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Electrocatalysis of modified carbon materials

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The Ohio State University, 1994
ELECTROCATALYSIS OF MODIFIED CARBON MATERIALS

DISSERTATION

Presented in Partial Fulfillment of the Requirements for

the Degree Doctor of Philosophy in the Graduate

School of The Ohio State University

By

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** **

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To My Wife

Wen Zhang
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TABLE OF CONTENTS

ACKNOWLEDGMENT ................................................................. iii
VITA ................................................................................................ v
TABLE OF CONTENTS ............................................................. vi
LIST OF TABLES ........................................................................ viii
LIST OF FIGURES .................................................................... x
CHAPTER PAGE

I INTRODUCTION .................................................................... 1
   Electrochemistry and Carbon Materials .................................. 1
   Electrode Activation and Electrocatalysis ............................... 9
   Fuel Cell and Their Development ......................................... 17
   Research Objectives ............................................................ 24

II. EFFECT OF CARBON ELECTRODE PRETREATMENT ON THE
   ELECTRON TRANSFER KINETICS OF OXYGEN REDUCTION
   REACTION IN ALKALINE SOLUTIONS ................................. 27
   Introduction ........................................................................ 27
   Experimental ..................................................................... 40
   Results .............................................................................. 42
   Discussion .......................................................................... 62
   Conclusions ....................................................................... 93

III. STRUCTURE AND ACTIVITY OF NANOSCALE PLATINUM
    CLUSTERS IN A SYNTHETIC GLASSY CARBON MATRIX .... 97
   Introduction ........................................................................ 97
   Experimental ..................................................................... 100
   Results and Discussion ..................................................... 114
   Conclusions ....................................................................... 160
IV. SYNTHESIS, CHARACTERIZATION AND ELECTROCHEMICAL ACTIVITIES OF HALOGEN DOPED AND IRON DOPED GLASSY CARBON ............................................................... 163

Introduction ................................................................. 163
Experimental ................................................................. 168
Results and Discussion .................................................. 173
Conclusions ................................................................. 202

APPENDIX

A ELECTRON TRANSFER KINETICS OF Fe(CN)$_6^{3-4}$ ON LASER ACTIVATED AND CN$^-$ MODIFIED PLATINUM MICROELECTRODE ................................................................. 205

Introduction ................................................................. 205
Experimental ................................................................. 208
Results ................................................................. 210
Discussion ................................................................. 219
Conclusions ................................................................. 225

B STRUCTURAL EVOLUTION OF CARBON SUPPORTED FUEL CELL CATALYSTS STUDIED BY IN SITU EXTENDED X-RAY ABSORPTION FINE STRUCTURE SPECTROSCOPY ................................................................. 227

Introduction ................................................................. 227
Experimental ................................................................. 230
Results ................................................................. 233
Discussion ................................................................. 245
Conclusion ................................................................. 249

LIST OF REFERENCES ................................................................. 251
# LIST OF TABLES

<table>
<thead>
<tr>
<th>TABLE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Observed $k^o$ for Fe(CN)$_6^{3+/4}$ on pretreated carbon electrodes</td>
<td>36</td>
</tr>
<tr>
<td>2. The first reduction peak potentials for O$_2$ reduction reaction on carbon electrodes after various pretreatment in 1M KOH/H$_2$O and 1M KOD/D$_2$O solutions at 50mV/s</td>
<td>60</td>
</tr>
<tr>
<td>3. HO$_2$ oxidation potentials on polished, fractured and ECP GC electrodes in 1M KOH/H$_2$O and 1M KOD/D$_2$O solutions at 50mV/s</td>
<td>61</td>
</tr>
<tr>
<td>4. The second reduction peak potentials for oxygen reduction reaction on carbon electrodes after various pretreatment in 1M KOH/H$_2$O and 1M KOD/D$_2$O solutions at 50mV/s</td>
<td>91</td>
</tr>
<tr>
<td>5. Comparison of selected physical and electrochemical properties of glassy carbon materials</td>
<td>120</td>
</tr>
<tr>
<td>6. XPS analysis of Pt-DGC thin film electrodes with different precursor structure (1:2, 1:6 and 1:10)</td>
<td>121</td>
</tr>
<tr>
<td>7. Summary of the effect of high surface area carbon support on the catalytic activities of Pt-DGC materials</td>
<td>132</td>
</tr>
<tr>
<td>8. Least square curve fit results for 3-shell fits to Fourier-filtered EXAFS data of Pt-DGC catalysts after various thermal treatment</td>
<td>159</td>
</tr>
<tr>
<td>9. Selected physical properties of GC6, GC10 and halogen doped glassy carbon materials</td>
<td>179</td>
</tr>
<tr>
<td>10. Electron transfer rate constants ($k^o$) for Fe(CN)$_6^{3+/4}$ under various conditions on platinum, gold and glassy carbon electrodes</td>
<td>207</td>
</tr>
<tr>
<td>11. Observed electron transfer rate constants ($k^o$) for Fe(CN)$_6^{3+/4}$ under various conditions on platinum microdisk electrodes</td>
<td>214</td>
</tr>
</tbody>
</table>
12. Effect of CN⁻ concentration on the electron transfer rate constants (kₒ) of Fe(CN)₆³⁻⁴ on Pt microdisk electrode determined at 600V/s .................................................. 217

13. Summary of the composition and selected physical properties of the four carbon supported fuel cell catalysts ................................................................................................... 231

14. Curve-Fitting Results for 3-shell fits to Fourier-filtered EXAFS data of dispersed Pt/C catalysts .............................................................................................................. 244
<table>
<thead>
<tr>
<th>FIGURE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>5</td>
</tr>
<tr>
<td>2.</td>
<td>7</td>
</tr>
<tr>
<td>3.</td>
<td>10</td>
</tr>
<tr>
<td>4.</td>
<td>11</td>
</tr>
<tr>
<td>5.</td>
<td>14</td>
</tr>
<tr>
<td>6.</td>
<td>19</td>
</tr>
<tr>
<td>7.</td>
<td>44</td>
</tr>
<tr>
<td>8.</td>
<td>47</td>
</tr>
<tr>
<td>9.</td>
<td>50</td>
</tr>
<tr>
<td>10.</td>
<td>51</td>
</tr>
<tr>
<td>11.</td>
<td>52</td>
</tr>
<tr>
<td>12.</td>
<td>54</td>
</tr>
</tbody>
</table>
13. Effect of 2,4-dinitrophenylhydrazine (DNPH) adsorption on O₂ reduction reaction in 1M KOH on ECP-GC electrode .................................. 55

14. Effect of β-carotene adsorption on O₂ reduction reaction in 1M TBAP/CH₃CN solutions ............................................................................. 56

15. Effect of cations (Na⁺, Li⁺, K⁺ and TEA⁺) on O₂ reduction reaction on polished GC electrodes ............................................................................. 58

16. Voltammograms of HO₂⁻ oxidation on polished, ECP and fractured GC electrodes in 1M KOH ..................................................................................... 59

17. Voltammograms of O₂ reduction reaction on polished electrode in 2.4M and 1M TEAOH solution ............................................................................. 66

18. Background uncorrected cyclic voltammograms of O₂ reduction reaction on PQ and AQDS adsorbed polished GC electrodes in 1M KOH ............................................................................. 75

19. Background voltammograms of fractured GC electrodes in 1M KOH ..................................................................................... 76

20. Simulated ORR peak one potentials and current densities for various Kₑₒ, kᵣ and kᵢ° ..................................................................................... 84

21. Simulated ORR voltammograms at two kᵢ° values and two kᵣ values to show the kinetics effect and the H/D isotope effect ..................................................................................... 87

22. Illustration of the membrane and electrode (M&E) assembly in making polymer electrolyte membrane (PEM) fuel cell electrodes ..................................................................................... 109

23. Illustration of the polymer electrolyte membrane fuel cell assembly ..................................................................................... 110

24. Illustration of the single cell hardware in PEM assembly ..................................................................................... 111

25. Illustration of the details of a PEM fuel cell front panel control system ..................................................................................... 112

26. Comparison of Raman Spectra of GC10, GC6 and Pt-DGC ..................................................................................... 116

27. Background corrected voltammograms of O₂ reduction reaction on thin film Pt-DGC electrodes in 1M HClO₄ ..................................................................................... 119

28. Hydrogen evolution curves on Toray "felt" supported Pt-DGC electrodes in comparison with a polycrystalline platinum electrode and an undoped "felt" electrode ..................................................................................... 124
29. Current densities of hydrogen evolution reaction at -0.1V vs NHE on Toray "felt" supported Pt-DGC electrodes as a function of Pt loading  

30. Effect of the high surface area carbon support on the fuel cell performance of Pt-DGC catalysts  

31. Illustration of dispersing the Pt-DGC precursor onto a high surface area carbon substrate  

32. Effect of the ink composition, the M&E assembly and the ink painting method on the catalytic activities of Pt-DGC materials in air fuel cells  

33. Effect of the thermal treatment environment on the fuel cell performance of Pt-DGC catalysts  

34. Effect of the final curing temperatures on the fuel cell performance of Pt-DGC catalysts  

35. Transmission electron micrographs of Pt-DGC fuel cell catalysts prepared with different thermal treatment conditions.  

36. Effect of the degree of precursor dispersion on the fuel cell performance of Pt-DGC catalysts  

37. Comparison of the Pt-DGC material with commercial ETEK and Pt black catalysts in both air and oxygen fuel cells  

38. Transmission electron micrograph of commercial ETEK catalyst  

39. Comparison of the stability test of Pt-DGC catalyst with the commercial ETEK catalyst for a period of 11 days  

40. Illustration of the basic principles and typical data analysis procedures in EXAFS  

41. Raw $k^3$-weighted Pt EXAFS of Pt metal, PtO$_2$ and Pt-DGC samples  

42. The Fourier Transform (FT) moduli of Pt-DGC materials cured to different final temperatures in comparison with a platinum foil  

43. Comparison of the Fourier Transform (FT) moduli of a 600°C cured Pt-DGC catalyst after gas phase oxidation and reduction  

