

Facile Preparation of Active Glassy Carbon Electrodes with Activated Carbon and Organic Solvents

Srikanth Ranganathan, Tzu-Chi Kuo, and Richard L. McCreery*

Department of Chemistry, The Ohio State University, 100 West 18th Avenue, Columbus, Ohio 43210

Pretreatment of glassy carbon (GC) electrodes with 2-propanol, acetonitrile, or cyclohexane had a significant effect on electrode kinetics, adsorption, and capacitance. Reagent grade solvents slowed electron transfer rates for dopamine, ascorbic acid, $\text{Fe}^{3+/2+}$, and $\text{Fe}(\text{CN})_6^{3-/4-}$ and decreased adsorption of anthraquinone-2,6-disulfonate (AQDS) and methylene blue (MB). However, if activated carbon (AC) was present in the solvent during pretreatment, the result was increased electron transfer rates and adsorption for several commonly studied redox systems. The large surface area of AC acts as a “getter” for solvent impurities and for species desorbed from the GC surface, leading to a carbon electrode surface with higher capacitance, higher adsorption of AQDS and MB, and faster electron-transfer rates for $\text{Fe}(\text{CN})_6^{3-/4-}$, dopamine, and ascorbic acid. In addition, the treated surfaces were more reproducible, and aged electrodes were reactivated by AC in 2-propanol. The results imply that large, polar organic impurities are present on the polished GC surface which are removed by the combination of an organic solvent and activated carbon. These impurities contain oxygen detectable by XPS and appear to be weakly catalytic toward the $\text{Fe}^{3+/2+}$ redox system.

The goal of understanding the factors which control electron transfer (ET) kinetics at carbon electrodes has remained elusive, despite the wide use of carbon electrodes and the extensive investigations of their electrochemical behavior.^{1–5} A prerequisite to determining ET mechanisms at carbon electrodes is the preparation of reproducible and hopefully well-defined surfaces for which surface structure and electrochemical behavior may be correlated. However, the propensity of most carbon surfaces to oxidize and/or adsorb impurities leads to generally variable surface structures and accompanying variability in properties. A wide variety of surface preparations for carbon electrodes has been

described, particularly for glassy carbon.^{5–12} Depending on the application, surface preparation can be critical to performance, with apparently minor changes in procedure leading to large effects. In addition to practical considerations of reproducibility and stability, surface preparations bear heavily on the larger question of the relationship of surface structure and ET reactivity. To further complicate matters, results from several laboratories including our own have established that carbon surface properties can affect ET kinetics for different redox systems in very different ways.^{13–17} For example, $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ is fairly insensitive to surface preparation, with the observed heterogeneous ET rate constant (k^0) varying by less than a factor of 10 for a wide range of surface modifications. In contrast, k^0 for $\text{Fe}^{3+/2+}$ in 0.2 M HClO_4 can vary by factors of 100–1000, due to catalysis by surface carbonyl groups.¹⁴ Pretreatment procedures which dramatically affect ET kinetics for dopamine and ascorbic acid may have little effect on “outer-sphere” systems such as $\text{Ru}(\text{NH}_3)_6^{3+/2+}$, $\text{IrCl}_6^{3-/2-}$, or $\text{Co}(\text{en})_3^{3+/2+}$. Therefore, several redox systems with different ET mechanisms should be considered when the effects of surface preparation techniques are examined. Previous reports from our laboratory have proposed systematic procedures for assessing surface variables which affect ET kinetics for particular redox systems.^{5,14,17}

Polishing is the most common preparation procedure for carbon electrodes,^{4,12} particularly for glassy carbon (GC) and microdisk electrodes made from carbon fibers. During the process of developing chemical modifications for polished GC surfaces, we often noted large effects of organic solvent exposure on ET kinetics. It became apparent that understanding these solvent

- (1) McCreery, R. L.; Cline, K. K.; McDermott, C. A.; McDermott, M. T. *Colloids Surf.* **1994**, *93*, 211.
- (2) Kinoshita, K. *Carbon: Electrochemical and Physicochemical Properties*; Wiley: New York, 1988.
- (3) McCreery, R. L. In *Electroanalytical Chemistry*; Bard, A. J., Ed.; Dekker: New York, 1991; Vol. 17, pp 221–374.
- (4) McCreery, R. L. In *Laboratory Techniques in Electroanalytical Chemistry*, 2nd ed.; Kissinger, P. T., Heineman, W. R., Eds.; Dekker: New York, 1996; Chapter 10.
- (5) McCreery, R. L. Electrochemical Properties of Carbon Surfaces. In *Interfacial Chemistry*; Wieckowski, A., Ed.; Dekker: New York; in press.

