

## Comment on Electrochemical Kinetics at Ordered Graphite Electrodes

Richard L. McCreery\* and Mark T. McDermott

Department of Chemistry, National Institute for Nanotechnology, University of Alberta, Edmonton, Alberta, Canada T6G 2A1

Although carbon electrodes have been used in electrochemistry for more than a century, there has been renewed recent interest in electron transfer at carbon surfaces due to the development of graphene and carbon nanotube (CNT) materials. This Comment regards reports of heterogeneous electron transfer (ET) rates on highly ordered pyrolytic graphite (HOPG), which is often used as a model for single crystal graphite. The atomically smooth, hexagonal “basal” plane is exposed by cleaving HOPG, and then voltammetry and related techniques are used to investigate ET rates to various redox systems, often ferrocene (Fc),  $\text{Fe}(\text{CN})_6^{3-/4-}$ , or  $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ . The resulting heterogeneous electron transfer rate constant ( $k^0$ , cm/s) is used to investigate the factors which affect the reactivity of the electrode, including any differences between graphene, CNTs, basal plane HOPG, and other carbon materials.<sup>1–3</sup> Since HOPG basal plane is the most ordered and best characterized graphite surface, it is appropriate to compare ET kinetics on the basal plane to more recently developed carbon electrodes. In the early 1990s,<sup>4–8</sup> we concluded that HOPG basal plane exhibits  $k^0$  values for 18 redox systems which are 1–3 orders of magnitude slower than those on glassy carbon, which has mixed basal and edge plane. For  $\text{Fe}(\text{CN})_6^{3-/4-}$  in 1 M KCl, the observed  $k^0$  on low-defect basal plane was  $10^{-5}$  to  $10^{-6}$  cm/s,<sup>7</sup> while that on glassy carbon with its many exposed graphitic edges was  $>0.1$  cm/s, depending on pretreatment.<sup>4,9</sup> We attributed the low  $k^0$ , low capacitance, and low electrochemically observed adsorption of anthraquinone 2,6 disulfonate (AQDS) to the low density of electronic states on basal plane originally reported by Gerischer<sup>10</sup> and Yeager.<sup>11</sup> However, more recent publications from several authors have reported a wide range of  $k^0$  values for  $\text{Fe}(\text{CN})_6^{3-/4-}$  and Fc on basal plane HOPG,<sup>12–14</sup> CNTs,<sup>15,16</sup> and graphene.<sup>2,13</sup> For example, reports regarding kinetics of  $\text{Fe}(\text{CN})_6^{3-/4-}$  on basal plane HOPG have concluded that “basal plane HOPG is highly active”<sup>14</sup> or “the basal plane was effectively inert”.<sup>12,17</sup> In order to fully understand the dependence of ET kinetics on the nature of the graphite surface, two discrepancies need to be resolved. First, why do reported  $k^0$  values for supposedly simple outer-sphere redox reactions vary by orders of magnitude on basal plane HOPG? Second, should we expect  $k^0$  on basal plane HOPG for such redox systems to be similar to that on the sides of CNTs or the basal surface of a single-layer graphene sheet?