xii
44. Illustration of the synthetic schemes to the preparation of halogen doped glassy carbon material including Cl-DGC, F-DGC and F-Pt-DGC. 170
45. Illustration of the synthetic schemes to the preparation of iron doped glassy carbon material (Fe-DGC) 171
46. Raman spectra of various DGC materials in comparison with a conventional GC10 material - effect of the dopants on the carbon lattice formation. 174
47. X-ray photoelectron spectra of thin film Cl-DGC and F-DGC. 176
48. Cyclic voltammograms of 1mM Fe(CN)₆³⁻ on thin film Cl-DGC, F-DGC and GC6 electrodes with background. 180
49. Cyclic voltammograms of 2,6-anthraquinone disulfonate (AQDS) on a high vacuum heat treated GC20 electrode with and without laser irradiation. 181
50. O₂ reduction voltammograms on F-Pt-DGC thin film electrode in comparison with polycrystalline Pt and Pt-DGC electrodes in 1M HClO₄ and 1M KOH. 185
51. Hydrogen evolution curves on Pt-DGC, F-Pt-DGC and polycrystalline Pt in 1M HClO₄ at 50mV/s. 186
52. Comparison of the hydrogen evolution on polycrystalline Pt and F-Pt-DGC in 1M HClO₄ at -44mV vs Ag/AgCl. 187
53. Effect of the final curing temperature on the carbon lattice formation in iron doped glassy carbon (Fe-DGC) materials. 190
54. X-ray photoelectron spectrum of a 600°C vacuum (10⁻⁶ torr) heat treated Fe-DGC electrode. 191
55. High resolution XPS scans of the Fe 2p region on Fe-DGC electrode after exposure to air for various amount of time. 192
56. O₂ reduction voltammograms on Fe, GC and Fe-DGC in 1M KOH. 196
57. HO₂⁻ reduction on Fe-DGC and GC20 in comparison with the ORR voltammogram on Fe-DGC. 197
58. O₂ reduction voltammograms on Fe-DGC as a function of solution pH. 198
59. O₂ reduction curve on Fe-DGC electrode at -0.95V vs Ag/AgCl .... 200
60. Voltammograms of O₂ reduction on Fe-DGC in 1M HClO₄ ........ 201
61. The experimental and simulated voltammograms of Fe(CN)₆⁻³/₄ in 1M KCl on platinum microdisk electrodes with and without CN⁻ ... 211
62. The heterogeneous electron transfer constant (k°) determined at 600V/s on Pt microdisk electrodes for Fe(CN)₆⁻³/₄ as a function of time and [CN⁻] ................................................................. 215
63. The heterogeneous electron transfer constant (k°) for Fe(CN)₆⁻³/₄ on Pt microdisk electrode in 5mM KCN + 1M KCl as a function of laser irradiation power density ......................................................... 218
64. k° for Fe(CN)₆⁻³/₄ (with 5mM CN⁻ added) as a function of time after 25, 50 and 75 MW/cm² laser irradiation ............................................. 220
65. Scanning electron micrographs of polished Pt microdisk electrodes followed by various degrees of laser activation .................................................. 221
66. Raw k³-weighted Pt EXAFS of Pt metal, PtO₂ and catalyst sample 10K20 after various treatments ................................................................. 234
67. EXAFS Fourier Transform moduli of Pt metal, PtO₂ and catalyst sample 10K20 after various treatments ......................................................... 235
68. Pt L₃ absorption edges of Pt metal, PtO₂ and catalyst sample 10K20 after various treatments ................................................................. 237
69. EXAFS Fourier Transform moduli of catalyst sample 10C20 after various treatments ................................................................. 238
70. EXAFS Fourier Transform moduli of catalyst sample 10BH20 after various treatments ................................................................. 239
71. EXAFS Fourier Transform moduli of catalyst sample 10G25 after various treatments ................................................................. 240
72. EXAFS curve-fits for catalyst sample 10K20 after various treatments in k space ................................................................. 242
73. R-space plots of EXAFS curve-fits for catalyst sample 10K20 after various treatments ................................................................. 243
CHAPTER I
INTRODUCTION

ELECTROCHEMISTRY AND CARBON MATERIALS

Electrochemistry is a science discipline that measures the electrical responses from a given chemical system in the form of current, potential or charge. It originated from the late 1800s when Galvani and Volta placed a copper hook into a frog leg and noticed a "twitch". They explained that the junction potential of two dissimilar metals produced an electrical current which then passed through the frog leg to give it the shock (1). An electrochemical system includes at least an anode and a cathode separated by an electrolyte. Electrochemical reactions occur on both electrodes and as a result electrons are produced or consumed. Externally, the electrons flow from one electrode to the other through a load. But internally, the charges are carried by ions which move under an electrical field to complete the circuit.

Electrochemical methods have been major analytical techniques for decades. They can be used to analyze trace amounts of metal ions or organic species in solutions or can be used to generate unstable radical intermediates for spectroscopic studies. They have been used to obtain quantitative and thermodynamic information about an electrochemical system and have been applied to industrial processes such as electrosynthesis, electrocatalysis, batteries and fuel cells.
Most electrochemical studies focus on the interface between the electrolyte and the electrode. Although chemical reactions within the solution phase can have significant effect on the outcome of a reaction, it is at the electrode-electrolyte interface where electron transfer occurs and where many fundamental problems arise. A sound understanding of the basic principles governing the electron transfer process at this interface is therefore the important step in gaining insight to the given system and obtaining the chemical information.

The interfacial properties of any electrochemical system depend on many factors. In particular, the specific redox reactions and the electrode structure are the most influential. A wide variety of electrode materials have been successfully used. Noble metals such as Pt, Au and Ag were almost exclusively utilized in the early days due to their chemical inertness and efficient catalytic activities. However, the high cost and low availability of these noble metals have prevented their widespread use, especially for industrial applications. Significant effort, therefore, has been spent on searching and applying alternative electrode materials for the ever increasing field of electrochemical studies. Among them, carbon is the most intensively studied.

The use of carbon as an electrode material started in the 19th century (2). Sir Humphrey Davy used graphite as an inexpensive alternative to noble metals to isolate alkali metals from molten salts (1). Around 1840 carbon electrodes were used to replace Cu electrodes in Volta batteries and Pt electrodes in Grove cells. However, it was not until 1896 when E.G. Acheson developed synthetic graphite that carbon materials have found important applications in many industrial electrochemical processes (2).
Carbon exists in a wide variety of forms, each with a unique combination of crystalline and electronic structure. The most common ones are diamond and graphite. Diamond has a sp³-hybridized structure which consists of covalently bonded atoms in a 3-D network. This rigid structure gives diamond an unusually high hardness. However, diamond itself has very low electrical conductivity and is of little value as an electrode material. Graphite, on the other hand, is sp²-hybridized and contains a delocalized electronic structure that yields good electrical conductivity. For this reason, only sp²-hybridized carbon can be used as alternative electrode material. The term "carbon" used throughout this dissertation refers specifically to this type of material.

Carbon is selected for a number of reasons, e.g., it has good electrical and thermal conductivities; it has low density and adequate corrosion resistance. Carbon can be relatively easily machined and it is generally inexpensive. Several types of carbon materials are readily available, including carbon blacks, active carbon, graphite, carbon fiber and glassy carbon. These materials have very different physical and chemical properties and have found a wide variety of industrial and commercial applications. Among them, carbon blacks play a major role as a conductive support and electrocatalyst in batteries and fuel cells.

The wide variety of carbons that are available makes selection of the appropriate type for electrochemical systems difficult. In this dissertation, only two kinds of carbon were used, namely, highly ordered pyrolytic graphite (HOPG) and glassy carbon (GC). HOPG (3) is made by stress annealing hydrocarbon precursors at high pressures and temperatures (3000°C) while GC (4) is produced by a thermal treatment of selected...
organic polymers to a final temperature of between 1000°C and 3000°C. The physical and chemical properties of GC materials are dependent on the final temperature. A nomenclature has been adopted to distinguish these materials. For example, GC10, GC20 and GC30 refer to glassy carbon that has been heat treated to 1000°C, 2000°C or 3000°C, respectively.

HOPG and GC are structurally quite different (Figure 1). HOPG is composed of evenly spaced sheets of carbon. Each sheet is a continuum of adjoining six member rings where carbon atoms are covalently bonded and all the valences are satisfied. The sheets are held together by the weak van der Waals attraction. There are two principle characteristic surfaces on HOPG: the basal plane which consists of the unbroken continuum of the carbon sheet, and the edge plane which is formed by the adjacent ends of the basal planes. HOPG has a interplanar distance of 3.35Å and a microcrystallite sizes of over 10,000Å. Its density is close to a single carbon crystal (~2.26g/cm³) (5). However, HOPG exhibits highly structural anisotropy, e.g., the electrical conductivity and thermal conductivity along the a-axis is 4000 times and 200 times higher than those along the c-axis, respectively (2, 4, 5).

In contrast, glassy carbon has a tangled ribbon-like structure that is isotropic with an average microcrystallite size of ca. 25Å (5). The porous structure as shown in Figure 1 gives GC a lower density, lower electrical conductivity and lower thermal conductivity than the HOPG a-axis. Glassy carbon is also impermeable to gases and liquids despite its apparently open structure because these pores are small and the majority of them are not connected. Electronically, glassy carbon behaves more like metals where there is a
Figure 1 Structural illustration of highly ordered pyrolytic graphite (HOPG) and glassy carbon (GC) with X-ray crystallographic parameters La, Lc and D$_{002}$.
sufficient overlap between its conduction band and valence band, whereas HOPG basal plane possesses properties of a semiconductor due to the very small overlap between its conduction band and valence band (6). These dissimilarities have resulted in significantly different electrochemical reactivities. For example, the heterogeneous electron transfer constant \( k^0 \) for \( \text{Fe(CN)}_6^{3-/4} \) system is 3-5 orders smaller on a well prepared basal plane than on a GC electrode (7). A small perturbation in the surface structure, e.g., an increase in the defect densities, can drastically increase the electron transfer kinetics on HOPG basal plane. Because the electrochemical behavior on HOPG is very sensitive to the surface preparation and often times these parameters are difficult to control, HOPG has only limited use in electrochemical studies.

As mentioned above, carbon materials possess considerably different microstructures that affect their activities. An understanding of these structures will help to predict their electrochemical behaviors. There are a number of techniques that are available to study graphite material's surface structure. They include electron spectroscopy (ESCA, Auger), x-ray spectroscopy (XPS, XRD), microscopy (SEM, TEM, STM), neutron scattering and mass spectroscopy (SIMS). These techniques generally require high vacuum environment and might alter the surface properties of the materials.

To obtain structural information that is more representative of the actual surface, Raman spectroscopy has been extensively used. Raman spectroscopy measures the vibrational modes through the change in polarizability. Since graphite materials have relatively high polarizability due to their conjugated structure, they are suitable for Raman studies. Two characteristic Raman bands, one at \( \sim 1360 \text{cm}^{-1} \) and one at \( \sim 1580 \text{cm}^{-1} \), are
Figure 2  Raman spectra of GC10, GC20, GC30 and HOPG. All spectra were obtained on SPEX 1403 spectrometer with a double monochromator and a water cooled photomultiplier tube (PMT) detector using the 514.5nm Ar$^+$ laser line as the excitation source.
typically observed on glassy carbon materials (Figure 2). The 1580cm$^{-1}$ band corresponds to the allowed $E_{2g}$ vibrational mode while the 1360cm$^{-1}$ band, sometimes referred to as the "disordered" band, has been assigned to the $A_{1g}$ mode which is not expected for an infinite graphite sheet (26). For this reason, only the 1580cm$^{-1}$ band is observed on HOPG. The band at $\sim$2300cm$^{-1}$ is due to the atmospheric N$_2$.

The Raman peaks have been related to the carbon microstructure (26). For example, the occurrence of 1360cm$^{-1}$ band suggests disordered graphitic matrix formation. An increase in the intensity ratio of 1360cm$^{-1}$ to 1580cm$^{-1}$ band and a higher resolution between them indicate a higher degree of graphitization. Figure 2 compares the Raman spectra of commercial GC10, GC20, GC30 and HOPG material. It is apparent that as the final curing temperature increases, the $I_{1360}/I_{1580}$ ratio increases and the two bands become better resolved. HOPG only exhibits the 1580cm$^{-1}$ band, as expected. There are other bands that occur at higher wavenumber region (2400-2700cm$^{-1}$). These bands are the overtones or combinations of the fundamental bands and they appear distinctively on GC30 and HOPG.

In addition to the different graphite microstructures, electrode pretreatment also has significant effects on carbon material's activities. Most as-received carbon materials are inactive for electrochemical applications. In order to increase their activities, carbon electrodes must be pretreated or activated. Activation not only reduces the effect from polishing but may also introduces surface functionalities. Electron transfer kinetics are strongly dependent of these pretreatments.
ELECTRODE ACTIVATION AND ELECTROCATALYSIS

There are many activation procedures that have been adopted to increase the activity of GC electrodes. Most treatments are performed with the purpose of removing the surface contaminants and/or generating active sites. Commonly used techniques include: polishing (8, 9), heat treatment (10, 11), intense pulsed laser irradiation (12, 13), electrochemical pretreatment (ECP) (14-16), radio frequency plasma activation (17) and fracturing the electrode immediately prior to the experiment to uncover a new graphite surface (18). These pretreatments increase the electron transfer ability on the electrodes and in most cases the results are more reproducible. However, in practice, these electrodes have limited applications due to the very small currents they are capable of producing.

