Surface Electrochemistry

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Nanotrench Arrays Reveal Insight into Graphite Electrochemistry**

*Trevor J. Davies, Michael E. Hyde, and Richard G. Compton**

Over the past few decades the popularity of carbon as an electrode material has increased dramatically. The fact that so many different types of carbon materials are commercially available has led to their use in a wide range of applications.[1] However, despite the large amount of research conducted with carbon electrodes, there still remains uncertainty about the individual roles of the edge-plane and basal-plane regions in the electrochemical response of a graphite surface. Herein, we address this fundamental problem and introduce a novel approach to investigate the source of the electrochemical reactivity of graphite.

A good way to understand the electrochemical properties of graphite electrodes is to study the voltammetry of well-defined graphite surfaces. For this reason, basal-plane highly ordered pyrolytic graphite (HOPG) is an attractive material; the surface consists of atomically flat basal-plane graphite terraces separated by steps and defects which expose extremely thin bands (multiples of 0.335 nm) of edge-plane graphite.[1,2] Accordingly, the voltammetric characteristics of basal-plane HOPG electrodes in simple redox couples are well-documented.[1,3,4] HOPG cyclic voltammograms provide relatively poor fits to linear diffusion simulations and display an increased peak-to-peak separation, indicative of slow electron-transfer kinetics relative to other electrode materials.[1,3–5] These characteristics become more pronounced if fewer defects are present on the surface.[6–8]

With the aid of a 2D simulation approach that allowed us to take the actual size and separation of surface defects into account, we recently demonstrated that the characteristics of HOPG cyclic voltammograms are consistent with the voltammetry of a macroarray of nanobands (edge-plane steps).[9,10] In other words, for the range of redox couples considered, the basal plane was effectively inert (Supporting Information). Given that edge-plane steps can make up less than 0.5 % of the total electrode area, and heterogeneous electron-transfer electrons are known to occur at basal-plane terraces as well as edge-plane steps,[11,15] the suggestion that basal-plane graphite makes no contribution to HOPG voltammograms is quite controversial.

For the work reported herein, we sought to prove beyond any doubt that the cyclic voltammetry response of basal-plane HOPG is solely due to the edge-plane steps present as defects on the electrode surface by selectively blocking the basal-plane terraces to leave only the edge-plane defects uncovered; covering the basal-plane terraces with inert material should make no difference to the observed voltammetry. Although heterogeneous electron-transfer reactions occur at basal-plane terraces, a combination of nonlinear diffusion and the large difference in reactivity between basal- and edge-plane graphite gives cyclic voltammograms in which the basal-plane terraces appear to be inert. For example, a previous study in which we compared experimental and simulated cyclic voltammograms for the oxidation of ferrocyanide at an HOPG electrode produced results suggesting that the electron-transfer rate constant for the edge-plane oxidation was 0.022 $\mathrm{cm\,s^{-1}}$, whereas that for the basal-plane reaction was less than 10^{-9} $\mathrm{cm\,s^{-1}}$. Furthermore, as all graphite electrodes are made from essentially the same building blocks (graphene sheets) we can expand our conclusions to other carbon materials such as pyrolytic graphite, carbon fibers, and even carbon nanotubes.[10]

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[*] T. J. Davies, M. E. Hyde, Prof. R. G. Compton
Physical and Theoretical Chemistry Laboratory
Oxford University
South Parks Road, Oxford OX1 3QZ (UK)
Fax: (+44) 1865-275-410
E-mail: richard.compton@chemistry.ox.ac.uk

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To generate an HOPG surface upon which the basal plane is selectively covered, we employ a three-stage method that involves the initial "protection" of the edge-plane steps, followed by "passivation" of the remaining carbon, and then the re-exposure of the edge-plane sites. This results in the formation of "nanotrenches" (relatively long grooves in the electrode surface with nanometer-scale dimensions in width and depth) which we identify by using AFM. The contribution of edge-plane steps to basal-plane HOPG voltammograms can then be assessed by comparing the cyclic voltammetry of the nanotrench arrays with that of the freshly cleaved basal-plane HOPG.