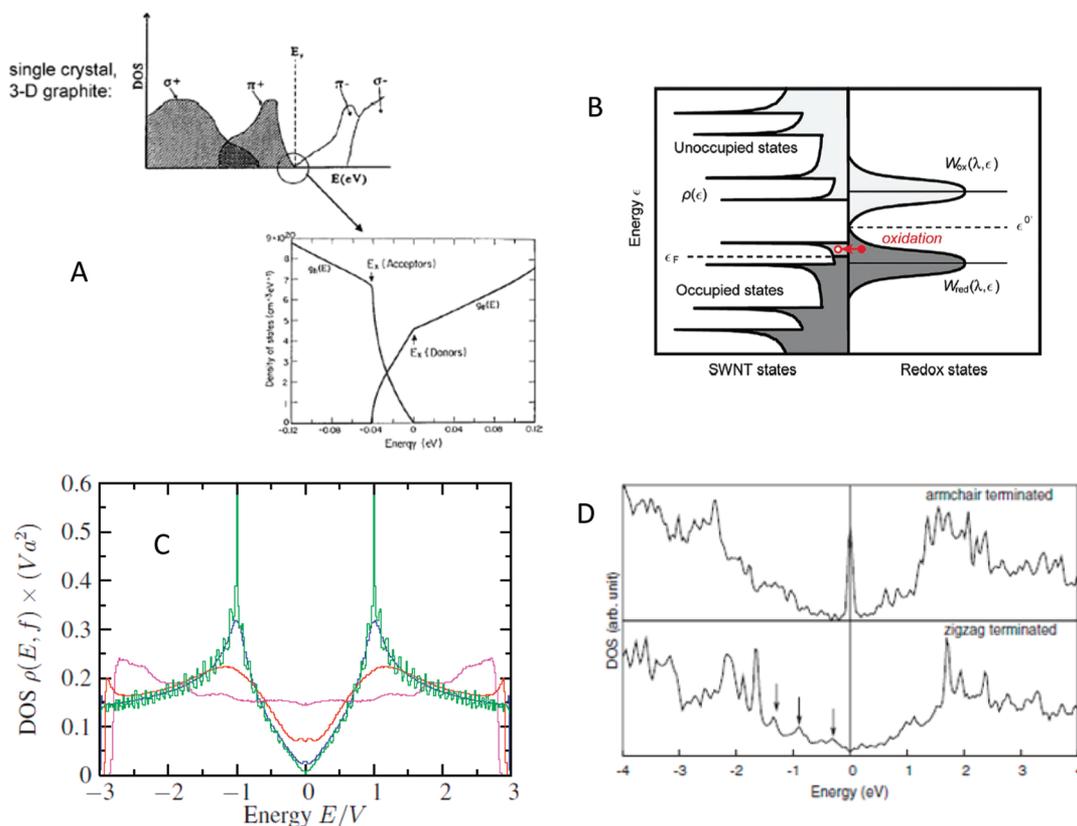
When comparing ET rates for different carbon electrode surfaces, there are at least three significant phenomena which can dramatically affect the observations: redox mechanism, surface density of electronic states, and the presence of edge plane sites on the electrode surface. Regarding mechanism, a recent review<sup>3</sup> described how “electrocatalytic” redox systems such as  $\text{Fe}^{3+/2+}$  and dopamine oxidation in water have observed

ET rates which are strongly dependent on the presence of specific sites on the carbon surface, such as oxygen-containing functional groups<sup>18–20</sup> or hydrogen bonding sites.<sup>21,22</sup> Metal deposition<sup>23</sup> and surface modification by diazonium-derived radicals<sup>24</sup> are both much faster at edge plane defects than on low-defect HOPG basal plane, thus permitting “decoration” of the edges with metals or organic molecules. In contrast, the “outer sphere” redox reactions such as Fc and  $\text{Ru}(\text{NH}_3)_6^{3+/2+}$  do not require specific surface sites but are still affected by the electronic structure of the electrode material. Fc and  $\text{Fe}(\text{CN})_6^{3-/4-}$  are often used as “simple” outer sphere redox systems but deserve special note. Fc and its derivatives have a high  $k^0$  ( $>5$  cm/s) on Pt electrodes<sup>25</sup> and appear “reversible” at commonly used scan rates. Since determination of such high rates is difficult, kinetic variations due to the carbon surface may be masked by the upper limit of the kinetic measurement technique.  $\text{Fe}(\text{CN})_6^{3-/4-}$  is notorious for various surface interactions and nonideality,<sup>3,19,26</sup> notably degradation with time and exposure to light.  $\text{Fe}(\text{CN})_6^{3-/4-}$  can be a useful indicator for the nature of the surface, but it is definitely not “simple” or well behaved.