Another way of enhancing the electrode activities is to physisorb or chemisorb certain catalytically active species onto the electrode surface. Carbon electrodes possess many surface functional groups such as quinone, carbonyl, phenol, carboxylic acid and lactone (Figure 3). These functional groups allow one to prepare chemical modified electrodes (CMEs). Figure 4 illustrates the four methods commonly involved in preparing CMEs. They include: (1) physisorption of molecular catalysts or mediators to the electrode surface (A); (2) covalent bonding of electroactive catalysts to the electrode surface (B); (3) vapor deposition or electrodeposition of metals directly onto the electrode surface (C); and (4) entrapment of metals within a polymer film affixed to the electrode (D). The chemically modified electrodes often exhibit much higher activities due to the modifier’s ability to affect the interaction of the reactants and the electrode surface. The chemisorption of iron porphyrins onto a graphite electrode surface is an example of the
Figure 3  Possible oxygen functionalities on carbon electrode surface.
Figure 4  Various methods used for the preparation of superficially chemically modified electrodes (CMEs), including (A) physisorption; (B) covalent bonding; (C) vapor deposition or electrodeposition of metal particles; and (D) entrapment of metals within a polymer film affixed to the electrode.
CMEs where oxygen reduction occurs at over 400mV more positive than simply polished electrode (19-21). Iron porphyrin effectively catalyzes O$_2$ reduction and serves as the mediators.

Unfortunately, these CMEs suffer from two major drawbacks: the mechanical instability of the catalytic layer and the irreproducibility of the surface. Since the active species are adsorbed onto electrode surface as thin layers, these electrodes are naturally fragile and tend to lose the adsorbed films quickly. The physisorption or chemisorption of a catalyst to a carbon surface is sometimes weak such that only low concentration of catalyst is retained on the surface. Although direct vapor deposition or electrodeposition of metal particles to carbon surface will increase the catalytic site density, without a protective overlayer, the rapid loss of these metal particles becomes intolerable. In the case of generating metal particles in a porous polymer structure, the electrode reactivity depends on the chemical stability of the catalyst and the polymer matrix. When the electrodes become deactivated, the process involved in regenerating the surface catalyst layer is often lengthy and the result is rarely reproducible. The chemically modified carbon electrodes, again, have little practical values.

To avoid these problems, a bulk modified rather than superficially modified carbon material is needed. The surface of a bulk modified electrode may be easily renewed by means of polishing. Several groups have reported procedures to prepare bulk modified carbon. Shaw and Creasy synthesized an electrode by polymerization of carbon black in vinyl ferrocene, styrene (or methylacrylate) and divinylbenzene (22). The catalytic activity of this electrode can be restored by polishing the electrode when it becomes deactivated.
Ingersoll and Huskisson prepared molybdenum and tungsten doped carbon films on quartz plates. They noticed different electrochemical response on these films (23). Wang and co-workers (24) described metal (Pt, Ru, or Pd) dispersed carbon paste electrodes (CPEs) based on mixing an organic binder with metallized graphite. Significant increase in response to H$_2$O$_2$, ascorbic acid, NADH, hydrazine and butanol peroxide were observed for doped CPEs. New surfaces of doped CPEs can be generated by smoothing the deactivated electrode on a weighing paper.

A new approach to the preparation of glassy carbon materials was developed recently (27-29). In this approach, relatively low temperatures ($\leq$600°C) are required instead of the extremely high temperatures used in commercial GC preparation. These high temperatures have excluded the incorporation of dopants in conventional glassy carbon matrix, which is independent of the starting materials. The low temperature route, however, allows the incorporation of a significant amount of foreign atoms at the atomic level (>15 atom%). Figure 5 shows the schematics of the synthesis of a platinum doped glassy carbon material. In this procedure, dibromobenzene (A) is first converted to diethynylbenzene (B) followed by reaction with phenylacetylene to give the oligomer as shown in (C). This oligomer can be directly heat treated to produce a sp$^2$-hybridized carbon material but it would have low catalytic activities just like commercial GC, or the oligomer can further react with the platinum triphenylphosphine complex to produce a precursor (D) where platinum becomes an appendage to the backbone structure. Pyrolysis of the precursor under controlled atmosphere to ~600°C produces a glassy carbon matrix where nanoscale platinum clusters are homogeneously incorporated (E).
1. Precursor is soluble.
2. Pt loading is user controllable.
3. Dopants can be incorporated.

**Figure 5** Illustration of the synthetic schemes for the preparation of platinum doped glassy carbon material.
A variety of species have been incorporated into the GC matrix, including: halogen (F, Cl), phosphorus, Pt, Fe, Ru, Pd, Co and Ni. All these DGCs possess three very useful properties: (1) the precursor is soluble in toluene, tetrahydrofuran and acetone. This allows the preparation of different sizes and shapes of thin film electrodes by casting the precursor solution onto appropriate substrates. It also allows the preparation of supported fuel cell catalysts by mixing the precursor solutions with a high surface area carbon support; (2) the dopant loading level is user-controllable by varying the stoichiometry of the reaction. This makes it possible to synthesize a wide spectrum of materials that contain different amount of heteroatoms; and (3) because of the relatively low temperature required to create the GC matrix, most of the heteroatoms in the precursor backbone can survive the thermal treatment and become homogeneously dispersed in the GC structure.

The activated or modified carbon electrodes are often used for electrocatalysis. The incorporated heteroatoms or the surface functionalities can serve as the catalytic sites for electrochemical reactions. The word "catalysis" was coined in 1836 by Berzelius to describe an enhanced chemical reaction due to an agent (the catalyst) that exerted more-than-proportional influence over some changes(25). A catalyst is often described as a material that accelerates the chemical reaction without itself undergoing changes. This is the ideal case. In practice, the catalyst is involved in the reaction and its structure and reactivity changes with use. Sometimes the changes are irreversible and the catalyst eventually loses its activity.

Many industrial processes require catalysts to achieve the desired products. The importance of a catalyst is in that it provides sites for the reactant molecules to interact
with the surface. This can be illustrated with the simple hydrogen dissociation reaction in an aqueous electrolyte on a platinum electrode. The hydrogen gas first reaches an equilibrium with the solution. Some of the dissolved gas molecules then attach loosely to the platinum electrode by donating valence electrons. A number of these atoms become detached, leaving electrons in the metal sites and exit to the solution as $\text{H}^+$ ions:

$$\frac{1}{2} \text{H}_2\text{(gas)} \rightleftharpoons \frac{1}{2} \text{H}_2\text{(dissolved)}$$  \[1.1\]

$$\frac{1}{2} \text{H}_2\text{(dissolved)} + \text{Pt} \rightleftharpoons \text{Pt-H} \rightleftharpoons \text{Pt}+\text{H}^++\text{e}^-$$  \[1.2\]

The process eventually reaches an equilibrium. Since it involves electrons, a current will be produced. When the current flows to an external load, the equilibrium is no longer maintained and a change in the electrode potential is required to re-establish the equilibrium. This excess potential is called overpotential.

Depending on the electrode material, the hydrogen dissociation process can be significantly different. For example, the adsorption of dissolved hydrogen onto platinum group metals is relatively weak thus enable a rapid formation and breaking of the metal-hydrogen bonds. The reaction is fast. However, on metals such as mercury, lead, zinc and cadmium, the metal-hydrogen bond is very weak compared to hydrogen-hydrogen bond and only a small portion of the molecules have sufficient energy to dissociate and bond to the metal surface. The reaction thus is slow. On the other hand, metals such as molybdenum, tungsten and tantalum exhibit very strong metal-hydrogen bonds and the dissociation becomes restricted. In this case, the reaction is also slow.
The hydrogen dissociation reaction demonstrates that only appropriate catalyst can enhance the electrochemical reactions. Noble metals are commonly chosen because they have the proper energy to form and break the catalyst-reactant complex (30). On carbon electrodes, the catalysts come from different sources. It can be the surface oxides created by electrochemical pretreatment, or the active species on the CMEs, or in the case of DGCs, the incorporated heteroatoms. Among many available catalysts, platinum appears to be the most effective one for both hydrogen dissociation and oxygen reduction reaction. Since the low temperature route enables the incorporation of nanoscale platinum particles into the GC matrix, these type of materials are suitable for electrocatalysis applications such as fuel cells.

FUEL CELLS AND THEIR DEVELOPMENT

One of the most challenging tasks in modern electrochemistry is the direct conversion of chemical energy into electrical energy. Since electrochemical reactions result in electrons, it is conceptually possible to design an apparatus to generate electricity by means of electrode reactions. Batteries and fuel cells are directly based on these ideas.

Although batteries are used in everyday life, most people are not familiar with fuel cells. A fuel cell is a device that directly converts the chemical energy of reactants (a fuel and an oxidant) into low voltage d.c. electricity (31-43). It differs from the ordinary batteries (primary or rechargeable) in that the fuel cell is simply a converter. It does not consume materials that form an integral part of its structure. The fuel and oxidant are stored outside of the reaction area and as long as the fuel and oxidant are fed into it, a fuel
cell will continue to operate.

The principle of fuel cells is relatively straightforward and has been known for about 150 years (40). Figure 6 illustrates a hydrogen-oxygen fuel cell. This fuel cell consists of a fuel electrode (the anode) and an oxidant electrode (the cathode) separated by an ion-conducting electrolyte. The circuit is completed by connecting the two electrodes with a working load where electric is transported externally by the flow of electrons and internally by the flow of ions (H\(^+\)). The electrochemical reactions involved in this fuel cell are the reverse of water electrolysis. At the anode, H\(_2\) gas (the fuel) ionizes to produce H\(^+\) ions and electrons. Since the electrolyte is not an electronic conductor, electrons flow away from the anode via the external metallic circuit whereas H\(^+\) ions migrate toward the cathode via the electrolyte. At the cathode, O\(_2\) gas (the oxidant) reacts with the migrating H\(^+\) ions and the incoming electrons from the external circuit to produce water. Depending on the operating temperature of the cell, water may enter the electrolyte and increases its volume or be lost through the cathode as vapor. Depending on the circumstance, careful water management may or may not be necessary to remove the water product.

Since fuel cells convert fuels directly into electrical energy by an electrochemical route, its efficiency is not limited by the Carnot cycle. In the traditional fashion, electricity is generated by alternators driven by steam turbines. The steam is produced by burning fossil fuels (coal or hydrocarbons) or by nuclear fission. This long process (fuel to heat, heat to steam, steam to electricity) involves efficiency loss at every stage. The Carnot cycle defines the maximum thermal efficiency of any heat engine as:
Anode: $H_2 = 2H^+ + 2e^-$  
Cathode: $O_2 + 4H^+ + 4e^- = 2H_2O$  
Overall: $2H_2 + O_2 = 2H_2O$

Figure 6 Illustration of a hydrogen-oxygen fuel cell.
where $T_2$ and $T_1$ are the temperatures at which heat is supplied to and rejected by the system. In practice, the upper temperature is limited to about 500°C and the lower temperature is at least 30°C. These temperatures limit the maximum efficiency of a heat engine to less than unity. And due to other losses at every stages, the most efficient power stations nowadays are able to achieve only 38-40% efficiency (34, 35).

In fuel cells, the chemical energy is directly converted to electrical energy according to the following relationship:

$$E = -\frac{\Delta G_T}{nF}$$

where $\Delta G_T$ is the free energy change of the reaction at temperature $T$, $n$ is the number of electrons involved in the reaction, $F$ is the Faraday constant and $E$ is the electromotive force that can be produced by the system at temperature $T$. In the case of $\text{H}_2/\text{O}_2$ fuel cell, the theoretical thermodynamic reversible potential at 25°C is 1.229V.