- (6) Wightman, R. M.; Deakin, M. R.; Kovach, P. M.; Kuhr, W. G.; Stutts, K. J. *J. Electrochem Soc.* **1984**, *131*, 1578.
- (7) McDermott, M. T.; Kneten, K. R.; McCreery, R. L. *J. Phys. Chem.* **1992**, *96*, 3124.
- (8) Kneten, K. R.; McCreery, R. L. *Anal. Chem.* **1992**, *64*, 2518.
- (9) Engstrom, R. C.; Strasser, V. A. *Anal. Chem.* **1984**, *56*, 136.
- (10) Cabaniss, G. E.; Diamantis, A. A.; Murphy, W. R., Jr.; Linton, R. W.; Meyer, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 1845.
- (11) Deakin, M. R.; Stutts, K. J.; Wightman, R. M. *J. Electroanal. Chem. Interfacial Electrochem.* **1985**, *182*, 113.
- (12) Hu, I. F.; Karweik, D. H.; Kuwana, T. *J. Electroanal. Chem. Interfacial Electrochem.* **1985**, *188*, 59.
- (13) Cline, K. K.; McDermott, M. T.; McCreery, R. L. *J. Phys. Chem.* **1994**, *98*, 5314.
- (14) Chen, P.; McCreery, R. L. *Anal. Chem.* **1996**, *68*, 3958.
- (15) Fagan, D. T.; Hu, I. F.; Kuwana, T. *Anal. Chem.* **1987**, *59*, 131.
- (16) Baur, J. E.; Kristensen, E.; May, L.; Wiedemann, D.; Wightman, R. M. *Anal. Chem.* **1988**, *60*, 1268.
- (17) Chen, P.; Fryling, M. A.; McCreery, R. L. *Anal. Chem.* **1995**, *67*, 3115.

effects would provide new insights into the relationship between surface structure and ET reactivity. Toward that end, we undertook a broad study of understanding the effects on surface structure brought about by three common solvents and how these changes affect the electrochemical behavior of several redox systems. Since even reagent grade solvents contain impurities which may adsorb on the GC surface, activated carbon (AC) was present in the solvents during electrode treatment. The relatively large surface area of the suspended AC compared to the GC electrode results in preferential adsorption of solvent or electrode impurities on the AC rather than the GC surface. Scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), and Raman spectroscopy were applied to understand changes in surface morphology and structure. Electrochemical studies including cyclic voltammetry and adsorption and capacitance measurements were conducted, and the results were related to the effects of solvent treatment.

EXPERIMENTAL SECTION

GC electrodes (GC-20) were obtained from Bioanalytical Systems Inc. (West Lafayette, IN). The two commercial GC electrodes studied (designated "A" and "B") yielded slightly different electrochemical behaviors, but the trends upon solvent treatment were the same. For electrodes subjected to XPS analysis, a GC-20 plate (Tokai) was cut into approximately 1 cm² samples before polishing. There have been reports of Kel-F carryover onto mounted GC electrodes during polishing,⁹ but we chose to emphasize the commercial electrodes here because of their wide use. A previous report comparing electron transfer kinetics at mounted and unmounted GC electrodes showed only minor differences for a range of redox systems.¹⁴ The polishing procedure, described previously, employed dry alumina powders from Buehler (Lake Bluff, IL) slurried with "Nanopure" water (Barnstead, Dubuque, IA).^{4,14,17} The glassy carbon electrodes were hand polished successively in 1.0, 0.3, and 0.05 μm alumina/water slurries on Buehler microcloth polishing cloth. Commercial alumina slurries containing organic deagglomerating agents were avoided. The electrode was rinsed with Nanopure water upon changing from one grade of alumina to another and then sonicated in Nanopure water for 10 min after polishing. Electrodes were polished this way before every experiment, unless stated otherwise, and will be referred to as "conventionally polished" electrodes. To prepare the AC/solvent mixture, AC was mixed with 2-propanol (IPA), acetonitrile, Nanopure water, or cyclohexane in a 1/3 (v/v) AC/solvent ratio. The mixture was covered and allowed to stand for 30 min before use. IPA, CH₃CN, and cyclohexane were of reagent grade and were used without further purification unless noted otherwise. For solvent treatment, the electrode was immersed in the sonicated solvent or AC/solvent mixture for 10 min, followed by an additional 10 min sonication in Nanopure water.

The redox systems examined were as follows: 1 mM Fe²⁺ in 0.2 M HClO₄ made from Fe(NH₄)₂(SO₄)₂·12H₂O (Mallinckrodt Inc.) and 70% HClO₄ (GFS Chemicals); 1 mM Fe(CN)₆⁴⁻ in 1 M KCl from K₄Fe(CN)₆ (Mallinckrodt Inc.); 1 mM [Ru(NH₃)₆]³⁺ in 1 M KCl from Ru(NH₃)₆Cl₃ (Aldrich); 1 mM ascorbic acid (AA, Aldrich Chemical Co.) in 0.1 M H₂SO₄; 1 mM Dopamine (DA, Sigma) in 0.1 M H₂SO₄. The solvents used in this study were cyclohexane (Fischer Scientific), 2-propanol (Mallinckrodt Inc.),