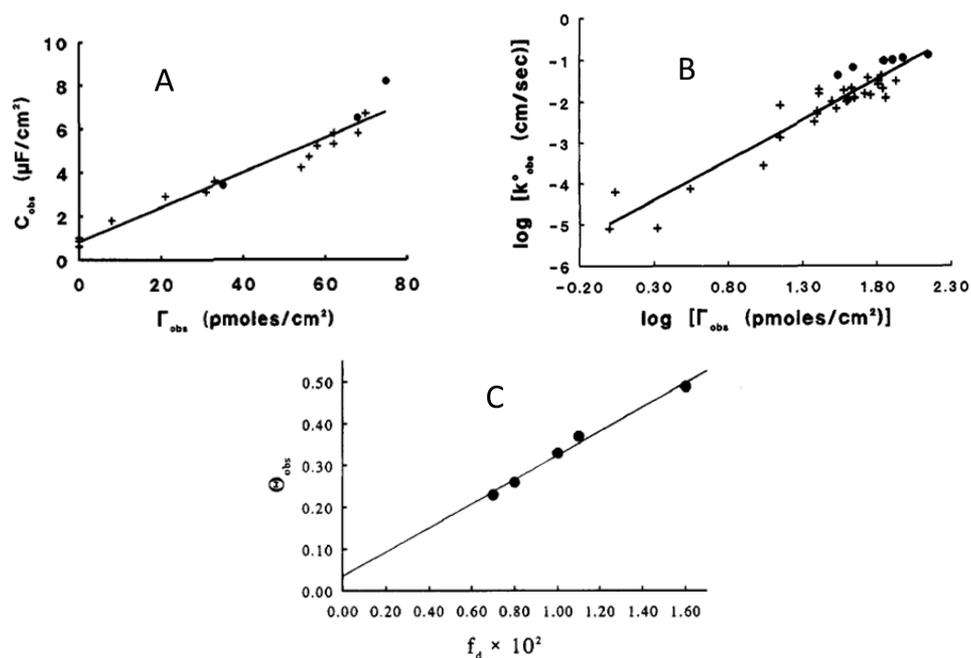
Regarding the second point of the electronic structure of the electrode, it has long been recognized that  $k^0$  for outer-sphere ET should depend on the density of electronic states (DOS) on the surface of the electrode and that most metals have a high DOS with no gaps or large variations with potential.<sup>27</sup> The much slower ET for outer-sphere redox systems on silicon surfaces at potentials within the band gap is a prominent example of the effect of low (or zero) DOS on electrode kinetics. This and related phenomena are the basis of the large body of research on semiconductor electrochemistry.<sup>28</sup> Figure 1 shows several examples of the calculated density of electronic states (DOS) for graphitic materials. Single crystal graphite (Figure 1A) has a small overlap of valence and conduction bands at the Fermi level, with a factor of  $>100\times$  lower DOS than Au.<sup>6</sup> Yeager<sup>11</sup> and Gerischer<sup>10</sup> first noted that the low capacitance of an HOPG basal plane electrode is a consequence of its low DOS near the Fermi level. The DOS of CNTs depends on their diameter, and they occur as both “metallic” and “semiconductor” tubes.<sup>16,29</sup> Figure 1B shows that the DOS for a CNT can vary significantly relative to the orbital energies of redox systems, with significant effects on the observed electron transfer rates. Most preparation methods for CNTs lead to a mixture of metallic and semiconducting tubes, with a range of DOS distributions. Although the “sidewall” surface of CNTs and the basal surface of graphene are similar to basal HOPG in terms of structure and the lack of functional groups, they differ substantially in electronic structure, notably the

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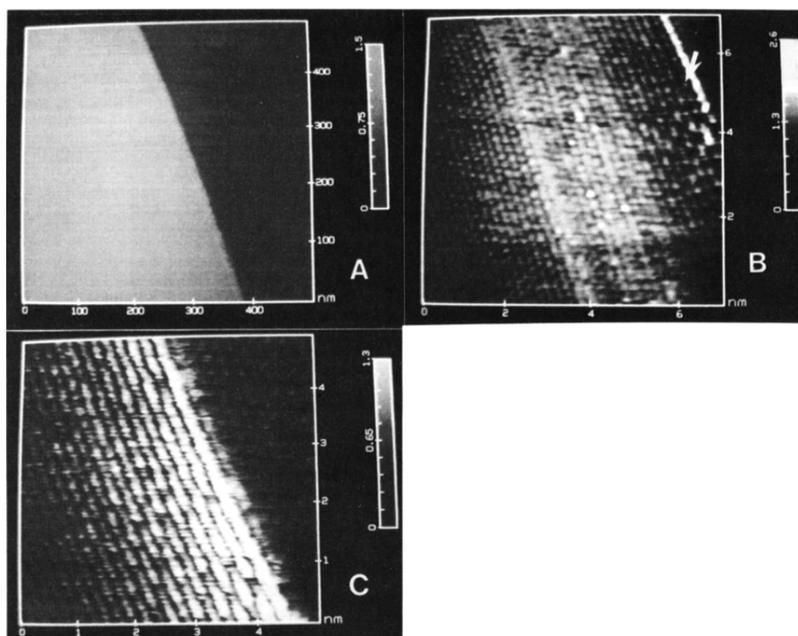




**Figure 1.** Density of electronic states for graphitic carbon materials. (A) single crystal graphite (Reprinted from ref 3. Copyright 2008 American Chemical Society); (B) a semiconducting CNT (Reprinted from ref 29. Copyright 2006 American Chemical Society); (C) pristine graphene (green curve) and with increasing disorder (black, red, lavender) (Reprinted with permission from ref 30. Copyright 2009 American Physical Society); (D) graphene terminated by zigzag or armchair carbon nanotubes (Reprinted with permission from ref 31. Copyright 2011 American Physical Society). Panel B shows one possible arrangement of the energy levels of a redox system relative to the DOS of a CNT.