The conversion efficiency of the chemical energy to electrical energy by fuel cells can be expressed by the following equation:

$$\eta = \frac{\Delta G_T}{\Delta H}$$
where $\Delta G_T$ and $\Delta H$ is the Gibbs free energy change and the enthalpy change of the reaction, respectively, at temperature $T$. Because there is no engine or heat transfer involved and there are no upper and lower temperature limits, the intrinsic efficiency of the fuel cell energy conversion is not subjected to the Carnot limitation. Thus it is theoretically possible to achieve 100% efficiency. Although in practice, this 100% efficiency is rarely achieved due to the presence of impurities, side reactions such as peroxide formation and electrode activation, the currently existing fuel cell units in the world have routinely demonstrated 40% electrical efficiency and 45% heat recovery in a combined heat and power system (37, 38). In addition to the much higher efficiency, fuel cell's characteristics of compactness, silence and cleanliness make them attractive candidates to replace urban power stations. Their freedom from pollution also help to make them economically competitive with existing power plants which face huge capital investment to ensure "clean" operation.

However, fuel cells are not in widespread use today despite their inherent advantages over the conventional power sources. The lack of their application is mainly caused by the problems associated with the catalyst. A brief historical overview should help to gain some understanding of the difficulties in fuel cell technology.

The fuel cell was invented by Sir William Robert Grove in 1839 (41-43). While carrying out experiments to dissociate water into hydrogen and oxygen gases by electrolyzing dilute sulfuric acid between platinized platinum electrodes, Sir William Grove noticed that the process can be reversed. He thus constructed an array of 50 cells to produce electricity (40) but soon abandoned this device because it was not capable of
delivering sufficient power to compete with more conventional galvanic cells. He noted the problem being a lack of "notable surface of action" between the electrode and the electrolyte where all the reactions take place.

In 1889, Ludwig Mond and Charles Langer constructed an operational apparatus (1.5W at 50% efficiency) which they called a fuel cell (44). For practical reason, they used air and industrial gas instead of oxygen and hydrogen. Due to the extremely high cost of platinum catalyst which was rapidly poisoned by traces of carbon monoxide in the industrial gas, they again quit pursuing the fuel cell concept.

With the advanced understanding of thermodynamics, more attempts were made to build practical fuel cells by converting carbon directly to electricity throughout the first half of the twentieth century. A high temperature molten carbonate fuel cell was built by E. Baur (45). However, because of the lack of the understanding of electrode kinetics, none of these attempts succeeded.

The first major fuel cell development was launched by Francis T. Bacon in 1932 (46). Bacon used a less corrosive alkaline electrolyte and less expensive nickel electrodes in his fuel cell and he operated the system at elevated temperature (205°C) and pressure (4MPa). To increase the active electrode area, Bacon applied porous gas diffusion electrodes upon which he was able to demonstrate a 5 kW system (46).

The 1950s and 1960s yielded the most rapid advances in fuel cell technologies due to the incentive from American space technology. Since fuel cells generate electricity by consuming hydrogen and oxygen and produce water, they have been successfully used by the Gemini mission and the Apollo missions in the U.S. space program. This success has
resulted in many predictions that fuel cells would be the solution to the world's energy problems. However, as certain inherent difficulties were gradually discovered, these hopes began to diminish.

First, hydrogen was recognized as the only really effective fuel. In order to use other fuels such as hydrocarbons and alcohols, impractically high noble-metal catalyst loading was needed to achieve sufficient activity. Second, the expensive platinum seemed to be the only effective catalyst. Although it is possible to use a less expensive catalyst such as nickel, high temperature and high pressure were needed. Third, even if platinum was used for high activity, a residual amount of carbon monoxide in the fuels can quickly poison it thus the catalyst life time was short. And finally, the concept of fuel cells was oversold after the success of the space program with no clear understanding of the nature and the magnitude of the interrelated problems. As more problems were realized, less enthusiasm and less funding were invested and fuel cell investigation has almost come to a stop.

It is not until recently that the energy crisis and atmospheric pollution become such a problem that a clean and renewable energy source is needed more than ever. Because of this, fuel cells studies have regained some momentum. Through many people's dedicated efforts, some of the early problems were now solved or better understood. For example, the catalyst cost has been dramatically lowered as the loading level continues to decrease, the catalyst life time has been significantly increased, and the electrode kinetics were further understood. These development has brought to reality mega-watt-sized demonstrators that have been successfully operated.
There are five major types of fuel cells, with each using a different kind of electrolyte and operating at a different temperature (33). The phosphoric acid fuel cell (PAFC) is the most intensively studied and is the nearest to commercial use. Other types include those with molten carbonate, solid oxide, alkaline and solid polymer electrolyte. Since these fuel cells operate at different temperatures, they can achieve different efficiencies and may have different applications. However, these differences due to temperatures are not caused by the Carnot cycle limitation. Instead, the temperature affects the kinetics of the reaction thus changes the efficiency of the system. Currently, there are about 100 fuel cell power plants that are or will be in operation world-wide (47).

RESEARCH OBJECTIVES

The research presented here was attempted in order to correlate the catalytic activities of modified carbon materials with their structural properties. Glassy carbon was modified by means of surface pretreatment and homogeneous dopant incorporation. These modifications result in structural changes as well as catalytic activity enhancement. The oxygen reduction reaction was investigated on these materials due to its technological and biological importance. The benchmark system of Fe(CN)$_6^{3-/4}$ was also studied to assess the electron transfer kinetics after the modification.

The effect of the surface pretreatment of undoped glassy carbon on the oxygen reduction reaction (ORR) in alkaline solution is described in Chapter II. This was accomplished by studying the kinetics of O$_2$ reduction on several well defined GC electrodes including polished, laser irradiated, fractured and electrochemically pretreated.
Some of these electrodes were further modified with cations and layers of adsorbates. A basic understanding of the influence of these pretreatment on oxygen reduction reaction was achieved by analyzing the effect of the surface oxide on the adsorption, the chemical reaction and the electron transfer kinetics, all of which are involved in the reduction mechanism. ORR was also investigated on a near perfect HOPG basal plane. Since HOPG basal plane is electronically and structurally very different from glassy carbon, investigation of oxygen reduction reaction on this electrode reveals the effect of surface defects and electronic structure. However, because of the magnitude and complexity of oxygen reduction reaction, this research did not embrace all aspects of the problem. Instead, the emphasis of the current investigation is to obtain an understanding of which surface oxides are responsible for the enhanced catalysis and how they affect the reaction.

Since the undoped glassy carbon material is not capable of producing high enough current for practical utilization in fuel cells, it is necessary that other high efficiency materials are used. The low temperature synthetic route illustrated in Figure 5 allows the incorporation of a variety of metal catalysts in the GC matrix. Chapter III describes the structure and activities of nanoscale platinum clusters in a synthetic glassy carbon matrix. Thin film electrodes made from the Pt-DGC materials were first applied to oxygen reduction and hydrogen evolution reactions. These primary studies indicate that Pt-DGC material has high catalytic activity for both reactions. Because of these, Pt-DGC was subsequently applied to polymer electrolyte membrane (PEM) fuel cells where the effect of substrate, pyrolysis environment, curing temperature and dispersion were further investigated to increase their activities. The fuel cell performance data were correlated to
the catalyst's atomic and electronic structures by Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy and Transmission Electron Microscopy (TEM).

In chapter IV, two more kinds of DGCs are discussed. The halogen DGC contains more than 15% of Cl or F which could significantly change the material's physical and chemical properties. The iron doped glassy carbon (Fe-DGC) is an alternative material for the oxygen electrode in alkaline solutions. Its activity toward the oxygen reduction reaction was investigated and compared to pure GC and pure Fe.
CHAPTER II

EFFECT OF CARBON ELECTRODE PRETREATMENT ON

THE ELECTRON TRANSFER KINETICS OF OXYGEN REDUCTION REACTION

IN ALKALINE SOLUTIONS

INTRODUCTION

Oxygen redox reactions are involved in many electrochemical technologies and biological processes. For example, oxygen reduction occurs at the positive electrodes in fuel cells and metal/air batteries to produce electricity while oxygen evolution takes place in rechargeable batteries during charge. Industrial $\text{H}_2\text{O}_2$ production uses $\text{O}_2$ as the reactant. In chlor-alkali cells, oxygen serves to lower the cell voltage in improving energy efficiency. But in metal corrosion reactions, oxygen promotes the reaction rate and is not desirable. Modern automobiles and industrial processes often use oxygen sensors as an integral part of the emission control systems. In biological systems, many reactions also involve oxygen. A well known example is the photosynthesis reaction in green plants which produces oxygen to become the primary $\text{O}_2$ source in the atmosphere. Due to their technological as well as biological importance, oxygen redox reactions have become one of the most widely studied electrochemical reactions. Among them, the oxygen reduction reaction (ORR) received the most attention because of the interest in energy conversion devices such as fuel cells.
ORR has been extensively studied on both metal electrodes and non-metal electrodes. In the former, platinum, mercury, silver and gold are commonly used. In the latter, carbon is the most popular electrode material. Many different types of carbons have been used, including: highly ordered pyrolytic graphite, pyrolytic graphite, graphite powder, porous graphite, natural graphite, glassy carbon, pyrolytic carbon, active carbon, carbon black and carbon single crystals. These materials exhibit a wide range of electrochemical activities for oxygen reduction that are dependent on their physicochemical properties. Since carbon has been widely employed in energy conversion applications where oxygen reduction reactions are involved, a better understanding of ORR on carbon electrode will be invaluable for the preparation of more efficient oxygen electrodes.

Brief Review of ORR Mechanism

The oxygen reduction reaction is a complex, four-electron, four-proton process. The mechanism of $O_2$ reduction to $H_2O_2$ on carbon materials in alkaline solutions have been examined several times. Despite many efforts by electrochemists, there is still no clear agreement on the steps involved. A number of mechanisms have been proposed but they are somewhat controversial. The overall reaction in acid and basic solutions are as follows:

\[
\begin{align*}
\text{In Acid:} & \quad O_2 + 4H^+ + 4e^- & \rightarrow 2H_2O \quad E^0 = 1.229V \quad [2.1] \\
\text{In Base:} & \quad O_2 + 2H_2O + 4e^- & \rightarrow 4OH^- \quad E^0 = 0.401V \quad [2.2]
\end{align*}
\]
Direct four electron, four proton reduction is possible on noble metal catalysts (e.g., Pt, Ag, Pd) and some transition metal macrocyclics (e.g., iron tetrasulfonated phthalocyanine), but the reduction does not complete in one single four electron process. Instead, it usually involves a number of steps where intermediates may be adsorbed. On carbon, gold, mercury and some transition metal macrocyclics (e.g., cobalt tetrasulfonated phthalocyanine), most workers agree that the reaction involves a peroxide pathway:

In acid: \[ O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O_2 \]  
followed by \[ H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O \]  
or \[ 2H_2O_2 \rightleftharpoons 2H_2O + O_2 \]

In base: \[ O_2 + H_2O + 2e^- \rightleftharpoons HO_2^- + OH^- \]  
followed by \[ HO_2^- + H_2O + 2e^- \rightleftharpoons 3OH^- \]  
or \[ 2HO_2^- \rightleftharpoons 2OH^- + O_2 \]

Under these circumstances, oxygen reduction often proceeds only to the first two electron step (i.e., \( O_2 \rightarrow H_2O_2 \) in acid and \( O_2 \rightarrow HO_2^- \) in base) and the full thermodynamic potentials cannot be utilized. This limitation is mainly caused by the extremely high energy required to break the O-O bond in the subsequent third and fourth electron reductions. In order to achieve four electron, four proton reduction on carbon, either very high overpotential have to be applied or a proper catalyst that can decompose the
peroxide or catalyze the peroxide reduction must be used. If one allows the peroxide to build up, a quick decrease in electrode activity and in some cases electrode failure will result.