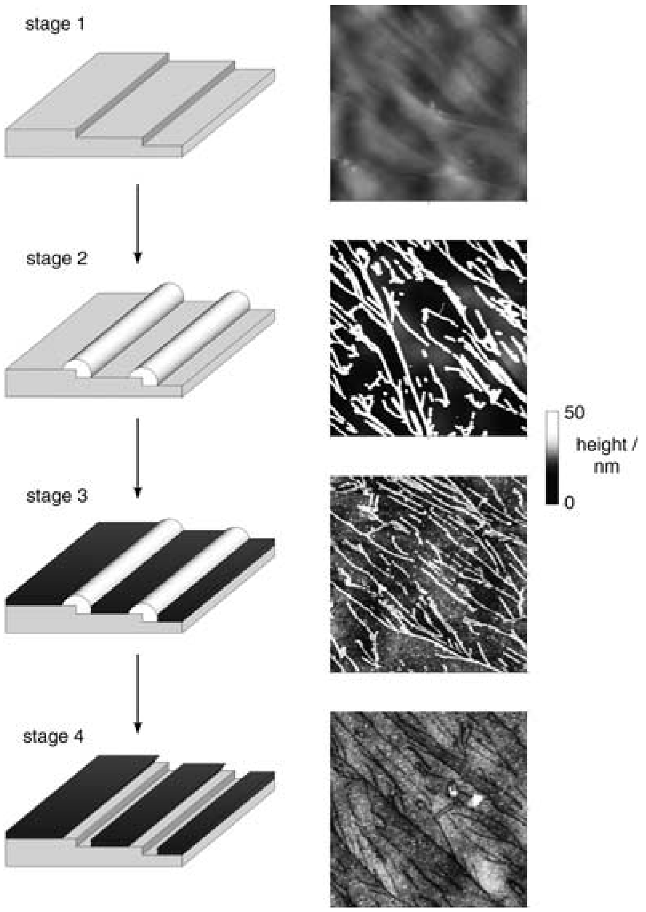

Figure 1. Schematic diagram and corresponding AFM images ($5\times5\mu m^2$ each) of the four stages involved in nanotrench fabrication.

Figure 1 outlines the stages involved in nanotrench formation, along with the corresponding AFM images ($5\times 5\,\mu m^2$ each). Initially, a HOPG slab of the highest quality ($10\times10\times2$ mm^3, SPI 1 grade, equivalent to ZYA grade of Union Carbide[12]) was adhesively cleaved to produce a fresh surface, as illustrated in Figure 1, stage 1 (only relatively large edge-plane steps are resolved owing to the resolution limits of the AFM scanner used). The following electrochemical experiments with the HOPG slab were conducted with the HOPG housing previously described, which resulted in an exposed electrode area of 0.32 cm^2.[13]

Recently, Penner and co-workers reported that the electrodeposition of MoO_2 (by Equation (1)) at a basal-plane HOPG surface occurs exclusively at edge-plane sites (at the appropriate deposition potential) resulting in the formation of MoO_2 nanowires along the edge-plane steps.[14–16]

$$MoO_4^{2-} + 2\,H_2O + 2\,e^- \rightarrow MoO_2 + 4\,OH^- \qquad (1)$$

Following the procedure of Penner and co-workers, MoO_2 nanowires were electrodeposited on HOPG from a solution of sodium molybdate (1.1 mM) in sodium chloride (1M) and ammonium hydroxide (1M) adjusted to pH 8.5 with sodium hydroxide. The AFM image in Figure 1 for stage 2 was recorded immediately after nanowire deposition at -1.0 V versus standard calomel electrode (SCE) for 130 s, and illustrates an ensemble of nanowires ≈ 50 nm in diameter (the average thickness has been shown to depend on the deposition time, which permits the preparation of specific diameters[15]). Further experiments confirmed that the wires were indeed on edge-plane steps. Experiments at short deposition times produced incomplete nanowires for which it was possible to see the edge-plane steps emerging from the ends of the nanowires (that is, these further experiments confirmed the wires had been formed along the edge-plane steps).

