Control of Electron Transfer Kinetics at Glassy Carbon Electrodes by Specific Surface Modification

Peihong Chen and Richard L. McCreery*

Department of Chemistry, 120 West 18th Avenue, Columbus, Ohio 43210

Various well-established and novel surface modification procedures were used on glassy carbon (GC) electrodes to yield surfaces with low oxide content or which lack specific oxide functional groups. In addition, monolayers of several different adsorbates were formed on GC surfaces before electrochemical evaluation. Both the non-specific monolayer adsorbates and reagents which chemisorb to specific functional groups were observed on the surface with Raman and photoelectron spectroscopy. The various GC surfaces were then evaluated for their electron transfer reactivity with nine redox systems in aqueous electrolyte, including $Ru(NH_3)_6^{2+/3+}$, $Fe(CN)_6^{3-/4-}$, ascorbic acid, and $Fe_{aq}^{3+/2+}$. The nine systems were categorized according to their kinetic sensitivity to surface modification. Several, including $Ru(NH_3)_6^{2+/3+}$, are insensitive to surface modifications and are considered outer sphere. $Fe_{aq}^{3+/2+}$, $V_{aq}^{2+/3+}$, and $Eu_{aq}^{2+/3+}$ are catalyzed by surface carbonyl groups and are very sensitive to the removal of surface oxides or derivatization of C=O groups. Ascorbic acid and $Fe(CN)_6^{3-/4-}$ constitute a third group which are not catalyzed by oxides but which do require a specific surface interaction. A procedure for classifying redox systems by their kinetics on modified carbon surfaces is proposed.

The importance of surface chemistry to the electrochemical behavior of carbon electrodes is well established and has been reviewed extensively.[1-5] The low cost and broad applicability of carbon electrodes, particularly in electroanalysis and electrosynthesis, have driven years of research to find the relationship between surface structure and electrochemical phenomena, particularly adsorption, heterogeneous electron transfer, and surface stability. The process of relating carbon surface structure to electrochemical reactivity is hindered by two formidable barriers. First, the carbon surface varies greatly with origin and pretreatment and is often difficult to characterize structurally. Thus, the surface structure is often unknown and can vary from laboratory to laboratory or day to day.[1,6,7] Second, redox systems vary greatly in their sensitivity to surface structure and, therefore, to surface history.[8-10] In order to understand the relationship between carbon surface structure and electrochemical reactivity, redox systems must be classified to some degree, according to their electron transfer kinetics or other relevant behavior.

While understanding structure/reactivity relationships at carbon electrodes is the main goal of our research in this area, this objective is certainly not new. It is generally believed that microstructure of carbon materials,[1,11-13] cleanliness of the electrode surface,[14-16] and surface functional groups[17-22] are important determinants of electrode reactivity. Much success has been achieved in understanding the effects of electrode microstructure on electron transfer reactivity as a result of many recent studies.[1,4,23,24] All of the carbon electrode materials in common use share sp^2 bonding and the basic structure of a six-member ring. The main differences in microstructure lie in crystallite size. Researchers have generally agreed that the graphite edges are much more reactive than the graphite basal plane toward electron transfer and adsorption.[25,26] The low reactivity of the graphite basal plane has been attributed to its low density of electronic

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states and to the lack of functional groups and adsorption sites.[10,23,27,28] However, our understanding of the nature and chemistry of the graphitic edges present on all but a few types carbon electrodes is much less complete. The ease with which carbon combines with other elements makes carbon materials rich in surface chemistry, leading to a variety of modifications. On the other hand, because of this richness in surface chemistry, the final properties of solid carbons are invariably difficult to predict, to evaluate, and often to reproduce. Largely for this reason, there is limited systematic understanding of what role surface chemistry plays in electron transfer kinetics.

The objectives of the present work are twofold and are directed at the two main barriers to understanding structure/reactivity relationships at carbon surfaces. Specifically, the approach is directed toward understanding surface structural factors which control heterogeneous electron transfer rates at glassy carbon electrodes. First, GC surfaces were modified by mainly well-established procedures to reproducibly yield surfaces with known structural features. XPS and surface Raman spectroscopy were used extensively to characterize the surfaces of interest. Second, a collection of nine redox systems was subdivided into classes, according to the sensitivity of their electron transfer rates to surface structure. At least for the limited number of redox systems examined, the combination of these two approaches leads to a useful understanding of the effects of carbon surface preparation on electron transfer reactivity.

EXPERIMENTAL SECTION

Both Tokai GC-20 plates and commercial GC electrodes from Bioanalytical Systems Inc. (MF2070) were used in this work. In the case of Tokai GC-20 plates, electrodes were mounted in a homemade Teflon electrode holder after polishing or other modification procedures. Before any modification procedures, glassy carbon electrodes were always polished in Nanopure water/alumina slurries. The polishing procedure can be found elsewhere,[5] but it was important to avoid commercial alumina slurries, which contain organic deagglomerating agents which contaminate the electrodes.

To physisorb 2,6-anthraquinonedisulfonate (AQDS), methylene blue, and 1,4-bis(2-methylstyryl)benzene onto glassy carbon surfaces from their solutions, procedures described previously were followed.[8,29,30] To chemisorb nitrophenyl on glassy carbon surfaces, the method developed by Saveant et al.[31,32] was used.

Vacuum heat treatment (VHT) was carried out in the XPS-ultrahigh-vacuum chamber. A heatable molybdenum sample stub was used to hold a Tokai glassy carbon plate in the vacuum chamber. A electrical circuit was used to heat the sample stub, and the temperature at the sample was monitored by a thermocouple. The pressure in the vacuum chamber without sample heating was normally under 10^{-8} Torr. When the stub and glassy carbon were heated, the pressure of the chamber rose to about 10^{-5} Torr and then dropped gradually when sample temperature was above 200 °C. The final pressure was about 10^{-7} Torr when the final temperature (650–700 °C) of treatment was reached. The sample was kept at the final temperature for 1 h and was allowed to cool under the high-vacuum conditions.

To polish glassy carbon electrodes with cyclohexane/Al_2O_3, cyclohexane was first saturated with argon for 15–20 min, and then slurries were prepared with dry 1, 0.3, and 0.05 μm alumina powders (Buehler). Glassy carbon electrodes were polished in cyclohexane/Al_2O_3 slurries on bare glass plates and were sonicated in cyclohexane and then nanopure water for 2 min each. When this procedure was carried out in a glovebag purged with argon gas, the surface O/C ratio was slighly lower.