Since carbon itself is an effective electrocatalyst for oxygen reduction to peroxide in alkaline solutions, many detailed mechanistic studies have been conducted. Morcos and Yeager (48) proposed a two step reduction mechanism on graphite electrodes followed by the disproportionation of adsorbed HO₂:

\[
O_2 \quad \rightleftharpoons \quad O_{2(\text{ads})} \quad [2.9] \\
O_{2(\text{ads})} + H_2O + e^- \quad \rightleftharpoons \quad HO_2(\text{ads}) + OH^- \quad [2.10] \\
2HO_2(\text{ads}) + OH^- \quad \rightleftharpoons \quad O_2 + HO_2^- + H_2O \quad [2.11]
\]

This mechanism does not involve O-O bond breaking and is consistent with their experimental Tafel slope of 0.12 V/decade if [2.10] is the rate determining step.

On glassy carbon electrodes, Taylor and Humffray (49) concluded the following mechanism:

\[
O_2 + e^- \quad \rightleftharpoons \quad O_2^- (\text{ads., before migration}) \quad [2.12] \\
O_2^- (\text{ads., before migration}) \quad \rightleftharpoons \quad O_2^- (\text{ads., after migration}) \quad [2.13] \\
2O_2^- (\text{ads., after migration}) + H_2O \quad \rightleftharpoons \quad O_2 + HO_2^- + OH^- \quad [2.14]
\]
The surface migration of adsorbed $O_2^-$ to active sites (step [2.13]) was believed to be the rate determining step. Similarly, Zhang et al (55), proposed two different forms of adsorbed $O_2^-$ on glassy carbon surface. They suggested the following reaction as the rate determining step:

$$\{O_2(ads)\}^+ + H_2O \rightleftharpoons HO_2(ads) + OH^- \quad [2.15]$$

where the surface active species of $\{O_2(ads)\}^+$ has a structure like:

![Structure of surface active species](attachment:image.png)

On carbon black electrodes in alkaline solution, Appleby and Marie (51) proposed that the most probable mechanism involves a second electron transfer:

$$O_2 + e^- \rightleftharpoons O_2^- \quad [2.16]$$

$$O_2^- + H_2O + e^- \rightleftharpoons HO_2^- + OH^- \quad [2.17]$$

or

$$O_2 + H_2O + e^- \rightleftharpoons HO_2(ads) + OH^- \quad [2.18]$$

$$HO_2(ads) + e^- \rightleftharpoons HO_2^- \quad [2.19]$$

where step [2.17] or [2.19] was considered the rds on certain carbon materials.
There are many other mechanisms that have been reported in the literature but they are somewhat arguable. For example, Sawyer and Seo (52) reported that the first electron reduction from $O_2$ to $O_2^-$ was reversible and was independent of the electrode material. But Sen, Zagal and Yeager (53) disagreed. Based on the Tafel slope of 0.12V/decade on graphite, Yeager et al (53), concluded that the first electron reduction was the rate determining step and therefore could not be reversible. A more exotic review of the different reaction pathways for oxygen reduction on carbon materials can be obtained from reference (57).

The above mechanistic studies have mainly applied the rotating disc electrode (RDE) technique and conclusions were mostly based on the Tafel slopes measured with steps where electrons were involved. However, little effort has been made to understand the influence from those steps where electrons are not involved, e.g., the adsorption in step [2.9] or the proton transfer in step [2.15]. It has been suggested that peroxide intermediates are adsorbed onto the electrode surface, presumably to the "active" sites which consist of the oxygen-containing functionalities. Studies carried out on stress-annealed pyrolytic graphite (48, 54) and single-crystal graphite (48) have shown that oxygen reduction or peroxide oxidation on the basal plane surface are typically two to three orders of magnitude slower than on the edge plane surface or glassy carbon surface. The sluggish kinetics were explained in terms of a lack of adsorption sites for the intermediates on the basal plane which then inhibit the reduction process.

In addition to the controversial rds proposed, the role of surface oxides is as poorly understood as the reaction mechanism. Schreurs et al (64), Kuwana et al (10) and
Zhang et al (55), all concluded that o-quinones like structures are the possible candidates as the functional groups. Evans et al. suggested that the oxygen-containing groups might serve as mediators for electron transfer between the electrode and the electroactive species (65). Recently Yeager et al, studied oxygen reduction on 9,10-phenanthrenequinone modified HOPG and 2-aminoanthraquinone modified ordinary pyrolytic graphite electrodes (172). They proposed a quinone mediated reduction mechanism:

\[
\begin{align*}
Q_{(\text{ads})} + e^- & \rightleftharpoons Q_{(\text{ads})}^- \quad [2.20] \\
Q_{(\text{ads})}^- + O_2 & \rightleftharpoons Q_{(\text{ads})} + O_2^- \quad [2.21] \\
Q_{(\text{ads})} + O_2^- + H_2O + e^- & \rightleftharpoons Q_{(\text{ads})} + HO_2^- + OH^- \quad [2.22]
\end{align*}
\]

where Q stands for a generic quinone. On adsorbed quinone surfaces, the kinetics of the initial electron transfer (to the quinone, [2.20]) were fast and ORR was limited by the reaction of the reduced quinone with solution-phase O\(_2\) ([2.21]). On chemically attached quinone surfaces, the quinone could not serve as the mediator since it was further away from the surface and in an unfavorable configuration for electron tunneling, thus the first electron transfer to O\(_2\) (O\(_2\) + e\(^-\) \rightleftharpoons O_2^-) was the rate determining step. Nagaoka et al, investigated ORR on electrochemically pretreated GC electrodes (62) and found that adsorbed naphthazarin mediated O\(_2\) reduction reaction while quinones of electrochemically treated electrodes could not serve as mediators for O\(_2\) reduction reaction.

It is still not clear which oxygen groups are responsible for the enhanced electrode activities and how they facilitate the kinetics. However, it is apparent that controversial
mechanistic results have been observed on different kinds of carbon materials. To a large extent, these discrepancies are caused by the different physicochemical properties of the materials, which in turn alter the reaction energetics. Factors such as the surface structure, chemical treatment and electrochemical treatment have been observed to drastically change ORR kinetics. Some of these factors are inherent to the materials but the majority of them result from the different electrode pretreatment. In order to gain an insight understanding of how these factors influence the reaction process, it is necessary to prepared electrodes where surface variables can be controlled.

**Electrode Pretreatment Techniques**

Before investigating the effect of electrode pretreatments on the complicated oxygen reduction reaction, it is helpful to review these techniques and how they affect the electron transfer kinetics for the well studied benchmark system of Fe(CN)$_6^{3/-4}$.

There are a number of techniques that are commonly used to activate glassy carbon electrodes. They include mechanical polishing, ultra high vacuum heat treatment, laser irradiation, fracturing and electrochemical pretreatment. These treatments enable one to obtain faster electron transfer kinetics and often more reproducible results. However, the electrode activity strongly depends on the particular treatment. For example, the heterogeneous electron transfer constant, $k^e$, for Fe(CN)$_6^{3/-4}$ system ranges from $<0.001$ cm/s on polished electrodes to $>0.5$ cm/s on laser irradiated surfaces. Table 1 lists some of the literature $k^e$ values for Fe(CN)$_6^{3/-4}$ after various treatment. Clearly, the electrode pretreatment has significant effect on their activities.
Polishing usually is the first step toward electrode activation. It is done by either hand polishing or mechanical polishing the electrode in a slurry of fine alumina particles on a polishing cloth. This "conventional" procedure yields a surface that is not reproducible and has slow electron transfer rate. Carefully controlled polishing, e.g., ultra-clean polishing (9) and Soxhelt extraction after polishing (11), can result in higher $k^o$ for Fe(CN)$_6^{3/-4}$. Polishing eliminates the electrode history but creates a large amount of microscopic roughness due to the size of the alumina particles ($\geq 500\AA$). The electrode surface is believed to consist of a layer of the abraded carbon particles and contaminants. Polished electrode shows a significant amount of surface oxide. XPS analysis gives the surface O/C ratio range from 0.084 to 0.17 (8, 9, 15).

High vacuum heat treatment is typically performed at $\leq 10^{-6}$ torr pressure and 550-750°C. This process increases the electron transfer kinetics by desorbing the physisorbed contaminants from the polishing step (10). However, high vacuum heat treatment does not seem to affect the surface roughness. XPS shows the O/C ratio decreases from 0.22 on a polished electrode to 0.06 after high vacuum heat treatment (10).

Laser irradiation utilizes intense Nd:YAG laser pulses to generate a temporary high temperature on the electrode surface which then cleans the electrode in a similar fashion as heat treatment. The local temperature can go higher than 1500°C with pulses of 25MW/cm$^2$ laser irradiation (58). This procedure can be done in situ and has resulted in a dramatically increased $k^o$ for Fe(CN)$_6^{3/-4}$ (59). Lower power density laser irradiation (e.g., 25MW/cm$^2$, up to 18 pulses) only slightly alters the carbon micro-structure and slightly increase the microscopic area (60). XPS and Auger analysis show the surface oxide is
Table 1: Observed $k^0$ for Fe(CN)$_6^{3-4}$ on pretreated carbon electrodes *

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Pretreatment</th>
<th>$k^0$ (cm/s)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOPG, basal</td>
<td>cleaved</td>
<td>$&lt; 10^{-7}$</td>
<td>173, 174</td>
</tr>
<tr>
<td>HOPG, edge</td>
<td>laser</td>
<td>0.10</td>
<td>174</td>
</tr>
<tr>
<td>HOPG, basal</td>
<td>laser, 50mW/cm$^2$</td>
<td>0.004</td>
<td>11, 173, 174</td>
</tr>
<tr>
<td>Pyrolytic Graphite (0.5M KCl)</td>
<td>cleaved</td>
<td>0.002</td>
<td>175</td>
</tr>
<tr>
<td>Pyrolytic Graphite (0.5M KCl)</td>
<td>ground</td>
<td>0.007</td>
<td>175</td>
</tr>
<tr>
<td>GC-20</td>
<td>vacuum heat treatment</td>
<td>0.14</td>
<td>10</td>
</tr>
<tr>
<td>GC-20</td>
<td>high speed</td>
<td>0.098</td>
<td>8</td>
</tr>
<tr>
<td>GC-20</td>
<td>ultraclean polish</td>
<td>0.14</td>
<td>9</td>
</tr>
<tr>
<td>GC-20</td>
<td>conventional polish</td>
<td>0.05</td>
<td>13, 16</td>
</tr>
<tr>
<td>GC-30</td>
<td>fractured</td>
<td>0.5</td>
<td>59</td>
</tr>
<tr>
<td>GC-30</td>
<td>polished, laser 25MW/cm$^2$</td>
<td>$&gt;0.5$</td>
<td>59</td>
</tr>
<tr>
<td>Graphite/hexane paste</td>
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<td>0.003</td>
<td>176</td>
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<tr>
<td>Graphite/Nujol paste</td>
<td>none</td>
<td>$10^{-4}$</td>
<td>176</td>
</tr>
</tbody>
</table>

* In 1M KCl unless otherwise noted.
decreased by as much as 40% after laser activation (13), indicating a significant reduction of the adsorbed surface species. High power density or large number of pulses, however, can damage the carbon structure by means such as local melting.

Fracturing is a relatively new technique that involves the breaking of a GC post immediately before the electrochemical measurement (18). In this pretreatment, a pristine carbon electrode surface is created in the solution of interest without exposing the electrode to airborne impurities. Since there is no intentional structural alteration and the surface is likely to have much less impurities, $k^o$ of 0.5cm/s has been observed for Fe(CN)$_6^{3/-4}$ on fractured surfaces (59). Fracturing provides a surface that might be more representative of the bulk glassy carbon material.

Another activation method often used is the electrochemical pretreatment (ECP). In this procedure, the electrode is typically placed in 0.1M KNO$_3$. A positive potential, usually around 1.8V vs Ag/AgCl, is applied to the electrode for ~5 minutes, then the potential is switched to a negative value of about -1.0V for approximately 1 minute. Electrodes after ECP exhibit mixed kinetics changes. For a large number of systems such as hydroquinone, catechol, ascorbic acid, Fe$^{+2}$ and O$_2$, the electron transfer kinetics are faster. However, for the benchmark system of Fe(CN)$_6^{3/-4}$, $k^o$ is in fact decreased (14, 15, 61, 62).

