

Preliminary note

Fast heterogeneous electron transfer rates for glassy carbon electrodes without polishing or activation procedures

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INTRODUCTION

Glassy carbon (GC) is an attractive choice for an electrode material because it has a wide potential range, is inexpensive, readily available, and chemically inert in most electrolytes [1]. The typical preparation of a GC electrode includes the removal of gross surface features by abrasion with silicon carbide paper and subsequent polishing with alumina. The electrochemistry of many redox systems such as ascorbic acid (AA), ferri/ferrocyanide, and dopamine on GC are very sensitive to the polishing procedure, with variations in the heterogeneous electron transfer rate constant, k° , for the $\text{Fe}(\text{CN})_6^{3-/4-}$ redox system covering at least three orders of magnitude [2]. This variation has been attributed primarily to superficial impurities and polishing debris [2–9].

Several activation methods have been developed which may be used to enhance k° for the GC surface. These methods include electrochemical pretreatment [10–14], laser irradiation [15,16], vacuum heat treatment (VHT) [6,7], and ultraclean polishing [2]. All of these approaches yield GC surfaces that have higher k° for benchmark systems than that of a conventionally polished surface, with a few yielding a k° for $\text{Fe}(\text{CN})_6^{3-/4-}$ comparable to that observed on clean Pt [2,15]. The mechanism of GC activation procedures remains a topic of active discussion, with surface cleaning, oxide film formation, formation of graphite edge planes, and changes in microscopic surface being invoked, to name a few [6,12,16–19]. Of particular relevance to the current report are mechanisms based on the removal of surface impurities and oxide films. Several workers have concluded that activation is related to removal of polishing debris and exposure of the underlying GC substrate [2,3,7–9]. For example, vacuum heat treatment removes surface oxides and results in

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a surface with low capacitance having high electron transfer rates for $\text{Fe}(\text{CN})_6^{3-/4-}$ and AA [7]. Much of the uncertainty about activation mechanism results from the many variables which determine k° . A given pretreatment procedure may alter simultaneously surface cleanliness, surface oxides, and microscopic roughness, so it is difficult to correlate the observed k° to only one of these variables.

It is not the purpose of the present report to resolve the complex question of which variables most affect the observed k° for GC. However, we will describe a combination of Raman spectroscopy, laser activation, and a new GC preparation method which provides new information about GC activity. The unpolished end of a fractured GC rod is unperturbed by abrasion, and presumably has a structure which represents the underlying GC substrate. We examined the fractured surface with Raman spectroscopy, and evaluated its electron transfer kinetics for AA oxidation. As will be demonstrated below, the fractured GC surface is unusually active for AA oxidation, and provides new insight into GC activation.

EXPERIMENTAL

All solutions were prepared daily using Nanopure water degassed with argon for 20 min. L-Ascorbic acid was used as received from Baker, Inc. for the preparation of 1 mM ascorbic acid in a supporting electrolyte of 1 M KCl and 0.1 M NaH_2PO_4 adjusted to pH 7.0 with KOH.

The working electrode was a 3 mm diameter Tokai glassy carbon GC 30s rod. Electrical contact was made by attaching a wire to one end of the rod with Tra-con silver epoxy. The entire rod was covered with Torr-seal (Varian), leaving only one end exposed. A surface referred to as "conventionally polished" was obtained by polishing the exposed end with 1, 0.3, and 0.05 μm polishing alumina (Buhler) on a texmet cloth and rinsing with Nanopure water. Although more active GC surfaces have been prepared with more rigorous procedures [2,8], we used the procedure most commonly reported by other laboratories.

The electrode area was determined by chronoamperometry with a diffusion coefficient for ascorbic acid of $6.5 \times 10^{-6} \text{ cm}^2/\text{s}$. Chronoamperometric areas for fractured surfaces were typically a factor of two higher than the geometric area. Laser pretreatment was performed in solution with three 9 ns FWHM laser pulses generated by a Quantel model YG 580 Nd:YAG laser operating at 1064 nm. Semi-integral analysis of the voltammograms was performed using the Gl algorithm of Oldham as described elsewhere [20]. All Raman spectra were obtained on a CCD spectrometer operating with an argon ion laser at 514 nm (100 mW) and an integration time of 100 s.

