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# Laser Activation of Carbon Electrodes. Relationship between Laser-Induced Surface Effects and Electron Transfer Activation

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**Several effects of intense laser pulses, including ablation, desorption, and structural changes are correlated with electron transfer activation of glassy carbon (GC) electrodes. By use of ferri-/ferrocyanide, ascorbic acid, and dopamine as test systems, it was found that ablation of bulk GC is a sufficient but not necessary process for activation. In addition, no correlation was found between increases in background current and activation, and several arguments are made against the promotion of electron transfer by oxygen-containing functional groups. Furthermore, adsorption of ascorbic acid and dopamine occurred with several pretreatment procedures but was unnecessary to achieve electron transfer activation. Fast electron transfer for ferri-/ferrocyanide, dopamine, and ascorbic acid is uncorrelated with background current, adsorption, ablation, surface oxygen content, and microscopic surface area. The most likely laser effects that promote electron transfer are desorption of impurities and formation or exposure of active regions on the GC surface.**

Due largely to the complex surface chemistry of carbon, solid electrodes made from graphite or glassy carbon (GC) often exhibit severe variation in electrochemical performance. An example of the problem is the wide range of heterogeneous electron transfer rates observed for the ferri-/ferrocyanide couple on GC under apparently identical conditions, with different electrode pretreatments leading to a range of a factor of  $10^3$  (1). A wide variety of mechanical (1-7), thermal (8, 9), and chemical pretreatments (10, 11) have been used to improve or alter the performance of carbon electrodes, with the objectives of enhancing electroanalytical utility or increasing electrocatalytic performance. An example of relevance to the present report is the observation that oxidation of a GC surface at high potentials in the 1.5-2.8 V range accelerates several redox events, including ascorbic acid and dopamine oxidation (11-21). One hypothesis for this acceleration is a proton transfer mechanism involving carbon surface phenolic functional groups (13). This hypothesis is controversial, however, with other investigators attributing acceleration to surface cleanliness (1, 12), other functional groups (22, 23), exposure of the GC microstructure (24), and other effects.

The major common question of the many investigations of GC is the relationship between surface structure, as determined by surface history, and electron transfer kinetics. The variety of effects that may be involved can be divided into three general classes. First, a pretreatment procedure will affect the concentration of physisorbed impurities on the GC surface, i.e. electrode cleanliness. Second, chemisorbed species, particularly oxygen, may affect electron transfer by electrostatic effects, proton or oxygen transfer, or redox mediation. The commonly invoked surface functional groups fall in this class. Third, the GC substrate structure may be altered by thermal or mechanical treatment, to create or remove defects

or to alter the microscopic surface area. The relationship between these three classes of surface structural effects and heterogeneous electron transfer kinetics is rather difficult to establish for two major reasons. First, the variations in cleanliness, functional group density, and substrate structure are potentially great from surface to surface and sample to sample. Second, the variety of pretreatments is also great, making it difficult to compare results from different labs using different procedures. In addition, a given procedure may alter more than one class of surface structural effects.

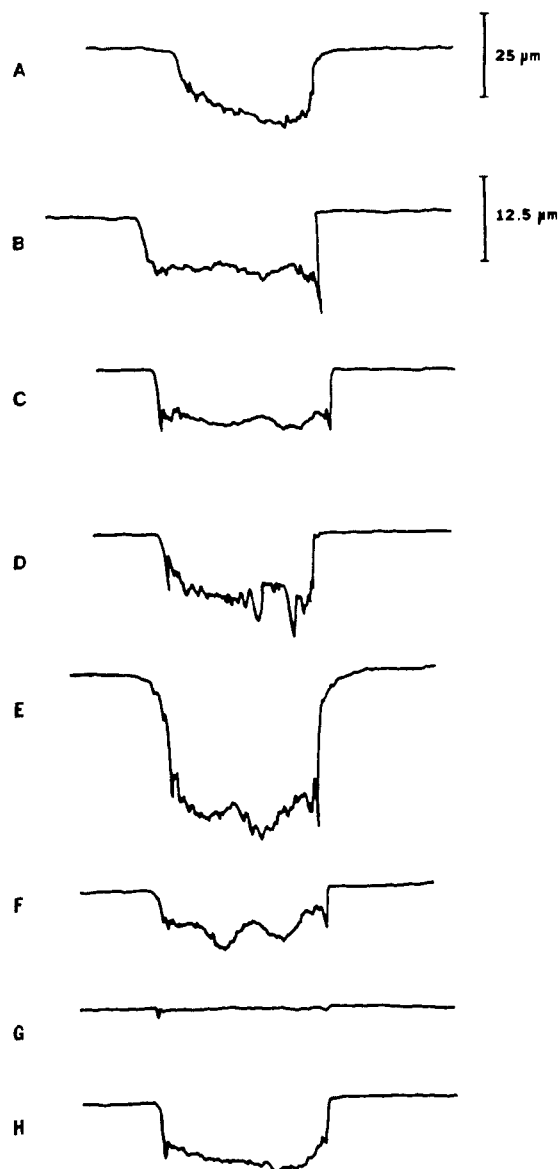
In three previous publications (25-27), our research group reported that an intense laser pulse dramatically increased the heterogeneous electron transfer rate for several redox systems. The increase was long-lived and reproducible and exhibited a rate constant for the benchmark  $\text{Fe}(\text{CN})_6^{3-/4-}$  system on glassy carbon that is comparable to the highest values reported for other pretreatment methods (1). We showed that the activation process could be repeated thousands of times and that a variety of redox systems exhibited electron transfer rate enhancements of factors of 600 or more. While laser activation has inherent value as a reproducible pretreatment procedure for analytical applications, the present report is directed more toward the mechanism of laser activation and what it can reveal about carbon surfaces. By using the laser to alter the surface, we will correlate surface structural changes with electron transfer rates, in order to infer which surface effects are important to activity. We will also compare laser activation with conventional polishing and with oxidative electrochemical pretreatment to provide insight into the activation mechanism.

