Activation of Highly Ordered Pyrolytic Graphite for Heterogeneous Electron Transfer: Relationship between Electrochemical Performance and Carbon Microstructure

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Abstract: The electrochemical and vibrational spectroscopic properties of highly ordered pyrolytic graphite (HOPG) were determined before and after modification by anodization or pulsed laser irradiation. Both treatments greatly accelerated the heterogeneous electron transfer rate constants for the Fe(CN)₆³⁻/⁴⁻ and dopamine redox systems on HOPG by approximately six orders of magnitude. Modification also caused significant changes in the Raman spectrum of HOPG, with new bands appearing at 1360 and 1605 cm⁻¹ for both pretreatments. The 1360-cm⁻¹ band is spectroscopically indicative of graphitic edge plane, and the results indicate that electron transfer activation correlates with edge plane density. The intensity of the 1360-cm⁻¹ band correlated with electron transfer activation, with a high intensity corresponding to higher \( k^o \) for either electrochemical or laser pretreatment. At intermediate electrochemical pretreatment (ECP) potentials, a spatially heterogeneous surface resulted, with surface regions exhibiting the 1360-cm⁻¹ band being separated by tens of microns. Such heterogeneity was verified by voltammetry, with distinct waves being observed for active and inactive surface regions. Such heterogeneity was not observed for laser treated surfaces, with a sudden and spatially uniform activation occurring between 40 and 50 MW cm⁻². The results clearly indicate that graphitic edge plane is necessary for fast electron transfer, and that the pretreatment procedures accelerate \( k^o \) by generating edge plane defects in the HOPG lattice. The mechanisms of defect generation for the two procedures appear very different, with ECP appearing to follow a nucleation process leading to a spatially heterogeneous surface, while the laser pulse appears to shatter the HOPG lattice, leading to a more uniform distribution of active sites. The results provide important conclusions about the relationship between carbon electrode microstructure and heterogeneous electron transfer activity.

A large body of literature has appeared over several decades on the electrochemical properties of carbon, with the most recent comprehensive review appearing in 1988.¹ The important commercial and analytical applications of carbon electrodes combined with complex and interesting surface chemistry have provided the driving force for examining the relationship between interfacial structure and electrochemical activity.²,³ Of particular interest is the heterogeneous electron transfer rate between carbon electrodes and various well-known redox systems such as ascorbic acid, ferri/ferrocyanide, and the catecholamines. Not only are these systems of significant analytical interest, but they serve as benchmarks for comparisons of electrode performance. Until relatively recently, the observed heterogeneous rate constants for these redox systems (\( k^o \)'s) were extremely irreproducible (by factors of up to 10⁵) due to variations in surface history and carbon type. Such variation frustrated attempts to determine which aspects of surface structure or preparation determined the value of \( k^o \), and any systematic examination of electrode kinetics on carbon was very difficult if not impossible.

With the development of heat treatment procedures,⁴⁻⁵ ultraclean polishing techniques,⁶⁻¹¹ and electrochemical activation,¹²⁻²⁰ it became possible to prepare reproducibly active carbon surfaces, particularly from glassy carbon substrates. With adequate care, glassy carbon exhibits a \( k^o \) value for the ferri/ferrocyanide redox system close to that for platinum, and 10⁻¹⁰ times faster than less successful pretreatment procedures.⁷⁻⁸ Our group added to the list of successful pretreatments by reporting that intense laser pulses can activate glassy carbon at least as well as other methods, with activation occurring in situ, repeatedly if desired.²¹⁻²⁴ While careful polishing, heat treatment, electrochemical anodization, and laser activation result in roughly comparable increases in \( k^o \) for several benchmark systems, there are major differences in surface chemistry for the various methods. Vacuum heat treatment and laser activation have low apparent capacitance (ca. 20 \( \mu F/cm² \)) while polishing and electrochemical pretreatment lead to much higher values (70⁻²⁰₀ \( \mu F/cm² \)).²⁻²⁴ Polished surfaces exhibit a pH dependent \( k^o \) for ferri/ferrocyanide,²⁻²⁴ while laser treated surfaces do not.²⁴ Polished or electrochemically pretreated surfaces exhibit a pH dependent quinone-like surface bound redox couple, while heat or laser treated GC do not.⁴⁻¹²,²⁰,²⁴ Electro-

