

Anomalously Slow Electron Transfer at Ordered Graphite Electrodes: Influence of Electronic Factors and Reactive Sites

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Electron-transfer rates for 17 inorganic redox systems plus methyl viologen were determined on highly ordered pyrolytic graphite (HOPG) and glassy carbon (GC). Provided the HOPG defect density is low, the electron-transfer rates of all systems are much slower on the basal plane of HOPG than on GC. The slow rates on HOPG show a trend with the homogenous self-exchange rate constants, but in all cases the HOPG rate constants are substantially lower than that calculated via Marcus theory from self-exchange rates. The low HOPG rates do not exhibit any trends with redox system charge or $E_{1/2}$, as might be expected in the presence of double-layer or hydrophobic effects. The results are consistent with the semimetal properties of HOPG, which have been invoked to explain its low interfacial capacitance. Both the density of electronic states (DOS) and carrier density for HOPG are much lower than those for metals. By analogy to theories developed for electron transfer at semiconductor electrodes, the rate depends on an effectively bimolecular reaction between the redox system and carriers in the electrode. The low DOS and carrier density of HOPG leads to low electron-transfer rates compared to those of metals, or to those predicted from exchange rates. Disorder in the graphite increases electron-transfer rates and the DOS, thus yielding much faster rates on both GC and defective HOPG. For the 14 outer-sphere systems studied here, this electronic factor is much more important than any interaction with specific surface sites present at defects. The evidence indicates that, for $\text{Fe}(\text{CN})_6^{3-/4-}$, $\text{Eu}_{\text{aq}}^{+2/+3}$, $\text{Fe}_{\text{aq}}^{+2/+3}$, and $\text{V}_{\text{aq}}^{+2/+3}$, specific surface interactions provide inner-sphere routes which have a large effect on the observed rate constant.

Introduction

Electrode kinetics at carbon electrodes have been the subject of many investigations by our laboratory and many others, and several reviews are available.^{1–3} In general, carbon electrode surfaces are ill-defined on the atomic level, and electron-transfer rates are strongly dependent on surface history.^{4–11} In an attempt to examine electrode kinetics on well-defined carbon surfaces, we studied the basal plane of highly ordered pyrolytic graphite (HOPG),^{12–15} a material considered originally by Yeager et al.^{16–18} and more recently by Wightman et al.,¹⁹ Gerischer et al.,^{20–22} Kim et al.,²³ and Goss et al.²⁴ If the density of defects on HOPG is kept low, all of the redox systems studied exhibit slow electron-transfer rates, often several orders of magnitude slower than those on glassy carbon (GC).¹⁵ After a study of 13 redox systems on HOPG, we concluded that slow electron transfer can be caused by the lack of specific chemical sites on the basal plane or the low density of electronic states (DOS) exhibited by low-defect HOPG.¹⁵

Speaking more generally, the concept of reactive sites is particularly prevalent when carbon electrodes are considered. There are several examples of electrocatalysis by surface functional groups, particularly oxides. These include redox mediation by surface quinones,^{25,26} binding sites for cytochromes,^{27,28} inner-sphere catalysis of aquated $\text{Fe}^{+2/+3}$, $\text{Eu}^{+2/+3}$, and $\text{V}^{+2/+3}$ by oxides,²⁹ and a variety of catalytic effects on oxidized carbon.^{10,11,29–31} Kinetic effects of the electrode's electronic properties are conceptually distinct from reactive sites. For example, electron transfer at semiconductor electrodes is often much slower than that on metals, not necessarily because of surface functional group chemistry but rather because of a low density

of electronic states (DOS) and a corresponding low density of charge carriers.^{32–36} As shown in detail by Gerischer,^{33,36} the rate-controlling process at semiconductors is often the availability of electrons or holes of suitable energy, rather than activation of the redox system involved. Thus both reactive sites and electronic properties of the electrode can affect electrode kinetics, but by conceptually distinct mechanisms.

A perfect basal surface of HOPG has no edge plane and therefore no locations for functional groups. Furthermore, the carbon atoms are satisfied in the valence sense and have no dangling bonds like edge plane carbon atoms or metals. In addition, perfect HOPG has the low DOS noted earlier. When the basal plane is disordered, the DOS increases and sites are created. It is difficult to modify electronic structure without also creating potentially reactive sites, so it is not obvious how to establish which factor more strongly affects observed kinetics.

The current paper is an extension of the previous effort on HOPG kinetics¹⁵ to a larger number of outer-sphere redox systems. By correlating observed kinetics at HOPG with capacitance and known physical properties, we sought to clarify the role of electronic properties and reactive sites on electrode kinetics at carbon electrodes.