**Figure 2.** (A) Capacitance (1 M KCl) vs AQDS adsorption ( $\Gamma_{\text{obs}}$ ) for cleaved (pluses) and laser activated (points) HOPG surfaces. Line is a least-squares fit to all points. (B) Log–log plot of  $k^0$  for  $\text{Fe}(\text{CN})_6^{3-/4-}$  in 1 M KCl vs AQDS adsorption measured on the same surface. Point labels are same as panel A. (C) AQDS surface coverage ( $\Theta_{\text{ads}}$ ) vs STM observed edge plane fractional area ( $f_d$ ) determined on the same surface for five separate HOPG surfaces, with least-squares determined line. Panels A and B reprinted from ref 7. Copyright 1992 American Chemical Society. Panel C reprinted from ref 5. Copyright 1994 American Chemical Society.



**Figure 3.** STM images of a step-edge defect (height  $\sim 0.8$  nm) on basal plane HOPG at three different magnifications. (A)  $500 \times 500$  nm image ( $z$ -scale =  $0$ – $1.5$  nm) shows the step edge, with the increased height of the terminated graphite plane. (B and C) Close-ups covering  $7 \times 7$  ( $z$ -scale =  $0$  to  $2.6$  nm) and  $5 \times 5$  nm images ( $z$ -scale =  $0$  to  $1.3$  nm), with the arrow indicating the maximum apparent height at the step edge. The electronic disturbance shown extending from the step edge into the top layer was observed at a large number of step edges. Reprinted from ref 5. Copyright 1994 American Chemical Society.

DOS.<sup>29</sup> A single graphene sheet with infinite in-plane dimensions has  $\text{DOS} = 0$  at the Fermi level (Figure 1C, green curve), in contrast to the  $\sim 60$  meV overlap of the valence and conduction bands in HOPG. We note also that the DOS plots shown in Figure 1 are calculated for ideal structures and are strongly affected by defects. As with silicon, defects in the graphite lattice may significantly alter the DOS, usually by increasing the DOS due to “mid-gap” or “defect” states. In the case of graphene, disorder can fill in the DOS near the Fermi level (Figure 1C), and the nature of the termination at the edge of a finite sheet of graphene can dramatically alter the DOS at the Fermi level (Figure 1D). Experimental determination of the DOS in carbon electrodes is not trivial, but the likely consequence of disorder is partial “filling” of the low DOS region near the Fermi level. Estimates of the DOS for low-defect HOPG indicate it is  $\sim 1\%$  that of Au,<sup>8</sup> but it is not known if the actual value is low enough to suppress electron transfer rates. As described next, such electronic changes are observable with both electrochemistry and scanning tunneling microscopy (STM).

In addition to the redox mechanism and the DOS of the carbon material, edge plane defects are particularly important on HOPG basal plane in terms of electrochemical reactivity. Regardless of the surface considered, if defects are much more reactive than a perfect surface toward a particular redox process, the apparent  $k^0$  values will be controlled largely by such defects. In the case of  $\text{Fe}(\text{CN})_6^{3-/4-}$  on HOPG, the  $k^0$  on low-defect basal plane is  $\sim 6$  orders of magnitude slower than that on glassy carbon with its many edge defects.<sup>6,7</sup> In our studies of HOPG kinetics, we correlated the capacitance, AQDS adsorption, and  $k^0$  for  $\text{Fe}(\text{CN})_6^{3-/4-}$  to the STM-observable coverage of edge plane defects on the basal plane, as shown in Figure 2. AQDS adsorption was undetectable by voltammetry on low-defect basal HOPG surfaces, and it was used as a sensitive indicator of the presence of edge plane sites. Later