chemical pretreatment of GC produces a porous, hydrated film up to at least 0.9 μm in thickness, but there is no evidence for such a film on laser treated or VHT surfaces. Severe electrochemical pretreatment leads to a partially insulating surface which retains high k^0 over a fraction of its surface. These observations indicate that different procedures yield structurally distinct surfaces, and the question of which surface structural properties are necessary for rapid k^0 remains unanswered.

Both the recent and older literature discuss the possibility that active sites may exist on carbon, and activation procedures may produce or uncover such sites. Kuwana et al. concluded that heat treatment removed oxygen functional groups and impurities from GC. If the activation resulted in a clean surface containing active sites,6-10 Wightman came to a similar conclusion,11 while other workers have attributed activation to oxygen functional groups16-29 or exposure of the underlying GC substrate structure.30 It has long been observed that exposed graphic edges correlate with electron transfer activation. For example, the ferri/ferrocyanide redox system exhibits a 3-fold higher exchange current on edge vs basal plane graphite,31 and exposure of edge plane has been proposed as the mechanism of several activation procedures.3,5,7 In none of the previous reports on carbon activation has there been a direct correlation between the population of active sites and electron transfer activation. The objective of the present work was the investigation of the relationship between a spectroscopically observable surface feature and the observed k^0 value. In particular, we sought to explain the origin of k^0 enhancement by laser activation.

The approach presented here differs from the large bulk of previous investigations in three ways. First, the electrode material was highly ordered pyrolytic graphite (HOPG) rather than glassy carbon. Unlike GC, HOPG is a microstructurally well-defined material, and the initial surface structure is known, at least before activation. Second, we used Raman spectroscopy as a probe of carbon microstructure, to permit structural inferences during and after activation. Third, we used both laser activation and electrochemical pretreatment (ECP) to modify the HOPG surface. Both methods provide a controlled, and in certain cases gradual, removal of superficial layers with common adhesive tape, and the GC-20 shows a strong 1360-cm^{-1} band,33,36 and the 1580-1620-cm^{-1} band is dependent on the origin of the material. Several spectra for the materials used here are shown in Figure 1. GC-20 shows a strong 1360-cm^{-1} band,33,36 and the 1580-1620-cm^{-1} band is dependent on heat treatment temperature.37 HOPG basal plane shows only a very weak 1360-cm^{-1} band, plus the strong 1582-cm^{-1} E_2^g mode.38-41 Spectrum D of Figure 1 is a microprobe spectrum on a visible tear on the HOPG basal plane, shown in the SEM of Figure 2A. Such defects are infrequent, representing less than 1% of a carefully exposed surface. While the 1360-cm^{-1} band for the defect is weak, its frequency matches that of the edge plane HOPG, shown in Figure 1 C. The 1360-cm^{-1} mode has been assigned to the A_g mode for D_{6h} symmetry, and Raman allowed only for small graphite crystals.34 It is present wherever significant edge density is present, as in GC, edge plane HOPG, and the HOPG defect. The 1582-cm^{-1} band is complex, being composed of two components.42,43 For extremely disordered graphite or intercalation compounds,45 it shifts to higher wavenumber in a range of 1590-1630 cm^{-1}. This shift has been explained by attributing the higher energy band to "boundary layer" graphite, which is adjacent to zero or one neighboring graphitic planes. The ca. 1620-cm^{-1} mode is prominent for graphitic planes bounded by intercalant layers and is the only band observed for Stage 1 intercalation compounds where the graphite layers are never adjacent to each other. The 1582-cm^{-1} mode is attributed to "inner layer" graphite which is bounded by two adjacent graphite planes. In Stage 4 intercalation compounds, for example, the "inner layer" and "boundary layer" planes are equal in number and the 1582- and 1620-cm^{-1} bands are equal in intensity.45 The higher energy band frequency is dependent on sample history, and in the results reported here it occurred most frequently at 1605 cm^{-1}. For the purposes of this report, it is important to recognize the association of the 1360-cm^{-1} band with the size of the graphitic plane, whereas the 1600-1630-cm^{-1} mode is related to the stacking of graphite planes.