Electrochemical pretreatment produces a surface that is quite different from the other techniques. The surface oxides concentration is greatly increased, e.g., the O/C ratio increased from 0.084 on freshly polished to 0.22 on cathodized ECP surface (15). XPS shows that both phenolic and carbonyl groups are increased (63). These oxides were
found to reside in the outer 20-30 nm (8). Phenol like oxides have been proposed as the active sites that catalyze oxygen reduction reaction (10, 64, 65). However, the reason that ECP electrodes show higher activities over polished electrodes is still unknown. It has been partially attributed to a surface cleaning effect.

In addition to the above pretreatment techniques, carbon electrodes can be further modified with certain organic species. For example, β-carotene was found to adsorb onto laser activated GC that can not be removed by sonication in acetone (66). Since β-carotene is not electroactive, its adsorption onto GC electrode surface may block the active sites and deactivate the electrode. This in turn can slow down the electron transfer kinetics if the electrochemical reaction involves adsorption of the redox species. Another reagent that has been used to modify glassy carbon electrode is 2,4-dinitrophenylhydrazine (DNPH). DNPH binds specifically and quantitatively to the surface \( \gamma C = O \) groups including carbonyl, quinone or ketone-like groups through the following scheme (67):

\[
\begin{align*}
R \gamma C = O + H_2N-NH & \rightarrow R \gamma C = N-NH \quad + \quad H_2O \\
\end{align*}
\]

The \( \gamma C = O \) bonds are converted into hydrozone after DNPH treatment. Therefore, if \( \gamma C = O \) sites are involved in the electrochemical reaction, it can be expected that DNPH modification will have significant influence on the reaction kinetics.

Similar to electrochemical treatments, chemical treatments have also been found to dramatically affect carbon electrode's activities for oxygen reduction. Zhang et al (55),
observed that dipping a GC electrode in nitric acid enhanced its activity while maintaining the electrode at 0 to 0.4V vs Ag/AgCl decreased its activity for oxygen reduction in 1M KOH. Sysoeva et al (56), reported that either chemical or electrochemical treatments decreased the activity of activated carbon electrodes for oxygen reduction. However, Taylor and Humffray (49) observed increased activities after both treatments. Quinone like groups have been accounted for the increased activity by Zhang et al (55).

In this chapter, the oxygen reduction reaction will be explored on four types of carbon surfaces, including electrochemically pretreated GC, laser treated GC, fractured GC and low-defect highly ordered pyrolytic graphite (HOPG) basal plane surfaces. A polished GC electrode serves as the basis for comparison. Some GC electrodes are further modified with β-carotene, butylated hydroxytoluene (BHT), DNPH, anthraquinone-2,6-disulfonic acid, disodium salt (AQDS), 9,10-phenanthrenequinone (PQ) and Ba\(^{2+}\). These electrodes provide surfaces where certain variables are modified. For example, ECP results in an oxide-rich surface; in situ laser activation at low power densities yields a clean electrode surface without altering its morphology; fracturing exposes the pristine carbon structure but contains no adventitious adsorption of impurities. HOPG basal plane is an electronically and structurally very different type of carbon that contains the fewest surface functional groups when carefully prepared. All the valences within the HOPG basal plane are satisfied and the material possesses an electronic property similar to semiconductors. By studying the effect of the different pretreatments on ORR mechanism, it is possible to assess some of the important factors that govern oxygen reduction kinetics on carbon materials.
EXPERIMENTAL

Electrode Preparation

A BAS GC-20 electrode was conventionally polished with successive 1.0, 0.3, and 0.05 μm alumina slurries on Buehler polishing cloth followed by sonication in NANOpure water (Barnstead) for 5 minutes before subsequent treatments. In situ laser activation was performed by delivering 5 pulses of Nd:YAG laser beam operating at 1064nm onto the polished electrode surface. Laser power density varies from 25MW/cm² to 100MW/cm². Electrochemical pretreatment (ECP) was done by oxidizing the polished electrode at 1.8V vs Ag/AgCl for 5 minutes in 0.1M KNO₃ solution followed by reduction at -1.0V for 1 minute in the same solution. The procedures of preparing fractured GC electrode is given elsewhere (18). Briefly, an epoxy ("Eccobond") mounted GC electrode was first filed down to expose a short length of GC post. The electrode was then sonicated in NANOpure water to clean the filing debris before placed into the electrocell. The cell was filled with argon or oxygen saturated analyte. Electrode surface was created by breaking the GC post immediately before a measurement. The newly exposed surface remaining embedded in the epoxy. Typical exposed area was 0.003-0.005cm². HOPG was a gift from Union Carbide and was cleaved with an Exacto knife to expose the basal plane. Inverse drop cyclic voltammetry of Fe(CN)₆³⁻/⁴⁺ (Mallinckrodt) was performed to validate the surface. Further modification of GC electrode was done by sonicating the polished or pretreated electrodes in a 10mM solution of the desired species (BaCl₂·2H₂O, β-carotene/acetone, BHT/acetonitrile, or DNPH/dry alcohol) followed by rinsing with large amount of NANOpure water.
**Electrochemical Measurement**

Cyclic voltammetry was performed in a custom-designed three-electrode cell immediately after the electrode was prepared. In the event of electrode transfer, the electrode surface was kept wet to reduce its exposure to air. The reference electrode was Ag/AgCl with glass frit and its potential was frequently checked (E°=0.203V vs NHE). The auxiliary electrode was a platinum wire. A triangular waveform triggered by a personal computer was delivered to the electrocell through a conventional three-electrode potentiostat (Advanced Idea Mechanics, Columbus, OH) with a RC setting according to nvRC<4mV criteria (68). Electrolyte was saturated either with argon (Linde Gas, prepurified, for background measurement) or oxygen (Linde Gas, ultra high purity) for 20 minutes prior to experiments under ambient temperature and pressure. During data acquisition, the system was maintained under the designated gas environment. In between scans, electrolyte was further saturated with the gas for 1 minute. When studying ORR on HOPG electrodes, inverse drop cyclic voltammetry was performed according to the method described elsewhere (69, 70).

**Reagents**

All chemicals were of AR grade. 1M KOH solution was made using pre-boiled NANOpure water and low carbonate KOH pellet. 1M KOD was made from D₃O (>99.9 atom% D) and KOD solution (40 wt.% in D₂O, >98 atom% D). 1M solution of tetraethylammonium hydroxide (TEAOH), NaOH and LiOH were substituted for KOH to study the effect of cations. In addition, ORR was examined in aprotic media of 1M
tetrabutylammonium perchlorate (TBAP) in acetonitrile solution. K$_3$Fe(CN)$_6$, BaCl$_2$·2H$_2$O, KOH and LiOH were from Mallinckrodt. TEAOH, KOD and D$_2$O were from Aldrich. BHT, β-carotene, acetone and acetonitrile were from Sigma. DNPH was from J.T. Baker. H$_2$O$_2$ solution was made from a 30% H$_2$O$_2$ stock (Fisher Scientific). All electrolytes were made fresh and used without pre-electrolysis.

RESULTS

Figure 7 shows the typical cyclic voltammograms of oxygen reduction in 1M KOH solution at 50mV/s. The solid lines were obtained with O$_2$ present and the dashed lines were the corresponding background voltammograms. The dependence of ORR on the electrode pretreatment becomes clear from these voltammograms. On conventionally polished electrode (Figure 7A), there is one reduction peak at -0.33V and the background current density is quite significant, e.g., 0.13mA/cm$^2$ at -0.5V. On 25 MW/cm$^2$ laser irradiated surface (Figure 7B), the background current decreases to 8.5×10$^{-3}$mA/cm$^2$ at -0.5V but there is still only one reduction peak at -0.35V. On ECP surface (Figure 7C), however, two reduction peaks are observed at -0.23V and -0.97V, respectively. The background current increases to 0.20mA/cm$^2$ at -0.5V. On a GC electrode fractured in O$_2$ saturated solution (Figure 7D), two reduction peaks are also found but the one at -0.97V is much smaller than the one at -0.27V. The background on this electrode is much smaller than that on ECP electrode, with a current density of only 0.01mA/cm$^2$ at -0.5V. When fracturing is done in argon saturated solutions before introducing O$_2$, the reduction peak at -0.97V disappears.
The ORR voltammograms on HOPG basal plane depends on the quality of the surface. A validation procedure to determine the quality of a HOPG basal plane has been described recently by McDermott et al (70). In this procedure, the surface double layer capacitance (C°) in 1M KCl was correlated to the Fe(CN)\textsubscript{6}^{4/-2} kinetics. They reported that surfaces yield k° < 10^-5 cm/s for Fe(CN)\textsubscript{6}^{3/-4}, which corresponds to C° < 1.5μF/cm^2, were considered "validated" surfaces; that is, they have sufficiently low defect densities to be used for basal plane kinetics studies and should yield rates near the true basal plane values. Surfaces with higher C° values are considered more defective and they exhibit faster kinetics for the Fe(CN)\textsubscript{6}^{3/-4} system. Figure 7E and 7F shows the ORR voltammograms on two HOPG basal plane surfaces. In Figure 7E, the electrode has a double layer capacitance C° of 4.8 μF/cm^2 and two reduction peaks are observed. In Figure 7F, the double layer capacitance C° is only 1.1μF/cm^2. This surface is considered "near-perfect" and only one peak is observed at -1.2V. The peak potentials on HOPG vary dramatically with C°. In both cases, the background at -0.5V is less than 0.3 μA/cm^2.

Figure 8 compares the background corrected CVs (cathodic half) on the above electrodes. The drastic differences lie in the peaks appear at between -0.2 to -0.4V. Peaks show in this region are referred to as peak one hereafter and their peak potentials and peak current densities are referred to as Ep\textsubscript{1} and ip\textsubscript{1}, respectively. Similarly, peaks appear at around -0.97V are referred to as peak two and their peak potentials and peak current densities are referred to as Ep\textsubscript{2} and ip\textsubscript{2}, respectively. In Figure 8, Ep\textsubscript{1} is -0.234, -0.289, -0.326 and -0.347V on ECP, fractured, polished and 25MW/cm^2 laser irradiated electrodes, respectively. Using the polished electrode as a reference point, Ep\textsubscript{1} on ECP
Figure 7 Cyclic voltammograms of oxygen reduction (solid line) and corresponding background curves (dashed line) in 1M KOH on pretreated GC electrodes.

(A) conventionally polished; (B) 25MW/cm² laser irradiated, 5 pulses; (C) electrochemically pretreated; (D) fractured in O₂ saturated solution; and HOPG basal plane with C°=4.8μF/cm² (E) and C°=1.1μF/cm² (F).
Figure 7 (Continued)

![Graph C and D](image)

**Graph C**
- Current Density (mA/cm²) vs Potential (V vs Ag/AgCl)
- Indicates changes in current density with potential variation.

**Graph D**
- Current Density (mA/cm²) vs Potential (V vs Ag/AgCl)
- Provides another perspective on the relationship between current density and potential.