XPS spectra were acquired with a VG Scientific ESCALAB MKII spectrometer with Mg X-ray radiation source. Both survey spectra and high-resolution spectra for C_{1s} and O_{1s} were collected. Software provided with the instrument was used to deconvolute the constituent peaks under C_{1s} and O_{1s} peaks and to integrate peak area. Instrumental sensitivity factors for the elements were used when surface coverage was calculated.

The redox systems used in this experiment were as follows: 1 mM ascorbic acid (AA, Aldrich Chemical Co.) in 0.1 M H_2SO_4 solution; 1 mM Fe^{2+} in 0.2 M $HClO_4$ made from $Fe(NH_4)_2$-$(SO_4)_2 \cdot 6H_2O$ (Mallinckrodt, Inc.) and 70% $HClO_4$ (GFS Chemicals); 3 mM V^{3+} in 0.2 M $HClO_4$ solution made from VCl_3 (Aldrich Chemical Co.); 5 mM Eu^{3+} in 0.2 M $HClO_4$ solution made from $Eu(NO_3)_3 \cdot 5H_2O$ (Aldrich); $Ru(NH_3)_6^{3+}$ in 1 M KCl solution made from $Ru(NH_3)_6Cl_3$ (Strem Chemicals); 0.5 mM $IrCl_6^{2-}$ in 1 M KCl solution made from K_2IrCl_6 (Aldrich); 1 mM $Fe(CN)_6^{4-}$ in 1 M KCl solution made from $K_4Fe(CN)_6$ (J.T. Baker); 2 mM $Co(en)_3^{3+}$ in 1 M KCl solution made from $Co(en)_3Cl_3$ (J.T. Baker); 2 mM $Co(phen)_3^{2+}$ in 1 M KCl solution made by mixing 2 mM $CoCl_2 \cdot 6H_2O$ (J.T. Baker) and 6 mM 1,10-phenanthroline (J.T. Baker). Additional reagents used in this study included cyclohexane (J.T. Baker), 2,6-AQDS, sodium salt (Aldrich), methylene blue (Aldrich), bis(4-methylstyryl)benzene (BMB, Aldrich), dinitrophenylhydrazine, (DNPH, J.T. Baker), dinitrobenzoyl chloride (DNBC, Aldrich), absolute ethyl alcohol (Mallinckrodt), and pyridine (Mallinckrodt).

RESULTS

(i) GC Surface Preparation. Figure 1 illustrates simplified drawings of target surfaces relevant to the current report. A typical polished surface (Figure 1A) has a 7–20% O/C ratio, with various functional groups and usually surface impurities. Figure 1B represents a polished surface after nonspecific physi- or chemisorption of a monolayer adsorbate such as anthraquinone-2,6-disulfonate. The monolayer is presumed to cover both functional groups and graphitic regions. Figure 1C is "oxide-free" carbon consisting of a variety of carbon sites but no oxygen-containing functional groups. Figure 1D is a polished surface following *specific* chemisorption of derivatizing agents which react with particular function groups, namely dinitrophenylhydrazine (DNPH) for carbonyl groups[33] and dinitrobenzoyl chloride (DNBC) for hydroxyl groups.[29] Procedures leading to GC surfaces approximating those of Figure 1 will be summarized, along with characterization results.

Polished GC. Unless stated otherwise, Tokai GC20 was polished in air to a mirror finish on a Buehler "Texmet" polishing cloth on glass, with a slurry of alumina in Nanopure water (Barnsted, Inc.). Provided that commercial alumina slurries were avoided, special procedures to minimize contamination appeared

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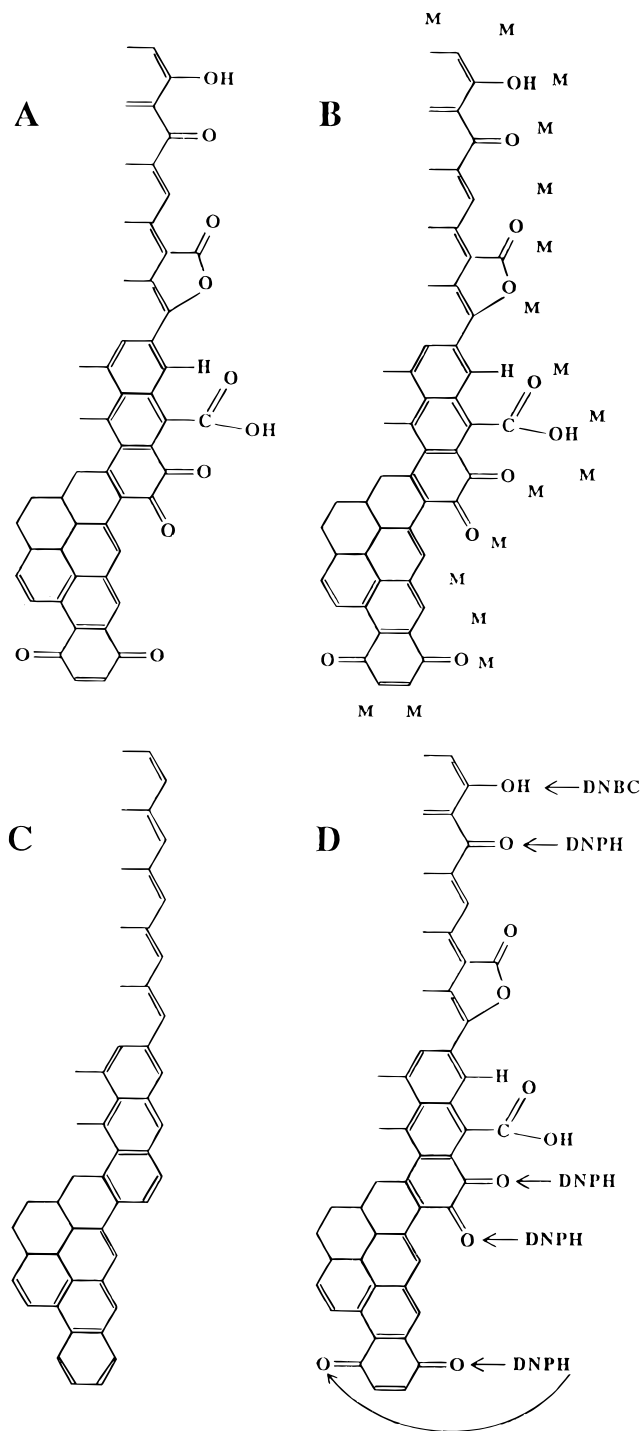(33) Fryling, M. A.; Zhao, J.; McCreery, R. L. *Anal. Chem.* **1995**, *67*, 967.