With the edge-plane sites covered, the HOPG surface was effectively passivated by nitrophenyl radicals, formed from the electrochemical reduction of 4-nitrobenzenediazonium cations. Savéant and co-workers demonstrated that the reduction of diazonium salts yields N_2 and a radical, which aggressively chemisorbs to both the edge and basal planes of graphite.[17–18] Stage 3 in Figure 1 illustrates the HOPG surface after electroreduction at -0.5 V versus SCE for 30 s in a stirred solution containing 4-nitrobenzenediazonium tetrafluoroborate (1.2 mM) and tetrabutylammonium perchlorate (0.1M) in acetonitrile. The AFM image displays a clear change in texture of the material surrounding the nanowires (the basal-plane terraces) consistent with the formation of a thin film. Because the nanowires are composed of MoO_2 (an electrically conductive metal oxide), chemisorption of the nitrophenyl radicals to the nanowire surface should not be possible. Furthermore, comparison of the images for stages 2 and 3 in Figure 1 reveals that the surface surrounding the nanowires is relatively higher after treatment with diazonium salt. Thus the nanowires are not as prominent after the modification which also suggests the presence of a thin film formed over the basal-plane terraces.

In the final stage, the nanowires are removed by placing the HOPG surface in a stirred solution of hydrochloric acid (1M) for 300 s.[19] As observed for stage 4 in Figure 1, this results in the formation of nanotrenches along which the edge-plane steps reside. Figure 2 illustrates more AFM images of these nanotrenches at various scan ranges. Similar nanotrenches were observed on a large number of different sections of the HOPG surface which confirms that the acid treatment only removed the nanowires and not the basal-plane coating. As observed from the inset section analysis, the depth of the nanotrenches is ≈ 8 nm, which is significantly deeper than expected from a monolayer coverage. Given that

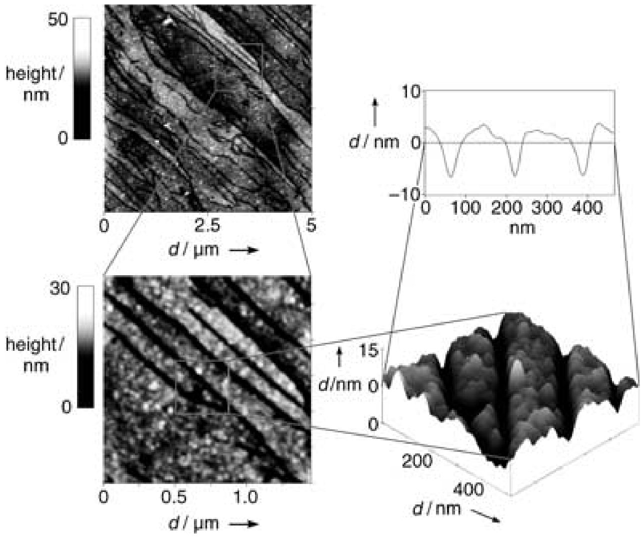

Figure 2. AFM images of nanotrenches at various scan ranges and perspectives.

the length of a nitrophenyl group is ≈5 Å,[20] the walls of the nanotrenches correspond to approximately 15 monolayers. Previous work by more than one research group has concluded that a monolayer is formed when diazonium salts are reduced at carbon electrodes.[17,18,21,22] However, our system is slightly different in that the nitrophenyl radicals should not chemisorb to the MoO_2 nanowires. This allows more nitrophenyl radicals to be generated than would be on a pure graphite surface. The AFM images provide clear evidence of a "multilayer" film which could be caused by the attack of nitrophenyl radicals on an already modified surface. Indeed, for experiments in which no MoO_2 was present, no evidence was found of a multilayer film after reduction of the diazonium salt. Alternatively, the nitrophenyl radicals could induce a polymerization reaction that forms a thin polymer film over the electrode surface rather than a chemisorbed multilayer.