RESULTS

As shown in Fig. 1, the Raman spectra in the carbon phonon region exhibit significant differences between the fractured and polished surfaces. The average $1360 \text{ cm}^{-1}/1582 \text{ cm}^{-1}$ peak intensity ratio for fractured GC 30s is 1.1 ± 0.1

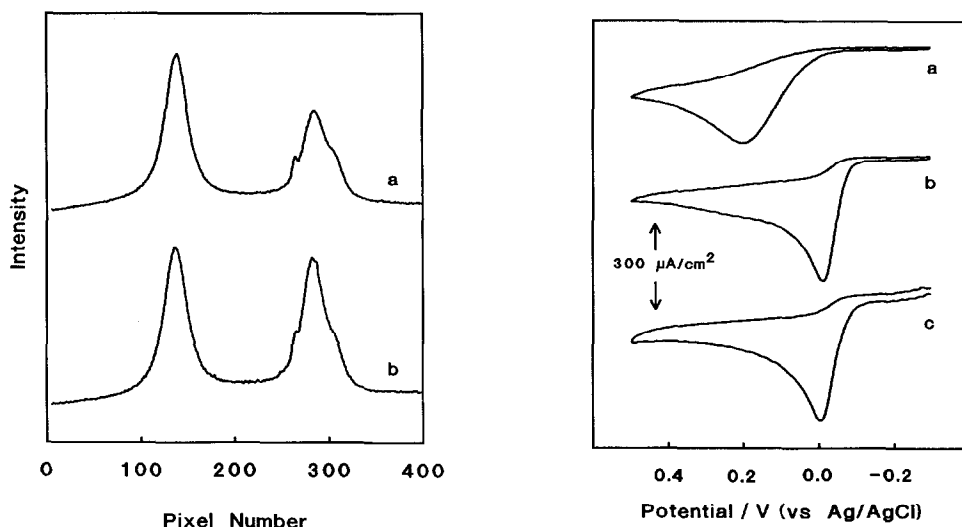


Fig. 1. Raman spectra for GC 30s obtained with a 515 nm laser and CCD detector. Abscissa is uncalibrated for Raman shift, but the peak at pixel 130 is ca. 1360 cm^{-1} while that at pixel 280 is ca. 1600 cm^{-1} . The small feature at pixel 260 is atmospheric oxygen. Detector integration time was 100 s, laser power at sample was ca. 50 mW.

Fig. 2. Voltammogram for 1.0 mM AA in 0.1 M phosphate buffer (pH 7.0) containing 1 M KCl. (a) Polished surface; (b) polished then laser activated at 40 MW/cm^2 ; (c) fractured surface. Scan rate was 0.1 V/s.

($N = 3$), while that for polished GC 30s is 1.8 ± 0.3 ($N = 3$). A similar change was observed by Nakamizo after an unspecified polishing procedure [21].

Figure 2 compares the voltammograms for polished, fractured, and laser activated GC 30s obtained at 0.1 V/s. The peak potential for AA oxidation serves as a relative measure of electron transfer activity, with a more negative E_p indicating a faster k° . As shown in Table 1, laser activation and fracturing both increase k°

TABLE 1

Peak potentials for AA oxidation^a

Surface	$v/\text{V s}^{-1}$	E_p/mV^b	
		0.1	10
Polished		200	> 500
Polished + 40 MW/cm^2		-7	83
Polished + 80 MW/cm^2		-19	24
Fractured		-6	50

^a pH 7.0, 1 M KCl, 0.1 M H_2PO_4^- buffer.

^b vs. Ag/AgCl (3 M KCl).

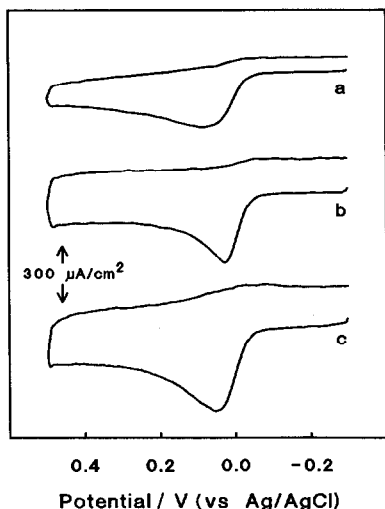


Fig. 3. Voltammogram for same solution conditions as Fig. 2, but a scan rate of 10 V/s. (a) Laser activated at 40 MW/cm²; (b) laser activated at 80 MW/cm²; (c) fractured.