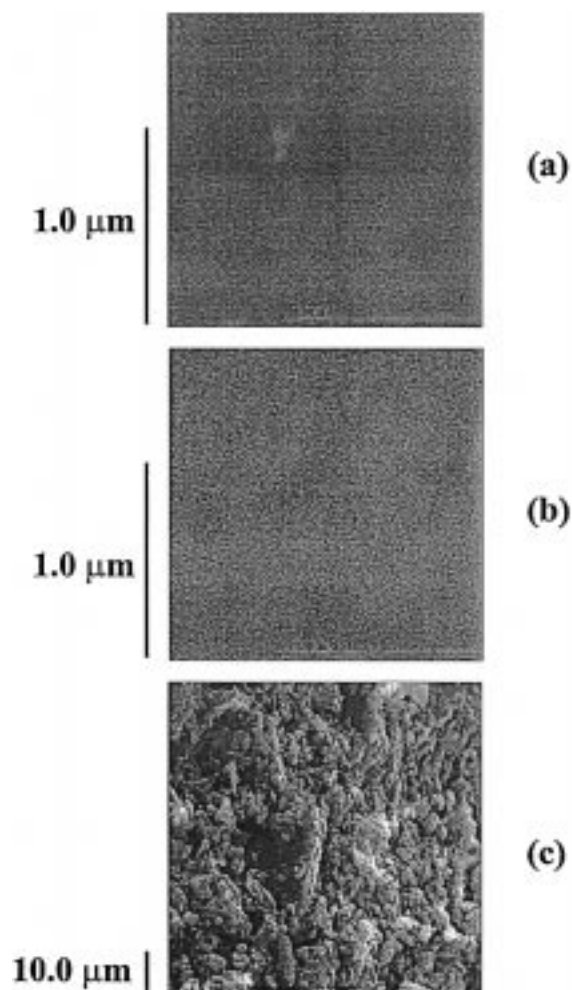


Figure 1. SEM images of (a) polished GC, (b) polished GC treated with AC/IPA, and (c) activated carbon particles. Note scale change between (b) and (c).

and acetonitrile (Mallinckrodt Inc.). Other materials included sulfuric acid (Mallinckrodt Inc.), activated carbon (Norit A, Jennele Chemical Co., Cincinnati, OH), anthraquinone-2,6-disulfonate (AQDS) sodium salt (Aldrich), and methylene blue (MB, Aldrich).

XPS spectra were obtained using a VG Scientific ESCALAB MKII spectrometer with an Mg X-ray radiation source. Both survey and high-resolution spectra for C_{1s} and O_{1s} were collected, and peak areas were used to calculate surface oxygen/carbon ratios. Sensitivity factors were taken into account when calculating the atomic O/C ratios.

The adsorption procedure for AQDS and methylene blue adsorption has been reported previously.^{7,14} A 40 μM AQDS solution in 0.1 M HClO₄ and 40 μM methylene blue in 0.1 M H₂SO₄ solution were used to examine adsorption on GC surfaces.

RESULTS

Surface Characterization. X-ray photoelectron spectroscopy (XPS), SEM, and Raman spectroscopy were used to observe possible surface changes caused by AC/solvent sonication. As noted in the Experimental Section, electrodes were always sonicated in Nanopure water after solvent treatment, in part to remove residual activated carbon. The SEM images in Figure 1

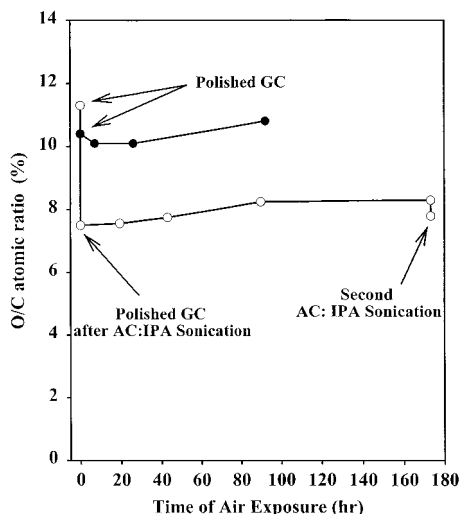


Figure 2. XPS O/C atomic ratio as a function of air exposure time for polished GC (closed circles) and AC/IPA treated GC (open circles). A second AC/IPA treatment occurred after 175 h.

are typical and show no AC particles on the treated surface, even though SEM of the AC is obviously different from GC. Higher magnification images of polished and AC/solvent treated GC revealed only pits inherent in GC.^{18,19} In addition, the XPS line width (fwhm) for the C_{1s} band of polished GC (1.12 eV), AC/IPA treated GC (1.11 eV) and AC (1.32 eV) indicated no observable broadening of the C_{1s} band by residual AC on the treated surface.

The O/C atomic ratio determined from the ratio of the O_{1s} and C_{1s} XPS band areas is typically 8–15% for polished GC.^{4,14} Following AC/2-propanol treatment, the O/C decreased to 7–8%. As shown in Figure 2, O/C ratios for both the polished and AC/IPA treated surfaces slowly increased, with the treated GC reaching a maximum of ~8% after 7 days in air. Previous reports on GC with lower O/C ratios prepared by vacuum heat treatment (VHT), sputtering, or anaerobic polishing showed an increase in O/C ratios, from <3% to 6–9% in 6 h.¹⁴ The rapid drop in O/C ratio with AC/IPA treatment implies that an oxygen-containing adsorbate is removed by the solvent. At least for the AC/IPA, VHT, sputtered, and anaerobically polished GC surfaces, air exposure resulted in an increase in O/C ratio to a maximum of 7–9%, and return to the polished value of >10% was not observed upon standing in air.