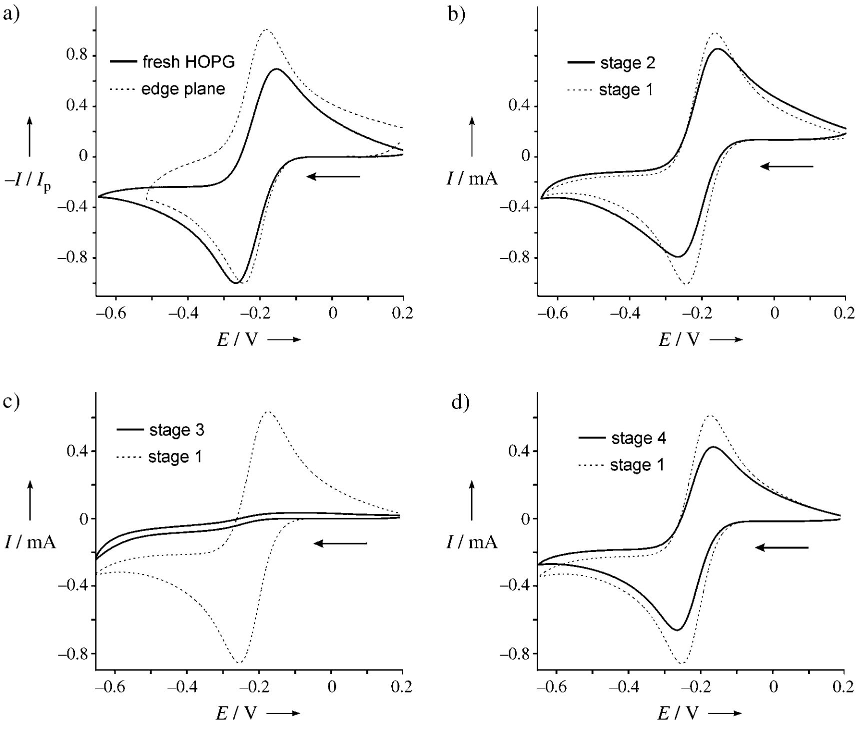

Figure 3. Cyclic voltammograms for the reduction of 1.1 mM $[Ru(NH_3)_6]^{3+}$ at a HOPG electrode (versus SCE) after each stage of nanotrench fabrication (——): a) stage 1, b) stage 2, c) stage 3, d) stage 4. The voltammogram ----- in a) was obtained from the same experiment with an edge-plane pyrolytic graphite electrode. Voltammograms ----- in b)–d) were obtained after stage 1 of nanotrench fabrication; experimental details are given in the text.

Having developed an experimental method that selectively blocks the basal-plane terraces, we were next able to turn our attention to identifying the role of edge-plane defects in HOPG cyclic voltammetry. Figure 3 illustrates four cyclic voltammograms taken with an HOPG electrode in $[Ru(NH_3)_6]^{3+}$ (1.1 mM) at each of the four stages of nanotrench synthesis. Figure 3a illustrates a cyclic voltammogram with a freshly cleaved HOPG electrode taken at 2.0 V s^{-1}. Overlaid as a dashed curve is the corresponding response from an edge-plane pyrolytic graphite electrode 5 mm in diameter (in this case, the difference in surface area between the two electrodes required that the y axis be represented by I/I_p instead of I). Analysis of the edge-plane experimental data with DigiSim gave $D_{[Ru(NH_3)_6]^{3+}} = 8.0\times10^{-6}$ cm^{2}s^{-1} and $k^\circ_{edge} = 0.4$ cm s^{-1} for the $[Ru(NH_3)_6]^{3+}/[Ru(NH_3)_6]^{2+}$ system. The corresponding fit of the HOPG voltammogram to DigiSim gives the effective electron transfer rate constant: $k^\circ_{eff} = 0.018$ cm s^{-1}. The term "effective electron transfer rate constant" is used rather than k°_{basal} because the surface is electrochemically heterogeneous, and its response is clearly dependent on the population of defects.[9] If our previous conclusion is correct, then the HOPG voltammogram in Figure 3a is solely the result of the tiny amount of edge-plane defects on the HOPG surface.[9] By using the method outlined in reference [9], the coverage of edge-plane defects can be approximated as: $\Theta_{edge} = \frac{k^\circ_{eff}}{k^\circ_{edge}} = 0.045$. Thus, 4.5% of the surface is edge-plane graphite, which agrees well with the appropriate STM studies of Bard and Chang.[2] It follows that selective blockage of the basal-plane terraces should have no effect on the voltammetry.

