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Laser induced microstructural and morphological alterations and their effects on electron transfer kinetics at glassy carbon electrodes

Pontikos, Nicholas Michael, Ph.D.

The Ohio State University, 1992
LASER INDUCED MICROSTRUCTURAL AND MORPHOLOGICAL ALTERATIONS AND THEIR EFFECTS ON ELECTRON TRANSFER KINETICS AT GLASSY CARBON ELECTRODES

DISSERTATION

Presented in Partial Fulfillment of the Requirements for the Degree Doctor of Philosophy in the Graduate School of The Ohio State University

By

Nicholas Michael Pontikos

* * * *

The Ohio State University

1992

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Approved By:

[Signature]
Adviser
Department of Chemistry
To My Family
ACKNOWLEDGEMENTS

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CHAPTER I

INTRODUCTION

Electrochemical methods are important analytical tools and are useful in both science and commerce. Electrical response, in the form of current, is usually measured as a function of potential in order to deduce information regarding a solution species. The relationships between current and potential, some developed more than a century ago, are employed both in the classroom for beginning students and in the laboratory for more advanced researchers. The combination of thermodynamics and kinetics allows the electrochemist to characterize the chemistry of heterogeneous electron transfer reactions at the electrode solution interface. It has also become possible to observe adsorption as well as coupled chemical reactions. Electrochemistry is becoming a more widely practiced application evident from its use in chromatographic detection and the fact that electrochemical processes provide the basis for numerous chemical industries that are important in the commercial value of products and their derivatives [1].

Electrochemical methods are used in many industrial processes and are involved in over $40 billion of the U.S. annual gross national product (GNP) in
applications such as electrosynthesis, corrosion, batteries and fuel cell production, and electrochemical sensors [2]. It is also estimated that between the years 1990 to 2000 new markets utilizing electrochemistry will emerge and amount to another $20 billion annually [1]. Solid electrodes have virtually replaced the dropping mercury electrode partly due cost, ease of use, and to the toxicity of mercury, and carbon is becoming more widely accepted as a solid electrode material as it replaces platinum in many applications. Several different forms of carbon have been successfully used to manufacture satisfactory electrodes.

Forms of carbon used in electrolysis include spectroscopic grade graphite, carbon black, pyrolytic graphite, highly oriented pyrolytic graphite, carbon paste, and glassy carbon. In terms of analytical applications, the suitability of an electrode material is dictated in part by the heterogeneous electron transfer rate constant $k^\circ$ of a benchmark redox couple. Other important factors include the mechanical properties of the electrode, background current, stability of the electrode in a particular medium, potential range for which the electrode remains useful, and the surface structural properties of the electrode. The one significant difference between carbon electrodes and their metal counterparts is that carbon has an anisotropic structure. One must have an understanding of the surface structure in order to relate surface structure to electrode reactivity and alterations of the surface.
Carbon as an Electrode Material

The introduction of carbon into the electrochemical field began in the early nineteenth century and since has escalated to the point where carbon is extensively and diversely used as an electrode material. Many types of carbon have been used for industrial and academic electrochemical purposes; however, no one kind of carbon is standard since suitability as an electrode material is governed by many factors. For example, carbon materials are available in a variety of structures such as powders, sheets, fibers, and blocks. These materials have similar bonding yet electroanalytical applications often favor one material over another since chemical, electrical, thermal, and mechanical properties of these materials are often distinct. For example, glassy carbon (GC) is in many instances replacing mercury in electroanalytical studies and the pronounced symmetry of highly oriented pyrolytic graphite (HOPG) makes it a standard in scanning tunneling microscopy [3].

Solid carbon occurs naturally in two allotropic forms, diamond and graphite, with graphite being the thermodynamically more stable allotrope under ambient conditions. Recently, a third form known as buckminsterfullerene, $C_{60}$ commonly referred to as buckyballs, was discovered as another natural form [4-6]. Diamond is a crystalline form of elemental carbon where each carbon atom is covalently bonded to four neighbors through $sp^3$ hybrid sigma bonds. Although diamond is one of the best conductors of heat, it is not suitable as an electrode material since it is electrically insulating. Graphite is a black, lustrous, electrically
conducting, slippery solid which consists of flat sheets or layers of carbon atoms which are covalently bonded in the x-y plane into hexagons through sp² hybrid bonds. Bonding between sheets is through weak van der Waals interactions enabling the sheets to easily slide over each other. Electrons can move easier within the layers, but much less readily between the layers permitting graphite to exhibit metallic properties parallel to the layered planes and nonmetallic properties perpendicular to the planes. Thus, with respect to electric conductivity, graphite is anisotropic and is a better conductor through the length of the sheets than perpendicular to them.

Several types of carbons with a network consisting of sp² hybridized atoms are widely used for many electrochemical applications due to their chemical inertness, electrical and thermal conductivities, low densities, adequate corrosion resistivities, low cost, and general availability. These types of carbons are commonly termed graphitic when the layers of carbon atoms arranged in hexagonal rings are stacked in a specific sequence. Throughout this document, a network of sp² hybridized carbons atoms will be referred to as graphitic. Some major types include single crystal graphite, pyrolytic graphite (PG), highly oriented pyrolytic graphite (HOPG), glassy carbons (GC), carbon fibers, and carbon films. The discovery of buckminsterfullerene (C₆₀) lead, within the past year, electrochemists to conceive many applications for this new form of carbon [5-6]. Many reviews which discuss various aspects of the physiochemical properties of carbon exist, yet few are extensive when it comes to the discussion
of electrochemical behavior [7-9]. To be able to use carbon with a high degree of confidence, additional information relating surface structure to reactivity is necessary.

Carbon paste and pyrolytic graphite are two forms of carbon which have been commonly used as electrode materials; however, two forms of graphitic carbon which have received much attention as electrode materials in the past twenty years are HOPG and GC [10-13]. Their practical potential range in aqueous solvents is usually limited by hydrogen and oxygen evolution, and in some cases, the limit may even be corrosion of the electrode. In general, carbon electrodes can be used in a wider potential range than either mercury or platinum in the same electrolyte solution. Another advantage of carbon electrodes is that they can be used in either acidic or basic media with reports of pH values as low as -1.0 [14-15]. Concentrations higher than 1 M sulfuric acid are inadvisable since surface oxidation may occur under these conditions.

HOPG is a product of the Union Carbide Corporation and is manufactured by compression annealing pyrolytic graphite at high temperatures. This process yields a highly crystalline material of varying grades with two different symmetry planes, La and Lc. As seen in Figure 1, La is defined as the average size of the microcrystallites along the axis which lies in the plane of the hexagonal lattice. Lc in contrast, refers to the collection of the graphite planes over which a specific sequence of stacking is defined and is orthogonal to the La axis. The plane containing the hexagonal lattice is referred to as the basal plane and the plane of
Figure 1

Structures of HOPG and glassy carbon.
Figure 1

EDGE PLANE

BASEAL PLANE

HOPG

GC

Figure 1
stacking is referred to as the edge plane. In general, $L_a$ may vary in the range from 10 to $10^5 \text{Å}$ and $L_c$ may cover a range between 10 Å to greater than 5 \text{μm} depending on the type of carbon [16]. Typical values for HOPG are of the order 1 \text{μm} for $L_a$ and 10 \text{μm} for $L_c$. It has also been observed that many of the physical and chemical properties of HOPG are anisotropic for the c and a axes [2, 17-19].

First synthesized and used as an electrode material in the early 1960's, and reviewed recently [2-3], glassy carbons (GCs), also known as vitreous carbons, are characterized by their black glass-like appearance and silicate-like fracture mechanics [20-23]. GC is a proprietary material of the Tokai Electrode Manufacturing Company, but analogous materials have been formulated by others [24-25]. The structure of GC was first proposed by Jenkins and Kawamura and a schematic representation is shown in Figure 1 with selected physical and chemical properties displayed in Table 1 [12, 26-27]. The model suggests a randomly oriented interwoven sp$^2$ hybridized carbon backbone with substantial porosity which may be responsible for GC’s low density relative to metals and HOPG. The porosity accounts for small and closed void spaces of about 30%; thus, low permeability is observed [3]. Typical values as obtained by X-Ray diffraction analysis yield values of about 50 Å for $L_a$ and 15 Å for $L_c$ [2-3].

Synthesis of most GCs begins with curing, carbonizing, and heat treatment of polyacrylonitrile at characteristic temperatures required to produce an sp$^2$ hybridized network. A thorough procedure is presented by Dresselhaus [28]. Other commonly used precursor materials include phenol formaldehyde, acetone-
Table 1: Physical and chemical properties of HOPG and GC's.

<table>
<thead>
<tr>
<th>Property</th>
<th>HOPG a-axis</th>
<th>HOPG c-axis</th>
<th>GC-10</th>
<th>GC-20</th>
<th>GC-30</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk Density (g/cm³)</td>
<td>2.26</td>
<td>2.18</td>
<td>1.55</td>
<td>1.55</td>
<td>1.55</td>
</tr>
<tr>
<td>Gas Permeability (cm²/s)</td>
<td>10⁻⁶ to 10⁻¹² for glassy carbons</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thermal Conductivity (W/cm⁻²K)</td>
<td>24</td>
<td>0.10</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>Thermal Expansion (°C⁻¹ x 10⁶)</td>
<td>27</td>
<td>3.0</td>
<td>3.0</td>
<td>3.0</td>
<td></td>
</tr>
<tr>
<td>Resistivity (Ω·cm)</td>
<td>4.1 x 10⁻⁵</td>
<td>0.5</td>
<td>4.5 x 10⁻³</td>
<td>4.2 x 10⁻³</td>
<td>3.7 x 10⁻³</td>
</tr>
<tr>
<td>Lx (Å)</td>
<td>&gt;10000</td>
<td>~20</td>
<td>~25</td>
<td>~55</td>
<td>~70</td>
</tr>
<tr>
<td>Ly (Å)</td>
<td>&gt;100000</td>
<td>~10</td>
<td>~12</td>
<td>~70</td>
<td></td>
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Sources: [2, 3, 7, 11, 28-32]
fural, furfuryl alcohol, and furfural alcohol-phenol copolymers [3]. Many physical properties of GCs are a function of the characteristic heat treatment temperature, with 2000°C being the temperature which produces properties satisfactory for many electrochemical applications. Heat treatment temperatures of 1000°C, 2000°C, and 3000°C produce glass-like carbons which respectively are termed GC-10, GC-20, and GC-30. It is worth mentioning that GC-10 and GC-20 have similar properties and that GC-30 shows variations in properties mentioned in Table 1 except density.

The use of glassy carbon electrodes in voltammetry is widespread due to GC’s chemical inertness, wide potential range, electrical conductivity, low porosity, low cost, high purity, and availability. Another important feature of GC from an electrochemical standpoint is its relatively wide potential window allowing many redox systems to be studied. In general, GC electrodes can be used at more positive and negative potentials than platinum under identical electrolyte conditions [3]. Also, unlike many metals, GC is relatively unaffected by strongly acidic or basic solutions. From a mechanical standpoint, carbon is an attractive choice since it is hard. These two features make carbon ideally suited for bulk industrial processes as well as smaller microelectrodes for laboratory experiments.
Spectroscopic and Structural Analysis

As stated earlier, several types of carbons share the sp\(^2\) hybridized network yet each exhibits microcrystallite sizes ranging from angstroms to micrometers. Since the microcrystallite sizes vary for carbons sharing the same network, structural properties should be monitored to deduce how they change and what consequences changes may have on electrochemical activity. Several spectroscopic techniques such as Infrared spectroscopy, X-Ray photoelectron spectroscopy (XPS or ESCA), Electron spin resonance spectroscopy (ESR), Auger spectroscopy, and Raman spectroscopy have been employed to investigate the physical properties of carbon materials [3]. Infrared and ESR spectroscopy are perhaps the two most common techniques used for carbon, yet meaningful information about carbon is often difficult to obtain with IR spectroscopy due to weak absorption bands caused by small dipole moment changes from lattice vibrations [2-3]. Since it is desirable to obtain structural information in the same media as electrochemical measurements were obtained, some of the above mentioned techniques are not always appropriate for structural elucidation since they require high vacuums or environments which may modify surface properties. Also, from a practical standpoint, IR radiation penetrates deeper than the visible radiation used in typical Raman experiments implying that Raman spectroscopy may be better suited for surface structural information [2].

When monochromatic radiation is incident on a sample most of the light is elastically scattered (Rayleigh effect); that is, the radiation is scattered without
a change in energy. Some of the photons however exchange energy with the sample and either loose or gain energy. This process is termed inelastic scattering and was predicted theoretically in 1923 by Smekal [33-34]. In 1928, this phenomenon was first observed by the Indian physicist C. V. Raman and was later termed the Raman effect [33, 35]. Usually less than one photon in $10^6$ is inelastically scattered which means that it is necessary to use powerful light sources when obtaining Raman spectra. Also, since the scattered frequencies are usually displaced from the Rayleigh line by only 1 to 4000 cm$^{-1}$, it is necessary to use highly monochromatic incident radiation. The advent of lasers has greatly inspired the use and development of Raman spectroscopy. In the fifties commercial Raman spectrometers were produced and the availability of the photomultiplier tube allowed for direct recording of spectra. However, Raman spectroscopy was less widely used than IR spectroscopy and the development of experimental Raman techniques did not keep pace with IR spectroscopy. This was primarily due to the limitations of the incident radiation source, the mercury arc lamp, which has only one strong excitation line at 438 nm thus restricting samples to those which are colorless or pale yellow [33]. Today, Raman spectrometers are commercially available by many manufacturers, and source intensity is no longer a limitation. Thus, the task of obtaining a Raman spectrum for most any sample is fairly routine.

Figure 2 depicts the process of Raman scattering. When incident monochromatic radiation of energy, $h\nu_o$, interacts with a molecule, the molecule
Figure 2

Energy level diagram of spontaneous and resonance Raman scattering.
Figure 2

Rayleigh Scattering

Stokes Spontaneous Raman

Anti-Stokes Stokes Resonance Raman

h_0

h_0 + h_0

h_0 - h_0\text{vib}

h_0 + h_0\text{vib}

h_{veI} - h_0\text{vib}

h_{veI} + h_0\text{vib}

Excited electronic state

Virtual state

Excited vibrational state

Ground state
is excited to a higher energy state and upon relaxing, it emits radiation either with the same energy or with a loss or gain. The relaxation of the excited molecule back to the ground state by emitting a photon of equal energy $h\nu_0$ is termed Rayleigh scattering. In contrast, the relaxation by emitting a photon of less energy, $h(\nu_0 - \nu_{\text{vib}})$, is termed Stokes scattering, while emitting a photon of greater energy, $h(\nu_0 + \nu_{\text{vib}})$, is termed anti-Stokes scattering. The anti-Stokes branch is generally less useful since it is less intense than the Stokes branch. This is true since Boltzman distributions favor ground state populations at room temperature. The resonance Raman effect, also depicted in Figure 2, occurs when the molecule is excited to a virtual state near an excited electronic state. This enables the molecule to interact more efficiently with the incident radiation, and vibrational transitions coupled to the excited electronic state are enhanced usually by factors of $10^4$ to $10^6$. It is important to note that in such cases, the incident laser radiation should be reported [33].

The Raman spectra of freshly cleaved basal plane HOPG and conventionally polished GC-20 are shown in Figure 3. Of the twelve possible vibrational modes associated with the $D_{6h}$ space group symmetry of graphite and GC, only the two $E_{2g}$ modes Raman active [16, 36]. These modes are used to characterize carbons with the widths at half maximum providing an estimate of the sample crystallinity [3]. The Raman spectrum of HOPG has a sharp band at 1582 cm$^{-1}$ that has been assigned to the in-plane $E_{2g}$ mode which is present in all graphitic carbons [16, 36]. Bands beyond 2000 cm$^{-1}$ are attributed to overtones and
Figure 3

Raman spectra of basal plane HOPG and polished GC-20 at 515.5 nm. Typical laser power at the sample was about 75 mW, with 1 second integration per point, and a spectral bandpass of 10 cm$^{-1}$. 
Figure 3
combinations. Glassy carbons in contrast exhibit a 1582 cm\(^{-1}\) band as well as a disorder mode at about 1360 cm\(^{-1}\). The band which appears at about 2250 cm\(^{-1}\) is due to atmospheric nitrogen. Tuinstra and Koenig demonstrated that the first order spectrum of graphitic carbons are sensitive to microcrystallite size [16]. More specifically, the relative Raman intensity ratio of the 1360 cm\(^{-1}\)/1580 cm\(^{-1}\) varies as the inverse of \(L_e\). The origin of the disorder mode is controversial, yet it has been attributed to two factors. First, the breakdown of the lattice symmetry results in the creation of graphitic edges which lead to a collapse of the selection rules. Second, smaller microcrystallite sizes exhibit changes in polarizability which also result in a collapse of the selection rules [37-38]. Thus, there is some agreement on the semi-quantitative correlation of the 1360 cm\(^{-1}\) band with smaller microcrystallites and the presence of edge plane carbon [16, 38]. As will be shown later, the 1360 cm\(^{-1}\)/1580 cm\(^{-1}\) ratio is dependent on surface pretreatment.

**Kinetic Parameters**

Carbon has played a prominent role in electrochemistry since the early applications of amorphous graphites. The introduction of glassy carbons has allowed electrochemists to take full advantage of the properties of solid electrodes and to exploit their wide range of applications without the high cost of using platinum [39] Establishing a relationship between structure and electrochemical performance is of paramount importance since heterogeneous electron transfer between a solid electrode and a solution redox couple is the basis for many
electrochemical reactions in batteries, electrosynthesis, and corrosion. Oxidation/reduction reactions may be represented by the general equation

\[ \frac{k_f}{k_b} \quad \text{Ox} + n\text{e} \rightarrow \text{Red} \]  

(1)

where \( k_f \) and \( k_b \) are the rate constants for the forward and reverse reactions respectively, at potential \( E \) and temperature \( T \). Also, an accurate representation of a dynamic equilibrium process must incorporate a thermodynamic equation. For the above case, the Nernst equation, shown below as Equation 2, accomplishes this since the equation combines the electrode potential with the bulk concentration of the solution species.

\[ E = E^f + \frac{RT}{nF} \ln \left( \frac{C^*_{\text{ox}}}{C^*_{\text{red}}} \right) \]  

(2)

In Equation 2, the terms \( E \), \( E^f \), \( R \), \( T \), \( C^*_{\text{ox}} \), and \( C^*_{\text{red}} \) refer to the electrode potential versus a reference cell, the formal potential of the electrode, the gas constant, the temperature, the bulk concentration of the oxidized form of the redox couple, and the bulk concentration of the reduced form of the redox couple respectively. The rate of the forward and reverse reactions may be expressed as

\[ (\text{rate})_f = k_f \ C_{\text{ox}} \]  

(3)

\[ (\text{rate})_b = k_b \ C_{\text{ox}} \]  

(4)

where \( C_{\text{ox}} \) and \( C_{\text{red}} \) refer to the concentrations of the oxidized and reduced forms of the electroactive species respectively, and \( (\text{rate})_f \) and \( (\text{rate})_b \) refer to the forward
and reverse rates respectively. Upon using either free energy curves or a kinetic model based on electrochemical potentials, it is possible to define \( k_f \) and \( k_b \). At potential \( E \) and temperature \( T \), \( k_f \) and \( k_b \) are given by Equations 5 and 6 respectively [40].

\[
k_f = k^o e^{-\alpha nF/RT(E-E^\circ)} \tag{5}
\]

\[
k_b = k^o e^{(1-\alpha)nF/RT(E-E^\circ)} \tag{6}
\]

The transfer coefficient, \( \alpha \), in the above equations is a parameter which describes the potential dependence of the standard heterogeneous rate constant, \( k^o \). The physical interpretation of \( k^o \) is that it is simply a measure of the kinetic facility of a redox couple to undergo electron transfer [40]. A system with a large \( k^o \) will achieve equilibrium on a shorter time scale than a system with a small \( k^o \). The transfer coefficient is a measure of the symmetry of the energy barrier between the oxidized and reduced forms of the redox species when a free energy model is used to derive Equations 5 and 6 [40]. The assumptions employed were that \( \alpha \) is potential independent and that the sum of \( \alpha \) and \( (1-\alpha) \) is unity. A value of \( \alpha \) greater than 0.5 implies that the forward reaction is favored while a value of \( \alpha \) of less than 0.5 implies the converse. At the formal potential \( E = E^\circ \),

\[
k_f = k_b = k^o \tag{7}
\]

and we term the quantity \( k^o \) the standard heterogeneous rate constant with units of cm/s [40]. The magnitude of the rate constant denotes the type of electrochemical condition under which we are operating. That is, reversible (\( k^o \)
= 1 to 10 cm/s), quasi reversible (0.0001 < \(k^0\) < 1), and totally irreversible (\(k^0 < 0.0001\)) reactions [40].

Using the method of Nicholson [41], it is possible to calculate a value for \(k^0\) if the peak potential separation between the cathodic and anodic cyclic voltammogram peaks, termed \(\Delta E_p\), is known. The peak separation and its relationship to a dimensionless rate parameter, \(\Psi\), has been tabulated [40-41]. The parameter \(\Psi\) is obtained from the measured \(\Delta E_p\) and \(k^0\) is calculated according to the following equation

\[
\Psi = \left( \frac{D_0}{D_R} \right)^{1/2} k^0 \left[ D_n \pi v (nF/RT) \right]^{1/2}
\]

where \(D_0\) and \(D_R\) refer to the diffusion coefficient for the oxidized and reduced forms of the electroactive species, in cm\(^2\)/s, respectively, and \(v\) is the scan rate employed in V/s. This equation is valid for 0.3 < \(\alpha\) < 0.7, and it is assumed that \(\alpha\) is 0.5 for most work utilizing Fe(CN)\(_6^{3/-4}\) in 1 M KCl.

It is important to note that the apparent value of \(k^0\) is not usually reproducible on carbon electrode surfaces due to the variability associated with pretreatment procedures. In some instances, \(k^0\) is not reproducible for a specific pretreatment procedure [2]. Also, carbon is a prominent adsorber of airborne and solution impurities and it is often difficult to obtain an atomically smooth surface. This results in an initially prepared surface which is rough and contaminated to some extent prior to obtaining voltammetric data. Thus, when pretreating the
electrode surface and calculating $k^o$, one must take care so that surface contaminants are minimized and that the roughness factor essentially remains constant.

When using carbon electrodes, one must account for the variability of the surface caused by the pretreatment procedure employed. Thus, $k^o_{\text{obs}}$ will be used in this document to denote the observed heterogeneous electron transfer rate constant on a surface which is not atomically smooth and involves complications introduced by pretreatment procedures. Figure 4 illustrates the difference between these two quantities, where $k^o$ would represent the textbook rate constant as described above, and $k^o_{\text{obs}}$ would be the rate constant obtained under normal operating conditions of physisorbed and chemisorbed impurities and surface roughness for carbon. The measurements discussed in this manuscript will be for $k^o_{\text{obs}}$.

Predicting the electrochemical behavior, specifically the heterogeneous electron transfer rate constant, on GC is complicated due to the enigmatic nature of carbons [2-3]. Electrochemical applications of GC are complicated by the fact that its behavior is highly dependent on surface history and like most solid electrodes, GC passivates upon use [39]. A significant body of literature has been devoted to the understanding and explanation of the many factors which affect $k^o$, with several surface pretreatment procedures being developed to enhance $k^o$ by renewing the glassy carbon surface. Reproducible electrode surfaces may have resulted for a given pretreatment, but the level of surface activity, as measured
Figure 4

Comparison of $k^o$ and $k_{obs}^o$ on glassy carbon.
Ideal:

```
Ox
```

Actual:

```
Ox + ne\(^-\) \rightleftharpoons \text{Red}
```

```
\text{Red}
```
by calculating $k^{0}_{\text{obs}}$ has been known to vary among pretreatment procedures. Since carbon electrodes are usually pretreated prior to use, one must also be aware of how pretreatment procedures affect the carbon surface.