significantly compared to polished surfaces, but there are only slight differences among the activated surfaces. After adjusting for reference electrodes, the -19 mV E_p for AA is about 30 mV negative of that for heat treated GC [22]. The E_p values obtained at 0.1 V/s are close to the thermodynamic potential for AA, and it is difficult to discriminate among the fractured and laser treated surfaces. At 10 V/s, however, the 40 MW/cm² laser treated surface exhibits slower kinetics than the fractured or 80 MW/cm² surface. Figure 3 shows a reduced peak current and more positive E_p for the 40 MW/cm² surface, while the 80 MW/cm² is distorted much less. At least part of the shift in E_p from 0.1 to 10 V/s is due to ohmic potential error, because for the 80 MW/cm² surface the shift in E_p is linear with peak current for a 1 to 10 V/s range of scan rates.

Semi-integrals of the voltammograms of Figs. 2 and 3 were sigmoidal, exhibiting no evidence for AA adsorption for any of the surfaces [20].

DISCUSSION

Raman spectroscopy is sensitive to the microstructure of sp^2 carbon materials. A breakdown of symmetry at graphitic edges permits the A_{1g} mode at 1360 cm⁻¹ to become Raman active for carbon materials with average microcrystallite size (L_a) less than about 50 nm. Tuinstra and Koenig have reported an empirical linear correlation between $1/L_a$ and the Raman intensity ratio of the 1360 cm⁻¹ band and the E_{2g} intensity at 1582 cm⁻¹ [23]. Thus, greater 1360 cm⁻¹ intensity implies more graphitic edges in the material. The Raman spectra for the polished and fractured GC surfaces obtained here indicate that the superficial microstructure of conven-

tionally polished GC electrodes is different from that of the bulk GC matrix. As shown in Fig. 1, the $1360\text{ cm}^{-1}/1582\text{ cm}^{-1}$ Raman peak intensity ratio for polished GC 30s is considerably higher than that observed for the freshly fractured surface, implying that the polished surface is composed of smaller microcrystallites. Based on the empirical study performed by Tuinstra and Koenig [23], the microcrystallite size of the polished GC surface is crudely 2.6 nm while that of the freshly fractured surface is in the vicinity of 4.4 nm. This observation may be related to the microparticle layer reported by Kuwana [3], but in any case indicates severe disruption of the GC structure upon polishing. Furthermore, the Raman sampling depth is in the region of 10–20 nm, implying that polishing affects a region much deeper than one monolayer.

The electrochemical properties of polished GC 30s differ greatly from those of the fractured surface. As shown in Fig. 2, the cyclic voltammogram of ascorbic acid at the polished electrode exhibits an oxidation peak at approximately 200 mV vs. Ag/AgCl (3 M NaCl). This high peak potential is reflective of the typically poor electron transfer kinetics for ascorbic acid on conventionally polished GC. Upon laser irradiation at a power density of 40 MW/cm^2 the oxidation peak for AA shifts to approximately -7 mV , indicating that a substantial increase in k° has taken place. This enhancement in rate for ascorbic acid on GC 30s is typical of that previously observed in this lab for a GC 20 surface upon laser pretreatment and by Kuwana et al. [4,7] and Wightman et al. [18] for vacuum heat treatment and ultraclean polishing. This rate enhancement is not only observed for AA but has been observed for many different electroactive species. Also shown in Fig. 2 is a CV for ascorbic acid on a freshly fractured GC surface. The observed peak potential of -6 mV is indicative of a very high k° and is virtually identical to that of the polished surface after laser irradiation at 40 MW/cm^2 . It is also comparable to that observed for VHT of a GC surface of 0 mV vs. SSCE for AA in pH 7.0 phosphate buffer [22].