Figure 1. Normally polished and desired GC surfaces: (A) normally polished GC surface, (B) GC surface covered by a monolayer absorber, (C) oxide-free GC surface, and (D) GC surface on which carbonyl and hydroxyl groups are derivatized.

Table 1. Coverage of Nonspecific and Specific Adsorbates on Polished GC

adsorbate	coverage (pmol/cm²)	monolayer (%)	method	ref
BMB	120[a]	100[a]	Raman[a]	30
AQDS	289 ± 12	160[b]	voltammetry	8
MB	198 ± 20	141[b]	voltammetry	29
NP	650 ± 50	54[b]	voltammetry	31
DNPH	~90	1.2[c]	Raman[d]	33
DNBC	~48	0.96[c]	XPS[e]	29

[a] Calculated from Raman observed adsorption isotherm assuming close packing of BMB. [b] 100% is for close packing of adsorbate on a flat surface. [c] Percent coverage relative to carbon atom surface density (100% = one carbonyl/carbon atom). [d] Estimated from area of 1104 cm^{-1} Raman band. [e] From N_{1s}/C_{1s} XPS intensity ratio.

term "polished GC" will always refer herein to surfaces polished in air with Al_2O_3/water, and such surfaces are assumed to be approximated by Figure 1A. These surfaces should not be confused with GC surfaces polished in Al_2O_3/cyclohexane slurries, which are discussed below.

Monolayer-Coated GC. A variety of adsorbates have been shown to form monolayers on GC and in some cases have been characterized spectroscopically. Of note here are AQDS,[35] methylene blue (MB),[29] BMB,[30] and chemisorbed nitrophenyl.[31] Table 1 lists coverages and characterization techniques which have been reported elsewhere. AQDS, MB, and BMB are strongly physisorbed under the conditions employed and do not appreciably desorb in blank electrolyte. BMB is not electroactive in the region studied, but AQDS ($E_{1/2} \cong -0.2$ V) and MB ($E_{1/2} \cong +0.1$ V) exhibit surface redox waves. Nitrophenyl (NP) chemisorbs after electrochemical formation from nitrophenyl diazonium ion[31] and is electroactive only at quite negative potentials (-1.1 V in acetonitrile). In all situations studied, these nonspecific adsorbers remained on the GC surface during electrode kinetic measurements.

Low Oxide GC. Vacuum heat treatment in various forms has yielded GC surfaces with low O/C ratios, in the 1−6% range.[15,35,36] Survey XPS for several pretreatments used here are shown in Figure 2. Ar$^+$ ion sputtering reduces the O/C ratio but with significant disturbance of the GC microstructure. Table 2 lists the O/C ratios for four procedures used in this work. An obvious issue is the stability of these surfaces after removal from the vacuum chamber. Figure 3 shows the O/C ratios after exposure to air. The abscissa is the exposure time in air following pretreatment, after which the sample was reinserted into UHV and analyzed with XPS. Although there is an initial rise in O/C ratio, it is not rapid, and the O/C very slowly approaches the value on polished surfaces. After 4 days in air, the O/C ratio of the sputtered surface reached 10.1%, still lower than that of the polished surface. For the few minutes required for electrode kinetic measurements discussed below, the O/C ratio increases only slightly after removal of the samples from UHV.

While UHV techniques are effective in reducing the surface O/C ratio, they are also slow and cumbersome. We found that polishing in an alumina/cyclohexane slurry was almost as effective and much simpler. The cyclohexane was argon saturated, and a

unnecessary. Following sonication, polished GC exhibited a $k°$ for Fe(CN)$_6^{3-/4-}$ (1 M KCl) of 0.08 cm/s, and an E_p for AA in 0.1 M H_2SO_4 of 318 mV. The values for Fe(CN)$_6^{3-/4-}$ are close to those obtained on "activated" surfaces following laser activation (>0.5 cm/s, ref 34), vacuum heat treatment (~0.1 cm/s, ref 15), and ultraclean polishing (0.14 cm/s, ref 6). The O/C ratio determined from XPS on GC polished in Al_2O_3/water slurries was 14% and was constant for several days of air exposure. Thus, the

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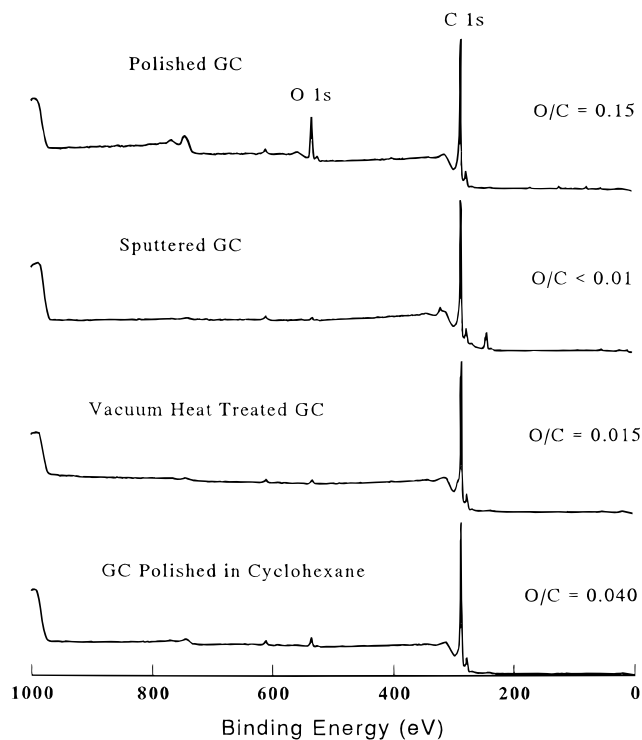
Figure 2. XPS spectra of normally polished amd modified GC electrodes.