## EXPERIMENTAL SECTION

The laser, cell, optical arrangement, and profilometer have been described previously (27). Cyclic voltammograms were obtained with a digital oscilloscope as before (26) or with a computer-assisted potentiostat controlled by a Tecmar labmaster interface in a PC-Designs ET 286i computer. Semiintegrals were calculated with the G1 algorithm of Oldham (28). In all cases reported here, Tokai GC-20 glassy carbon disks served as the electrode material and were polished conventionally with 1.0-, 0.3-, and 0.05- $\mu\text{m}$  alumina on a Texmet polishing cloth before activation experiments. Electrochemical activation of GC was performed in 0.1 M  $\text{KNO}_3$  for 5 min at +1.8 V and 1 min at -1.0 V (vs Ag/AgCl (3 M NaCl)).

## RESULTS

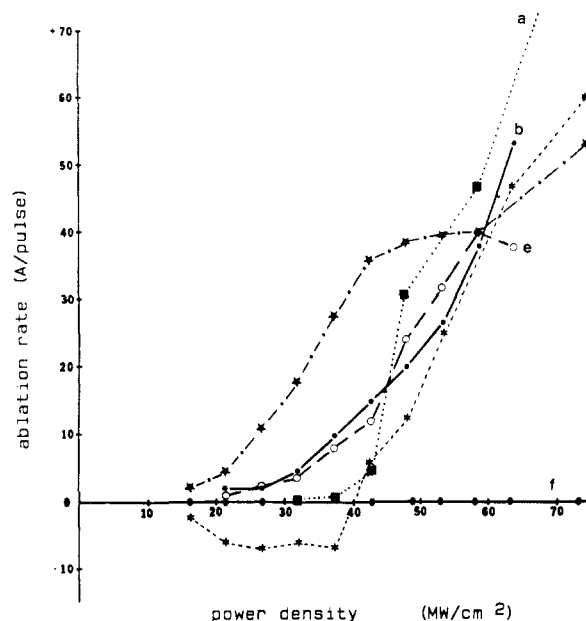
The rate of carbon removal from GC surfaces by the laser was determined in order to assess the importance of substrate ablation to activation. The method we employed to measure carbon removal involved determination of an average ablation rate by dividing a laser-generated crater depth by the (large) number of pulses required to make the crater. Since the craters were several micrometers deep, the ablation rate observed is characteristic of the carbon substrate, *not* the initial superficial layer present after polishing. Thus, "ablation" as used here refers to bulk carbon removal, and any superficial layers such as oxides or particle layers present on the initial



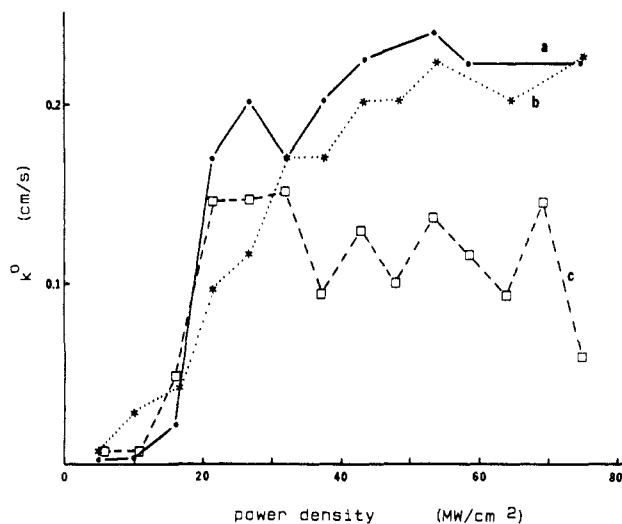
**Figure 1.** Profilometer traces of GC surfaces that have been treated with 3000 laser pulses at  $43 \text{ MW/cm}^2$  in the presence of different media: trace A,  $0.1 \text{ M Ce}^{4+}$ ; trace B, saturated  $\text{Na}_2\text{SO}_3$ ; trace C,  $1 \text{ M H}_2\text{SO}_4$ ; trace D,  $1 \text{ M NaOH}$ ; trace E,  $8 \text{ M HNO}_3$ ; trace F,  $8 \text{ M HCl}$ ; trace G, air; trace H, water. All except trace A are on same vertical scale; width of each crater is  $1 \text{ mm}$ .