**Experimental Section**

HOPG was a gift from Arthur Moore at Union Carbide, Parma, Ohio, and the GC was Tokai GC 20S. A fresh HOPG surface was exposed by removal of superficial layers with common adhesive tape, and the GC-20 was polished conventionally with the final abrasive being 0.05-μm alumina. Electrochemical apparatus was conventional, consisting of a Princeton Applied Research Corporation 173/176 potentiostat controlled by a PC compatible computer and Tescar Labmaster analog interface. HOPG was mounted in a Kel-F holder and the active electrode region was defined by a viton o-ring which prevented solution contact with the edge plane. The exposed basal plane area was 0.70 cm^2 for ECP experiments. ECP was conducted with a procedure similar to that of Engstrom,21,22 with a 2 min controlled potential anodization in 0.1 M KNO_3, followed by a cathodic step to -0.1 V vs Ag/AgCl for 30 s. For voltammetry, a small O-ring defined a 0.70 cm^2 area, the GC-20 was defined by a viton O-ring which prevented solution contact with the edge plane. For both scanning and multichannel spectral acquisition, it was necessary for rapid beam unifor-
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Figure 1. Raman spectra of various forms of carbon, obtained with 515-nm laser light. A and B are gross spectra of GC-20S and HOPG basal plane, respectively, 20 mW at sample covering a 0.1 x 1 mm spot. Spectral resolution was 10 cm⁻¹. Shoulder at 1565 cm⁻¹ is dioxygen in the room air in which spectra were obtained. C and D are microprobe spectra of the HOPG edge plane and a visible defect on the HOPG basal plane, respectively, obtained with 5 mW of laser light on a ca. 5 μm diameter spot.

with Nd:YAG pulses of varying power, dramatic changes occur in the voltammetry and Raman spectra. At laser peak powers equal to and above 45 MW cm⁻², the 1360-cm⁻¹ band appears in the Raman spectra of the irradiated region, as shown in Figure 4. The spectrum of the irradiated area was obtained with the microprobe on a region similar to the gray area apparent in the SEM of Figure 2B. The spectrum was essentially uniform across the laser-treated area, and no significant differences were observed between gross and microprobe spectra. No distinct 1620-cm⁻¹ band was observed for laser-treated surfaces, but a weak shoulder on the 1582-cm⁻¹ band was observed at 45 MW cm⁻² and above. The voltammetric peak separation for Fe(CN)₆³⁻/⁴⁻ and dopamine decreased strongly at 45 MW cm⁻² and above, as shown in Figure 3. The effect occurred suddenly between 40 and 50 MW cm⁻², with no intermediate peak separations between the two extremes. Figure 5 summarizes the gross Raman intensity data and voltammetric ΔE_p values for dopamine and Fe(CN)₆³⁻/⁴⁻. Assuming a value of α = 0.5 for Fe(CN)₆³⁻/⁴⁻, the increase in rate constant upon laser activation at 45 MW cm⁻² was from <10⁻⁹ to 1.7 x 10⁻⁷ cm s⁻¹, as determined from ΔE_p.⁴⁶

The SEM obtained from surfaces after laser treatment in air shows no structure or spatial heterogeneity, only a “grey” region corresponding to the laser spot (Figure 2B).