Experimental Section

The inverted drop cell and HOPG preparation procedure were the same as described previously.^{14,15} Unless noted otherwise, "HOPG" refers to the basal plane of material obtained from Arthur Moore at Union Carbide (Parma, OH). HOPG surfaces were "validated" as before, with the requirement that ΔE_p for $\text{Fe}(\text{CN})_6^{3-/4-}$ on a given surface be greater than 700 mV at 0.20 V/s in 1 M KCl.¹⁵ "Defective HOPG" describes an unvalidated surface of low-grade HOPG (ZYH, Union Carbide) with no special care taken to reduce defects during cleavage. Voltammetry was performed with a triangle wave generator and digital oscilloscope as described previously.¹⁵ HOPG capacitance was measured with a 100-Hz, 20-mV peak-to-peak triangle wave as described by Gileadi et al.^{37,38}

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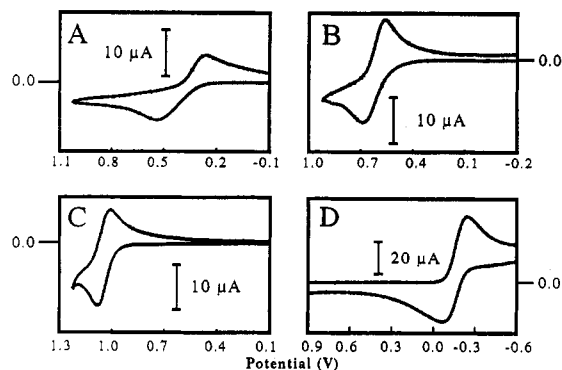


Figure 1. Voltammograms at validated basal plane HOPG, all at 0.2 V/s in 1 M KCl: (A) 1 mM $W(CN)_8^{3-/4-}$; (B) 1 mM $Mo(CN)_8^{3-/4-}$; (C) 1 mM $Ru(bpy)_3^{2+/3+}$; (D) 1 mM $Ru(NH_3)_6^{2+/3+}$. Potentials are relative to a silver quasireference electrode.

The following solutions were prepared as indicated: 0.25 mM potassium hexachloroiridate(IV) (Aldrich Chemical Co.) in 1 M KCl; 1 mM hexaammineruthenium(III) chloride (Strem Chemicals) in 1 M KCl; 1 mM pentaammine(pyridine)ruthenium(II) chloride (gift from Bruce Bursten, Ohio State) in 1 M KCl; 1 mM cobalt(III) sepulchrate trichloride (Aldrich) in pH 7 phosphate buffer + 1 M KCl; 2 mM tris(1,10-phenanthroline)-cobalt(II) chloride (from 2 mM cobalt chloride hexahydrate (reagent grade, J. T. Baker Chemical Co.) and 6 mM 1,10-phenanthroline (reagent grade, J. T. Baker Chemical Co.)) in 1 M KCl; 1 mM methyl viologen (Sigma) in 1 M KCl; 1 mM 1,1'-ferrocenedicarboxylic acid in pH 7 phosphate buffer + 1 M KCl; 2 mM tris(1,10-phenanthroline)iron(II) (from 2 mM ferrous ammonium sulfate (reagent grade, J. T. Baker) and 6 mM 1,10-phenanthroline) in 1 M KCl; 1 mM tris(2,2'-bipyridyl)-ruthenium(II) chloride hexahydrate (Strem Chemicals) in pH 7 phosphate + 1 M KCl; 1 mM potassium ferrocyanide or potassium ferricyanide (J. T. Baker) in 1 M KCl; 10 mM tris(ethylenediamine)cobalt(III) chloride (Johnson Matthey) + excess ethylenediamine (reagent grade, J. T. Baker) in 1 M KCl; tris(ethylenediamine)ruthenium(II) chloride (Johnson Matthey) in 0.2 M $HClO_4$; 1 mM potassium hexacyanoruthenate(II) (Johnson Matthey) in pH 7 phosphate buffer + 1 M KCl; 1 mM potassium octocyanomolybdate(IV) (gift from Tom Mallouk, University of Texas) in 1 M KCl; 1 mM potassium octocyanotungstate(IV) dihydrate (gift from Tom Mallouk) in 1 M KCl. For brevity, these redox systems will be referred to by the numbers listed in Tables 1 and 3. The electrolyte was 1 M KCl in most cases, due to the availability of comparative homogeneous and electrochemical kinetic data. In all cases, the GC and HOPG rates were compared under otherwise identical conditions.

Phosphate buffer solutions were prepared from 0.1 M H_2PO_4 (Matheson, Coleman and Bell) and additional NaOH (Mallinckrodt) to pH 7.0. Potassium chloride (Jennele Chemical Co.), perchloric acid (GFS Chemicals), and all other chemicals were used as received. All solutions were prepared daily with distilled water purified with a Nanopure water purification system (Barnstead) and degassed with argon.