High-resolution XPS of the C_{1s} band revealed small but reproducible changes in the “shoulder” region from 286 to 289 eV. AC/IPA treatment reduced the intensity of this “shoulder”, implying reduction in carbon oxide coverage. As noted above, the C_{1s} band for AC has a quite different line shape, which was not observed following AC/IPA treatment. For comparison purposes, the O/C ratio for the AC used was ~7%. The Raman spectrum of activated carbon is quite distinct from that of GC, with D/E_{2g} ratios of 2.34 for AC and 1.86 for polished GC. Polished GC exhibits nearly baseline-resolved D and E_{2g} bands,^{3,19} while the corresponding AC bands are broadened and overlapped. The D/E_{2g} ratio was constant across the AC/IPA treated GC surface, with no indication of AC particles observable with repeated macro- (~50 μm spot size) or microsampling (~1 μm spot size).

(18) Kazee, B.; Weisshaar, D.; Kuwana, T. *Anal. Chem.* **1985**, *57*, 2739.

(19) Ray, K.; McCreery, R. L. *Anal. Chem.* **1997**, *69*, 4680.

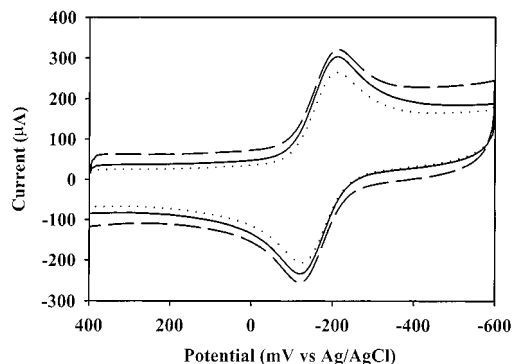


Figure 3. Voltammograms of 1 mM $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ (1 M KCl) at 20 V/s on polished GC (solid curve), IPA treated GC (dots), and AC/IPA treated GC (dashes). Background current was not subtracted.

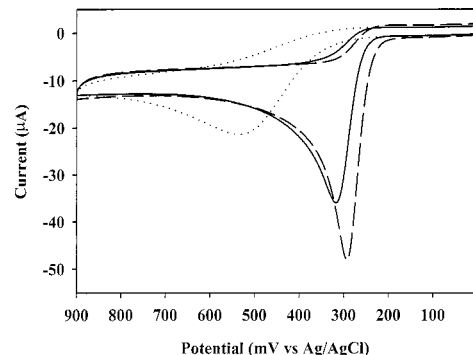


Figure 4. Voltammograms of 1 mM ascorbic acid in 0.1 M H_2SO_4 (0.10 V/s) on polished GC (solid curve), IPA treated GC (dots), and AC/IPA treated GC (dashes). Background current was not subtracted.

Electrode Kinetics. Five redox systems were selected to evaluate the effects of solvent treatment on GC electrodes, on the basis of previous experience and extensive correlative results from the literature. $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ is relatively insensitive to surface conditions (as noted earlier), and k^0 for GC is similar to that for metals, with values ranging from 0.1 to 1.0 cm/s .¹⁴ $\text{Fe}(\text{CN})_6^{3-/4-}$ exhibits much greater sensitivity to preparation procedures, with rates ranging from <0.01 cm/s for conventional polishing to >0.5 cm/s for laser activation.^{1,4,12} $\text{Fe}^{3+/2+}$ (0.2 M HClO_4) has been shown to be very sensitive to surface oxide coverage, particularly that of carbonyl groups.^{17,20} It has an uncatalyzed k^0 of ca. 10^{-5} cm/s in the absence of surface carbonyls and $k^0 > 10^{-2}$ cm/s on intentionally oxidized GC. Ascorbic acid (AA) and dopamine (DA) have long been studied on carbon due to their biochemical importance, and both exhibit ET kinetics which are sensitive to surface cleanliness and oxidation.^{3,16,21–23} Although the ET kinetics of DA and AA have not been demonstrated to depend directly on surface oxides, the adsorption of DA (a cation) is increased and that of AA is decreased (an anion above pH 4) when oxides are present.²⁴

Figures 3 and 4 show the effect of solvent treatment on $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ and AA voltammetry. 2-Propanol and AC/IPA have

(20) McDermott, C. A.; Kneten, K. R.; McCreery, R. L. *J. Electrochem. Soc.* **1993**, *140*, 2593.

(21) Deakin, M. R.; Kovach, P. M.; Stutts, K. J.; Wightman, R. M. *Anal. Chem.* **1986**, *58*, 1474.

(22) Deakin, M. R.; Wightman, R. M. *J. Electroanal. Chem. Interfacial Electrochem.* **1986**, *206*, 167.

(23) Hu, I. F.; Kuwana, T. *Anal. Chem.* **1986**, *58*, 3235.

(24) Allred, C. D.; McCreery, R. L. *Anal. Chem.* **1992**, *64*, 444.