Electrochemical Pretreatment of HOPG. The SEM of electrochemically pretreated HOPG in Figure 3C exhibits a complex pattern of defects, which may emanate from a few points on the surface. These complex defect networks were surrounded by sometimes large (~20 μm) regions of apparently undamaged HOPG. The bright lines associated with defects may be edge planes, but their brightness implies electron beam charging and perhaps some insulating character. Figure 6 shows the effect of ECP at three potentials on the gross Raman spectra of fresh HOPG surfaces. Spectrum B exhibits a 1605-cm⁻¹ band which first appears at a pretreatment potential of about 1.6 V. In addition, the 1360-cm⁻¹ band appears and becomes more intense as the ECP potential is increased. These modes indicate that the initial nearly defect free HOPG surface is delaminating and fracturing, resulting in smaller crystallites. The 1605- and 1360-cm⁻¹ bands do not vary together, however, showing different onset potentials, and occasionally varying in opposite directions. Three microprobe spectra of an HOPG surface pretreated at 1.85 V are shown in Figure 7. Some regions sampled by the 5 μm laser spot exhibit both the 1360- and 1620-cm⁻¹ bands, but translation of the microprobe to a region only 20 μm away yields a spectrum without the 1360-cm⁻¹ band. The Raman microprobe indicates spatial heterogeneity on a scale of tens of microns for a surface treated at 1.85 V. The effect of ECP on the electrochemical properties of the HOPG surface is apparent by comparing curves A and B in Figure 8. The 1.85-V ECP has activated dopamine and Fe(CN)₆³⁻/⁴⁻ dramatically, with both systems showing large reductions in ΔE_p. The existence of two voltammetric waves for dopamine and the distortion of the Fe(CN)₆³⁻/⁴⁻ wave imply spatial heterogeneity on a scale larger than (Dt)⁻¹/² (D = diffusion coefficient, t = approximate scan time through voltammetric wave). For the scan rate employed, (Dt)⁻¹/² is about 25 μm, implying that activated regions are separated from each other by at least this distance.

Figure 2. SEM's of carbon samples obtained in secondary electron mode. (A) Freshly cleaned HOPG with arrow indicating a defect similar to that exhibiting spectrum D of Figure 1. (B) Laser treated (50 MW cm⁻², 1064 nm, 3 pulses) HOPG. The gray area is the laser spot, and the large defect to the right was present before laser treatment and serves as a marker. Laser treatment occurred in air. (C) Electrochemically pre-treated HOPG (1.95 V vs AgCl, 2 min, 0.1 M KNO₃).

Both the gross Raman spectrum and microprobe spectra of HOPG after a 1.95-V ECP have the appearance of Figure 6C. Unlike the 1.85-V ECP, the 1.95-V surface exhibits no spatial heterogeneity and shows only slight variation in the Raman spectrum for many microprobe positions on the activated surface. The voltammetry of dopamine and Fe(CN)₆³⁻/⁴⁺ on the more vigorously activated surface (Figure 8) shows full activation, with no observed peak from an inactive region. Thus, any spatial heterogeneities are small relative to the microprobe spot size (5 μm) or (Dt)¹/² for a 0.2 V/s voltammogram.

Figure 3. Voltammograms of dopamine and Fe(CN)₆³⁻/⁴⁺ on untreated and laser-treated HOPG: (A) Fe(CN)₆³⁻/⁴⁺, 1 M KCl, 0.2 V s⁻¹; (B) dopamine in 0.1 M H₂SO₄, 0.2 V s⁻¹. Upper curve in both cases is before laser treatment, and lower curves are after laser treatment (50 MW cm⁻², 3 pulses). Laser treatment was performed in air before immersion in electrochemical solutions.