Table 2. ΔE_p and O/C Ratios on GC Electrodes

surface treatment	ΔE_p (mV)[a] $Ru(NH_3)_6^{3+/2+}$	ΔE_p (mV)[b] $Fe_{aq}^{3+/2+}$	XPS O/C ratio (%)
polishing in water−alumina	123	150	14 ± 1 $(N = 5)$[c]
Ar^+ sputtering	119	908	<1
vacuum heat treatment	115	439	1.6 ± 0.3 $(N = 3)$
polishing in cyclohexane−alumina	109	352	4.0 ± 0.2 $(N = 3)$

[a] 1 M KCl, 20 V/s. [b] 0.2 M HClO$_4$, 0.2 V/s. [c] Number of surfaces examined.

polishing pad was not used, but the polishing was otherwise conventional. As shown in Figure 3, the O/C ratio was reduced to 4% by cyclohexane/Al$_2$O$_3$ polishing and then slowly increased with exposure to air.

Specific Chemisorption to Functional Groups. As reported previously, DNPH covalently bonds to surface carbonyl groups on GC to form a resonance Raman-active hydrazone.[33] The resulting adduct may be observed with Raman spectroscopy and has a large effect of Fe$^{3+/2+}$ kinetics.[29] This reaction was used as a modifier for carbonyl groups, as indicated in Figure 1. Similarly, DNBC reacts with surface hydroxyl groups to yield an adduct which can be observed with XPS.[29] DNBC is not a sufficiently strong Raman scatterer to be observed with present techniques. In addition, DNPH does not react with lactone, carboxylate, or phenolic groups and is therefore quite selective.[33]

(ii) Electron Transfer Kinetics. Heterogeneous electron transfer rate constants ($k°$ values) were determined for several redox systems on GC surfaces prepared as described. Once this process was complete, the nine redox systems examined fell into several kinetic classes, depending on their sensitivity to surface modifications. The results reported here are subdivided according to these kinetics classes.
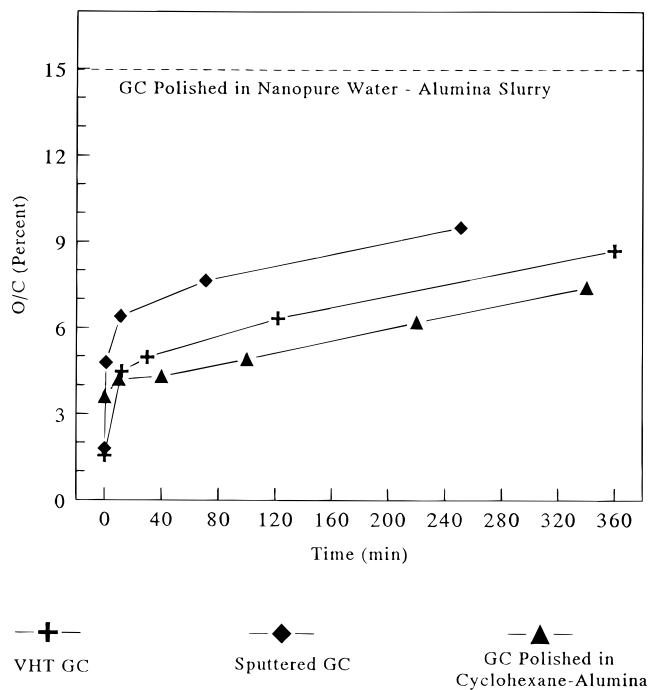

Figure 3. Stability of surface O/C ratio of low oxide GC surfaces as a function of exposure time in air.

Systems Which Are Relatively Insensitive to Surface Chemistry. If the $k°$ for a given redox system is not affected by the presence of monolayer films, a catalytic mechanism involving interaction with a surface group is unlikely to be important. $Ru(NH_3)_6^{2+/3+}$ is such a system, as indicated in Figure 4. Adsorption of a monolayer of BMB, AQDS, NP, or MB has very minor effects on ΔE_p, compared to the polished surface. Table 3 lists changes in ΔE_p following pretreatments leading to the surfaces represented by Figure 1. Note that the first column of Table 3 is the ΔE_p (or E_p^a for AA) for polished GC, but all other columns are *changes* in ΔE_p caused by surface modification. The ΔE_p values for $Ru(NH_3)_6^{2+/3+}$, $IrCl_6^{2-/3-}$, $Co(phen)_3^{2+/3+}$, and $Co(en)_3^{2+/3+}$ behave similarly, with little change in ΔE_p when the surface is coated with a monolayer or the oxides are removed. Therefore, the kinetics of these four systems are observed to be insensitive to surface modification, with the strong implication that electron transfer does not depend on an interaction with a surface site or functional group.

Systems Dependent on Surface Oxides. If electron transfer to a particular redox system is dependent on an oxygen-containing surface functional group, its kinetics should be slower if the surface O/C ratio is decreased, if a monolayer of nonspecific adsorbers is present, or if the oxides are derivatized. We have noted previously that $Fe_{aq}^{3+/2+}$, $V_{aq}^{2+/3+}$, and $Eu_{aq}^{2+/3+}$ exhibit these characteristics,[29] with all three systems having much slower electron transfer on low oxide GC. Figure 5 and Table 2 show the example of $Fe_{aq}^{3+/2+}$ for heat treatment and cyclohexane/Al$_2$O$_3$ polishing. When the surface O/C ratio is reduced to ~1.5% with VHT or ~4% with cyclohexane/Al$_2$O$_3$, the ΔE_p for $Fe_{aq}^{3+/2+}$ increases significantly, indicating a decrease of $k°$ by 1−2 orders of magnitude. In addition, nonspecific adsorption by NP, BMB, and MB increases ΔE_p, as expected if the adsorber covers oxide as well as carbon sites (see Table 3). AQDS adsorption *decreases* ΔE_p for $Fe_{aq}^{3+/2+}$, but we have reported previously that carbonyl groups catalyze $Fe_{aq}^{3+/2+}$.[29] Apparently, the significant increase