surface have a small effect on the ablation rates discussed below. Profilometer traces of GC surfaces subjected to 3000 laser pulses ( $43 \text{ MW cm}^{-2}$ ) while immersed in various media are shown in Figure 1. Note that the crater depth varies significantly with medium, with a deeper crater formed in oxidizing media such as  $\text{Ce}^{4+}$  and  $\text{HNO}_3$  and no measurable ablation occurring in air. Acetonitrile, reducing media such as  $\text{Na}_2\text{SO}_3$  in water, or acidic and basic solutions exhibit ablation rates similar to water.

The depth of the crater may be converted to an average ablation rate, with units of angstroms per pulse, by dividing by the number of pulses. The average ablation rates were strongly power dependent, as shown in Figure 2. Laser exposure in air produced ablation rates below the detection limit for the measurement (ca.  $0.1 \text{ Å/pulse}$ ), even at high laser power. The negative ablation rate for toluene apparently resulted from deposition of unknown materials produced from the solvent. Such deposits also appeared on the cell window. Of the aqueous media,  $0.5 \text{ M HNO}_3$  had a high ablation rate in the  $20\text{--}40 \text{ MW cm}^{-2}$  range, while water,  $\text{CH}_3\text{CN}$ , and  $1 \text{ M KCl}$  exhibited significantly lower ablation rates.



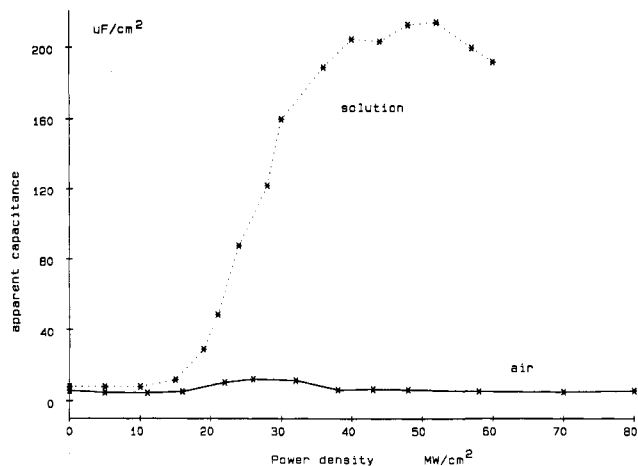
**Figure 2.** Plot of ablation rate in the presence of various media as a function of power density of the laser radiation: (a)  $\text{CH}_3\text{CN}$ ; (b)  $1 \text{ M KCl}$ ; (c) toluene; (d)  $0.5 \text{ M HNO}_3$ ; (e)  $\text{H}_2\text{O}$ ; (f) air.



**Figure 3.** Plot of observed  $k^\circ$  for ferri-/ferrocyanide ( $1 \text{ mM}$  in  $1 \text{ M KCl}$ ) at GC as a function of power density after laser irradiation was performed in three different media: (a)  $1 \text{ M KCl}$ ; (b)  $0.5 \text{ M HNO}_3$ ; (c) air.

The solution in which laser ablation was carried out was examined by fluorescence spectroscopy for two solvents in which polynuclear aromatic hydrocarbons are soluble. After ablation of GC in both toluene and octane at  $50 \text{ MW cm}^{-2}$ , the solvent exhibited intense fluorescence upon dye laser excitation at  $360 \text{ nm}$ .

The heterogeneous kinetic performance for activation in three media is shown in Figure 3. The rate for the  $\text{Fe}(\text{CN})_6^{3-/4-}$  redox system was measured in  $1 \text{ M KCl}$  after laser activation in either  $1 \text{ M KCl}$ ,  $0.5 \text{ M HNO}_3$ , or air. As shown in Figures 1 and 2, these media exhibit quite different ablation rates, with  $0.5 \text{ M HNO}_3$  being as much as 4.5 times as high as  $1 \text{ M KCl}$  (at  $27 \text{ MW cm}^{-2}$ ) and the ablation rate in air was near zero.  $k^\circ$  for  $\text{Fe}(\text{CN})_6^{3-/4-}$  showed the previously reported activation to ca.  $0.2 \text{ cm/s}$  at about  $20 \text{ MW cm}^{-2}$ , with no substantial increase at higher power densities. The rate constant for an electrode activated in  $0.5 \text{ M HNO}_3$  required slightly higher power density for activation but eventually reached a plateau at  $0.2 \text{ cm s}^{-1}$ . Electrodes activated in air (or argon) also exhibited a large rate enhancement at about



