNT. (two magnifications are displayed at right and left panels, respectively).

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Depending on the presence of sidewall defects, MWCNTs can also be separated in hollow-type MWCNTs (hCNTs), which present ideally defect-free sidewalls, and bamboo-like MWCNTs (bCNTs) that are characterized by having transverse walls regularly located along the tubes resulting in edge planes of graphene material at regular intervals along the walls [8, 25]. [Figure 3.2b](#) shows the bamboo-shaped structure of bCNTs.

CNTs can be obtained by electric arc discharge, laser ablation, high-pressure carbon monoxide, and catalyzed chemical vapor deposition. The multiple synthesis methods for CNTs are outside the scope of this chapter and had been extensively reviewed elsewhere [26–28]. The first three methods produce a large amount of by-products such as graphitic debris, metallic NPs, and fullerenes. On the contrary, CNTs obtained by chemical vapor deposition are highly crystalline and have low defect densities, although a minimal amount of amorphous content and NPs is present [27].

Several alternatives have been proposed to purify the as-produced CNTs. Mixtures of $\text{HNO}_3/\text{H}_2\text{SO}_4$ are most effective in removing amorphous carbon [29], while HCl treatment together with sonication is more useful to remove catalytic NPs [30]. These impurities, particularly the metallic NPs, are probably responsible for the “electrocatalysis” seen at some CNT-modified electrodes [31]. On the other hand, extensive exposure to oxidant solutions generates cut ends and defects/oxygen functionalities in the carbon sp^2 structure, which cause significant changes in the CNT electronic states near the Fermi level. Therefore, special care should be taken in the purification step in order to minimize such changes.

3.3 Structure of CNTs versus Electrochemical Properties

Considering the interfacial nature of electrochemical processes, CNTs are ideal candidates for electron transfer analysis as has been widely demonstrated. Since the pioneering work of Britto *et al.* [32], several studies have been conducted to determine the electrochemical properties and their relationship with structural and/or electronic features.

Gooding's group [33] reported interesting results mainly based on the control of the orientation of SWCNTs. They modified Au electrodes with acid-treated SWCNTs using two strategies: (i) covalent link to the electrode derivatized with cysteamine thiol to obtain vertically aligned SWCNTs and (ii) drop-coating Au electrode to obtain the horizontally spread SWCNTs.

[Figure 3.3](#) depicts the cyclic voltammograms for $[\text{Fe}(\text{CN})_6]^{3-}$ at both surfaces. The peak-to-peak separation (ΔE_p) for the SWCNT-edge exposed electrode is 59 mV ([Figure 3.3a](#)) while for the SWCNT-wall exposed electrode, it is 99 mV ([Figure 3.3b](#)). The favorable electron transfer at the vertically aligned SWCNTs demonstrates that the ends of the nanotubes possess electrocatalytic properties different from those at the sidewalls. This conclusion was broadly confirmed in several reports [34]. Even though $[\text{Fe}(\text{CN})_6]^{3-}$ is considered an *inner-sphere* redox couple at carbonaceous surfaces, and the electrochemical response is highly dependent of the surface oxygen content [35], similar results were obtained with $[\text{Ru}(\text{NH}_3)_6]^{3+}$, a truly *outer-sphere* species with a surface-independent electron transfer behavior [36].

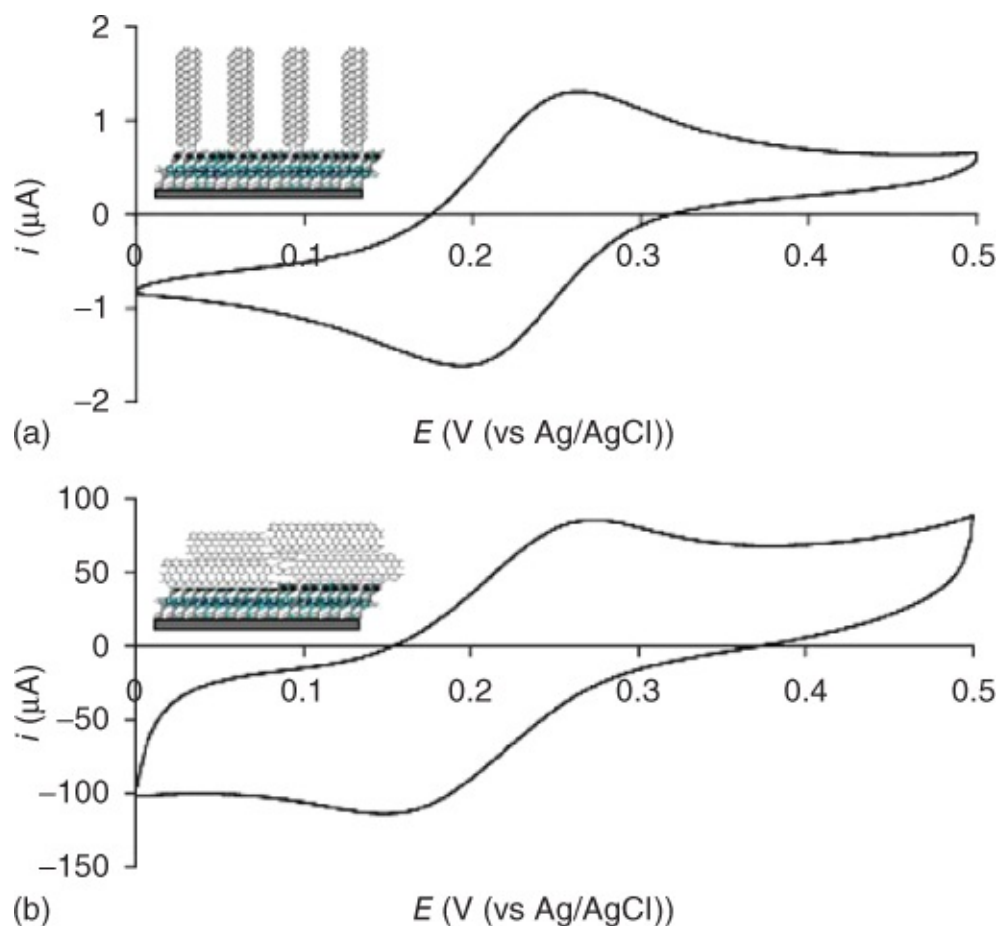


Figure 3.3 Cyclic voltammograms in 1 mM $[\text{Fe}(\text{CN})_6]^{3-}$ over (a) covalently aligned and (b) drop-coated SWCNT-modified Au/cysteamine electrode. Supporting electrolyte: 0.05 M phosphate buffer solution pH 7.0 and 0.05 M KCl solution.

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The oxidation state of CNTs is a key factor when considering the electron transfer rate of the selected redox probe. Gong *et al.* [24] performed an elegant experiment with superlong (5 mm) pristine and oxidized vertically aligned SWCNTs as shown in [Figure 3.4](#). They selectively masked the sidewalls or tips with a polystyrene insulating coating and tested different redox probes ([Figure 3.4a](#)). In the case of H_2O_2 , they found a significant improvement in the electron transfer rate at both the oxidized tip-exposed SWCNT ([Figure 3.4b](#)) and oxidized sidewall-exposed SWCNT ([Figure 3.4c](#)). In the case of ascorbic acid (AA) oxidation ([Figure 3.4d,e](#)), the electrocatalysis was favored at the tip compared to the sidewalls, $E_{\text{p,a}} = 0.350 \text{ V}$ and $E_{\text{p,a}} = 0.450 \text{ V}$, respectively. In the case of both reactions, the oxidation was catalyzed when oxygen groups are present ($E_{\text{p,a}}$ oxid-tip = 0.030 V and $E_{\text{p,a}}$ oxid-sidewall = 0.130 V). This is also true for MWCNTs [37], although in this case it is difficult to separate the effect of oxygen-containing functionalities from the effect of edge-plane defects, since their effects are in the same direction.

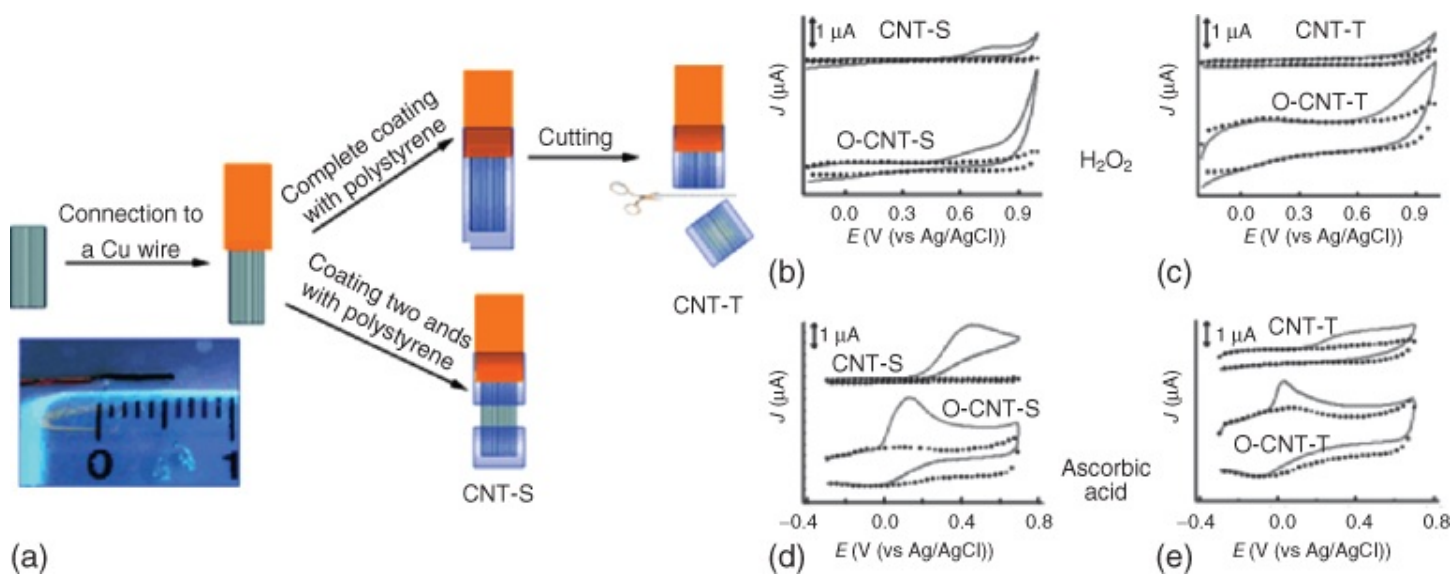


Figure 3.4 (a) Schematic representation of the procedure for preparing the CNT electrodes with tip exposed (CNT-T) or sidewall (CNT-S) accessible to electrolyte. CVs of 2.0 mM H_2O_2 (b,c), and 2.0 mM ascorbic acid (d,e) recorded in phosphate buffer solution pH 6.5 at the CNT-S (upper curves in b and d), O-CNT-S (lower curves in b and d), CNT-T (upper curves in c and e), and O-CNT-T electrodes (lower curves in c,e). The dotted curves were recorded at the corresponding CNT electrodes in the absence of the electrochemical probe molecules. Scan rate: 0.100 V s^{-1} .

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Regarding the latter, Compton *et al.* [38–40] reported a series of works where they compared the electrochemical response of CNTs with basal plane pyrolytic graphite (BPPG) and edge-plane pyrolytic graphite (EPPG). They found that the pristine walls of CNTs behave as a basal plane of graphite with the heterogeneous electron transfer constant (k_{ET}) close to zero, while the ends of the CNTs and the defects present on their walls resemble the behavior and fast electron transfer of EPPG. Even though this last conclusion is well established in the electrochemical community, there is still no absolute electrochemical evidence that a nanotube sidewall is completely inactive [34].

Pacios *et al.* [41] analyzed the charge transfer resistance (R_{ct}) derived from impedance spectroscopy experiments with the $[\text{Fe}(\text{CN})_6]^{3-/4-}$ redox couple of several epoxy composite electrodes with different pristine CNTs; shown in Figure 3.5. The similar R_{ct} for EPPG and bCNT is due to its high density of edge-plane defects [25]. This also explains the decrease in R_{ct} of bCNT versus SWCNT. Another interesting result is that upon increasing the MWCNT diameter, the electrocatalytic properties are less important. *Ab initio* calculations have shown that upon increasing the curvature of the CNTs, there is a decrease in the k_{ET} [42], indicating that when the MWCNT diameter increases the structure tends to resemble a graphitic surface.

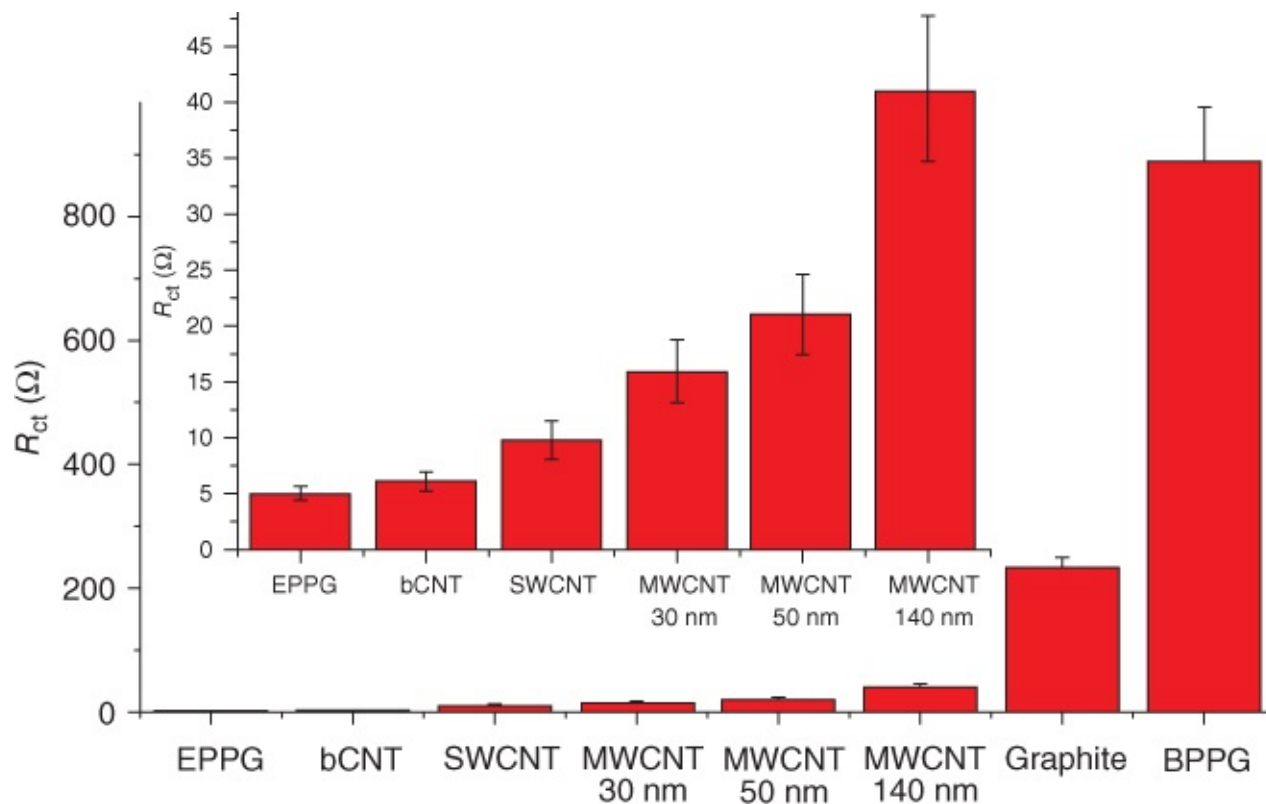


Figure 3.5 Values of charge transfer resistance (R_{ct}) obtained by fitting with an equivalent circuit of the impedance spectra performed in $[\text{Fe}(\text{CN})_6]^{3-/4-}$ for several electrodes (from left to right): EPPG, bCNT, SWCNT, MWCNT with diameter equal to 30, 50, and 140 nm, graphite and BPPG. The inset shows values at a lower resistance scale.

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Regarding the use of nanoscale carbon-based electrode materials, there are still some issues that need to be resolved; mainly regarding the relationship between electrochemical properties and electronic features of the CNTs (i.e., semiconducting or metallic) [34]. In this sense, the main inconvenience is that electrochemistry is essentially a macroscopic methodology while CNT features occur at the nanometer scale. Therefore, special care must be taken in the reproducibility of the synthesis methodology, the degree of purity of CNTs, and the strategy used for the immobilization to the conductive substrate before drawing conclusions from electrochemical measurements.

3.4 Strategies for the Preparation of Carbon Nanotube-Based Electrodes

As was previously explained, CNT-based electrodes exhibit excellent electrocatalytic properties, mainly contributed by the activity of edge-plane-like graphite sites at the CNT ends [43, 44]. The inconvenience is that they exist as bundles of SWCNTs, or aggregates of MWCNTs held together by van der Waals forces; thus the poor dispersion of CNTs in aqueous and organic solvents, due to strong van der Waals forces and π - π stacking interactions between the tubes. This fact produces a serious limitation for the manipulation and processing of CNTs

and further integration into more complex systems. To overcome this problem, much effort has been made to develop several strategies for the immobilization of CNTs on electrochemical transducers, such as functionalization of CNTs or incorporation into pastes [45, 46].

3.4.1 Functionalization

To facilitate the incorporation of CNTs at different electrodes, diverse surface modification protocols have been evaluated [47]. These mainly follow two functionalization routes, covalent and noncovalent.

One of the main advantages of the covalent functionalization is the increased efficiency to obtain proper dispersions, although it presents the disadvantage that it disrupts the conjugation of the π -bonds of the CNT, altering in most cases the intrinsic properties of the CNTs, such as conductivity and mechanical strength, since it destroys the regular graphene-type structure [48].

Noncovalent functionalization offers the advantage of preserving the intrinsic properties of CNTs, and, consequently, their original electronic and optical properties. In this case, the adsorption of functional molecules does not occur with disruption of the extended π -conjugated system ($sp^2 \rightarrow sp^3$ rehybridization) but via van der Waals-type or electrostatic interactions. As a consequence, the original electronic and optical properties of the CNTs are preserved almost completely. However, the main drawback of this functionalization type is the problem of the possible reaggregation of the nanotubes due to the inherently weak interactions [48].

The criteria for selecting one approach over others depend on the application purpose. The main challenge is to choose a protocol that allows obtaining the best compromise between the efficiency of the dispersion and the inherent properties of CNTs, mainly the electronic one [45].

3.4.1.1 Covalent Functionalization

This strategy is based on the covalent attachment of functional groups to the C=C double bonds of the polyaromatic network of CNTs. By adjusting the reaction conditions (i.e., catalysts and reactants concentration, temperature and solvent), this strategy has allowed the selective and controlled modification of CNTs and, due to the nature of the bonds, has provided long-term stability to the dispersion. Nevertheless, the two main drawbacks of covalent surface modification are: (i) the inevitable loss of their electrical and/or electronic properties [49] and (ii) the low degree of functionalization.

The covalent chemistry of CNTs may be classified into two categories, depending on the different reactivities of the bare nanotubes. The first involves the semifullerene tips and the defects over the sidewalls and the second one, the sp^2 hybridized sidewalls.

The Tip and Defect Covalent Chemistry

This strategy involves the hemispherical fullerene caps and several kinds of sidewall defects (π -orbital misalignments between adjacent carbons, pentagon–heptagon pairs called **Stone–Wales defects or vacancies**). The reactivity arises from the strain and torsional strain relief by

the transformation of sp^2 - into sp^3 -hybridized carbons [50]. This type of chemical modification involves mainly the oxidation to carboxylic groups using strong oxidant mixtures and ultrasonication [51]. Even though this methodology produces drastic changes in the electrochemical properties of CNTs [52], it improves the dispersibility of CNTs in organic solvents and water [47], and also gives a wide range of possibilities of functionalization with several types of (bio)molecules, taking advantage of the condensing reaction of the carboxyl groups with amines and alcohols. Some examples are presented in [Table 3.1](#).

Table 3.1 Main covalent functionalization strategies for the modification of CNTs with general applications in electrochemistry

Methodology	Part of the CNT which reacts	Functionality added	General procedure and considerations	Application electrocher
Oxidation	Cap ends and defects. Under certain circumstances, the sidewalls	$-\text{COOH}$, $-\text{OH}$, $=\text{O}$ groups	1) Liquid-phase: hot concentrated HNO_3 or $\text{HNO}_3/\text{H}_2\text{SO}_4$; <i>piranha</i> solution. Ultrasound treatment 2) Gas-phase: UV irradiation in O_3 , O_2 plasma, and HNO_3 vapor	Dispersion oxidized C. in a wide v of solvents, electrode modificac [53]
Oxidation, esterification/amidation	Carboxylated groups	$-\text{OH}$, $-\text{NH}_2$ groups	1) Activation via formation of acyl-chloride: reaction with SOCl_2 , usually in DMF, high temperatures 2) Activation via aqueous solution of EDC/DCC and NHS or HOBt, mild conditions	Electrochei biosensing Immobiliza of proteins, DNA, and antibodies 55]
Oxidation and thiolation	Carboxylated groups	$-\text{SH}$ groups	1) Reduction with NaBH_4 , activation with SOCl_2 , and thiolation with $\text{Na}_2\text{S}/\text{NaOH}$ 2) Activation with SOCl_2 and thiolation with $\text{H}_2\text{N}-\text{R}-\text{SH}$	Self-assem thiolated C [56, 57] Functionali of CNTs w MNps [58]
<i>Cycloadditions</i>				
Nitrenes addition	Sidewalls	Molecules with	—	—

		alkoxycarbonyl azide groups		
1,3-Dipolar cycloaddition	Sidewalls	Pyrrolidine rings fused to C–C bonds	Addition <i>in situ</i> of azomethine ylides by thermal condensation of aldehydes and α -amino acids	Immobilization of ferrocene Electrochemical detection of anions, amino acids, and peptides [6]
Cu(I)-catalyzed Huisgen [3+2] dipolar cycloaddition	Cap ends, defects, and sidewalls, depending on the strategy	Any molecule that bears an azide or alkyne group. It can be added through azo-coupling (radical way) or EDC/DCC coupling, previous oxidation of the CNTs	Addition of azide and alkyne groups via Cu(I) catalyzer generated:	Immobilization of polymer: amino acid MNPs, antibodies, redox-active molecules for biosensing [62] Improving biocompatibility of CNTs [6]
			1) <i>In situ</i> from CuSO ₄ and ascorbate 2) By mixing a Cu(I) halide with DBU/PMDETA.	

Radical additions

Diazonium salts	Sidewalls	Substituted aryl groups	<i>In situ</i> generation of aryldiazonium cations by mixing the arylamine with NaNO ₂ in acidic media. The aryl radicals are coupled by application of current/potential/potential scan or by heating the mixture	Electrode modification [64–66]
				Immobilization of enzymes [68]
Electrochemical radical addition	Sidewalls	Substituted aryl groups	<i>In situ</i> formation of radical species by	Attachment MNPs [69]

			electron transfer from CNTs at constant potential/current	
				Grafting of polymer br via atom tr: radical polymeriza [70]
				Immobiliza of hydrogei enzyme [71 DNA [72]

Symbols: EDC: 1-ethyl-3-(3-methylaminopropyl)carbodiimide, DCC: *N,N'*-dicyclohexylcarbodiimide, HOBt: hydroxybenzotriazole, NHS: *N*-hydroxysuccinimide, MNps: metal nanoparticles, DBU: 1,8-Diazabicyclo[5.4.0]undec-7-ene, and PMDETA: *N,N,N',N',N''*-pentamethyldiethylenetriamine, DMF: dimethylformamide.

The Sidewall Covalent Chemistry

Direct covalent sidewall functionalization is associated with a change of hybridization from sp^2 to sp^3 and a simultaneous loss of the π -conjugation system in the graphene layer. This methodology takes advantage of the organic chemistry associated with the addition to C=C bonds and, due to the lower reactivity of these bonds, it requires the use of highly reactive species [73]. The most important ones, which have been responsible for intriguing applications in the field of electrochemistry, are: (i) radical addition, specially through the diazonium salt route and further electrochemical modifications, (ii) addition of nitrenes, (iii) 1,3-dipolar cycloaddition, and (iv) Cu(I)-catalyzed Huisgen [3+2] dipolar cycloaddition. The latter has been of special interest in the past few years due to the emergence of the so-called **click chemistry** and its promising advantages [74].

3.4.1.2 Noncovalent Functionalization

In the last few years, the noncovalent treatment of CNTs has been widely used in the preparation of both aqueous and organic solutions to obtain a high weight fraction of individual nanotubes or small aggregates of dispersed nanotubes [75]. Noncovalent functionalization of nanotubes is of particular interest, because it improves solubility and processability without compromising their physical properties. The noncovalent approaches are based on the interaction of the hydrophobic part of the dispersing agents with the nanotube sidewalls through electrostatic interaction, π - π stacking, CH- π [76], or van der Waals forces, facilitating the aqueous solubility through the hydrophilic part of the molecules. This type of functionalization mainly involves a great variety of molecules and biomolecules, including small ones such as flavonoids, pyrene, porphyrin and their derivatives, (bio)macromolecules (simple saccharides and polysaccharides, peptides, proteins, enzymes, oligonucleotides,

DNA), surfactants, ionic liquids (ILs), and other polymers [77, 78].

Among the diversity of molecules reported, ILs emerged as an alternative material for obtaining well-dispersed CNTs due, principally, to their high ionic conductivity and solvation ability. The combination of ILs and CNTs was first reported in 2003, when Fukushima and coworkers [79] found that CNTs could form gelatinous materials, called *bucky gels*, upon being ground with room temperature ionic liquids (RTILs). Since then, CNT–IL hybrids have attracted great attention and their applications in different fields, from electrochemistry to polymer composites, have been extensively studied. Furthermore, by simple anion exchange reactions, the solubility of the nanomaterials modified by ILs can be easily tuned.

Polymers [80–86] have allowed the successful dispersion of CNTs. The main advantage is that they reduce the entropic penalty of micelle formation and have significantly higher energy of interaction with nanotubes than with small molecules. The main problem in the use of polymers is that the interaction with the mechanically rigid CNTs may force them into energetically unfavorable conformations. It has been suggested that to minimize their strain conformations, the polymers, in general, wrap around the nanostructures through π -stacking interaction [87]. In this way, polymers have been widely adopted to achieve effective disentanglement of CNTs allowing thus, their dispersion, and showing enhanced electrical properties.

Electrochemical sensors modified with a CNT dispersion have been prepared by various techniques that basically consist of casting on the electrode, usually glassy carbon, screen-printed electrodes (SPEs), or gold. The most common coatings of electrodes with dispersions are obtained by “dipping” or “dropping” the given CNT–polymer dispersion, followed by a drying step under different conditions [88]. One important aspect to take into account for the electrochemical applications of CNT–polymer dispersions is to know the distribution of the nanotubes at the electrode surface, to correlate this behavior with the electrochemical one. Primo *et al.* [89] compared scanning electron microscopy (SEM) images of glassy carbon electrodes (GCE) modified with different CNT–polymer dispersions: (a) MWCNT-GOx; (b) MWCNT-PEI; (c) bCNT-dsDNA; and (d) MWCNT-Polyhis ([Figure 3.6](#)).

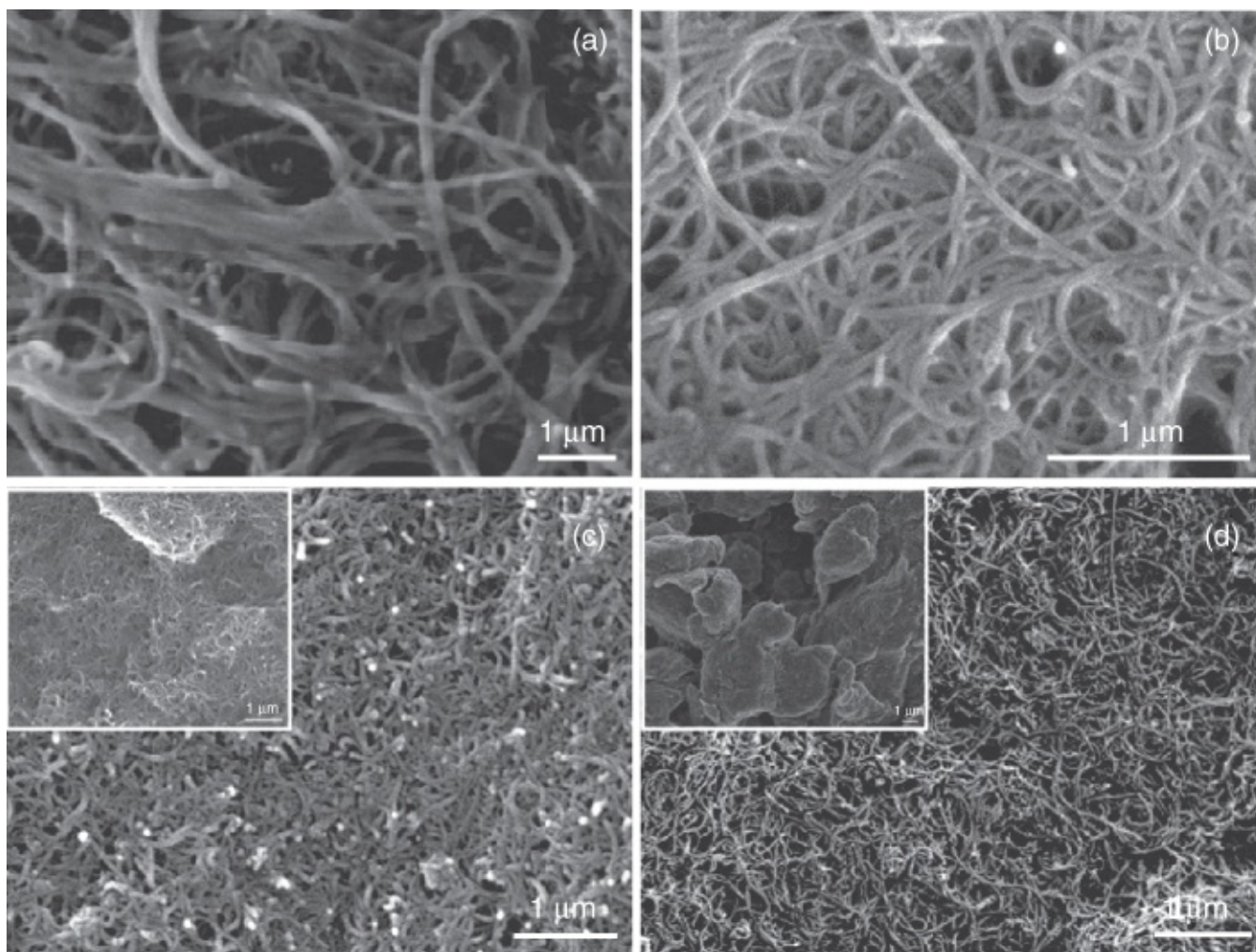


Figure 3.6 SEM micrographs of glassy carbon disks modified with different dispersions of MWCNT: (a) 1.00 mg ml^{-1} MWCNT in 1.00 mg ml^{-1} GOx solution prepared in 50 : 50 (v/v) ethanol/water; (b) 1.00 mg ml^{-10} MWCNT in 1.00 mg ml^{-1} PEI solution prepared in 50 : 50 (v/v) ethanol/water; (c) 1.00 mg ml^{-1} bCNT in 100 ppm dsDNA solution prepared in 50 : 50 (v/v) ethanol/water (inset: bCNT in dsDNA solution prepared in water); and (d) 1.00 mg ml^{-1} MWCNT in 0.25 mg ml^{-1} Polyhis solution prepared in 75 : 25 (v/v) ethanol/acetate buffer solution pH 5.00 (inset: MWCNT in 2.00 mg ml^{-1} Polyhis).

(Reference [89]. Copyright (2013), with permission from Elsevier.)

In all cases, even when the surfaces of GCEs are completely covered by the CNT dispersions, the coverage is not homogeneous ([Figures 3.6a–d](#)). In general, there is a pattern of a fully covered surface with areas containing different densities of CNTs, which depend on diverse factors such as the solvent used to prepare the dispersion, the nature of the polymer selected to disperse the CNTs, and the CNT/polymer ratio. The GCE modified with bCNT-dsDNA ([Figure 3.6c](#)) prepared in 50 : 50 v/v ethanol/water (main picture) and water (inset) demonstrated that ethanol largely improves the quality of the dispersion and its deposition on the glassy carbon surface. The use of water produces a deposit with an important number of aggregates. Another aspect to consider is the influence of the polymer concentration on the quality of the dispersion and further deposition at the glassy carbon surface. [Figure 3.6d](#) reveals that when the

concentration of Polyhis (poly(histidine)) increases, there is a segregation of the CNTs entrapped in the polymer net, which is followed by a poor electrochemical response due to the nature of the polymer (see inset).

Bollo *et al.* [53] reported an interesting comparison of the electrochemical behavior of GCE modified with 1.0 mg ml⁻¹ of chemically oxidized MWCNT dispersed in water, dimethylformamide (DMF), chitosan (CHI) (in 1.0% v/v acetic acid solution) and Nafion (Naf) in ethanol ([Figure 3.7](#)).

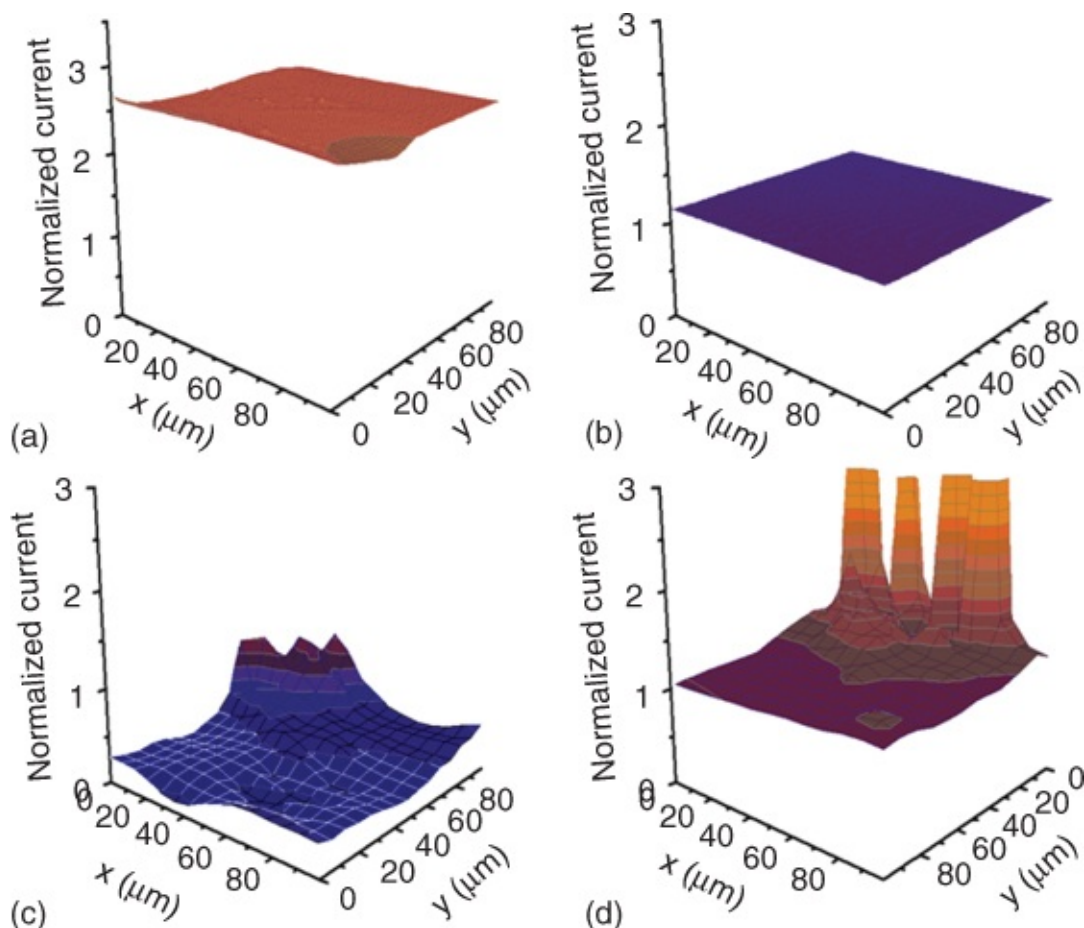


Figure 3.7 SECM surface plot images of (a) GCE/MWCNT-H₂O, (b) GCE/MWCNT-DMF, (c) GCE/MWCNT-CHI, and (d) GCE/MWCNT-Naf modified with 1.0 mg ml⁻¹ of CNT dispersion. Experimental conditions: 5.0×10^{-4} M FcOH solution in 0.050 M phosphate buffer pH 7.40. Image parameters: $1 \mu\text{m s}^{-1}$ tip scan, $E_{\text{tip}} = 0.500$ V, $E_{\text{substrate}} = 0.000$ V.

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Scanning electrochemical microscopy (SECM) experiments gave interesting information about the topography and electroactivity of GCE modified with different CNT dispersions. For MWCNT–water, there is a homogeneous surface from the electrochemical point of view with a normalized current higher than that for GCE ([Figure 3.7a](#)). The profile for MWCNT–DMF is more homogeneous although the resulting electrode is less electroactive ([Figure 3.7b](#)). A completely different behavior appears when using polymers as dispersing agents: in both cases, there are regions with different electroactivity due to the diverse density of CNTs. It is

important to mention that in the absence of CNTs, either in the case of Naf or CHI, there is a partial blockage of the surface, effect that is reversed by the presence of CNTs. Therefore, the deposition of CNT–polymer dispersions at the surface of the electrodes generates areas with different densities of CNTs, that are associated with heterogeneous local increments in the redox probe currents transduced in SECM electroactive spots.

Primo *et al.* [89] have showed that AA ($pK_a = 4.1$) gives important information for evaluating the electrochemical behavior of GCE/CNT-polymer since its electrochemical behavior is sensitive to changes in the electroactive surface. [Table 3.2](#) compiles the corresponding voltammetric parameters for different platforms: GCE/MWCNT-Plys, GCE/MWCNT-PEI-Do, GCE/MWCNT-PEI, GCE/bCNT-dsDNA GCE/MWCNT-Polyhis, and GCE. Compared to GCE, the overvoltage for AA oxidation decreases at all the GCE/CNT-polymer, although this decrease depends on the nature of the dispersing agent. Therefore, the improved electrochemical activity for AA at GCE/CNT-Polyhis, even despite the blocking activity of Polyhis, is attributed to the catalytic activity of the CNTs and the electrostatic interaction between the negatively charged redox marker and the electrode surface. In the case of the dispersion prepared with dsDNA, the overvoltage for AA decreases compared to bare GCE, although the decrease is not as pronounced as in the case of GCE modified with CNT-polycations due to the repulsive effect of the polyanion with AA.

Table 3.2 Voltammetric parameters obtained from the cyclic voltammograms for 1.0×10^{-3} M AA

Electrode	j_p (mA cm ⁻²)	E_p (V)
GCE	1.55	0.378
GCE/MWCNT-Plys	2.64	-0.055
GCE/MWCNT-PEI-Do	2.78	-0.028
GCE/MWCNT-PEI	2.78	-0.050
GCE/bCNT-dsDNA	1.81	0.160
GCE/MWCNT-Polyhis	1.25	0.022

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Therefore, when preparing dispersions of CNTs in polymer solutions, it is necessary to take into account that: (i) ethanol has to be used as a cosolvent to obtain a more efficient dispersion and better distribution of the wrapped CNTs on the electrode surface due to the decrease in the viscosity of the medium and the improvement in the mobility of the polymeric chains; (ii) the nature and the concentration of the polymer are critical factors, since the concentration has to be high enough to ensure the dispersion of the nanotubes, but not too high to block the electron transfer. Thus, the incorporation of CNTs at the glassy carbon surfaces always produces a decrease in the overvoltage for AA oxidation due to their catalytic activity; the magnitude of this decrease in the overvoltage depends on both the catalytic activity of CNTs and the nature of the polymer (net charge, secondary and tertiary structure, degree of cross-linking, and length

of the polymeric chains).

Examples of GCE Modified with Diverse Dispersions

This section describes the electrochemical behavior and characteristics of modified electrodes with the most reported and relevant CNT dispersions mediated by different polymers, ILs, and small molecules. A summary of them can be found in [Table 3.3](#).

Table 3.3 Noncovalent functionalization of CNTs: comparison of different types of dispersing agents and their general applications in electrochemistry

Type of CNT	Dispersing agent	Solvent	Optimum CNT concentration (mg ml ⁻¹)	Procedure	Redox probes/EQ analysis performed	Applications	References
<i>Polymers</i>							
MWCNT	p(MAA-co-AAM)	Water	1.0	Sonication 4 h, centrifugation 20 000 rpm 30 min	H ₂ O ₂	Direct biodection of H ₂ O ₂	[90]
oxMWCNT	CHI (1.0 wt%)	Acetic acid solution	0.5	Sonication	[Fe(CN) ₆] ^{3-/4-} , QCA	Electrochemical sensor for determination of QCA in pork samples	[91]
oxMWCNT	CHI (0.5% w/v)	2 M acetic acid solution	3.0	Sonication 3 h	[Fe(CN) ₆] ^{3-/4-}	DNA biosensor the for determination of amitrole in water and soil samples	[92]
MWCNT	PDDA (2.0 mg ml ⁻¹)	Water	2.0	Sonication, centrifugation 10 000 rpm 10 min	[Fe(CN) ₆] ^{3-/4-} , choline, acetylcholine	Amperometric acetylcholine (bio)sensor	[93]
oxMWCNT	PDDA (1.0 mg ml ⁻¹)	0.5 M NaCl solution	1.0	Sonication 3 h	[Fe(CN) ₆] ^{3-/4-} , codeine and morphine	Simultaneous determination of codeine and morphine with DNA	[94]
oxMWCNT	P4VP	DMF	1.0	Sonication 3 h	[Fe(CN) ₆] ^{3-/4-} , paracetamol	Determination of paracetamol in formulation tablets and urine samples	[95]
oxMWCNT	PAH (0.1 mM)	Water	0.033	Sonication 30 min	Ciprofibrate	Determination of ciprofibrate in pharmaceutical formulations	[96]
MWCNT	PAA (0.1 wt%)	HCl or NaOH solutions	Variable	Sonication 10 min	Do, AU, and AA	Selective detection of UA and Do in the presence of AA	[97]
MWCNT	Nafion	Water	2.0	Sonication 10 min	D-Xylose, NAD ⁺	Detection of beer and product of lignocelluloses degradation	[98]
MWCNT	Nafion	Water	2.0	Sonication 5 min	Glucose, UA, AA, catechol, Do, and catechin	Enzymatic biosensors based on the self-assembling of QCHI and different oxidases	[99]

MWCNT	PEI	Ethanol	1.0	Sonication 30 min	$[\text{Fe}(\text{CN})_6]^{3-/4-}$, chlorpromazine, acetaminophen, UA, AA, Do	Sensor for the determination of chlorpromazine	[100]
MWCNT	PEI (1.0 mg ml ⁻¹)	50% v/v ethanol/water	1.0	Sonication 15 min	H ₂ O ₂ , AA, Do, DOPAC, serotonin, glucose	Enzymatic biosensors and electrochemical sensor	[101, 102]
MWCNT	Plys (1.0 mg ml ⁻¹)	50% v/v ethanol/water	1.0	Sonication 15 min	H ₂ O ₂ , AA, UA, glucose, dsDNA, oligo(dG) ₁₁ , oligo(dC) ₁₁	Glucose biosensing Hybridization studies	[103–105]
MWCNT	Polyhis (0.25 mg ml ⁻¹)	75 : 25 (v/v) ethanol/0.200 M acetate buffer solution pH 5.00	1.0	Sonication 30 min	Paracetamol, glucose, AA, UA, and Do	Electrochemical sensor for Do, AA, and UA Glucose amperometric biosensor LbL self-assembly of GOx	[106–108]
MWCNT	HBPE	THF	2.0	Sonication 1 h, stirring overnight	—	Characterization of electrical conductivity and rheological properties	[109]
<i>Proteins and enzymes</i>							
MWCNT	HFBI (20 mg ml ⁻¹)	Water	2.0	Strong stirring and then dispersed in sonication 30 min	$[\text{Fe}(\text{CN})_6]^{3-/4-}$, glucose, acetaminophen, AA, and UA	Glucose biosensing	[110]
MWCNT	GOx (1.0 mg ml ⁻¹)	50% v/v, ethanol/water	1.0	Sonication 15 min	Glucose, $[\text{Fe}(\text{CN})_6]^{3-/4-}$, H ₂ O ₂ , dsDNA, ssDNA, oligo(dG) ₇ , oligo(dG) ₁₁ , and oligo(dY)	Glucose biosensing Adsorption and electro-oxidation of DNA and oligonucleotides	[111, 112]
SWCNT-COOH/ SWCNT-OH	GOx (1.0 mg ml ⁻¹)	Water	1.0	Tip sonication 5 and 60 min centrifugation 33 000 g, 4 h, 4 °C	—	Sonication effect SWCNT-GOx dispersions	[113]
SWCNT	BSA, LSZ, or γ -G (the concentration was varied)	Water	1.0	Tip sonication 0–12 h centrifugation 21 000 g 7 min	—	Sonication effect on SWCNT-protein dispersions	[114]
<i>DNA</i>							
bCNT	Calf thymus dsDNA (100 ppm)	50% v/v ethanol/water	1.0	Sonication 45 min	Electroactive DNA's adsorbed bases, $[\text{Fe}(\text{CN})_6]^{3-/4-}$, FeOH, H ₂ O ₂	Determination of promethazine [115]	[115, 116]
SWCNT	17 mer poly(C) heterosequence ssDNA (10 μ M)	Water	Not reported	Tip sonication 90 min	—	Hybridization (bio)sensing based on FET measurements of desorption of wrapped DNA with complementary sequence	[117]

oxMWCNT	20 mer ssDNA sequence (20 mM)	pH 7 buffer solution	—	Sonication 120 min, centrifugation 2000 rpm 60 min	—	Detection of <i>Escherichia coli</i> O157:H7 DNA sequence	[118]
<i>Surfactants</i>							
oxMWCNT	1% solution of SDS or CTAB	Water	1.0	Sonication 30 min	Capacitance measurements of the assembly process	LbL assembling over ITO electrodes with PDDA	[119]
SWCNT	1% (w/v) solution of SDS	Water	$(1.5, 2.0, 5.5, 7.0) \times 10^{-3}$	Sonication	Resistance measurements	Self-assembly on silicon wafer to create aligned thin-film stripes	[120]
SWCNT	Triton X-100 (10 mg ml ⁻¹), Tween 20 (5 mg ml ⁻¹), sodium chlorate (20 mg ml ⁻¹), NaDDBS (5 mg ml ⁻¹)	Water	0.4	Tip sonication 60 min	Polymer redox moieties, glucose, [Fe(CN) ₆] ³⁻ , [Ru(NH ₃) ₆] ³⁺	Glucose biosensing	[121]
SWCNT	1% (w/v) solution of SDS	Water	0.3	Tip sonication 120 min	Electrical transport properties, <i>i</i> – <i>V</i> curves	H ₂ S gas sensor	[122]
<i>Ionic liquids</i>							
oxMWCNT	[OMIM]PF ₆	[OMIM]PF ₆	—	Grounded 20 min to form a <i>bucky gel</i> [35] 5 mg of the gel were transferred to a 1% (w/v) CHI solution	[Fe(CN) ₆] ^{3-/4-} , NO ₂ ⁻	Detection of NO ₂ ⁻ in soil, sewage, and sausage samples	[123]
SWCNT	[BMIM]PF ₆	[BMIM]PF ₆	—	0.2 ml of hematin solution (4 mM) in IL were grounded with 1 mg of SWCNT to form a <i>bucky gel</i>	Fe ^{II/III} moieties of porphyrin, [Fe(CN) ₆] ^{3-/4-} , TCA	Detection of TCA acid in polluted waters	[124]
MWCNT	poly[VEIM]Br	[VEIM]Br	—	1.56 g of IL and 200 mg of MWCNT were grounded 30 min and mixed with 76 mg of AIBN to form the PIL	FAD group of GOx, O ₂ , H ₂ O ₂ , and glucose	Immobilization of GOx/Nafion for glucose biosensing	[125]
oxSWCNT	[EMIM]BF ₄	[EMIM]BF ₄	—	SWCNTs were grounded with 20% of IL 5 min and compressed under 20 MPa	Electrical conductivity and capacitance	Fabrication of a “buckypaper” supercapacitor	[126]
<i>Small molecules</i>							
SWCNT	PTCA (0.4 mg ml ⁻¹)	Ethanol	1.0	Sonication 2 h, stirring 5 h	9-Anthracene-carboxylic acid	Electrochemical sensing of 9-anthracenecarboxylic acid	[127]
SWCNT	Congo red	Water	2.6	SWCNT grounded with Congo red (weight ratio 5 : 1) 4 h and mixed in water	Congo red, [Fe(CN) ₆] ^{3-/4-} Do, UA, and AA	Biosensing of Do in the presence of UA and AA	[128]
Pretreated SWCNT	Pyrene-butanol biotin ester	THF	—	Stirring in THF for 3 h	Glucose	Immobilization of avidin-GOx for glucose biosensing	[129]
MWCNT	Pyrene-B18C16 (1.0 mg ml ⁻¹)	THF	1.0	Sonication 3 h	Potentiometric analysis of K ⁺ , NH ₄ ⁺ , Na ⁺ , Li ⁺ , Ca ²⁺ , Mg ²⁺	K ⁺ -ion selective electrode	[130]

Symbols: p(MAA-co-AAM): poly(methacrylic acid-co-acrylamide), oxMWCNT: oxidized multiwall carbon nanotubes, CHI: chitosan, QCA: quinoxaline-2-carboxylic acid, PDDA: poly(diallyldimethyl-ammonium chloride), P4VP: poly(4-vinylpyridine), PAH: poly(allylamine hydrochloride), PAA: poly(acrylic acid), AA: ascorbic acid, Do: dopamine, UA: Uric acid, DOPAC: 3,4-

dihydroxyphenylacetic acid, Polyhis: poly(histidine), QCHI: quaternized chitosan, PEI: polyethylenimine, HBPE: hyperbranched polyethylene, THF: tetrahydrofuran, HFBI: hydrophobin, GOx: glucose oxidase, oligo(dY): 3'-TAC ACC TTT TAGAGA TCG TCA-5', LSZ: lysozyme, BSA: bovine-serum albumin, γ -G: γ -globulin, FET: field effect transistors, SDS: sodium dodecyl sulfate, CTAB: cetyltrimethylammonium bromide, LbL: layer-by-layer, ITO: indium tin oxide-coated glass slides, NaDBBS: sodium dodecyl benzenesulfonate, Fc: ferrocene, FcOH: ferrocene methanol, GCr: gel chromatography, DOC: sodium deoxycholate, IL: ionic liquid, [OMIM]PF₆: 1-octyl-3-methylimidazolium hexafluorophosphate, [BMIM]PF₆: 1-butyl-3-methylimidazolium hexafluorophosphate, [VEIM]Br: 1-vinyl-3-ethylimidazolium bromide, AIBN: 2,2'-azobisisobutyronitrile, PIL: polymerized ionic liquid, TCA: trichloroacetic acid, B18C6: benzo-18-crown-6, and PTCA: 3,4,9,10-perylene tetracarboxylic acid.

CNT-PEI

Rubianes and Rivas [101] proposed the highly efficient dispersion of MWCNTs by the polycation polyethylenimine (PEI) as well as the excellent performance of GCE modified with this dispersion, not only in batch measurements but also as detector in flow injection analysis and capillary electrophoresis [131]. The resulting electrodes showed excellent electrocatalytic activity with decrease in the overvoltages for the oxidation of AA, hydrogen peroxide, 3,4-dihydroxyphenylacetic acid, and even dopamine (Do). Taking advantages of the polycationic nature of PEI and the electrocatalytic response toward hydrogen peroxide, the platform GCE/MWCNT-PEI was also used for building architectures based on the self-assembly of polyelectrolytes such as glucose oxidase (GOx) to obtain a supramolecular multistructure for glucose biosensing, with very low detection limits (11 μ M). GCE/MWCNT-PEI has also been shown to be highly efficient for the voltammetric resolution of Do in the presence of a large excess of AA and serotonin [132]. The modified electrode was successfully used for recovery assays in human blood serum. Luque *et al.* [133] used MWCNT-PEI dispersion for dsDNA quantification based on the well-known complex formation between the polycation and DNA (double-stranded calf thymus DNA (dsDNA), homo and heteronucleotides). The capability of PEI to disperse MWCNTs (hCNT type and bCNT type) with an ultrasonic bath and probe was also evaluated by Eguílaz *et al.* [134] by comparing the electrochemical response of GCE modified with both dispersions using AA as redox marker.

Unnikrishnan *et al.* [100] reported the fabrication of a selective voltammetric sensor for the determination of chlorpromazine (an antipsychotic drug) using GCE modified with MWCNT-PEI, in the presence of uric acid (UA), Do, and acetaminophen. The GCE/MWCNT-PEI platform was also employed for the quantification in batch of flavonoid compounds in onion samples [135] and peanut hull samples [136], and as a detector in capillary electrophoresis, for the simultaneous detection of eight polyphenols (*t*-resveratrol, (+)-catechin, quercetin and *p*-coumaric, caffeic, sinapic, ferulic, and gallic acids) in Spanish white wines [137].

Gasnier *et al.* [138] also reported the catalytic determination of reduced nicotinamide adenine dinucleotide (NADH) at very low potentials (-0.25 V), with excellent sensitivity and stability by using a GCE modified with PEI functionalized with Do and glutaraldehyde as a linker (PEI-Glu-Do). The presence of Do covalently bonded to PEI promotes hydrophobic π -interactions with the CNT walls conferring better stability and mechanical strength to the dispersion compared with nonmodified PEI.

CNT-Plys

Jalit *et al.* [103] reported for the first time the efficient dispersion of MWCNT with Plys (polylysine) due to the large amount of amine residues of the polymer that facilitates the interaction with the MWCNT. GCE modified with the resulting dispersion showed an excellent electrocatalytic activity toward AA, UA, and hydrogen peroxide. The platform was used for the construction of supramolecular architectures for glucose quantification by self-assembling of polyelectrolytes. GCE/MWCNT-Plys was also used for the determination of UA in the presence of AA [104], allowing the efficient quantification of UA in a complex matrix, such as human blood serum samples.

Another interesting application of this electrode was the development of a platform for detecting the hybridization event [105]. Oligo(dG)₁₁ was immobilized at GCE/MWCNT-Plys for the selective detection of oligo(dC)₁₁ through the evaluation of the decrease in the guanine oxidation signal.

Recently, Ling *et al.* [45] reported the use of the dispersion of MWCNT-Plys as a bio-nanomaterial in applications such as sensing, nanoelectronics, and drug delivery systems based on the pH response of the dispersion.

CNT-GOx and CNT-dsDNA

Biomolecules have received particular attention not only as efficient dispersing agents for CNTs, but also to give them biorecognition properties.

The first example of the use of an enzyme to disperse MWCNTs was reported by Gutierrez *et al.* [111]. They used GOx and reported that, even under the drastic conditions for preparing the dispersion (ultrasonic bath and ethanolic medium), the enzyme kept its biocatalytic activity. The intimate contact of MWCNT and GOx made possible the efficient electron transfer to the GCE as well as an excellent biocatalytic activity, allowing the highly sensitive detection of glucose. The GCE/MWCNT-GOx was also used as a platform to build supramolecular architectures by self-assembling polydiallyldimethylamine (PDDA) and dsDNA [112]. The presence of GOx allows a most favorable environment that promotes the adsorption and electro-oxidation of dsDNA. The adsorbed layer could be successfully used for evaluating the interaction of methylene blue (MB) with the adsorbed DNA layer, allowing the study of DNA–drug interaction and DNA damage.

Karunwi and Guiseppi-Elie [113] proposed the dispersion of SWCNT with GOx, and analyzed the effect of tube length, sonication time, and SWCNT functionalities on the structure and kinetics of the enzyme. They demonstrated that the nanotube length presented the highest effect on the structure of the enzyme, while SWCNT functionality had the largest effect on the kinetic efficiency of the enzyme. They concluded that longer SWCNT caused some partial denaturation and release of the oxidized flavin adenine dinucleotide (FAD) group.

Another interesting biomolecule to functionalize CNTs is DNA due to its unique biorecognition properties. Since the first report in 2003 by Zheng *et al.* [139], some advances have been made to use DNA as a dispersing agent for CNTs, taking into account that this molecule is amphiphilic. However, an important challenge is, as in the case of GOx, to transfer to the

carbon nanostructures the excellent biorecognition properties of DNA. In this way, Primo *et al.* [116] demonstrated that double-stranded calf thymus DNA (dsDNA), about 50 kbp, effectively dispersed bCNTs by dissolving the dsDNA in ethanol: water 50% (v/v) and bath-sonicating for 45 min. The partial denaturation produced as a consequence of these conditions facilitated the contact between the hydrophobic bases of the nucleic acid and the CNT sidewalls, making possible, in this way, the dispersion. Taking advantage of the electroactivity of adenine and guanine bases, the authors showed the increased electrocatalysis of the bamboo structure when compared to the hollow CNTs. The platform GCE/bCNT-dsDNA allowed the highly sensitive determination of promethazine (PMZ), a known intercalator within the double-stranded regions of DNA that supports the MWCNTs, indicating that even under those drastic conditions of dispersion preparation, the biomolecule maintains biorecognition properties [115]. Electrochemical and spectroscopic experiments, combined with quantum dynamics calculations at the density functional-based tight binding (DFTB) level, confirmed that the increased accumulation properties of the GCE/bCNT-dsDNA platform toward PMZ were due principally to the intercalation effect.

In a different approach, Jung *et al.* [117] used poly(C)- and human papilloma virus (HPV)-related sequences for dispersing SWCNTs. In both cases, the dispersion was dielectrophoretically deposited between the source and drain electrodes of a field effect transistor (FET)-based sensor. The sensing mechanism was based in the change from metallic to p-type semiconducting behavior of SWCNTs. The authors demonstrated by Raman spectroscopy, electrophoresis, and molecular dynamics (MD) simulations that the ssDNA wrapped around the SWCNT could detach in the presence of a complementary sequence, returning the SWCNT to the metallic state. This process can be monitored in a $I-V_{\text{Gate}}$ diagram and opens new possibilities for hybridization (bio)sensors.

CNT-Ionic Liquids

A gel of MWCNT and 1-octyl-3-methylimidazolium hexafluorophosphate hydrophobic IL was obtained by Xiao *et al.* [123], which was entrapped in the three-dimensional CHI network to serve as ionic and electric conductor. The MWCNT-IL gel/CHI composite was immobilized at GCE and the resulting GCE/MWCNT-IL gel/CHI sensor demonstrates a strong electrocatalytic effect on the oxidation of nitrite, which was successfully determined in different real samples. Tu *et al.* [124] reported the construction of a highly sensitive biosensor for trichloroacetic acid, modifying a GCE with a bucky gel prepared using SWCNTs functionalized with hematin (a water-insoluble porphyrin) in the presence of 1-butyl-3-methylimidazolium hexafluorophosphate. The SWCNTs were dispersed by π - π noncovalent interaction with porphyrin, and the IL produced a synergic effect that accelerated the electron transfer between GCE and the redox probe or the FeIII/FeII redox couple in hematin. Meanwhile, a novel strategy in which IL monomer of 1-vinyl-3-ethylimidazolium bromide is directly polymerized on the surface of MWCNT to form a stable MWCNT-PIL composite was reported by Xiao *et al.* [125]. The MWCNT-PIL-modified GCE showed excellent electrocatalysis toward O_2 and H_2O_2 , and a new biosensor (GCE/MWCNT-PIL/GOx/Nafion), with GOx as a model protein, was designed for studying the direct electron transfer of a redox protein. The proposed

biosensor showed a good analytical performance for glucose without the interference signal of AA and UA. Zheng *et al.* [126] proposed the first dispersion of SWCNT in 1-ethyl-3-methylimidazolium tetrafluoroborate, which was converted to a buckypaper by compression. The debundling effect of IL on SWCNTs was effective to fabricate an IL-coated SWCNT buckypaper that exhibited supercapacitor properties such as increased electrical conductance, high mechanical strength, and excellent capacitance.

3.4.2 Preparation of Carbon Nanotube Paste Electrodes Using Different Binders

The CNT-based paste electrodes obtained using CNTs and different binders are an additional strategy to obtain very efficient electrodes as a result of the advantages of CNTs and the well-known properties of composite materials (also see Chapter 11). In this sense, it is important to distinguish between the *properly called carbon nanotube paste electrodes* (CNTPEs), composed exclusively of CNTs as conductive materials combined with different binders and *graphite carbon paste electrodes (CPEs) modified with CNT (CPE-CNT)*. These materials may also include different additives, such as ILs, polymers, DNA, and metal or metal oxide particles, among others, to gain sensitivity and selectivity toward the desired analyte. In general, the resulting materials are usually packed into polypropylene syringes, Teflon, plastic, or glass tubes. The electrical contact is made through a copper wire inserted in the paste or a stainless steel screw, and the surface is renewed by expelling an excess of paste and then polishing it onto a soft paper.

Wang *et al.* [140, 141] reported for the first time the successful use of Teflon as a binder for dispersing MWCNTs. Hill *et al.* [142] showed the feasibility of using CNT as an electrodes material, dispersed in bromoform, Nujol, deionized water, or mineral oil. Britto *et al.* [32] proposed the first CNT-based electrode by dispersing CNTs in bromoform. Rivas and Rubianes [143, 144] were the first in reporting a composite material prepared in an easy and very efficient way by dispersing MWCNTs within mineral oil (60 : 40% w/w CNT : oil). The resulting CNTPE presents an excellent combination of the classic CPE, keeps the properties of the classical CPE and those of the CNT. Pedano and Rivas [145] demonstrated for the first time the adsorption and electro-oxidation of nucleic acids on the CNTPE. Chicharro *et al.* [146] also used an electrochemically activated CNTPE for the highly sensitive detection of amitrole. CNTPE was highly useful as electrochemical detector in flow systems [147]. Palleschi *et al.* [148] reported a composite electrode obtained by mixing SWCNTs and mineral oil (60/40% w/w CNT : oil). CNTPE using mineral oil as binder was also proposed for the detection of homocysteine [149] and amitriptyline in pharmaceutical formulations [150].

Surfactants, such as sodium dodecyl sulfate (SDS) and Triton X-100, and particularly ILs, have been lately used as binders, since the latter improve the conductivity of the paste material and, depending on the molecular structure of the IL, can also provide catalytic properties or selectivity toward certain compounds. SWCNTs were dispersed in a 1 wt% SDS aqueous solution and sonicated for several hours to fabricate a transparent heating film on a glass or

poly(ethylene terephthalate) (PET) substrate, where Cu electrode plates were attached with silver paste [151]. The IL 1-octyl-3-methylimidazolium hexafluorophosphate (OMIMPF6) was used as a binder to form an SWCNT-IL paste and transferred to the electrode, to obtain a GCE/SWCNT-OMIMPF6-modified electrode for the detection of folic acid [152].

The resulting CNTPE can also be modified by immersion, drop coating, or electrodeposition of different molecules, polymers, biomolecules, or metals. Some examples include 3,4-dihydroxybenzaldehyde [153] and polyOs-GDH-Di-NAD⁺ for the detection of glucose in alcoholic beverages [154] or pyrrole polymerized at CNTPE with a DNA probe for the detection of the hybridization event [155].

In the case of CPE modified with CNTs, two main general ways were reported to disperse the additives within the paste: (1) the mortaring of the desired amounts of the graphite powder (mostly 60–75% w/w), CNT in proportions from 1% to 40% w/w, the additive in small percentages (1, 3, 5, 8 or 15% w/w), and the binder (typically in 15–42% w/w); (2) or the dissolution of the additive in a volatile solvent (CH₃Cl, CH₃Cl₂, diethyl ether, methanol, acetone, hexane, or DMF), mixing with the CNT and stirring until complete solvent evaporation. Sometimes, the graphite powder is added to the volatile solvent additive–CNT mixture while in other cases it is added later on, after the solvent evaporation, together with the binder, and further mixed with mortar and pestle to obtain a uniformly wetted paste. The selected procedure will depend on the chemical nature of the modifier and its physical properties, such as solubility in a given solvent and physical state at room temperature. The binder employed (paraffin, Nujol or mineral oil, silicone, Teflon or ILs) can affect the sensor response. For example, by employing the mortaring method, the use of IL as the paste binder made it possible to obtain lower detection limits compared to paraffin oil [156], while when using the solvent evaporation method, better detection limits were obtained using silicone as a binder rather than mineral oil [157].

The surface incorporation of SDS to a graphite electrode modified with MWCNT was reported for the amperometric determination of epinephrine (EP) [158]. Triton X-100 was incorporated into CPE-CNT to prepare an electrode for the detection of acetaminophen, aspirin, and caffeine [159]. Gorton *et al.* [160] developed a microbial biosensor based on the incorporation of *Pseudomonas putida* DSM 50026 within a graphite paste electrode modified with MWCNT by drop-coating with poly(1-vinylimidazole)12-[Os-(4,40-dimethyl-2,20-dipyridyl)₂Cl₂]^{2+/+} aqueous solution. In another strategy, a graphite paste electrode modified with oxMWCNTs (oxidized multiwall carbon nanotubes) in a 90 : 10% w/w ratio and bonded with paraffin oil was coated with dsDNA by immersion in 10 mg ml⁻¹ solution (in 0.50 M acetate buffer) at 0.50 V for 400 s and used for the quantification of UA [161].

Afkhami *et al.* [162] used a graphite paste electrode containing MWCNT modified by the electrodeposition of gold NPs from a HAuCl₄ solution to successfully determine cefixime, methadone [163], and nitrite [164] in a pharmaceutical form, in urine and saliva; in several food stuffs; and water samples, respectively. Fe₂O₃ was also electrodeposited from a solution containing 10% of the nanodispersion at a similar electrode just modified with Triton X-100

onto the surface of the aforementioned electrode and dried at room temperature and used to simultaneously detect orange G and orange II by differential pulse voltammetry (DPV) [165].

3.4.2.1 Screen-Printed Electrodes (SPE)

Another interesting strategy proposed by Wang and Musameh [166] was the preparation of a composite material based on the dispersion of CNTs to form an ink, in a way similar to that for preparing the classical graphite SPEs (see also Chapter 12). The electrodes were fabricated following two strategies: (i) using the same ink as the one for preparing the SPE and (ii) mixing 60 mg CNTs with 500 μl of isophorone solution containing different compounds until homogeneous in appearance. The ink was then printed on alumina ceramic plates and the resulting electrodes were cured for 1 h at 150 $^{\circ}\text{C}$ and then allowed to cool down at room temperature.

Costa-García *et al.* [167] proposed another type of CNT-based carbon or gold SPE (DropSens) obtained by dropping 5 μl of carboxylated multiwalled carbon nanotubes (MWCNT-COOH) dispersed in a 1 mg ml^{-1} mixture of DMF:water (1 : 1) printed onto plastic or ceramic substrates. Significant improvement in the electron transfer for Do, H_2O_2 , and NADH was obtained at the resulting electrodes that were stable for up to 2 months allowing the detection of alkaline phosphatase [168] and paracetamol using flow injection analysis [169].

A nanohybrid electrochemical transducer was prepared by casting MWCNT or carbon nanofibers onto a carbon SPE, followed by *in situ* generation of gold NPs by electrochemical deposition of HAuCl_4^- [170], being used for the quantification of Hg(II) by square wave voltammetry (SWV) [171] or anti gliadin antibodies for the diagnosis of celiac disease [172]. Recently, they evaluated the electrochemical signal of MB-modified ssDNA sequences on AuSPE modified with MWCNT-NH₂ dispersed in a 0.5% Nafion/ethanol solution for the detection of ss-oligonucleotides [173].

3.5 Prospective Work

The important research on CNTs performed in the last two decades has made it possible to generate the knowledge necessary to obtain successful developments in different fields. However, there are still many aspects that require attention for further CNT-based electrochemical devices.

It is necessary to have efficient control of the morphology of the nanotubes, with special emphasis on their chirality. The heterogeneity of CNTs is another critical aspect to be considered, in order to obtain reproducible electrochemical behaviors. The selection of the dispersing agent and dispersing conditions for CNTs has to be critically made to obtain nanostructures with particular properties to ensure the construction of efficient electrochemical (bio)electrodes. The generation and exposure of defects in general and edge-plane defects in particular, must be controlled in order to facilitate an efficient distribution of the CNTs on the surface of the electrodes.

From the point of view of bioelectronics it is very important to obtain more information about the mechanism of integration of CNTs into living biological systems. The toxicity of CNTs is a critical aspect that requires important research to know about the uptake of CNTs by living cells and their distribution in the environment. Another important topic that requires more attention is the application of CNTs for future efficient development of devices for drug release and gene therapy.

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Chapter 4

Electrochemistry of Graphene

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4.1 Overview of Graphene Properties

If one were to define the ideal properties that an electrode material should possess, along with the prerequisite of good electrical conductivity, strength, low mass, chemical stability, high specific surface area, flexibility, and – for certain applications – transparency would also feature on the list. Until very recently, no material combined all these properties: noble metal electrodes possess strength and stability although flexibility and weight are sacrificed; the converse is true for conducting polymers. When cost factors are included, it is not surprising that bulk forms of carbon (whether graphitic or amorphous phases) have become the “workhorse” electrode materials for technological applications, whether in energy storage/conversion, electroanalysis, or metal extraction. It is, therefore, logical that the discovery of low-dimensional forms of carbon – fullerenes, nanotubes and, most recently, graphene – should have prompted significant interest from the electrochemical perspective, particularly because of the likely technological applications of these materials. In particular, one of the most potent attributes of graphene is that it satisfies all of the material performance criteria outlined in the opening sentence. It is no exaggeration to say that there has been an avalanche of publications on the electrochemical properties of graphene, the two-dimensional form of elemental carbon, over the last decade. This is partly due to the intrinsic interest in the properties of the material, provoked by a publication from the University of Manchester in 2004 [1], which led to a Noble Prize 6 years later, and partly because the interest in the fundamental properties of graphene has also coincided with an upsurge in interest in electrochemical energy storage and conversion, particularly in the development of batteries and supercapacitors to store energy on a variety of scales [2].

It was rapidly realized that the physical properties of graphene made it a potentially useful electrode material, first in the context of supercapacitors [3], then as an electrode material (or conductive additive) for battery applications [4]. Much of this interest in the electrochemical properties of graphene, and related two-dimensional materials, has been “device” driven, that is, motivated by their potential use in energy storage or conversion technologies, or in electroanalytical detection. Welcome though this interest is, the sheer volume of the available literature makes it difficult for the casual reader to assess general trends in the electrochemistry of graphene. (The search term *graphene and electrochem** produces more than 15 000 hits on ISI Web of Science at the time of writing in June 2014, a rate of publication over the preceding 18 months corresponding to 16 articles per day.) There have been numerous reviews, initially trying to summarize the broader field of graphene electrochemistry [5–7], with more recent reviews focusing on specific aspects such as fabrication and general applications of graphene-based electrodes [8] or specific applications in energy storage [9–

11] or electroanalysis [12, 13]. We feel that a significant omission, due to the rush to develop technologies based on graphene, is a thorough understanding of how the properties of graphene manifest themselves in fundamental electrochemistry. Specifically, although various types of graphene biosensor [14] and supercapacitor [15] have been proposed based on Faradaic and non-Faradaic electrochemistry, respectively, we still do not have a complete understanding of the underlying physical chemistry of graphene (e.g., how electron transfer and interfacial capacitance change with substrate or the number of graphene layers present). In any case, as is noted below, most of these applied electrochemistry reports in fact use graphene oxide (GO), rather than pristine graphene, as their electrode material. The aim of this chapter is to redress this balance somewhat, by discussing the more fundamental aspects of graphene electrochemistry that have been reported to date, and identifying where future efforts should be concentrated. There is also a strong, but often neglected, link between the route used to prepare graphene and resultant physical properties of the sample: we therefore also devote some space to preparation methods, with specific emphasis on the various electrochemical routes that have been reported for graphene preparation. Even though the focus here is specifically on graphene in the electrochemical context, it is useful to give a brief summary of the physical properties of graphene to understand the significance of this material for electrochemistry.

The properties of graphene, as an idealized two-dimensional material, had attracted the interest of theoreticians since the 1940s [16]; however, it was generally thought that a strictly two-dimensional material could not be isolated, with thermodynamic arguments advanced to justify this [17]. The two-dimensional nature of the material gives rise to unusual electronic properties, where the charge carriers behave as massless Dirac fermions, whose energy follows a linear dispersion relation (energy proportional to the magnitude of the wavevector) [18]. The existence of the linear Dirac cones means that graphene exhibits an ambipolar electric field effect: application of a potential produces charge carriers (electrons or holes) whose density is proportional to the applied voltage. The mobility of these charge carriers is exceptionally high (room temperature values of $2.5 \times 10^5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ are reported) [19], but is intimately linked to the number of defects present, the size of the individual graphene flakes (or the individual grain size in a larger film), and the substrate on which the material is placed. Consequently, for investigations of graphene as an electrode material, or indeed any investigation of its physical properties, both defect concentration and flake size must be optimized for the application in mind. Accordingly, it is essential to discuss the methods used to make graphene: a survey of this area is given in [Section 4.2](#).

It is worth returning to the strict definition of graphene: it is a monolayer carbon material, with the carbon atoms in “sp²” hybridization. In practice, many experimental samples are (at least in parts) more than one atom thick. Furthermore, there is the difficulty of ensuring that a given graphene sample is “atomically pure,” i.e., that it only consists of carbon atoms, with no heteroatoms (e.g., oxygen) or strongly bound adsorbates. Given that synthetic processes often involve oxidation, there is no strict definition of what constitutes graphene, what constitutes GO, and where the domain of the intermediate material, reduced graphene oxide (rGO), should lie. Finally, even if we can be reasonably confident of the atomic purity of the sample, there is the question of the existence of structural defects, such as Stones–Wales defects or other

vacancies, in the two-dimensional network.

4.2 Preparation of Graphene

The preparation methods of graphene, as with other nanomaterials, can be divided into “bottom-up” – where the carbon network is assembled from some source of carbon atoms, that is, a molecule – and “top-down,” where a larger layered structure (i.e., graphite) is broken apart into individual graphene layers. One overview of the production methods of graphene, taken from a 2012 graphene “road map” is presented in [Figure 4.1](#) [19]. Factors to consider in the choice of a specific graphene synthesis route are quality (purity, doping, number of defects), size (lateral size and thickness, if the sample contains flakes or domains that are thicker than a monolayer), the extent of surface functionalization and, for industrial applications, the scalability, and cost of the route.

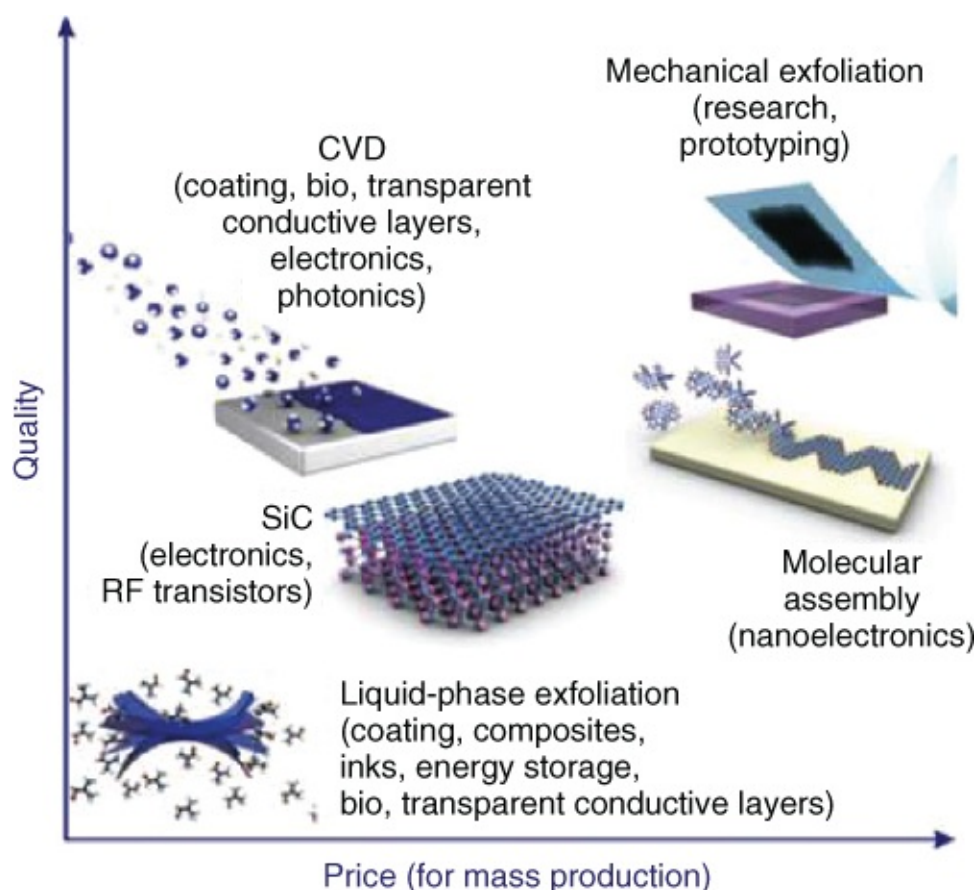


Figure 4.1 Overview for the production methods of graphene [19].

4.2.1 Top-Down Fabrication of Graphene

Most electrochemical studies of graphene reported to date have used samples generated via “top-down” methods, where some kind of energy input is used to cleave the individual layers within the initial graphite sample. There is generally a compromise to be made between the ease of the graphite exfoliation process, the purity of the resultant sample, and also the thickness and lateral size. Particularly for applications of “graphene” in electrochemical

energy storage, samples are usually prepared using chemical methods, where graphite is exfoliated as GO (using a combination of oxidizing agents and acids) [20], which are then reduced using a combination of chemical and/or heat treatment to materials that are frequently called **graphene**. The reduction process is, however, not completely reversible, and hence it is more accurate to label the reduced materials as rGOs. Unfortunately, many research articles do not make this distinction, making it more difficult for the reader to gauge the purity of the sample material: the term *graphitic sludge* has also been employed to describe oxide-derived graphene by the discoverers of mechanically exfoliated (ME) graphene [18]. The latter term is, perhaps, an exaggeration, but it highlights the problem with synthetic routes based on rGO, namely the relative lack of control over the nature, density, and distribution of defects (mainly oxygen atoms, but other atoms can be introduced during the reduction step), which complicates comparative studies of rGOs derived from different reduction procedures. A specific example, which is discussed further in [Section 4.4](#), is a recent study showing that detectable amounts of manganese, derived from the permanganate used as an oxidizing agent in the Hummers' method [20], remain in rGO materials [21].

The opposite extreme of the GO/rGO pathway to graphene samples is the ME (or “scotch tape,” see [Figure 4.2](#)) [22] route developed by Geim and Novoselov [1]. The great advantage of this method is that it, essentially, preserves the structure of the initial graphite material, hence the flake dimensions and purity of the resultant graphene are limited by the crystallite size and impurity levels of the graphitic source. Accordingly, ME is still the method of choice for studies of electronic properties of graphene (e.g., measurements of charge carrier mobility): work at the contributor's University has shown that the accessible flake size has grown over the past decade from a few microns to over 1 mm. The disadvantage of this method is its relative complexity: the method involves “hunting” for exfoliated fragments on a silicon wafer (graphene samples are visible on oxide-covered silicon, with an optical contrast that is layer dependent [23]), and fabrication of a usable device for electrochemistry, or other applications, requires several steps of sample masking, cleaning, and, in some cases, transfer to a different substrate. These steps generally use quite standard photolithographic procedures that are compatible with modern clean rooms; however, the lithographic residues can contaminate the sample, leading to doping, an effect which has only recently been studied in depth [24–26]. The effect of such residues on the electrochemical properties of graphene is largely unknown. Despite the high quality of ME samples, there are only a few reports describing their use in electrochemistry (dealt with under the relevant sections later). This underexploitation of ME is regrettable, given that it is the preferred route to the best-defined graphene samples.

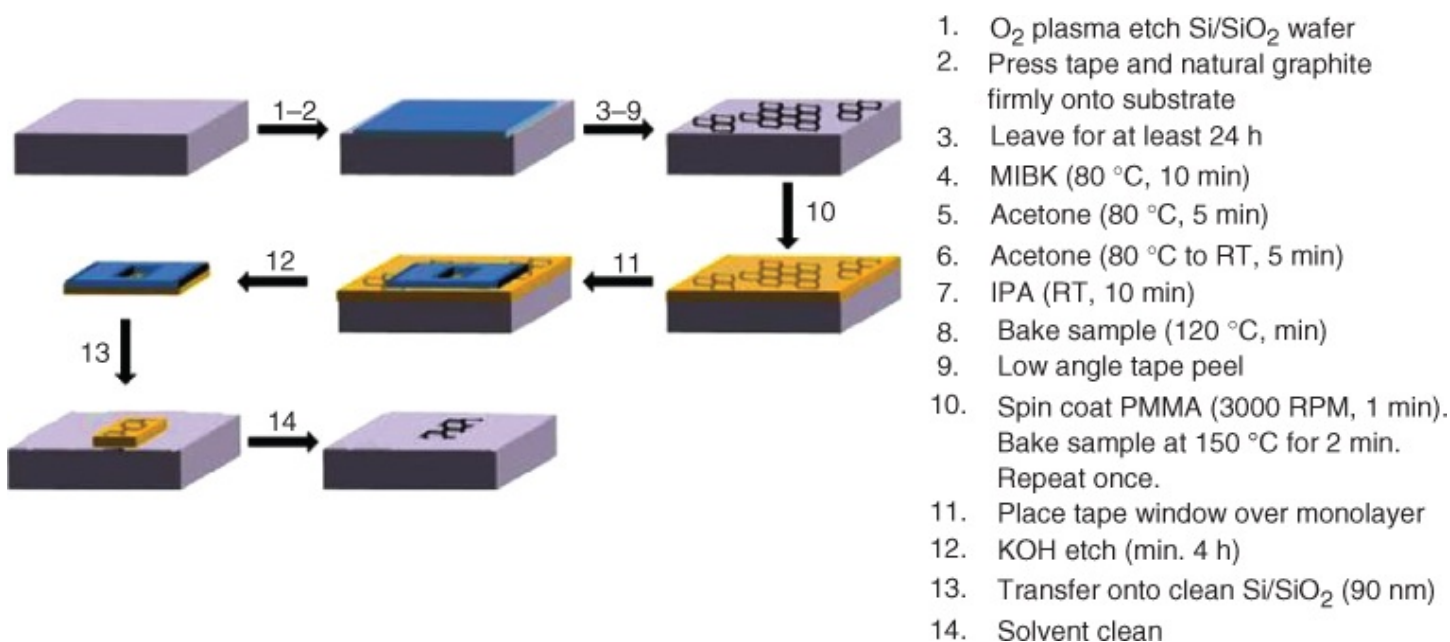


Figure 4.2 A schematic to show the preparation of the ME graphene samples and transfer process [22].

The exfoliation process can be “scaled up” by applying external sources of energy, rather than relying on manual cleavage of graphite. Ultrasonic treatment of graphite yields stable dispersions of exfoliated material in solvents where the interfacial energy of the solid–solution interface matches the cohesive energy of the graphite. A range of organic solvents has been investigated; however, the optimal one appears to be *N*-methylpyrrolidone (NMP), which was previously shown to be an efficient dispersant for carbon nanotubes [27]. The ultrasonic exfoliation method necessarily produces a distribution of product thicknesses: prolonged sonication can be used to reduce flake thickness of the resultant liquid-exfoliated graphene (LEG) toward the desired monolayer level [28], but sample thinning is accompanied by a reduction in the lateral size of the material. Stable LEG dispersions with concentrations as high as 25 g dm⁻³ in NMP have been reported [29]. Monolayer material can be separated from thicker fragments using centrifugation, but the overall yield is low (about 1%). Films of LEG can be used as electrodes, but such studies are hampered because the high purity of the sample is counteracted by the random assembly of graphene flakes, of varying dimensions and uncontrolled relative orientation [30]. Again, specific examples of the use of LEG are discussed under the relevant applications later. Chemical intercalation, via exposure to gases followed by rapid thermal expansion of samples to induce exfoliation, is another scalable route to graphene materials. For example, a solution-phase route to bilayer and trilayer graphene has been reported using thermally induced intercalation of mixed halides, followed by mild sonication, which leads to films with larger individual crystallite sizes than those formed solely from sonication [31].

The formation of graphite-intercalation compounds is not new: the electrochemical formation of such compounds is the basis of the lithium-ion battery. It was thus realized, at a relatively early stage in the graphene story, that electrochemical intercalation could be a useful way to exfoliate graphene, with the added advantage that an electrochemical route could allow

tailoring of the preparation to optimize the resultant material for a specific application. Given that the focus of this chapter is graphene electrochemistry, we devote some space to reviewing electrochemical routes to graphene exfoliation.

The basic principle behind the electrochemical exfoliation of graphite to graphene, or materials approaching monolayer graphene, rests on the ability to intercalate ions under an electric field into bulk forms of graphite. The interlayer spacing in graphite is around 0.34 nm, the exact value depending on the specific form of graphite: [32] the reversible operation of the Li^+ -ion battery rests on the smaller crystallographic diameter of Li^+ (0.12 nm) [33]. Intercalation of larger ions should distort and expand the structure, ultimately leading to exfoliation under the correct conditions. Organic ions are ideal candidates for this role, their sizes being tunable, with their inherent flexibility allowing the penetration of cations with diameters significantly larger than 0.34 nm. The first published electrochemical approach to a graphene-like structure was the work of Liu *et al.*, [34] who used a two-electrode arrangement with a water–ionic liquid (IL) mixture. The work reports exfoliation from a graphite anode shown as the negative electrode in [Figure 4.3](#) [34]. Typical preparations involved the application of very large (15 V) potential differences between the two terminals, which produced some individual monolayers (based on atomic force microscopy (AFM)), although the material is reported to be heavily functionalized with the imidazolium cation of the IL, based on the nitrogen signal seen in the X-ray photoelectron spectrum. Cationic functionalization of the graphene is surprising, given that anodic exfoliation is implied by [Figure 4.3](#). The Raman spectra reported for the exfoliate do not show any strong features, which is also surprising for a graphene material, even if heavily functionalized. More convincing work was reported by Lu *et al.* in 2009 [35], who described a one-pot synthesis of fluorescent carbon nanoribbons, nanoparticles (NPs), and graphene by the exfoliation of graphite. The electrolyte solution was again a water–IL mixture, which was, once more, imidazolium-based with large (up to 15 V) potentials applied in a two-electrode configuration, although lower potentials (2 V) could be used with higher added water content. This article specifically questioned the mechanism proposed in the earlier work by Liu *et al.* [34] and, instead, stated that anodic exfoliation of graphite occurred with a mechanism involving the oxidative attack of the water on the graphite. “Ultrathin” graphene sheets are quoted as one product from this process, although X-ray photoelectron spectroscopy again reveals functionalization, presumably covalent, of the product with atoms derived from the IL. Variations on this anodic exfoliation theme have been reported in ILs or aqueous acid solutions or mixtures of these phases, and also in aprotic solvents such as acetonitrile [36–38], but the oxidative nature of the processes raises questions about the suitability of this approach for the production of high-purity graphene samples. Similarly, anodic exfoliation using aqueous surfactant solutions has been employed, which at least minimizes the extent of oxidative damage to the exfoliate because of the less-acidic pH of the electrolyte [39, 40]. More recently, sulfate-based electrolytes have been used to achieve exfoliation at near-neutral pH, although the procedure is also anodic, impressive product distributions are reported, with the average flake thickness in the bilayer region [41].

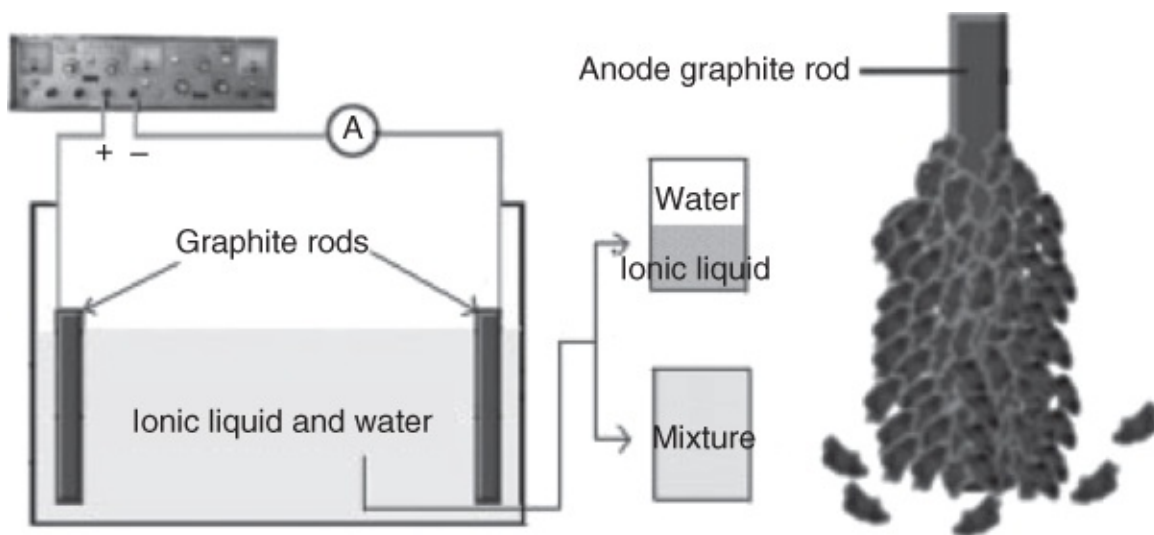


Figure 4.3 Showing the experimental setup used by Liu *et al.* [34] for the electrochemical exfoliation of graphite.

A more interesting approach is, therefore, the possibility of cathodic exfoliation of graphite to graphene materials, which should minimize the extent of sample oxidation. Salavagione and coworkers [42] have reported the production of few-layer graphene using electrochemical exfoliation as a pretreatment, followed by microwave and ultrasonic exfoliation, where evolution of hydrogen is identified as the key cathodic process. Lithium intercalation into graphite, the basis of the lithium-ion battery, was exploited by Loh and coworkers [43] to achieve direct electrochemical exfoliation of few-layer graphene in propylene carbonate. The solvent is seen as key: propylene carbonate co-intercalates with the cation; this lack of a stable solid–electrolyte interface is deleterious to battery performance, but in this case enhances exfoliation. Electrochemical intercalation is not, however, sufficient to produce exfoliated material on its own: as with the work of Salavagione, post-electrochemical ultrasound treatment is required to exfoliate the expanded material that results from the lithium intercalation process. Zhong and Swager [44] have developed a two-step exfoliation process based solely on cation intercalation: the first step involves graphite expansion driven by lithium intercalation from propylene carbonate, as employed by Loh [43]. The second step involves the intercalation of tetrabutylammonium cations to yield a few-layer graphene material. In fact, the formation of expanded graphite through the cathodic intercalation of tetra-alkylammonium ions was reported in the 1970s, although the possibility of graphene formation was not considered in the “pre-graphene” era [45, 46]. More recently, a detailed study of chemical intercalation compounds derived from tetra-alkylammonium ions has been reported [47]. Returning to electrochemistry, cationic intercalation has been performed in a single step using the pyrrolidinium cation of a room temperature IL: the product was less than five layers thick, as judged by Raman spectroscopy and transmission electron microscopy, with a low oxygen content [48]. No posttreatment, using either ultrasound or microwave exfoliation, was apparently required. Similarly, Cooper and coworkers reduced the tetra-alkylammonium intercalation route, as reported by Swager, to a single step by skipping the lithium intercalation stage. NMP, due to its polarity and stability at reductive potentials, was also shown to be a viable solvent for cathodic exfoliation, with few (about – four to five)-layer graphene shown

to be the major exfoliate via this route [49]. Simultaneous use of lithium and alkylammonium cations, yielding few-layer samples with significantly larger (10 μm diameter) lateral dimensions, was also demonstrated by this research group [50].

The focus of this chapter is on the electrochemical properties of graphene, rather than GO, but it should be noted that the latter material can also be produced electrochemically, and used as a route to graphene (or, more correctly, rGO) through electrochemical reduction. The latter pathway involves the electrochemical reduction of GO produced using conventional, chemical oxidation: even though the oxygen content cannot be eliminated completely, it has been shown that some degree of control over reduction can be obtained through repeated voltammetric cycling in aqueous solution [51]. Similarly, electrochemical oxidation can be used as a route for the direct synthesis of GO from graphite, avoiding the use of acid solutions and/or oxidizing agents that may remain adsorbed in the product [52].

4.2.2 “Bottom-Up” Routes to Graphene Production

Although not based on electrochemistry “bottom-up” methods, where the graphene is prepared from molecular (generally hydrocarbon) components, are worthy of a brief discussion. Chemical vapor deposition (CVD) has attracted enormous attention as a scalable route to graphene production. The method rests on the catalytic decomposition of hydrocarbons: nickel can be used as the growth substrate, but the lower solubility of carbon in copper gives more uniform films with better control over thickness [53], although very recent results suggest that germanium is also a promising substrate material for the growth of graphene (see [Figure 4.4](#) for a general schematic [54] of the CVD process) [55, 56]. The advantages of graphene synthesis via CVD are scale, coverage approaching the meter square scale [57], and the ease with which heteroatoms can be incorporated by introduction of the relevant feed into the gas supply: [58] this point is particularly important given the interest in electrocatalysis using heteroatom-containing graphene, as discussed in [Section 4.4](#). From the electrochemical viewpoint, the scale of the samples produced by CVD offers immediate advantages. Similarly, the method produces graphene – as opposed to its oxide – although there is a wide range in the quality (e.g., uniformity of monolayer coverage, the presence of pinholes, and other defects) of samples produced by this route. Care is therefore required in the interpretation of electrochemical data obtained from CVD samples supplied commercially [59], for example, with independent sample characterization being important. Another important factor is the role of the substrate – to be discussed later in the context of Faradaic and non-Faradaic electrochemistry. The electrochemistry of CVD-derived samples can be studied directly with the sample present on their growth substrates, although this leads to the need to distinguish between the responses of the graphene and the growth substrate. Alternatively, CVD samples can be “transferred” to insulating substrates such as the oxide-covered silicon wafers that are routinely used as substrates for ME graphene. This transfer procedure involves the coating of the sample in a polymer film (e.g., poly(methyl methacrylate), PMMA) and subsequent etching of the underlying metal. While relatively straightforward, the transfer process brings with it the possibility of contamination through polymer residues and solvent exposure referred to above. More exotic “bottom-up” procedures to graphene production also exist: chemical reduction of

dry ice using magnesium metal has been proposed as a route to thin graphitic films, although the production of monolayer material and ease of scale-up remain to be confirmed [60]. Similarly, arc discharge has been reported as a route to multilayer graphene samples [61].

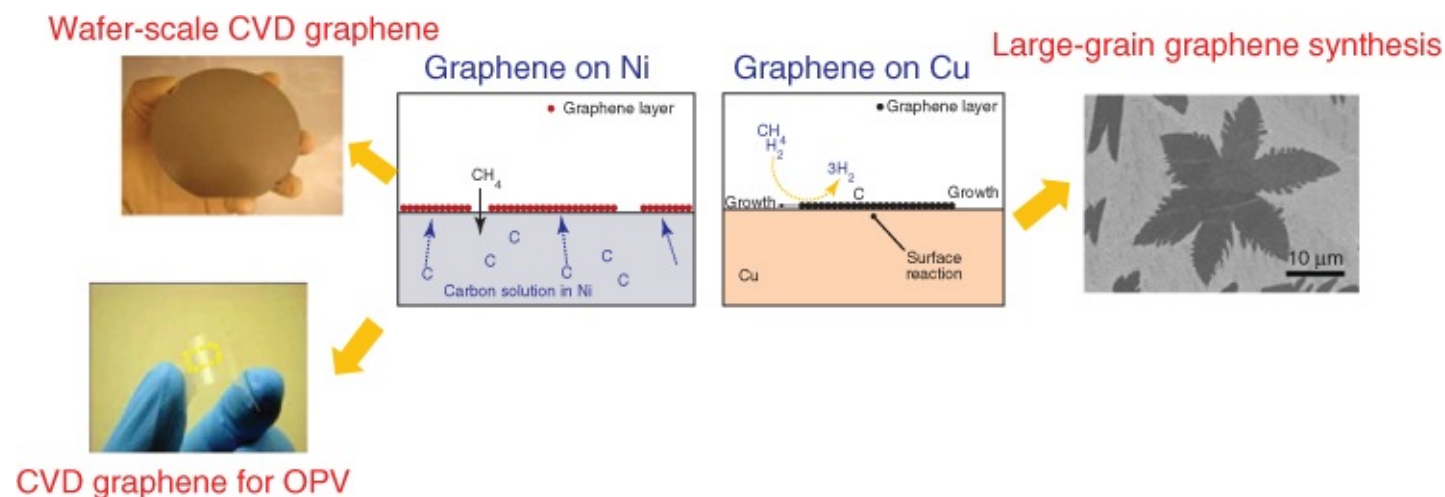


Figure 4.4 Schematic of CVD-grown graphene on Ni and Cu substrates [54].

Finally, a route to very high purity graphene, which has been largely overlooked by the electrochemical community, is through epitaxial growth from silicon carbide. This method relies on the relative ease of sublimation of the Si atoms, thus leaving an epitaxial deposit of graphene [62]. As with CVD, the method relies on high ($>1000^{\circ}\text{C}$) growth temperatures, but a major drawback (compared to CVD) is the inertness of SiC, meaning that the graphene layer is confined to this substrate. The electrochemical properties of graphene grown on nanostructured SiC have been investigated, for example, in the context of methanol oxidation [63], although we are unaware of electrochemical studies using large-scale graphene samples grown on SiC substrates.

4.3 Capacitance of Graphene Electrodes

In order to utilize and exploit the unique properties of graphene for energy storage/conversion applications, such as fuel cells, batteries, and supercapacitors, the double-layer or interfacial capacitance (C_{int}) provides invaluable data to aid in the production of materials that will achieve the most promising structure and configuration for each particular application. Briefly, the C_{int} is caused by an accumulation of charge at the electrode–electrolyte interface on the application of a potential. It is measured in solution-containing background electrolyte only, for example, aqueous salt solutions, where no Faradaic process is occurring. Graphene, as a two-dimensional material with an intrinsically high specific surface area, has naturally attracted attention as an electrode material for supercapacitors [3].

Early studies on graphite, as the bulk analog of graphene, provided a platform for the investigation of C_{int} for carbon materials. The first investigation of the double-layer capacitance on pyrolytic graphite was by Bauer *et al.* in 1968 [64]. Here, disk electrodes sealed in glass were employed [65] where the graphite surface was prepared by either

polishing with an abrasive paper or cleaved using a sharp scalpel. Measurements were then taken in aqueous and organic solvents by varying either the frequency (between 50 and 25 000 Hz) or the potential with a fixed frequency. A frequency dependence for both the series capacitance and resistance was observed. Moreover, the latter experiments using aqueous KCl electrolyte demonstrated a potential dependence with a shallow minimum between -0.2 and -0.4 V versus a saturated calomel reference electrode saturated calomel electrode (SCE) when using a polished graphite surface. This study does not provide any in-depth explanation for the value of C_{int} , and in common with many other studies, a reproducible well-defined and characterized surface was not demonstrated; one of the explanations given for the observed frequency dependence.

It is of utmost importance to use a material that is well defined and of high quality, especially with graphite, as the cleavage method and quality of material will produce surfaces with varying step densities and hence edges exposed [66], which, as will be described later, will affect the capacitive response [64, 67]. Early studies using a better-defined surface were those comparing polished basal and edge planes of pyrolytic graphite and also the basal and edge planes of stress-annealed graphite (where the disk electrodes were formed under compression) [67, 68]. The basal plane stress-annealed samples were prepared by using the tape peel method, enabling a fresh and renewable surface to be used before each measurement. Use of a 0.9 M NaF electrolyte demonstrated little or no frequency dependence of the capacitance, although again there was a potential dependence with a fixed frequency. This potential dependence was almost symmetrical with the minimum at about 0 V versus the normal hydrogen electrode (NHE) and independent of the concentration of electrolyte in the range of 0.01–1 M. However, employing lower electrolyte concentrations, in the range of 10^{-5} to 0.9 M, resulted in a concentration effect where the minimum value in the capacitance–potential curve is sharper at the lower concentrations ([Figure 4.5](#)). A change in solution pH ruled out surface heterogeneities as the cause of this [69]. Studies on graphene also revealed an influence of concentration on capacitance when employing low concentrations of electrolyte (*vide infra*). Interestingly, the lowest observed C_{int} was reported at around $3 \mu\text{F cm}^{-2}$ (in agreement with subsequent research), which is significantly lower than the minimum capacitance values of more than $15 \mu\text{F cm}^{-2}$ reported for metallic electrodes under comparable conditions [70, 71].

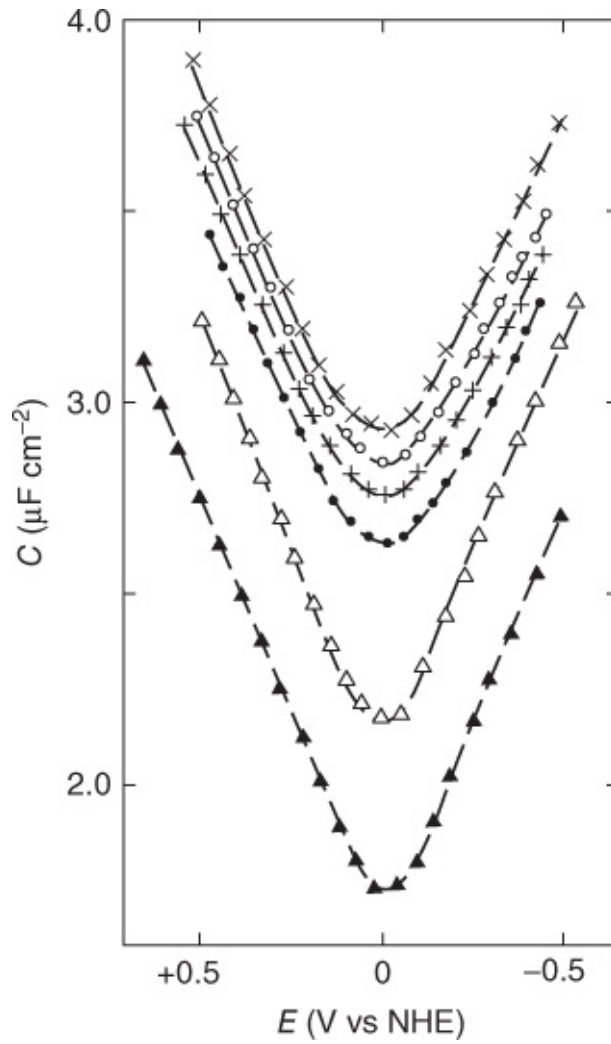


Figure 4.5 Capacitance–potential curves for the basal plane of stress-annealed graphite for a range of concentrations (0.9, 10^{-1} , 10^{-2} , 10^{-3} , 10^{-4} , and 10^{-5} M from top to bottom) in NaF (pH = 6) [69].

Randin and Yeager gave the first explanation for the low C_{int} observed for the basal plane stress-annealed graphite; they attributed this to a space-charge component. For semiconductors or semimetallic electrodes, such as carbon materials, there is a contribution to the overall capacitance from the “space-charge” region, which occurs due to a limited density of charge carriers. For metals, this contribution to the capacitance is not present due to the higher number of charge carriers. This “space-charge” capacitance (C_{sc}) becomes a quantum capacitance (C_{Q}) when employing low-dimensional materials with singularities in their density of states (DOS): physically, both effects arise because the electronic structure of the solid influences the overall charge distribution at the solid–electrolyte interface. Therefore, the overall measured C_{int} in electrochemistry has contributions from the Helmholtz layer, diffuse layer, and also the space-charge region as seen in Equation (4.1) [71] as follows:

$$C_{\text{int}}^{-1} = C_{\text{H}}^{-1} + C_{\text{D}}^{-1} + C_{\text{sc}}^{-1} \quad 4.1$$

where C_{int} is the measured interfacial capacitance, C_{H} is the Helmholtz capacitance, C_{D} is the

corresponding diffuse layer term, and C_{SC} is the space-charge capacitance. Under high-ionic strength conditions, $C_D \gg C_H$ and so contributes negligibly to the overall measured C_{int} . In the initial study of pyrolytic graphite [69], the data were interpreted using the framework for semiconductor electrodes where the minimum interfacial capacitance ($C_{int(0)}$) measured for an intrinsic semiconductor can be calculated as:

$$C_{int(0)} = (2\epsilon\epsilon_0 e^2 c / kT)^{1/2} \quad 4.2$$

where ϵ is the dielectric constant, ϵ_0 is the permittivity of free space, e is the elementary charge, c is the electronic charge density, k is Boltzmann constant, and T is the absolute temperature. The dependence of potential on the capacity is given by Equation (4.3) as follows:

$$C_{SC} = C_{int(0)} \cosh(V_s e / 2kT) \quad 4.3$$

where V_s is the potential at the surface [69, 72]. Randin and Yeager's data do not fit this theory well: two possible explanations given were the possible existence of imperfections on the graphite surface resulting in degenerate surface electronic states, or that the semiconductor theory was not, in fact, appropriate for a material such as graphite because of the relatively high carrier concentration. Therefore, an alternative more representative model is sought. Gerischer interpreted results and explained the capacitance in terms of a low DOS near the Fermi level [71].

Further studies demonstrating the low C_{int} of graphite have been performed by several research groups on the basal plane of different grades of highly oriented pyrolytic graphite (HOPG) [66, 73–75] where the quality and step density of the samples varied. Measurements of C_{int} on ZYA-grade HOPG (high quality with low step density) were reported in the range of 1.2–2.8 $\mu\text{F cm}^{-2}$ in 1 M KCl [66]. These values are slightly lower than reported for a lower grade HOPG with a higher step density, ZYH grade, which have been in the range of 3.4–7.1 $\mu\text{F cm}^{-2}$ [74, 75]. Even though the studies do report similar C_{int} values, a range of factors may have influenced the data obtained for the different types of HOPG, such as the supplier (SPI supplies [66], Union Carbide [74], or Advanced Ceramics) [75], cleaving method used (scotch tape [66] or scalpel cleave) [74], the experimental setup, or the duration the sample may have been exposed to air (HOPG has been reported to degrade over time as seen through the influence on electron transfer kinetics) [66].

One notable difference is the higher C_{int} reported for ZYH-grade HOPG compared with ZYA-grade HOPG. One study using ZYH HOPG demonstrated that surface polishing and deliberate introduction of defects, such as step edges, increased the capacitance [75]. Studies specifically investigating the capacitive response on edge-plane stress-annealed graphite have been conducted by Randin and Yeager with values measured between 50 and 70 $\mu\text{F cm}^{-2}$ quoted. These values, which are much higher than those of the basal plane, are explained by higher surface roughness, and some contribution from the surface groups. In a separate study, a

measurement of $16 \mu\text{F cm}^{-2}$ was recorded for the capacitance of polished basal plane of ordinary pyrolytic graphite, which was quite different to the value of $60 \mu\text{F cm}^{-2}$ reported in the previous study on a similar material [64]. The authors state that this discrepancy could be purely because of a different origin and preparation of the material [68].

It is imperative that fundamental studies to determine the C_{int} of graphene samples are carried out on well-characterized materials, and, to date, there are only a very limited number of reports that meet this criterion. To the best of our knowledge, these fundamental studies have mainly been performed on graphene grown via CVD, with only one study using graphene produced by ME [76]: by contrast, supercapacitor devices are usually constructed as porous architectures, using graphene prepared from chemical (rGO) methods, the aforementioned uncertainty in the structure of the materials produced via this approach makes it difficult to perform detailed studies that relate observed capacitance to structure. Consequently, and also because of the preponderance of the “applied” studies of graphene capacitance in the literature, in this chapter we focus purely on the fundamental capacitive studies. The single study using ME graphene was produced by the ME of Kish graphite, which was then transferred onto a Si/SiO₂ (290-nm-thick oxide layer) substrate [77]. Many samples of graphene for fundamental studies are prepared by transferring them onto a substrate that potentially has little effect on the desired measurement. This includes samples grown via CVD where the graphene is transferred from a metallic substrate, which would give rise to a capacitive current, to an inert surface such as Si/SiO₂ [78] (although it should be noted that substrates generally dope the graphene) [79, 80]. For these studies, a 10- μm -diameter window surrounded by photoresist defined the working electrode and each sample was cleaned and annealed at 200 °C in a H₂/Ar atmosphere (a commonly used method to clean the graphene removing any contamination such as transfer residues) [24, 81–83]. Capacitance measurements were performed in an IL, 1-butyl-3-methylimidazolium hexafluorophosphate (BMIM-PF₆), and also in NaF at a range of concentrations (0.1, 0.5, and 1 mM). For BMIM-PF₆, the C_{int} was modeled as two capacitors in series due to the small Debye length when employing ILs (meaning the C_D term of Equation (4.1) could be neglected); however, when using NaF as the electrolyte at the above concentrations, a capacitance dependence was observed, which is most likely due to a contribution from the diffuse layer. In all cases, the measured capacitance will be dominated by the smallest term in the series, see Equation (4.1): for ideal and pristine graphene, the C_Q term can be calculated from the following equation [77, 84, 85]:

$$C_Q \approx \frac{8\pi e^3 V_s}{(h v_F)^2} = \frac{4\pi^{1/2} e^2 n^{1/2}}{h v_F} \quad 4.4$$

where h is the Planck's constant, v_F is the Fermi velocity of carriers in the graphene, and n is the carrier concentration. According to Equation (4.4) a plot of quantum capacitance versus potential shows two linear branches, with a minimum around 0 V (where there is a low DOS near the Dirac point), which is essentially an experimental manifestation of the linear dispersion of the Dirac cone structure mentioned in [Section 4.1](#). Experimentally, the

capacitance minimum shows a more rounded response, and always has a nonzero value, which is greater than the minimum expected, due to thermal effects. Also, the measured slope of the C_Q versus potential plot showed a lower value than expected. These discrepancies were taken as indications of the presence of defects, or charged impurities, arising from the contact of the monolayer with the substrate and therefore the addition of a charge carrier density due to impurities (n^*) can be included in Equation (4.4), in addition to the carrier concentration caused by the gate potential (n_G), as shown in Equation (4.5) [77, 78, 86, 87]

$$n = |n_G| + |n^*| \quad 4.5$$

where

$$n_G = \left(\frac{2\sqrt{\pi}eV_{ch}}{h\nu_F} \right)^2 \quad 4.6$$

Tao *et al.* state “...a complete interfacial capacitance theory including quantum contribution and impurities is yet to be developed”, although more recent works have achieved this to some extent (*vide infra*) [85, 88].

Ruoff *et al.* have performed some of the most in-depth studies on the capacitance of PMMA-transferred CVD graphene. One of their studies used a monolayer sample where either one, or both sides, of the graphene were exposed to solution (for details on electrode fabrication, see [Figure 4.6](#)) before electrochemical impedance spectroscopy (EIS) measurements were performed (amplitude: 10 mV; frequency: 100 kHz to 1 Hz) in 4 M sulfuric acid [89]. In order to determine the capacitance, the results were fitted to an $R(RC)$ equivalent circuit.

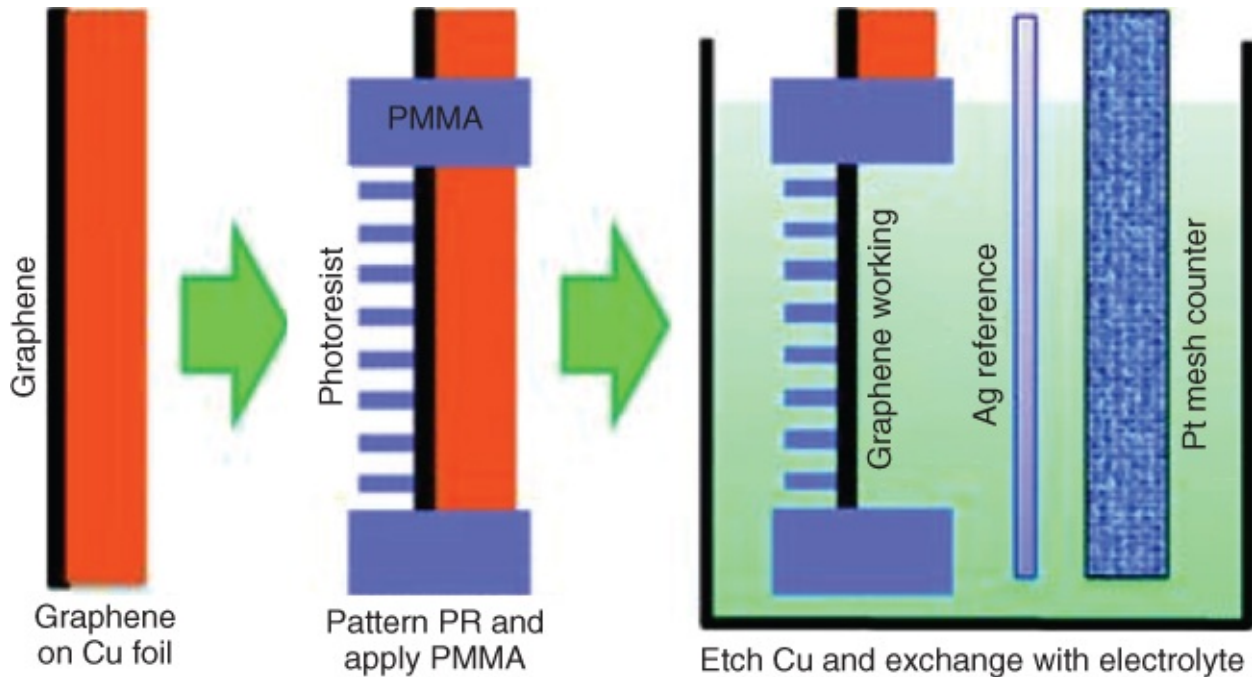


Figure 4.6 Schematic of the electrode fabrication [3].

[Figure 4.7](#)a,b compares the calculated and experimental C_{int} when one, or two sides, of the

graphene are exposed to electrolyte. Logically, when two sides were exposed to solution, the C_H term in Equation (4.1) was doubled. The potential dependence is clearly evident with the measured minimum correlating to the theoretical minimum at 0 V, when the Ag reference electrode is taken into account. Also demonstrated in Figure 4.7 is the dominance of C_Q as the surface area is increased, that is, when both sides of the graphene are exposed to solution, the smallest capacitance dominates.