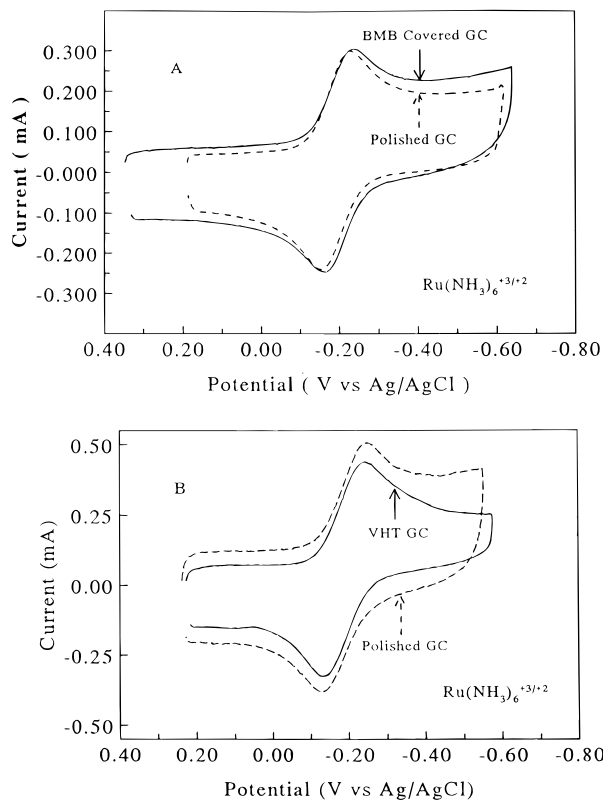**Figure 4.** Cyclic voltammograms of 1 mM $Ru(NH_3)_6^{3+/2+}$ in 1 M KCl on BMB monolayer covered (A) and vacuum heat treated (B) GC electrodes compared to that on normally polished GC electrodes. Scan rate was 20 V/s.
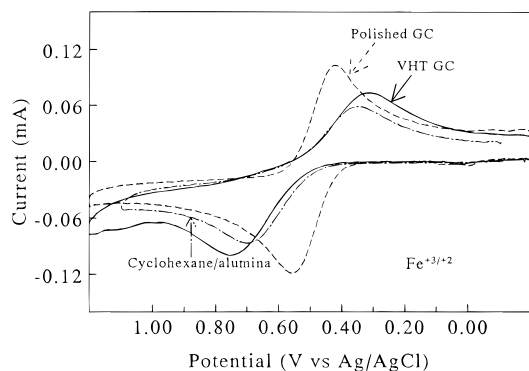

Figure 5. Cyclic voltammograms of $Fe^{3+/2+}$ on VHT and cyclohexane/Al_2O_3 polished GC electrodes.

in surface carbonyl groups upon AQDS adsorption accelerates $Fe_{aq}^{3+/2+}$ electron transfer.

We reported previously that derivatization of surface carbonyl groups with DNPH greatly inhibited $Fe_{aq}^{3+/2+}$ kinetics,[29] and these results are repeated in Table 3. Unlike the nonspecific adsorbers, DNPH specifically modifies carbonyl groups. Control experiments lacking DNPH confirm that the inhibition is not due to sample manipulation or exposure to ethanol. A surface modifier specific for OH groups had a significant but much smaller inhibitory effect on $Fe_{aq}^{2+/3+}$, $Eu_{aq}^{2+/3+}$, and $V_{aq}^{2+/3+}$, as shown in Table 3. Thus, removal of all oxides with UHV, or coverage with nonspecific adsorbers, or specific blocking of surface carbonyls inhibits electron transfer to this class of redox systems.

Surface Sensitive but Not Oxide Sensitive. A third class of redox systems is represented by $Fe(CN)_6^{3-/4-}$ and ascorbic acid (AA). Since AA oxidation is chemically irreversible, E_p^a rather

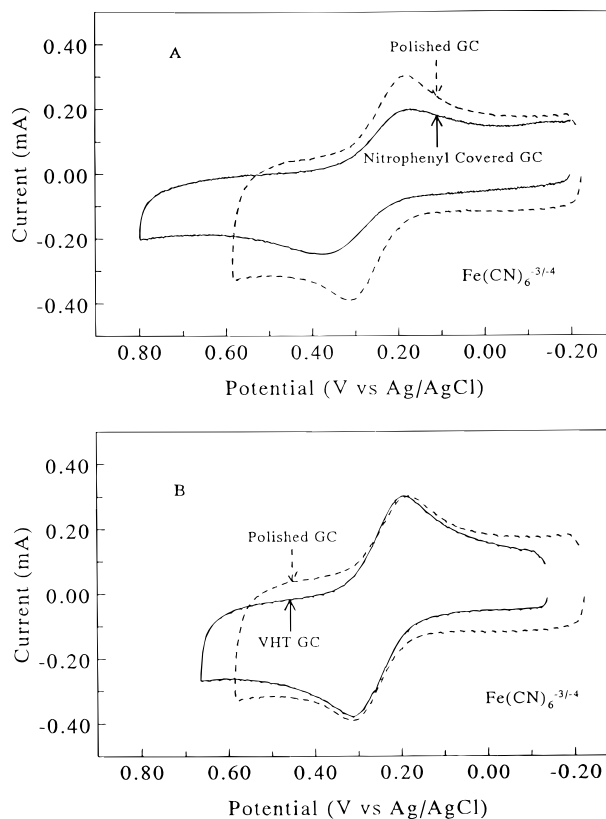**Figure 6.** Cyclic voltammograms of 1 mM $Fe(CN)_6^{3-/4-}$ in 1 M KCl obtained on nitrophenyl monolayer covered (A) and VHT (B) GC electrodes compared to that on normally polished GC electrodes. Scan rate was 20 V/s.

than ΔE_p reflects electron transfer rate, with a more negative value of E_p^a indicating faster electron transfer kinetics. Figure 6 shows the behavior of $Fe(CN)_6^{3-/4-}$ on low oxide and monolayer-coated GC surface. BMB, AQDS, and MB have small inhibitory effects (Table 3), while chemisorbed NP significantly slows electron transfer (Figure 8A). Reduction of the surface O/C ratio has minor effects on ΔE_p for $Fe(CN)_6^{3-/4-}$. Other investigators have also concluded that surface oxides have minor effects on $Fe(CN)_6^{3-/4-}$, except for a fairly small (factor of 3) Frumkin effect when surface carboxylates are deprotonated at neutral pH.[15,20]

AA is a more complex redox system than those discussed so far, involving two electron and one or two protons, depending on pH. Deakin et al.[37] and Hu and Kuwana[38] have shown that the voltammetric oxidation peak shape depends on the relative rates of the two electron transfers, both of which are potential dependent. Nevertheless, E_p^a is a reliable indicator of changes in oxidation rate caused by surface modification. Figure 7 shows the effects of MB physisorption and a reduction of surface O/C ratio of AA voltammetry. The redox couple at about +0.08 V is MB itself, and MB causes a postive shift of 80 mV in E_p^a for AA. Other nonspecific adsorbers have similar effects (Table 3), while specific adsorbers (DNPH and DNBC) have significantly smaller effects on E_p^a.