Table 1. Variation of Capacitance and Peak Separation for Ascorbic Acid and Ru(NH₃)₆^{3+/2+}

	capacitance ($\mu\text{F}/\text{cm}^2$)	E_p (anodic) for 1 mM AA in 0.1 M H ₂ SO ₄ , ^a mV vs Ag/AgCl (scan rate 100 mV/s)	ΔE_p for Ru(NH ₃) ₆ ^{3+/2+} in 1 M KCl, ^a mV (scan rate 20 V/s)
electrode A ^b			
polished GC	55 ± 10 (12) ^c	323 ± 7 (5) ^c	78 ± 7 (5) ^c
IPA sonicated	39 ± 3 (3)	338 ± 9 (5)	79 ± 10 (5)
CH ₃ CN sonicated	39 ± 5 (3)	554 ± 27 (5)	86 (2)
cyclohexane sonicated	24 ± 3 (3)	378 ± 12 (5)	80 (2)
water sonicated	51 ± 13 (3)	325 ± 9 (5)	83 (2)
electrode B ^b			
polished GC	38 ± 16(12)	321 ± 7 (5)	82 ± 7 (5)
AC/IPA sonicated	66 ± 11 (3)	299 ± 5 (5)	85 ± 5 (5)
AC/CH ₃ CN sonicated	72 ± 9 (3)	299 ± 10 (5)	80 (2)
AC/cyclohexane sonicated	36 ± 6 (3)	314 ± 9 (5)	83 (2)
AC/water sonicated	30 ± 1 (3)	316 ± 6 (5)	80 (2)

^a Electroactive species concentrations were 1 mM. ^b Electrodes A and B were different commercial GC electrodes (Bionalytical Systems).
^c All the values reported are mean ± standard deviation; values in parentheses indicate number of trials.

Table 2. Variation of ΔE_p and the Rate Constant for 1 mM Fe(CN)₆^{3-/2-} in 1 M KCl as a Result of Solvent Sonication and AC/Solvent Sonication^a

solvent	electrode A		electrode B	
	conventionally polished	solvent sonicated	conventionally polished	solvent/AC sonicated
2-propanol	118 ± 21 (0.047) ^a	145 ± 24 (0.034) ^a	95 ± 3 (0.085) ^a	93 ± 5 (0.090) ^a
acetonitrile	123 ± 19 (0.043)	142 ± 24 (0.034)	96 ± 7 (0.083)	94 ± 10 (0.088)
cyclohexane	114 ± 26 (0.051)	139 ± 9 (0.035)	102 ± 8 (0.069)	108 ± 16 (0.059)
water	128 ± 19 (0.040)	122 ± 16 (0.044)	101 ± 7 (0.071)	98 ± 9 (0.078)

^a Peak potential difference (mV) reported as mean ± standard deviation of five trials. Values in parentheses are rate constants calculated from the mean value in cm/s.

Table 3. ΔE_p Values for 1 mM Dopamine in 0.1 M H₂SO₄ (Scan Rate 200 mV/s)

solvent	electrode A			electrode B		
	conventionally polished	solvent sonicated	AC/solvent sonicated	conventionally polished	AC/solvent sonicated	solvent sonicated
2-propanol	52 ± 3 ^a	70 ± 10 ^a	58 ± 4 ^a	47 ± 3 ^a	41 ± 2 ^a	68 ± 8 ^a
acetonitrile	53 ± 2	114 ± 15	57 ± 8	54 ± 7	39 ± 1	79 ± 11
cyclohexane	52 ± 4	109 ± 14	66 ± 12	47 ± 5	45 ± 3	101 ± 7
water	53 ± 4	53 ± 3	52 ± 3	47 ± 2	47 ± 1	50 ± 2

^a Peak potential difference (mV) reported as mean ± standard deviation of five trials.

minor effects on Ru(NH₃)₆^{3+/2+} except for the changes in background current. These changes are due primarily to changes in observed capacitance discussed in the next section. As shown in Table 1, the ΔE_p (20 V/s) for Ru(NH₃)₆^{3+/2+} ranges from 78 to 86 mV for treatments with three solvents and water, with the presence of AC having little effect. The AA voltammograms in Figure 4 show very different behavior. CH₃CN sonication *without* AC results in an ~200 mV increase in E_p , indicating substantially slower ET kinetics. However, CH₃CN containing AC results in a voltammogram characteristic of fast ET, as fast as that observed for laser activation or VHT.^{3,15} As shown in Table 1, IPA, CH₃CN, and cyclohexane have varying kinetic effects, but the polar solvents studied (IPA and CH₃CN) both yield rapid AA kinetics when AC is present. Table 2 lists the kinetic results for Fe(CN)₆^{3-/4-} in 1 M KCl, which demonstrate that untreated solvents decrease k^o while AC/solvent system have little effect.

The effects of solvent treatment on DA and Fe^{3+/2+} were fairly large and were studied in more detail. For both systems, a

polished electrode was treated with a given solvent containing AC, a voltammogram was recorded, and then the electrode was treated again with the same solvent lacking AC. For a different electrode, the sequence was reversed. This procedure clearly distinguished the kinetic effects of AC/solvent from those of the solvent alone. For all cases except water, the reagent grade solvents lacking AC increased ΔE_p for DA (Table 3). The addition of AC during solvent treatment decreased ΔE_p for this activated electrode to values slightly larger than that of the initial polished surface. If the AC/solvent sonication step followed polishing immediately, quite small ΔE_p values resulted for DA, in the range 39–45 mV. In addition, AC/IPA sonication dramatically decreased ΔE_p for GC electrodes intentionally contaminated by soap solution or prolonged air exposure, as indicated by Table 4. Since DA oxidation is a multistep process, it is difficult to estimate ET rate constants,²² but the directions and approximate magnitudes of the kinetic effects of solvents are obvious.