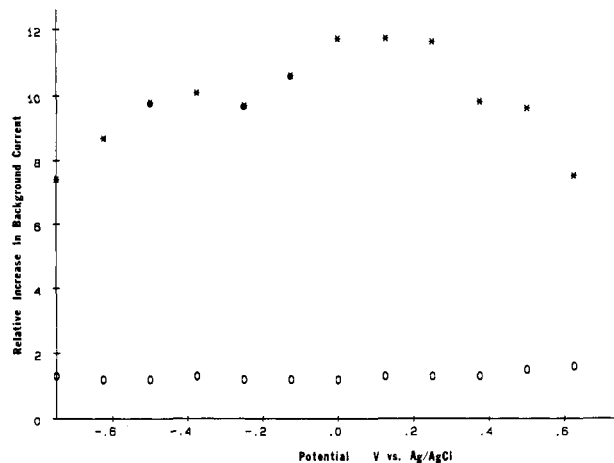
**Figure 4.** Plot of capacitance measured by chronocoulometry (potential step from  $-0.05$  to  $0.00$  V) vs power density for a GC electrode that has been laser treated in the presence of air (solid line) and in  $1$  M KCl (dotted line). Data for  $1$  M KCl is from ref 26.

$20 \text{ MW cm}^{-2}$ , but the rate constant never reached  $0.2 \text{ cm s}^{-1}$ , and higher power densities exhibited large fluctuations in observed rate. While this fluctuation is both significant and at present unexplained, it should be noted that even the varying value of  $k^\circ$  is much greater than the value before activation, which was  $0.004 \pm 0.002 \text{ cm s}^{-1}$ . After Figure 2 and 3 were considered together, it is clear that activation in  $\text{HNO}_3$  or water occurs when the ablation rate is  $1\text{--}2 \text{ \AA/pulse}$  and that ablation is not required for activation when laser treatment occurs in air. Despite the fact that  $\text{HNO}_3$  produces a much higher ablation rate,  $k^\circ$  for  $\text{HNO}_3$  is equal to or lower than that for water. One concludes that there is no correlation between average ablation rate and electron transfer activation. However, this conclusion does not rule out the removal of superficial impurity layers by the first several laser pulses.

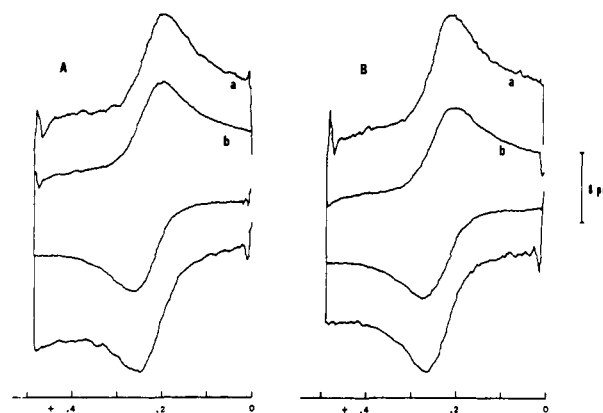
The background current for carbon electrodes varies greatly with surface history and nearly always contains components from double layer capacitance and surface faradaic processes such as the redox reactions of surface functional groups. The background current will be expressed here as apparent capacitance, determined either by the method of Fagan, Hu, and Kuwana (8) or from the background current from cyclic voltammetry. The effect of power density and medium on apparent capacitance is shown in Figure 4. As reported previously (26), the capacitance increases as a function of power density when activation is carried out in solution. After laser treatment in air, the capacitance remains low, even at quite high ( $80 \text{ MW cm}^{-2}$ ) power density. Recall that for laser pretreatment in either air or KCl, comparable electron transfer activation is observed. Thus, the capacitance increase correlates with ablation but not activation.

An alternative activation procedure that affects both background current and activation is electrochemical pretreatment. Its effects on background current are compared to laser activation in Figure 5, as a function of potential. Note that oxidative electrochemical pretreatment produces a background that is not only larger than the laser treated surface but that also varies with potential. The larger current observed for electrochemical treatment at about  $0.2$  V has been attributed to redox reactions of surface quinones (8), which are not apparent on laser-treated surfaces. Furthermore, a comparison of Figures 2 and 4 shows that laser treatment in solution produces a substantially higher apparent capacitance than laser treatment in air and that capacitance shows a trend similar to that of ablation rate.