Figure 7 also shows the effect of reducing the surface O/C ratio from ~15% to ~4% on AA voltammetry. As noted by our laboratory and others,[15] AA voltammetry on clean GC is not

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Table 3.

| | | change in ΔE_p relative to polished GC (mV) | | | | | | | |
| | ΔE_p (mV) polished GC | low oxide | | nonspecific adsorber | | | | specific adsorber | |
		VHT	cyclohexane/Al$_2$O$_3$	NP	BMB	AQDS	MB	DNBC	DNPH
Ru(NH$_3$)$_6$$^{2+/3+}$ 1 M KCl, 20 V/s	$(76 \pm 7)^b$ $N = 6^d$ 113 ± 7^a $N = 4$	0	0 ± 14 $N = 3$	+12	(9 ± 9) $N = 3$	(6 ± 8) $N = 3$	(16 ± 10) $N = 3$	(6 ± 9) $N = 3$	(6 ± 9) $N = 3$
IrCl$_6$$^{2-/3-}$ 1 M KCl, 20 V/s	(68 ± 2) $N = 3$				(9 ± 4) $N = 3$	(2 ± 3) $N = 3$	(7 ± 4) $N = 3$		(7 ± 4) $N = 3$
Co(phen)$_3$$^{2+/3+}$ 1 M KCl, 0.2 V/s	(65 ± 2) $N = 3$				(6 ± 5) $N = 3$		(-1 ± 0) $N = 3$		
Co(en)$_3$$^{2+/3+}$ 1 M KCl, 0.2 V/s	(95 ± 5) $N = 3$				(21 ± 6) $N = 3$		(12 ± 6) $N = 3$		
Fe$_{aq}$$^{3+/2+}$ 0.2 M HClO$_4$, 0.2 V/s	(164 ± 9) $N = 6$ 165 ± 22 $N = 5$	+265	293 ± 77 $N = 4$ $(+300)$	+523	(342 ± 20) $N = 3$	(-52 ± 10) $N = 3$	(195 ± 6) $N = 3$	(88 ± 22) $N = 3$	(533 ± 63) $N = 3$
Eu$_{aq}$$^{3+/2+}$ 0.2 M HClO$_4$, 0.2 V/s	(267 ± 11) $N = 3$ 216		212				(>183)	(58)	(>543)
V$_{aq}$$^{3+/2+}$ 0.2 M HClO$_4$, 0.2 V/s	(280 ± 22) $N = 3$				(>620)	(-107 ± 29) $N = 3$	(561 ± 27) $N = 3$	(210 ± 32) $N = 3$	(>800)
Fe(CN)$_6$$^{3-/4-}$ 1 M KCl, 20 V/s	(91 ± 4) $N = 3$ 108 ± 10 $N = 3$	−5		+138	(9 ± 6) $N = 3$	(30 ± 9) $N = 3$	(9 ± 6) $N = 3$	(5 ± 2) $N = 3$	+65
AA 0.1 M H$_2$SO$_4$, 0.1V /s	$318 \pm 4(E_p)$ $N = 5$ (312)		-8 ± 8^c $N = 3$ $(+4)$	$+120^c$	$+46^c$	$+40^c$	$+80^c$	-12^c	$+28^c$

^{a} Values without parentheses were obtained from Tokai GC20 sheet, polished in the absence of Kel-F, mean and standard deviation. ^{b} Values in parentheses were obtained with Tokai GC20 in commercial Kel-F mount (BAS, Inc.). ^{c} Change in E_p^a with pretreatment. ^{d} Number of surfaces averaged.

sensitive to surface oxides. However, AA is inhibited by monolayer adsorption, implying some chemical interaction with the GC surface.

While surface oxides did not affect E_p for AA immediately after pretreatment, they did affect E_p^a after prolonged exposure of the electrode to air. Figure 8 shows E_p^a for GC electrodes exposed to laboratory air for several hours, *without* any intervening voltammetry. After polishing in water/Al$_2$O$_3$ or cyclohexane/Al$_2$O$_3$, the surface was exposed to air for 1–18 h, followed by a single AA voltammogram. It was observed that repeated voltammetry on a single surface degraded AA response, so a newly polished surface was prepared for each data point. E_p^a on the polished electrode increased with time, while E_p^a on the cyclohexane/Al$_2$O$_3$ polished surface did not, for at least 18 h.

DISCUSSION

The main objective of this report and of extensive efforts by several laboratories is identification of the surface structural factors which determine electron transfer rates at carbon electrodes. The success of the approach described herein depends on two issues: the extent to which the idealized surfaces of Figure 1 are realized and the categorization of redox systems into subclasses depending on their sensitivity to surface structure. In the end, an understanding of electron transfer mechanisms at carbon electrodes should emerge if these goals are realized.

Given the reactivity of carbon surfaces toward dioxygen, it is difficult to maintain an oxide-free carbon surface in an aqueous electrochemical environment. Even if dioxygen could be rigorously excluded, the carbon can oxidize in water at fairly mild

positive potentials. However, VHT, sputtering, and the cyclohexane/Al$_2$O$_3$ polish greatly reduce the O/C ratio to the point where kinetic effects are obvious (e.g., for Fe$^{3+/2+}$). Of these methods, the cyclohexane/Al$_2$O$_3$ polish is the simplest and may be used with either loose GC20 pieces or commercial GC electrodes mounted in Kel-F. At least for the redox systems examined here, no negative effects of cyclohexane exposure were observed, even for AA, which is quite sensitive to surface impurities. Overall, the cyclohexane/Al$_2$O$_3$ polish provides a simple means to reduce the surface O/C ratio and to test the importance of surface oxides to the kinetics of a given electron transfer reaction. The involvement of particular oxygen-containing functional groups may be assessed with the specific derivatization reactions of DNPH and DNBC, as discussed below.