Table 4. ΔE_p Values for 1 mM Dopamine in 0.1 M H_2SO_4 during a Sequence of Electrode Treatments (Scan Rate 200 mV/s)

sequence	ΔE_p , mV
polished	52
after AC/IPA	41
after exposure to soap solution	322
AC/IPA treatment after soap	53
repolished	52
after 1 week in air	164
after AC/IPA	41
repolished (three trials)	47 ± 6^a
stirred, not sonicated, in AC/IPA, three trials	36 ± 3
repolished (five trials)	47 ± 4
purified IPA, AC not present, sonicated	45 ± 4

^a Mean \pm standard deviation.

Results for the same sequence of solvent and AC/solvent treatment for $Fe^{3+/2+}$ in 0.2 M $HClO_4$ are listed in Table 5. In all cases, including Nanopure water, solvent without AC increased ΔE_p , often significantly. AC/solvent treatment only partly restored the electrode activity. In contrast to the other redox systems, AC/solvent treatment immediately after polishing *increased* ΔE_p , more so with CH_3CN and IPA.

Control experiments were performed with dopamine to determine if sonication, the presence of AC, or both during treatment were required for kinetic changes. As shown in Table 4, stirring in AC/IPA without sonication decreased ΔE_p for DA, at least as much as sonication in AC/IPA. So a mechanism related to the high local energies associated with sonication is unlikely. A sample of AC/IPA was allowed to stand for 3 months with occasional stirring, and then the purified IPA was decanted. An electrode sonicated in this IPA with AC absent showed a modest decrease in ΔE_p for DA (from 47 to 45 mV) but did not exhibit the significant increase (from 52 to 70 mV) observed for reagent grade IPA.

Capacitance and Adsorption. Interfacial capacitance was determined from the voltammetric background current and expressed as microfarads per square centimeter of geometric area. The effects of solvent treatment on observed capacitance are apparent in Figure 3 and are listed in Table 1 for two different GC electrodes. Although the initial, polished surface showed variation in capacitance for the two electrodes, the effects of solvent treatment were consistent. Reagent grade solvents without AC decreased the capacitance significantly in all cases except water. Treatment with AC suspended in the two polar organic solvents (IPA and CH_3CN) significantly increased capacitance, while AC in water or cyclohexane had minor effects.

Interfacial capacitance depends on microscopic surface area and the presence of adsorbed molecules, among other factors. Sonication would not be expected to change the microscopic area of GC, so the capacitance changes are likely to reflect deposition or removal of adsorbed films. Generally speaking, adsorbed films decrease the capacitance on GC, with the surfaces having the highest capacitance being the most active toward electron transfer and adsorption.^{4,24–26}

Adsorption on solvent treated GC was evaluated with anthraquinone-2,6-disulfonate (AQDS) and methylene blue (MB).

Both redox systems have been shown to yield monolayer coverage on clean GC surfaces, and both have readily observed voltammetric features for the adsorbed species.^{7,14} Voltammograms of dilute (10^{-5} M) AQDS in 0.1 M $HClO_4$ are shown in Figure 5. Pretreatment with CH_3CN without AC reduces the observed AQDS adsorption, while AC/ CH_3CN pretreatment increases adsorption above the polished surface value. Integration of the voltammetric reduction wave yields the AQDS coverages (relative to geometric area) listed in Table 6. For comparison, GC following laser activation exhibits saturation coverage of 228 pmol/cm².⁷ MB showed qualitatively similar behavior on a GC electrode treated with IPA. The reagent grade solvent decreased surface coverage, and AC/solvent pretreatment increased it above the polished surface value. When AQDS was adsorbed to GC *before* solvent treatment, sonication in water or IPA produced little change in AQDS coverage. However, sonication in AC/IPA removed AQDS below detectable levels.

DISCUSSION

It would normally be assumed that reagent grade organic solvents should remove impurities from a polished GC surface, thus increasing electron transfer to solution redox species. In addition, removal of impurities would be expected to increase the adsorption of those solution species which normally compete with impurities for adsorption sites. However, IPA, CH_3CN , and cyclohexane all caused increases in ΔE_p when activated carbon was absent, implying that they are depositing rather than removing impurities from the conventionally polished surface. Apparently, the adsorption of impurities from the solvent is sufficiently strong on polished GC that the three organic solvents considered have negative rather than positive effects on electrode kinetics. Addition of activated carbon to the solvent provides a large active surface area both to purify the solvent and to trap adsorbates which are desorbed from the GC. The practical advantage of AC/solvent treatment over solvent alone is the “getting” action of the AC, allowing the AC to compete with the GC for the solvent and electrode impurities, thus leading to a cleaner GC surface.