Results

The voltammetry of the one-electron inorganic complexes studied here was qualitatively similar to that observed previously for a different set of one-electron systems. Voltammograms on validated HOPG for three systems not reported previously (numbers 10, 14, and 15) are compared to that of $Ru(NH_3)_6^{2+/3+}$ in Figure 1. In a few cases (e.g. $Co(sep)^{2+/3+}$, $Mo(CN)_8^{3-/4-}$), weak adsorption of the redox system on GC, indicated by nonideal peak shape and semiintegrals, limited the scan rate and the maximum measurable k^0 value. The results for the seven new systems plus the eight studied previously on

TABLE 1: Redox Potential and Kinetic Data for Validated HOPG

system	$E_{1/2}^a$ (V vs SSCE)	ΔE_p^b (mV)	k_b^0 (cm/s)	k_{exc}^c ($M^{-1} s^{-1}$)	ref ^d
1 $IrCl_6^{2-/3-}$	0.74	146	0.003	2×10^5	39
2 $Ru(NH_3)_6^{3+/2+}$	-0.19	285	9×10^{-4}	4000	40, 41
3 $Co(phen)_3^{3+/2+}$	0.10	715	2×10^{-5}	40	42
4 $MV^{2+/+}$	-0.67	76	0.017	10^7	43
5 $Fe(phen)_3^{3+/2+}$	0.86	66	>0.07	3×10^8	44
6 $Fe(CN)_6^{3-/4-}$	0.25	700-1500	10^{-6} ^e	2×10^4	45, 46
7 $Co(en)_3^{3+/2+}$	-0.48	770	2×10^{-5}	8×10^{-5}	47
8 $Ru(en)_3^{3+/2+}$	-0.08	502	1×10^{-4}	4000	41
9 $Fc(COOH)_2$	0.42	150	0.003	10^7	48
10 $Ru(bpy)_3^{3+/2+}$	1.04	72	>0.02	2×10^9	50
11 $Ru(NH_3)_5py^{3+/2+}$	0.04	156	0.002	5×10^5	51
12 $Co(sep)^{3+/2+}$	-0.62	265	7×10^{-4}	5	52
13 $Ru(CN)_6^{3-/4-}$	0.78	350	4×10^{-4}	8000	45
14 $Mo(CN)_8^{3-/4-}$	0.60	148	0.002	3×10^4	39
15 $W(CN)_8^{3-/4-}$	0.33	340	4×10^{-4}	$>4 \times 10^4$	49

^a Average of voltammetric peak potentials on laser-activated GC. ^b On validated HOPG basal plane surfaces, 0.2 V/s scan rate. ^c Homogeneous self-exchange rate constant. ^d Reference for k_{exc} . Electrochemical results for some systems were reported previously,¹⁵ and others are from this work. ^e Value for HOPG exhibiting minimum AQDS adsorption, from ref 14.

TABLE 2: Comparison of Rate Constants for HOPG and GC

system	k_b^0 (cm/s) ^a	k_{GC}^0 (cm/s) ^b	k_{GC}^0/k_b^0
1 $IrCl_6^{2-/3-}$	0.003	>0.5	>200
2 $Ru(NH_3)_6^{3+/2+}$	9×10^{-4}	>0.4	>400
3 $Co(phen)_3^{3+/2+}$	2×10^{-5}	0.08	4000
4 $MV^{2+/+}$	0.017	>0.1	>6
5 $Fe(phen)_3^{3+/2+}$	>0.07	>0.2	
6 $Fe(CN)_6^{3-/4-}$	10^{-6}	>0.5	$>6 \times 10^5$
7 $Co(en)_3^{3+/2+}$	2×10^{-5}	0.03	2000
8 $Ru(en)_3^{3+/2+}$	1×10^{-4}	>0.5	>5000
9 $Fc(COOH)_2$	0.003	>0.5	200
10 $Ru(bpy)_3^{3+/2+}$	>0.02	>0.2	
11 $Ru(NH_3)_5py^{3+/2+}$	0.002	>0.03	>300
12 $Co(sep)^{3+/2+}$	7×10^{-4}	>0.1	>100
13 $Ru(CN)_6^{3-/4-}$	4×10^{-4}	0.4	1000
14 $Mo(CN)_8^{3-/4-}$	0.002	>0.05	>30
15 $W(CN)_8^{3-/4-}$	4×10^{-4}	>0.5	>1500

^a Same as k_b^0 from Table 1. ^b From laser-activated GC surfaces.

validated HOPG are listed in Table 1. As before, validated HOPG provides a well-defined carbon surface with minimal surface defects. We previously used laser-activated glassy carbon as a reference surface for disordered carbon,^{4,15} and the relevant rate constants for GC are shown in Table 2. Note that GC rates are consistently higher than those on HOPG, but the magnitude of the difference is often uncertain due to instrumental limitations on measuring fast GC rates.

In a previous report, we concluded that the rates of $Fe_{aq}^{2+/3+}$, $Eu_{aq}^{2+/3+}$, and $V_{aq}^{2+/3+}$ in $HClO_4$ can be accelerated by surface oxides present on polished or anodized GC surfaces.²⁹ For example, k^0 for $Eu_{aq}^{2+/3+}$ was increased by a factor of 500 when GC was oxidized electrochemically, and the effect was reversed by silanization. Fractured GC provides a surface with minimal surface oxide coverage, thus reducing the effect of an inner-sphere route.⁴ A comparison of the rate constants for these systems on HOPG and fractured GC is reproduced as Table 3.