**Pretreatment Procedures For Glassy Carbon Electrodes**

Solid electrodes such as noble metal, carbon, and semiconductor electrodes have found numerous applications in the areas of electrochemical analysis, electrochemical synthesis, energy conversion, and thermodynamic and electrochemical studies [7, 39-40, 42]. However, one inherent problem with solid electrodes is their degradation upon use; the surface of many solid electrodes often passivates upon exposure to atmospheric or solution impurities thus reducing the heterogeneous electron transfer rate [7, 40]. Thus, a preparation technique for renewing or activating the electrode surface is required prior to using the electrode or after the surface has been passivated.

Electrode activation techniques should generate a surface which is reproducible with a known surface area, produce the maximum number of active sites on the surface, and minimize or eliminate contamination [43]. The former, generation of a reproducible surface, was a realization suggested by Heyrovsky as being essential if electrochemistry was to be recognized as an analytical tool when he introduced the dropping mercury electrode in 1922 [44]. These procedures are well established for platinum electrodes [45-46], yet remain a challenge for glassy carbon.
Much effort has been spent by many researchers in an attempt to develop a method for preparing an active and reproducible carbon electrode surface. There is no standard method for pretreatment, yet generally, one begins by mechanically polishing followed by a subsequent treatment since electrode activity is usually low after polishing. Some of these subsequent treatment procedures include polishing [47-49], chemical and electrochemical pretreatment [50-56], vacuum heat treatment [57-58], thermal and rf plasma treatments [57,67, 59-60], and laser irradiation [15,61, 62-64].

In general, electrode polishing is accomplished by physically grinding or pressing the carbon electrode, usually a circular disk, on polishing cloth to which abrasives and water have been added until a mirror-like finish is obtained. The abrasive is usually 1.0 μm alumina, Al₂O₃, followed by 0.3 μm and 0.05 μm particles. Usually, sonicating the electrode between successive alumina polishings is recommended to minimize residual particles or debris. Electrode activity is then assessed by measuring ΔE_p and calculating the observed heterogeneous electron transfer rate constant, k°_obs, usually for Fe(CN)₆³⁻/⁴⁻ in 1 M KCl. However, since values for k°_obs after polishing range from 0.0001 to 0.15 cm/s [2], it is unclear what effects polishing has on the electrode surface. Thus, subsequent treatment procedures are recommended, and in general, they produce values for k°_obs which are larger than those obtained from polishing and also more reproducible. Kuwana et al. have introduced novel approaches to polishing which produce k°_obs values on carbon comparable to those obtained on platinum
by polishing on a glass plate and exercising caution regarding cleaning of the surface [47, 65-66].

Although the effects of polishing glassy carbon surfaces are not completely understood, subsequent treatment of the electrodes by vacuum heat treatment (VHT) helps to elucidate some of the mystery of the GC surface. Wightman et al. [10, 67] were the first to report use of VHT at 550 °C and millitorr pressures to activate ascorbic acid, Fe(CN)$_6^{3/-4}$, and catechol on carbon. The electrode was observed to retain its activity for an extended period of time even in ambient laboratory air while cooling; however, polishing in alumina destroyed this activity. The extent of activation was also reported to be independent of the heating duration. The possibility remains, however, that the surface may react when exposed to air prior to cooling, which is why Fagan, Hu, and Kuwana introduced a modification to this technique in 1985 [65]. Instead of cooling the electrode under low vacuum, Fagan et al. cooled under high vacuum, $<2 \times 10^6$ torr, where reactive gases were essentially absent. This approach produced an electrode surface which was active toward heterogeneous electron transfer of Fe(CN)$_6^{3/-4}$ and ascorbic acid and also produced a surface with substantially reduced concentrations of surface oxides, commonly referred to as surface functionalities, and low electrode capacitance. Reducing the amount of functionalities is desirable so that faster heterogeneous electron transfer is not related to surface modification while a low electrode capacitance is associated with surface cleanliness and a lack of surface roughness. Usually a lower
electrode capacitance value implies a less rough surface. The observed effects of VHT on $k_{\text{obs}}$ are similar to those of ultra clean polishing, as demonstrated by Kuwana, for Fe(CN)$_6^{3/4}$, ascorbic acid, and catechol although the surface properties are quite different. One important difference is the oxygen to carbon ratio is lower substantially after VHT over that of a polished surface [65]. These results imply that neither surface oxides nor excess roughness are necessary for a high heterogeneous electron transfer rate.

Another pretreatment procedure which increases $k_{\text{obs}}$ on glassy carbon electrodes is electrochemical pretreatment, ECP [50-51]. Although ECP increases electrode activity, it does so by a mechanism different than that employed in VHT. The variables modulated during ECP include the supporting electrolyte, the applied potential waveform type and amplitude, and the duration of the applied potential. In general, one applies a dc potential, whose magnitude falls in the range between 1.5 and 2.5 V vs. Ag/AgCl, to the electrode for a given length of time. Once this oxidation step is finished, a mild reduction step, -1.0 V vs. Ag/AgCl, is employed next for a shorter duration of time. The length of oxidation and magnitude of applied potential is used to characterize the type of ECP, soft or hard. No standard procedure exist for ECP because most laboratories adopt a procedure which best suits the intended use of the electrode.

ECP produces electrodes which have a high oxygen to carbon ratio as well as fast electron transfer kinetics [2]. Also, Engstrom et al. observed a color change on the electrode surface which is not present after polishing or VHT. This color
change is attributed to a semi transparent oxide film comprised of phenolic or alcoholic surface functional groups [2, 52, 68]. The term surface oxides will refer to chemisorbed oxygen or functional groups containing oxygen. The identity of the supporting electrolyte was shown to be directly responsible for increases or decreases in electrode capacitance even though polishing impurities were removed from the GC surface. Also, larger $k_{obs}^0$ were measured for many redox couples, as was an increase in adsorption and electrode capacitance. Although some agreement on ECP results exists, this technique produces surfaces which are not always characterized with constant morphology or microstructure and in all cases, surface oxides are greater than those observed after polishing or VHT.

A recent addition to the battery of activation techniques for GC electrodes is laser irradiation. Like VHT, laser irradiated surfaces have a greater carbon to oxygen ratio when compared to polished surfaces and the electrode capacitance is usually greater on laser irradiated surfaces [2]. A experimental design for laser irradiation will be described in Chapter II. Usually, laser irradiation employs a Nd:YAG laser operating 10 Hz at the fundamental 1064 nm, with a 9 ns pulse duration. Nitrogen and iodine lasers have also been used successfully [2, 61, 69]. One advantage of laser irradiation is that it may be performed repeatedly in solution with no solvent removal or cell disassembly. Also, laser irradiation may be conducted in a shorter time period, as fast as 10 Hz if desired and one may synchronize the laser with an electrochemical measurement [2]. The laser pulses rapidly heat the GC surface, in some instances melting the surface, thus increasing
electron transfer possibly by removing debris, generating active sites, or roughening the surface. Values of $k_{\text{obs}}$ for Fe(CN)$_6^{3/4}$, ascorbic acid, and dopamine have increased by orders of magnitude over results obtained on polished surfaces. Laser irradiation produces surfaces which show increases in heterogeneous electron transfer for Fe(CN)$_6^{3/4}$ on carbon comparable to values obtained on platinum [70], and there is no evidence of a passivating film which develops after ECP [2]. Despite the many advantages of laser irradiation, the mechanism for activation is still unclear.

The final activation technique for GC electrodes is fracturing of the electrode surface in solution. This technique is unique since it does not involve intentional pretreatment of the surface in order to observe large $k_{\text{obs}}$ for Fe(CN)$_6^{3/4}$ [71]. The pristine surface exposed has a low oxygen to carbon ratio and results in the largest $k_{\text{obs}}$ obtained to date for many redox systems [2]. Part of the focus of this work is to characterize this surface and to attempt to elucidate the mechanism for fast heterogeneous electron transfer.

It is not clear which surface variables are changing during pretreatment. In fact, most pretreatment procedures alter many variables making the elucidation and correlation of surface microstructure with electrochemical activity difficult. Kuwana et al. and Wightman et al. proposed that active sites exist on carbon and that removal of impurities expose these sites [47, 53, 65, 66], while others propose that surface functionalities enhance the rate for certain redox systems. [52, 72] Most approaches are designed to generate reproducible surfaces, but usually this
results in unknown surface structure. There are no standard polishing procedures yet it is usually best to pretreat in this manner when GC is freshly obtained [9]. Hu and Kuwana, using a novel polishing technique, achieved a rate constant of 0.14 cm/s for Fe(CN)$_6^{3/-4}$ in 1M KCl, comparable to values of 0.2 cm/s obtained on platinum [47]. Since polishing does not produce a smooth surface, their results may have been artificially enhanced due to surface roughness.

Electrochemical pretreatment by Cabaniss et al. has activated Fe(CN)$_6^{3/-4}$, but not to the same degree as Kuwana’s polishing technique [52]. Laser activation and fracturing the surface, have produced comparable and larger rate constants than Kuwana obtained [15, 61-64]. Although each technique produces an increase in $k^o$, it is not clear that this is done uniquely by removal of debris. This may be substantiated by noting that basal plane HOPG, though atomically clean upon cleavage, exhibits poor electron transfer kinetics for several redox couples [10, 73]. Clearly, the electrode surface is clean, [74] yet deficient in active sites which Kuwana and Wightman suggested were necessary for fast electron transfer at GC. Surface oxygen catalysis has been ruled out for these surfaces, [3, 64, 66] suggesting the possibility that enhancement may be due to other surface variables. Thus, the surface at which electron transfer occurs must be understood to gain a fundamental insight of the variables which change during pretreatment procedures.
Surface Variables

Although GC is probably the one of most popular forms of carbon used as an electrode material, there is much discrepancy as to which surface variables affect its electrochemical behavior, and to date there is no agreement as to which variables have the greatest effect on $k_{obs}$. These structural surface variables are of fundamental scientific interest since they ultimately control the rate and thus the efficiency of electron transfer. The difficulty in elucidating structure and reactivity relationships arises from the inability to reproduce and characterize solid electrode surfaces. This is primarily due to the complex nature of glassy carbon. Unlike HOPG, one does not know the exact surface structure prior to performing an experiment since the GC surface exposed a combination of basal and edge plane carbon as depicted in Figure 1. The primary variables involved in the characterization of carbon surfaces toward heterogeneous electron transfer are intricate and usually interrelated thus frustrating attempts to separate them. The four major variables studied here are the carbon microstructure, surface roughness ($\sigma$), surface coverage by impurities ($\theta$), and surface oxygen functionalities.

Surface microstructure will affect kinetics and manifest itself in the form of edge plane density [18]. This variable, $f_v$, is defined as the percent of exposed edge plane for a particular surface [2] and is most influenced by carbon type. The creation of edge plane sites on GC was proposed by many authors as a possible explanation for activation [2-3, 6]. However, surface microstructure for glassy
carbons is poorly defined and there is considerable doubt as to whether the edge plane density is consistent for various pretreatment procedures. Raman spectroscopy is suited for determining structural information since it provides the required structural information.

Surface roughness (σ) will affect kinetics by increasing the active surface area for all carbon surfaces except basal plane HOPG. \( k_{\text{obs}} \) will be proportional to the roughness provided the roughness scale is less than \((Dt)^{1/2}\). Surface roughness is defined as the ratio of the microscopic to the geometric or macroscopic area \( (A_m/A_g) \). It should be stated that roughness does not imply edge plane density and as such is an average over the entire surface.

Surface coverage (θ) will affect \( k_{\text{obs}}^{\theta} \) by shielding some active sites available for electron transfer. Many authors have discussed the ramifications of covered surfaces and have applied numerous pretreatment procedures to reduce surface impurities and hence increase \( k_{\text{obs}} \) [10, 51, 47, 75-77]. One aspect which still remains uncertain, due to the use of carbon as a purifier, is whether the remaining surface has been efficiently cleaned and has an unaltered surface structure [2].

Finally, surface functionalities, primarily oxides, may affect \( k_{\text{obs}}^{\theta} \) [3, 8, 52, 55-56]. Their existence causes variability in electrochemical performance since the surface oxides may be neutral, basic, or acidic depending on their reactivity with known acids or bases. Also, the type and quantity of functional groups varies with pretreatment procedures and carbon type, and various functional groups
exist for a given pretreatment procedure [2].

**RESEARCH OBJECTIVES**

The goal of this work is to investigate the microstructural and morphological alterations induced in glassy carbon electrodes by various pretreatment procedures and to gain insight into how these changes influence $k_{\text{obs}}$ for $\text{Fe(CN)}_6^{3/-4}$, $\text{IrCl}_{2/-3}$, and $\text{Ru(NH}_3)_6^{2+/3}$ on polished, fractured, and laser irradiated glassy carbon surfaces. The approach adopted here was to hold as many of the surface variables constant as possible and monitor changes in the Raman intensity ratio, the electrode capacitance, surface adsorption of an organic molecule, and microscopy photographs in order to obtain information regarding surface morphology and microstructure.

In Chapter II, the application of Raman spectroscopy and electrochemistry is used to deduce if surface coverage, microscopic surface area, or surface microstructure are changing during laser irradiation. The laser power density will be varied in order to determine a threshold value where the laser irradiated surface is altered significantly from the starting polished or fractured surface. Also, the GC surface will be subjected to repetitive 25 MW/cm² laser pulses in order to determine if further increases in $k_{\text{obs}}$ are obtained and to ascertain if the morphology and microstructure are altered. The changes in $k_{\text{obs}}$ will be studied and related to the changes observed on the surface before and after laser irradiation.
In Chapter III, the dependence of $k_{\text{obs}}^0$ on monolayer surface coverage of a physisorbed species will be investigated. Rate constants for $\text{Fe(CN)}_6^{3/4}$, $\text{IrCl}_6^{2/3}$, and $\text{Ru(NH}_3)_6^{2+/3}$ in various supporting electrolytes will be calculated from cyclic voltammetry data on GC surfaces before and after adsorption. The various supporting electrolytes will help in determining a model for electron transfer on carbon surfaces which have been modified by monolayer adsorption. Explanations regarding hydrophobicity, cation hydration radius, identity of the supporting electrolyte, and space charge effects will be offered to explain the observed values for $k_{\text{obs}}^0$.

In Chapter IV, the observation of $\text{O}_2$ effects on $k_{\text{obs}}^0$ for $\text{Fe(CN)}_6^{3/4}$, and $\text{Ru(NH}_3)_6^{2+/3}$ will be investigated. The observed heterogeneous electron transfer rate constant will be investigated as a function of dissolved oxygen. An attempt will be made to correlate the decay in $k_{\text{obs}}^0$ with the formation of surface oxides.
BACKGROUND

The surface condition of solid electrodes is one of the most important aspects of electrochemical measurements and also one of the most difficult to control. One inconvenience of GC is the sensitivity of the heterogeneous electron transfer rate constant of many redox systems to the surface state of the electrode. Carbon, like many other solid electrodes, passivates upon use and exposure to either air or solution species; thus, it is necessary to devise techniques and procedures which will retard this transient decay [39]. Any procedure which will improve the reproducibility of electrochemical measurements and enhance electrochemical activity, increasing $k_{obs}$, and selectivity is termed electrode activation.

The choice of a redox system as a probe for activation must meet several criteria so that $k_{obs}$ can be reliably determined. First, the redox couple must not adsorb to the electrode. Adsorption is a common occurrence on carbon and this feature is exploited to purify many solutions. As mentioned in the previous
chapter, \( k_{\text{obs}} \) should depend to surface coverage implying that adsorption will hinder electron transfer. Also, many pretreatment procedures create a surface which has a strong tendency to adsorb organic functionalities [78-79]. Second, the redox couple should be a simple, one electron transfer reaction, preferably outer sphere since such electron transfer reactions are not sensitive to the electrode material. Finally, the redox couple should be widely studied so that it may be compared with many types of activation procedures on various electrodes.

Before any subsequent activation, GC electrodes are usually polished since it is customary to remove any residual surface debris as well as part of the surface from newly purchased GC due to its unknown surface history. To accomplish this task, most laboratories mechanically polish their electrodes. Although there is no standard polishing procedure, many researchers agree that the strategy is to manually grind the electrode using a series of silicon carbide sandpapers of decreasing roughness, followed by polishing with slurries of alumina particles or diamond pastes of micron dimensions on polishing cloth or glass until a mirror-like finish is obtained. Rinsing with water or detergents, or sonicating between successive polishings is recommended to remove any residual polishing debris. There are many variations using the above criteria which is why \( k_{\text{obs}} \) is known to vary from 0.0001 cm/s to 0.14 cm/s for Fe(CN)\(_6^{3/-4}\) in 1M KCl on polished surfaces [3, 47, 80-81]. The value of 0.14 cm/s is comparable to the highest values obtained on platinum [72]. Because of the irreproducibility of polishing procedures, many other techniques have emerged as replacements for
activating carbon electrodes. What remains unclear however is the mechanism of activation for any particular procedure.

Laser irradiation, first reported in 1984 for activating glassy carbon and platinum electrodes, [82] is a relatively new pretreatment technique. It has many potential advantages over previously employed procedures. After short and intense pulses were delivered to the electrode in situ, increased electron transfer rates, by several orders of magnitude, for ascorbic acid, dopamine, and hexacyanoferrate (II/III) resulted. Typical pulse durations were between 7 and 10 nanoseconds, with the pulse intensity of 25 MW/cm² for Nd:YAG lasers operating at 1064 nm with a flashlamp frequency of 10 Hz [61-64, 82].

Activation has also been attained by using an iodine laser operating at 1315 nm with pulse durations of 150 microseconds. Under these conditions, typical power densities required for activation were on the order of 0.4 MW/cm², substantially lower than those used with Nd:YAG activation [69]. The use of lower power density for activation was attributed to the longer pulse duration of the iodine laser (150 μs vs. 9 ns) which deposits more energy onto the surface resulting in more efficient activation. Since laser activation is weakly dependent on the laser wavelength, the mechanism by which $k_{obs}$ is enhanced appears to be thermal rather than photochemical [2]. Laser activation has been compared to vacuum heat treatment, but it surpasses this technique in one aspect; laser activation does not require cell disassembly for pretreatment. Analytical advantages of laser activation include lower electrode capacitance, better
sensitivities due to increase in $k_{obs}$ [62], rapid, (nanoseconds compared to hours with other techniques), reproducible and repetitive application without complex reassembly procedures [62].

The mechanism of laser activation at glassy carbon surfaces has been proposed to be due primarily to surface cleaning and generation of active sites [65, 76]. Although there is evidence suggesting that surface cleaning is the primary activation mechanism, it is not logical to preclude the involvement of the remaining surface variables since it is not clear which parameters are altered during the laser activation process. Similar arguments, relating the alteration of more than one surface variable with enhanced electron transfer kinetics, also may be applied to other pretreatment procedures. Early conclusions demonstrating no correlation of microscopic surface area, surface ablation, or surface O/C ratios with enhanced electron transfer kinetics for many redox systems, may be in error if careful procedures were not used to assure that only the appropriate surface variable was altered [64, 69, 76, 83].

Perhaps one of the most important aspects of laser activation is the penetration depth of the Nd:YAG laser light. The laser beam penetration depth is given by Equation 9.

$$I(z) = I(0) \exp(-4\pi kz/\lambda)$$  \hspace{1cm} (9)

where $I(z)$ is the laser intensity at depth $z$, $I(0)$ is the surface irradiance, $\lambda$ is the wavelength of incident radiation, and $k$ is the imaginary part of the refractive index at wavelength $\lambda$ [84-85]. Using typical values reported by Vidano and
Fischbach, the penetration depth of the Nd:YAG laser was calculated to be about 900 Å. Thus, one may conclude that the laser is altering the surface on the same order as polishing since the smallest alumina particle used is 500 Å. The question now arises as to whether the Raman sampling depth is less than the penetration depth of the Nd:YAG laser. Using values obtained from Williams and Arakawa [86] and data compiled by McCreery et al. [2, 87], a Raman sampling depth of approximately 300 Å using 515 nm excitation was calculated. Thus, the Raman sampling depth is less than the region altered by the Nd:YAG laser upon activation implying that Raman spectroscopy is probing the transformed surface.

Pretreatment procedures have been introduced within the past twenty five years for the purpose of removing the irreproducibility associated with polishing. Since a proposed mechanism for the enhancement of $k_{\text{obs}}$ involves the removal of debris and exposure of pristine carbon, it has been accepted that pretreatment procedures tend to alter more than just the first few layers of an electrode. Also, pretreatment procedures tend to alter more than one of the surface variables which control electron transfer thereby requiring that as many variables as possible be controlled for a given pretreatment procedure. It has therefore been recommended that a better representation of the bulk carbon material is required in order to assess the enhancement in $k_{\text{obs}}$ without interference from the activation procedure. Such a technique was presented in 1989 and involves fracturing the electrode in situ [71, 88]. Some major advantages of fractured surfaces are that the exposed carbon is pristine and the electrode has not been intentionally
pretreated or altered prior to use.

Fractured surfaces were studied electrochemically and spectroscopically and found to differ considerably from conventionally pretreated surfaces. This was primarily due to the fracture mechanics of the fabricated electrodes [15, 88]. When glass like materials are fractured, three distinct zones of varying roughness are produced. These zones are referred to as mirror, misty, and hackled. The appearance of the zones is dependent on the velocity of the fracture wave through the material and the cross section of the electrode [89-90].

Initially, 3 mm diameter GC rods (Tokai) were fractured. The resulting surface was heterogeneous and had a very high background current. Rate constants for Fe(CN)$_6^{3/-4}$ were greater than 0.5 cm/s, the surface excess of phenanthrenequinone (PQ) was high, and the Raman intensity ratio was similar to that of a freshly polished surface. The electrochemical data implied that the surface roughness had changed greatly whereas the Raman intensity ratio suggested that the fractured and polished surfaces were similar.

Since these data were peculiar, evidence was sought which might explain the observed data. Upon fracturing, three distinct zones were produced on the carbon surface, and it was suspected that these regions were responsible for the irregular electrochemical and spectroscopic effects observed. Rice, Allred, and McCreery [71] demonstrated that the Raman intensity ratio for a bulk fractured electrodes was different from the Raman intensity ratio obtained within a specific zone on the surface. They chose the "mirror" region of the surface and used
Raman microprobe to prove their supposition. Their conclusions were that the "mirror" region had a Raman intensity ratio which was lower than that of the bulk fractured carbon electrode. The data provided by Rice et al. [71], influenced the fabrication and fracturing of electrodes which had an area no greater than 0.005cm². By reducing the electrode size, only the mirror region was produced [89], and the Raman intensity ratio was no longer similar to that obtained from a polished surface [2, 15, 71]. Since the high capacitance and adsorption values were unacceptable it was established that GC electrodes of dimensions 0.5 mm x 0.5 mm were required in order to obtain low capacitance and adsorption values.

Also, these smaller electrodes exhibited a large rate constant for Fe(CN)₆³⁻⁴ and lower PQ adsorption and electrode capacitance values [15]. Thus, a mirror region must be produced upon fracturing in order to obtain low capacitance and adsorption.