Figure 3b illustrates the voltammogram recorded at 0.2 V s^{-1} immediately after stage 2 of the nanotrench fabrication process, in which MoO_2 was deposited along edge-plane steps. Overlaid is the corresponding voltammogram from stage 1, that is, the freshly cleaved HOPG surface at 0.2 V s^{-1}. As observed, the HOPG with MoO_2 nanowires instead of edge-plane steps gives a response with a larger peak-to-peak separation (ΔE_p) than the freshly cleaved HOPG. This indicates slower electrode kinetics and agrees with the hypothesis that the HOPG response is that of a nanoband array.[9] Although MoO_2 is electrically conductive, one might expect an MoO_2 electrode to display slower electrode kinetics than that of a noble metal, for example. For a random array of nano- or microbands in which the surface coverage is Θ, the peak-to-peak separation is approximately that expected for a cyclic voltammogram in the same system at a macroelectrode with an electron transfer rate constant of $\Theta k^{\circ}_{\text{mat}}$, in which k°_{mat} is the electron transfer rate constant of the nano- or microband material.[9,23] Therefore, as k°_{edge} is expected to be greater than $k^{\circ}_{\text{MoO}_2}$, the increased ΔE_p is easily explained. The decrease in peak current was a general characteristic observed after each stage of the process and is probably due to relatively large defects created as a result of adhesive cleaving,[2] and thus becoming inactive or separated from the surface.

Figure 3c illustrates the cyclic voltammogram recorded immediately after stage 3, in which the scan rate is $0.2\,\text{V}\,\text{s}^{-1}$. As before, the corresponding voltammogram obtained from a freshly cleaved HOPG surface is overlaid (-----). The reduction of the diazonium salt appears to have passivated the entire surface (both the MoO_2 nanowires and basal-plane terraces), with only a tiny response from the modified electrode. As discussed above, nitrophenyl radicals are not expected to chemisorb to MoO_2. This suggests a more plausible result of generating nitrophenyl radicals in the absence of edge-plane graphite through a polymerization reaction which effectively blocks the entire surface. Although this may be unexpected, it does show that the surface is sufficiently blocked by the generation of nitrophenyl radicals.

Figure 3d shows the cyclic voltammogram obtained immediately after the final stage, along with the corresponding response obtained at stage 1 (freshly cleaved HOPG). As observed, the two voltammograms are almost identical, with the small difference in ΔE_p probably the result of a slight loss in activity of the edge-plane sites caused by the preceding treatments. In the case of the modified electrode, only the edge-plane steps located along the bottom of the nanotrenches are exposed to the solution (that is, we have effectively created an array of nanobands).[24] Thus, as predicted for a simple redox couple, the cyclic voltammetric response of a basal-plane HOPG electrode is solely due to the edge-plane defects, no matter how small their coverage may be (which can be as low as 0.2 %[11]). The basal-plane graphite terraces have no influence on the voltammetry and are effectively inert; blocking the basal-plane sites results in no overall change to the observed voltammetry.

Cyclic voltammetry with the nanotrench arrays was performed in other redox couples and gave exactly the same results. Figure 4 shows the voltammetric response at $200\,\text{mV}\,\text{s}^{-1}$ taken at stage 1 (-----) and stage 4 (——) for the oxidation of a) 2,3,5,6-tetramethyl-1,4-phenylenediamine (TMPD, 1.1 mM) and b) ferrocyanide (1.1 mM) for which the background electrolyte is KCl (0.1M) in both cases. Figures 4a and b clearly show that the ensemble of nanotrenches gives almost identical I-E signals to the freshly cleaved HOPG.