work correlating scanning force microscopy and voltammetry showed that AQDS adsorbs very weakly on HOPG basal plane and much more strongly on defects.<sup>7,32</sup> Due to the difference in interaction energy and/or the availability of hydrogen bonding sites on edge plane,<sup>22</sup> adsorbed AQDS is electroactive only at the defect sites. While Figure 2 shows that  $k^0$ , capacitance, and electrochemically determined AQDS coverage ( $\Theta_{\text{AQDS}}$ ) correlate linearly with defect area, the electrochemically determined fractional coverage of AQDS was  $\sim 30$  times larger than the geometric edge plane area determined from STM. Both the AQDS electroactive area and the geometric fractional area were measured on the same basal plane surface in Figure 2C. While there are several possible explanations for this anomaly, another piece of information is critical. High resolution STM examination of HOPG defects revealed that a physical defect induces a significantly larger electronic disturbance of the surface, as shown in Figure 3. We proposed at the time that the electrochemically determined AQDS coverage more closely correlates to this electronically disturbed region near the edge defect visible in Figure 3B,C. This disturbance may have different polarizability and local dipoles than the perfect basal plane and thus promotes AQDS adsorption. As already noted, the electronic effects of a defect on both kinetics and adsorption occur over a much larger area than that of the defect itself.

Our attempts to obtain near defect-free HOPG surfaces lead us to several observations concerning surface preparation and use. We found that HOPG is quite mechanically fragile, and standard methods to define the electrode area with an elastomeric O-ring under mechanical pressure resulted in quite defective surfaces. To minimize this effect, we performed electrochemical experiments using an “inverted-drop” cell geometry. In addition, we noted the often-used method to remove HOPG layers with adhesive tape introduces many more defects than cleaving a thick HOPG sample with a razor blade

and allowing the sample to spontaneously delaminate.<sup>7</sup> Since HOPG consists of rotationally disordered microcrystallites with diameters of <10  $\mu\text{m}$ , flexing of the sample may expose the boundaries between such crystallites. It should also be noted that commercial HOPG samples are “graded” according to their X-ray diffraction properties, with the ZYA (highest) grade having the most interplanar order. This grading process would be expected to only indirectly reflect surface properties important to electrochemical behavior.

Given the unusually high sensitivity of the  $k^\circ$  for  $\text{Fe}(\text{CN})_6^{3-/4-}$  on defects, we used it to “validate” HOPG surfaces before determining  $k^\circ$  for another 16 redox systems. This practice was certainly not arbitrary, since the choice of  $\text{Fe}(\text{CN})_6^{3-/4-}$  was based on the correlation of its  $k^\circ$  with other indicators of surface defect coverage (Figure 2). In addition, the “validation” and measurement of  $k^\circ$  for a test redox system were performed quickly after exposing the basal plane (<1 min total), and the order the redox systems was tested was often reversed,<sup>4</sup> with no apparent effect on  $k^\circ$ . Given that  $k^\circ$  is so strongly affected by the presence of defects on basal HOPG, we concluded that every surface under study should be validated with a sensitive measure of defect coverage. Furthermore, when “validated” HOPG surfaces are purposely damaged with laser pulses, the  $k^\circ$  increases greatly, to values similar to those observed on HOPG edge plane or glassy carbon.<sup>7</sup> We should stress here that glassy carbon is an example of an extremely “defective” surface, which is expected to have a higher DOS than basal HOPG, and which exhibits  $k^\circ$  values much higher than those observed on low-defect basal HOPG.

The most likely origin of the discrepancy in reported  $k^\circ$  values for  $\text{Fe}(\text{CN})_6^{3-/4-}$  and  $\text{Ru}(\text{NH}_3)_6^{3+/2+}$  under the same conditions on basal plane HOPG is the variation in edge plane defect coverage, particularly when the electronic disturbance is significantly larger than the defect itself (Figure 3). This mechanism is consistent with the proposal that a low DOS surface exhibits slow ET kinetics to outer-sphere redox systems and that defects increase the DOS near the Fermi level. We emphasize that electronic differences between graphene, CNTs, basal HOPG, and glassy carbon are likely responsible for variation in electrode kinetics for outer-sphere electron transfer reactions, but significant reactivity differences are also expected for electrocatalytic redox systems. Such variations in electronic structure for carbon materials are scientifically very interesting, and it would be unfortunate if the observation of the resulting kinetic effects was significantly perturbed by defects or experimental details. In addition to kinetic effects of the electronic structure of carbon electrodes, we expect the various types of carbon to exhibit very interesting behavior for redox reactions with specific interactions with the carbon surface, such as dopamine oxidation,<sup>21,22</sup> metal deposition,<sup>23</sup> ET to aquated  $\text{Fe}^{3+/2+}$ ,<sup>19,20</sup> and dioxygen reduction.<sup>33</sup>

## AUTHOR INFORMATION

### Corresponding Author

\*Tel.: 780-641-1760. E-mail: richard.mccreery@ualberta.ca.

### Notes

The authors declare no competing financial interest.

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