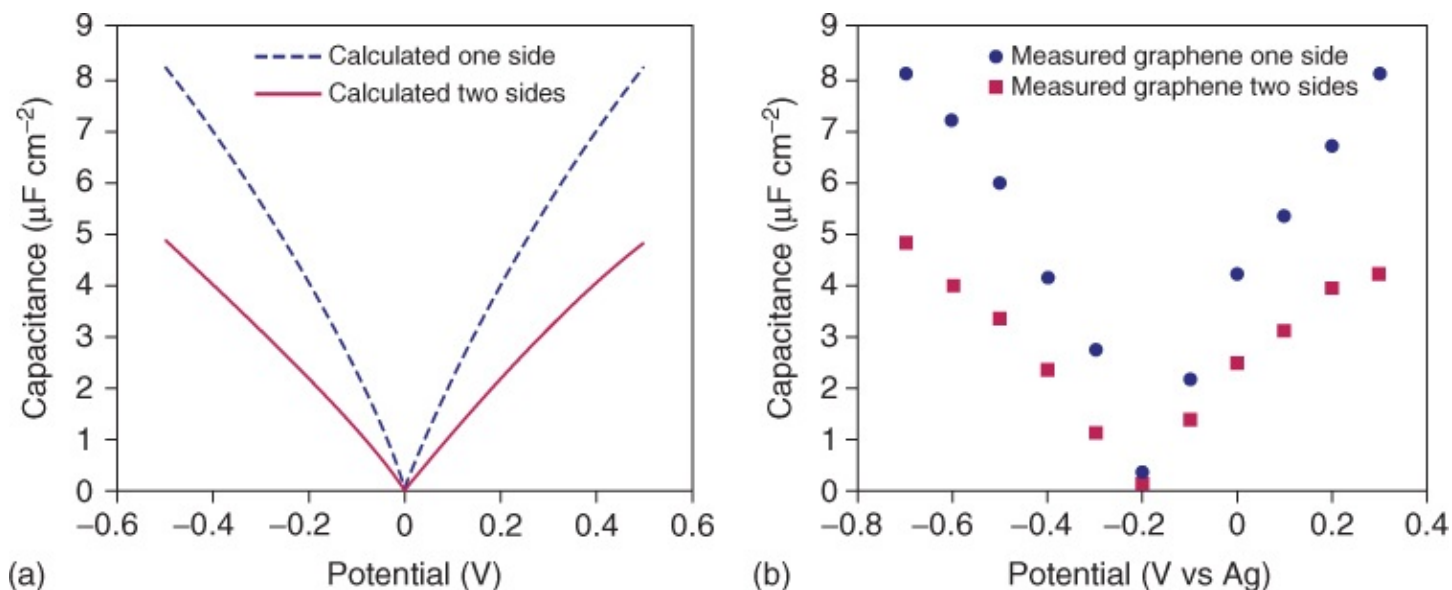


Figure 4.7 A comparison for the (a) calculated and (b) measured capacitance of monolayer graphene when either one or two sides are exposed to 4 M H₂SO₄ electrolyte solution.

(Taken from Ref. [3].)

Later studies were performed to explore the effect on C_{int} when multiple CVD-grown graphene layers were used as the electrode (one to five layers) [88]. The electrodes were prepared using PMMA to transfer each layer on top of the previous one (this method of fabrication is relevant as described later). As is evident from Figure 4.8, the C_{int} -potential curves follow the same shape as reported previously [77, 88] with minimum C_{int} in the range of 2.5–3.5 $\mu\text{F cm}^{-2}$, consistent with other values reported for basal plane HOPG and graphene.

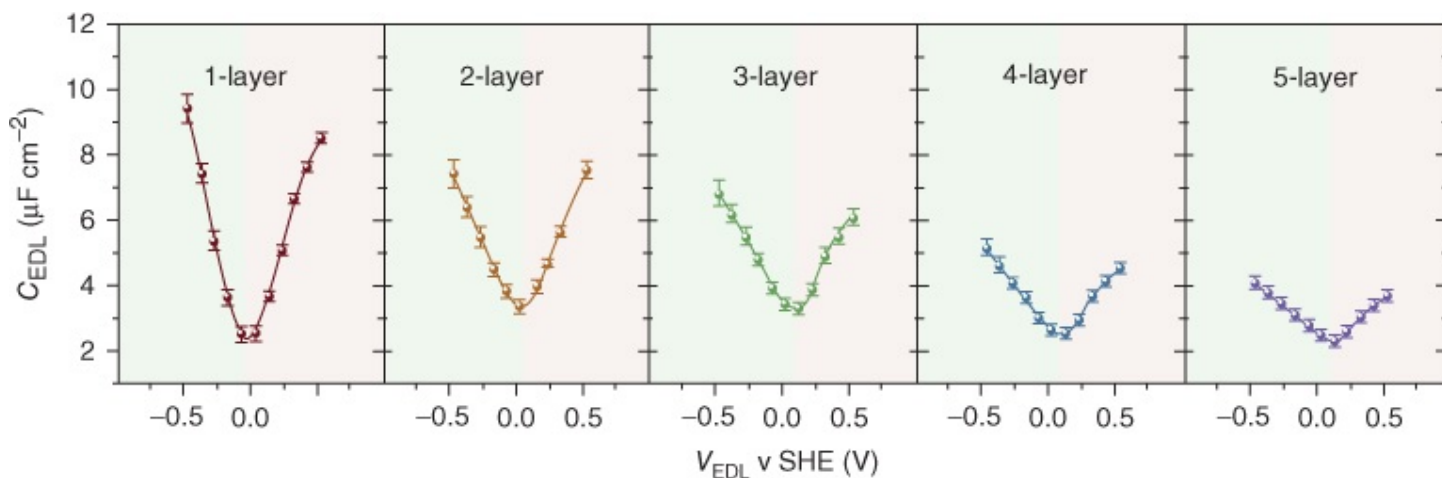


Figure 4.8 C_{int} versus potential plots for electrodes prepared with one to five layers of graphene in a 6 M potassium hydroxide aqueous electrolyte [88].

The curves in [Figure 4.8](#) show a decrease in C_{int} for this potential range as the number of layers is increased. However, as the number of layers is decreased to the monolayer, C_H is found to be higher in the electrolyte used (6 M aqueous KOH solution) and more sensitive to potential. Interestingly, there is evidence of doping, most likely resulting from the transfer residues, which is apparent from the potential at which the capacitance is at its minimum. For samples that are deliberately n-doped, through introduction of nitrogen, the potential of zero charge (the PZC, which is the Dirac point of the graphene) is shifted positive, likewise for p-doped samples this potential shifts negatively.

From studies using the undoped graphene, Ruoff *et al.* concluded that a monolayer electrode with a higher DOS would be ideal for a capacitor: hence the addition of the nitrogen source during the CVD growth process increased the capacitance of the resultant electrode by 66% [88]. [Figure 4.9](#) demonstrates that as the concentration of nitrogen is increased, the potential for minimum capacitance is shifted notably positive and also the minimum value of capacitance is increased. Where the DOS would be lowest, at the PZC, it is clear that this is where the doping has the most pronounced effect on capacitance.

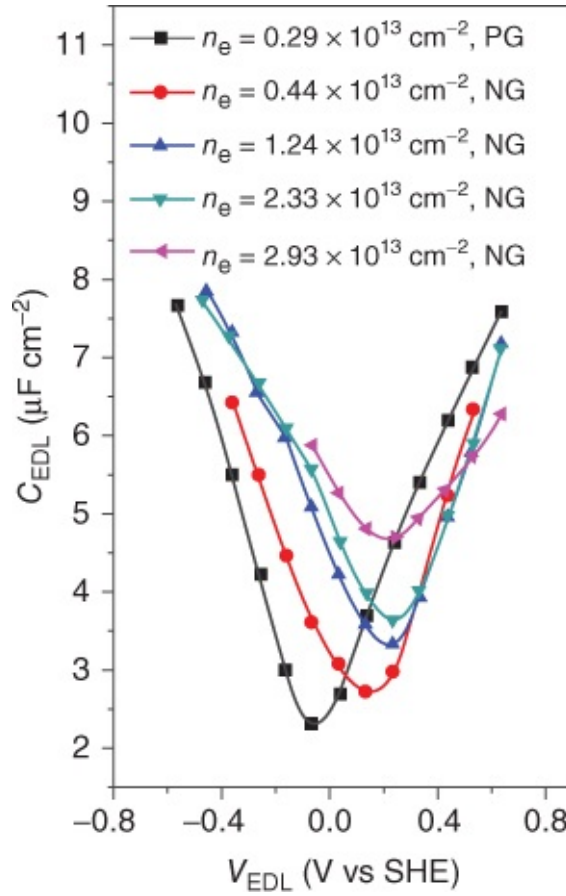


Figure 4.9 Effect of n-doping on capacitance of graphene with various concentrations using 6 M potassium hydroxide aqueous electrolyte.

In situ Raman spectroscopy can be used to identify if a sample is n- or p-doped and can provide insight into the impact on C_Q [90] (see Equation (4.7)):

$$C_Q = \left(\frac{4e^2}{\hbar v_F 2\alpha'} \right) \Delta\Omega \quad 4.7$$

where v_F is the Fermi velocity of the Dirac electron, α' is a numerical coefficient (4.39×10^{-3}) [90], and $\Delta\Omega$ is the measured frequency shift of the Raman spectrum G band. The G band peak position shifts depending upon the type of doping in the material and therefore provides ready insight into the charge carrier concentration. Again, this study also measured the minimum C_{int} , which was found to be $4.5 \mu F cm^{-2}$ in NaCl.

As with HOPG described previously, both basal plane and edge studies have been carried out on CVD graphene and values of 4 and $1 \times 10^5 \mu F cm^{-2}$ were reported, respectively, when employing 0.1 M KCl in 0.1 M phosphate-buffered saline (PBS) [91]. The enormous capacitance for the edge plane (although caution should be taken when using the quoted value due to difficulties in determining the actual size and area of electrolyte contact with a monolayer edge plane) of graphene is at least qualitatively consistent with the higher capacitance seen on HOPG. The related differences between the DOS of the edge and basal planes [92, 93] are also thought to impact on the heterogeneous electron transfer (HET)

kinetics.

Fundamental studies of the C_{int} of graphene are very much lacking particularly for methods of production other than via CVD. All research on graphite and graphene to date have demonstrated a low C_{int} compared with metallic electrodes, which has been attributed to a C_{SC} (or C_{Q}) component. Graphene properties can be tuned to give a higher or lower C_{int} by either electrochemical (application of potential) or chemical (i.e., addition of atoms during the growth process) doping. These can give desired effects dependent upon the application required. For energy storage applications, a high C_{int} is sought; however, for biological and sensing applications, a low C_{int} is desirable, which would give rise to a high signal-to-noise ratio and hence detect low concentrations of analyte. In addition to doping, electrolyte as well as pH plays a role on the C_{int} .

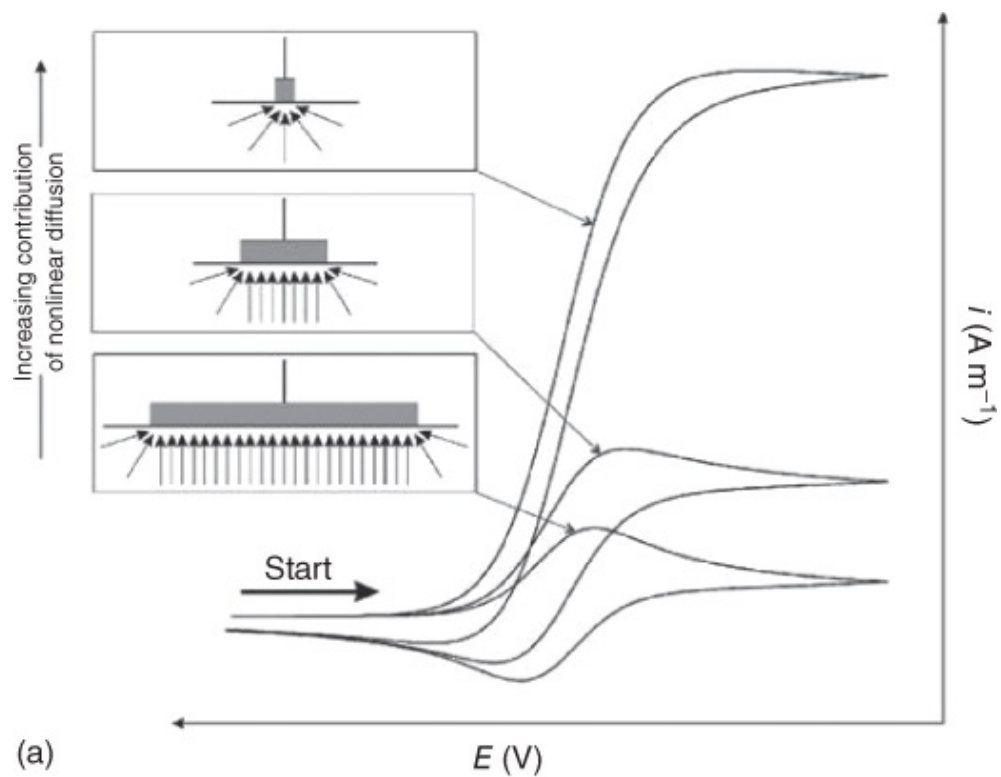
More research is required to gain a deeper insight and understanding of the C_{int} of graphene electrode. Studies using well-defined samples are vital, where there are no contributions from the production or transfer process. Information on the electrical properties of the material would aid in determining the local DOS [94] and hence provide a greater ability to tune the electrode properties for the desired applications.

4.4 Electron Transfer Kinetics at Graphene Electrodes

As noted earlier, several unique properties of graphene, namely high electron mobility, high specific surface area, flexibility, and high transparency, could be directly exploited in electrochemical applications, such as energy conversion/storage, sensing, and corrosion protection. Keeping these applications in mind, the standard HET rate constant, k^0 , between the graphene and a redox-active molecule is of significant importance when evaluating its performance as an electrode material. In particular, two fundamental questions arise: (i) how do the HET kinetics of the basal plane, edge plane, and defects of graphene compare? and (ii) how do the HET kinetics change with the number of graphene layers, going from mono- to multilayer graphene and bulk graphite?

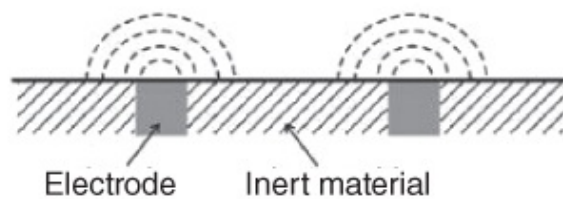
The first question has been a focus of intensive research a long time before the first isolation of graphene [1]. HOPG is an ideal crystalline surface and was, for that reason, popular for these investigations. Now the “traditional” view of crystalline carbon electrochemistry is that the edge plane and defects are the electrochemically active sites of the surface, whereas the pristine basal plane is electrochemically inactive or at least exhibits kinetics of many orders of magnitude slower than the active sites [32, 95]. One of the first experimental proofs for this hypothesis was given by McCreery *et al.*, [74] who studied HOPG surfaces using anthraquinone disulfonate adsorption and ferri/ferrocyanide ($\text{Fe}(\text{CN})_6^{3-/4-}$) electrochemical measurements. They reported significant surface-to-surface variation in HET kinetics, adsorption, and capacitance, and most interestingly, laser irradiation was used to intentionally create defects. The measured k^0 was found to linearly correlate with the laser power, indicating that the higher concentration of defects accelerates the HET kinetics. The

quantitative conclusion of the work was that the pristine basal plane has $k^0 < 10^{-6} \text{ cm s}^{-1}$ (corresponding to peak separations larger than 1500 mV for $\text{Fe}(\text{CN})_6^{3-/4-}$ reduction/oxidation at a scan rate of 1 V s^{-1}). We note that $\text{Fe}(\text{CN})_6^{3-/4-}$ is traditionally regarded as an “inner-sphere” complex, that is, it should be very sensitive to the structure/history of the electrode surface and is also known to form “Prussian blue.” [96] The reports in support of the “slow basal plane kinetics” theory were further expanded by the work of Compton *et al.*, [97] who performed both experimental and simulated electrochemical experiments with $\text{Fe}(\text{CN})_6^{3-/4-}$ and hexaammineruthenium ($\text{Ru}(\text{NH}_3)_6^{3+/2+}$) redox probes. They concluded that HOPG can be described as a heterogeneous surface containing both the electrochemically inactive basal plane and the active edge and defect sites, analogous to a highly inactive surface containing electrocatalytically active metal NPs. This gives rise to individual radial diffusion layers around the active surface sites, which can be isolated or overlapping, depending on the overall charge passed through the electrode, concentration of the active surface sites, and so on, as shown in [Figure 4.10](#). The numerical simulation of mass transport/HET kinetics for $\text{Fe}(\text{CN})_6^{3-/4-}$ reduction/oxidation showed that when the kinetics of the basal plane were several orders of magnitude (2–7) smaller than those of edge plane (10^{-9} to $10^{-4} \text{ cm s}^{-1}$, but not zero!), the cyclic voltammogram (CV) should contain two pairs of reduction and oxidation peaks, rather than one pair as in a conventional one-electron transfer process. This phenomenon is more evident as the size of the diffusion domain is increased, that is, a smaller concentration of edges/defects scattered on the basal plane surface as indicated in [Figure 4.11](#). Because such voltammograms had not been observed experimentally, the authors concluded that the HET rate of ferrocyanide oxidation at the pristine basal plane of HOPG is much slower than $10^{-9} \text{ cm s}^{-1}$ or possibly even zero [97, 98]. The same group used a fabrication method, in which the edge planes of HOPG were temporarily covered with MoO_2 nanowires and the exposed basal plane blocked with inert material. After acid treatment and MoO_2 dissolution, only the edge-plane “nanotrenches” were exposed and electrochemistry performed on them. Because no difference was observed in the voltammetry between the modified surface and plain HOPG, the authors reached the same conclusions about the edge/basal plane activity [99].

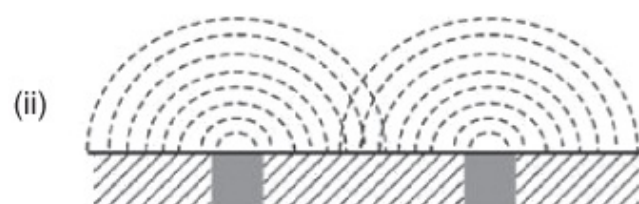


(a)

(i) Individual diffusion layers

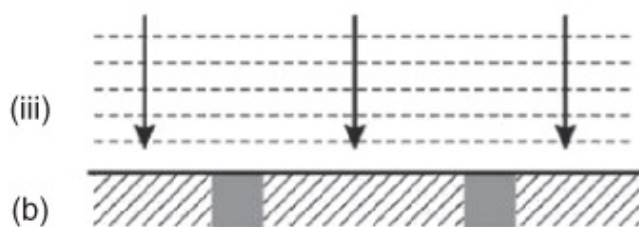


Overlapping diffusion layers



(ii)

linear diffusion



(iii)

(b)

Figure 4.10 (a) Shape of the voltammetry for radial and linear diffusion. (b) Schematic diagram showing the development of the diffusion layer with increasing time (or charge passed), that is, from (i) to (iii).

(Reprinted from Ref. [98].)

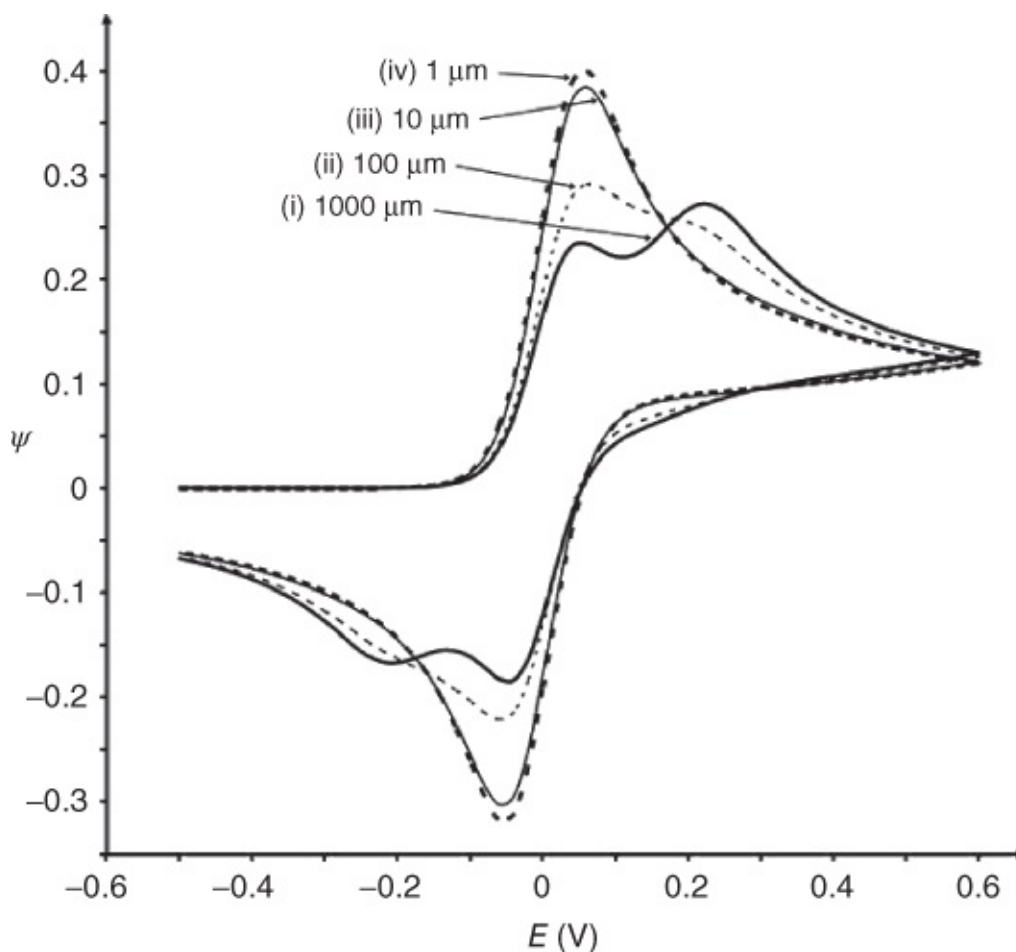


Figure 4.11 Simulated dependence of the voltammetric shape (dimensionless current vs potential) on the domain size of a heterogeneous surface. The k^0 of the “slow” and “fast” kinetics domains were $1 \times 10^{-4} \text{ cm s}^{-1}$ and $1 \times 10^{-2} \text{ cm s}^{-1}$, respectively.

(Reprinted from Ref. [97].)

Nevertheless, the above views of edge-plane versus basal plane electrochemistry on carbon surfaces are not uniformly accepted throughout the scientific community. Unwin *et al.* [66, 100, 101] have published a series of studies, which showed evidence of significant electrochemical activity of the HOPG basal plane. In order to avoid the problem of overlapping diffusion layers of the heterogeneous surface as mentioned earlier, a Nafion film was used to slow the diffusion to the surface, and experimental voltammograms were compared with numerical simulation of the diffusion response. The observed currents were 1–2 orders of magnitude larger than predicted had only the edge plane of HOPG been active, which led the authors to conclude that the basal plane is active with $k^0 = 4.5 \times 10^{-5} \text{ cm s}^{-1}$ for the $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ redox probe [102]. In another article, they correlated high-resolution electrochemical measurements using scanning electrochemical cell microscopy (SECCM) with AFM measurements over the

same surface area, again showing that the basal plane of HOPG is electroactive, and furthermore, showing evidence of rapid deterioration of the kinetics within 1 h after the fresh cleave of the HOPG surface [100]. The reciprocal dependence of the kinetics, and also conductivity, on repeated voltammetric sweeps, significant for a surface-sensitive inner-sphere ferricyanide mediator, was further investigated by the same group [66]. It is clear that the discussion around edge-plane versus basal plane electroactivity on graphite is still an open arena with many unanswered questions and deserves further detailed and careful attention to gain full understanding of sp^2 carbon electrochemistry. A subtle, but important, experimental question is the grade/purity of the graphite samples used, the surface treatment before experimentation and method used to obtain the data [95].

The above discussion relates to graphite electrochemistry: however, identical questions also arise – how do the HET kinetics of the basal plane, edge plane, and defects of graphene vary and how do the kinetics change with the number of graphene layers? – with graphene. One response to the questions posed (as with the graphite case) is: it depends on the type of “graphene” used. Graphene electrochemistry is a very young area with very few papers before 2010. Unfortunately, the fact that the large number of research groups involved used different graphene sources (described previously for samples derived from GO) complicates the efforts to summarize a cohesive set of conclusions about electron transfer kinetics on graphene.

The bulk of published work has been carried out using rGO and LEG, aimed at applications in sensing and electrocatalysis [7, 103–105]. The samples are usually prepared by filtration or compression of the liquid-based nanoflake dispersion to obtain a thin film of stacked flakes. Alternatively, many researchers simply drop-cast and dry the suspension on a conductive support, such as glassy carbon (GC) or gold. There are inherent problems with such sample preparation, namely the stacking of graphene/graphite layers, which significantly reduces the conductivity, as well as the interference of the conductive support. Furthermore, the measured electrochemical response is an “average” of basal and edge-plane contribution due to nanocrystallinity of the graphene flakes. Wang *et al.* compared the electrochemical activity of rGO and electrochemically reduced GO with that of single-wall carbon nanotubes (SWNTs) and concluded that the latter exhibits faster HET kinetics, attributed to the surface groups on carbon surface. The voltammetric analysis, using ferricyanide, β -nicotinamide adenine dinucleotide (NADH) and ascorbic acid (AA) as redox probes, is, however, only qualitative and the k^0 values were not provided [106]. Keeley *et al.* developed an AA sensor prepared from graphene nanosheets, initially exfoliated in *N,N*-dimethylformamide and then immobilized on a conductive polymer. The graphene electrodes exhibited an overall resistance of about 0.8 k Ω and yielded near-reversible kinetics for the $Ru(NH_3)_6^{3+/2+}$ redox probe. The AA oxidation provided quite a narrow effective concentration window of 0.4–6.0 mM, and a detection limit (0.12 mM) much higher than that typical for UV/Vis spectrophotometry [30]. Pumera *et al.* published an early study on commercially available stacked graphene platelets with different ratios of mono- and multilayer flakes immobilized on a GC surface. Electrochemistry on these samples (dopamine and AA) did not reveal any significant variation in voltammetric response and the authors concluded that the HET kinetics are independent of the number of graphene layers [107]. It is important to note that stacking of the platelets does not provide a good

control over the edge/basal plane content and simply results in an averaged nano- and microscale response. The same group compared the HET rate on open and folded edges of stacked graphene nanofibers (again immobilized on GC) and concluded that, in accordance to the “inactive” basal plane hypothesis discussed earlier, the electroactivity of the folded edges decreased in comparison to that of the open edges ([Figure 4.12](#)) [108]. Xie *et al.* used graphene nanosheets prepared by arc-discharge method to modify n-octadecyl mercaptan self-assembled monolayer (SAM) on a gold electrode. The Au electrode was firstly deactivated by SAM deposition, however, upon placement of the graphene nanosheets on the SAM, the electron transfer was restored as confirmed using CV and scanning electrochemical microscopy (SECM) with $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ mediator [109]. Questions remain as to whether the restored electroactivity originates from incorporation of graphene into the SAM or a physical contact between the nanosheets and Au surface. Similarly, Zhang *et al.* [110] prepared n-dodecanethiol-modified SAM Au microelectrodes decorated with hydrazine-treated rGO and, using numerical simulations of the measured voltammetric curves, they obtained very fast k^0 for $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ ($\sim 10 \text{ cm s}^{-1}$) and $\text{Fe}(\text{CN})_6^{3-/4-}$ ($\sim 1 \text{ cm s}^{-1}$) ([Figure 4.13](#)). Banks *et al.* [111] attempted to investigate graphene sheets placed on both the basal and edge planes of HOPG and stated that increased amounts of graphene sheets decrease the HET kinetics of the electrode and therefore lowered the electrochemical performance for various redox mediators. The same group reported a comparative study of a graphene- and graphite-based paste electrode, prepared by mixing the graphene/graphite nanosheets with mineral oil, and reported no generally observable difference between the electroactivity on graphene- and graphite-based electrodes for the most studied redox mediators, although an increased HET rate was observed for $\text{Fe}(\text{CN})_6^{3-/4-}$ reduction/oxidation on graphene-based ones [112].

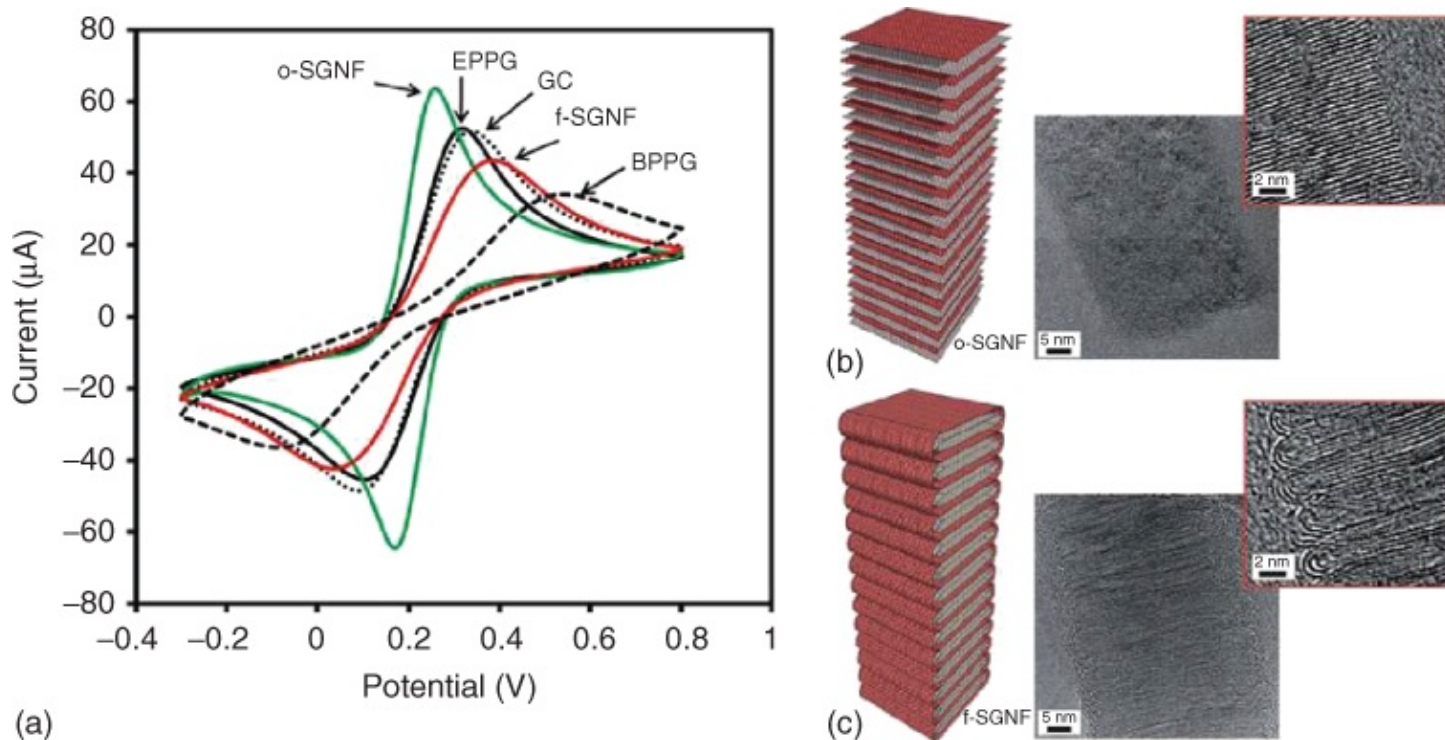


Figure 4.12 (a) Comparison of CVs obtained for open-edge graphene nanofibers (o-SGNFs) and folded-edge graphene nanofibers (f-SGNFs). Schematic and TEM micrographs of the (b) o-SGNF and (c) f-SGNF.

(Reprinted from Ref. [108].)

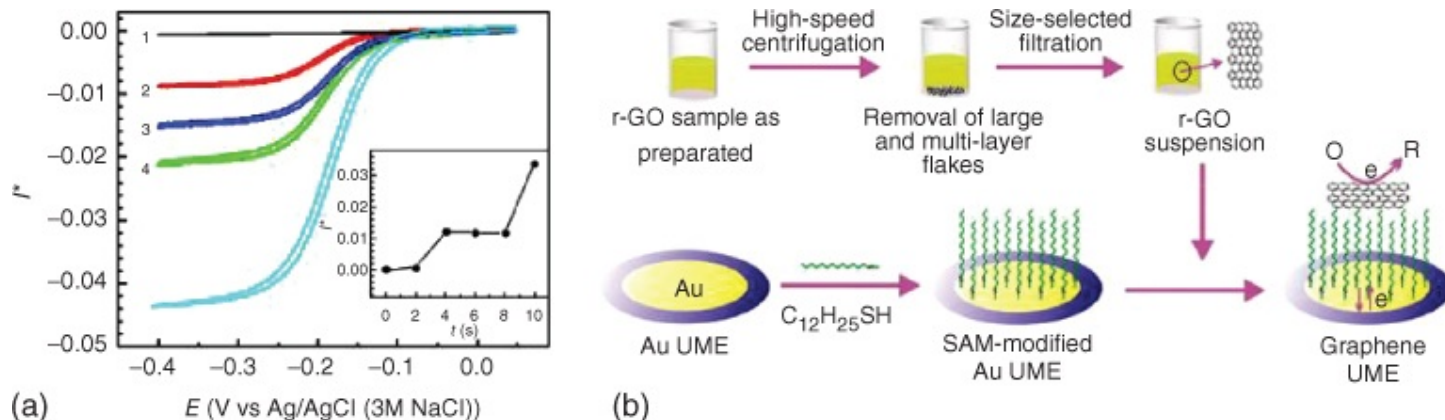


Figure 4.13 (a) Microelectrode-shaped voltammograms obtained on the graphene-decorated SAM Au electrode. (b) Schematic of the microelectrode fabrication.

(Reprinted from Ref. [110].)

The above overview is not a comprehensive list as the relatively simple preparation of rGO and LEG resulted in an overwhelming number of publications in the recent years. Even though some fundamental studies using these graphene-based materials were carried out [107, 108, 111, 112], one has to recognize that the uncontrolled nature of the graphene “nanoflake” or “nanosheet” electrodes makes any fundamental conclusions, such as dependence of the HET kinetics on the flake thickness or the basal plane, edge plane, defects content, quite unreliable. These samples suffer from inherently high resistivity, resulting from the discontinuous

character of the flake mixture, and also impurities from the preparation process, which can significantly affect the voltammetric performance. Moreover, the simple voltammetric analysis is not suitable to quantify the complex mass transport to rough or porous electrodes. On the other hand, both rGO and LEG seem to be suitable materials for use in the development of sensors, high-surface electrodes, or composite materials with desirable electrocatalytic properties.

More significant understanding of questions pertaining to graphene electroactivity has been gained using electrodes prepared via CVD. The main advantage of CVD-grown graphene, as noted earlier, is the large sample area ($> \text{cm}^2$) of continuous graphene film, which can be easily transferred onto different substrates. Li *et al.* [113] were the first to report the electrochemical measurements on individual samples of monolayer CVD graphene, and significantly, they also reported some data with ME graphene deposited onto a Si/SiO₂ substrate using ferrocenemethanol (FeMeOH) as a redox mediator. The researchers reported a microelectrode, sigmoidal response for ME graphene electrodes and a classic “macroelectrode” response for large-area CVD graphene, with fast HET kinetics of ME (a lower bound of $\sim 0.5 \text{ cm s}^{-1}$ was quoted) about 10 times faster than that of the CVD sample ($\sim 0.042 \text{ cm s}^{-1}$, resistance corrected), which was attributed to the lower electron mobility within the CVD graphene. Interestingly, the authors also observed CV peak separations smaller (40–54 mV) than the theoretical limit of 59 mV at room temperature, which was explained as the adsorption of the mediator on the graphene surface [113]. The research group followed the CVD graphene investigation using SECM and confirmed that the sites with large concentration of intentionally formed defects (both mechanically and via chemical oxidation) are more electroactive than the rest of the surface (FeMeOH and $\text{Fe}(\text{CN})_6^{3-/4-}$) [114]. Furthermore, the high reactivity of the defective graphene could be reversed by passivation using *o*-phenylenediamine electropolymerization as shown in [Figure 4.14](#) [114]. The same group reported HET kinetics on a monolayer CVD graphene for an extensive library of redox mediators in both aqueous and organic (acetonitrile and *N,N*-dimethylformamide) media, ranging from quasi-reversible to near-reversible kinetics, although the data were interpreted in terms of the Butler–Volmer formalism, the transfer coefficient, α , values fell outside the usual range expected ($0.3 < \alpha < 0.7$). Significantly, an enhancement in kinetics was observed upon intentional coverage of a fraction of the surface (1/100th) with osmium complex “impurities,” demonstrating that even the smallest amount of impurities can alter the apparent kinetics on a graphene surface [115]. Brownson *et al.* studied mono- and multilayer polycrystalline CVD graphene, which was left on the Ni-film growth substrate. Slower kinetics of $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ reduction/oxidation was found on the graphene-covered Ni-film ($k^0 = 2.5 \times 10^{-3} \text{ cm s}^{-1}$) when compared with the bare Ni substrate ($\sim 7.2 \times 10^{-2} \text{ cm s}^{-1}$) but a very poor, or possibly microelectrode-like, response with no voltammetric peaks was found for $\text{Fe}(\text{CN})_6^{3-/4-}$ [59]. The authors attempted to attribute the observed difference between the inner-sphere and outer-sphere mediator to the existence of the electroactive part of graphitic “islands” on the substrate; however, the complexity of the polycrystalline substrate gives little room for any convincing conclusions to be drawn. More detailed correlations between local graphene

structure and electroactivity have been extracted by Unwin *et al.*, who looked at the relationship between the number of graphene layers using (ferrocenylmethyl) trimethylammonium mediator ($\text{FcTMA}^{+/2+}$) and SECCM. They investigated Ni-grown CVD turbostratically stacked graphene multilayers transferred on a Si/SiO₂ substrate, which showed a clear trend of a two- to fourfold increase in kinetics from bilayer to seven layers ([Figure 4.15](#)). Also, little difference in the HET kinetics was found between monolayer and turbostratic bilayer, which was explained by lack of AB stacking in the bilayer, resulting in its “monolayer-like” behavior [116].

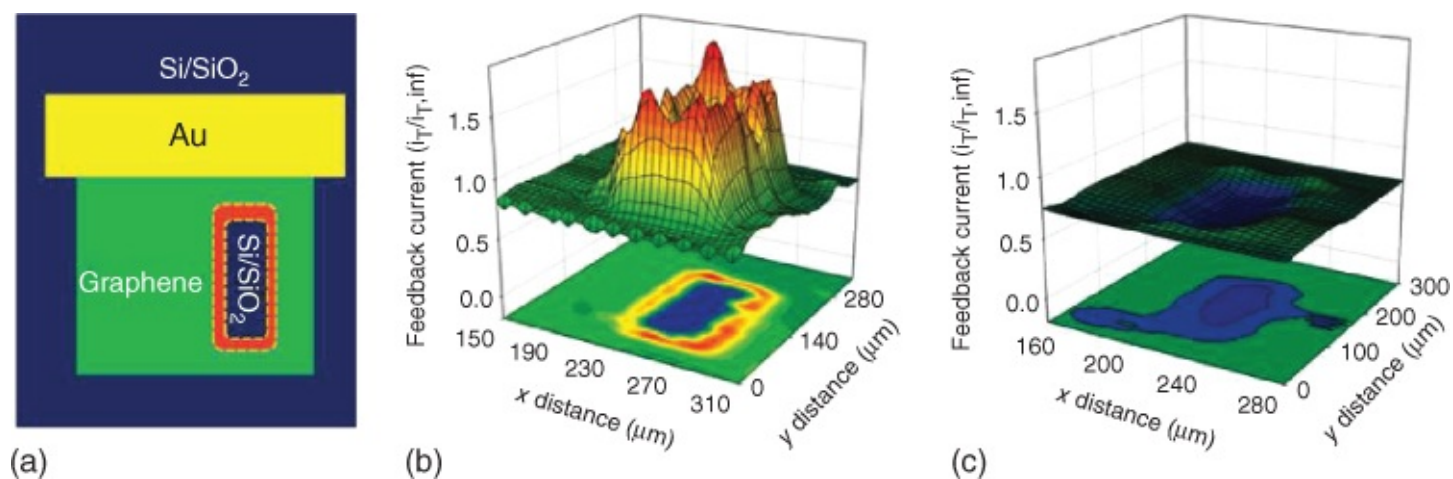


Figure 4.14 (a) Schematic of the monolayer CVD graphene (grey, labelled) with induced defects (light grey zone with dashed outline) deposited on a Si/SiO₂ substrate (black). Panels (b) and (c) show SECM maps of the graphene with induced defects and the same area passivated using *o*-phenylenediamine electropolymerization, respectively.

(Reprinted from Ref. [114].)

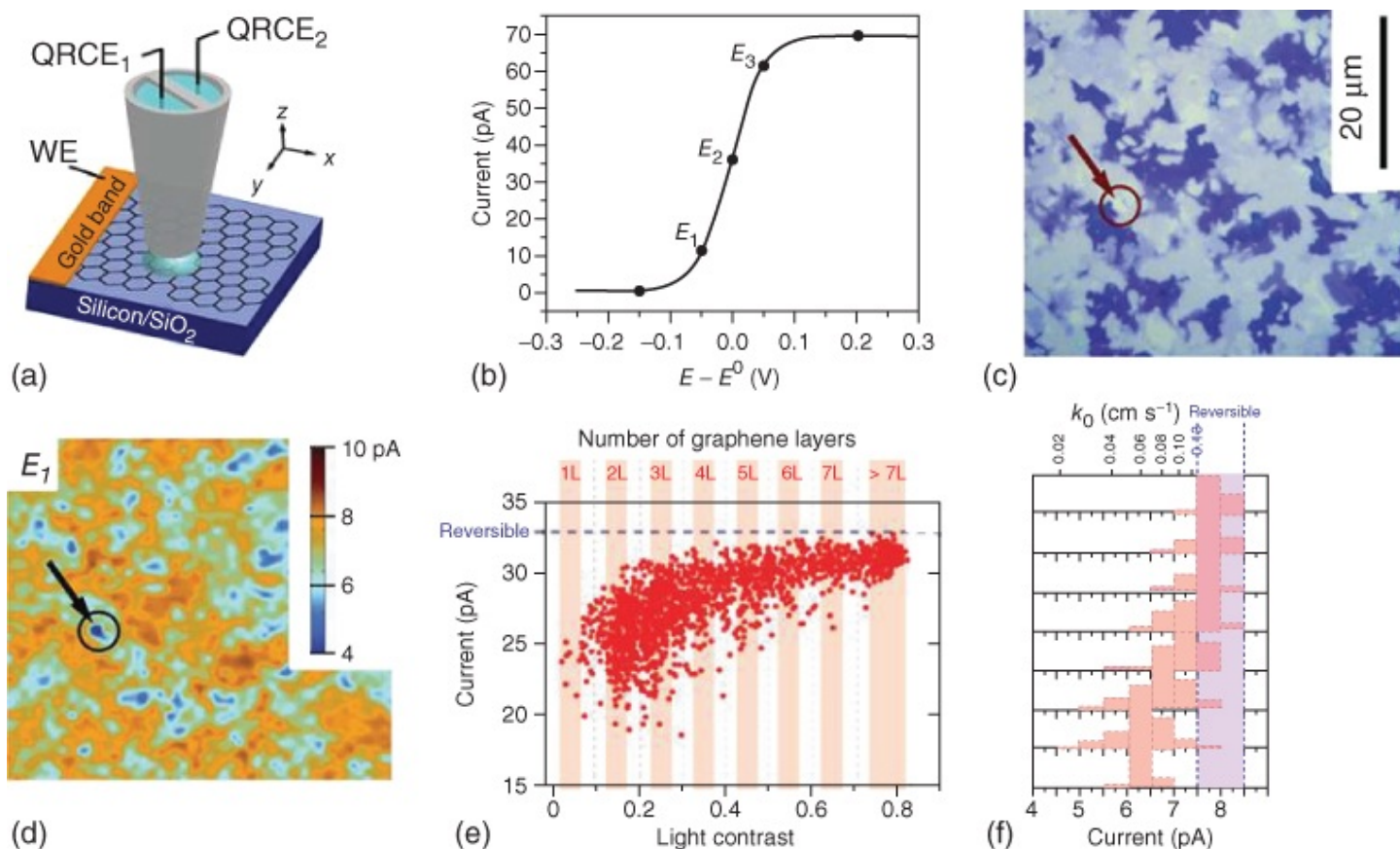


Figure 4.15 (a) Schematic of the SECCM setup, (b) voltammetry obtained on a graphene surface. Scanned area with varied flake thicknesses of different light contrast and electrochemical activity is shown as (c) optical micrograph and (d) corresponding SECCM map. Panels (e) and (f) show correlation between the feedback current or HET rate and the light contrast (number of graphene layers), respectively.

(Reprinted from Ref. [116].)

Dryfe *et al.* employed a microscale approach in determining the HET kinetics on Cu-grown CVD graphene transferred onto Si/SiO₂ substrate. Microsized droplets, yielding macroscopic voltammetric responses were deployed to probe the electroactivity of the basal plane surface of the graphene monolayer and turbostratic bilayer, for both Fe(CN)₆^{3-/4-} and IrCl₆^{2-/3-} redox mediators. The analysis provided contrasting results for the two mediators attributed to the inner-sphere and outer-sphere nature: Fe(CN)₆^{3-/4-} reduction/oxidation was approximately fivefold faster on monolayer than bilayer, whereas the IrCl₆^{2-/3-} redox kinetics was found approximately twofold slower on monolayer than bilayer [117]. Most recently, Yuan *et al.* used CVD-grown graphene to fabricate a sophisticated device in order to investigate the HET kinetics and capacitance measurement on a true basal and edge-plane monolayer (Figure 4.16). Nevertheless, despite the quality of the voltammetric data presented for Fe(CN)₆^{3-/4-}, the quantitative analysis of the HET rate is absent and the authors merely restricted themselves to stating that the kinetics on edges are faster than on the basal plane. The edges were also shown to have superior electrocatalytic properties toward AA and NADH oxidation as well as the oxygen reduction reaction (ORR), which is explained by the existence of the defective and

oxygen-containing sites at the graphene edge [118]. Questions remain about the extent to which the authors considered the very different diffusion profiles at the edge (extreme radial) and the basal plane (planar) when comparing the current densities. It is evident that CVD graphene is certainly better defined than the nanoflake-type graphene/graphite electrode, produced from LEG, for example, and therefore has been a popular choice for fundamental electrochemistry studies in recent years. However, the CVD technique still suffers from the inherent polycrystallinity of the graphene layers, in some cases, and especially on Ni substrates, the existence of domains of multilayered growth. These are the limiting factors that can only be overcome when a well-defined “single crystal” of graphene is used. This is possible using ME graphene.

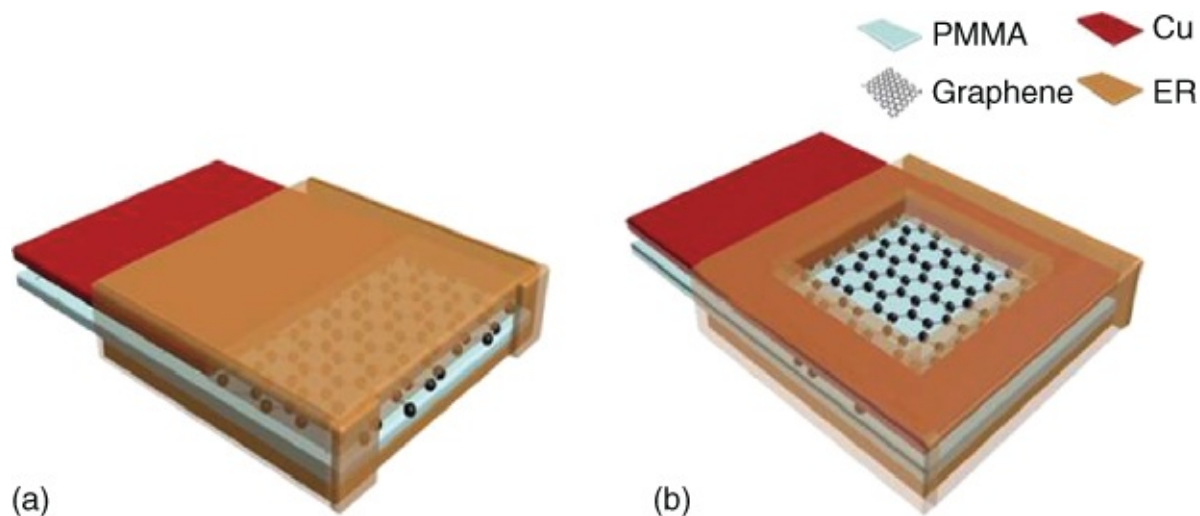
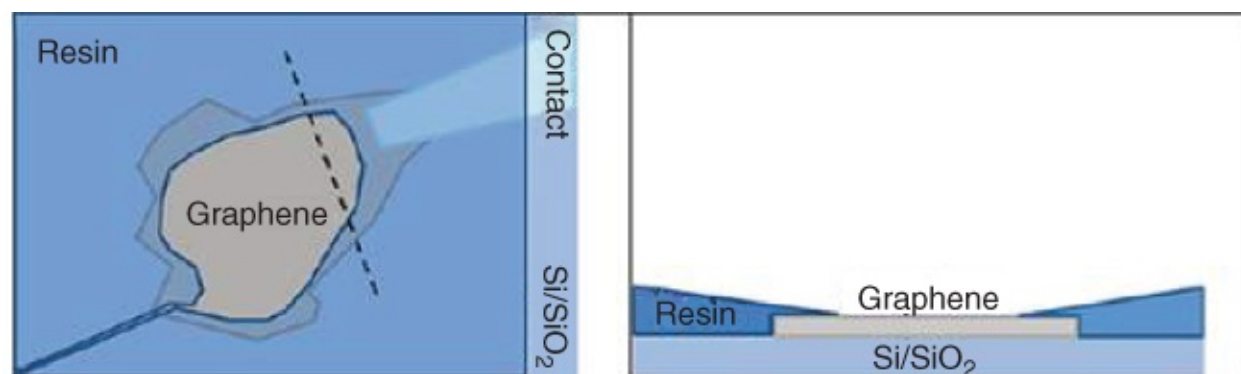


Figure 4.16 Schematic of the edge-plane (a) and basal plane (b) monolayer graphene device, fabricated using poly(methyl methacrylate) (PMMA) and epoxy resin (ER).

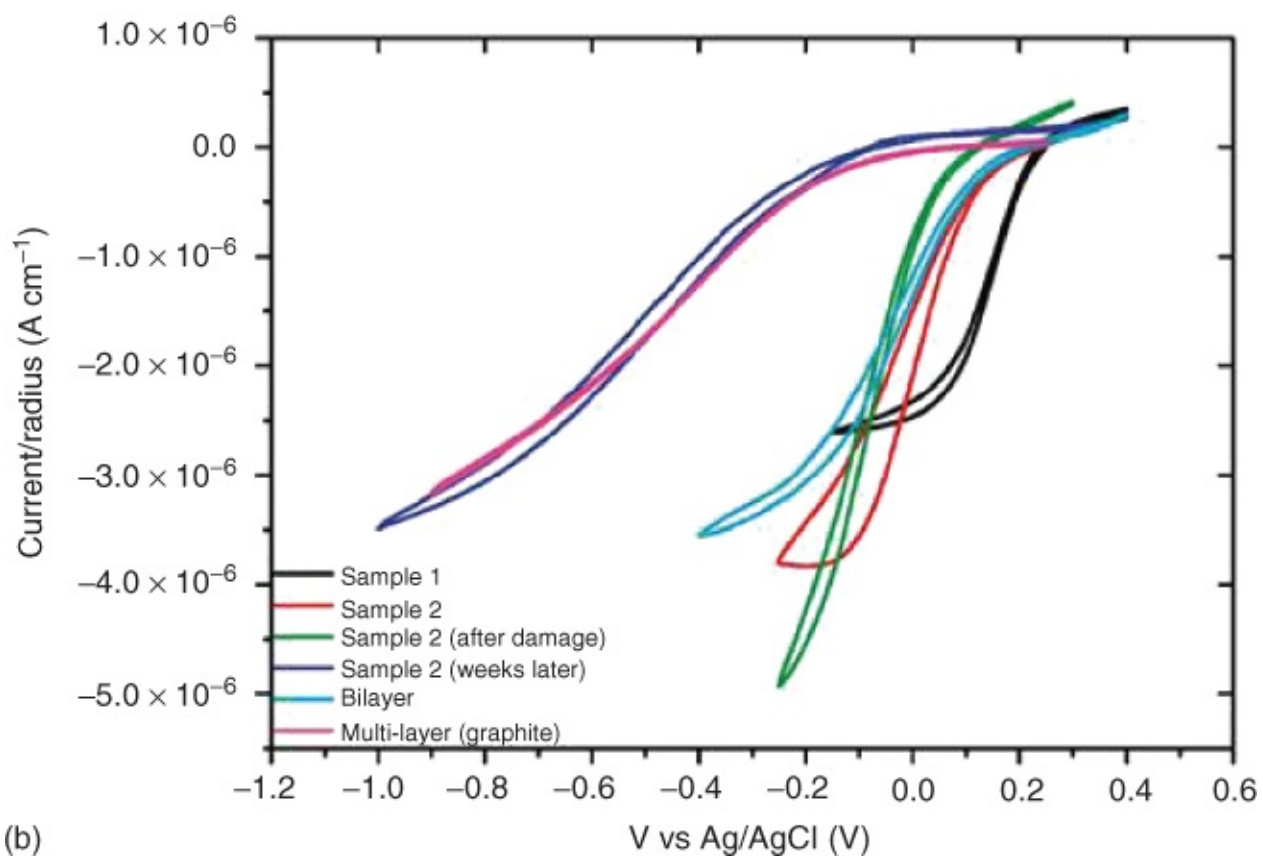
(Reprinted from Ref. [118].)

Surprisingly, given the high-quality reputation of ME graphene, which was gained simultaneously with the avalanche of physics and nanotechnology publications in the early years after its discovery, there are very few electrochemical studies using ME graphene. The article by Li *et al.* [113] was mentioned earlier; this group was among the first to study this pristine type of graphene. An early, nonelectrochemical determination of electron transfer rate using a reaction of graphene surfaces with 4-nitrobenzene diazonium tetrafluoroborate was reported by Strano *et al.*, who deposited the ME flakes onto a Si/SiO₂ substrate and assessed changes in reactivity through the extent of functionalization using Raman spectroscopy. The authors demonstrated that monolayer graphene exhibits kinetics about an order of magnitude faster than bilayer and multilayers, and also found increased reactivity (approximately twofold) on the graphene edges [119]. Dryfe *et al.* were among the first researchers to measure the HET kinetics electrochemically. The ME graphene monolayer and bilayer flakes were deposited on Si/SiO₂ substrate and Fe(CN)₆^{3-/4-} used as a redox mediator in voltammetric measurements. The contacting/masking of the graphene flakes resulted in a graphene microelectrode with the typical response shown in Figure 4.17. The HET kinetics was found to be about twice as fast on monolayer ($\sim 1.2 \times 10^{-3} \text{ cm s}^{-1}$) than on multilayered flakes and

interestingly, the presence of defects/edges made little difference to the observed kinetics [120]. The same group followed with a more detailed study of ME graphene mono- and multilayer flakes deposited on Si/SiO₂ and polymer-coated Si substrates employing microdroplets controlled using the micromanipulator aligned with an optical microscope [121, 122]. The schematic of the setup, previously used by the for CVD graphene measurements, is shown in [Figure 4.18](#). The results in this case showed a similar trend to that of the article by Unwin *et al.*, where the HET kinetics increases with the increasing number of graphene layers. The HET rate for the IrCl₆^{2-/3-} mediator varied from $3.1 \times 10^{-3} \text{ cm s}^{-1}$ on the graphene monolayer up to about $1 \times 10^{-2} \text{ cm s}^{-1}$ and $2 \times 10^{-2} \text{ cm s}^{-1}$, for multilayer and bulk graphite, respectively [121]. An extended study on a large number on graphene multilayers, however, did not reveal any convincing trends between the HET kinetics and number of graphene layers [122]. Furthermore, a very recent high-resolution SECCM study on HOPG-derived ME graphene has shown a complex dependence of the HET kinetics on the applied potential, local topography and surface history [123]. Interestingly, significant damage of the graphene monolayer was found upon deposition of liquid for the flakes prepared via conventional exfoliation directly on Si/SiO₂ substrate, which was the reason for using the polymer-coated substrate, as this resulted in greater flake stability on exposure to liquids [124].



(a)



(b)

Figure 4.17 (a) Schematic of the ME graphene monolayer electrode preparation. (b) Microelectrode voltammetric response obtained on mono-, bi-, and multilayer graphene flakes, normalized to the flake radius.

(Reprinted from Ref. [120].)

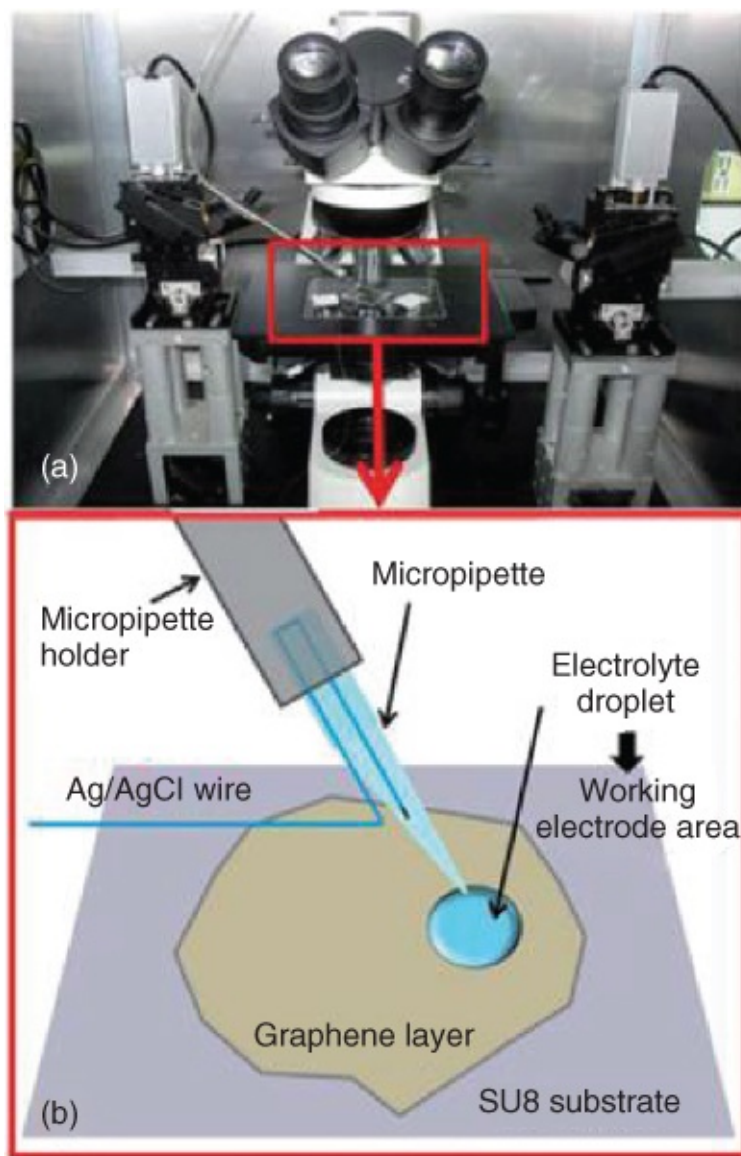


Figure 4.18 (a) Photograph and (b) the schematic of the micromanipulator setup used for deposition of liquid microdroplets on the surface of graphene electrodes.

(Reprinted from Ref. [121].)

To summarize, the studies of the HET on graphene have been of great scientific interest in the last few years, yet fundamental understanding of some of its aspects is lacking significantly as most of the work has focused directly on graphene applications. Namely, the roles of flake thickness, underlying substrate and edge/basal plane content, surface contamination, and so on, are not fully understood and deserve a detailed and careful investigation. There are only a few, detailed studies to date of the electrode kinetics of well-characterized graphene samples and, at the time of writing, rather contradictory conclusions have emerged from these studies. One issue is that the length scales of these studies differ, from the 10–100 μm scale (the typical scale of ME graphene and also the length scale of SECM used to probe CVD graphene samples [114]) to the few hundred nanometer scale of the SECCM [125]. Perhaps surprisingly, the best-suited material for this job, the high-quality ME graphene, has attracted less attention in fundamental electrochemical investigation than its more accessible yet problem-ridden

counterparts, namely CVD graphene, LEG, and rGO.

4.4.1 Modification and Doping of Graphene for Applications in Electrocatalysis

Significant effort has been focused on modification/doping of graphene to achieve desirable catalytic performance, namely in fuel cells, solar cells, and sensing [126–130]. A handful of articles covered some fundamental aspects of doping, for example, Das *et al.* reported changes in Raman spectra of ME graphene, subjected to *in situ* top-gated (i.e., electrochemical) doping via a solid electrolyte. The authors demonstrated that the resistivity of graphene is much more sensitive to changes in the top-gate than back-gate bias and also showed that positions of both G and 2D Raman peak change with the charge carrier concentration induced by doping [131]. Wang *et al.* [132] studied the effect of underlying substrate on the electron transfer of CVD graphene monolayer using covalent functionalization via diazonium salts and Raman spectroscopy as a measure of the electroactivity (mentioned in [Section 4.4](#)), and found that graphene exhibited high reactivity when supported on SiO₂ and Al₂O₃ in contrast to negligible reactivity when on alkyl-terminated surface and hexagonal boron nitride. Beyond the doping of the graphene induced by the substrate, the reactivity variations were interpreted in terms of local fluctuations in the Fermi level, which are more pronounced for a less-homogenous (rougher) substrate, such as SiO₂. A lot of interest has been devoted to manufacturing of metal/graphene composites or using graphene as a support for metal NP for various catalytic functions. Li *et al.* [133] formed Pt/graphene nanocomposites by “one-pot” reduction of GO and H₂PtCl₆ using NaBH₄ and claimed that the composite's catalytic behavior toward methanol oxidation was superior to that of a Pt/Vulcan catalyst. Dao *et al.* [134] used dry plasma reduction under atmospheric pressure to synthesize Pt NPs on CVD graphene, which served as a counterelectrode in a dye-sensitized solar cell (DSSC), and, despite limited experimental details, showed good performance for triiodide to iodide reduction. Graphene decorated with NPs was also used in the development of bio-relevant sensors (Pd NP on rGO for detection of dopamine and diclofenac) [135] and as effective catalyst for ORR (Pt NP on sulfur-doped rGO) [136]. Iron NPs incorporated in a nitrogen-doped rGO were also studied and showed promise for ORR electrocatalysis [137].

Modification of graphene in order to enhance catalytic performance for the abovementioned ORR with its application in fuel cells has been rapidly explored in the recent years, in particular, using nonmetallic heteroatom doping of the graphene lattice [138]. Qu *et al.* [139] prepared nitrogen-doped CVD-grown graphene (with methane and ammonia as carbon and nitrogen sources, respectively) and showed that its electrocatalytic performance toward ORR and stability is superior to that of the costly Pt/C catalyst. Xu *et al.* used a combination of sulfur and nitrogen doping in CVD graphene preparation. Despite the moderate oxygen content (up to 12%), the authors referred to their product as GO and found an optimum concentration ratio of S and N precursors (thiophene and pyrimidine), which gave an ORR response comparable to that of Pt/C [140]. As in the case of fundamental graphene electrochemistry studies, the source of graphene is very important. This was shown by Pumera *et al.*, [21] who

reported that manganese impurities left over in rGO from the oxidation process significantly enhance ORR kinetics, even at concentrations below 0.01 wt%.

Graphene is showing promise for use in solar cells as well, its high transparency, flexibility combined with conductivity being the most obvious advantages, which could rival the established indium tin oxide (ITO) counterelectrodes. Choi *et al.* manufactured a stacked multilayer CVD graphene device supported on a glass substrate with excellent transparency of over 80% throughout the visible spectrum and low sheet resistance. The multilayer collector electrode had a power conversion efficiency (PCE) of ~1.2% (about 30% of that of ITO) in conjunction with the active organic film and conductive polymer [141]. Miao *et al.* reported impressive 8.6% PCE for a solar cell based on a graphene monolayer/n-doped silicon Schottky junction, with the CVD graphene chemically doped with bis-(trifluoromethanesulfonyl)amide, drop-cast, and spin-coated from nitromethane solution. Nitrogen-doped graphene was also used as a metal-free catalyst for DSSC. Hou *et al.* [142] explored triiodide to iodide reduction using quite high levels of nitrogen doping in rGO (4–18 at%) and suggested that the nitrogen states affect the electrocatalytic activity more than the overall nitrogen content. Jeon *et al.* [143] showed similar catalytic properties for edge-nitrogenated graphene multilayer nanoplatelets produced by dry ball-milling of natural graphite. Interesting work has been done in the development of “3D graphene”, that is, high-surface-area 3D structures, comprising thin, few-layer graphene walls, which have significant potential in most of the catalytic applications. An example of such work is a preparation of a high-performance material developed by Wang *et al.*, [144] using a disproportionation reaction between CO and Li₂O ([Figure 4.19](#)). The sheet resistance of resultant honeycomb-like graphene “sponge” seemed to be tunable by the reaction time, and the material exhibited excellent PCE of ~8%.

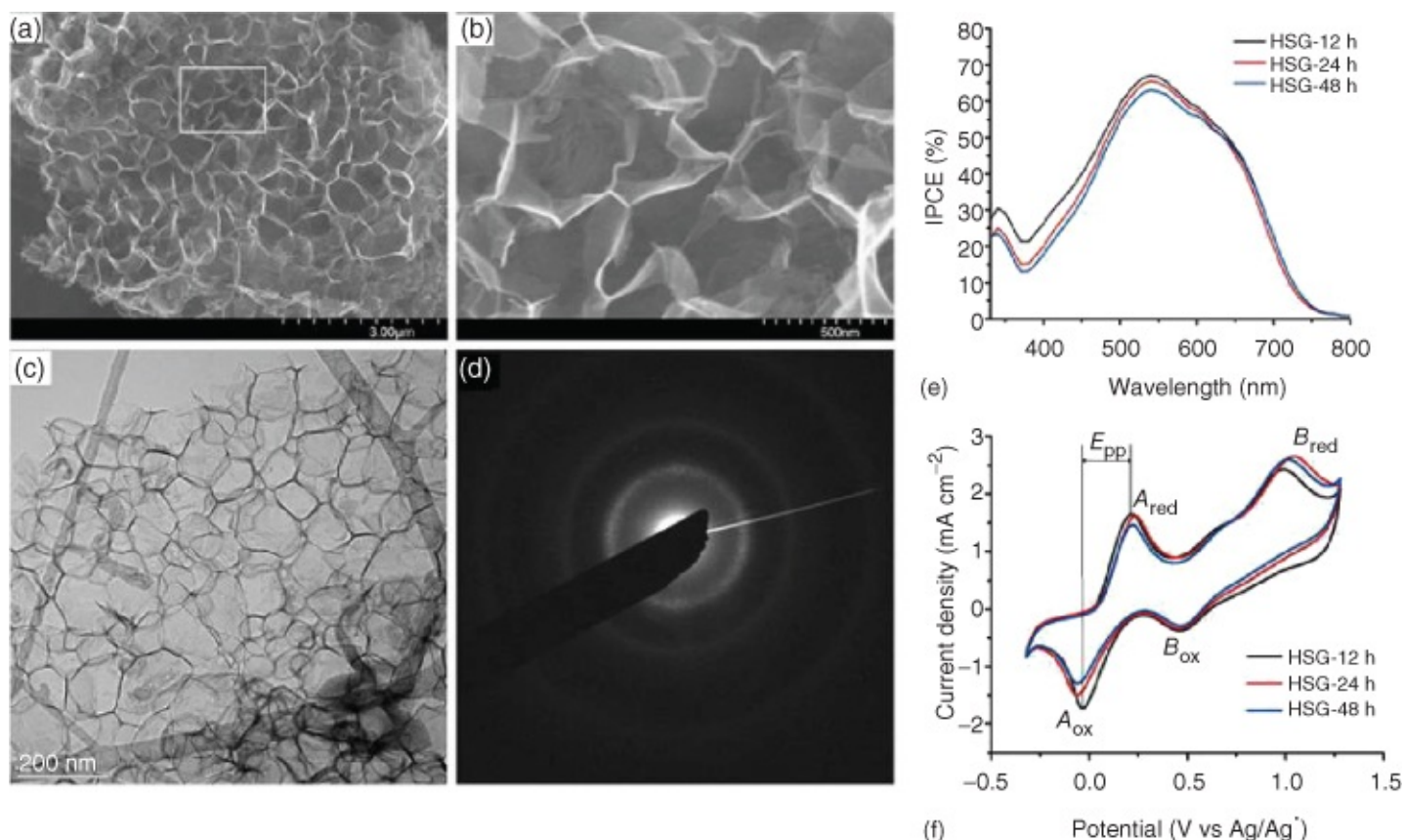


Figure 4.19 (a,b) Scanning electron micrographs, (c) transmission electron micrograph, and (d) electron diffraction pattern of the “3D graphene” catalyst. Panels (e) and (f) show the photovoltaic and voltammetric characterization of the material prepared using three different reaction times.

(Reprinted from Ref. [144].)

A significant amount of work also focused on development of graphene-based materials for sensing applications, mostly for detection of bio-relevant molecules, including glucose [14], cytochrome *c* [145], or dopamine [146, 147] although sensors of inorganic molecules such as hydrogen peroxide [148], cadmium [149], or protons/hydronium ions [150] were also successfully fabricated [6].

4.5 Conclusion and Future Directions

As a two-dimensional material, graphene presents unique opportunities for fundamental and applied studies in an electrochemical context. Its high surface area, transparency, and flexibility have been widely studied in the context of solar cells and supercapacitors. Graphene electrodes can be readily fabricated through LEG via rGO, so electroanalytical studies using some kind of graphene structure are readily accessible. The task for the future is to further exploit the unusual physical properties of graphene in fundamental electrochemistry by better understanding the relationship between graphene structure, double-layer capacitance, and HET kinetics. This requires the production and characterization of well-defined samples, using either CVD methods or, better still, ME graphene. Some efforts in these directions have

been reported recently [88, 151], but further experimental and theoretical developments are certainly needed to harness the full potential of this unique material in an electrochemical context.

Abbreviations

AA	ascorbic acid
AFM	atomic force microscopy
BMIM-PF ₆	1-butyl-3-methylimidazolium hexafluorophosphate
CV	cyclic voltammogram
CVD	chemical vapor deposition
DOS	density of states
DSSC	dye-sensitized solar cell
EIS	electrochemical impedance spectroscopy
Fe(CN) ₆ ^{3-/4-}	ferri/ferrocyanide
GC	glassy carbon
GO	graphene oxide
HET	heterogeneous electron transfer
HOPG	highly oriented pyrolytic graphite
IL	ionic liquid
ITO	indium tin oxide
KCl	potassium chloride
LEG	liquid-exfoliated graphene
ME	mechanically exfoliated
NADH	b-nicotinamide adenine dinucleotide
NaF	sodium fluoride
NHE	normal hydrogen electrode
NMP	<i>N</i> -methylpyrrolidone
NP	nanoparticle
ORR	oxygen reduction reaction
PBS	phosphate-buffered saline
PCE	power conversion efficiency
PMMA	poly(methyl methacrylate)
PZC	point of zero charge
rGO	reduced graphene oxides
SAM	self-assembled monolayer

SCE	saturated calomel electrode
SECCM	scanning electrochemical cell microscopy
SECM	scanning electrochemical microscopy
SWNTs	single-wall carbon nanotubes

Symbols

c	electronic charge density
C_D	diffuse layer capacitance
C_H	Helmholtz capacitance
C_{int}	interfacial capacitance
$C_{\text{int}(0)}$	minimum interfacial capacitance
C_Q	quantum capacitance
C_{SC}	space-charge capacitance
e	elementary charge
h	Planck's constant
k	Boltzmann constant
k^0	standard heterogeneous electron transfer constant
n	carrier concentration
n^*	charge carrier density due to impurities
n_G	gate potential
T	absolute temperature
v_F	Fermi velocity of carriers
V_s	potential at the surface
$\Delta\Omega$	measured frequency shift of the Raman spectrum G band
ϵ	dielectric constant
ϵ_0	permittivity of free space

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Chapter 5

The Use of Conducting Diamond in Electrochemistry

Julie V. Macpherson

5.1 Introduction

The properties synonymous with the use of diamond electrodes in electrochemical research are well documented and include extended solvent window, low capacitive currents, significantly reduced fouling compared to conventional electrode materials, and the ability to be used in extreme (high-temperature and corrosive) environments without damaging structural integrity. Original experiments back in 1983, where natural and colorless diamond implanted with zinc [1], showed wider potential windows and lower background currents than glassy carbon electrodes, first highlighted the potential for using diamonds in electrochemistry. However, since these early experiments, the field has moved considerably on, the quality of the diamond materials produced has dramatically improved, the range of electrode geometries available to diamond greatly increased, and the range of applications diversified. Diamond electrochemical research has been driven notably by the considerable efforts of research groups in the United States (Swain, Angus, Carlisle, and Hamers), Japan (Fujishima and Einaga), Germany (Nebel), Russia (Pleskov), and the United Kingdom (Compton, Marken, Foord, and Macpherson).

Boron incorporated during a chemical vapor deposition (CVD) process is now proving to be the most popular means of imparting electrical conductivity on the diamond lattice for use in electrochemistry, both from a research perspective and commercially, for reasons that will be discussed later. There have been many reviews since 1983, both in journals [2–9] and books [10] on the use of diamonds in electrochemistry. This chapter aims to review the field and provide a comprehensive discussion on the current understanding of the fundamental factors controlling the response of boron-doped diamond (BDD) electrodes. Latest developments (as of 2014) are also highlighted.

5.1.1 Boron-Doped Diamond: Electrical Properties

Diamond is an exceptional material, the complete sp^3 hybridization of carbon results in extensive tetrahedral bonding throughout the lattice, leading to the extreme properties summarized in [Table 5.1](#); most notable are hardness, very high thermal conductivity, and extremely high electrical resistivity. The latter makes diamond, at first glance, useless to an electrochemist as diamond is a wide-band gap semiconductor (5.47 eV at 300 K). However, just as with silicon, where dopant impurities can be added to modulate the electrical properties of the material the same is true of diamond. In the periodic table, either sides of carbon are boron (p-type dopant) and nitrogen (n-type dopant). Phosphorous also acts as an n-type dopant. Dopants in wide-band gap semiconductors tend to have high activation energies. Doping with nitrogen at ~ 1.7 eV does not result in any appreciable conductivity for

electrochemical applications. Phosphorous (~ 0.6 eV) being a much larger atom, when substituted into the lattice results in a five-coordinated, strained structure; achieving high doping levels with phosphorous is challenging and in practice is limited to high-temperature applications [13]. It is easier to substitute boron atoms in the diamond lattice as they will effectively take up the same position as displaced carbon atoms, with an activation energy of ~ 0.37 eV, hence p-type boron doping has proved a practical method of achieving room temperature conductivity in diamond.

Table 5.1 Physical properties of diamond [11, 12].

Property	Value
Broad transmission spectra	226 nm to 500 μm
Highest thermal conductivity	2200 $\text{W m}^{-1} \text{K}^{-1}$ (300 K)
Highest resistance to thermal shock	1000 MW m^{-1}
Low thermal expansion coefficient	0.9 ppm K^{-1}
Good electrical insulator	$10^{15}\text{--}10^{16}$ W cm
Low dielectric constant	5.68 ± 0.15 (35 GHz)
Low dielectric loss	$8\text{--}20 \times 10^{-6}$ (145 GHz)
Wide electronic band gap	5.47 eV
High electronic mobility	4500 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ (electron), 3800 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ (hole)

It is crucial to dope the diamond with enough boron to impart sufficient electrical conductivity on the matrix that the material can be considered “metal-like.” It is thus essential to consider how the boron dopant density, denoted in B atoms per cubic centimeter, affects the electrical resistivity of the material [14], as shown in [Figure 5.1a](#). Note that diamond contains $\sim 2 \times 10^{23}$ C atoms per cubic centimeter. Boron doping introduces a band acceptor level 0.37 eV above the valence band. In the boron dopant range $10^{16}\text{--}10^{19}$ B atoms per cubic centimeter (i.e., ~ 1 in 2×10^7 – 1 in 2×10^4 C atoms are replaced with B), the material shows resistivity changes in accordance with p-type semiconductor behavior. The implications for using semiconducting BDD (i.e., B-dopant density at the relatively high $\leq 10^{19}$ B atoms per cubic centimeter levels) as an electrode means that the user must be aware that as the electrode potential is made more negative of the flat band potential, the BDD becomes more depleted of charge carriers. This typically results in cyclic voltammeteries (CVs), which look “resistive” in nature, that is, for macroelectrodes, where linear diffusion dominates, the peak-to-peak separation, ΔE_p , increases beyond that expected for the reversible case, that is, $59/n$ mV (at a temperature of 298 K), where n is the number of electrons transferred per redox event. Interpretation of electron transfer (ET) kinetics for semiconducting electrodes (SCEs) is challenging [16, 17].

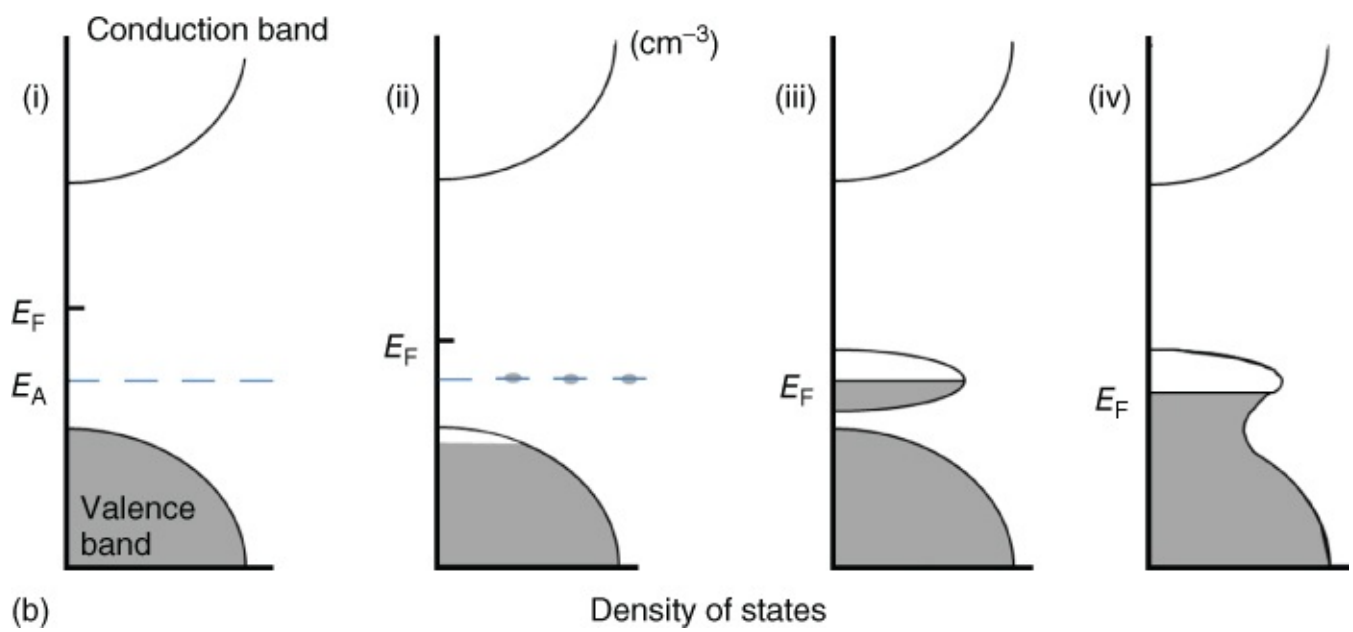
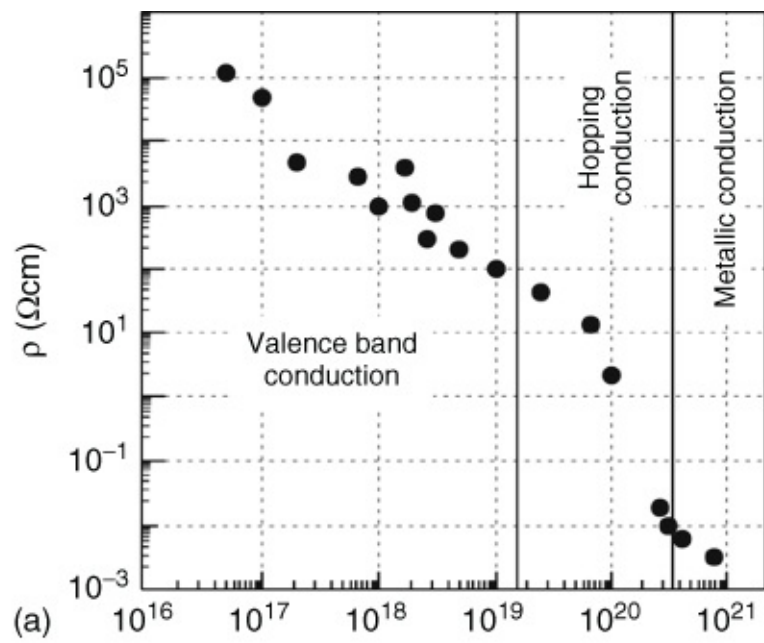


Figure 5.1 (a) Room temperature resistivity as a function of boron doping concentration. (Taken with permission from [14]). (b) p-type low-doped BDD at (i) absolute 0 K, no carriers are thermally excited from the valence band to acceptor states; the diamond is an insulator and the Fermi level, E_F , is mid-gap and (ii) nonzero temperature; the number of free carriers in the valence band will depend on the concentration and the ionization energy of the boron acceptors (E_A) and the temperature, yielding an activated electrical resistivity intermediate between that of an insulator and that of a metal; the Fermi level will move downward toward the top of the valence band. (iii) p-type heavily doped BDD ($\sim 10^{20}$ B atoms cm^{-3}), when the impurities are close enough, quantum overlapping of their wave functions results in delocalization leading to metallic behavior at zero temperature with a Fermi level pinned inside the impurity band; the metal–insulator transition takes place. (iv) Very high doping levels $> 10^{20}$ B atoms cm^{-3} ; screening of the impurities modifies the acceptor activation energy and the intrinsic band gap energy will reduce.

(Adapted from Ref. [15].)

As the boron doping level is pushed above 10^{19} , the resistivity drops sharply as hopping conduction dominates, until at boron dopant levels typical $\sim \geq 10^{20}$ (i.e., ~ 1 in 2000 carbon atoms replaced by boron), the material becomes “metal-like” in terms of electrical conduction. At these levels, the acceptor density is so high that there is significant wave function overlap of acceptor atoms and hole propagation in these states is possible without thermal activation to the valence band, as shown schematically in [Figure 5.1b](#) [15]. Hence, to be considered useful for electrochemistry, and akin to metal electrodes, BDD electrodes should contain B-dopant densities $\geq 10^{20}$; these electrodes are referred herein as *highly doped*. Note BDD electrodes, by virtue of metal-like status conferred through doping, will still present a much lower density of states (DOS) than metallic electrodes [18], the implications for this are discussed in [Section 5.4.1](#).

5.1.2 Growth of Synthetic Boron-Doped Diamond for Electrochemical Applications

There are several challenges associated with the synthesis of BDD suitable for electrochemistry. Since diamond is a semiconductor with exceptional properties, precise control of dopant impurities and extended defects is required to dope the diamond lattice with sufficient boron to make the material conduct. However, as the boron levels increase, it can be harder to maintain crystallinity and control the amount of nondiamond carbon (NDC) both within crystal defects and at grain boundaries. While NDC can increase material conductivity, it is detrimental to a diamond electrochemist, as the widely recognized electrochemical properties of BDD (wide solvent window, low background currents, reduced susceptibility to electrode fouling, corrosion resistance) are impaired and the electrochemical response becomes more akin to glassy carbon. If the presence of NDC is unaccounted for, electrical resistivity measurements will mislead the user into believing that there is more boron than actually present in the matrix.

5.1.2.1 High-Pressure High-Temperature (HPHT) Growth

The first industrialized process for the synthesis of diamond employed the HPHT method, which mimics nature in that thermodynamically stable conditions are used for growth [19]. In HPHT, typically a synthesis capsule containing graphite, seed crystals, and a metal solvent is compressed to tens of thousands of atmospheres (3–5 GPa) and heated to over 1800 K [20]. Even though this process has been used to synthesize single-crystal (sc) industrial-grade diamond for decades, the diamonds produced are often small, in the micron to millimeter range, typically doped with nitrogen ($\sim 10^{19}$) and are typically used for grinding and abrasive tools. The addition of boron to commercial HPHT processes achieves B-doping levels of $\sim 10^{20}$; however, the materials exhibit lower than expected conductivity due to compensation with co-doping nitrogen.

Exceptional process control is required to produce large (>1 carat) sc HPHT diamond relatively free from impurities [21]. Small heavily boron-doped HPHT diamond crystals $<10 \text{ mm}^3$ have been fabricated using ultrahigh pressures, 8–20 GPa, and temperatures of $>2500 \text{ K}$, and diamond superconductivity at 4 K has been reported. However, such synthesis conditions require highly specialized HPHT capabilities and to date these materials remain a research curiosity [22].

5.1.2.2 Chemical Vapor Deposition Growth

The most commonly used method for growing BDD both in the laboratory and commercially is CVD [11], due the efficiency of the process in controlling dopant incorporation and the ability to grow over large areas and on structured substrates [23]. CVD is the method used to produce the vast majority of diamond electrodes for the electrochemical work discussed later. Where alternative growth techniques such as HPHT have been employed, discussed in [Section 5.1.2.1](#), this will be highlighted.

CVD BDD growth typically operates at high temperatures of $>2000 \text{ K}$ (temperature of the plasma), and requires a carbon source, usually methane, typically present at $\sim <5\%$ in the mixture, and boron (often in the gaseous form B_2H_6 or $\text{B}(\text{OCH}_3)_3$). The boron concentration in the gas phase is often expressed in ppm. However, but to quantify the amount taken up in the material during growth, expressed in B atoms cm^{-3} , independent verification using e.g. secondary ion mass spectrometry (SIMS) is required.

To suppress the formation of the thermodynamically more stable sp^2 carbon and enable sp^3 growth on the substrate, excess hydrogen is added and the gaseous mixture activated thermally or through a plasma. Plasma use is most common and generated either using a hot filament (HF) or via microwaves (MWs). The principle benefit of MW diamond CVD is that it is possible to generate higher plasma temperatures than HF, where the temperatures are limited by the melting point of the filaments. The resultant higher temperatures result in higher concentrations of hydrogen (H) atoms [24]. The plasma-generated H atoms are crucial for terminating dangling bonds on the growing diamond surface, preventing both reconstruction of the surface and the formation of NDC. Diamond growth is thus kinetically not

thermodynamically driven. Atomic H also reacts with sp and sp² carbon sites on the surface, preferentially etching them away and removing them from the growth layer [25]. Most commercial BDD electrode manufacturers adopt the HF-CVD approach due to its ability to grow over larger areas; however, with MW-CVD it is possible to achieve higher phase purity and faster growth rates [26].

In the laboratory, researchers can obtain diamond electrodes from three different sources: (i) from their own home-built systems, typically HF-CVD; (ii) from commercial growth systems, for example, MW plasma CVD reactors from Seki Diamond Systems, Microwave Enterprises, Diamond Materials, and iPlas Cyrannus; and (iii) purchase the diamond electrodes from a commercial source, as listed in [Table 5.2](#).

Table 5.2 List of commercial companies selling BDD electrodes.

Diamond supplier	Material
Advanced Diamond Technology Inc., http://www.thindiamond.com/	Ultranan thin-film electrode water tre
CCL-Diamond, http://www.ccl-diamond.com/HTML/Products_Electrodes.html	Microcry thin-film electrode
	Coated o Nb, Si
Condias (DIACHEM®), http://condias.de/en/products/diachem/index.html	Microcry thin-film electrode
	Coated o Si, graph conductiv ceramics
	Thicknes µm
Element Six Ltd, http://www.e6.com/wps/wcm/connect/E6_Content_EN/Home/Applications/sensors/	DIAFILM (electroc processir
	Microcry free-stan µm thick
	Boron co ~ 3 × 10 ²⁰
	Resistivi

	cm
NeoCoat-Electrodes, http://www.neocoat.ch/en/products/electrodes/	Microcry thin-film electrode
	Coated o or Si
	Boron co (3×10^{19} – 3×10^{21})
	Thicknes
	Resistivi mΩ cm
	Recessec interdigit electrode available
Pro-Aqua, http://www.proaqua.cc/en/products/pro-aqua-diamond-electrode/	HPHT B. a flexible fluoropol substrate
	Electrode 260 mm × 270 mm × 0.5 mm water tre applicati

A variety of polycrystalline substrates have been employed during CVD growth, including silicon and self-passivating metals such as niobium, molybdenum, titanium, tantalum, and tungsten. The substrate is often treated before growth to increase the density of nucleation sites to promote the formation of continuous diamond layers, for example, abrasion, seeding with diamond nanoparticles (NPs), and electrical biasing of the growth substrate [27].

Polycrystalline films containing diamond crystals of different growth facets, or grains, result. The grain size of the resulting growth face can vary from ultra-nanocrystalline (UCN: <10 nm) [27], nanocrystalline (NC: <1 μm) [27], microcrystalline (MC: >μm) [28], to even millimeter size. Facet size can be controlled by changing seeding methods, growth conditions, gas composition, temperatures, and pressures, for example, for high ratios of atomic hydrogen to methyl radicals, larger facets result; however, as this ratio is reduced, the crystallite size decreases to the micrometer or even nanometer scale [26].

NDC incorporation is thought to occur predominantly at grain boundaries, and thus can be electrochemically significant in UNC and NC BDD [27], given that the grain boundary density is significantly higher compared to MC BDD. For example, UNC, typically produced by adding high concentrations of argon to the gas composition during growth, contains a high

volume fraction of sp^2 and grain boundaries. As boron concentrations are increased, it is harder to prevent NDC formation in MC BDD; however, it is still possible to control growth such that highly doped MC BDD containing negligible NDC can be produced [17].

[Table 5.2](#) lists the current commercial suppliers of BDD and the form the diamond is supplied in (information obtained from company Web sites).

For fixed growth conditions, the size of the crystalline facets on the growth face increases with film thickness, controlled by growth time, as shown schematically in [Figure 5.2](#). For example, higher quality NC BDD films (lower NDC content) can be obtained by growing using the conditions for MC BDD growth but stopping growth before the grains become too big [27]. The different shading on the crystallites in [Figure 5.2](#) refers to the fact that different crystallographic orientations take up boron differently; for example, the (111) orientation can incorporate approximately ten times as much boron as the (100) [29]. For UNC and NC BDD, the films are thin, while for MC BDD the substrate can be grown as thick as required.

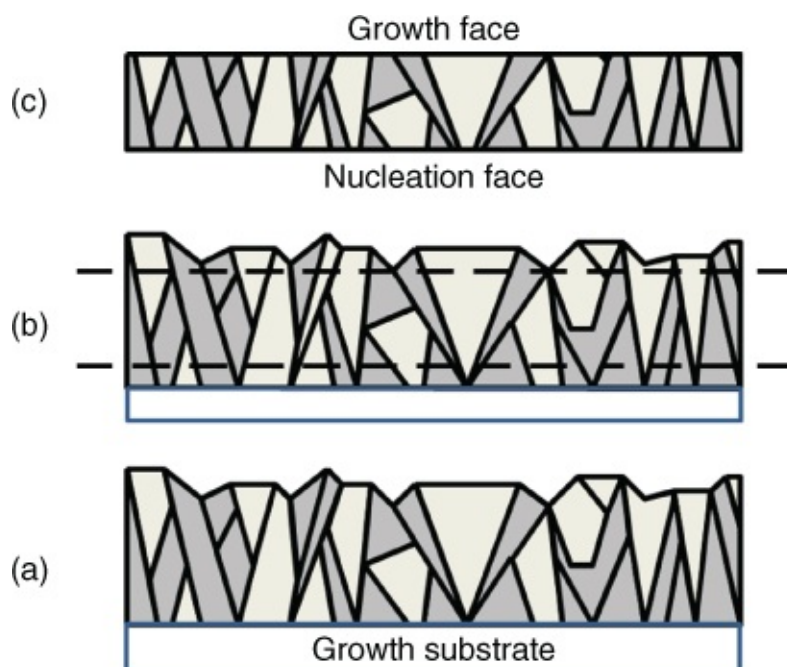


Figure 5.2 (a) Schematic showing grain structure of a thick polycrystalline diamond film. Differential boron uptake in different grains indicated by dark and light regions. (b) Processing of sample to remove growth and nucleation surfaces. (c) Resultant sample for investigation. Note the complex interconnection of grains with different dopant densities.

(Adapted from Ref. [28] with permission.)

When the BDD films are thin, it is not possible to remove the film from the growth substrate, however for thicker MC films the growth substrate can be removed and then polished, using diamond lapping techniques to reveal approximately nanometer flat, free-standing BDD. Note, for highly doped electrodes as the carrier concentration is high, surface polishing damage, where defects are created which trap charge carriers, has a negligible effect on the electrochemical characteristics of the electrode [17].

For the growth of sc BDD via the CVD process, sc diamond itself is used as the growth

substrate in order to encourage homoepitaxial growth under step-flow growth conditions. These substrates are typically grown using HPHT technology (see [Section 5.1.2.1](#)). In the literature, there is only one report of a different substrate used to grow sc diamond by CVD; sc iridium [30]. HPHT has also been used to grow sc BDD specifically for electrochemical studies [31]. Understanding the CVD growth mechanism and optimizing growth conditions [32] to minimize defect formation and impurity incorporation is essential for obtaining high-quality, highly doped sc BDD materials [33] suitable for electrochemistry.

Finally, when the BDD is removed from the CVD diamond reactor, it is hydrogen (H-) terminated, which also confers hydrophobic properties on the surface. Contact angles of $\sim 90^\circ$ have been measured using water [34]. The question of how long the hydrogen termination lasts, especially after oxidative electrochemical treatment [4, 17], is an important one to consider; therefore at the minimum, simple contact angle verification before and after experiment is a necessary and important measurement to make.

5.2 Electrode Geometries and Arrangements

Of importance to any electrochemist is how to work with an electrode material so it can be used for the widest range of experiments imaginable. Conventionally, in the laboratory, electrodes are packaged such that they can be handled efficiently, easily cleaned, and are of a known geometry, often macro or microdisk. For some applications, different electrode geometries and/or multiple electrodes in an addressable format are required. Typical electrodes, such as Pt, Au, and glassy carbon, are available from a range of commercial suppliers, in macrodisk form, sealed in solvent-resistant insulating plastics, such as Kel-F or polytetrafluoroethylene. Microdisk electrodes are also available and are often sealed in glass.

For BDD, electrodes in the recognized format, akin to Pt, Au, and glassy carbon, are not currently widely available. For any BDD thin-film electrode, where the BDD still resides on the (semi)conducting growth substrate, for example, Nb, W, silicon, electrochemical cells of the required geometry are typically fabricated by clamping an insulating cell, for example, polydimethylsiloxane (PDMS), Teflon, and glass onto the BDD film electrode, supported by an O-ring, as shown in [Figure 5.3a](#) [35, 39, 40]. In this way, a freshly H-terminated surface (from the CVD reactor) can be electrochemically interrogated, without damaging the surface during electrode construction. Alternatively, the entire front face of the BDD electrode is insulated in epoxy and polished flat [41]; this procedure obviously removes the H-termination of the growth surface. Electrical contact is made to the back of the (semi)conducting growth substrate.

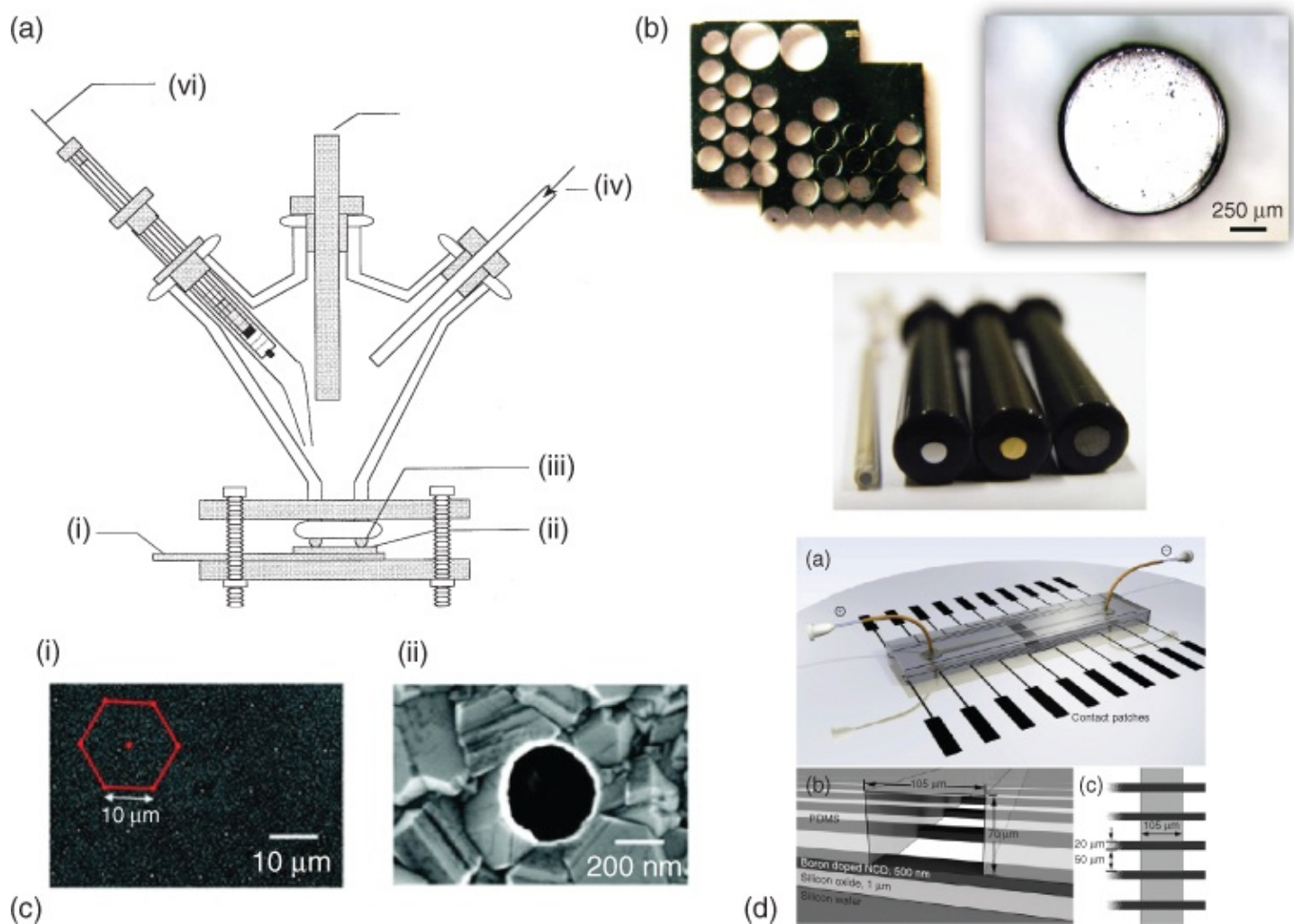


Figure 5.3 Different experimental arrangements used by researchers when working with BDD electrodes. (a) For thin-film BDD still attached to the growth substrate an glass electrochemical cell can be used. (Adapted from Ref. [35].) (i) Cu or Al metal current-collecting plate; (ii) the diamond film electrode; (iii) the Viton O-ring seal; (iv) the input for nitrogen purge gas; (v) carbon rod or Pt counterelectrode; and (vi) reference electrode. (b) Preparation of BDD free-standing electrodes. (Adapted from Ref. [36] with permission.) (i) Laser micro machining is used to cut the required BDD electrode geometry from a BDD free-standing wafer; (ii) here a cylinder is revealed. The electrode is ohmically contacted, sealed in glass, and polished flat to reveal the electrode structure in the left of (iii). Also shown are conventional polymer-sealed Pt, Au, and glassy carbon electrodes. (c) Scanning electron microscopy (SEM) images of a nanoelectrode array. (Adapted from Ref. [37].) (i) Overview of the design with distances of 10 μm between neighboring electrodes with hexagonal order (indicated in red) and (ii) recessed diamond electrode, the insulating diamond layer is clearly visible. (d) Schematic views of a top contacted BDD multiply addressable band electrode device, where the BDD band electrodes lie on insulating silicon oxide.

(Taken from Ref. [38] with permission.)

For free-standing BDD, the material is typically cut to shape using a laser cutter; note this process leaves NDC around the cut edges so the material must be acid-cleaned to try and

remove as much of the NDC as possible. BDD, like a semiconductor, does not form an ohmic contact simply by adding Ag paint, solder, or some such conductive adhesive, as with conventional metals. Ohmic contacts to BDD can be achieved by thin-film deposition of Ti to control interface impurities, followed by an Au barrier layer, to passivate and finally a high-temperature anneal [42] to form an ohmic titanium carbide contact. The laser-cut BDD is then insulated in glass or epoxy to produce the electrode, as shown in [Figure 5.3b](#). Macrodisk [36] and microdisk electrodes [43] have been made this way; the latter by sealing a “top-hat” structure in epoxy, where the larger base provides the structural support for handling during electrode construction.

Thin-film BDD attached to the growth substrate can also be processed using photolithography or laser micromachining to produce a range of different electrode geometries, often at the multiple level. When BDD is overgrown on top of an insulating material, a protruding electrode is formed. Coating the top surface of the BDD film with an insulating material results in a recessed electrode structure. For example, recessed ultramicroelectrode arrays (typical disk size 10 μm) insulated by a top coating of insulating diamond have been produced this way [44]. The counter- and reference electrodes were also present on the same device and fabricated from BDD. By using e-beam lithography, it is possible to produce recessed nanoelectrodes, less than 250 nm in diameter, as shown in [Figure 5.3c](#) [37]; the use of NC BDD was advocated to reduce the risk of electrode heterogeneities arising from differently doped grains dominating the response. Other materials have also been used to insulate the BDD electrode and alternative techniques to lithography employed to remove the insulating layer. For example, silicon oxide has been used in the lithographic processing of microband arrays [45, 46]; here, BDD was grown into recessed silicon oxide structures. In addition, laser micromachining has been employed to reveal recessed BDD electrode structures by removing the insulator-coated BDD in selected areas [47]. Protruding BDD microband arrays have also been fabricated by lithographically defining the BDD bands on top of insulating silicon dioxide [38]. In this case, top contacts to the BDD electrodes were required on the active face of the BDD device, as shown schematically in [Figure 5.3d](#). Solution was confined to the area of interest using PDMS channels.

Alternatively, it is possible to use free-standing BDD or insulating diamond as the starting material. For the former, microstructuring of the top surface of the BDD film using laser machining, subsequent overgrowth with insulating diamond followed by polishing has been employed to reveal coplanar microelectrode arrays [48–50], as shown in [Figure 5.4a](#). However, as the BDD base is still continuous over large areas, as here and in the examples given earlier, the resulting micro- and nanoelectrode arrays are not individually addressable. In order to configure multiple addressable electrode devices on the same substrate, it is preferable to commence fabrication with an insulating substrate. Here patterning of the insulating diamond with appropriate recessed structures (reflecting the electrodes of choice, e.g., disks, bands, and rings) subsequent overgrowth with BDD and polishing to reveal the diamond-insulated BDD structures, produced individually addressable coplanar electrode devices, such as those shown in [Figure 5.4b](#) [51]. Electrical contact can be made to the top ([Figure 5.4c](#), bottom) or bottom BDD face ([Figure 5.4c](#), top), depending upon the ultimate

application. Both macro and microelectrodes can be produced using this methodology. Finally, by using a layered growth approach, here starting with insulating diamond, overgrowing with first BDD and then, insulating diamond and finally machining a hole through the middle of the structure, an all-diamond microring electrode can be fabricated for flow studies [52].

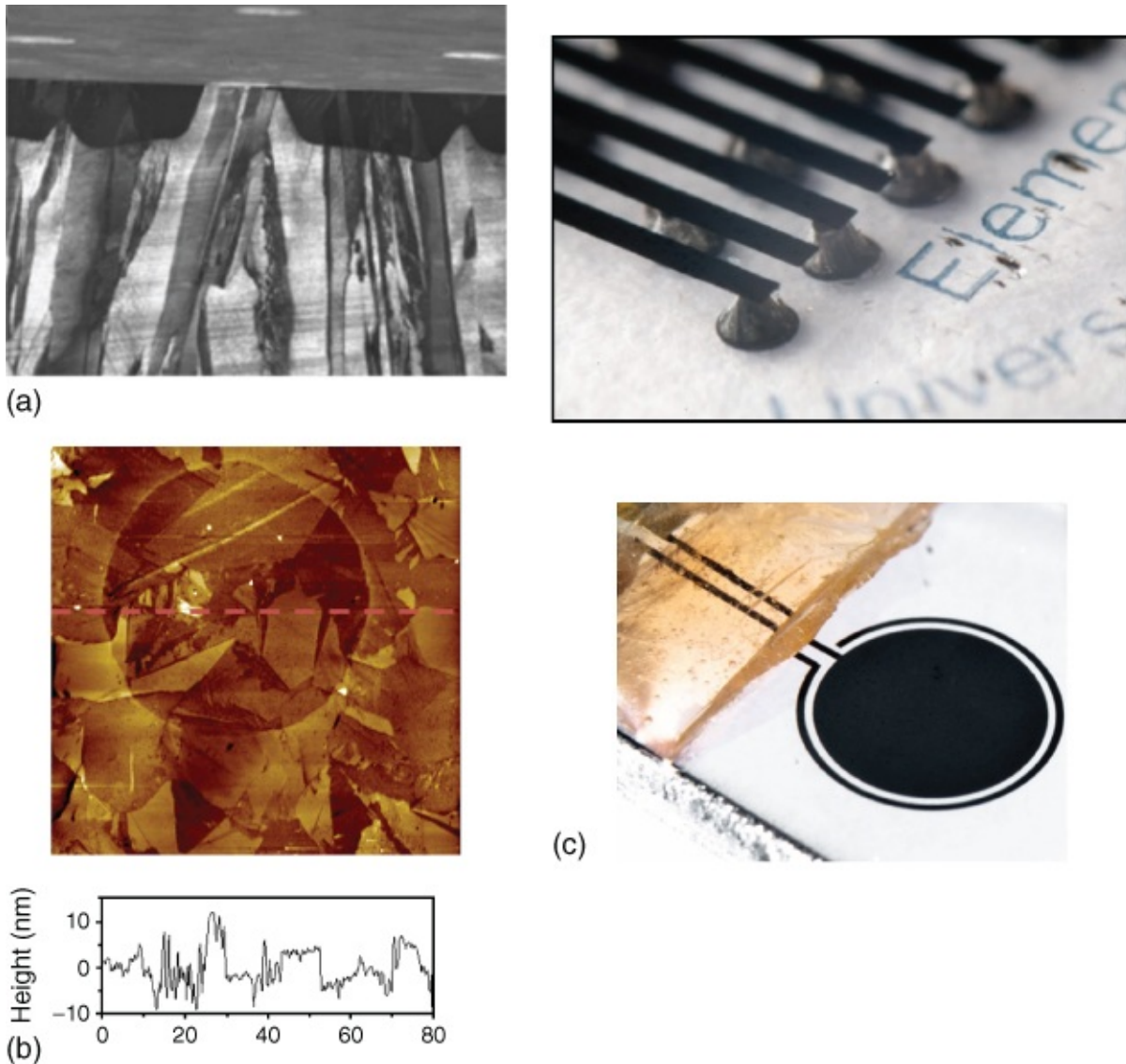


Figure 5.4 All-diamond coplanar micro- and macroelectrodes. (a) Multiple microelectrode array formed from machining pillar structures in free-standing BDD, overgrowing with insulating diamond, and then polishing flat to reveal a coplanar structure. SEM side on view of cross-sectioned microelectrode array. (Taken from Ref. [50] with permission.) (b) Atomic Force Microscopy (AFM) topography image of one of the electrodes in the array; the location of the BDD microdisk ultramicroelectrode is clearly visible. (Taken from Ref. [28] with permission.) (c) Top: multiple individually addressable microband array electrodes, of width $200\text{ }\mu\text{m}$, formed by growing BDD into trench structures in insulating diamond. The NDC back contact to each electrode is visible. Bottom: top contacted BDD ring-disk electrode formed using the same procedure. The diameter of the disk electrode is 3 mm .

(Adapted from Ref. [51] and Jon Newland copyright with permission.)

Using thick free-standing, all-diamond electrodes have the advantage that the electrodes are

more likely to survive certain operating environments. For example, using thin-film BDD electrodes in organic electrosynthesis can result in coating perforation and dissolution of the underlying growth substrate. In particular, Ti and Nb substrates have been found to degrade quickly for a thin-film BDD electrode operated under anodic conditions in organic solvent [53].

As CVD enables growth on structured surfaces, BDD microelectrodes can be produced by growing BDD on chemically sharpened metal (W or Pt) wires [54–56]. Both NC and MC films can be formed, with the MC films having a rougher surface but less NDC content, as expected [55]. The wires are typically seeded with diamond NPs before growth. The challenge with BDD-coated wires, as with any metal wire, is how to reliably insulate the wire such that only a defined (micro) portion of the tip is exposed and there are no pinholes in the insulating film. This problem is exacerbated when the roughness of the BDD film increases. A variety of insulating films have been employed, such as glass, epoxy, polyimide, nail polish, polypropylene tubing, and electrophoretic paint, however, to date the problem has still not been reliably solved. Such electrodes are currently finding use for *in vivo* [57] and *in vitro* neurotransmitter, antioxidant, and pH measurements associated with a range of different medical research areas, such as irritable bowel syndrome [58], cancer [59], stomach disorders [60], and genetic variability [61].

5.2.1 Characterization of BDD Electrochemical and Material Properties

Many of the electrochemical properties synonymous with the use of BDD result from the sp^3 nature of the electrode surface, the more NDC (sp^2) present the more the properties will change. From [Section 5.1.2](#), it is clear that growth of BDD does not always result in NDC-free diamond, especially when working with thin-film MC, NC, or UNC BDD. In this section, the key properties and characterization techniques are reviewed.

5.2.1.1 Assessment of Surface Morphology

Scanning electron microscopy (SEM) is an extremely useful tool for assessing the surface morphology of the different forms of BDD that can be synthesized, providing information predominantly on grain size and morphology. [Figure 5.5](#) shows SEM images of (a) as-grown MC BDD, (b) polished MC BDD, [18] (c) NC diamond [63], and (d) UNC diamond [63]. It is clear from [Figure 5.5](#) the dramatic effects changing growth conditions can have on crystallite morphology. The as-grown MC BDD material shows differently shaped crystal structures originating from the different crystal facets present: [100] cubic, [110] dodecahedral, and [111] octahedral (the preferred growth plane for diamond). Previous SEM studies have shown that secondary electron emission yields from BDD reach a maximum at boron concentrations of 10^{19} – 10^{20} cm^{-3} , hence difference in SEM contrast can indicate differently boron-doped regions [64]. This is most obviously seen in the polished MC BDD electrode shown in [Figure 5.5b](#) (left), where the dark regions represent the more highly doped areas of the surface. Quantitative information on surface roughness is often obtained using atomic force microscopy

(AFM) while X-ray diffraction provides knowledge on crystal orientation.

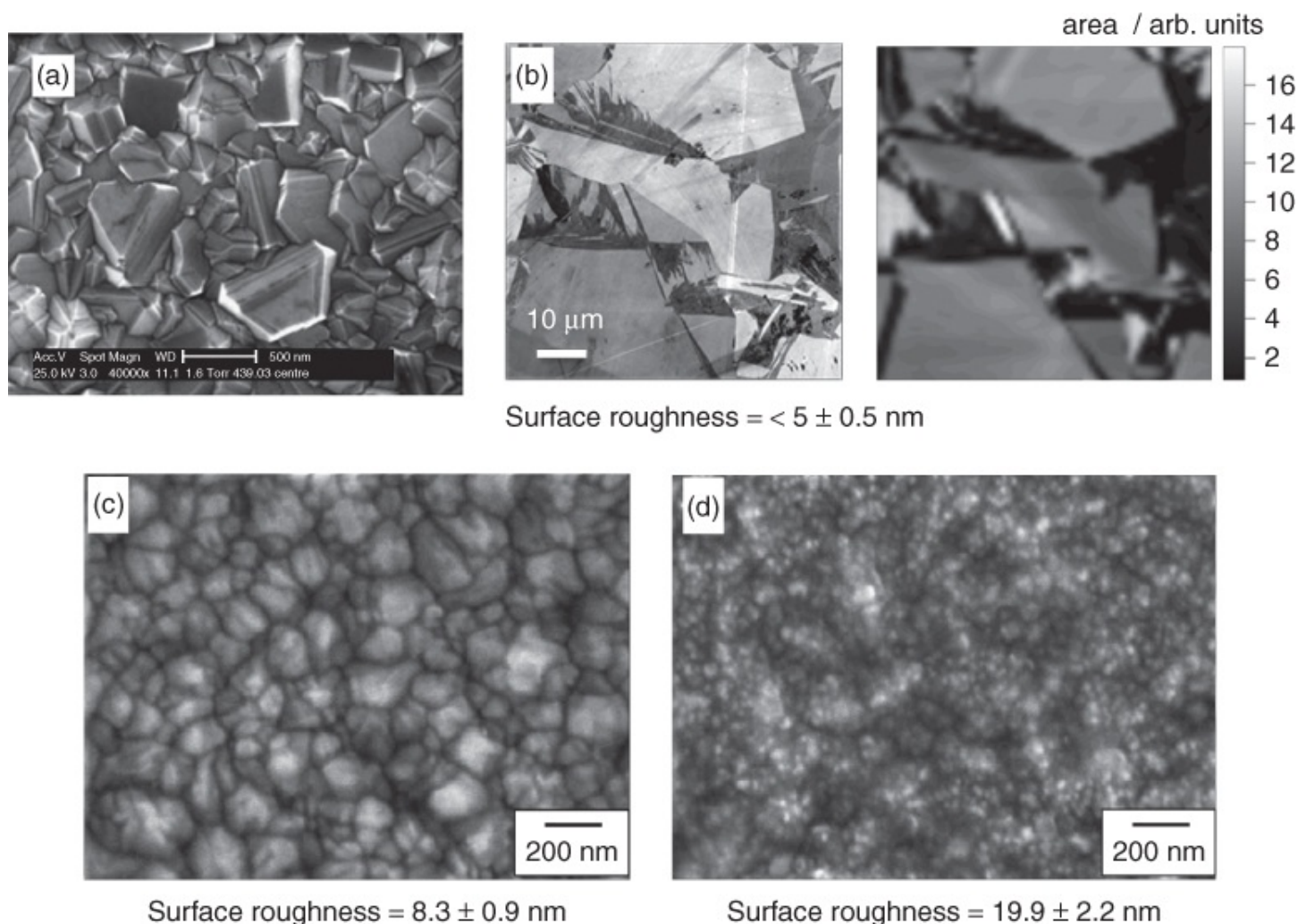


Figure 5.5 (a) SEM of an as-grown MC BDD electrode. (Taken from Ref. [62] with permission.); (b) Left: SEM of lapped surface of MC BDD; Right: corresponding Raman map of the same area. For both, zones of darker intensity correspond to more heavily boron-doped regions of the surface. (Taken from Ref. [18] with permission.) (c) SEM of thin-film BDD NC and (d) SEM of thin-film BDD UNC.

(Both (c, d) taken from Ref. [63] with permission.)