The nonspecific adsorbers provide an initial test of the involvement of an interaction between the surface and the redox system in the charge transfer reaction. It is important to distinguish between an "outer sphere" electron transfer, where the electrode acts merely as a source or sink of electrons, and a more complex process involving chemisorption, bridging, etc. In the outer sphere case, a monolayer of adsorbate would increase the electron tunneling distance and probably modify double-layer properties, but it would not be expected to have a large effect on observed electron transfer rates for thin (<5 Å) monolayers. For example, if electron transfer were dependent solely on electron tunneling, one could estimate the decrease in $k°$ from the tunneling constant observed for alkanethiol films, $e^{-1.06}$ per CH$_2$ group.[39] For a monolayer equal in thickness to 1–2 CH$_2$ groups (approximately the case for MB, AQDS, or BMB), $k°$ would
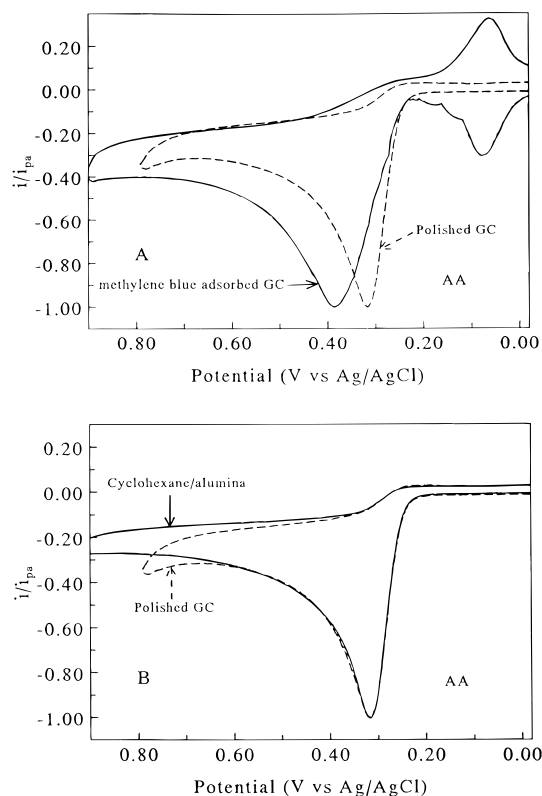
Figure 7. Cyclic voltammogram of 1 mM ascorbic acid in 0.1 M H_2SO_4 obtained on methylene blue monolayer covered (A) and cyclohexane/Al_2O_3 polished (B) GC electrodes compared to that on normally polished GC electrode. Scan rate was 0.1 V/s.
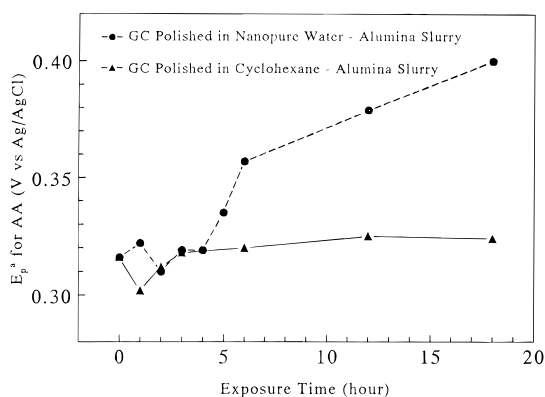

Figure 8. Oxidation peak potential of ascorbic acid versus air exposure time of polished electrodes.

decrease by $1/e$ to $1/e^2$, or 64−86%. If the effect of a monolayer film on a given redox reaction is much larger than this range, some factor other than tunneling distance is indicated. According to this argument, NP would be expected to have a larger effect than MB, AQDS, or BMB, since the increase in tunneling distance would be greater.

The variety of nonspecific adsorbers examined is useful, since two are uncharged (BMB and NP), one is cationic (MB), and one is anionic (AQDS). Furthermore, two are not electroactive in the potential range studied (BMB and NP) and will not be involved in redox mediation. If all of these adsorbers have similar effects (or lack of effects) on a given redox system, it is unlikely that double-layer or mediation effects play a significant role in controlling electron transfer. It is probably an oversimplification to state

that nonspecific absorbers affect only the tunneling distance for outer sphere systems. However, the important observation here is to determine if a redox system is catalyzed by a chemical interaction with the carbon surface. If electron transfer reaction is significantly inhibited by a monolayer of nonspecific adsorber, such an interaction is likely.

The DNPH and DNBC reactions are examples of a variety of surface modifications directed toward altering electron transfer behavior. They have the advantage of reacting with specific surface groups and providing a label for spectroscopic observation. Of particular importance is the fact that a low coverage of the DNPH/carbonyl adduct (<2%) has a large effect on certain reactions (2 orders of magnitude for $Fe^{2+/3+}$). This distinguishes the specific adsorbers from the nonspecific absorbers, since the latter cover everything with a monolayer. As an example, the fact that a 1−2% coverage of DNPH has a large effect on the $Fe^{3+/2+}$ rate clearly indicates the importance of surface carbonyl groups to $Fe^{3+/2+}$ kinetics and distinguishes this effect from a decrease in rate caused by monolayer adsorption of BMB, NP, etc. The effects of these three distinct tests of surface structure on reactivity, i.e., removal of oxides, nonspecific monolayer adsorption, and specific adsorption at functional groups, and their effects on the nine redox systems are summarized in Figure 9. To a large degree, the surfaces examined herein approximate the idealized surfaces of Figure 1.

The categorization of redox systems according to their sensitivity to surface modification naturally leads to questions about electron transfer mechanisms. A variety of possible mechanisms have been identified for carbon surfaces, including but not limited to (1) outer sphere,[10] (2) bridging by either a ligand or a surface group,[29,40,41] (3) redox mediation,[10,18,42,43] (4) adsorption to surface sites,[44−46] (5) electrostatic effects (Frumkin effects),[20] and (6) proton transfer in series or in parallel with electron transfer.[19] In principle, the outer sphere rate should depend only on the distance of closest approach of the redox system to the electrode and the inherent self-exchange rate of the redox system. The other mechanisms, if operative, should increase the observed $k°$ over this outer sphere value. The three classes of redox systems observed for the nine systems examined will be discussed in turn.