The kinetics of neither the polished, laser irradiated nor the fractured electrode surfaces may be deduced from the CV of ascorbic acid at 0.1 V/s because the observed E_p is close to the thermodynamic value. At faster scan rates, however, some kinetic information is accessible. The voltammograms using a scan rate of 10.0 V/s clearly vary for the different surfaces (Fig. 3). The peak potential for the polished GC surface, even after laser irradiation at 40 MW/cm^2 , has a value of 83 mV while that for the fractured surface is approximately 50 mV. The lower peak potential for the fractured surface indicates a higher k° . Due to the relatively high currents and consequently the non-negligible ohmic potential error, the true electron transfer rate for the fractured surface is not reflected by the observed peak potential. A linear plot of peak potential vs. peak current at scan rates of 2, 5, and 10 V/s indicates that the peak potential of AA on the fractured surface is determined primarily by ohmic potential drop. If a more intense laser pulse is used for laser pretreatment of the polished surface, more negative values for E_p are obtained. While ohmic potential errors do not permit an accurate comparison of peak potentials, the relative values are clear. The 40 MW/cm^2 surface exhibits

slower electron transfer than the fractured surface, while the 80 MW/cm² exhibited the fastest kinetics of all surfaces examined.

On the basis of the voltammetric background current, the apparent capacitance differs for the various pretreatment procedures. Upon activation at 40 MW/cm², the observed capacitance increases from 20 μF/cm² for the polished surface to 30 μF/cm² after activation. Because k° increased by several orders of magnitude while the capacitance increased by only 50%, the rate increase must be due to more than an increase in microscopic surface area, as stated previously [15]. The 80 MW/cm² and fractured surfaces have an observed capacitance of 75 and 110 μF/cm², respectively. Although these values are large relative to the polished surface, they are not large enough to explain the rate enhancement solely by a microscopic area increase. The relationship between surface cleanliness, microscopic area, and k° is currently under more detailed examination.

The observations lead to two distinct conclusions. First, the fractured GC 30s surface is very active toward electron transfer, with rates for AA oxidation at least as fast as VHT or 40 MW/cm² laser activated surfaces. Second, the 80 MW/cm² laser activated surface is similar to the fractured surface, at least with respect to capacitance and E_p . The fact that the fractured surface exhibits fast kinetics for AA has several implications. First, any gross modification of the GC microstructure by polishing is unnecessary for high activity toward AA. Polishing debris and impurities may in fact be deleterious to electron transfer. Second, a thick oxide film similar to that formed by electrochemical activation is unnecessary for activation. There may be oxides on the freshly fractured surface, but several arguments against their involvement in activation have been presented [24,25]. Any oxides involved in electron transfer must form immediately upon exposure of the freshly fractured surface to air.

These preliminary results on fractured GC indicate that the GC substrate microstructure is itself sufficient for fast electron transfer for AA. In addition, laser activation of an electrode deactivated by polishing yields a similarly active surface, either by exposing the underlying microstructure or by some other mechanism. The fact that laser activation slowly (~ 1 nm/pulse) removes GC substrate may imply that substrate exposure is a mechanism common to laser activation and fracturing. As pointed out by Jordan et al. [8], polishing may also activate GC by exposure of substrate. However, extreme care must be taken to avoid deactivation during polishing by impure polishing materials. Similarly, Kuwana et al. [7] attribute high activity of VHT GC to "pristine" carbon.

As a closing point, the results presented here and by others are consistent with activation mechanisms based solely on exposure of graphite edge planes. The GC substrate microstructure is already rich in edge planes. Several workers have concluded that GC activity is a function of active site density and surface cleanliness [2,6,7,16,22,24], and we have reported that the active sites are located on graphitic edge planes [19,25]. In the case of GC 20, the edge plane density is high throughout the material, so activity primarily reflects surface cleanliness. If one assumes that the fractured GC surface is at least as clean as that obtained from

careful polishing, then the observed high activity for fractured surfaces is reasonable. When the surface is polished, however, the surface may be deactivated to widely varying degrees depending on the cleanliness of the procedure. A major effect of laser activation on polished surfaces may be removal of polishing debris. It is also quite likely that VHT and electrochemical pretreatments act mainly by removing surface impurities, microparticle layers, etc. While area effects may be less important than surface cleaning, an increase in microscopic area by polishing or laser activation may further enhance activity. Whatever mechanisms are invoked to explain GC activation by various procedures, they must be consistent with the observation of high electron transfer activity for the fractured surface.

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