The effects of laser treatment on the  $\text{Fe}(\text{CN})_6^{3-/4-}$  system and on background currents are shown in Figure 6 which was obtained for solutions of lower concentration than those re-



**Figure 5.** Relative increase in background current of a cyclic voltammogram ( $0.1 \text{ M KNO}_3$ ) as a function of potential for electrochemically pretreated GC (asterisks) and laser-treated GC (circles). Ordinate is the ratio of voltammetric background current treatment after activation to that before.



**Figure 6.** Cyclic voltammograms for ferri-/ferrocyanide ( $1 \text{ M KCl}$ ) at laser-activated GC. Voltammograms A were activated at  $27 \text{ MW cm}^{-2}$  and voltammograms B at  $80 \text{ MW cm}^{-2}$ . Scans a were after activation in the presence of the electrolyte; scans b were after activation in the presence of air only.

ported previously (26). Note that laser treatment either in solution or in air decreases the peak separation to about the same value. As reported previously, this decrease in  $\Delta E_p$  corresponds to a factor of 30–50 increase in  $k^\circ$ , and the present results show this increase to be the same for air or solution activation. In contrast, the background current increases substantially for solution activation but not for air. Additional data on the  $\text{Fe}(\text{CN})_6^{3-/4-}$  rate are shown in Table I. Polished surfaces show a higher rate at pH 4 than pH 7, while partially or fully laser activated surfaces show no such pH dependence. A comparison of electrochemical and laser activation of ascorbic acid oxidation at neutral pH is shown in Figure 7. Electrochemical activation leads to not only a large negative shift of the peak potential but also a large increase in the background current. Laser activation results in a comparable peak shift, but much lower background current. The semi-integral voltammograms confirm this observation.

The involvement of reactant adsorption may be determined by using semiintegral methods, as described previously (28). Voltammograms of ascorbic acid at pH 1.0 are shown in Figure 8A, with their semiintegrals in Figure 8B. Note that laser activation in air or solution leads to comparable shifts in peak position, but that an electrode activated in solution shows an excursion above the diffusion plateau of the semiintegral, indicating reactant adsorption (28). For similar conditions, electrochemical activation leads to severe reactant adsorption. Note that the power density used to produce Figure 8 was  $27$

**Table I. Peak Separation and Heterogeneous Electron Transfer Rate Constants for  $\text{Fe}(\text{CN})_6^{3-/4-}$  as a Function of pH**

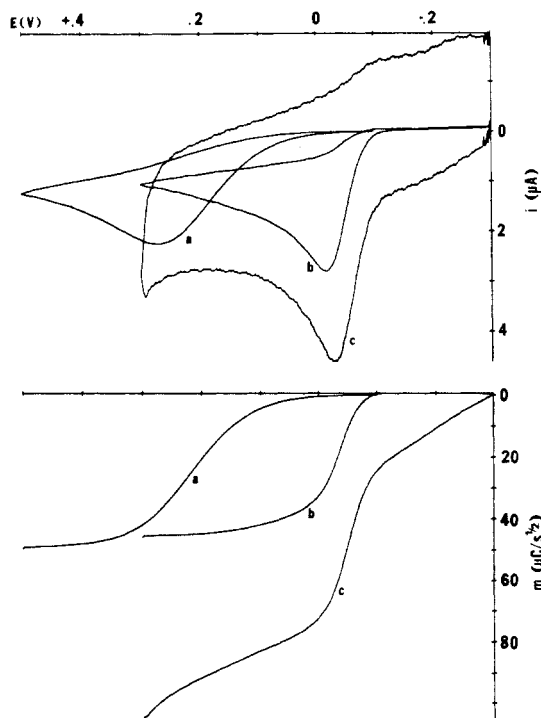
Polished Electrode		
pH <sup>a</sup>	$\Delta E_p$ , mV	$k^\circ$ , cm s <sup>-1</sup>
7.0	140	0.003
6.0	110	0.005
5.0	92	0.008
4.0	79	0.014
5.0	97	0.007
6.0	120	0.004
7.0	145	0.003
4.0	84	0.011