5.2.1.2 Extended Solvent Window and Low Capacitance

The sp^3 surface of BDD can be described as catalytically inert. To be efficient, water electrolysis requires the presence of catalytic sites on the electrode surface (inner-sphere ET) [65]. Water electrolysis is thus hindered at highly doped BDD electrodes, compared to electrode materials such as glassy carbon and platinum, due to a lack of available binding sites on the surface to mediate ET. On platinum and glassy carbon, both unfilled d orbitals and reactive quinone-like groups are present, respectively, enabling more efficient water–electrode interactions. Thus, wide solvent windows are reported in the literature for highly doped BDD for a variety of aqueous solutions (typically >3.5 V; depending on the definition of solvent window applied). A solvent window of 5 V has been reported for fluorinated diamond

electrodes in aqueous solutions [66].

As the concentration of NDC in the electrode surface increases, the solvent window decreases and the presence of a kinetically retarded oxygen reduction wave is often seen due to NDC impurities providing catalytic sites for oxygen reduction, as shown in [Figure 5.6](#), blue line. High-quality (negligible NDC) highly doped BDD should not show an oxygen reduction wave in aqueous acidic and neutral solutions, and is one way to quickly assess the quality of the BDD electrode. Furthermore, in the anodic potential window, close to the anodic solvent window, when NDC is present, currents due to the oxidation of sp^2 -bonded carbon impurities at the diamond surface are often seen [67, 68], which increase with NDC content. These are thought to be due to, for example, hydroquinone/benzoquinone-like surface reactions associated with sp^2 carbon [68, 69]. As summarized by Swain [35], “The magnitude of the background current, the working potential window, and the voltammetric features present within the working potential window are all sensitive to the presence of nondiamond (amorphous or graphitic) carbon impurities.”

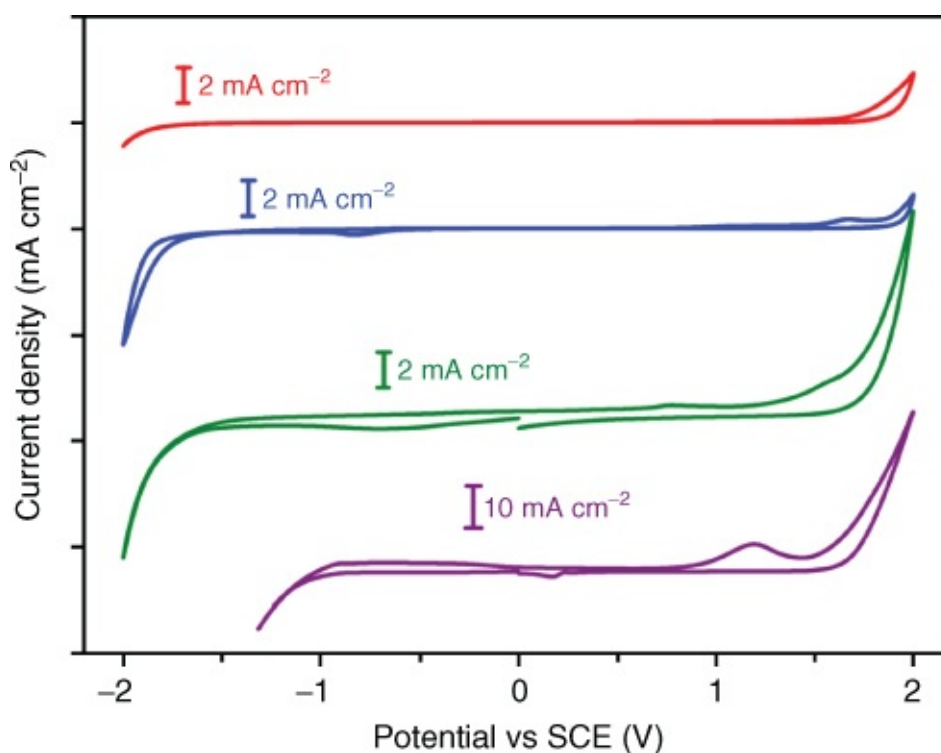


Figure 5.6 CVs recorded in 0.1 M KNO_3 at a scan rate of 0.1 V s^{-1} for highly doped NDC-free free-standing, microcrystalline BDD (top), NDC-containing free-standing, microcrystalline BDD (second down), glassy carbon (third down), and platinum (bottom). The CVs have been plotted on different scales and vertically offset for clarity.

(Taken from Ref. [17] with permission.)

For as-grown surfaces that contain significant NDC, it has been reported that acid washing followed by rehydrogenation of the surface or anodic polarization by cycling in acid solutions can result in a reduction of sp^2 content [35, 70]. It has also been noted that a similar effect can be achieved by employing a slow cool-down procedure in atomic hydrogen, post growth [71].

NDC removal is typically ascertained by examination of the CV response before and after treatment, as shown in [Figure 5.7](#), employed in conjunction with Raman microscopy ([Section 5.2.1.3](#)).

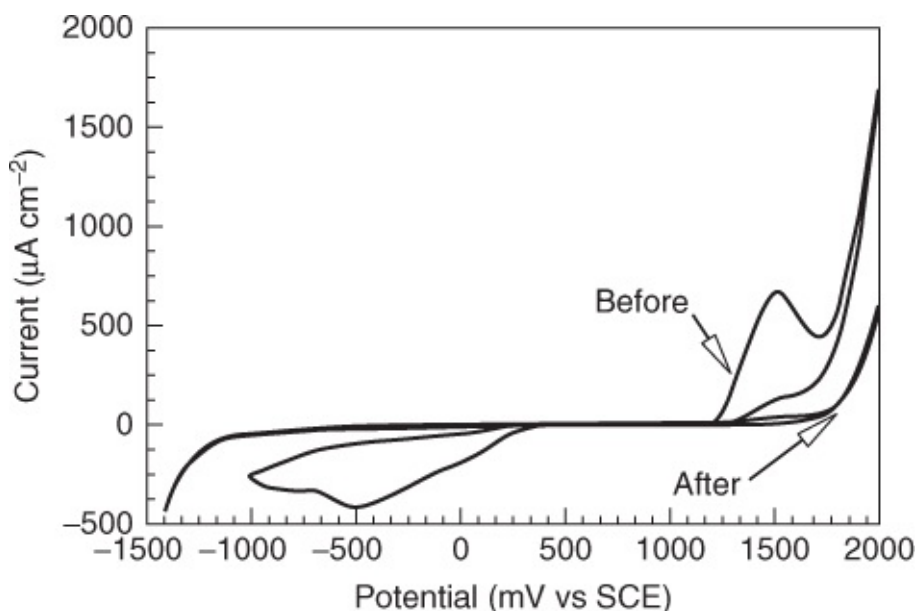


Figure 5.7 Cyclic voltammetric curves for a lower quality, NDC-containing thin film diamond film electrode in 0.1 M H₂SO₄ before and after acid washing and rehydrogenation. Scan rate, 0.1 V s⁻¹.

(Taken from Ref. [35] with permission.)

Also of note in [Figure 5.6](#) (red line) is the observation of very low current signals in the solvent window for high-quality (negligible NDC content), highly doped diamond. This is attributed to the low capacitance of the material (10 μF cm⁻²) compared to conventional electrode materials such as Pt and Au (~30 μF cm⁻²). This originates from (i) the lower DOS for BDD [18] compared to classical electrode materials and a significant reduction in surface-driven ET processes, especially in the case of negligible NDC content. Increasing boron content increases the measured capacitance, most likely due to an increase in local DOS [17], and (ii) the chemical stability of the sp³ diamond surface.

5.2.1.3 Raman Interrogation of sp²/sp³ Ratio in BDD

Raman microscopy is an ideal tool for probing carbon materials. The Raman effect is a form of inelastic scattering of monochromated light. Laser wavelengths from visible to near-ultraviolet region can be used to probe a variety of compounds. Excitation photons interact with rotational and vibrational modes associated with atoms or molecules, exciting them from a ground state to a virtual energy state. Molecular relaxation results in photon emission. The shift in frequency of the emitted and excitation photons is related to the energy difference in the molecular states. This shift can be to a lower frequency (Stokes shift) or a higher frequency (Anti-Stokes shift). Micro-Raman is also non-destructive technique, which can give qualitative and quantitative analysis on very small samples.

Pure diamond contains only sp^3 carbon (σ bonds), which in the Raman spectra results in a single diamond zone center optical phonon peak, occurring at 1332 cm^{-1} . The line width is a qualitative measure of the crystalline quality of the film. The more defects in the probed area, the shorter the phonon lifetime and the broader the width. NDC (sp^2 -containing diamond – π bonds) in the diamond matrix interacts with the Raman laser differently. Two peaks can result, the G and D peaks, the G peak is as a result of stretching of pairs of sp^2 sites (rings and chains) while the D peak is the breathing mode of sp^2 rings. In crystalline graphite, the G peak occurs at 1575 cm^{-1} , while the disordered D peak occurs at 1355 cm^{-1} . For amorphous carbon, the peak widths of the D and G peaks are generally broader, depending on the ordering of the NDC material.

sp^2 π bonds are more polarizable than sp^3 σ bonds, and thus have a larger Raman cross section ($\sim \times 50$ for 514.5 nm excitation). Furthermore, with visible light, resonant enhancement of the sp^2 signal is possible; this is not possible with sp^3 diamond. In Raman spectra, selection of the correct laser wavelength is important to accentuate the features of interest. The relative intensity of the diamond-central phonon peak to the NDC G peak is often used as a qualitative assessment of the quality of the diamond material. However, as resolution (depending on optical magnification) tends to be of the order of microns, it is important to make many measurements across the sample, especially when dealing with MC diamond where grain size is bigger than laser spot size.

In the presence of boron, as the boron concentration increases the diamond phonon peak shifts slightly to lower wavenumbers [72], as shown in [Figure 5.8a](#) for a diamond sc sample doped with successively increasing concentrations of boron in the range 60–2000 ppm. The diamond peak also moves from being symmetrical to deforming asymmetrically, typically observed for boron concentrations $\sim \geq 10^{20}\text{ B atoms cm}^{-3}$, also seen in [Figure 5.8a](#).

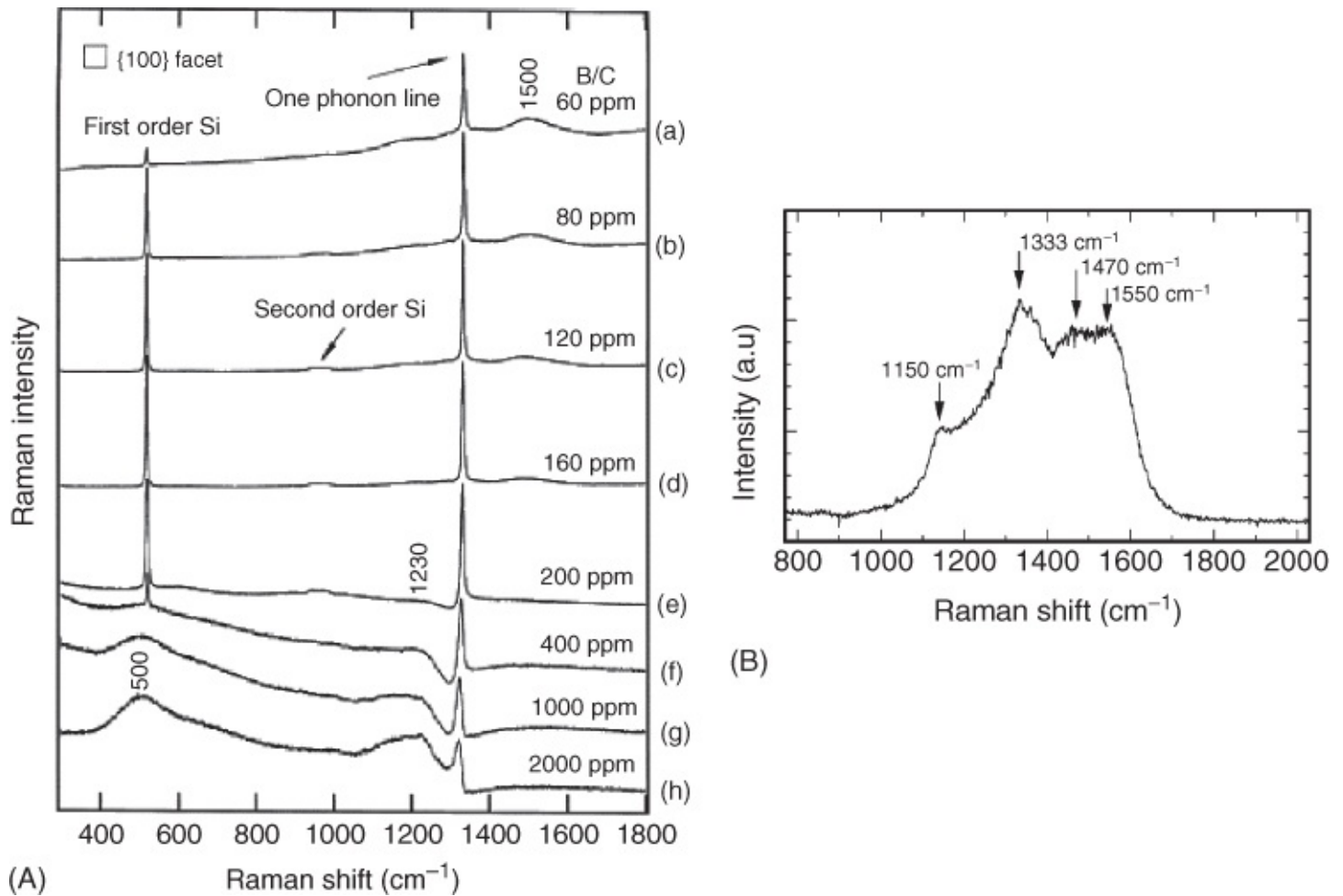


Figure 5.8 (a) Raman spectra of the [100] facet of B-doped individual diamond crystals recorded with a single-mode 514.5 nm line of an Ar-ion laser at low power (about 5 mW). “B/C” refers to B/C in the gas phase. (Taken from Ref. [73] with permission.) At low B, a NDC G peak is evident at $\sim 1500 \text{ cm}^{-1}$; as the B concentration increases, the diamond phonon peak becomes more asymmetric and reduces in size. (b) Visible Raman spectrum for a boron-doped NC diamond thin film at laser wavelength = 532 nm and power = 50 mW. Integration time = 5 s.

(Taken from Ref. [74] with permission.)

This feature is attributed to a Fano-type interference between the discrete zone center optical phonon and a continuum of electronic excitations [73], and signifies the onset of metallic conductivity on the boron impurity band [75]. Hence, observation of a Fano resonance is further proof that the diamond has been doped with sufficient boron to be suitable as an electrode material. Broad features at about 500 and 1220 cm^{-1} have also been observed for highly doped BDD in the range 10^{20} – $10^{22} \text{ atoms cm}^{-3}$ [73] (Figure 5.8a). Analysis of the peak position and shape at 500 cm^{-1} has been postulated as a means of nondestructively analyzing the boron content of highly doped materials [76]. Features in the range 1350–1580 cm^{-1} are often associated with NDC.

UNC and NC BDD has proven popular due to factors such as inherent low surface roughness compared to as-grown MC BDD, film homogeneity, and high Young's modulus. However, by

virtue of the growth process and increased density of grain boundaries, NDC is often higher in NC BDD and especially in UNC BDD. Furthermore, as the crystallite size decreases and the material becomes more disordered, the Raman spectra become more complicated to interpret, due to selection rules breaking down. This results in the shifting, broadening, and asymmetry of existing peaks and even the occurrence of new ones [74], compared to the MC BDD spectra. For example, the spectra shown in [Figure 5.8b](#) for highly doped NC BDD (1.4×10^{20} B atoms cm^{-3}) at $\lambda = 532 \text{ nm}$ display a broad diamond phonon peak and broad peaks at 1150, 1470, and 1550 cm^{-1} . The broadening of the diamond-central phonon peak is attributed to the reduced crystallite size and overlap with the D band associated with NDC, present in grain boundaries [27]. The 1470 and 1550 cm^{-1} peaks are also attributed to NDC.

The 1150 cm^{-1} peak has been the subject of some controversy in the literature. Initial thoughts believed it to be a characteristic sign of an NC phase in diamond, resulting from a diamond phonon mode [77]. However, it has now been proven that this is not the case and most likely originates from sp^2 -hybridized structures present on the surface and at grain boundaries, such as polyacetylene-type molecules [78–80].

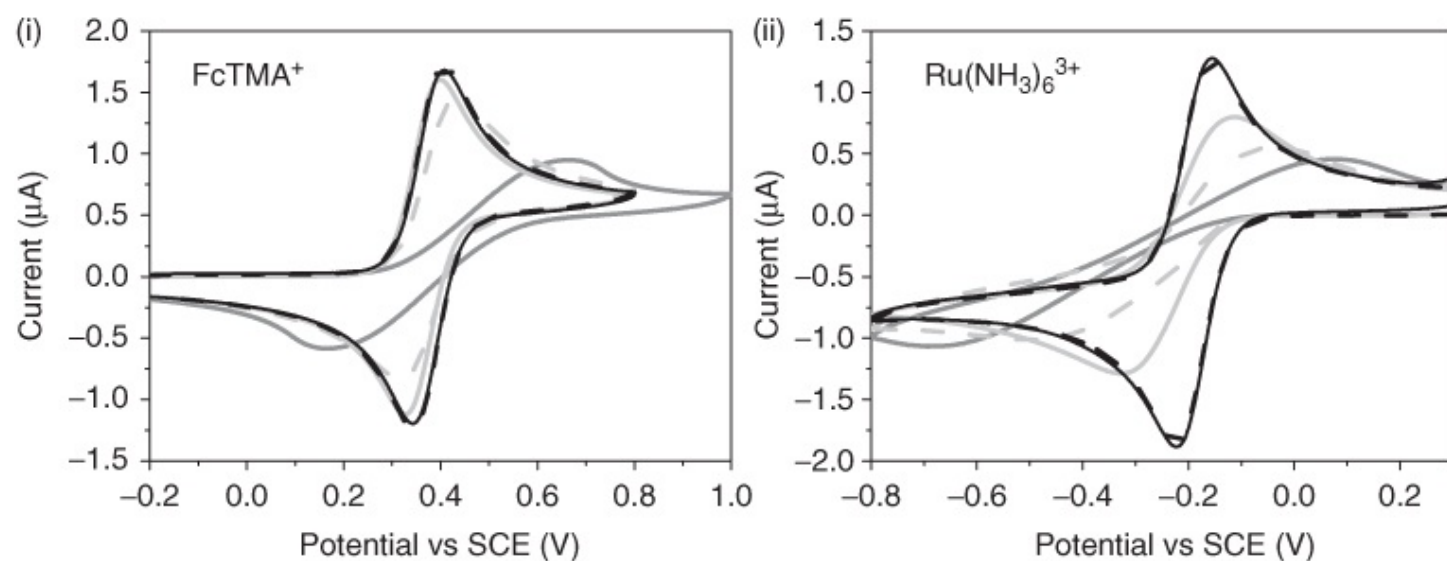
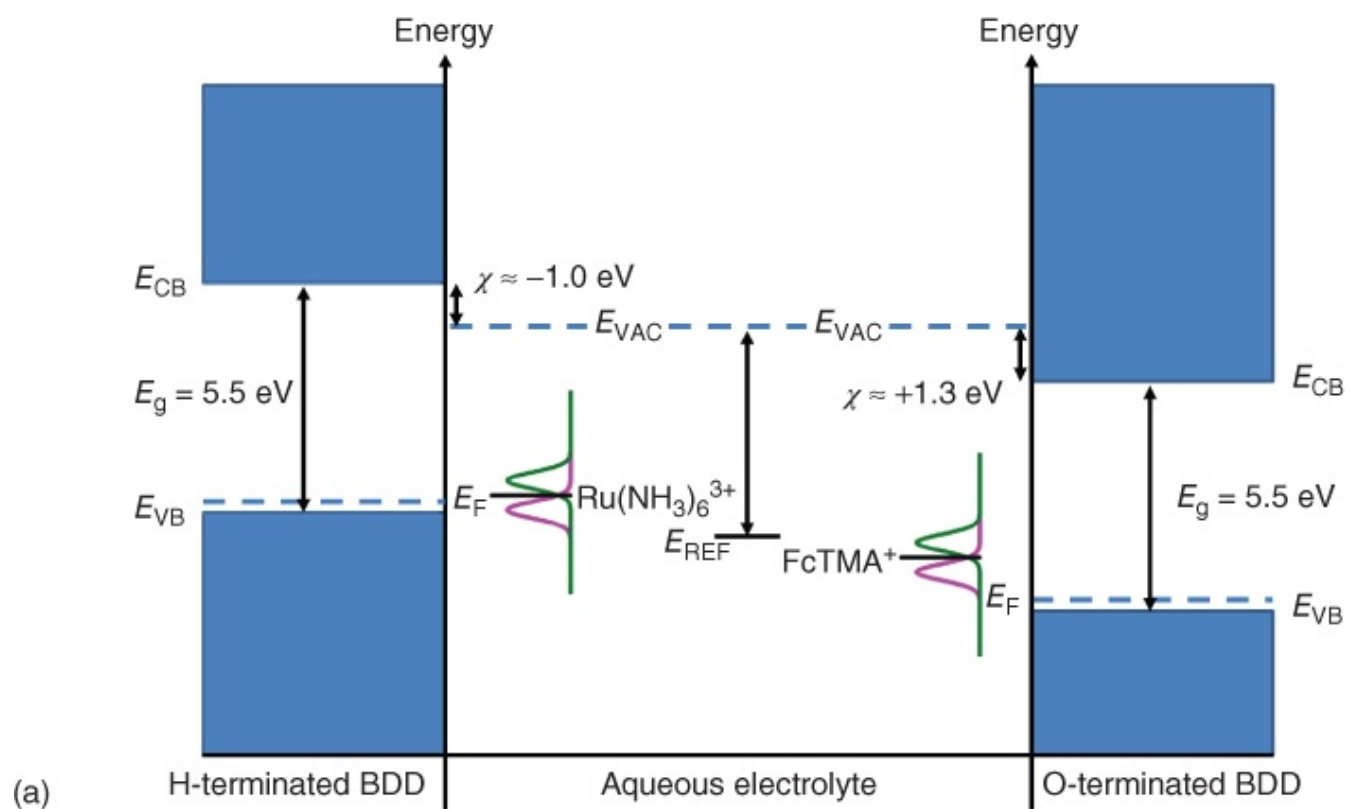
When the surface is flat enough and grain sizes large such that the laser spot size can interrogate individual grains, as in MC BDD, it is also possible to both qualitatively map BDD dopant density [18, 81] and identify regions of NDC. As the area under the diamond sp^3 peak decreases with increasing boron content, integration of the Raman spectra recorded on a spot-by-spot basis qualitatively provides information on local boron concentration, with a spatial resolution governed by the size of the spot. A typical image is shown in [Figure 5.5b\(ii\)](#), alongside the corresponding SEM image of the BDD surface. Similarly, analysis of spectra in the region associated with NDC provides spatial information on NDC location.

5.2.1.4 Outer-Sphere Redox Species Characterization

Boron dopant density clearly plays a significant role in governing the electrochemical characteristics of the material [17, 82]. The redox species of choice for characterizing a newly prepared BDD electrode or any carbon material used to be the ferri/ferrocyanide redox couple. However, many articles have now shown this couple to be surface sensitive and can result in electrode fouling unless special precautions are taken [83]. To prove that the BDD electrode is sufficiently doped to be considered metal-like, the best redox species to use is one that is thus surface insensitive, that is, outer sphere, and undergoes fast ET. Under these conditions, the response should only be controlled by mass transport in the system, providing the electrode can supply sufficient charge carriers to maintain a Nernstian equilibrium. The resulting CV should display reversible characteristics as with other classical electrodes. The question is which redox couple to use for BDD assessment?

BDD doped below the metallic threshold is a p-type semiconductor (see [Figure 5.1](#)). To identify semiconducting BDD electrodes it is important to use a redox couple which shows ET activity in a potential region the BDD electrode is strongly depleted of surface charge carriers. An ideal redox mediator is $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ due to its outer-sphere characteristics and E^0 value = -0.16 V (vs SCE), which sits in the band gap of semiconducting BDD, as shown in [Figure](#)

5.9a. [Figure 5.9b](#) displays CVs recorded in stationary solution for O-terminated BDD MC electrodes containing boron at different dopant densities in the range $9.2 \times 10^{16} - 3 \times 10^{20}$ B atoms cm^{-3} for both FcTMA^+ (a fast ET outer-sphere species) which has a more positive $E^{0'} = 0.35$ V (vs SCE) and $\text{Ru}(\text{NH}_3)_6^{3+/2+}$.



BDD Electrode	1 mM FcTMA^+ ΔE_p (mV)	1 mM $\text{Ru}(\text{NH}_3)_6^{3+}$ ΔE_p (mV)
9.2×10^{16} (grey)	589 (± 7)	642 (± 6)
2×10^{18} (light grey dashed)	105 (± 6)	615 (± 8)
mid 10^{19} (light grey)	72 (± 9)	212 (± 9)
1.9×10^{20} (black dashed)	62 (± 3)	68 (± 4)
3.2×10^{20} (black)	61 (± 2)	65 (± 2)

Figure 5.9 (a) Schematic representation showing the position of the $\text{Ru}(\text{NH}_3)_6^{3+}$ and FcTMA^+ couples with respect to valence (E_{VB}) and conduction (E_{CB}) bands for both O- and H-terminated semiconducting BDD. H-termination (O-termination) is known to induce a negative (positive) electron affinity, with a value of -1.3 eV ($+1.7$ eV) measured in vacuum [84]. The presence of water molecules screening the C–H (C–O) surface dipole is expected to reduce the value of the electron affinity (χ) toward less-negative (positive) values. We have chosen a value of approximately $\chi = -1.0$ eV and $\chi = +1.3$ eV for H- and O-terminated surfaces, respectively. In the electrolyte region, the level of the Ag/AgCl reference electrode (E_{ref}) is shown, and all applied voltages are referred to its energy. (b) CVs performed with a 1 mm diameter disk electrode of freestanding polished microcrystalline BDD electrode of dopant density 9.2×10^{16} (black line), 2×10^{18} (red line), mid- 10^{19} (blue line), 1.9×10^{20} (pink line), and 3.2×10^{20} (green line) at a scan rate of 0.1 V s^{-1} for (i) the oxidation of 1 mM FcTMA^+ and (ii) the reduction of 1 mM $\text{Ru}(\text{NH}_3)_6^{3+}$ in 0.1 M KNO_3 . (Taken from Ref. [17] with permission.) The resulting peak-to-peak (ΔE_p) separations are given for the differently doped electrodes in the two different redox mediator solutions.

For both redox species, as the boron concentration increases ΔE_p decreases until a value close to that synonymous with “metal-like” behavior is reached at boron concentrations $\sim >10^{20} \text{ B atoms cm}^{-3}$. Note the change in ΔE_p is much more dramatic with $\text{Ru}(\text{NH}_3)_6^{3+}$ and is evident for all boron dopant densities less than 10^{20} . In comparison for FcTMA^+ , the mid- 10^{19} boron dopant density electrode shows close-to-reversible-like CV behavior, which could lead to misinterpreting the boron content of this electrode. Hence, $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ is the preferred redox mediator. Note that this electrode also showed no evidence of a Fano resonance in the Raman spectra [17], advocating characterization methodology must be used in parallel.

It is also crucial to take note of the surface termination when making these measurements, even though the redox species is outer sphere. A H-terminated BDD electrode doped $\leq 10^{20} \text{ B atoms cm}^{-3}$ in the presence of $\text{Ru}(\text{NH}_3)_6^{3+}$ will produce CV results with smaller ΔE_p values than the corresponding O-terminated electrode. The data thus can be misleading in suggesting a much higher boron dopant concentration for the H-terminated electrode. The reasons for this are discussed in the [section 5.3](#) and highlight an interesting physical phenomenon associated with H-terminated diamond surfaces. For $\text{Ru}(\text{NH}_3)_6^{3+}$, it has also been shown that for highly doped BDD ($>10^{20} \text{ B atoms cm}^{-3}$), the CV response of O-terminated BDD is independent of the surface treatment process [85, 86].

5.3 Effect of Surface Termination on the Electrochemical Response of BDD

5.3.1 Inner-Sphere Versus Outer-Sphere Electron Transfer Mechanisms

In any electrode/electrolyte system, attention must not only be given to the electrode and its surface termination (or surface chemistry) but also for the redox species of interest and the heterogeneous ET mechanism. For species that are purportedly outer sphere, ET is often fast and the species comes close enough to the surface for electrons to tunnel or hop across at least a monolayer of solvent, but they do not directly interact; outer-sphere species are often referred to as **surface insensitive** [87]. By contrast, for inner-sphere species there is a strong interaction between either the reactant or product with the surface, whereby reactants, intermediates, or products are often specifically adsorbed on the surface. Inner-sphere species are therefore surface sensitive; heterogeneous inner-sphere processes are often referred to as **electrocatalytic**, as changing the electrode material can strongly influence the rate of the reaction [87]. The difference between outer- and inner-sphere ET processes is illustrated in [Figure 5.10](#).

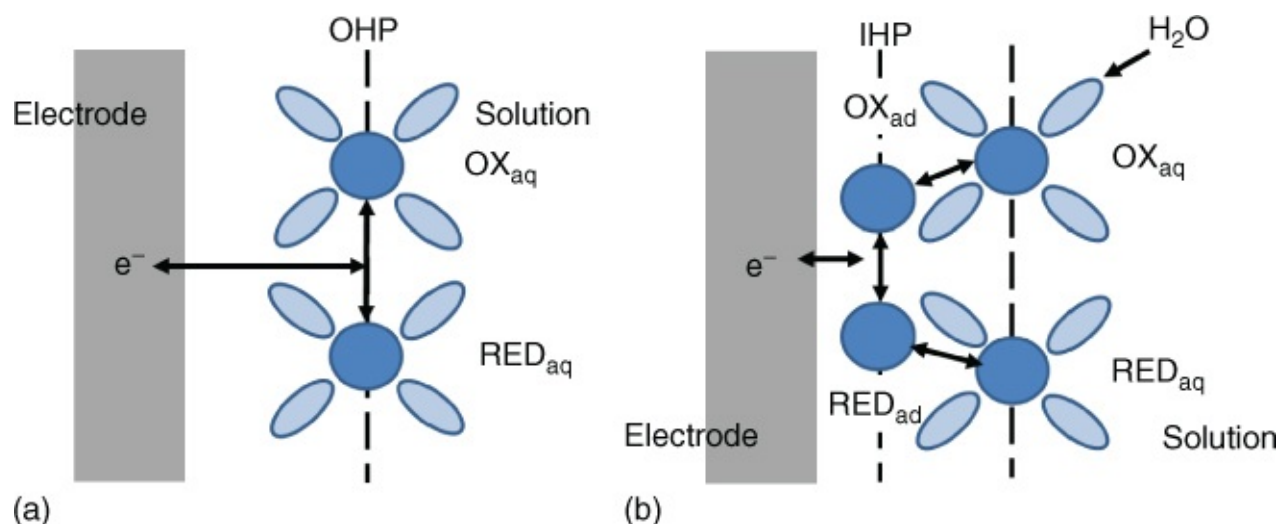


Figure 5.10 Schematic illustration of (a) outer-sphere and (b) inner-sphere redox process. OHP is the outer Helmholtz plane and IHP is the inner Helmholtz plane.

Diamond is an interesting material, as its sp^3 surface, whether H- or O-terminated, does not lend itself to surface adsorption as readily as classical metal electrodes, with their available d orbitals or sp^2 materials, which encourage adsorption through electrostatic effects and π - π^* interactions. This is why diamond is often referred to as **electrocatalytically inert** and is a significant reason for why diamond electrodes show reduced fouling compared to other electrode materials [88] and has a low capacitance (and low background currents); the surface does not charge readily or undergo surface redox processes.

The inertness of the surface raises interesting questions. The aqueous solvent window is pushed out as a result of water electrolysis being an inner-sphere mechanism. As a result, it is often stated in the literature that BDD can detect species which other electrodes cannot due to the extended solvent window. This is certainly true of outer-sphere species, but care must be taken when considering inner-sphere species. Heterogeneous ET will be retarded for many of these species on BDD, as there are no favorable adsorption sites, pushing out their electrochemical detection potential. Therefore, each species should be considered on a case-by-case basis, in combination with the effect of surface termination. For example, both $Ce^{3+/4+}$

oxidation [89] and $\text{Eu}^{3+/2+}$ reduction, in acidic solutions [90] are detectable on BDD electrodes, but are very difficult to differentiate from the water electrolysis signature on electrode materials, such as platinum, gold, and glassy carbon.

5.3.2 Hydrogen- and Oxygen-Terminated Diamond

As discussed in [Section 5.1.2.1](#), the as-grown surface leaves the CVD reactor H-terminated and hydrophobic. Since 1989 it has been known that the H-terminated insulating diamond surface shows a measurable conductivity [91–93], with p-type carriers present in an accumulation layer [94]. This was initially attributed to doping via subsurface hydrogen [95]. However, it was not until 2000 that it was realized atmospheric adsorbates play a significant role through a process called **surface transfer doping** [84, 96, 97], as shown in [Figure 5.11](#).

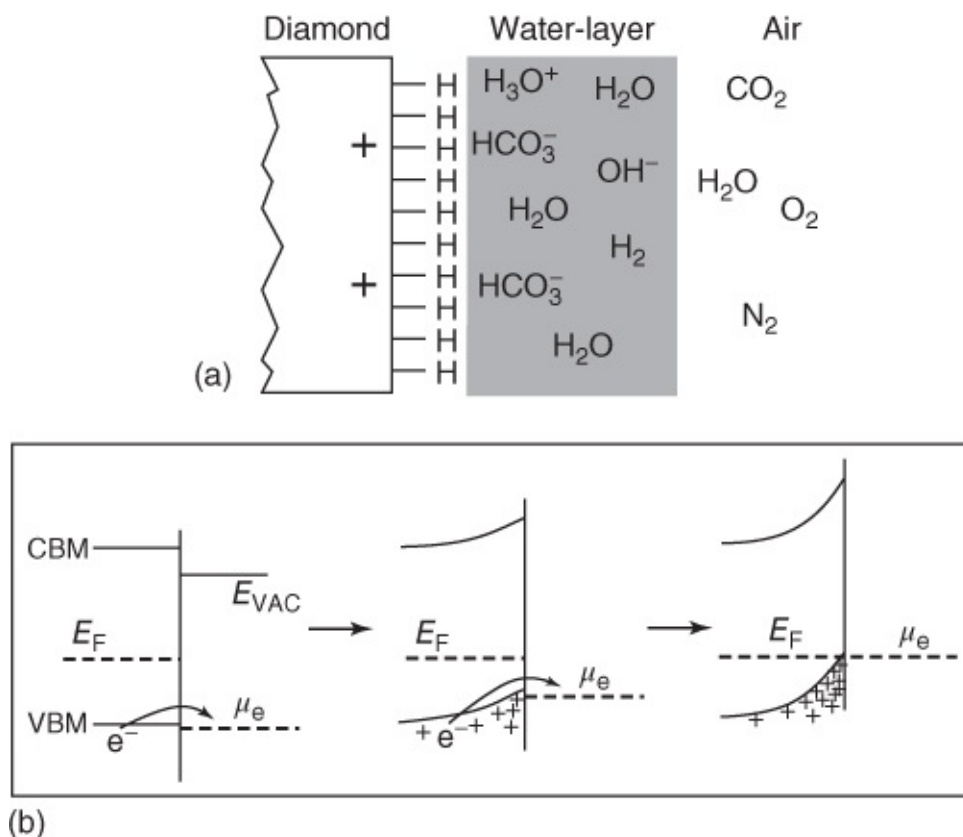


Figure 5.11 (a) Schematic of the hydrogenated diamond surface in contact with a water layer as it forms in air. (b) Evolution of band bending during the electron transfer process at the interface between diamond and the water layer. VBM = valence band maximum, CBM = conduction band maximum, E_F = Fermi level, μ_e = chemical potential of the liquid phase.

(Taken from Ref. [84] with permission.)

In brief, saturation of surface dangling bonds by donor-like monovalent hydrogen atoms results in a dense surface dipole layer (C^-H^+), which results in an electrostatic potential step perpendicular to the surface. This negative electron affinity increases all energy levels of diamond by a defined amount (see [Figure 5.9a](#)). The valence band maximum (VBM) is now raised sufficiently with respect to the vacuum level to place it just above the chemical potential of a mildly acidic water layer ($\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HCO}_3^- + \text{H}_3\text{O}^+$) physisorbed on the surface. ET

from diamond to H_3O^+ ($2\text{H}_3\text{O}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2 + 2\text{H}_2\text{O}$) is now possible, providing an electron sink for subsurface hole accumulation. This layer of positive charge is compensated by anions such as HCO_3^- , present on the diamond surface. The surface conductivity will remain for as long as the holes remain charge compensated by the adsorbed anions. Adsorbed neutral molecules can also cause the same effect provided they have sufficiently high electron affinity [96, 97], for example, fullerenes.

For electrochemical measurements, the additional surface conductivity H-termination imparts will impact negligibly on highly doped “metal-like” electrodes, due to the high number of already available charge carriers. However, for lower doped electrodes, H-termination will have an effect as the density of charge carriers increases at the diamond surface, decreasing the potential drop across the depletion layer and resulting in an observed increase in ET. This is likely to be the reason that H-terminated BDD electrodes doped in the 10^{18} and 10^{19} range have been reported as showing significantly faster ET kinetics than should be expected for these dopant densities with redox species such as $\text{Ru}(\text{NH}_3)_6^{3+}$ [17, 35].

The H-terminated layer will slowly become air-oxidized with time [98, 99], and its stability in the oxidative potential window has also been questioned [17]. Therefore, there has been much interest in whether cathodic treatment of the surface can be used to rehydrogenate the surface. This is coupled with the fact that some researchers report enhanced electrochemical response after cathodic treatment [99–101], discussed in more detail in [Section 5.3.2.1](#). It has been proposed that the surface can be reconverted to a H-terminated one by applying a negative voltage in acidic solutions (typically ~ -3 V vs Ag/AgCl in 0.5 M H_2SO_4) to generate hydrogen. However, as no direct comparisons were made between the quality of the resulting surface after electrochemical treatment and one prepared by hydrogen plasma, it has been questioned whether these treatments are really replicating the as-grown H-terminated surface [102]. Interestingly, many articles in the literature will simply refer to a cathodically treated BDD as H-terminated. Nebel and colleagues advocated the use of a more severe potential treatment, -35 V for 5 min in a 2 M HCl solution, to produce a H-terminated surface more akin to that produced by the H-plasma process, which was characterized using X-ray photoelectron spectroscopy (XPS) and contact angle measurements [102]. However, to date, it is still widely believed that the only reliable way to reconvert the surface to its fully H-terminated state is exposure to hydrogen plasma or a hydrogen dose [94].

Converting to an O-terminated surface is much easier and a variety of techniques have been employed including boiling in acid [103], alumina polishing [17], exposure to oxygen plasma [63, 104], photochemical oxidation [34], reaction with oxygen at high temperatures [105], and probably the most common anodic polarization [70, 104, 106, 107]. O-terminated hydrophilic diamond results in water contact angles ranging from 0.6° to 65° depending on the method of termination, surface roughness, and so on [86]. An O-terminated surface also has a positive electron affinity, due to the C^+-O^- polar bond causing energy levels to decrease by a defined amount. Depending on the crystal orientations present at the growth surface and the oxygenation treatment employed, the ratio of different oxygenated groups on the surface will vary. Hence, it is important to clarify the surface chemistry before interpreting the electrochemical data. This

can be achieved using XPS, although conventional XPS averages over large areas of the surface and does not provide crystallite-specific information [63, 107].

[Figure 5.12a](#) shows contact angles recorded on O-terminated BDD and cathodically treated BDD (-35 V for 5 min in 2 M HCl) [102]; and [Figure 5.12b](#) XPS C1s spectra recorded on semiconducting H-terminated BDD; formed via hydrogen plasma treatment (i) before and (ii) after electrochemical oxidation at 1.5 V for 10 min in 0.1 M KH_2PO_4 [108]. The largest component in the XPS spectra is found at ~ 284.6 eV, attributed to the sp^3 C–C present in the diamond bulk; all other component peaks are given relative to this one. Higher binding energies are associated with carbon in the form of adsorbed hydrocarbons ($+0.6$ to $+0.9$ eV) and different forms of oxidation (e.g., alcohol (C–OH) and ether (C–O–C) ($+1$ – 2 eV), carbonyl $>\text{C}=\text{O}$ ($+2.9$ – 3.8 eV), and carboxyl COOH ($+3.7$ – 4.3 eV)) [86, 106, 109, 110]. Lower binding energy peaks (-1 to -2.1 eV) can be assigned to sp^2 C–C, where reconstruction of the diamond surface, especially at the polycrystalline grain boundaries may give rise to π -bonding.

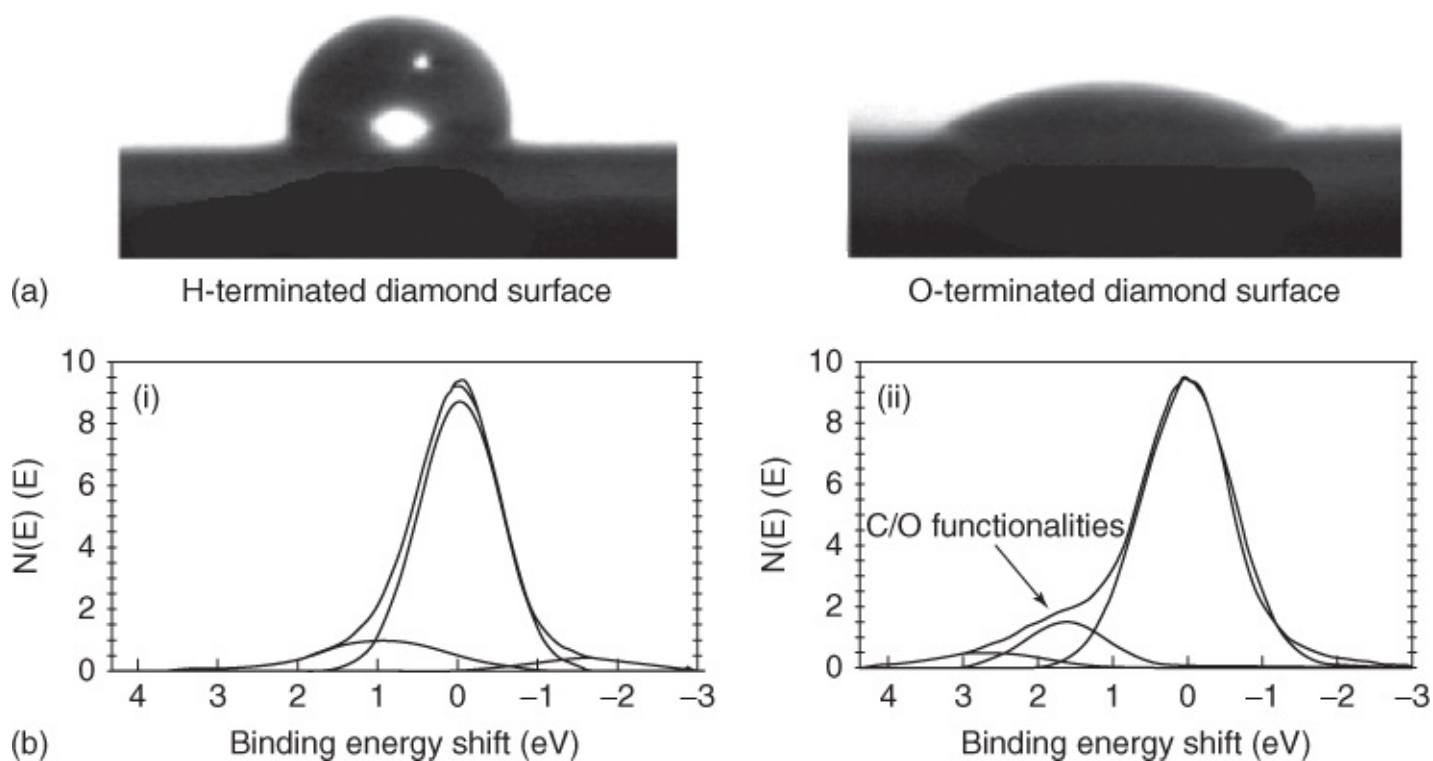


Figure 5.12 (a) Contact angles for H- and O-terminated BDD [102] (b) XPS C1s spectra of semiconducting H-plasma-treated BDD (i) before and (ii) after electrochemical oxidation at 1.5 V for 10 min in 0.1 M KH_2PO_4 [108].

O-terminated polycrystalline BDD shows a range of oxygen-containing functional groups on the surface [108, 111]. Studies on sc diamond show that C–OH groups are most abundant on the (111) diamond surface, while C–O–C and $>\text{C}=\text{O}$ groups are dominant on the (100) face [112]. In the literature, XPS shows that the oxygen termination treatment strongly affects the ratio of the different groups on the surface. Grain structure (e.g., MC vs NC vs UNC) and NDC content will also play a role. For example, in one study, XPS showed that oxygen termination

of BDD by anodic, UV, and plasma treatment all produced a low number of $>\text{C}=\text{O}$ groups, with UV resulting in the largest percentage of $\text{C}-\text{OH}$ groups compared to the other two oxidation processes [113].

In another investigation, it was shown that alumina polishing MC BDD resulted in $\text{C}-\text{OH}$, $\text{C}-\text{O}-\text{C}$, and $\text{C}=\text{O}$ groups on the surface [17]. The $>\text{C}=\text{O}$ groups, decreased significantly after heating to $300\text{ }^{\circ}\text{C}$ and were almost completely removed after heating to $500\text{ }^{\circ}\text{C}$, whereas the $\text{C}-\text{O}-\text{C}$ and $\text{C}-\text{OH}$ groups appeared stable at these temperatures. This observation was in agreement with reports which show that $\text{C}=\text{O}$ groups are more weakly bound to the surface than $\text{C}-\text{O}-\text{C}$ groups and are thus more easily removed at elevated temperatures ($\leq 400\text{ }^{\circ}\text{C}$). However, when the same surface was subjected to anodic polarization in acid, peaks at higher binding energies spanning $+2.2$ to $+5.4\text{ eV}$ appeared in the XPS spectra [17], indicating the presence of highly oxidized carbon functional groups such as COOH and even polycarbonate groups [110, 114].

5.3.2.1 Heterogeneous Electron Transfer Kinetics at Hydrogen- Versus Oxygen-Terminated Electrodes

There have been many articles written over the last 30 years on how different surface treatments affect the ET characteristics, for both inner- and outer-sphere ET species at BDD. Qualitatively, ΔE_p values from the CV are reported or quantitative analysis undertaken to extract the rate constant. However, as the field of diamond electrochemistry has grown and understanding has improved in order to interpret the wide ranging data obtained, often with the same redox systems, the reader should also take into account: (i) the boron dopant density of the material (does it contain enough boron to be considered metal-like); (ii) the crystalline morphology (UNC, NC, or MC; as grown or polished) and NDC content (sp^2 carbon can catalyze ET reactions compared to sp^3 BDD); (iii) the treatment conditions employed and an understanding of the resulting surface chemistry; and (iv) the experimental scan speed and electrode size when kinetic limitations are apparent.

[Table 5.3](#) is an attempt to summarize some of the data presented in this area for some of the simpler redox systems, note it does not by any means represent an exhaustive list. Where NDC has been noted as being present or absent by the author, this is included in the table as either high, low, or absent. Note, as-grown films will be H-terminated.

Table 5.3 Nonexhaustive table of ΔE_p values recorded for simple redox species by different authors using differently prepared BDD electrodes.

Electrode type	Boron dopant density	Redox couple and scan speed	Surface treatment and ΔE_p	Surface treatment and ΔE_p	Surface treatment and ΔE_p
MC 1 μm thin (200–800 nm grains) Area = not given Reference [70] 2004	$10^{20} - 10^{21}$	0.1 V s ⁻¹ Fe(CN) ₆ ⁴⁻ Q/H ₂ Q	As grown (NDC _{high}) =240 mV =740 mV	Mild anodic (NDC _{low}) =530 mV =1420 mV	Severe anodic =520 mV =930 mV
MC 8 μm thin ($\sim 3 \mu\text{m}$ grains) Area = 0.2 cm ⁻² Reference [100] 1999	$10^{19} - 10^{20}$	0.1 V s ⁻¹ Fe(CN) ₆ ⁴⁻	As grown =70 mV	Cycle from +2 to -1 V in 1 M H ₂ SO ₄ =198 mV	Acid clean, rehydrogenate =84 mV
Polycrystalline, thin film, no further details provided Area = not given Reference [86] 1999	$>10^{20}$	0.1 V s ⁻¹ Fe(CN) ₆ ⁴⁻ Fe ²⁺ Ru(NH ₃) ₆ ³⁺ IrCl ₆ ³⁻ Co(en) ₃ ²⁺	As grown =120 mV =637 mV =117 mV =93 mV =1853 mV	1 min O ₂ plasma treatment =1072 mV =466 mV =135 mV =667 mV =1879 mV	—
MC (free-standing polished approximately nanometers) Element Six, Ti/Au contact Reference [17] 2013 Area = 0.00785 cm ²	3×10^{20}	0.1 V s ⁻¹ Fe(CN) ₆ ⁴⁻ Fe ²⁺	Polished (NDC _{negligible}) =65 mV =803 mV	Anodic (+3 V 60 s in 0.1 M H ₂ SO ₄) =500 mV =472 mV	—
MC (free-standing polished $\sim$ nm, 600 μm thick) – commercial Windsor Scientific, Ag epoxy contact Area = 0.5 $\times$ 0.5 cm ² Reference [85] 2002	$\sim 10^{20}$	0.1 V s ⁻¹ Fe(CN) ₆ ³⁻ Ru(NH ₃) ₆ ³⁺ Q/H ₂ Q	Polished =280 mV =70 mV =1000 mV	Anodic (cycle $\times$ 5, 0–5 V in 1 M HNO ₃) =430 mV =70 mV =1670 mV	Cathodic (cycle $\times$ 5, 0 to -3 V V in 1 M HNO ₃) =77 mV =70 mV =970 mV
MC $\sim$ grain size 5–10 μm Area = 7.9 $\times 10^{-3}$ cm ² Reference [115] 2005	10^{20}	0.05 V s ⁻¹ Fe(CN) ₆ ³⁻ Ru(NH ₃) ₆ ³⁺	As grown =700 mV $\sim 80 - 90$ mV	Alumina polished =200 mV $\sim 80 - 90$ mV	Anodic polarization (no details supplied) =90 mV $\sim 80 - 90$ mV
MC thin films 1.5–2 μm thick Area = not given Reference [113] 2009	3×10^{19}	0.1 V s ⁻¹ Fe(CN) ₆ ³⁻ Ce ⁴⁺	As grown =60 mV =670 mV	Anodic 40 min in 0.5 M H ₂ SO ₄ (0.1 mA cm ⁻²) =4000 mV =2900 mV	1 min oxygen plasma treatment =2690 mV =3260 mV

The Fe(CN)₆^{4-/3-} system seems one of the most studied for BDD electrochemistry and gives the most conflicting results, again highlighting why this should not be the redox species of choice for BDD electrode assessment. Note, attention must be paid to the anions present, as well as the pH, as these have been shown to influence the Fe(CN)₆^{3-/4-} kinetic response [116]. The general trend from Table 5.3 shows that certain oxidative treatments of the surface have a detrimental effect on the ET kinetics for the Fe(CN)₆^{4-/3-} redox couple. However, the results also suggest that close-to-reversible ET kinetics can be obtained on both H-terminated and O-terminated surfaces. In the latter case, XPS analysis indicated that provided the O-terminated surface did not contain highly oxidized surface species such as >COOH and polycarbonates, ET was fast for Fe(CN)₆⁴⁻ [17]. These surface groups are the ones that can become negatively

charged, dependent on the pH of the solution, and will either encourage electrostatic interactions with appropriately positive charged inner-sphere species, or hinder interactions with surface-sensitive negative ions, such as $\text{Fe}(\text{CN})_6^{4-}$. This observation appears to be supported by $\text{Fe}^{2+/3+}$ CV behavior; $\text{Fe}^{2+/3+}$ is thought to be inner sphere. Here oxidative treatment acts to increase the rate of ET compared to a H-terminated surface, most likely due to favorable interactions between the $\text{Fe}^{2+/3+}$ and O-terminated species created on the BDD surface.

Also of interest, by H-terminating semiconducting electrodes, the rate of ET for $\text{Fe}(\text{CN})_6^{4-}$ is increased considerably compared to the same O-terminated electrode [82], as shown in [Figure 5.13](#) for a BDD electrode doped $\sim 10^{18}$ B atoms cm^{-3} . Also shown for comparison is the response recorded at an O-terminated highly doped electrode, $\sim 10^{20}$ B atoms cm^{-3} [82]. No information was provided in [82] on the method of O-termination. Similar results have been seen with the redox couple $\text{Ce}^{4+/3+}$ ($E^0 = 1 \text{ V}$) for semiconducting BDD electrodes [117]. O-termination was achieved by either thermally annealing in ultra-high vacuum or anodically polarizing the electrode. The H-terminated surface showed a peak separation $\sim 800 \text{ mV}$, while for the annealed O-terminated surface, ΔE_p increased to 1500 mV . For both couples, the effects observed were attributed to the role surface transfer doping plays in increasing the number of available charge carriers at the H-terminated electrode surface. In the latter study, emphasis was also placed on the lowering of the BDD valence band energy at the surface, due to O-termination, which was also believed to result in retarded ET [103, 117].

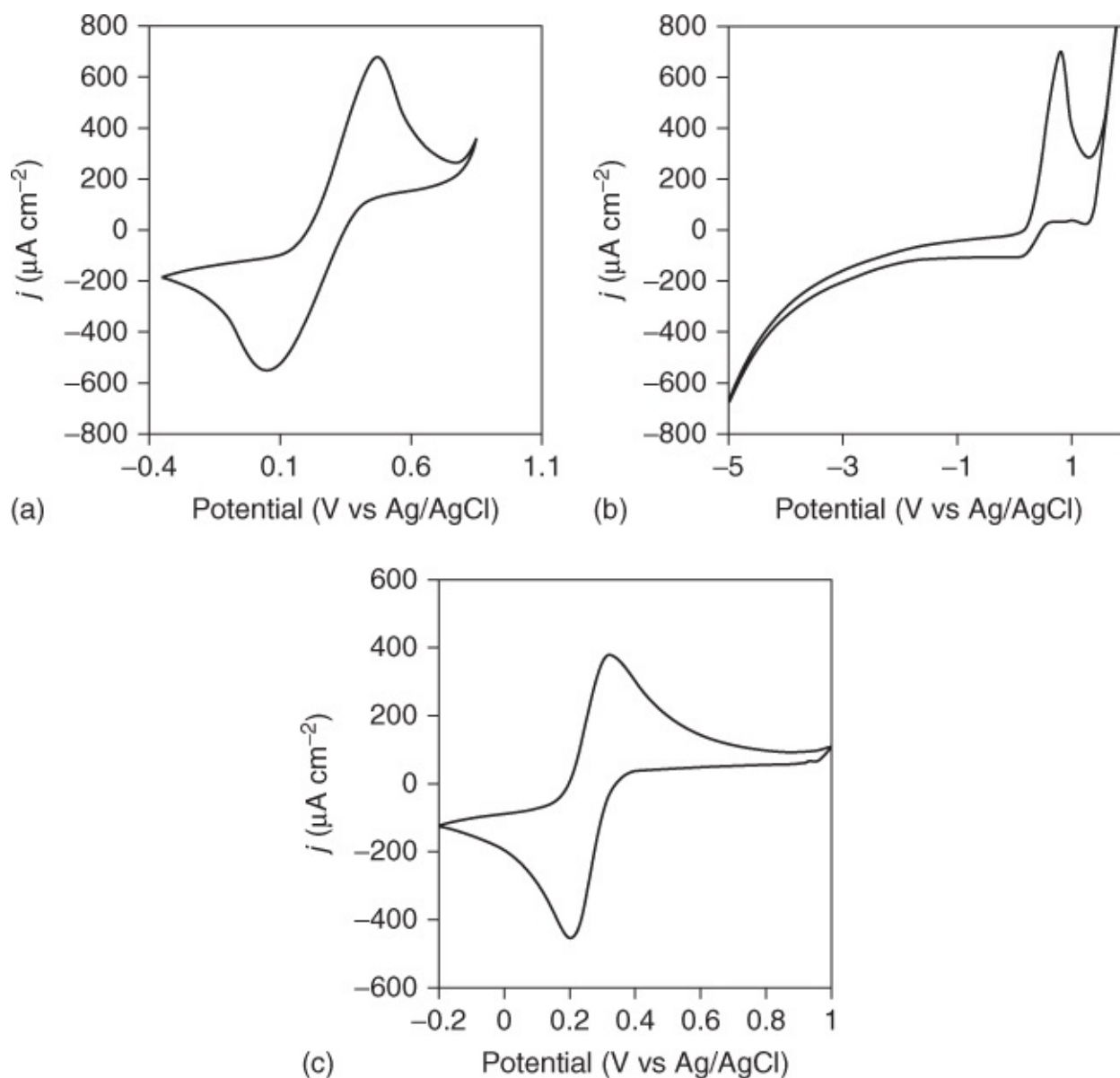


Figure 5.13 CV curves. (a) H-terminated low-doped ($\sim 10^{18}$) BDD electrode in 10 mM $\text{Fe}(\text{CN})_6^{3-/4-}$ with 1 M KCl, scan rate = 25 mV s^{-1} . (b) O-terminated low-doped ($\sim 10^{18}$) BDD electrode in 10 mM $\text{Fe}(\text{CN})_6^{3-/4-}$ with 1 M KCl, scan rate = 25 mV s^{-1} . (c) O-terminated high-doped ($\sim 10^{20}$) BDD electrode in 3 mM $\text{Fe}(\text{CN})_6^{3-/4-}$ with 1 M KCl, scan rate = 20 mV s^{-1} .

(Taken from Ref. [82] with permission.)

5.4 Polycrystalline Versus Single-Crystal Electrochemistry

In the early days of diamond electrochemical studies, there was some debate over the electrochemical origin of the signature. It was postulated that the response could be dominated by a network of electrochemically active NDC inclusions, most probably residing at grain boundaries, within a less-active diamond matrix [100]. Alternate theories questioned the role boron doping density and local DOS played in controlling ET in BDD [71, 118]. However,

pioneering work with single crystals and electrochemical imaging techniques, the latter where it is possible to probe the electrochemical response on a grain by grain basis, has now irrefutably demonstrated that BDD itself is capable of transferring electrons, albeit at a slightly slower rate (for an outer-sphere redox species) compared to a classical metal electrode.

5.4.1 Electrochemical Imaging of Polycrystalline BDD

Scanned probe microscopy and related techniques, often employed in combination, enable the activity of heterogeneous materials to be resolved. In the electrochemical arena, two such techniques that have had significant impact are scanning electrochemical microscopy (SECM) [119] and scanning electrochemical cell microscopy (SECCM) [120]. In the former, the probe is an ultramicroelectrode (UME), where the spatial resolution is controlled by the size of the UME (tip) employed. In SECCM, the probe is a glass capillary typically of micron and smaller tip-opening dimension, filled with the electrolyte/redox analyte solution of interest. Both techniques have been used to probe the electrochemical heterogeneities associated with polycrystalline BDD. [Figure 5.14a](#) shows a schematic of SECM applied to the study of a polycrystalline BDD electrode.

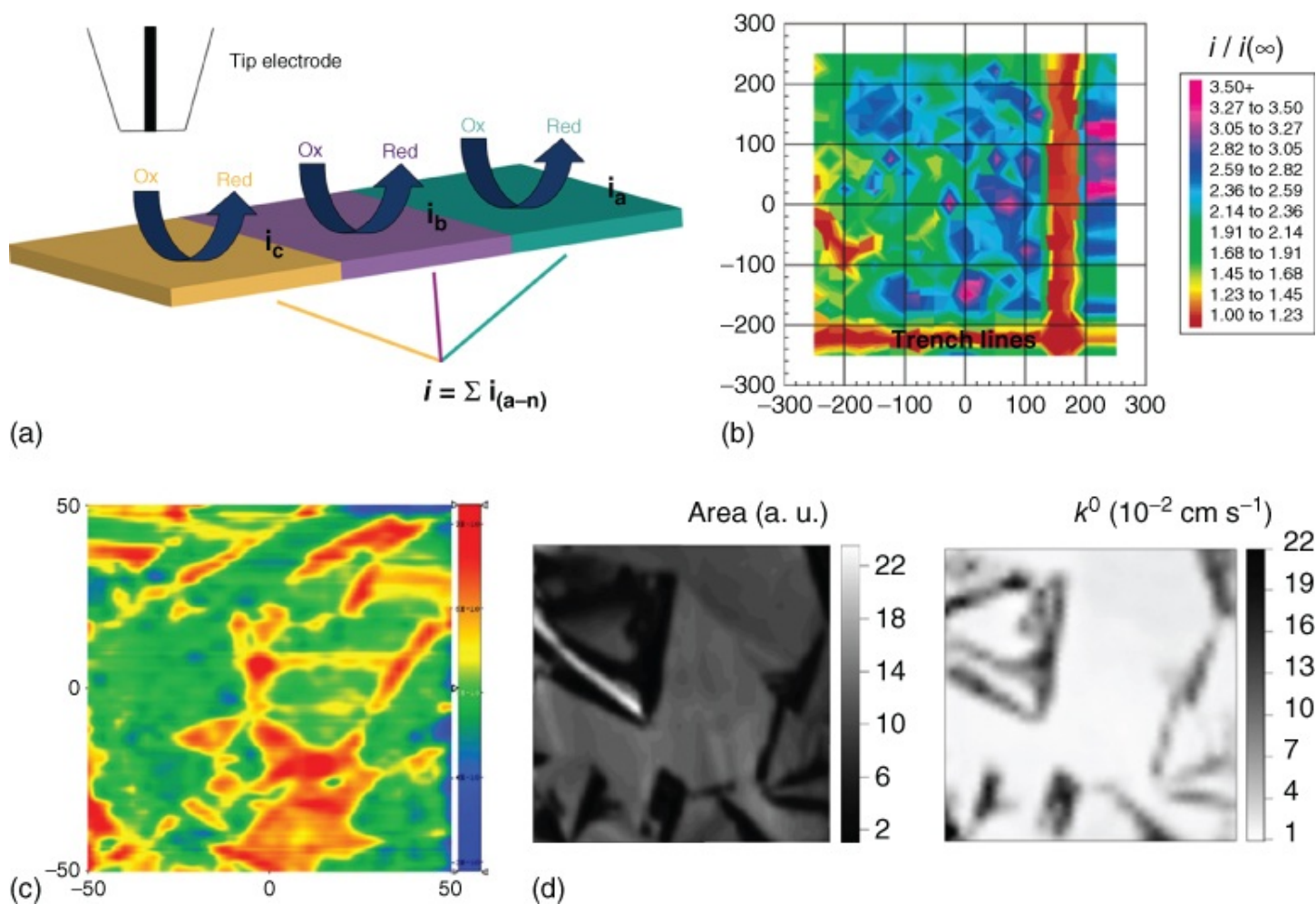


Figure 5.14 (a) Schematic illustrating SECM SG-TC mode. The heterogeneously active BDD electrode is biased at a potential to electrolyze the redox couple (Ox to Red or Red to Ox). The tip is biased at a suitable potential to convert the electro-generated species back to its original form at a diffusion-controlled rate. Variations in tip current reflect variations in the underlying ET capabilities of the surface. In feedback, the tip is biased to electrolyze the redox couple and the substrate left unbiased or biased to turn over the electro-generated form of the redox couple at a diffusion limited rate. (b) SECM SG-TC image of polished free-standing MC BDD, $500\mu\text{m} \times 500\mu\text{m}$, for substrate generation of $\text{Ru}(\text{NH}_3)_6^{2+}$ from $\text{Ru}(\text{NH}_3)_6^{3+}$ at a $25\text{-}\mu\text{m}$ -diameter imaging tip. (Taken from Ref. [28] with permission.) (c) SECM feedback image of polished free-standing MC BDD, $100\mu\text{m} \times 100\mu\text{m}$, recorded with a $2\mu\text{m}$ tip electrode biased at a potential to convert $\text{Ru}(\text{NH}_3)_6^{3+}$ to $\text{Ru}(\text{NH}_3)_6^{2+}$. (Taken with permission from Ref. [121].) (d) Scanning Raman image (left) and intermittent contact SG-TC SECM image (right) of the surface of polished free-standing MC BDD, $70\mu\text{m} \times 70\mu\text{m}$, with a $2\mu\text{m}$ tip electrode, biased at a potential to convert FcTMA^{2+} to FcTMA^+ .

(Taken with permission from Ref. [18].)

In early studies, SECM was employed in both constant height, substrate generation–tip collection (SG-TC) mode [28] and feedback mode [121], to examine the ET activity of free-standing, thick, MC highly doped, O-terminated BDD, as shown in Figure 5.14b,c. $\text{Ru}(\text{NH}_3)_6^{3+}$ was employed as the redox mediator. The electrode surfaces were polished to approximately

nanometer roughness and the boron-doped crystal facets ranged from ~ 1 to $50\ \mu\text{m}$ in dimension. Tip sizes were $25\ \mu\text{m}$ (Figure 5.14b) and $2\ \mu\text{m}$ (Figure 5.14c). As Figure 5.14b,c show, the SECM tip current, which results from either reduction of $\text{Ru}(\text{NH}_3)_6^{3+}$ (feedback: Figure 5.14c) or oxidation of substrate-generated $\text{Ru}(\text{NH}_3)_6^{2+}$ to $\text{Ru}(\text{NH}_3)_6^{3+}$ (Figure 5.14b), was heterogeneous at the applied substrate potential; a phenomenon attributed to the differently doped boron grains turning over the redox species at different rates. No quantitative information was presented on the spatially dependant ET kinetics due to the uncertainty in the tip–substrate separation at each imaging position.

Electro-generated chemiluminescence (ECL) was used to image the spatial variations in electrochemical activity of a heavily doped ($\sim 10^{21}$ B atoms cm^{-3}) MC diamond film electrode [122]. The ECL was generated by the reaction of $[\text{Ru}(\text{bpy})_3]^{3+}$ (generated by oxidizing $\text{Ru}(\text{bpy})_3^{2+}$ at the electrode surface) and tripropylamine. Images of the chemiluminescence patterns at the MC electrode indicated that the electrochemical reactivity was microscopically heterogeneous, with the ECL intensities for the (100)-oriented growth sectors much lower than those for other growth sectors.

SECM SG-TC images (tip size $2\ \mu\text{m}$) and C-AFM images were also recorded on H-terminated NC BDD thin-film electrodes, grain size $15\text{--}20\ \text{nm}$, of different dopant densities in the range of approximately 0 to mid- 10^{20} B atoms cm^{-3} [118]. For the undoped NC electrodes, C-AFM revealed a number of conducting pathways, attributed to NDC content at grain boundaries, a conclusion also reached by others in complementary experiments [123]. SECM was used to map the electrochemical activity of the highest doped NC electrodes and revealed a spatial heterogeneity for all three redox systems investigated ($\text{Ru}(\text{NH}_3)_6^{3+}/\text{Fe}(\text{CN})_6^{4-}/\text{IrCl}_6^{3-}$).

By building in a feedback mechanism which enables the tip–substrate separation to be accurately controlled and known, it is possible to extract intrinsic ET rate constant values, k_0 , as a function of tip position. Intermittent contact mode SG-TC SECM ($2\text{-}\mu\text{m}$ -diameter tip) was employed on highly doped polished freestanding MC BDD, of a similar grain size to the studies above (Figure 5.14d (right)) [18]. For the redox couples $\text{FcTMA}^{+/2+}$ and $\text{Ru}(\text{NH}_3)_6^{3+/2+}$, two characteristic k_0 values were extracted, differing in value by a factor of ~ 4 , associated with the high and lower doped grains on the surface. The k_0 values were about $10^2\text{--}10^3$ times smaller than found at a typical metal electrode, such as Pt or Au. Scanning Raman microscopy and EM were also used in the same scan area to confirm the different boron doping densities of the area examined. By using the small probe of SECCM, it was possible to measure the capacitance for these two different regions: $5.2 (\pm 0.8)$ and $3.1 (\pm 0.4)\ \mu\text{F cm}^{-2}$ at 0 V versus Ag|AgCl. From these values, a local DOS was extracted at 0 V versus Ag|AgCl $\sim 6.3 (\pm 2.0) \cdot 10^{20}\ \text{cm}^{-3}\ \text{eV}^{-1}$ and $\sim 1.7 (\pm 0.7) \cdot 10^{20}\ \text{cm}^{-3}\ \text{eV}^{-1}$, respectively, that is, a difference of about 4, correlating well with the factor of 4 difference in k_0 for the differently doped regions of the surface. For comparison, metals have a DOS $\sim 10^{23}\ \text{cm}^{-3}\ \text{eV}^{-1}$.

This important study showed that for polycrystalline BDD electrodes doped above the metallic

threshold, the k^0 values appeared to correlate with the differences in local capacitance and DOS associated with differences in the boron doping levels. Whether this applies to other carbon electrodes is still open to debate [124, 125]. Note, even though the k^0 values were lower than seen at a metal electrode, they are still fast enough that macro BDD electrodes operated in stationary conditions with fast outer-sphere redox couples, at typical scan speeds, appear reversible. Complementary, C-AFM [28] and SECCM images [126] recorded at higher resolution than the intermittent contact SECM study, on the same electrode material, also revealed, no increase in current associated with grain boundaries. This suggests that there is no significant preferential uptake of boron at the grain boundary, with this BDD material (grown using MW-CVD to film thickness of $\sim 500\text{ }\mu\text{m}$); NDC content for this material was also negligible.

5.4.2 Single-Crystal BDD Electrochemistry

As sc electrodes are significantly more challenging to synthesize than their polycrystalline counterparts, the number of electrochemical studies performed on sc electrodes is far less than on polycrystalline materials. Notable work in this area has been primarily carried out by Ramesham [127], Pleskov [31, 128–131], and Fujishima [132–134], using electrodes grown by CVD, HPHT, and from a Ni–Fe–C melt. Most of the work took place over the period 1998–2006. As sc BDD electrodes are still in their infancy compared to polycrystalline BDD, measurements were often made on lower doped semiconducting sc BDD electrodes, thus the reported rate constants for different redox analytes were low. In some cases, the dopant density was unknown or inferred from resistivity values. Moreover, when comparing different crystal faces in all but one study were comparable boron dopant densities employed. Moreover, results were often compared against polycrystalline electrodes of much higher dopant density. Researchers typically used the as-grown surface (H-terminated) or an O-terminated one resulting from polishing, acid cleaning or deliberate anodic polarization. For a fair comparison, it is important to keep boron dopant density and surface termination, in particular either O- or H-, the same.

Note, when comparing data from different papers the following observations were made, which are mostly in agreement with the current understanding of polycrystalline BDD electrochemistry.

(i) The diamond electrode response is a combination of the large potential window of the diamond single-crystal faces and reactivity at the grain boundaries; for NDC-free materials, the electrochemical response is controlled only by the diamond crystallites [128, 135]. (ii) Boron uptake in (111) is about $\times 10$ greater than (100); this difference in doping density and acceptor concentration leads to faster ET rates for $\text{Fe}(\text{CN})_6^{3-}$ reduction [133]. For (111) and (100) crystals grown with similar dopant densities, the ET rate for $\text{Fe}(\text{CN})_6^{3-/4-}$ was similar [131]. (iii) The ET rates are faster on a H-terminated semiconducting surface [133] than an O-terminated one [130]. (iv) The rate of ET for $\text{Ru}(\text{NH}_3)_6^{3+}$ is faster than $\text{Fe}(\text{CN})_6^{3-}$ for the same crystal faces [131]. (v) The (111) crystal gives electrochemical characteristics comparable to a thin film polycrystalline electrode [133]. (vi) An anodically polarized (100) surface

produces both $>\text{C}=\text{O}$ and $\text{C}-\text{O}$ groups while the (111) surface produces predominantly $-\text{C}-\text{OH}$ [134]. Studies made led one author to claim, sc homoepitaxial diamond films of the correct orientation should be superior materials for electroanalytical detection, with lower detection limits and less tendency for surface adsorption [133].

It is clear to see that more work is needed in the area of sc electrochemistry, notably the ability to reliably prepare highly doped, high-quality BDD electrodes of a known crystallographic orientation. Such materials are now being grown [136] in bulk form, as shown in [Figure 5.15](#), for applications such as high-power electronics [33] and as delta-doped layers [137], where thin-film sc BDD is overgrown on insulating diamond, for field effect transistor and Schottky diode applications. One recent article described the overgrowth of a diamond-attenuated total reflection prism with homoepitaxial BDD (thickness ~ 100 nm, boron dopant density $\sim 5 \times 10^{20}$ B atoms cm^{-3}) [138]. The BDD electrode was employed to drive the electrodeposition (ED) of a polymeric species on the surface, monitored by changes in the simultaneously recorded IR signals. Thus, it should be only a matter of time before sc BDD electrodes start appearing routinely in the electrochemical arena.

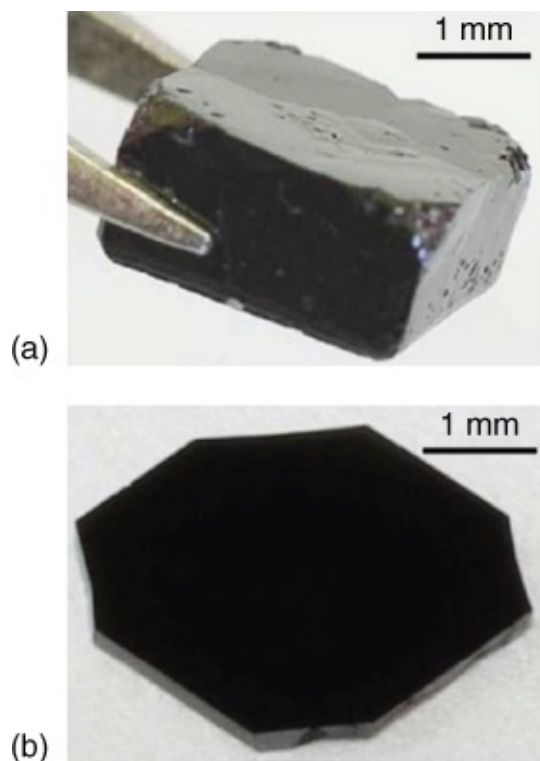


Figure 5.15 (a) Boron-doped film with its HPHT substrate before cutting and polishing. (b) Freestanding boron-doped diamond film.

(Taken from Ref. [33] with permission.)

5.5 Imparting Catalytic Activity on BDD

For some applications, the O- or H- terminated sp^3 surface of BDD is not sufficiently active to promote the redox process of interest. To this effect, researchers have been deliberately imparting catalytic activity on the BDD electrode in a number of ways.

5.5.1 Metal Nanoparticle-Coated BDD Electrodes

Metals such as Pt, Au, Ni, and Pd are well known as electrocatalysts; however, as a consequence, the background currents associated with metal electrodes are significantly greater than for BDD. The goal is thus to impart electrocatalytic activity on the BDD electrode by covering with enough metal NPs [139] to produce a measurable catalytic response but not too many that the background signals rise significantly. NPs also show considerably higher electrocatalytic activity than a bulk metal, due to the increased surface-to-volume ratio. The BDD, ideally highly doped to be semimetallic, thus acts as an electrochemically inactive electrical support for the metal NPs. This subject area was extensively reviewed in 2010 by Toghiani and Compton [140]. [Table 5.4](#) is an adapted list [140] of some of the target analytes for metal NP-BDD electrodes. [Figure 5.16](#) shows SEM and AFM microscopy images of a range of different metal NP-BDD electrodes used in electroanalysis.

Table 5.4 Nonexhaustive list of different metal NPs deposited on BDD electrodes for the electrocatalytic detection of a range of different analytes.

Metal NP	Analyte	References
Gold (ED)	Oxygen	[141]
Gold (EVAP)	Oxygen	[142]
Gold (ED)	Hemoglobin	[143]
Gold (LBL)	Dopamine	[144]
Gold (ED)	Tyrosine	[145]
Nickel (IED)	Glucose, ethanol, methanol	[146]
Nickel (IED)	Ethanol, glycerol	[147]
Copper (ED)	Nitrate	[148]
Platinum (ED)	Arsenite	[149]
Platinum (ED)	Oxygen	[36]
Platinum (ED)	Hydrazine	[150]
Platinum (ED)	Methanol	[151]
Palladium (ED)	Hydrazine	[152]
Nickel (IED)	Adenine, DNA	[153]

ED, electrodeposited; EVAP, vacuum evaporated; LBL, layer-by-layer assembly; IED, indirect electrodeposition.

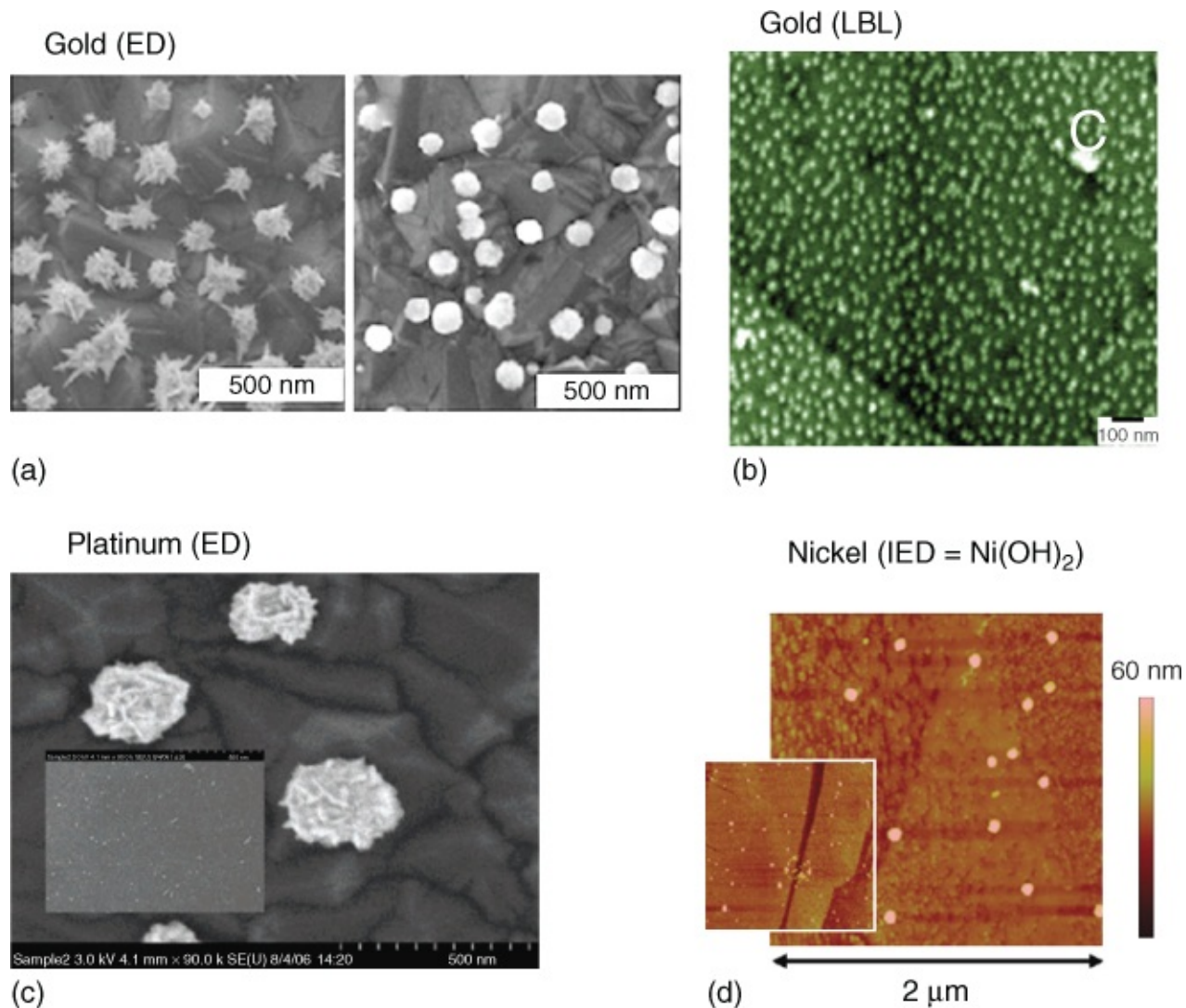


Figure 5.16 SEM and AFM images of different metal NPs deposited under different conditions on BDD. (a) SEM images of flower-like (left) and spherical gold NPs electrodeposited on MC BDD by varying the electrodeposition conditions. (Taken from Ref. [143] with permission.) (b) SEM of citrate-capped gold NPs formed on as-grown BDD by the layer-by-layer assembly procedure. (Taken from Ref. [154] with permission.) (c) SEM of platinum nanoparticles electrodeposited on BDD microelectrodes after two deposition cycles. (Taken from Ref. [149] with permission.) (d) AFM image of nickel hydroxide nanoparticles deposited on free-standing polished MC BDD by electrochemically generating OH^- in the presence of Ni^{2+} .

(Taken from Ref. [146] with permission.)

As can be seen from [Table 5.4](#), a variety of techniques have been used to coat the BDD electrodes with metal NPs, including direct ED and indirect ED, where the electrode is used to generate a species which results in a precipitation reaction with metal ions in solution, evaporation, and sputtering, self-assembly using presynthesized ligand-stabilized metal NPs [154], layer-by-layer assembly, and sol-gel techniques [155]. Note that when using the popular ED approach, it is important to take into account the nonuniform doping levels of especially MC BDD; this is evident when small overpotentials are used to drive ED [49]. Under these conditions, metal NP density is often reported to be higher in the higher doped regions of the

surface. However, by using large overpotentials, differences in boron dopant density become less apparent [36, 156]. Furthermore, for the self-assembly approach, it was demonstrated that the duration of surface treatment effected the spatial distribution of the metal NPs [157]. In particular, for UV/ozone-treated BDD surfaces, for short treatment times, citrate-stabilized Au NPs were found to adhere only to the (111) face, whereas longer periods resulted in Au NP adsorption over the entire surface.

Most of the articles highlighted in [Table 5.4](#) deal with 2D surfaces. In complementary work, Nebel and colleagues evaporated Ni NPs onto a BDD electrode and used the Ni as an etch mask to produce a BDD nanowire electrode terminated with Ni NPs. This 3D electrochemical platform has been utilized for the electrochemical detection of glucose [158], immobilization of histidinylated biomolecules [159], and the immunosensing of immunoglobulin G [160].

5.5.2 Ion Implantation

As an alternative to metal NP deposition, where the stability of the metal NPs on the BDD has been in some cases questioned, ion implantation (II) was proposed by Einaga and colleagues as an alternative methodology. II modifies the near-surface structure of the BDD by heavy-ion bombardment and has been used to implant a range of different metal ions in the surface of BDD, including Ir^+ [161], Ni^{2+} [162, 163], Cu^{2+} [162], and Pt^{2+} [164] for the detection of a range of different species, including arsenic [161], as shown in [Figure 5.17](#), glucose [162], hydrogen peroxide [164], and tetracyclines [163].

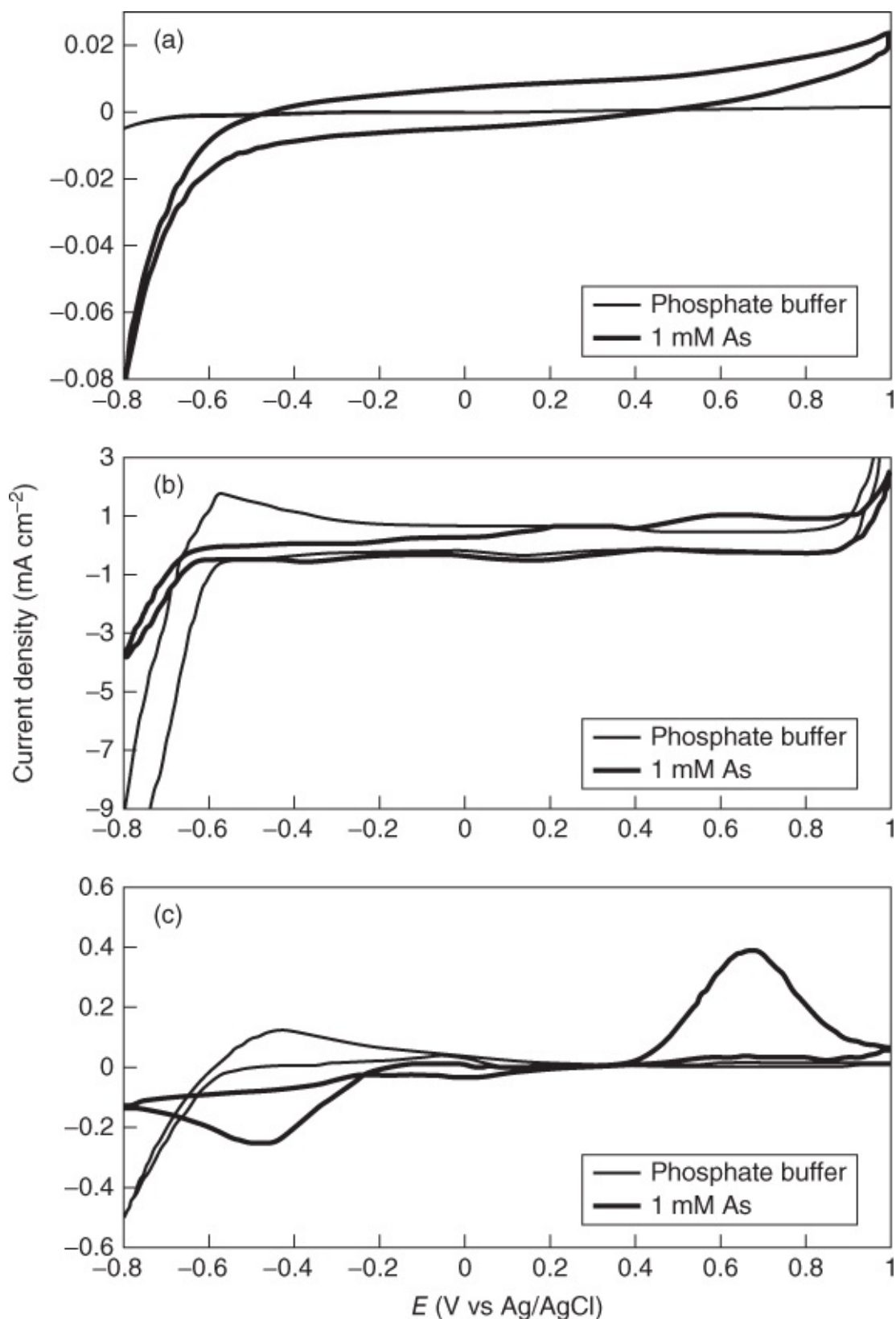


Figure 5.17 CV responses of 0.1 M phosphate buffer solution pH4 at a scan rate of 50 mV s^{-1} in the absence and presence of 1 mM arsenic(III) at (a) BDD electrode, (b) Ir-wire electrode, and (c) Ir-BDD electrode.

(Taken from Ref. [161] with permission.)

During ion implantation, some of the sp^3 bonds are broken and thus an annealing step is

advocated to restore the surface, providing the critical damage level has not been exceeded. Annealing in a hydrogen atmosphere or plasma is also thought to be necessary to bring the metal to the surface. Nanoscopic holes, up to ~200 nm, are also observed on the surface post treatment. The presence of the metal is confirmed by XPS.

5.6 Chemical Functionalization of BDD Electrodes

For many applications, especially in the biosensing arena it is advantageous to be able to chemically functionalize the surface of BDD with linker molecules to enable attachment of molecules, such as DNA and peptides. Functionalization can also be employed to reduce nonspecific binding events [165, 166]. State-of-the-art chemical, photochemical, and electrochemical strategies for the grafting of different organic functionalities on diamond was reviewed in 2008 by Szunerits and Boukherroub [167], and then more recently by Szunerits *et al.* in 2014 [168]. Today, these methodologies enable the preparation of halogenated, aminated, carboxylated, oxidized, and other types of diamond surfaces, which can be used for further functionalization depending on the desired application. A few procedures are given below, followed by some recent applications.

For halogenation with, for example, fluorine [169, 170] and chlorine [170], it is first necessary to activate the halogen gas to form free radicals; this is typically achieved using high temperature, UHV conditions. A milder approach is to employ UV photochemical activation in the presence of halogen gas [171]. The chlorinated surface can be further functionalized to the amine by photochemical substitution in the presence of UV light and ammonia [172] or via reaction with a quaternary pyridinium salt [173]. Direct amination of the H-terminated surface is also possible using a plasma [174] or UV treatment [175] in the presence of ammonia or a long-chain end group-protected amine (UV only) [176].

For the formation of organic layers grafted to the surface via a C–C bond, UV irradiation of H-terminated diamond covered with liquid films of an appropriate alkene [177] is also viable. The addition of aminosilane groups to the diamond surface is possible by reacting O-terminated diamond with 3-aminopropyltriethoxysilane (APTES). Carboxylation of the surface involves reacting an aminated surface with succinyl chloride and triethyl amine [178]. For boron-doped surfaces, C–C bond formation between diamond and organic molecules can be achieved via the electrochemical reduction of diazonium salts enabling the introduction of a wide range of functional groups (–COOH, X, NO₂, etc.) onto the surface in one step [179].

Szunerits *et al.* [180], for example, presented a chemical functionalization scheme on BDD to enable the electrochemical detection of DNA hybridization events, as shown in [Figure 5.18a](#). In brief, the H-terminated surface was aminated and then reacted with pentatonic acid, resulting in alkynyl termination. Thiolated molecules of interest, for example, oligonucleotides, were then “clicked” onto the surface via the alkynyl groups using mild UV conditions. Electrochemical impedance spectroscopic (EIS) measurement of the charge transfer resistance was employed to monitor hybridization events, with a detection limit of 1 nM reported for DNA–DNA recognition events. Yeap *et al.* [181] also used EIS to characterize DNA

immobilized on their BDD electrodes. However, the attachment procedure differed slightly and advocated the use of electrografting as the first step in the reaction mechanism. In particular, as shown in [Figure 5.18b](#), an azidophenyl layer was grafted onto the BDD surface through electrochemical reduction of the corresponding (*in situ* generated) 4-azidophenyldiazonium chloride salt. This was followed by chemoselective coupling of the terminal alkyne-bearing molecule of interest via a click reaction.

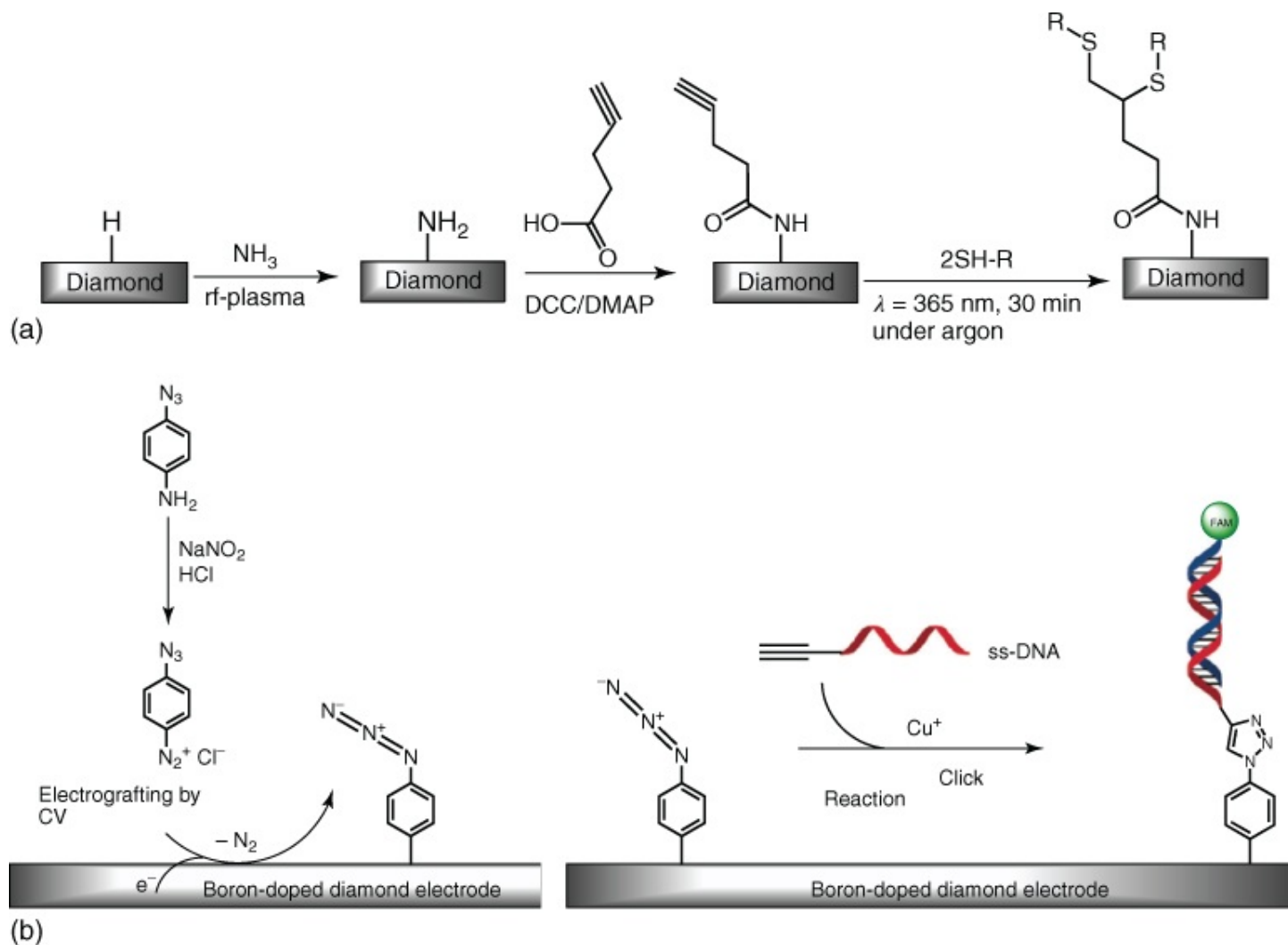


Figure 5.18 (a) Description of the successive diamond surface functionalization steps: first, amination with rf plasma, then aminolysis with 4-pentynoic acid, yne coupling using a thiolated oligonucleotide. (Modified from Ref. [180] with permission.) (b) Illustration of the multistep functionalization of BDD electrodes: first, diazotization, then electroreduction of the diazonium salt for electrografting of phenylazide molecules and finally click cycloaddition between the immobilized phenylazide molecules and ss-DNA (fluorescently labeled).

(Modified from Ref. [181] with permission.)

5.7 Electroanalytical Applications of BDD

The range of electroanalytical applications of BDD is huge and has been highlighted in two fairly recent extensive reviews by Luong *et al.* [4] and Tryk [6]. To avoid repetition, the

research themed areas will only be briefly highlighted for areas where diamond electrodes have made an impact. These include: (i) inorganic trace metal determination. Due to outlawing the use of mercury electrodes in stripping voltammetry, and related techniques, solid electrodes with an extended cathodic window have been sought. BDD has thus been the subject of intense investigation for the detection of a wide variety of metal ions, including Pb^{2+} , Cd^{2+} , Ag^+ , Cu^{2+} , and Hg^{2+} , in a field of work first instigated by Fujishima [182]. (ii) Organic species analysis. BDD electrodes have been employed to electrochemically detect a vast range of organic species ranging from (a) nitrogen-containing compounds (such as catecholamines [46], ethylamine, and ethylenediamine [183]), polyamines (such as cadaverine, putrescine, and spermine) [184], NADH [185], nitrogen-containing pesticides [186], xanthine [187], caffeine [187], cytochrome *c* [85, 188], and nucleic and amino acids [189, 190] to (b) sulfur-containing species, such as sulfadiazine [191], sulfamerazine [192], sulfamethazine [192], l-cysteine [193], sulfides [194], d-penicillamine [195], tiopronin [196], and captopril [197] (this is not an exhaustive list). Many of these studies are often carried out in combination with flow injection analysis, high performance liquid chromatography, or capillary electrophoresis.

One very recently reported application of BDD by Hamers and coworkers describes the formation of solvated electrons by irradiating H-terminated conducting diamond with light >5.5 eV (<225 nm) [198, 199]. As described in [Section 5.3.2](#), the negative electron affinity of H-terminated diamond places the conduction band, 0.8–1.3 eV above the vacuum level. Irradiation enables the diamond to become a solid-state electron source and when placed in solution, solvated electrons are produced with a reduction potential of about -5.5 V versus the normal hydrogen electrode. These electrons are now capable of reducing species that cannot be reduced directly at conventional electrodes, due to their extremely high reduction potential, such as CO_2 or N_2 and offers significant promise in the field of heterogeneous catalysis. Complementary to this study, Einaga and colleagues showed that a BDD electrode in the solvent methanol was able to directly reduce CO_2 [200]; however, electrochemical detection of N_2 was not possible, as its reduction potential lay outside the solvent window.

Finally, BDD electrodes have also found extensive use in the areas of water treatment (ozone and hydroxyl radical generation), and organic and inorganic synthesis processes, but it is beyond the scope of this chapter to provide detailed information. The reader is directed to references [7, 10] for further information.

5.8 Conclusions

The aim of this chapter has been to put into context the vast body of research since the early 1990s on the use of diamonds in electrochemistry; a unique sp^3 material. As the field has progressed so has both understanding of the properties of this amazing material and the ability to produce higher quality materials. BDD can be routinely grown in UNC, NC, and MC forms with the method of growth dictating the quality of the diamond synthesized, in terms of NDC content. Novel synthesis and fabrication routes mean that all-diamond electrodes of any electrode geometry at the single and individually addressable level are now possible. This has

even been extended to the entire electrochemical cell, working, counter, and reference electrode, being fabricated from BDD.

Understanding the role surface termination plays in the resulting electrochemical performance has led to an increased awareness of how best to use diamond electrodes for electrochemical analysis. As H-termination confers an additional surface conductance due to transfer doping, dependant on the redox potential of the mediator employed, a semiconducting BDD electrode can appear metal-like. Hence, thorough material characterization of any new diamond electrode is advocated before use. H-terminated surfaces can also be used to produce high-energy solvated electrons for the reduction of high redox potential species, such as CO₂ and N₂. Changing surface termination can also enhance the ET kinetics of inner-sphere redox couples and for BDD, there are a myriad of methods available now to present a variety of chemical groups at the electrode surface, over and above the standard O- and H-terminations.

The advantages of a pure sp³ surface, such as extended solvent window, low capacitance, low background currents, and reduced electrode fouling, also bring out disadvantages in that certain species which need to bind to the diamond surface in order to transfer electrons efficiently do this sluggishly. However, strategies are in place, which couple metal and inorganic NPs to BDD electrodes to enhance electrocatalytic activity while retaining many of the properties associated with BDD. Finally, the literature is still biased toward the use of polycrystalline BDD, but with recent advances in highly doped sc BDD for a range of different electronic applications, it should not be long before the balance begins to be addressed in the electrochemical field.

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Chapter 6

Modification of Carbon Electrode Surfaces

Muhammad Tanzirul Alam and J. Justin Gooding

6.1 Introduction

The chemical modification of carbon surfaces with different functional groups has received considerable interest because of its multitude of applications, including as model systems for understanding electron transfer [1], molecular electronics [2, 3], bioelectronics [4, 5], and sensors [6]. Modification actually starts from the choice of the carbon material to be used and then continues with how the surface is terminated, cleaned, and activated followed by the attachment of other different molecules of interest to get the desired activity. Unlike metals, carbon materials have a diverse density of states (DOS), ranging from undoped diamond with a large band gap containing no states to highly oriented pyrolytic graphite (HOPG) with low DOS, nanotubes with significant DOS, and disordered graphite with a relatively evenly distributed DOS at the Fermi level [7]. The surface chemistry of carbon materials is also quite complex not only because of the varied underlying microstructures, but also because carbon forms a wider variety of surface bonds and functional groups. Since the electrochemical response is essentially an interfacial phenomenon, the nature of the carbon electrode surface is of obvious importance, and the choice of electrode material and surface preparation method are usually dictated by the suitability of the electrode for observing a desired electrochemical response in a particular experimental condition.

Surface preparation is of obvious importance for any heterogeneous process, and the literature on carbon materials is quite rich [6, 8–15]. Hence, different ways of modifying carbon surfaces with external molecules are the focus of this chapter. Since the early 1990s, significant new approaches to surface modification have been reported by several laboratories [7–10, 15–17]. The most common approach of modification via a covalent bond is the generation of a radical of the molecule to be attached by electrochemical reduction/oxidation (e.g., reduction of aryl diazonium and oxidation of amine and alcohol) at the surface. The radical, being highly reactive, interacts with the surface rapidly and is attached via a covalent bond. Recently as a noninvasive approach, π – π stacking-based surface modification strategy has also been used and has become popularized with the advent of graphene. These processes of modification have significantly broadened the utility of carbon materials. However, whatever the process of modification is, the modified layer is generally required to be compatible with the immobilization of further functionality so that the developed interface can be used to detect or electrocatalyze species of interest selectively or specifically. For example, in biosensors, biological recognition species, such as enzymes, antibodies, and DNA, must be attached to the carbon electrode. However, while performing the experiment in complex samples, the surface chemistry must also resist other Faradaic or non-Faradaic reactions. Typically, in complex biological samples, further chemical functionality, apart from immobilization of the biological

recognition molecule, must be incorporated into the interface. This additional functionality could be oligo(ethylene glycol), which provides the surface with some resistance to nonspecific adsorption of protein so that spurious proteins in a sample do not interfere with the measurement. Hence, not only are surface modification strategies required to allow further modification but they must also provide the ability to incorporate multiple chemical functionalities into an interface.

Modification procedures for carbon electrodes are quite diverse. For convenience, in this chapter, they are broadly divided into two parts: covalent and noncovalent modifications. It is worth mentioning that this chapter is not intended to cover the entire literature on carbon modification, instead the focus is given on basic features of each process of modification and how it changes the nature of carbon electrode surfaces. From the wide variety of applications of modified electrodes, a few selected articles are discussed in short at the end of each modification process to demonstrate its utility.

6.2 Covalent Modification

6.2.1 Reduction of Diazonium Cation

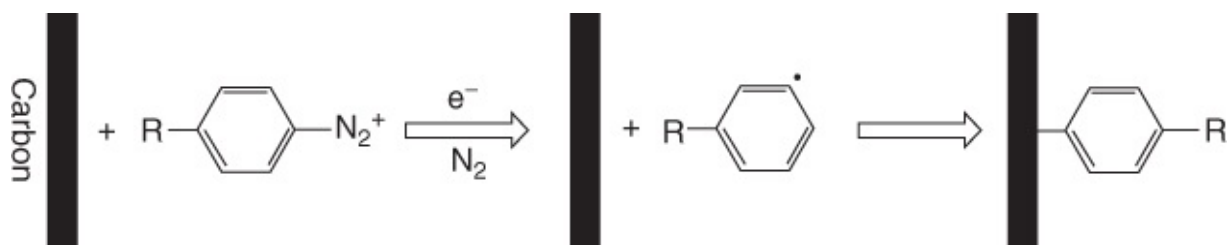
The electrochemical reductive grafting of aryl diazonium salt has been receiving increasing attention as a versatile method for the covalent derivatization of not only all sorts of carbon materials [9, 18–21], but also metals [12, 22], semiconductors [23–27], indium tin oxide, and organic materials [28, 29]. Since the first demonstration [17], this procedure has been expanded to include a wide variety of molecules attached to phenyl [30–32] and heteroaryl rings [33]. This feature is exciting as it allows us to use one method of modification for a diverse range of applications using different electrode materials. Aryl diazonium salts are stable in aqueous acidic solution, but their stability decreases at $\text{pH} > 2\text{--}3$ [34]. They are also stable in acetonitrile, but their stability in other aprotic media has not been investigated systematically [8–10]. The diazonium salts are easy to prepare; the traditional synthesis involves mixing an aromatic amine with NaNO_2 in an ice-cold aqueous acidic solution, filtering, and washing the precipitate [35]. The synthesis can also be performed in an aprotic medium (acetonitrile) in the presence of tert-butyl nitrite. Instead of isolating the diazonium salt, it can be prepared *in situ* by mixing amine with either an acidic aqueous solution of NaNO_2 [36] or tert-butyl nitrite in acetonitrile [37]. Protic ionic liquids (e.g., based on 2-methoxypyridine and trifluoroacetic acid) have also been used recently as electrolytes for the functionalization of carbon surfaces by electrochemical reduction of *in situ* generated diazonium cations [38]. The protic ionic liquid supplies protons, as in an acidic aqueous medium, required for the generation of the aryl diazonium cation from the corresponding arylamine in the presence of NaNO_2 . The resulting electrografted organic layers exhibit similar properties to those obtained from the *ex situ* derived of diazonium salts. Whatever the method used for the production of diazonium salts, one must start from an aromatic amine, and a large number of these compounds are available commercially. This *in situ* method of modifying surfaces can be used advantageously where the generation of the aryl diazonium salt from a

particular aniline followed by purification is difficult.

Because of the strong electron-withdrawing power of the diazonium group, generation of the radical for reductive electrografting usually requires quite low potential; typically applied by either cyclic voltammetry or using a potential step approach. The corresponding cyclic voltammogram (CV) usually shows a broad irreversible peak resulting from the reduction of diazonium to its radical, which is suppressed on successive scans [19, 39]. The suppression of the peak is related to the blockage of the access of electroactive aryldiazonium to the electrode by the developed organic film. The chronoamperogram is also very characteristic as instead of following the Cottrell law that describes the current decrease expected for the reduction of electroactive species in solution, one observes a rapid drop of the current that is related to the blocking of the electrode. The involvement of radicals during the electrochemical reduction of aryldiazonium salts was demonstrated through the Pschorr synthesis of phenanthrene [40] and also by electron spin resonance in acetonitrile in the presence of a spin-trap (nitron) [41]. At the modified surface, cyclic voltammetry shows attenuated response for the $[\text{Fe}(\text{CN})_6]^{3-/4-}$ redox couple, compared to that at the unmodified surface, and is usually used as a quick test to verify the success of modification. X-ray photoelectron spectroscopy (XPS) is also routinely run to confirm the modification.

The C–C bond formed through this process is very stable compared to say a gold-thiol bond. It can resist temperatures up to 700 K without being lost from the surface [42] and is stable in a wide potential window. A further advantage over other common surface modification techniques (e.g., self-assembly of silane monolayers on oxide) is that the process is quite fast, deposition times are usually on the order of 10 s. In contrast to the enhanced stability, formation of these layers on electrode surfaces is less controlled than for the alkanethiol system. In addition, not all the radicals generated participate in the formation of C–C bonds. It varies based on the surface condition and the substituent in the para position of the aryldiazonium salt. It has been reported that 84% of radicals form bonds with a glassy carbon (GC) surface while only 56% form bonds with the basal planes of HOPG [42]. Hence, the area under the reduction peak, or the charge passed during the modification of the electrode surface, will always give an upper limit to the surface coverage. In addition, the reaction shown in [Scheme 6.1](#) is only the dominant reaction but due to the high reactivity, the electro-generated radical also takes part in side reactions, the nature of which depends on the alkyl substituent and the surface being modified. The two most significant side reactions are (i) radical attack at the ortho position of a surface-bound aryl group [9], leading to the formation of multilayers and (ii) bonding to the surface without the loss of diazonium group, resulting in the generation of a surface with hydrazine attached to it [43]. Consequently, aryldiazonium salt-derived films are typically inhomogeneous multilayers with thickness of up to 10 nm [12]. Multilayers might even be present when the surface coverage estimated from the charge passed suggests a monolayer, or submonolayer, indicating that the layer has a porous structure [44]. On occasions, scanning probe microscope (SPM) techniques have been successfully used to demonstrate the formation of multilayers. This inferior control in modifying a surface is probably the main disadvantage of using aryldiazonium salts to modify electrode surfaces with organic layers. However, in the vast majority of sensing applications, the control achieved

with aryldiazonium salts is more than adequate. Only in a few instances, where the sensing principle is such that the exact position of the biorecognition or redox species relative to the electrode surface must be known, as is the case for some DNA sensors [45, 46] and some strategies for wiring proteins [47, 48], a special precautionary measure might be required to get a better control over the side reactions of the aryldiazonium salt.



Scheme 6.1 Reductive electrografting of aryldiazonium on a carbon surface.

A simple strategy using a radical scavenger was recently proposed to control side reactions of aryldiazonium salts [49]. Under an applied potential, the aryldiazonium salts generate reactive radicals at the electrode–solution interface, which couple with either the surface or other diazonium ions leading to the formation of multilayers. However, the kinetics of surface coupling is greatly favored compared to the polymerization reaction that takes place further away (not on carbon) from the surface. The kinetic gap between the surface coupling and the polymerization reaction is exploited to prevent the growth of the layer without interfering with the grafting. The molecule 2,2-diphenyl-1-picrylhydrazyl (DPPH) is used as the radical scavenger to achieve a monolayer surface coverage of 4-nitrobenzenediazonium on vitreous carbon. The radical capture was confirmed by isolating the aryl radical/DPPH coupling product. [Figure 6.1](#) shows two characteristic reduction peaks of 4-nitrobenzenediazonium at 0.07 and –0.21 V in the absence of DPPH. As the surface becomes passivated, no peak is observed in the subsequent cycles. When DPPH is added at an equivalent amount of 4-nitrobenzenediazonium, the reduction peak corresponding to the formation of anion (DPPH → DPPH^{•–}) is observed at –0.06 V and gets superimposed with the diazonium reduction peaks. A pair of reversible redox peaks is also observed for DPPH to DPPH^{•+} at 0.48 V. Interestingly, in the presence of DPPH, the surface does not get passivated indicating that the surface reaction is controlled to a greater extent. [Figure 6.2](#) demonstrates the corresponding mass (frequency) versus time curves recorded at carbon-coated quartz with and without radical scavenger at –0.5 V. The mass increase obtained without radical scavenger fits well with the previously reported results on such coated quartz with a deposition rate of 0.39 mol s^{–1} cm^{–2} and absence of stabilization, that is, the polymer continues to grow with time at the applied potential [50]. On the contrary, the deposition rate is quite slow (0.16 mol s^{–1} cm^{–2} in the initial stage) in the presence of DPPH, and the mass reaches a maximum with a steady-state value just after 20 s. The surface coverage calculated from this curve is 5.7 × 10^{–10} mol cm^{–2}, which corresponds to a monolayer of 4-nitrobenzenediazonium on the carbon surface [51].

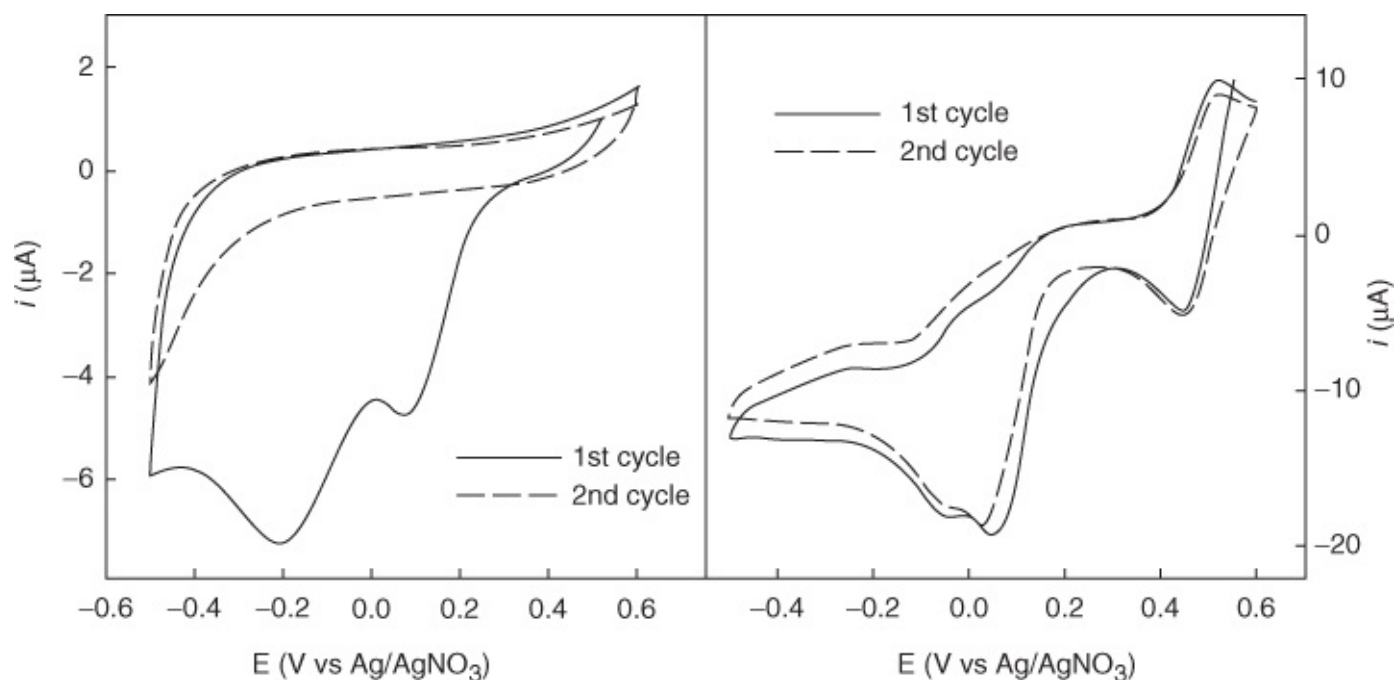


Figure 6.1 Cyclic voltammograms recorded at a GC electrode without DPPH (left) and with 1 mM of DPPH (right) in a solution of CH_3CN containing 0.1 M tetrabutylammonium hexafluorophosphate and 1 mM of 4-nitrobenzenediazonium at a scan rate of 50 mV s^{-1} .