The AC need not be present during sonication, nor is sonication itself required for improved electrode behavior. If the solvent is prepurified with AC before being used to clean the electrode, the ET rates increase relative to that of the polished surface, although not as much as for simultaneous AC and sonication (Table 4). Stirring in the presence of AC rather than sonication decreases ΔE_p for DA, to a value comparable to that observed after sonication. These results argue against a mechanism based on abrasion of the GC by AC during sonication or an increased microscopic surface area due to residual AC particles remaining after treatment. Several additional observations support the conclusion that the AC is acting to purify the solvent and is not directly responsible for electrode activation. First, SEM shows no residual AC particles on GC after treatment, nor are there any visible changes to the GC surface. Second, the C_{1s} peak for AC is broader than that for GC, but the observed line width after treatment corresponds to GC. Third, Raman microscopy reveals a constant D/E_{2g} ratio on the GC surface, equal to that of GC and not AC. We cannot completely rule out the possibility that some

(25) Hance, G. W.; Kuwana, T. *Anal. Chem.* **1987**, *59*, 131.

(26) Rice, R. J.; Pontikos, N.; McCreery, R. L. *J. Am. Chem. Soc.* **1990**, *112*, 4617.

Table 5. ΔE_p Values for 1 mM $\text{Fe}^{3+/2+}$ in 0.2 M HClO_4 (Scan Rate 200 mV/s)

solvent	electrode A			electrode B		
	conventionally polished	solvent sonicated	AC/solvent sonicated	conventionally polished	AC/solvent sonicated	solvent sonicated
2-propanol	126 \pm 28 ^a	274 \pm 49 ^a	244 \pm 19 ^a	137 \pm 20 ^a	194 \pm 11 ^a	290 \pm 53 ^a
acetonitrile	134 \pm 40	407 \pm 36	277 \pm 21	150 \pm 28	219 \pm 34	367 \pm 31
cyclohexane	122 \pm 13	352 \pm 38	270 \pm 22	143 \pm 24	162 \pm 15	379 \pm 63
water	140 \pm 24	194 \pm 37	185 \pm 28	142 \pm 30	157 \pm 29	190 \pm 40

^a Peak potential difference (mV) reported as mean \pm standard deviation of five trials.

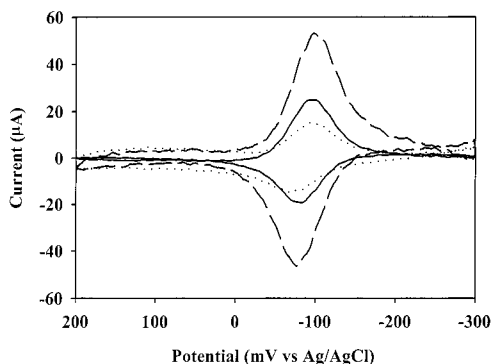


Figure 5. Voltammograms (1 V/s) of 40 μm AQDS in 0.1 M HClO_4 , after standing for 10 min in the solution. The electrode was polished GC (solid curve), CH_3CN treated GC (dots), or AC/ CH_3CN treated GC (dashes). The background voltammogram was subtracted.

Table 6. Surface Coverages (pmol/cm^2) of Physisorbers on GC Surfaces

	AQDS ^a	methylene blue ^b
polished GC	135	168
solvent sonicated GC	68	112
AC/solvent sonicated GC	246	300
purified solvent sonicated GC	125	
laser activation (25 mW/cm^2)	228 ^c	

^a Solvent was acetonitrile. ^b Solvent was IPA. ^c From ref 7.

AC particles may remain on the GC, but there is no evidence that they are responsible for the kinetic effects observed. The fact that the kinetic effects are larger when AC is present is likely to be due to trapping of impurities desorbed from the GC surface during solvent treatment.

The decrease in the O/C ratio accompanying AC/IPA treatment (Figure 2) implies that the solvent removes oxygen-containing physisorbed species. Air exposure caused a small (<1%) and slow (7 days) increase in the O/C ratio, which was reduced again with AC/IPA treatment. In previous reports, we noted that GC surfaces with initially low O/C ratios (1–4%) increased their ratios to 7–9% over several hours but did not return to the values observed for polished surfaces.¹⁴ Apparently the GC surface exposed to air reaches a maximum O/C ratio of about 8%, substantially less than that observed on the polished surface. It is quite reasonable to assume that polishing produces oxygen-containing organic compounds which physisorb to the GC surface. After these physisorbed species are removed by the AC/solvent treatment, the O/C ratio does not return to the >10% value typical of a polished surface, even after prolonged exposure to air. The greater effectiveness of IPA and CH_3CN compared to

cyclohexane may be due to the polar nature of these physisorbed oxygen-containing polishing products.

A mechanism based on removal of physisorbed impurities is further supported by the capacitance and adsorption results in Tables 1 and 5. As the surface impurities are removed, the capacitance increases as well as the adsorption of AQDS or MB. Hance and Kuwana reported that capacitance correlated linearly with the adsorption of 1,2,4-trihydroxybenzene and attributed the effect to changes in the number of adsorption sites per unit area.²⁵ In the present case, contamination by solvent impurities decreases capacitance and AQDS adsorption, while removal of polishing products with AC/solvent increases adsorption and capacitance. As was the case with Hance and Kuwana's observation, these changes are consistent with impurity removal rather than changes in microscopic area. Rice, Pontikos, and McCreery reported that increases in capacitance caused by laser activation correlated with increases in ET rate,²⁶ but the capacitance increase was not as large as that reported in Table 1 for AC/IPA or AC/ CH_3CN treatment. Finally, we observed that AC/IPA can remove AQDS adsorbed to GC.