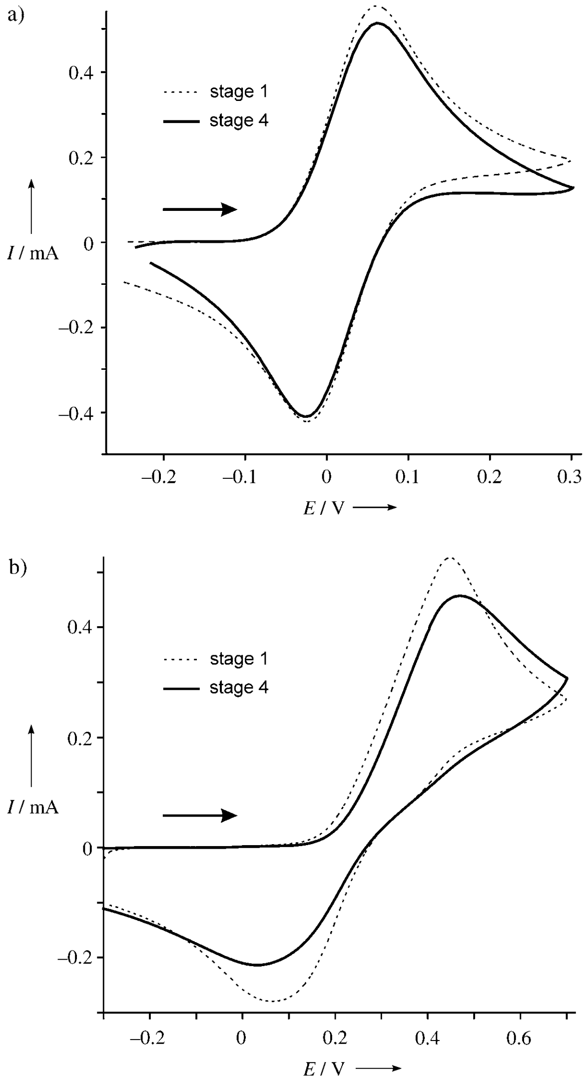

Figure 4. Cyclic voltammograms (versus SCE) taken at stage 1 (-----) and stage 4 (——) of nanotrench fabrication for the oxidation of a) TMPD (1.1 mM) and b) ferrocyanide (1.1 mM); experimental details are given in the text.

In conclusion, performing cyclic voltammetry with our nanotrench arrays has answered and raised some fundamental questions. For example, we now know categorically that edge-plane sites are responsible for the cyclic voltammetric response of a basal-plane HOPG electrode; there is no reason why these findings cannot be applied to other carbon materials such as carbon nanotubes (which are effectively rolled-up graphene sheets).[10,25] Furthermore, our nanotrenches could have major applications for the synthesis of nanowires, which is currently under investigation. What, however, are the implications for basal-plane graphite? The results of electrodeposition experiments demonstrate that basal-plane graphite cannot be electrochemically inert.[15] Conversely, our simulations show that k°_{basal} is significantly smaller than k°_{edge}. Otherwise, we would observe strange voltammetric characteristics.[9] The value of k°_{basal} could be determined by performing the inverse of this experiment and selectively blocking the edge-plane steps. This is currently under investigation. However, an important question to consider is why there is such a large difference in electrochemical reactivity between basal and edge-plane graphite.

To answer this question one must attempt to link electrochemical activity with electronic structure.[4] Theoretical calculations predict graphite to have both semiconductor and metallic properties, in that the density of states (DOS) at the Fermi Level, E_f, is smaller than that of a metal, but there is no band gap.[26,27] The problem to consider is how the 3D pristine graphite DOS relates to our HOPG electrode surface.