Results have been reported signifying the importance of the surface variables which control the observed heterogeneous electron transfer rate constant, \( k_{obs} \), and some method of quantitation may be formulated with a few assumptions to allow one to predict electrochemical behavior on GC electrodes. Recall that the major surface variables discussed here are carbon microstructure (\( f_c \)), surface roughness (\( \sigma \)), and surface coverage of impurities (\( \theta \)). This model was constructed using laser activation and fractured GC experimental data for Fe(CN)₆³⁻⁴, dopamine, and ascorbic acid and may not be applicable to all activation procedures [15]. Many authors have reported effects of observed rate
constant variations on GC electrodes [71, 91-92]. It has been suggested that both edge and basal domains exist on GC and that each region differs in size and in electrochemical properties. In previous reports, the number of surface variables was reduced by starting with the basal plane of highly oriented pyrolytic graphite [18, 73, 77]. It was concluded that $k_{\text{obs}}^o$ for Fe(CN)$_6^{3/4}$ was larger on graphitic edge plane than on basal plane, and that $k_{\text{obs}}^o$ was determined primarily by the fractional density of edge plane on the surface. That is $k_{\text{e}}^o \gg k_{\text{g}}^o$. This strategy was applied to glassy carbon and a hypothesis describing a simple relationship of the variables which affect $k_{\text{obs}}^o$ was formulated [15]. If one assumes that surface heterogeneities are small compared to $(D\theta)^{1/2}$, then Equation 10 applies [15]

$$k_{\text{obs}}^o = k_{\text{e}}^o f_{\text{e}} \sigma (1-\theta)$$

where $k_{\text{e}}^o$ is the observed rate constant for clean edge plane carbon, $f_{\text{e}}$ is the edge plane density, $\sigma$ is the surface roughness factor, expressed as the ratio of the microscopic surface area to the geometric surface area, and $(1-\theta)$ is the fraction of surface area not covered by impurities. Thus, for the systems studied, Equation 10 dictates $k_{\text{obs}}^o$ and incorporates the major surface variables and furnishes some insight for predicting $k_{\text{obs}}^o$ on glassy carbon electrodes.
Raman spectra of glassy carbon surfaces were obtained in air using a Spex 1403 spectrometer. A Spex 1460 monochromator was incorporated to reject emission lines from a Coherent Innova 90 argon ion laser allowing the excitation wavelength, 514.5 nm, to pass unobstructed. Spectral bandpass was 10 cm$^{-1}$, and actual laser power at the sample was typically 25 to 40 percent less than that at the laser head. Photon counting using a RCA 31034A PMT was employed for detection, and spectra were collected using SPEX DM3000 software running on an IBM compatible 286 personal computer. A schematic is shown in Figure 5. The Raman intensity ratio, or Raman ratio, of the 1360 cm$^{-1}$ and 1580 cm$^{-1}$ bands were used to assess any changes in the surface microstructure.

Laser activation was performed in solution using a Continuum (Quantel) model 580-10 Nd:YAG laser operating at 10 Hz and delivering 9 ns pulses at the fundamental wavelength, 1064 nm. Laser pulses were usually delivered in groups of three in order to average spatial and temporal variations. Power density (PD), in MW/cm$^2$, was determined by measuring the average power, in watts, through a 1.4 mm metal aperture and dividing by the aperture area, flash lamp frequency, and pulse duration according to Equation 11

$$PD = \left( \frac{\text{average power (W)}}{\text{area (cm}^2)} \right) \left( \frac{\text{sec}}{10 \text{ pulses}} \right) \left( \frac{\text{pulses}}{9 \times 10^{-9} \text{ sec}} \right) \left( \frac{1 \text{ MW}}{10^6 \text{ W}} \right)$$ (11)

Average power was measured with a Scientech 365 thermal power meter, and
Figure 5

Configuration of the excitation laser (Innova 90) and Spex 1403 double monochromator for single channel Raman Spectroscopy.
Figure 5
was accurate to within ±20 percent due to the variations in the Nd:YAG beam intensity and profile. A schematic of the Nd:YAG apparatus is shown in Figure 6, with a helium neon laser serving as the alignment laser. The electrochemical cell used in all experiments was constructed of Teflon with a BK-7 quartz window (> 95% transmittance) to allow the 1064 nm laser radiation to impinge upon the working electrode in solution.

Working electrodes (GC-20 or GC-30, Tokai) were fabricated from a corresponding plate by first diamond sawing the carbon then sanding the piece obtained into a small rectangle of approximate dimensions (0.05 cm x 0.05 cm x 1.00 cm). The carbon microrod was mounted onto a conducting surface with silver epoxy and coated with Eccobond epoxy (Emerson & Cumming, Inc., Woburn, Mass.). Torr Seal epoxy (Varian) was previously used to encapsulate the carbon microrods, but soluble organic materials in the epoxy resin appeared to contaminate the GC surface with time. This resulted in substantially lower $k_{obs}$ for Fe(CN)$_6^{3/4}$, ascorbic acid, and dopamine with time after fracture as well as lower adsorption values for PQ. Electrodes encapsulated in Eccobond yielded higher $\Gamma_{PQ}$ (pmoles/cm$^2$) values over time. Prior to fracturing, the Eccobond epoxy was filed away exposing a short post. The post was scored at the epoxy junction, and the electrode was placed in the solution of interest. The post was fractured by swift impact from the side thus exposing the pristine surface. Typical areas, as measured by single step chronoamperometry of Fe(CN)$_6^{3/4}$ in 1 M KCl, were on the order of 0.005 cm$^2$ for the bare face. If a polished surface
Figure 6

Configuration of Nd:YAG laser, HeNe alignment laser, optics, and electrochemical cell arrangement for laser activation. The Nd:YAG laser was operated at the fundamental wavelength (1064 nm).
Figure 6
was to be investigated, the electrode was polished to a mirror-like finish with
slurries of 1.0, 0.3, and 0.05 μm alumina powder in Nanopure (Barnstead, Boston
MA.) water on microcloth (Buehler) then the polished electrode was sonicated for
5 minutes to remove polishing debris prior to use. A Bioanalytical Systems (BAS)
Ag/AgCl (3M NaCl) electrode was used as the reference while a platinum wire
served as the auxiliary electrode.

Electrochemical measurements were performed using customized computer
software [93] and a Scientific Solutions Labmaster analog interface board which
controlled an Advanced Ideas Mechanics model 18709 potentiostat (Columbus,
Ohio). The potentiostat was driven by a triangular potential versus time ramp
from a Tektronix 501A function generator. All data were collected on an IBM
clone 286 personal computer. For fast voltammetry, scan rate greater than 5 V/s,
the data were collected on a Lecroy 9400A digital oscilloscope then transferred to
the personal computer for analysis.

The effects on the microscopic surface area were assessed by monitoring
the adsorption of phenanthrenequinone (PQ) from either 1.0 M perchloric (HClO₄)
or 1.0 M hydrochloric (HCl) acid. PQ was recrystallized three times from benzene
prior to use. In all cases, PQ exhibited well behaved voltammetry at the scan rate
of 100 mV/s employed. The magnitude of PQ adsorption was determined by the
method of Anson [14] which involved integration of the reduction peak above the
capacitive background to determine the charge, \( Q_{\text{adv}} \), and then calculating the
amount of adsorbed PQ in moles/cm² via Equation 12.
where \( Q_{ads} \) is the total charge due to adsorption of PQ corrected for capacitive background, \( n \) is the number of electrons transferred (2 in the case of PQ), \( A_g \) is the chronoamperometric area in cm\(^2\), and \( \Gamma_{PQ} \) is the equilibrium coverage of PQ expressed in moles/cm\(^2\). The chronoamperometric area was determined 1 mM Fe(CN)\(_6^{3/-4}\) in 1 M KCl on a 1-5 second time scale. The resulting currents were background corrected and plots of current vs. \( t^{1/2} \) were linear in all cases.

Apparent differential capacitance was measured by the method of Gileadi [94-95] which involved applying a 100 Hz, 20 mV peak to peak triangle wave centered on 0.0 V vs. Ag/AgCl from a Tektronix function generator to the working electrode and recording the response on a Lecroy 9400A digital oscilloscope. The double layer capacitance (\( \mu \text{F/cm}^2 \)) was calculated from Equation 13

\[
i_{p-p} = 2 v A_g C_{dl}^o \tag{13}
\]

where \( i_{p-p} \) is the peak to peak current due to double layer charging, \( v \) is the slope of the triangle wave in volts/sec, \( A_g \) is the chronoamperometric area in cm\(^2\), and \( C_{dl}^o \) is the double layer capacitance in \( \mu \text{F/cm}^2 \).

Scanning Electron Microscopy (SEM) was performed using a Hitachi model S-510 scanning electron microscope. All SEMs were acquired in secondary electron detection mode, in order to obtain greater surface information, at an acceleration voltage of 25 KeV, a beam current of approximately 100\( \mu \text{A} \), and a tilt angle of 0°. For SEMs presented in this work, the GC samples were sputter
coated with gold in all cases.

RESULTS AND DISCUSSION FOR SPECTROSCOPIC DATA

Investigations of microstructural changes after laser activation and fracturing of glassy carbon surfaces were conducted by observing the Raman 1360 cm$^{-1}$ to 1580 cm$^{-1}$ intensity ratio. A higher ratio indicates that more edge plane carbon is present and correlates with smaller microcrystallites. Figure 7 shows the effects of Nd:YAG power density on the Raman spectra of laser irradiated polished and fractured GC-20. All surfaces were freshly prepared prior to obtaining Raman spectra by either polishing or fracturing then exposing the surface to the appropriate number of Nd:YAG laser pulses. Although the second order spectra were obtained, no correlation with microcrystallite size was attempted. Also, the band which appears at about 2350 cm$^{-1}$ is due to atmospheric nitrogen, and the sharp intense band at 2625 cm$^{-1}$ was identified as a grating ghost.

For polished and fractured surfaces which have not been laser pretreated, as shown in the top box of Figure 7, the Raman spectra exhibit different features. The top spectrum is for a conventionally polished surface and has an intensity ratio $I_{1360}/I_{1580}$ of 1.8 while the bottom spectrum of a fractured surface has an intensity ratio $I_{1360}/I_{1580}$ of 1.1. This observation indicates that the two surfaces are microstructurally distinct with the fractured surface exhibiting less edge plane density and larger microcrystallites. Since a fractured surface is presumably
Figure 7

Raman spectra of conventionally polished and fractured GC-20 following Nd:YAG laser irradiation. Figure 7A depicts freshly prepared polished and fractured surfaces and figures 7B and 7C were obtained after the carbon was irradiated with three 40 MW/cm$^2$ and three 70 MW/cm$^2$ pulses. The band at 2350 cm$^{-1}$ is due to atmospheric nitrogen, and the sharp intense band at about 2625 cm$^{-1}$ is the result of a grating ghost.
representative of the unmodified bulk GC, the higher Raman intensity ratio observed after polishing is due to exposure or creation of edge plane sites conceivably by mechanically grinding the electrode through the polishing alumina.

When the polished and fractured surfaces were exposed to three 40 MW/cm² laser pulses, the spectra shown in Figure 7B were obtained. No discernible changes between the Raman intensity ratios for the polished and polished plus 40 MW/cm² surface are detected; in fact, the Raman intensity ratio remains relatively constant at 1.8 for these surfaces. However, a noticeable change has occurred for the 40 MW/cm² laser irradiated fractured surface as the Raman ratio has increased from 1.1 to 1.55 indicating that microstructural alterations have transpired. Exposing the polished and fractured surfaces to three 70 MW/cm² laser pulses again has little apparent effect on the Raman intensity ratio of the polished surface and substantial influence on the Raman intensity ratio of the fractured surface. The Raman ratio for the fractured surface exposed to three 70 MW/cm² laser pulses has now approached that of the initially polished surface signifying that the two surfaces are comparable in terms of microstructure as indicated by Raman spectroscopy. Also, it is difficult to distinguish between the Raman ratio for the polished plus 70 MW/cm² and fractured plus 70 MW/cm² surfaces, in Figure 7C, further indicating that the microstructure of the laser irradiated fractured surface is now similar to that of the polished surface. These results, along with those for intermediate power
densities, are presented in Figure 8A. Based exclusively on the Raman ratio, increasing the Nd:YAG power density on a fractured surface causes significant microstructural alterations implying that \( f_e \) is being modified. Although the Raman intensity ratio of the polished surface originates at a higher value, there are few if any changes observable with laser activation implying that no prominent additional microstructural changes are induced.

Successive 25 MW/cm\(^2\) Nd:YAG laser pulses were used to assess whether reduced power densities would also induce the Raman intensity ratio changes indicative of microstructural alterations for fractured surfaces. A lower power density, 25 MW/cm\(^2\) was chosen, since activation was observed previously for several redox couples at this power density. The pulses were delivered in groups of three followed by acquisition of the Raman spectrum with the sequence being repeated until 99 pulses had been delivered. As shown in Figure 8B, the Raman ratio increases from 1.1 to 1.8 upon polishing, but it changes little with further laser irradiation up to 60 pulses. However, for a fractured surface, the Raman ratio slowly increases with repeated irradiation, approaching the value observed for a polished surface after about 80 Nd:YAG pulses. These results, like those presented above for increased power density, indicate that irradiation by the Nd:YAG laser produces microstructural alterations for a fractured surface similar to those present on a polished surface. Along with the results presented for increasing power density, it may be concluded that laser irradiation does not affect the edge plane density (\( f_e \)) or microcrystallite distribution of a polished
Figure 8

Raman spectra of polished and fractured laser irradiated GC-20 as a function of increasing Nd:YAG power density and successive 25 MW/cm² pulses.
Figure 8
surface in any way observable by Raman spectroscopy; however, it does induce microstructural alterations for a fractured surface presumably by shattering the lattice and producing edge plane sites.

RESULTS FOR ELECTROCHEMICAL AND MICROSCOPY EXPERIMENTS

The effect of laser irradiating polished and fractured surfaces on the microscopic surface area and surface coverage of impurities was assessed by monitoring the adsorption of PQ from either 1.0 M HClO₄ or 1.0 M HCl and the apparent electrode capacitance in 1 M HClO₄. A typical PQ voltammogram is shown in Figure 9. One sees that the peak separation is nearly zero implying that both produce and reactant are strongly adsorbed at the electrode surface. Also, \( E^{\circ} \) is 0.2 V vs. Ag/AgCl. To determine an appropriate working bulk concentration of PQ one needs to determine the adsorbate's behavior on the surface and in the bulk. The relationships between the amount of a species adsorbed on an electrode and the bulk activity of that species is known as an adsorption isotherm. Various isotherms result depending on the assumptions employed which relate the surface concentration to the bulk. Prior to choosing an operating concentration of PQ, isotherm calculations were required in order to assess the behavior of PQ molecules on glassy carbon surfaces. Bulk concentrations of PQ ranged from 0.2 \( \mu \)M to 10 \( \mu \)M, and cyclic voltammograms were obtained every five minutes until equilibrium coverage resulted. For a
Figure 9

Current vs. Potential for the adsorption of $10^6$ M PQ onto GC.
Figure 9
Langmuir isotherm, the following relationship results

$$\Gamma_i = \frac{\Gamma_i^s \beta C^b}{1 + \beta C^b}$$  \hspace{1cm} (14)

where $\Gamma_i$ is the equilibrium coverage of adsorbed species $i$ (moles/cm$^2$), $\Gamma_i^s$ is the saturation coverage of adsorbed species $i$ (moles/cm$^2$), $C^b$ is the bulk concentration of species $i$ (molar), and $\beta$ is an energy parameter (M$^{-1}$). Rearranging the above expression, the following relation is obtained from which the values of $\Gamma_i^s$ and $\beta$ may be extracted using experimental data.

$$\frac{C^b}{\Gamma_i^s} = \left( \frac{1}{\Gamma_i^s} \right) C^b + \left( \frac{1}{\beta \Gamma_i^s} \right)$$  \hspace{1cm} (15)

If a Langmuir isotherm is obeyed, then a plot of $C^b/\Gamma_i$ vs. $C^b$ should be linear with a slope of $1/\Gamma_i^s$ and a y-intercept of $(1/\beta \Gamma_i^s)$. For both polished and laser irradiated surfaces, linearity is observed up to a bulk PQ concentration of $10^6$ M. Thus, using this information and data obtained from Anson [14], a working bulk concentration of $10^6$ M was used for PQ.

For measurements where the power density was increased, fresh polished and fractured surfaces were prepared in all cases prior to laser irradiation. These effects are shown in Figure 10A. Initially, $\Gamma_{PQ}$ for a fractured surface (618 pmoles/cm$^2$) is about twice that of a polished surface (320 pmoles/cm$^2$). Also, $\Gamma_{PQ}$ increases slightly with laser irradiation below 25 MW/cm$^2$ both for the polished and for the fractured surfaces; however, this increase is relatively small.
Figure 10

Phenanthrenequinone (PQ) adsorption of polished and fractured laser irradiated GC-20 as a function of increasing Nd:YAG power density and successive 25 MW/cm² pulses.
Figure 10
for the fractured surface. As the power density is increased, $\Gamma_{PQ}$ for the fractured surface slowly ascends and reaches a value of about 950 pmoles/cm$^2$ after three 70 MW/cm$^2$ pulses, an increase of about 50 percent. In contrast, for a polished surface, $\Gamma_{PQ}$ reaches a value of about 454 pmoles/cm$^2$ after three 25 MW/cm$^2$ pulses. This 50 percent increase is dwarfed after the electrode is irradiated with three 70 MW/cm$^2$ pulses resulting in a 270 percent increase in $\Gamma_{PQ}$, which corresponds to greater than 1200 pmoles/cm$^2$.

Successive 25 MW/cm$^2$ pulses were used to determine if changes in roughness or surface cleanliness occur after multiple low power density pulses were delivered. This specific power density was employed since increases in heterogeneous electron transfer kinetics were observed previously at this value for systems such as Fe(CN)$_6^{3/-4}$, dopamine, and ascorbic acid [2]. After initial adsorption onto the polished or fractured surface, the electrode was irradiated with laser pulses in groups of three and cyclic voltammograms were obtained every five minutes until equilibrium coverage by PQ was achieved. This sequence was repeated until 21 pulses had been delivered. For a polished surface, laser irradiation with three pulses increased $\Gamma_{PQ}$ from 318 pmoles/cm$^2$ to 454 pmoles/cm$^2$, but further irradiation caused only a slight increase in $\Gamma_{PQ}$ for up to 21 pulses as shown in Figure 10B. In contrast, $\Gamma_{PQ}$ for a fractured surface consistently began at a higher value and ascended slightly after each set of pulses, but no initial jump after the first three pulses were delivered was observed. In both cases however, $\Gamma_{PQ}$ increased by at most 40 percent over the initial values.
Surface excess values, $\Gamma_{RO}$, as well as $k_{obs}$, Raman ratios, and calculated roughness factors are shown in Table 2. Explanations regarding the calculation of the roughness factors will be given in the discussion section.

The effects of laser irradiation on the apparent double layer capacitance, $C_{dl}$, was also monitored in order to obtain additional information concerning the surface variables and the electrode solution interface. On mercury electrodes, the apparent double layer capacitance has been used to study this interface and the effects induced due to adsorption and electrolyte identity and concentration. The overall objective is to understand the changes observed in $k_{obs}$ and how these changes relate to the double layer structure [2]. Since the electrode/solution interface at carbon electrodes is more complicated and harder to define, attempts made to elucidate surface structure from $C_{dl}$ are usually frustrated. In fact, surface roughness, surface functional groups, the surface microstructure, surface adsorption, and possible surface faradaic reactions may complicate the observed double layer capacitance on carbon electrodes. In this work, $C_{dl}$ will be referred to as $C_{obs}$ since this quantity, like $k_{obs}$, incorporates the complications which may be introduced due to a surface pretreatment procedure and existing complexities mentioned above.

The conclusions reached from changes in observed capacitance are similar to those reached from studies of $\Gamma_{RO}$ and are shown in Figure 11. Figure 11A depicts $C_{obs}$ as a function of power density. The initial $C_{obs}$ for a fractured surface is about twice that of a polished surface. As the power density is increased from
0 to 25 MW/cm², $C_{obs}$ does not change significantly for a fractured surface, but beyond 30 MW/cm², $C_{obs}$ increases until after three 70 MW/cm² pulses, the capacitance had increased to 82 μF/cm². In contrast, laser irradiating a polished surface greatly altered $C_{obs}$. There was no apparent change in $C_{obs}$ until three 25 MW/cm² pulses were delivered. After three 25 MW/cm² pulses were delivered to the electrode, $C_{obs}$ increased from an initial value of 25 μF/cm² to 32 μF/cm². At 30 MW/cm² $C_{obs}$ jumped to a value of 50 μF/cm², and when three 40 MW/cm² pulses were delivered to the electrode, $C_{obs}$ reached a value of 60 μF/cm². This $C_{obs}$ value is the same as the value reported for a fractured surface which had not been exposed to laser irradiation. Beyond 40 MW/cm², $C_{obs}$ increased by more than 500% with a value of 140 μF/cm² after three 70 MW/cm² pulses were delivered.

Figure 11B shows $C_{obs}$ as a function of successive 25 MW/cm² laser pulses. The pulses were delivered in groups of three followed by measurement of the peak to peak current and subsequent calculation of $C_{obs}$. These data are similar to those obtained for $\Gamma_{p2}$. For up to 21 pulses, successive 25 MW/cm² pulses did not cause a significant increase in $C_{obs}$ for the fractured surface. Data for the polished surface shows a slow rise in $C_{obs}$ followed by a leveling in the value of $C_{obs}$. In fact, $C_{obs}$ did not change by more than 20% and the value leveled after nine pulses were delivered.
Figure 11

Apparent capacitance of polished (A) and fractured (B) laser irradiated GC-20 as a function of increasing Nd:YAG power density and successive 25 MW/cm² pulses.
Figure 11

A

Power Density (MW/cm²)

B

Total # Nd:YAG Pulses

Figure 11
Table 2: Raman intensity ratio, surface excess of PQ, observed double layer capacitance, surface roughness, and $k^o_{obs}$ for Fe(CN)$_6^{3/4}$ on laser irradiated GC-20 surfaces.

<table>
<thead>
<tr>
<th>Surface</th>
<th>$I_{1350}/I_{1580}$</th>
<th>$\Gamma_{PQ}$ (pmoles/cm$^2$)</th>
<th>$\sigma$</th>
<th>$C^o_{obs}$ (µF/cm$^2$)</th>
<th>$k^o_{obs}$ Fe(CN)$_6^{3/4}$ (cm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GC-20</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>POL</td>
<td>1.80 ± 0.10 (N = 10)</td>
<td>318 ± 15 (N = 40)</td>
<td>1.80</td>
<td>25 ± 5 (N = 30)</td>
<td>0.05 ± 0.01 (N = 10)</td>
</tr>
<tr>
<td>POL + 25</td>
<td>1.70 ± 0.14 (N = 10)</td>
<td>454 ± 20 (N = 40)</td>
<td>2.56</td>
<td>32 ± 5 (N = 30)</td>
<td>0.45 ± 0.11 (N = 20)</td>
</tr>
<tr>
<td>POL + 70</td>
<td>1.80 ± 0.09 (N = 10)</td>
<td>1200 ± 20 (N = 40)</td>
<td>6.78</td>
<td>140 ± 9 (N = 30)</td>
<td>0.50 ± 0.10 (N = 20)</td>
</tr>
<tr>
<td>FRA</td>
<td>1.10 ± 0.05 (N = 10)</td>
<td>618 ± 18 (N = 40)</td>
<td>3.49</td>
<td>58 ± 8 (N = 10)</td>
<td>0.50 ± 0.10 (N = 20)</td>
</tr>
<tr>
<td>FRA + 25</td>
<td>1.30 ± 0.06 (N = 10)</td>
<td>645 ± 20 (N = 40)</td>
<td>3.64</td>
<td>63 ± 4 (N = 10)</td>
<td>0.50 ± 0.08 (N = 25)</td>
</tr>
<tr>
<td>FRA + 70</td>
<td>1.55 ± 0.08 (N = 10)</td>
<td>920 ± 20 (N = 40)</td>
<td>5.20</td>
<td>82 ± 9 (N = 10)</td>
<td>0.50 ± 0.10 (N = 10)</td>
</tr>
</tbody>
</table>

The instrumental limits for the measurement of $k^o_{obs}$ are believed to be 1.0 cm/s. Values of $k^o_{obs}$ greater than this value were unattainable, and it is not known whether laser irradiation of a surface whose $k^o_{obs}$ value is 1.0 cm/s would induce activation.

Values for the surface roughness, $\sigma$, were calculated assuming a molecular area of 94 Å$^2$ calculated by the method of Hubbard using Van der Waals radii and a theoretical surface coverage of 177 pmoles/cm$^2$ [96].

Typical literature values of $k^o_{obs}$ for polished surfaces range from 0.001 to 0.005 cm/s. Results from our laboratory are larger due to incorporating ultra clean conditions.

The value for "N" in parenthesis refers to the number of surfaces on which the specific quantity was measured.
In order to observe changes in the surface morphology, scanning electron microscopy was performed on the same surfaces mentioned above. Scanning electron micrographs are presented in Figures 12 and 13. All micrographs were obtained at high magnification (80K times) in order to observe morphological alterations induced by laser irradiation. The bar in the lower right corner is a distance marker and represents 1.0 μm in all photographs. Micrographs obtained at lower magnification normally showed no indication of alteration with the features present in this work not visible [62, 97]. However, polishing striation and surface indentations were seen to be randomly oriented throughout the polished GC surface in earlier work. Other distinct features from earlier works include circular and oblong cavities and remains of cracks, possibly formed during diamond sawing, and subsurface inclusions. These features have been observed elsewhere and have been attributed to the underlying carbon substrate [46, 97]. In contrast, fractured surfaces exhibited nodules in all cases and it was difficult to discern any indentations, pits or crevices.