The graphs illustrate the electrochemical behavior of the system under study, showing how current density changes with potential fluctuations.
Figure 7  (Continued)
Figure 8 Background corrected cyclic voltammograms of oxygen reduction reaction in 1M KOH. Scan rate = 50mV/s. LA-25 = 5 pulses of 25MW/cm² laser irradiation.
electrode is 92mV more positive, $E_{p1}$ on fractured is 37mV more positive and $E_{p1}$ on laser activated electrode is 21mV more negative. The only peak observed on HOPG (with $C^\circ = 1.1\mu F/cm^2$) appears at -1.22V, almost 900mV more negative than on the polished electrode. Note that current is used instead of current density for the results on HOPG basal plane in Figure 7E and 7F due to the difficulties in obtaining the electrode area in an inverse drop experiment. However, the area of the drop is estimated to obtain the current density values for the HOPG voltammogram in Figure 8. Oxygen reduction on HOPG basal plane is quite different when the surface becomes slightly more defective, e.g., an increased $C^\circ$ as shown in Figure 7E. Not only are two peaks detected, but the peak currents are also increased. Another notable difference in ORR behavior on these electrodes is the presence of second reduction peak. On ECP electrode, peak two appears at -0.97V and its current density is 0.43mA/cm², similar to $i_{p1}$ value. On fractured electrode, peak two occurs at that same potential but its current density decreases to 0.32mA/cm². On polished electrode, only residual peak two is observed. There is a broad wave on the laser activated electrode with a maximum at about -0.87V. Except for HOPG, peak one current densities are similar among electrodes.

$E_{p1}$ on laser irradiated electrodes depends on the laser power density. Figure 9 shows that $E_{p1}$ shifts negative with increasing power densities. The laser irradiation was performed in air saturated solutions. At less than 40MW/cm² power density, the peak potentials were relatively stable, but they were slightly negative than the $E_{p1}$ on polished electrode. Above this value, $E_{p1}$ became more negative almost linearly with increasing power density. The increased overpotential with $>40$MW/cm² laser irradiation suggests an
unfavorable change in the electrode properties for oxygen reduction.

Ep₂ in Figure 8 corresponds to HO₂⁻ reduction potential in alkaline solutions. This is shown in Figure 10 where an argon saturated H₂O₂ solution was reduced on polished and ECP electrodes. No reactivity of H₂O₂ reduction was observed on polished electrode at potential positive of -1.2V. However, on the ECP electrode, the reduction peak occurred at -0.96V which correlates to Ep₂ (-0.97V). When the reduction started at -0.05V vs Ag/AgCl (solid line), a portion of the H₂O₂ was pre-oxidized to O₂. As a result, a small O₂ reduction peak at -0.21V was also observed. These results demonstrated the dramatic influence of surface oxidation on HO₂⁻ reduction.

The background corrected ORR cyclic voltammograms in 1M KOD/D₂O are shown in Figure 11 on polished, ECP and fractured electrodes. Compared to ORR in KOH/H₂O (Figure 8), difference in the first reduction peak potential is smaller. Ep₁ is -0.268, -0.312 and -0.345V on ECP, fractured and polished electrodes, respectively. These potentials represent a negative peak potential shift with deuterium substitution. For peak two, its potential on fractured and polished electrodes are the same but both moved negative to -1.02V. Ep₂ on ECP electrode remains unchanged at -0.97V. Note that peak one current densities are again similar among electrodes and they are quite the same as those obtained in KOH/H₂O solutions. Peak two, however, becomes more distinctive than those found in KOH/H₂O, particularly for the polished electrode.

Since oxygen reduction has been proposed to involve adsorption of either molecular oxygen or the reaction intermediates, we have modified GC electrodes to test the influence of these adsorbed species. Figure 12 shows the CVs of ORR on polished
Figure 9 The first reduction peak potentials ($E_{p1}$) of oxygen reduction reaction on laser irradiated GC electrodes as a function of the laser power density.
Figure 10  $\text{HO}_2^-$ reduction on ECP and polished glassy carbon electrodes in 1M KOH at 50mV/s.
Figure 11  Background corrected cyclic voltammograms of oxygen reduction reaction in 1M KOD/D$_2$O solution. Scan rate = 50mV/s.
electrodes after β-carotene and BHT modification. The reduction peak obtained with either species pre-adsorbed has smaller current density and occurs at about 40 mV more negative. However, the reduction remains distinctive, indicating that β-carotene or BHT does not severely obstruct the reaction.

Figure 13 reveals the effect of DNPH treatment on the oxygen reduction kinetics at ECP electrodes. DNPH is believed to bind quantitatively with carbonyl or quinone-like oxides which are present on the ECP surface. However, Figure 13 shows that both peak one and peak two are not significantly hindered by DNPH treatment. Ep₁ shifts negative by 24 mV but Ep₂ becomes slightly more positive. The peaks current densities also increase slightly after DNPH treatment. The modulation observed on the (ECP+DNPH) electrode seems to be associated with the DNPH treatment, as it occurs consistently.

The oxygen reduction reaction in aprotic media was also studied. Figure 14 shows the CVs obtained on a polished GC electrode in 1M TBAP/CH₃CN. The reaction is quasi-reversible with a peak separation of 112 mV at 50 mV/s. Note that the cathodic peak potential in TBAP/CH₃CN is ~580 mV more negative than Ep₁ on polished electrode in KOH solution. It is known that in the absence of proton sources such as in pyridine solution, O₂ is reversibly reduced to O₂⁻ with E⁰ = -0.84 V vs Ag/AgCl (52, 71). The shift of E⁰ from -0.13 V in KOH solution (177) for the O₂ + e⁻ ⇌ O₂⁻ reaction to -0.84 V in pyridine is mainly due to the much lower solvation energies of pyridine to O₂⁻ than H₂O to O₂⁻. Also shown in Figure 14 is the influence of adsorbed β-carotene. It is apparent that the kinetics of the first electron reduction are unchanged, evidenced by the same peak potentials and peak separation. The current density, on the other hand, is decreased.
Figure 12 Effect of β-carotene and BHT adsorption on O₂ reduction at polished GC electrodes in 1M KOH/H₂O solution. Scan rate = 50mV/s.
Figure 13 Background corrected voltammograms of O₂ reduction on ECP and 2,4-dinitrophynylhydrazine (DNPH) treated ECP-GC electrodes in 1M KOH. Scan rate = 50mV/s.
Figure 14 Voltammograms of $O_2$ reduction in 1M TBAP/CH$_3$CN on polished GC electrode before and after $\beta$-carotene adsorption. CVs are NOT background corrected. Scan rate = 50mV/s.
Figure 15 demonstrates the effect of cations on oxygen reduction. Four different cations were used, including TEA⁺, K⁺, Na⁺ and Li⁺. These cations have quite different ionic radii which result in very different ORR behavior. More positive Ep₁ and higher ip₁ were observed with smaller cations (non-hydrated radii), e.g., Ep₁ in LiOH is 65mV more positive than Ep₁ in TEAOH and ip₁ is almost doubled. Slight change is found between NaOH and LiOH. These results suggest that cations in the electrolyte are involved in the reduction pathways. Table 2 summaries all peak one potentials after various treatments and in the four different cation solutions.

Figure 16 shows the CVs of HO₂⁻ oxidation in 1M KOH at 50mV/s. The oxidation peaks appear at very similar potentials of ~0.6V on all three electrodes, despite these electrodes have significantly different activities for oxygen reduction reaction (see Figure 8). When the surface is further modified with Ba²⁺ by sonicating the pretreated electrode in 10mM BaCl₂2H₂O solution followed by rinsing the electrode with large amount of H₂O, the HO₂⁻ oxidation kinetics are greatly enhanced on all three electrodes. Table 3 lists the observed peak potentials. It can be calculated that after Ba²⁺ treatment, HO₂⁻ oxidation peaks occur at 175, 146 and 148 mV more negative on polished, fractured and ECP electrodes, respectively (in KOH/H₂O solution). When HO₂⁻ oxidation is performed in KOD/D₂O solutions, the kinetics are found to be slower than in KOH/H₂O solutions, evidenced by a peak potential shift of +5mV on Ba²⁺ modified polished electrode to +138mV on Ba²⁺ modified fractured electrode. The difference in the peak potentials with and without Ba²⁺ modification is relatively smaller in KOD/D₂O solutions.
Figure 15 Effect of cations on O$_2$ reduction at polished GC electrodes. Voltammograms are background corrected. All electrolyte solutions are 1M. Scan rate = 50mV/s.
Figure 16  \( \text{HO}_2^- \) oxidation on polished, ECP and fractured GC electrodes in 1M KOH. Voltammograms are background corrected. Scan rate = 50mV/s.
<table>
<thead>
<tr>
<th></th>
<th>KOH/H$_2$O (mV)</th>
<th>KOD/D$_2$O (mV)</th>
<th>$\Delta$Ep (D-H) (mV)</th>
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</thead>
<tbody>
<tr>
<td>Polished</td>
<td>-326.4±2.6 (n=10)</td>
<td>-345.4±8 (n=2)</td>
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<tr>
<td>LA-25</td>
<td>-347.2±15.1 (n=5)</td>
<td>-367.8±10.6 (n=2)</td>
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<tr>
<td>Fracture-O$_2$</td>
<td>-288.7±10.3 (n=4)</td>
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<td>-23.2</td>
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<tr>
<td>Fracture-Ar</td>
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<td>-16.9</td>
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<tr>
<td>ECP-pH14</td>
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<td>ECP-pH13</td>
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<td>ECP + DNPH</td>
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<tr>
<td>Polished + β-carotene</td>
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<td>Polished + BHT</td>
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<td>Polished, with Na$^+$</td>
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<td>Polished, with TEA$^+$</td>
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<tr>
<td>polished, in MeCN</td>
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<td></td>
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</tr>
<tr>
<td>polished + PQ</td>
<td>-290</td>
<td></td>
<td></td>
</tr>
<tr>
<td>polished + AQDS</td>
<td>-310</td>
<td></td>
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<tr>
<td>HOPG (C$^\circ$=1.1μF/cm$^2$)</td>
<td>-731</td>
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</table>

Note: (1) $E_{p1}$ is vs Ag/AgCl reference ($E^\circ$=0.203V) and is obtained from 50mV/s scans. (2) n is the number of data points used to get the average.
Table 3  \( \text{HO}_2^- \) oxidation peak potentials in alkaline solutions

<table>
<thead>
<tr>
<th></th>
<th>KOH/H(_2)O (mV)</th>
<th>KOD/D(_2)O (mV)</th>
<th>( \Delta \text{Ep (D-H)} ) (mV)</th>
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<tbody>
<tr>
<td>Fractured</td>
<td>629.8±2.2 (n=2)</td>
<td>702.5±6.2 (n=2)</td>
<td>+72.7</td>
</tr>
<tr>
<td>Fractured + Ba(^{+2})</td>
<td>483.7±15.5 (n=2)</td>
<td>621.9±3.8 (n=2)</td>
<td>+138.2</td>
</tr>
<tr>
<td>Polished</td>
<td>603.4±1.7 (n=3)</td>
<td>654.0±1.0 (n=2)</td>
<td>+50.6</td>
</tr>
<tr>
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<td>427.9 (n=1)</td>
<td>432.9±16 (n=2)</td>
<td>+5</td>
</tr>
<tr>
<td>ECP</td>
<td>595.2±9.3 (n=3)</td>
<td>654.0±1.0 (n=2)</td>
<td>+59</td>
</tr>
<tr>
<td>ECP + Ba(^{+2})</td>
<td>446.8 (n=1)</td>
<td>491.1±5.0 (n=2)</td>
<td>+44.3</td>
</tr>
</tbody>
</table>

Note:  (1) Peak potentials are measured from background corrected CVs at 50mV/s.  
(2) n is the number of data points used to get the average.
DISCUSSION

Oxygen reduction reaction has been studied for over 130 years and is still not well understood due to the complexity involved in this reaction (178). As mentioned earlier, there are many reduction pathways that have been proposed on carbon electrodes. Generally, these mechanisms concern only the first two electron reduction and little has been done to the investigation of the third and fourth electron reduction on carbon materials. However, even with the first two electron reduction, results reported by various people are controversial. Most workers agree that the first step involves a 1e\textsuperscript{-} reduction of O\textsubscript{2} to superoxide, which may be adsorbed to the carbon surface:

\begin{equation}
O_2 + e^- \rightleftharpoons O_2^-
\end{equation} \[2.24\]

The O\textsubscript{2}\textsuperscript{-} ions can then react with H\textsubscript{2}O and a second electron to become HO\textsubscript{2}\textsuperscript{-}:

\begin{equation}
O_2^- + H_2O + e^- \rightleftharpoons HO_2^- + OH^-
\end{equation} \[2.25\]

or they can react with H\textsubscript{2}O to become HO\textsubscript{2} which then disproportionate to form O\textsubscript{2} and be recycled back to step \[2.24\]:

\begin{equation}
O_2^- + H_2O \rightleftharpoons HO_2^- + OH^-
\end{equation} \[2.26\]

\begin{equation}
2HO_2^- + OH^- \rightleftharpoons HO_2^- + H_2O + O_2
\end{equation} \[2.27\]
These mechanistic steps were derived by various authors to explain their experimental data. Because different types of carbon or different pretreatments were involved in the experiment, the results were very diversified. Therefore, the mechanisms suggested were wide spread.