As noted by Yeager et al.¹⁶⁻¹⁸ and Gerischer et al.,^{20,21} interfacial capacitance is an indication of the electronic properties of HOPG. For semiconductors and HOPG, a space charge capacitance develops which is usually smaller than the ionic double-layer capacitance. Since the space charge and double-layer capacitance are in series, the observed capacitance is dominated by the space charge for a semiconductor electrode. Thus a low observed capacitance is a marker for the presence of a space charge layer

TABLE 3: Kinetic Results for Fractured GC and HOPG

system	k_b^0 ^a (cm/s)	k_{frac}^0 ^d (cm/s)	k_{exc}^b (M ⁻¹ s ⁻¹)
16 Fe _{aq} ^{+3/+2}	1.4×10^{-5}	$(2.3 \pm 0.5) \times 10^{-3}$ (<i>N</i> = 8) ^c	1×10^{-3}
17 Eu _{aq} ^{+3/+2}	2.5×10^{-6}	$(9 \pm 4) \times 10^{-5}$ (<i>N</i> = 8)	2×10^{-4}
18 V _{aq} ^{+3/+2}	$<3 \times 10^{-6}$	$(4.5 \pm 0.5) \times 10^{-4}$ (<i>N</i> = 4)	0.05
6 Fe(CN) ₆ ^{-3/-4} e	10^{-6}	≥ 0.5	2×10^4
2 Ru(NH ₃) ₆ ^{+2/+3} e	9×10^{-4}	0.3	4×10^3

^a HOPG rate constants obtained from comparison to simulations for HOPG CV's; surfaces were not "validated". ^b k_{exc} for aqueous complexes data from ref 71. ^c Rate constants indicate mean and standard deviation; *N* is number of trials. ^d GC-20 fractured in situ. ^e Data from ref 15.

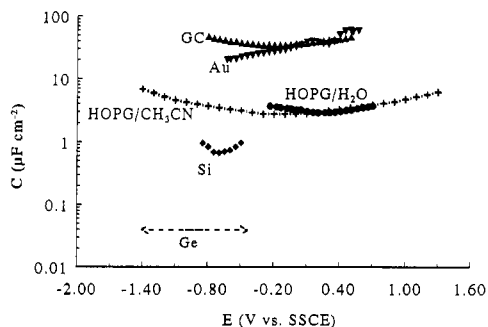


Figure 2. Comparison of observed interfacial capacitance for several electrode/electrolyte systems. GC in 1 M KCl curve was determined in the present work; others are from the literature: Au(III), 1 M K₂SO₄,⁵³ *n*-silicon, pH 7;⁵⁴ HOPG, aqueous;⁵⁵ HOPG, acetonitrile.²⁰ Value for Ge³⁺ is noted but reference potential is uncertain.

TABLE 4: Effects of AQDS Adsorption on k^0

system	k_{GC}^0 ^a (cm/s)	$k_{\text{GC,AQDS}}^0$ ^b (cm/s)	k_b^0 (cm/s)	$k_{b,\text{AQDS}}^0$ ^c (cm/s)
1 IrCl ₆ ^{-2/-3}	0.50 (laser) ^d	0.24 (laser) ^d	.003	.003
	0.55 (fract) ^d	0.26 (fract) ^d	(validated) 0.052 (defective)	(validated) 0.022 (defective)
2 Ru(NH ₃) ₆ ^{+2/+3}	0.5 (laser) ^d	0.5 (laser) ^d		
	0.27 (fract) ^d	0.30 (fract) ^d		
12 Co(sep) ^{+2/+3}	0.1 (laser) ^d	0.6 (laser) ^d	0.001	0.003
6 Fe(CN) ₆ ^{-3/-4}	>0.5 (laser) ^d	0.05 (laser) ^d	10^{-6} e	
	0.5 (fract) ^d	0.02 (Fract) ^d	(validated) 0.045 (defective)	(validated) 0.0007 (defective)

^a Laser-irradiated (polished) GC, no AQDS. ^b Same as k_{GC}^0 , but with 10^{-5} M AQDS in solution. ^c Validated or defective (ZYH) basal plane with 10^{-5} M AQDS in solution. ^d Data from ref 56. ^e From ref 14.

in the electrode. Figure 2 shows differential capacitance vs potential curves for several surfaces. Note that Si and Ge electrodes have very low capacitance ($<1.0 \mu\text{F}/\text{cm}^2$), GC and Au are much higher ($>10 \mu\text{F}/\text{cm}^2$), and HOPG is intermediate ($1-5 \mu\text{F}/\text{cm}^2$). Furthermore, the HOPG capacitance is nearly independent of the electrolyte composition, implying minimal effect of the ionic double layer.²⁰