The SEM photographs depicted in Figure 12 are for surfaces which were initially polished. Figure 12A is an SEM of a typically polished carbon electrode surface. At this magnification, no holes or scratches are visible but apparent microcracks and fissures are present. After three 40 MW/cm² Nd:YAG pulses had been delivered to the electrode surface, the photograph in Figure 12B was obtained. Nodules of approximately 0.1 μm in diameter are now present in a random fashion across the surface. The underlying GC surface is still visible and
the alterations induced by the laser cover less than 25 percent of the surface. These new features were not present to a great extent when the polished surface was subjected to three 25 MW/cm² laser pulses. Although not shown, the 25 MW/cm² laser irradiated surface resembles the initially polished surface. There is an indication that some nodules are present, but they account for less than one percent of the surface. When the polished surface was irradiated with three 70 MW/cm² pulses, Figure 12C, the surface was significantly altered as compared to the initially polished surface. The 70 MW/cm² surface is characterized by occasional large defects in a sea of nodules of approximately 0.1 μm in diameter. Thus, major morphological alterations have occurred to the polished surface as a result of laser irradiation. These morphological changes appear to have occurred between 25 and 70 MW/cm², starting below 40 MW/cm².

Similar SEM images were also obtained for fractured surfaces. Figure 13A is an SEM photograph of a freshly fractured GC surface. This surface is characterized by nodules distributed fairly uniformly throughout the surface. The underlying structure which includes cracks, crevices, and valleys is not visible; however, if the surface were polished, these features would appear. Thus, the nodules must be inherent in the GC matrix, possibly formed when the GC was fabricated, and polishing flattens the nodules by mechanical grinding of the electrode surface. No obvious changes are apparent upon laser irradiation with three 40 MW/cm², Figure 13B, or 70 MW/cm², Figure 13C, pulses. The fractured and fractured plus 70 MW/cm² surfaces, Figures 13A and 13B, are virtually
Figure 12

Scanning electron micrographs of laser irradiated polished GC-20. SEMs were obtained in secondary electron detection mode using an accelerating voltage of 25 KeV and a beam current of 100 μA. Figures 12A, 12B, and 12C are of polished, polished plus three 40 MW/cm² Nd:YAG pulses, and polished plus three 70 MW/cm² Nd:YAG pulses.
Scanning electron micrographs of laser irradiated fractured GC-20. SEMs were obtained in secondary electron detection mode using an accelerating voltage of 25 KeV and a beam current of 100 μA. Figures 12A, 12B, and 12C are of polished, polished plus three 40 MW/cm² Nd:YAG pulses, and polished plus three 70 MW/cm² Nd:YAG pulses.
indistinguishable and they, in turn, resemble the polished surface which has been irradiated with three 70 MW/cm² surface, Figure 12C. An elementary image analysis revealed an average diameter of the nodules for the fractured surface of 0.16 ± 0.05 μm, where 0.05 represents the standard deviation for 109 nodules. Upon laser irradiation with three 70 MW/cm² pulses, the average nodule size slightly decreased to 0.09 ± 0.03 μm for 100 measured nodules. One interesting characteristic however is the nodules appear to have increased in diameter after the fractured surface was irradiated with three 40 MW/cm² pulses. The average nodule size for the 40 MW/cm² laser irradiated fractured surface is 0.25 ± 0.08 for 100 measured nodules.

These nodules have also been observed and verified using scanning tunneling microscopy (STM). Figure 14 shows STM images of the polished and fractured surfaces before and after laser irradiation. Figures 14A, 14B, and 14C are of polished, polished plus three 40 MW/cm², and polished plus three 70 MW/cm² surfaces respectively; while Figures 14D, 14E, 14F are of fractured, fractured plus three 40 MW/cm², and fractured plus three 70 MW/cm² surfaces respectively. STM images were obtained on a scale similar to the SEM images in order to compare the results. In all cases, the results are similar suggesting that the SEM results that the nodules are not artifacts of accumulations of gold particles is valid. Also, STM results of uncoated carbon surfaces show virtually identical results to those depicted here implying that the gold coating is not interfering with the STM imaging.
Figure 14

STM images of polished and fractured laser irradiated GC-20.
Since SEM images reveal apparent microcracks on the polished surface and fissures between nodules on the fractured surface, it is reasonable to suspect that these features will affect voltammetry and hence produce a erroneous \( k_{\text{obs}} \). This may occur since electroactive species in the cracks and fissures will follow thin layer behavior rather than semi infinite linear diffusion (SILD). This hypothesis was tested by comparing the voltammograms for \( \text{Fe(CN)}_6^{3/-4} \) (1 M KCl) at 100 V/s with simulated curves calculated with the SILD assumption and a \( k_{\text{obs}} \) of 0.4 cm/s. The results are presented in Figure 15. The voltammograms are for fractured, Figure 15A, and fractured plus 70 MW/cm\(^2\) surfaces, Figure 15B, and the shapes agree well with the simulated curves. Background subtraction was not completely effective at removing the background signal since the background current decreased when the solution was changed from \( \text{Fe(CN)}_6^{3/-4} \) to electrolyte. The predicted and experimental peak currents and voltammogram shapes for the conditions in Figure 13A are similar, 32 \( \mu \text{A} \) vs. 35 \( \mu \text{A} \) respectively, implying that the nodules and fissures do not cause any deviation from planar diffusion. Also, semi integration of the experimental data yields the expected sigmoidal shape with no evidence of adsorption or thin layer behavior. Thus, semi infinite linear diffusion is obeyed.
Comparison of simulated (dotted) and experimental (solid) voltammograms for 
Fe(CN)$_6^{3/-4}$ in 1 M KCl at 100 V/s. Voltammogram A was obtained on fractured 
GC-20 and voltammogram B was obtained on a fractured surface which has been 
irradiated with three 70 MW/cm$^2$ Nd:YAG pulses. Simulated $k^0$ is 0.4 cm/s.
Figure 15
DISCUSSION AND CONCLUSIONS

The dependence of \( k_{\text{obs}} \) on the electrode's surface history complicates attempts to correlate structural changes with electrochemical reactivity. Since such correlations are important for understanding surface behavior, establishing methods for determining which variables change upon various pretreatment procedures is important so that separation of these variables may be attempted. Common dependent variables such as \( k_{\text{obs}} \), the Raman intensity ratio, surface coverage, and differential capacitance have been shown here to depend on more than one independent surface variable dealing with the fraction edge plane carbon present, \( f_e \); the surface roughness, \( \sigma \); and the fraction of the surface covered by impurities, \( \theta \). Thus, one monitors these dependent surface variables with the formentioned observables. The Raman intensity ratio is an indicator for carbon microstructure, with a larger intensity ratio implying smaller microcrystallites and presumably more edge plane density, with little interference from other variables since the microcrystallite sizes would not be expected to depend on surface roughness or cleanliness. In contrast, adsorption, \( \Gamma_{\text{PQ}} \), and capacitance, \( C_{\text{obs}} \) would both be expected to depend on surface cleanliness, roughness, and fraction of edge plane density.

Figure 9 confirms that the Raman intensity ratio is altered upon laser irradiation for a fractured surface but not for a polished surface. When comparing the initial surfaces, one notes that a fractured surface has larger
microcrystallites, thus less edge plane density, since the Raman ratio is 1.1 as opposed to 1.8, the value of the initially polished surface. Thus, the apparent microcrystallite size of the polished surface remains unaltered with increasing or successive laser irradiation. Presumably, the surface was modified upon polishing and laser irradiation does not affect the microcrystallite size as measured by Raman spectroscopy. In contrast, the Raman intensity ratio for a fractured surface indicates a decrease in the microcrystallite size with laser irradiation for either increasing power density or successive 25 MW/cm² pulses. Also, with extensive or high powered irradiation, the Raman ratio for the fractured surface eventually approaches that of the polished surface implying that the function of laser irradiation is to decrease the microcrystallite size and presumably increase the fraction of edge plane. From a broad perspective, the nature of the surface following considerable or repetitive low power density laser irradiation does not appear to depend on whether the surface initially was fractured or polished.

Unlike the carbon microstructure, the remaining surface variables are convoluted. Measurements of adsorption and capacitance depend not only on surface coverage and roughness but also on the microstructure and various other items. Considering adsorption first, one would expect $\Gamma_{PO}$ to depend on both surface cleanliness and microscopic surface area. However, from Figure 10, it is seen that $\Gamma_{PO}$ does not increase greatly for a surface which was initially fractured and laser irradiated in the range from 0 to 25 MW/cm². Also, this same trend is observed for laser irradiation of a polished surface which implies that cleanliness
is not a predominant factor affecting $\Gamma_{PQ}$. Since three 25 MW/cm$^2$ laser pulses increase $k_{\text{obs}}^0$ for Fe(CN)$_6^{3-}$ by two orders of magnitude for a polished electrode, as shown in table 2, one would deduce that the surface is cleaned significantly by the laser [71]. Also, SEM and STM results indicate that no major morphological alterations are produced until 40 MW/cm$^2$ pulses are used to irradiate the polished surface. Thus, the appearance of nodules is not necessary in order to observe an increase in $k_{\text{obs}}^0$ by two orders of magnitude. Apparently PQ adsorbs strongly enough that adsorbed impurities, at least those affected by the laser, have only minor effects on $\Gamma_{PQ}$ [98]. This leads to the conclusion that $\Gamma_{PQ}$ is primarily a measure of surface roughness.

Given the results above, a few factors can be concluded from Figure 10 and Table 2. First, surface roughness does not change significantly for up to twenty one 25 MW/cm$^2$ laser pulses or up to about 25 MW/cm$^2$ power density. This is consistent with the SEM and STM results which showed minor morphological alterations for up to 25 MW/cm$^2$. Second, the initially fractured surface has a higher roughness factor when compared to the initially polished surface, and a freshly polished surface does not have a roughness factor of one. Roughness factors reported in Table 2 were calculated on the basis of a molecular area for PQ of 94 Å$^2$ calculated by the method of Hubbard using Van der Waals radii [96]. It was possible to determine roughness factors ($\sigma$) for these surfaces based on a theoretical surface coverage of 177 pmoles/cm$^2$ [96]. The roughness factor for a freshly fractured surface is about twice that of a freshly polished surface and
these values do not change significantly during laser pretreatment below 30 MW/cm² or a total of twenty one successive 25 MW/cm² laser pulses for a fractured surface. For a polished surface, the roughness factor increased by about 30% after three 25 MW/cm² pulses were delivered. Successive 25 MW/cm² pulses had no profound effect on surface roughness. These conclusions are consistent with SEM and STM results which show minor changes in surface morphology under these conditions. These observations of minor changes in surface roughness are consistent with other reports for several activation procedures [83]. Laser irradiation beyond 30 MW/cm², increases the surface roughness of both the initially polished and fractured surfaces with the 70 MW/cm² laser irradiated polished surface eventually having a roughness factor greater than a freshly fractured surface. Thus, the roughness factor is seen to be strongly dependent on the surface history and pretreatment procedure.

One would expect $C_{obs}$ to be a less direct indicator of surface roughness than $\Gamma_{pq}$ since $C_{obs}$ should also depend on additional surface variables such as oxides, supporting electrolyte concentration, and potential. Thus, the double layer structure may be probed by monitoring the observed capacitance which then provides information about the electrode solution interface. The overall objective is a better understanding of the double layer structure and its relationship and effects on $k_{obs}$ and electrode kinetics. The changes in $C_{obs}$ shown in Figure 11 are similar to those in $\Gamma_{pq}$, however, where $\Gamma_{pq}$ increased by 40 percent, $C_{obs}$ increased by 70 percent for a polished surface after three 70 MW/cm² pulses. The initial
C\textsuperscript{obs} for a fractured surface is about twice that of a polished surface. As the power density is increased, C\textsuperscript{obs} remains relatively constant for both polished and fractured surfaces irradiated with less than 30 MW/cm\textsuperscript{2}. At 30 MW/cm\textsuperscript{2} and beyond, C\textsuperscript{obs} does not increase greatly for a fractured surface, but it does increase markedly for a polished surface implying that the double layer structure is being altered.

The trends observed for C\textsuperscript{obs} as a result of successive 25 MW/cm\textsuperscript{2} pulses are similar to the trends observed in \(\Gamma_{PQ}\). There are no significant increases in C\textsuperscript{obs} for the fractured surface and an increase of 30% for the polished surface after 21 successive pulses for the polished surface. Since one cannot further clean a surface which is initially free of debris, it follows that C\textsuperscript{obs} does not change significantly upon laser irradiation of a fractured surface with successive 25 MW/cm\textsuperscript{2} pulses. This argument may be extended to the fractured surface which has been impacted with increasing power density pulses. Since C\textsuperscript{obs} is relatively constant in the range from 0 to 25 MW/cm\textsuperscript{2}, there are no observable changes in surface cleaning for a fractured electrode. The increases in C\textsuperscript{obs} observed beyond 30 MW/cm\textsuperscript{2} may possibly be attributed to roughening since the laser pulses should not subsequently be cleaning the surface. Similarly, since no changes are observed for a polished surface below 30 MW/cm\textsuperscript{2}, arguments for surface cleaning may be extended to the polished surface as well.

The entire collection of observables which include the Raman intensity ratio, \(\Gamma_{PQ}\), C\textsuperscript{obs}, k\textsuperscript{obs}, SEM, and STM data shown in Figures 10 to 15 and in Table
2, a model for the GC surface and the variables influenced during laser activation may be formulated. As shown in Table 2, $k_{obs}^o$ increases significantly for a polished surface once the electrode is irradiated with three 25 MW/cm$^2$ pulses. There is no increase in $k_{obs}^o$ with laser irradiation for a fractured surface, but the surface is already active since $k_{obs}^o$ is initially 0.5 cm/s with no intentional surface pretreatment. Looking at the SEM and STM data, the fractured GC surface is characterized by a sea of nodules with a mean diameter of $0.16 \pm 0.05 \mu m$. The nodules are presumably present throughout the material, and were formed when the original GC material was fabricated. Laser irradiation with three 70 MW/cm$^2$ does not affect the SEM or STM data; however, the nodule size has been slightly reduced to $0.09 \pm 0.03 \mu m$.

SEM and STM data indicate that, if one begins with a fractured surface, polishing flattened the exposed hemispheres of each nodule to yield a surface which consists of fissures. Data from Figure 15 showed that these fissures were shallow and that the diffusion to the electrode was in accordance with semi infinite linear diffusion (SILD) theory. Upon laser irradiating the polished surface with 40 MW/cm$^2$, the nodules reappear. The minor effects on $\Gamma_{PO}$, $C_{obs}^o$, and SEM appearance for surfaces irradiated below 25 MW/cm$^2$ are dwarfed by the two orders of magnitude increase in $k_{obs}^o$ on a polished surface. Thus, it is concluded that the presence of nodules is not necessary in order to observe increases in heterogeneous electron transfer for a polished surface. For the fractured surface, up to 25 MW/cm$^2$ laser irradiation has relatively minor effects on $\Gamma_{PO}$, $C_{obs}^o$, SEM,
and STM appearance, but the Raman intensity ratio increases. The increase corresponds to a reduction in the lattice microcrystallite size from approximately 5.0 nm to 2.5 nm [16]. The affects on $C_{\text{obs}}$ and $\Gamma_{\text{pt}}$ are small since these electrochemical variables do not appear to track the Raman ratio. The laser induced microstructural changes are presumably caused by thermally induced mechanical shock during the rapid heating associated with laser irradiation. Thus, for power densities at or below 25 MW/cm$^2$, the results are consistent with a laser activation mechanism based on surface cleaning.

The reduction in nodule size may be a clue as to why there was an increase in $\Gamma_{\text{pt}}$ and $C_{\text{obs}}$ upon laser irradiation with greater than 30 MW/cm$^2$. Obvious changes occurred in $C_{\text{obs}}$, $\Gamma_{\text{pt}}$, SEM, and STM data upon laser irradiation for a polished surface. Nodules are evident in Figures 12 and 14 for the 40 MW/cm$^2$ laser irradiated surface, and they are dominant for the 70 MW/cm$^2$ surface. The nodules are present at all times for a fractured surface, and laser irradiation is not necessary for nodule formation; however, there is a decrease in size upon irradiation with 70 MW/cm$^2$. The decrease in nodule size for a fractured surface and the appearance of nodules for a polished surface indicates that major morphological alterations are induced by laser irradiation. Once possible cause of this alteration is local melting.

If phase changes are ignored, laser irradiation at 25 MW/cm$^2$ is predicted to cause a maximum surface temperature excursion of about 3900 K and this excursion is linear with power density [99]. Since the melting point of carbon is
about 4300 K, laser irradiation at or above 30 MW/cm² is sufficient to induce local melting of the surface. For a fractured surface, melting and resolidifying may be responsible for the decrease in nodule size, and for a polished surface, melting distorts the flattened surface and produces nodules upon cooling. Thus, melting and resolidifying revert a polished surface back to a surface which is more characteristic of bulk glassy carbon. Unlike the polished surface, melting of the polished surface causes no obvious structural changes. Changes in \( C_\text{obs} \) and \( \Gamma_{\text{ROI}} \) beginning at 30 MW/cm², are likely to be attributed to local melting and surface restructuring induced by the Nd:YAG laser. Since power densities well below this melting threshold are sufficient to activate the GC electrode surface toward heterogeneous electron transfer of ferri and ferrocyanide in 1 M KCl, melting is probably not a necessity for increased heterogeneous electron transfer. It is also possible to transcend laser irradiation thus producing a surface with a high capacitive background and a high microscopic surface area and roughness factor. Conversely, laser irradiation at 25 MW/cm² produces increases in \( k_\text{obs} \) without obvious morphological alterations [61-64]. Also, laser irradiation at 25 MW/cm² does not create a surface with a high roughness, and at this power density, the data presented for a polished surface is consistent with a phenomenon not probed by \( \Gamma_{\text{ROI}} \), the Raman ratio, or microscopy data and probably involves cleaning by removal of surface impurities. Thus, for a polished surface, it appears as if surface cleanliness is important in order to observe laser induced increases in \( k_\text{obs} \) and surface roughness, \( \sigma \), and the fraction of edge plane density, \( f_e \), do not appear
to change significantly during activation.
CHAPTER III
ELECTROCHEMICAL INVESTIGATION OF ELECTRON TRANSFER DEPENDENCE ON ADSORPTION

Background

The GC/solution interfacial region may be considered to be a complex matrix consisting of numerous layers between the carbon electrode surface and the solution species undergoing electron transfer. This matrix usually consists of surface debris, surface oxide functionalities, adsorbed organics, and possibly a disrupted layer of carbon particulates. The various layers of this complex matrix compromise the interface at which charge transfer occurs. Beyond these surface films lies the bulk solution whose properties are quite different from those of the double layer.

For the idealized case the electrode surface is smooth and, the double layer is well defined. In general, the layer closest to the electrode surface, sometimes referred to as the Stern layer, consists of solvent molecules and species which have a strong interaction with the electrode surface. These species either partially or completely cover the electrode surface and are said to be specifically adsorbed. The electrical centers of the specifically adsorbed species is referred to as the inner
Helmholtz plane (IHP). Solvated ions which have long range interactions with the surface occupy the next domain which is known as the outer Helmholtz plane (OHP). Beyond the OHP lies a diffuse layer of ions in solution which may extend from angstroms to micrometers into the bulk solution [40]. The structure of the double layer plays an important role in heterogeneous electron transfer, and the electroactive species must interact with the electrode surface as well as the structured solvent at the helmholtz planes, each of which may inhibit the transfer of an electron. Since carbon surfaces are heterogeneous, the double layer is ill defined and it is difficult to discern the distinct regions defined in the case of the idealized electrode. Also, unless a species is specifically adsorbed, the distance of closest approach to the electrode is limited to the OHP.

Since charge segregation exists at the electrode/solution interface, theories regarding the electrical double layer are concerned with charge distribution and electrical potentials which arise because of this charge separation. Many models have been formulated to describe the ion ordering within the double layer in an attempt to elucidate information as to its structure. The simplest model was proposed by Helmholtz who envisioned neutralization of the excess surface charge by a monolayer of oppositely charged ions. However, because charges are free to move in an electrolyte solution, one must account not only for charge neutralization but for the random thermal motion which is also possible under such conditions. This is the basis for the Gouy-Chapman model which assumes a diffuse layer of charge where the concentration of counterions is greatest near
the electrode surface and progressively decreases until a homogeneous
distribution of ions exists in the bulk. Introduction of ionic size by Stern allowed
for the modification of the Gouy-Chapman model and incorporated the theory of
closest approach into his model [40]. In an attempt to interpret thermodynamic
data fully, Grahame proposed a model which required two planes of approach
[100]. One plane was needed to describe the position of specifically adsorbed ions
and the other for non-specifically adsorbed ions. Also, a diffuse layer was
assumed which extended into the bulk solution. This theory is the basis for
current models for the structure of interfacial regions with added factors to
rationalize the roles played by solvent species. Grahame’s basic model is the
beginning for interpreting the solution side of the electrical double layer as being
comprised of three distinct regions. The understanding of the electrical double
layer is also a prerequisite for the comprehension of charge transfer and the
associated electrochemistry.

Measurements of heterogeneous electron transfer kinetics at solid electrodes
is of fundamental importance since this information may provide insight and
support in the development of batteries, electrosynthesis techniques, corrosion
resistance, and fuel cell improvement. The concepts of electron transfer are
important in chemical industries because the designers of plants, processes, and
equipment must know how reaction rates are affected by changes in temperature,
pressure, and concentration. Also, complex electron transfer kinetics which occur
in biological systems require a underlying basis in order to extrapolate data and
draw conclusions for these more complex systems. In biology and medicine, there is a balance between a large number of reactions each of which must coexist with others. Illness is often an indication that the rates of biologically important reactions have been altered substantially. The study of kinetics is also important if one wishes to comprehend the conditions which will expedite the reaction to proceed on a commercially feasible time scale. A further reason to study reaction rates is to obtain a fundamental understanding of how chemical reactions occur. Insight at the molecular level may be obtained by varying the reaction conditions.

For the study of electron transfer, one usually begins with a well defined surface and proceeds to deduce the mechanism by which electron transfer occurs. This task is not always simple since electron transfer may occur via different mechanisms, and may be affected by catalysis or adsorption. The problem is further complicated by the fact that it is difficult to ensure a reproducible surface which is free of contamination and defects when one is dealing with carbon. Since the double layer structure is important, one must also contend with solution properties such as pH, hydrophobicity and hydration, and interfacial properties such as bridging ions, ion ordering at the surface, and potential [7, 39, 40, 42]. Most existing theories available to predict the value of $k_{\text{obs}}$ are usually frustrated by many of the actual conditions mentioned which complicate electrochemistry. Thus, choosing a redox system to probe heterogeneous electron transfer kinetics is important, and it is necessary to determine which factors are responsible for the magnitude of $k_{\text{obs}}$ on the chosen electrode.
It is difficult to achieve situations where the working electrode behaves ideally since there is ample evidence suggesting that the rate of heterogeneous electron transfer is dependent on the physical properties of the electrode material. Also, perturbations such as applied potential affect the rate of an electrode reaction. Many efforts have been designed specifically to elucidate this mystery. Some of the qualities which an ideal electrode should possess include chemical inertness, high purity, a wide potential range, invariant electrochemical activity, resistance to passivation, durability, easily machinable, and relatively inexpensive. Most electrodes do not satisfy all the above criteria yet they are acceptable for the situations employed.