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From multilayer to monolayer using radical scavenger

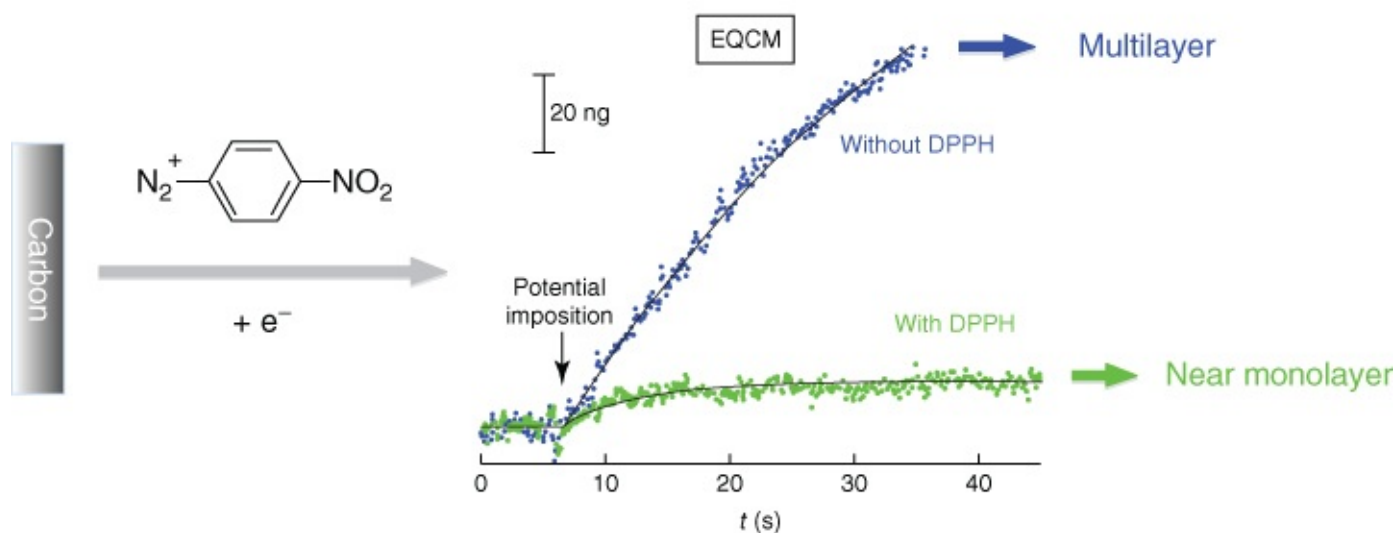
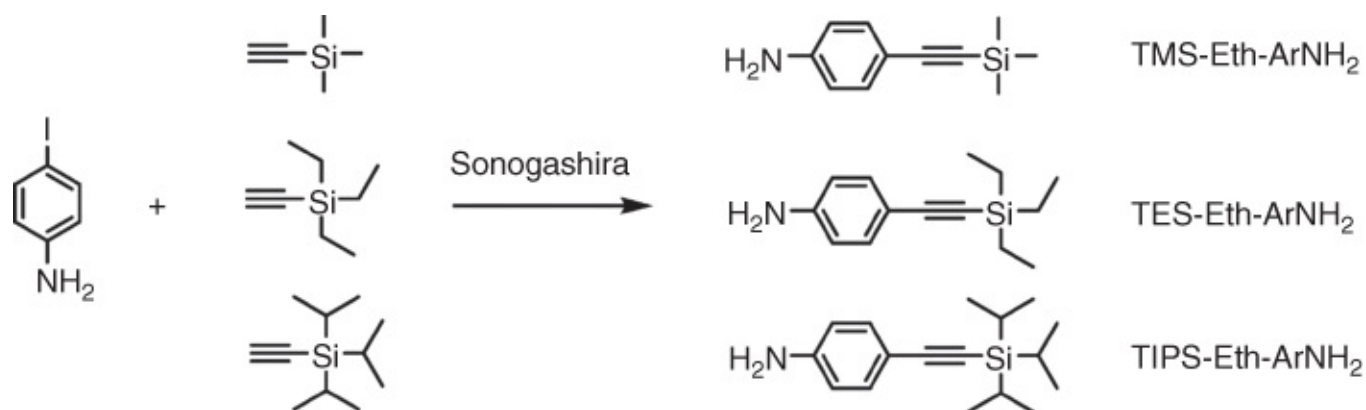


Figure 6.2 Mass versus time response of a carbon coated quartz crystal microbalance for the electrochemical grafting of 4-nitrobenzenediazonium (1 mM) at a fixed potential of -0.5 V versus Ag/AgNO_3 . Data are fitted using the Langmuir model (solid lines).

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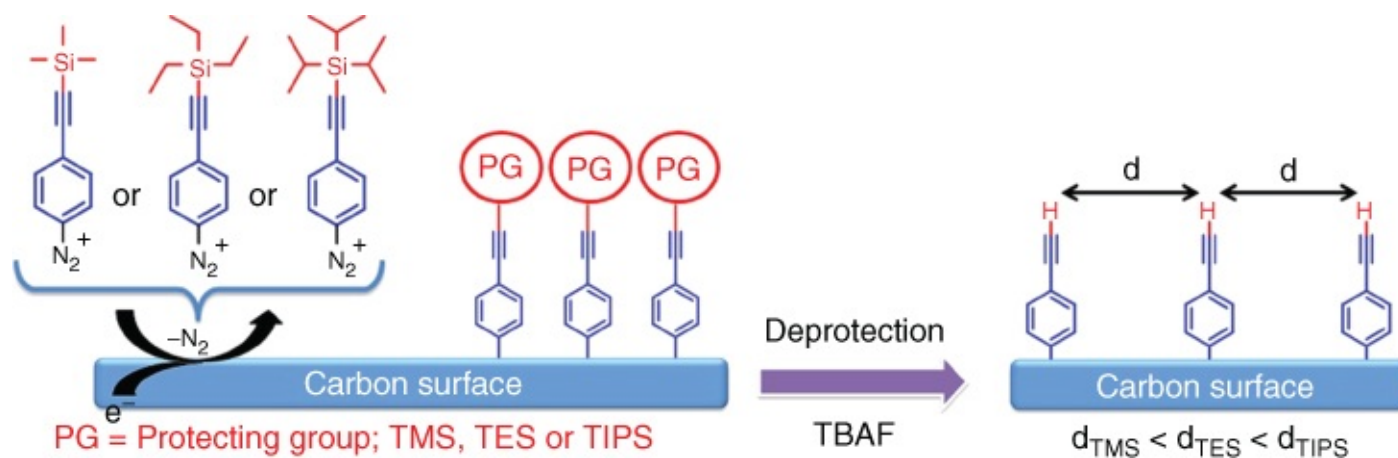
Recently, it has also been shown that a monolayer from aryldiazonium can also be formed by attaching silyl groups at the para position of aryldiazonium [52], which function as a barrier for the already attached aromatic groups against the attack of aryl radicals, that is, silyl groups

prevent the formation of multilayers. Aryldiazonium is functionalized with the silyl group before electrochemical grafting ([Scheme 6.2](#)), and after the formation of monolayer, it is removed by treating in a solution of tetrabutylammonium fluoride in tetrahydrofuran ([Scheme 6.3](#)) to generate a robust ethynylaryl monolayer on the surface. However, the bulkiness of the protecting group means that once it is removed there is a possibility of the surface monolayer possessing pinholes. Taking advantage of the distal alkyne group on the monolayer, the copper-catalyzed azide–alkyne cycloaddition “click reaction” can be performed such that the initial monolayer can be used as a versatile platform for immobilizing many molecules of interest with controlled spatial arrangements.



Scheme 6.2 Reaction to attach silyl groups at the para position of aryldiazonium.

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Scheme 6.3 Modification process to get monolayer surface coverage on carbon using different protecting groups. **TMS**, **TES**, **TIPS**, and **TBAF** represent trimethylsilyl, triethylsilyl, tri(isopropyl)silyl, and tetrabutylammonium fluoride, respectively.

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A two-step “formation–degradation” procedure has also been applied to form a thin layer of benzaldehyde on GC [53]. In the first step, an aryldiazonium salt of a long and bulky hydrazone is electrografted on GC. Being bulky in size, the molecule itself decreases the grafting rate (after the formation of first layer) by preventing the aryl ring, which is buried inside, from the attack of radical. In the second step, hydrazone group is deprotected (degradation step) by converting hydrazone to aldehyde via acid hydrolysis. In this manner, a thin and well-defined

film of covalently attached benzaldehyde with an estimated coverage of 4×10^{-10} mol cm⁻² was formed. In another study, a monolayer derived from aryldiazonium salts was formed on metal by blocking 3- and 5-positions of surface-bound aryldiazonium with large alkyl group [54].

Aryldiazonium chemistry for modifying the surface has also been utilized to prepare mixed layers of two components [21, 55]. Importantly, the ratio of the two components on the surface is dominated by the reduction potentials of the two aryl diazonium salts as distinct from their ratio in solution [8, 19, 56]. That is, the species that dominates on the surface is the one that has the more positive reduction potential. One exception to that rule has been demonstrated by Gui *et al.* [57], where supramolecular interactions between the two species in solution ensured that the ratio of the surface of the two components was always 1 : 1. A sophisticated example of forming mixed layers is where a surface was modified with a mixture of a molecular wire and a diluent to provide efficient interfacing of electrodes with redox proteins [58, 59] and immunosensors [60–62]. In the protein electrochemistry study, an oligophenylethynylene molecular wire and an oligo(ethylene glycol)-terminated antifouling component were attached on a GC surface to achieve direct electron transfer with horseradish peroxidase (HRP) [58]. The molecular wire enables electrochemical communication between the electrode and the protein, and the oligo(ethylene glycol) molecules resist nonspecific adsorption of proteins to the surface. The rate of electron transfer through the layers has been investigated. The electrochemistry of the heme center showed a close-to-ideal full-width half-maximum for the oxidation peak with a very high rate of electron transfer (13.4 s^{-1}). The electrochemistry indicates that the proteins are all in a similar environment. Then, challenge in controlling the ratio of the two components on the surface was also highlighted with this system where, despite solutions that were dominated with the oligo(ethylene glycol) molecules, there was always a high proportion of the molecular wires in the surface because these molecules had the more positive reduction potential [63].

Diazonium ions that are easily reducible have also been observed to graft spontaneously on carbon. For instance, 4-nitrophenyldiazonium ($E_p = 0.25 \text{ V/saturated calomel electrode (SCE)}$) gets spontaneously grafted on GC from a solution of 0.1 M tetrabutylammonium tetrafluoroborate in acetonitrile whereas diazonium salts of diethyl, aminodiphenyl, or triphenylaniline ($E_p = -0.42, -0.35, \text{ and } -0.45 \text{ V}$, respectively) do not [64]. Spontaneous grafting depends on the reduction potential of the diazonium salt and on the nature of the carbon surface, that is, how well the surface supports the reduction process. Carbon surfaces are quite diverse ranging from highly ordered basal plane of HOPG to highly disordered and oxidized carbon black; consequently, their activity toward the reduction process is also quite different. Spontaneous grafting can be monitored from the change in open-circuit potential. Open-circuit potential of GC in a solution of acetonitrile containing 0.1 M tetrabutylammonium tetrafluoroborate solution changes by about 0.25 V with the addition of 4-nitrophenyldiazonium [64]. However, such a change was not observed with the diazonium molecules that are difficult to reduce. Spontaneous grafting on diamond has also been observed [65]. It was claimed that the aryl diazonium salts form a monolayer on hydrogenated nanocrystalline diamond after immersing it for 72 h in a solution of 4-nitrophenyldiazonium in acetonitrile. Raman

spectroscopy measurements have revealed that the spontaneous grafting of 4-nitrophenyldiazonium on graphene involves two steps: (i) adsorption, followed by (ii) grafting, and the grafting rate on bilayers of graphene is slower compared to that on single-layer graphene [66].

Electrografting of diazonium salts has been widely used to create platforms for the detection of biomolecules, cofactors, proteins, enzymes, DNA, and eukaryotic cells [8–10, 67]. Once the substituted phenyl group is attached to the surface, the realm of organic chemistry is available for the modification of these substituents. For instance, Michael addition and click chemistry between an azide and an alkyne molecule have been used for the attachment of ferrocene or biotin [68]. As for biosensors, either the substrate is electrografted with a diazonium salt substituted with a group that can bind, directly [58, 69, 70] or after modification [71–73], to the protein, or the protein is modified with an aniline group that is diazotized and electrochemically attached to the substrate [74–76]. For instance, the amino groups of the protein rabbit IgG (essentially lysine) were reacted with 4-aminophenylacetic acid and the free amino groups were diazotized under gentle acidic conditions to be electrografted on carbon. Alternatively, aryldiazonium salt-modified HRP and antibodies have been prepared and attached to the electrode [74, 77] via electroreduction of diazonium. Electrodes modified with aryldiazonium salts have also been used for a range of other sensing applications, for instance, to detect metal ions using peptide motifs as the recognition element on top of diazonium salt-modified carbon electrode [78], to form nonspecific protein-resistant film (e.g., polyethylene glycol) [79, 80], and so on. Interested readers may wish to check review articles [7, 9, 10, 12] on this topic for more detail.

Considering the good stability of aryldiazonium salts, this process of modification has recently been applied to fabricate molecular junctions in molecular electronics, that is, to construct electrical connection between two conducting substrates [81, 82] (see Chapter 10). The possibility that molecules can be used as microelectronic circuit components was first stated in 1974 in an article entitled “Molecular Rectifiers” [83]. Not only can such “molecular circuits” conceivably increase device density compared to today's state-of-the-art electronic devices, but molecules might also add a wide range of functions and structures that are not possible to achieve with conventional semiconductors. This covalent strategy of modification generates surface with the ability to withstand the direct evaporation of various top contact materials, including copper [84], carbon [85], and silicon [86]. Metal-free, all-carbon (i.e., carbon/nitroazobenzene (NAB)/carbon) molecular electronic junction has been fabricated by reductive electrografting of NAB on pyrolyzed photoresist film (PPF) and electron beam-assisted deposition of carbon (e-C) film on top of NAB (as top contact) [85]. The voltammogram for PPF/NAB/Cu ([Figure 6.3](#)) shows that the junction collapses at approximately -1.86 V ($\sim 300\text{ A cm}^{-2}$) (when Cu is positively biased) with a dramatic and irreversible increase in junction conductance. This behavior has been attributed to the electrochemical oxidation of Cu, resulting in the formation of Cu cations, which undergo electromigration under the applied electric field and get reduced at the PPF electrode to form Cu filaments [87]. The curve for PPF/NAB/e-C ([Figure 6.3](#)) shows that when both the bottom and top contacts are composed of carbon materials, the junction can be swept up to 3.5 V

($\sim 1500 \text{ A cm}^{-2}$), without breakdown. The enhanced electrochemical stability of all-carbon molecular devices is likely related to the difficulty of oxidation or electromigration of both PPF and e-C as compared to most metals. PPF/NAB/e-C junction can sustain temperatures up to 300°C in vacuum for 30 min and can be scanned at $\pm 1 \text{ V}$ for at least 1.2×10^9 cycles in air at 100°C without a significant change in the voltammogram.

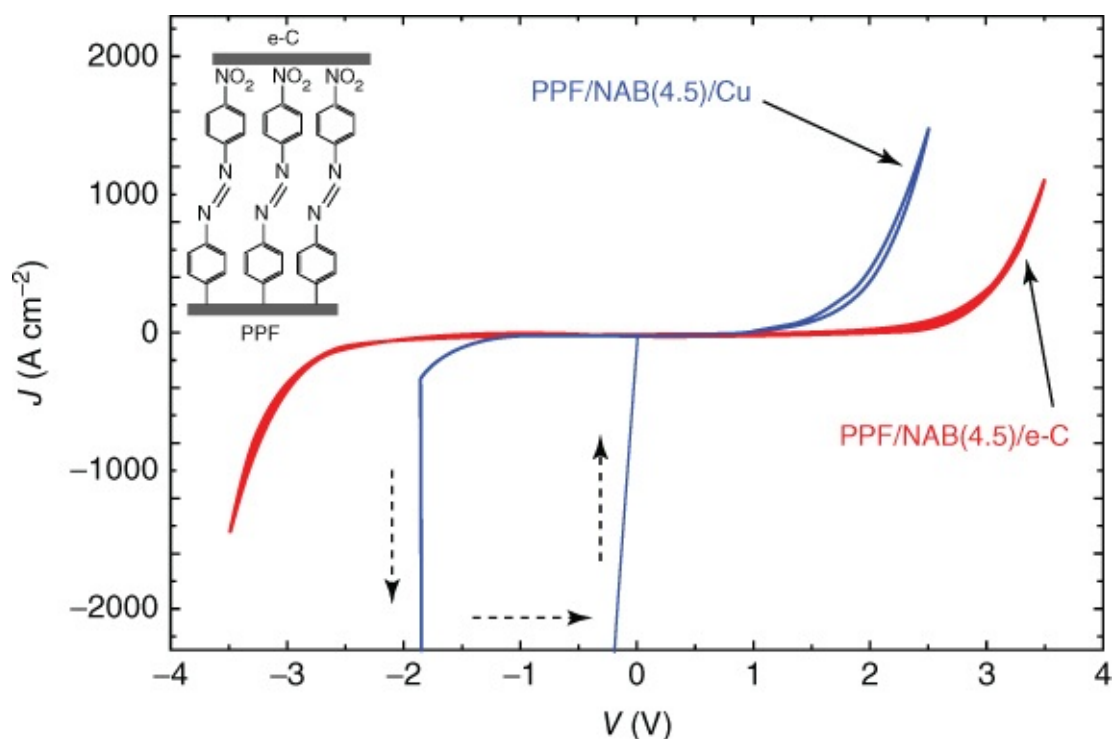
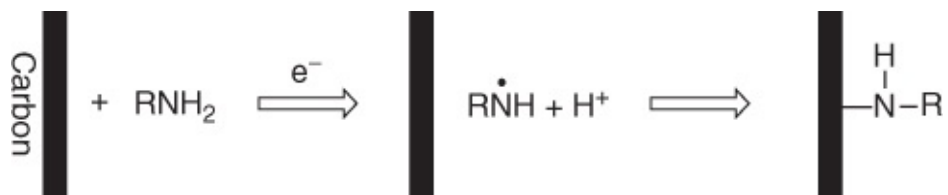


Figure 6.3 Comparison of bias stability of molecular junctions with Cu and e-C as top contacts. Cu junction breaks down at approximately -1.86 V , due to electrochemical oxidation of Cu, while e-C is stable up to a bias of 3.5 V .

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6.2.2 Oxidation of Amine

A variety of amines have been covalently attached through their electro-oxidation onto carbon surfaces. The mechanism ([Scheme 6.4](#)) proceeds via one-electron oxidation of amine moieties to the corresponding radical cation, which deprotonates [88]. The generated radical reacts with the carbon surface, leading to a covalent attachment of the compound via an amine linkage. Oxidation of amine is usually conducted in anhydrous solvents, however aqueous solutions also support this process [89].



Scheme 6.4 Oxidative electrografting of amine on carbon surface.

The attachment of amine groups is usually demonstrated through the observation of

electrochemical signal of a surface-bound redox-active moiety (e.g., anthracene, anthraquinone, or nitrobenzyl) of a molecule or from the blockage of the electrochemical response of a redox species in a solution. For instance, the 4-nitrophenylamine-modified GC electrode shows a pair of reversible peaks for the nitrophenyl group in acetonitrile containing 0.1 M tetrabutylammonium tetrafluoroborate [88, 90]. The redox response of the surface-bound species is also used to assess the coverage of the attached amine on the electrode. Electrografting of amine can also be confirmed by XPS analysis, where the ratio of N/C increases with increasing oxidation potential or the duration of oxidation at a particular potential. Similarly, secondary ion mass spectroscopy is utilized to confirm the attachment (e.g., 2-amino-4-methylthiazole on carbon fibers) [91].

The feasibility of electrografting primary, secondary, and tertiary amines on a carbon surface is demonstrated in [Figure 6.4](#) [89]. Irreversible oxidation waves are observed for all the amine-containing compounds. Oxidation peaks shift more negative, with increased sharpness, as alkyl substituents are added to the amine group. Therefore, the generation of radical cations is most facile for tertiary amines and least facile for primary amines, and is related to the stabilization of cation radical by the alkyl substituents [92, 93]. Intramolecular electron transfer from a redox group conjugated with the amino group also favors the electrografting [94]. The electrografting potential of amino-ferrocifen shifts from 0.7 to 0.4 V/SCE when amine moiety is indirectly oxidized through an intramolecular electron transfer from the amino moiety to the ferrocenyl group after oxidation of the ferrocene moiety at 0.40 V. The XPS spectrum in [Figure 6.5a](#) shows that butylamine is electrografted with an N/C value of 3.7, a value reasonably consistent with other amines. Attachment of primary amines on the electrode surface is further supported by the attenuation of the oxidative adsorption peak current with increasing number of cycles in CV. By contrast, in spite of the facile and extensive oxidation of secondary and tertiary amines, their corresponding cation radicals do not bind effectively to the GC surface. Careful inspection of [Figure 6.5a–d](#) reveals that the extent of electrografting is strongly influenced by the presence of substituents on the nitrogen atom. For example, the surface coverage of the methyl-substituted secondary amine ($N/C = 1.4$) is less than half to that of the primary amine ($N/C = 3.7$), whereas no detectable coverage is observed for tertiary amine. The reason for observing an intense oxidation current without electrografting (in case of tertiary amine) is that for oxidation, amines do not need to come into contact with the electrode surface. Electrons can transfer through an outer-sphere mechanism, but for electrografting the active amine site is believed to be required to come into contact with electrode surface. The presence of additional substituents impedes it from coming into contact with the electrode surface and also due to the absence of a proton that can be lost in the mechanism ([Scheme 6.4](#)), the reaction pathway is not suitable for tertiary amine. Electrografting also depends on the surface condition. The basal plane of HOPG is not active for electrografting of amine, grafting takes place mostly at the edge plane though amine can be oxidized at both planes [7, 8]. However, surprisingly the exact structure and thickness of amine-grafted layers on carbon have not been studied in much detail.

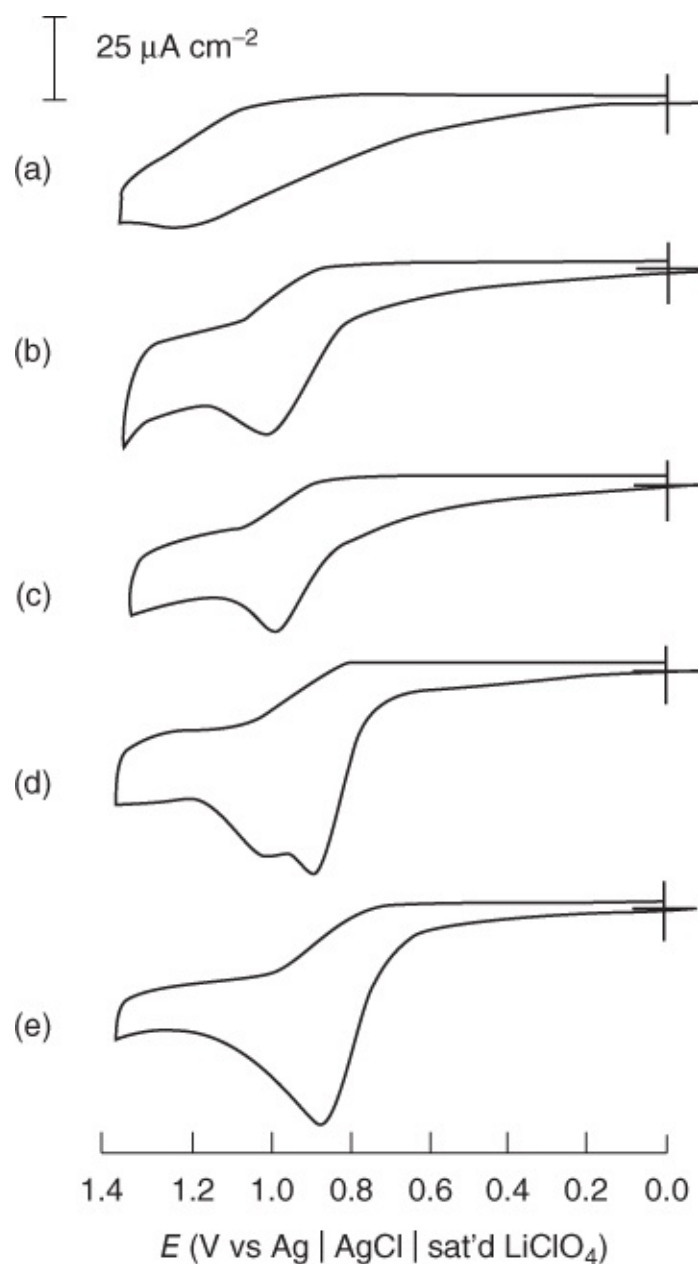


Figure 6.4 CVs obtained at GC in a solution of ethanol containing 0.1 M LiClO₄ and 1 mM (a) butylamine, (b) *N*-methylbutylamine, (c) *N*-ethylbutylamine, (d) *N,N*-dimethylbutylamine, and (e) triethylamine. The scan rate was 10 mV s⁻¹.

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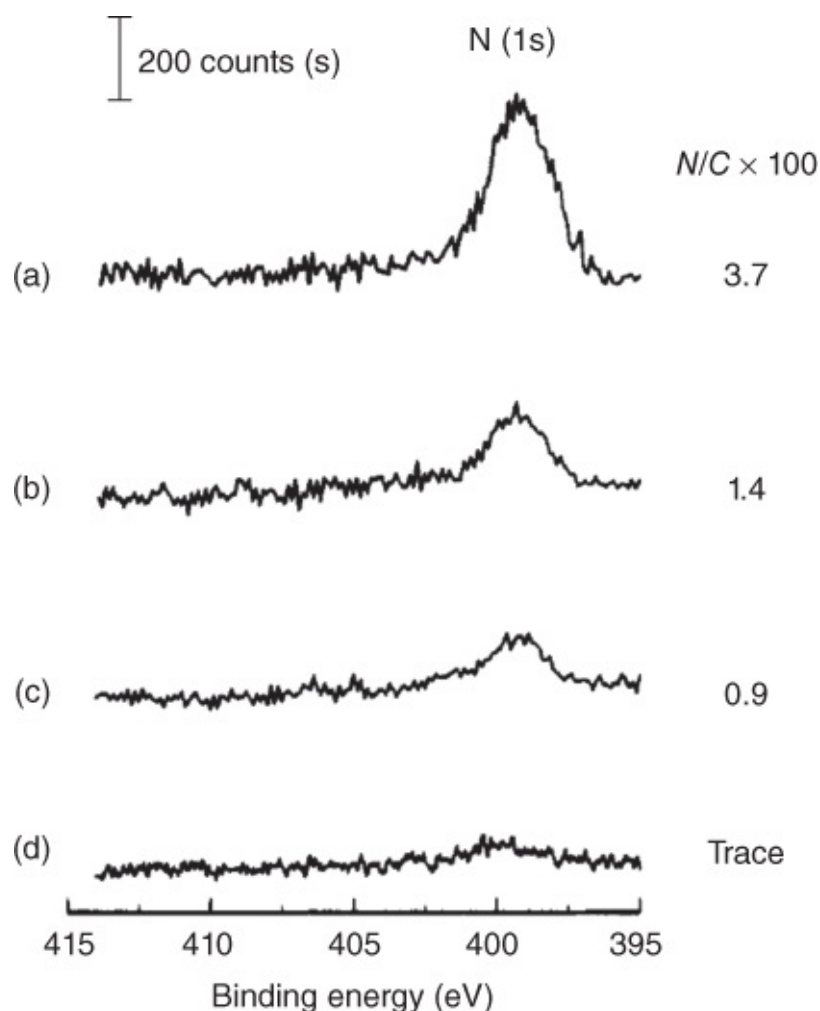


Figure 6.5 XPS spectra in the N(1 s) region for GC electrode modified by cycling the potential once between 0.0 and 1.4 V versus Ag/AgCl in ethanolic solutions of 1 mM (a) butylamine, (b) *N*-methylbutylamine, (c) *N*-ethylbutylamine, and (d) *N,N*-dimethylbutylamine. Scan rate was 10 mV s⁻¹

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In the case of diamines, both amines can be oxidized, but the preference for attachment on a carbon surface with by only one amine, or both, depends on the length of alkyl chain. A single oxidation peak is observed for the two identical and electronically independent amines of ethylenediamine at carbon fibers and 75% of the surface gets covered via a loop-like arrangement of ethylenediamine, that is, both amines are surface bound. The remaining 25% of the surface is covered with molecules where only one amine is attached to the surface [91]. On the other hand, in the case of longer diamines, such as 1,7-diaminoheptane, 1,10-diaminodecane, and 1,12-diaminododecane, typically only one amine binds covalently to the carbon surface. The other amine does however remain free to participate in a reaction to form multilayers [95]. Localized electrografting has been achieved by scanning electrochemical microscopy (SECM), aniline was generated by reducing nitrobenzene at the tip of the microscope ($E_{\text{tip}} = -0.8$ V/SCE), and the generated amine was oxidized (at 0.8 V) on the substrate just beneath the tip, in this way 15 mm modified spots can be drawn on the substrate [96]. Even though monolayers have been claimed in many instances [97], it is likely that

multilayers are often obtained but this has not been definitively confirmed either way.

Mixed monolayers, *N*-(2-aminoethyl)acetamide and mono-*N*-Boc-hexamethylenediamine, have been fabricated recently on GC by electro-oxidation of the corresponding amines to design a maleimide-functionalized electrode, which is then used for the covalent attachment of proteins [98]. The monolayer was functionalized with maleimide through subsequent *N*-deprotection, amide coupling, and solid-phase synthetic steps [99, 100]. The maleimide group is chosen due to its spontaneous reaction with cysteine groups, which can be exploited to immobilize proteins that are genetically engineered to contain cysteine to place them at a suitable position of an interface. The efficacy of this approach has been demonstrated using bovine heart cytochrome *c* as a redox-active model protein. The oxidation of amines for surface modification has also been used extensively to attach metal complexes for the electrocatalysis of oxygen, hydrogen peroxide, and to modify surface for the selective detection of ascorbic acid, dopamine, and uric acid in the presence of other electroactive molecules [7, 9]. Diamines have been electrografted to attach enzymes and proteins with the distal amine group via the carbodiimide chemistry [8]. As the distal end of a grafted molecule can be tuned with the functional group of interest, the scope of using this process of modification as a basis for fabricating sophisticated molecular architectures on surfaces is immense.

6.2.3 Oxidation of Carboxylate

Aryl films can also be electrografted by oxidizing corresponding carboxylates such as 1-naphthylmethylcarboxylate and 4-methoxybenzylcarboxylate on carbon surfaces ([Figure 6.6](#)). The voltammograms show an irreversible oxidation peak, which for simple carboxylates continues to diminish with repeated potential cycling due to the passivation of surface by grafted carboxylate [7, 8, 92, 102]. The apparent rate of electron transfer for the $[\text{Fe}(\text{CN})_6]^{3-/4-}$ redox couple is very low at 1-naphthylmethylcarboxylate- and 4-methoxybenzylcarboxylate-grafted GC and PPFs [101]. Since direct oxidation of aliphatic carboxylates gives rise to carbocations, they cannot be electrografted via covalent bonding on the carbon surface. Mediated decarboxylation is used as an alternative to generate alkyl radicals. In [Scheme 6.5](#), ferrocene/ferricenium (Fc/Fc^+) is used as a mediator to generate $\text{CH}_3\text{COO}^\bullet$ [103]. As a mediator is used, radical generation can occur away from the surface. Consequently, the chance of a radical being trapped by other species (e.g., by other $\text{R}^\bullet$) is high. Hence to get a completely passivated surface, an oxidizing potential needs to be applied for a long time. For instance, at GC in a solution of acetonitrile containing 40 mM tetrabutylammonium acetate and 2 mM ferrocene, the potential was cycled 11 times between 0.0 and 0.9 V versus SCE at a scan rate of 0.1 V s^{-1} to get appreciable coverage.

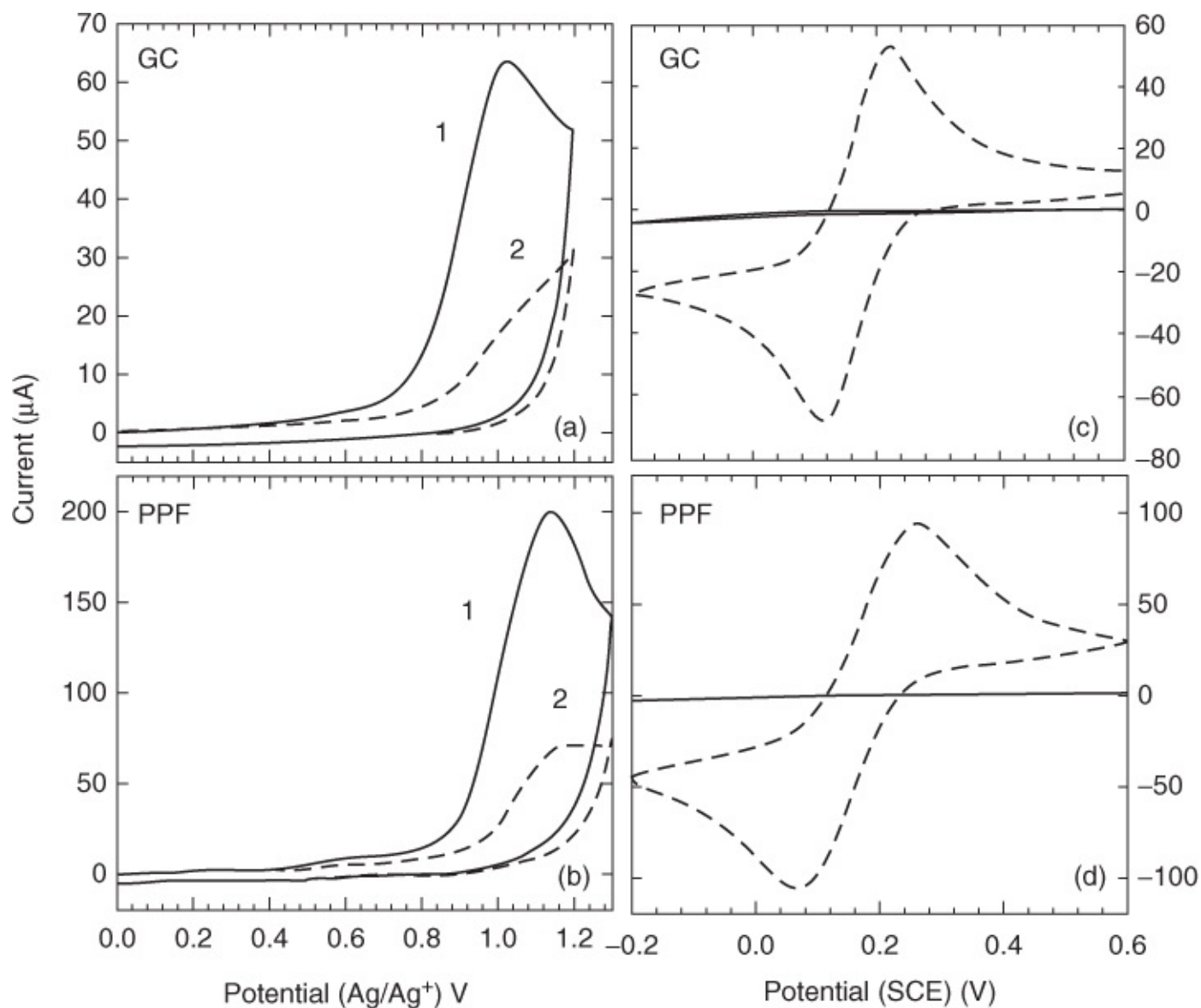
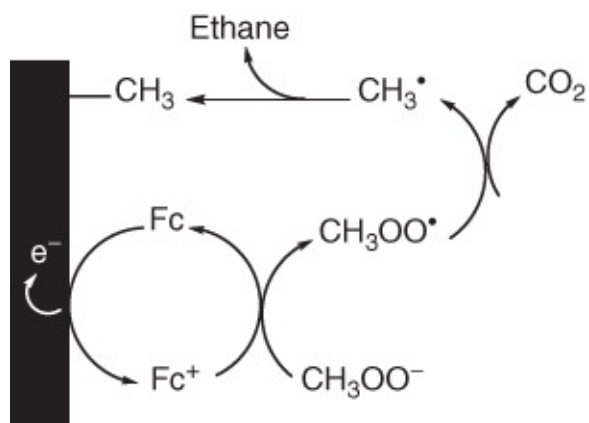


Figure 6.6 CVs measured at GC (a,c) and pyrolyzed photoresist films (b,d). (a,b) First scan (—) and second scan (- - -) (0.2 V s^{-1}) with stirring between scans in a solution of 5.2 mM 1-naphthylmethylcarboxylate and 0.1 M tetrabutylammonium tetrafluoroborate in acetonitrile. (c,d) Scans of 3.1 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ in aqueous 0.2 M KCl at bare (- - -) and 1-naphthylmethylcarboxylate modified (—) surfaces.

(Adapted from Ref. [101]. Copyright 2005 American Chemical Society.)



Scheme 6.5 Mechanism of grafting by using a redox mediator.

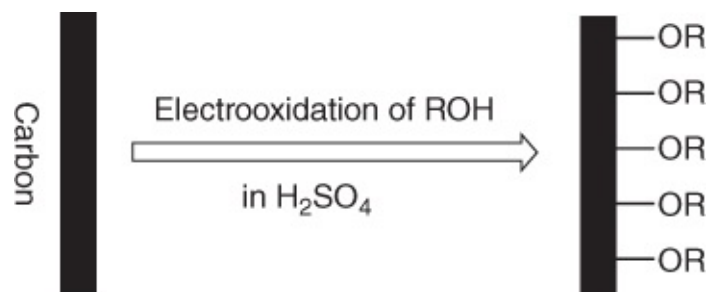
Atomic force microscopy (AFM) depth profiling reveals that the thickness of the films prepared from 1-naphthylmethylcarboxylate and 4-methoxybenzylcarboxylate with two potential cycles ranged from 2.0 to 3.1 nm and 3.3 and 4.7 nm, respectively [101]. The thicknesses of the films are clearly greater than one molecular layer as the lengths of 1-naphthylmethylcarboxylate and 4-methoxybenzylcarboxylate from the carbon surface atom to the outermost atomic radii are 0.72 and 0.82 nm, respectively. Assuming the molecules are perpendicularly oriented with respect to the surface, the average thicknesses are estimated to be three to four molecular layers for 1-naphthylmethylcarboxylate and four to six molecular layers for 4-methoxybenzylcarboxylate.

Thus prepared layers have been further modified to develop electrocatalysts and sensors. Polypyridyl ruthenium–oxo complexes are of particular interest as efficient oxidants for a wide variety of organic molecules, including aromatic hydrocarbons, olefins, alcohols, and ketones. One such electrocatalyst was prepared by first electrografting bipyridine at an applied positive potential followed by treating the modified surface with $[\text{Ru}^{\text{II}}\text{Cl}_2(\text{DMSO})(\text{terpyridine})]$ and then $\text{CF}_3\text{SO}_3\text{H}/\text{H}_2\text{O}$ [104]. Enhanced electrochemical activity has also been observed for the reduction of oxygen at anthraquinone-modified GC electrodes in 0.1 M KOH solution [105, 106]. Anthraquinone was grafted by oxidizing 10-anthraquinone-2-ethanoic acid in dimethylformamide.

6.2.4 Oxidation of Alcohol

Oxidative treatment of a carbon electrode in a solution of 1-alkanol, in the presence of H_2SO_4 or LiClO_4 , results in the alkyl group attaching to the surface via the formation of an ether linkage ([Scheme 6.6](#)). In common with amine and carboxylate grafting on carbon surfaces, electrodes modified in this way become passivated by the organic layer with repeated potential cycling or with increasing time of electrolysis as demonstrated by the reduced Faradaic electrochemistry of these modified electrodes in $[\text{Fe}(\text{CN})_6]^{3-/4-}$ solutions [107, 108]. However, the produced alkyl films on GC have been shown to be less densely packed than alkanethiol layers on gold formed via the self-assembly [108]. Contact angle and capacitance are usually measured to confirm the attachment [109]. Contact angle increases with a concomitant decrease of capacitance as the length of the attached alkyl group increases. It has

been shown that the suppression of the voltammetric response of $[\text{Fe}(\text{CN})_6]^{3-/4-}$ at a GC electrode modified with 1-octanol can be restored with the addition of alkaline earth metal ions. In fact, this phenomenon has been used to detect metals ions [110]. The cathodic current of $[\text{Fe}(\text{CN})_6]^{3-/4-}$ is found to be linearly dependent in the concentration range of 10^{-5} – 10^{-3} M for Ca^{+2} , Mg^{+2} , Sr^{+2} , and Ba^{+2} .



Scheme 6.6 Oxidative electrografting of alcohol on carbon surface.

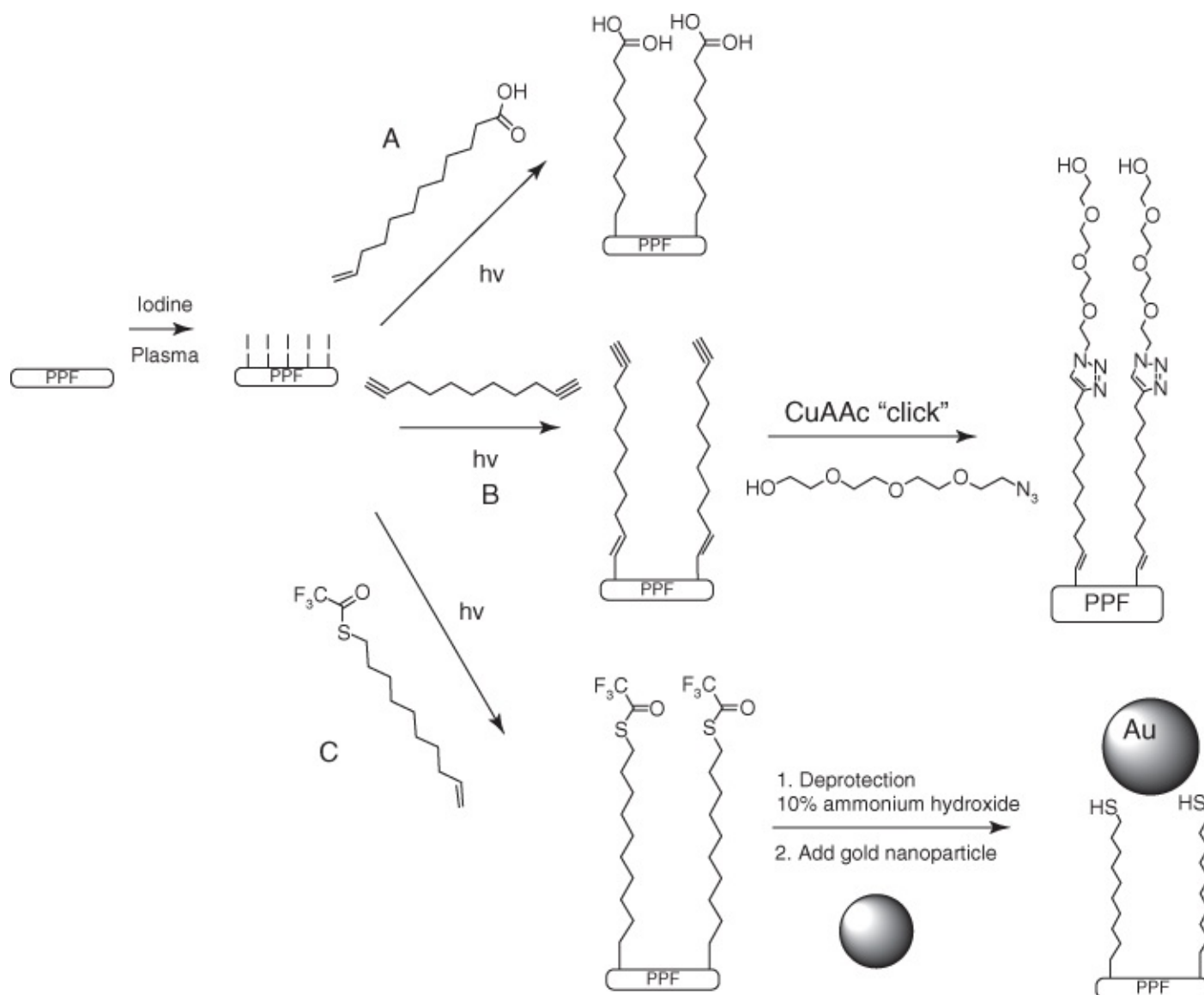
In contrast to using 1-alkanol, the modification of a GC electrode with 1, ω -alkanediol results in the formation of a hydrophilic surface [111]. It has been proposed that during the anodic electrografting, the distal hydroxyl group of the grafted 1, ω -alkanediol oxidizes to carboxyl moiety, and at such surfaces oxidation of ascorbic acid gets blocked completely due to electrostatic repulsion, while a well-defined anodic peak is observed for dopamine [111]. Triethylene glycol [112–114] has also been attached to carbon by oxidative electrografting to produce carbon–O–(CH₂CH₂O)₂CH₂COOH as the modified surface. Oligo(ethylene glycol)-modified surfaces are frequently used as antifouling layers to the nonspecific adsorption of protein.

6.2.5 Hydrogenation and Halogenation of Carbon

One of the most powerful ways of activating carbon materials is H-termination, a process commonly performed using hydrogen plasma [115]. However, electrochemical techniques have also been used recently. H-terminated diamond electrode was prepared by applying –35 V versus Ag/AgCl in 2 M HCl solution [116]. The exceptional high stability of the diamond electrode allows the application of such high potential generating a hydrophobic surface with virtually no oxide. The same approach also works for other materials such as amorphous graphite. Electrochemical hydrogenation is proposed to begin through the production of hydrogen radicals. At sufficiently high negative potential, protons in the acidic solution reduce to hydrogen radicals and bind with the surface to give a hydrogenated surface. According to density functional theory, the energy level of the electron in the hydrogen radical is 3.68 eV higher than the energy of the electron in the σ -bond of H₂. Hence, theoretically, a potential of 3.68 V versus the normal hydrogen electrode should be sufficient to generate hydrogen radicals. However, in practice, higher negative potentials need to be applied, which is argued to be related to the inhomogeneous doping (i.e., conductivity) and surface contaminants on boron doped diamond (BDD) [116]. In support of this argument, recently it has been reported that GC (conductivity higher than BDD) can be hydrogenated by applying –5 V versus Ag/AgCl in 2 M HCl solution for 15 min. Hydrogenation results in the formation of C–H

dipoles with electropositive hydrogen slightly susceptible to nucleophilic attack [117]. H-terminated surfaces have been exploited to form stable layer of alkenes, azides, and alkylthiols [118–120]. The hydrogen–carbon bond is quite stable, such that a high energy source such as UV light is required to break the bond for further modifications. Photoejection of electrons into the acceptor levels of the alkenes initiates the functionalization reaction and controls the overall rate [118, 121, 122]. On the other hand, the strength of carbon–halogen bonds is lower than carbon–hydrogen bonds, hence recently the halogen-terminated surface is preferred as an activated platform for further modification.

Iodination of the PPF surfaces was performed using a radio frequency plasma generator in a reaction chamber. Iodine plasma can roughen the surface hence, using plasma of optimized power for an optimized time is crucial. The surface constructs explored to demonstrate the scope of this new carbon electrode modification strategy are shown in [Scheme 6.7](#) [123]. As the strength of the carbon–iodine bond is less, modification of the iodinated PPF surface with both alkenes and alkynes was conducted with visible light ($\lambda = 514 \text{ nm}$). The use of 1,8-nonadiyne enables further modification via “click” chemistry, while S-undec-10-enyl-2,2,2-trifluoroethanethioate (C11-S-TFA) facilitates the investigation of the layer on the surface with XPS due to fluorine being an excellent XPS marker. Deprotection of the thiol on C11-S-TFA allows the attachment of gold nanoparticles, which could be imaged by scanning electron microscope. Formation of layers and their stability were characterized using cyclic voltammetry. This surface modification strategy has potential for various sensing applications, such as formation of molecular wires, DNA patterning, and cell adhesion. In another study [120], a two-step process has been described for the electrochemical hydrogenation of a GC electrode followed by either chemical or electrochemical chlorination to provide a highly reactive surface for further functionalization. The GC surface was hydrogenated by applying a potential of -5 V versus Ag/AgCl and 20 mA current in a solution of 2 M HCl for 15 min , whereas for chlorination 2 V and 20 mA current was applied at the hydrogenated surface for 5 min in a solution of $2 \text{ M HCl}/2 \text{ M HNO}_3$ ($3 : 1$ ratio). A ferrocene-labeled alkylthiol was used as a model system to demonstrate the potential application of the resulting chlorinated surface. Chemical halogenation of H-terminated carbon surfaces can be performed using benzoyl peroxide and phosphorus pentachloride in an anhydrous organic solvent. The surface obtained, following electrochemical chlorination, was observed to be markedly less damaged, and consequently, more organized as compared to the surface obtained from chemical chlorination.



Scheme 6.7 Various surface construction strategies on iodinated PPF. Firstly, PPF surface is iodinated by exposing it to iodine plasma. Iodinated surface can then be reacted with different alkene and alkyne compounds in the presence of appropriate light (A, B, and C). Further surface modification can then be achieved via “click” reaction (B) or attachment of nanoparticle (C).

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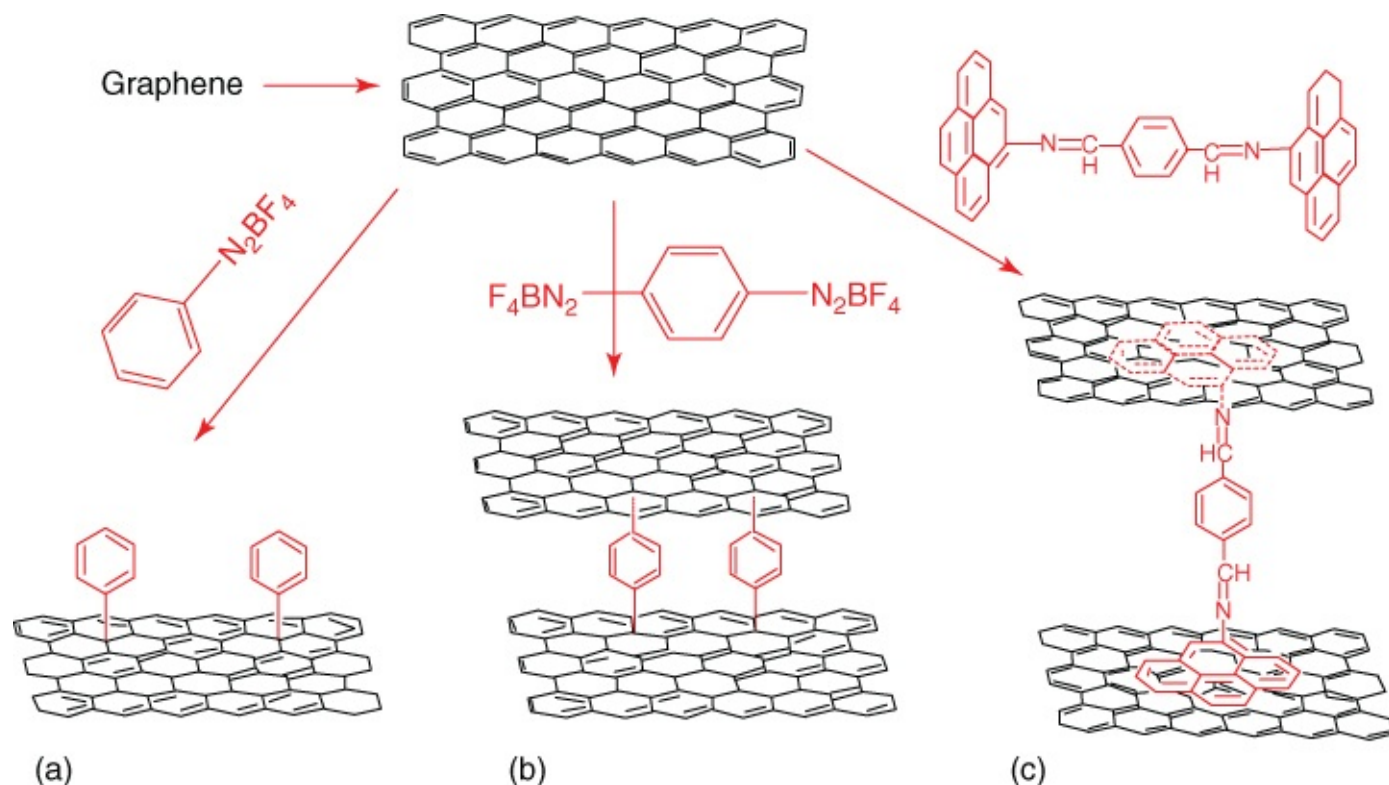
To extend the hydrogen evolution potential in an aqueous media, a fluorine-terminated diamond surface is prepared in a radio frequency plasma reactor of CF–He [124]. Fluorine-terminated diamond is usually used to study electrode reactions that require high overpotential. For covalent attachment of different biomolecules, hydrogen-terminated diamond electrodes are also treated with ammonia plasma to prepare the surface with terminal amine groups [125].

6.3 Noncovalent Modification

6.3.1 π – π Stacking

As the name implies, π - π stacking requires continuous π -conjugation on the surface of the electrode to be modified and in the molecule to be used for the modification. So far, most of the studies on this type of modification have been performed using graphene or carbon nanotubes [16] (see Chapter 3 and 4), as an electrode substrate and pyrene as a molecule of attachment [13]. Graphene is used as it displays unique physical and chemical properties, such as extremely high electric and thermal conductivity [126–128], high strength, and large surface area [129, 130]. Electrons in a graphene layer move ballistically without collision and scattering with mobilities as high as $15\,000\text{ m}^2\text{ V}^{-1}\text{ s}^{-1}$ at room temperature [131]. Pyrene is used as its four benzene rings, as compared to one or two aromatic rings in other molecules, provide enough strength in the π - π stacking interaction so that the molecules do not get detached during successive experiments done to further modify the surface and/or to detect analyte. Also pyrene precursors can be freely synthesized with a range of functional side chains [132]. The strategy of using functional pyrene derivatives is commonly employed when interfacing graphene with biological systems. However, besides pyrene [133, 134], pentacene [135], dopamine [136], and some other aromatic derivatives were also used [137–139]. By functionalizing graphene with different chemical compounds, it can be endowed with the desired properties.

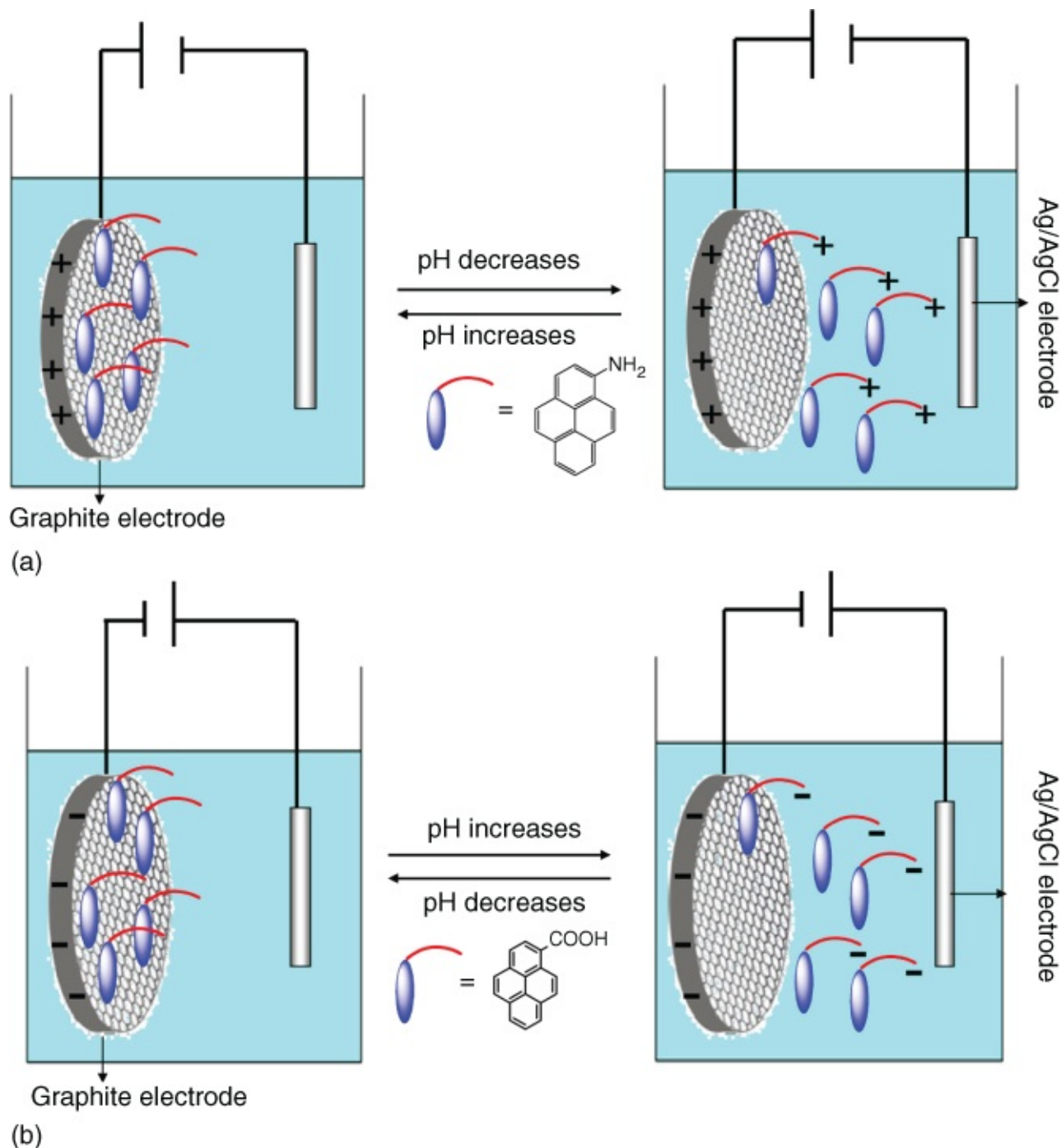
The basic process of modifying an electrode with π - π stacking is quite simple. Simply, the carbon material with π -conjugation is incubated in a solution of an appropriate molecule. Apart from washing, no other surface treatment is required. π - π stacking does not destroy the conjugated structure of graphene, hence the unique properties of graphene are not compromised. A significant decrease in electrical conductivity of graphene paper has recently been observed while modified with monoaryldiazonium and biaryldiazonium salts through a covalent bond compared to the graphene paper modified with bipyrene-terminated molecular wire via π - π stacking ([Scheme 6.8](#)) [140]. When graphene is modified with monoaryldiazonium or biaryldiazonium salt, its in-sheet charge transfer is disturbed as the π -conjugation is destroyed partially due to its covalent attachment with the diazonium functionalities of monoaryldiazonium or biaryldiazonium salt, resulting in the decreased conductivity. The biaryldiazonium salt might function as a molecular conduit enhancing the inter-sheet charge transfer, but its contribution to the overall conductance is less compared to the decrease in in-sheet charge transfer due to the formation of a covalent bond. However, when a bipyrene-terminated molecular wire is attached via π - π stacking interaction, π -conjugation of graphene remains undisturbed, and the rate of inter-sheet charge transfer increases as the bipyrene-terminated molecular wire works as a conduit for electron transfer.



Scheme 6.8 Modification of graphene with (a) monoaryldiazonium salt, (b) biaryldiazonium salt, and (c) bipyrene-terminated molecular wire.

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The reversibility of the π - π stacking interaction has recently been studied by using pyrene molecules with appropriate functionality [141]. The molecules that were studied are 1-aminopyrene, 1-pyrenecarboxylic acid, and doxorubicin hydrochloride. For the π - π stacking attachment, graphite electrodes were incubated in an appropriate solution of pyrene for an optimized amount of time, while for desorption, charge on the surface (i.e., of the functional moieties) was controlled by changing pH, and under a sufficiently high potential of opposite charge, the pyrene can be desorbed from the surface ([Scheme 6.9](#)). For instance, 1-aminopyrene is positively charged at pH 2 as $-NH_2$ becomes $-NH_3^+$ in this pH, and at an applied potential of 0.8 V versus Ag/AgCl for 60 s, 90% of the attached molecules could be desorbed from the surface. The reversibility of the π - π stacking interaction was monitored using CV and XPS. Cyclic voltammogram of bare graphite electrodes does not show redox response in phosphate buffer of pH 7; however, when the pyrene molecule (e.g., 1-aminopyrene) is attached on the surface, well-defined redox peaks were observed indicating its attachment. While desorbing, the redox response decreases with applied potential and time. The surface coverage of pyrene derivatives were calculated from this redox response. However, as expected, neutral pyrene molecules do not desorb under an applied potential.



Scheme 6.9 Reversible interaction of charged pyrene derivatives on graphite surface.

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Using density functional theory, the binding energy between pyrene and graphene is calculated to be $26.8 \text{ kcal mol}^{-1}$, which increases with the presence of $-\text{NH}_2$ and $-\text{COOH}$ functional moieties in the pyrene molecules. Positively charged 1-aminopyrene has a much stronger binding energy ($54.1 \text{ kcal mol}^{-1}$) than that of neutral 1-aminopyrene ($35.2 \text{ kcal mol}^{-1}$), while with 1-pyrenecarboxylic acid the interaction energy changes little between the neutral and the negatively charged states ($35.7 \text{ kcal mol}^{-1}$) providing a guide to how large the applied potential has to be and for how long it needs to be applied to gain a required reversibility of an interface. A potential application of this approach in drug delivery was demonstrated by

studying the release of adsorbed doxorubicin.

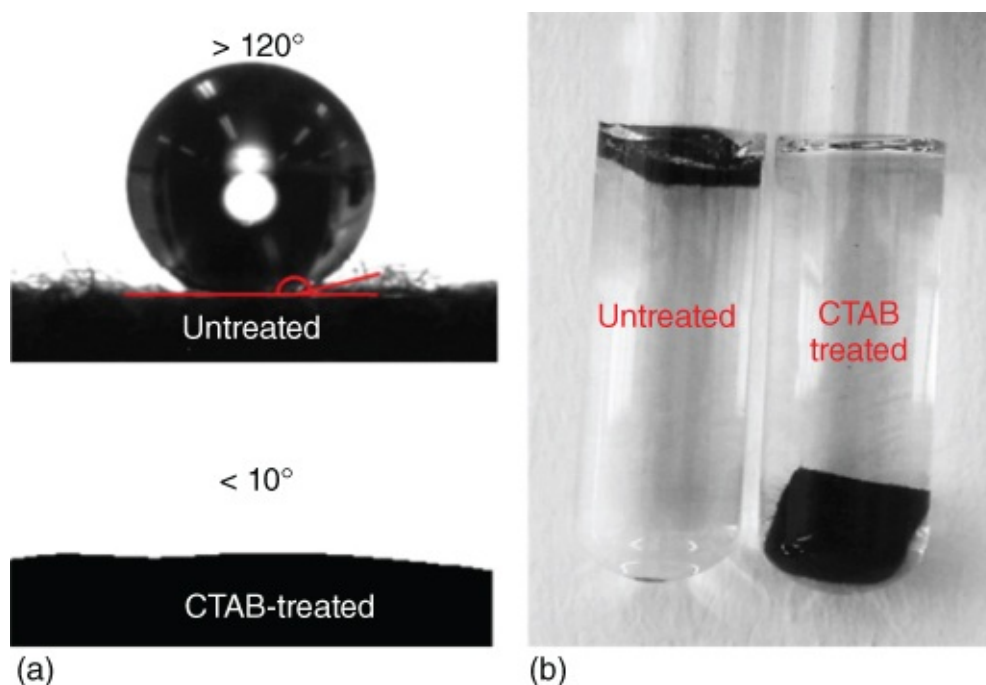
Single- and double-layered graphene nanosheets from graphite oxide have been exfoliated by π - π interaction [11]. During the exfoliation process, the planar structure of the pyrene group works like a “sucking disk” to drag the bound graphene sheet off the graphite precursor demonstrating the strength of the π - π stacking interaction. Simple ultrasonication is usually used to assist the top graphene layer(s) to exfoliate from the graphite [142–144]. π - π functionalization of graphene sheets with a conducting polymer (sulfonated polyaniline) is also exploited to produce a water-soluble and electroactive composite [145]. Synthetic DNA has begun to be incorporated into graphene-based electrochemical sensors too [146], at least partially because of its potential of being physically adsorbed by π - π stacking. Using labeled quantum dots as signal probes, a “signal on” electrochemiluminescence detection strategy has been proposed for selective and sensitive detection of dopamine [147]. In this process, a boronic acid-functionalized pyrene probe is self-assembled on the side walls of carbon nanotubes via π - π stacking, as a capture probe on a GC electrode and then quantum dots with appropriate functionalization were captured on the surface as electrochemiluminescence emitters.

6.3.2 Surfactant

Two important aspects of surfactants, (i) adsorption at the interface and (ii) aggregation into supramolecular structures, are advantageously used in electrochemistry for different purposes. The amphiphilic property allows surfactants to be self-assembled into single or ordered stacks of bilayer with many functions, including microporosity, selective permeability, and binding biomolecules on or within bilayers [148–150]. Because of these properties, surfactants have been used in the development of electrochemical sensors to entrap proteins in the surfactant bilayer, arrange proteins into a correct orientation, and facilitate the electron transfer between proteins and electrode [151, 152].

Surface modification is conducted simply by soaking the electrode of interest in a vigorously stirred solution of surfactant usually for 5–20 min followed by rinsing in deionized water. Contact angle measurements are used as a quick test ([Scheme 6.10](#)) to confirm the success of the modification [148, 153]. It was found that the adsorption of cetyltrimethylammonium bromide (CTAB) onto the active carbon–water interface mainly takes place through ion exchange, ion pairing, and hydrophobic bonding [154]. The predominant mechanisms at a lower concentration of CTAB have been shown to be ion exchange and ion pairing. The hydrophobic bonding mechanism predominates as CTAB concentration increases. The amount of CTAB adsorbed on the surface decreases with increasing temperature indicating that the adsorption process is exothermic, hence the isosteric adsorption enthalpy for this system is found to be negative. On the contrary, the value of the isosteric adsorption entropy was found to be positive as the degree of freedom of the water molecules increases with adsorption. Because of the adsorption of the alkyl groups on the surface, the number of water molecules surrounding the hydrophobic moiety decreases, increasing the freedom of water molecules. Also, the higher the oxygen content in an activated carbon, the lower the amount of surfactant adsorbed on it [155], hence no obvious relationship can be drawn between the surfactant

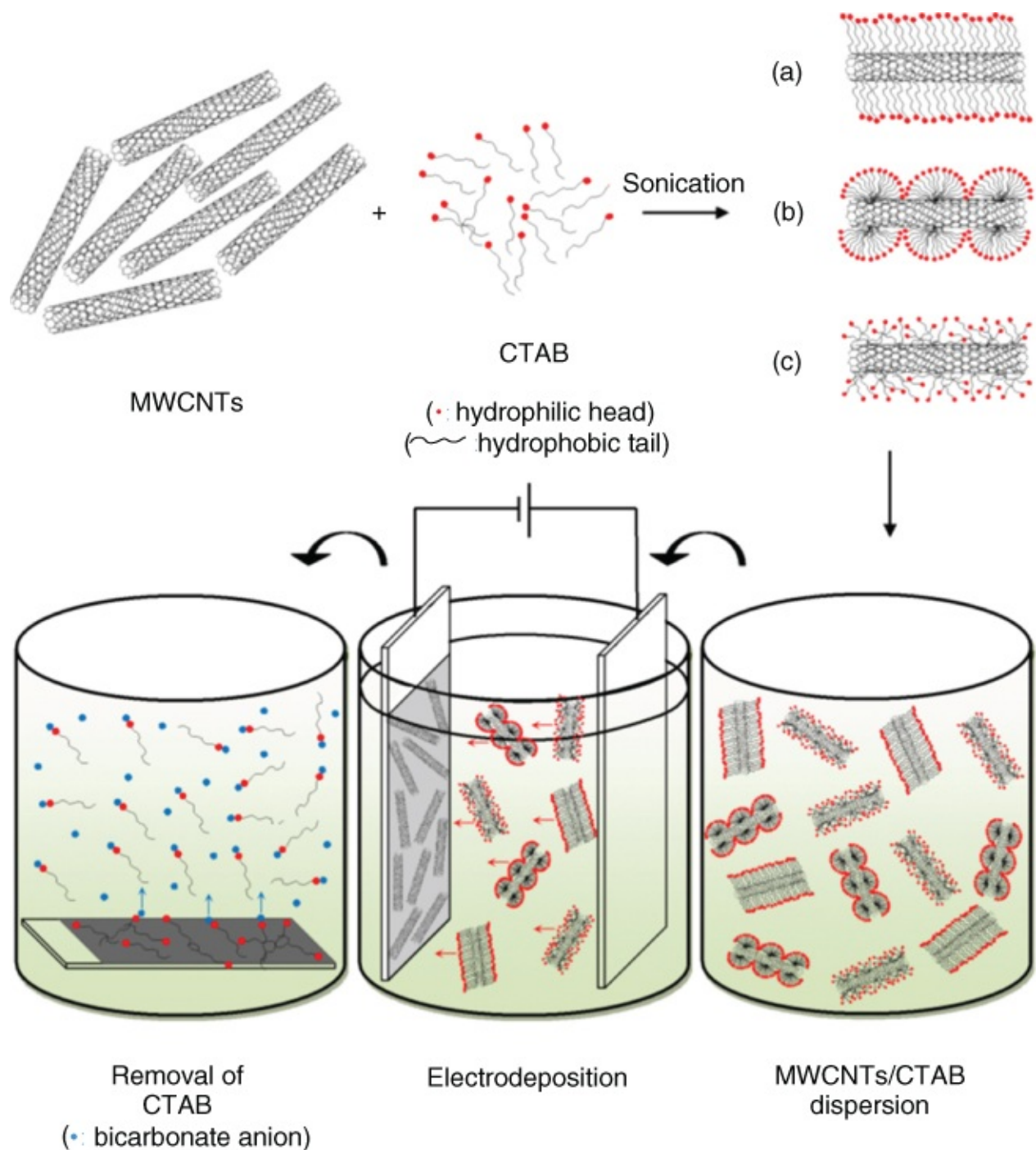
amount adsorbed with the surface area.



Scheme 6.10 Water contact angle (a) and water absorption (b) images of untreated and CTAB-treated carbon felts.

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Surfactant-assisted dispersion of multiwalled carbon nanotubes (MWCNTs) has been studied to examine the effects of nanotube diameter, surfactant concentration, and pH of the solution on the dispersibility of nanotubes [156]. The surfactants used in this study were sodium 4-dodecylbenzenesulfonate, CTAB, sodium dodecane-1-sulfonate (SDS), Pluronic® F-68, Pluronic® F-127, and Triton® X-100. Dispersion of MWCNTs in aqueous media was strongly dependent on the diameter of nanotubes suggesting that information gathered for the dispersion of single-walled carbon nanotubes (SWCNTs) may not be applicable to the dispersion of MWCNTs. At SWCNTs and graphite, the interaction of surfactant was primarily hydrophobic, whereas Coulombic interactions and Lewis acid–base complexation were found to play a key role in surfactant-assisted dispersion of MWCNTs. CTAB was the best surfactant for MWCNTs at neutral pH. MWCNTs have been successfully electrodeposited on carbon electrodes using a cationic surfactant, CTAB [149]. Cationic surfactant makes the nanotubes positively charged, and through simple electrodeposition process, these charged nanotubes are driven toward the cathode to form a thin layer at the electrode surface. For better dispersion of MWCNTs and CTAB, the mixture is ultrasonicated before electrodeposition. Possible arrangements of CTAB on MWCNTs are illustrated in [Scheme 6.11](#)a–c.



Scheme 6.11 Electrodeposition of MWCNTs using CTAB surfactant. (a), (b) and (c) show the possible arrangements of CTAB on MWCNTs.

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Carbon felts treated with CTAB were found to accelerate the formation of biofilm and enhance current output of microbial bioelectrochemical systems. The current density at the treated electrode is 23.8% higher than that of the untreated counterparts as biomass grows favorably at the treated electrode compared to the untreated electrode. CTAB treatment makes the surface of carbon felt hydrophilic and positively charged by introducing the $-N^+(CH_3)_3$ groups on which the bacterial colony grows favorably [157]. Besides CTAB, other surfactants, such as SDS, trimethyl benzoyl chloride (TMBC), and Umonium³⁸® were also tested. CTAB-modified

carbon paste electrodes have also been applied for the simultaneous determination of different analytes, such as ascorbic acid, dopamine, and uric acid [158–161]. Hemoglobin has been successfully immobilized on these surfactant monolayers to form stable protein–surfactant composites [162, 163]. The resulting surface-confined hemoglobin exhibits well-defined direct electron transfer behavior in all positively, neutral, and negatively charged surfactant films demonstrating the important role of hydrophobic interactions in the adsorption of hemoglobin on surfactant films. The hydrophobicity of the surfactants rather than their charge is found to be crucial in promoting the electrode response. Ultraviolet–visible (UV–vis) and reflection–absorption infrared (RAIR) spectra suggest that the native conformation of hemoglobin in these films remains unchanged; consequently, its catalytic activity toward hydrogen peroxide and nitric oxide was found to be almost the same as compared to its activity in the absence of surfactant [164]. The electrochemical response of screen-printed electrodes toward hydrogen peroxide increases 8- to 10-fold while modified with nonionic surfactants, for example, Triton X-100 and Tween 20 [165].

Surfactants are routinely used in the production of graphene and additionally in their stabilization with the aim of reducing the likelihood of coalescing [166]. Surfactant is an integral part of graphene and sometimes its presence might be disadvantageous [167] in electrochemical processes, for example, in the electrochemical oxidation of nicotinamide adenine dinucleotide (NADH) [168]. Control experiments, that is, with and without the surfactant that is used in the preparation of graphene is particularly encouraged in deconvoluting the origin of the electrochemical response of graphene-modified electrodes.

6.4 Future Directions

Modification strategies that are described in this chapter are quite versatile. A wide range of classes of molecules can be attached on carbon. If in case a molecule is not attachable in its native form, appropriate functionalization can be carried out to enable attachment. However, the formed layers on carbon, especially with covalent strategies, are often ill-defined. As the covalent strategies are radical mediated, multilayers can form or there can be branching due to the high reactivity of the radical. After electrochemical generation of the radical, it reacts with either the electrode surface or the molecule that is already grafted on the surface leading to branching. The electrode-radical reaction is favorable as compared to molecule-radical reactions. Hence, to form a monolayer or to gain a precise control over modification, the kinetic gap between the reactions needs to be exploited. Little research has recently been directed in this track. There is a lot more to do to develop a simple strategy for forming monolayers, which is crucial when the exact position of biorecognition or redox species relative to the electrode surface must be known. Also as today's microelectronics include intricate parallel fabrication and operation of millions of active devices, this knowledge will provide an extra grip in “wiring up” the molecular junction of microelectronics with the polymer of diazonium salts or others.

While forming the top contact in a molecular junction via direct deposition of a metallic film, the underlying molecular layer sometimes get damaged or sometimes the deposited metal

penetrates into the molecular layer and forms “short circuits” coming in contact with the electrode substrate. The π – π modification strategy that is described in this chapter can be utilized to circumvent this problem. To the best of the authors' knowledge, no studies have been done so far in molecular junctions using this strategy. π – π stacking is not as strong as the covalent bond is, hence researchers may want to increase the strength of π – π stacking by increasing the number of aromatic rings at the distal end of the molecule to be connected via the top contact. For π – π stacking, the top contact just needs to come into contact with the molecule such that it will not be damaging to the underlying molecular layers.

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Chapter 7

Carbon Materials in Low-Temperature Polymer Electrolyte Membrane Fuel Cells

Michael Bron and Christina Roth

7.1 Introduction

Carbon is a material commonly used in electrochemical energy devices, such as fuel cells, electrolysis cells, and redox flow and lithium-ion batteries. In these systems, it fulfills various functions, which can be as diverse as serving as catalytically active material, nanoparticles' anchor, intercalating electrode, or electron-conducting additive.

Carbon itself is so vital because it is cheap, chemically inert, electron conductive, and also (more or less) stable under fuel cell operation conditions. Furthermore, it may offer high surface area and sometimes even add to the catalytic activity, as for instance in the oxygen reduction reaction (ORR) at the fuel cell's cathode. However, the *material* “carbon” is not unambiguously defined. And more often than not researchers referring to “carbon” are not discussing the C element in group IV (or 14) of the periodic table, but rather mean the broad range of carbonaceous materials, mostly containing not only carbon in a crystalline arrangement (which makes up sp^2 graphite and sp^3 diamond) or in a disordered manner, but also H, O, and other elements. A straightforward classification is indeed not easy. For instance, carbon materials can be categorized with respect to their shape or morphology, their graphitic content, porosity, surface area, and surface functionalities, to name just a few ([Figure 7.1](#)). The following two examples may serve to demonstrate the broad spectrum of structures and properties, which are covered by the term *carbon materials*. It includes among many others, for example, mostly amorphous carbon black (CB), the most prominent CB type in fuel cells being Vulcan XC-72, and also perfectly hexagonally arranged two-dimensional (2D) single-layer graphene. These two not only differ in dimensionality, but also in defect density, graphite content, and surface area, making a direct comparison impossible.

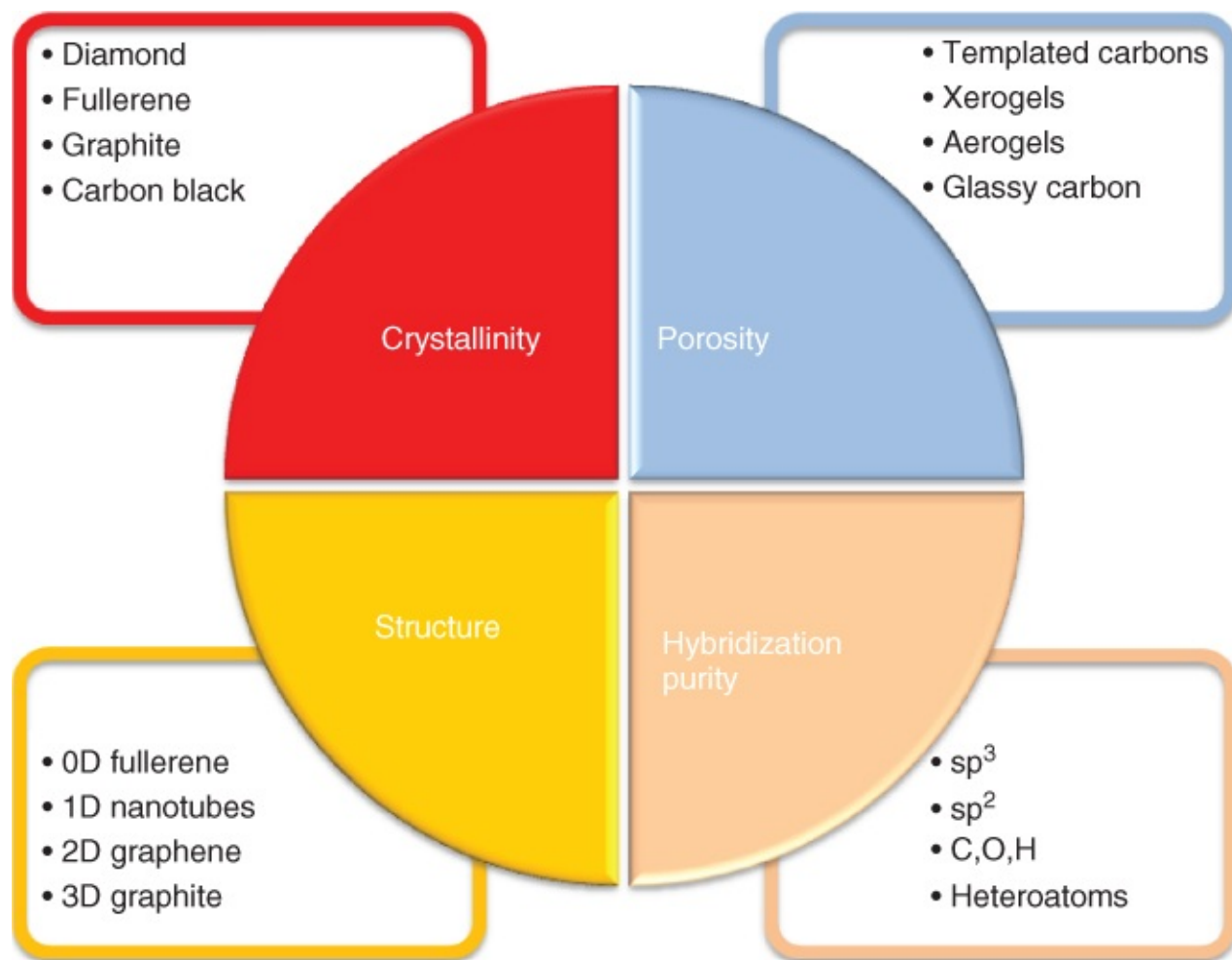


Figure 7.1 Schematic illustration to categorize the most prominent carbon materials.

Carbon materials are organized in a multiscale hierarchical structure built up from subunits from the subnanometer to the millimeter scale in entities, such as crystallites, particles, and 2D and three-dimensional (3D) agglomerates. This multiscale organization can serve as a fingerprint of their preparation conditions (i.e., synthesis, fractioning, and milling) and is also responsible for some of their later properties. Moreover, each carbon material may be functionalized by various treatments in order to modify its surface functional groups or to integrate heteroatoms, such as N and B, into the structure. An effort to classify the different kinds of carbon materials, some of which are also applied in fuel cells and related experiments, has been made in [Figure 7.1](#).

7.1.1 Brief History of the Most Prominent Carbon Materials Applied in Fuel Cell Research

For many years, carbon science was a backwater field [1], which entered the limelight only at the end of the twentieth century with the discovery of *fullerenes* in 1985 by Kroto *et al.* [2], carbon nanotubes (CNTs) by Iijima in 1991 [3], and – most recently – *graphene* by Geim *et al.* in 2004 [4]. Fullerenes, CNTs, and graphene have well-defined crystalline structures with fascinating properties, but only the latter two play a significant role in fuel cell research.

CNTs consist in a specifically rolled single graphite layer, the so-called graphene sheet, which depending on the folding geometry results in armchair, zigzag, and chiral nanotubes offering different related properties [1] (see [Chapter 3](#)). Such single-walled CNTs, however, were so far only scarcely used in applied fuel cell research. By contrast, multiwalled CNTs consisting of multiple rolled concentric graphene layers either in single-walled nanotube within larger single-walled nanotube manner or as one single sheet rolled in around itself have been applied manifold with promising results. In contrast to their single-walled counterparts, they are also cheaper and therefore more compelling with respect to future commercialization. And apparently, when applied in fuel cells, CNTs may offer higher long-term stability in the electrochemical environment, since Pt nanoparticles anchored to CNTs are more strongly attached and less prone to coalescence. Furthermore, the carbon structure itself appears to be less sensitive to carbon corrosion in the conditions at the fuel cell cathode (see also [Section 7.2.4](#)). A drawback in the preparation of electrocatalysts, however, consists in the fewer anchoring sites on CNT for Pt nuclei, so that a high dispersion of Pt nanoparticles on CNT is difficult to obtain.

The new star in the carbon family, however, became **graphene**, which has been discovered in 2004 by Geim *et al.* [4] (see [Chapter 4](#)). Graphene strikes us with a unique 2D structure with sp^2 -bonded carbon atoms densely arranged in a honeycomb crystal lattice. It is thus the missing link, the 2D building block of all carbon allotropes to be stacked into 3D graphite, rolled into one-dimensional (1D) nanotubes or folded into zero-dimensional (0D) fullerenes [5]. Since its recent discovery, graphene nanosheets have already found widespread application as 2D flat catalyst support. This is due to their large theoretical specific surface area of approximately $2600 \text{ m}^2 \text{ g}^{-1}$, which is twice that of single-walled CNTs, as well as their ultrahigh electrical conductivity. Moreover, lattice defects and surface functional groups, such as carbonyls and hydroxyls, can be used to immobilize the catalytically active metal nanoparticles on its surface. The strong metal–support interaction keeps the nanoparticles in place and thus enhances the stability of such catalysts [6, 7]. Because of its unique properties, it is anticipated that graphene-supported catalytically active nanoparticles will become promising electrocatalysts in the future.

Up to the discovery of CNTs and graphene, their more “potty” siblings, CB and graphite were the most commonly applied carbon materials in electrochemical energy applications. **CB** is a largely amorphous, nanoparticulate material, which is produced in a closed reactor by incomplete combustion or thermal decomposition of liquid or gaseous hydrocarbons under controlled conditions ([Section 7.2.1](#)) [8]. It is formed of disordered layers in a so-called turbostratic structure. The separation of individual graphene layers is between 3.5 and 3.8 Å, in contrast to 3.35 Å for graphite, with usually three to four layers stacked in parallel. Its main applications lie in the rubber industry, where it is used as mundane as a reinforcing filler material to improve the mechanical properties of car tires. Its application as a support material in catalysis is in weight-wise comparison negligible. Observing CB particles under the electron microscope reveals the materials' complex multiscale structure: the so-called primary particles are fused together to form discrete entities called **aggregates** ([Figure 7.2](#)). These are relatively robust, chain-like structures held together with van der Waals forces, which arrange

into the CB's coiled “tertiary structure” with voids between the irregular 3D agglomerates. Primary particle size (about 10–75 nm), aggregate size (about 50–400 nm), surface area (about 20–1500 m² g⁻¹), and structure (agglomerate size, about 100–1000 nm) are controlled during the production step. Similar to the aforementioned carbons, various functional groups, such as phenols, ketones, and acids, are found in the surface of CB, determining its rich catalytic properties [9]. The hydrogen content is approximately 0.2%, the total oxygen content usually less than 1%.

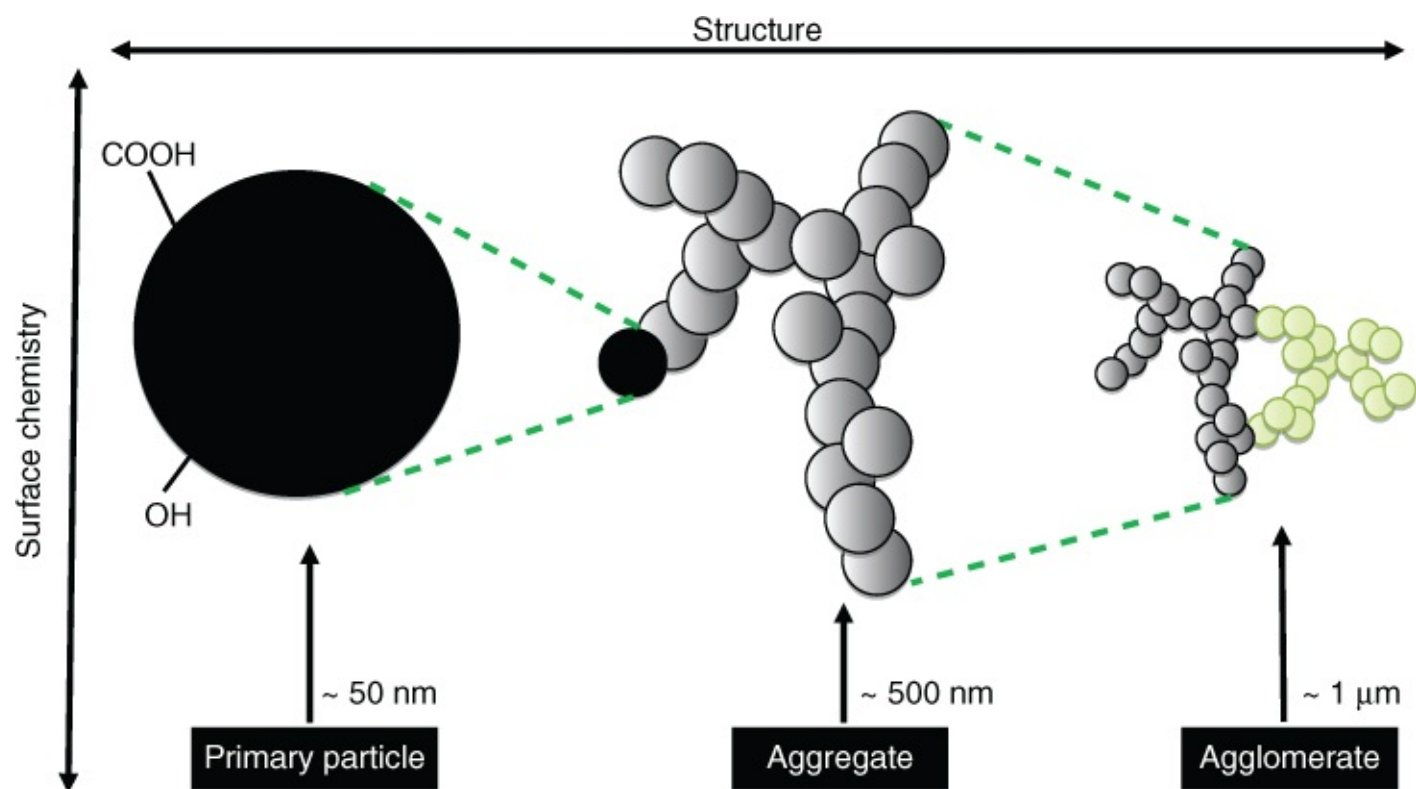


Figure 7.2 The three characteristics of carbon black determining its rich properties: particle size, aggregate structure, and surface chemistry.

Graphite is by far the most important carbon material in electrochemical applications, in particular so, as it is widely used as intercalating anode in lithium-ion batteries. In this function, it accommodates lithium ions between its 2D stacked graphene layers during charging of the battery. With very few exceptions, graphite consists of polycrystalline particles, in which each particle is a composition of numerous single crystals. In the case of natural flake graphite, these individual single crystals show a preferential orientation. Compared to CB, graphite appears to be an ordered and well-defined material with known chemical and physical structures. The reality, however, is different, since graphite can be obtained either naturally or synthetically, and can be found in platelet-, potato-, or needle-like morphology. The graphite particles' shape is directly important to their application in fuel cells, since the morphology of the carbon material predetermines the 3D electrode structure (see also [Section 7.4](#)) and hence the water management in the catalytic layer. A dense packing of platelet-like graphite might build up an effective “diffusion barrier” for the water transport in the cathode and therefore largely hinder the removal of product water from the working fuel cell.

Apart from crystallinity and shape, porosity is also an essential feature of carbonaceous materials. Sp^2 carbons have the exceptional ability to form porous materials with very high surface areas [1]. **Carbon aerogels**, for instance, can be fabricated via a supercooling process and consist of interconnected nanometer-sized carbon particles. This morphology leads to high surface areas, wide distribution of pore diameters, and very low bulk densities, all of which are favorable for fuel cell applications. Other types of porous carbons are **carbon xerogels**, and **mesoporous carbon microbeads** (MCMB).

Ordered mesoporous carbons (OMCs) offer most of all controllable pore sizes in a well-defined cubic or hexagonal arrangement and large pore volumes, which are advantageous in fuel cell operation, as they improve the mass transport of products and reactants [8]. They are obtained by using ordered mesoporous silica, such as MCM-41 and SBA-15, as hard templates. After their infiltration with a suitable carbon precursor and its subsequent carbonization, the template is removed and the templated carbon powder recovered ([Figure 7.3](#)). The pore structure of the carbon thus depends on the 3D porous structure of the template, with, for instance, CMK-3 carbon being an exact replica of SBA-15 silica [10]. A controlled porosity is of significant importance in fuel cell applications, since mass transport of the reactants to and the products away from the catalytically active sites plays an essential role in the device performance. It has been observed that the structural collapse of the electrode during durability tests impacts the performance of the fuel cell even more than the loss of active platinum particles [11]. In addition to the tailored properties, which can be achieved by rational design of the template, another advantage is that the synthesis route is comparatively simple and not too expensive to be developed to industrial scale. One such material prepared by a related templating approach, which has been recently commercialized by the Heraeus group, is PorocarbTM [www.heraeus-porocarb.com]. When a subsequent graphitization step is applied to enhance the material's durability (as discussed in more depth in [Section 7.2.4](#) below), the structural integrity of the PorocarbTM is maintained, while its electron conductivity is significantly improved.

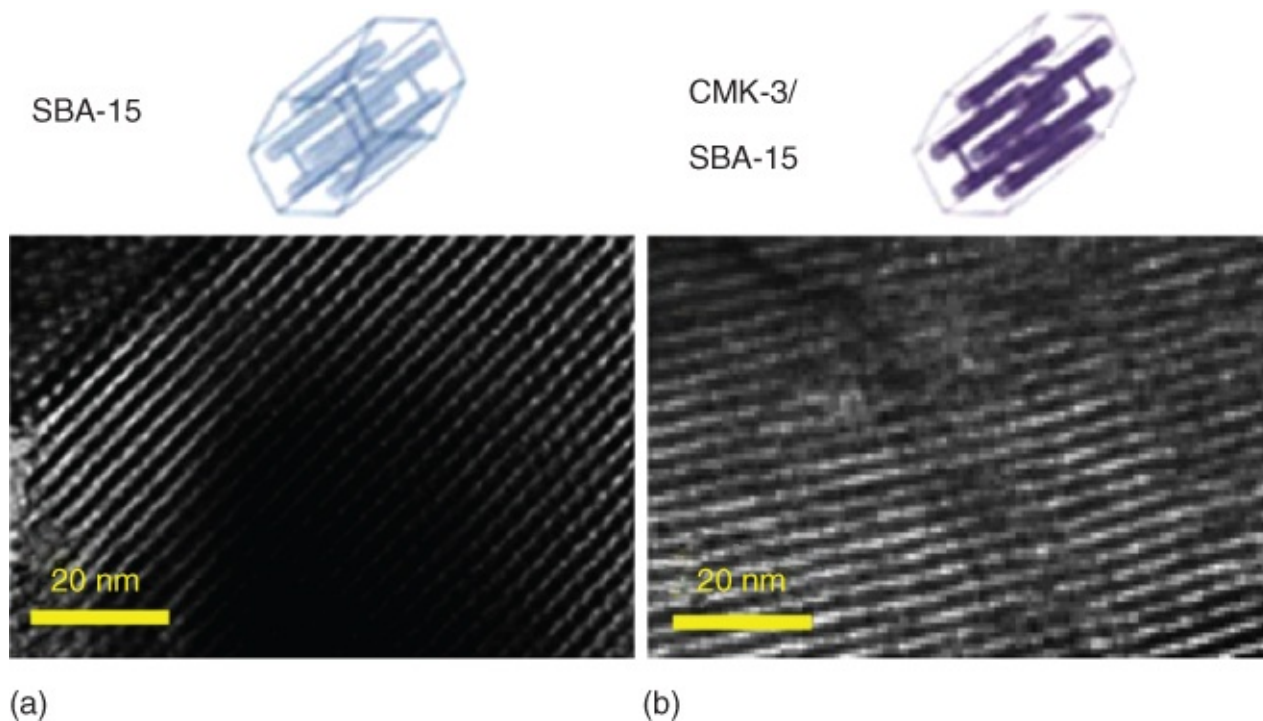


Figure 7.3 Templating strategy for obtaining CMK-3 carbon from SBA-15 silica [10].

And, not surprisingly, all of these very different types of carbon materials are used in fuel cells, either for model studies due to their fascinating properties or even directly in realistic fuel cell tests.

7.1.2 Carbon Characterization

In the early 1970s, purity, crystallinity/structure, porosity/texture, and particle size were defined as the four primary carbon properties ([12], see also [Figure 7.1](#)). These are also the fundamental features, which determine almost all other, so-called application properties, for example, the electrical and thermal conductivities and powder compactibility. For example, it has been observed that the electrical resistivity of compacted graphite powders primarily correlates with the negative logarithm of the particle size and the crystallite dimension in the *c*-axis direction. Suitable characterization methods should consequently be capable of providing information on morphology and shape, crystallinity and graphitic content, porosity and pore size distribution, aggregate, agglomerate, and particle size as well as surface chemistry with respect to applications in (electro)catalysis.

In contrast to, for example, crystalline oxidic supports, the physicochemical characterization of carbon materials proves to be rather complex. Since carbons are often largely amorphous and black, routinely applied X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) get pushed to their limits. Analysis of the XRD patterns, that is, width and intensity of the (002) reflection, can be applied to investigate the degree of graphitization in carbons, which is helpful with respect to carbon corrosion and durability. The presence of the (110) reflection gives a further estimate for the expected corrosion resistance of the carbon material [13]. FTIR studies of carbon materials still prove challenging, but may be mitigated by using an attenuated total reflection (ATR) setup with Germanium crystal or dispersing the carbon

powders in high dilution in KBr. By these approaches, functional groups at the surface of, for example, CB have been identified, such as carboxylic or quinone groups.

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) can be applied to investigate shape, morphology, and – to a lesser extent – crystallinity. In [Figure 7.4](#), TEM images of graphite and CB (Vulcan XC-72) are compared and display the characteristic features of the two different carbon materials. While TEM images of graphite show bundled stacks of parallel lattice planes ([Figure 7.4a](#)), the CB is characterized by an onion-like turbostratic structure.

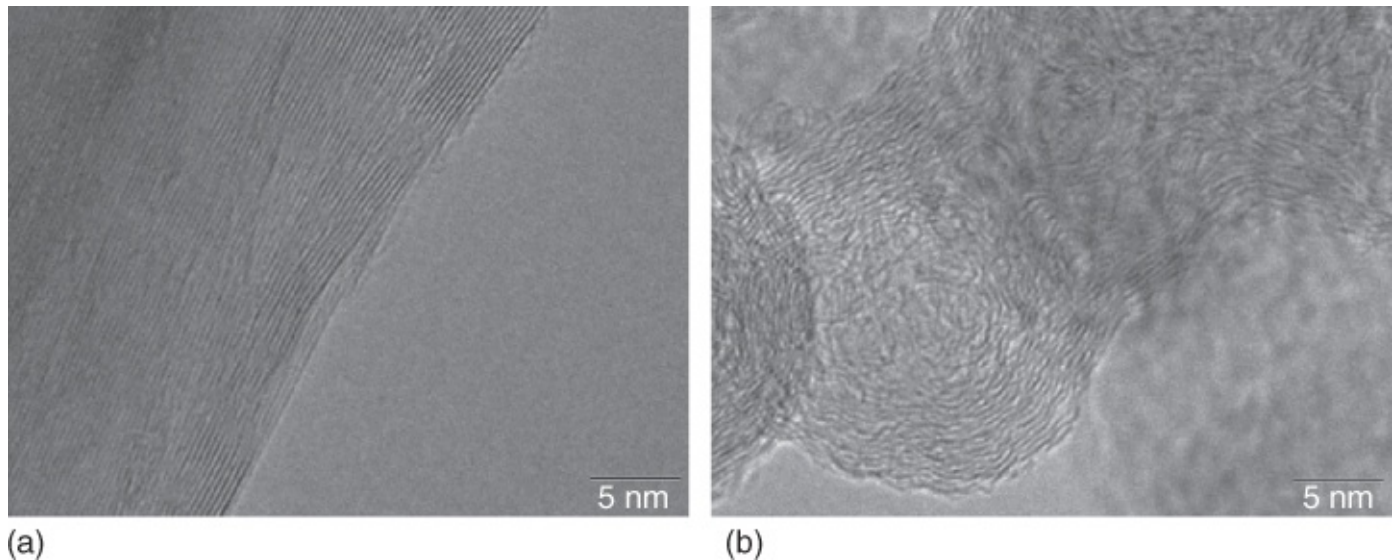


Figure 7.4 Images of the most prominent carbonaceous support materials: (a) graphite and (b) Vulcan carbon. (Taken from Ref. [14]. Copyright (2014), with permission from Elsevier Limited).

A very detailed fuel cell-related TEM study of CB and CB corrosion can be found in Liu *et al.* [15]. Gas adsorption, Hg intrusion porosimetry, and small-angle X-ray scattering (SAXS) provide information on porosity and pore size distribution, each of them having its own advantages and limitations. Methods that can be used to probe the functional groups at the carbon surface are X-ray photoelectron spectroscopy (XPS) and near-edge X-ray absorption spectroscopy (NEXAFS). [Table 7.1](#) gives an overview of characterization techniques applied to carbonaceous materials and the information contained. The most prominent characterization tools are discussed in more detail in the following.

Table 7.1 Overview of characterization methods applied to unravel the geometric and electronic structures of different carbons

Technique	Abbreviation	Information	Applicability
Electron microscopies	SEM, TEM	Shape, morphology, crystallinity	+
X-ray diffraction	XRD	Crystallinity	±
Pair distribution function	PDF	Near range order	±
Raman spectroscopy	Raman	Disorder, defects	++
X-ray photoelectron spectroscopy	XPS	Surface functional groups, sp^2/sp^3 content	+
X-ray absorption spectroscopy	NEXAFS	Surface functional groups, sp^2/sp^3 content	+
Fourier transform infrared spectroscopy	FT-IR	Surface functional groups	±
Small-angle X-ray or Small angle neutron scattering	SAXS, SANS	Porosity, pore size distribution	++
Hg intrusion porosimetry, gas adsorption		Porosity, pore size distribution	+

7.1.2.1 Raman Spectroscopy

In order to be appealing, a characterization tool should be most of all fast, nondestructive, with high specific, spatial, and time resolution. Furthermore, sample preparation should be easy, free of producing artifacts, and the method of choice should give maximum structural and electronic information. That is why Raman spectroscopy comes to mind first. However, it comes at a price, since the spectral interpretation is not so straightforward. Raman spectra of all carbon materials show only few prominent features [5]. But their shape, intensity, and positions allow us to distinguish CB from graphite and CNTs ([Figure 7.5](#)).

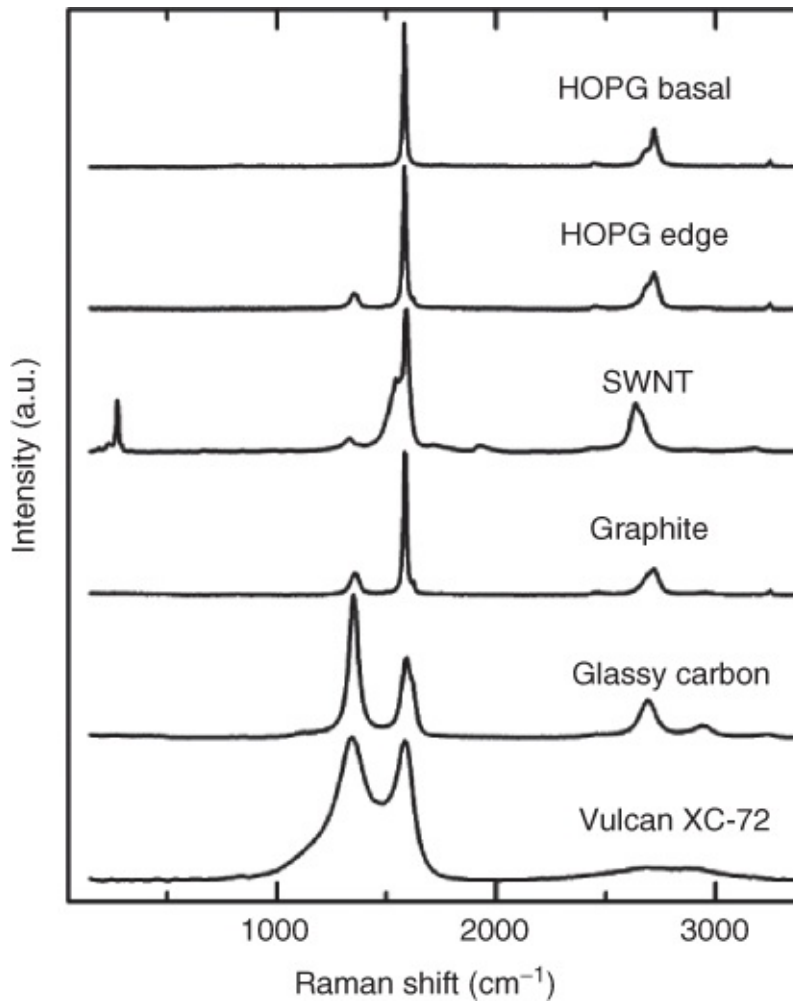


Figure 7.5 Comparison of Raman spectra of different carbon materials [16].

The main features in the Raman spectra are the so-called *G*, *graphitic* (approximately 1560 cm^{-1}) and *D*, *disorder* (approximately 1360 cm^{-1}) bands. Graphite, for instance, displays an intense G peak at 1580 cm^{-1} and a band at about 2700 cm^{-1} , historically attributed to as G', as it is the second most prominent feature in the Raman spectrum of graphite. This signal is significantly different in shape and intensity for graphene and bulk graphite, therefore suitable to distinguish between these two carbon materials [5]. In single-walled CNTs, the shift and splitting of the G peak is a measure for the tube diameter [17]. For graphite used as an anode in Li-ion batteries, the intensity ratio between D and G bands decreases, while eventually a D band at 1520 cm^{-1} appears indicating lithium intercalation in between the graphene planes [18]. The ratio of intensity of the D peak to that of the G peak varies and is proposed to be related to the size of graphitic domains in the in-plane direction (L_a , obtained by XRD measurements). On the basis of a series of measurements on microcrystalline graphite samples with various microcrystalline sizes, Tuinstra and Koenig [19] suggested a linear correlation between I_D/I_G and $1/L_a$. But this correlation holds only up to a certain crystallite size, as discussed by Zickler *et al.* [20].

In agreement with the above, Raman spectroscopy allows the study of the degree of disorder in carbonaceous materials and the size of graphitic domains. Moreover, confocal Raman

microscopy gives spatially resolved information, for example, on the distribution of defects, which can be displayed in 2D false-color plots [17]. The various Raman bands and corresponding information are summarized in [Table 7.2](#).

Table 7.2 Overview of various Raman bands and their interpretation

Signal	Raman shift (cm^{-1})	Information
G	Approximately 1580	Undisturbed graphitic lattice
D1 (D)	Approximately 1350	Disordered graphitic lattice (edges)
D2 (D')	Approximately 1620	Disordered graphitic lattice (surface)
D3	Approximately 1500	Amorphous carbon
D4	Approximately 1200	Disordered graphitic lattice (polyenes, ionic impurities)

7.1.2.2 Small-Angle Scattering Techniques

A number of techniques have been proposed to study the porosity and surface area in carbon materials. Among them, small-angle scattering techniques offer the intrinsic advantage over gas adsorption and, in particular, Hg intrusion porosimetry that they are essentially nonintrusive [21]. X-rays (i.e., SAXS) or neutrons (i.e., small angle neutron scattering (SANS)) under a very small angle, typically below 1° , are elastically scattered, changing direction and providing an inverse relationship between object size (from 1 nm to about 20 μm) and wavevector. The scattered intensity varies with fluctuations in the electron density and contains contributions from scatterers of all sizes, pores (voids), and particles (material) alike. Consequently, the analysis of the scattering data is complex and tedious and only possible with sophisticated mathematical models. Only recently, two notable developments to porosity characterization in carbons have been reported: Lozano-Castello *et al.* [22] at the ESRF in Grenoble used an X-ray microbeam and were able to resolve anisotropic features related to the porosity development across the diameter of a single activated carbon fiber. Calo *et al.* [23] combined SAXS and thermogravimetric analysis to directly monitor the development of porosity in carbon in real time. While SAXS and SANS provide basically similar information, SANS is slightly better suited to pick up on the difference between “open” and “closed” porosity. By a so-called contrast-matching technique, difference curves between the pristine samples and samples filled with a liquid with close to the same neutron scattering cross section as the solid can be obtained, which then only display the closed porosity. This difference between open and closed pores is also of importance to fuel cell applications, since only accessible pores are good pores.

7.1.2.3 Surface Chemistry by X-ray Photoelectron Spectroscopy (XPS) and Near-Edge X-ray Absorption Spectroscopy Fine Structure (NEXAFS)

For the electrocatalytic application of carbon materials, apart from their crystallinity and porosity, their surface chemistry is also of importance. XPS and NEXAFS are both capable of determining the surface functional groups on the carbon surface. In XPS, the sample is

irradiated with X-rays ejecting photoelectrons into the vacuum. The kinetic energies of the photoelectrons can be detected and hence related to the binding energies (BEs) of the electrons in the sample. Because each element is defined by a unique set of BEs, XPS can be applied to identify and measure the concentration of the elements within the escape depth of the photoelectrons in the near-surface region [24]. It is a powerful tool to analyze carbon materials without excessive sample damage, for example, able to distinguish sp^3 and sp^2 carbon. For instance, the C1s peak position in diamond is 285.50 eV, which is about 1.4 eV higher than that in graphite (284.15 eV). When analyzing this peak splitting, the proper peak fitting can thus reveal the sp^3 to sp^2 ratio. Oxygen-related groups with single bonds, such as carboxyl, are observed as peak broadening at about 288.5 eV, a contribution of surface oxygen groups with multiple carbon–oxygen bonds is proposed at 289.5 eV [25]. And also the incorporation of N atoms into the graphene layers can be studied by XPS measurements.

NEXAFS of the C K-edge probes the chemical state of the carbon and is sensitive to the hybridization and the bonding of functional groups to the carbon surface. Compared to XPS, it is even more sensitive to the surface. NEXAFS measurements of highly oriented pyrolytic graphite (HOPG), which is often used as a reference system, display the typical π^* and σ^* transitions for C=C and sp^3 carbon at 285.7 and above 292 eV. When oxygen bonds to the carbon, the binding energy will be shifted accordingly, so that, for instance, the π^* transition for =COOH will be observed at 288.2 eV, for phenolic =OH at 286.3 eV, and for quinone groups at 283.6 eV. In a comparison of different carbon materials for application in all-vanadium redox flow batteries, Melke *et al.* [14] found that carboxyl groups produce a comparatively sharp peak at 288.8 eV, whereas carbonyl groups or O-alkyl groups appear only as a small shoulder at 290.7 eV. A comparison of different carbon materials using NEXAFS C K-edge analysis is shown in [Figure 7.6](#). The downside of NEXAFS experiments is that they rely on synchrotron radiation and are thus not readily available.

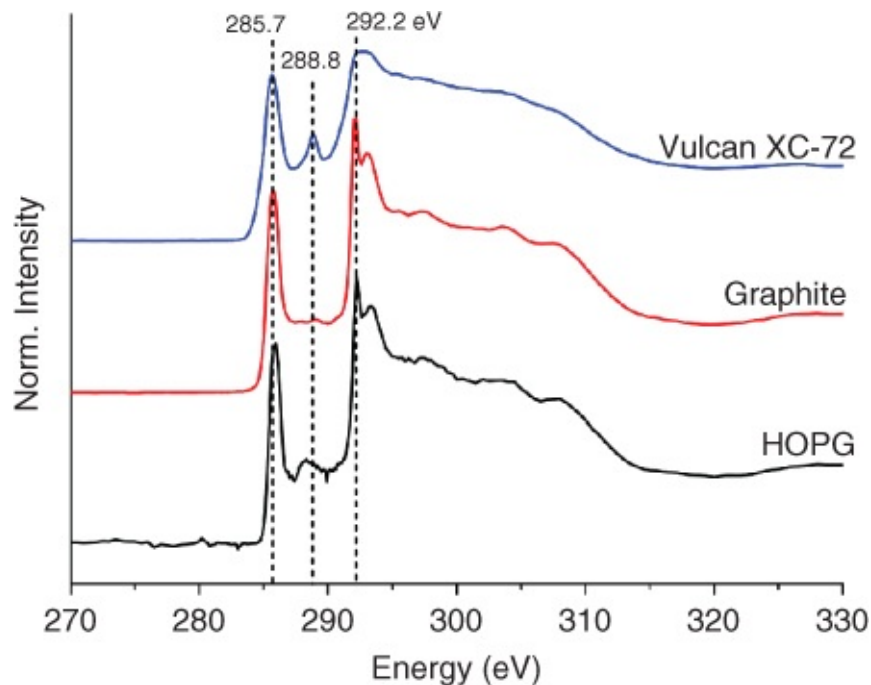


Figure 7.6 C K-edge NEXAFS spectra of different carbon materials (J. Melke, unpublished results).

7.1.2.4 Other Methods and In situ Studies

Other methods which can also be applied include electron paramagnetic resonance (EPR) and nuclear magnetic resonance (NMR). Information on the charge carrier concentration and their mobility can be obtained by EPR thus rendering a deeper insight into the conduction behavior of carbons [14]. NMR furthermore provides structural information, such as quantitative sp^2/sp^3 ratio comparable to Raman and XPS.

Even more valuable than the *ex situ* characterization of carbon materials with the aforementioned methods, is their *in situ* characterization during operation or at least under conditions very similar to their application. However, not all measurements can be applied *in situ*, as for instance in XPS, the mean free wavelength of the electrons in “not-vacuum” conditions is too low and in TEM ultrahigh vacuum (UHV) is required to detect the electrons. Consequently, electron probe techniques relying on UHV are not (or only with immense effort) applicable *in situ* [26]. Novak *et al.* [27] give an overview of advanced *in situ* characterization applied to carbonaceous materials for Li-ion batteries.

Depending on the final application of carbon materials, very different properties and structures on different length scales need to be analyzed in detail using the aforementioned methods and, most favorably, a combination of them. A systematic Raman, TEM, SEM, NEXAFS, and EPR study of various carbon materials for impregnation into carbon felts used as positive electrode in all-vanadium redox flow batteries is given by Melke *et al.* [14].

Of importance to fuel cell applications is the electron conductivity of carbons, when used as electron pathway in the porous electrode. Moreover, their functional groups with respect to hydrophobicity and water transport phenomena are also important. Also their defect density

plays a role, when these defects function as nucleation sites during the synthesis of nanoparticulate catalysts and also when anchoring the particles to hinder Ostwald ripening during degradation. This chapter is further subdivided into three parts corresponding to the carbon's three main functions in polymer electrolyte membrane fuel cell (PEMFC):

1. Carbon as support material
2. Carbon as a catalytically active component
3. Carbon as structure-forming element in porous fuel cell electrodes.

The use of carbon in gas diffusion layers (GDLs) and bipolar plates is not discussed here.

7.2 Carbon as Support Material in Fuel Cell Electrocatalysts

Most fuel cell electrocatalysts use platinum as the catalytically active site for both hydrogen oxidation reaction (HOR) and ORR. Platinum is active and stable, but unfortunately also hideously expensive. Dispersing the catalytically active noble metal particles onto support materials has effectively reduced the noble metal loading required for fuel cell electrodes in the past, and consequently also reduced the fuel cell cost. And high-surface-area carbon has been the most popular choice for decades. But since in particular disordered carbon materials suffer from corrosion in the harsh conditions at the fuel cell cathode, also electron-conducting polymers, such as polyaniline (PANI) [28–31] and transition metal oxides, carbides, nitrides, and borides, such as doped titanium oxides [32–35] and doped tin oxides [36, 37], have been investigated as alternative supports in the past.

An ideal support material has to fulfill a vast list of criteria. It has to combine high surface area with a good electrical conductivity and a suitable pore structure in order to be filled with proton-conducting ionomer to connect reactants, catalytic sites, and transport pathways in the so-called three-phase boundary (TPB). A schematic illustration of the TPB is shown in [Figure 7.7](#). Other important criteria to be taken into account are inertness, stability, toxicity, and cost. Requirements for a good support material are listed in [Table 7.3](#) along with exemplary data for Vulcan XC-72.

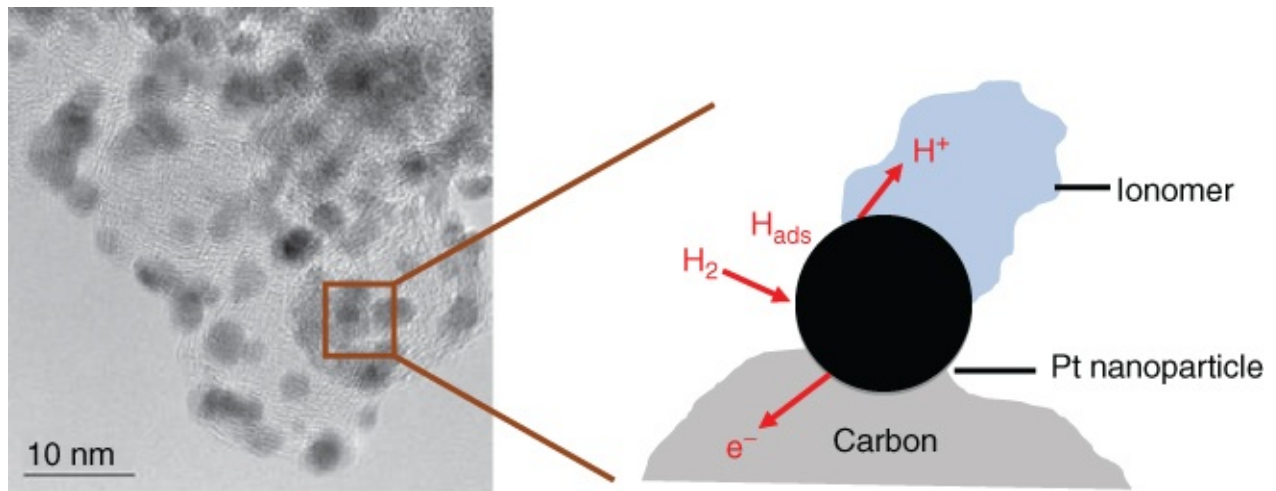


Figure 7.7 Schematic illustration of the three-phase boundary in fuel cell electrodes.