An additional probe of the effects of interfacial structure on k^0 is provided by intentional adsorption of anthraquinone-2,6-disulfonate (AQDS). We showed earlier that AQDS adsorbs strongly on HOPG defects, and on GC, reaching saturation coverage at $<10^{-5}$ M solution concentration.¹⁴ If electron transfer depends on a specific chemical interaction at the carbon surface, one would expect AQDS to significantly modify k^0 by interfering with the site of interaction. Table 4 shows the effect of 10^{-5} M AQDS on the observed rate constants for several systems. Although the AQDS is also electroactive, both oxidized and reduced forms adsorb strongly, and the AQDS current is too small to interfere with kinetic measurements. On laser-activated or fractured GC, AQDS has little effect on k^0 for IrCl₆^{-2/-3}, Ru(NH₃)₆^{+2/+3}, or Co(sep)^{+2/+3}. However, the rate constant for

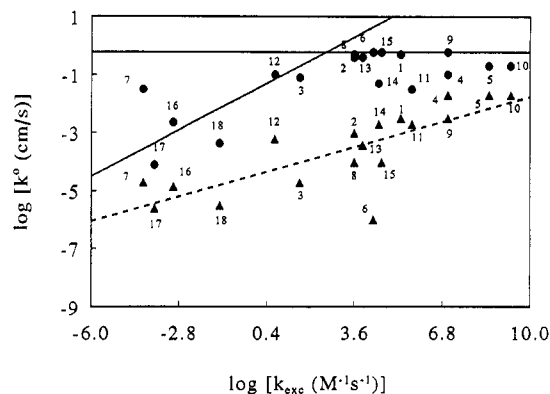


Figure 3. Correlation of k^0 and k_{exc} for redox systems 1–15 on validated HOPG (triangles) and laser-activated GC (circles). For systems 16–18, triangles are validated HOPG and circles are fractured, unoxidized GC. Horizontal line is instrumental limit; solid, sloping line is calculated as before¹⁵ from the simple Marcus relation $k^0 = 0.03k_{\text{exc}}^{1/2}$. Dashed line is a least-square fit to HOPG points.

Fe(CN)₆^{-3/-4} on GC is reduced by a factor of 10–25.⁵⁶ AQDS has little effect on kinetics on HOPG for any system, unless the surface is initially defective.

Discussion

An initial qualitative question involves the distinction between reactive sites and electronic properties noted in the Introduction. In a preceding publication, we reported that oxide sites on oxidized GC or HOPG catalyzed electron transfer to Eu_{aq}^{+2/+3}, Fe_{aq}^{+2/+3}, and V_{aq}^{+3/+2} and that this inner-sphere route could be blocked by silanization.²⁹ In the case of Eu_{aq}^{+2/+3}, the inner-sphere route was 500 times faster than the outer sphere route, indicating the importance of active sites (oxides in this case) to this system. Another example is provided by the effect of AQDS adsorption on k^0 for Fe(CN)₆^{-3/-4}. Monolayer coverage of AQDS on GC decreases k^0 for Fe(CN)₆^{-3/-4} by factors of 10–25 but has only minor effects on Ru(NH₃)₆^{+3/+2}, IrCl₆^{-2/-3}, or Co(sep)^{+2/+3}. This decrease for Fe(CN)₆^{-3/-4} is larger than the factor of 2 attributed to electrostatic effects of surface carboxylates by Deakin et al.⁵⁷ and is also much larger than the decrease in k^0 observed here for the anionic IrCl₆^{-2/-3}. These results imply an inner-sphere route for Fe(CN)₆^{-3/-4}, or some other factor which depends on specific surface chemistry. The Fe(CN)₆^{-3/-4} system has been shown to be nonideal on both carbon and metal electrodes,^{1,6,58,59} with a common problem being degradation caused by CN⁻ chemisorption.^{60,61} The sensitivity of Fe(CN)₆^{-3/-4} to AQDS implies that some surface site is important on carbon, but the specific mechanism is unclear. The well-known variation of k^0 for Fe(CN)₆^{-3/-4} on GC with surface history^{3,6,13} may be a consequence of the dependence of Fe(CN)₆^{-3/-4} on surface chemical sites.

In contrast to Fe(CN)₆^{-3/-4}, Eu_{aq}^{+2/+3}, Fe_{aq}^{+2/+3}, and V_{aq}^{+2/+3}, the rates for Ru(NH₃)₆^{+2/+3}, IrCl₆^{-2/-3}, and Co(sep)^{+2/+3} do not depend strongly on AQDS adsorption. We concluded previously that Ru(NH₃)₆^{+2/+3} shows a slight (2–3-fold) decrease in k^0 with surface oxidation by O₂, H₂O, or anodization,⁶² and Hsueh and Brajter-Toth observed a similar inhibition by oxides on carbon fibers.⁶³ The behavior of systems 1–5 and 7–15 is consistent with outer-sphere electron transfer in which an oxide or AQDS layer causes a slight decrease in rate. It is possible that the AQDS acts merely as a spacer, increasing the distance of closest approach and decreasing the tunneling probability. In addition, all of the redox systems studied, excluding Fe(CN)₆^{-3/-4} but including Eu_{aq}^{+2/+3}, Fe_{aq}^{+2/+3}, and V_{aq}^{+2/+3} on low oxide surfaces, show a similar depression in rate for HOPG compared to GC. As shown in Figure 3, the HOPG rate approximately tracks the homoge-