In a differential capacitance study on basal-plane HOPG, Gerischer and co-workers determined the DOS around E_f to be both qualitatively and quantitatively similar to the most popular theoretical models for graphite.[28] It can therefore be inferred that the theoretical calculations for graphite are relevant to basal-plane terraces. This is not surprising; the major contribution to the DOS diagram for graphite comes from orbital overlap in the planes of individual graphene sheets, so exposing the basal plane should not have a significant effect. (Indeed, the DOS diagrams for a 2D graphene sheet and 3D graphite are similar.[27]) In addition to well-established parameters such as reorganization energy, the rate of electron transfer (reflected in the value of $k°$) also depends on the surface concentration of electrons. The electron-transfer reaction proceeds by electron tunneling; the more electrons present, the more likely it is that a tunneling event will occur.[4,29]

For metals such as gold, the DOS at E_f is relatively large, and the rates of electron transfer depend on the properties of the redox system with the electrode band structure having no limiting effect.[4,30] However, redox reactions for which the DOS at E_f is much smaller (or even zero) are limited by the low surface concentrations of electrons.[4,29] Basal-plane graphite appears to fall into this category, effectively behaving like a semiconductor with zero band gap, in agreement with the DOS diagram for graphite.

McCreery and co-workers have shown edge-plane graphite to have a capacitance over 30-fold that of basal-plane graphite.[7] Furthermore, electrochemical reactions at edge-plane pyrolytic graphite electrodes for a wide range of redox couples possess similar $k°$ values to those conducted at metal electrodes. Therefore, electron surface concentration is not a limiting factor for edge-plane graphite, and the theoretical calculations for pristine graphite are clearly not relevant. Indeed, exposed edge-plane graphite is expected to have a far different electronic structure than 3D pristine graphite, with the "cut-off" along the surface severely disrupting the main orbital interactions.

There is notable overlap between the conclusions reported herein and those of Gerischer et al.[28] In a differential capacitance study, the experimentally observed capacitance (C_{obs}) for the HOPG surface is expected to scale with the relative areas of edge-plane and basal-plane graphite, as expressed in Equation (2) in which C_i is the capacitance of the

$$C_{obs} = \frac{A_{basal}}{A_{HOPG}} C_{basal} + \frac{A_{edge}}{A_{HOPG}} C_{edge} \tag{2}$$

given electrode material, A_{HOPG} is the total area of the HOPG electrode, and A_i is the total surface area of the given electrode material. Therefore, by using high quality basal-plane HOPG, Gerischer and co-workers were able to minimize the contribution of edge-plane graphite and obtain experimental data attributable to basal-plane graphite. In the case of cyclic voltammetry, the experimental observation is an $I-E$ response, $I-E$(HOPG). Owing to the depleting effects of nonlinear diffusion, the individual contributions of edge and basal-plane graphite do not scale with relative areas; Equation (3) is thus a more appropriate description in which

$$I-E_{HOPG} = \beta[I-E_{basal}] + \varepsilon[I-E_{edge}] \tag{3}$$

$I-E_i$ is the cyclic voltammetry response for the given electrode material and β and ε are complicated functions that take into account the relative areas and sizes of the two electrode materials as well as nonlinear diffusion. For HOPG cyclic voltammetry at scan rates of $\approx 1\,\mathrm{V\,s^{-1}}$ and diffusion coefficients greater than $\approx 10^{-6}\,\mathrm{cm^2\,s^{-1}}$, $\beta = 0$, so there is no contribution from the basal-plane terraces as evidenced by the work reported herein. This means that unlike the results of Gerischer et al.,[28] the use of HOPG in cyclic voltammetry experiments (with the aforementioned parameters) will not provide experimental results that are attributable to basal-plane graphite. The same can be said for all other types of graphite electrodes. Therefore, to obtain a response from which kinetic parameters for basal-plane graphite could be determined would require setting ε to zero (by selectively blocking edge-plane sites) or by making $\beta > 0$. This approach is currently under investigation.

Previously, researchers described anomalously slow kinetics for basal-plane HOPG electrodes relative to their edge-plane counterparts. Our work herein shows that edge-plane defects are responsible for the voltammetric response at basal-plane HOPG electrodes, with the basal plane being effectively inert. A k°_{basal} value significantly less than that of a metal (that is, k°_{edge}) agrees with the extensive amount of theoretical work on the electronic structure of graphite.[26,31–33] Therefore, we suggest the more appropriate perception that *electrochemical reactions at edge-plane graphite are anomalously fast*. Whatever the reason for this, the fact that massive changes in electronic structure occur over the traverse of a basal-plane HOPG surface is quite fascinating.

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