Figure 4. Gross Raman spectra of laser-treated HOPG (3 pulses, 50 MW cm⁻²): (A) off the laser spot, (B) in the gray region shown in Figure 2B. Relative to the 1582-cm⁻¹ band for a large observation area as a function of pretreatment potential. The I₃₁₆₀/I₁₅₈₅ ratio indicates the spatially averaged intensity of the A₁₉ mode within the sampled area. Figure 9 also shows the ΔEₚ for Fe(CN)₆³⁻/⁴⁺ as a function of ECP potential. The dramatic decrease in ΔEₚ coincides with...
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Figure 5. Effect of laser power density on $\Delta E_p$ for Fe(CN)$_6^{3-/4-}$ (curve A), intensity ratio of 1360 to 1582 cm$^{-1}$ gross Raman band (curve B), and intensity ratio of 1605 to 1582 cm$^{-1}$ band (curve C). Three laser pulses in air, and spectra obtained in air. Data in curve C are approximate due to the difficulty of determining the intensity of the 1605-cm$^{-1}$ shoulder.

Figure 6. Gross Raman spectra obtained in air after electrochemically pretreating HOPG for 2 min in 0.1 M KNO$_3$. 1565-cm$^{-1}$ peak is di-oxygen: (A) 1.6 V vs Ag/AgCl; (B) 1.85 V; (C) 1.95 V. Laser spot on surface was 0.1 x 1 mm in size.

Figure 7. Raman microprobe spectra of HOPG electrochemically pretreated at 1.85 V. Same conditions as Figure 6 except the laser spot size on surface was ca. 5 $\mu$m in diameter. Spectra B and C were obtained on the same surface as A, after two successive ~20-$\mu$m translations of the microprobe.

Discussion

The Raman spectra of laser treated HOPG indicate a damage mechanism with a well-defined threshold. The sudden appearance of the 1360-cm$^{-1}$ band intensity in addition, the 1605-cm$^{-1}$ intensity occurs after ECP potentials significantly lower than those required for electron transfer activation. The $k^0$ for Fe(CN)$_6^{3-/4-}$ observed for ECP potentials below 1.6 V was $<10^4$ cm/s, while that for the 1.95-V ECP was $6.5 \times 10^{-3}$ cm s$^{-1}$. The Raman spectra of laser treated HOPG indicate a damage mechanism with a well-defined threshold. The sudden appearance of the 1360-cm$^{-1}$ band at power densities above 45 MW cm$^{-2}$ demonstrates laser induced fragmentation of the graphitic lattice, resulting in edge plane defects in the initially smooth HOPG basal plane. Compared to ECP, the laser treated surface exhibits weak 1605-cm$^{-1}$ intensity, implying that little or no delamination of...
The spatial heterogeneity of the HOPG surface following a 1.85-V ECP is apparent from both Raman microprobe and voltammetric data. Untreated HOPG shows widely separated regions with observable 1605-cm\(^{-1}\) bands, but these are only present on visible defects which comprise less than 1% of the total surface area. After a 1.85-V ECP, regions with 1605-cm\(^{-1}\) intensity are more frequent, but they are separated on the surface by tens of microns. At higher ECP potential, the 1605-cm\(^{-1}\) band is uniformly present on the surface, and the voltammetry exhibits a single, activated redox couple. It may be significant that not all defects visible by light microscopy showed the 1605-cm\(^{-1}\) Raman band. However, the spatial heterogeneity observed for both the 1605-cm\(^{-1}\) band and fast \(k^0\) supports the association between an electrochemically active surface and graphitic edge plane defects.

While ECP undoubtedly creates oxygen-containing functional groups on the carbon surface, the role of oxygen in the spectral and electrochemical results of ECP is unclear. None of the three Raman bands shift when the ECP is carried out in \(\text{H}_2\text{O}\), indicating that surface oxygen is weakly coupled to the observed vibrational modes. Furthermore, carbon materials that contain little or no known oxygen (e.g., GC30, ground graphite) exhibit any or all of the 1605-, 1620-, and 1582-cm\(^{-1}\) bands. As reported for vacuum heat treatment and laser activation, surfaces with immeasurably low surface oxygen content (as determined from ESCA) can exhibit fast \(k^0\) for ascorbic acid, \(\text{Fe(CN)}_6^{3-/4-}\), and dopamine. The absence of a role of oxygen in the activation process is substantiated by the laser pretreatment. The laser has been shown to reduce surface oxygen on GC, even in water, and the laser pulse is not a fundamentally oxidative process.
like ECP. The laser does activate the surface, however, and the activation correlates with the 1360-cm\(^{-1}\)-band intensity. Thus, the correlation between activation and Raman spectral properties is consistent, while neither the spectrum nor activation correlate with oxygen content. There is no doubt that formation of an oxide film by ECP results in activation,\(^ {12,14,16,17,20}\) and it has been shown that the oxide film thickness correlates with the extent of activation.\(^ {20}\) However, activation by ECP appears to result from oxidation-induced fracturing of the graphite lattice rather than any more direct effect of surface oxides on heterogeneous electron transfer.