(Adapted from Rolison [38].)

Table 7.3 List of requirements which a good support material has to fulfill and exemplary data for VulcanXC-72

Requirement	What for...	Optimal values	Data Vulcan XC-72
High surface area	To enhance particle dispersion	Minimum 100–300 m ² g ⁻¹ , preferable higher 400–1000 m ² g ⁻¹	245 m ² g ^{-1a}
Good electronic conductivity	To provide electron transport pathways	—	4.5 S cm ^{-1b}
Suitable pore size distribution	To ensure accessibility of particles in three-phase boundary (TBP)	Micro-porosity less than 1 nm, meso-porosity 10–100 nm	0.06 cm ³ g ^{-1c}
Multiscale structure	To build up porous catalytic layers	—	178 cm ³ /100 g ^d (aggregates)
			30 nm (primary particle size)
High stability	To withstand corrosive fuel cell conditions	Low solubility at pH 1–2	—
Sufficiently low toxicity	To allow for customer-friendly application	—	—
High chemical inertness	To be suitable for long-term use	Not prone to organic reaction chemistry	—
Low cost	To allow for scale-up and later commercialization	—	<45 EUR/100 g

^a Measured by BET.

^b Measured at packaging fraction of 0.3, since conductivity is affected by particle size and crystallite dimension (see above).

^c Given as the averaged micropore volume, thus no information on pore size distribution.

^d As determined by standard dibutyl phthalate (DBP) absorption.

But while carbon appears to be the ideal choice, when it comes to the aforementioned requirements, also certain challenges have to be overcome. The most important drawback is the low equilibrium potential for carbon corrosion [39]. Already at a potential of 207 mV versus standard hydrogen electrode (SHE), the carbon may get oxidized to CO₂ according to Equation (1) as follows:



Even though the mechanisms of corrosion are not completely understood yet, for the electrochemical oxidation in acids several reaction pathways are proposed either directly to CO_2 or via hydroxyl, keto, or carboxylic groups. It is furthermore assumed that the active sites for carbon corrosion are associated with carbon atoms at edges, defects, dislocations, and single-layer planes, that is, amorphous regions within the carbon materials. One strategy to reduce carbon corrosion could therefore focus on removal, reduction, and inhibition of such active sites in order to slow down the carbon's oxidation.

Luckily, the rate of carbon oxidation is negligible during normal operation of PEMFCs [40]. Previous studies in half-cell tests found that carbon oxidation occurred only above 1.0 V versus SHE. Such high potentials will be reached in automotive applications during fuel starvation and start-up and lead to significant performance losses due to support corrosion and collapse of the porous electrode structure [11]. In general, it is found that carbon corrosion is accelerated during start/stop cycles, at high voltages (open circuit potential), at high operation temperatures, and operation in low humidity.

Ways to circumvent these issues will be (i) the application of alternative polymeric or oxidic support materials, (ii) rigorous control of the operation conditions, and (iii) surface modification and/or graphitization of the routinely applied carbon supports. Since most metal oxides offer only comparatively low electronic conductivities, are difficult to disperse into an ink for electrode preparation and also form mostly very dense electrode layers [41], a lot of effort is still put into the modification of either the surface or the bulk of the CB supports (see [Section 7.2.4](#)).

7.2.1 Carbon Blacks

CB is also known by the names furnace black, acetylene black, channel black, lamp black, and thermal black with the names referring to the respective manufacturing process. It is produced by the pyrolysis of hydrocarbons, thus being in principle the product from their incomplete combustion. The most commonly applied CB is produced with the furnace process by blowing petroleum oil or coal oil as raw material into high-temperature gases resulting in their partial combustion. This method is suitable for mass production due to its high yield and good control over the product's properties, such as particle size or structure. For instance, the primary particle diameter can vary between 5 and 100 nm depending upon the processing conditions [12]. [Table 7.4](#) gives an overview of the most prominent CB support materials listing their surface areas and primary particle sizes.

Table 7.4 Overview of prominent carbon black materials applied in fuel cell research

Carbon black	DBP absorption (cm ³ g ⁻¹)	Surface area BET (m ² g ⁻¹)	Primary particle size (nm)
Vulcan XC-72R	1.93	254	30
Black Pearl 2000	3.30	1475	15
Ketjenblack DJ-600	3.50	1300	40
Acetylene Black	2.62	64	42

For more information, see also: [42].

CB, and in particular Vulcan XC-72, is the standard support material in fuel cell research. Therefore, it is hardly surprising that most recent publications do no longer focus on ways to describe, analyze, and optimize the support, but rather report on strategies to, for example, increase the dispersion of the catalytically active metal nanoparticles on the carbon surface by various treatments [43–47]. Apart from that, also the investigation of CB composites, such as CB blended with CNT [48] and CB/reduced graphene oxide [49], came into the focus of recent fuel cell research, as well as its application in the microporous layer (MPL) of the GDLs, which are not subject of this chapter [50, 51]. In addition, the comparison of low-surface-area Vulcan XC-72 with high-surface-area black pearls or Ketjenblack with respect to their electrochemical properties, capacitive behavior [52], and durability [53] has been a frequent subject of recent publications.

But while CBs are the respected literature standard, which every new material has to compete with, novel carbonaceous materials, such as CNTs, graphene, and OMCs, moved into the limelight during the last years and are discussed in more detail in the following.

7.2.2 CNTs and Graphene

Because of their high electrical and thermal conductivities, a lower degradation rate compared to CBs and their 1D structure, which offers new ways in the 3D design of catalytic layers, there is a high interest in using CNT as support material in catalysis. Already in 1994, only 3 years after the discovery of CNTs, the first communication on the applicability of CNTs as support in heterogeneous catalysis was published by Planeix *et al.* [54]. However, it took another 5 years until the first report on the electrocatalytic reduction of dissolved oxygen using CNT as support material was published [55]. In this work, Britto *et al.* prepared microelectrodes from CNT samples, which they investigated by cyclic voltammetry (CV). The use of microelectrodes was indeed necessary, as the first preparation techniques for CNT did not allow for the production of significant amount with sufficiently high purity. Therefore, new large-scale purification processes had to be developed, like the one invented by Rinzler in 1998 [56] for single-wall CNT. This is only one example of a large number of purification and scale-up processes enabling the broad utilization of CNT in different fields of science and technology. With respect to PEMFCs, there are three main fields of application: CNTs can be

used to prepare a thin MPL on the GDLs [57], in corrosion-resistant coatings of the bipolar plates [58] and, more prominent, as catalyst supports. The first application of CNT as support material in fuel cell electrodes known to us was published in 2002 by Liu *et al.* [59]. After that, a number of publications followed mostly aiming at more stable carbon-based catalysts [59–61]. These studies demonstrated that platinum nanoparticles supported on CNT are superior to platinum nanoparticles supported on CB. Shao *et al.*, for instance, used accelerated stress tests to determine the long-term stability of Pt on multi-walled carbon nanotubes (MWCNT) in comparison to Pt/C. The loss in electrochemically active surface area (ECSA) for Pt/C was almost twice the reduction observed in Pt/MWCNT (49.8% vs 26.1%). The authors correlated this finding with the Pt/MWCNTs' higher resistance toward sintering as well as their higher resistance against electrochemical oxidation. Another favorable feature of using CNT as catalyst supports in fuel cells is that, due to their 1D shape, they lend themselves to the design of highly porous and even 3D aligned electrode structures [62]. It is thus possible to grow well-aligned CNT arrays, which are subsequently electrochemically decorated with catalytically active platinum nanoparticles. Tang *et al.* observed higher electrocatalytic activity in such systems as compared to Pt on graphite, which they attributed to the higher dispersion of the platinum and the particular properties of the CNT support.

For the successful deposition of platinum nanoparticles on CNT, most deposition methods known previously from the impregnation of carbon supports can be applied [63]. However, in order to achieve a homogeneous distribution of the metallic nanoparticles on all nanotubes, these have to be activated before deposition. Moreover, since they are often entangled, such that the reduction agent cannot access the core of the nanotube bundles, novel synthesis strategies have to be developed. For instance, Soehn *et al.* [64] reported the application of multi-walled carbon nanotubes (MWNT)/Nafion® emulsions in the reduction reaction of hexachloroplatinate with ethylene glycol and butyl acetate. In contrast to other syntheses described in the literature, the emulsion step allows effective debundling and a good dispersion of MWNTs in the solvent resulting in a narrow Pt particle size distribution and a homogeneous dispersion of the nanoparticles on the CNT, even at loadings of up to 50 wt%.

Inspired by the observation, that binary Pt= Ru nanoparticles supported on CNT showed a promising performance as anode catalysts in PEMFCs, Harris *et al.* [65] used density functional theory calculations to study the anchoring of the nanoparticles to the nanofibers. They found a strong metal–carbon bond (~ 3 eV) with covalent character between the graphene structure and the metal (111) crystal planes, which might be the reason for the higher stability found in these systems.

Apart from using CNT as stable and high-surface-area supports, they can also be applied as the catalytically active component in fuel cells (see [Section 7.3](#) exclusively).

Similar to CNT described earlier, other groups dedicated their research to graphene as support material expecting to create more stable catalysts with well-structured electrodes. Shortly after the discovery of graphene, the first theoretical calculations predicted a strong metal–support interaction in case platinum or gold nanoparticles were supported on graphene sheets and flakes [66, 67]. The first practical work decorating platinum nanoparticles on graphene we

know about was published in 2008 by Xu *et al.*, [68] only 4 years after its discovery. The authors produced graphene–metal particle nanocomposites in a water–ethylene glycol system, characterized them using electron microscopy and XPS, and showed their potential application in direct methanol fuel cells applying CV. Only 1 year later, Kou *et al.* [69] were able to synthesize platinum nanoparticles with an average diameter of 2 nm on graphene, and demonstrated both their higher activity and stability for the ORR when compared to a commercial Pt/C catalyst. In 2014, Sung *et al.* [70] observed a durability improvement by adding small amounts of graphene to a platinum-on-CB catalyst. In real fuel cell tests, they could observe improved durability at high current densities (3 A cm^{-2}). Another idea was to produce sandwich-like 3D networks on the nanoscale with homogeneously distributed noble metal nanoparticles, which show enlarged ECSA and a high mass activity toward the methanol oxidation reaction (MOR) [71].

For both materials, CNT and graphene, numerous publications demonstrate their applicability as promising support materials in PEM FCs. In lab-scale tests, their higher stability, durability, and activity have been shown manifold. Yet, up to now nobody knows which drawbacks have to be overcome to commercially apply CNTs and graphene on a larger scale in real fuel cell stacks. This, only time will tell.

7.2.3 (Ordered) Mesoporous Carbons

(Ordered) mesoporous carbons are an interesting class of carbon materials for fuel cell applications, as they offer a means to control the porosity on the micro- and mesoscale, which is important with respect to the accessibility and addressability of the active metallic nanoparticles. The pores should allow access of the ionomer to transfer protons away from the reaction sites. Moreover, the pores should not be too small so that they can get clogged or expensive noble metal particles buried inside them. In this case, they would not contribute to the electrochemical performance.

As one example of a mesoporous material, a carbon xerogel consisting of coral-like amorphous structures is compared to carbon nanocoils and nanofibers [72]. In contrast to the nanocoils and nanofibers, the porosity in the xerogel is a consequence of both the interparticular spaces and the intraparticle voids. It offers a BET surface area of $441 \text{ m}^2 \text{ g}^{-1}$ and a total pore volume of $1.62 \text{ cm}^3 \text{ g}^{-1}$, which are four times higher than the values measured for the carbon nanofibers. The same is true for the pore volume in the mesopore range between 10 and 100 nm. Another approach to obtain materials with pores in the mesopore regime is presented by Afsahi *et al.* [73]. An ordered metal–organic framework (MOF; MOF-253) structure was synthesized and Pt as reactive centers introduced directly in a second step. The resulting solid was used as a precursor, which was subsequently subjected to pyrolytic carbonization at different temperatures under an Ar atmosphere. N_2 adsorption isotherms indicate the presence of meso- and micropores in the carbonized material, although both pore volume and BET surface area get reduced from $0.51 \text{ cm}^3 \text{ g}^{-1}$ and $1155 \text{ m}^2 \text{ g}^{-1}$ in the original MOF to $0.27 \text{ cm}^3 \text{ g}^{-1}$ and $540 \text{ m}^2 \text{ g}^{-1}$ in the Pt-MOF and $0.22 \text{ cm}^3 \text{ g}^{-1}$ and $160 \text{ m}^2 \text{ g}^{-1}$ in the carbonized material, respectively.

Not only mesoporous, but also ordered carbon materials for application in electrocatalysis were reported first in 2001 by Joo *et al.* [74]. By a templated synthesis, OMCs were obtained, which could be decorated by platinum nanoparticles in high dispersion exceeding that of common microporous carbons, such as CB or activated carbon fibers, by far. A review on the application of OMC in PEMFC is given by Chang *et al.* [75]. However, the applicability of this class of materials is strongly dependent on their structure. Banham *et al.* [76] demonstrated for the first time a significant effect of the wall thickness on the ORR activity. Moreover, the micropore volume affects the mass activity for the ORR, and an almost inverse relation has been observed by Kim *et al.* [77]. The effect of pore size and electronic conductivity on alcohol electro-oxidation has also been discussed by Song *et al.* [78]. Obviously larger pore sizes, which facilitate mass transport, decrease the electronic conductivity. And this is a significant drawback, since OMCs already suffer from comparatively low electron conductivities [79].

In an attempt to further optimize the fuel cell performance of OMC, the materials can also be functionalized and oxygen-containing groups introduced into the surface [80] (see also [Section 7.3.2](#)), as well as doped with heteroatoms, such as phosphorus [81], which proves to be beneficial for methanol electro-oxidation (see also [Section 7.3.3](#)).

7.2.4 Graphitization as a Means to Fight Carbon Corrosion

As mentioned earlier, CB is prone to oxidation, the so-called carbon corrosion, which results in the loss of surface area, changes in the pore structure and finally also leads to sintering of the supported nanoparticles and eventually their loss from the support surface. This affects both the kinetics of the reaction and the electrode's mass transport behavior resulting in a significant loss of performance with operation time. Consequently, carbon support durability is considered to be a major barrier for the successful commercialization of fuel cell technology in the automotive sector. So much so, during the last decade, more than 60 publications dealt with carbon corrosion mechanisms in fuel cell application [82].

For instance, Wang *et al.* [53], already quoted above, compared the mechanism of carbon corrosion for the standard CB Vulcan XC-72 and the high-surface-area Black Pearl 2000 in a model experiment. Instead of a realistic fuel cell test, which is difficult to control, they used an accelerated aging process by steam etching. When steam etched for 3 h at 800 °C, the high-surface-area carbon loses almost twice as much weight as the Vulcan material. Moreover, corrosion of the Vulcan XC-72 begins at the center, whereas in the case of the Black Pearl 2000 oxidation starts from the carbon surface. Therefore, one way to remedy support corrosion would be to synthesize carbons with lower surface area, larger primary particle size, and dense-layered structure (see also [Table 7.4](#)). These findings are in good agreement with an earlier study of Wang *et al.* [83], who also found a significantly lower corrosion resistance for the high-surface-area black pearl than for Vulcan XC-72 by CV, XPS, and XRD analysis. Electrochemical quartz crystal microbalance (EQCM) and online mass spectrometry (MS) investigations are also useful tools in the characterization of carbon corrosion. In 2011, Hung *et al.* [84] applied EQCM as a simple and fast screening tool, and also observed that high surface area causes increased corrosion. Furthermore, they demonstrated that the corrosion

resistance of Vulcan XC-72 was boosted by a graphitization treatment. Oh *et al.* [85] reached a similar conclusion when testing a graphitized and nongraphitized carbon by online MS. In their experiment, the generation of CO₂ was followed by MS when the carbon support material was held at a constant potential of 1.4 V, and the highly graphitized sample showed only negligible CO₂ formation.

Graphitization, that is, heat treatment of carbonaceous materials between roughly 1500 and 2800 °C in argon, predominantly induces the growth of ordered graphitic domains. By contrast, carbonization occurs already at lower temperatures between 500 and 1000 °C, can be carried out under nitrogen atmosphere and essentially eliminates functional groups from the surface. (Note: One has to be careful, since the two terms get sometimes mixed up in the respective literature.) Of course not only CB can be subjected to a heat treatment at high temperatures under Ar, but also all other forms of carbon, such as carbon nanospheres, carbon nanofibers, carbon nanohorns, and tubes, can be subjected to graphitization treatment. Miyazaki *et al.* [86] report the use of graphitized nanospheres as a highly corrosion-tolerant support material in PEMFCs. Pristine and graphitized multiwalled CNTs have been investigated by Selvaganesh *et al.* [87]. During accelerated stress tests, a lower overall loss in electrochemical surface area and cell performance has been found for the graphitized specimens; in particular, only 6% performance degradation for the Pt-decorated graphitized MWCNTs as compared to 54% for a standard CB. At the ECS Spring meeting 2014, Stamatina *et al.* [88] even proposed a graphitization stability relation for carbons heat-treated at different graphitization temperatures correlated to their electrochemical behavior at positive potentials.

However, one significant drawback of graphitization is the “healing” of defect sites at the carbon surface. As nucleation of the catalytically active nanoparticles occurs preferably at defect sites, less defects also means less nucleation sites and larger particles in general [89]. As a consequence, the synthesis of electrocatalysts with high metal loadings is significantly impeded.

7.3 Carbon as Catalytically Active Component in Fuel Cells

Besides the more common use of conductive carbon materials as catalyst supports and GDLs in fuel cells, their application as catalytically active material has also been investigated. Earlier reports were focusing on fundamental studies related to “pure” carbon materials, such as pyrolytic graphite, natural graphite, and glassy carbon, while in recent times a wealth of publications appeared with a focus on heteroatom-modified carbons and their possible application. The latter were, for instance, highlighted in a recent review by Wang and Su in 2014 [90].

7.3.1 ORR Activity of Carbons

The ORR is catalyzed at the cathode of fuel cells, but also in lithium-air batteries and others, and unfortunately appears to be a very sluggish and therefore limiting reaction. It has been

studied extensively throughout many decades due to its importance to electrochemical energy conversion [91]. However, the challenging problem of the electrocatalytic reduction and generation of dioxygen at low and moderate temperatures in aqueous solutions had already been identified before fuel cells and Li-air batteries were *en vogue* [92], and for instance discussed in detail by Yeager in 1984 [93].

Depending on the electrode material, the ORR can either proceed via a direct $4e^-$ process transferring oxygen directly to water. The other option would be a sequential reaction mechanism involving two $2e^-$ steps and H_2O_2 as an intermediate on metallic electrodes. The direct oxygen reduction step is catalyzed by expensive platinum, whereas carbon materials predominantly favor the indirect pathway via H_2O_2 or HO_2^- as an intermediate depending on pH [94]. Moreover, the reduction kinetics appears to be much slower on carbon surfaces than on the costly noble metals. But, while the effect of electrode material on the ORR has been reviewed extensively and plausible reaction mechanisms controlled by oxygen chemisorption on metallic electrodes have been proposed [95], on carbon surfaces there seems to be no consensus as to the individual reaction steps in a detailed reaction scheme and even the identity of the (adsorbed) intermediates remains largely unclear [96]. It has been suggested in the literature that the adsorption of O_2 or superoxide is involved in the reaction. However, different pretreatments and activation procedures of carbon materials may significantly impact their surface functional groups and thereby affect the observed electrode behavior, so that there is a controversy in the community as to the rate-determining step of the ORR. For instance, it is well established that there is a very large overpotential on graphite. By contrast, kinetic measurements on single-walled carbon nanotubes (SWNTs) were inconclusive, since the experiments proved difficult with respect to well-defined electrode areas, material properties, and mass transport in conventional electrode setups [94]. Since the major goal of fuel cell catalysis is the direct $4e^-$ ORR, which did not seem possible by application of cheap and abundant carbon materials, researchers started to become discouraged. But not for long, not until the activity of heteroatom-doped carbons was demonstrated, as, for example, described in [90] and discussed in detail below.

7.3.2 N-Doped Carbons and Functionalized CNTs

On the basis of earlier fundamental studies, however driven by the need to replace expensive Pt-based catalysts, research and development has focused on modified carbon materials, which have in many studies been shown to be active for the electrocatalytic oxygen reduction under conditions of PEM FCs. As discussed earlier, pure carbon materials are of insufficient activity for ORR in acid medium, and catalyze the two-electron reduction of oxygen to hydrogen peroxide. In 1964, Jasinski [97] showed that carbon-supported Co phthalocyanines are active oxygen reduction catalysts albeit of their low stability. These findings opened a new field of electrocatalysis research, and it was shown that oxygen reduction activity is not restricted to phthalocyanines, but can be found also in other so-called N_4 -chelates, including porphyrins and tetraazaannulenes complexing a variety of transition metals, including iron and nickel [98]. The research on modified carbon materials gained momentum after it was demonstrated that heat

treatment of carbon-supported metal phthalocyanines, porphyrins, and other N_4 -chelates leads to enhanced stability of the catalysts in an electrochemical environment and sometimes also to enhanced activity [98, 99]. There was some debate in the literature as to the nature of the active site. An opinion shared by many researchers is, that it consists of nitrogen atoms embedded in the carbon structure and that the metal ion (mainly Fe, but other central metals like Co have also been investigated) is coordinated to these nitrogen atoms. Representations of the active sites Me-N-sites as MeN_4C_X or $MeN_{2+2}C_X$ (or similar) appeared in the literature. The developments in this field have been discussed in detail in recent reviews [100–102]. For practical applications, most of the N_4 -chelates do not provide a good starting material since they are not easily available as a bulk chemical. However, it has been demonstrated that modification of carbon with Me-N-centers can also be realized with much less complex starting materials. As a general requirement for the synthesis of active catalysts, it was concluded that a nitrogen source, a metal source, and a carbon material suffice when subjected to a heat treatment step to form materials active for the electrocatalytic oxygen reduction [103]. Indeed, the used nitrogen sources range from simple ammonia to nitrogen-containing polymers, and as metal sources simple metal salts of, for example, iron or cobalt can be used, as will be exemplified in the following.

7.3.3 Modification of Carbon Black and Other Carbon Materials

Initial research in the field of modified carbons focused on CB-based materials as substrates for the formation of active materials. Typically, those carbons also employed as support in fuel cell catalysts, such as Vulcan XC-72 and black pearls from Cabot or Printex XE2 from Evonik, were used. The most facile approach consists of an impregnation of the carbon with both the transition metal salt and the nitrogen source and a subsequent heat treatment step in inert atmosphere, as reviewed earlier [100, 102]. Alternatively, heat treatment of a carbon impregnated with a metal salt in an atmosphere containing the nitrogen precursor (NH_3 [104] or acetonitrile [105]) was proposed. As mentioned earlier, a broad variety of nitrogen precursors have been used for impregnation. One of us (MB) introduced iron phenanthroline as possible precursor molecule, a material much simpler than the above-mentioned N_4 -chelates, however with already existing N-Fe-coordinations, which should aid in the formation of the active sites [106, 107]. Besides simple impregnation and heat treatment, other approaches for catalyst preparation were proposed. Using iron phenanthroline as iron-nitrogen precursor and black pearls as carbon material, Dodelet and coworkers achieved very high catalytic activities by employing ball milling instead of impregnation for preparation of the catalyst precursor, which is subjected to a heat treatment step for catalyst formation [108]. Highly active catalysts were also reported by the Zelenay group employing N-containing polymers as precursors [109].

Crucial parameters in the preparation of Me-N-modified carbons are the metal content and the heat treatment temperature and atmosphere. Several studies indicated that a too high metal content is impeding high activity and optimal metal contents as low as 2% [107] or 0.2% [104] were found, depending probably on the metal precursor. As a possible reason for the reduced

activities, it was claimed that the metal might destroy active sites. Recent activities in this field led to more sophisticated approaches comprising two heat treatment steps with intermediate leaching of the metal [110].

7.3.3.1 CNT-Based Materials

Given their favorable properties such as high chemical and thermal stabilities and good conductivity (see above), it is no surprise that CNTs have also been employed as carbon substrate for the synthesis of active ORR catalysts. Similar approaches as for CBs have been used. For instance, impregnation with iron phenanthroline or N_4 -chelate complexes and subsequent heat treatment led to catalysts active for the ORR in acid media [111]. Besides impregnation, also other approaches such as electropolymerization of N-containing precursors onto CNTs and subsequent heat treatment have been reported [112]. The challenge in the latter case, however, is to prepare larger quantities of catalysts. In all cases, the activity, albeit much higher than that of unmodified CNTs, is still too low to be considered for practical applications.

7.3.3.2 Graphene

Another carbon material currently in the focus of researchers is graphene. Its excellent conductivity and high specific surface, among other favorable properties, render it advantageous for electrocatalytic applications. However, it has been claimed that the basal planes of graphene are inactive in catalysis and it is the edges that provide activity [113]. This would be in agreement with the statements on active sites in carbon nanofibers (CNF) and CNT oxygen reduction catalysts (see below). Similar to CNTs and CBs, its application as electrocatalyst usually involves modification with heteroatoms (typically nitrogen and a transition metal, but also B [114]). However, due to practical reasons, the majority of the studies deals with reduced graphene oxide (rGO) obtained by oxidation of graphite and reduction of the obtained graphene oxides according to Hummers' method, rather than with graphene. The term **rGO** implies that the material is not completely reduced and still contains defects and oxygen functional groups. Furthermore, it should be pointed out that the term **graphene** strictly refers to a one-layered material, while most electrocatalytic studies utilize few-layered samples. Several studies deal with metal (oxide)/N-doped rGO composites [e.g., [115–118]]. Kottakkat and Bron prepared CoN/rGO composites by a one-step reduction from rGO in the presence of a cobalt salt and a nitrogen source (phenanthroline). Depending on preparation conditions, nitrogen-doped rGO with about five layers was obtained with embedded CoO_x species. The materials showed appreciable ORR activity in alkaline media [119].

7.3.3.3 Nanostructured Carbon Grown over Metal Catalysts

As mentioned earlier, a widely accepted model of the active site is that it consists of a central metal ion, which is coordinated to nitrogen atoms embedded as heteroatoms into the carbon structure. However, this view was challenged by contrary findings, that virtually metal-free nitrogen-doped carbons are also active catalyst materials. In this context, it has also been

proposed that the presence of a metal ion is necessary during active site formation with an active site void of any metal. Among other reasons, this hypothesis emerged based on the observation that electrocatalytically active materials can also be prepared by direct growth of nitrogen-doped carbon nanostructures (mainly CNTs and carbon nanofibers) over metal-based catalysts. Ozkan *et al.* grew nitrogen-containing nanofibers over carbon- or alumina-supported metal (Fe, Ni) catalysts in a typical chemical vapor deposition (CVD) process using acetonitrile and tested their activity toward the ORR. The noticeable activity of the N-modified carbon was attributed to higher edge-plane exposure and accordingly the presence of pyridinic nitrogen at these edge planes [120–122].

Similarly, Kundu *et al.* grew CNTs over Co-based catalysts. Significant catalytic activity for the ORR was observed, depending however on the conditions of the CVD growth process. Even though Co was found in the CNTs after pyrolysis, it was concluded that the high activity is related to pyridinic-type nitrogen embedded into the carbon structure [123]. In an earlier study, Maldonado and Stevenson correlated ORR activity of nitrogen-doped carbon nanofibers with the nitrogen doping level and the edge-plane exposure [124]. A correlation of the reducing activity with the basicity of heteroatom-doped carbon has also been suggested [125].

A critical issue concerning the aforementioned studies on virtually metal-free catalysts is that they were conducted on nanostructures grown over metal/support catalysts. Thus, doubts remained whether these materials still contain (minute) amounts of active metal species from the production process. However, recently it was shown that N-doped carbons synthesized without any metal are active for electrocatalytic oxygen reduction. Xia *et al.* prepared ORR catalysts by heat treatment at temperatures ranging from 400 to 800 °C of mixtures of polypyridine and CB, and observed reasonable catalytic activity for the ORR [126].

Even though this issue has not been completely solved yet, research is ongoing in this field. It is likely that various active sites exist, some of them with a central metal ion, some of them metal free, consisting of nitrogen embedded into the carbon structure. With detailed evidence still missing, it is not unlikely that the metal-containing centers are of high activity in both alkaline and acid media, whereas the metal-free ones seem to be mainly active in alkaline media.

Besides growth of nitrogen-containing nanostructures, the possibility of functionalizing the CNT surface in a more or less defined way offers additional approaches to introduce heteroatoms like nitrogen into the carbon surface. A comparably straightforward approach is to oxidize CNTs with suitable agents and to use the introduced oxygen functional groups for further synthesis steps. As an example, heat treatment of oxidized CNTs in ammonia has been reported to yield active electrocatalysts with the activity depending on heat treatment temperature in the range of 400–800 °C. Considerably high activity was found in alkaline solution [127].

7.4 Carbon as Structure-Forming Element in Porous Fuel Cell Electrodes

Fuel cell electrodes are built up from porous layers of the electrocatalysts and have to fulfill many functions. Above all, they form the porous structure, in which the transport of the gaseous or liquid reactants and products has to be accommodated. Furthermore, they anchor the active sites and expose them in a way accessible to the fuel feeds and offer interdigitated pathways for proton and electron transport from electrode-to-membrane or electrode-to-current collectors. And all of these functions have to be maintained over at least 3.000 operation hours for fuel cells in automotive applications.

7.4.1 How the Support Material Affects the Electrode Structure

Since the electrodes are manufactured from supported electrocatalysts, the choice of the support material apparently also affects the porous structure of the formed electrode layer. This is demonstrated in the false-color TEM image of a thin cross section of a porous fuel cell electrode in [Figure 7.8](#). The connection between the morphology of the support (inset) and the 3D structure of the electrode can be clearly observed. Shown in black and lilac are electron-conducting regions, that is, carbonaceous support agglomerates, whereas green and red mark the proton-conducting ionomer strands and white are pores. The black regions appear in size and shape extremely similar to the particle agglomerate (shown in the inset). Changing the support material, for instance, from a platelet-shaped graphite to a voluminous carbon xerogel, would thus not only result in different catalytic and stability properties, but also significantly influences the 3D architecture of the electrode. In reverse conclusion, this would also mean that it is not easily possible to change only the morphology of the carbon material, while keeping its physicochemical properties and structural characteristics, such as, for example, the electron conductivity and graphite content, the same.

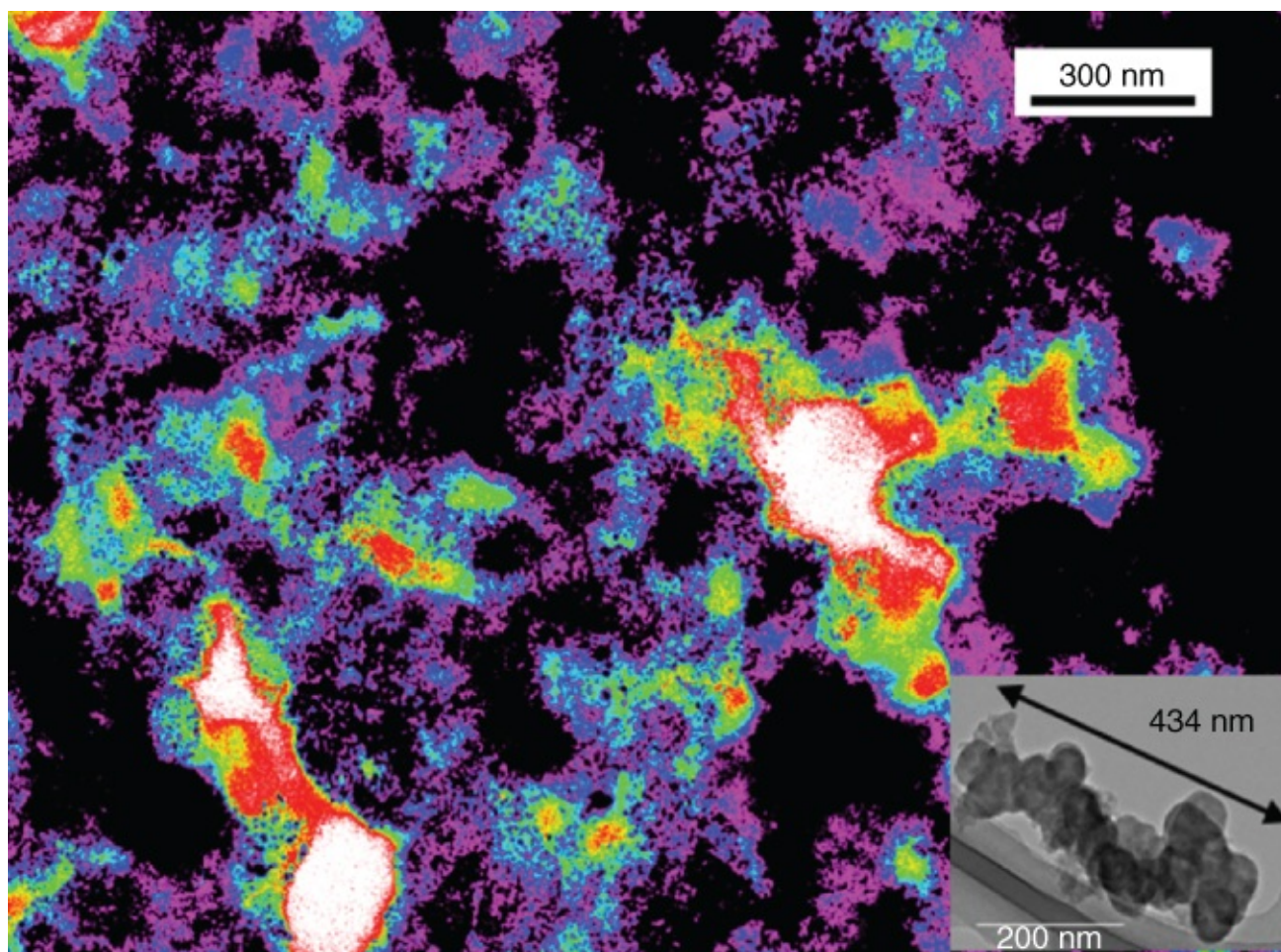


Figure 7.8 False-color image of an ultrathin section of a fuel cell electrode; the inset shows a typical carbon agglomerate.

(Adapted from our other book chapter: [128]. Copyright Woodhead Publishing. Reproduced with permission.)

Peter *et al.* [129] report an interesting approach to synthesize chemically identical carbon materials with significantly different morphology by pyrolysis of a precursor polymer. In this article, the effect of the support morphology on the electrode structure and fuel cell performance is studied in detail. PANI was chosen as the polymeric precursor, as it can be easily prepared in different morphologies [130]. Carbonization of this material yields N-doped carbon spheres, short and long fibers, and the shape is maintained during the temperature treatment under nitrogen atmosphere. From single cell fuel cell tests, significant differences in performance were observed with the long fibers showing the highest and the carbon spheres giving the lowest performance, although electrode thickness and Pt loading were almost identical. Differences between the electrodes fabricated from the carbons with different morphology were revealed using focused ion beam tomography (FIB-SEM) slice and view of a porous volume of $4 \times 4 \times 4 \mu\text{m}^3$. The illustration of the pore space showed in particular a higher amount of pores $>500 \text{ nm}$ for the electrode prepared from the long fibers. This was in good agreement with the chord length analysis (Figure 7.9). It is proposed that this structure is favorable for mass transport and water management, but this assumption has to be verified by further simulations.

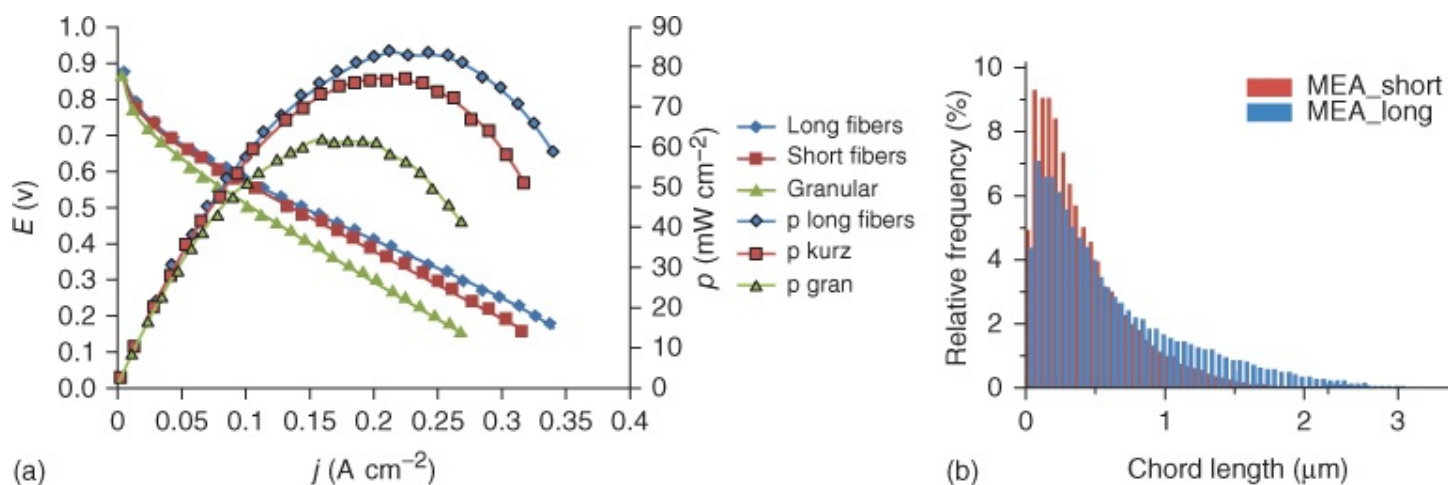


Figure 7.9 (a) Current–voltage characteristics of the three morphologically different support materials with the long fibers displaying the highest power output. (b) The chord length distributions for the long and short fibers are compared.

7.4.2 How the Chosen Fabrication Step Affects the Electrode Structure

In most industrial processes, the electrodes are prepared from a so-called ink consisting of the supported catalyst powder, ionomer, and additives. Already here, the chosen carbonaceous support material will affect the ink properties, such as homogeneity and viscosity, and therefore necessitate adapted ink recipes for each support material. The ink is then either airbrushed, sieve-printed, inkjet-printed, or DECAL transferred onto the membrane or the GDL; and – like the ink ingredients – also the chosen manufacturing process strongly affects the electrode properties.

Zils *et al.* [131] were among the first to study the effect of electrode structure on cell performance using FIB-SEM. In their work, two differently prepared membrane electrode assemblies – one airbrushed, one by the horizontally sprayed fast multilayer method (see also below) – were analyzed by FIB-SEM and 3D reconstruction with respect to porosity, pore size, and tortuosity. Polarization curves were recorded in order to point out the influence of the electrode structure on the PEMFC performance. The results show a higher porosity and a smaller pore size for the LbL-prepared (layer-by-layer) electrode at a four times higher Pt utilization of 1670 mW mg^{-1} and a peak power density of 210 mW cm^{-2} . This favorable behavior is assumed to be due to the improved water management in this electrode. The advantages of the novel spray coating technique are, for example, a high homogeneity of the electrode with respect to pore size (see [Figure 7.10](#)), Pt distribution, and also the expected cost reduction of 60%, since a decreased amount of catalyst allows for a sufficiently good performance.

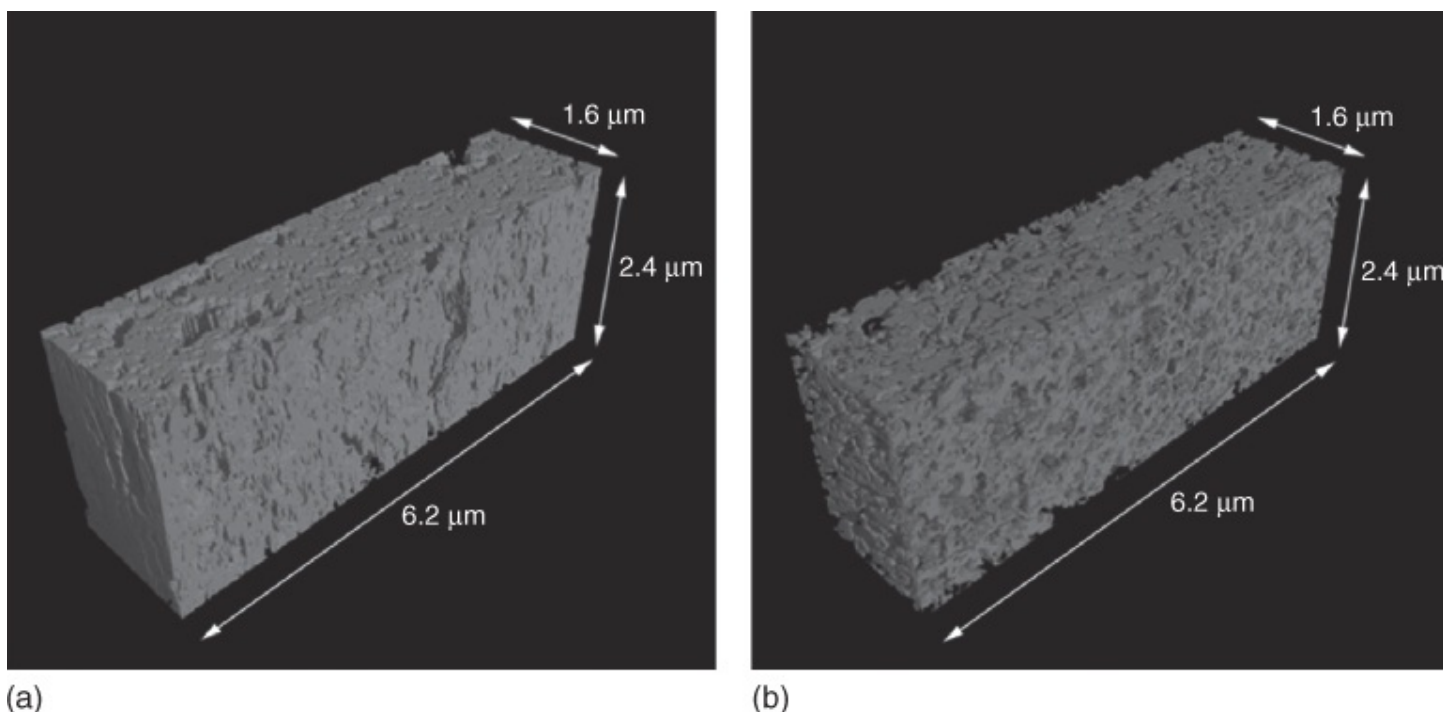


Figure 7.10 Comparison of 3D-reconstructed volumes of (a) an airbrushed electrode and (b) an LbL-prepared electrode (b). [131] (

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7.4.3 How Electrode Structuring Holds Promise to Improve Electrode Performance

Typical processes for the electrode manufacture include airbrushing, sieve-printing, and a DECAL transfer step. In these processes, it is difficult if not impossible to control the integration of active sites, pores, and interconnected proton and electron pathways. That is why the systematic manufacture of (aligned) 3D nanoarchitectures came into focus of recent research [38]. Advantages of such well-defined, ion-electron conductive pathway-integrated 3D architectures are, in addition to the small areal footprint, the short transport lengths for ions in the solid-state electrode as well as between the anode and cathode. In lithium-ion batteries, the 3D design minimizes both distances and hence yields concomitant improvements in the achieved power density. Sophisticated 3D preparation techniques also hold great promise in fuel cells.

Among other techniques, Rolison *et al.* [38] discussed LbL *deposition* and *self-assembly* as viable ways toward more controlled 3D designs. LbL deposition, which was first introduced in 1991, offers several advantages, such as simple incorporation of conductive components, uniform coating of surfaces with complex geometries, as well as nanometer-scale control over film porosity and thickness. Multilayers are built up by alternately dipping a substrate (in fuel cell research: the membrane) into two reservoirs containing solutions of polyelectrolytes of opposite charge. Attracted via electrostatic forces, a layer of polymer adds to the oppositely charged surface, reversing the surface charge and thus priming the film for the addition of the next layer. In fuel cell research, LbL was frequently employed in the horizontally controlled

design of porous electrode layers [132–134]

Self-assembly is another interesting approach toward controlled porous layers in three dimensions. Rolison *et al.* [38] report that colloidal particles can modify electrochemical interfaces in a self-limiting manner. This only happens under very controlled conditions capable of balancing the repulsive and attractive forces between particles, electrode surfaces, and solvents, such that colloids will subsequently self-assemble into continuous aperiodic networks. A respective example has been described by Chiang and coworkers [135] for the positive electrode in lithium-ion batteries. In suspensions of MCMC colloids in an electrolyte of 0.1 M LiClO₄ in 2-butanone containing poly(ethylene glycol), the carbon colloids are strongly attracted to one another, yet repelled from the surface of LiCoO₂ in the absence of an applied voltage. The resulting carbon colloid network self-limits before short-circuiting with the LiCoO₂ as driven by dispersion forces that defeat the interparticle electrostatic interactions.

Here, we would like to point out the specifics of carbon materials applied as the structure-forming element in the porous electrodes in classical electrode design ([Section 7.4.4](#)), in advanced designs applying, for example, horizontal and vertical structuring techniques ([Section 7.4.5](#)), and also highlight novel concepts, such as electrospinning and “self-assembled” Pickering emulsions ([Section 7.4.6](#)).

7.4.4 Classical Electrode Designs

The standard PEMFC is built up in a sandwich-like manner with the membrane as a mirror plane. The proton-conducting membrane is at the core of the device, covered on both sides by the catalytically active porous electrodes, next to them GDLs for fine gas distribution, heat and water management, and flow fields for the coarse distribution of the feeds. The electrodes can then be bound to either the membrane (so-called catalyst-coated membrane = CCM) or the GDL (so-called gas diffusion electrode = GDE).

Historically, separating the fabrication of the catalyst layer from the gas diffusion backings has been an important step toward enhanced performances [136, 137]. By this approach, each layer can be manufactured individually with the properties adapted to its respective function. In the case of the catalyst layer, this would mean an optimized hydrophilicity, thin electrode, and suitable ionomer-to-electrocatalyst ratio. Wilson and Gottesfeld found out that such thin-film catalyst layers, in which the traditionally employed hydrophobic polytetrafluoroethylene (PTFE) binder is replaced by hydrophilic perfluorosulfonate ionomer (Nafion), show performances comparable to GDE designs utilizing several times as much platinum. This observation is also linked to the existence of sufficient amounts of three-phase boundaries and the corresponding accessibility of active Pt nanoparticles, also referred to as **Pt utilization** (compare [Figure 7.7](#)). Their approach was patented in 1993 [138]. In a later study covering not only fuel cells, but GDEs in general, Wendt proposed that matching the thickness of the porous catalyst layer, that is, adjusting particle size and coating thickness, would indeed help to increase the catalyst utilization [139]. But also the optimum ink recipe and ratio between ionomer and supported catalyst was subject of several investigations (e.g., [140, 141]). An

excellent overview on electrodes and electrode fabrication is given by Litster *et al.* [142]. More recent articles discuss the 3D structure of realistic fuel cell electrodes using the rather tedious process of FIB-SEM and 3D reconstruction to link electrode structure to fuel cell performance [143, 144].

7.4.5 Advanced Designs

Another important step was the partial replacement of more or less arbitrary electrode fabrication techniques with only little control over the final electrode structure with more controlled methods. Advanced and more sophisticated preparation techniques should allow for more control over the porous electrode structure, should be able to tailor the formation of its 3D architecture focusing on important aspects, such as pore sizes and pore size distribution, Pt accessibility, and distribution of TPB. For their adoption by the industrial players, however, these advanced manufacturing technologies should also be cost effective (which they still have to demonstrate in practice).

7.4.5.1 Horizontal Structuring by LbL

In 2005, Farhat *et al.* [145] described for the first time the use of a slightly modified technique based on LbL to fabricate components for PEM FCs. Compared to spraying, DECAL transfer or sieve-printing, LbL offers many advantages, such as the facile incorporation of conductive components, uniform coating of surfaces of complex geometries as well as nanometer-scale control over film thickness and film porosity. These make LbL an attractive new tool in fuel cell technology [133]. An alternating horizontal structure is achieved by successively dipping a substrate into two reservoirs, which contain solutions of polyelectrolytes of opposite charge [146]. Electrostatic forces between the oppositely charged polyelectrolytes lead to the formation of bilayers. However, this process is rather tedious when membrane electrode assemblies MEAs of a suitable thickness are required. Less time consuming is a sequential fast multilayer spraying procedure, which has been developed by Wolz *et al.* [134]. It has been demonstrated that a deposition sequence of a few seconds can be applied without impairing the quality of the films. For example, a film composed of 40 bilayers may be fabricated in less than 10 min as compared to about almost 5 h by the conventional LbL method. [Figure 7.11](#) shows differently magnified electron micrographs of a cross section of a multilayer electrode as an example. Here, 20 wt% Pt on Sb-doped tin oxide (ATO) was successively sprayed with multiwalled CNTs.

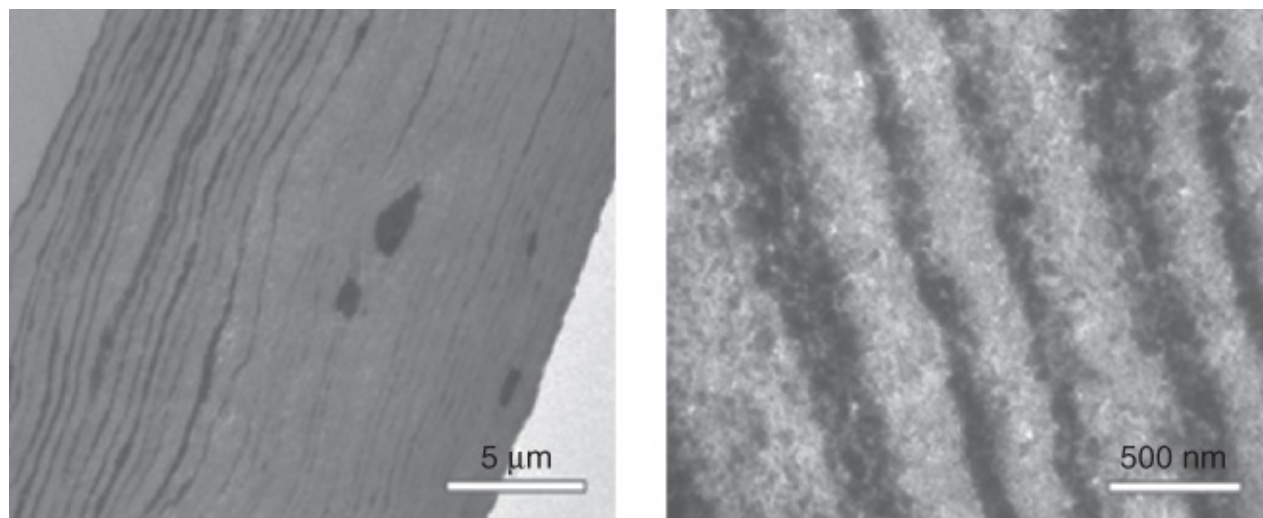


Figure 7.11 Electron micrographs of a cross section of a multilayer electrode composed of bilayers of Pt on Sb-doped tin oxide and multiwalled carbon nanotubes in different magnifications [147].

In the above example ([Figure 7.11](#)), the successful incorporation of Pt nanoparticles supported on ATO into a porous CNT network is demonstrated. By this strategy, porous electrodes were obtained, which is usually rather difficult to achieve, since oxidic supports tend to form very dense catalytic layers. Moreover, it has been found that the tailored architecture favored the gas permeability and likewise a better accessibility of the active Pt sites. The oxide-supported catalyst showed a performance and Pt utilization comparable to an MEA using a standard carbon support, but most probably with a reduced corrosion tendency.

The LbL technique may be utilized also with other novel support materials, for example, PANI fibers before and after carbonization [148] and incorporation of indium tin oxide nanoparticles [149]. Or might be linked to the vertical structuring techniques discussed below. In any case, it is an approach, which might open the way to the manufacturing of structured, but at the same time, cost-efficient fuel cell electrodes.

7.4.5.2 Nanostructured Electrodes

In order to achieve full utilization of active catalyst material (e.g., Pt), high conductivity throughout the electrode, an extended TPB, as well as optimum porosity for facile diffusion of educts and products while at the same time avoiding flooding, it would be desirable to develop a bottom-up approach, in which porous electrodes are assembled in a defined way. Indeed, first fundamental studies have been published, which used the concept of CVD growth of carbon nanostructures to the stepwise build up of the respective nanostructures.

7.4.5.2.1 Bottom-Up Approaches

The simplest approach to prepare nanostructured electrodes in a bottom-up approach is the growth of aligned CNTs on a suitable substrate. Gong *et al.* [150] grew aligned nitrogen-doped CNT on quartz substrates, which showed very promising activity toward ORR, albeit in alkaline media. The growth of NCNTs on glassy carbon using acetonitrile is described by

Alexeyeva *et al.* [151]. High catalytic activity in alkaline media was observed, whereas in acidic media the activity was insufficient for possible practical applications. Prehn *et al.* grew aligned NCNTs from ferrocene/acetonitrile on a silicon substrate and fabricated these into GDEs using sulfonated polyetheretherketone (PEEK) as a binder. The catalytic activity in acid media was moderate [152]. These electrodes have also been used as catalyst support for Pt, demonstrating that the concept can be extended beyond the growth of active carbon nanostructures.

However, to be able to introduce further functionality, additional synthesis steps on the structured electrodes could be performed. Branching of primary CNTs grown on graphite foil with secondary nanotubes has been demonstrated by Li *et al.* and Xia *et al.* [153, 154], resulting in the so-called hierarchically structured electrodes with high electrical conductivity. In a follow-up study, this concept has been transferred to hierarchically structured electrodes grown on carbon cloth, which is frequently used as GDL in fuel cell electrodes. After Pt deposition onto the carbon cloth/carbon fiber/CNT composites, reasonable activity for ORR was obtained [155]. The application of similar structures in fuel cells has also been reported and makes this approach a promising concept for the immediate future [156, 157].

7.4.6 Novel Concepts

Novel concepts of electrode fabrication focus on ways to realize well-defined 3D porous electrode architectures, in which the distribution of TPB is fine-tuned for maximum fuel cell performance. In principle, this means electrode manufacture with pore sizes and pore size distributions in an optimum range and a controlled interplay between electron- and ion-conducting pathways. In recent years, electrospinning and self-assembly have attracted significant interest and some examples of their application in fuel cell technology are described in the following.

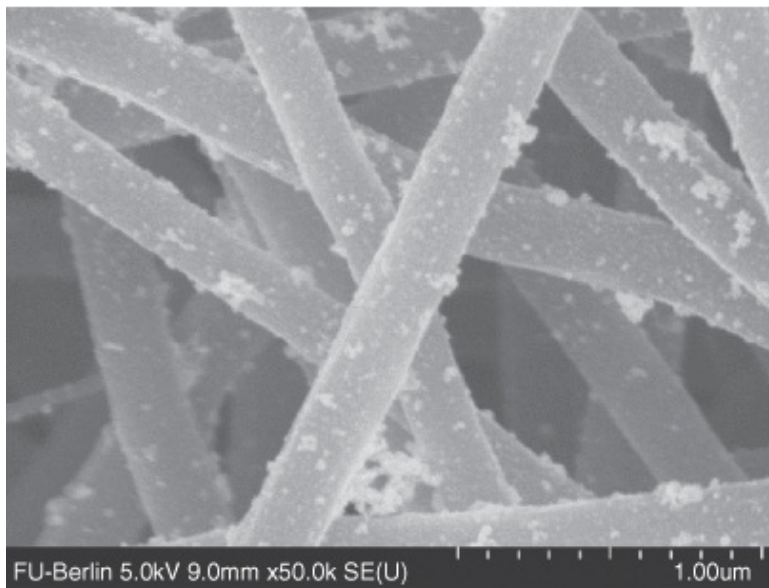
7.4.6.1 Electrospinning in Fuel Cell Technology

Electrospinning is a versatile and low-cost process to fabricate polymer nanofibers, nanofiber mats, and aligned nanofiber structures, but also ceramics and composite materials [158]. Moreover, it offers the potential of a facile and inexpensive scale-up. In the past years, it has been applied in the area of biotechnology for tissue engineering, wound dressings, drug delivery, and enzyme immobilization, and also in filtration and biosensors, to name just a few of its applications [159]. However, despite early publications already in the 1990s, only recently the electrospinning technology grabbed the attention of fuel cell and battery researchers worldwide. An extensive review on the use of electrospinning in energy conversion and storage devices can be found in the article by Cavaliere *et al.* [160]. In low-temperature fuel cells, the obtained fibrous materials find application as catalyst, support material, or even mechanical reinforcement of the polymer electrolyte membrane.

The electrospinning apparatus utilizes a rather simple setup with a so-called spinneret, consisting of pump, tube and needle, and a collector plate. When the polymer solution is pumped and reaches the needle tip, a high voltage is applied between needle tip and collector

plate. The electric field interacts with the droplet deforming its shape. At a threshold potential, electrostatic repulsion is almost equal to surface tension of the liquid and the so-called Taylor cone forms. On further increasing the voltage, the surface tension in the droplet is overcome and a charged polymer thread will be ejected from the needle tip. On its way toward the collector plate, the solvent vaporizes and deposits in the form of continuous, nanometer-thin fibers on the collector. Depending, among others, on the high voltage, the distance between needle tip and collector plate and the viscosity of the solution, fiber length, fiber thickness, and network interdigitation can be adjusted over a wide range. Consequently, skillfully varying these parameters allows us to tailor the resulting porous fiber mat structure. In the most convenient case, such a freestanding fiber mat would be directly implemented as the electrode into an MEA for fuel cells.

In a recent approach of the Roth group, fiber mats from an aqueous polyacrylonitrile (PAN) solution have been electrospun, stabilized at 300 °C, and graphitized in nitrogen atmosphere at 1000 °C. After graphitization of the polymer, the mat structure is largely maintained. In a next step, platinum nanoparticles were decorated into the 3D porous carbon structure by impregnation ([Figure 7.12a](#)). The Pt-decorated electrospun fiber mat was then fabricated into an MEA by hot-pressing it with GDL and membrane. [Figure 7.12b](#) shows a photograph of the obtained MEA, which can be readily used in a fuel cell test bench with promising results despite its rather low Pt loading (not shown). The good performance at low loading can be attributed to the enhanced control over electrode fabrication and the increased number of TPB [161].



(a)

(b)

Figure 7.12 Electrospun and carbonized PAN fibers decorated with Pt (a; bright spots attributed to Pt particles) and an overview of the final freestanding porous electrode structure (b).

Further investigations and an optimization of the process conditions are under way. Hopefully, the results will interest many more potential users in this flexible, low-cost, and promising technology inviting both academia and industry to think outside the box and use it to its full

advantage.

7.4.6.2 “Self-Assembly” by Pickering Emulsions

Another novel concept to obtain structured porous electrodes is based on self-assembly (see also above, work by Rolison [38], already cited), and a modified self-assembly approach for carbon/oxide composite electrodes of the AG Roth is discussed below.

Electrodes utilizing oxidic supports very often suffer from poor porosity. In contrast to catalytic layers built up from CB (see [Figure 7.8](#)), low-surface-area oxides tend to form dense layers, which cannot easily be penetrated by reactants and products. Hence, despite their advantages in durability-limited mass transport is a significant drawback to their routine application. Since they also often possess only low electron conductivities, usually carbon material/oxide support composites are applied instead. One approach toward a controlled porous electrode structure utilizing the so-called Pickering emulsions is shown below ([Figure 7.13](#)).

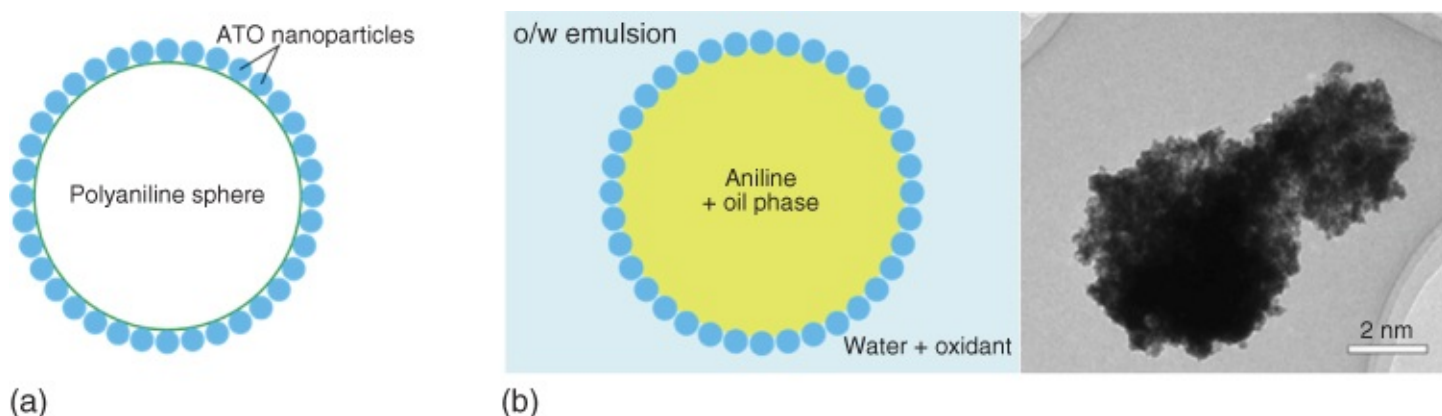


Figure 7.13 (a) Schematic illustration of a Pickering emulsion and (b) SEM picture of the respective Pt/SnO₂ shell around a polyaniline (PANI) core sample.

A Pickering emulsion is an oil-in-water or water-in-oil emulsion, which is stabilized by solid particles, such as metal oxides, clay mineral particles, noble metal particles, and polymer as well as colloidal particles. This effect has been described as early as in 1907 by Pickering [162]. For successful stabilization, the surface charge of the particles (depending on pH, salt, and solid-phase concentration) and the contact angle (depending on the surface groups and the polarity of the oil phase) are key parameters. Because of their unique properties, Pickering emulsions have already been used manifold in various technological applications.

Inspired by He and Yu [163], Wolz and Hein [164] applied the Pickering approach in the synthesis of a porous electrode structure, in which the porosity is predefined by the oxide–polymer sphere size. Sb-doped SnO₂ (ATO) nanoparticles were used to stabilize a PANI core, while the size of these spheres and the stability of the emulsion could be tailored by the chosen synthesis conditions (pH value and solid content) between ATO, toluene/aniline, and water (A. Wolz and S. Hein, unpublished results). An optimized Pickering solution was stable for about 40 min without visible coalescence of the organic phase.

The hollow ATO-PANI spheres obtained via the Pickering approach were decorated by Pt nanoparticles using a standardized polyol process. The chosen synthesis protocol for Pt decoration used mild conditions, which hence did not impact the hollow sphere structure. The hollow spheres were then sprayed onto a commercial Nafion membrane and applied at the cathode side of an MEA. [Figure 7.14a](#) depicts a cross-sectional SEM image of the oxidic hollow spheres. It can be clearly observed that the sphere structure is maintained after the polyol process for Pt decoration. Single cell tests of the novel electrode design showed a maximum power density of 58 mW cm^{-2} and a platinum utilization of 10.3 gPt kW^{-1} ([Figure 7.14b](#)). In comparison to a Pt-ATO electrode prepared in the standard way, the Pt utilization was increased by more than 30%. The enhanced activity is most probably due to the different porosity and structure of the electrode. However, this is only a concept study of the applicability of Pickering emulsions and their self-assembling properties as a way to structure the electrode. Further optimization of the approach is necessary, since the nanoparticle shells are still too inhomogeneous and partially block access of the individual hollow spheres in the catalytic layer.

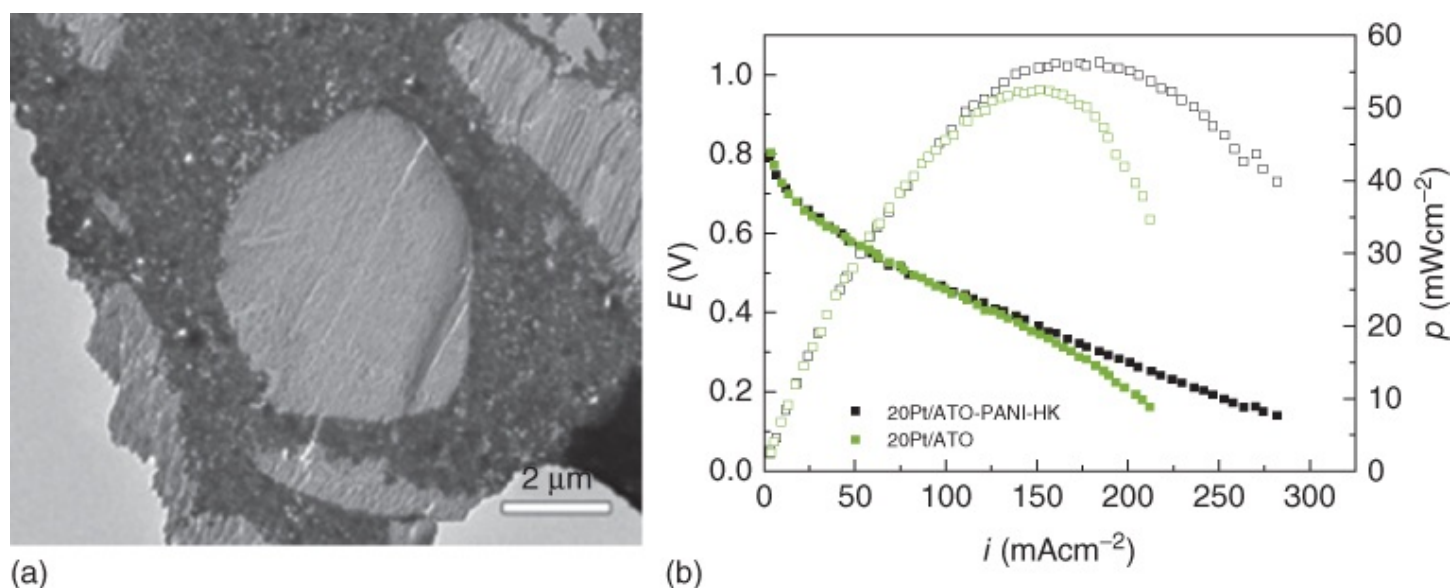


Figure 7.14 (a) Cross section through a catalytic layer formed by “self-assembly” of the Pickering emulsion and (b) the corresponding fuel cell polarization curve.

7.5 Summary and Outlook

After decades literally in the darkness, the impressive versatility of carbon materials appeared in the spotlight only recently, with “carbon materials” meaning materials as different as graphene and CB. Not surprisingly, due to their unique properties, both of them are being utilized in energy applications, and in particular, in low-temperature fuel cells. Nevertheless, because of the huge variety of carbon materials, a thorough classification is necessary, which has been reviewed in [Section 7.1](#). Here, crystallinity, structure, porosity, and hybridization/purity come to mind, which can be accessed via suitable characterization tools, such as Raman spectroscopy, NEXAFS, and XPS studies as well as various microscopy

techniques (SEM, TEM, FIB-SEM, etc.).

In fuel cells, carbon materials are being used in different functions. For instance, in a straightforward approach, high-surface-area carbons serve as support and anchoring sites for the catalytically active nanoparticles, so that the overall material usage and thereby fuel cell cost can be reduced. CB, graphite, CNTs, graphene, and also composites have all been used in the past. Apart from that, carbon materials can even play a much more active role in electrochemical energy applications. Catalytically active ensembles on the carbon surface can enhance the ORR at the cathode side of the fuel cell. And carbon functionalization with nitrogen groups appears to be extremely favorable in this respect, although the nature of the active site is still under debate.

But not only the physicochemical properties of carbon materials play an important role, already the 3D morphology of the carbonaceous material has a significant effect on the porosity, tortuosity, and overall structural integrity of the porous electrode. Therefore, Section 7.4 dealt with material science aspects highlighting the structure-forming effect of the carbon material. Here, the classical electrode fabrication, but also advanced designs applying, for example, horizontal and vertical electrode structuring techniques, have been described, which hold the promise of even better fuel cell performances. Novel concepts, such as electrospinning and self-assembly, have only just emerged, but need to be followed more closely in the future.

Despite the black appearance of most carbon materials, their future in electrochemical energy applications appears to be really bright!

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Chapter 8

Electrochemical Capacitors Based on Carbon Electrodes in Aqueous Electrolytes

Elżbieta Frąckowiak, Paula Ratajczak and François Béguin

8.1 Introduction

In recent years, as the level of technological development of humanity has increased, the demand for energy has increased with the simultaneous increase in CO₂ emissions and the depletion of fossil fuels. For these reasons, attention worldwide is concentrated on introducing renewable sources based on the use of wind and solar energy. However, due to the intermittent character of power generation by these sources, their wide-scale introduction in the grid requires energy storage systems in order to better adapt the delivery to the demand. Among the various storage systems available to date, the most attractive for this target seem to be Li-ion batteries [1], Ni-MH accumulators [2], redox flow batteries [3], and electrochemical capacitors (ECs), also known as **supercapacitors** or **ultracapacitors** [4]. Because of their specific characteristics, where a nanoscale layer of ions from the electrolyte is attracted to the surface of a polarized electrode material, ECs are high-power devices, while they store lower amounts of energy than batteries [5]. Therefore, research attention on the development of ECs is essentially focused on enhancing their energy density while realizing environmentally friendly and low-cost systems. Nanoporous carbons, for example, activated carbons (ACs), are unique electrode materials for ECs, which offer the advantages of low cost, facility in processing, compatibility in composites, highly developed specific surface area (SSA) (up to 2500 m² g⁻¹), versatility, and high electrical conductivity, the latter being a decisive parameter for enhancing power [6–9].

Generally, the proposed solutions to increase the energy density of ECs are based on extending the cell potential and/or enhancing capacitance. In order to increase the capacitance values, researches are focused on analyzing the relationship between capacitance and available surface area/porosity of carbons, pore size and shape, tortuosity, size of ions, and so on [10–13]. Since the operating cell potential is essentially controlled by the stability window of the electrolyte, most of the industrial devices are based on the use of organic electrolytes [14], while ionic liquids (ILs) are still expected to be an alternative especially for high-temperature applications [15, 16]. However, when ecological and economical aspects as well as power demands are considered, aqueous electrolytes offer clear advantages. Especially, recent works have shown that ECs with neutral aqueous sulfates are able to operate at potential values as high as 1.6 V in Na₂SO₄ [17, 18] and 2 V in Li₂SO₄ [19]. It is noteworthy to stress that hydrogen electrosorbed on the negative electrode and strong solvation of ions can be at the origin of cell potential extension.

This chapter presents an overview of carbon-based ECs, paying a special attention on systems

operating in aqueous electrolytes, where the most novel developments have appeared during the last years. Perturbation phenomena, such as positive electrode degradation (oxidation), electrolyte decomposition, and corrosion of stainless steel current collectors, have been disclosed by potentiostatic floating on AC/AC capacitors in aqueous lithium sulfate. Interesting alternatives providing capacitance enhancement, long-term performance, and lack of corrosion products on steel current collectors at high cell potential are also presented. Finally, redox-active electrolytes are shown as an efficient way to increase energy density of ECs using aqueous electrolytes.

8.2 Fundamentals on Carbon/Carbon Electrical Double-Layer Capacitors

ECs store charges in an electrical double layer (EDL) by electrostatic interaction at the electrode–electrolyte interface [5, 20]. Over the years, scientists have developed various models of the EDL describing the aggregation of ions at the surface of electrodes and in the electrolyte. These models explain the phenomena that occur at the solid conductor–electrolyte boundary. In the Helmholtz double-layer model [21], the interface consists of an excess of electrons or holes at the surface of the electrode and a monolayer of ions in the electrolytic solution. According to this model, the specific capacitance has a constant value depending on the dielectric constant, the surface area of the electrode, and the EDL thickness. In the 1900s, Gouy and Chapman formulated another model according to which the capacitance depends also on the applied potential and concentration of the ions [22]. Because of their motion, ions do not accumulate on the electrode surface but form a diffuse space charge.

After 20 years, Stern [23] modified these models by including both a compact and a diffuse layer. At the same time, Grahame [24] divided the Stern layer into two regions: (i) an inner Helmholtz plane consisting of a layer of adsorbed ions at the surface of the electrode and (ii) an outer Helmholtz plane (referred to as **Gouy plane** as well), which is formed by the closest approach of diffuse ions to the electrode surface. From the Grahame model, the capacitance C of the double layer is described by [Equation 8.1](#) as follows:

$$\frac{1}{C} = \frac{1}{C_H} + \frac{1}{C_G} \quad 8.1$$

where C_H corresponds to the specific capacitance of the Helmholtz-type compact double layer, and C_G results from the Gouy diffuse layer ([Equation 8.2](#)):

$$C_G = \frac{\epsilon \kappa}{4\pi} \cosh \frac{z}{2} \quad 8.2$$

with z – the valency of ions and κ – the Debye–Hückel length (m). When n is the number of ions per cubic centimeter, T – the absolute temperature (K), and k – the Boltzmann constant ($1.3806488 \cdot 10^{-23} \text{ J K}^{-1}$), the Debye–Hückel length is described in [Equation 8.3](#) as follows:

$$\kappa = \sqrt{\frac{8\pi ne^2 z^2}{\epsilon kT}} \quad 8.3$$

The model of the EDL that is currently used was proposed by Bockris *et al.* [25], who suggested that a water layer is present at the surface of the electrode (within the inner Helmholtz plane) and some other water molecules are displaced by adsorbed ions. This model may be extended to charge transfer reactions occurring in organic electrolytes with polar solvents, for example, acetonitrile (AN), contributing to the potential drop across the electrode–electrolyte plane.

It is noteworthy that, in all these models, the electrode surface is considered as a plane whereas, practically in an electrical double-layer capacitor (EDLC), it is a porous material – most often carbon – of highly developed SSA, which might be approximately estimated by gas (generally nitrogen) physisorption. Since the gas molecule used to probe the pore volume and the electrolyte ions display different size and interaction with the material surface, it is obvious that the active surface area that takes part in EDL charging is different from the one evaluated by gas adsorption.

An EC is generally constituted of two identical electrodes made of carbon coating on a current collector. These electrodes are separated by a porous membrane impregnated with the electrolyte. [Figure 8.1](#) shows that, in the charged state, an EDLC is equivalent to two capacitors of capacitances C_+ and C_- and resistances R_{f+} and R_{f-} in series. The capacitance C of the total system is given by [Equation 8.4](#) as follows:

$$\frac{1}{C} = \frac{1}{C_+} + \frac{1}{C_-} \quad 8.4$$

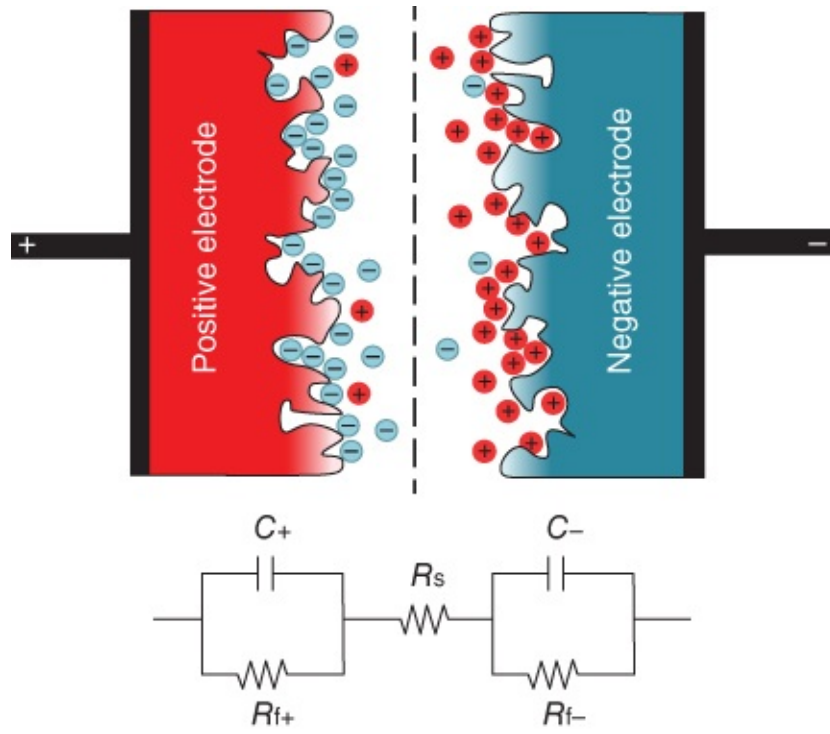


Figure 8.1 Schematic representation of the charged state of a symmetric electrical double-layer capacitor using porous electrodes and its simplified equivalent circuit.

(From Ref. [26].)

Because of the different size of cations and anions in the electrolyte, the capacitance of the electrodes is generally different, even in a symmetric capacitor; in that case, according to [Equation 8.4](#), the capacitance of the capacitor is determined by the electrode with the smallest capacitance.

Since the performance of ECs is based on the attraction of oppositely charged species (polarized electrode and ions from the electrolyte), it is usually assumed that the amount of charge stored in the EDL is directly proportional to the SSA of the interface, according to the following formula ([Equation 8.5](#)) [5]:

$$C_n = \frac{\epsilon_r \epsilon_0 S}{d} \quad 8.5$$

where C_n is the capacitance of one electrode, S is the surface area of the electrode–electrolyte interface, ϵ_r is the relative permittivity of the electrolyte, ϵ_0 is vacuum permittivity ($\epsilon_0 = 8.854 \cdot 10^{-12} \text{ F m}^{-1}$), and d is the EDL thickness. Hence, a highly developed SSA is found as a crucial parameter in energy storage of EDLCs. Moreover, [Equation 8.5](#) presents the technological advantage of EDLCs over conventional capacitors; since d is usually around 1 nm, it gives a huge specific capacitance of around 0.1 F m^{-2} [27].

The energy density of an EC is given by [Equation 8.6](#) as follows:

$$E = \frac{1}{2} C U^2 \quad 8.6$$

where U is the operating cell potential.

The maximum power density also depends on the maximal applicable cell potential and is given by the following formula ([Equation 8.7](#)):

$$P_{\max} = \frac{U^2}{4R_s} \quad 8.7$$

where R_s states for the equivalent-series resistance (ESR) of the EC, which represents the electrical losses during the charging and discharging processes, while the charges flow to and from the electrolyte–electrode interface. The electrolytic solution as well as separator and electrodes are the main components responsible for the value of ESR.

Generally, energy and power of electrochemical storage systems are plotted against each other in a so-called Ragone plot ([Figure 8.2](#)). Dividing the energy density by power gives the time constant τ of a device – presented as diagonal dashed lines in [Figure 8.2](#) – which is the product of series resistance and capacitance ($\tau = R_s C$). The time constant informs how fast the energy can be distributed.

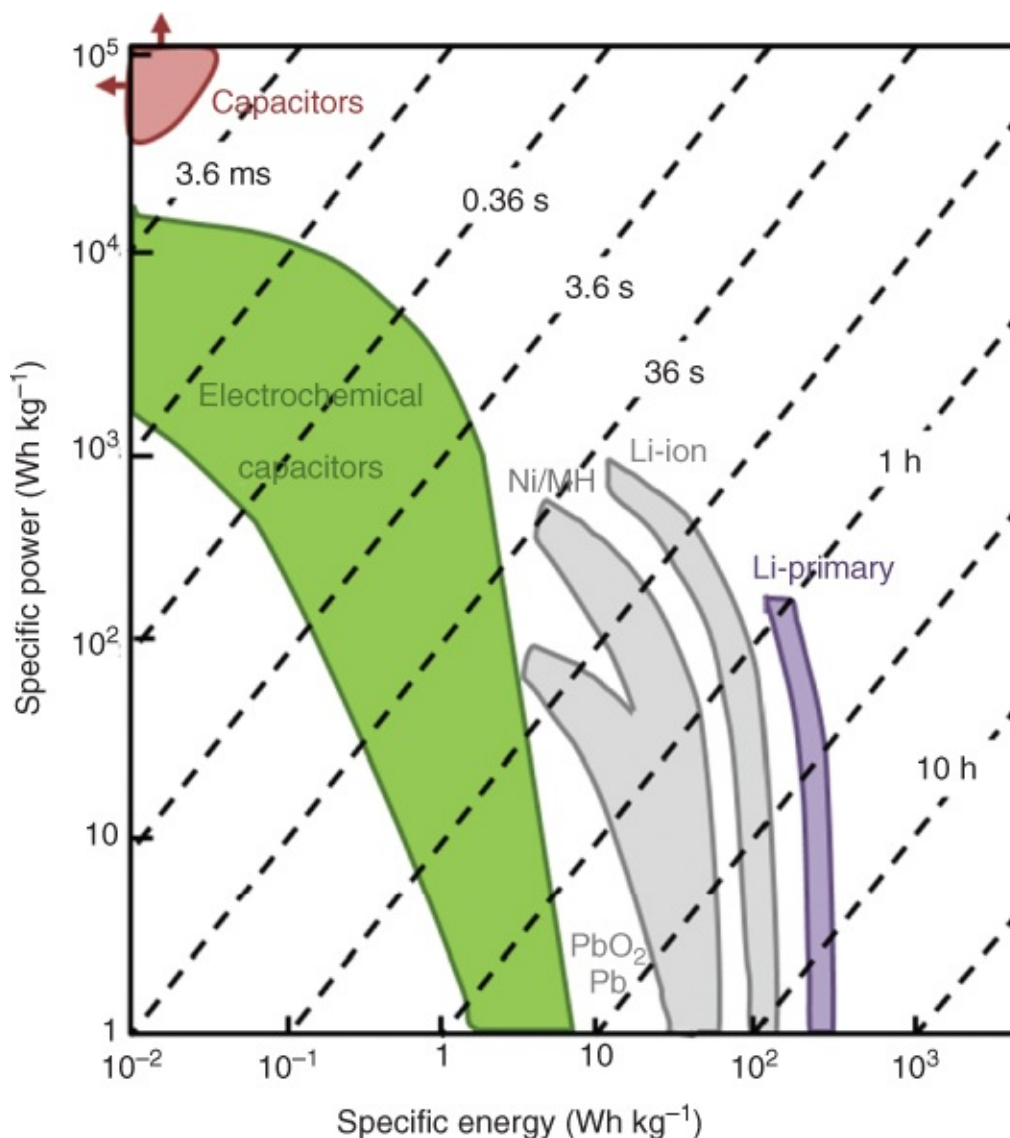


Figure 8.2 Ragone plot of various electrochemical energy storage systems.

(Adapted from Ref. [6].)

Because the storage mechanism is based purely on physical interaction, charging of EDLCs is very rapid. This is the difference with accumulators, where energy is stored through redox reactions in the bulk of the electrode material. An EDLC can deliver power density as high as 15 kW kg^{-1} , which is much more than Li-ion batteries (up to about 2 kW kg^{-1}) [28]. By contrast, since the charge is not stored through electrochemical redox reactions, the specific energy is much lower than for Li-ion batteries ($5\text{--}8 \text{ Wh kg}^{-1}$ compared to up to 180 Wh kg^{-1} , respectively) [29]. Notwithstanding, the storage mechanism in EDLCs is fully reversible with a charge/discharge efficiency close to 100%. The commercially available ECs are characterized by a high life cycle of more than 1 000 000 charge/discharge cycles [30]. Since EDLCs can deliver all the stored energy within around 5 s, they can be used as energy storage and power deliverers for many applications, for example, electric and hybrid vehicles, tramways, buses, cranes, forklifts, wind turbines, electricity load leveling in stationary and transportation systems, opening emergency doors of aircrafts, diesel engines, and renewable energy harvesting [28, 31].

In order to extend the range of possible applications of ECs, the current research strategy is to improve their energy density. According to [Equation 8.6](#), the energy can be enhanced by either increasing the capacitance C or extending the operating cell potential U ; the latter is closely determined by the stability window of the applied electrolyte. The optimization of these two parameters will be considered in the next paragraph. Notwithstanding, most of the scientific publications are rather dedicated to improving the capacitance of electrode materials [32–35].

8.3 Carbons and Electrolytes for Electrical Double-Layer Capacitors

8.3.1 Electrical Double-Layer Capacitors Based on Carbon Electrodes

The most common carbons used as electrodes for EDLCs include ACs [7, 20], carbon nanotubes [36], onion-like carbons [37], graphene [38], and carbide-derived carbons [39]. From the industrial point of view, low cost and high specific capacitance are the essential criteria that determine the choice of AC as material for EDLCs. Compared to some other carbon structures, ACs are characterized by a slightly lower conductivity which, however, can be easily compensated by using a good percolator and appropriate electrode manufacturing process. Finally, in ACs, a large number of pores are opened/created during the activation step, and the development of porosity is usually estimated by the SSA (up to $2500 \text{ m}^2 \text{ g}^{-1}$) and pore size distribution [40].

In order to understand the capacitance properties of electrodes based on ACs, many authors in literature have assumed that the surface area of the electrode–electrolyte interface in [Equation 8.5](#) is equivalent to the BET SSA (S_{BET}) of the electrode material, and have plotted capacitance against S_{BET} . As example, [Figure 8.3a](#) shows that the gravimetric capacitance of ACs and carbon blacks increases almost linearly with the SSA up to $S_{\text{BET}} \approx 1500 \text{ m}^2 \text{ g}^{-1}$, and then exhibits a plateau for carbons with higher activation degree [41]. Taking into account that the BET model generally overestimates the actual surface area values [42, 43], the regularized density functional theory (DFT) model assuming slit-shaped pore geometry is generally proposed as a more accurate way to correlate capacitance with SSA. As shown in [Figure 8.3b](#) for the same carbons, the proportionality region of capacitance with S_{DFT} is more extended than when using S_{BET} , but still saturation of capacitance is observed for S_{DFT} higher than $1200 \text{ m}^2 \text{ g}^{-1}$. In order to explain this saturation phenomenon, Barbieri *et al.* [41] suggested that the pore wall thickness decreases with the increase in pore volume, and for large values of SSA, the average pore wall thickness approaches the screening length of the electric field (δ_{SC}). For carbon materials with $S_{\text{DFT}} \approx 1200 \text{ m}^2 \text{ g}^{-1}$, the walls become too thin and adjacent space charge regions inside the carbon material begin to overlap, resulting in lower capacitance values.

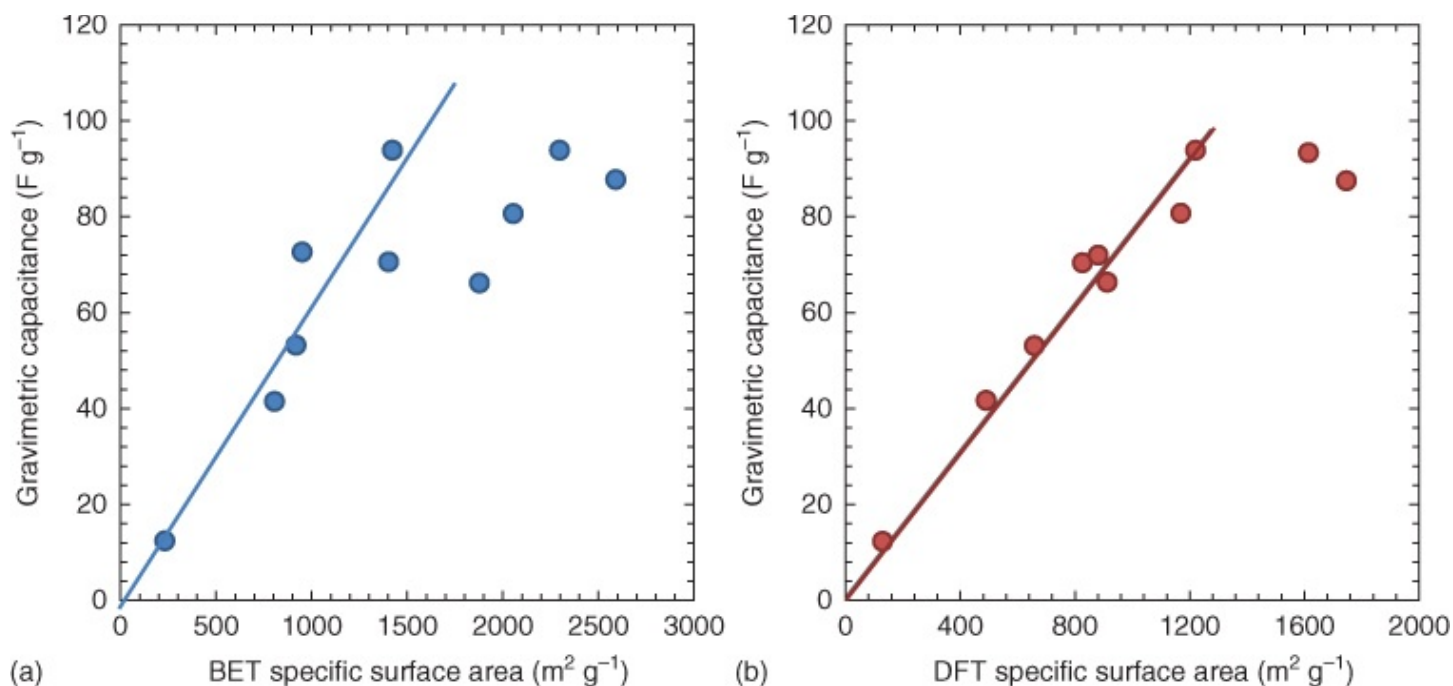


Figure 8.3 Gravimetric capacitance versus (a) BET and (b) DFT specific surface area.

(Adapted from Ref. [41].)

In fact, parameters closely connected with the SSA – pore volume of carbons, size and shape of pores, tortuosity – play an important role in charge storage. It is now well established that ions are efficiently adsorbed in micropores (less than 2 nm in diameter), while mesopores (with 2–50 nm in diameter) are intended to allow the ions to be transported to micropores [44–46]. Moreover, an appropriate volume ratio of meso/micropores is necessary to enhance the capacitance and lower the ESR values [47, 48]. The optimum mesopore volume ratio for AC/AC ECs in 1 mol l⁻¹ H₂SO₄ electrolytic solutions was found to be in the range of 20–50% [49]. A carbon with comparable micro- and mesopore volumes exhibits good charge propagation in cyclic voltammetry while increasing the scan rate from 10 to 50 mV s⁻¹. Because of the role of micropores in charging the EDL, the capacitance values are higher at a low scan rate (2 mV s⁻¹), while the beneficial effect of mesoporous transportation channels is pronounced at higher rates [49].

Above all, according to [Equation 8.5](#), it is important that the pore diameter and the size of the attracted ions fit with each other to enable effective electrostatic interactions and enhance the value of EDL capacitance [50]. Since the size of, for example, K⁺ and N₂ are comparable, it should be possible to assume that the micropores measured by nitrogen adsorption at 77 K (>0.38 nm) should be almost fully accessed by potassium ions. However, according to studies on the accessibility of micropores to aqueous solutions, it turns out that potassium ion sorption occurs only in pores larger than 0.5 nm, meaning that these ions are at least partly hydrated [51]. In such case, since the size of ions depends on their hydration degree, it becomes impossible to establish a direct correlation between the electrochemical properties and the nitrogen adsorption data. Electrochemical measurements conducted with carbons containing a large amount of ultramicropores (<0.7–0.8 nm) and tetraethylammonium tetrafluoroborate

(TEA⁺ BF₄⁻) in AN suggest that ions need to be at least partly desolvated to enable their access into the pores of electrodes [50]; the sizes of desolvated TEA⁺ and BF₄⁻ are 0.67 and 0.48 nm, respectively, as compared to 1.3 and 1.16 nm, respectively, of the solvated ions [51]. Desolvation of ions was confirmed by nuclear magnetic resonance (NMR) on AC electrodes extracted from capacitors charged up to different cell potential values in this electrolyte; for each cell potential, the molar proportions of TEA⁺ and BF₄⁻, as well as the relative amount of AN were expressed versus the total amount of electrolyte species ([Figure 8.4](#)) [52]. As expected, during charging, the NMR signals of cations and anions show that anions are replaced by cations. Simultaneously, the solvent concentration decreases rapidly, and at 2.7 V no AN molecules are left in the micropores of carbon. In the positive electrode, due to charging, large TEA⁺ cations are replaced by smaller BF₄⁻ anions, leaving the place for solvent molecules, which amount remains nearly constant up to 4.0 V. In the case of the negative electrode, the incoming TEA⁺ expels AN, which is further stored in the mesopores, or evaporates from them after opening of the cell.

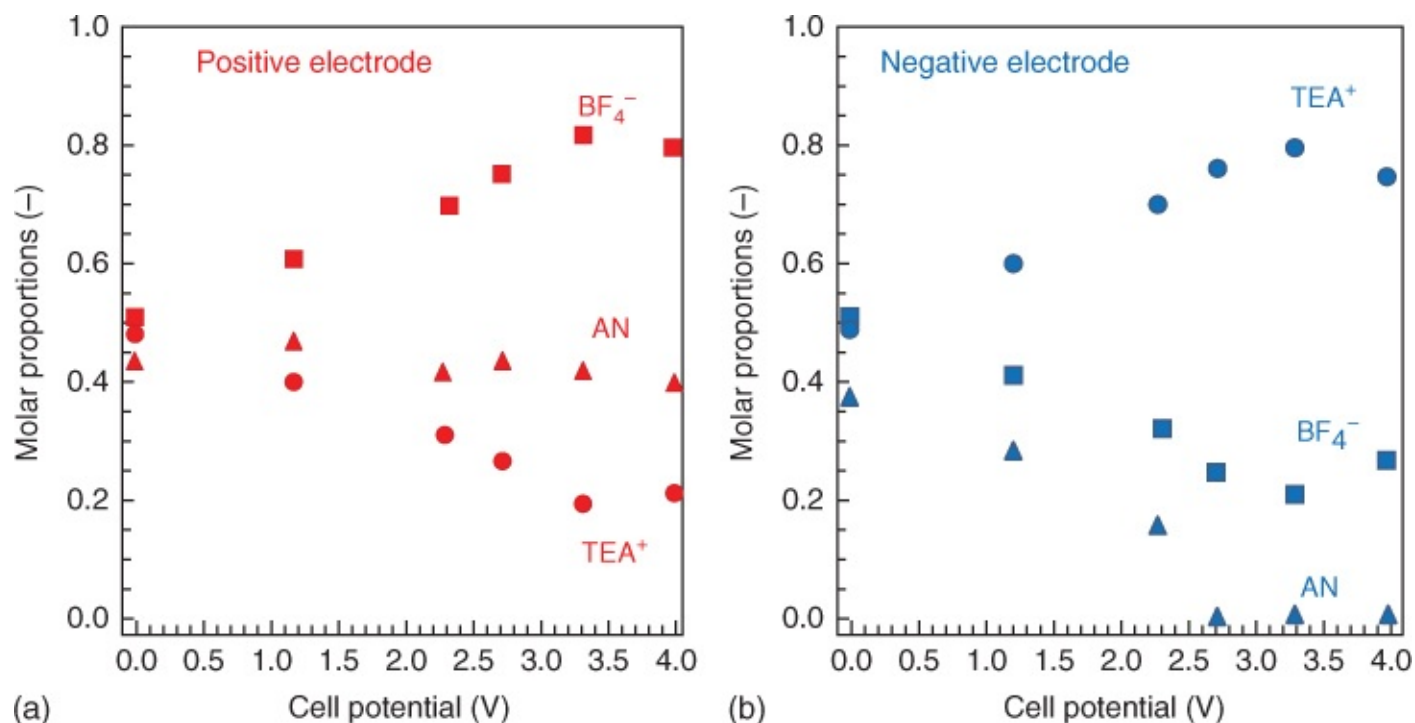


Figure 8.4 Molar proportions of TEA⁺ and BF₄⁻ calculated from the NMR spectra, and relative amount of AN versus the total amount of electrolyte species, after polarization at various cell potentials for 30 min in the (a) positive and (b) negative electrodes of AC/AC electrochemical capacitor.

(Adapted from Ref. [52]).

Because of the fact that in all computational methods there are some assumptions and limitations, Stoeckli *et al.* [53, 54] have correlated the capacitance properties of 28 porous carbons of different origins with their average surface area S_{av} determined by combining gas adsorption and immersion calorimetry. Contrary to the anomalous increase of C/S_{BET} (F m⁻²)

for TiC-based carbons in pores of less than 1 nm for the TEABF₄/AN electrolyte [55], the C/S_{av} values remain relatively constant in slit-shaped micropores of 0.7–1.8 nm [54, 56, 57]. It also appears that, in this pore size range, the volumetric capacitance (C/W_0) increases with decreasing pore width ([Figure 8.5](#)); W_0 represents the volume of micropores deduced from the carbon tetrachloride (CCl₄) isotherm, assuming that the diameters of the largest ion (in the present case, TEA⁺: 0.68 nm and CCl₄: 0.63 nm) are comparable. Interestingly, while assuming slit-shaped pores, the linearization of volumetric capacitance versus L_0 led to similar trend in 1 mol l⁻¹ TEABF₄/AN and 6 mol l⁻¹ KOH electrolyte for two series of ACs [58]. However, taking into account [Equation 8.5](#), when the average pore width L_0 decreases, the capacitance should increase, assuming constant electrolyte dielectric permittivity ϵ_r . Hence, the almost constant value of C/S based on the “sandwich” model of Feng *et al.* [59] led Stoeckli and Centeno [54] to the conclusion that there is a gradual decrease of TEABF₄/AN relative permittivity in micropores. Since slit-shaped micropores contain a constant amount of ions surrounded by a variable amount of solvent molecules that fill the rest of the micropore volume, the relative permittivity of an ionic solution can decrease with the solvent to ion ratio. Even though the theory of variable ϵ_r leads to new considerations involving changes in the number of solvent molecules with the size of micropores, modeling still assumes ideal conditions, for example, that the solvated ion occupies a central position in micropores.

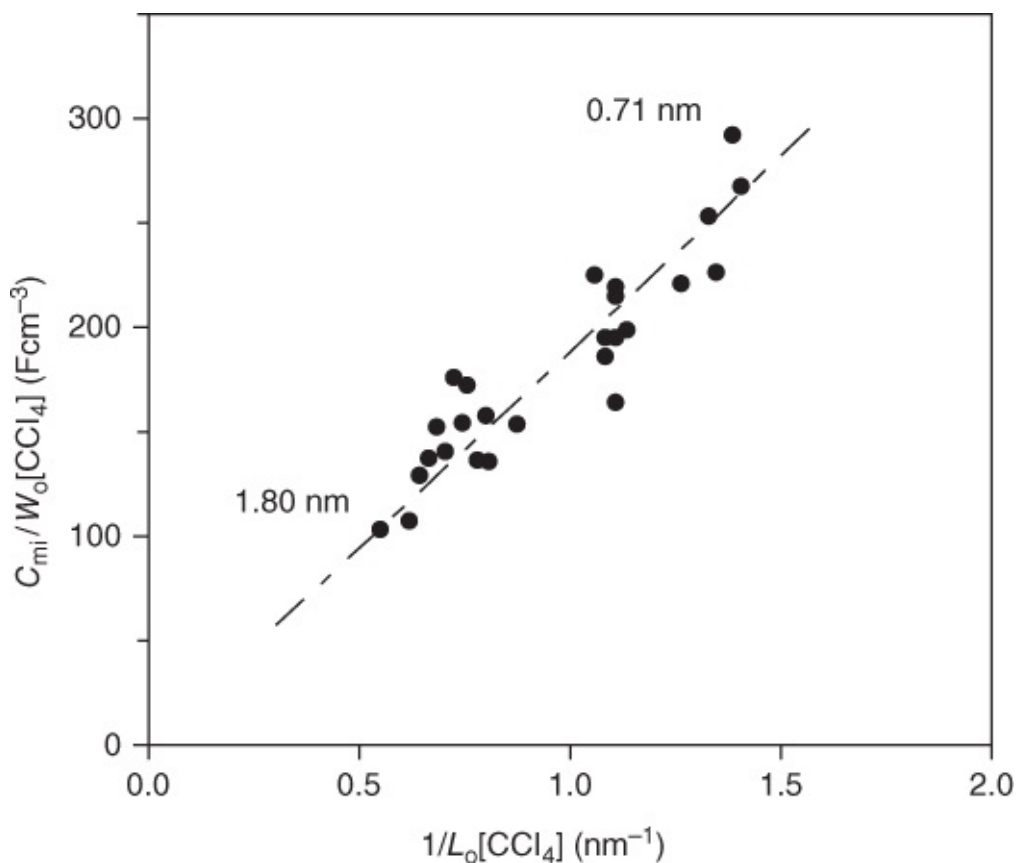


Figure 8.5 Volumetric capacitance of microporous carbons in TEABF₄/AN electrolyte vs average width (L_0) of pores accessible to CCl₄ [57].

The weak point of computational methods is still that they assume well-defined shape pores, rigid, and not interconnected, and thereof are inaccurate for real microporous carbons. In addition, all correlations presented in literature assume that the porosity of electrodes is identical to that of the carbon powder and do not take into account the additives, that is, binder and carbon black. As shown in [Figure 8.6](#) presenting nitrogen adsorption isotherms recorded at 77 K ([Figure 8.6a](#)) and pore size distribution (PSD) ([Figure 8.6b](#)) of an industrial AC powder (NORIT, DLC Supra 30, further named AC) and of electrodes with 80% AC, 10% conductivity additive and 10% polyvinylidene difluoride (PVdF) or polytetrafluoroethylene (PTFE) as binder, the porosity drops due to the binder implementation into the electrodes. The SSA is less reduced for electrodes incorporating PTFE (11% loss), as compared to PVdF containing electrodes, where a 25% decrease is observed. The PSD curve ([Figure 8.6b](#)) demonstrates that all pores are significantly blocked when PVdF is used; this is especially emphasized for the micropores responsible of the adsorption of ions and charge accumulation in the EDL. The cumulative volume of pores <1 nm is 0.32 and 0.28 $\text{cm}^3 \text{g}^{-1}$ for electrodes with PTFE and PVdF binder, respectively, against 0.38 $\text{cm}^3 \text{g}^{-1}$ for the powder, confirming less impact in case of PTFE binder. Furthermore, electrodes with PTFE as binding agent show higher amount of mesopores (V_{meso} reduction by 9%, compared to a decrease by 24% in case of PVdF application) allowing mobility of ions in the pores of the carbon electrode. As a consequence, it has been shown that the different porous texture originated from the type of binder affects the electrochemical performance of both types of electrodes in $1 \text{ mol l}^{-1} \text{ NaNO}_3$ [60].

Nonetheless, one must be always aware that the porosity changes for whichever AC can differ from the above-presented case, and that for establishing correlations between porous characteristics and electrochemical properties, SSA and PSD of electrodes should be always determined.

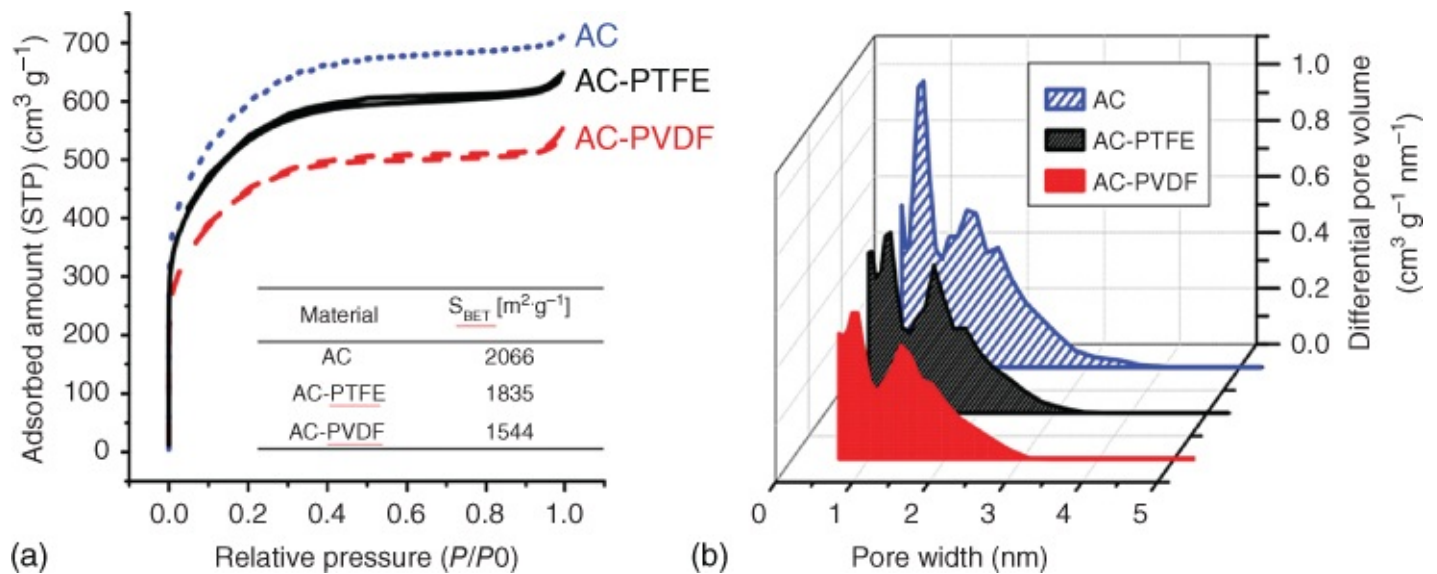


Figure 8.6 Nitrogen adsorption/desorption isotherms obtained at 77 K (a) and quenched solid density functional theory (QSDFT) pore size distribution (b) of AC, AC-PTFE, and AC-PVDF electrodes. For the electrodes, the amount of nitrogen adsorbed is referred to the mass of AC [60].

In organic TEABF₄ electrolyte, good electrochemical performance and mechanical stability was observed for electrodes with 3.5 wt% of polyvinylpyrrolidone (PVP) binder [61]. This amount of PVP has a negligible impact on porous texture characteristics, with total pore volume of 0.71 cm³ g⁻¹ as compared to 0.73 cm³ g⁻¹ for the as-received AC. ECs with AC-PVP, AC-PTFE, and AC-PVdF electrodes in 1 mol l⁻¹ TEABF₄ in PC exhibited specific capacitance values of 112, 107, and 70 F g⁻¹, respectively. Hence, this fluorine-free material appears competitive to the commonly used binders in organic electrolyte, due to not only its suitability in AN and PC, but also its solubility in nontoxic solvents such as ethanol and facile production of electrodes by spray coating or drain casting.

8.3.2 Electrolytes for Electrical Double-Layer Capacitors

Apart from the porous characteristics of electrodes, the kind of electrolyte strongly influences the energy and power density of ECs. Especially, [Equations 8.6](#) and [8.7](#) point out that the performance of ECs is dominantly controlled by the operating cell potential. A good electrolyte for ECs should be characterized by: (i) a good stability in a wide potential range; (ii) good ionic adsorption, which determines the specific double-layer capacitance; (iii) a good conductivity, which determines the power capability; and (iv) a high dielectric constant, which also determines the capacitance value. Besides, the desired electrolytic solution should be also thermally stable, have low viscosity, low toxicity, and low cost [62].

The most commonly used electrolytes are aqueous solutions (sulfuric acid and potassium hydroxide), organic electrolytes, and ILs [14]; however, none of these electrolytes can be considered as ideal in the sense that the previously mentioned criteria are never all satisfied. Aqueous electrolytes display high values of ionic conductivity up to ~1 S cm⁻¹ for 30% H₂SO₄ [63], while the latter is only ~0.02 S cm⁻¹ for the most common organic electrolyte, for example, tetraethylammonium tetrafluoroborate in propylene carbonate [64], and ~0.01 S cm⁻¹ for typical room temperature ionic liquids (RTILs) [65]. According to [Equation 8.5](#), the capacitance values of cells implementing the same electrodes from high-SSA carbons are significantly higher in aqueous electrolytes, of high dielectric constant, as compared to nonaqueous solutions [66, 67]. Finally, when using organic electrolytes, all components (carbon material, separator, electrolyte itself) need to be exceptionally well dried in order to ensure a long life cycle of the system, while drying is not needed in case of aqueous electrolytes, that significantly drops the production price of ECs in the latter media. Despite all the aforementioned advantages of aqueous electrolyte, a major disadvantage of water, when considering [Equations 8.6](#) and [8.7](#), is its low thermodynamic stability and consequently low reachable cell potential of 1.23 V [68]. In practice, it is even less than 1.00 V in symmetric carbon-based SCs with H₂SO₄ and KOH aqueous electrolytes [17, 69–72], whereas AC/AC capacitors in organic medium can be cycled at 2.7–2.8 V [73]. Hence, most of the industrial EDLCs available in the market are based on organic electrolyte, for example, tetraethylammonium tetrafluoroborate in AN.

Recently, attention has been also focused on AC/AC capacitors in ILs, which are able to

operate at high temperatures with almost zero vapor pressure, and feature nonflammability and high electrochemical stability up to around 4.5 V [14, 16, 62, 74]. However, galvanostatic cycling in *N*-methyl-*N*-butylpyrrolidinium bis(trifluoromethylsulfonyl)imide (PYR₁₄TFSI) demonstrated 3.5 V as maximum working cell potential at 60 °C with an efficiency of 95% [74]. The application of 1-ethyl-3-methylimidazolium tetrafluoroborate ([Emim]BF₄) with mesoporous carbon black (BP 2000) enables long-time operation (500 h) at constant cell potential hold (floating) of 3.4 V [75]. Despite the claims on high electrochemical stability of ILs, industrial applications of ILs in ECs are still limited, due to their relatively high viscosity, low conductivity at room temperature, and high cost. Therefore, recently, a by-product of the polyamide industry (Azepane compound) was used for the synthesis of Azp₁₄TFSI and Azp₁₆TFSI [76]. However, the large cation size of this new class of electrolyte results in higher viscosity and lower conductivity as compared to Pyr₁₄TFSI and still requires further study on their potentials as electrolytes for EDLCs [77]. Apart from these applied aspects, from the fundamental point of view, since solvent-free ILs do not possess a solvation shell, thus offering a well-defined ion size, they may be applied to understand the behavior of ions in the pores of carbons.

8.4 Attractive Electrochemical Capacitors in Aqueous Solutions

8.4.1 Extension of Stability Window in Neutral Aqueous Electrolytes

It is well known that higher capacitance values and better electrochemical performance are achieved with aqueous electrolytes due to their greater ionic conductivity, faster mobility of ions, and greater activity of oxygenated groups on the surface of the carbon electrode material [68, 69, 78]. Even though the thermodynamic stability of water is 1.23 V, the cell potential of symmetric carbon-based SCs with H₂SO₄ and KOH aqueous electrolytes is generally less than 1.00 V [17, 69–72], because the potential range of the individual electrodes is not controlled, and one of them might operate out of the stability limits. Consequently, for a long time, it has been accepted that the energy density of capacitors in aqueous electrolyte is much lower than in organic electrolyte. Notwithstanding, aqueous electrolytes based on neutral sulfates lately revealed potentialities for developing high-energy density AC/AC ECs, with cell potential reaching values as high as 1.6 V in 0.5 mol l⁻¹ Na₂SO₄ (around 12% capacitance fading after 8000–10 000 galvanostatic cycles at 1 A g⁻¹) [17, 18] and 2 V when using 1 mol l⁻¹ Li₂SO₄ [19]. The Ragone plots of AC/AC ECs in Li₂SO₄ and KOH aqueous electrolytes ([Figure 8.7](#)) show that the energy density in Li₂SO₄ is enhanced by 80% as compared with KOH [70]. At 25 s time constant, the energy and power density in Li₂SO₄ are 12.3 Wh kg⁻¹ and 1.6 kW g⁻¹ against 7.2 Wh kg⁻¹ and 1.0 kW g⁻¹, respectively, in KOH.

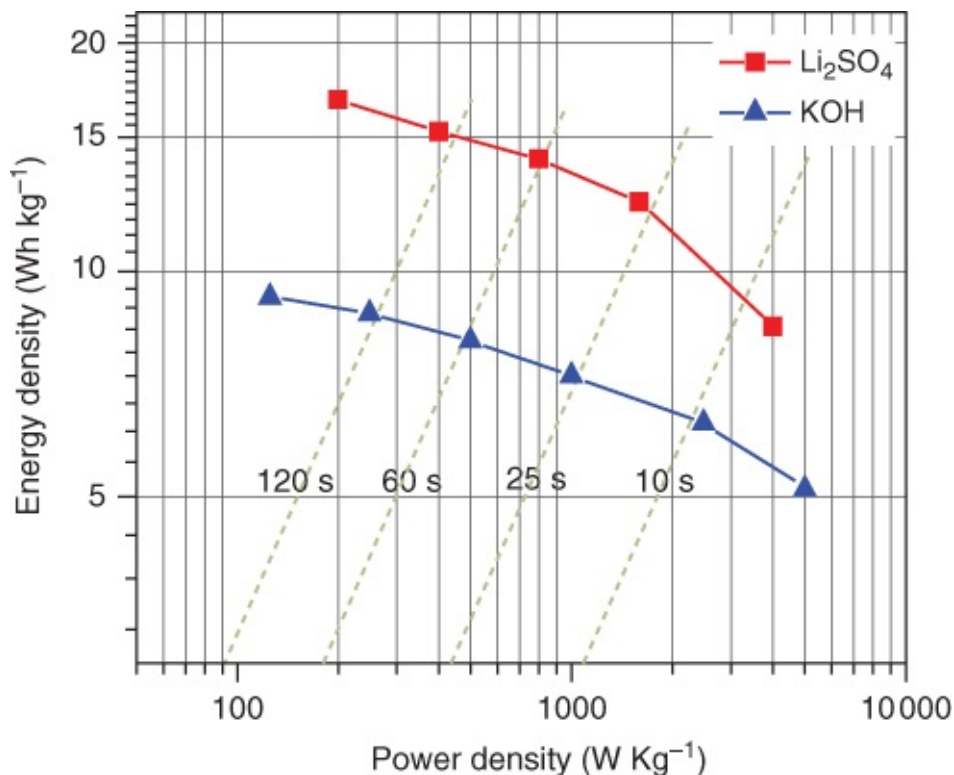


Figure 8.7 Ragone plots of AC/AC capacitors in 1 mol l⁻¹ Li₂SO₄ and 6 mol l⁻¹ KOH aqueous solutions with cell operating potential windows 0–1.6 and 0–1.0 V, respectively. Values calculated for the total mass of active materials.

(From Ref. [70].)

These differences between neutral, acidic, and basic electrolytes are well highlighted in [Figure 8.8](#) by the three-electrode cyclic voltammograms of AC. The potential window of the carbon/Na₂SO₄ system is roughly twice that in the traditional KOH and H₂SO₄ electrolytes [17, 69–71]. Such enhancement has been attributed either to the high overpotential for dihydrogen evolution at the negative electrode [79] or to the strong solvation of cations and anions [19]. For further scaling-up to an industrial production, these neutral electrolytes are by far much preferable, due to much less corrosive properties than sulfuric acid, and allow the cell potential to be extended by appropriate combinations of electrode materials [72, 80, 81].