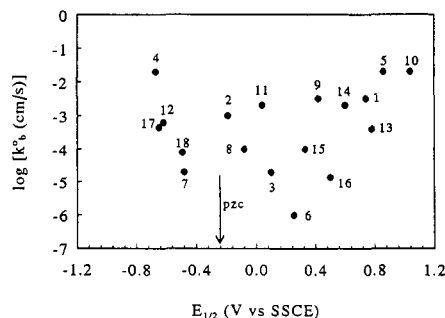


Figure 4. Plot of k^0 for validated HOPG vs $E_{1/2}$ for 18 outer-sphere systems. Potential of zero charge in 1 M KCl is indicated.

neous self-exchange rate constant (k_{exc}), as would be expected for outer-sphere reactions through Marcus theory.¹⁵ If the rate depression for HOPG vs GC were due solely to the lack of reactive sites on HOPG, one would expect the depression to be quite variable for different systems (since different systems would presumably interact differently with the sites) and not depend on k_{exc} . Furthermore, all systems should be markedly affected by AQDS if inner-sphere routes and specific sites are important. On the basis of the systems in Tables 1 and 3, we conclude that reactive chemical sites are important to $\text{Fe}(\text{CN})_6^{-3/4}$, $\text{Eu}_{aq}^{+2/+3}$, $\text{Fe}_{aq}^{+2/+3}$, and $\text{V}_{aq}^{+2/+3}$, but also that inner-sphere routes are comparatively unimportant for the other systems and for the aquated ions on low oxide surfaces.

Restricting the discussion to the apparent outer-sphere systems (1–5 and 7–15) and considering reactive sites to be unimportant, we have yet to answer the question of why rates on HOPG are suppressed by several orders of magnitude relative to GC. The observed rates are also much lower than those predicted from k_{exc} by Marcus theory,¹⁵ as noted in Figure 3. On the basis of a smaller set of redox systems, we argued previously that the lower rate on HOPG is unlikely to be caused solely by double-layer or hydrophobic effects, since the rate depression was independent of $E_{1/2}$ or charge of the redox system.¹⁵ A more complete plot of k^0 for HOPG vs $E_{1/2}$ appears in Figure 4. If the lower rate resulted solely from differences in ionic double-layer effects between HOPG and GC, one would expect the rate to depend strongly upon the position of $E_{1/2}$ relative to the potential of zero charge (-0.2 V vs Ag/AgCl for HOPG, ca. $+0.1$ V for GC).^{16–18} A trend in k^0 is not observed when k^0 is plotted vs $E_{1/2}$, nor does k^0 show a trend with redox system charge. If a similar plot of $k^0/k_{exc}^{1/2}$ is constructed to compensate for variations in k_{exc} , no trends with $E_{1/2}$ or redox system charge are apparent. Any modification in driving force caused by a potential drop across the space charge region in the HOPG should be strongly dependent on $(E_{1/2} - E_{pzc})$. In addition, systems with quite varying hydrophobicity show similar rate differences between GC and HOPG. These observations confirm the previous arguments¹⁵ that the slow rates on HOPG are unlikely to be caused solely by hydrophobic or double-layer effects.

After concluding that sites are not important to the outer-sphere systems, we turn to the solid-state electronic properties of HOPG. The calculated band structure for perfect HOPG is shown in Figure 5. As noted earlier, Yeager et al.^{16–18} and Gerischer et al.^{20,21} attributed the low capacitance of HOPG to a space charge layer caused by the low DOS of HOPG at the Fermi level. McDermott et al.¹⁴ showed that the low capacitance is very sensitive to the presence of defects on the HOPG surface, as are k^0 for $\text{Fe}(\text{CN})_6^{-3/4}$ and AQDS adsorption. Spain⁶⁴ has proposed that disorder in graphite generates new electronic states, some of which are near the Fermi level (Figure 5c). These have the effect of filling in the band overlap region, as occurs with disordered semiconductors. The capacitance data in Figure 1 support this model, with semiconductors having low capacitance, metals and GC much higher capacitance, and HOPG intermediate capaci-