While both laser and ECP result in similar changes in the Raman spectrum and similar \(k^0\) activation, it is the differences between them that provide insight into the activation mechanism. Since HOPG is initially very clean and is quite inert toward adsorption, activation of HOPG probably does not involve surface cleaning. Both laser and ECP create defects in the HOPG surface that result in the edge plane Raman peak and increased \(k^0\) but the two pretreatments differ in the spatial distribution of defects. ECP leads initially to widely spaced defects while the laser appears to create an even distribution of both the 1360-cm\(^{-1}\) Raman peak and electrochemically active sites. The observations are consistent with a nucleation mechanism for defect growth during ECP. The few defects on fresh HOPG may act as nuclei for the delamination and fracturing of nearby graphite planes. As implied earlier, it is quite possible that the formation of surface oxides during ECP produces strain on the graphite lattice which produces fracturing and delamination. The result is spatially separated active regions, at least at a low ECP potential. At higher potentials, defect growth extends over the entire surface, and uniform activation and 1360-cm\(^{-1}\)-band intensity result. The absence of spatial heterogeneity on a greater than micron scale for laser-treated HOPG implies that the laser-induced temperature excursion or associated mechanical strains create many defects that do not grow from a few nuclei. Given the 10-ns duration of the laser pulse compared to the 2-min ECP, a slow nucleation and growth process may not be possible for laser treatment. The fact that rate enhancement and 1360-cm\(^{-1}\)-band intensity occur suddenly and completely at 40 and 50 MW cm\(^{-2}\) may imply that laser-induced thermal stresses shatter the graphite lattice, leading to a fine network of edge plane defects but little delamination or surface oxidation.

To our knowledge, these results constitute the first correlation of a surface feature observable with vibrational spectroscopy and electron transfer activation on carbon electrodes. The rate enhancement is monotonic with the 1360-cm\(^{-1}\) Raman band associated with edge plane graphite with higher edge plane density always correlating with higher \(k^0\). The important question of the mechanism by which edge plane defects enhance electron transfer remains open. The basal plane of HOPG exhibits some properties of a semiconductor electrode, particularly anomalously low capacitance due to space charge effects.\(^ {57}\) On the basis of the measured internal resistance of 0.15 \(\Omega\)-cm, the internal resistance of the working electrode for our geometry is \(<1\ \Omega\) and is not sufficient to significantly increase the observed \(\Delta E_p\). However, the low density of states at the Fermi level for an HOPG basal plane in solution of Raman spectroscopy techniques (R.T.P.) was funded by the Chemical Analysis Division of the National Science Foundation. The authors thank A. W. Moore of Union Carbide (Parma, Ohio) for the HOPG samples used throughout the project.

**Note Added in Proof.** A recent report (Gewirth, A. A.; Bard, A. J. Phys. Chem. 1988, 92, 5563) has also concluded a nucleation and growth mechanism for ECP of HOPG, based on scanning tunnelling microscopy.

Registry No. HOPG, 7782-42-5; GC, 7440-44-0; KNO\(_3\), 7757-79-1; Fe(CN)\(_6\)\(^{3-}\), 13408-63-4; Fe(CN)\(_6\)\(^{4+}\), 13408-62-3; dopamine, 51-61-6.

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