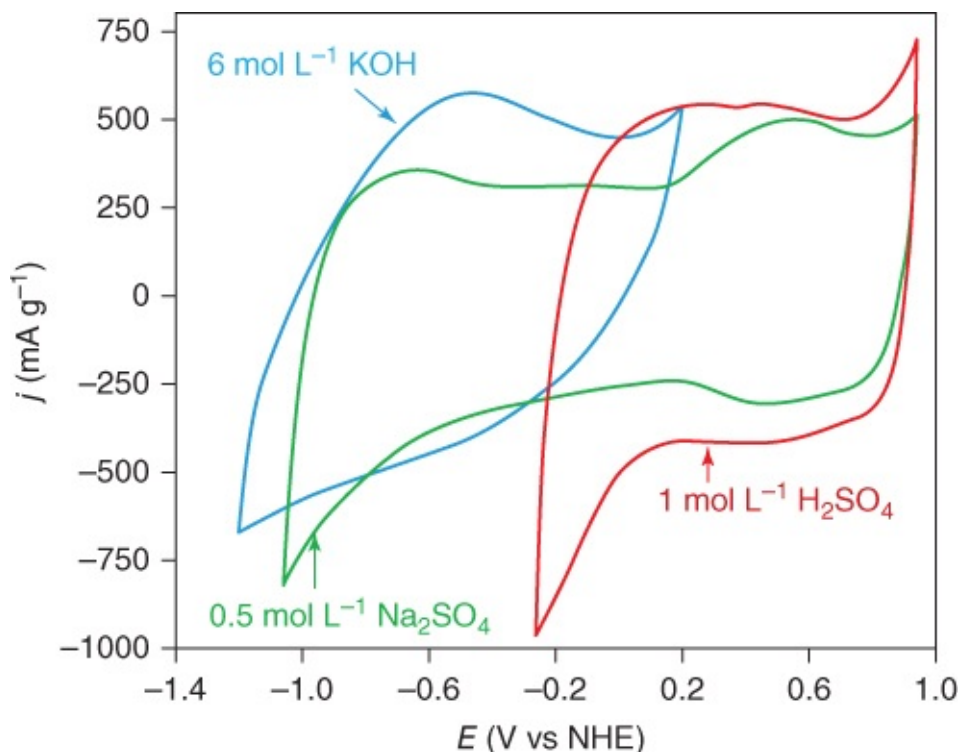


Figure 8.8 Three-electrode cyclic voltammograms (2 mV s^{-1}) showing the potential stability window of AC in $6 \text{ mol l}^{-1} \text{ KOH}$, $1 \text{ mol l}^{-1} \text{ H}_2\text{SO}_4$, and $0.5 \text{ mol l}^{-1} \text{ Na}_2\text{SO}_4$ [17].

Three-electrode cyclic voltammograms of AC in $2 \text{ mol l}^{-1} \text{ Li}_2\text{SO}_4$ ($\text{pH} = 6$), recorded with a gradual decrease of negative cutoff potential, are shown in [Figure 8.9](#). According to the Nernst law, at this pH, hydrogen evolution should start to occur at -0.35 V versus NHE. At cutoff potential higher than this value, rectangular-shaped voltammograms, typical of the double-layer charging, are obtained. For cutoff potentials lower than -0.35 V versus NHE, one can observe a cathodic current leap due to the formation of nascent hydrogen and its rapid chemisorption onto the carbon surface [82, 83]:



and a corresponding anodic peak at around 0.3 V versus NHE [79]. The negative current increases sharply from potentials below -1.0 V versus NHE, indicating H_2 gas evolution according to [Equation 8.9](#) as follows:



and the plausible limit for negative polarization. Part of the chemisorbed hydrogen can also lead to the formation of dihydrogen [84]:



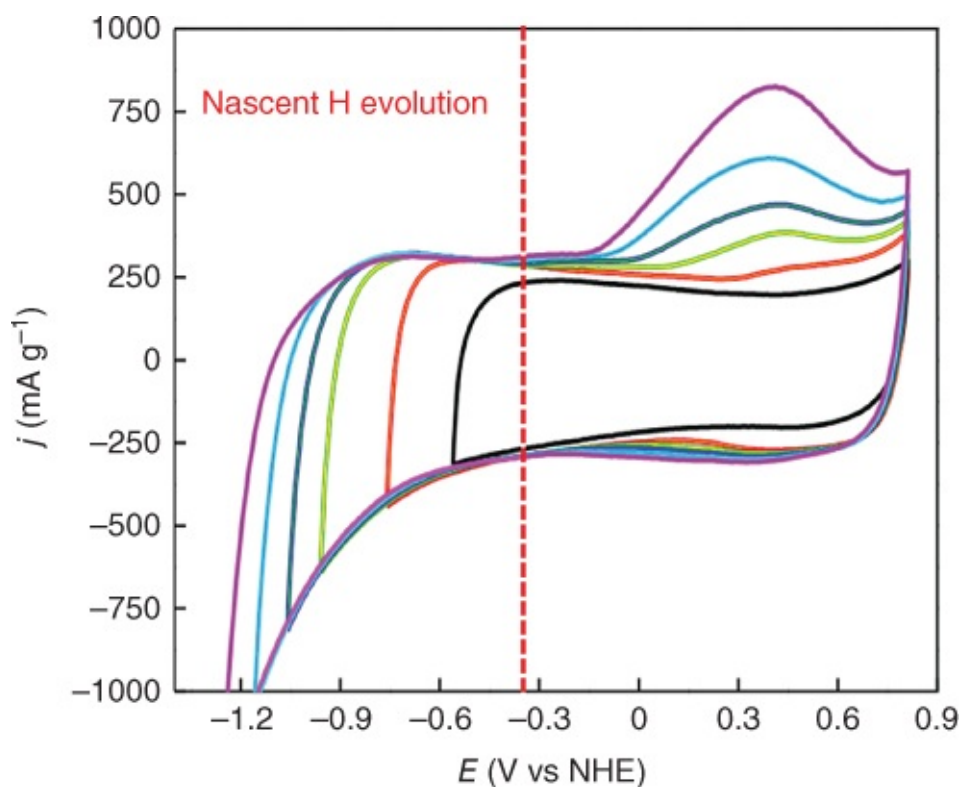
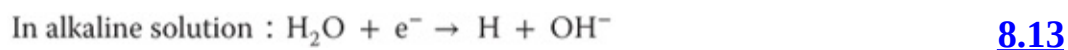


Figure 8.9 Three-electrode cyclic voltammograms of AC in 2 mol l⁻¹ Li₂SO₄. The various loops are obtained by stepwise shifting of the negative potential limit. The vertical dashed line at -0.35 V versus NHE corresponds to the thermodynamic potential for water reduction.

(Adapted from Ref. [79].)

The high overpotential for dihydrogen evolution can be easily explained by the increase of pH in the porosity of the AC electrode. The supply of electrons to carbon under negative polarization leads to the formation of nascent hydrogen by reduction of the electrolyte, according to [Equation 8.12](#) or [8.13](#) depending on pH [84]:



When cathodic charging at -500 mA g⁻¹ was applied for 12 h, Chun *et al.* [85] detected *in situ* pH variations of the electrolyte on the carbon electrode surface ([Figure 8.10](#)). At the end of charging, the pH value in all electrolytes approached approximately 11, except for the medium with pH ~2 where it remained unchanged. For example, in the solution with starting pH = 4, the pH increases due to either reduced amount of H₃O⁺ or formation of OH⁻. On the contrary, for pH = 2, due to the excessive amount of H₃O⁺, the reduction of hydronium ions according to [Equation 8.12](#) results in negligible pH increment. The estimation of local pH changes is particularly difficult with highly porous electrodes where these species are unable to leave the pores rapidly via diffusion or electromigration [85]. Also, owing to their high porosity, ACs are able to store more than 1.5 wt% of the nascent hydrogen formed by electrochemical reduction of water, under ambient pressure and temperature conditions [86–90]. Coming back

to the example presented in [Figure 8.9](#), according to the Nernst law, a change of pH from 6 (initial) to 11 (final) would generate a potential shift of -0.3 V. This lower shift as compared to the experimentally observed one is easily explained by a higher pH in the porosity of the AC electrode than on its outer surface.

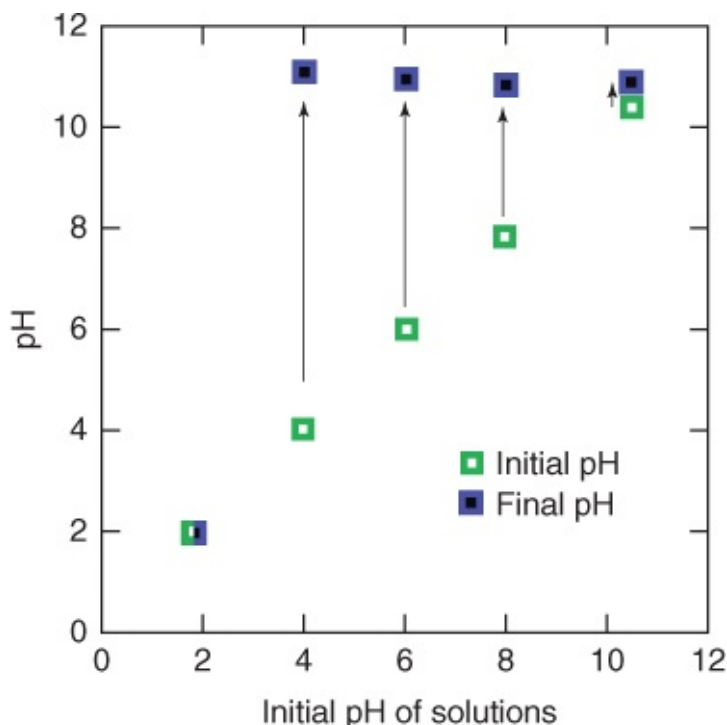


Figure 8.10 Variation of pH value after cathodic charging (-500 mA g^{-1} for 12 h) of AC electrodes in $0.5 \text{ mol l}^{-1} \text{ Na}_2\text{SO}_4$ solutions where the initial pH was adjusted by addition of $1 \text{ mol l}^{-1} \text{ H}_2\text{SO}_4$ or $1 \text{ mol l}^{-1} \text{ NaOH}$.

(Adapted from Ref. [85].)

8.4.2 Determination of Cell Potential Stability Limits by Floating

Even if the positive and negative electrodes initially operate in a given potential window, during long-term cycling, their potential range can progressively shift toward uncontrolled values. It can result in stability limits to be exceeded and finally lead to electrolyte decomposition [79, 91]. The rate of the electrolysis reactions depends on the applied potential, current density and local pH values [92, 93]. During capacitor operation, the local pH of the electrolyte can change through the consumption of hydronium ions or evolution of hydroxide ions during the electrolysis process at the negative electrode.

The test protocols used to determine the operating limit conditions are usually based on galvanostatic charge/discharge cycling. In order to keep an acceptable length of investigation period, the number of cycles is generally limited to about 10 000, which is a few orders of magnitude lower than the number of expected working cycles of these systems.

Therefore, accelerated aging by keeping the system at an imposed high cell potential (so-called “floating”), and in some cases using temperature higher than the ambient, is considered as a

pertinent method to examine the state of health (SOH) of a cell, while not requiring extremely long investigation time [94, 95]. The floating tests are usually applied on commercially available AC-based ECs in organic electrolytes [96], and recently they have been adjusted to examine systems with aqueous electrolytes [97, 98].

The SOH of an EC is evaluated by monitoring capacitance and ESR at various lifetimes of the system. An EC is usually considered by manufacturers as out of service when the ESR is increased by 100% or the initial capacitance is reduced by 20% [99]. Generally, it is typical that the ESR reaches the end-of-life limit earlier than capacitance [98]. The failures which can appear during the working time of a capacitor may be

1. Opening of the system due to gas evolution and internal overpressure
2. A capacitance loss of the carbon electrode caused by (i) reduced accessible surface area due to oxidation of the carbon surface or pore blockage by electrolyte decomposition products and (ii) electrolyte decomposition leading to ionic starvation in the electrode [100]
3. An increase in ESR due to weakening of the adhesion between the active mass and the current collector (it is often caused by gas evolution or corrosion of the current collector) or to the formation of decomposition products on the electrode.

This test of ECs is based on a combination of few galvanostatic charge/discharge cycles followed by floating periods at constant high cell potential ([Figure 8.11](#)). Since a prolonged period at high cell potential may promote better packing of ions, resulting in an increase of capacitance and a lower value of resistance, few galvanostatic cycles are necessary for the system to return to its initial state after a floating period. Therefore, only capacitance and ESR determined from the fifth discharge are considered to be representative of the system performance. The ESR R_s is calculated from the cell potential drop when the sign of current I changes from charge to discharge ($R_s = \Delta U_1/2I$), whereas capacitance C is deduced from the galvanostatic discharge in the range ($\Delta U_2; 0$) by the time this process takes (Δt), and R_s and C are plotted against the cumulated floating time. In the case of carbon-based ECs in aqueous electrolyte, it is sufficient to repeat the floating and galvanostatic sequences 60 times for a total floating time of 120 h to distinguish the main failures that can appear during operation as: internal overpressure, increase of ESR, capacitance loss, and corrosion of the positive current collector.

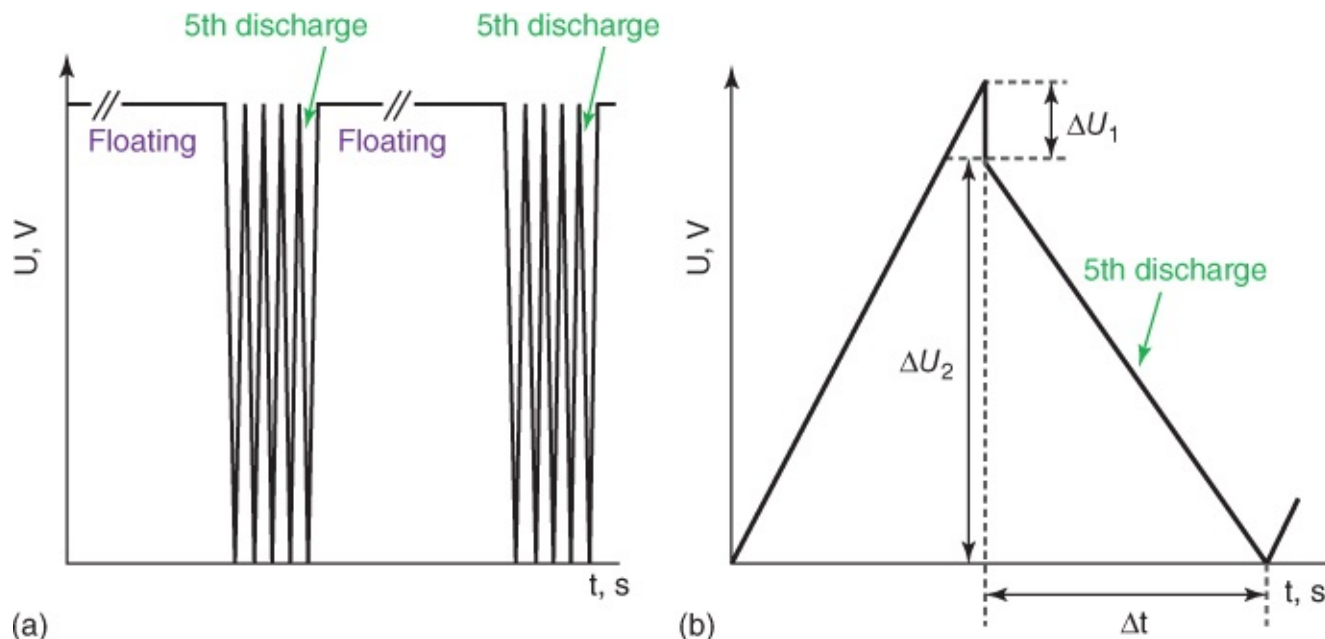


Figure 8.11 Scheme of the accelerated aging protocol (a) and magnification of the fifth galvanostatic cycle (b). The fifth discharge cycle of each series is considered to estimate the capacitance and ESR values.

The effect of cell potential hold on capacitance and resistance versus cumulated floating time is shown in [Figure 8.12](#) for an AC/AC EC in $1 \text{ mol l}^{-1} \text{ Li}_2\text{SO}_4$. The initial capacitance increase when floating proceeds is due to the improved access of ions to narrow micropores of the carbon electrodes under the effect of polarization. At 1.5 V, the capacitance value reaches stabilization after about 75 h. At higher cell potentials of 1.6 and 1.7 V, the stabilization period is reached more quickly (higher cell potential enhances the access of ions to the narrow pores), and the capacitance decays more or less rapidly depending on the cell potential, which is the proof of side reactions leading to partial blockage of porosity. The noticeable resistance increase during floating at 1.6 and 1.7 V is also the proof of carbon degradation and/or electrolyte decomposition with possible accumulation of gases/solids at the current collector–electrode material interface and in the porosity of carbon. The presence of deposits, mainly on the positively polarized collector, indicates that aging is also related to corrosion of the stainless steel current collectors under floating cell potential higher than 1.5 V [98]. Consequently, such tests prove that ECs using aqueous Li_2SO_4 with stainless steel current collectors can operate safely up to 1.5 V [97, 98]. Such value is obviously lower than the claims coming from galvanostatic cycling with gold current collectors [17–19], and confirms that only floating with non-noble metal collectors is relevant for the validation of systems.

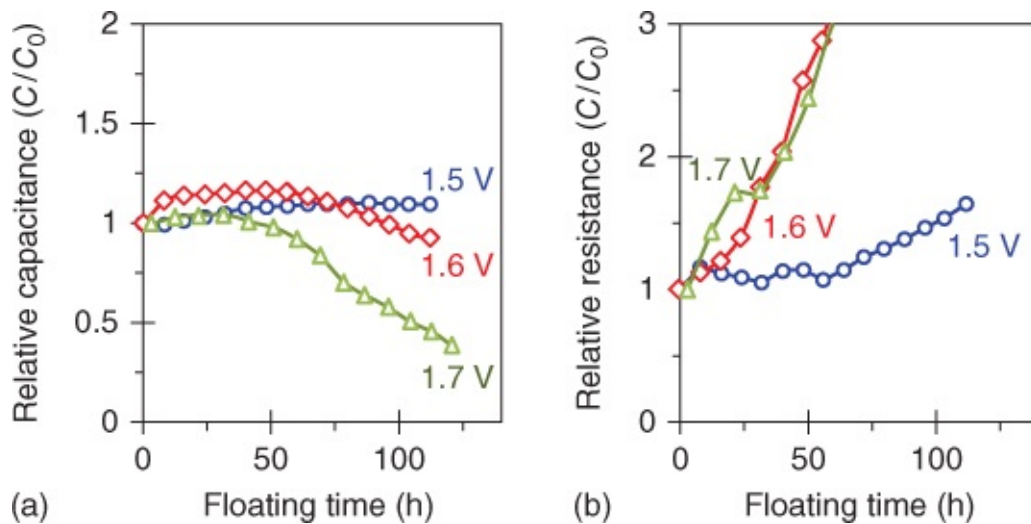


Figure 8.12 Effect of floating cell potential at 24 °C on the (a) relative capacitance and (b) relative resistance of an AC/AC capacitor in 1 mol l⁻¹ Li₂SO₄ [98].

Nitrogen adsorption isotherms were recorded at 77 K on the pristine powder and on the powder of fresh and aged electrodes after 120 h floating at 1.7 V in 1 mol l⁻¹ Li₂SO₄; all textural data were further referred to the mass of active material [98]. As shown by the PSD (Figure 8.13), all pores of the positive electrode are affected after floating, and the volume of micropores (V_{micro}) and mesopores (V_{meso}) is 3.5 times lower compared to the fresh electrode, which results in a reduction of S_{BET} from 1560 to 440 m² g⁻¹. By contrast, in the case of the negative aged electrode, only the volume of ultramicropores (<0.7–0.8 nm) decreases, and the BET SSA is slightly reduced by 205 m² g⁻¹ [98]. It leads to the conclusion that floating at 1.7 V causes a loss in positive electrode porosity, thus reducing performance of the whole cell.

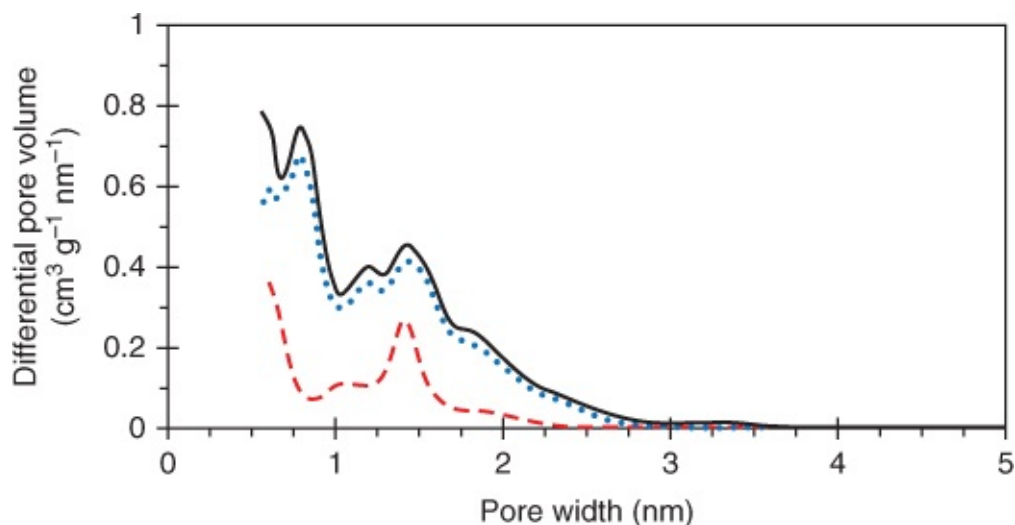


Figure 8.13 Pore size distribution (PSD) of a fresh electrode (full dark gray line) and of aged positive (dashed light grey line) and negative (dotted light grey line) electrodes after 120 h of floating at 1.7 V in 1 mol l⁻¹ Li₂SO₄. The Quenched Solid Density Functional Theory (QSDFT) was used to determine the PSD [98].

The reduction of electrode accessible surface area for ions is not only related to a blockage of

pores by corrosion products, but also to the formation of surface functional groups [98, 101, 102]. The effect of aging at high cell potential of 1.7 V in aqueous lithium sulfate electrolyte on the surface functionality of the carbon electrodes has been analyzed by thermoprogrammed desorption (TPD – thermogravimetric analysis coupled with mass spectrometry analysis of evolved gases), and is shown in [Figure 8.14a,b](#) [97]. In order to avoid the interferences that could be especially due to the presence of binders, the electrodes were made from self-standing activated carbon cloth (ACC). The aged positive electrode exhibits an important mass loss and a large amount of CO₂- and CO-evolving groups. From the patterns of the untreated ACC and electrochemically aged positive electrode, it is clear that new oxygenated functionalities have been formed, and also that some CO₂-evolving groups at temperature higher than 750 °C have disappeared. After deconvolution of the CO₂ and CO patterns ([Figure 8.14c,d](#)), the CO₂ desorption peaks at 270, 500, and 620 °C were attributed to carboxylic and two kinds of peroxide groups, respectively [103]. The quite stable oxygenated complexes desorbed as CO at 710 and 920 °C were attributed to carbonyl/quinone groups and pyrone-type structures, respectively [103, 104]. These new oxygenated complexes formed on the surface of the electrode material block a part of the entrances of the pores, explaining at least partly the decrease of capacitance during floating hours presented in [Figure 8.12](#). Interestingly, it might be observed that the oxygenated functionalities on the surface of the aged negative electrode are more developed than in the pristine ACC, although one could expect that it should not occur under negative polarization of this electrode. Dioxygen, which is formed at the positive electrode, is dissolved in the electrolyte, being able to diffuse to the negative electrode to form peroxide ions and to oxidize the carbon material [105]. The new oxygenated groups appeared on the surface of the negative electrode can be recognized as peroxide groups, desorbing as CO₂ at 550–600 °C [103].

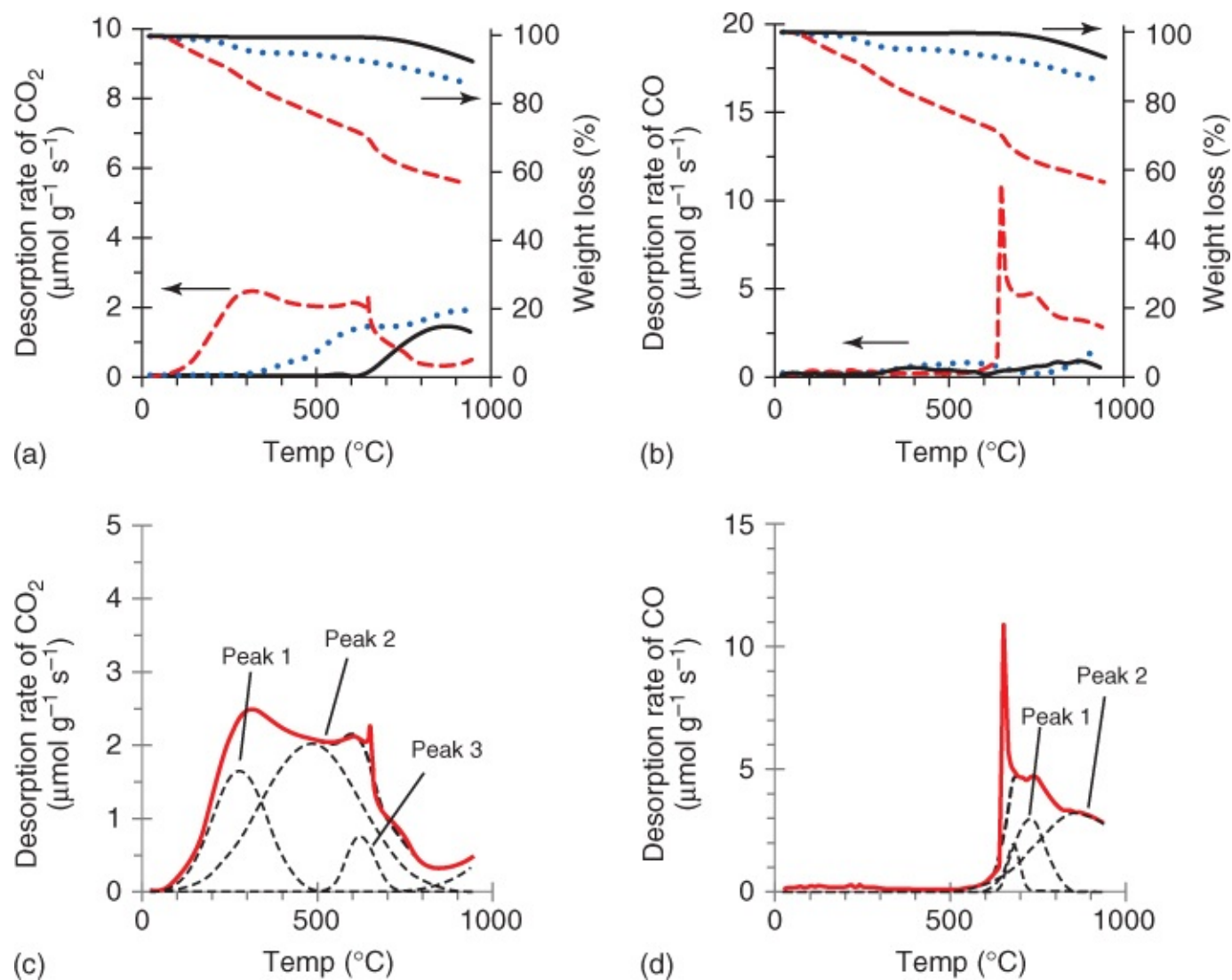


Figure 8.14 TPD on pristine ACC (full dark grey line) and on aged positive (dashed light grey line) and negative (dotted light grey line) carbon electrodes after 120 h of floating at 1.7 V in 1 mol l⁻¹ Li₂SO₄: (a) mass loss and CO₂ evolution; (b) mass loss and CO evolution; (c) deconvolution of CO₂; and (d) CO patterns (full light grey line: TPD experimental data; dashed lines: individual peaks; thick dashed line: sum of the individual peaks).

(Adapted from Ref. [97].)

Recently, the cell potential could be increased up to 1.6 V by adding a corrosion inhibitor of stainless steel, for example, sodium molybdate, to the Li₂SO₄ aqueous electrolyte [106]. After 120 h of floating with this electrolytic solution, a gray deposit is formed on the separator, positive and negative current collector [98]. This gray layer was assigned as a protective passive film, composed mainly of MoO₂ and some traces of MoO₃ [107]. Besides, a pseudo-capacitive contribution of the MoO₄²⁻ ions enhances the capacitance of the whole cell to 120 F g⁻¹, as compared to 103 F g⁻¹ when only 1 mol l⁻¹ Li₂SO₄ is used. [Figure 8.15](#) compares the Nyquist plots of AC/AC capacitors in Li₂SO₄ and in Li₂SO₄ + Na₂MoO₄ before and after 120 h of floating at 1.6 V [106]. The significant increase of charge transfer resistance (R_f), due to

the corrosion products generated on the positive stainless steel current collector, indicates an uneven current distribution after floating in Li_2SO_4 (Figure 8.15a). By contrast, no significant increase of R_f is noticed after 120 h of floating in $\text{Li}_2\text{SO}_4 + \text{Na}_2\text{MoO}_4$ (Figure 8.15b), confirming an inhibitory effect of molybdate anions preventing the formation of a poorly conducting layer of corrosion products. For the AC/AC capacitor in Li_2SO_4 , the ESR calculated from galvanostatic cycling was doubled after 90 h of floating at 1.6 V, whereas it remains almost constant in $\text{Li}_2\text{SO}_4 + \text{Na}_2\text{MoO}_4$ electrolyte. This difference is related to the fact that the maximum operating potential of the positive electrode is shifted from 0.96 to 0.798 V versus NHE when Na_2MoO_4 is added to $1 \text{ mol l}^{-1} \text{Li}_2\text{SO}_4$. Such a shift of the positive electrode potential range prevents electrolyte decomposition, and in consequence AC electrode oxidation and stainless steel collector corrosion at 1.6 V floating.

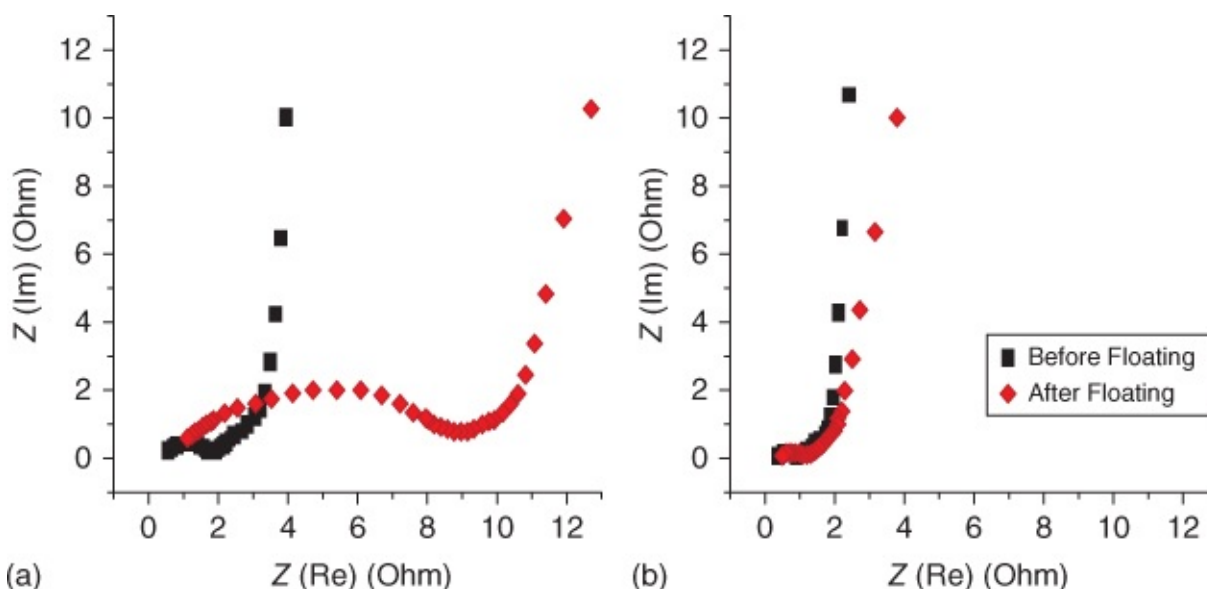


Figure 8.15 Nyquist plots of AC/AC capacitors at 0 V before and after floating at 1.6 V for 120 h in (a) $1 \text{ mol l}^{-1} \text{Li}_2\text{SO}_4$ and (b) $1 \text{ mol l}^{-1} \text{Li}_2\text{SO}_4 + 0.1 \text{ mol l}^{-1} \text{Na}_2\text{MoO}_4$ [106].

8.4.3 Capacitance Enhancement through Faradic Reactions at the Carbon–Electrolyte Interface in Aqueous Media

Besides the EDL electrostatic interactions, redox processes with electron transfer at the electrode–electrolyte interface may also contribute to energy enhancement by pseudo-capacitive charge storage processes. However, due to the faradic origin of these reactions, the performance might be limited by the diffusion of the electrochemical species. There is a recent trend, where the origin of the additional charge comes from redox reactions involving electrolyte species at the surface of an AC electrode. The first reports about this new kind of pseudo-capacitive contribution concerned the carbon–iodine interface formed in aqueous KI electrolyte [108–110]. The cyclic voltammetry investigations on the individual electrodes of an AC/AC cell operating in $1 \text{ mol l}^{-1} \text{KI}$ solution with gold current collectors clearly show reversible redox peaks at the positive electrode (Figure 8.16a) in a narrow potential range from 0 to 0.14 V versus saturated calomel electrode (SCE) [108]. The electrochemical activity

of this electrolyte is based on the following possible redox reactions (8.14)(8.15)(8.16)(8.17):



The extremely high capacitance of 1840 F g^{-1} at 1 mHz for the positive electrode is not only related to the above redox reactions, but also to physicochemical parameters such as hydration effects, interactions between ions under electrical polarization and kinetic considerations such as species diffusion coefficients and their mobility [109]. Since the negative electrode has a typical EDL behavior (Figure 8.16a), the CVs of the hybrid AC/AC cell display the typical rectangular shape for a capacitor (Figure 8.16b). The capacitance of the device (expressed per mass of one electrode) is 260 F g^{-1} at a scan rate of 1 mV s^{-1} [108] showing that, according to (Equation 8.4), this capacitance is around twice that in a system, where both positive and negative electrodes would have the same capacitance. It is worth mentioning that a moderate decrease of capacitance (less than 20%) was observed after 10 000 galvanostatic cycles at current density of 1 A g^{-1} with gold current collectors.

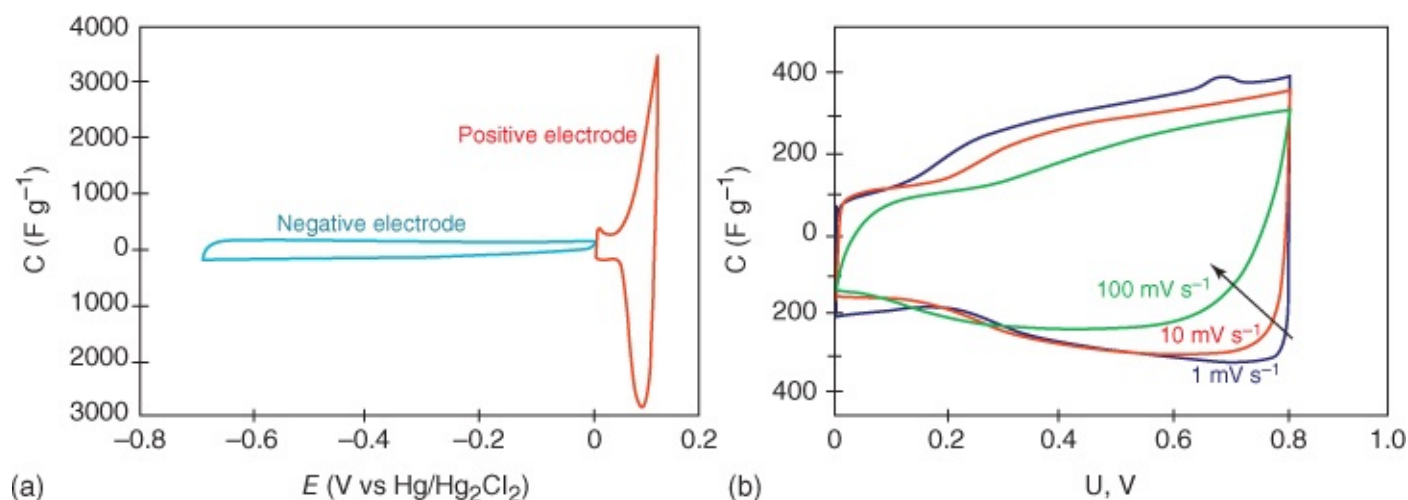


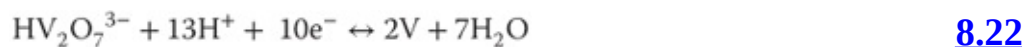
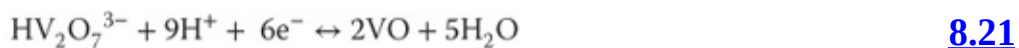
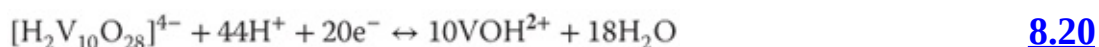
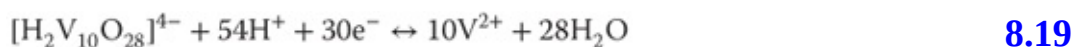
Figure 8.16 Voltammetry characteristics of an AC/AC cell in 1 mol l^{-1} KI solution: (a) AC/AC cell with SCE reference at 5 mV s^{-1} ; (b) two-electrode system at 1, 10, and 100 mV s^{-1} potential scan rate.

(From Ref. [108].)

Another important advantage of iodide salts as electrolytes for EC application is the possibility to use cheap stainless steel current collectors. AC/AC cells with stainless steel collectors in 2 mol l^{-1} NaI did not show any trace of corrosion after 15 000 charge/discharge cycles at 2 A g^{-1} as well as after 150 h of floating at 1.2 V [110]. During floating of the cell with stainless steel collectors, the potential range of the electrodes shifts, and as a consequence a slight redox contribution starts to appear when the potential of the negative

electrode reaches its highest values. Because of that, the linearity of the galvanostatic curves is restricted to the cell potential range from 0.1 to 1.2 V, where the discharge (at 2 A g⁻¹) capacitance is stable in the range of 250–280 F g⁻¹.

As explained earlier, and due to the application of [Equation 8.4](#), the capacitance of the AC/AC capacitor is limited by the relatively low capacitance of the negative EDL electrode. For this reason, an AC/AC capacitor has been developed by using 1 mol l⁻¹ KI as anolyte and 1 mol l⁻¹ VOSO₄ as catholyte separated by a Nafion membrane [111]. High capacitance values of 1200 and 670 F g⁻¹ were measured at 5 mV s⁻¹ for the positive and negative electrodes, respectively. The high values at the negative electrode were explained by the multielectron reactions [\(8.18\)](#)[\(8.19\)](#)[\(8.20\)](#)[\(8.21\)](#)[\(8.22\)](#):



The capacitance values for the full cell with different carbons (AAC 1 or AAC 2) are equal to 521 and 685 F g⁻¹ at 0.8 V and a scan rate of 1 mV s⁻¹ ([Figure 8.17](#)).

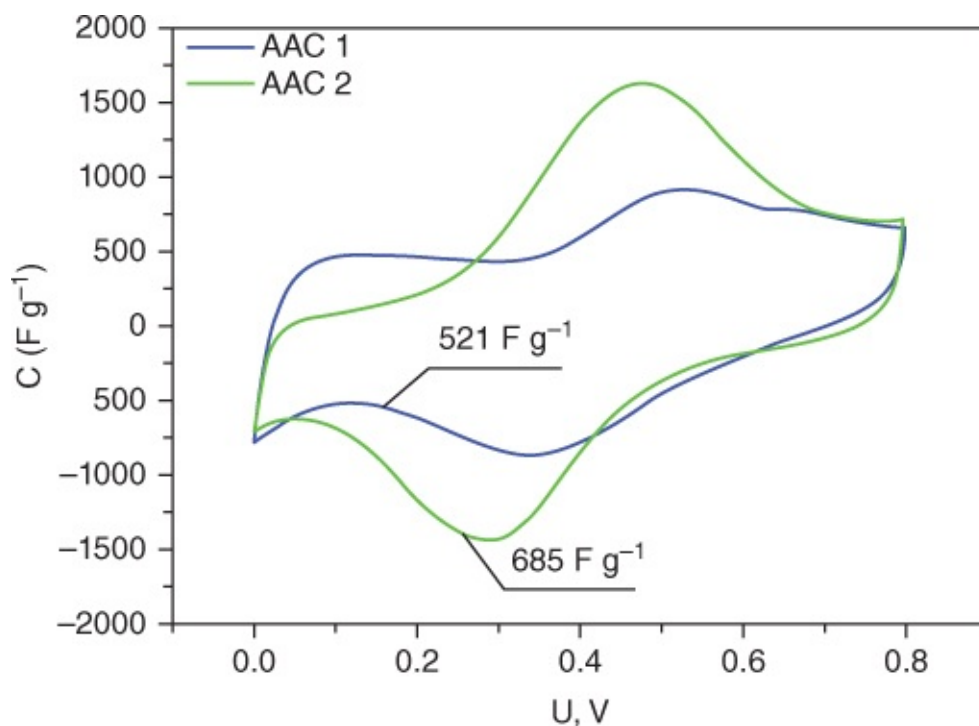


Figure 8.17 Cyclic voltammograms (at 1 mV s^{-1}) of two-electrode cells operating with activated carbons AAC 1 or AAC 2 in iodide/vanadium conjugated redox couples as electrolyte solutions [112].

Another example of pseudo-capacitance related to redox couples at the interface with a carbon electrode is given by the addition of hydroquinone into $1 \text{ mol l}^{-1} \text{ H}_2\text{SO}_4$, which transforms a symmetric AC/AC EC into a hybrid redox system, where the charge storage mechanism becomes different in each electrode [113, 114]. Because of the development of the quinone/hydroquinone redox reaction on the carbon surface [115], the positive electrode exhibits a battery-like behavior, whereas the negative electrode remains of the EDL type. A tremendous capacitance value of 5017 F g^{-1} was recorded by cyclic voltammetry (at 1 mV s^{-1}) for the positive electrode, as compared to 477 F g^{-1} for the negative one. Thus, according to [Equation 8.4](#), with capacitance of the positive electrode (C_+) assumed as infinite, the overall capacitance of the system should be equal to the capacitance of EDL electrode ($C = C_-$), as opposed to the case of the symmetric EDLC, where $C = 0.5C_-$ [100]. This trend was confirmed by galvanostatic (2.7 mA cm^{-2}) cycling up to 1 V, where the capacitance values of the negative electrode and full cell in H_2SO_4 were 9 and 4.2 F, respectively, while after HQ addition $C_- = 15 \text{ F}$ and $C_{\text{cell}} = 13.5 \text{ F}$ [113]. The long-term galvanostatic (4.4 mA cm^{-2}) cycling of a cell in HQ/ H_2SO_4 electrolyte up to 1 V showed a decrease in the initial capacitance of 65% after 4000 cycles. The main loss occurred during the first 1000 cycles and was assigned to the noncompleted quinone/hydroquinone redox reactions within the 0–1 V cell potential window; during the next 3000 cycles, the capacitance of the cell remained stable [114]. Even though this hybrid system appears as an attractive way to increase the capacitive characteristics, it is important to point out that, during long-term cycling, such a cell behaves as a battery than a capacitor. Moreover, practically, it seems difficult to realize a light cell with cheap current

collectors resistant to sulfuric acid corrosion.

8.5 Conclusions and Perspectives

In this chapter, an overview of ECs based on nanoporous carbon electrodes (essentially from ACs) has been presented. Since the operating mechanism of these devices is based on physical interactions of electrolyte ions with the surface of the carbon electrodes, without any electron exchange in typical EDL capacitors, the power is much higher than in lithium batteries. In turn, because of these electrostatic interactions, the energy density is lower than in batteries. For these reasons, most research efforts are dedicated to enhance the energy density by playing on the two factors that control this energy – the capacitance and the cell potential. In EDLCs, the capacitance depends obviously on the development of pore volume, but some other factors such as the pore size and tortuosity are extremely important. At the moment, the correlations between the electrochemical properties of carbons and their nanoporous texture data are still not well understood, especially due to nonorganized porosity, ill-defined pore shape, different size and interactions of ions and gas adsorption probes, not completely satisfactory adsorption techniques and models to interpret experimental data. The cell potential is controlled essentially by the electrochemical stability of the electrolyte. Even though aqueous electrolytes present many advantages, today industrial capacitors prefer organic electrolytes, despite their high cost, environment unfriendliness, and low conductivity, because they allow high potential window – around 2.7–2.8 V to be reached, against around 1 V for conventional electrolytes usually applied in battery systems, for example, sulfuric acid and potassium hydroxide.

After this general presentation of the state of the art, the chapter is focused on recent and novel research developments in the domain of low cost and environmentally friendly AC/AC capacitors using neutral salt electrolytes, for example, essentially alkali electrolytes. Besides fundamental investigations to understand the operating principles and properties of these new systems, attention has been paid to use a common technique from industry to evaluate their life cycle, for example, so-called floating.

By a careful selection of the salt composition (kind and concentration), it is possible to extend the operating cell potential of ECs. AC/AC capacitors with aqueous lithium sulfate are able to operate up to 1.8–2.0 V under galvanostatic cycling when using noble metal (gold) current collectors. When using stainless steel current collectors, the reachable cell potential under potentiostatic floating is 1.5 V, which is approximately twice higher than in H_2SO_4 or KOH. It is noteworthy to stress that hydrogen electrosorbed in the negative electrode and strong solvation of ions can be at the origin of the cell potential extension. The role of carbon, its texture, micro-mesopore ratio, and surface functionality should not be neglected. Among the two electrodes, the positive one is mainly responsible for performance decay during operation, due to carbon degradation (oxidation), electrolyte decomposition, and corrosion of the current collector. The cell performance can be improved by the use of sodium molybdate additive, which allows the cell potential to be enhanced to 1.6 V due to its anticorrosive effect and the capacitance to be increased due to a pseudo-capacitive contributions related with various oxidation states of molybdenum.

AC/AC capacitors involving pseudo-capacitive contributions related with redox reaction at the carbon electrolyte interface are an interesting option to enhance the capacitance in aqueous electrolytes. The most studied electrolytic solutions are based on alkali iodides and quinone/hydroquinone redox couples in sulfuric acid, both types of electrolytes being characterized by a higher conductivity than sulfates. An important interest of iodides is their high compatibility with stainless steel current collectors, whereas gold is corroded in iodide solutions. However, the maximum cell potential reachable with iodide electrolytes is lower (1.2–1.4 V) than in alkali sulfates. Synergetic effects leading to good cyclability without corrosion, higher energy, and power could be expected from mixed electrolytic solutions.

Hence, one can expect that aqueous electrolytes will soon become strong competitors to organic electrolytes (mainly based on AN) because of ecological and economical aspects, while providing comparable energy density. The assembly of capacitors in aqueous electrolytes obviously does not require moisture-free conditions and extremely expensive drying of the carbon material. In addition, the nonflammability of the solvent (H₂O) and the high conductivity of the electrolyte, which enhances energy and power of ECs, seem to be the main paybacks of this future technology.

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Chapter 9

Carbon Electrodes in Electrochemical Technology

Derek Pletcher

9.1 Introduction

Electrochemical technology has a history dating back deep into the nineteenth century and carbon electrodes have been major players in this success [1–4]. In the early cells for both the two largest electrolytic industries, chlor-alkali and aluminum extraction, the electrodes were blocks of carbon or graphite. The past 50 years, however, has seen the development of carbons with different structures and often their availability in a range of forms. Thus, it is possible to purchase electrodes based on graphites, carbons, thermally treated carbons (e.g., vitreous or glassy carbon), expanded carbons, carbon/polymer composites, and doped diamond materials. Moreover, some of these materials are available in many forms as follows:

- Plates, disks, rods
- Powders and pastes
- Coatings usually on Si, Ti, or Nb
- Spheres, microspheres, granules
- Raschig rings
- Fibers
- Cloths and felts
- Foams.

In many forms, carbon is a comparatively cheap electrode material. In addition, it is a poor catalyst for both H_2 and O_2 evolution so that, in many conditions, it is expected to act as an inert electrode for both laboratory experiments and applications in technology. Hence, it is an obvious choice for testing as both anode and cathode in many new technologies. In reality, however, experience shows that graphite and cheaper forms of carbon are not necessarily stable to corrosion and even disintegration on passing current. When used as an anode, oxidation and surface crumbling are common while even as a cathode, intercalation or absorption of species into the structure can cause extensive physical damage; porosity of the carbon is a major factor determining the stability. Certainly, the demonstration of stability in the electrolysis conditions is an important part of programmes to develop electrolysis involving carbon electrodes. The demand for stability has been a major driver for the development and application of more expensive forms of carbon, such as diamond and vitreous carbon.

This chapter will focus on the carbon materials used in the manufacture of chemicals, flow

batteries, and effluent/water treatment. Applications in fuel cells will be dealt with in other chapters. The applications of carbon electrodes have been reviewed previously [2, 3].

9.2 Comments on the Carbons Met in Electrochemical Technology

Some comment about the carbon structures to be met in this chapter is essential. Unlike most chapters in this textbook where the carbons employed are well defined and often fully characterized, the carbon electrodes employed in electrochemical technology are seldom fully characterized and commonly only identified by a manufacturer's/supplier's code [5]. Even when a series of materials are compared, the differences, in terms of structure, are usually poorly specified.

Both diamond and graphite occur in nature and the structures of the pure materials are well defined (see Chapter 1 and Refs [5–8]). Pure diamond has a three-dimensional structure with sp^3 -hybridized carbon atoms forming a tetrahedral lattice. The synthetic diamond used for electrodes is prepared by chemical vapor deposition and doped, commonly with boron, to increase its conductivity. Graphite is a structure based on parallel sheets with each sheet consisting of sp^2 -hybridized carbon atoms in a hexagonal array and the sheets bound together by van der Waals forces. It is manufactured by high-temperature (>3000 K) decomposition of hydrocarbon gases such as acetylene followed by hot pressing at high temperature and pressures.

In reality, materials labeled “diamond” or “graphite” can deviate significantly from this perfection. They may differ in the number/type of imperfections and the “quality” of the structure; for example, in graphite the scale of the order perpendicular to the parallel sheet structure. In addition, real materials will be based on crystallites with the theoretical structures and these crystallites may differ in their size, size distribution, and the orientation to neighboring crystallites. With graphite, there is a further possibility of ions or molecules intercalating between the layers, and this leads to graphite being somewhat porous. The interlayer spaces are also a natural home for impurities that can influence the properties. Moreover, with all carbon materials, the structure of the surface (where the electrochemistry occurs) will not be the same as the bulk. Most importantly, carbon surfaces have “dangling bonds” and may be oxidized with carbonyl, carboxylate, and hydroxyl groups with variable coverages depending on their preparation, history, and pretreatment.

Materials labeled as “carbon” are the least defined. There is a material known as **amorphous carbon** where the carbon atoms are randomly arranged in a three-dimensional array. In reality, however, these materials are probably more likely to be low-quality graphites, maybe with small or highly variable crystallite size, very limited number of layers in each stack or consisting of sheets that are bent and distorted so that they appear to be fragments of fullerene structures. Pores can also be present, increasing the surface area and making the material more porous. Such materials are manufactured by heat treatment at 1000–3000 K of carbonaceous solids or natural gas in an atmosphere containing limited oxygen. Their structures can be

refined by, for example, thermal treatments; prolonged heating to above 3000 K in an inert atmosphere can lead to high-quality graphite.

A number of other forms of carbon will be discussed in this chapter. Vitreous (also called **glassy**) carbon is prepared by slowly carbonizing a polymer resin (commonly, polyacrylonitrile) and then further heated at higher temperature, up to 3000 K under pressure of an inert gas. It is hard and largely impermeable to both liquids and gases. The structure is based on sp^2 -hybridized carbon atoms but the polymer backbone remains largely intact; it has been modeled as consisting of interwoven ribbons, each with a graphite-type structure. Vitreous carbon is also used as a foam (reticulated vitreous carbon) with pores of controlled dimensions (available commercially with pores ranging from 250 μm to 2.5 mm) and manufactured in a similar way starting from a polymer foam. Electrodes for technology have been manufactured from a number of particulate forms of carbon [5]. These particulates are prepared by thermal decomposition of a variety of carbonaceous materials (hydrocarbon gases, sawdust, coconut shells, charcoal, etc.) employing different programmed thermal regimes and atmospheres. As a consequence, they differ in particle shape (from microspheres to irregular chips) and particle dimensions (0.03–5 μm) as well as regularity of both shape and dimensions. The particles are generally made up of microcrystallites of much smaller size, maybe 1–10 nm; although based on sp^2 -hybridized carbon atoms, the structure within varies substantially from highly disordered to a graphite structure. These particulate forms have a high surface area up to 5000 $\text{m}^2 \text{g}^{-1}$ and this may be further increased by the presence of enhanced pores. The pore structure and surface properties may be enhanced by “activation,” heating either in aqueous solutions of acid, alkali, or oxidizing agents or in a controlled atmosphere. Finally, electrochemical technology is making increasing use of carbon/polymer composites. These are polymers or polymer blends filled with carbon blacks [9] or carbon fibers to make them electrically conducting.

9.3 Manufacture of Chemicals

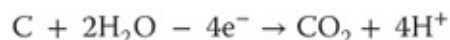
In addition to the two largest electrolytic industries, chlor-alkali and aluminum extraction, carbon anodes have been used for the manufacture of other inorganic products. These include fluorine and ozone manufacture, two chemistries requiring the anode to operate at extreme positive potentials. In organic electrosynthesis, carbons have been used as both anodes and cathodes.

9.3.1 The Chlor-Alkali Industry

Initially, the electrolysis of aqueous brine was carried out in amalgam cells [4, 10, 11]. Typical conditions employed were: an electrolyte feed of 25% NaCl at pH 4, a temperature of 343 K, and a current density in the range of 0.7–1.4 A cm^{-2} . The desired anode reaction, the evolution of chlorine, was accompanied by corrosion of the carbon at a rather rapid rate. Sodium amalgam was formed at the mercury cathode, which was then reacted with water to give 50% sodium hydroxide and hydrogen gas in a catalytic reactor known as a **denuder**.

The anodes were blocks of carbon entering the cell from the top and adjustable downward toward the mercury cathode surfaces so as to maintain a constant interelectrode gap as the carbon corroded. By the 1940s, the carbon was replaced by graphite because of its better chemical stability, higher conductivity and mechanical strength, and lower overpotential for chlorine evolution. Graphite was also the anode material for early diaphragm cells where the chlorine and sodium hydroxide + hydrogen are formed directly at the anode and cathode, respectively. The electrodes were separated by a porous diaphragm (e.g., asbestos) and cells were operated at a lower current density, 0.1–0.2 A cm⁻². Graphite was a cheap choice of anode material but, in both amalgam and diaphragm cells, it was consumed in competing reactions to chlorine evolution at a high rate of 2–3 kg of graphite/ton of Cl₂. The resulting requirement to routinely replace anodes limited developments in cell design and the introduction of more energy-efficient technology. A consequence was the development of the RuO₂-based coatings on titanium (“dimensionally stable anodes” or “DSAs”) that were very stable to corrosion as well as giving lower overpotentials for Cl₂ evolution. They have almost totally replaced graphite as the anode and their development also made possible the introduction of the much superior, membrane cell technology [4, 10, 11].

Even though the involvement of graphite in the chlor-alkali industry is now history, this application remains important to this chapter, because it remains the largest and most reliable source of information about the mechanism of graphite corrosion and ways to limit the rate of corrosion [1–3]. The graphite lost from the anode was found partly as sludge in the base of the cells, but CO and CO₂ were also found to contaminate the chlorine off-gas. Evidently, graphite consumption results from anodic oxidation



9.1

and “active” oxygen species from the oxidation of water and an “oxide” layer have a dominant role in the mechanism for chemical corrosion. Some attack by Cl₂ species leading to chlorinated hydrocarbon gases was also seen. But the dominance of oxygen species in the corrosion mechanism was consistent with the dependence of the corrosion rate on electrolysis parameters. In both laboratory and industrial cells, the rate of corrosion increased with

- a decrease in the concentration of Cl⁻
- an increase in pH becoming rapid above pH 3
- the presence of other anions, particularly sulfate
- increasing current density.

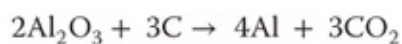
In parallel to chemical corrosion, there is mechanical erosion of the graphite to give graphite particles in the electrolyte. Graphite has a high porosity (up to 30% of the total volume) and a structure consisting of interconnecting carbon crystals – hence, many grain boundaries. During chlorine evolution in the cell operating conditions (elevated temperature, high current density), pores were found to become bigger and the surface became rougher by a factor >10. Both changes lead to an increase in the rate of loss of carbon and gas within the internal structure

leading to swelling, and surface crumbling was considered to have a key role. The corrosion rate is decreased by an increase in the graphitization of the anode material (by thermal treatment), an observation thought to result from an increase in the carbon crystal size leading to fewer grain boundaries. Organics such as linseed oil impregnated into the graphite structure also lower the corrosion rate and were considered to act by adsorption at points of contact between crystals in the graphite.

9.3.2 Aluminum Extraction

Even today, almost all aluminum is manufactured by the Hall–Héroult process [4, 12–16]. Unlike the chlor-alkali industry, the anode technology remains based on carbon, and the stoichiometric consumption of the carbon anode is an essential part of the anode chemistry.

In the Hall–Héroult process, the overall chemical change



9.2

is achieved by the electrolysis of the alumina in a cryolite (Na_3AlF_6) melt at a temperature of 1200–1250 K. Typically, the current density is $\sim 1 \text{ A cm}^{-2}$. The aluminum is formed at a molten aluminum cathode in the base of the cell, and the anode reaction is the stoichiometric conversion of the carbon anode to carbon dioxide. Inevitably, the carbon anodes are consumed at a rate of >0.5 tons of C/ton of Al. Hence, the carbon anodes must be cheap and in a form in which they can be lowered into the cell continuously so as to maintain a constant gap between the anode surface and the pool of molten aluminum.

In fact, the anodes are large blocks, up to $1 \text{ m} \times 1 \text{ m} \times 1 \text{ m}$ in dimensions and made by heating high-purity, calcined petroleum coke and pitch. Two types of anode are used (i) self-baking or Soderberg anodes, where a mixture of coke and pitch is fed to the top of the anodes within the cell and this mixture is cured as it is moved downward (typically at a rate of $\sim 2 \text{ cm day}^{-1}$) through the high-temperature cryolite melt to the bottom of the block facing the aluminum pool, where it becomes the anode surface and (ii) prebaked anodes, where the curing is carried out external to the cell. The self-baking technology is cheaper but leads to carcinogenic, polycyclic aromatic hydrocarbons in the cell off-gases (mainly CO_2). The prebaked anodes are produced in more controlled conditions leading to better-defined structures. These lead to lower cell voltages and higher current efficiencies. In addition, external thermal treatment allows much superior control of emissions to the environment.

Because of the highly aggressive conditions in the high-temperature, molten salt media, attempts to find alternative anode materials or cell chemistries have been unsuccessful and developments in anode technology have been limited to minimizing the carbon consumption toward the stoichiometric requirement. Indeed, carbons are one of the few materials to be stable to cryolite at the operating temperature and hence, for example, it is also employed as an internal lining to the steel cell bodies.

9.3.3 The Extraction of Group 1 and 2 Metals

Lithium, sodium, and magnesium are all produced in significant tonnages by electrolysis at steel cathodes in molten chloride electrolytes [4]. Eutectics are used to lower the operating temperature and hence the rate of cell and component corrosion. The specific conditions (see [Table 9.1](#)) are selected to attain the lowest possible operating temperature and to ensure that only a single metal is formed in the cell. In all cases, the anode reaction is chlorine evolution at a graphite surface using a high current density. Once again, because of the aggressive conditions and the corrosion of the graphite leading to the need for routine replacement, cell designs are simple, typically a graphite cylinder surrounded by a cylindrical steel cathode. Although corrosion of the carbon anodes certainly occurs, details of its rate and mechanism have not been published.

Table 9.1 Typical conditions for the manufacture of metals by molten salt electrolysis

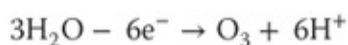
Metal	Eutectic	Temperature (K)
Li	55% LiCl + 45% KCl	720
Na	42% NaCl + 58% CaCl ₂	870
Mg	15% MgCl ₂ + 30% CaCl ₂ + 55% NaCl	1000

9.3.4 Fluorine Generation

Elemental fluorine is an important chemical in the nuclear industry for separation of uranium isotopes and also for the manufacture of SF₆, fluorinated organics, and polymers. The only source of fluorine is electrolysis usually carried out in the eutectic KF·2HF at a temperature of 355–383 K and using a current density of 70–200 mA cm⁻² [4, 17–19]. The selection of cell components and cell design is again determined by stability of materials to the very aggressive electrolysis conditions, both the electrolysis medium and the very positive anode potential. The anodes are blocks of carbon (preferred to graphite in this application), and discussion of their performance is dominated by the so-called “anode effect.” This is a large increase in the cell voltage from <10 to >40 V resulting from fluorination of the anode surface with a consequent loss of wetting of the surface by the eutectic electrolyte. While the anodes also suffer corrosion and disintegration during extended operation, avoiding “anode effects” is the main factor determining the selection of anode material. Two approaches have been successful in practice: (i) the use of a carbon with pores of a sufficient size that fluorine gas will pass through the carbon to a central gas collection space without the pores becoming flooded with electrolyte and (ii) the use of a nonporous carbon with an electrolyte rigorously free of water and with additives, particularly Ni in a higher oxidation state.

9.3.5 Ozone Generation

The electro-generation of ozone has recently been reviewed [20, 21]. Ozone is electro-generated by the anodic oxidation of water:



a reaction with a standard potential of +1.51 V vs SHE and hence again necessitating a very positive potential, where O_2 evolution is inevitably a competing reaction and corrosion of the anode is likely. Ozone is formed with a low current efficiency from many electrode materials and in many electrolytes and such systems may be of interest in effluent treatment (see later). The criteria for the preparation of ozone are, however, more demanding, namely (i) an energy efficiency not significantly higher than that for conventional ozone preparation procedures (corona discharge or UV excitation) and (ii) a high concentration of ozone in the cell off-gas. Few anode materials and electrolytes approach these requirements. In fact, it is the energy demand (determined by the cell voltage and the current efficiency) that is difficult to meet and a high ozone content of the cell off-gas is one of the major attractions of the electrolytic approach.

An electrolytic technology for the preparation of ozone was based on glassy carbon as the anode material in concentrated fluoroboric acid (HBF_4) [22–24]. The cells also employed a Pt-catalyzed, oxygen reduction cathode (gas diffusion electrode (GDE)) to lower the cell voltage (and hence the energy consumption) and to avoid the need to handle H_2 off-gas from the cathode. It was necessary to operate with cooling, and the preferred temperature was 268 K.

The current efficiency for ozone increased sharply with acid concentration (see [Table 9.2](#)) reaching 40–45% in the specially prepared 62 wt% acid (commercial grade is 48 wt%). The glassy carbon also shows increased stability in the higher acid concentration. In prolonged cell operation, it was necessary to avoid an “anode effect” (an increase in cell voltage from ~5 to >15 V) by control of the fabrication conditions for the glassy carbon, current density and temperature. Different glassy carbons prepared from different resin compositions and treatment temperatures (1250–3250 K) led to variations in process performance. Higher treatment temperature led to glassy carbon with greater sp^2 character and higher thermal conductivity and resistance to anode effects but lower stability to corrosion.

Table 9.2 Current efficiency for the formation of ozone as a function of HBF_4 concentration for cells with glassy carbon anodes and air GDE cathodes

HBF_4 concentration (wt%)	Current efficiency (%)
13	1.5
33	12
48	34
62	42

Temperature: 268 K. Current density: 0.4 A cm^{-2} .

Data taken from [23].

The technology was scaled to a 40 A unit with tubular anodes and planar air cathodes in an undivided cell. The tubular geometry for the anodes was preferred since cracking during thermal fabrication, cell assembly, and sealing was less of a problem than with large flat plates of glassy carbon; they also allowed more facile and efficient internal cooling to temperatures

as low as 250 K. On the other hand, planar air cathodes were easier to fabricate and the unusual cell geometry consisting of multiple cylindrical cathodes (diameter 2.5 cm) between two planar air cathodes allowed operation with a lower current density (by a factor of 2) at the cathode than the anode. Indeed, all the operating conditions selected were a compromise between the optimum for anode and cathode and also to ensure that the ozone concentration in the cell off-gas remained below 15 wt% because of safety concerns. Hence the electrolyte is commercial 48 wt% HBF_4 and the anode current density is 0.4 A cm^{-2} , and there was air purging to maintain the ozone level.

This ozone concentration is, of course, much higher than can be achieved with corona discharge or UV excitation ozone generation and this enhances the kinetics for the removal of microorganisms and oxidation-resistant organics from water and effluents. The 40 A cell and all the auxiliary equipment was packaged into a $50 \text{ cm} \times 40 \text{ cm} \times 40 \text{ cm}$ unit weighing 35 kg. It produced 5 g h^{-1} of pure ozone and had potential markets in the production of potable water, control of cooling tower water, sterilization, and effluent treatment.

Doped diamond is the alternative carbon material to glassy carbon for ozone generation [20, 21], but the technology is much less developed. Boron-doped diamond is prepared by chemical vapor deposition and has been used as an anode when (i) deposited as a thin film on substrates such as silicon, titanium, or niobium or (ii) fabricated as a bulk plate – for example, Element Six supplies Diafilm EP as a free-standing polycrystalline plate capable of supporting current densities of $>1 \text{ A cm}^{-2}$ [25]. Typically, the boron-doping concentration is 10^{20} – 10^{21} atoms cm^{-3} when its resistivity is of the order of $0.05 \text{ } \Omega \text{ cm}$. These boron-doped diamond materials are stable to corrosion in most aqueous electrolytes and give very low background currents over a wide potential region. Unfortunately, the boron-doped diamond films on metal substrates can be subject to high residual stress leading to spalling over a period of operation.

Some articles report the use of diamond-coated anodes for the preparation of solutions of ozone in water (without electrolyte) [26]. Honda *et al.* [27] used electrodes with a boron-doped diamond film, thickness $13 \text{ } \mu\text{m}$, on a perforated p-Si(111) wafer in a water-fed, zero gap (SPE) cell where two such diamond electrodes were pressed either side of a Nafion® N-117 membrane. The electrodes were prepared using acetone as the carbon source and trimethoxyboron as the boron source, and the B/C ratio in the diamond was varied between 0.001 and 0.05. With the highest doping level, it was possible to achieve a current efficiency of 42% for ozone although with the absence of electrolyte in the cell feeds, the cell voltage was high, 10–15 V. With the flow rates and current densities used, the ozone level in the water exiting the cell was $\sim 8 \text{ mg l}^{-1}$. The materials with high boron doping level were most efficient for ozone production and this was ascribed to an increase in sp^2 impurity. Kraft *et al.* [28] also used an SPE configuration where the electrodes (areas 13 cm^2) were boron-doped diamond on a niobium, expanded metal mesh. The membrane was Nafion® N-324 and the cell was again fed with pure water. The maximum current efficiency was 24% achieved with a current density of 0.3 A cm^{-2} , and ozone was formed at a rate of $\sim 160 \text{ mg h}^{-1}$.

A cell with a boron-doped diamond film on an n-Si(111) plate has also been used to generate

ozone in the gas phase [29]. A simple undivided, parallel plate cell with sulfuric acid electrolyte was employed. The diamond anode was shown to give more stable performance than PbO₂. When operated at 2.3 A cm⁻², it gave a cell off-gas with 0.8% ozone for a period of >3000 h.

Free-standing, bulk, boron-doped diamond has also been proposed for the generation of solutions of ozone in water. Nishiki *et al.* [30] have described a simple small cell with a diamond rod (diameter 2 mm and length 4 cm) anode surrounded by strips of Nafion® membrane and steel wire cathode. The cell was fed with both pure water and tap water, and pure water was shown to give higher yields of ozone (probably because of the absence of chloride ion to react with the initially formed ozone). Small additions of surfactants increased yields of ozone. With pure water flow rates of 100–600 cm³ min⁻¹, the current efficiency was 2–8% and the exit ozone concentration a few mg l⁻¹, sufficient to kill microorganisms from pets with dermal symptoms. A parallel plate, zero gap cell was developed by Arihara *et al.* [31–33]. The anode was a plate (1.5 cm × 5 cm × 0.54 mm thick) with 1 mm diameter holes (160–410 per plate) drilled out and cell was constructed by pressing these anodes and a Pt mesh anode either side of Nafion® N-324 membrane. With a flow rate of pure water of 2 l min⁻¹ to the anode and a current density of 0.5 A cm⁻², the current efficiency was 42% and the ozone exit concentration was ~5 mg l⁻¹ (increasing to 10 mg l⁻¹ with a current density of 1.5 A cm⁻²). These results were obtained without cooling of the water substantially below room temperature before entry into the cell.

9.3.6 Hydrogen Peroxide

At many forms of carbon, the reduction of oxygen occurs by a 2 × 2e⁻ mechanism and the potentials for the reactions



are well separated particularly in alkaline media. This leads to the possibility of the selective conversion of oxygen to hydrogen peroxide using carbon-based electrodes. The low solubility of oxygen in water limits the rate of conversion (current density) at planar carbon surfaces but a wide range of three-dimensional electrodes as well as GDEs have been used for the formation of hydrogen peroxide for effluent treatment (see later). Commercial concentrated (30–70%) hydrogen peroxide solutions are all manufactured by a chemical route, the anthraquinone-catalyzed combination of oxygen and hydrogen. There has, however, been interest in electrolytic processes for the manufacture of more dilute hydrogen peroxide solutions for specific applications, particularly 1–5% hydrogen peroxide in sodium hydroxide solution for bleaching in the paper and pulp industry. On-site production of this solution is envisaged to avoid the hazards associated with the transport of concentrated hydrogen peroxide.

Dow/H-D Tech developed a process based on a trickle bed electrolyzer [4, 34] that has been

operated as a demonstration plant within a mill. In this cell, the cathode was a bed of “composite carbon chips,” that is, a bed of granular pieces of graphite (0.8–2 mm) coated with a layer of high-surface-area carbon black and fluorocarbon binder. The anode was Pt/Ti and the separator was an inexpensive polypropylene microporous material. This allowed the cathode to be fed with NaOH from the anode compartment (saturated with O₂ formed at the anode) so as to form a film of electrolyte over the carbon bed within an oxygen atmosphere. The desired concentration of H₂O₂ (3–4%) with a NaOH/H₂O₂ ratio of 1.6 : 1.8 was achieved in a single pass through the cell. At atmospheric pressure and room temperature and with a current density of 67 mA cm⁻², it was possible because of the thin layer of catholyte over the high area of carbon surface. The cell voltage was 2.3 V and the current efficiency 80–95%. Oloman and coworkers [35, 36] have sought to increase the space-time yield of such cells by using a graphite felt cathode. In their largest cell with a graphite felt cathode, 63 cm high × 4 cm wide × 0.32 cm thick, that was constricted at interval up the cell to prevent the segregation of the two-phase oxygen/electrolyte flow through the felt, it was possible to obtain current efficiencies ~80% with a current density of 0.3–0.5 A cm⁻². A typical outlet solution was 2% H₂O₂ in 2 M NaOH solution.

Electrolysis cells with a planar GDE have also been developed to produce H₂O₂ + NaOH solutions for the same market [34]. In such cells, the cathodes operate similarly to those in a fuel cell, but are fabricated from carbon materials without the presence of catalyst (usually present to promote the 4e⁻ reduction of oxygen). A Nafion® N-324 membrane was used as the separator and a nickel-based anode. In fact, the cathodes were fabricated from PWB-3 carbon cloth (a densely woven, 0.4 mm thick cloth) coated with a layer of Vulcan XC-72® and Teflon®. The ink was prepared by ultrasonic dispersion, then worked into both sides of the cloth and sintered at 610 K for 30 min. Initial data were obtained in a 10 cm × 10 cm cell and the cell was operated at slightly elevated temperature, 318–328 K, to improve the kinetics of O₂ reduction and hence reduce the cell voltage and also to prevent precipitation of Na₂O₂ in the pores of the GDE. Over a 6000-h operation, 5% H₂O₂ with a 2.2–2.3 ratio of NaOH/H₂O₂ was obtained with a current efficiency of ~80% and a cell voltage of ~1.5 V. With the cell design developed, there was a limitation in the height that could be used due to the need to balance gas and electrolyte pressures on the two sides of the GDE. Hence, the FM21 SP electrolyzer (an ICI chlor-alkali cell) with electrode dimensions of 0.21 m height and 1 m width was selected for scale-up. The cell modifications to incorporate the GDE were engineered and the process economics set out, but it is not clear whether a pilot plant based on the FM21 SP electrolyzer was actually constructed.

Good performance is also reported by a Spanish group for the combination of hydrogen and oxygen to give hydrogen peroxide in an alkaline fuel cell with an uncatalyzed carbon cathode. With a 1 M KOH electrolyte, the current efficiency was close to 100% at a current density of 130 mA cm⁻² [37].

9.3.7 Other Strong Oxidizing Agents

Their chemical stability and the large overpotential for oxygen evolution at boron-doped diamond make them attractive materials for the anodic generation of strong oxidizing agents [38, 39]. Early articles reported successful preparation of several strong oxidants at boron-doped, diamond-coated p-silicon or niobium electrodes ([Table 9.3](#)). These reports do not seem to have been followed up probably due to delamination of the diamond coatings away from the substrates during extended electrolysis at high current densities. It would be interesting to explore the generation of strong oxidants at stand-alone, bulk doped diamond anodes.

Table 9.3 The electro-generation of strong oxidants at boron-doped, diamond-coated anodes

Oxidant	Medium, anode	Current density	Current	References
	substrate,	(mA cm ⁻²)	efficiency	
	temperature (K)		(%)	
Peroxodisulfuric acid, H ₂ S ₂ O ₈	3 M H ₂ SO ₄ , p-Si, 282 K	23	95	[40]
Peroxycarbonate, C ₂ O ₆ ²⁻	1 M NaOH, Nb, 278 K	50	65	[41]
Silver (II), Ag ²⁺	10 M HNO ₃ , p-Si, 298 K	a	81	[42]
Permanganate, MnO ₄ ⁻	1 M HClO ₄ , 298 K	a,b	48	[43]

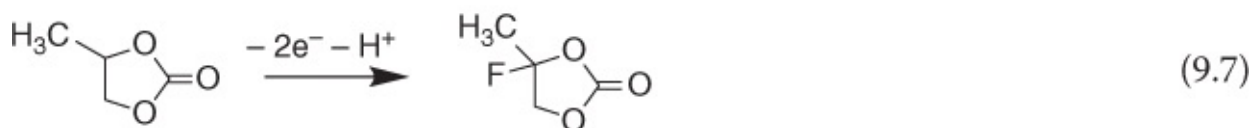
a: controlled potential. b: Bi(III) catalyzed.

9.3.8 Organic Products

There is a very extensive academic literature on the electrosynthesis of organic molecules [44–48]. Unfortunately, academic laboratories have commonly, without thought, used platinum as the electrode for anodic oxidations and mercury for cathodic reductions. While other electrode materials have been employed, their selection appears random and there have been few systematic studies to find how the choice of electrode material influences selectivity and/or current efficiency. Carbon (usually of unspecified type) is among the electrode materials that have been used but its advantages and comparison of performance with other materials and, indeed, between forms of carbon are seldom discussed. It is only as scale-up and process costs become important, that carbon becomes important and more thoroughly investigated. The product selectivity can certainly depend on the electrode material. An oft-quoted example is the oxidation of carboxylates at Pt and C anodes where the trend is for Pt to give products from radical intermediates and C to give products from carbenium ion intermediates. It should, however, be noted that the products from carboxylate oxidation also depend on solvent, pH, current density, temperature, and so on, so that simple conclusions can be misleading.

Fluorinated organic compounds are now an important component of the fine chemicals industry because of their distinctive physical and biological properties. Electrolysis has always been

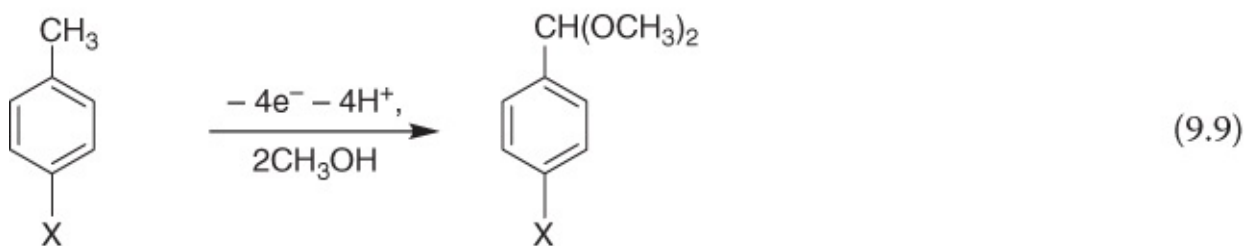
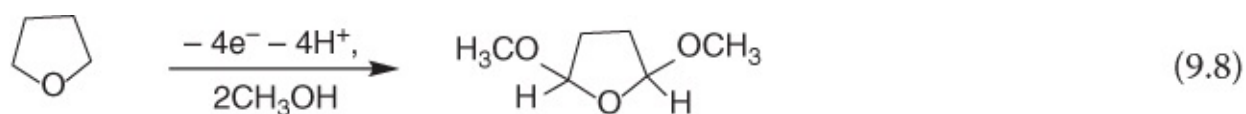
an important route to perfluorinated organic compounds. Initially, production was based on the Simons process [49] that employs a nickel anode with the substrate dissolved in a liquid hydrogen fluoride electrolyte and was used to manufacture perfluorinated amines, ethers, carboxylic acids, and sulfonic acids. It is always difficult to control and generally leads to low yields and complex mixture of products. Childs *et al.* [50–52] developed an alternative approach that gave improved selectivity, control, and safer operation. It employs a porous carbon tube as the anode and molten $\text{KF} \cdot 2\text{HF}$ at 370 K as the electrolyte. The feedstock is fed to the cell as a vapor from the inside of the anode tube and it is critical that electrode reaction occurs within the pores of the carbon and that reactant and product do not escape into the electrolyte. This is achieved by the selection of a carbon with appropriate permeability and pore size. An early article [52] describes the electrofluorination of ethane. Over 95% of the ethane consumed was recovered as fluoroethanes and the current efficiency was >98%. While the cell exit stream contained all fluorocarbons between C_2H_6 and C_2F_6 as well as minor amounts of C_1 and C_3 fluorocarbons, by variation of the feed rate it was possible to obtain good yields of $\text{CH}_3\text{CH}_2\text{F}$ (42%), CFH_2CHF_2 (21.6%), or C_2F_6 (33%). The technology has again been applied to the fluorination of amines, ethers, and carboxylic acids (perfluorooctanoic acid being commercially the most successful product). The following work has focused on seeking conditions for more selective fluorination of larger, polyfunctional substrates. Fuchigami and coworkers [53, 54] have been very successful in using anodic oxidation in ionic liquids and mixtures of ionic liquids with aprotic solvents; a large number of monofluorinated compounds have been synthesized, but, in general, the anode is Pt and it is not clear whether a carbon anode could have been used. Interestingly, however, a recent BASF patent [55] has described the use of an uncatalyzed, carbon-based GDE in electrolytes based on the ionic liquid $(\text{C}_2\text{H}_5)_3\text{NH}^+\text{F}^- \cdot 2\text{HF}$ for the fluorination of ethylene carbonate and propylene carbonate as follows:



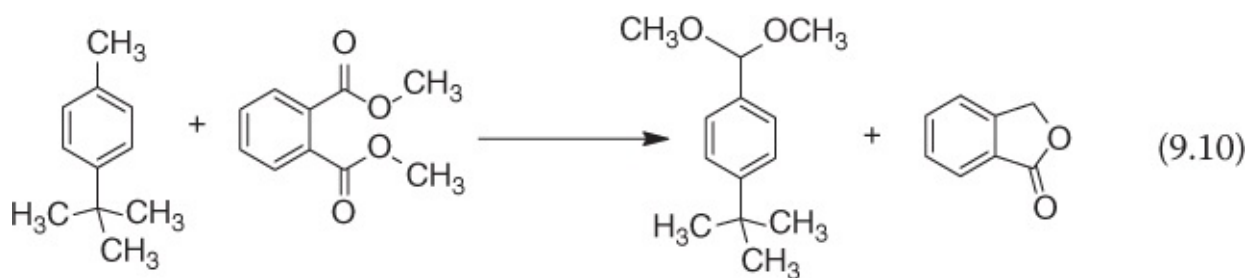
Unusually with a GDE, the substrates were dissolved in the electrolyte. With a current density of 0.1 A cm^{-2} , conversions after the passage of a charge of 2F were ~60% and the selectivity to the monofluorinated products 60% and >40%.

BASF in Germany operated a number of commercial, electrolytic processes [44, 56, 57] using a strategy based on the availability of a reliable and simple cell design and then noting the chemistry that can be carried out within this cell. In this cell, a series of horizontal carbon disks (diameter ~1 m) were stacked with a separation of ~1 mm (maintained by polymer spacers) and the electrolyte was pumped outward from the center of the disks. The cell is operated undivided and as a bipolar stack with bypass currents minimized because the stack is not immersed in electrolyte. The cell is well suited to methoxylation reactions carried out in

methanol as the solvent. For example, BASF have carried out the following conversions:

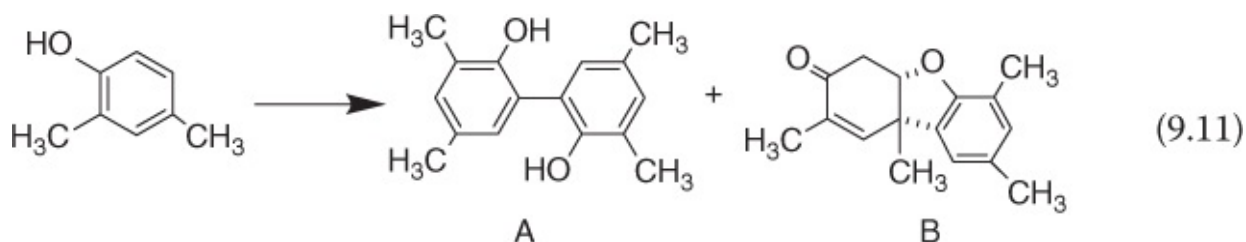


The first reaction is carried out as an indirect electrolysis with bromine as the active intermediate, and the product can be converted into the food additive, maltol. The second one is a direct oxidation leading to a product that is readily hydrolyzed to the aldehyde. The cathode reactions maintain the neutrality of the electrolytes by reducing protons and/or forming methoxide by reduction of methanol. Reaction (9.9) has been used to produce a number of substituted benzaldehydes with, for example, $X = -\text{CH}_3$, $-\text{OCH}_3$, and $-\text{C}(\text{CH}_3)_3$. Using a current density of $30\text{--}50 \text{ mA cm}^{-2}$ and electrolyte recycle, it was possible to achieve $>90\%$ conversions with a selectivity for aldehyde of $\sim 85\%$; a small amount of overoxidation to acid was observed. Reaction (9.9) with $x = -\text{C}(\text{CH}_3)_3$ is also the anode reaction in an usual paired electrosynthesis where both electrode reactions lead to wanted products. In the BASF process, the cathode reaction is the reduction of dimethyl phthalate to phthalide so that the overall cell conversion is



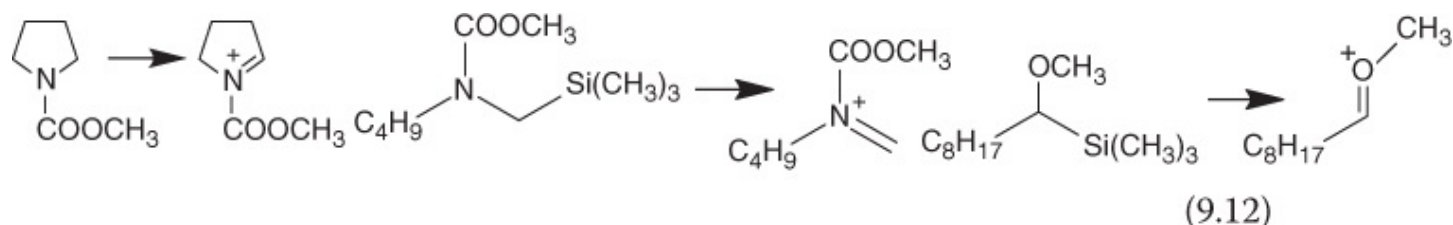
The cell chemistry is fully balanced. Moreover, both products are obtained in good yields and are used together in equimolar quantities in downstream chemistry, making this electrolysis particularly attractive from an economic viewpoint. The process also employed a specially developed electrolyte to allow simple recovery and recycle.

The opening paragraph of [Section 9.3.8](#) should not be read as a statement that particular forms of carbon do not have a role in electrosynthesis. In aqueous media, boron-doped diamond tends to give total oxidation to CO_2 (see [Section 9.3.1](#)) but in nonaqueous solvents, such as methanol, selective, partial oxidation as well as reduction is possible [58, 59]. Moreover, in some cases, the products (and presumably the reaction mechanism) at Pt- and B-doped diamond can be quite different. For example [60], the phenol oxidation



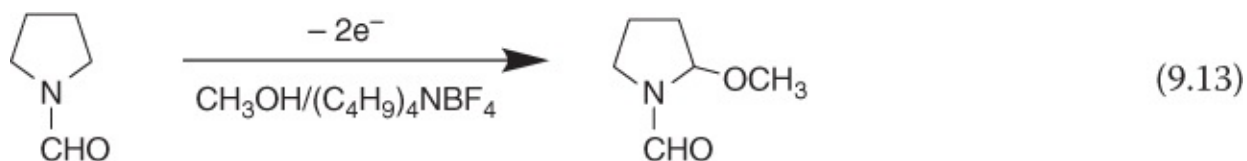
at Pt in methanol leads to a ratio of products A:B = 1 : 11 with oligomers also formed while at B-doped diamond in a medium without added solvent (but a few % water) and $(\text{C}_2\text{H}_5)_3\text{NH}^+ \text{CH}_3\text{OSO}_3^-$ as the electrolyte, the ratio of A:B was 18 : 1. This is a unique synthesis of the dimer.

Use of the high surface area of three-dimensional forms of carbon, particularly reticulated vitreous carbon and carbon/graphite felt, to increase the rate of organic conversions when the current density for reactions is low, has, of course, long been recognized. Examples of the use of reticulated vitreous carbon in flow cells are articles that describe studies of the oxidation of *p*-cymene [61] and the generation of *o*-quinones for coupling with nucleophiles [62]. An interesting application of a carbon felt anode is in a small flow cell giving a high conversion in a single pass of electrolyte and used for the low-temperature generation of reactive N-acyliminium and alkoxy-carbenium ion intermediates [63–65]. Dichloromethane at a temperature of 195 K could be used to generate highly reactive intermediates by the oxidations,



and these could then be reacted with a family of nucleophiles external to the cell to give a wide range of interesting products.

The past 10 years have seen the rapid development of microflow electrolysis cells to catalyze the routine application of electrolysis in pharmaceutical and similar laboratories. The design of these cells targets the rapid synthesis of a few grams of pure product with a high conversion in a single pass through the cell. The ability to achieve this as well as minimizing the use of electrolyte makes the technique of greater interest to synthetic organic chemists and also aids the isolation of pure product. Several designs have been reported [65–69] and some are making use of carbon-filled polymer composites as ideal electrode materials; they combine chemical inertness and flatness with acceptable conductivity and they are less brittle than vitreous carbon or graphite, making them easier to fabricate and handle. For example, one design [69] uses a flat anode plate made from carbon-filled polyvinylidene fluoride (PVDF). Combined with a polymer spacer and a flat steel cathode, it permits the design of a cell with a convoluted channel 1.5 mm wide $\times$ 0.2 mm interelectrode gap $\times$ 700 mm long to be fitted into a device 6 cm $\times$ 5 cm $\times$ 3 cm. Using the test reaction



the cell was capable of giving 2 g product h⁻¹ with a yield of >95% or 5 g h⁻¹ with a conversion of 85% in single-pass operation using a substrate concentration of 0.1 M. Indeed, the use of higher concentration of substrate and higher flow rates allows the productivity to be increased to >10 g h⁻¹ although with a slight drop in conversion [70].

9.4 Water and Effluent Treatment

Improvement in the quality of water, both that supplied by utilities and that recycled in loop systems (e.g., cooling towers) is an important goal. In addition, the treatment of effluents containing toxic materials or an unacceptably high COD (chemical oxygen demand) or TOC (total organic carbon) is an essential technology in the modern world. Electrochemical technology has approached these objectives in different ways. Anodic oxidation at boron-doped diamond and Fenton's reagent (H₂O₂ + Fe(III)) chemistry using cathodically generated hydrogen peroxide are the two main approaches to the removal of organics. By contrast, the application of three-dimensional cathodes dominates the removal of inorganics, particularly heavy and transition metals. Carbon-based electrodes are central to all these technologies.

9.4.1 The Removal of Organics

Because of the diverse mechanisms and the forcing conditions achievable in electrolytic cells, it is possible to oxidize a very wide range of organic molecules (even to CO₂). In addition, unlike, for example, treatments with chlorine compounds, electrolytic treatments including those via ozone and hydrogen peroxide, do not have the possibility of leaving toxic residues. It should, however, be noted that, even when the chemical change occurs with a high current efficiency, complete oxidation of organic compounds can be an energy-intensive process because of the large number of electrons involved in the reaction (e.g., >100e⁻ for many dyes). Such reactions are also multistep often requiring prolonged treatment times. For these reasons, improvement in water/effluent quality that can be achieved for a smaller charge input can be more attractive. Such situations include (i) oxidizing/reducing toxic materials to compounds acceptable to conventional water treatment processes; (ii) decoloration – dyes often bleach for 2–4e⁻/dye molecule; and (iii) killing viruses and microorganisms.

9.4.1.1 Boron-Doped Diamond

The past two decades have seen the establishment of a very extensive literature on the application of boron-doped diamond electrodes for the decoloration and the removal of COD and TOC from effluents, the disinfection and quality improvement of water, and the complete oxidation of particular organic molecules [26, 38, 39, 71–75]. There can be no doubt that boron-doped diamond anodes allow the effective killing of microorganisms and the complete

oxidation of a wide range of organic compounds to carbon dioxide (and other inorganic fragments). Both direct and indirect mechanisms have been invoked. The direct mechanisms involve electron transfer and oxidation via weakly adsorbed $\text{OH}^\bullet$ radicals, while the indirect mechanisms have seen a role for solution-free $\text{OH}^\bullet$ radicals, ozone, sulfate radicals, or chlorine compounds if suitable anions are present or added. Indirect routes via ozone [20, 21] and sulfate radicals [40, 74, 76–78] can, of course, become dominant with appropriate selection of the conditions. This literature has been extensively reviewed and the interested reader is referred to these reviews [26, 38, 39, 71–75].

Even though the published literature is dominated by the use of boron-doped diamond electrodes using a p-Si substrate, their fragility and susceptibility to delamination has not been a total barrier to commercialization. DiaCell® units employ short bipolar stacks of electrodes (up to four) where the electrodes are circular disks (diameter 100 mm) of boron-doped, diamond-coated p-silicon (Adamant Electrodes) [73, 78]. The stability of the boron-doped diamond under strongly oxidizing conditions allows the use of current densities $>1 \text{ A cm}^{-2}$. A single unit has a maximum flow rate of $1.2 \text{ m}^3 \text{ h}^{-1}$, with higher flow rates handled with multiple units in parallel. The cells produce a mixture of peroxydisulfate, hydrogen peroxide, percarbonates, and ozone (concentration depending on feed stream), and the solutions leaving the cell have a high enough concentration of remaining oxidants that it can be used for treatment of larger volumes or maintaining activity for an interval. Systems with multiple cell units have been marketed for inactivation of viruses and other microorganisms in swimming pools, spas, rainwater, process water, and sewage.

9.4.1.2 Hydrogen Peroxide Chemistry

As noted in [Section 9.3.6](#), carbon is the cathode of choice for the generation of hydrogen peroxide by the reduction of oxygen. This cathode reaction can be efficient in aqueous acid (pH 0–4) and the reduction of Fe(III) to Fe(II) can occur in parallel. Hence, the cathodic generation of Fenton's reagent ($\text{H}_2\text{O}_2 + \text{Fe(II)}$) is a facile reaction and the use of this chemistry in the cathode compartment works well for the decoloration of dyes, disinfection, and even the removal of COD. The practical challenge is a cell that allows the high rate of generation of the active species. The early work by Sudoh *et al.* [79] using a graphite plate cathode spawned a large volume of papers using more realistic cathodes including reticulated vitreous carbon [80, 81], graphite felt [82, 83], and uncatalyzed carbon GDEs [84–86].

While such studies have continued, the recent trend has been to increase the rate of the water/effluent treatment by incorporation of the Fenton's chemistry into “advanced oxidation processes” [87–91]. In these, the reduction of oxygen at the carbon cathode is combined with (i) photochemical enhancement of the rate of peroxide oxidation [92–94], (ii) a boron-doped diamond anode in an undivided cell [92, 95, 96], (iii) electrocoagulation (using a dissolving Fe anode to give fine Fe(OH)_3 particles for the adsorption of organics) [97–99], and (iv) sonochemistry [100]. “Advanced oxidation processes” are proving successful and recent reviews have highlighted their application to the treatment of dye effluent [101], pharmaceutical residues [102–104], and landfill leachate [105].

9.4.1.3 Other Technologies

High-surface-area three-dimensional electrodes (e.g., beds of granular activated carbon or carbon aerosols, graphite felts, and carbon fiber materials) have been used to adsorb organics from effluents [106, 107]. The potential of the carbon surface is used to control the adsorption and desorption processes. Unless combined with a destruction procedure, these are essentially concentration procedures but they also have a low energy consumption because adsorption and desorption do not involve Faradaic processes. Foo and Hameed [108] have summarized the literature on the electrosorption of organics on activated carbon, but we are aware of no scale-up from laboratory experiments.

In all its forms, the surface of carbon has oxygenated functional groups and these have been used as the starting point for the covalent bonding of functional groups to the surface. Moreover, in order to enhance the coverage by the functional groups, it has become common to preoxidize the surface by either an anodic treatment or the use of a chemical oxidant. While the properties of these modified surfaces are more suited to sensors, such modifications have been explored for effluent treatment applications. For example, an oxidative treatment of carbon felt was found to enhance the rate of destruction of 4-nitrophenol by an electro-Fenton approach [109] while chemical modification with hydrazine [110] and an anthraquinone polymer [111] has also been reported to increase the efficiency of electro-Fenton treatment.

Carbons modified with fluorine [112] and nitrogen [113, 114] have also been extensively studied as catalysts in fuel cells leading to improvements in performance for both oxygen reduction and methanol oxidation. Both decrease in overpotentials and increase in lifetimes have been reported. The application of similar concepts to electrode materials for effluent/water treatment is likely to lead to electrodes with greater stability. A nitrogen-doped diamond-like carbon has been shown to be effective for generation of ozone in water and the resulting solution employed to sterilize water of *Escherichia coli* [115].

9.4.2 The Removal of Inorganics

The use of electrolysis to remove heavy and transition metal ions from industrial effluents is now a mature technology. Provided that, within the environment of the effluent, hydrogen evolution does not overwhelm the cathodic deposition of a metal, the metal can be removed from the effluent and recycled; metals including Au, Ag, Pt, Pd, Cu, Ni, Pb, Hg, Cd, Zn, Sn have been successfully removed using electrochemical technology. The challenge is to remove the metal ion, present in low concentration, at an acceptable rate (current density) and energy consumption (and hence current efficiency).

One approach to achieve these goals employs three-dimensional electrodes [4, 116, 117] where the mass transfer-limiting current, I_L , for metal ion removal is given by

$$I_L = nFk_m A_e V_e c$$

9.14

where n is the number of electrons involved in the reduction of the metal ion to metal, F is the Faraday constant, k_m is the mass transport coefficient, A_e is the active electrode area/unit

volume of electrode, V_e is the volume of the three-dimensional electrode, and c is the concentration of metal ion. The rate of reduction in the concentration of the metal is given by

$$\frac{dc}{dt} = -\frac{I_L}{nFV_s} \quad 9.15$$

where t is time, I_L is the limiting current, and V_s is the volume of effluent to be treated in unit time. Three-dimensional electrodes are effective because they combine (i) a high surface area per unit volume with (ii) an efficient mass transport regime due to the local turbulence resulting from the flowing solution hitting the electrode structure. For example, replacing a carbon plate by a carbon foam of 5 mm thick can reduce the electrolysis time by a factor >100 [118]. In general, such cell can be set up to (i) decrease the metal ion concentration to <1 ppm before discharge of the effluent [119] or (ii) maintain the concentration at a preset level (commonly 10–100 ppm) in a recycled process stream.

A number of carbon materials are ideal for the construction of three-dimensional electrodes for metal ion removal, and commercial cells have been marketed based on beds of granular carbon [120], reticulated vitreous carbon [121], and carbon felt [122]. Details of the cell designs and examples of their performance have been described previously [4, 116, 117].

9.5 Flow Batteries

The introduction of a substantial fraction of renewable energy into a practical energy economy requires technology for large-scale energy storage. The time frame for energy production is determined by nature (when the sun shines, the wind blows, or tides are suitable), while the pattern of usage is determined by customer demand; these are quite different and hence the need for a buffer technology. A possible technology is based on flow batteries [123–125]. These are very large battery systems designed to either (i) meet the daily energy demand for a hotel, office block, or group of houses, up to 100 kWh or eventually (ii) store the energy from, for example, a wind farm or solar panel facility or a power station maybe with a capacity of >1 MWh. The energy storage is achieved by driving a chemical change to two electrolytes in a flow electrolysis cell during charge and allowing the reverse, spontaneous chemistry to occur during discharge. The overall cell chemistry should involve a large Gibbs free energy change so as to achieve a high battery voltage, redox couples with rapid kinetics to avoid overpotentials, and high solubilities to avoid mass transport limitations during both charge and discharge. When the redox couples at both electrodes only involve soluble species, it should be noted that (i) the energy storage capability is determined by the volume of the electrolytes and the concentrations of species within the electrolyte while (ii) the rate of charge/discharge is determined by the active electrode area and the current density for the electrode reactions, ultimately limited by mass transport considerations.

Several cell chemistries for flow batteries have been developed to a significant scale [123–125], including the all vanadium battery, iron/chromium, zinc/bromine, bromine/polysulfide, and zinc/ferricyanide while on a smaller scale, other chemistries (e.g., soluble lead, zinc/air,

and zinc/cerium) have been shown to have advantages. In all the flow batteries, because of the desire to charge/discharge at high rates (current densities) and also work toward complete charge and discharge (when the concentrations of reactants for the electrode reactions are approaching low values), mass transport control of species to the electrodes will be an issue at some state of charge. For the reasons highlighted in the previous section, three-dimensional electrodes are attractive and again, carbon materials predominate. The application of carbon materials in redox flow batteries has been reviewed [126].

Most commonly, the battery will be configured with a stack of bipolar cells (10–100 cells per stack) to give a useful output voltage and with parallel flows for the electrolytes to each of the cells in the stack. Hence, the electrodes will be bipolar with a solid core from carbon, graphite, or a carbon/polymer composite and the three-dimensional elements bonded or pressed onto either side of the solid core. The composites are a blend of a chemically stable polymer and a micron-scaled carbon powder, most commonly an activated carbon; Radford *et al.* [127] have considered the influence of the source of the carbon and the chemical and thermal treatments on the properties of such activated carbons, especially the pore size and distribution [126]. Even though reticulated vitreous carbon has been used for the three-dimensional elements [117], the predominant materials are graphite cloths or felts with a thickness of up to 5 mm, and it is clear that such layers are essential to scale the current density and thereby achieve an acceptable power density. Details of electrode performance in the more developed flow batteries are not available but, for example, Skyllas-Kazacos *et al.* [124] have tabulated an overview of the development of the all vanadium redox flow battery that includes the electrode materials and the chemical and thermal treatments used to enhance activity and stability.

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Chapter 10

Carbon Electrodes in Molecular Electronics

Adam Johan Bergren and Oleksii Ivashenko

10.1 Introduction

Molecular electronics is broadly defined as the study of charge transport involving molecular entities [1–9]. However, such a broad definition overlaps with several other related areas, including, electrochemistry [6], organic electronics [10–12], and donor–acceptor electron transfer studies [13, 14]. Indeed, insights from all of these areas have been important to advances in understanding molecular electronic systems. Two key distinguishing factors separate molecular electronics from other areas of study [15]: (i) the charge transfer distance is of molecular scale (rather than the much longer distances involved in, for example, organic electronic devices) and (ii) the use of two conductors or semiconductors to “wire” the molecules to larger circuitry that is used to measure charge transport properties. Thus, in one sense, molecular electronics can be thought of as the study of interrupting a conductor with a nanoscopic molecular region, where the primary goal is observing and understanding how the electronic properties of the entire circuit depend on the details of the molecular region.

A key component in molecular electronics is the molecular junction (MJ), the fundamental electronic component that is constructed in molecular electronics. The details of the structure of a MJ is dependent on the specific way in which it is fabricated, as discussed in [Section 10.2](#). However, all types of MJs have a basic common structure, as shown in [Figure 10.1](#), where some of the main features are highlighted, including the type of surface interactions that anchor the molecule to a contact, and the externally applied voltage leading to electron flow across the molecules. In all cases, either a single molecule or a molecular mono- or multilayer is sandwiched between two conductors (or semiconductors). As we will see, the details of exactly how the MJ is made can impact the electronic properties in some nonintuitive ways. For this reason, a MJ must be treated as a system, and not as isolated components that are brought into contact. Thus, the initial goal outlined earlier of “understanding how the electronic properties of the entire circuit depend on the details of the molecular region” often requires considerations of physical factors that arise when molecules interact with conductors. Thus, when comparing the electronic properties of different MJs, it does not suffice to compare only the molecular structure and make predictions based on only this factor. It is especially critical to emphasize consideration of the nature of the entire MJ given that molecular electronics grew out of a desire to utilize the great variety of electronic systems available through chemical synthesis. As discussed later, the reason for this idea emerging is based on the historical development of electronics.

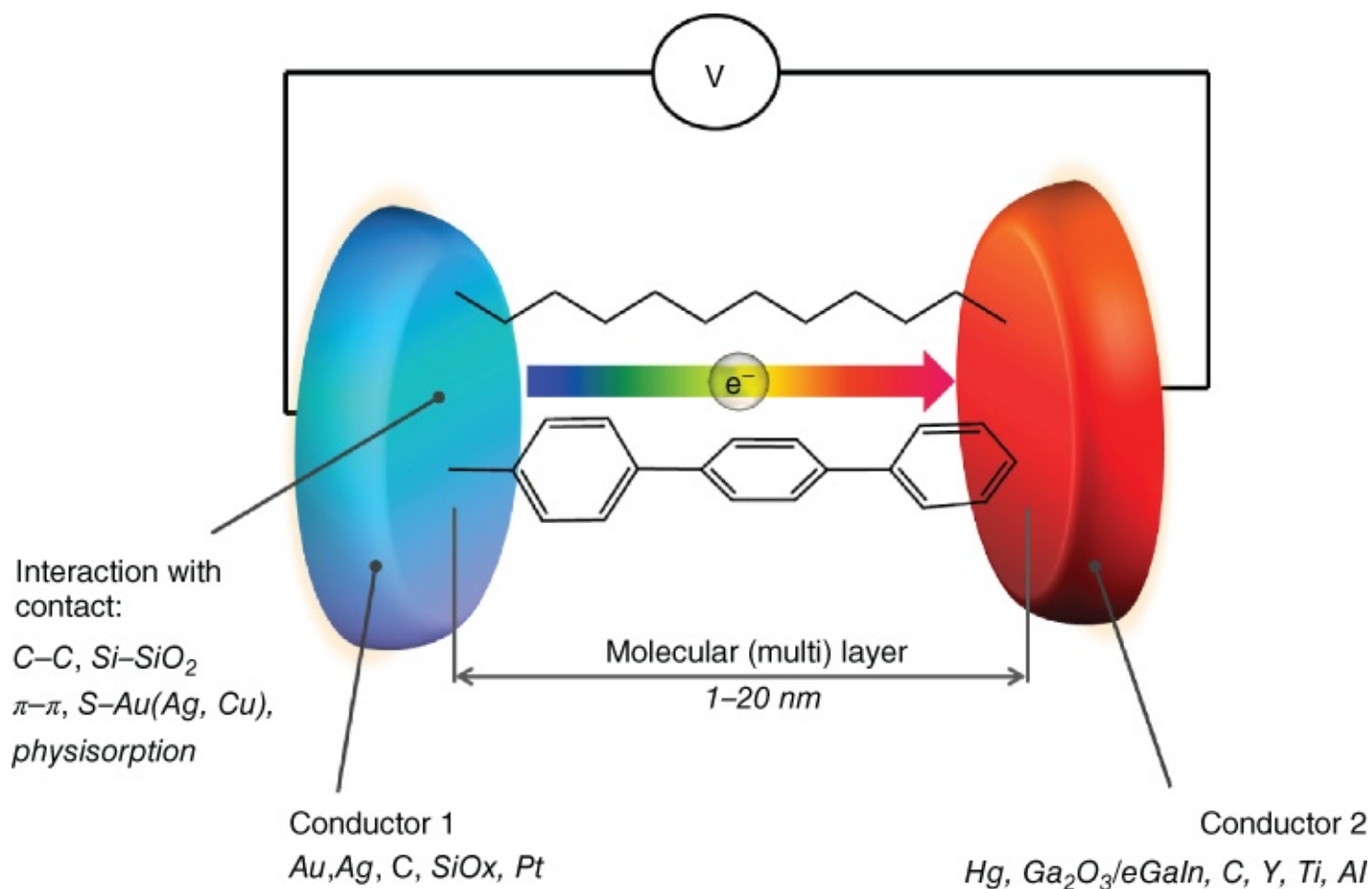


Figure 10.1 Generalized schematic of a generic molecular junction, consisting of a molecule (can be one or many) placed between two conductors (examples for each contact are for illustrative purposes). As shown, a wide variety of materials can be used, and the choice of molecules and contacts can impact the specific electronic interactions at the interface – chemisorption (C-C, Si-SiO_x) or physisorption (π - π , S-Au, etc.), which can exert a controlling influence on junction behavior. Upon application of voltage across the junction, current flows across the molecular layer. However, the system should be treated as whole, as the thickness and electronic properties of the molecule are not the only factors that will dictate conductivity.

The basic concept of making an electronic device of molecular or atomic size has been around for many decades, with well-documented discussion in Feynman's famous lecture "There is Plenty of Room at the Bottom" in 1959 [16]. As described later in the context of molecular-scale electronic devices, Moore's law was postulated in 1965 (shortly after the advent of the integrated circuit [17]), which stated that the number of components able to be fit onto a given chip area would increase with time, largely due to a concurrent decrease in device size. Thus, even though the concepts of circuit and component miniaturization were being discussed during the 1960s, molecular electronics was not formally recognized as a distinct idea until 1974, when Aviram and Ratner [18] published a theoretical article that proposed the use of a single molecule as a rectifier. This work suggested that by controlling the electronic properties of a molecule (i.e., essentially the energy of molecular orbitals located at specific points in space – in this case, by careful arrangement of donor and acceptor molecular fragments), a particular

electronic function could result (in this case, rectification). Thus, an electronic function normally carried out by constructing a macroscopic p–n junction (i.e., a discrete diode) might also be enabled by a single molecular entity. Even though this article did not contain experimental data, as the methods and techniques that have become commonplace in constructing molecular electronic devices were not developed until more than a decade later, it has served as motivation for many of the experimental efforts that followed. Thus, theoretical molecular electronics preceded experiments by approximately two decades: while some experiments had been done in the 1980s, it was not until the mid-1990s that experimental molecular electronics came into its own.

The burgeoning of experimental molecular electronics was enabled by some key advances during the 1980s. First, the ability to chemically modify the surface of conducting materials (often electrodes) with molecular layers of controlled structure boomed following the advent of self-assembled monolayers (SAMs) [19]. Second, the development of high-resolution imaging techniques (especially scanning tunneling microscopy, STM) enabled measurements of the electronic structure of matter in unprecedented detail. These two techniques would be combined often in the 1990s to measure charge transport across molecular layers. It was also during this time that electroanalytical studies were being carried out using modified electrodes. Consequently, in addition to the STM-based charge transport measurements, studies of electron transfer rates of redox couples in solution also served to inform future efforts in molecular electronics by analysis of charge transport mechanisms across molecular layers, and by refinement of the construction techniques for the bottom half of a MJ.

Electroanalytical measurements of charge transport across molecular monolayers to/from a redox couple in solution have been carried out extensively since the initial methods for modifying electrode surfaces were described in the 1980s [20–23]. [Figure 10.2](#) shows the basic scheme for using chemically modified electrodes in electrochemical studies for a variety of purposes, including electron transfer studies. An electrode surface is chemically modified to provide a set of desirable properties, such as specificity through chemical recognition elements or barrier properties. In the case that the main topic being studied is electron transfer reactions, there are two different experiments to consider. First, a redox-active molecule can be tethered to the terminus of a molecule that is attached to the electrode [24–26]. This allows surface-confined electrochemistry to be carried out and studied as the structure of the tether is altered (e.g., the length of the tether changes, but the same redox species is bonded as the end group in all cases). A second experiment can be carried out where a redox species is added to the solution to study electron transfer across an inert molecular layer [27–32]. In either case, a normal electrochemical cell is used to measure electron transfer, and properties such as the rate of the heterogeneous electron transfer are correlated to the properties of the molecular layer [33]. These studies were especially popular in the 1990s, during which time SAMs on gold were being intently studied for a wide variety of applications. In [Section 10.4](#), we detail some of the results of these studies and relate electrochemical measurements of particular parameters to those measured using solid-state MJs.

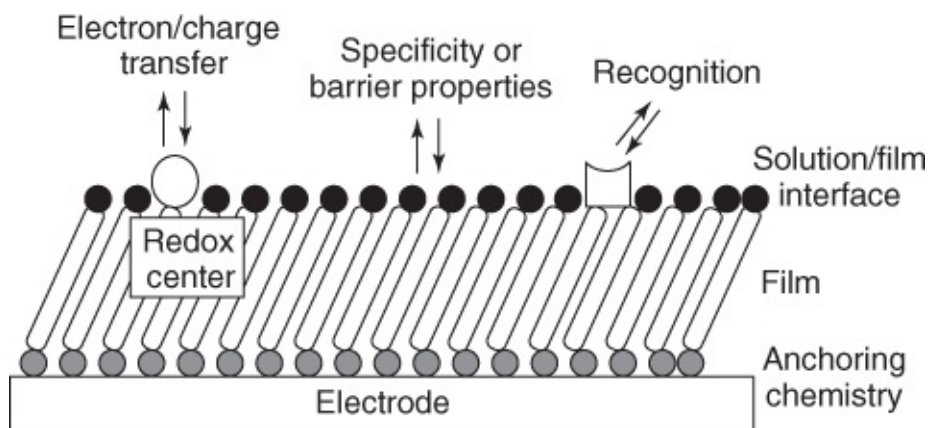


Figure 10.2 Scheme showing chemically modified electrodes that are used to study various electrochemical processes, including electron transfer rates across molecules.

(Reprinted from: Ref. [23].)

As described earlier, the convergence of modified electrodes and (especially) high-resolution electronic measurements using STM led to studies of charge transport across molecules between two conductors. Since the methods were in place to modify conductors with molecular layers of controlled structure, the addition of a top contact to result in a solid-state MJ was a natural evolution. By the late 1990s and early 2000s, the development of the mechanically controlled break junction [34, 35] (see [Figure 10.3d](#)) enabled statistically significant measurements of single-molecule devices to be made routine. Simultaneously, methods were being developed to deposit conductive materials onto the top of molecular layers. Indeed, Science magazine declared nanoelectronics a breakthrough of the year in 2001 [38]. Since this time, the field has grown rapidly, but not without some growing pains. As discussed elsewhere [15], around the turn of the millennium, a tremendous hype surrounded the area, with several cases of promising results failing to live up to expectations, and data had even been fabricated [39]. Issues related to excessive hype were due in part to difficulties in producing reliable and reproducible results such that a particular phenomenon under study, which may have formed the basis of a highly promising set of claims, became difficult to verify. However, despite setbacks in realizing dependable results, interest in molecular electronics remains intense due to some powerful motivators, and efforts over the last decade have begun to make inroads, with several platforms capable of yielding acceptably reproducible results having emerged (part of this is due to the use of carbon electrodes, as will be discussed).

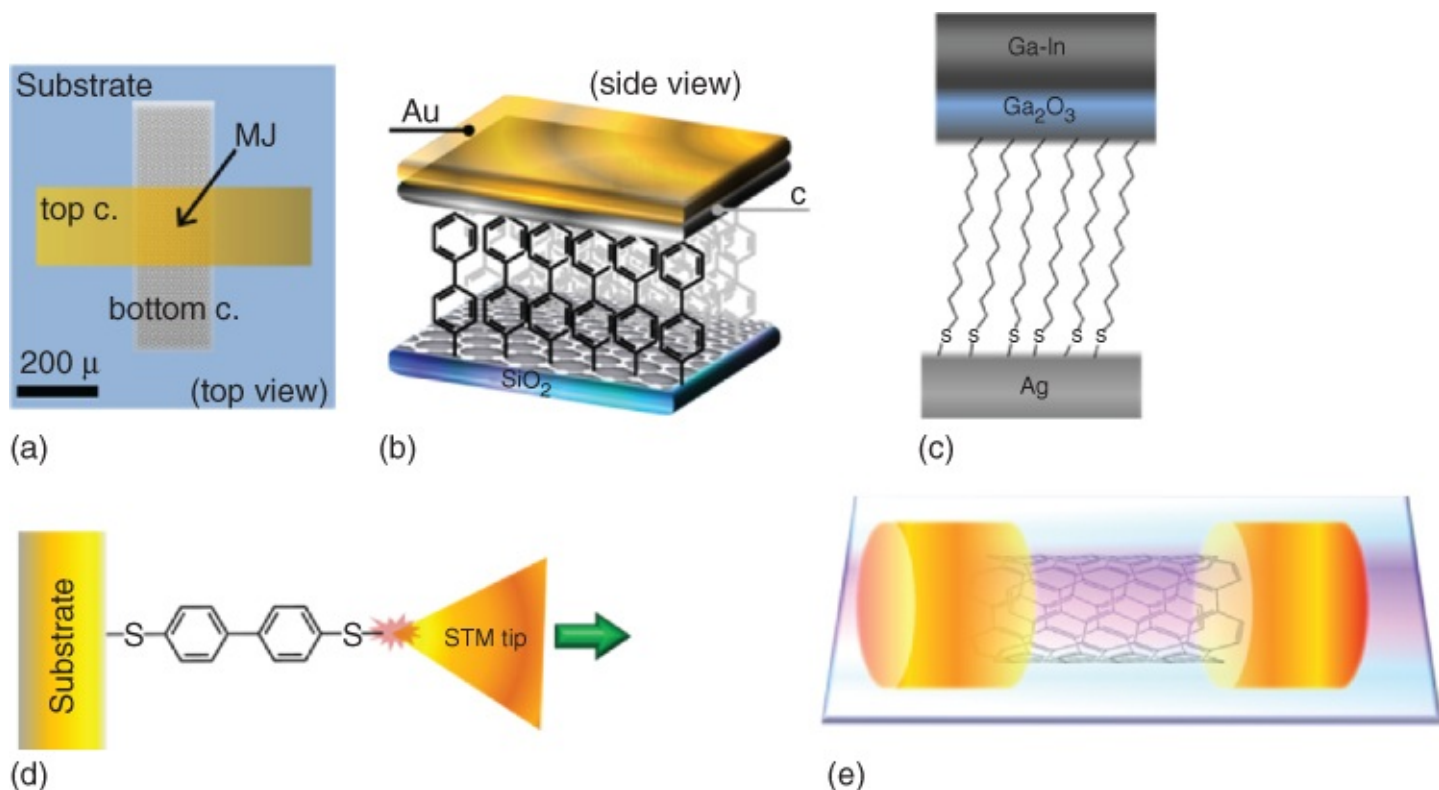


Figure 10.3 Various structures of molecular junctions commonly used in molecular electronics: (a) Cross junction formed by perpendicularly oriented bottom and top contacts with a molecular layer sandwiched between the conductors. Typical junction sizes range from several square microns to a square millimeter. (b) An all-carbon molecular junction formed using pyrolyzed photoresist film (PPF) (on SiO_2 support) as a bottom contact, an evaporated carbon (eC) top contact, and a molecular layer consisting of a multilayer of biphenyl grafted using diazonium chemistry. (c) Molecular junction made by contacting a thiols-based self-assembled molecular layer on Ag with a liquid-metal (in this case, a eutectic alloy of Ga and In). ((c) Reproduced from Ref. [36].) (d) A mechanically controlled break junction formed using *retractable* electrodes controlled with an STM, where molecules in solution bridge the gap to result in a junction [37]. (e) Other experimental geometries for studying electronic properties of single carbon nanotubes or a graphene nanoribbon can be made through forming contacts with lithographic methods.