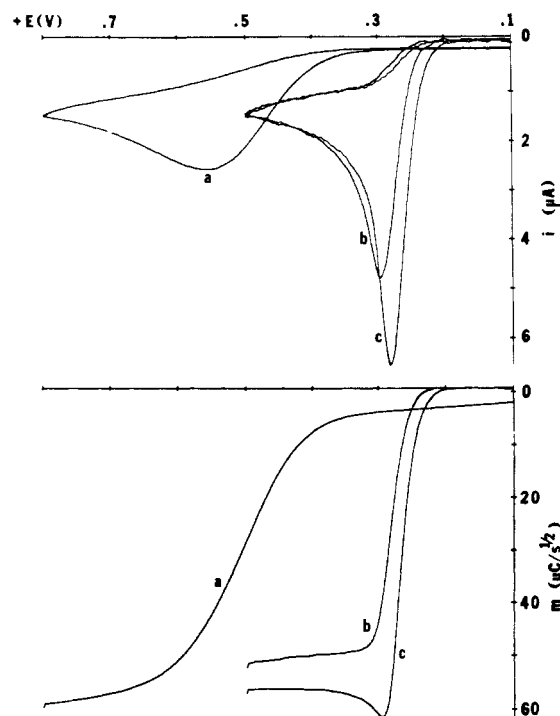
Laser-Treated Electrode (in Solution, 27 MW/cm <sup>2</sup> )		
pH	$\Delta E_p$ , mV	$k^\circ$ , cm s <sup>-1</sup>
4.0	72.3	0.182 cm s <sup>-1</sup>
7.0	72.3	0.182
6.0	73.2	0.171
5.0	72.3	0.182

Laser-Treated Electrode (in Air, 80 MW/cm <sup>2</sup> )		
pH	$\Delta E_p$ , mV	$k^\circ$ , cm s <sup>-1</sup>
7.0	99.6 mV	0.054
4.0	99.6	0.054
5.0	99.6	0.054
6.0	100.6	0.052

<sup>a</sup> Experiments performed sequentially as listed.**Figure 7.** Cyclic voltammograms (upper) and semiintegral voltammograms (lower) of ascorbic acid (pH 7.4, 1 mM in 0.1 M phosphate buffer, 0.1 V/s) at GC. Scans a were obtained with polished surfaces, scans b after laser treatment at 27 MW/cm<sup>2</sup>, and scans c after electrochemical pretreatment for 5 min at +1.8 V and 1 min at -1.0 V.

MW/cm<sup>2</sup>, enough to ablate the surface in solution but not in air. Dopamine exhibits similar behavior in acidic solution, with laser activation leading to adsorption when carried out in solution. Further involvement of adsorption was demonstrated in the cyclic voltammetry of 1,4-naphthoquinone. At a freshly polished electrode, the oxidation was diffusion-

**Figure 8.** Cyclic voltammograms (upper) and semiintegral voltammograms (lower) for ascorbic acid oxidation (1 mM in 0.1 M H<sub>2</sub>SO<sub>4</sub>, 0.1 V/s). Scans a were obtained with a polished surfaces, scans b after laser treatment in air at 27 MW/cm<sup>2</sup>, and scans c after laser treatment in solution at the same power density.

controlled as determined by a linear relationship between peak height and the square root of scan rate. After laser activation, peak height remained linear with the square root of scan rate, whereas after electrochemical activation, the peak height became linear with scan rate, indicating a surface-controlled process. Both treatments resulted in significant activation for the naphthoquinone system; the peak separation decreased by 65 mV upon laser activation and by 70 mV upon electrochemical pretreatment.

A final comparison between electrochemical and laser activation is the oxidation of hydrazine. When a polished GC electrode is oxidized at 1.75 V for 5 min in 0.1 M KNO<sub>3</sub>/0.1 M H<sub>2</sub>PO<sub>4</sub><sup>-</sup> at pH 7, then reduced at -1.0 V for 1 min, the oxidation of hydrazine shifts from a virtually nonexistent wave to a well-defined peak at +0.34 V vs SCE. Laser activation of polished GC surface also shifts the hydrazine oxidation wave negative, but no peak is observed and the electron transfer rate is slower than that on the electrochemically activated surface. Laser treatment of an electrochemically activated electrode shifts the hydrazine wave positive, while electrochemical activation of a laser-treated surface restores the peak at +0.34 V. Thus, the two methods differ with respect to hydrazine oxidation and the GC surface may be repeatedly transformed from one surface to another. Laser treatment is capable of removing the effects of electrochemical activation, and vice versa. While the results were not definitive, the electrochemical surface exhibited a hydrogen/deuterium isotope effect for hydrazine oxidation, while the laser-treated surface did not. The oxidation peak shifted to significantly more negative potentials (40–90 mV) in H<sub>2</sub>O than in D<sub>2</sub>O for the electrochemically pretreated surface, but no such shift was observed on a laser-treated surface.

While there was little question that an intense laser pulse can remove physisorbed impurities, this fact was tested by activating an intentionally fouled electrode. At relatively low power, 10 MW cm<sup>-2</sup>, a polished electrode was activated for Fe(CN)<sub>6</sub><sup>3-/4-</sup> ( $k^\circ = 0.15\text{--}0.2$  cm s<sup>-1</sup>) after ca. 15 laser pulses. If the electrode was polished, then intentionally fouled by

handling with ungloved hands, activation required ca. 50 laser pulses at  $10 \text{ MW cm}^{-2}$ . Thus, a seriously fouled electrode can be laser activated, but it requires more laser pulses than a freshly polished surface. At higher power (ca.  $30 \text{ MW cm}^{-2}$ ), only a few additional pulses are necessary to activate an intentionally fouled electrode.