The goal in this chapter is the understanding of surface structure and how it relates to electrochemical reactivity. The electrode surface must be well defined, as was described in Chapter II, and the redox system employed must be simple one electron transfer redox couple since it is commonly observed that a redox species may behave differently on two dissimilar electrodes. The ideal redox system should be widely studied so that data may be compared to published results. Also, the redox system should undergo a simple one electron transfer and neither the reactant nor the product should adsorb to the electrode surface since such interactions would complicate the electron transfer mechanism.
**Heterogeneous Electron Transfer**

Electrochemical reactions of inorganic systems have been studied experimentally for a long time due to the fundamental importance of electron transfer in condensed media; one paramount reason being the development of fuel cells. Thus, it is necessary to develop a fundamental understanding of the processes and mechanisms controlling heterogeneous electron transfer kinetics. The theoretical treatment of electron transfer at metal electrodes may be similar to that of homogeneous electron transfer in that there are two reactants in both cases; however, for heterogeneous electron transfer, the metal electrode now serves as one of the reactants providing a rigid two dimensional environment for a reaction to occur. The homogeneous case must first be considered in order to provide a basis for extrapolation into the heterogeneous case.

There are two mechanistic classes into which homogeneous kinetics may be divided. These are classified as inner and outer sphere electron transfer reactions. For the homogeneous case, the first evidence of an inner sphere reaction was provided by Taube and Meyer who investigated the Cr$^{2+}$ reduction of $[\text{Co(NH}_3)_6]^{3+}$ [101-103]. Inner sphere reactions often include covalent bonds which are not well understood. A generalized mechanism for inner sphere reactions may be represented in three steps as follows,

$$M^{II}L_5 + XM^{III}L'_5 \rightleftharpoons L_5M^{II+}X^{--}M^{III}L'_5 + L$$

$$L_5M^{II+}X^{--}M^{III}L'_5 \rightleftharpoons L_5M^{III--}X^{--}M^{II}L'_5$$

$$L_5M^{III--}X^{--}M^{II}L'_5 \rightarrow \text{products}$$
where $M$ refers to the metal of interest, $L$ refers to a ligand, and $X$ refers to a bridging group [104]. The mechanism is explained as follows:

1. Substitution of a ligand into the coordination sphere of the reactant by the bridging group $X$ to form the precursor complex $L_sM^{III}--X--M^{III}I_5$.  
2. Reorganization of the precursor complex now occurs to give the successor complex $L_sM^{III}--X--M^{III}I_5$.  
3. The successor complex now collapses to produce products.

Any of the above steps may be rate determining and often inner sphere interactions include covalent bonds and hence these mechanisms are often referred to as ligand bridging reactions since direct bonds to a common atom or small group are formed prior to electron transfer. Thus, the ligand belongs to both coordination shells simultaneously.

In contrast, an outer sphere mechanism occurs when the two separate coordination spheres remain unaltered and the electron must eventually pass through both coordination spheres. The following representation is an explanation of the outer sphere mechanism.

\[
\begin{align*}
A + B & \rightarrow A||B \\
A||B & \rightarrow A||B' \\
A||B' & \rightarrow A||B^+ \\
A^-||B^+ & \rightarrow A^- + B^+
\end{align*}
\]

where $A$ and $B$ may be either individual ions, or fully coordinated molecular species, $B'$ represents an excited form of $B$, and the two vertical bars, $||$, represent contact between the valence electrons of the two coordination spheres without
electron sharing or bond formation [104]. In the case where one of the reactants is a solid electrode, the two vertical bars represent contact of a coordination sphere with the electrode surface without bond formation.

For the heterogeneous case, one of the reactants is essentially replaced by an electrode surface. Like homogeneous kinetics, heterogeneous kinetics may also be divided into the two mechanistic classes of inner and outer sphere electron transfer reactions. A reactant or a coordinated ligand is bound to the electrode surface in the transition state followed by electron transfer. Simple heterogeneous electron transfer may be considered to occur in two steps. The first is the location of the reacting species at a suitable site within the interfacial region where electron transfer can occur, and the second is thermal activation of the precursor species followed by electron transfer then deactivation to form the products. Because the inner layer of solvent molecules adjacent to the electrode surface remains intact during the formation of the precursor state and subsequent transition state, the reaction site is sufficiently far from the electrode surface resulting in weak, possibly electrostatic, reactant/electrode interactions. Hence, redox species undergoing an outer sphere electron transfer should be independent of electrode material.

Predicting $k^o$ for a specific redox species is not a trivial task since the rate constant is expected to depend on the free energy change of the overall reaction. Also, the metal ion which will undergo electron transfer is generally surrounded by shields of ligands and solvating molecules. The above factors were
incorporated on a firmer theoretical basis by Marcus [105] who derived an equation for predicting rate constants for heteronuclear reactions from the homogeneous self exchange rate constant, $k_{\text{exc}}$, and the overall equilibrium constant. This equation is shown below.

$$\left(\frac{k_{\text{exc}}}{Z_{\text{exc}}}\right)^{1/2} = \frac{k^o}{Z_{el}}$$  \hspace{1cm} (16)

The Marcus equation neglects work terms associated with the electrode surface; the terms $k_{\text{exc}}$ refers to the homogeneous self exchange rate constant, $k^o$ is the heterogeneous electron transfer rate constant, and $Z_{\text{exc}}$ and $Z_{el}$ are frequency factors, usually taken as $10^{11}$ and $10^4$ respectively, which incorporate the equilibrium constant and the self exchange rate constants for the reductant and oxidant [106]. The use of Marcus theory in this chapter is for comparison purposes only. Rates obtained on polished, laser irradiated, and fractured surfaces will be compared to the predicted values as described by Marcus theory.

The work presented in this chapter deals with the effects of an adsorbate on electron transfer kinetics of several redox systems. The reactants were chosen because we could expect an adsorbate to affect outer sphere and inner sphere reactions differently. As discussed in Chapter 1, the observed heterogeneous electron transfer rate constant, $k^o_{\text{obs}}$, reflects changes in the character of the electrode surface which are manifested in the form of microstructure or morphology and are commonly due to pretreatment procedures. An additional, and sometimes less understood, factor which may also influence $k^o_{\text{obs}}$ is the double
layer structure. Likely origins of double layer effects include the presence of surface functionalities and/or specifically adsorbed molecules. Oxide formation, hydrophobicity, and solution viscosity, which influence the double layer structure, or tunneling through surface films all can affect the observed heterogeneous electron transfer rate constant. Double layer structure and adsorption affects on $k^o_{\text{obs}}$ were recognized by Frumkin in 1933 and these affects were shown to give rise to a number of anomalies when rate constants were measured [107]. The rate constant for a given system will be measured on polished, fractured, and the surfaces resulting after laser irradiation before and after adsorption of anthraquinone-2,6-disulfonate (AQDS) and 9,10-anthraquinone-2-monosulfonate (AQMS).

**EXPERIMENTAL**

Electrode fabrication, laser irradiation, fracturing of the electrode surface, and voltammetric measurements were described in Chapter 2. Solutions of redox species were 1 mM unless otherwise noted, and potentials were measured against a BAS Ag/AgCl (3 M NaCl) reference electrode. Solutions of AQDS and AQMS were either 2 μM or 5 mM unless otherwise noted. Rate constants were calculated as described in Chapter 2 by the method of Nicholson.

For unmodified surfaces, cyclic voltammograms were obtained for Fe(CN)$_6^{3/-4}$, IrCl$_6^{2/-3}$, and Ru(NH$_3$)$_6^{2/-3}$ in the appropriate supporting electrolyte on
polished, fractured, and laser irradiated surfaces using a power density of 25 MW/cm². The apparatus and cell arrangement are shown schematically in Figure 6. The GC electrode was polished, as described in Chapter 1, placed into the cell, and the cell was filled with a solution containing the appropriate redox couple. After obtaining cyclic voltammograms, the difference in the anodic and cathodic peak potentials, \( \Delta E_p \), was measured, and then \( k_{obs} \) was calculated as described in Chapter 1.

In the cases were the GC electrodes are modified by adsorption of either AQDS or AQMS, solutions were prepared which contained both the redox couple of interest and the adsorbate with the appropriate supporting electrolyte. Concentrations employed were usually 5 mM for the redox couple and 5 mM for the adsorbate unless otherwise noted. At a concentration of 5 mM, monolayer coverage of the GC surface by the adsorbate was attained in less than 1 seconds. The solution was placed into the cell and cyclic voltammograms were obtained within 5 seconds of laser irradiation or fracturing.

**UNMODIFIED SURFACES**

**Results**

Examples of voltammograms for the three redox systems chosen as a diagnostic are shown in Figure 16 on polished and laser irradiated GC-20. Table 3 lists \( k_{obs} \) values for the three redox couples used [108-109] along with the homogeneous self exchange rate constant and the predicted \( k^o \) value based on the
Figure 16

Cyclic voltammograms on polished and laser irradiated GC-20 surfaces for IrCl$_6^{2/-3}$ (1 M HClO$_4$), Fe(CN)$_6^{3/-4}$ (1 M KCl), and Ru(NH$_3$)$_6^{2/-3}$ (1 M KCl).
Figure 16

A

IrCl$_{2}^{2+/3}$  
(1M HClO$_{4}$)

POL
LAS

B

Fe(CN)$_{6}^{3-/4}$  
(1M KCl)

POL
LAS

C

Ru(NH$_{3})_{6}^{2+/3}$  
(1M KCl)

POL
LAS

(V vs. Ag/AgCl)
**Table 3:** Observed heterogeneous electron transfer rate constants and homogeneous self exchange rate constants for the three redox systems investigated. 25 MW/cm² refers to laser irradiation at that power density. GU = Guanidine hydrochloride. Units for $k_{\text{obs}}^o$ are cm/s, and $N$ refers to the number of distinct surfaces used to obtain the statistics.

<table>
<thead>
<tr>
<th></th>
<th>$k_{\text{obs}}^o$ Polished</th>
<th>$k_{\text{obs}}^o$ 25 MW/cm²</th>
<th>$k_{\text{obs}}^o$ Fractured</th>
<th>$k_{\text{exc}}$</th>
<th>$k^o$ Predicted</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(CN)$_6^{3/-4}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(1 M KCl)</td>
<td>0.05 ± 0.01 (N = 12)</td>
<td>0.50 ± 0.10</td>
<td>0.50 ± 0.10</td>
<td>2 x 10⁴</td>
<td>4.5</td>
</tr>
<tr>
<td>(1 M LiCl)</td>
<td>0.001 ± 0.002 (N = 8)</td>
<td>0.13 ± 0.06</td>
<td>0.18 ± 0.05</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(1 M NH$_4$Cl)</td>
<td>0.19 ± 0.02 (N = 5)</td>
<td>0.30 ± 0.03</td>
<td>0.27 ± 0.05</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(1 M GU HCl)</td>
<td>0.15 ± 0.03 (N = 5)</td>
<td>0.25 ± 0.03</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IrCl$_6^{2/-3}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(1 M HCl)</td>
<td>0.14 ± 0.02 (N = 10)</td>
<td>0.50 ± 0.05</td>
<td>0.55 ± 0.05</td>
<td>2 x 10⁵</td>
<td>14</td>
</tr>
<tr>
<td>(1 M LiCl)</td>
<td>0.04 ± 0.02 (N = 10)</td>
<td>0.07 ± 0.02</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ru(NH$_3$)$_6^{2/-3}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(1 M KCl)</td>
<td>0.62 ± 0.11 (N = 10)</td>
<td>0.70 ± 0.02</td>
<td>0.27 ± 0.07</td>
<td>4 x 10³</td>
<td>2.0</td>
</tr>
<tr>
<td>(0.5 M KCl)</td>
<td>0.12 ± 0.04 (N = 10)</td>
<td>0.12 ± 0.02</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(1 M LiCl)</td>
<td>0.19 ± 0.02 (N = 10)</td>
<td>0.24 ± 0.02</td>
<td>0.16 ± 0.02</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(50 mM K$_2$PF$_6$)</td>
<td>0.03 ± 0.03 (N = 4)</td>
<td>0.04 ± 0.01</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(50 mM (NH$_4$)$_2$PF$_6$)</td>
<td>0.03 ± 0.04 (N = 4)</td>
<td>0.03 ± 0.01</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Typical literature values of $k_{\text{obs}}^o$ for polished surfaces range from 0.001 to 0.005 cm/s.
Marcus equation. The three redox systems are the Fe(CN)$_6^{3/-4}$ couple, the IrCl$_6^{2/-3}$ couple, and the Ru(NH$_3)_6^{2/-3}$ couple, and they were chosen since other researchers have also used these couples as models of systems which exhibit outer sphere electron transfer [75, 110]. The values reported in Table 3 for the polished surfaces were obtained within 30 seconds of polishing. Values for the laser irradiated and fractured surfaces were obtained within 5 seconds of pretreating or fracturing. Various supporting electrolytes were used in order to assess information regarding double layer effect.

For the Fe(CN)$_6^{3/-4}$ couple, $k_{obs}^o$ increased after laser irradiation and fracturing by at least two orders of magnitude in both 1 M KCl and 1 M LiCl. A similar trend was observed for IrCl$_6^{2/-3}$ except the increase in $k_{obs}^o$ at most a factor of 3. Also, unlike $k_{obs}^o$ for Fe(CN)$_6^{3/-4}$, $k_{obs}^o$ for IrCl$_6^{2/-3}$ began at a larger value. In contrast, Ru(NH$_3)_6^{2/-3}$ kinetics showed nominal improvement after laser irradiation, and fracturing did not improve $k_{obs}^o$. In fact, $k_{obs}^o$ on the fractured surface was always slower than the polished surface for Ru(NH$_3)_6^{2/-3}$. The initial value of $k_{obs}^o$ for Ru(NH$_3)_6^{2/-3}$ on a polished surface was large when compared to Fe(CN)$_6^{3/-4}$ and IrCl$_6^{2/-3}$. Varying the supporting electrolyte concentration resulted in a significant decrease in $k_{obs}^o$ for laser irradiated surfaces. For each system studied, $k_{obs}^o$ was always lower than the $k^o$ value predicted by Marcus theory, and $k_{obs}^o$ was dependent on the supporting electrolyte.

The heterogeneous electron transfer rate constant $k_{obs}^o$ was monitored as a function of time on polished, fractured, and the laser irradiated surfaces in order
Figure 17

Observed rate constant, $k_{\text{obs}}$, vs. time for $\text{Fe(CN)}_6^{3/4}$ (1 M KCl) and $\text{IrCl}_6^{2/3}$ (1 M HClO$_4$)

Graph A shows kinetics as a function of solution exposure time for $\text{Fe(CN)}_6^{3/4}$ and graph B shows the same results for $\text{IrCl}_6^{2/3}$.

$\text{Fe(CN)}_6^{3/4}$ rate constants were obtained at 100 V/s and $\text{IrCl}_6^{2/3}$ rate constants were obtained at 400 V/s.
Figure 17
to determine why $k_{obs}$ varied with solution exposure time. Figure 17 shows $k_{obs}$ as a function of solution exposure time on polished, laser irradiated (25 MW/cm$^2$), and in situ fractured GC surfaces for Fe(CN)$_{6}^{3/4}$ and IrCl$_{6}^{2/-3}$. Scan rates were chosen to obtain peak separations sufficient to produce reliable rate constants. These criteria were satisfied when $\Delta E_p$ greater than 88 mV.

The experiments were performed by first polishing the electrode surface then monitoring $k_{obs}$ as a function of time. After an hour had elapsed, the surface surface was exposed to three 25 MW/cm$^2$ Nd:YAG pulses and $k_{obs}$ was again monitored for an hour. There was no difference in the behavior of $k_{obs}$ as a function of exposure time when the experiment was performed without waiting an hour after polishing. In this case, the electrode was polished then immediately laser irradiated. The voltammetry was then obtained within five seconds of irradiation and $k_{obs}$ was monitored for an hour by repeating the acquisition of cyclic voltammograms. Finally, the surface was fractured by impact and kinetics were again monitored for an hour. Initial values for $k_{obs}$ after laser irradiation and fracturing were obtained within five seconds of laser irradiation or fracturing. In all cases, the values for $k_{obs}$ are larger for laser irradiated and fractured surfaces than they are for surfaces which were polished. Also, it was observed that solution exposure of all surfaces resulted in a decrease in $k_{obs}$ over time.

For the case of Fe(CN)$_{6}^{3/4}$ in 1 M KCl, $k_{obs}$ increased by approximately two orders of magnitude, after the polished surface had been laser irradiated with three 25 MW/cm$^2$ Nd:YAG pulses or fractured in solution, were observed.
Average $k_{\text{obs}}$ values were 0.05 ± 0.05 cm/s (N=10) for a polished surface, 0.50 ± 0.11 (N=10) for a 25 MW/cm² laser irradiated surface, and 0.50 ± 0.2 cm/s (N=10) for a fractured surface. The values of "N" reported are for the number of freshly prepared surfaces studied. Kinetics were monitored for an hour and it was observed that for Fe(CN)$_6^{3/-4}$ the decay in $k_{\text{obs}}^o$ over time did not reach the lower limit obtained upon polishing. That is, $k_{\text{obs}}^o$ increased from 0.05 cm/s to 0.50 cm/s upon laser irradiation and after an hour, $k_{\text{obs}}^o$ decayed to 0.2 cm/s. Values of 0.50 cm/s for $k_{\text{obs}}^o$ on GC are the highest reported to date [2], and the value of 0.05 cm/s for the polished surface was the highest obtained in these studies.

Two other supporting electrolytes were used in order to assess the behavior of Fe(CN)$_6^{3/-4}$ on GC surfaces. These supporting electrolytes were ammonium chloride, NH$_4$Cl, and guanidine hydrochloride, GU HCl. GU was chosen since it is known to decrease the hydrophobic interactions of water [111-112]. For these studies on GC-20 surfaces, Figure 18 shows a plot of $k_{\text{obs}}^o$ for Fe(CN)$_6^{3/-4}$ kinetics as a function of solution exposure time and supporting electrolyte on laser irradiated surfaces. The results for KCl may be compared to the decay in $k_{\text{obs}}^o$ on laser irradiated and fractured GC shown in Figure 19. Supporting electrolyte concentrations were 1 M in all cases, and various supporting electrolytes were used in order to assess effects of solution viscosity, hydrophobicity, pH, or hydration of the supporting electrolyte cation on $k_{\text{obs}}^o$. The observed trend for initial $k_{\text{obs}}^o$ on laser irradiated GC, as shown in Figure 18, follows the same trend as $k_{\text{obs}}^o$ values on gold and platinum [114-115]; that is $k_{\text{obs}}^o$...
Figure 18

$k_{obs}^o$ for Fe(CN)$_6^{3/4}$ as a function of time and supporting electrolyte on laser irradiated GC-20. Supporting electrolyte concentrations were 1 M in all cases. GU HCl is guanidine hydrochloride C(NH$_2$)$_3^+$ HCl.
Figure 18
Figure 19

$k_{obs}^0$ for Fe(CN)$_6^{3/4}$ in 1 M KCl on fractured and laser irradiated GC-20 as a function of solution exposure time.
Figure 19

Solution Exposure Time (min.)

$k_{obs}^o$ (cm/s)

- • LASER
- • FRACTURED
increases with supporting electrolyte identity in the order Li⁺ < NH₄⁺ < K⁺. The trend on glassy carbon is identical except that guanidine hydrochloride, GU, is placed between Li⁺ and NH₄⁺, as follows Li⁺ < GU = NH₄⁺ < K⁺. Data for the fractured and laser irradiated surfaces in Figure 19 are similar both initially and after long solution exposure times.

Similar k⁰obs results were obtained for IrCl₆²⁻⁻ in either 1 M HCl or 1 M HClO₄, as were obtained for Fe(CN)₆³⁻⁻, except the increase in k⁰obs after laser irradiation or fracturing was only a factor of five as opposed to 100. These results for IrCl₆²⁻⁻ are shown in Figure 17B. For IrCl₆²⁻⁻ however, decay was observed for only 10 minutes of solution exposure time. The observed rate constant on laser irradiated and fractured GC surfaces correlates well with the results obtained by Saji et al. [115] on platinum; their value was 0.5 cm/s. Table 3 shows data for IrCl₆²⁻⁻ kinetics in HCl and LiCl, and the decay results were summarized in Figure 17B. Values for k⁰obs were larger in 1 M HCl than in 1 M LiCl in all cases. For the laser irradiated surfaces, an effort was made to reactivate with successive laser pulses after passivation. As in chapter 2, laser pulses were delivered in groups of three. As before, decay over time still occurred, perhaps caused by passivation of the surface due to solution impurities. An attempt was made to retard the decay by introducing 30% acetonitrile (CH₃CN) into the IrCl₆²⁻⁻ solution. It was believed that if trace organic impurities were responsible for the decay, then they would be more soluble in acetonitrile and not adsorb to the carbon surface to as great an extent. No retardation of the decay was
observed implying that the decay in $k_{\text{obs}}$ could still be due to impurities in acetonitrile or some other phenomenon.

Kinetic data for $\text{Ru(NH}_3\text{)}_3^{2/3+}$ is also shown in Table 3. For this couple however, there is little change in $k_{\text{obs}}$ with laser irradiation of a polished surface, and when the surface is fractured, $k_{\text{obs}}$ decreases. Supporting electrolytes however have an effect on $k_{\text{obs}}$ as was demonstrated by comparing data for 1 M KCl and 1 M LiCl. In this case, $k_{\text{obs}}$ was three times faster in 1 M KCl than in 1 M LiCl, and laser irradiation did not significantly improve $k_{\text{obs}}$ in LiCl either. Fracturing the electrode in a LiCl solution also had no effect on $k_{\text{obs}}$. In order to compare rate constants to those reported by Penner et al. [116], kinetics were measured in a K$_2$PF$_6$ medium. Also, the cation was varied, from potassium to ammonium, to deduce whether there would be an effect.

Conclusions

Although the Fe(CN)$_6^{3/4-}$ redox couple has served as a benchmark system for many years on metal electrodes, there are many discrepancies in the literature regarding the rate constant of electron transfer for Fe(CN)$_6^{3/4-}$ using various electrode surfaces under a variety of conditions [2, 39, 108, 113-114, 117-125]. The observed heterogeneous electron transfer rate constant is reported to vary with the concentration and identity of the supporting electrolyte and pretreatment procedures. Also, $k_{\text{obs}}$ is known to depend on the anion present, particularly when CN$^-$ and I$^-$ were introduced into the system. The reasons for these variations are
not well understood, but several authors have offered explanations regarding the behavior of this redox couple. Table 4 lists $k_{obs}^{o}$ for Fe(CN)$_{6}^{3/-4}$ on platinum electrodes following various pretreatment procedures by various authors. Values for $k_{obs}^{o}$ range from 0.002 to 0.23 cm/s on platinum and from 0.002 to 0.5 cm/s on glassy carbon.