With respect to motivators, electronics are ubiquitous in modern society. Given the enormous value of the global consumer electronics market place, it is not surprising that concerted efforts toward realizing the potential of exploiting molecules in electronic devices are ongoing. Part of the reason for the success of modern electronics is the remarkable improvement in the performance possible over time, during which the per-component production costs decrease due to miniaturization. It is for this same reason that the concept of molecular electronic devices began to take hold; continuous miniaturization inevitably leads to device sizes on the molecular scale by extrapolating Moore's law [40] (described earlier). This observation-turned prediction has been remarkable in its accuracy over the last 40 years. However, even before its accuracy was verified, it was clear that if such a trend continued uninterrupted, device sizes would approach molecular and atomic size scales at some point. Following the

current international technology roadmap for semiconductors (ITRS), that point is in approximately within one decade of 2014, when parameters such as gate and channel lengths for high-performance logic devices are expected to approach the 5–8 nm range [41].

While size represents perhaps the most commonly cited motivator in molecular electronics, there are other reasons to study MJ systems. Moreover, it should not be mistaken that shrinking device size represents the actual goal: much of the increase in performance for conventional semiconductors that results from decreasing device footprint is not inherent to the actual device size, but rather the ability to fit more components onto a single chip. In order to generate potential improvements in performance, molecular electronics seeks to utilize the wide range of molecular structures available relative to the number of semiconductors. In addition to this potential, molecular devices provide some unique possibilities, including new electronic functions and decreased production costs. First, some examples of unique electronic functions might include specific molecular interactions for use in sensors, unique interactions with photons (molecule-specific switches), and nonlinear circuit applications (e.g., generation of Fourier components). Thus, whatever the size of the MJ, if a function is achieved that is valuable AND difficult to accomplish using conventional components, then the value proposition for the use of MJs need not include size. Second, if the use of high-purity crystalline semiconductors can be replaced using organic moieties, then electronic functions may be achieved at much lower cost. Finally, it is critical to emphasize that regardless of the specific advantage offered by a molecular electronic device, the devices themselves must be manufacturable, durable, and reproducible in order to serve a practical use (and we would also argue that this requirement must be satisfied to enable the reliable study of charge transport phenomenon). This last consideration dictates that strategies for making cost-effective and robust molecular electronic junctions are a basic requirement for any type of commercial application. As we will see, the use of carbon materials in junction fabrications meets these needs nicely.

This chapter discusses the use of carbon-based electrode materials in the construction of MJs and the use of carbon-based materials in related studies (such as electrochemical experiments and in the construction of other electronic devices). The methods for making MJs are first outlined, followed by the use of the more novel allotropes of carbon. These materials have interesting electronic properties that provide additional opportunities for their application in molecular electronics relative to more conventional carbon materials. Finally, some of the considerations that dictate charge transport across molecular layers in MJs are discussed before we leave with some future prospects.

10.2 Fabrication

As briefly alluded to in earlier discussion, various methods for making single- and many-molecule junctions have been devised, and several of the more prominent structures are illustrated in [Figure 10.3](#), where large-area cross junctions (a,b), and liquid metal top contact (c) junctions are shown, along with a single-molecule STM-based junction (d) and a carbon nanotube (CNT) device (e). Here, we discuss a few of the more popular MJs before narrowing

the focus to carbon-based devices. This is done in order to provide some context that illustrates the strengths and weaknesses of carbon electrodes as contacts in MJ fabrication. In addition, we compare the general properties of devices made in different ways to illustrate that MJs must be considered as a complete system, where their electronic properties arise not only from the structure of the molecular component, but from the way in which the contacts and molecule interact.

The most common way to construct a complete and discrete component MJ (as opposed to using an STM or conductive atomic force microscopy (AFM) tips as a contact method) is a “bottom-up” approach, where a conductive material is used as a substrate support, and a molecular layer is placed onto the initial “bottom” contact. In order to complete the circuit, a top contact is placed onto the molecular layer in a way that enables a bias voltage to be applied across the molecule. As we will see, the reasons for this methodology being adopted relate to the available techniques for placing molecular layers onto surfaces. However, bottom-up fabrication also places limitations on the types of layers that can be used without going to great lengths to ensure that the process of placing the top contact does not disrupt or destroy the molecular layer.

As is clear in the historical context provided in the introduction, SAMs were the initial favorite choice for constructing MJs. The ease of preparing a well-defined molecular monolayer on stable and readily available metals (especially gold) made SAMs a natural choice. Most of the earliest studies that can be considered to be a complete MJ involve STM-based measurements of SAM-based junctions starting in the mid-1990s [42]. However, many of the early efforts to fabricate discrete solid-state MJs using SAMs were hindered by the deposition of the top contact disrupting or even destroying the molecular layer, resulting in short circuits, high variability in device behavior, and nonreproducible results. As an example that illustrates these difficulties, studies of noble metal deposition onto thiolate monolayers on gold revealed that gold penetrates the molecular layers, and even that the molecules could reassemble onto the top of the deposited gold layer [43, 44].

Alternative methods for making top contacts that avoided some of these issues were developed; many of these have resulted in the ability to make reliable MJs, and are sometimes referred to as *soft-contact* methods [45, 46]. One such method involved the use of a conductive polymer buffer layer (PEDOT) before deposition of Au [47, 48]. The deposition of the conducting polymer layer prevented the reordering of the labile thiolate molecules on the underlying Au surfaces and also protected the layer from penetration of Au atoms. A second method that has been employed is the use of liquid metals. This generally started with mercury [49–53] and proceeded to the use of a eutectic mixture of Ga and In, often abbreviated eGaIn [54–58]. The use of a liquid metal largely circumvents the penetration of the top conductor into the molecular layer, and has been employed in many systematic studies of charge transport in molecular devices. Third, since the direct vapor deposition of metals had often resulted in disruption of the molecular layer, various forms of shielded deposition have been carried out. For example, indirect deposition of Au, where the evaporation sources are shielded from the sample such that the Au atoms can arrive at the sample only after several collisions (which it is thought reduces the kinetic energy of the impinging atoms) was shown to have less effect on a

molecular layer than direct deposition [59]. Finally, another notable method that has been employed to make MJs using SAMs on metallic substrates is conducting AFM tips [60–67]. Here, an AFM tip that is coated with a conductive metal is brought into contact with a preexisting SAM on a metal substrate, resulting in a metal–molecule–metal junction of relatively small area. The ability to control the force exerted on the molecular layer during the contacting procedure prevents disturbing or destroying the molecular structure.

A large part of the limitations in using SAMs as the molecular component in molecular electronics is due to the lability of the metal–S bond in the thiolate molecules. More generally, any method of placing a contact onto a molecular layer that requires the dissipation of energy equal to, or exceeding, the stabilization energy between the molecular layer and the substrate is likely to yield inconsistent results at best. As discussed earlier, another likely scenario is the complete disruption of the MJ, possibly including changes to the chemical structure of the molecular layer. As discussed in a 2009 Progress Report [68], the surface bond energy of a SAM is ~ 1.9 eV, while that for covalently bonded molecules on carbon is in the range of 3.5–4 eV (for more information, see Figure 3 of the original article [68]). For this reason, MJs made using the covalent modification of carbon surfaces have several advantages that enabled the fabrication of MJs with a high degree of stability, which enables the reliable and reproducible fabrication of molecular devices. Next, we discuss the fabrication of MJs using carbon electrodes, and draw out both the limitations and advantages of this method.

A form of conducting carbon that can be made easily, and that has an excellent set of properties for use as a bottom contact in molecular electronics is pyrolyzed photoresist films (PPFs) [69, 70]. This form of conductive carbon material is made by the pyrolysis of photoresist films, which can be patterned into any desirable feature (for some examples, see literature [69, 71]) using standard photolithographic techniques, which enable a wide range of geometries to be accommodated. In addition to good conductivity, PPF has a surface that is very flat, with measured root mean square (RMS) roughness values (via AFM) of ~ 0.5 nm (see [Figure 10.4b](#)). This feature is critical, since a substrate that has a surface roughness comparable to, or larger than, the thickness of the targeted molecular layer is not suitable for making MJs, due to the increased possibility of short circuits resulting from conductor–conductor contacts providing the primary current pathway. Finally, a method for covalently binding molecular layers to carbon surfaces using the electrochemical reduction of aromatic diazonium ions (see Sections 2.4.4 and 6.2.1 and [Figure 10.4a](#) for an example voltammogram recorded during the deposition of a molecular layer from a dilute solution of a diazonium ion precursor) was presented in the early 1990s [74], and this sets the stage for the fabrication of stable MJs.

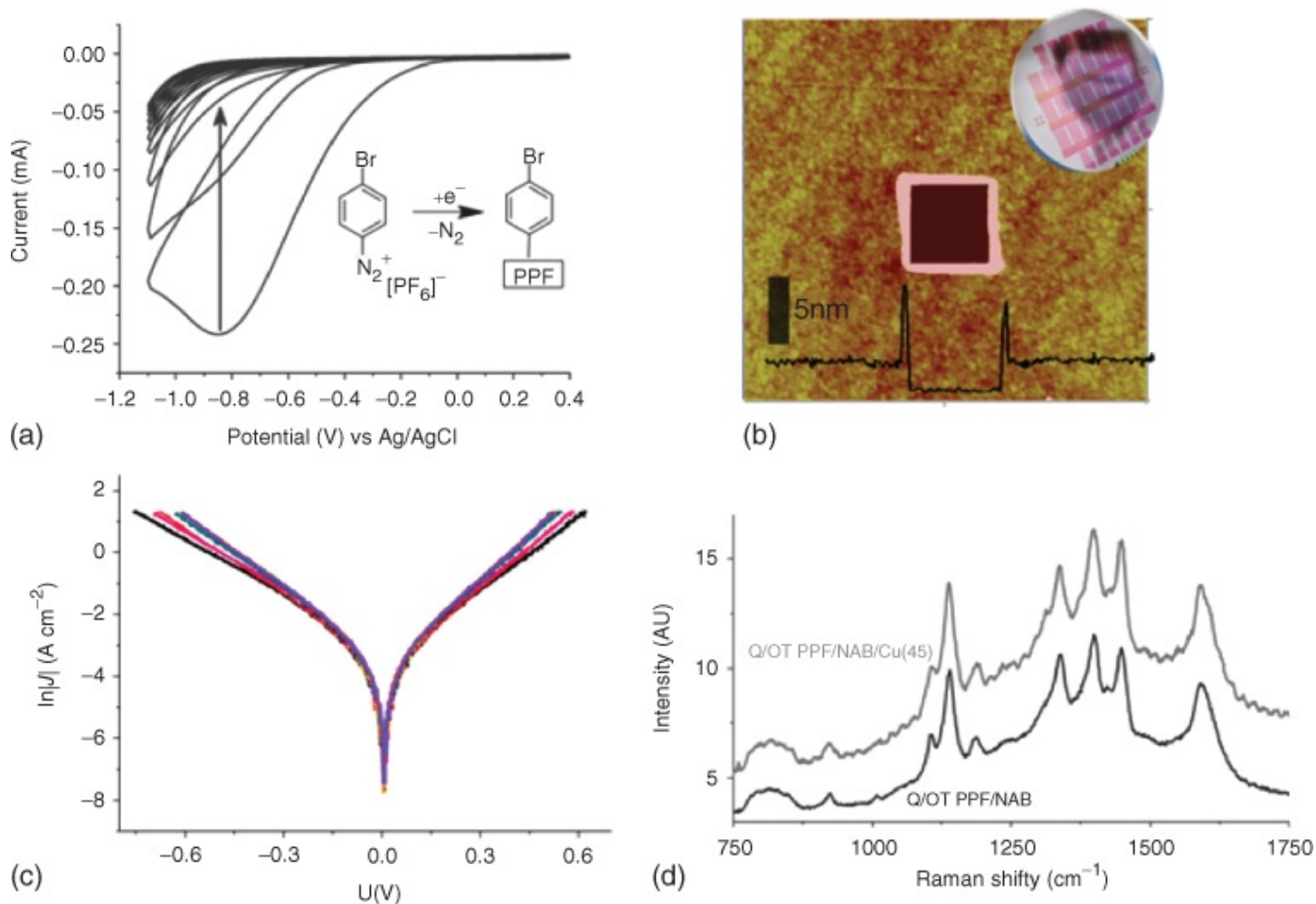


Figure 10.4 Fabrication and measurements of molecular junction formed on PPF using diazonium chemistry. (a) Cyclic voltammogram measured at a PPF electrode featuring an irreversible reduction peak at approximately -0.8 V that corresponds to the reduction of diazonium ions with subsequent formation of a C–C with PPF. Growth of the molecular layer results in the increased blocking of electron transfer from the electrode and gradual decrease of the peak intensity (see also Chapter 6 on carbon electrode modification). (b) AFM image of the molecular layer obtained in (a), showing that film is homogeneous, and that the thickness can be measured using AFM. (c) Overlay of the current density–voltage characteristics (semilogarithmic scale) of eight junctions showing good reproducibility. (d) Raman spectra (measured with a 514 nm probe through an optically transparent quartz/PPF substrate made by diluting the photoresist) of a Q/PPF/NAB/Cu junction with and without a Cu top contact showing no changes in the structure of a nitroazobenzene molecular layer. (c) (Reprinted with permission from Ref. [72]. Copyright (2010) American Chemical Society). (d)

(Reproduced from Ref. [73].)

The fabrication of PPF/molecule samples as a starting point for making a MJ at first utilized a liquid–metal contact (Hg) [75, 76]. As will be shown, the increased stability of covalently bonded molecular layers on carbon enabled the electronic characteristics of such devices made using the direct deposition of metals [77] reproducible. In particular, the use of Cu metal, deposited via electron beam evaporation (directly, without any shielding), yields MJs with

excellent reproducibility. [Figure 10.4c](#) shows a series of current density–voltage (J – V) curves for an example set of large-area PPF/molecule/Cu junctions, where an overlay is shown of the J – V curves (semilogarithmic scale) of eight MJs containing a 3.5 nm layer of azobenzene. Here, the yield was 100% (while for 72 junctions fabricated in the study, the yield was 96%), and the relative standard deviation of the current density at 0.1 V was less than 10%. Importantly, this level of reproducibility in the measured values of J is a requirement for studying the changes in current density as the molecular layer thickness changes, which is an important mechanistic diagnostic (see discussion in [Section 10.4](#)).

While several demonstrations of reproducible electronic properties of carbon/molecule/Cu MJs have been presented [72, 77, 78], because molecular materials are “soft,” it is important to assess the structure of the molecular layer after deposition of contact materials. As recently reviewed [79], various analytical techniques for assessing the structure of molecular layers within MJs have been developed in order to determine if the molecule survives various fabrication processes. In the case of molecular layers grown by diazonium reduction on PPF surfaces, UV/vis, Raman, and X-ray photoelectron spectroscopy (XPS) have been used to verify that molecular layers can survive the direct electron beam deposition of Cu, Ag, Au [73, 80], Si [81], and carbon [82] with no detectable changes in structure. However, in the case of Au contacts, the electronic properties of the junctions were not reproducible, indicating that Au can penetrate the molecular layers to some degree [73]. Moreover, the use of Ti or Pt contacts resulted in significant disruption of the molecular layer [73], illustrating that structure must be verified after fabrication. To illustrate an example, [Figure 10.4d](#) shows a comparison of the Raman spectra of a 5 nm layer of nitroazobenzene measured through a transparent layer of PPF on quartz (made by diluting the photoresist before pyrolysis [83]) for a region of the sample without any top contact (gray line) and for a region where a 45 nm layer of Cu was deposited directly onto the molecular layer (black line) [73]. Additional analysis by XPS, UV/vis, and AFM confirmed this result.

From the discussion earlier, it is clear that the use of the electrochemical reduction of diazonium reagents on carbon leads to reproducible molecular layers that can withstand fabrication and packaging procedures. In addition to the ability to readily fabricate reproducible junctions, another aspect of the excellent stability of this system is the excellent temperature stability of PPF/molecule/Cu MJs [73]. While the stability of Au/SAM/PEDOT/Au MJs was shown to be limited to temperatures of 50 °C [84] or 60 °C [85], molecular layers on PPF made using diazonium reduction are stable to 400 °C, while completed PPF/molecule/Cu MJs are stable to at least 250 °C [73]. Moreover, when employing a “covalent” top contact material, also made of carbon, both temperature and bias stability are improved, as discussed later.

The use of covalent conductors in electronics eliminates some of the potential problems when metallic conductors are used, including redox reactions and migration of the conductors driven by applied electric fields. These processes can cause short circuits and/or disruption of the device structure, and can lead to limited device stability under applied voltages. In terms of molecular electronics, these restrictions can be heightened since nanoscopic molecular layers are used. As shown earlier, the use of Cu metal as a top contact in carbon–molecule–metal junctions has been highly effective at producing reliable and reproducible MJs. However, a

more recent advance has employed electron beam deposition of carbon (e-C) as a top contact [82]. This material behaves as a covalent conductor, and increases both the temperature and bias stability. Figure 10.5a–e highlights the high stability of PPF/molecule/e-C/Au devices toward AC, DC, time aging, and temperature, respectively. Thus, the “all-carbon” molecular tunnel junction provides a platform for making reliable, reproducible, and robust MJs. Next, we discuss the use of some of the novel allotropes of carbon in molecular electronics.

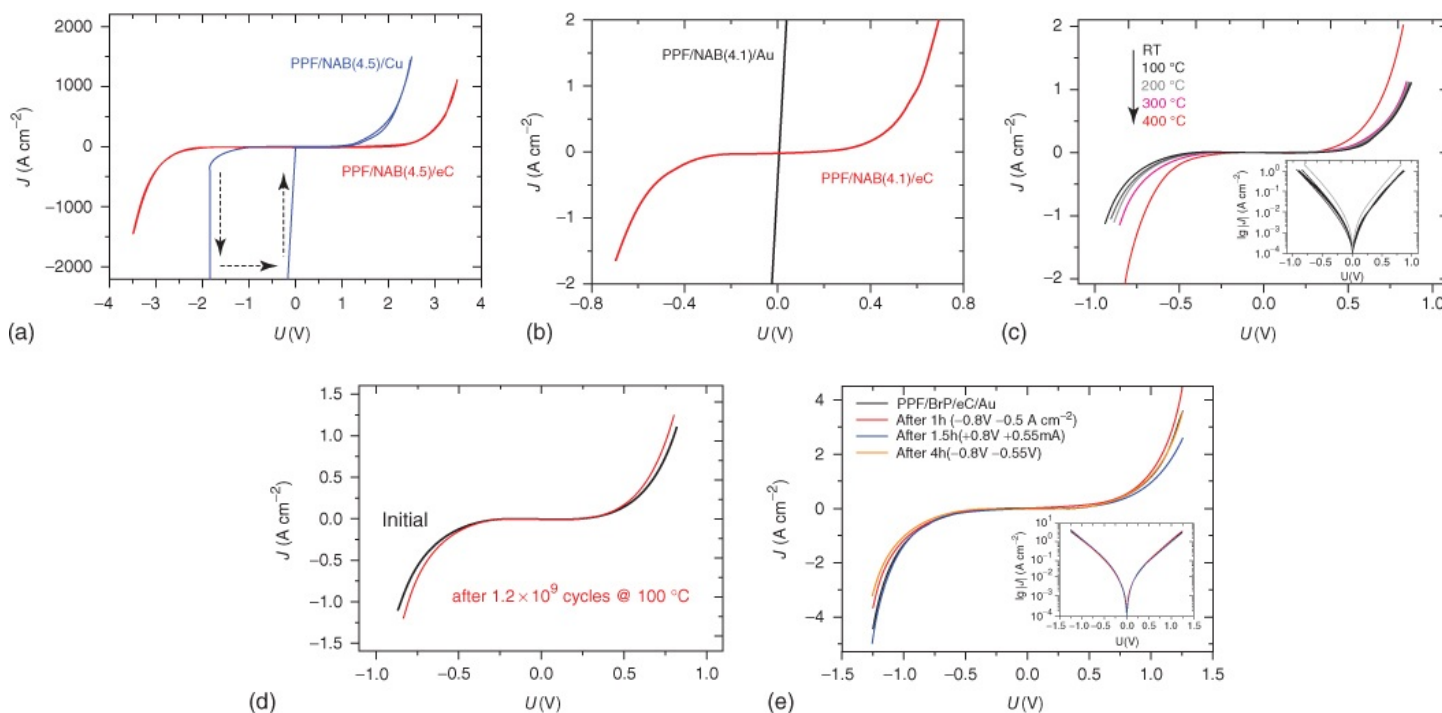


Figure 10.5 Bias and temperature stability of all-carbon MJs: (a) Comparison of Cu and e-C as top contacts, showing that the use of Cu leads to breakdown at approximately -1.86 V (due to electrochemical reactions of Cu), while e-C shows stability to ± 3.5 V (with current densities up to ~ 1500 A cm⁻²), junction area: $15\mu\text{m} \times 15\mu\text{m} = 225\mu\text{m}^2$). (b) Overlay of J - V curves for PPF/NAB(4.1)/Au and PPF/NAB(4.1)/eC(10)/Au junctions showing that 10 nm of e-C prevents penetration of Au. (c) J - V curves of PPF/NAB(4.5)/e-C junction after heating in vacuum ($2-4 \times 10^{-6}$ Torr) for 30 min at each temperature. (d) J - V curves of a PPF/NAB(4.5)/e-C junction before and after 1.2×10^9 cycles at 100°C in lab ambient (air) over the course of ~ 68 h. (Adapted with permission from Ref. [82].) (e) J - V curves of a PPF/BrP(3)/e-C/Au junction before and after the application of ± 0.8 V DC bias for 1–4 h at room temperature. Insets display the same data plotted in a semilog scale.

10.3 Novel Allotropes of Carbon in Molecular Electronics

This section focuses on the electronic properties of other, novel carbon materials as relevant to their use in molecular electronics. The appropriate background regarding properties and preparation methods is discussed, while an interested reader may refer to Chapters 1-4 for more details on electrochemistry of highly oriented pyrolytic graphite (HOPG), graphene, and

CNTs. Here, we specifically consider electrodes made of confined sp² carbon layers, and limit the discussion to graphene and CNTs as prominent examples.

10.3.1 Graphene

Gradually after the experimental isolation of graphene 10 years ago [86] and accelerating with the awarding of the 2010 Nobel Prize to Andre Geim and Konstantin Novoselov for their initial experiments with this material, it has gained widespread attention. Many different application fields in different branches of electronics are being explored. The main reason for this boom in graphene research is due to its extraordinary mechanical, optical, and electronic properties: single-layer graphene (SLG) is strong, with a strength [87] of 42 N m⁻¹; it has high surface area [87] (2630 m² g⁻¹); good optical transparency in the visible region [88] (~97.7% in the infrared limit for SLG); a high electron mobility [89] of 200 000 cm² V⁻¹ s⁻¹; excellent thermal conductivity [90] (3000 W m⁻¹ K⁻¹); and can sustain remarkably high current densities [91]. A variety of preparation methods are available, including mechanical and chemical exfoliation [92], reduction of graphene oxide GO, chemical vapor deposition [93], and graphitization of SiC [94]. Each method yields graphene in different ranges of quality [95], with flakes of 1–1000 nm in size, with variable electron mobility (1–200 000 cm² V⁻¹ s⁻¹). These parameters vary depending on the types and density of defects, doping level, and the types of functional groups found in the graphene layers – all of which stem from the preparation methods so that its electronic properties can be controlled as desired. Finally, the different preparations lead to a different degree of electronic coupling with the substrate on which the graphene is supported, which also influences its charge transport behavior.

10.3.1.1 Electrochemistry of Graphene (see also Chapter 4)

Graphene sheets are typically composed of two faces: (i) high-quality sp² carbon network without defects (the basal plane) and (ii) carbon network rich in defects and oxides (the edge plane). When graphene is transferred to a surface, a mixture of these planes will be present in different proportions. Conventionally, it has been proposed that each plane displays distinct rates of heterogeneous electron transfer (HET), with the edge plane exhibiting an HET rate constant of ~0.01 cm s⁻¹, while the basal plane shows an essentially inactive rate of about 10⁻⁹ cm⁻¹ s⁻¹. This line of reasoning has been used to establish that the overall electrochemical response of graphene is attributed primarily to edge sites. High-quality graphene with a low density of defects exhibits poor EC behavior, even up to blocking the underlying electrode surface [96]. By contrast, defects arising from functionalization, oxidation, or other treatments exhibit increased rates for heterogeneous electron transfer [97], and defects introduced by anodization of graphene show superior electron transfer rates as compared with pristine graphene, glassy carbon (GC), or boron-doped GC [98]. We note here that studies with HOPG, which is often considered as a model surface to study electrochemistry of graphene and CNTs, have shown that both edge and basal planes of HOPG support fast HET rates, and ET is not confined to step edges [99]. This inconsistency around the activity of basal plane HOPG present in the literature is justified by different quality, since defects in these materials result in variable electronic properties and electrochemical activity [100].

In the context of molecular electronics, the presence of two planes with different electrochemical reactivity implies that band gap opening and functionalization will occur mainly at the edge-plane sites. The number of graphene layers exhibit different chemical reactivity toward electrochemical sensing and functionalization also, where SLG shows the lowest activity, with increasing reactivity as the number of layers grows [101] (e.g., double-layer graphene is expected to be 1.6 times more reactive than an SLG [102]). The high surface area and electrochemical properties of graphene have tremendous potential for sensing and energy storage applications. For example, defect and oxide sites in graphene represent active redox centers for bioelectrochemical sensing, which are connected by a defect-free sp²-hybridized graphene network [103].

10.3.1.2 Graphene in Molecular Electronics

Graphene's sp²-hybridized carbon atoms are arranged in a honeycomb manner and possess a lattice structure consisting of two equivalent interpenetrating sublattices. The equivalence of the two sublattices results in the absence of the gap in the band structure of graphene, where the conduction and valence bands touch at the two K (Dirac) points (Figure 10.6). The zero band gap nature of graphene in relation to semiconductors shows that graphene can become a semiconductor when the gap is “opened,” which can be achieved by breaking the symmetry of the two lattices, and which is desirable when making various molecular electronic devices using graphene. As a result of its electronic, optical, and mechanical properties, the utilization of graphene in molecular electronics largely includes three main directions – use of graphene as a top/bottom contact material due to its electronic coupling with a molecular layer; as a top contact that serves as a protecting layer; and, in its pristine or functionalized form, as the active part of a MJ.

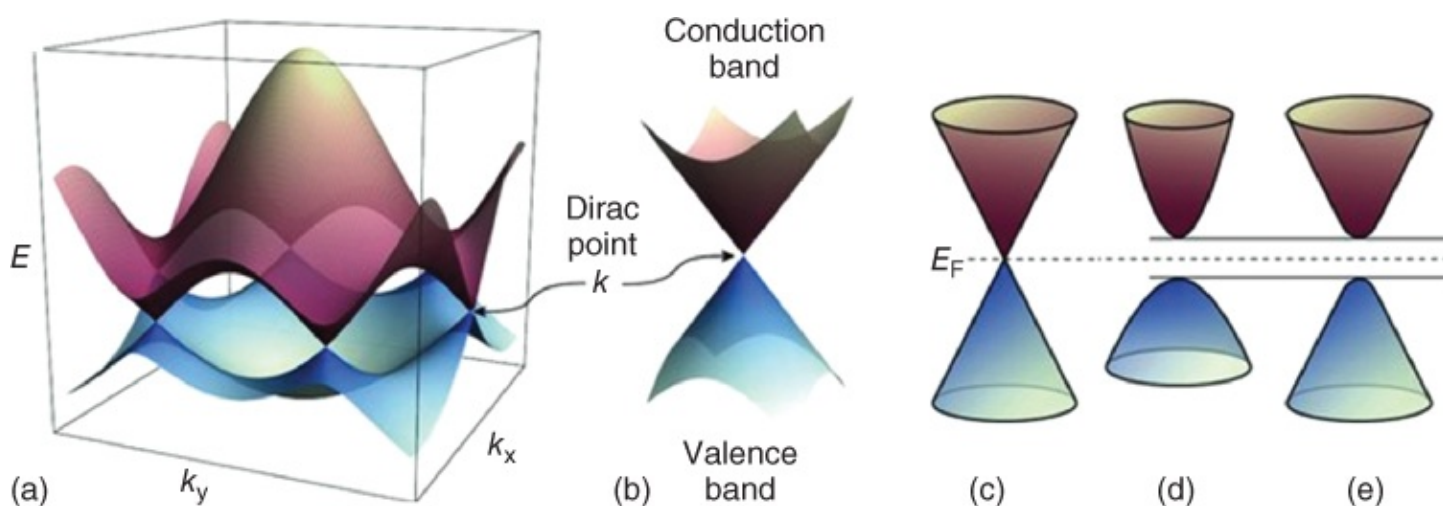


Figure 10.6 (a,b) Electronic band structure of graphene showing valence and conduction bands touching at the Dirac points and having a linear dispersion relation around the Fermi level. Comparison of (c) zero-band gap graphene, (e) band gap-opened graphene, and (d) a semiconductor, suggesting the possible use of zero-band gap graphene as a conductor for MJIs and with a band gap as a molecular layer.

(Reproduced from Ref. [104].)

Before listing a few examples, it is useful to describe in brief the basic concept of field-effect transistors (FETs). In an FET, as in a MJ, current flows between two terminals, called the **source (S)** and **drain (D) electrodes**. The channel between the source and the drain is typically composed of a semiconductor or a molecule (in the case of molecular electronics). In order to control the conductance in the semiconducting channel, a third electrode, called the **gate (G)** is added to the structure and is insulated from the channel, usually through a nonconducting dielectric layer. In FETs, two situations can be considered: when there is no applied voltage between S and G (or V_{SG} is less than certain threshold value V_T), and no current is passing in the channel (OFF state); when $V > V_T$, and a negative bias is applied at the gate, hole current flows in the channel (ON state), in the case of a p-type FET (alternatively, a positive bias at the gate can result in an electron current for an n-type FET).

Graphene has been successfully utilized as an active layer in FETs, where graphene surfaces are functionalized with a photochromic spiropyran molecule ([Figure 10.7](#)) [105]. In this case, spiropyran with a pyrene linker was noncovalently immobilized on graphene through π - π interactions, with negligible introduction of defects. As prepared, such FETs exhibited n-type behavior. Photochromic ring opening of the spiropyran molecules using ultraviolet light yielded a zwitterionic conjugated structure with a large dipole moment, resulting in changes to the position of Dirac point of graphene, which could be reversed upon exposure to visible light ([Figure 10.7b](#)). The modulation of the Dirac point relative to the Fermi level resulted in concomitant changes of conductance of the FET ([Figure 10.7c,d](#)).

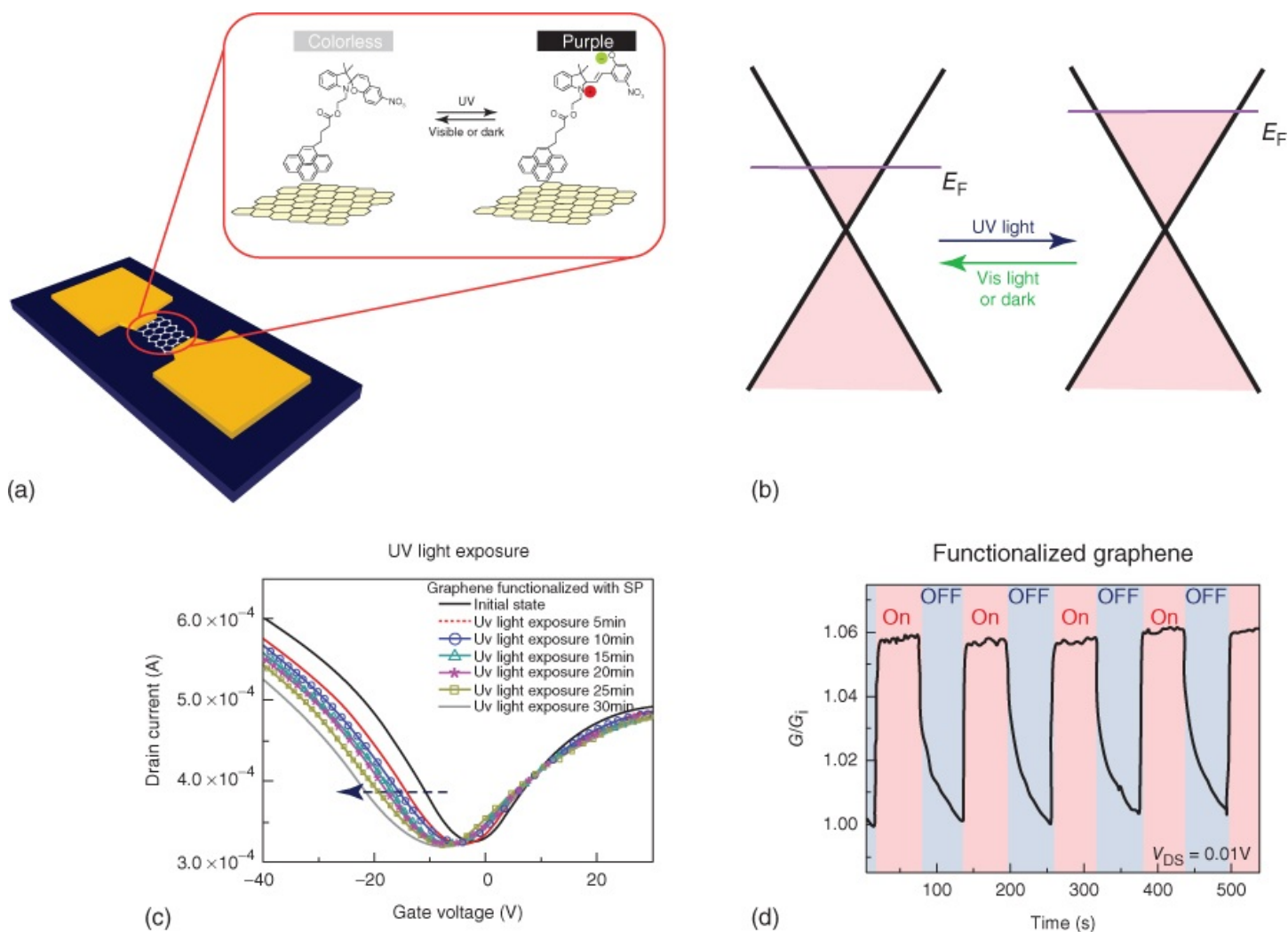
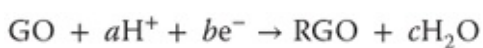


Figure 10.7 Reversible switching of conductance in a junction consisting of graphene functionalized with spiropyran. Spiropyran, a photochromic switch attached to G noncovalently, is able to change states between the ring closed (small dipole moment) and ring open (larger dipole moment) upon irradiation with UV and visible light. (a) Changes in the electronic configuration of spiropyran are translated into changes of the position of Dirac point of graphene (b), resulting in changes in the applied gate voltage (c) and conductance (d).

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In an independent application, graphene was utilized as a top electrode for solid-state MJs consisting of alkanethiol SAMs on Au (Figure 10.8a–b) [106]. Good electronic coupling of graphene with molecules resulted in better contact resistance and good durability, improved thermal and operational stabilities and lifetime. In addition, similarly to the role of eC discussed in Section 10.2 (fabrication), the presence of the intermediate graphene [108] or reduced graphene oxide (RGO) [109] (multi) layer between the SAM and Au evaporated as a top contact served to protect the molecules from damage, including short circuits. In the latter case, graphene with a high density of oxygen groups, or GO, can be reduced electrochemically, resulting in RGO according to [110]



and the resulting RGO can be used as contact material for an MJ [109]. On the other hand, graphene-coated Au AFM tips have been suggested for use as a top contact for MJs and showed very small tip-to-tip variance, good operational stability, endurance, and long shelf-life [111].

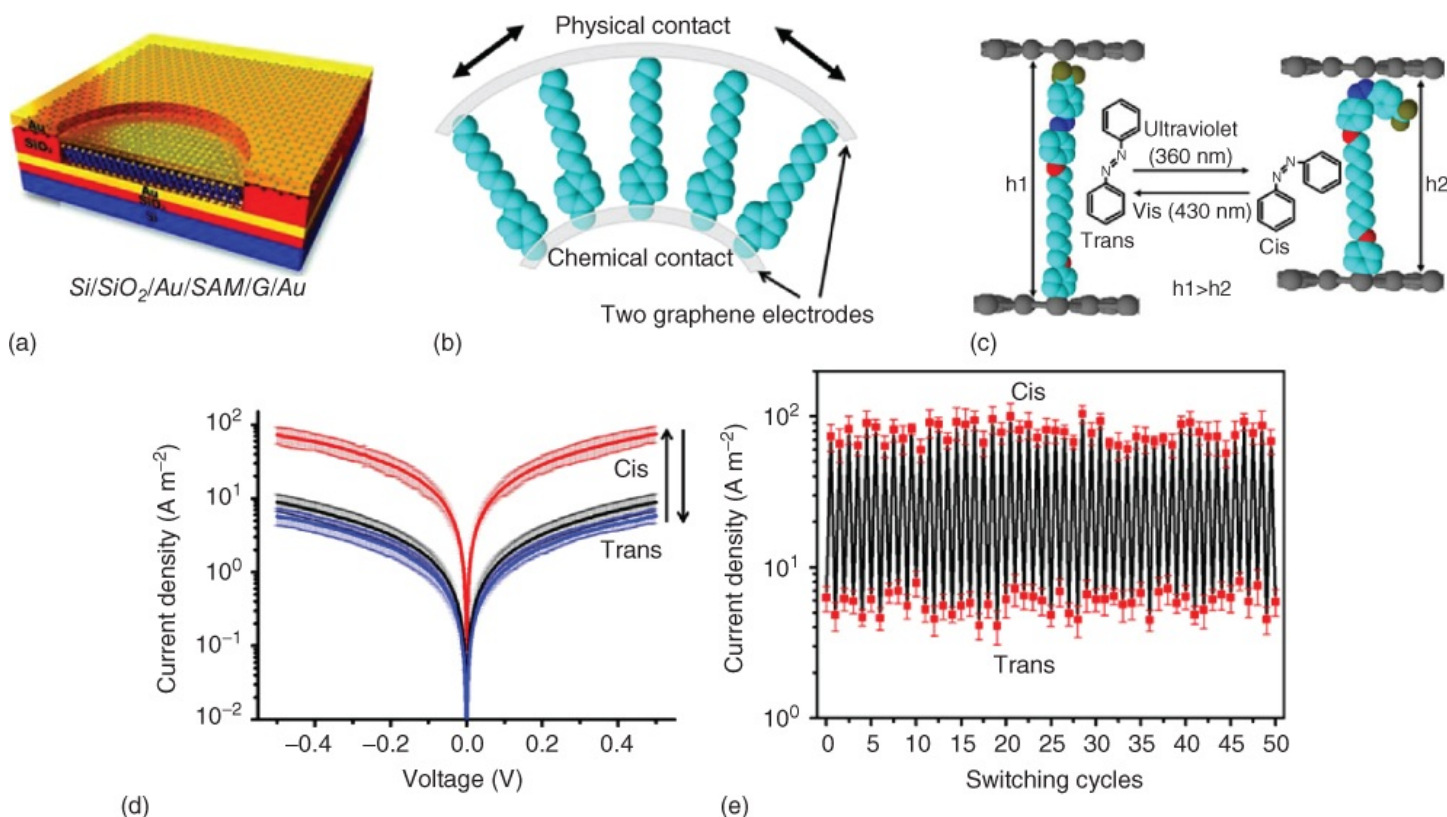


Figure 10.8 Graphene functioning as top and bottom electrodes for MJs. (a) Similarly to eC, the presence of graphene between molecular layer and Au top contact protects the junction from short circuits between electrodes. (Reproduced from Ref. [106].) (b) Using diazonium chemistry, an azobenzene layer was grown covalently on a graphene bottom contact, while a top graphene electrode was contacted physically. The mechanical and optical properties of graphene electrodes allowed testing of electronic properties under mechanical stress, and (c) photochemical switching of azobenzene between cis- and trans-isomers induced by multicycle switching (d) of the conductance of the junction, which was reversible (e).

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Combining the advantages of graphene as an optically transparent, mechanically flexible, and chemically stable electrode with the photoactivity of molecular switches, all-carbon MJs have been prepared using graphene bottom and top contacts, with azobenzene-based molecular layers of 1.5–2 nm thickness (Figure 10.8c–d) [107]. Here, azobenzene was used to derivatize graphene using diazonium chemistry to allow covalent anchoring to the bottom graphene contact, with the top graphene layer contacted noncovalently. Fabricated on a plastic substrate, devices showed excellent performance under mechanical stress. Reversible multicycle modulation of conductance was achieved by switching azobenzene between cis- and trans-isomers using UV and visible light, respectively. Similarly, a junction consisting of a single azobenzene molecule sandwiched between two graphene contacts showed modulation of

conductance upon light exposure, and additionally by changes in pH [112]. The latter effect originated from sulfonic acid groups present in the azobenzene derivative. This example demonstrates the multiresponsiveness and versatility of devices based on molecular components. An important advantage of using graphene over CNTs as an electrode material is that it gives more controlled performance due to lack of chirality, which can affect the conductance of the device [113, 114].

Currently, there are several hurdles related to the fabrication of graphene devices and the manipulation of the electronic properties of (functionalized) graphene. Some of these include the need to create a band gap (as discussed earlier), which limits its applications in high-performance integrated logic circuits and the contact resistance between graphene and other electrode materials. For these reasons, it has been suggested that the controlled integration of graphene layers into circuits using a top-down, bottom-up, or hybrid approach [115] is likely to appear after 2020 [95].

10.3.2 Carbon Nanotubes

CNTs can be considered as a sheet of graphene folded to form a tube, which can also be capped on-ends with a (half) fullerene-like cage ([Figure 10.9](#)). This one-dimensional curved graphene allotrope shows excellent mechanical strength, good thermal and chemical stability, a high aspect ratio, helicity, and exceptional electron mobility and conductivity. These properties arise, at least in part, from satisfied aromatic bonds. In the following, we summarize briefly some preparation methods and discuss relevant electrochemical and electronic properties of these materials before touching on some electronic applications.

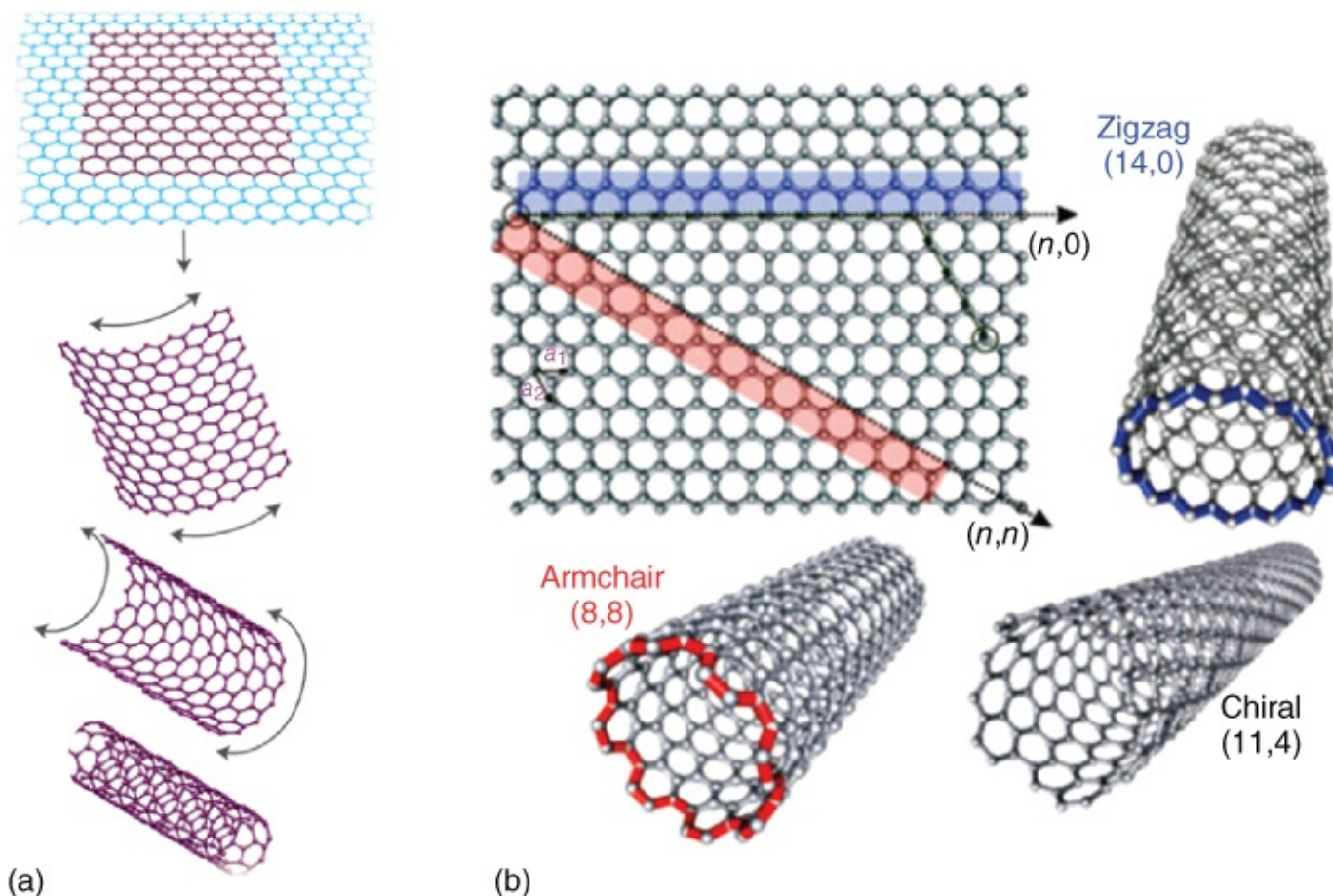


Figure 10.9 Formation of a carbon nanotube by rolling up a graphene sheet. Depending on the chiral vector along which the nanotube is rolled, zigzag, armchair, and other chiral options are possible resulting in metallic or semiconducting CNTs.

(Reproduced from Ref. [116], copyright Wiley.)

The preparation of CNTs, including laser ablation and the original method of electric arc discharge, uses solid-state carbon precursor materials [117]. Alternatively, (HiPCO) nanotubes are produced with high-pressure carbon monoxide in the presence of iron carbonyl. A common graphene production method – chemical vapor deposition is also suitable for the synthesis of CNTs, if a suitable precursor and catalyst are used [118, 119]. While high-quality CNTs can be produced with these methods, without proper purification, when CNTs are used as electrodes, a high electrochemical activity is observed, originating from metallic impurities present in the as-synthesized CNTs. Therefore, successful utilization of CNTs in molecular electronics requires that further purification and isolation methods are employed to remove these side products, including graphitic clusters, metal nanoparticles, and fullerenes from the final product. For this reason, it has been challenging to obtain, unambiguously, the intrinsic electrochemical properties of CNTs [120, 121]. A multistep purification procedure that yields high-quality CNTs consists of several treatments that are focused to remove specific contaminants: dry oxidation by annealing in air at 350 °C is used to remove amorphous carbon; heating in a nonoxidizing acid solution is used to remove metal particles (HCl or HNO₃); a final annealing at 1000–1100 °C in vacuum is used to repair defects created in the previous step [116, 122].

10.3.2.1 Electrochemistry of CNT Electrodes

CNT electrodes do not typically show well-defined redox peaks, but continuous cathodic current originating from a mixture of variable CNTs in the film. A detailed spectroelectrochemical study of a range of single-walled carbon nanotubes (SWCNTs) in solution showed how the redox potentials of individual nanotubes depend on their diameter and chirality [123]. The overall electrochemical activity consists of highly active defect-rich areas, including edges, oxides, and the comparably inert basal plane [120]. If CNTs are being functionalized for further use in molecular electronics, this difference in electron transfer rates at the edge and basal plane dictates the morphology and distribution of the functional groups. CNTs also have unique electronic properties that have led to some unique uses in molecular electronics.

10.3.2.2 Electronic Properties of CNTs

The electrical properties of CNTs are related to the electronic properties of graphene, since a nanotube can be considered a rolled sheet of graphene ([Figure 10.9](#)). Therefore, depending on the CNT chirality, several options are possible related to the specific chiral indices (n,m) of the chirality vector $C = na_1 + ma_2$ of hexagonal lattice: metallic behavior (m-CNT), when $n = m$; a semiconductor behavior (s-CNT), when $|n - m| = 3i \pm 1$ (i – integer). As synthesized, an average sample of CNTs contains semiconducting and metallic CNTs in a ratio of $\sim 2 : 1$. From the perspective of molecular electronics, the utilization of CNTs is distinguished between the use of metallic CNTs as contacts to molecules and use of semiconducting CNTs as a p–n junction element.

In metallic CNTs, confinement results in allowed bidirectional ballistic movement of electrons along the nanotube axis, provided that energy and momentum conservation laws are satisfied. These constraints result in the reduced probability of electron-scattering processes, and mobility [124] up to $10^4 \text{ cm}^2 \text{ Vs}^{-1}$, significantly higher (~ 2 orders of magnitude) relative to typical organic semiconductors [125] allowing m-CNTs to carry current densities [125–127] up to 10^9 A cm^{-2} . This combination of features might be useful in applications where high-electric field and high-frequency operations are essential [128]. The ballistic electronic properties of metallic SWCNTs lend this material to use as a contact to molecules. Calculations suggest that alignment of the Fermi level of m-SWCNTs and the energy levels of connected molecules may enable the use of such systems in a new generation of nanoscale devices [129–131].

10.3.2.3 CNT-Based Electronic Devices

By leveraging the electronic properties outlined earlier, various electronic devices, including MJs, can be made using CNTs. However, a distinction between metallic and semiconducting CNTs must be made, as the ability to modulate the conductance of FETs requires s-CNTs, and is not feasible for m-CNT channels. Moreover, the use of m-CNTs as a contact in a MJ is feasible, while additional flexibility can be provided by s-CNTs. Thus, s-CNTs can be modulated between ON and OFF states with gate voltage, while the conductance of pristine

(defect-free) m-CNT is effectively independent of applied bias. For these reasons, CNT-based electronic devices can be built using two approaches: individual CNTs and arrays consisting of multiple quasi-ordered, nonisolated, overlapping CNTs ([Figure 10.10](#)). The first method allows more control over the device properties, and remarkable performance for s-CNT FET has been shown with current ON/OFF ratios of 10^4 , high conductance [134] (up to $0.5 \times 4e^2 h^{-1}$), and channel lengths ranging from 500 nm [135] down to <10 nm [136]. As prepared, CNT-FETs show p-type behavior with holes as main carriers due to the lower Schottky barrier for holes at the nanotube–metal interface. To generate n-type CNT-FETs, chemical doping of p-type tubes can be carried out by functionalization [137, 138], annealing the CNTs [139, 140], or selecting a special electrode material [141, 142]. The necessity of special treatment of p-type CNT-FETs to convert to n-type has the consequence that p-type CNTs are more developed and have more reproducible characteristics than n-type [143].

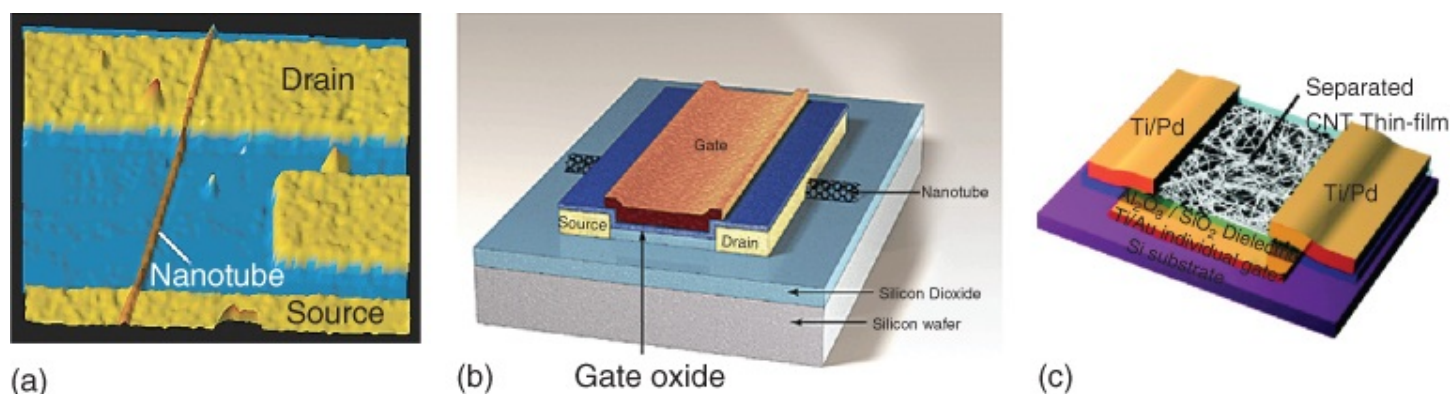


Figure 10.10 Construction of FETs with individual (a and b) and collective (c) nanotubes. (a) AFM image of an FET composed of gold source and drain electrodes and an individual carbon nanotube as a channel. A heavily doped wafer served as a back gate electrode. Alternatively, an individual top gate electrode made of Ti can be employed (b). (a,b) (Reprinted with permission from Ref. [132], Copyright (2002) American Chemical Society.) (c) FET composed of an array of CNTs, with an individual gate Ti/Au electrode, separated with an Al_2O_3/SiO_2 insulating layer and Ti/Pd source and drain electrodes.

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Importantly, films of nonpurified SWCNTs behave as a collective array of randomly oriented semiconducting CNTs, functioning as a unified network in an electronic device ([Figure 10.10c](#)). The performance of such an array depends on the geometry of the device (including the channel length) and the alignment and surface density of the NT. For example, ON/OFF state currents can be optimized [144–146] by manipulating the alignment and density of CNTs, and by adjusting the proportion of semiconducting CNTs in the film from the as-prepared 2 : 1 ratio, ensuring that a channel is long enough (but not bridged by an individual CNT). In terms of molecular devices, CNTs have many possible and demonstrated uses, as outlined below.

Theoretical studies of MJs based on placing a molecule between two CNTs showed that it may be possible to control the conduction properties of the junctions by varying the topology and chirality (zigzag, armchair) of the nanoscale CNT contacts [113, 147, 148]. Several experimental realizations of single and multiple CNT junctions are also available. For

example, the use of CNTs as a top contact [140] and in all-carbon junctions with both contacts made of CNTs [149] has been demonstrated. In the latter case, a single MJ consisting of oligoaniline covalently attached to two CNTs (Figure 10.11a) [114] showed reversible conductance switching through changes in pH (Figure 10.11b and c). Alternatively, CNTs can also be combined with graphene to make interesting electronic devices. When a MJ is formed of graphene and SWCNTs, electronic interactions can result in mutual doping, such that the SWCNT donates electrons to graphene, yielding p-doped CNT and n-doped graphene [150]. This last example highlights the possibility of developing hybrid graphene-CNT devices where the metallic properties of graphene and the semiconducting properties of CNTs are combined.

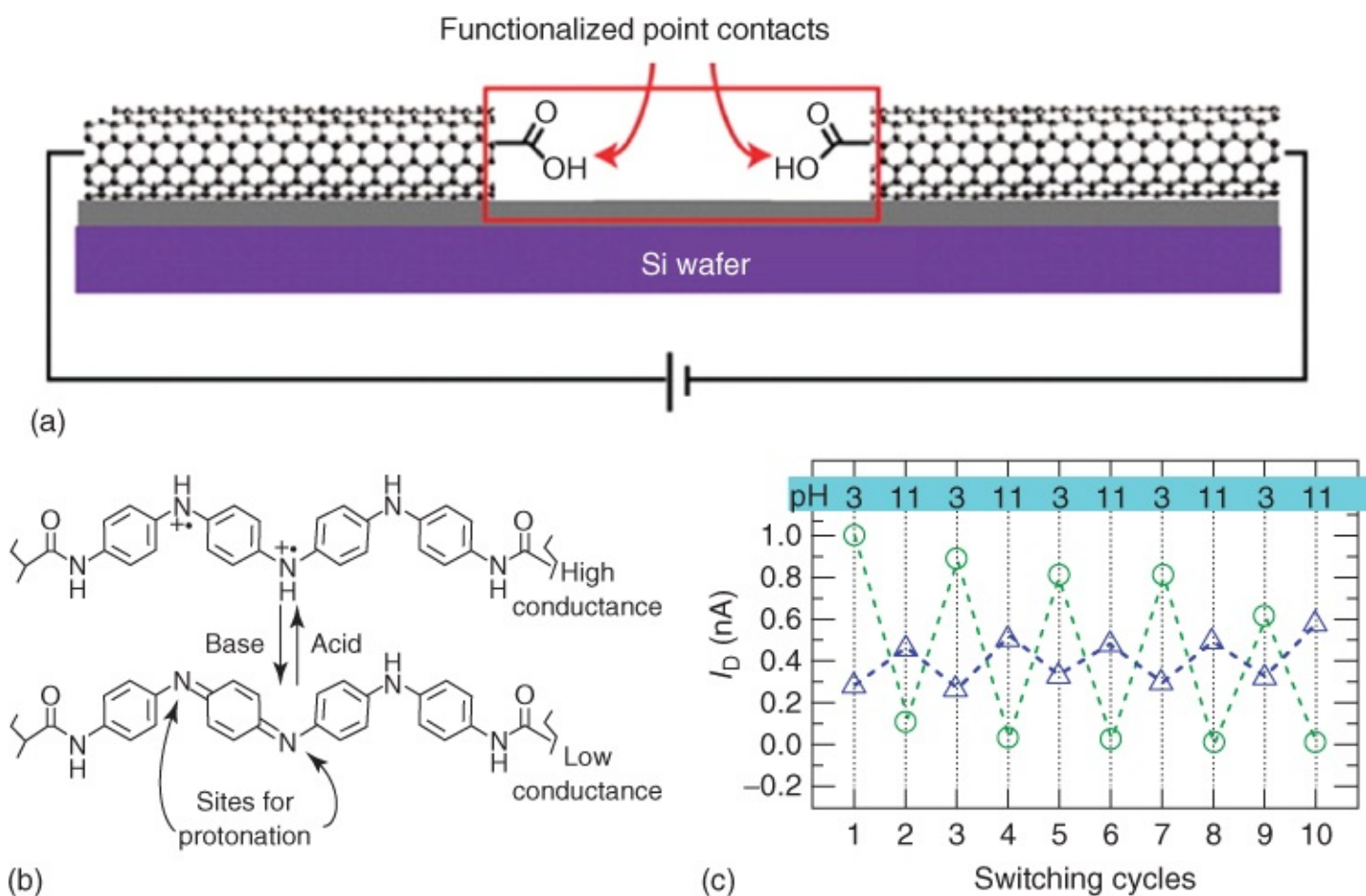


Figure 10.11 (a) A gap in a nanotube is created using an oxygen plasma to yield a space of few nanometers, which is suitable for the formation of a molecular junction. The ends of carbon nanotubes terminated with carboxylic groups and serving as a point of contact for further functionalization. (b) Oligoaniline placed between CNT contacts allows (c) reversible switching of the conductance in the junction by changes in the pH due to protonation/deprotonation.

(Reproduced from Ref. [114]. Copyright AAAS.)

A final illustrative and interesting example of an individual CNT FET device was prepared using a DNA origami method in which two-dimensional structures of nanotubes were obtained [151]. Using noncovalent labeling of CNTs with nucleic acids physisorbed on the side walls of individual SWCNTs, it was possible to arrange them on complementary single-stranded DNA

origami substrate in a desirable manner. Subsequent transfer to a silicon oxide substrate preserved the structure and electronic properties of the semiconducting CNTs, and cross junctions consisting of two crossing SWCNTs were obtained, one of which was serving as a conduction channel and the other functioning as a gate.

10.4 Charge Transport

One of the fundamental issues from the onset of molecular electronics, regardless of the fabrication method or the specific materials used, was the question of the charge transport mechanism in MJs, where the “active” region is a nanoscopic molecular layer. In contrast to the macroelectronic transport mechanisms that dominate device behavior in traditional semiconductor devices or even organic electronics, when the total distance separating two conductors decreases below a particular size, unique charge transport mechanisms become possible in MJs, and efforts to understand the “rules” that dictate the electronic properties of molecular devices have led to much work in this area. This section reviews some of the studies that have been carried out in order to determine what these mechanisms are and what some of these “rules” are – specifically regarding “transitions” between charge transport regimes. We also touch here on some of the models that have been applied to describe charge transport in molecular electronics, and how the way a molecule interacts with a surface leads to some special considerations.

Before discussing the details of any particular charge transport mechanism, it is instructive to consider an energy level diagram that describes the energetic situation of charge carriers in the contacts and molecular region. [Figure 10.12](#) shows an energy level diagram that is often used in molecular electronics; we will discuss some of the pitfalls of using these types of diagrams later. Thus, while this figure does not capture several important aspects of MJs, it does illustrate some fundamental concepts that are critical to understanding possible charge transport mechanisms, and serves as an excellent starting point. As shown, the Fermi level (E_f , which represents the energy at which the probability of finding an electron is $\frac{1}{2}$) of the conductors on either side of the molecular component are offset from the energy of the orbitals of the molecular component (E_{HOMO} and E_{LUMO}). The amount of offset, denoted by ϕ , defines an interfacial injection barrier for holes (ϕ_h , $E_f - E_{\text{HOMO}}$) or electrons (ϕ_e , $E_{\text{LUMO}} - E_f$). It is important to note that energy levels are often given with respect to the vacuum level (E_{vac}), the energy of an electron in vacuum. Here, these energies are treated as positive values for mathematical simplicity. However, the situation is much more complex than this, as different researchers use different conventions. Furthermore, the absolute vacuum level is generally not an experimentally accessible parameter [153], and in most cases, the concept of a local vacuum level immediately above a molecularly modified surface must be introduced to account for the energy level alignment situation (more details about these issues are discussed below) [154].

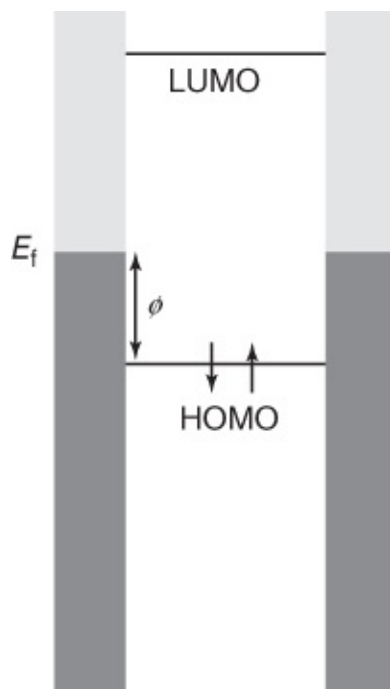


Figure 10.12 A generic energy level diagram of a molecular junction showing the Fermi level of the contacts offset from molecular HOMO and LUMO levels to define interfacial barriers (here, a barrier to hole transport mediated by the HOMO is shown, (ϕ)). Filled states in the conductors are shaded. A parallel situation can be drawn for electron tunneling (using the LUMO).

(Reproduced from Ref. [152].)

In an electrochemical context, the situation is somewhat simplified since the value of E_f for an electrode surface can be controlled (with the aid of a stable reference electrode and an electrical double layer, which serves to screen electrons that reside in the electrode such that the energy level of a molecular orbital in solution is not impacted by the applied potential). Thus, in electrochemical studies, the value of ϕ can be reduced to zero, enabling electrons to be removed from the HOMO orbital of solution-based molecules (oxidation), or to be added to the LUMO orbital (reduction). However, in the context of a solid-state molecular electronic junction, the value of a nonresonant interfacial barrier remains essentially static at different voltages. We discuss some of the reasons in more detail below that it cannot be assumed that their energy levels in a completed junction are set by the properties of the individual, isolated components. In any case, the presence of an interfacial barrier in a solid-state junction is a critical parameter in determining the electron transport properties of the device, regardless of the specific mechanism in operation. Thus, the appearance of [Figure 10.12](#) needs to be taken in the context of the specific mechanism(s) under study.

The various transport mechanisms possible in molecular materials are briefly summarized in [Table 10.1](#). Taking the transport dimension that is of interest here as the middle region of [Figure 10.1](#) and combining this with the energy level diagram in [Figure 10.12](#), we can define a few different limits. First, in the limit of bulk materials, where a molecular material is very thick, and/or the value of ϕ is very large, there will be essentially no charge transport. Instead, such materials can behave as pure dielectric insulators, and devices made from such materials

are capacitive. While leakage currents in capacitive structures can result from impurities or defects in the dielectric, in general, DC conduction is small and might proceed through a series of steps between defect sites. However, even for a dielectric film that does not have any defects, when the distance between the electrodes is made small enough, transport can proceed via quantum mechanical mechanisms. In addition, when the molecular component is redox-active, or can form polarons (i.e., conducting polymers), a wider range of transport mechanisms can take place, including redox-based hopping.

Table 10.1 Thickness, voltage, and temperature dependence for various charge transport mechanisms relevant in molecular electronics

Mechanism	Thickness	Voltage	Temperature	Notes/References
Diffusive	d^{-3}	V^2	N/A ^a	[155]
Ballistic	d^{-2}	$V^{3/2}$	N/A ^a	[156]
Coherent tunneling	$\exp(-bd)$	Linear (low V), exponential (high V)	Weak ^b	[157]
Incoherent tunneling	$\exp(-cd)$	Linear (low V), exponential (high V)	Weak ^b	[158]
Field-emission tunneling	$\exp(-cd)$	$V^2 \exp(-b/V)$	Weak ^b	[159]
Schottky Emission	$\exp(-cd^{1/2})$	$\exp(b/V^{1/2})$	$\exp(-a/T)$	[160]
Poole-Frenkel	$\exp(-cd^{1/2})$	$\exp(b/V^{1/2})$	$\exp(-a/T)$	[161]
Redox exchange (hopping)	d^{-1}	Linear (low V)	Strong, activated	[162]

^a The temperature dependence for these mechanisms is system (material and environment) dependent.

^b The various tunneling mechanisms are not fundamentally dependent on temperature; however, the Fermi function of metallic conductors does depend on temperature, and this can impact the apparent barrier of the system. See [72, 163, 164] and other for a discussion.

We will start by considering a basic nanoscale charge transport mechanism that is common in molecular electronics: quantum mechanical tunneling. Starting with the energy level diagram in [Figure 10.12](#), when there is an interfacial barrier present, charge transport cannot occur via a classical mechanism since the energy of a charge carrier in the bulk conductor(s) does not have an energy that matches a corresponding state in the molecular material (i.e., the energy levels are nonresonant). However, if the thickness of the molecular layer is made small, the wavefunction of a carrier in one contact can overlap with the conduction band of the second contact, leading to a finite probability that a charge carrier can be transported into (i.e., “show up”) in the second conductor. Thus, if we consider the situation of two conductors separated by a vacuum gap over a small enough distance, charge transport can proceed, and current can be measured, even for voltages much lower than ϕ .

Nonresonant tunneling can be identified by several features, including an exponential decay of the tunneling current as the thickness of the molecular layer increases, a very weak temperature dependence (with essentially zero activation over a fairly wide temperature range), and a somewhat distinctive current–voltage curve shape. However, a few features of tunneling should be clarified. First, it is often stated that tunneling current is completely independent of temperature. While the tunnel process itself is not activated, the magnitude of the tunnel current does depend on the Fermi function of the contact, as described in Simmons' elegant derivations [163]. Thus, the current can increase with temperature due to the spreading of carrier energies in the contacts, as originally described by Simmons [163] and later shown to be consistent with the temperature dependence of MJs [72, 164]. Second, while the shape of the current–voltage curve can be used to indicate mechanism, it is often the case the very little or no distinctions can be made between different mechanisms on the basis of curve shape alone. Instead, an approach that can work well when attempting to identify mechanisms is to make various plots that are based on mathematical modeling of a variety of charge transport mechanisms (see [Table 10.1](#)). Finally, tunneling can only proceed over a limited range of molecule thickness ($< \sim 5$ nm) due to the limited extension of wavefunctions through molecular materials (it is even more limited for the case of a vacuum gap, as the dielectric constant of the medium adjacent to the electrode plays a role in how fast the wave function decay occurs [165]). Thus, it is expected that a transition from tunneling to some alternative mechanism, such as field ionization and hopping, will take place at a particular thickness.

To illustrate how charge transport mechanisms can be determined, we will start with a related area of study – electrochemical measurements at chemically modified electrodes. Before molecular electronic devices could be made in a reliable manner, numerous measurements of heterogeneous electron transfer reaction rates at electrodes modified with molecular layers had been carried out. Because carbon electrode materials such as GC and HOPG had long been used in electrochemical studies, these materials were also used in studies of modified interface electrochemistry. In one example, modified GC surfaces displayed rate constants with an exponential fall-off with increasing molecular layer thickness. By analyzing the plot of $\ln k$ versus thickness (d), often called an **attenuation plot**, the value of the slope yields the attenuation constant (β). [Figure 10.13a](#) shows an example of one measured attenuation plot for a series of electrochemical measurements [166], along with a diagram showing how the experiment is carried out [Figure 10.13c](#). In the case of carbon surfaces modified with aromatic molecular layers shown here, the value of β in the electrochemical experiment was measured to be 2.2 nm^{-1} (this value of β is consistent with the use of aromatic molecular layers; see the literature [15, 167, 168] for extensive discussions). The linearity of the attenuation plot is one indication of tunneling as a primary mechanism for charge transport. By studying related systems in MJs, additional experiments are enabled that help elucidate mechanism, as described later.

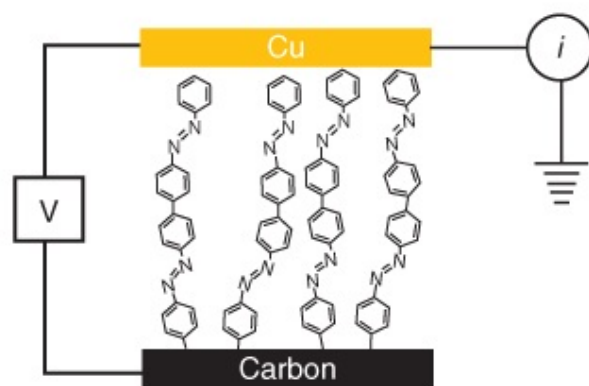
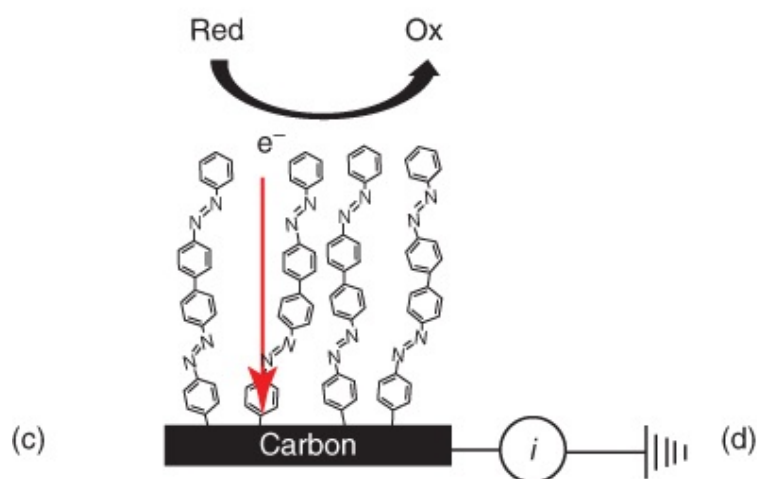
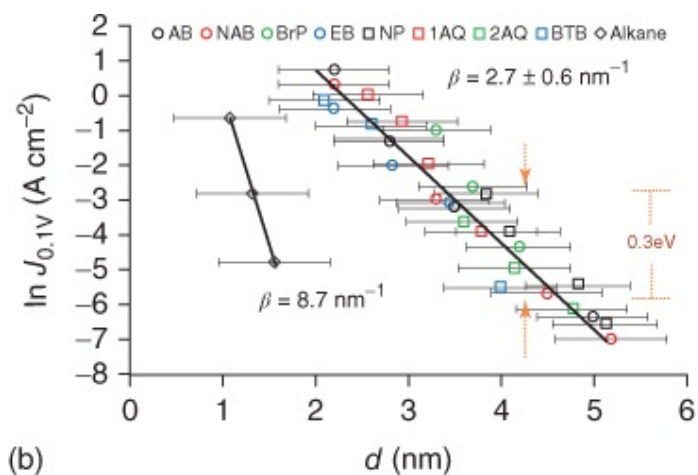
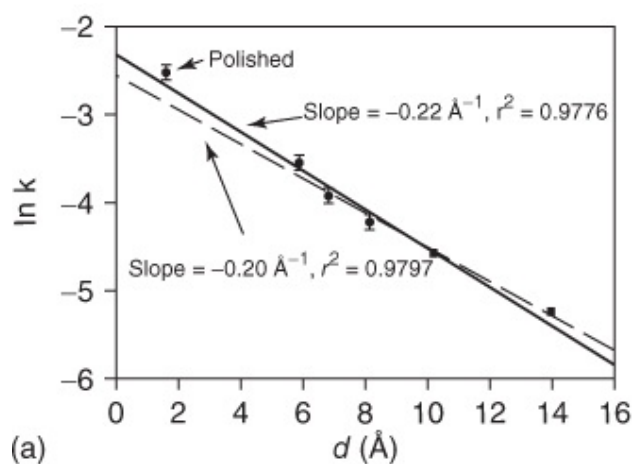


Figure 10.13 (a) Attenuation plot for an electrochemical experiment shown in (c). Here, the $\ln$ of the electrochemical rate constant is plotted against thickness to yield a slope of 0.22 Å^{-1} (or 2.2 nm^{-1}). (b) Attenuation plot for a series of aromatic molecules and an aliphatic species by molecular junctions of different thickness of each (a corresponding diagram of the molecular junction is illustrated in (d)). See original text for structures and abbreviations. Here, the aromatic molecules give similar behavior due to the interactions between the molecular layers and the substrate, as discussed in the text. (a) (Reprinted with permission from Ref. [166]. Copyright (1999) American Chemical Society.) (b), (d)

(Reproduced from Ref. [152].)

As discussed earlier, electrochemical rate constant measurements provide one platform upon which to evaluate charge transport across molecules. However, the electrochemical system contains a lot of complexity, including the presence of ions (i.e., the impact of the electrical double layer cannot be ignored), and relies on electron transfer reactions that may or may not be straightforward to probe the properties of a molecular layer located at the electrode surface. However, fabrication of a MJ by deposition of a top contact onto a molecular layer bonded to carbon avoids all of these complexities, and enables the direct measurement of current flow across molecular layers. Measurement of the junction current density–voltage curve can be carried out, with the advantage that many solid-state charge transport mechanisms have been derived so that the dependence of the current on voltage, thickness, and other

variables can be used as diagnostics (see, e.g., [Table 10.1](#)).

[Figure 10.13b](#) shows an attenuation plot for a series of MJs, along with a diagram that illustrates the general structure that is used in the measurement [Figure 10.13d](#). The data used to construct the attenuation plot in this case are typically a series of J – V curves for different molecular layer thicknesses, here ranging from 2 to 5 nm. Examples of J – V curves can be seen in [Figure 10.5](#), where it can be noted that a strongly nonlinear dependence of J as a function of V results. The shape of the J – V curve provides another hint regarding transport mechanism – the general J – V curve shape in [Figure 10.5](#) is consistent with quantum mechanical tunneling as a transport mechanism. The value of β for eight different aromatic structures, as determined from the data in [Figure 10.13b](#) is 2.7 nm^{-1} , which is similar to the value obtained in the electrochemical experiments outlined earlier and in [Figure 10.13a](#). Several other articles have shown that similar aromatic MJs display temperature dependence and other characteristics that are consistent with tunneling [78, 72, 82]. There are two important issues that arise when considering molecular tunnel junctions: (i) what is the value of the tunneling barrier for charge transport in a molecular tunnel junction, how can it be evaluated, and what controls it and (ii) over what distance can tunneling proceed, and what mechanisms become important at longer distances. We consider these questions below.

10.4.1 Charge Transport Depends on the System

As stated in [Section 10.1](#), the primary goal of molecular electronics was to determine how structural factors determine electronic behavior. Because chemists have long used molecular orbital theory to determine rules related to chemical reactivity and stability, a natural starting point for determining the electronic behavior of molecules in MJs is to use a model as shown in [Figure 10.12](#), and correlate the energy of molecular orbitals with tunneling barrier values. Thus, an initial expectation can be derived by considering that if the molecular HOMO is changed by controlling structure, then the value of the hole tunneling barrier will follow. However, for this to hold true, the system must follow closely to the Schottky–Mott limit, where the molecular layer and the contacts do not interact [152–154, 169, 170]. A second limit, referred to as **the Bardeen limit** [171], exists where the two species interact without impediment, leading to the formation of a dipole barrier (described below), and leading to the situation wherein small changes in the structure of the molecule are not expected to result in a change in the barrier.

In or close to the Bardeen limit (where unimpeded interaction takes places between the molecule and contact, as would be expected in the case when using strongly bonded molecules, such as that described earlier for PPF–molecule–Cu junctions), the impact of small changes in molecular structure or changes in the contact material will not have an impact on the interfacial tunneling barrier, regardless of changes in the molecular HOMO or LUMO energy. The reasons for this have been discussed in detail elsewhere [171], and are summarized here by considering a much simplified example: when considering a series of homologous aromatic molecules like derivatized benzenes, the value of the molecular HOMO energy will be correlated to the properties of the specific functional group(s) used to modify the base benzene ring. Thus, if we compare an unmodified benzene ring to that with an electron-withdrawing

group such as NO₂, the latter will have a HOMO level that is deeper (relative to vacuum) than the underivatized benzene unit, which would correlate to a larger hole tunneling barrier in [Figure 10.12](#). Thus, in a system that follows the Schottky–Mott limit, the electronic behavior of junctions containing these two different molecules could be predicted, where the benzene-containing junction would show higher current than the nitrobenzene-containing junction. However, in the Bardeen limit, the interaction between the molecule and electrode leads to the formation of a dipole barrier.

Staying with the example used above, the deeper HOMO level of the nitrobenzene would act to withdraw electrons from the surface, leading to a partial transfer of charge from the surface to the nitro group until the potential energy stored in the system through the introduction of the NO₂ group is equilibrated, a process that results in a surface dipole that, in an ideal situation, is equal in magnitude to the shift in the molecular HOMO energy. Simplistically, an electron propagating within the conductor will therefore “see” this surface dipole when approaching the surface as an effective lowering or raising of the barrier depending on the direction of the surface dipole (the former for cases where the electron is attracted to the surface, and the latter for cases where it is repelled from the surface). In the case of our example of nitrobenzene, the magnitude of the surface dipole, dictated by the amount of shift in the molecular HOMO, will result in a tunneling barrier, given by the difference between hole tunneling barrier ($E_f - E_{\text{HOMO}}$) and the shift of the local vacuum level induced by the surface dipole, Δ , with the direction in this case indicating a negative value [154]. Thus, the barrier is expected to take a value equal to that of the unmodified benzene case. This leveling effect was recently shown to apply for carbon–molecule–Cu junctions [152], and illustrates that a MJ must be considered as a whole system, and not as a union between isolated components.

While larger structural changes have been observed to change the value of the measured barrier (such as moving from an aromatic molecule to an aliphatic series – see [Figure 10.13b](#)), it has been challenging to obtain unambiguous information regarding the interfacial barrier. For example, fitting of J – V curves to tunneling equations has been used [48, 72] to obtain estimates of the tunneling barrier, but validating these estimates has been difficult. One method for obtaining interfacial barrier heights that has been applied is the use of ultraviolet photoelectron spectroscopy, UPS [67]. This method is similar to the more familiar XPS, but utilizes an ultraviolet source in order to probe valence states. In the case of molecular electronics, UPS is applied to surfaces modified with molecules to determine the photon energy at which an onset of photoemission is observed. Thus, the detection of any valence states in the molecular layer-modified sample that are not present in the unmodified substrate represents occupied states that correlate the molecular HOMO energy, and the energy at which the onset occurs can be related to the hole tunneling barrier [67, 152].

While UPS provides a valuable characterization, it does not enable the measurement of a barrier in a completed MJ. In order to provide such information, a method termed internal photoemission (IPE), which had been used to measure tunneling barriers in oxide tunnel junctions [172–174], has been proposed for use in determining molecular tunnel junction barriers for intact MJs [175]. In this case, absorption of light by the molecule must be carefully

considered, but assuming that issue can be addressed, IPE shows promise for providing critical information about interfacial energy barriers in molecular electronics.

10.4.2 Mechanism Transitions

Finally, various measurements have been carried out to determine what the range of thickness over which tunneling can operate, and what mechanisms take over beyond this thickness. As described in detail elsewhere [63, 64, 68, 176], beyond a thickness of 5–7 nm, the electronic behavior displays features of hopping, represented by thermal activation and a decrease in the value of β . However, an alternative, nonactivated transport mechanism was recently noted for thicknesses between 7 and 20 nm, with thicker films showing evidence of hopping at higher temperatures and lower voltages [177]. In this latter case, a Poole–Frenkel type of mechanism involving ionization of “trap” sites (which may be particular structures of the molecular layer, or even the molecular HOMOs themselves), followed by ballistic transport into the second contact was proposed. While it is clear that each particular system may show different characteristics, transition regions, and mechanisms, it is clear that beyond ~ 7 nm, there are many possible transport mechanisms that may be different from bulk transport mechanisms, and which may prove to be fundamentally different for molecular devices (relative to say, organic electronics) [15]. It is also important to note that several transport mechanisms can occur simultaneously, or at least different mechanisms can be dominant for slightly different conditions [178] (e.g., applied voltage, thickness, or temperature), such that it can be difficult to disentangle behavior, and as many variables as possible should be tested when studying charge transport mechanisms [68].

10.5 Conclusions and Prospects

Molecular electronics was born out of a desire to utilize the rich variety of electronic structures that can be prepared through chemical methods. While some techniques for placing well-defined molecular layers onto conductors have been devised, much care must be taken to verify structure and ensure that the molecular layer remains intact [79]. One solution to some of these issues makes use of the properties of carbon materials and the covalent bonding of molecules to carbon through diazonium chemistry. The use of these techniques enables reproducible and robust MJs to be prepared, enabling systematic studies and potential commercial applications. As of the writing of this chapter, we are working toward the first commercial use of molecular electronics in the area of audio processing – a feat that could not even be attempted without the excellent stability of the electronic behavior as presented in [Section 10.2](#).

In addition to traditional carbon materials, novel allotropes of carbon have unique electronic properties that may be exploited to provide some advantages to electronic device fabrication. These may serve as electrode materials in molecular electronics, or may form the basis of extant electronic devices with specifications that exceed those of existing electronics. In any case, carbon electrodes provide a rich area of study for molecular electronic systems.

The examples described in this chapter highlight the possibilities to make high yield, stable, and reproducible molecular electronics components using the unique advantages of carbon electrodes. Carbon-based molecular electronics has features, including the covalent C–C bond between the molecule and electrode, which yields high temperature and chemical stability; strong electronic coupling between molecular layer and electrode; protection from mechanical damage/penetration when eC or graphene is used as the top contact; ballistic conduction of m-CNTs contacts; and pathways to include a large number of molecular structures that can be placed between carbon electrodes using covalent and noncovalent chemistry.

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Chapter 11

Carbon Paste Electrodes

Ivan Švancara and Kurt Kalcher

11.1 Introduction: Carbon Paste Electrodes – The State of the Art

Half a decade ago, carbon paste had celebrated a notable jubilee: 50 years of existence and extraordinarily wide applicability across the areas of electrochemistry and electroanalysis [1–3]. Herein, it can be remembered that carbon paste – that is, a thick mixture of a carbonaceous moiety with a suitable (usually liquid) binder – had originally been discovered as a certain by-product, coming from unsuccessful experimentation with carbon powder-based suspension intended to accomplish an electrode with renewable surface for anodic oxidations [2, 3].

Since then, carbon paste-based electrodes, sensors, and detectors became soon quite common in both electrochemical and electroanalytical measurements, representing apparently the most popular electrode material that could be made in the laboratory without special equipment. This is well documented by nearly 3000 scientific articles, which is an estimate coming from the real literature search made recently and concerning the reports on carbon paste in all its forms and imaginable applications published within the periods 1958–2010 [3–5] and 2011–2013 [6].

In this chapter with rather narrower focus and limited scope, it is impossible to refer to all the facts surveyed, commented, and discussed via standard way of citing the corresponding original literature, but, for these purposes, it has been decided to select the hitherto existing reviews and related articles, together with a representative collection of original articles of principal importance and often also with priority in a topic or area within the field.

Concerning the reviews, one can classify the respective contributions in the following way:

1. The very first review by the inventor himself [7] plus his legendary monograph referring to carbon paste-based electrodes in several subsections, as well as inside many other pages throughout the text (see [2] and the corresponding pagination given)
2. Generally orientated and typically extensive articles commonly accessible from international high impact journals [8–13]
3. Special compilations of the review type [14–23] focused on a particular area within electrochemistry or applied electroanalysis
4. Reviews published in regional or even local periodicals [24–32]; however, always abstracted by a majority of world's scientific databases and thus available upon request
5. Book chapters; again, either general and covering the field as a whole [4] or specially

tailored compilations [33–35]

6. A textbook released a couple of years ago [5] and – despite the above-emphasized half-century history and tremendous literature archives – being the first monograph of its kind, covering the field on 666 pages from which a good third is a set of tables surveying more than 1000 electroanalytical applications and the rest then the literature gathering nearly 3300 references in the full-citation format.

11.2 Carbon Paste as the Electrode Material

11.2.1 Basic Considerations and Classification

In the most general approximation, carbon paste is a **compact mixture of a carbonaceous material with a suitable binder**, representing the two-component basic formula [1–5, 10–13]. These simple configurations with typical paste (soft, plastic) consistency are also occasionally termed as **binary carbon pastes** [5, 16], whereas their classification as *unmodified carbon pastes* is a more complex task, requiring further commentary (see later).

From a traditional point of view, the first major component is **carbon powder**, namely highly pure *graphite* with particle size typically in micrometers or tens of micrometers [5, 7–9, 36, 37]. However, the spectrum of carbonaceous materials applicable in carbon paste mixtures is much wider (see, e.g., [4, 5, 7, 9, 11, 35]), comprising (i) *natural graphite* (specially crushed and chemically purified), (ii) various forms of *synthetic graphite* (produced by controlled pyrolysis of macromolecular resins), (iii) *new forms of carbon* (e.g., nanostructures and graphene), (iv) *special forms of carbon* (microspheres, carbon template, porous foam, electrospun microfibers), and (v) *natural and synthetic diamond* (both undoped but somehow conducting due to the presence of trace impurities). Finally, one should quote also (vi) *crude forms of carbon* (anthracite, black coal, activated charcoal, as well as soot); all having been reported to be tested in some preliminary experiments (see [5, 11, 35] and references therein).

Similarly, the second constituent of carbon paste mixtures is the **pasting liquid** [4, 5, 7, 9, 11, 38–41] – also a solute [42] or even mulling agent [43] – when the traditional binders are (i) *mineral/paraffin oils*, predominantly *Nujol*® (a commercially marketed mixture of liquid aliphatic hydrocarbons used as the solvent in spectroscopy) or (ii) *silicone fluids* such as macromolecular alkyl siloxanes. Besides these two principal agents, the field has seen during the lengthy decades many other substances that can be divided into the following categories: (iii) *liquid and fluid hydrocarbons*, (iv) *their halogen derivatives*, and (v) some *organic ethers and esters*. All these substances share two key features – (i) chemical inertness and (ii) immiscibility with water and aqueous solutions (for other ones, see below). Thus, it is worth noting that there is quite a wide family of binary carbon pastes containing pasting liquids with completely opposite properties – the so-called **electroactive carbon pastes** [4, 5, 9, 15] whose carbon particles are bound by means of a few droplets of *highly concentrated solutions* of mineral acids or alkaline hydroxides. Finally, another seemingly principal property of a binder – (iii) its liquid state – is not the case of carbon paste mixtures whose binding agent is being intentionally solidified, giving rise to heterogeneous materials of the

carbon composite type, also known as **solid-like** or **pseudo-carbon pastes** [4, 5, 11, 43–46].

On the special occasion of being invited to contribute to this textbook, we have prepared a brand new survey of two-component carbon paste mixtures gathered in [Table 11.1](#). Its two parts present for the first time in such a concise way about 20 different types of carbon paste mixtures that have ever been employed – or, at least, examined – in electrochemical and electroanalytical measurements, when the respective data complete the list of all possible constituents introduced earlier.

Table 11.1 Survey of (unmodified) carbon pastes and the corresponding carbon paste electrodes

Type of CP (^a)	Carbonaceous moiety (^b) (specification)	Usually mixed with (^{c,d})	Classification of respective carbon paste (^d) (specification)	Abbreviation(s) of the respective electrode (^{d,e})
Part A: Types and variants distinguished according to the carbonaceous constituent				
trad. (unm.)	Carbon powder (^f) (spectroscopic graphite, sC)	PO, SO, AH, XH, OE, IL, sf-, sm-B	Classical, common, standard carbon paste	CPE (syn.: GPE, for others, see part B)
–"–	carbon powder (^f) (natural graphite (ch.p.), nC)	MO, SO, AH, OE, IL	Common, standard carbon paste	–"–
spec.	Glassy carbon powder (carbon microspheres, GC (glassy carbon))	–"–	Glassy carbon paste electrode	GCPE
–"–	Colloidal graphite, cG	PO	–"– (CP made of colloidal graphite)	(cGPE)
–"–	Acetylene black, AB	–"–	Acetylene black paste electrode	ABPE (syn.: ABE)
–"–	Carbon black, CB	PO, SO	–"– (CP made of carbon black)	(CBPE)
exp.	Soot (crude) (^g)	SO	–"– (CP made of soot)	–"–
–"–	Coal (natural (ch.p.)) (^g)	PO, SO	–"– (CP made of coal)	–"–
–"–	Activated charcoal	PO	–"– (made of "USP"-powder)	USPE
spec.	Diamond powder (^{f,h}) (natural (ch.p.), nD)	–"–	Diamond paste electrode (type "n")	(_n)DPE
spec.	Diamond powder (^{f,h})	–"–	Diamond paste electrode	(_s)DPE

	(synthetic (ch.p.), sD)		(type “s”)	
new	Carbon nanopowder, nC ^(f)	–”–	Carbon paste microelectrode	(n)CP μ E
–”–	Carbon (nano)fibers, Cfi ^(f)	–”–	Carbon fiber paste electrode	(CfiPE)
–”–	Carbon nanotubes ^(f) (SW-CNTs, MW-CNTs)	PO, SO, OE, IL, sf-, sm-B	Carbon nanotube paste electrode carbon nanotube-modified CPE carbon nanotube ionic liquid el.	CNTPE, CNT-CPE, CNTILE ⁽ⁱ⁾
–”–	Carbon nanohorns, CNH	PO	Carbon nanohorn paste electrode	(CNHPE)
–”–	Fullerene (e.g., C ₆₀)	–”–	Fullerene (C ₆₀) paste electrode	(C ₆₀ PE)
–”–	Porous carbon (foam)	–”–	Porous carbon paste electrode	(pCPE)
–”–	Graphene, graphene oxide	–”–	Graphene (oxide) paste electrode	G(r)PE, G(r)OPE
–”–	Ordered mesoporous carbon, OMC	–”–	Ordered mesoporous carbon paste electrode	OMCPE
Part B: Types and variants distinguished according to the binding agent chosen				
trad. (unm.)	Paraffin/mineral spectroscopic oil (l) (e.g.,: Nujol®, Uvasol®) ^(f)	C, GC, AB, D, CNTs, CFi, nC	Classical, common, standard carbon paste	CPE(s) (syn.: C/MO, C/PO, C/Nj, C/Uv)
–”–	Silicone oil/grease/rubber ($M_{(r)} = 500\text{--}50\,000$) (l,f,s)	C, GC, CNTs	Common, standard carbon paste	–”– (syn.: C/SO, C/SG)
–”–	Aliphatic hydrocarbon [C ₈ H ₁₈ –C ₂₀ H ₄₂] (l,f,s)	C	–”–	CPE
–”–	Aromatic hydrocarbon [C ₆ H ₆ (l), phen. (sf)]	–”–	–”– (for “phen”: solid-like, heterogeneous CP)	–”– (syn.: s-CPE, h-CPE)
–”–	Halogenated hydrocarbon [CCl ₄ , CHBr ₃ , C ₁₂ H ₉ Br] (l,f)	–”–	Electroactive carbon paste, reactive carbon paste	C(R)PE
spec.	Organic ester, organic ether (TCP (tricresyl phosphate), DOP (dioctyl phthalate), DINP, DPE) (l)	C, GC, CNTs	Electroactive, chemically active carbon paste	–”– (syn.: OE-CPE TCP-CPE or C/TCP)

–"–	Vegetable oil (l) (castor oil)	C	–"–	CPE
–"–	Industrial oil (l) (Vaseline, lubricating oil) ^(g)	–"–	–"–	–"–
–"–	Two-component binder (mineral oil + glycerol) (l)	–"–	CP with mixed binder	–"–
–"–	Strong electrolyte, highly conc. aqueous solution (l) (e.g., 2 M H ₂ SO ₄ , 1 M KOH)	–"–	Electroactive carbon paste, CP with electrolytic binder	CPEE(s)
new	Polycationic electrolyte (e.g.,: el.-gen. polypyrrole) (f)	–"–	Binder paste(s)	BPE(s)
–"–	(r-t.) ionic liquid (l,f,sf) (e.g.,: BPPF6 and BMIMPF6)	C, GC, CNTs	Carbon ionic liquid electrode	CILE(s)
sl-CP	e.g., polypropylene, ceresin and paraffin waxes, Kel-F® ^(l) synthetic and natural rubbers ^(m)	C, CNTs	Solid-like carbon paste electrode	(s-CPE)
ps-CP	e.g., polypyrrole + dispersed polystyrene ⁽ⁿ⁾ , polyethylene	C	Pseudo-carbon paste electrode	(ps-CPE)

Symbols and abbreviations: ^(a) according to a general classification, ^(b) carbon, graphite, and related material (with abbreviations used in Part B), ^(c) for abbreviations in this column, see Part B, ^(d) typical and/or prevailing terminology, ^(e) abbreviations in parentheses used solely by the authors; ^(f) further characterization in the text, ^(g) in preliminary experiments only; ^(h) undoped, that is, chemically pure, ⁽ⁱ⁾ three different configurations (for details, see text); ^(j) with specified consistency: (l), pasting liquid; (f), fluid; (sf), solidified binder; (s), (sm), solid (-like matrix); ^(k) for abbreviations in this column, see Part A, ^(l) poly(chlorotrifluoroethylene); ^(m) chloroprene and butadiene products; and ⁽ⁿ⁾ porous structure formed after dissolving PS. – "–, *ibid.* (as above);/, or, also; B, binder/pasting liquid/mulling agent; el., electrode; new CP-mixtures made from new forms of carbon; B, binder; ch.p., chemically purified, CP, carbon paste; conc., concentrated; e.g., for example; el.-gen., electrogenerated; exp., experimental; (f), fluid (very thick liquid); (l), liquid; M(r), relative molecular weight; new, new mixtures (from 2000s to 2010s); phen, phenanthrene; ps-, pseudo-; r-t., room temperature; (s), solid or solid-like, (sf), solidified, solidifying binder; spec., special; syn., synonym (less or even scarcely used); trad., traditional, unmodified; and TCP, tricresyl phosphate.

As can be seen, the table does not list any chemically or biologically modified variant, which is in accordance with the consensus that, at present, the most common classification of carbon pastes and, eventually, the respective electrodes, sensors, or detectors distinguish between **(i) unmodified** and **(ii) modified carbon paste mixtures**. Retrospectively, this fundamental divide is logical and, in detail, being of interest in our two review articles from the early 1990s [8, 9], where the carbon paste had been discussed as maybe the most flexible electrode material with respect to the diversity and effectiveness of its physical, chemical, and biological

modifications. It can be estimated that if [Table 11.1](#) would have an analog compiled for the hitherto known modified carbon pastes and all related combinations, it could gather surely several hundreds of types of different mixtures. Also, this documents the potential of modified carbon pastes and a need to cover the area in a separate section; herein, in the second part of this chapter.

When going back to the classification of carbon pastes and the respective electrodes, the term **carbon paste electrode (CPE)** means a setup of *carbon paste fixed in a suitable body*, which may be of quite different construction (see, e.g., [1, 2, 26, 46–49] and many others in [5]); nevertheless, only exceptionally being reflected in naming of the electrode itself. Historically, some of the first definitions had classified CPEs as a *special type of solid carbon electrode* [2, 7], later taxonomy preferred the classification *among heterogeneous carbon electrodes* [4, 8, 9]. Finally, there were also other ways to classify or sort carbon pastes and the corresponding CPEs; for instance, (i) the electrodes made of mixtures from spectroscopic graphite and mineral (or even silicone) oils are commonly quoted as *classical CPEs* [5, 10, 11], (ii) notable nuances in the final consistency gave rise to a differentiation between (a) *dry* and (b) *wet carbon pastes* [7, 9, 10, 50]; or (iii) according to the demand whether or not the electrode of choice needs additional maintenance – then, one can distinguish between (i) *untreated* [51, 52] and (ii) *pretreated* CPE [53, 54].

The resultant behavior of each carbon paste and the corresponding CPE(s) always reflects the type and quality of carbonaceous and binding moieties used. With certain simplification, it can be stated that mechanical, physicochemical, and electrochemical properties of CPEs are close to those exhibited by related solid electrodes from graphite and similar materials; nevertheless, because of the presence of the pasting liquid, there are also some specific characteristics or even completely unique features [4, 5, 7, 9, 16, 40, 43, 51–60].

11.2.2 Characterization of Two Main Carbon Paste Components

11.2.2.1 Carbonaceous Moiety

Carbon Material in Traditional Mixtures

Any carbon powder chosen for the preparation of carbon paste or its possible alternative with the *primary function* to act as the sensor proper should obey three *principal criteria*: (i) particles in the micrometric scale and with uniform distribution, (ii) high chemical purity, and (iii) controlled adsorption capabilities.

Together with other typical features such as (iv) high chemical inertness and (v) excellent conductivity, this is fulfilled by the majority of so-far used synthetic graphite available under various trademarks (*Acheson, UCP, GP, SMMS, RW-B*, etc., see [2, 7, 9] and references therein) or supplied as “*graphite powder for spectroscopy*” by renowned international chemical companies, such as Merck, Sigma-Aldrich, Fluka, or Riedel-de-Haën.

Highly suitable is also the specially refined natural product from South Bohemian graphite mines; in Middle Europe marketed as a gear lubricant “CR” [35]. For common carbon paste

mixtures, both synthetic and natural graphite are dominant in the final formulas, whereas other related materials listed in [Table 11.1](#) are used only scarcely.

New Forms of Carbon

As almost everywhere in science, grandiose commencement and a remarkable progress in the use of newly synthesized allotropic forms of carbon on the verge of the new millennium has principally changed electrochemistry with carbon pastes and, in fact, kicked off a completely new era in the field [5, 11, 12].

More specifically, it has been shown that the original and already somehow exploited concept of carbon pastes with graphitic carbon can be revived by using qualitatively new materials that give rise to heterogeneous mixtures offering more or less comparable electrochemical behavior and similar applications [5, 11, 12].

Moreover, due to some specific features of new forms of carbon, the spectrum of applications of traditional CPEs could be further extended. (This trend was prophesized already in the mid-1990s [28, 29] in association with the rapid progress in the use of *carbon inks* for manufacturing of screen-printed carbon electrodes, SPCEs (see Chapter 12), that had for a certain time been considered as a derivative or successor of the CPEs themselves; see also note in [5].)

On the other hand, these newly acquired properties – primarily, distinct catalytic capabilities of most of these materials [5, 20, 35] – evoke an undeniable dilemma. Are such binary composites still unmodified carbon pastes if the respective carbon moiety behaves like typical modifier? One possible answer came with the quickly advancing research, when many propagators of these new configurations had started to prefer ternary mixtures with the new carbon added as the third constituent [5, 11]. Then, the resultant formulas contain two carbonaceous materials: (i) the ordinary graphite, representing the electrode proper and (ii) the new one acting as a modifier. And if one adopts this distribution of both possible functions, the two-component mixtures containing new carbon can be classified as a *novel type of (binary) carbon paste with carbonaceous moiety in the dual role* (it means, without further specification by the term **unmodified**).

Perhaps the first representative of a new carbon is (i) **glassy carbon (GC) powder**, tested first in the mid-1990s [37] and forming fine microspheres that may also have a specially treated surface. The second newly appearing carbonaceous material was (ii) **diamond powder** [61] applicable in both natural and synthetic forms as chemically pure, that is, undoped. (Reportedly – see [5] and a discussion inside – a certain conductivity of this otherwise totally insulating material was ensured by the presence of unspecified trace impurities.)

Next was (iii) **fullerene** (namely: soccer ball-shaped “C-60”), added as the third component into the common silicone oil-based carbon paste, together with (iv) **carbon nanohorns (CNHs)** and (v) **carbon nanotubes (CNTs)**, forming altogether three major classes of *molecular carbon nanomaterials*. And whereas the “C + C₆₀/SO” and “CNH/PO” mixtures exist so far in their prototypes (see [62, 63]), the use of *single-walled* (SW) or *multiwalled*

(MW) CNTs – both with nearly equal preference – in the paste configuration had meant a real boom in the field [5, 11, 20, 59], quickly establishing an extra group of numerous subtypes or variants (with three basic combinations shown in [Table 11.1](#), reported for the first time in [64–66]) and positioning these mixtures at the top of popularity among new carbon pastes as shown again below – in a special paragraph, surveying typical properties of all basic types of CNT-based paste electrodes.

The table lists also some *other new materials* examined with more or lesser success in mixtures with typical binders. Up until now, this is the case of (vi) “**carbon nanoparticles**” (with diameter of about 30 nm [67]), (vii) “**ordered mesoporous carbon**” (OMC [68]), (viii) “**carbon (nano)fibers**” (CFis; obtainable either with the aid of chemical vapor deposition or, more effectively, by electrospinning [69]), and (ix) “**graphene**” (Gr [70]); the last one being known as the ***two-dimensional (2D) graphite*** that can be prepared, similarly as carbon nanofibers, in an ordinary laboratory and, eventually, also printed as *three-dimensional (3D) graphene*.

11.2.2.2 Binder/Pasting Liquid Moiety

In all carbon pastes, the main function of a binder is **mechanical connection** of the individual particles of the carbonaceous material chosen. Besides this, however, the binding component codetermines some typical properties of carbon pastes and therefore, its selection is always important. (In context with this advice, it is interesting to mention the authors' own experience that numerous users of CPEs are rather conservative, preferring to use the same binders even in situations, when a good alternate choice would have resulted in notable improvement of the overall performance in some particular experiments.)

Classical Pasting Liquids

Characteristic parameters of these binders, that is, (i) **paraffin** and (ii) **silicone oils**, are as follows: (a) chemical inertness and electroinactivity, (b) *high viscosity*, (c) *low volatility*, (d) *minimal solubility in water* and aqueous solutions, and in some special applications also (e) *resistivity toward common organic solvents*.

Yet another advantage of paraffin and silicone oils is their (f) *low toxicity*, which is now – in the era of ecologically oriented sciences – almost a principal requirement that has practically eliminated the third group of classical pasting liquids – (iii) *halogenated hydrocarbons*; by the way, the very first CP-binders in the pioneering years of the field [1, 7].

Other Binders

As mentioned earlier, there are a number of other substances whose use can be characterized as occasional or, in some particular cases, also entirely intentional. Concerning fairly **liquid binders**, one can choose among (iv) *aliphatic and cyclic hydrocarbons* [7, 38–41] and (v) *organic ethers and esters* (e.g., tricresyl phosphate and dioctyl phthalate [57]). Thicker but still **fluid binders** can be some (vi) *aromatic hydrocarbons* [39, 51, 52] and (vii) *highly viscous polysiloxanes* (such as silicone fluids with $M_{(r)} > 20\ 000$ [56]). Their advantage is a

more compact carbon paste mixture, but its manual preparation may be less comfortable [16].

Almost or totally **solid binders** are being represented by (ix) *heavier hydrocarbons* [41, 46] (x) *silicone greases and rubbers* [42, 44], (xi) *ceresin and paraffin waxes* (e.g., [45]), or – finally – some (xii) *special polymers* such as waxy polypropylene (PP) or *Kel-F®* oil ([43]; for chemical composition, see [Table 11.1](#) and the respective specification in the legend).

Regarding these solid-like composite mixtures, the initial paste-like consistency is being utilized for more effective homogenization of both main components (and, eventually, of yet another constituent like modifier or stabilizer), where the binding moiety is a melted form or a monomer and the proper solidification is then the result of the subsequent cooling down or a cold polymerization/vulcanization, respectively [44–46].

New Types of Binders

In the late 1990s, there was another attempt to abandon the concept of traditional pasting liquids by introducing the so-called “binder paste” (BP [71]), based on (i) *polycationic electrolytes*, such as polypyrrole. Even though this type of CPE did not find other adaptors, it can be regarded as a predecessor of (ii) **(room temperature) ionic liquids, (RT)ILs**, representing another important group of substances in the recent period of the field, having spawned a brand new type of carbon pastes [72, 73] with the respective electrodes termed *carbon ionic liquid electrodes (CILEs* [60, 74]). Concerning the individual ionic liquids (ILs) tested in carbon paste configurations, about 20 different (RT)ILs have already been examined in the CILE configuration during the first years of their use [5].

Specifically, preferred are the ion associates with quaternary cations of the alkyl/heterocyclic structure, such as [*n*-alkyl-pyridium]⁺, [*N*-butyl-*N*-methyl-pyrrolidinium]⁺, and [R,R'-imidazolium]⁺; anionic moieties being hexafluorophosphate, PF₆[−], tetrafluoroborate, BF₄[−], and less often bis(trifluoromethylsulfonyl)imide, NTf₂, ethylsulfate, Et–O–SO₃[−], or bromide, Br[−]. When using the established abbreviation system for these compounds, the most often chosen ILs in CIL(E) configurations are (i) **BPyPF6** and (ii) **BMImPF6**, where “M” is “methyl”; “B” *n*-butyl; “Py” pyridinium; and “Im” imidazolium.

Through the late 2000s, carbon IL pastes had been attracting almost equal attention as CNT-based configurations, giving rise to the second, very successful family of new carbon pastes and the corresponding electrodes. A symbolic connection of these two categories is a composite of the “CNT-IL” type [66], yielding a *CNT IL electrode*, in which both traditional carbon paste constituents have been replaced by the new alternate materials. This, together with compatibility with other new carbons, such as nanofibers [68] or graphene [70], documents clearly the vitality of ILs as the new binders and deserves a more detailed concern within the following section.

11.2.3 Physicochemical and Electrochemical Characterization of Carbon Pastes and the Respective Carbon Paste Electrodes

11.2.3.1 A Few Notes to the Preparation of Common Carbon Paste Mixtures

The carbonaceous moiety and a binder are mutually mixed in a ratio typically based on empirical experience [5, 7, 9, 16, 38–41, 50–52, 58]; the optimal **carbon-to-pasting liquid ratio** for traditional carbon pastes usually being **1.0 g : 0.5 ml**. The two main components are usually hand-mixed in a mortar using a pestle with sufficient pressure, and advisably in two or three consecutive steps, when the formed mass is ripped off from the vessel wall to the bottom and homogenized again. Typically, soft and noncompact pastes have to be *packed/filled into a suitable body*, which can be accomplished by using (i) *glass tubes* and *plastic rods* with a cavity [1, 2, 5, 46] in the simplest arrangements, via specially designed (ii) *piston-driven holders* [5, 16, 26, 47], up to (iii) *unique constructions* with special geometry [48] or continuously renewable surface [49]; in all cases being devised with appropriate electric contact.

11.2.3.2 Typical Properties and Behavior of Traditional Carbon Paste (Electrode)

In the previous text, attention was paid to a feature of carbon pastes as a **unique electrode material** of *heterogeneous nature*, reflecting both main carbon paste constituents in rather specific behavior that differs from mixture to mixture, depending not only on the type and quality of the respective component, but also on the way in which the respective electrode or sensor is constructed and employed in practical experiments. Typical properties and some specific features of traditional carbon paste mixtures are as follows:

1. Structure and microstructural morphology: The physical constitution of common carbon pastes can be described as a *solid dispersion* (of the individual graphite particles in liquid binder). Practically from the very beginning of carbon pastes in electrochemistry, the microscopic structure of their surface was of continuing interest (see, e.g., [7, 36, 37] and other references therein [5]).

In our laboratories, SE(T)M (scanning electron (tunneling) microscopy) imaging of various carbon pastes – either as such or in the role of electrode substrates for other objects of interest – is an inevitable tool of research within experimentation with CPEs, starting from the mid-1990s [37], continuing through the 2000s [75] up until now ([35] with references therein). In brief, the typical microstructure of the carbon paste surface is an *unconsolidated array of carbon particles linked together with pasting liquid* whose thin film covers intimately almost every piece of graphite in the mixture.

[Figure 11.1](#) depicts a series of SEM micrographs, inspired by some previous studies [35, 37, 58–60], but mostly acquired especially for this presentation. The respective gallery features the surface microstructure of two related carbon powder materials (see images “a” and “b” on top) and the surface morphology of four different carbon paste mixtures (“c–f”) made of these carbon powders and three different pasting liquids: (i) highly viscous silicone fluid, as the representative of traditional oils [2–4, 7–11], (ii) tricresyl phosphate, as an organic ester and special pasting liquid [57], and (iii) an IL of the BMImPF6 type [74].

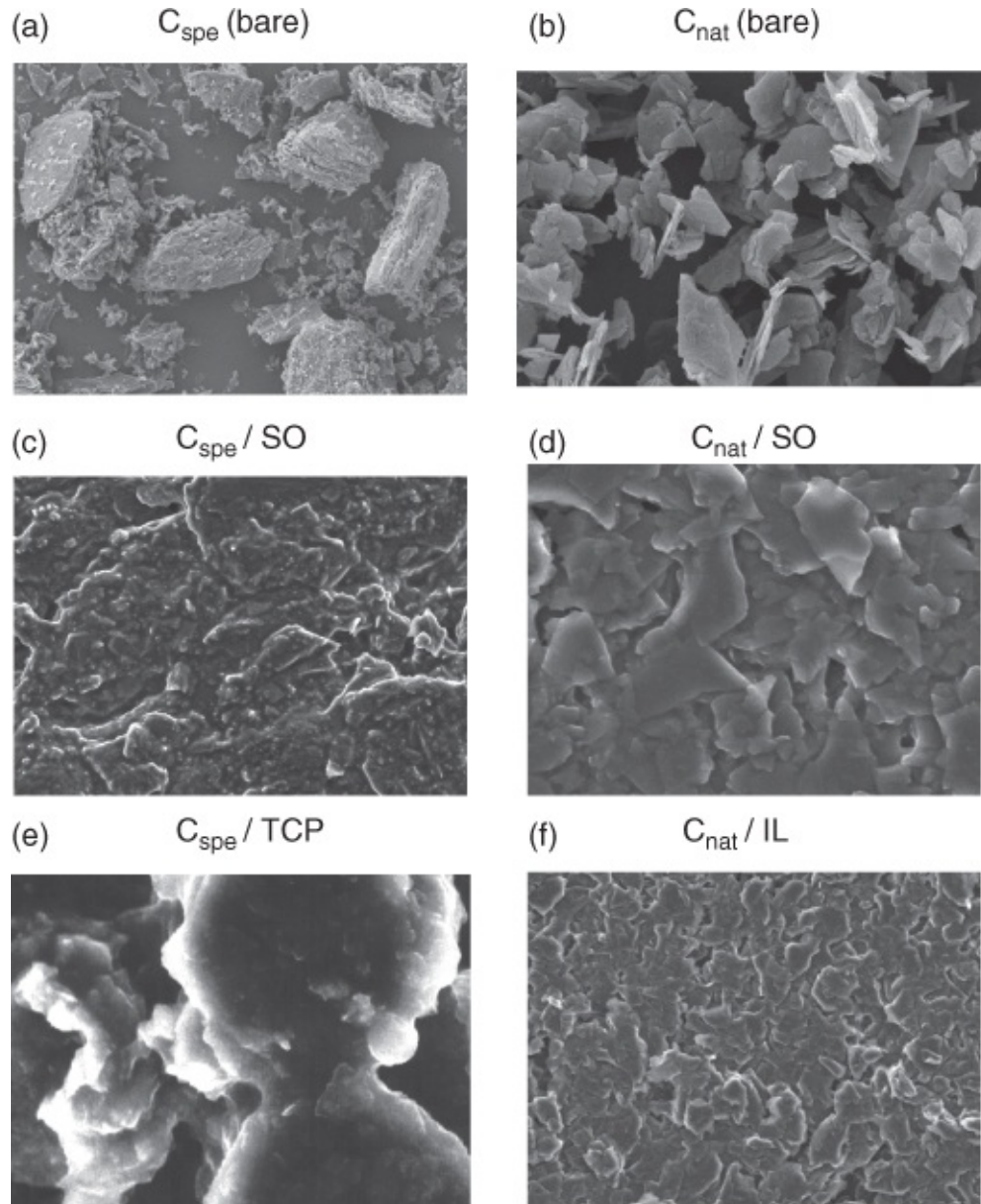


Figure 11.1 Typical microstructures of two related graphite powders and four different carbon paste mixtures made of these carbons. Abbreviations and symbols used: C_{spe} , spectroscopic (or spectral) graphite; C_{nat} , refined natural graphite; SO, silicone oil; TCP, tricresyl phosphate; and IL, ionic liquid (BMImPF6); the individual carbon pastes denoted accordingly above the respective images (a–f). Experimental conditions: scanning electron microscopy, magnification: 1 : 1000 (a–e); scale: the actual size of photos corresponds really to (25 μm $\times$ 35 μm), 1 : 500 (f; $s = 50 \mu\text{m}$). Hitherto unpublished photos from authors' archives, except “(e)” being the alternate view of an image published in [37]. For other specification and details, see [35, 37, 58, 60].