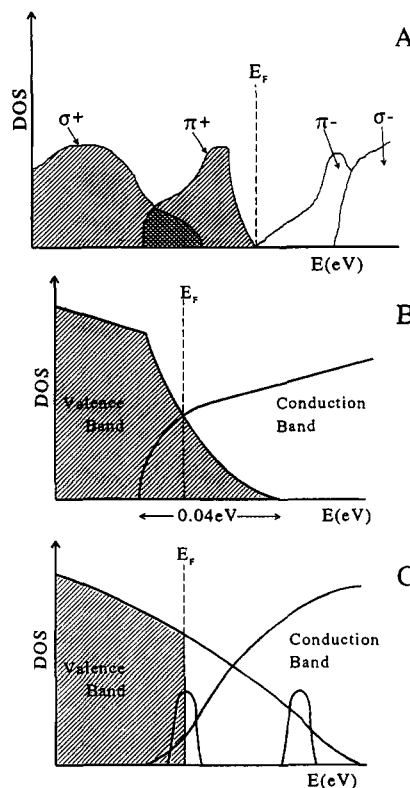


Figure 5. Band structure for a graphite crystal; shading indicates filled bands (A). σ^+ and π^+ indicate valence band derived from bonding orbitals; σ^- and π^- indicate conduction band. B is an enlargement of the band overlap region. C has been proposed for disordered graphite, with additional features attributed to localized states associated with disorder. Adapted from Spain.⁶⁴

TABLE 5: Density of Electronic States and Carrier Density for Several Electrode Materials

	free electron density (cm^{-3})	DOS at Fermi level states/atom/eV
Au	6×10^{22} (ref 65)	0.28 (ref 66)
HOPG	5×10^{18} (ref 64)	2.2×10^{-3} (ref 20)
semiconductor (typical)	10^{13} – 10^{17} (ref 33)	varies, zero in band gap

tance. Although HOPG does not have a band gap and the carrier density is higher than in semiconductors, its electronic properties have a large effect on capacitance. The relevant properties for HOPG, metals, and semiconductors are summarized in Table 5.

The effects of electronic factors in the electrode on kinetics have been considered in some detail for semiconductors. The model was originally proposed by Gerischer³³ and Doganadze and Levich⁶⁷ for semiconductors, and a brief summary is provided here. For a reduction, the electron transfer is modeled as a bimolecular reaction between the oxidized species in solution and the electron in the electrode, with a rate proportional to the product of their concentrations:³⁶

$$i_{\text{redn}} \propto k^- W_{\text{ox}}(E) C_{\text{ox}}^0 N_s(E) \quad (1)$$

where k^- = forward rate constant, $W_{\text{ox}}(E)$ = distribution function of Ox as a function of energy, C_{ox}^0 = surface concentration of oxidized form of redox couple, and $N_s(E)$ = surface concentration of electrons at a given energy. $N_s(E)$ is determined by the DOS at the surface and by the distribution of electrons populating these states. Gerischer^{33,36} further notes that electron transfer will be fastest when the electron has the same energy in the electrode as it does in Ox at the point of transfer. So the rate will be proportional to the DOS, which determines N_s , and to a distribution function for Ox ($W_{\text{ox}}(E)$) which determines its energy. This approach has been successful for describing electron transfer

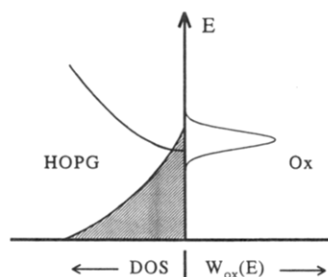


Figure 6. Model for electron transfer at semiconductors developed by Gerischer^{33,36} and Levich,⁶⁷ adapted to a reduction at HOPG.

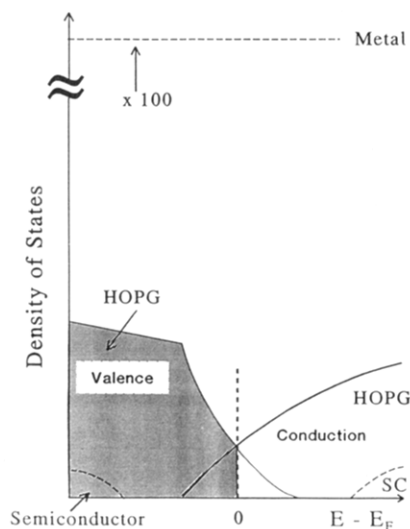


Figure 7. Semiquantitative comparison of band structure for a metal, HOPG, and a semiconductor (SC), in the region of band overlap. Although HOPG does not have a band gap, its DOS near the Fermi level is very low.

at semiconductors, leading to the conclusion that electron-transfer rates depend strongly on the availability of charge carriers (electrons or holes) of suitable energy. For several metals, Iwasita, Schmickler, and Schultze⁶⁸ concluded that electron-transfer rates for $\text{Ru}(\text{NH}_3)_6^{2+/+3}$ did not track the DOS of the metal, perhaps because the semiconductor model does not apply at such high carrier densities.

While HOPG is not a semiconductor and does not have a band gap, its low density of states may be important to electron transfer. The semiconductor model is adapted to HOPG in Figure 6. Randin² used a similar model to predict slow electron transfer at graphite electrodes but did not have kinetic data available. The DOS for Au, HOPG, and a semiconductor are compared semiquantitatively in Figure 7. Although HOPG has a higher DOS than a semiconductor, it is much lower than that of a metal such as Au.