Some explanations regarding the variations in $k_{obs}^{o}$ on platinum electrodes have been suggested. Iodide adsorption was proposed to block the surface of platinum from other impurities and thus $k_{obs}^{o}$ was slightly increased. A K$^+$ ion bridging mechanism was proposed by Sohr et al. [125] for fast electron transfer on platinum which was not affected by iodide adsorption, while Peter et al. concluded that the transition state must contain at least one cation [114] implying that the predominant species is KFe(CN)$_{6}^{2/3}$. Complex stability for Fe(CN)$_{6}^{3/-4}$ was reduced as K$^+$ concentration was decreased as suggested by Galus [121]. Others measured reproducibly high $k_{obs}^{o}$ on platinum after CN$^-$ adsorption. These complications had been restricted to metal electrodes owing to the difficulty in preparing reproducible carbon surfaces; however, Fe(CN)$_{6}^{3/-4}$ in 1 M KCl was commonly incorporated as a benchmark system for rating electrodes toward heterogeneous electron transfer. The highest $k_{obs}^{o}$ obtained to date has been reported on fractured glassy carbon [15].
Table 4: $k_{\text{obs}}^o$ for Fe(CN)$_{6}^{3/-4}$ on platinum and GC electrodes under various pretreatment procedures

<table>
<thead>
<tr>
<th>Pretreatment Procedure</th>
<th>Electrolyte</th>
<th>$k_{\text{obs}}^o$ (cm/s)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aqua regia, anodization, flame</td>
<td>1 M KCl</td>
<td>0.23 ± 0.07</td>
<td>72</td>
</tr>
<tr>
<td>Nitric acid, flame</td>
<td>1 M KCl</td>
<td>0.23 ± 0.23</td>
<td>72</td>
</tr>
<tr>
<td>Flame only</td>
<td>1 M KCl</td>
<td>0.22 ± 0.01</td>
<td>72</td>
</tr>
<tr>
<td>Nitric acid, anodization</td>
<td>1 M KCl</td>
<td>0.11 ± 0.04</td>
<td>72</td>
</tr>
<tr>
<td>Nitric acid</td>
<td>1 M KCl</td>
<td>0.22 ± 0.007</td>
<td>72</td>
</tr>
<tr>
<td>Aqua regia</td>
<td>1 M KCl</td>
<td>&lt; 0.01</td>
<td>72</td>
</tr>
<tr>
<td>HClO$_4$, reduction in KCl</td>
<td>1 M KCl</td>
<td>0.24</td>
<td>119</td>
</tr>
<tr>
<td>HClO$_4$</td>
<td>1 M KCl</td>
<td>0.028</td>
<td>119</td>
</tr>
<tr>
<td>Potential cycling</td>
<td>1 M KCl</td>
<td>0.10</td>
<td>114</td>
</tr>
<tr>
<td>Potential cycling</td>
<td>1 M LiNO$_3$</td>
<td>0.01</td>
<td>114</td>
</tr>
<tr>
<td>Aqua regia, cathodization, flame</td>
<td>1 M KCl</td>
<td>0.21</td>
<td>72</td>
</tr>
<tr>
<td>Aqua regia, cathodization, flame</td>
<td>1 M NaCl</td>
<td>0.17</td>
<td>72</td>
</tr>
<tr>
<td>Aqua regia, cathodization, flame</td>
<td>1 M LiCl</td>
<td>0.07</td>
<td>72</td>
</tr>
<tr>
<td>Aqua regia, cathodization, flame</td>
<td>1 M NaClO$_4$</td>
<td>0.15</td>
<td>72</td>
</tr>
<tr>
<td>Potential cycling</td>
<td>1 M KCl/0.01 M NaCN</td>
<td>&gt; 0.1</td>
<td>106</td>
</tr>
<tr>
<td>Potential cycling</td>
<td>1 M LiCl</td>
<td>0.08</td>
<td>106</td>
</tr>
<tr>
<td>Potential cycling</td>
<td>1 M LiCl</td>
<td>0.002</td>
<td>106</td>
</tr>
<tr>
<td>Gold electrode</td>
<td>1 M KCl</td>
<td>0.10</td>
<td>126</td>
</tr>
<tr>
<td>Tokai GC-20 (Al$_2$O$_3$ on glass)</td>
<td>1 M KCl</td>
<td>0.14 ± 0.01</td>
<td>47</td>
</tr>
<tr>
<td>Tokai GC-20 (Al$_2$O$_3$ on glass)</td>
<td>0.5 M K$_2$SO$_4$</td>
<td>0.12 ± 0.02</td>
<td>47</td>
</tr>
<tr>
<td>Tokai GC-20 (Al$_2$O$_3$ on polishing cloth)</td>
<td>1 M KCl</td>
<td>0.002</td>
<td>2</td>
</tr>
<tr>
<td>Glassy Carbon (ECP procedures)</td>
<td>KNO$_3$/H$_2$SO$_4$</td>
<td>0.002 - 0.15</td>
<td>2</td>
</tr>
<tr>
<td>GC-20 (VHT)</td>
<td>1 M KCl</td>
<td>0.14</td>
<td>65</td>
</tr>
<tr>
<td>GC-20 (Laser irradiated or Fractured)</td>
<td>1 M KCl</td>
<td>0.50 ± 0.10</td>
<td>This work</td>
</tr>
</tbody>
</table>
Unusual kinetic behavior of the Fe(CN)$_6^{3/4}$ redox couple in the presence of various cations was reported by Peter et al. [114] and confirmed by Goldstein and Van De Mark [72]. The observed trend was that $k_{\text{obs}}^o$ on gold and platinum increased, as the radius of the alkali metal increased, or as the cation hydration sphere decreased, in the order Li$^+$ < Na$^+$ < K$^+$ ≈ Cs$^+$. Values for crystal ionic radii and hydrated ionic radii for selected cations and anions are shown in Table 5. Kuta and Yeager reported $k_{\text{obs}}^o$ values for Fe(CN)$_6^{3/4}$ in the presence of Rb$^+$, and placed Rb$^+$ between K$^+$ and Cs$^+$ in the above order [126]. Goldstein and Van De Mark explained this trend as an interaction, either direct or indirect, between the electrons of Fe(CN)$_6^4$ and the empty orbitals of the cation which could lead to increases in the observed heterogeneous electron transfer rate constant. Also, solvation differences and/or ion pairing interactions were suggested as being possible explanations for the increase in $k_{\text{obs}}^o$ with increasing cationic size. The cation solvent interaction for Li$^+$ is much stronger than for larger metal cations which implies that Li$^+$ may not associate with Fe(CN)$_6^4$ as readily as the larger K$^+$. Thus, the highly solvated Li$^+$ cation would tend not to interact whereas the less solvated K$^+$ would probably associate with the Fe(CN)$_6^4$. Hence, when KCl is the supporting electrolyte, the species KFe(CN)$_6^2$ is predominant as opposed to Fe(CN)$_6^3$.

GU was chosen since it is known to decrease the hydrophobic interactions of water [111-112]. Also, the decay of $k_{\text{obs}}^o$ was noticed to be dependent on the identity of the supporting electrolyte. That is, in 1 M KCl, $k_{\text{obs}}^o$ reached 0.15 cm/s
Table 5: Crystal ionic and hydrated ionic radii for selected ions. Data taken from reference 127.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Crystal Ionic Radii (Å)</th>
<th>Hydrated Ionic Radii (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li⁺</td>
<td>0.78</td>
<td>3.82</td>
</tr>
<tr>
<td>Na⁺</td>
<td>0.95</td>
<td>3.58</td>
</tr>
<tr>
<td>K⁺</td>
<td>1.33</td>
<td>3.31</td>
</tr>
<tr>
<td>Rb⁺</td>
<td>1.48</td>
<td>3.29</td>
</tr>
<tr>
<td>Cs⁺</td>
<td>1.69</td>
<td>3.29</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>1.48</td>
<td>3.31</td>
</tr>
<tr>
<td>(Me)₄N⁺</td>
<td>3.47</td>
<td>3.67</td>
</tr>
<tr>
<td>(Et)₄N⁺</td>
<td>4.00</td>
<td>4.00</td>
</tr>
<tr>
<td>F⁻</td>
<td>1.36</td>
<td>3.52</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>1.81</td>
<td>3.32</td>
</tr>
<tr>
<td>Br⁻</td>
<td>1.95</td>
<td>3.30</td>
</tr>
<tr>
<td>I⁻</td>
<td>2.16</td>
<td>3.31</td>
</tr>
<tr>
<td>ClO₃⁻</td>
<td>2.88</td>
<td>3.41</td>
</tr>
<tr>
<td>BrO₃⁻</td>
<td>3.08</td>
<td>3.51</td>
</tr>
<tr>
<td>IO₃⁻</td>
<td>3.30</td>
<td>3.74</td>
</tr>
<tr>
<td>ClO₄⁻</td>
<td>2.92</td>
<td>3.38</td>
</tr>
<tr>
<td>IO₄⁻</td>
<td>3.19</td>
<td>3.52</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>2.90</td>
<td>3.79</td>
</tr>
</tbody>
</table>
after a 60 minute solution exposure time, while in 1 M NH₄Cl, it reached 0.22 cm/s. Also, the values of $k_{\text{obs}}$ in KCl varied markedly, 0.5 cm/s initially after the laser pulses were delivered to 0.15 cm/s after 60 minutes of solution exposure; whereas, in NH₄Cl, the value of $k_{\text{obs}}$ was fairly constant, 0.29 cm/s initially and 0.24 cm/s after 60 minutes of solution exposure. Furthermore, in LiCl and GU, $k_{\text{obs}}$ was more constant over the 60 minute exposure, although smaller in magnitude than in 1 M KCl.

Supporting electrolytes were varied in order to assess the effects of solution viscosity, hydrophobicity, pH, or hydration of the supporting electrolyte cation on $k_{\text{obs}}$. Figure 18 shows a plot of $k_{\text{obs}}$ for Fe(CN)$_6^{3/-4}$ kinetics as a function of solution exposure time and supporting electrolyte on laser irradiated surfaces. In determining which electron transfer mechanisms could be excluded for Fe(CN)$_6^{3/-4}$ electron transfer, it was concluded that surface oxides probably played no role in electron transfer since $k_{\text{obs}}$ values and decays were similar for a fractured and laser irradiated, 25 MW/cm$^2$, surface as shown in Figures 18 and 19 for Fe(CN)$_6^{3/-4}$ in 1 M KCl. Since $k_{\text{obs}}$ values, both initially and after the 60 minute decay, are virtually identical, one may conclude that surface oxides are probably not important in electron transfer [2]. Solution viscosity is probably not important for electron transfer unless the measured values differ significantly albeit measured diffusion coefficients for Fe(CN)$_6^{3/-4}$ were slightly larger in 1 M KCl, $6.3 \times 10^{-6}$ cm$^2$/s, than in 1 M LiCl, $5.6 \times 10^{-6}$ cm$^2$/s. Cation hydration should be significant for electron transfer since the hydrated radius is larger for Li$^+$ than
K⁺. A larger hydrated radius will change the supporting electrolyte medium which will alter the double layer structure, in turn relocating the OHP, thus changing the distance of closest approach for Fe(CN)₆³⁻/⁴; hence, $k_{\text{obs}}^o$ should be decreased as the hydration sphere is increased. This is exactly what is observed when $k_{\text{obs}}^o$ values for Fe(CN)₆³⁻/⁴ are compared in 1 M KCl and 1 M LiCl on laser irradiated GC electrodes. Thus, it would seem as if the decrease in $k_{\text{obs}}^o$ for Fe(CN)₆³⁻/⁴ in KCl and LiCl may be explained via a cation hydration argument. However, if NH₄Cl is used as a supporting electrolyte, unexpected results are obtained. Since K⁺ and NH₄⁺ have identical hydrated radii, 3.31 Å [127], then one would expect similar behavior in $k_{\text{obs}}^o$ for Fe(CN)₆³⁻/⁴ in either medium. If identical results for $k_{\text{obs}}^o$ are obtained, then a hydration argument is supported. Figure 18 shows these results and they are distinct. Electron transfer rates for Fe(CN)₆³⁻/⁴ are slower in 1 M NH₄Cl than in 1 M KCl implying that a hydration radius is not the only issue.

Guanidine hydrochloride, GU, was chosen as a supporting electrolyte since it is known to decrease hydrophobic effects. Thus, a redox species should be closer to the carbon surface when GU is the supporting electrolyte as opposed to LiCl or KCl. This suggests that $k_{\text{obs}}^o$ should be lower if the supporting electrolyte is LiCl rather than GU [111]. As shown in Figure 18, this does occur for Fe(CN)₆³⁻/⁴ which implies that hydrophobic effects may be an issue for Fe(CN)₆³⁻/⁴ electron transfer kinetics on GC electrodes. In essence, the redox couple is hydrophilic while the GC surface is hydrophobic, and if GU reduces the
hydrophobicity of the GC surface then it should promote electron transfer. Another possibility is that GU is solubilizing organic impurities which would normally adsorb on the carbon surface. If this were the case, then \( k_{\text{obs}} \) would be larger in GU as opposed to KCl or LiCl. Also, it is possible that GU adsorbs to the glassy carbon surface. If adsorption were to occur, then the effects observed may be explained via this argument. An adsorbed layer of GU on the GC surface may prevent further passivation of the surface thus possibly causing \( k_{\text{obs}} \) to remain relatively constant as is observed in Figure 24.

An interesting outcome from the data in Figure 18 is that \( k_{\text{obs}} \) for \( \text{Fe(CN)}_{6}^{3/4} \) behaves similarly when the supporting electrolyte is GU or \( \text{NH}_{4}^{+} \). This effect is suggests that although hydrophobic effects may be a possible cause of the reduced \( k_{\text{obs}} \), it is probably a surface phenomenon or interaction between the \( \text{Fe(CN)}_{6}^{3/4} \) and the carbon surface which is responsible for the unusual kinetic behavior of \( \text{Fe(CN)}_{6}^{3/4} \) on glassy carbon. Also, local pH effects may be responsible for the observations obtained with GU and \( \text{NH}_{4}^{+} \). Solutions of \( \text{Li}^{+} \) and \( \text{K}^{+} \) would have different pH values than solutions of GU and \( \text{NH}_{4}^{+} \) thus altering the double layer and affecting \( k_{\text{obs}}^{0} \). In summary, \( \text{Fe(CN)}_{6}^{3/4} \) kinetics on pretreated or fractured glassy carbon electrodes appear to be sensitive to the underlying GC surface and that a surface sensitive interaction between \( \text{Fe(CN)}_{6}^{3/4} \) and carbon probably exists.

The effects observed for the \( \text{IrCl}_{6}^{2/3} \) couple were different from those of the \( \text{Fe(CN)}_{6}^{3/4} \) couple. Kinetics of \( \text{IrCl}_{6}^{2/3} \) were sensitive to solution pH as suggested
by Deakin et al. [108], and possibly to the supporting electrolyte cation. One major difference however is IrCl$_6^{2/3}$ is less sensitive to the surface conditions than Fe(CN)$_6^{3/4}$. This can be seen since $k_{\text{obs}}^o$ on the polished surface is fast when compared to $k_{\text{obs}}^o$ for Fe(CN)$_6^{3/4}$. Since this was the case, laser irradiation did not improve $k_{\text{obs}}^o$ to the same magnitude as was observed for Fe(CN)$_6^{3/4}$. The instrumental limit for our measurements was 0.5 cm/s suggesting that the actual rate constant may be significantly larger. This may be the case since the predicted rate constant, via Marcus theory, is 14.0 cm/s which is almost three times greater than that for Fe(CN)$_6^{3/4}$. The fact that $k_{\text{obs}}^o$ is similar for laser irradiated and fractured surfaces for this redox couple suggests that surface oxides are probably not important for electron transfer and that IrCl$_6^{2/3}$ is less surface sensitive than Fe(CN)$_6^{3/4}$.

The Ru(NH$_3$)$_6^{2+/3}$ couple was investigated next and its behavior on glassy carbon was unanticipated. Data from Table 3 show that $k_{\text{obs}}^o$ for Ru(NH$_3$)$_6^{2+/3}$ is not only dependent on the nature of the supporting electrolyte, the concentration of the supporting electrolyte, and the supporting electrolyte cation, but $k_{\text{obs}}^o$ does not increase upon laser irradiation. This observation was unexpected, and it does suggest that Ru(NH$_3$)$_6^{2+/3}$ is not as sensitive to the GC surface condition as IrCl$_6^{2/-3}$ or Fe(CN)$_6^{3/4}$. For the case where 1 M KCl is used as the supporting electrolyte, $k_{\text{obs}}^o$ is shown to be significantly slower on a fractured surface as compared to a laser irradiated or polished surface. Since a fractured surface is assumed to be initially free of debris and is probably contains fewer surface oxides when
compared to a polished or laser irradiated surface, the observation that \( k_{\text{obs}} \) is slower on a fractured surface would imply that Ru(NH\(_3\)\(_6\))\(^{2+/3}\) kinetics are surface oxygen sensitive. This behavior was also observed by Deakin et al. [108] who treated the GC electrodes with Vitride, a chemical reducing agent, to derivitize the surface oxides. The rate constant was pH dependent, but upon treatment with Vitride, \( k_{\text{obs}} \) for Ru(NH\(_3\)\(_6\))\(^{2+/3}\) on the GC surface showed no pH dependence suggesting that surface oxides were important for electron transfer to the Ru(NH\(_3\)\(_6\))\(^{2+/3}\) species on carbon electrodes.

A comparison with the results of Penner et al. [116] showed that rate constants obtained by Penner et al. [116] were always greater than those obtained here, by about a factor of 100; however, comparisons were not possible since he used electrodes of much smaller dimensions thus minimizing any effects of solution resistance. It is possible that solution resistance effects in this experiment are responsible for the low values of \( k_{\text{obs}} \). Since fabrication of smaller electrodes was not possible, the kinetic results in K\(_2\)PF\(_6\) may be anomalously low. From the data in Table 3, it appears as if Ru(NH\(_3\)\(_6\))\(^{2+/3}\) kinetics are not sensitive to the choice of cation when the supporting electrolyte is PF\(_6\)_2\(^-\). The observations and conclusions for this work were that \( k_{\text{obs}} \) for Ru(NH\(_3\)\(_6\))\(^{2+/3}\) was slower when the supporting electrolyte was K\(_2\)PF\(_6\). In fact, the rate constant decreased in a similar order, for different electrolyte cations; that is, \( k_{\text{obs}} \) was fastest when KCl was the supporting electrolyte and slower when LiCl was used.
Overall, the three redox couples behave unexpectedly on GC electrodes. Deakin et al. were the first to observe similar behavior for these couples when they noticed that the couples were pH dependent on GC electrodes but not on metallic electrodes [108]. From the data presented in Table 3 and in Figures 18 and 19, it is concluded that IrCl\textsuperscript{2/3} and Ru(NH\textsubscript{3})\textsuperscript{2+/3} kinetics do not appear to be as sensitive to the state of the GC surface, and that Fe(CN)\textsubscript{3/4} kinetics appear to be more dependent on the nature of the GC surface. Hydrophobic interactions appear to affect Fe(CN)\textsubscript{3/4} since k\textsubscript{obs} for this couple remains relatively constant with time in GU HCl. The other redox couples exhibit a decrease in k\textsubscript{obs} over time regardless of supporting electrolyte. Thus, it is shown that Fe(CN)\textsubscript{3/4} behaves differently than either IrCl\textsubscript{2/3} or Ru(NH\textsubscript{3})\textsubscript{2+/3} and one possible reason may be that Fe(CN)\textsubscript{3/4} is sensitive to impurity adsorption.

MODIFICATION OF GC ELECTRODES BY ADSORPTION

Background

When an electrode is immersed in a solution, the surface becomes covered with a layer of solvent molecules and possibly by other species in solution which are present as impurities or reactants. The electrochemical behavior of the electrode surface is often modified due to interactions of the adsorbed species with the redox system under investigation. In some instances, purposely altering the electrode by adsorption, polymerization, or covalent bonding provides a rational approach for fabricating interfaces with a well-defined structure,
composition, and thickness. Fundamental investigations of modified surfaces have provided an insight into the nature of heterogeneous charge transfer phenomena including catalysis, corrosion, lubrication, and adhesion [128-132]. The ability to control interfacial processes and to elucidate the manner by which electron transfer occurs for a large separation between donor and acceptor sites has important implications for the fundamental advancement of technology. A detailed understanding of electron transfer on modified surfaces would have an impact on current efforts in electrochemistry, biomembrane technology, and microelectronics.

The choice of an adsorbate for surface modification is crucial since the adsorbate should be structurally well-defined on the surface of interest. Quinone adsorbates are usually an ideal choice since they are well understood on carbon surfaces. Soriaga and Hubbard demonstrated that anthraquinone-2,6-disulfonate (AQDS) adsorbs onto platinum in a close packed flat arrangement [96]. Recently, Faulkner et al. [133] have characterized the adsorption of AQDS on mercury electrodes and showed that Langmuirian behavior was observed for a range of bulk concentrations below $10^{-5}$ M. Brown and Anson were the first to adsorb PQ and 9,10-anthraquinone-2-monosulfonate, AQMS, onto carbon electrodes [134-135] and report saturation coverages for these species. PQ was not the adsorbate of choice for these studies because PQ is a slow adsorber when the bulk concentration is $10^4$ M. It takes approximately 45 and 75 minutes to reach equilibrium coverage on polished and laser irradiated surfaces respectively. Also,
PQ is relatively insoluble in an aqueous medium with a saturated solution having a concentration of approximately 0.08 mM [136].

To address the problem of slow adsorption due to the inability to increase the bulk adsorbate concentration, a new adsorbate was sought. Since AQDS was similar to PQ in terms of structure and was shown to obey a Langmuir isotherm on platinum [96], it was considered. In an effort to characterize AQDS adsorption on GC, it was necessary to determine if a Langmuir isotherm was obeyed and if monolayer coverage was achieved from the dilute solution concentrations employed to minimize diffusion currents. Figure 20 shows a typical AQDS voltammogram obtained at a scan rate of 100 mV/s on laser irradiated GC-20. Note that the peak separation is less than 8 mV and that the formal potential is at approximately -0.08 V vs. Ag/AgCl. For a nernstian reaction under Langmuir isotherm conditions the peak separation is 0.0 mV [40]. A non-zero peak separation implies that either the reduced or oxidized form of the adsorbate is more strongly adsorbed or the kinetics are slow [40]. The supporting electrolyte employed was 1 M HClO₄ but similar results are observed in 1 M HCl. To verify that a Langmuir isotherm was obeyed, bulk AQDS concentrations in the range from 10⁻⁸ to 10⁻⁵ M were used in either 1 M HCl or 1 M HClO₄.

Adsorption onto GC-20 was monitored using cyclic voltammetry until equilibrium coverage was reached. Cyclic voltammograms were recorded every five minutes and the area under the reduction peak above the capacitive background was integrated to determine the total excess surface charge. The
Figure 20

Cyclic voltammogram of $10^6$ M AQDS (Bulk Concentration) adsorbed onto laser irradiated GC-20. The scan rate employed was 100 mV/s.
Current (µA)

Potential (V vs. Ag/AgCl)

Figure 20
excess surface charge was then used in Equation 12 to calculate \( \Gamma \), the surface excess in moles/cm\(^2\). The results are shown in Figure 21. The top plot shows \( \Gamma_{AQDS} \) as a function of the bulk AQDS concentration. A plateau occurs in the range from \( 1 \times 10^{-4} \) to \( 1 \times 10^{-5} \) M implying that saturation coverage is reached for any bulk concentration in this range with the time required for saturation coverage decreasing as the bulk concentration increases. These results were desired since voltammetry at low bulk AQDS concentration would neglect diffusion currents. Thus, when AQDS at \( 10^{-5} \) M, and a redox couple at 1 mM would be in solution together, the diffusion current from the redox system would greatly exceed that from AQDS.

The bottom plot of Figure 21 shows \( C^b/\Gamma_{eq} \) vs. the bulk AQDS concentration. If a Langmuir isotherm is obeyed, then this plot should be linear over a wide concentration range. This is the case in the bottom plot implying that AQDS obeys a Langmuir isotherm on GC. Similar saturation coverages, \( \Gamma_{sat} \), are observed \( 1 \) M KCl, \( 1 \) M LiCl, and \( 1 \) M NH\(_4\)Cl with \( \Gamma_{sat} \) being \( 218 \pm 20, 232 \pm 15, \) and \( 227 \pm 18 \) pmoles/cm\(^2\) respectively. The adsorption isotherms in these supporting electrolytes were also obtained for bulk AQDS concentrations in the range of \( 5 \times 10^{-8} \) to \( 1 \times 10^{-5} \) M. Observed saturation coverage was 228 pmoles/cm\(^2\) for \( C^b \) in the range from 0.5 \( \mu \)M to 10 \( \mu \)M; the calculated saturation coverage was 232 pmoles/cm\(^2\) assuming flat adsorption. Thus, AQDS obeys a Langmuir isotherm on laser irradiated GC surfaces at low bulk concentrations, and monolayer coverage is achieved for a wide concentration range suggesting that
Figure 21

$\Gamma_{AQDS}$ as a function of $C^b$ and $C^b/\Gamma_{AQDS}$ as a function of $C^b$ on laser irradiated GC-20. All solutions were prepared in 1 M HCl.
Figure 21
\( \Gamma_{AQMS} \) as a function of \( C_b \) on laser irradiated GC-20. All solutions were prepared in 1 M HCl.
Figure 22
AQDS is a better choice for an adsorbate than PQ for the conditions required.

Similar studies were performed for AQMS. Figure 22 shows $\Gamma_{AQMS}$ as a function of the bulk AQMS concentration. From the plot, one may extract the saturation coverage which is 240 pmoles/cm$^2$ and Langmuirian behavior was observed over the same concentration range as AQDS.