As can be seen, the overall morphology of three of the CP-mixtures resembles that of native graphite, copying their characteristic *corn flake-like texture* but viewing also the *glaze of a very thin film* of pasting liquid spread over groups or individually distributed solid particles. In contrast to these mixtures, the morphology of the remaining one, “ C_{spe} /TCP (tricresyl phosphate),” is completely different revealing more or less *isolated*

clusters with a markedly thicker layer of the binder. (Here, it should be added that this unusual structure had been attributed to be the reason for rather specific behavior of the corresponding CPE(s) [37, 57].)

2. Soft/plastic consistency: As the term *carbon paste* suggests, a mixture of powdered graphite with liquid binder is a *paste-like, incompact mass* whose consistency has been related – for many, amusingly – to a peanut butter by the inventor himself [1, 2, 7]. This characterization fits quite well for classical mixtures from mineral oils [2, 4, 38–40, 50–52], whereas carbon pastes made of silicone fluids are markedly thicker (up to nearly solid state [16, 58]) and, in contrast to the typically matte appearance of most C/MO (mineral oil) configurations, the C/SO and C/SG formulas may exhibit a fine metallic luster [5, 16]. Needless to say that the resultant thickness of carbon pastes depends on the mutual ratio of both main components.

3. Minimal Ohmic resistance/excellent conductivity: Quite surprisingly, even intimately coated graphite particles in the CP(E) configurations exhibit a very low ohmic resistance; often, *in tens of ohms* [5, 39, 40, 50–52, 55] and, in special cases, even below 10 Ω [5, 16].

(The phenomenon of negligible resistance of two-component mixtures in which one is an almost insulating substance had been of interest as early as in the mid-1960s [55]; nevertheless, its likely interpretation came very recently [58–60] with the aid of “*Theory of the Closest Arrangement (of Solid Particles)*” adopted from crystallography and helping to define also the optimal carbon-to-pasting liquid ratio for traditional CP-mixtures [58], as well as some new types of carbon pastes [59, 60].)

4. Chemical and electrochemical inactivity: Similar to solid carbons used in electrode configurations, carbon pastes keep the property of chemical and electrochemical inactivity and can be characterized as a fine material with high resistance against unwanted transformations during electrode processes [2, 5, 35, 50]. However, polarization at extreme potentials may cause substantial changes at the carbon electrode surface as shown later, in point (8-f).

5. Instability in organic solvents: Because of a certain miscibility of carbon paste binders with organic solvents, such as methanol, acetonitrile, or dimethyl formamide, the corresponding mixtures are vulnerable in measurements, requiring the use of these solvents. The result is usually a spontaneous *disintegration of the paste* [2, 5, 21, 56] recognizable first by largely increasing background currents and, subsequently, in an uncontrollable signal with frequent random oscillations [16, 56]. To some extent, the *stability of carbon pastes* can be improved by (i) choosing more *resistant pasting liquids* (e.g., some silicone fluids [56]), (ii) adding a highly *lipophilic stabilizer* [76] or – rather unexpectedly – (iii) with special carbonaceous material, namely glassy carbon microspheres with thermally pretreated surface [5, 77].

6. Aging of handmade mixtures: This phenomenon is more pronounced for carbon paste mixtures containing more volatile binders, such as organic esters or halogenated

hydrocarbons [5, 16, 57], whereas for common mineral- or silicone oil-based CPEs, it can remain unnoticed.

7. Hydrophobic character of carbon pastes: Consensually, it is the most typical feature of traditional carbon pastes due to the lipophilic nature of both paraffin and silicone oils forming the electrode material [2, 4, 5, 8–10, 35, 36, 50]. The principal consequence of such hydrophobicity is *moderated reaction kinetics* at carbon paste-based electrodes [2, 5, 7, 50], reflected in more or less *irreversible behavior* of numerous inorganic redox pairs and organic systems involved in chemical transformations at the electrode surface. (The reason for such behavior is mainly a repelling effect between the hydrophobic surface of CPEs and typically hydrophilic character of the compounds participating in the individual reactions [2, 5, 7–10, 16, 50].)

8. Diverse interactions at the carbon paste surface and in the carbon paste bulk: The nature of carbon as one of the most flexible electrode materials [2, 4, 35] together with the presence of a specifically behaving liquid binder gave, individually or together, rise to an unprecedented variety of principles and processes that characterize measurements with CPEs. They involve typical redox transformations, physicochemical interactions of nonelectrolytic origin, as well as some synergistic mechanisms and multistep pathways. The individual possibilities and limitations featured by common CPEs can be highlighted in this way:

a. Electrolytic processes. In experiments associated with electron transfer and current flow – that is, in *faradic transformations* – the processes measured involve the change of oxidation state of a species or, more generally, of the actual chemical state of a compound; both by oxidation and reduction in the voltammetric, amperometric, or coulometric mode. Concerning *polarization characteristics*, traditional carbon pastes and the respective CPEs can be polarized within a potential range of about -1.0 and $+1.0$ V versus SCE, when considering common supporting media and measurements out of extreme pH [5, 16, 38–40, 51, 52]. (In special cases, the operational potential range can be markedly extended; for instance, the anodic limit up to $+1.8$ V versus SCE at a CPE with specially impregnated graphite [78] or cathodic limit down to -2.0 V versus Ag/AgCl by using an atypical binder containing trace impurities that inhibit the hydrogen evolution in the buffered solution [79].)

Otherwise, faradic measurements with CPEs are typified for fairly low background currents between 0 and $+1.0$ V versus SCE, whereas polarization in the negative direction suffers from the reduction of oxygen contained in the paste, enhancing the background between about -0.3 and -0.6 V, but still enabling cathodic reductions to be observed as responses superposed upon a deformed baseline [2, 7]. (Also, this phenomenon varies from paste to paste, where some mixtures may exhibit only minimal evidence of unwanted reduction of O_2 [79].)

b. Nonelectrolytic processes. Carbon paste-based electrodes and sensors are also widely applicable in electrochemical measurements that are not connected with current flow. Herein, one can mention classical potentiometry [21, 80] or computer-controlled

stripping (chrono)potentiometry [81]; both with indication of the actual equilibrium potential.

c. Adsorption onto the carbon paste surface. Reportedly, pasting liquid in carbon paste mixtures may enhance the resultant adsorptibility [25]; nevertheless, such interactions seem to be more complex and represent a combination with electrostatic effects, extraction, and ion-pairing affinity rather than adsorption alone [4, 5, 8–13, 35].

d. Extraction (penetration) into the carbon paste bulk. One of the most valuable features of carbon pastes and the respective electrodes [4, 7–12, 16, 41, 42, 82] that can comparably be accomplished solely at electrodes with additional membrane(s) [5, 80] is extraction into the carbon paste bulk. Having utilized the controlled distribution of a substance between two liquid phases – that is, the carbon paste binder and the sample solution – there is a simple relation: the more lipophilic the liquid binder or the substance distributed, the more pronounced the penetration into the carbon paste interior and the more effective extraction [4, 16, 42]. Moreover, this process can be coupled with ion-pairing when the ion associates formed are particularly willing extractants [5, 8, 9].

e. Ion-exchange and ion-pair formation. Both terms symbolize electrostatic interactions between the charged counterions [4, 5] and, in fact, may give rise to the same reaction pathway [33]. In these cases, carbon pastes usually represent electrode substrates, into which the ion-pairing agent is being added as a modifier, this is discussed in more detail below, in a special section.

f. Forced electrocatalysis. Mediated reaction processes at CPEs are quite frequent in practical electroanalysis in order to enhance the sensitivity during the proper detection [83]. However, they are a domain of chemically and/or biologically modified electrodes, containing catalyst(s) as the additional constituent [4, 5, 8–11]. For binary mixtures, one can assume a specific form of catalysis associated with suppression of (the aforementioned) irreversible behavior at the hydrophobic carbon paste surface [5, 16, 21, 50]. This operation is feasible by (i) electrolysis at extreme potentials [53], (ii) chemical pretreatment with aggressive oxidants [50], or (iii) erosion effect of some surfactants [54]; all three alternatives leading to a partial removal of the lipophilic binder from the surface, its hydrophilization, and the resultant improvement of reaction kinetics at CPEs [16, 50, 81].

11.2.3.3 Specific Features of New Types of Two-Component Carbon Pastes

In accordance with the above-presented classification and due to the wide diversity of new carbon pastes, solely binary mixtures of the GCP(E), CNTP(E), CIL(E), and CNT-IL(E) configurations are considered in the following paragraphs (1–5).

1. Consistency and overall appearance: Compared to rather predictable forms of classical pastes, the “new generation” mixtures exhibit a wider variety in their final consistency; for example, homogenization of glassy carbon microspheres with paraffin oil

yields a “muddy” and almost fluidic mass, but also a very compact composite difficult to handle; depending on the surface pretreatment of these special carbons [37, 58]. Quite dense and notably deep black are also mixtures from Nujol® and CNTs [59], whereas similarly tough masses of spectral graphite with (RT)ILs of the RR’ImPF₆ type have somewhat lighter tone with a waxy surface [60].

2. Microstructure and compact character: In accordance with the rather atypical consistencies of binary mixtures from new carbons or ILs, the corresponding microstructures also differ considerably from those manifested by traditional carbon pastes as depicted in [Figure 11.1](#). Identically assembled [Figure 11.2](#) illustrates well these differences, representing “GC/MO” (b) “CNT/MO” (c), “CNT/SO” (d), “C_{spe}/IL” (e), and “CNT/IL” (f) mixtures together with the original morphology of both carbonaceous materials being imaged before their mixing with the corresponding binders.

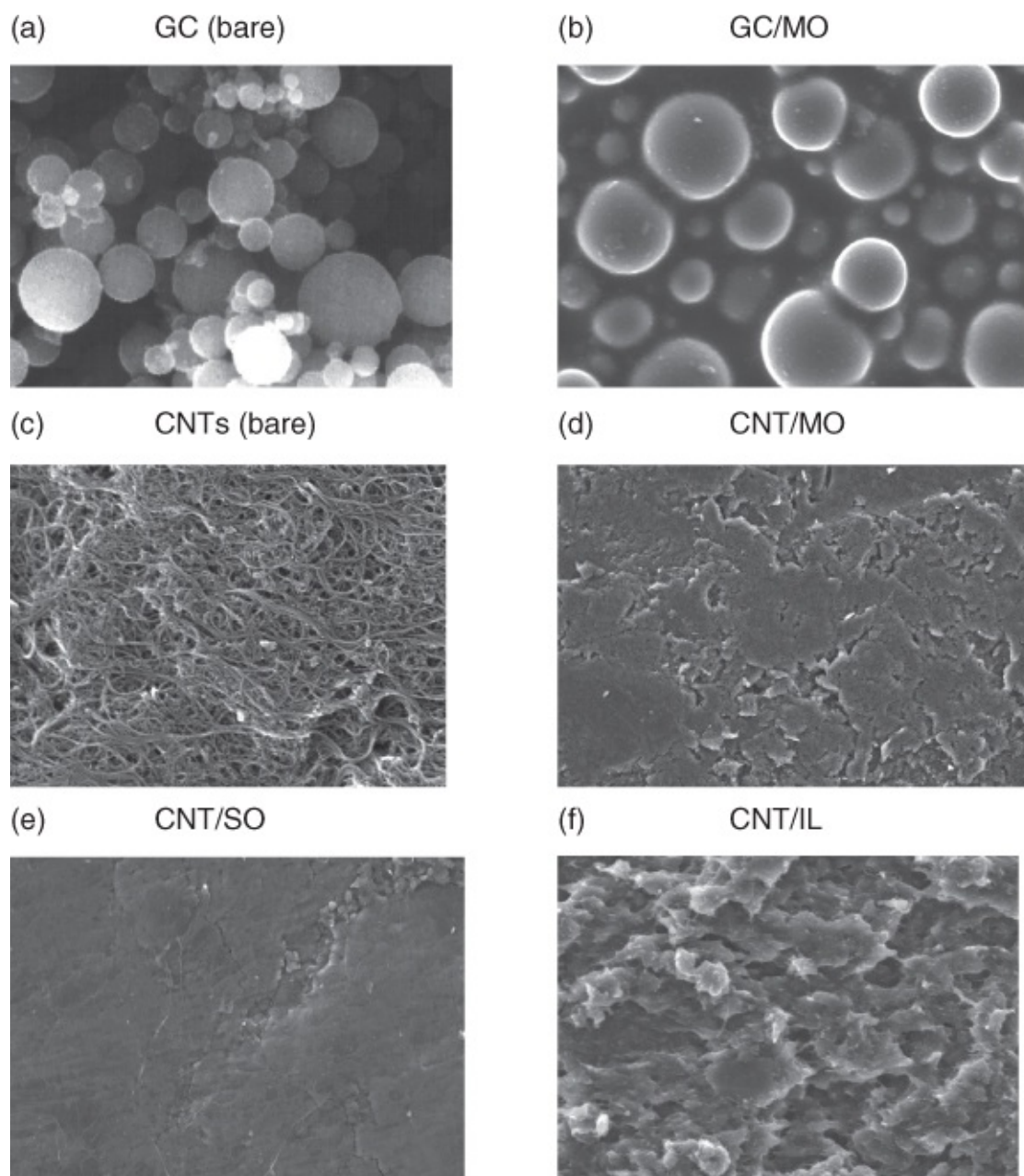


Figure 11.2 Typical microstructures of two new forms of carbon and four carbon paste mixtures, made of traditional oil binders and ionic liquid. Abbreviations and symbols used: C_{spe} , spectroscopic graphite powder; GC, glassy carbon powder (“Sigradur®”); CNTs, carbon nanotubes (“SW-” type); MO, mineral oil; SO, silicone oil (highly viscous type); and IL, ionic liquid (BMImPF₆); the individual carbon paste mixtures denoted accordingly above the respective images (a–f). Experimental conditions: scanning electron microscopy, magnification: 1 : 1000, scale as in [Figure 11.1](#). Hitherto unpublished photos from authors' archives, except “(a)” being the alternate view of an image published in [37]. For other specification and details, see [35, 37, 58–60].

It is interesting to note that the surface appearance of the “GC/MO” resembles again the original pattern of irregularly spread clusters of globules – while a very thin film of the binding oil is visible, too – whereas the highly homogeneous surface of “CNT/MO” and especially “CNT/SO” does not resemble the characteristic morphology of the SW-CNTs.

Regarding the remaining “CNT/IL” paste, its surface is again rather similar to traditional pastes, and also to the “C_{nat}/IL” mixture featured in the previous set in [Figure 11.1](#).

3. Ohmic resistance and capacitance: The individual types of GCP-, CNTP (carbon nanotube paste)-, and CIL-mixtures exhibit *slightly higher resistance* compared to C/MO and C/SO formulations – typically within 50–200 Ω [59, 60] – despite their more compact texture and the fact that some sources quote opposite trend in pastes with ILs [72, 73]. However, the presence of ILs amplifies *the capacitance signal*, which can be beneficial but problematic at the same time [66].

4. Electrochemical characteristics: A very typical sign of all these new carbon pastes is their substantially *enhanced signal-to-noise ratio*; that is, higher analytical signal with the increased background in parallel. In the case of GC-powder and SW- or MW-CNTs, the reason has been attributed to their specific surface geometry [5, 59, 64, 65], whereas the interpretation of the same effect by ILs is not so consensual [5].

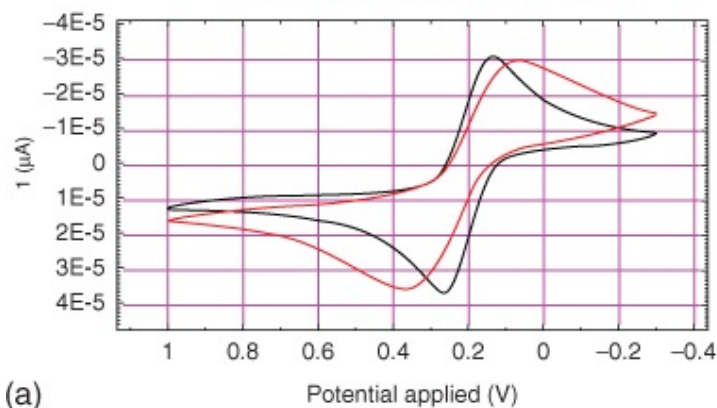
A further observable nuance in behavior of these mixtures in comparison with traditional pastes is *lowered irreversibility* for some redox systems, which is in direct relation with the most distinctive property of all new carbon pastes – their (electro)catalytic capabilities (see below). Finally, in the CIL(E) arrangement, yet another benefit is enhanced chemical activity toward some ion-exchange and ion-pairing reactions [59, 72, 73].

5. (Electro)catalytic properties: Undoubtedly, *the most frequently emphasized feature* of CNT- and IL-based carbon pastes is their **(self)catalytic character** [5, 11, 12, 20, 64, 65], allowing the detection of numerous electrode reactions with markedly higher efficiency and, in some respect, substituting the function of specially added chemical modifier(s). Concerning the interpretation of (electro)catalysis by CNTs, it has been related with the electronic properties of carbon tubules, facilitating the mediation of electron transfer-based reactions [65]. Catalysis at ILs requires more explanations; one of them being a support of synergistic reactions via stabilization of some intermediate products and radicals by the respective IL(s); see [74] and references therein.

11.2.4 Survey of Applications of Two-Component and Unmodified Carbon Pastes

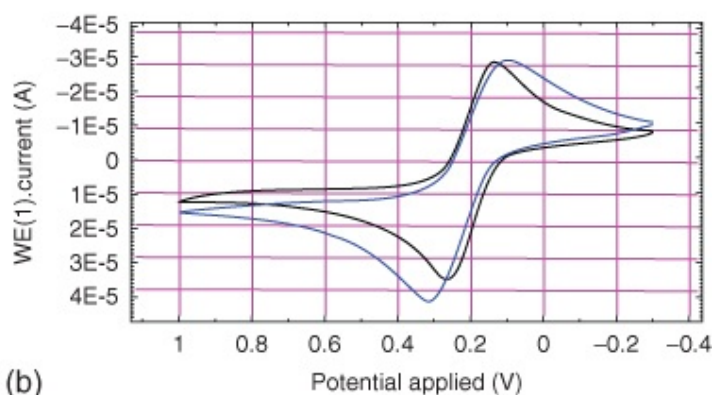
In the following lists, facts, and numbers, the possibilities and limitations of both traditional and new carbon pastes are summarized the applications of the corresponding electrodes, sensors, detectors, and the remaining devices; all being based on data from [3–5, 7, 9–11, 84, 85]. Some features surveyed earlier and interesting applications of CPEs in electrochemical investigation or practical electroanalysis are also illustrated in [Figure 11.3](#), together with further specification in the legend.

Moderated kinetics at C/MO



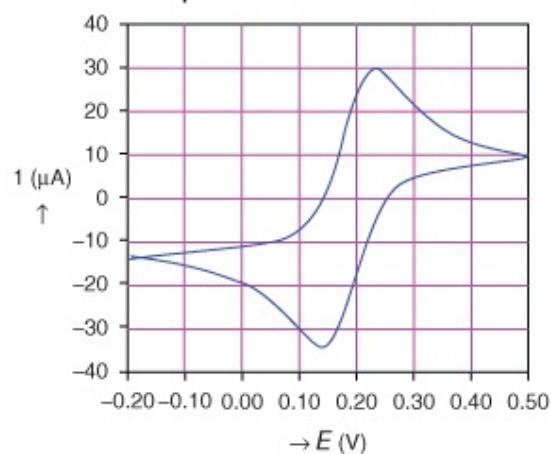
(a)

Moderated kinetics at C/SO



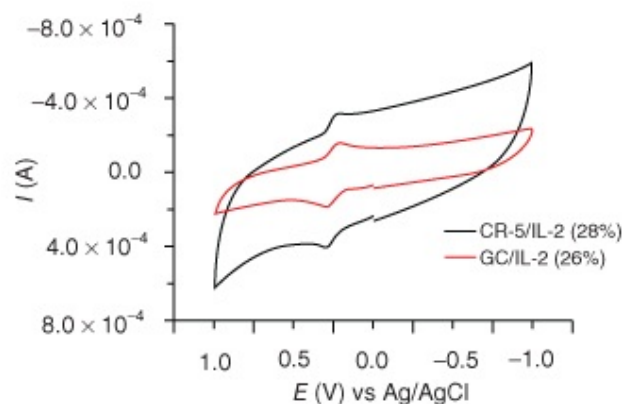
(b)

Improved kinetics at CNTPE



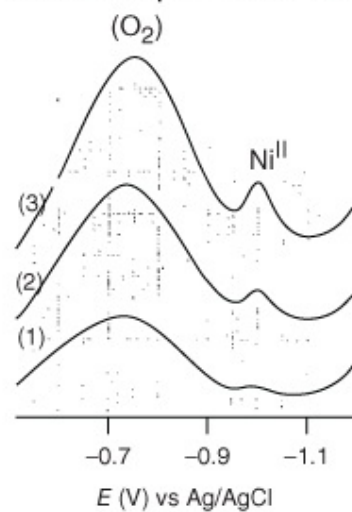
(c)

Enhanced currents at CILE



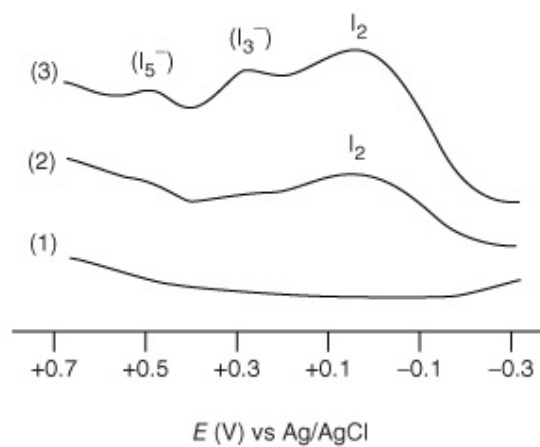
(d)

Cathodic desorption at MF-CPE



(e)

Re-extractive release at C/TCP



(f)

Figure 11.3 Typical features and behavior of traditional or new carbon pastes and the respective electrodes in current flow measurements. (a–d) Cyclic voltammetry of $[\text{Fe}(\text{CN})_6]^{3/4-}$ in 0.1 M KCl, $c(\text{Fe}) = 5 \text{ mM}$, lighter line, GCE (a,b) or GC-IL (c,d), hitherto unpublished records; (e) Adsorptive stripping voltammetry of Ni^{II} at the low parts per billion level in 0.1 M ammonia buffer containing $10 \mu\text{M}$ DMG (dimethyl glyoxime) + Hg^{II} . Legend: curve (1) blank, (2) $c(\text{Ni}^{\text{II}}) = 5 \text{ ppb}$, and (3) $c(\text{Ni}^{\text{II}}) = 10 \text{ ppb}$. Note: symbol O_2 denotes the reductive response of oxygen entrapped in the paste; an outtake from [84]; (f) Cathodic reduction of iodine at higher concentrations accumulated in 0.1 M HCl via ion-pairing and extraction. Legend: curve (1) blank, (2) $c(\text{I}^-) = 0.01 \text{ mM}$, and (3) $c(\text{I}^-) = 0.1 \text{ mM}$; an outtake from [85]. Abbreviations and symbols used: **C**, spectral or natural graphite powder; **MO**, mineral oil; **SO**, silicone oil; **TCP**, tricresyl phosphate; **MF-**, mercury film; **CNTPE**, carbon nanotube paste electrode (“SW-CNTs/SO” type); and **CILE**, carbon ionic liquid electrode (“ $\text{C}_{\text{nat}}/\text{BMImPF}_6$ ” type).

Even though only two-component and unmodified mixtures are of interest here – a similar summary for chemically and biologically modified variants is given later – such a selection shows carbon pastes as a versatile class of material with a myriad of applications and achievements in electrochemistry, electroanalysis, and related areas.

Types of carbon pastes and their popularity (expressed via a percentage estimated from the total appearance in the respective scientific articles): C/Nj and C/MO – 70%; C/SO – 10%; CNTPE – 10%; CILE – 5%; GCP – 4%; others – 1%.

Constructions of CPEs (compared again by the approximate percentage and comprising more frequent configurations and size variants): Common (macro)CPEs – 90%; CP-detectors in flowing streams – 5%; mini- and micro-CPEs – 1%; CP-arrays (ultra-microelectrodes, electronic noses, and tongues) – 1%; rotated disk- and dual arrangements – 1%; planar configurations – 1%; others – 1%.

Measuring and instrumental techniques in combination with CPEs: (i) *Abundant use*: voltammetry (CV (cyclic voltammetry), LSV (linear scan voltammetry), ACV (alternating current voltammetry), DPV, SWV) and amperometry (hydrodynamic, detection in FIA, and HPLC); (ii) *frequent use*: electrochemical stripping analysis (DP(A,AdS)V: differential pulse (anodic, adsorptive) stripping voltammetry), AdSV (adsorptive stripping voltammetry), PSA, and CCSA (constant current stripping analysis)) and equilibrium potentiometry (direct, titrations); and (iii) *occasional use*: chronoamperometry, (chrono)coulometry, detection in electrophoresis, detection of electrochemiluminescence, microscopic observations (by SEM, STM, AFM (atomic force microscopy)); *scarce/rare use*: conductometry, electrochemical impedance spectroscopy, and spectroelectrochemistry. *Note*: This survey has also considered special arrangements where the native carbon pastes had served as the *substrate for modification “in situ”* [4, 5, 10, 11, 16], or acted as *support for metallic film(s)*; that is, configurations of the following types: MF-CPE (MF = mercury film) [74], AuF-CPE [86], BiF-CPE (bismuth film-plated carbon paste electrode) [87], SbF-CPE [88], and PbF-CPE [89].

Major areas of electrochemical measurements with CPEs (in order of appearance): (I) Electrode reaction pathways and mechanisms of electroactive organic compounds (see also [Figure 11.3a–d](#)); (II) Pharmaceutical and clinical analysis; (III) Solid-phase voltammetry with electroactive CPEs; (IV) Analysis of (i) inorganic ions and molecules, (ii) organic compounds + environmental pollutants, and (iii) analysis of biologically important compounds (BICs); (V) Voltammetry “*in vivo*” (also known as **brain electrochemistry**).

Electroanalysis with carbon paste-based electrodes, sensors, and detectors in surveys of chemical species and compounds determined in model and real samples; after [3–5, 85]:

Inorganic species. Heavy metals: Zn^{II} , Pb^{II} , Cd^{II} , Tl^{I} , Sn^{II} , In^{III} , Sb^{III} , Bi^{III} , and Cu^{II} ; noble metals: Ag^{I} , Au^{III} , Hg^{II} , and Pt^{IV} ; iron metals: Fe^{III} , Co^{II} , Ni^{II} (see also [Figure 11.3e](#)); other metals and metalloids: Mn^{II} , Be^{II} , Mg^{II} , Ca^{II} , Al^{III} , and As^{III} . Nonmetal species and molecules: H^+ (pH), N_2H_5^+ ; Cl^- , I^- (see also [Figure 11.3f](#)), $[\text{Fe}(\text{CN})_6]^{3-/4-}$; H_2O_2 , O_2 , NO_x , SO_2 , and Cl_2 .

Inorganic compounds analyzed in the solid state (selected examples, according to [4, 5, 10, 14]): The elements: Fe, Zn, As, Si; oxides and related structures: FeO , Fe_2O_3 , Fe_3O_4 , $\text{FeO}(\text{OH})$; CoO , Co_3O_4 ; NiO ; Cu_2O , CuO ; PbO , PbO_2 , Pb_3O_4 ; $\text{MnO}(\text{OH})$, MnO_2 ; V_2O_3 , V_2O_5 ; MoO_3 . Sulfides and sulfidic ores: FeAsS , ZnS , PbS , CuS , CuFeS_2 , HgS , As_2S_3 , As_4S_4 ; selenides and tellurides: PbSe , CuSe , Ag_2Se , Ag_2Te , AuTe_2 ; others: Fe_3C , Ni_2Al_3 , $\text{Y}_A\text{Ba}_B\text{Cu}_C\text{O}_D$.

Pharmaceuticals and drugs (given as typical groups according to medical classification; see also [18, 19]): analgetics, antibiotics, antimycotics, antiseptics, anti-inflammatory drugs, antipyretics, antiasthmatics, bronchospasmolytics, antirheumatics, diuretics, cardiotonics, antihypertensive agents, antineoplastics, hypnotics, antidepressants, anxiolytics, antipsychotics, antitumor, and antileukemic drugs, selected narcotics plus their legal substitutes.

Organic compounds, including typical environmental pollutants (survey of typical groups and derivatives): amines^{1,2}, nitro compounds^{1,2}, nitroso compounds², hydrazines², hydroxylamines², azo compounds², phenol and substituted phenols³, aldehydes^{1,2}, quinones, carboxylic acids^{1,2}, halogen derivatives^{1,2}, thiols¹ and organosulfur compounds⁴, organophosphorus and organoarsenic compounds⁴, synthetic dyes and pigments, surfactants, plastic materials, and other industrial polymers.

Legend: (1) aliphatic, (2) aromatic, (3) substituted, and (4) selected derivatives.

Biologically important/active compounds, including some macromolecules and biological polymers (survey of typical groups): selected amino acids; purines (mainly uric acid) and pyrimidines; glucose, some disaccharides and polysaccharides; vitamins (B6, ascorbic acid, tocopherols), enzymes and coenzymes (NAD^+ , NADH); neurotransmitters (dopamine and catechols); and nucleic acids (DNA/RNA).

Note: The lists above comprise data from reports on carbon pastes in several possible forms: bare COES as such, native mixture(s) or CPEs in the role of electrode substrates, and *in situ* modified CPEs. The other types, that is, bulk- and covalently modified pastes and composites or enzyme- and tissue-containing mixtures are surveyed later.

Minor applications of carbon pastes in scientific laboratories and industry (selected examples taken from [4, 5, 85]): (i) conductive substrate in solar batteries; (ii) sample bed and sensing site of scanning devices in microscopic techniques; (iii) renewable electrodes for industrial electrolysis; (iv) electronic noses and tongues; electrode substrate for (v) generation of the electropolymerized films; and (vi) characterization of newly synthesized catalysts.

11.2.5 Current Trends in Using Carbon Pastes and Some Future Prospects

Before stepping into the realm of chemically and biologically modified carbon pastes with all their hitherto existing configurations and variants, it is useful to overview the latest advances with carbon pastes as such, which can be accomplished with the aid of a properly selected collection of newly appearing articles [90–100].

Such a brief summary can be started with a brand new review [90] that pursues the recent achievements with new carbon pastes made of alternate carbons and binders; for example, *graphite powder-based solgel electrodes*. Another review article then reflects the still stronger position of solid-state analysis; herein, in a new renaissance of solid-phase electrochemistry with *electroactive carbon paste electrodes, CPEEs* [91].

For everyone who has watched the field from the very beginning, it is a pleasure to see a couple of reports from Japanese authors [91, 92], concerning the successful revival of the already introduced *dropping carbon electrode, DCE* [1–3]. Reportedly, the new prototype was wholly functional for its primary purpose – polarographic oxidations in aqueous solutions – when a three-component mixture of graphite, dioctyl phthalate, and triiodomethane acted as the true DCE with a periodically renewable surface.

Of continuing interest are the new forms of carbon; for example, nanoparticles [93] and, in particular, graphene [94–97] whose momentary popularity is reminiscent of the boom of CNTs in the late 2000s. Similarly, also *ILs, ILs*, still attract considerable attention, and even now some authors come with completely new theoretical models [98]. Besides these main areas, other applications can be traced, such as the case of a new CP-array proposed as the scanning tip(s) for electrochemical microscopy [99].

Finally, there are continuing investigations of new alternate carbonaceous materials in binary CP-configurations, here one typical example is a contribution by our research group where we examined the powdered forms of some abrasives from the carbide family, namely TiC, WC, and B₄C [100]. It can be concluded that inspiration for these so-far inconclusive experiments came again from Adams, the inventor of CPEs, and his interesting results with a solid *boron*

carbide electrode, BCE, including its envisaged but never realized B₄C-paste analog (see [2] and references therein).

11.3 Modified Carbon Paste Electrodes

11.3.1 Modification – How to Alter the Electrode Properties in an Intentional Way

Plain electrode surfaces for electrochemical analyses, as well as for syntheses, offer only limited applicability due to the fact that their main purpose is to act as an electron source or sink depending upon the depolarizer present in the bulk solution. Concomitant adsorption, which is rather frequent with CPEs particularly with organic aromatic compounds, is – apart from stripping analysis – rather unwanted because it complicates handling and practical setups due to a necessary control of the exposure time of the electrode to the solution.

A convenient alternative to improve such drawbacks and limitations is *modification of the electrode surface*, which means that either chemically functional groups are introduced there allowing, apart from electron transfer processes, also chemical reactions or the physical and physicochemical properties of the surface are altered improving electron transport [3–5, 7–13]. Such modified electrodes have been frequently called **chemically modified electrodes**, a term propagated by Baldwin's and Durst's groups in the 1980s [101, 102] and still frequently used mainly by Chinese authors. According to IUPAC, a chemically modified electrode is *an electrode made of conducting or semi-conducting material that is coated with a selected monomolecular, multimolecular, ionic, or polymeric film of a chemical modifier and that by means of faradic reactions or interfacial potential differences exhibits chemical, electrochemical, and/or optical properties of the film* [103].

It should be mentioned that a *film-type modification*, as indicated here, is not a prerequisite for chemical modification of the electrode materials of heterogeneous character, such as solid composites or paste-like mixtures. The respective electrodes enable the so-called *bulk modification*; nevertheless, the chemical characteristics are altered at the surface, too. In this context, (i) *physical modification* may take place, comprising a change of the surface states [50] and giving rise to some observable electrochemical effects, which can be advantageously exploited for an improvement of the analytical performance of an electrode, such as potential shifts or decreased overpotential [4, 5]. Yet another variant is the already mentioned (ii) *electrochemical modification* utilizing the application of an initial conditioning potential, either cathodic (pre-cathodization) [104] or anodic (pre-anodization) [105], or even both [16]; often, at extreme conditions – outside of the usually attainable potential window. In the latter case, oxygen-containing groups (C=O, C–OH [50]) are formed improving the electron transfer or being electrocatalytically active in some way.

The *goals of modification* are straightforward: (i) improvement of detection ability by accumulation of the target species; (ii) generation of electrochemical signals and their characteristics (signal shape, signal separation, decrease of overpotentials) by mediation or

electrocatalysis; and (iii) improved selectivity or even specificity [5, 8].

Apart from this variety and the individual nuances, chemical modification of CPEs leads to qualitatively new configurations termed **chemically modified carbon paste electrodes (CMCPEs** [4, 5, 8, 9]).

11.3.2 Modification Processes

The “classical” modification processes for solid homogeneous electrodes are (i) *film* and (ii) *membrane* covering, as well as (iii) *adsorption*, and (iv) *covalent attachment/immobilization* of the modifier. These avenues are also open to modify carbon paste as the most popular representative of heterogeneous electrode materials. But, because of its composite character, it facilitates simpler ways of modification by direct addition of the modifier to the paste either during or after the preparation of the material. The term **direct mixing** was coined by Baldwin [106], though the history of modification of CPEs dates back to the mid-1960s, when Kuwana was the first who added electroactive components to the paste [107]. (In his case, however, there had been no intention to alter the CPE characteristics, and the purpose was to study the redox behavior of the adduct in a nonaqueous environment.)

Thin films (mono- and multistacked layers) as well as membranes may serve for various purposes [108]: protective layers with size exclusion, charge barrier or diffusion-inhibiting effects; immobilization and anchoring structures for modifiers, catalysts, and mediators; “preconcentrators” of analytes; modifiers of surface characteristics; wetting aids; and adhesion or insulation layers.

Monolayers as modifiers on electrode surfaces are prepared by sorption techniques. *Self-assembled monolayers* (SAMs) form by spontaneous adsorption of precursors on the electrode substrate with an ordered orientation by interaction of certain molecule areas protruding from the sorption plane [109–112]; most popular are SAMs prepared by thiol compounds on gold surfaces, but also SAM formation on CPEs is possible. *Langmuir–Blodgett layers* (LBLs) are monolayers made by surfactants by adsorption from the surface of a solution [113]. Highly ordered multistacked structures from polyelectrolytes can be obtained by layer-by-layer deposition, where the ensuing plane of the stack can be immobilized by sorption of a countercharged polyelectrolyte [114–116].

Thicker membranes from polymers are usually cast as solution (drop, spin, and spray coating), and the membrane forms after evaporation of the solvent. Alternate routes are *application of monomers*, *direct polymerization* on the electrode surface, and *mechanical attachment* of the ready-to-use *membranes*. Usually, modifiers (mediators, catalysts, enzymes, etc.) are dissolved in the membrane-forming solution. Membranes can be generated also by *electropolymerization*, most commonly from aniline, pyrrole, or thiophene [117–119]; the resulting 2D structure can entrap active molecules (e.g., enzymes) or serve as anchors for the actual modifier. Attachment of active molecules to polymeric structures can proceed via covalent binding, electrostatic attachment, biotin–avidin binding [120], or click chemistry [121]. Polymers may also act as templates for the analyte, a process called molecular imprinting, where the target molecule is present during polymerization and leached afterward

leaving behind cavities with the shape of the molecule of interest and occasionally combined with proper binding sites [122–124].

The most frequently applied modification procedure is still *the direct addition of the reagent to the paste material* – also known as **the bulk modification** – the simplicity of the method and the mildness of the modification conditions are probably responsible for the wide popularity of CPEs [3–5, 7–13]. Particulate modifiers must be intensively homogenized with the paste to yield uniformly modified surfaces (grinding, sonication); dissolution of the modifier in the binder being facilitated by its lipophilicity.

Covalent binding of modifiers is usually quite work intensive because the surface must be equipped with proper functional groups (usually achieved with oxidation) to which the active molecules or anchors for them are attached either directly or via spacers [125, 126].

11.3.3 Types of Modifiers

There seems to be numberless different modifiers which have been used with CPEs; one of the main reasons being certainly the ease of modification due to the composite nature of the electrode material. [Table 11.2](#) offers an approximate overview on the most common types of modifiers including some illustrative examples.

Table 11.2 Common modifiers for carbon paste electrodes with typical examples.

Type of modifier	Purpose of modification, main principle(s) of interaction with analyte	References
Examples (specification)	Examples	
<i>Metals</i>	<i>Catalytic effects mimicking metal electrodes</i>	
Platinum metals, platinized C	Catalytic effects for H ₂ O ₂ , biosensors	[127]
Spongy Os	Catalytic oxidation of oxalic acid	[128]
Bismuth powder	Mimicking Bi-electrode for the detn. of cysteine	[129]
<i>Metal oxides</i>	<i>Catalytic effects by valence change oxidation reaction with analyte precursors for metal films</i>	
MnO ₂	Catalytic effects for H ₂ O ₂ , biosensors	[130, 131]
RuO ₂	Oxidation of glucose in alkaline medium	[132]
Cu ₂ O	Oxidation of glucose via Cu(III)	[133]
Bi ₂ O ₃	Bismuth film electrode	[134]
<i>Metal complexes</i>	<i>Catalytic effects by valence change</i>	
Prussian blue	Catalytic effects for H ₂ O ₂ and O ₂ biosensors	[135]
Ferrocene	Electron donator or acceptor (as ferricinium)	[136]

Co-phthalocyanine	Electrocatalytic detn. of glutathione and cysteine	[137]
<i>Ion-exchangers</i>	<i>Accumulation of ions</i>	
Amberlite LA2	Accumulation of nitrite	[138]
Tricresyl phosphate (binder)	Accumulation of iodide	[139]
Humic acid	Accumulation of Cu^{2+} and other metals	[140]
<i>Ion-pairing reagents, surfactants</i>	<i>Accumulation of ions as ion pairs, improvement of surface characteristics</i>	
CTAB	<i>In situ</i> accumulation of Ti – oxalate complexes	[141]
Surfactant	detn. of NADH, improved current	[142]
<i>Complexants</i>	<i>Accumulation of ions</i>	
Dimethyl glyoxime	Accumulation of Ni^{2+} , Co^{2+}	[143, 144]
Crown ether	Accumulation of Cu^{2+}	[145]
<i>Sorbents</i>	<i>(ad)sorptive accumulation supported by ion-exchange and size exclusion</i>	[146, 147]
Zeolite Y loaded with Cu(II)	detn. of electroinactive small ions	[148]
<i>Ionic liquids</i>	<i>Ion-exchanging effects for accumulation of ions</i>	
Ionic liquids	Cysteine	[149]
<i>Nanosized materials</i>	<i>Catalytic effects, increased surface area, anchors</i>	
Nanoparticles	Act like micro- and macro-particles but with the increased activity;	
Core-shell nanoparticles	Core as support (e.g., magnetic) for active shell catalyst;	
CNTs	Electron conductor, anchor for decorations;	
Graphene	Signal improvement	
Cu nanoparticles	Catalytic oxidation of amino acids	[150]
Au nanoparticles – cysteamine	detn. of homocysteine	[151]
$\text{Fe}_2\text{O}_3@\text{Co(III)hexacyanoferrate}$	Magnetic nanoparticles for the detn. of N-acetylcysteine	[152]
(MW)CNT	detn. of pyranoses with pyranose oxidase via H_2O_2	[153]
Graphene paste electrode	detn. of chlorpromazine	[154]
Graphene (+ ionic liquid) (+ ZrO_2)	Signal improvement for oxidation of guanosine	[155]
<i>Host molecules</i>	<i>Formation of host-guest complexes</i>	

Cyclodextrins	detn. of phenols and polycyclic aromatic amines	[156–158]
Crown ethers	detn. of amino acids via host-guest complexes	[159]
Calixarenes	Metal ions, organics	[160]
<i>Membranes</i>	<i>Immobilizer</i>	
	Diffusion barrier	
	Ion-exchange membranes for immobilization	
	Electropolymerized membranes (various functions)	
Dialysis membrane	immob. of tissue and protection; detn. of phenols	[161]
Cation exchanger	immob. of NAD ⁺	[162]
Nafion-glutamate oxidase	immob. of glutamate oxidase	[163]
Poly(N-methylaniline)	Electropolymerization, detn. of nitrite	[164]
<i>Redox polymers</i>	<i>Electron shuttles</i>	
Os redox polymer	detn. of glucose with GOD, direct electron transfer	[165]

Abbreviations and symbols: detn., determination; e.g., for example; GOD, glucose oxidase; immob., immobilization; (MW)CNT(s), (multiwalled) carbon nanotubes; LA2, commercial denotation (abbreviation); NADH, nicotinamide adenine dinucleotide; and NAD⁺, oxidized form of NADH.

For more detailed or even almost complete insight, the corresponding reviews, book chapters, and the recent monograph can be recommended [3–5, 7–13, 28, 29, 33], whereas this chapter offers a brief and concise survey in the following paragraphs.

Metals: They can be used to mimic corresponding metal electrodes; they can be employed as metallic micro- or nanoparticles or as thin films in the form of metallized carbon [127–129]. The main goal is to exploit some specific characteristics of the element, for example, the catalytic activity of platinum for the determination of hydrogen peroxide [127].

Metal oxides: Being frequently assessed as modifiers for CPEs, their way of action may account for different purposes. Some are electrocatalysts due to a potential-dependent change of their valence state [130–133]. Another interesting approach is to add them directly to the paste as precursors for metal film electrodes which renders plating with a solution of the metal obsolete (e.g., [134]).

Metal complexes: Similarly to metal oxides, these compounds can be exploited for electrocatalytic (mediating) actions to facilitate electron transport between analyte and electrode surface [135–137]. Ferrocenes, phthalocyanines, and their derivatives are most frequently used for this purpose.

Ion-exchangers: Another important group of modifiers that act quite straightforward [138–140]. Counterions compensating the charge of their functional group can be exchanged by ions with the charge of the same polarity, where parameters, such as ion size, charge, and concentration, still control the binding affinity of competing ions. Ion-exchangers can be in

solid (grinded polymers, membranes) or in liquid form, the latter ones yielding more homogeneously modified electrodes. Ion-exchangers accumulate ionic analytes or immobilize target ions for other purposes.

Ion-pairing surfactants: Some substances of this type can be added directly to either the electrode material or the analyte solution, provoking an *in situ* modification of the electrode surface and – together or instead of the aforementioned erosion effect [54, 141] – acting as highly effective ion-pairing agents [80, 142, 143].

Complexing agents: Being known from chemical qualitative analysis as classical reagents for probe reactions, they represent yet another key group of modifiers for adsorptive stripping voltammetry and can be applied either *in situ* or as bulk modifiers [104, 144, 145]. By the way, many of them – for example, dimethylglyoxime (*Chugaev's* reagent), oxin, thiosemicarbazid, cupferron, ferroin, *Alizarine S*, *Beryllon IREA*, and so on – belong to the very first modifiers used in the CMCPE configurations (see [4, 5] and table sets included).

Sorbents: A wide group of modifiers, where **sorbent** is a very general term for substances in solid state that are used as macro- (pore size > 50 nm), meso- (2–50 nm), or microporous (<2 nm) materials [146] and combine more effects (ion-exchange, size exclusion, adsorption) to immobilize the target species. Zeolites and related compounds (artificial and natural clays and molecular sieves) are most frequently used [147]. An interesting application is their loading with an electroactive ion (Cu^{2+}) which can be released by nonelectroactive ions and determined amperometrically exploiting size exclusion effects [148].

ILs: Apart from two-component configurations of the CILE type discussed earlier, ILs can also be employed as special modifiers for accumulating ion-exchanging species, improving the resultant current height, shape, and peak potentials [149].

Nanoparticles and related materials: During the past two decades, the use of nanosized species as modifiers of choice for various electrodes and sensors has evolved exponentially [4, 5, 11]. Compared to macro- and micro-sized materials, nanoparticles possess increased surfaces intensifying the desired performance on the one hand, but also exhibiting additional electrocatalytic effects that are not pronounced with larger size and dimensions of the modifier. Some typical examples are copper and particularly gold nanoparticles fairly applicable, for example, to the determination of amino acids [150, 151] but also for many other analytes (see [4, 5] and table surveys therein). Core-shell nanoparticles contain a (usually nonreactive) core, which serves for purposes other than electrochemical ones – among others, magnetic particles of Fe_3O_4 facilitating handling and manipulation – covered by a shell with the desired chemical or electrochemical properties, for example, $[\text{Fe}(\text{CN})_6]^{3-}$ as electrocatalyst [152].

CNTs. As far the most popular, these new carbons with helical structures have been shown to be widely applicable – equally, in SW and MW forms – thanks to their specific surface morphology, high electrical conductivity, and electron transfer-

facilitating properties. Both types can be used as graphite substitutes (in the CNT-CPE arrangement; see above) or simply as the modifier only; a typical example being the determination of H_2O_2 at such an electrode because of much lower potentials needed for its oxidation and the respective detection compared to unmodified carbon pastes [153].

Graphene and graphene oxide. This planar nanocarbon [95, 154] together with its oxidized form [155] can also be employed as special modifiers with adsorptive and catalytic properties.

Host-guest coupling agents: This supramolecular affinity can be exploited for immobilization and accumulation, and the most popular examples are cyclodextrins [156–158], crown ethers [145, 159], and calixarenes [160].

Membranes: As a traditional tool for modification of electrodes from compact materials, various membranes are also very compatible with the carbon paste-based configurations [4, 5, 80]. On the one hand, the presence of a membrane usually hinders diffusion toward and from the electrode surface, but on the other, this drawback is compensated by further benefits. In the simplest case, a dialysis membrane establishes a diffusion barrier to prevent large molecules from either entering or leaving the space directly around the electrode surface [161]. In the form of a membrane, a *cation exchanger* can be applied to electrostatically attach the corresponding counter ions [162]. Similarly, *Nafion*® – a perfluorinated and sulfonated polymer acting as a special thin membrane (after application onto the electrode surface in dissolved form and evaporation to dryness) – is frequently used to entrap natural polymers (e.g., enzymes); but it may also bind some cations via its $-\text{SO}_3^-$ functional groups [163]. In the last decade, *electropolymerization* has become popular as an especially convenient procedure for creating thin films on the electrode surface with the advantage that, in many cases, the polymer layer is electrically conductive and even electroactive [4, 5]. This allows some polymers, including enzymes and enzymatic cofactors, to be entrapped and immobilized during such electropolymerization [164]. Finally, membranes can be made from *redox polymers* containing oxidizable/reducible groups that can shuttle electrons and exert electrocatalytic effects; the most popular being osmium-based polymers [165].

11.3.4 Carbon Paste Biosensors

In general, biosensors contain a biological (usually polymeric) entity in the recognition environment of the sensor [166, 167]. Enzymes are the most frequently used biomodifiers, in particular, such ones that catalyze oxidation or reduction reactions (oxidoreductases), that is, oxidases and dehydrogenases, when the former ones exploit oxygen as the electron acceptor with consequent reduction to hydrogen peroxide or water.

Electrode configurations relying on determining either O_2 or H_2O_2 (mainly glucose sensors) are termed **first-generation (bio)sensors** after the first and, at present, classical construction designed by Clark and Lyons [168].

Second-generation sensors replace oxygen by an artificial electron acceptor, whereas *third-generation sensors* wire the enzyme providing a direct electrical contact with the (electro)active enzyme center. Hydrogen peroxide, H_2O_2 , an intermediate from oxidases, is electroactive but displays high overpotentials for both oxidation and reduction, and therefore mediation (e.g., with MnO_2) is preferable [163]. Dehydrogenases often have NAD^+ as a cofactor, which is reduced during the oxidation of the substrate; the resulting NADH in turn being commonly the target for electrochemical detection by reoxidation [168]. Hydrolases are rarely used for the direct determination of analytes, but are convenient for indirect determinations with inhibition assays where an artificial nonelectroactive substrate (e.g., phosphate esters of phenols) is hydrolyzed to an active compound (phenol) [169]. Inhibition is provoked by many herbicides and pesticides, which can be employed for their quantification.

Concerning **carbon paste biosensors** – less often named *biologically modified CPEs* – their concise classification, characterization, and detailed survey of applications was for the first time reviewed by Gorton in the mid-1990s [15]. Since then, some other related but less-extensive articles can be found (see, e.g., the respective sections in [10, 12, 21]), summarizing the ongoing activities and/or some special achievements with CP-biosensors that rapidly gained a worldwide popularity and – for nearly a decade – dominated all the remaining types of CPEs (see the surveys in [3, 85]). Here, it can be highlighted that the most valuable feature of CP-biosensors is the carbon paste itself and, more specifically, its *biocompatibility* – that is, capability to host various enzymes that are mechanically embedded into CP-mixtures in the same way as bulk modifiers in CMCPEs. This can be advantageous for enzyme-containing tissues and whole cells (for the individual types and some practical examples, see the table survey overleaf), from which the isolation and the subsequent purification of an enzyme are complicated or should be circumvented as such [15].

The first example of this kind was the “bananatrode,” a CPE modified with banana tissue [170] containing phenol oxidase as a catalyst for the oxidation of dopamine (DOP, a neurotransmitter), followed by a similar construction some years later [171]. Another representative is a CP-biosensor with admixed yeast containing alcohol dehydrogenase that facilitates the determination of ethanol [172]. Some biomasses such as algae, lichens, or mosses then show quite a high affinity to some heavy and precious metals with the correspondingly modified electrodes (see [4, 5, 33] and references therein).

The **electrochemistry of nucleic acids** at carbon paste-based electrodes has become quite attractive as well, commencing also during the “golden era of carbon pastes” – on the verge of 1980s and 1990s [4, 5, 22]. This special area relies on the electroactivity of the guanine moiety, but also the other bases of DNAs and RNAs can be electrochemically oxidized at rather high positive potentials. The carbon paste material offers the additional advantage that nucleic acids strongly adsorb to their surfaces, which can be exploited for three purposes: (i) *stripping analysis of nucleic acids* (without much specificity) with further enhancement by special modifiers (e.g., ILs [173]); (ii) *immobilization of nucleic acids and interaction studies* with other substances [174] or accumulatable analytes [175]; and (iii) *hybridization studies*, where the single strands are immobilized as probes and intentionally hybridized with

complementary strands (analytes) from solution [176]. The whole hybridization process can then be monitored by electroactive “reporter molecules” exhibiting sufficiently high binding affinity to either single or double strands.

Also, **immunochemistry with CPEs** can be mentioned utilizing antibodies, antigens, and haptens in the form of the immunorecognition elements, when the antibodies are mostly immunoglobulin G, less frequently IgM [177]. Most common immunochemical analytical procedures are the competitive or sandwich assays; magnetic nanoparticles being very helpful with respect to easy handling (see, e.g., [178]).

All the important modifiers of biological origin are surveyed in [Table 11.3](#); again, with typical examples of the individual interactions and processes applicable in electrochemical research and/or practical electroanalysis.

Table 11.3 Modifying agents for carbon paste biosensors with typical examples.

Type of modifier	Purpose of modification, main principle(s) of interaction with analyte	References
Examples (specification)	Examples	
<i>Enzymes</i>	<i>Detection of substrates via products, intermediates</i>	—
Oxidases	detn. via O ₂ or H ₂ O ₂ , e-acceptors, direct e-transfer	
Dehydrogenases	detn. usually via NADH	
Hydrolases	detn. of electroactive products, indirectly via inhibition	
MnO ₂ + glutamate oxidase	detn. of glutamate via H ₂ O ₂	[163]
Alcohol dehydrogenase + NAD ⁺	Amperometric detection of EtOH	[168]
Alkaline phosphatase	Carbofuran	[169]
<i>Tissues and cells</i>	<i>Source of enzymes or biological organelles, accumulation of analyte</i>	[15]
Banana tissue	detn. of dopamine (via polyphenol oxidase)	[170]
Yeast	detn. of EtOH (via alcohol dehydrogenase)	[171]
<i>Chlorella pyrenoidosa</i>	acc. of [AuCl ₄] [−]	[172]
<i>Nucleic acids</i>	<i>dsDNA for accumulations or interaction studies</i>	
	<i>ssDNA for hybridization studies</i>	
Ionic liquid	acc. of dsDNA	[173]
dsDNA or ssDNA	Interaction studies with As ₂ O ₃	[174]
dsDNA	acc. of chloroquine	[175]
ssDNA	detn. of avidin in transgenic maize	[176]
<i>Antibodies</i>	<i>Immunosensors</i>	[177]
Picloram-ab on magnetic NP	detn. of picloram by competition	[178]

Abbreviations and symbols: acc., accumulation; detn., determination; DNA, deoxyribonucleic acid; EtOH, ethanol; ds, double stranded; ss, single stranded; and NADH, NAD⁺, see [Table 11.2](#).

11.3.5 Applications of CMCPes and CP-Biosensors in Surveys, Facts, and Numbers

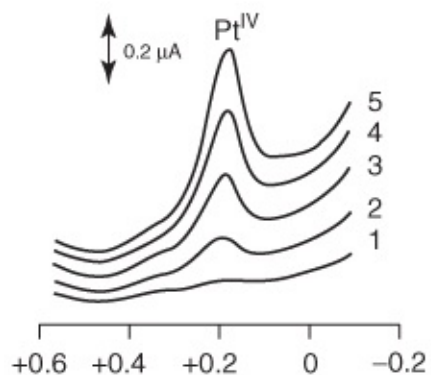
For everyone who is interested in the applicability of CMCPes and CP-biosensors in its entirety, there is a recently published monograph covering this topic almost completely [5]; the

latest years being updated by the newest review [91].

Nevertheless, also most of the remaining reviews [3, 4, 7–13, 15, 18, 21, 25–30, 33, 35] may provide a sufficiently representative information, moreover, with contemporary insight.

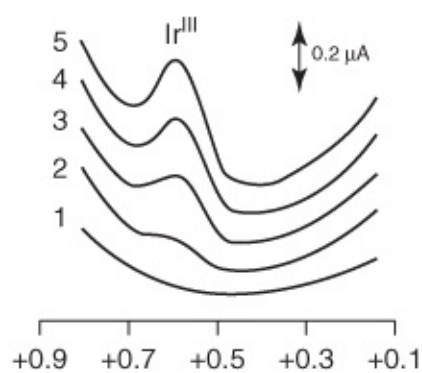
Herein, the individual areas of applications of CMCPEs and CP-biosensors are again overviewed by means of selected summaries, along with a few examples, taken from the authors' archives [179–181] and shown in [Figure 11.4](#)a–d with the corresponding legends.

Calibration of Pt^{IV} at μM level
using *in situ* modified CPE



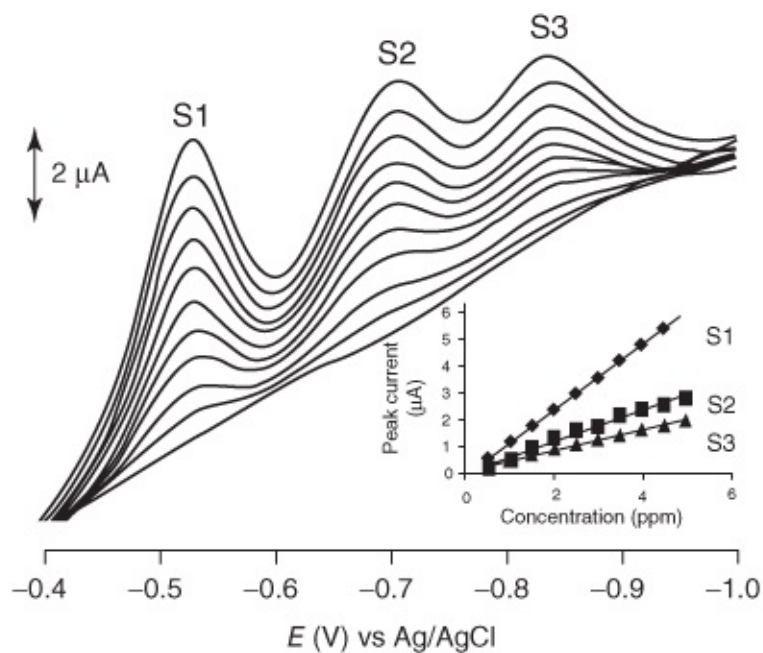
(a) E (V) vs Ag/AgCl

Calibration of Ir^{III} at μM level
using *in situ* modified CPE



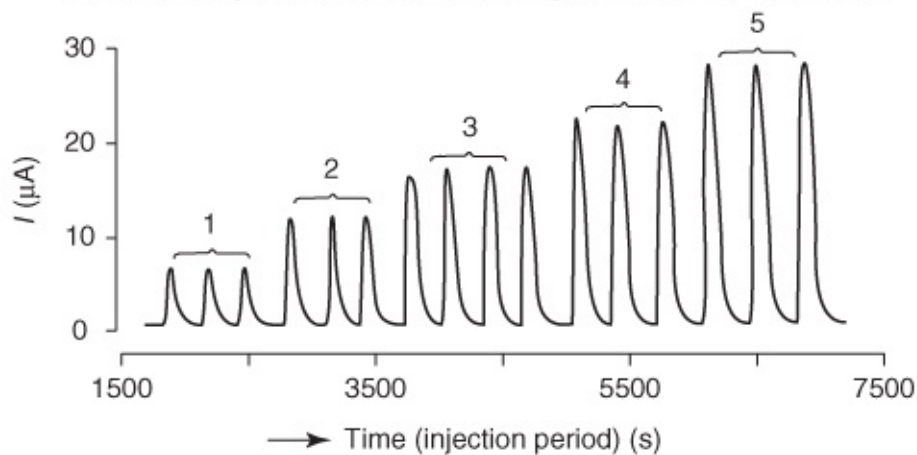
(b) E (V) vs Ag/AgCl

Calibration of three analytical signals for TNT at the BiF-GCPE



(c)

FIA-amperogram for calibration of glucose at CP-biosensor



(d)

Figure 11.4 Three examples of typical applications of chemically (a–c) and biologically (d) modified carbon paste electrodes. (a,b) Calibrations of Pt^{IV} and Ir^{III} at the micromolar concentration level at a CPE modified “*in situ*” with quaternary ammonium salt. Legend: (a) baseline, (2–5) 1, 3, 6, and 9 μM Pt^{IV} ; (b) (1) baseline, (2–5) 3, 6, 9, and 12 μM Ir^{III} experimental conditions: DPCSV; 0.1 M acetate buffer + 0.1 M KCl + 1×10^{-5} M cetyl-tributylammonium bromide (CTAB, pH 4.5); accumulation potential and time: +0.9 V versus 30 s; stripping: from +0.9 to -0.3 V; scan rate and pulse height: 10 mV s^{-1} ; $\Delta E = -25 \text{ mV}$.

(Taken and redrawn from [179].)

(c) Calibration of the multiple SWAdSV (square-wave (anodic, adsorptive) stripping voltammetry) signal (S1–S3) of trinitrotoluene at “*ex situ*” BiF-GCPE. Legend: main voltammograms, $c(\text{TNT}) = 0.5\text{--}1, 2, 3, 4, \text{ and } 5.0 \text{ mg l}^{-1}$; inset: calibration plots for S1, S2, and S3. Experimental conditions: Britton–Robinson buffer (pH 9.0); accumulation potential and time, -0.3 V versus 60 s; Square wave potential ramp: frequency, 25 Hz; increment, 4 mV; pulse height, 50 mV. BiF-GCPE prepared in plating solution of 0.1 M acetate buffer +5 ppm Bi(III); deposition potential and time, $E_{\text{DEP}} = -1.0$ V versus $t_{\text{DEP}} = 60$ s.

(Taken and redrawn from [180].)

(c) FIA-amperogram from testing of glucose detection with a CP-biosensor modified with 5% RuO_2 (serving as the mediator) and glucose oxidase (GOx) immobilized in the Nafion® membrane. Legend: (1–5) $c(\text{glucose}) = 0.25, 0.50, 1.00, 2.00, \text{ and } 5.00 \text{ g l}^{-1}$ (almost all in three replicates). Experimental conditions: FIA; phosphate buffer (pH 7.5); detection potential, +0.48 V versus Ag/AgCl.

(An outtake from [181].)

Types of modifications and their popularity (compared again via a percentage estimated from the respective original articles and based on approximate summaries in [3, 5, 85]): *manual bulk modification*, 40%; *chemical or biological immobilization*, 20%; “*in situ*” *modification* (in sample solutions), 20%; *other approaches*, 10%.

Atypical materials for chemical and biological modifications: Fresh banana tissue or yeast mentioned above is not the only unusual items as purposely chosen modifiers. In the database of electrochemistry and electroanalysis with CMPEs and CP-biosensors, one can find a long line of similarly unusual or indeed curious materials proposed for modifying carbon pastes and related mixtures. Needless to use any special characterization of the individual examples, the respective list can be set up in this way: (i) *materials of inorganic and organic nature*, selected minerals and ores (e.g., natural clays), liquid crystals, synthetic dyes, industrial catalysts, and pumice (“sea foam”) and (ii) *biological materials*, algae, lichen, moss, tobacco leaves, grass weed, pea, and soybean seeds, horseradish, apple, orange, pear, peach, avocado, annona, pineapple, tomato seeds, cucumber, cabbage, potatoes, mushrooms (*Agaricae* sp.), flower (*Asparagus* sp.), vegetable oil, natural macromolecules (chitin, chitosan, and keratin), living microorganisms (bacteria and viruses), or even chicken intestines.

Main areas of electroanalysis with CMCPes and biosensors: Similar to unmodified

CPEs, there are four major categories, in which the modified variants are widely employed: (i) *inorganic ions, complexes, and molecules*, 40%; (ii) *organic substances and environmental pollutants (of organic origin)*, 10%; (iii) *BIC*, 40%; and (iv) *pharmaceutical and clinical analysis*, 10%.

Electroanalysis with CMCPEs and CP-biosensors in systematic survey of the

analytes: In fact, chemically and biologically modified variants have been successfully used for almost all compounds determinable with the bare CPEs and surveyed above. Often, the respective methods and procedures with CMCPEs and CP-biosensors have offered better analytical performances, due to the improved selectivity and sensitivity provided by the modifier(s) [3–5, 85]. Thus, in the following text, listed are mainly the analytes that have not yet been – or, in principle, could not be – determined with “ordinary” unmodified electrodes and sensors.

Inorganic species. Metals, Li^{I} , Na^{I} , K^{I} , and Cs^{I} ; Ba^{II} , Ga^{III} , Ge^{IV} , La^{III} , Ti^{IV} , Zr^{IV} , and Th^{IV} ; $\text{V}^{\text{IV,V}}$, $\text{Cr}^{\text{III,VI}}$, $\text{Mo}^{\text{V,VI}}$, W^{VI} , $\text{Mn}^{\text{IV,VII}}$, $\text{Tc}^{\text{IV,VII}}$, Pd^{II} , Os^{IV} , $\text{Ir}^{\text{III,IV}}$ (also simultaneously with Pt^{IV} ; see [179] and [Figure 11.4a,b](#)), and some rare earths. Nonmetal species, NH_4^+ , NH_3OH^+ , NO_2^- , NO_3^- , and N_3^- ; CN^- , SCN^- , F^- , ClO_3^- , ClO_4^- , Br^- , I_3^- , and IO_3^- ; HPO_4^{2-} , S^{2-} , SO_3^{2-} , SO_4^{2-} , $\text{S}_2\text{O}_8^{2-}$, SeO_3^{2-} , $\text{B}(\text{O}_2)(\text{OH})_2^{3-}$, BF_4^- , and $\text{Si}(\text{Mo}_3\text{O}_{10})_4^{4-}$.

Organic substances. Examples of compounds determined only at CMCPEs and biosensors: nitromethane, nitropropane, polynitroaromates (see [180] and [Figure 11.4c](#)) aliphatic and aromatic peroxides, selected alkaloids (nicotine, caffeine, and brucine), trichloro- and pentachloro phenol.

Biologically important compounds. Again, mostly nondeterminable at common CPEs are: most of amino acids; glucose (typically, via the H_2O_2 release and its subsequent oxidation or reduction in the amperometric mode; see [180] and [Figure 11.4d](#)) and other monosaccharides; less-frequent vitamins (A, B1, B9, B12, D, K1, and K3), hormones, and steroids; lactic acid and lactates; and antioxidants (mainly flavanols and flavonoids), plus some bacteria and viruses.

Pharmaceuticals: Relatively infrequent methods developed for pharmaceutical and clinical analysis employ, for example, lipid-, fatty acid-, or vegetable oil-modified carbon pastes, together with some special biosensors [5, 15, 18, 19]. Otherwise, this rather wide group of analytes is still the domain of unmodified CPEs: in an estimate, with three times higher abundance compared to modified variants [3–5]. This atypical proportion may be explained by two factors: (i) prevailing extractive accumulations (onto the binder), with no need for additional modifiers [19] and (ii) lesser requirements with respect to selectivity for specific samples containing higher concentrations of analytes and often anticipated interfering species.

Typical samples analyzed with CMCPEs and biosensors: For practically oriented electroanalysts, it is useful to overview the spectrum of samples, certified specimens, and

other materials that have already been analyzed; some of them being of permanent interest. It should be admitted, however, that the respective list reflects rather the possibilities and limitations of electrochemical measurements than specifics of CMCPEs and CP-biosensors.

When considering first the samples for **inorganic analysis**, the individual categories in the order of appearance are (i) *aquatic samples* [33] comprising a wide range of real specimens: (a) natural waters (sea, lake, pond, and river water, mineral springs, underground sources, or atmospheric water in the form of raindrops and snow); (b) drinking and industrially treated water; or (c) heavily polluted wastewaters. Furthermore, there can be (ii) ores and minerals, (iii) soils and sediments, (iv) sewage sludge, (v) fly coal ash, (vi) metals and alloys, (vii) pure chemicals, (viii) industrial products (e.g., cosmetics, agricultural fertilizers, silicate bricks, ceramics, refined petroleum, or industrial explosives – again, see [Figure 11.4c](#)), (ix) selected drinks (juices, beer, cider, wine, and spirits), (x) pharmaceuticals and vitamin supplements, and (xi) human tissues and fluids (hair, liver slices, blood, and urine).

Within a palette of the samples for **organic and biological analysis**, both CMCPEs and CP-biosensor have been employed for determination of a wide variety of compounds in: (i) soft drinks; (ii) alcoholic beverages (beers, ciders, and wines); (iii) vegetable oils; (iv) food dyes, coloring additives, and antioxidants; (v) industrial detergents and plastics; and (vi) human tissues and fluids (kidney and liver cuts, spinal fluid, whole blood, serum, urine, and saliva). Among less frequently analyzed (vii) environmental samples, the dominant specimens were, for example, natural and industrial waters (see [4, 5, 33] and table surveys therein).

11.4 Latest Achievements in Electroanalysis with CMCPEs and CP-Biosensors and Perspectives for the Future

By analog to the closing notes on unmodified carbon pastes, the current status and position of chemically and biologically modified variants can be illustrated via a collection of more or less accidentally selected articles published in the last 2 years [182–200], taking into account also the advances highlighted in the newest review [90].

In fact, there are no breaking events when considering CMCPEs and/or CP-biosensors and the latest achievements follow faithfully the already discussed activities of the last one or two decades. Thus, among the **modifiers of choice**, (i) various *nanomaterials* are of continuing interest [184, 191, 196], including nanotubes [190, 197] applicable as an alternate component(s) or adduct(s) with distinct catalytic properties. Similarly acting are then (ii) *solgel* and *sonogel*-based modifiers [90, 194], or (iii) *mesoporous structures* [184, 198] that all are able of altering, in a significant way, the surface characteristics of the resultant CMCPE(s). The greening orientation of modern electroanalysis is represented by a special group of CMCPEs, based on (iv) *(pre)plated metallic films* [183, 188, 189], substituting nowadays the ecologically unacceptable mercury-based configurations. Regularly appearing combinations with flow systems and organic solvent-based media are, for years, feasible with

highly resistant glassy carbon paste electrodes (GCPEs) [77, 182] or similarly applicable CMCPs containing (v) *special stabilizers* [194]. Finally, *new types of CP-biosensors* are also regularly appearing, utilizing the carbon paste as biocompatible substrate for various (vi) *enzymes and enzyme-containing tissues* [90, 186, 194], although this family of formerly highly popular carbon paste-based configurations is now in continuing decline in confrontation with more robust and more handy screen-printed constructions with solidified carbon inks [28, 29, 118, 163, 179] (see Chapter 12).

Regarding the analytes in focus, one can mention the determination of frequently monitored toxic heavy metals [183, 184, 188, 189], some less-frequent and electrochemically challenging ions, such as Cs^+ [185], Lu^{3+} [195], and S^{2-} [190], permanent attention is paid to organic pollutants [182, 194, 196], pharmaceuticals [193, 198], food additives [187], and principal substances among BICs [186, 191, 197].

Despite indisputable dominance of chemically and biologically modified variants, there is still some position for “good old carbon pastes” – that is, *traditional mixtures* of graphite powders with mineral or silicone oils. This can be documented by three actual examples from the selection of newest contributions presented here [182–200], when common CPEs had surpassed in their performance even carbon nanotube paste electrodes (CNTPEs) or a CILE and could thus be proposed as the electrodes of choice for determination of caffeine [192], myristicin [199], and nicotine [200]. Also, this indicates that the carbon paste – regardless if one uses highly sophisticated chemically and biologically modified systems or remains faithful to classical formulations – still represents *one of the most popular materials used for preparation of electrode and sensors* in modern electrochemistry and electroanalysis, as well as in some other areas of instrumental measurements. And, so far, there is no sign that this could change in the near future.

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Chapter 12

Screen-Printed Carbon Electrodes

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12.1 Introduction

Over the past 20 years, the screen printing of electrodes and sensors has emerged as a major branch of electrochemical research, with hundreds of documents being published which refer to the technique or claim to apply it in a novel way [1–13]. During the same period, numerous screen printing techniques have also been adapted for electronic circuit fabrication, and today these form an essential part of a multibillion dollar industry. The great driving force for these historical advances has been the realization that screen printing can be much cheaper to implement than traditional methods of manufacturing. Given this insight, and the continuing need for miniaturization of advanced electronics, the time is perhaps ripe to take stock of these developments, and to collate some of the fundamental science behind this revolution in print technology. As a small contribution toward this goal, I here review certain physical and chemical aspects of the screen printing process relevant to the manufacture of carbon electrodes.

Screen printing provides the possibility of manufacturing large numbers of carbon electrodes in a reproducible, low-cost, and disposable format. It also permits the incorporation of chemically functionalized materials in a straightforward way. Currently, screen-printed carbon electrodes find application in many areas of electrochemistry, but most notably in chemical and biochemical sensing, energy conversion and storage, and microelectronics. They also find application in flexible electronics, which is a rapidly developing technology for printing electronic devices directly onto flexible plastic substrates, such as polycarbonate, polyimide, and PEEK. Almost all forms of carbon have been deposited by screen printing, with graphite, carbon black, and activated carbon being the most widely used. Other forms of carbon that are the subject of continuing interest include carbon nanotubes, carbon nanofibers, and graphene.

The screen printing process has three principal advantages over other methods of electrode manufacture. First, the electrode area, electrode thickness, and electrode composition are readily controlled. Second, statistical validation of experimental results is made possible by the existence of replicate electrodes. Third, catalysts can be incorporated simply by adding them to the screen printing ink (paste). The main disadvantage of screen printing is that it is restricted to flat substrates.

For electrochemical purposes, the chemical composition of the ink is paramount. Three components are absolutely essential: a conducting filler, a nonconducting binder, and a volatile solvent. After the ink is printed, the volatile solvent evaporates, leaving behind the conducting filler cemented into the binder. This process is known as **curing**. During curing, the binder may simply precipitate from solution, or it may polymerize depending on its composition. Because

some solvent residue inevitably contaminates the final product, the first rule of ink formulation is to ensure that the solvent is electrochemically inactive over a wide range of electrode potential (i.e., has a wide “electrochemical stability window”). The solvent must also be free of nonvolatile impurities. Preferably, it should also be nontoxic.

The ideal finished product of the screen printing process is a solid composite system consisting of small particles of conducting filler (such as particulate graphite) uniformly dispersed inside an inert binder (such as a σ -bonded polymer). Within the bulk of the composite, each particle of conducting filler must be physically located within electron tunneling distance of its neighbor (~ 1.4 nm), otherwise it will not contribute to the long-range conductivity of the total electrode. To ensure this latter criterion is met, very high volume fractions of conducting filler must be incorporated inside the composite ($>64\%$ for random close packing of spherical particles of the same size) [14, 15], and of course the spatial dispersion of the filler particles should be as statistically homogeneous as possible. The detailed relationship between the bulk conductivity of composites and their three-dimensional structure is the province of *Percolation theory* [16]. According to the latter, smaller volume fractions of conducting filler can be tolerated if the filler consists of nonspherical particles, such as platelets or long thread-like chains.

12.2 Conductivity of Composites

In order to enhance the conductivity of printed electrodes, ink slurries are commonly pulverized in ball mills. This process creates very small particles of conducting carbon known as *fines* (1–100 nm diameter), which, after printing, bridge the electron tunneling gaps between the larger particles. However, since milling always causes some attrition of the mill surface, the mill interior should be made of agate (a cryptocrystalline variety of silica), rather than stainless steel, in order to prevent the introduction of trace amounts of iron and chromium. An alternative method of enhancing the conductivity of printed electrodes is to add small quantities of carbon black to the test ink (typically 5–15% by weight of solids, depending on micromorphology) [17]. Carbon black is the generic name for a family of small-particle carbon powders, which are formed in the gas phase by thermal decomposition of hydrocarbons. Carbon blacks are commercially available in a wide variety of grades, which differ in the size and shape of their particles and the chain length of their aggregates. Different grades may also have different degrees of compaction.

When carbon black is used in the laboratory, it must be handled with great care because of its potentially adverse effects on human health. The safest type of carbon black is *acetylene black*. This consists of graphitized particles, usually between 8 and 80 nm diameter, aggregated into long chains, having a specific surface area of ~ 60 m² g⁻¹. After printing, the long chains lower the percolation threshold of the conductivity network without introducing toxic impurities. More hazardous types of carbon black are *furnace blacks*, which contain carcinogenic compounds such as polycyclic aromatic hydrocarbons (PAHs), and *thermal blacks*, which contain aggregates in the size range 1–5 μ m which may become trapped in human lungs. Regardless of provenance, however, inhalation of all carbon blacks should be strictly avoided.

12.3 Carbon Polymorphs

Just after World War II, Rosalind Franklin famously classified carbons as either “graphitizing” or “nongraphitizing,” depending on their ability to form graphite in response to high-temperature heat treatment [18]. By means of X-ray diffraction, she observed that graphitizing carbons had very few sp^3 defects, thus allowing them to form extended sp^2 layer planes. By contrast, nongraphitizing carbons (such as glassy carbons, activated carbons, and high-modulus carbon fibers) had large amounts of tetrahedral sp^3 bonding trapped inside their structures, and hence were structurally rigid.

Since Franklin's time, many new polymorphs of carbon have been discovered, and today these are generically classified as *foliated* (graphite and its intercalation compounds), *exfoliated* (graphene and graphene oxide), or *hierarchical* (carbon black). On the atomic scale, some remarkable valence-satisfying structures have also been discovered, such as icosahedra (fullerenes), cylinders (nanotubes), and semi-infinite sheets (graphene). Stress-relieving pentagonal and heptagonal carbon rings have also been observed. Adding to this superabundance of morphologies, many important carbon materials also display oxygen functionalities on their surfaces, either as remnants from their synthesis or as deliberately introduced features. In extreme cases, oxygen/carbon ratios may exceed 10% w/w.

12.4 Oxygen Functionalities

Carbon forms two different types of covalent bond with oxygen. A carbon-oxygen single bond contains one σ bond and no π bonds, whereas a carbon-oxygen double bond contains one σ bond and one π bond. The pure σ -bond motif is found in C–OH groups (as seen in phenols) while the mixed σ/π motif is found in C=O groups (as seen in carbonyls and quinones). In the terminology of quantum mechanics, the oxygen atoms in C–OH groups are said to be sp^3 hybridized, whereas the oxygen atoms in C=O groups are said to be sp^2 hybridized.

Some oxygen functionalities are redox active, such as carbonyl and quinone. Others influence pH, such as carboxylate (aqueous $pK_a \sim 4$) and phenolic hydroxide (aqueous $pK_a \sim 10$). Yet others are comparatively inert, such as lactone and ether. In all cases, however, oxygen functionalities occur more frequently on edge planes than basal planes, due to the termination of the graphitic lattice there. In the carbon industry, it has long been recognized that the hydrophilicity of carbon surfaces can be enhanced by the introduction of oxygen functionalities. Similarly, the wettability of pores inside bulk carbon can be improved by internal oxidation. The explanation of both effects is that oxygen atoms behave as negatively charged loci for hydrogen bonding to water molecules.

Oxygen functionalities are notoriously difficult to remove. To a first approximation, the C–OH functionality has a carbon-oxygen bond strength of $\sim 350 \text{ kJ mol}^{-1}$, while the C=O functionality has a carbon-oxygen bond strength of $\sim 745 \text{ kJ mol}^{-1}$. These values are very high, and they prevent the pyrolytic elimination of carboxylate groups until $T > 600^\circ\text{C}$, and the pyrolytic elimination of quinone groups until $T > 1000^\circ\text{C}$.

12.5 Activated Carbons

Historically, almost all forms of carbon have been used in the screen printing process. In recent times, however, activated carbons have aroused special interest because of their potential applications in batteries and supercapacitors. Industrially, activated carbons are synthesized from organic matter such as charcoal, wood, peat, or coconut shells. This typically involves a two-step process: (i) *carbonization* in which the parent material is pyrolyzed in a reducing atmosphere in the temperature range of 600–1200 °C, then (ii) *activation* in which the initial product is surface-oxidized by oxygen, carbon dioxide, or steam in the temperature range of 600–1200 °C. Provided the starting material resists full graphitization, the original porous structure of the organic matter is retained by the final product, typically yielding a B.E.T. specific surface area in the range of 500–1500 m² g⁻¹ for particles of 15 μm diameter. At the other extreme, mesophase carbon microbeads (MCMBs), which also consist of particles of 15 μm diameter, exhibit B.E.T. specific surface areas of only 1–3 m² g⁻¹. These are used as intercalation hosts in lithium-ion batteries.

Within the supercapacitor industry, it is widely speculated that stand-alone screen-printed carbon electrodes might one day attain equivalent-series gravimetric capacitances of ~100 F g⁻¹ (based on the total mass of carbon, binder, and ion-supplying solution), and equivalent-series volumetric capacitances of ~150 F cm⁻³ (based on the total volume of carbon, binder, and ion-supplying solution). However, at the present time, commercial electrodes typically attain less than half these figures. Even smaller equivalent-series gravimetric capacitances (10–50 F g⁻¹) are obtained from oxidized nanotubes, chopped nanofibers, and carbon aerogels. In general, the best electrode responses correlate with highly oxidized carbon materials, well-conducting electrolytes, slit-shaped micropores, long charging times (minutes), and thin films (<500 μm). For a 125 μm film of activated carbon, one finds a maximum equivalent-series areal capacitance of ~1 F cm⁻² (where the *area* is defined as the convex hull of the electrode). Methods of increasing this number would be of great interest to the supercapacitor industry. On the other hand, for sensors, *minimum* equivalent-series capacitance densities are also sought by analytical chemists, and these values may be as low as ~100 μF cm⁻² in the case of nonporous, oxygen-free, particulate graphite.

12.6 Binder–Solvent Combinations

Over the years, innumerable binder–solvent combinations have been trialled in screen printing formulations, but only a few successful compositions have been disclosed in the open literature. This is because of their commercial value. Nevertheless, it is clear that two different kinds of polymeric binder are in widespread use, *thermoplastic* and *thermosetting*. Among electrochemists, perhaps the most popular approach is to dissolve a thermoplastic polymer in a high-boiling solvent. Representative systems of this type are poly(vinylidene fluoride) (PVDF)/N-methyl-2-pyrrolidone (NMP), poly(carbonate)/solvent naphtha (PC/SN), poly(methyl methacrylate) (PMMA)/ethylene glycol diacetate (EGDA), poly(sulfone) (PS)/dimethylacetamide (DMAC), and ethyl cellulose (EC)/α-terpineol (AT). The main

advantage of using a thermoplastic polymer as a binder is that it has a low degree of cross-linking, which makes the finished product slightly flexible. At the other extreme, various thermosetting systems have also been developed, based mainly on acrylic melamine and epoxy resin formulations, and these create more brittle films. A shortcoming of thermosetting systems is their high initial reactivity, although this usually fades with time due to the formation of covalent cross-links during curing. The diglycidyl ether of bisphenol-A (DGEBA) is a particularly popular cross-linking agent in epoxy resins. It is formed by reaction of bisphenol-A with epichlorohydrin in the presence of a basic catalyst.

Even though they are widely available as components of complex commercial products, thermosetting binders are difficult to obtain pure. For example, acrylic melamine formulations almost always contain mixtures of industrial solvents as diluents (such as 2-heptanone and *n*-butanol), and they may also contain proprietary dispersing and wetting agents. Similarly, epoxy resin formulations commonly contain industrial xylene and/or methyl isobutyl ketone as diluents, plus silicones and wetting agents. Plasticizers such as dioctyl phthalate are also widely used to decrease viscosity, despite being suspected endocrine disruptors. The many and various consequences of including these ingredients should be carefully considered before scientific use. It should also be noted that the maximum operating temperature of epoxy-based carbon electrodes is 120 °C. Their surfaces also swell in small-molecule organic solvents.

PVDF is probably the most widely used thermoplastic binder. It is a partially fluorinated polymer produced by the polymerization of 1,1-difluoroethylene, and typically has a molecular weight in the range of 180 000–550 000 Da. Commercially, PVDF is synthesized by two different routes: *emulsion polymerization* and *suspension polymerization*, with the emulsion-polymerized PVDF having the smaller particle size. Hence it is easier to dissolve. The customary solvent for PVDF is NMP. After printing and curing, PVDF-bound electrodes are resistant to many room temperature solvents, acids, and bases. In recent years, PVDF has also emerged as the industry standard binder in lithium-ion batteries, partly because its high molecular weight improves the adhesion of electrode components.

Polycarbonate is another binder used in screen printing formulations. It typically has a molecular weight in the range of 20 000–200 000 Da and is attractive because it can undergo large plastic deformations without cracking or breaking. Unfortunately, it also contains potentially harmful traces of bisphenol-A. Complicating matters still further, the standard solvent for polycarbonate is solvent naphtha, which contains a complex mixture of aromatic hydrocarbons. Fortunately, solvent naphtha can be replaced by 1,2,4-trimethylbenzene when high purity is required. PMMA and poly(styrene-co-methyl methacrylate) are practical alternatives to polycarbonate, but more brittle. They do not contain the potentially harmful bisphenol-A subunits found in polycarbonate, and can be dissolved in EGDA. The latter is a slow-evaporating biodegradable solvent (bp 190 °C) that is used in some commercial lacquers and enamels. Polysulfone belongs to a lesser-known family of thermoplastic polymers that is able to function continuously at temperatures up to 160 °C. Commercial polysulfone has a molar mass of ~35 000 Da and a glass transition temperature of ~190 °C. This polymer is customarily dissolved in DMAC or butyrophenone, and finds use in carbon and silver inks. In addition, it has been recommended for use in electrochemical nanobiosensors [19]. Finally,

ethyl cellulose is a derivative of cellulose in which some of the hydroxyl groups on the anhydro-glucose units have been converted into ethyl ether groups. It is practically insoluble in water, but dissolves in α -terpineol (bp 217 °C). It is used in the manufacture of some gas sensors, and to form carbon catalyst layers in dye-sensitized solar cells [20].

12.7 PVDF Properties

For general electrochemical measurements, there are many powerful constraints on the choice of binder. In addition to supplying a strong adhesive bond to the conducting filler, and a strong cohesive bond inside itself, the binder must also be wettable by water (i.e., exhibit a contact angle $<90^\circ$). It should also have a wide electrochemical stability window, a high purity, and be insoluble in a wide range of common solvents. For all of these reasons, PVDF is a good choice. It is a partially fluorinated semicrystalline polymer with excellent electrochemical and thermomechanical properties. In particular, it is electrochemically stable in the range of 0 to +5 V versus Li/Li⁺, it exhibits no thermal degradation below 300 °C, and its volume resistivity is $\geq 10^{14} \Omega \text{ cm}$.

To a first approximation, PVDF can be thought of as a bulk combination of two components: a high-density crystalline component and a low-density amorphous component. The observed density (ρ) of a given specimen is then given by the following formula:

$$\rho = f_{\text{crys}}\rho_{\text{crys}} + f_{\text{amorph}}\rho_{\text{amorph}}$$

where f_{crys} is the volume fraction of the crystalline component, ρ_{crys} is the density of the crystalline component (g cm^{-3}), f_{amorph} is the volume fraction of the amorphous component, and ρ_{amorph} is the density of the amorphous component (g cm^{-3}). For a typical commercial PVDF,

$$\rho_{\text{amorph}} \approx 1.68 \text{ g cm}^{-3}$$

$$\rho_{\text{crys}} \approx 1.88 \text{ g cm}^{-3}$$

and

$$f_{\text{amorph}} \approx 60\%$$

$$f_{\text{crys}} \approx 40\%$$

yielding a density of $\sim 1.76 \text{ g cm}^{-3}$ (as observed). This is almost twice the value of high-density polyethylene (0.93 g cm^{-3}). From a mechanical point of view, the crystalline component imparts rigidity to the binder, while the amorphous component imparts elasticity. The crystallinity also affects the melting point. The crystalline component melts sharply at 177 °C, whereas the amorphous component melts gradually over the range of 165–175 °C.

It is well known that, in the absence of surfactants, fully fluorinated polymers, such as poly(tetrafluoroethylene) (PTFE) and poly(perfluoroalkoxy ethylene) (PFA), cannot be wetted

by polar solvents. For this reason, they are not recommended as binders for screen-printed electrodes (although they do find specialist use in gas diffusion electrodes and lithium-thionyl chloride batteries). The physicochemical origin of their nonwettability lies in the fact that their fluorine atoms are densely packed together, so that their surface dipole is zero. By contrast, PVDF displays alternating CF_2 and CH_2 units at its surface, which allows the highly electronegative fluorine atoms to extract electrons from the nearby hydrogen atoms. The resulting surface dipoles interact strongly with nearby solvent molecules through dipole–dipole coupling and hydrogen bonding. As a result, PVDF is surprisingly wettable by water (contact angle $\sim 80^\circ$).

Unfortunately, if left in laboratory air for any length of time, PVDF surfaces tend to adsorb solvophobic impurities. As a result, aged electrodes containing PVDF may sometimes be difficult to wet with electrolyte solution. In such cases, the natural wettability of PVDF can be restored by prewetting the printed electrodes with isopropyl alcohol (IPA) or by adding surfactants to the electrolyte solution. Poor wettability is also a problem with PVDF copolymers such as PVDF-HFP, poly(vinylidene fluoride-co-hexafluoropropylene), which is sometimes used as an alternative to pure PVDF when enhanced flexibility is needed. Even though the pendant trifluoromethyl groups ($-\text{CF}_3$) of HFP successfully disrupt the crystalline regions of the PVDF, they also introduce significant solvophobicity. At the same time, the melting point of the copolymer falls by about 3°C for each 1% of HFP added.

12.8 PVDF Solubility

One of the paradoxes of screen printing is that the binder material must not dissolve in any of the common solvents used in electrochemistry, but must dissolve in at least one solvent to create the printing ink. This enigmatic requirement is in fact met by PVDF. It is insoluble in solvents having low Hildebrand solubility parameter ($\delta_{\text{H}} < 20 \text{ MPa}^{1/2}$), such as hydrocarbons, perfluorinated solvents, ethers, and glymes, and it is also insoluble in solvents having high Hildebrand solubility parameter ($\delta_{\text{H}} > 28 \text{ MPa}^{1/2}$), such as water and alcohols. However, it does dissolve in an elite group of solvents that have intermediate Hildebrand solubility parameters ($\delta_{\text{H}} = 20\text{--}28 \text{ MPa}^{1/2}$). A list of these is given in [Table 12.1](#). What all of these solvents have in common is that they have large dipole moments and weak internal hydrogen bonding – just like PVDF itself. The solubility parameters of PVDF have been summarized by Bottino *et al.* [25].

Table 12.1 Halogen-free, high-boiling solvents for PVDF

	mp (°C)	bp (°C)	Dipole moment (debye)	δ_H (MPa ^{1/2})	Flash point (°C)	
Propylene carbonate	PC	−49	242	4.98	27.2	132
Hexamethylphosphoramide	HMPA	+7	230	5.38	23.2	106
Gamma butyrolactone	GBL	−45	204	4.27	26.2	98
N-Methyl-2-pyrrolidone	NMP	−24	202	3.92	22.9	86
Dimethylsulfoxide	DMSO	+16	189	3.96	26.7	85
Isophorone	IP	−8	214	3.96	20.0	84
Acetophenone	AP	+19	202	3.15	20.8	82
Tetramethylurea	TMU	−1	177	3.44	21.7	66
N,N-Dimethylacetamide	DMAC	−20	165	3.81	22.7	63
N,N-Dimethylformamide	DMF	−61	153	3.86	24.8	58
Cyclohexanone	CH	−47	155	3.25	20.2	47

δ_H is the Hildebrand solubility parameter.

Flash points mainly from WolframAlpha [21]. Hildebrand values mainly from Ref. [22]. Other data from Refs. [[23, 24]].

Warning: hexamethylphosphoramide and isophorone are confirmed animal carcinogens. Warning: DMF and NMP are suspected embryotoxins.

In principle, any of the solvents listed in [Table 12.1](#) could be used to manufacture PVDF-based inks. However, because the curing of carbon inks typically takes place at $T > 110\text{ }^{\circ}\text{C}$ (to ensure the removal of water and other volatile impurities), most of the listed solvents find themselves evaporating above their flash points. The *flash point* of a solvent is defined as the lowest temperature at which its equilibrium vapor will ignite in air. As a consequence, only propylene carbonate can be evaporated with complete thermal safety. Further advantages of propylene carbonate are that (i) it has a mild odor, (ii) it is not strongly hygroscopic, and (iii) it is nontoxic by inhalation [26]. By contrast, the more widely used NMP has an amine-like odor, is strongly hygroscopic, and is a suspected human reproductive hazard [27]. As regards electrochemistry, the electrochemical stability window of propylene carbonate containing 0.1 M LiClO₄ as supporting electrolyte extends from −3.2 to +2.6 V (vs Fc/Fc⁺), which is highly attractive for general electrochemical purposes.

At room temperature, the rate of dissolution of semicrystalline PVDF is low in all known solvents, even though its glass transition temperature is −35 °C, and even though the free energy of mixing is negative. The reason for this reluctance to dissolve is the high density of the crystalline material, which kinetically hinders the ingress of solvent molecules. As a result, the solvent/PVDF mixture must be maintained at $T > 60\text{ }^{\circ}\text{C}$ for at least 3 days to ensure that the dissolution of PVDF proceeds to completion. Lower temperatures and shorter dissolution times may result in the formation of gels. In gels, submicrometer remnants of the crystalline polymer remain undissolved [28]. To help avoid gel formation, the solvent should also be

scrupulously dried, since a few percent of water can also cause gelling. Fortunately, all the solvents listed in [Table 12.1](#) can be dried over molecular sieve and then distilled under inert atmosphere before use. Alternatively, they can be stored inside burettes containing a mixture of molecular sieve and activated carbon, which conveniently minimizes their water content while also removing trace impurities. Solid PVDF powder can be dried in a vacuum oven.

12.9 Flexible Substrates

Flexible substrates for screen-printed electrodes must meet a range of demanding requirements, especially for display applications. Besides the most obvious requirement – low flexural rigidity – they also need high temperature stability, high solvent resistance, good optical clarity, microrough surface texture (± 50 nm), and low cost.

In general, however, the most important requirement is low flexural rigidity (low bending stiffness) D (N m^2). From an engineering perspective, this is related to the first power of the tensile modulus and the third power of the substrate thickness as follows:

$$D = \frac{Eb h^3}{12(1 - \mu^2)}$$

where E is the tensile modulus (Young's modulus, N m^{-2}), b is the substrate width, h is the substrate thickness, and μ is Poisson's ratio for the substrate material (0.3–0.5). In the absence of an exact value of the latter, it may be assumed $\mu \approx 0.5$, since this gives the worst-case value (highest value) of flexural rigidity. Evidently, the third-power dependence on h makes the substrate thickness the most important parameter in the system.

Widely used substrate materials include poly(ethylene naphthalate) and poly(ethylene terephthalate) of thickness 25–75 μm . A cheap commercial source of poly(ethylene terephthalate) is laser inkjet transparency film. Interestingly, both PEN and PET can withstand temperatures up to 180–220 $^{\circ}\text{C}$. PEN also has the advantage that it is about three times less permeable to water and oxygen than PET. Other widely used substrate materials include polycarbonate, polyimide, and PEEK. Some commercial plastic films are also obtainable with oxygen plasma-treated poly(urethane) primer layers on one side, to raise the surface energy and thereby improve the adhesion of inks.

12.10 Screen Printing Process

The screen printing process is in fact a type of stenciling, in which the carbon ink is forced through the open regions of a mesh screen to form a pattern on a surface. When viewing the process for the first time, most people imagine that the entire image is deposited simultaneously. However, the mesh screen actually stops 1–2 mm above the substrate, and the two come into contact only when the edge of a poly(urethane) “doctor blade” (a corruption of *ductor* blade) sweeps over them. This prevents the screen and the substrate from sticking together. [Figure 12.1](#) is a simplified representation of the screen printing process.

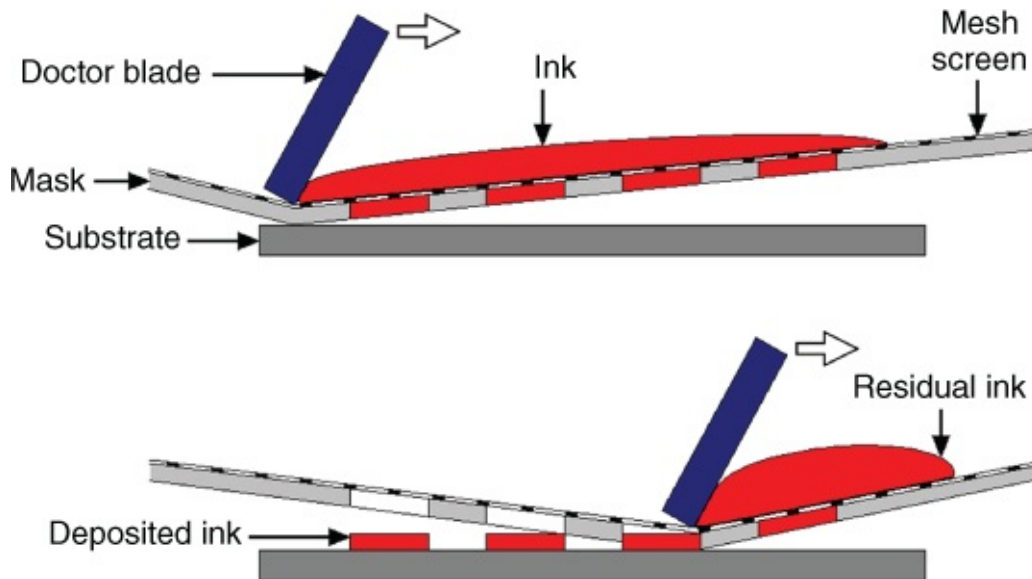


Figure 12.1 The screen printing process.

(From van Dijk [29].)

12.11 Screen Printing Materials

Screen printing uses mesh screens to support the ink before its extrusion onto the substrate. Three mesh materials are in common use: steel, polyester, and nylon. However, steel is preferred for making carbon electrodes because it possesses a greater open area, and thus allows more ink to transfer for each pass of the doctor blade. Steel is also very resilient, readily resuming its original position after the passage of the doctor blade.

Ink-free regions in the image are created by coating the mesh with a “mask” made of a rubbery ink-repelling polymer, usually poly(vinyl acetate). This mask defines the shape of the image by providing a boundary for the ink. The reproducibility of the printed image depends on the mesh's ability to form a gasket-like seal with the substrate when the doctor blade passes over it. In the laboratory, mask thickness and screen mesh size are commonly chosen by trial and error. The hole size and the wire diameter determine the thickness of the printed layer, while the wire spacing determines the resolution (and hence reproducibility) of the printed area. A physical model of the screen printing process has been described by Owczarek and Howland [30].

The screen mesh size is conventionally characterized by the number of wire strands per centimeter (spc), so larger spc values imply finer detail. High-definition stainless steel screens typically have 180 spc, creating apertures of 45 μm for strand diameters of 10 μm . To prevent screen blockage during printing, the maximum particle diameter should therefore be about one-third this value ($\sim 15 \mu\text{m}$). Particles above 20 μm can be removed by preliminary dry sieving. Mesh tensions are usually set around 30 N/cm, and printed film thicknesses are typically in the range of 15–150 μm ([Figure 12.2](#)).



Figure 12.2 Mesh and mask geometry.

In practice, there is a limit to layer thickness (and hence mask thickness) determined by the tendency of thick layers to crack during drying. At the other extreme, very thin layers tend to have high electrical resistance. After use, most screens can be safely cleaned with volatile esters (butyl acetate, ethyl acetate) or ketones (methyl isobutyl ketone, methyl ethyl ketone).

12.12 Ink Flow

From a colloid science point of view, carbon inks are two-phase gels. They consist of structured networks of solid particles thoroughly permeated by a polymer solution. As two-phase gels, they behave as classic non-Newtonian fluids, and commonly exhibit a decreased viscosity upon the application of a finite shear stress (thixotropy). The original viscosity is restored only after the shear stress is removed. Even though thixotropy is a nuisance in many industrial processes, screen printing in fact *requires* inks to be thixotropic. The reason for this is as follows. When first placed on the mesh screen, the ink must be so viscous that it remains immobile. Then, as the doctor blade passes over it, it must become so nonviscous that thousands of tiny droplets of ink extrude through the mesh and stick to the substrate. Finally, after the droplets have coalesced, the viscosity of the ink must rise again, in order to preserve the shape of the transferred image.

Because screen printing inks are thixotropic, they have a natural tendency to gel during storage. In most cases, this can be rectified by stirring (though not so vigorously that air bubbles are introduced). The optimum ink viscosity at the start of the screen printing process depends on the design parameters of the screen printer, but is generally about 10^3 poise ($= 10^5$ mPa s). Note, however, that an initial viscosity of this magnitude is no guarantee that a particular ink will print well, because it may not be shear-thinning enough to pass through the screen [31]. At a shear rate ($\dot{\gamma}$) of 10 s^{-1} (typical for a carbon ink passing through a steel mesh screen), the viscosity should fall to about 10 poise ($= 10^3$ mPa s).

12.13 Substrate Wetting

In order for a solvent to wet a substrate, its surface energy (surface tension) must be lower than that of the substrate. Since many common substrates such as polyester, polyimide, and polyacrylate all have surface energy values around 45 dynes cm^{-1} , screen printing solvents are normally chosen to have surface tension values around 40 dynes cm^{-1} . In this context, it should be noted that some common laboratory contaminants, such as silicone oils, have ultralow

surface energy values ($<22 \text{ dynes cm}^{-1}$), which means they must be excluded from screen printing apparatus.

The achievement of proper wetting is particularly problematic. There are only two ways of overcoming the failure of an ink to wet a substrate: (i) increasing the surface energy of the substrate and (ii) decreasing the surface energy of the ink. The surface energy of a substrate may be increased by oxygen plasma treatment to introduce polar functionalities. Alternatively, the surface energy of the ink may be decreased by the addition of surfactants. However, surfactants are a nuisance in many electrochemical systems. They aggregate in solution, adsorb at interfaces, and inhibit some electron transfer reactions. Indeed, the presence of surfactants in many commercial inks is a serious problem that is often overlooked by academic researchers. For biomedical applications, it should also be noted that some surfactants are endocrine disruptors, and therefore are not approved by the U.S. Food and Drug Administration (FDA).

The ability of an ink to resist detachment after deposition is known as **tack**. Tack is influenced by many different factors, both intrinsic and extrinsic. Intrinsic factors include (i) the surface energies of ink and substrate, (ii) the viscoelasticity (cohesive strength) of the ink, and (iii) the surface roughness of the substrate. Extrinsic factors include (iv) the printing force, (v) the contact time, and (vi) the ambient temperature.

Tack is quantifiable as the work per unit area needed to disbond an ink immediately after adhesion. This is given by the following formula:

$$w = \frac{1}{A} \int F \cdot v \, dt$$

where A is the geometrical contact area, F is the tensile force applied to the disbonding process, and v is the rate of separation. The work w (also known as **the adhesive failure energy**) was originally developed by Gent, Kinloch, and Andrews [32–34] to quantify the strengths of adhesives. Good tack is important in the screen printing process because inks must resist pull-away as the mesh screen relaxes. On the nanometer scale, tack is generated in a patch-wise manner by the formation of multiple molecular contacts between the polymer binder and the substrate. Unsurprisingly, therefore, the greater is the contact time, the greater is the number and size of adhesive patches, and the better the resulting tack.

12.14 Commercial Ink Additives

Commercial screen printing inks contain diverse mixtures of additives, including pigments, plasticizers, surfactants, extenders, dispersants, and waxes. Pigments are used to control color. Plasticizers are used to soften binders and improve the flexibility of the finished product. Surfactants are used to decrease the surface tension of the solvent. Extenders are used to lower cost. Dispersants are used to avoid particle coagulation, and waxes are used to improve the rub resistance and gloss of the finished product. All these additives are undesirable in electrochemistry and should be excluded from carbon inks.

12.15 Binder Percentage

Both laboratory experiments and computer simulations have shown that the random close packing of equal-sized, spherical-shaped particles occupies a volume percentage of 64%. It follows that, if we want to eliminate porosity in such a system, then we must fill the remaining 36% of space (the “dead volume”) with an inert binder. By contrast, if we want to retain some porosity, then a certain fraction of the dead volume must be kept free of binder. On the basis of a 50/50 compromise between electrode cohesion and solution access, one may therefore reasonably conjecture that the volume percentage of inert binder should be ~18%, and indeed this is a good starting point in the laboratory development of inks from equal-sized, spherical-shaped particles.

Of course, lower volume percentages of inert binder can be used if some of the dead volume is packed with smaller particles of the conducting material (fines). Indeed, if the fines are equally sized among themselves, then the revised dead volume falls to 13% (i.e., 36% of 36%) and the volume percentage of inert binder that is needed to create a functioning porous electrode falls to 6.5%. At the other extreme, a volume percentage of binder higher than 18% could conceivably be used, but this would also increase the electrical resistance of the electrode.

12.16 Multilayered Electrodes

The basic elements of a multilayered electrode are shown in [Figure 12.3](#). Each part has its own design specification, depending on end use. First, electrode materials have to withstand both oxidizing and reducing conditions. Second, total electrode resistance should be below $10\ \Omega$ to minimize errors associated with IR drop. Third, electrodes must have electroactive areas which are reproducible within 5% coefficient of variation. Fourth, during manufacture, all materials must withstand repetitive thermal cycling to $T > 110\ ^\circ\text{C}$. Fifth, all the electrode materials must be mutually adhesive. Sixth, there has to be a complete absence of electroactive impurities.

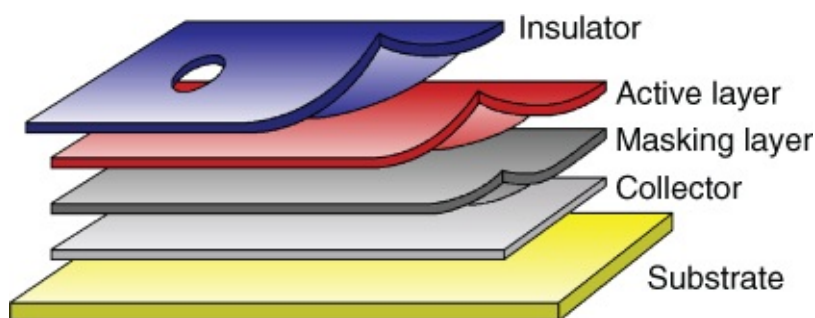


Figure 12.3 The basic elements of a multilayered electrode.

In addition to the above criteria, an insulator may be used to mask the final electrode layer and to define the size of the geometric area exposed to the solution. This insulator must be viscous enough not to creep (in order to create a well-defined electrode area) yet it must flow evenly under the pressure of the doctor blade to ensure good coverage. It must also be very pure. Preferably, it should also have a thermal expansion coefficient close to that of the printed ink,

to prevent disbonding of the printed layers.

12.17 IR Drop

The electrical resistance of printed carbon electrodes made from standard commercial inks is about $50 \Omega \text{ cm}^{-1}$, for a 1-cm-wide strip. Since practical test cells typically require a contact strip at least 5 cm long, this implies an *IR* drop of $\sim 250 \text{ mV}$ for a 1 mA current. For voltammetric work, this is completely unacceptable. To overcome this problem, a well-conducting silver layer is usually printed underneath the active layer. This decreases the total resistance to below $0.5 \Omega \text{ cm}^{-1}$, but makes it necessary to block the unwanted electrochemistry associated with the silver surface. This latter is readily achieved by overprinting the silver layer with a layer of nonporous graphite secured with an epoxy binder. A scanning electron microscope image of a cross section of an electrode of this type is shown in [Figure 12.4](#).

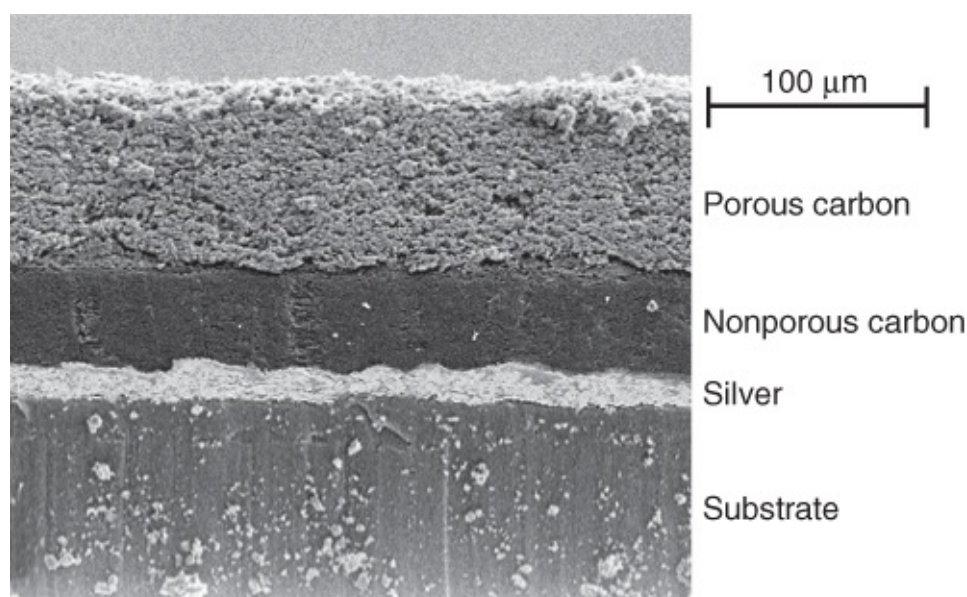


Figure 12.4 A scanning electron microscope image of a cross section of a screen-printed porous carbon electrode having a low *IR* drop.

(From van Dijk [29].)

12.18 Areal Capacitance

The areal capacitance of carbon electrodes depends strongly on carbon type. Graphite is the simplest case to consider, because it lacks surface functionalities. In this special case, the areal capacitance may be represented, to a first approximation, as the weighted sum as follows:

$$C_{\text{total}} = \theta \hat{C}_{\text{basal}} + (1 - \theta) \hat{C}_{\text{edge}}$$

where C_{total} is the total areal capacitance and $\hat{C}_{\text{basal}}$ and $\hat{C}_{\text{edge}}$ are the *areal capacitance components* of the basal plane and edge plane, respectively. Rough estimates, in strong electrolyte solutions, are $\hat{C}_{\text{basal}} = 2 \mu\text{F cm}^{-2}$ and $\hat{C}_{\text{edge}} = 70 \mu\text{F cm}^{-2}$. (The idea that the capacitance

of carbon can be decomposed in this way seems to have originated in the work of Randin and Yeager [35] and Rice and McCreery [36].)

By contrast, activated carbon, such as glassy carbon, has multiple surface functionalities which vary with provenance and pretreatment. Typically, these functionalities are oxygen-type and undergo reversible Faradaic reactions that manifest as a very large “pseudo-capacitive” component $\hat{C}_{\text{pseudo}} \approx 400 \mu\text{F cm}^{-2}$ in the total response. For some applications (e.g., supercapacitors), it is in fact desirable to increase the pseudo-capacitive component. However, because the surface coverage of oxygen functionalities is sterically restricted to ~25% by the need for them to be covalently attached to the carbon substrate, the maximum areal capacitance is $\sim 100 \mu\text{F cm}^{-2}$ on a flat electrode surface, and is often only one-fifth of that. For other applications, such as anodic stripping voltammetry on glassy carbon electrodes, functionality-free surfaces are preferred. These typically have areal capacitances in the range of $2\text{--}10 \mu\text{F cm}^{-2}$.

The origin of the high capacitance of edge-plane carbon ($70 \mu\text{F cm}^{-2}$) is somewhat mysterious, but may be due to a locally enhanced population of charge carriers inside the lattice edges. On the other hand, the surprisingly low-capacitance component of basal plane carbon ($2 \mu\text{F cm}^{-2}$) is almost certainly due to the presence of a space-charge capacitance (C_{sc}) in series with the capacitance in solution:

$$C_{\text{basal}}^{-1} = C_{\text{sc}}^{-1} + C_{\text{solution}}^{-1}$$

12.19 Equivalent Circuit

Recently, a new equivalent circuit was proposed for porous carbon electrodes ([Figure 12.5](#)). Naively, one might suppose that this would involve multiple ladder networks in parallel, in order to model the response of multiple pores in parallel. However, the somewhat surprising result is that the circuit in [Figure 12.5](#) is able to capture the complete multipore behavior [37].

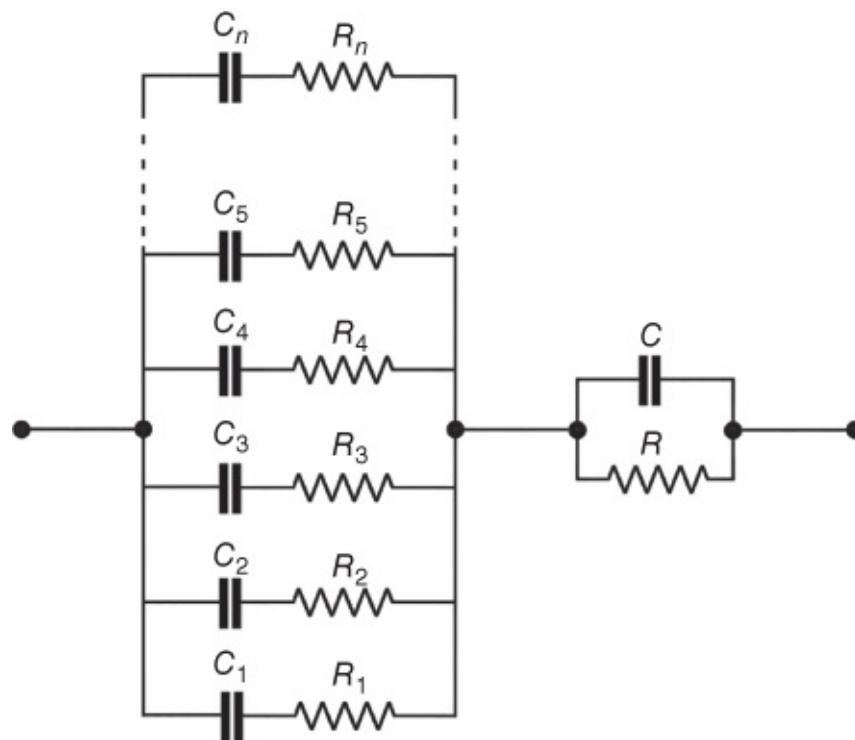


Figure 12.5 The equivalent circuit of a porous carbon electrode. It consists of a single vertical ladder network in series with an RC parallel network. The ladder network models the response of pores in the body of the electrode, whereas the solitary RC parallel network models the response of the electrolyte solution. (In many cases, the capacitance of the electrolyte solution is better represented as a constant-phase element.)

The equivalent circuit shown in [Figure 12.5](#) explains the three most striking properties of large-area carbon electrodes, namely their propensity to exhibit voltage decay at open circuit, their loss of equivalent-series capacitance at high frequency, and their voltammetric distortion at high scan rate. It also explains the shape of observed complex plane impedance plots over the entire frequency range. For screen-printed porous carbon electrodes (whether in aqueous, organic, or ionic liquid solution), one generally finds that the solitary RC parallel network on the right-hand side of [Figure 12.5](#) dominates the impedance response at high frequencies (>1 kHz, say), because this corresponds to the resistance of the electrolyte solution. By contrast, the vertical ladder network dominates the impedance response at low frequencies. In the latter case, the time constants of the “rungs” of the ladder network correspond to charge/discharge phenomena deep inside pores, and empirically these are found to occur over many orders of magnitude, from milliseconds to kiloseconds.

Finally, it should be noted that the resistance of all graphitic carbons is generally insignificant compared with the resistance of their liquid-filled pores, so it is the liquid-filled pores that determine the RC time constants in the system. For example, the room temperature conductivity of activated carbon is about $0.06 \times 10^3 \text{ S cm}^{-1}$, whereas that of aqueous sulfuric acid at its conductivity maximum (31 wt%) is $830 \times 10^{-3} \text{ S cm}^{-1}$. Hence, even in this extreme case, the pore channels containing sulfuric acid are more resistive than the pore walls by a factor of ~ 70 . The ratio is even more extreme in the case of organic solvents and ionic liquids.

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