Outer Sphere Systems. $Ru(NH_3)_6^{2+/3+}$, $IrCl_6^{2-/3-}$, $Co(phen)_3^{2+/3+}$, and $Co(en)_3^{2+/3+}$ are insensitive to the surface O/C ratio, intentional monolayer coverage, or specific adsorption to surface carbonyl or hydroxyl groups. Monolayer adsorption does produce a small (factor of 2) decrease in $k°$, approximately consistent with that estimated for an increase in tunneling distance. In addition, $Ru(NH_3)_6^{2+/3+}$ and $IrCl_6^{3-/4-}$ are activated only slightly by laser activation. Although exact comparisons are not readily available, the $k°$ values for $Ru(NH_3)_6^{2+/3+}$ and $IrCl_6^{3-/4-}$ on polished GC are similar to those on metals. For example, $k°$ values calculated from exchange current densities reported by Iwasita et al. for $Ru(NH_3)_6^{2+/3+}$ on Hg, Pt, Pd, Au, Cu, and Ag range from 0.51 to 1.24 cm/s.[47] $k°$ for $Ru(NH_3)_6^{2+/3+}$ observed here for polished GC is 0.24 cm/s, while laser activation yields values from 0.28 to 0.85 cm/s, depending on surface oxidation.[48]

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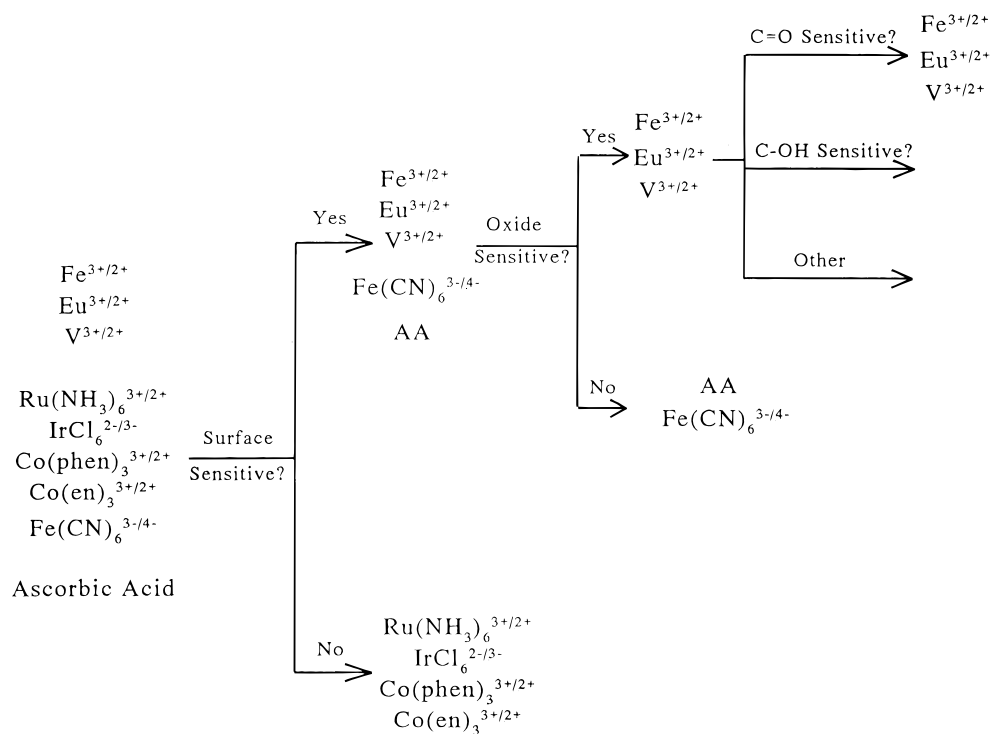
Figure 9. Categorization of redox systems according to the effects of surface modification on electrode kinetics.

Thus, the $k°$ values observed for $Ru(NH_3)_6^{2+/3+}$ on metals and GC agree to approximately a factor of 2. For $IrCl_6^{3-/4-}$, $k°$ on Pt was reported to be 0.50 cm/s,[49] while that observed here for polished GC was also 0.5 cm/s. Collectively, these results indicate that this group of redox systems is insensitive to surface chemistry or adsorbed monolayer films, intentional or otherwise. The GC is acting as a source or sink of electrons, with no catalysis (or inhibition) by chemical changes at the surface. A fairly small perturbation on this conclusion is the Frumkin effect present when surface oxides are deprotonated at neutral pH, leading to a factor of 2−3 decrease in $k°$ for $IrCl_6^{3-/4-}$ and increase in $k°$ for $Ru(NH_3)_6^{2+/3+}$.[20] This effect is larger when oxides are more prevalent but is attributable to electrostatic effects rather than a change in electron transfer mechanism.

Inner Sphere Systems Catalyzed by Surface Carbonyls. As noted earlier, $Fe_{aq}^{3+/2+}$, $Eu_{aq}^{2+/3+}$, and $V_{aq}^{2+/3+}$ are much slower on low oxide or DNPH treated GC surfaces. In a previous report, we concluded that these systems exhibit outer sphere behavior in the absence of carbonyl groups but were catalyzed significantly (by 1−3 orders of magnitude) when surface carbonyls were exposed.[29,50] The present results are entirely consistent with this conclusion, with large decreases in observed rate when carbonyls are removed or covered or specifically derivatized with DNPH. Although the mechanism must involve an interaction between the redox systems and surface carbonyls, the nature of the interaction is not obvious. We have considered both a ligand substitution of ligated water with a surface group[8] and an "outer sphere bridge" between the hexaaquo complex and the carbonyl.[29] The fact that the OH reagent DNBC causes a minor decrease in rate compared to DNPH might indicate an alternative but minor pathway involving both surface carbonyls and hydroxyls. In any case, it is clear that the inner sphere route dominates the electron transfer process unless the carbonyl coverage is very low.

Inner Sphere, Not Oxide Catalyzed. The rates of AA and $Fe(CN)_6^{3-/4-}$ do not vary significantly with surface oxide coverage, but they are sensitive to monolayer adsorption. Other investigators[37,38] have noted the insensitivity of $Fe(CN)_6^{3-/4-}$ and AA to surface oxides and have suggested other mechanisms, such as hydrophobic effects or the involvement of cations. AA oxidation is a multistep process, and any of the steps may be affected by surface modifcations. There are clear examples already cited available for the importance of redox mediation and/or chemisorption to electron transfer rates, but these mechanisms did not appear to be involved in the nine systems studied. For those cases where the redox mediator or chemisorption site are known, the effects of the pretreatment procedures discussed here should be predictable.

In conclusion, it is clear that every mechanism and possibly every redox system will depend to varying degrees on carbon surface pretreatment. The classification of redox systems according to their sensitivity to surface chemistry is informative but imperfect. At least initially, a more important outcome of this report is development of several tests for how carbon surface variables affect the kinetics of a given system of interest.

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