## DISCUSSION

A possible mechanism of laser activation is the gross removal of GC substrate by intense laser pulses and associated thermal effects. As noted earlier, we are defining ablation as substrate removal rather than surface cleaning. The measurements of average GC ablation rate show that the medium in which laser treatment occurs has a substantial effect on the rate of GC removal. Laser exposure in liquids causes much faster ablation than the same treatment in air or argon, and oxidizing solutions approximately double the rate compared to water. Acids, bases, or organic solvents produce ablation rates comparable to that observed in water. The apparent deposition of material observed in toluene may be caused by a laser-induced polymerization to form large polycyclic aromatic hydrocarbons that deposit both on the electrode and on the cell walls and window. The ablation process and associated reactions is undoubtedly complex, but its relevance to the issue of electron transfer activation may be appreciated from Figure 3. Although air,  $\text{HNO}_3$ , and  $\text{KCl}$  produce very different ablation rates ( $<0.1$ , 4, and  $18 \text{ \AA/pulse}$  at  $30 \text{ MW cm}^{-2}$ , respectively), the electron transfer activation is comparable for laser treatment in the three media. If anything, the higher ablation rate observed in  $\text{HNO}_3$  produces less activation of electron transfer. The lack of correlation between ablation and electron transfer activation indicates that ablation is a sufficient but not necessary process for enhancing electron transfer rates. This conclusion is relevant to pretreatment procedures involving polishing (1), particularly the rigorous "metallographic" procedures (4, 6). While these methods do remove layers of GC substrate, the laser experiments show that such removal is not a necessary step for activation. As noted below, a major effect of laser treatment may be removal of superficial impurity layers or polishing debris, whereas actual substrate removal is unnecessary.

Just as activation does not correlate with substrate removal, it also is not coupled to increases in background current or adsorption. The voltammograms of Figures 6, 7, and 8 show that high background current and adsorption may result from electrochemical activation or laser activation in solution, but these effects do not correlate with activation for  $\text{Fe}(\text{CN})_6^{3-/4-}$ , ascorbic acid, naphthoquinone, or dopamine. After considering the collected results from Figures 2, 4, 7, and 8, it is clear that increases in background current correlate with increased adsorption and that ablation can increase both effects. However, neither background current, ablation rate, nor increased adsorption correlate with improved electron transfer rate. Kuwana and Hance (30) have demonstrated a correlation between background current and 1,2,4-trihydroxybenzene adsorption for polishing and vacuum heat treatment. Kovach, Deakin, and Wightman have reported greatly increased adsorption for cations on electrochemically treated carbon fibers (31) and attribute the adsorption to surface oxide functional groups. In a different report, they reject the involvement of functional groups in rate enhancement on heat-treated GC and conclude that the activation mechanism is primarily surface cleaning (32). The important conclusion from the present work is that the surface properties that lead to high background current and adsorption are not the same as those that promote electron transfer between GC and  $\text{Fe}(\text{CN})_6^{3-/4-}$ , ascorbic acid, naphthoquinone, or dopamine.

Oxygen-containing surface functional groups have often been invoked to explain the behavior of GC electrodes (22,

23). In some cases they act as redox mediators catalyzing electron transfer but have also been associated with "proton assisted electron transfer" for electrochemically pretreated surfaces (13). Wightman et al. (29) showed that surface carboxylates can affect  $k^\circ$  through electrostatic effects, with slower rates observed for electroactive anions at pH 7, where surface carboxylates should be deprotonated. For the present case of laser activation of GC for  $\text{Fe}(\text{CN})_6^{3-/4-}$ , ascorbic acid, and dopamine, several strong arguments are available against the involvement of oxygen-containing functional groups in an activation mechanism. First, the oxygen to carbon ratio on the GC surface, as measured by Auger spectroscopy, decreases upon laser treatment in either a vacuum, air, or aqueous solutions (26). Even when the surface oxygen is undetectable by Auger spectroscopy, activation is observed. Second, there is no pH effect on the  $\text{Fe}(\text{CN})_6^{3-/4-}$  couple for laser-treated surfaces, while polished electrodes show a 3–4-fold lower rate at pH 7 vs pH 4. This decrease in rate has been attributed to electrostatic repulsion of the redox systems by deprotonated surface carboxylate groups on the polished surface. Since the effect is not observed on laser-treated surfaces, we infer that carboxylates are not prominent on the laser-treated surface. Third, activation is independent of the medium in which the laser treatment was conducted. Media with little or no oxygen present, such as acetonitrile, produced the same activation as a medium in which oxidation should be likely ( $8 \text{ M HNO}_3$ ). Fourth, there is no observable H/D kinetic isotope effect for hydrazine oxidation on laser-treated GC, while an effect was observed for the electrochemically pretreated surface. Such effects have been attributed to oxygen functional groups for other redox systems (13).