As noted for semiconductors, i_{redn} and therefore k^0 depend strongly on the DOS as a function of energy. Since the DOS in the band gap is zero, N_s is also zero, and electron transfer is very slow to redox systems with $E_{1/2}$ in the band gap. As a consequence, k^0 values at semiconductors are usually much more dependent on the band structure and on $E_{1/2}$ than they are on the kinetic properties of the redox system. For metals, the DOS is high and not very dependent on potential. The rate is more dependent on $W_{\text{ox}}(E)$, which is related to reorganization energy and other properties of the redox system. Thus rates on metals generally follow Marcus theory once double-layer factors and other work terms are taken into account.⁶⁹⁻⁷¹ In general, rates for outer-sphere systems will depend on $W_{\text{ox}}(E)$ at metals (and will track k_{exc}), while they will depend strongly on the electrode band structure at semiconductors.

Applying this model to HOPG reveals that the material has a DOS which is overall lower than metals but is particularly low

near the Fermi level. The observations of general suppression of outer-sphere rates and capacitance lead to the conclusion that the N_s term in eq 1 is small for HOPG. The observed rate is still dependent on k_{exc} , but all rates are lower than on GC or metals. Disorder in carbon (such as in GC) increases the DOS at all energies, yielding rates and capacitance comparable to those for metals. The importance of disorder-induced electronic effects is supported by the observation that very limited disorder can greatly enhance the rate on HOPG.^{14,15} For example, k^0 for $\text{IrCl}_6^{-2/+3}$ at defective HOPG is ~ 17 times greater than at validated HOPG (Table 4). Stated differently, the electronic effects and low rates are observed only for very low defect HOPG. The unusual electronic properties of HOPG will not be observed without significant care to reduce defect density.

Although approximate, due to the assumption that semiconductor theory applies to HOPG, Gerischer's calculation of the DOS for HOPG based on capacitance produces a parabolic shape of the DOS vs potential curve.³⁶ If DOS were the main factor controlling observed k^0 at HOPG, Figure 3 or an analogous plot of $k^0/k_{\text{exc}}^{1/2}$ should also be parabolic with a minimum at E_{pzc} . They are not, and show no particular trend with $(E_{1/2} - E_{\text{pzc}})$. However, the potential range of the 14 outer-sphere systems examined is +1.2 to -4 relative to the pzc for HOPG, over which the DOS is predicted to vary by a factor of about 10. Throughout this range, the DOS of HOPG remains much lower than that of a metal. So the lack of a trend in k_b^0 with $(E_{1/2} - E_{\text{pzc}})$ may be obscured by other relatively minor factors (such as hydrophobicity, etc.), but the overall depression of rates is still consistent with the large difference in the DOS for HOPG compared to metals. It should also be noted that the DOS shown in Figure 5A,B was calculated for *bulk*, crystalline graphite, while interfacial properties will be sensitive to a *surface* DOS. The low defect density on validated HOPG will reduce the influence of any localized defect states, but even a perfect basal surface should differ electronically from bulk graphite.

Finally, it is useful to refine the definition of the term "site" as applied to electron transfer on carbon surfaces. If "site" is defined generally to mean any location where electron transfer is facilitated, it could apply to either an electronically modified region (e.g. HOPG defects or GC) or specific functional groups involved in electrocatalysis. As a consequence of the results presented here, we are distinguishing emphatically between *disorder*, which affects the DOS and distribution of electron and hole energies, and *chemical sites*, which promote certain inner-sphere reactions, such as those of $\text{Eu}^{2+/+3}$ and $\text{Fe}^{2+/+3}$. Disorder is responsible for the acceleration of outer-sphere systems (1-5, 7-15, and 16-18 on low oxide surfaces) when HOPG is replaced with GC, and this rate enhancement is quite general for both outer- and inner-sphere systems. Chemical sites are responsible for the further increase in rate when the disordered surface is modified to produce the chemical sites, as occurs when GC is oxidized to enhance k^0 for $\text{Eu}^{2+/+3}$, $\text{Fe}^{2+/+3}$, and $\text{V}^{2+/+3}$. We have investigated the electronic perturbation induced by disorder with scanning tunneling microscopy, and the results will be reported separately.⁷²

Summary

To reconsider the issue of surface chemical sites vs electronic properties, it is clear that *all* systems studied are slower on validated HOPG compared to GC or metals, consistent with the lower DOS of HOPG. When the DOS is increased by disorder, all systems increase in rate, but by varying amounts. For most of the outer-sphere systems (1-5 and 7-15), the rate at GC was 3-5 orders of magnitude faster than that on the basal plane of HOPG. As noted previously,²⁹ an additional increase of the rate for $\text{Fe}^{2+/+3}$, $\text{Eu}^{2+/+3}$, and $\text{V}^{2+/+3}$ occurs when surface oxides are present on GC. $\text{Fe}(\text{CN})_6^{\text{aq}-3/+4}$ is affected both by electronic factors and by a specific surface interaction, whose nature is as

yet undetermined. For the outer-sphere systems, disorder increases the rate by modifying the electronic structure of the carbon, not by providing surface chemical sites.

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