Results

The effects of an adsorbed monolayer on the observed heterogeneous electron transfer rate constant were probed using IrCl$_6^{2/3}$, Fe(CN)$_6^{3/-4}$, and Ru(NH$_3$)$_6^{2+/3}$ in various supporting electrolytes. The redox couples were used by others as models for outer sphere electron transfer and it is hypothesized that an intervening monolayer should have minimal effects on the observed heterogeneous electron transfer rate constant at glassy carbon electrodes. All solutions consisted of one of the above redox couples at millimolar concentrations, and either AQDS or AQMS at millimolar concentrations, in the appropriate supporting electrolyte. Figure 23 shows the kinetic results for IrCl$_6^{2/3}$ on fractured GC surfaces after monolayer coverage of the electrode by AQDS. In Figure 23A the bulk AQDS concentration was 5 mM and in Figure 23B it was 2 µM. Increasing the bulk AQDS concentration decreased the time required to obtain equilibrium coverage by about a factor of 30. Thus, equilibrium coverage for the 5 mM AQDS solution occurred in less than a second. Since the results were virtually identical for different bulk AQDS concentrations, the extra time required
Figure 23

Electrode kinetics for iridium hexachloride kinetics (1 M HCl) as a function of solution exposure time on laser irradiated glassy carbon surfaces before and after the adsorption of AQDS. Figure A is for an AQDS bulk concentration of 5 mM and figure B is for a bulk concentration of 2 μM.
Figure 23
to reach equilibrium for the 2 μM AQDS solution did not result in any apparent contamination of the electrode surface by extraneous solution or airborne impurities. However, in order to avoid the possibility of surface contamination with long adsorption times, and to minimize the decay observed in $k_{\text{obs}}$ with time, a 5 mM solution of AQDS was used in all experiments. This will assure that the monolayer will be formed almost immediately after pretreatment or fracturing of the electrode surface, and lessen the chance of surface passivation with time.

In both Figures 23A and 23B, the decay of $k_{\text{obs}}$ after an hour had lapsed was lower when AQDS was in the solution. Figure 24 shows results for a similar experiment except the surface was laser irradiated as opposed to fractured. The results are very similar to those obtained for the fractured surface. Figures 24A and 23B show kinetics as a function of time for IrCl$_6^{2/-3}$ when the bulk AQDS concentration is 5 mM and 5 μM respectively. When the data in Figures 23 and 24 are compared, one notices that although the decays after an hours exposure to the solution are similar, the decay rate is greater for the laser irradiated surface, Figure 24. The decrease in $k_{\text{obs}}$ after AQDS adsorption is about 50% for both the laser irradiated and fractured surfaces.

Rate constants measured for IrCl$_6^{2/-3}$, Fe(CN)$_6^{3/-4}$, and Ru(NH$_3$)$_6^{2/-3}$ are summarized in Table 6. All values of $k_{\text{obs}}$ specified in the table are for the initial surfaces prior to any passivation and for adsorbate concentrations of 5 mM. For AQDS adsorption, data are also shown in Table 6 using LiCl as a supporting electrolyte. In this case, the values for $k_{\text{obs}}$ are much lower than the values
Figure 24

Electrode kinetics for iridium hexachloride kinetics (1 M HCl) as a function of solution exposure time on fractured glassy carbon surfaces before and after the adsorption of AQDS. Figure A is for an AQDS bulk concentration of 5 mM and figure B is for a bulk concentration of 2 µM.
Figure 24
Table 6: Observed heterogeneous electron transfer rate constants for the three redox systems investigated. Scan rates employed were 400 V/s for IrCl$_6^{3/3}$, 100 V/s for Fe(CN)$_6^{3/4}$, and 10 V/s for Ru(NH$_3$)$_6^{2+/3}$. AQDS and AQMS concentrations were 5 mM. Rate constants were determined by the method of Nicholson [41]. For all data, at least 10 separate experiments were performed. Statistics were given in Table 3. GU = Guanidine hydrochloride. Units for $k_{obs}$ are cm/s.

<table>
<thead>
<tr>
<th></th>
<th>$k_{obs}$</th>
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<tr>
<td></td>
<td>POL LAS FRA</td>
<td>LAS FRA</td>
<td>LAS FRA</td>
</tr>
<tr>
<td>POL LAS FRA (NO ADSORPTION)</td>
<td>0.14 0.50 0.55</td>
<td>0.24 0.26</td>
<td>0.08 0.08</td>
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<tr>
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<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>POL LAS FRA (AQMS)</td>
<td>0.25 0.08 0.08</td>
<td></td>
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<tr>
<td>IrCl$_6^{2/3}$</td>
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<tr>
<td>(1 M HCl)</td>
<td>0.02 0.50 0.50</td>
<td>0.05 0.02</td>
<td>0.02 0.02</td>
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<tr>
<td>(1 M LiCl)</td>
<td>0.001 0.13 0.18</td>
<td>0.05 0.01</td>
<td>0.02 0.002</td>
</tr>
<tr>
<td>(1 M NH$_4$Cl)</td>
<td>0.19 0.30 0.27</td>
<td>0.04</td>
<td></td>
</tr>
<tr>
<td>(1 M GU HCl)</td>
<td>0.15 0.25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe(CN)$_6^{3/4}$</td>
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<tr>
<td>(1 M KCl)</td>
<td>0.62 0.70 0.27</td>
<td>0.73 0.30</td>
<td>0.69 0.23</td>
</tr>
<tr>
<td>(1 M LiCl)</td>
<td>0.19 0.24 0.16</td>
<td>0.25 0.16</td>
<td>0.25 0.17</td>
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<tr>
<td>(0.5 M KCl)</td>
<td>0.13 0.12 0.12</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(50 mM K$_2$PF$_6$)</td>
<td>0.03 0.04</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(50 mM NH$_4$PF$_6$)</td>
<td>0.03 0.03 0.02</td>
<td>0.02 0.02</td>
<td>0.02 0.01</td>
</tr>
</tbody>
</table>

GU = Guanidine hydrochloride. Units for $k_{obs}$ are cm/s.
obtained when HCl was used. In all cases, for IrCl$_6^{2/-3}$, adsorption of AQDS did not affect $k^{\text{obs}}_\text{obs}$ by more than 50%.

The effects of surface charge due to the adsorbate were also investigated for IrCl$_6^{2/-3}$ in 1 M HCl using AQMS as the adsorbate. These data are summarized in Table 6. Adsorption of AQMS affected $k^{\text{obs}}_\text{obs}$ for IrCl$_6^{2/-3}$ to a greater extent than adsorption of AQDS for both laser irradiated and fractured surfaces. The intervening AQMS monolayer caused a decrease in $k^{\text{obs}}_\text{obs}$ by a factor of five over the value for AQDS adsorption.

Similar experiments using AQMS in place of AQDS were performed for Fe(CN)$_6^{3/-4}$ in 1 M KCl. Figure 25 depicts Fe(CN)$_6^{3/-4}$ kinetics as a function of time after laser irradiation in a solution containing 0.5 mM AQDS in various supporting electrolytes, and Figure 26 shows similar data except that AQMS, 0.5 mM is substituted for AQDS. Referring to Figure 25, $k^{\text{obs}}_\text{obs}$ in all cases decreased after AQDS adsorption when compared to the results obtained in the absence of AQDS, shown Figure 18. Also the trend observed in Figure 18 for $k^{\text{obs}}_\text{obs}$ as a function of supporting electrolyte cation is maintained after AQDS adsorption; that is $k^{\text{obs}}_\text{obs}$ decreases significantly with the identity of the supporting electrolyte cation in the order $K^+$, $NH_4^+$, $Li^+$. In fact, $k^{\text{obs}}_\text{obs}$ decreased by greater than a factor of 10 for KCl after laser irradiation and by about a factor of 2 and 5 for LiCl and $NH_4Cl$ respectively once AQDS had been adsorbed. These data are also summarized in Table 6. In all cases presented in Figure 25, the decay obtained after 40 minutes of solution exposure time was dependent on the supporting
Figure 25

$k_{\text{obs}}$ vs. time for Fe(CN)$_6^{3/-4}$ and AQDS on laser irradiated GC-20 in various supporting electrolytes.
Figure 25

Solution Exposure Time (min.)

$k_0^{obs}$ (cm/s)

- **KCl**
- **LiCl**
- **NH₄Cl**

5 mM Fe(CN)$_6^{3/-4}$
0.5 mM AQDS
Figure 26

$k_{\text{obs}}$ vs. time for Fe(CN)$_{6}^{3/4}$ and AQMS on laser irradiated GC-20 in various supporting electrolytes.
Figure 26

$5 \text{ mM Fe(CN)}_{6}^{3-/4}$

$0.5 \text{ mM AQMS}$

$KCl$

$LiCl$

$k_{obs}^{o} \text{ (cm/s)}$

Solution Exposure Time (min.)
electrolyte, and it appeared as if K$^+$ and Li$^+$ ions had a greater effect on the decay than NH$_4^+$ ions. The effects that AQDS had on the kinetics of Fe(CN)$_6^{3/4}$ were greater than the effects AQDS had on IrCl$_6^{2/-3}$ kinetics. The observed rate constants for IrCl$_6^{2/-3}$ (1 M HCl) and Fe(CN)$_6^{3/4}$ (1 M KCl) on laser irradiated and fractured surfaces with the addition of AQDS decreased by factors of 2 and 10 respectively. In the case where LiCl was used as the supporting electrolyte, Fe(CN)$_6^{3/-4}$ rates after AQDS adsorption were virtually identical to the values obtained for Fe(CN)$_6^{3/4}$ in 1 M KCl after AQDS adsorption, Figure 25.

When AQMS was substituted for AQDS, Fe(CN)$_6^{3/-4}$ kinetics were monitored in KCl and LiCl only. These data agree with the AQDS results when KCl is the supporting electrolyte. However, when LiCl is used, $k_{\text{obs}}^0$ for the fractured surface is ten times lower than the corresponding value obtained in KCl. The decay in $k_{\text{obs}}^0$ with time after AQMS adsorption is depicted in Figure 26 for KCl and LiCl as supporting electrolytes. When KCl is used, decay in $k_{\text{obs}}^0$ occurs for only five minutes then a limiting value is reached. The limiting value of $k_{\text{obs}}^0$ is 50% of the initial value after laser irradiation. When the supporting electrolyte was LiCl no significant changes were observed in $k_{\text{obs}}^0$ after laser irradiation and AQMS adsorption. In fact, $k_{\text{obs}}^0$ remained constant over the experiment length of an hour.

Thus far the redox couples investigated have been negatively charged inorganic complex ions. The use of a negatively charged redox couple along with a negatively charged adsorbate may result in a repulsion effect and a decrease in
for such redox systems. To study the effects of a negatively charged adsorbate on the kinetics of a positively charged redox species, AQDS and AQMS were once again employed as adsorbates and the Ru(NH₃)⁶²⁺/³⁺ couple was used for kinetic measurements. Referring back to Table 6, adsorption of AQDS and AQMS have an almost negligible effect on $k_{\text{obs}}^0$ for both laser irradiated and fractured surfaces when either 1 M KCl or 1 M LiCl were employed as supporting electrolytes for Ru(NH₃)⁶²⁺/³⁺. These results are unexpected since a monolayer of an adsorbate should in theory hinder electron transfer. There is a supporting electrolyte cation dependence as shown by the KCl and LiCl data in Table 6. Rate constants were lower in LiCl as was the case when there was no intentional adsorption. Data obtained in NH₄PF₆ also showed no changes in $k_{\text{obs}}^0$ after adsorption of either AQDS or AQMS with the exception that $k_{\text{obs}}^0$ was lower by a factor of 5. Since iR effects may be present in this solution because of the low supporting electrolyte concentration, these rate constants may not be completely reliable.

**Conclusions**

The kinetics of three redox systems were investigated on polished, laser irradiated, and fractured glassy carbon surfaces in order to assess the behavior of redox system hypothesized to undergo heterogeneous electron transfer by an outer sphere mechanism. With the information from Chapter 2 regarding surface structure and how it is altered upon laser irradiation and fracturing, it was
possible to investigate the changes in $k_{\text{obs}}$ and to attempt to deduce the mechanism by which changes in $k_{\text{obs}}$ occur. If these systems behave as though electron transfer were occurring via an outer sphere mechanism, then theoretically the electron transfer should be independent of the electrode material, and any changes observed should be indicative of alterations or modifications in the state of the electrical double layer or electrode surface.

Several authors have attempted to explain the behavior of electron transfer reactions on carbon electrodes. Some of these explanations include surface oxide effects, tunneling, local and solution pH effects, solution viscosity, hydrophobicity of the carbon surface, cation hydration of the supporting electrolyte, electrostatics, and bridging via a solution ion. All are possibilities depending on the conditions and the pretreatment procedure employed and in each case, the double layer is altered and significant changes in $k_{\text{obs}}$ usually result.

Two decay mechanisms are possible for $k_{\text{obs}}$ when a redox species is in solution with an adsorbate. The decay observed is a convolution of the transient decay in $k_{\text{obs}}$, whose origin is not well understood, and the decay which results as a function of surface coverage by the adsorbate. Since a decay in $k_{\text{obs}}$ occurred with time, it was not possible to monitor $k_{\text{obs}}$ for the three redox couples as a function of surface coverage. Instead, the AQDS or AQMS bulk concentration was high enough (5 mM) to attain monolayer coverage in under a minute.

For the three redox couples investigated, it was concluded that IrCl$_6^{2/3}$ and Ru(NH$_3$)$_6^{2+/3}$ kinetics were not greatly altered after an intentional monolayer was
adsorbed to the carbon surface. However, this was not the case for Fe(CN)$_6^{3/4}$ kinetics. Rate constants, from Table 6, decreased by factors of two, zero, and one hundred for IrCl$_6^{2/3}$, Ru(NH$_3$)$_6^{2+/3}$, and Fe(CN)$_6^{3/4}$ respectively on laser irradiated GC surfaces after an intentional monolayer was adsorbed.

For the IrCl$_6^{2/3}$ couple, the fact that the rate constant decreased only by a factor of two, after monolayer adsorption of AQDS, implies that the electron transfer mechanism does not change with substantial changes in surface condition. Although there was an effect due to the supporting electrolyte cation identity on $k_{obs}^o$ after adsorption, the trend observed for the decrease in $k_{obs}^o$ after monolayer coverage of AQDS, in KCl and LiCl, was virtually identical to the results obtained in a HCl medium. Since monolayer adsorption, of AQDS, does not greatly affect $k_{obs}^o$ for IrCl$_6^{2/3}$, it is likely that these changes could be accounted for by as cation hydration or local pH effects.

Since IrCl$_6^{2/3}$ is a negatively charged species, one would expect $k_{obs}^o$ to be influenced by a charged adsorbate. In particular, $k_{obs}^o$ should be greater if the adsorbate is AQMS as opposed to AQDS since AQDS has a negative charge which is twice that of AQMS. Also, since both AQDS and AQMS have similar monolayer coverages on GC electrodes, the excess negative surface charge should be greater for AQDS after adsorption. This being the case, $k_{obs}^o$ for IrCl$_6^{2/3}$ is expected to be greater when AQMS is adsorbed. This is not the case however, as demonstrated by the results in Table 6. AQMS adsorption decreased $k_{obs}^o$ by a factor five while AQDS decreased $k_{obs}^o$ by a factor of two. This is evidence
which does not favor an electrostatic mechanism. Thus, one of the other mechanisms is probably responsible for the decrease.

The Ru(NH$_3$)$_6^{2+/3}$ couple is also not as sensitive to the surface condition of GC electrodes as Fe(CN)$_6^{3-/4}$ although it is sensitive to the identity and concentration of the supporting electrolyte. The redox couple behaves similarly when either AQDS or AQMS is adsorbed to the surface implying that $k_{\text{obs}}^o$ is not dependent on surface charge. The observation that $k_{\text{obs}}^o$ is slower on a fractured surface implies that surface oxides may be important for electron transfer for this redox couple; however, once the surface is covered with a monolayer of AQDS or AQMS this sensitivity appears to be eliminated.

The only redox couple which exhibited extreme sensitivity to the GC surface conditions was Fe(CN)$_6^{3-/4}$. The rate constants measured in the presence of a monolayer of adsorbed AQDS are smaller than those obtained on a bare electrode. Also, these rate constants have been decreased further than would be anticipated based on a tunneling argument. If tunneling through an adsorbed monolayer were a pathway for electron transfer then Equation 17 should apply

$$ (k_{\text{obs}}^o)_{\text{ads}} = k_{\text{obs}}^o e^{-\beta r} $$

where $(k_{\text{obs}}^o)_{\text{ads}}$ is the observed rate constant after adsorption, $k_{\text{obs}}^o$ is the observed rate constant without adsorption, $\beta$ is an estimated parameter, taken as 0.72 Å$^{-1}$ [137], and $r$ is distance between the donor and acceptor [137-140]. In the case where flat adsorption occurs, the value of $r$ is between 2 to 3 Å which is the distance of a p-orbital. If tunneling were all that mattered for the reduction of
k^\text{obs}_\text{after monolayer adsorption then } k^\text{obs}_\text{should only decrease by at most a factor of 3 if the above numbers are used in equation 17. Since } k^\text{obs}_\text{for Fe(CN)}_{\text{6}}^{3/4}\text{ decreases by a factor of 100 after adsorption, one may conclude that tunneling is not the only mechanism which is influencing electron transfer for } \text{Fe(CN)}_{\text{6}}^{3/4}\text{. This leads one to hypothesize that } \text{Fe(CN)}_{\text{6}}^{3/4}\text{ is surface sensitive and the mechanism responsible for increases in } k^\text{obs}_\text{after surface pretreatment and intentional adsorption are more complicated that previously believed. The data presented in this chapter confirm that } \text{Fe(CN)}_{\text{6}}^{3/4}\text{ kinetics do not abide by an outer sphere electron transfer mechanism on GC electrodes.}

If an adsorbed monolayer is representative of surface impurities or contamination, then it is apparent from the data presented that } \text{Fe(CN)}_{\text{6}}^{3/4}\text{ kinetics are extremely sensitive to impurities on the electrode surface while } \text{Ru(NH}_3)_6^{2+/3}\text{ and } \text{IrCl}_6^{2-/3}\text{ kinetics are less sensitive. This conclusion is consistent with the conclusion from Chapter 2 which stated that for a laser irradiated surface, cleanliness is important in order to obtain a large heterogeneous electron transfer rate constant for } \text{Fe(CN)}_{\text{6}}^{3/4}\text{.}

**CHAPTER SUMMARY**

Many of the factors which affect electron transfer at glassy carbon electrodes should not influence outer sphere redox systems to a great extent. Increases in } k^\text{obs}_\text{after intentional surface pretreatment are the result of
modifications to the surface due to cleaning, roughening, restructuring, or any combination of the three. When monitoring the change in $k_{obs}$ with time as opposed to remaining constant with time after pretreatment. However, this is not the case on glassy carbon electrodes as was demonstrated for the three redox couples whose electron transfer was believed to be outer sphere. Observations from Figures 17, 18, and 19, depict transient decays for these redox couples which reach a limiting value after about an hour. It was not possible to retard this decay on polished or laser irradiated GC surfaces, but for IrCl$_6^{2/3}$ kinetics in 1 M HCl, the decay was retarded for about three minutes on a fractured surface. This is not clearly depicted in Figure 23 because of the scale used for the time axis.

Tables 3 and 6 summarize the measured values of electron transfer rate constants for the three redox couples investigated on polished then laser irradiated and fractured surfaces before and after monolayer adsorption of wither AQDS or AQMS. Table 3 also lists the theoretical rate constant which should be observed as predicted by Marcus theory according to Equation 10. Also shown in Table 3 are the values for $k_{sec}$, the homogeneous self exchange rate constant, which are different for each redox couple, hence the predicted rates are distinct. The measured rate constants were smaller than those calculated from Marcus theory for all systems studied.

The effects of cleanliness on $k_{obs}$ can best be observed from the Fe(CN)$_6^{3/4}$ data. From Table 6 and Figure 18 it is apparent that $k_{obs}$ is dependent on the supporting electrolyte. One interesting feature from Figure 18 is that when GU
HCl and NH₄Cl are used as supporting electrolytes then k_{obs} is relatively large and the decrease in k_{obs} with time is smaller. One explanation is that GU HCl is known to decrease the hydrophobic interactions of materials allowing hydrophilic redox couples to interact with a usually hydrophobic surface. If this is true, then the distance of closest approach is altered and k_{obs} is thus modified. Another possibility is that GU HCl, since it causes organics to become more soluble, is solubilizing the surface debris on carbon, hence effectively cleaning the electrode surface. Thus, once again, removal of surface impurities is the important factor which influences electron transfer.

Adsorption of a monolayer helped provide insight about the outer sphere electron transfer nature of the three redox couples. Although each couple shows some dependence on the identity of the supporting electrolyte, after adsorption the changes in k_{obs} should only be a function of the intervening monolayer. The rate constant after adsorption is not diminished greatly for Ru(NH₃)₆²⁺/³⁺ or IrCl₆²⁻/³⁻, but k_{obs} is greatly reduced for Fe(CN)₆³⁻/⁴⁻. This suggests that Fe(CN)₆³⁻/⁴⁻ is not behaving as an outer sphere electron transfer redox system on laser irradiated or fractured GC after the surface had been intentionally coated by an adsorbate. The kinetics of Fe(CN)₆³⁻/⁴⁻ appear to be complicated since the redox couple appears to be sensitive to the condition of the GC surface. In particular, Fe(CN)₆³⁻/⁴⁻ kinetics are extremely sensitive to surface contaminants. The other two couples do not seem to be greatly affected by the adsorbed monolayer and thus are not as sensitive to the surface conditions or to surface contaminants. Hence,
IrCl$_6^{2/-3}$ and Ru(NH$_3$)$_6^{2/-3}$ kinetics behave as though an outer sphere electron transfer mechanism was obeyed on GC electrodes while Fe(CN)$_6^{3/-4}$ kinetics depict more complex behavior.
CHAPTER IV

OBSERVATION OF OXYGEN EFFECTS ON ELECTRON TRANSFER KINETICS

Background

Electrochemical oxygen reduction is an significant reaction and it is of theoretical and practical interest because of its importance for energy conversion and industrial electrolysis. The practical importance of such an electrode process, as the anodic evolution of chlorine and oxygen, can hardly be overemphasized. In some instances, oxygen evolution is an unavoidable side reaction in many anodic processes; moreover, it is the most common anodic reaction coupled with most of the cathodic processes occurring in aqueous solutions. Thus, in most instances, oxygen interferes with electrochemical measurements. In this case, the intent is the removal of oxygen, and in many cases, the appropriate selection of the electrode material is a prerequisite for the optimization of the electrolysis parameters.

Because it is chemically reactive with various substances and electrochemically reducible, oxygen is usually excluded or removed from experiments. This is generally accomplished by degassing, deaerating,
deoxygenating, spraying, or evacuating. Deaerating and deoxygenating effectively result in purging the electrochemical cell with an inert gas such as argon, nitrogen, or helium and then maintaining a slight positive pressure of the inert gas over the solution. Usually a purging gas is favored which is more dense than air so that a blanket of inert gas will cover the solution and minimize the amount of atmospheric oxygen which will redissolve. Argon is an example of such a gas. Degassing implies the use of a vacuum technique to remove dissolved oxygen and then venting the gas to the atmosphere. The introduction of a chemical reducing agent to a sealed system may also aid in the removal of oxygen; however, this procedure is seldom used since the reducing agent may interfere with the redox couple under investigation. For voltammetric work, the presence of oxygen interferes because of its reducibility and usually purging the system with an inert gas is satisfactory. This procedure is capable of reducing the oxygen content in the electrochemical cell atmosphere to as low as 20 parts per million (ppm). This concentration is usually adequate and at this level oxygen does not usually interfere with the electrochemistry; however, care must still be taken since certain aqueous species, such as Cr$^{2+}$, react rapidly with oxygen at this concentration. Hence, an atmospheric concentration of 20 parts per million is unsuitable in this instance.