It is very difficult to rule out the existence of oxygen functional groups, since our experiments involve the exposure of activated GC to water. However, the preponderance of evidence indicates that the presence of such groups is uncorrelated with electron-transfer activation for the redox systems examined. A similar conclusion was reached for vacuum heat treatment, based on ESCA results and the absence of differential pulse voltammetric waves for surface functional groups on active surfaces (8). However, neither the laser nor heat treatment results rule out the possibility of functional group involvement in accelerating redox systems other than ascorbic acid, dopamine, and  $\text{Fe}(\text{CN})_6^{3-/4-}$ , or in cases when active carbon sites are unavailable (13, 22, 23, 34). Redox mediation or proton transfer may play a role for other redox systems on different carbon surfaces, but there is no evidence for their involvement on laser or heat-treated GC. While functional groups do not appear to be involved with activation on laser-treated surfaces, their presence does correlate with adsorption and background current. For the systems studied here, the only effects of oxygen functional groups may be adsorption and electrostatic effects.

The conclusions presented thus far are significant but negative. They rule out ablation, i.e. removal of significant layers of substrate, as the laser-activation mechanism. A previous report demonstrating a lack of correlation between capacitance and activation rules out a mechanism based solely on a laser-induced increase in microscopic surface area (26). In addition, the results argue strongly against the involvement of oxygen-containing functional groups in the activation of electron transfer for  $\text{Fe}(\text{CN})_6^{3-/4-}$ , ascorbic acid, or dopamine, except for relatively minor electrostatic effects. There is only negative evidence that a redox mediation or proton transfer mechanism is involved for these systems.

Of the possible remaining laser effects that may promote electron transfer, two appear most likely. First, the laser may remove the layer of physis- and chemisorbed impurities, microparticles, and polishing debris present on a polished surface

(24, 33). Such cleaning has been proposed for several pretreatments, and the laser may provide a fast, effective, in situ means to effect the process. Second, the laser pulse may generate active sites at which electron transfer occurs. (As noted by a reviewer of this paper, the absence of an increase in microscopic surface area implies that the active site density increases with laser activation, not merely their number.) While it is difficult to assess the relative contribution of these two effects to activation, they are likely to be the dominant factors involved in the laser activation mechanism. Kuwana concluded that cleaning and increases in site density were important for vacuum heat treatment (8), and Wightman reached a similar conclusion for the case of aggressive anodization (31). Despite the apparent similarity of activation mechanisms for these very different pretreatment procedures, the surfaces produced from them may differ greatly with respect to ancillary effects not directly related to activation. Electrochemical pretreatment and polishing can bring about gross oxidation and functional group formation, but not all of these effects are necessary or even beneficial toward activation. For example, the surface quinone functional group is likely to be formed during carbon oxidation but is not a prerequisite for activation, as demonstrated for heat treatment (8) and laser activation. For the case of  $\text{Fe}(\text{CN})_6^{3-/4-}$ , carboxylate functional groups may actually inhibit  $k^\circ$  at neutral pH through electrostatic effects (29). In terms of activity and background current, the laser activated surface is most similar to that produced by vacuum heat treatment (8), since both procedures produce high  $k^\circ$  and low background current. However, a 10-ns, 20 MW/cm<sup>2</sup>, in situ laser pulse is very different from slow ex situ heat treatment and may have a quite different mechanism at the microstructural level.

At least for the redox systems studied here, the results indicate that many effects of pretreatment are ancillary to the main processes of cleaning and/or active site generation. Ablation and surface oxidation may lead to increases in background current and adsorption but are not necessary for activation. The laser results contribute to the growing body of evidence from other activation procedures (1, 8, 9, 24, 31-34) indicating the importance of active sites and surface cleanliness.

#### ACKNOWLEDGMENT

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**Registry No.** GC, 7440-44-0; O<sub>2</sub>, 7782-44-7; HNO<sub>3</sub>, 7697-37-2; KCl, 7447-40-7; Ce, 7440-45-1; Na<sub>2</sub>SO<sub>3</sub>, 1313-82-2; H<sub>2</sub>SO<sub>4</sub>, 7664-93-9; NaOH, 1310-73-2; HCl, 7647-01-0; CH<sub>3</sub>CN, 75-05-8; H<sub>2</sub>O, 7732-18-5;  $\text{Fe}(\text{CN})_6^{3-}$ , 13408-62-3;  $\text{Fe}(\text{CN})_6^{4-}$ , 13408-63-4; toluene, 108-88-3; ascorbic acid, 50-81-7; dopamine, 51-61-6.

#### LITERATURE CITED

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