With the exception of the $\text{Fe}^{3+/2+}$ redox couple, the effects of AC/solvent treatment on ET kinetics are consistent with previous reports on the systems studied, whose results are listed in Tables 1–5. As expected, $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ is insensitive to solvent treatment and appears to behave like a classical outer-sphere system. The 80–85 mV peak separations at 20 V/s correspond to the k^o values from 0.12 to 0.10 cm/s, compared to 0.05–0.24 cm/s reported previously for polished surfaces. Since a chemisorbed monolayer decreases k^o for $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ by only a factor of 2,¹⁴ it is not surprising that the removal of physisorbed impurities by AC/solvent has minor effects.

$\text{Fe}(\text{CN})_6^{3-/4-}$ is significantly more sensitive to surface conditions, although the mechanism underlying this sensitivity is still not clear. k^o for $\text{Fe}(\text{CN})_6^{3-/4-}$ in 1 M KCl varies from <0.005 cm/s for polished surfaces¹² to >0.5 cm/s following laser activation,²⁶ and k^o does not appear to depend on surface oxides except for a fairly small (factor of 2–3) Frumkin effect.¹¹ The rate constants observed for AC/solvent treatments (Table 2) range from 0.06 to 0.09 cm/s. This range is near the k^o values reported for significantly more complex heat treatment or polishing procedures (0.14 cm/s)^{15,23} but not as high as those for laser activation (≥ 0.5 cm/s).²⁵ For both $\text{Fe}(\text{CN})_6^{3-/4-}$ and $\text{Ru}(\text{NH}_3)_6^{3+/2+}$, AC/solvent treatment yields quite active electrode surfaces, with $\text{Fe}(\text{CN})_6^{3-/4-}$ exhibiting greater variability.

Although the electrode kinetics of DA and AA on GC electrodes have not been studied as extensively as those of

$\text{Fe}(\text{CN})_6^{3-/4-}$ and $\text{Ru}(\text{NH}_3)_6^{3+/2+}$, the effects of solvent treatment are more dramatic. The ΔE_p 's for DA of 36–41 mV observed after AC/IPA or AC/ CH_3CN treatment are the smallest observed in our laboratory to date in 0.1 M H_2SO_4 . For laser activation at pH 7, ΔE_p decreases from 125 to 32 mV (0.1 V/s) at pH 7.²⁷ The kinetics are complicated by adsorption and the multistep redox process of these systems, but AC/solvent treatment clearly leads to a reactive electrode when the solvent is polar. Furthermore, a small ΔE_p for DA is restored by AC/IPA treatment even after intentional electrode abuse by exposure to soap solution or standing for a week in laboratory air (Table 4). Ascorbic acid exhibited the most negative E_p (and therefore fastest kinetics) on AC/IPA and AC/ CH_3CN surfaces. The mechanism of the catechol redox systems will be discussed in a separate publication,²⁸ but it is clear that AC/solvent treatment increases ET rates for DA and AA systems relative to polished surfaces.

$\text{Fe}^{3+/2+}$ differs from the other systems studied here in that AC/solvent treatment yields a surface with slower kinetics than the initial polished surface (Table 5). We infer that this shortfall is due to catalysis of $\text{Fe}^{3+/2+}$ by the polishing products which are removed by AC/solvent treatment. If these "impurities" contain carbonyl groups, they should catalyze $\text{Fe}^{3+/2+}$ electron transfer.^{17,20} Once they are removed by the solvent, they are not restored until the electrode is polished again.

Overall, the results provide strong evidence for removal of polishing residue by purified, polar solvents containing activated carbon. Removal of this residue occurs because the large surface area of the AC in the solvent prevents adsorption of solvent

impurities or readsorption of physisorbed materials removed from the GC surface. When the residue is removed, the capacitance increases, the capacity for AQDS or MB adsorption increases, and ET rates for DA, AA, and $\text{Fe}(\text{CN})_6^{3-/4-}$ increase as well. In addition, the surface O/C ratio decreases, implying that the residue contains oxygen, presumably in functional groups. It is likely that this oxygen is present in part as carbonyl groups and catalyzes the $\text{Fe}^{3+/2+}$ redox system.

From a practical standpoint, AC/solvent treatment provides a means to clean carbon electrodes which cannot be polished. With the exception of those of $\text{Fe}^{3+/2+}$, the kinetics and adsorption properties of the AC/solvent pretreated electrodes are comparable to surfaces prepared by more arduous techniques. In fact, AC/IPA treatment yields AA and $\text{Fe}(\text{CN})_6^{3-/4-}$ voltammograms comparable to that of the "pristine" GC prepared by vacuum heat treatment.¹⁵ The kinetic, adsorption, and capacitance results to date imply that GC treated with AC/IPA or AC/ CH_3CN sonication is close to the "clean" GC surface which has been so elusive in the past.

ACKNOWLEDGMENT

This work was supported by the National Science Foundation Division of Analytical and Surface Chemistry. The authors acknowledge Stacy DuVall for the AQDS adsorption data and Mark Wightman and Gregory Swain for valuable comments.

Received for review December 14, 1998. Accepted May 24, 1999.

AC981386N

(27) Poon, M.; McCreery, R. L. *Anal. Chem.* **1986**, *58*, 2745.

(28) DuVall, S.; McCreery, R. L. Submitted for publication.