Care must also be incorporated in the selection of the inert purging gas. Not only is the choice dependent on cost but more importantly on how much dissolved oxygen is present. Gases purchased in tanks always contain some
dissolved oxygen and using these gases will inevitably not eliminate all the oxygen in a cell, and in certain circumstances introduce oxygen into the cell environment. Nitrogen is the most common deaerating inert gas used since it is the cheapest and it is amply available in a prepurified grade that contains less than 20 parts per million oxygen. If this concentration of oxygen is unacceptable, residual oxygen may be removed by bubbling the inert gas through an aqueous solution of vanadous or chromous ions [141]. Oxygen may also be reduced to a concentration of less than a part per million in solution if a BTS (Badische Anilin und Soda-Fabrik) catalyst in conjunction with molecular sieves is employed [142]. This method involves the use of a catalyst in conjunction with molecular sieves to trap and remove oxygen dissolved in solution. Next the purified oxygen free inert gas, nitrogen or argon, is saturated with the solvent of interest in a gas cylinder that is filled with a solution identical to the test solution. As a last resort, the entire electrochemical and experimental apparatus may be situated in a glove box whose environment has been purged of oxygen and water.

This research presented in this chapter studies the effects of atmospheric oxygen and surface oxides on $k_{obs}^o$ for $\text{IrCl}_6^{2/3}$ and $\text{Fe(CN)}_6^{3/4}$ on glassy carbon electrodes and their relationship. In particular, the interest focuses on changes observed in $k_{obs}^o$ with time and electrode condition due to the possibility of surface oxidation as a result of increasing the solution oxygen concentration.
EXPERIMENTAL

Electrode fabrication, laser irradiation, fracturing of the electrode surface, and voltammetric measurements were described in Chapter 2. Solutions of redox species were 1 mM unless otherwise noted, and potentials were measured against a BAS Ag/AgCl (3 M NaCl) reference electrode. Rate constants were calculated as described in Chapter 2 by the method of Nicholson. Solutions were oxygenated via a similar procedure used for deaerating. This was accomplished using prepurified oxygen (Linde specialty gases) and teflon tubing was used to deliver the oxygen to the cell prior to obtaining voltammetry. Oxygen was bubbled into the solutions for at least 15 minutes at a moderate flow rate prior to obtaining any voltammetry.

RESULTS

Data was obtained for the IrCl$_6^{2/3}$ couple since results from Chapter 3 suggested that $k_{obs}$ for this redox species was only slightly sensitive to the surface state as compared to the Fe(CN)$_6^{3/4}$ couple. Figure 27 shows a plot of $k_{obs}$ as a function of solution exposure time for IrCl$_6^{2/3}$ in 1 M HCl. The results for the deaerated solution are comparable to those obtained in Chapter 3. When voltammetry was obtained before deaerating, the values for $k_{obs}$ were significantly smaller than the values obtained for the deaerated solutions. The results are
Figure 27

$k_\text{obs}$ as a function of solution exposure time for IrCl$_6^{2/-3}$ in 1 M HCl. The solution was deaerated with nitrogen (solid line, circles) as well as oxygenated (dotted line, squares), and not deaerated (dashed line, triangles). The surfaces were polished then laser irradiated with three 25 MW/cm$^2$ pulses.
Figure 27

- deaerating
- no deaerating
- \( O_2 \) sat.
shown Figure 27. Following this, the electrode was repolished and the sequence was repeated except that the solution was saturated with oxygen prior to laser irradiation. The data for each series were obtained on freshly irradiated surfaces so that no cumulative effects would be observed.

The results from Figure 27 show the initial value of $k_{\text{obs}}$ after laser irradiation is dependent on the amount of oxygen dissolved in the solution. In fact, the initial $k_{\text{obs}}$ decreases as the amount of dissolved oxygen increases. The decay reached for the deaerated solution was 0.2 cm/s, as was shown in Chapter 3 and in Figure 27, and it was reached after 40 minutes of solution exposure time. In comparison, the decay reached after an hour of solution exposure was similar for the deaerated, non-deaerated and the oxygenated solutions; however, it was reached more quickly for the oxygenated solution. That is, the value of 0.2 cm/s was achieved after 5 minutes of solution exposure time for the non-deaerated and oxygenated solutions. Also, no significant decreases below the value of 0.2 cm/s were observed over an hour.

Additional Nd:YAG pulses were also delivered to the electrode in the oxygenated and deaerated solutions to observe whether these added effects would increase $k_{\text{obs}}$. In Figure 28 $k_{\text{obs}}$ is plotted against exposure time and total number of Nd:YAG pulses for the deaerated and oxygenated solutions. Initially, after laser irradiation, $k_{\text{obs}}$ was 0.23 cm/s and remained relatively constant over the course of an hour. Further laser irradiation after the hour had elapsed produced no further change in $k_{\text{obs}}$. Also, repeating the procedure once more, until a total
Figure 28

$k_{obs}$ as a function of solution exposure time and 25 MW/cm² Nd:YAG pulses. The IrCl$_{2/3}$ solution was deaerated (circles) and saturated with O$_2$ (triangles) prior to irradiation. The arrows apply to both deaerated and oxygenated solutions.
Figure 28
of nine pulses had been delivered to the electrode surface, resulted in no change in \( k_{\text{obs}} \). The decay reached after an hour was 0.2 cm/s, and it appeared to be the lowest value obtained for \( k_{\text{obs}} \) even after exposure to oxygen.

Rate constants for Fe(CN)\(_{6}^{3/4}\) in 1 M KCl were next measured after oxygenating the solution and the results shown in Figure 29, were similar to those for IrCl\(_{6}^{2/3}\) in 1 M HCl. The initial \( k_{\text{obs}} \) appeared to be sensitive to the amount of oxygen dissolved in the solution. Not deaerating the solution prior to obtaining voltammetry produced \( k_{\text{obs}} \) values which were intermediate between deaerating and oxygenating. The decay reached after exposure to the solution for an hour also did not vary with the amount of dissolved oxygen. The limits reached were 0.18 cm/s, 0.20 cm/s, and 0.10 cm/s for deaerated, non deaerated, and oxygenated solutions respectively. Although this difference in \( k_{\text{obs}} \) is not larger, \( k_{\text{obs}} \) for the oxygenated solution appears to be lower than that of the other two solutions.
Figure 29

$k_{\text{obs}}^0$ as a function of solution exposure time for Fe(CN)$_6^{3/4}$ in 1 M KCl.
The solution was deaerated with nitrogen (solid line, circles) as well as oxygenated (dotted line, squares), and not deaerated (dashed line, triangles). The surfaces were polished then laser irradiated with three 25 MW/cm$^2$ pulses.
Figure 29
DISCUSSION AND CONCLUSIONS

The data for IrCl$_6^{2/-3}$ in Figure 27 demonstrates that oxygen dissolved in the solution significantly affects the rate constant, $k^o_{\text{obs}}$, initially after laser irradiation. Based on information from Lange's Handbook, the concentration of O$_2$ which is soluble in water at 25 °C is 1.22 mM; this corresponds to 39.3 parts per million [143]. Thus, the O$_2$ saturated solution contains no more than 39.3 parts per million oxygen. The deaerated solution contains much less than 39.3 ppm oxygen; in fact, a properly deaerated solution contains less than 20 ppm oxygen in the atmosphere above the liquid implying that much less oxygen is dissolved in solution. The non deaerated solution shows an initial $k^o_{\text{obs}}$ value which is intermediate to those of the deaerated and saturated solutions. Apparently this level of oxygen is sufficient to cause a decrease in the initial value of $k^o_{\text{obs}}$.

Oxidation of the carbon surface is a likely explanation for the observed effects. If the excess oxygen passivates the surface by oxidation, then $k^o_{\text{obs}}$ would be expected to decrease for a redox couple which is not dependent on surface oxides for rate enhancement. This is exactly the case for IrCl$_6^{2/-3}$. The oxide independence on $k^o_{\text{obs}}$ enhancement was discussed in Chapter 3 and is due to the fact that similar observed rates and decays are observed for both laser irradiated and fractured surfaces. The decrease in the initial $k^o_{\text{obs}}$ after saturating the solution with oxygen, is a direct result of the excess oxygen dissolved in the solution. Also, it is possible that the heat generated by irradiating the surface is causing a
reaction which involves formation of surface oxides. Since predicted surface temperatures after irradiation at 25 MW/cm² are on the order of 3000 K, it is possible the GC surface is oxidized in the presence of dissolved oxygen.

Since the decay after an hour of solution exposure for $k_{obs}^o$ is not dependent on the oxygen content of the solution, it is possible that formation of surface oxides are responsible for the decay observed in $k_{obs}^o$. From Figure 28, it is also demonstrated that repetitive laser irradiation does not improve $k_{obs}^o$ for an oxygenated solution over the value of 0.22 cm/s obtained initially; however, the deaerated solution shows increases in $k_{obs}^o$ after laser irradiation. Thus, it would appear as though further laser irradiation is not capable of removing the effects of the oxygen on the GC surface. It is known that on various carbon materials the rate of surface oxide formation is temperature dependent with more surface oxides forming at higher temperatures and pressures [144-145]. Walker et al. [145] demonstrated a mechanism for oxygen chemisorption onto carbon surfaces at low oxygen pressures and temperatures and found a correlation between the amount of adsorbed oxygen and the surface temperature. Lower temperatures required more time for saturation coverage to be reached; however, oxygen adsorption was almost immediate. Thus, a thin oxide coating forms virtually instantaneously regardless of the amount of oxygen present or the temperature.

Attempts were made to remove any residual oxygen from the surrounding atmosphere by enclosing the laser activation apparatus in a glove box and purging the system with nitrogen. The decay in $k_{obs}^o$ after laser irradiation was
still present, and the results were identical to those obtained in Figures 27 and 29. Thus, it is concluded that it is difficult to completely remove oxygen from the surroundings, and since laser irradiation is performed in an aqueous medium, oxygen elimination becomes impossible.

Data for the Fe(CN)$_6^{3/-4}$ couple shown in Figure 29 also show a significant dependence on the amount of dissolved oxygen on the initial value of $k_{obs}$. In fact, the initial values for $k_{obs}$ for this couple are practically identical to those for the IrCl$_6^{2/-3}$ couple. This implies that oxygen is affecting both redox species similarly. The decay reached after solution exposure for an hour for Fe(CN)$_6^{3/-4}$ is also virtually identical for all three trials and to the values obtained for the IrCl$_6^{2/-3}$ data. This suggests that the dissolved oxygen is partially responsible for the observed decay in $k_{obs}$ with time. Laser induced heating may accelerate the rate of surface oxide formation. Also, since there is more oxygen dissolved in the non deaerated and oxygenated solutions, the rate of surface oxide formation should be increased. If this is the case, then $k_{obs}$ will decrease with increasing amount of dissolved oxygen.

Surface oxides may also affect $k_{obs}$ differently for negatively and positively charged redox couples. There is a known pH dependence on $k_{obs}$ at glassy carbon electrodes which has been shown to be a property of the carbon/solution interface [75]. The chemical origin of this pH effect was attributed to surface carboxyl functionalities [146-151]. The pH dependence of $k_{obs}$ was assumed to occur due to the association of protons with the carboxyl functional groups. From
this data, an apparent pK\textsubscript{a} of the GC surface was reported to be near 4.0 which is consistent with the pK\textsubscript{a} of carboxyl functionalities on carbon. Repulsive forces would exist between the negatively charged carboxyl functionalities and either the Fe(CN)\textsubscript{6}^{3/-4} or IrCl\textsubscript{6}^{2/-3} redox couples. This being the case, k\textsuperscript{o,obs} would be smaller for these redox couples in the presence of surface oxides.

The preliminary data presented in this chapter provided additional evidence to support a model for laser irradiation of polished GC surfaces which involves removal of surface impurities in order to observe increases in k\textsuperscript{o,obs}. Surface oxides may be considered to be unwanted chemisorbed impurities and the function of the laser is to remove these surface impurities. Also, since more oxygen is present in a saturated solution, laser irradiation in a medium which has additional oxygen should produce more surface oxides. This being the case, the GC surface would then contain more impurities, in the form of oxides, and k\textsuperscript{o,obs} would be sensitive to these modified surface conditions. In fact, k\textsuperscript{o,obs} should decrease with increasing surface coverage, as was concluded in Chapters 2 and 3. This is exactly what is observed when excess oxygen is incorporated into the solution containing the IrCl\textsubscript{6}^{2/-3} and Fe(CN)\textsubscript{6}^{3/-4} redox couples. The values for k\textsuperscript{o,obs} decrease as the amount of oxygen is increased with the oxygenated solution having the lowest initial k\textsuperscript{o,obs}. The oxide surface impurities are not affected by further laser irradiation implying that oxides apparently hinder k\textsuperscript{o,obs} to a greater extent than other types of impurities. This leads to a hypothesis that there are various types of surface impurity, of which oxides are only a subset, and each
The influence of oxygen and oxides on $k_{\text{obs}}$ may be related to the results obtained in Chapters 2 and 3. It was shown that among the surface variables that coverage by physisorbed or chemisorbed impurities was the most paramount factor influencing $k_{\text{obs}}$. Specifically, a surface which was covered with impurities had a slower heterogeneous electron transfer rate constant. Removal of these impurities by laser irradiation resulted in increases in $k_{\text{obs}}$ followed by a decay in $k_{\text{obs}}$ with time until a limiting value was reached. Deliberately beginning with a surface which had no intentional pretreatment history, in situ fracturing, produced similar results for $k_{\text{obs}}$. Since a decay in $k_{\text{obs}}$ with time also occurred for the fractured surface, it was hypothesized that impurities were responsible for this process. Removal of surface impurities also was shown to activate redox couples by different amounts. For example, $k_{\text{obs}}$ for Fe(CN)$_6^{3/4}$ in 1 M KCl increased by a factor of 100 over the value obtained for a polished surface after laser irradiation at 25 MW/cm$^2$ or fracturing. This increase was attributed to removal of physisorbed or chemisorbed impurities. In contrast, $k_{\text{obs}}$ for IrCl$_6^{2/3}$ (1 M HCl) only increased by a factor of 2 upon laser irradiation, and $k_{\text{obs}}$ for Ru(NH$_3$)$_6^{2/3}$ (1 M KCl) did not improve. These results demonstrated that the Fe(CN)$_6^{3/4}$ redox couple was more sensitive to the state of the GC surface than the other two
Furthermore, intentionally adsorbing an organic species (AQDS) onto the GC surface as a model for impurities, resulted in decreases in $k_{\text{obs}}$ for all three redox couples after laser irradiation or fracturing. However, the decrease in $k_{\text{obs}}$ was greater for $\text{Fe(CN)}_6^{3/4}$ than for the other redox couples. Thus, it was concluded that the redox couple which is most sensitive to the condition of the GC surface is also affected the most after an intentional impurity is adsorbed to the surface. It is also known that polished and laser irradiated surfaces contain chemisorbed oxides which are difficult to eliminate [2]. Suppose that oxide formation inhibits electron transfer and that oxides form more readily when a clean activated surface exists [2, 145]. If this were the case, then addition of excess molecular oxygen into a solution prior to laser irradiation would accelerate the formation of surface oxides. Also, the elevated surface temperature would promote the formation of a surface saturated with oxides on a shorter time scale [145]. Wightman et al. [108] showed that the redox couples investigated here were sensitive to the formation of surface oxides. However, once the surface was treated with a chemical reducing agent which converted the surface oxides to alcohols, only the $\text{Fe(CN)}_6^{3/4}$ couple maintained a pH dependence. This implied that the $\text{Fe(CN)}_6^{3/4}$ couple was sensitive to all forms of surface oxides and impurities. It is not surprising then that $\text{Fe(CN)}_6^{3/4}$ is the redox species which activates the greatest since it is also the species which is most sensitive to all forms of impurities on the GC surface.
In conclusion, the GC surface is a complex matrix in its raw form and intentional pretreatment is necessary prior to using the material as an electrode. Of the various available pretreatment procedures, one usually begins by polishing the surface then post treating by vacuum heat methods, rf-plasma methods, thermal pretreatment, electrochemical anodization, chemical reduction, and laser irradiation. The focus of this work has been to elucidate the mystery behind laser irradiation and to understand why electrochemical activation is occurring. It was concluded that low power density laser pulses, 25 MW/cm², were sufficient to activate the surface without inducing major microstructural and morphological alterations. In particular, the microscopic surface area did not greatly increase upon laser irradiation implying that the increases observed in $k_{obs}$ are not solely a function of increases in area. The microcrystallite size was not affected which indicated that the fraction of edge plane site also were not changing. All that remains is the removal of physisorbed or chemisorbed impurities. This result was validated after an intentional layer was adsorbed to the GC surface and $k_{obs}$ for three redox species was found to be dependent on the monolayer formed. The couple which was most sensitive to the initial state of the GC surface was also the couple which was most sensitive to the physisorbed monolayer. Intentionally forming more surface oxides by saturating the solution of interest with oxygen then laser irradiating also demonstrated that the redox couples were sensitive to chemisorbed impurities. Thus, surface cleanliness is the primary factor responsible for the majority of the increases observed in $k_{obs}$ and the observed
decay is probably a result of micromolar impurities of oxygen which adsorb to the GC surface and passivate the electrode toward heterogeneous electron transfer.
APPENDIX A

KINETICS OF IrCl$_6^{2/3}$ ELECTRON TRANSFER AS A FUNCTION OF PQ ADSORPTION

Background

The effects of an adsorbed monolayer had on the observed heterogeneous electron transfer rate constant were probed in Chapter 3 using AQDS and AQMS as the adsorbates and Fe(CN)$_6^{3/4}$, IrCl$_6^{2/3}$, and Ru(NH$_3$)$_6^{2+/3}$ as the redox couples. PQ was rejected as an adsorbate due to its slow adsorption with time at a bulk concentration of 1 μM and Langmuir behavior of PQ was questionable. However, data concerning electron transfer when the surface is blocked by a neutral adsorbate would be beneficial in determining surface interactions with redox species. If a Langmuir isotherm is obeyed, then surface coverage as a function of bulk PQ concentration should eventually become constant; this does not occur for PQ adsorption on GC surfaces. A possible explanation for this behavior is that interaction parameters need to be considered in order to model PQ adsorption on GC electrodes. Also, it is difficult to obtain solution concentrations of PQ which are greater than 2 μM since dimerization is known to occur [134], and
constructing an isotherm over a wide bulk concentration range is difficult since a saturated PQ solution is approximately 0.08 mM [136].

The effects of an adsorbed monolayer of PQ on the observed heterogeneous electron transfer rate constant were probed using IrCl$_6^{2/-3}$ in 1 M HCl since it was possible to monitor kinetics and adsorption from the same solution. The hope was to be able to monitor the decay in $k_{\text{obs}}^o$ as a function of surface coverage. Since Fe(CN)$_6^{3/-4}$ decomposes in an acidic medium, IrCl$_6^{2/-3}$ was used for kinetic determinations. Acidic pH values were desired since adsorption of PQ was performed from this medium as described in Chapter 2. The data presented in Table 7 suggests a region of $C_b$ between 0.2 $\mu$M and 1 $\mu$M which is fairly invariant, then a region beyond which shows an increase in $\Gamma_{\text{PQ}}$ as $C_b$ increases. These data are also shown graphically in Figures 30 and 31. Two decay mechanisms are possible for $k_{\text{obs}}^o$ if IrCl$_6^{2/-3}$ and PQ are in the same solution. These mechanisms are the passivation of the electrode surface with time and the decrease in $k_{\text{obs}}^o$ as a function of PQ adsorption. Since a decay in $k_{\text{obs}}^o$ for IrCl$_6^{2/-3}$ occurred with time, it was not possible to monitor $k_{\text{obs}}^o$ as a function of increasing PQ coverage from a $10^{-6}$ M solution. Working under the assumption of Anson [14] which stated that a monolayer of PQ formed from a $10^{-6}$ M PQ solution on carbon, the following procedure was employed.

The electrode was polished and a $10^{-5}$ M PQ 1 M HClO$_4$ solution was placed into the cell. Varying the adsorption time on a polished surface allowed different amounts of PQ to be initially adsorbed. When the desired amount of
Figure 30

Linearized Langmuir isotherm for the adsorption of PQ onto polished GC-20.
Figure 30

Polished GC-20

Bulk PQ concentration (μM)

$C^b / T_{PQ} (M^* cm^{-2}/picomoles)$ (E-7)

0.00 0.02 0.04 0.06 0.08 0.10 0.12
Figure 31

Linearized Langmuir isotherm for the adsorption of PQ onto laser irradiated (25 MW/cm$^2$) GC-20.
Figure 31

$\frac{C^b}{T_{PQ}} \text{ (M}^*\text{cm}^2/\text{picomoles)}$ vs. 

Bulk PQ concentration (µM)

Laser Irradiated
GC-20
Table 7: Isotherm data for PQ adsorption onto polished and laser irradiated (25 MW/cm²) glassy carbon surfaces.

<table>
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<th>Surface</th>
<th>C₀ (µM)</th>
<th>Γ₁ (pmoles/cm²)</th>
<th>Number Points for linearization</th>
<th>slope (cm²/pmoles)</th>
<th>Γₛ (pmoles/cm²)</th>
<th>corr</th>
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<td>5</td>
<td>2.047 x 10³</td>
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<td>0.9987</td>
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surface coverage was obtained, the cell was quickly flushed with a solution obtaining $10^4 \text{ M } \text{PQ}$ and $10^3 \text{ M } \text{IrCl}_2^2$ in $1 \text{ M } \text{HClO}_4$. The surface was then immediately irradiated with three 25 MW/cm² laser pulses and the resulting voltammetry was recorded and corresponding $k_{\text{obs}}$ calculated. This procedure allowed for preconcentration of PQ on the surface while simultaneously permitting the equilibrium coverage of PQ to remain similar to the value obtained after adsorption from a $10^4 \text{ M } \text{PQ}$ solution. The results for $k_{\text{obs}}$ and $\Gamma_{\text{PQ}}$ are shown in Table 8.

A possible complication which may result is the lack of monolayer coverage by PQ. Recalling that if a Langmuir isotherm is obeyed, then a plot of $C_b/\Gamma_1$ vs. $C_b$ should be linear over a wide concentration range. This is not the case for PQ. Isotherms for polished and laser irradiated surfaces are shown in Figures 30 and 31 respectively. Linearity for both the polished and laser irradiated surfaces occurs for the first four to five concentrations employed. This limits the useful range for bulk PQ concentrations between 0.2 µM and 2.0 µM. Ideally, a concentration range of at least two orders of magnitude would be desirable. Extracting the relevant terms from the linearized isotherm section, one obtains the data shown in Table 7.

Linearity was best achieved using only the first four points since the slopes were quite different when the first five points were chosen. Also, saturation coverage, as measured experimentally and calculated according to Equation 12 resulted in values of $(\Gamma_{\text{exp}})$ of 320 pmoles/cm² and 435 pmoles/cm² for polished
and laser irradiated surfaces respectively. These values are in good agreement with those extracted from the linearized isotherm portion. However, since a good correlation exists when five points are used for linearization, there exists the possibility that the extracted value of $\Gamma_s$ (403 pmoles/cm$^2$, and 489 pmoles/cm$^2$ for polished and laser irradiated surfaces respectively) is best represented by this condition. That being the case, saturation coverage by PQ onto the glassy carbon surface is not achieved from a $10^4\text{ M}$ solution and the results presented, although in agreement with Equations 14 and 15, do not truly represent the surface conditions. Since saturation coverage is not theoretically achieved if five points are used from the linearized isotherm, then the rate constant of $0.10 \text{ cm/s}$ acquired with a $\Gamma_{pq}$ coverage of 320 pmoles/cm$^2$ is not representative of monolayer coverage. Thus, it was concluded that PQ was not the best adsorbate and to achieve more quantitative results, a new adsorbate was required.
Table 8: $\Gamma_{pQ}$ and $k_{obs}^o$ for IrCl$_6^{2/-3}$ in 1 M HCl on laser irradiated (25 MW/cm$^2$) GC-20.

<table>
<thead>
<tr>
<th>$\Gamma_{pQ}$ (picomoles/cm$^2$)</th>
<th>$k_{obs}^o$ (cm/s)</th>
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<tr>
<td>0</td>
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<td>57</td>
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LIST OF REFERENCES