Step [2.25] has been suggested to occur as:

\[
O_2^- + H_2O \rightleftharpoons HO_2^- + OH^- \quad [2.28]
\]

\[
HO_2^- + e^- \rightleftharpoons HO_2^- \quad [2.29]
\]

or as:

\[
O_2^- + H_2O \rightleftharpoons HO_2^- + OH \quad [2.30]
\]

\[
OH + e^- \rightleftharpoons OH^- \quad [2.31]
\]

Regardless of the actual steps involved in O$_2$ reduction, one can arbitrarily divide these schemes into three interconnected stages: the first electron reduction step [2.24], the proton transfer step [2.26], [2.28] or [2.30], and the second electron transfer step [2.29] or [2.31], or the disproportionation step [2.27]. Previous investigation have shown that the overall reaction is first order dependent on the partial pressure of O$_2$ and zero order dependent on [OH$^-$] and [HO$_2^-$] (48)

The above schemes do not include a step for adsorption, which is believed to play an important role in ORR mechanism. The effect of adsorption will be discussed later. But
for now, it is apparent that oxygen reduction involves both homogeneous chemical
reaction (e.g., proton transfer) and heterogeneous electron transfer. It would be difficult
to study the effect of the chemical reaction without the complication from the electron
transfer, or vice versa. However, with well defined carbon electrodes such as those used in
this investigation, it is possible to assess the influence of some of the surface processes.

Like many others, we find that oxygen reduction on carbon electrodes is strongly
dependent on the electrode pretreatment. The kinetics are faster on oxidized surfaces,
shown by more positive \( E_{p1} \). This is particularly evident on ECP electrodes where \( E_{p1} \) is
92 mV more positive than on a conventionally polished electrode (Figure 8). Nagaoka and
Yoshino observed +200 mV potential shift for ORR after ECP (61). Engstrom and
Strasser also reported +370 mV and +700 mV change in \( E_{1/2} \) for wave 1 and wave 2 in
RDE measurement after ECP (15). The different degree of improvement is related to the
initial state of the polished electrode. For an electrode fractured in \( O_2 \) saturated solution
(Figure 7D), \( E_{p1} \) is also more positive than the conventionally polished electrode by
37 mV.

The laser irradiated electrode, on the other hand, has a more negative \( E_{p1} \) than the
polished electrode. Laser irradiation at 25 MW/cm\(^2\) power density was believed to clean
the electrode surface by means of thermal desorption of the preadsorbed impurities
without altering the electrode microstructure (60). However, \( E_{p1} \) is 21 mV more negative
after laser irradiation of a polished electrode. \( E_{p1} \) continues to shift negative with
increasing laser power density, suggesting that certain species in the desorbed layer are
necessary for faster ORR kinetics.
The first electron oxygen reduction, \( \text{O}_2 + e^- \rightleftharpoons \text{O}_2^* \), in aprotic solutions such as CH\(_3\)CN and pyridine, was found to be reversible because the \( \text{O}_2^* \) ions cannot be protonated to allow subsequent reaction. Instead, they are stable in the aprotic solutions and can be oxidized back to \( \text{O}_2 \). However, in most aqueous alkaline solutions, \( \text{O}_2^* \) can further react with a proton to form \( \text{HO}_2^- \). Since \( \text{HO}_2^- \) oxidation only occurs at much more positive potentials (Figure 16), the reduction of \( \text{O}_2 \) to \( \text{HO}_2^- \) is generally considered irreversible. Surprisingly, ORR in 2.4M TEAOH solution gives a voltammogram corresponds to a quasi-reversible reaction, as shown in Figure 17A. The cathodic peak is at \( \sim -0.37\text{V} \) and the anodic peak is at \( \sim -0.26\text{V} \). Note that the anodic peak is smaller than the cathodic peak, indicating that a portion of the reduction product further reacted to form other species on the time scale of the experiment. The current density for the cathodic peak is only 0.066mA/cm\(^2\), much smaller than those shown in Figure 8 or Figure 15, which are about 0.47mA/cm\(^2\).

However, in 1M TEAOH, the cathodic peak current density increases to 0.26mA/cm\(^2\) while the anodic peak becomes diminished (Figure 17B). The cathodic peak current density corresponds to that expected for a reversible one electron reduction, as estimated from the following equation (184):

\[
\text{Current Density} = \frac{i_p}{A} = \frac{(2.69 \times 10^5) \times n^{3/2} \times D_0^{1/2} \times \nu^{1/2} \times C_0^*}{2.32}
\]

Given \( n=1, D_0=1.65 \times 10^{-5} \text{cm}^2/\text{s}, \nu=0.05\text{V/s} \) and \( C_0^* = 1.2\text{mM} \), the calculated current density is 0.29mA/cm\(^2\), close to the observed 0.26mA/cm\(^2\). Further more, the anodic peak
Figure 17 Cyclic voltammograms of O₂ reduction on polished GC electrodes in 2.4M (A) and 1M (B) TEAOH. CVs are background corrected. Scan rate = 50mV/s. The dashed line in (A) is simulated with $\alpha=0.52$, $T=298$K and $k^0 = 0.005$cm/s for the reaction $O_2 + e^- \rightarrow O_2^-$.
in TEAOH is unlikely to be due to HO$_2^-$ oxidation, as HO$_2^-$ oxidation occurs at $\sim +0.6$V (Figure 16). Therefore, the quasireversible reaction observed in TEAOH can be assigned to the $\text{O}_2 + \text{e}^- \rightleftharpoons \text{O}_2^-$ reaction. This is the first time a quasireversible O$_2$/O$_2^-$ reaction is observed in aqueous solutions. The smaller peak current densities found in 2.4M TEAOH solution probably result from a smaller O$_2$ solubility and a smaller diffusion coefficient of O$_2$ in more concentrated TEAOH. Note that equation [2.32] is only approximately correct under current conditions. A better simulation to the peak current densities is given later.

The $E_{1/2}$ calculated from the average of the reduction and oxidation peak potentials is $-0.31$V vs Ag/AgCl. This is more positive than the $E^\circ$ of $-0.53$V for the O$_2$/O$_2^-$ couple deduced from radiolysis studies in alkaline solutions (179, 180). However, it is known that $E^\circ$ for this couple is strongly medium dependent due to the differences in the solvation of the O$_2^-$ ions with the medium. As a comparison, the $E^\circ$ value in TBAP/CH$_3$CN solution is about $-0.8$V vs Ag/AgCl because the O$_2^-$ ions are difficult to solvate by CH$_3$CN (177).

From the peak separation of 118mV in Figure 17A, the heterogeneous electron transfer constant, $k^\circ$, for the O$_2$/O$_2^-$ couple is calculated to be 0.005cm/s, based on Nicholson and Shain's treatment (77). Using $k^\circ$ of 0.005cm/s, $E^\circ$ of $-0.31$V and $\alpha$ of 0.52 (172), a voltammogram of O$_2$/O$_2^-$ reaction can be simulated. Figure 17A compares the simulated CV with the experimental CV. Apparently, they agree well, suggesting that a $k^\circ$ value of 0.005cm/s is reasonable for the O$_2$/O$_2^-$ redox in aqueous solutions on polished GC electrode.
It has been suggested that oxygen reduction involves the adsorption of either molecular $O_2$ or the reaction intermediate such as $O_2^-$. Current data do not support this adsorption for several reasons. First, peak one current density $i_{p_1}$ is proportional to $\sqrt{v}$ which is typical of a diffusion controlled redox process with no adsorption of the active species. If adsorption is involved, $i_{p_1}$ will be proportional to $v$ instead. Second, intentional contamination of the surface with monolayer adsorption of either $\beta$-carotene or BHT cause slight changes in the voltammetry (Figure 12). Since both species are not electroactive, their adsorption to the electrode surface can be expected to cause severe inhibition to the electron transfer if adsorption of either $O_2$ or $O_2^-$ is involved. Third, $\beta$-carotene adsorption to a polished GC electrode has no effect on the kinetics of $O_2/O_2^-$ reduction in 1M TBAP/CH$_3$CN solution (Figure 14). Because only $O_2$ and $O_2^-$ species are involved in aprotic solution, any influence to their adsorption energetics will drastically change the reaction kinetics. The fact that the $O_2/O_2^-$ kinetics are not changed by $\beta$-carotene treatment weakens the possibility of $O_2$ or $O_2^-$ adsorption. Although this evidence does not rule out the possibility of subsequent adsorption of $O_2^-$ or other intermediates such as $HO_2^-$, they do imply that the initial $O_2/O_2^-$ reduction is not dependent on the adsorption of $O_2$ or $O_2^-$, hence it is considered here that the $O_2/O_2^-$ reduction proceeds via an outer-sphere mechanism. Similarly, the $O_2/O_2^-$ reduction in acetonitrile on GC electrode (185) and in aqueous solutions on Hg electrode (73, 74) have been proposed to be outer sphere. Yeager et al, also concluded that $O_2^-$ was produced by an outer
Helmholtz plane electron transfer process on the basal plane of stressed annealed graphite in 2M NaOH (50).

Figure 8 and Figure 11 show that the oxygen reduction kinetics are quite different among electrodes. The ECP electrode has the most positive Ep in either KOH/H$_2$O solution or KOD/D$_2$O solution. The enhanced kinetics have been proposed to due to the surface oxides catalysis. Both phenol and carbonyl type of oxides were found to be increased (63) after ECP and both of them have been attributed to catalyze oxygen reduction. However, the voltammetry on DNPH treated ECP electrode suggests that carbonyl type of oxide is not necessarily the active sites.

Figure 13 shows the ORR CVs with or without DNPH treatment. Although DNPH binds quantitatively to the carbonyl sites, they do not significantly affect the reduction kinetics. Ep only shifts 24mV negative after treating the ECP electrode in 10mM DNPH solution for 2 hours. Raman studies on such an electrode shows significant amount of resonance peaks due to the formation of hydrozones from the reaction of DNPH and the surface carbonyl groups. Since DNPH binds specifically to $\gamma$C = O groups (carbonyl, quinone or ketonic oxides), the slight influence to the ORR kinetics after DNPH treatment indicates that these $\gamma$C = O groups are not the catalytic center, at least carbonyls alone can not explain the dramatic peak shift (92mV) between polished electrode and ECP electrode. It is possible, though, that because of the thickness of the oxide layer created by ECP, DNPH might not penetrate inside and bind to all $\gamma$C = O groups that are not on the surface. However, it is unlikely that oxygen reduction will be
catalyzed by those oxides either, since they might not be accessible to O₂ molecules.

If \( \gamma C = O \) groups are not necessarily the active species, then the enhanced electrode activities on ECP electrode must due to other types of oxides. The most probable oxides on ECP surface other than the \( \gamma C = O \) type is of type \( \gamma C - OH \) which include semiquinone, phenol or alcohol groups. One can also argue that the faster ORR kinetics after ECP result from the surface cleanliness since the very positive potential applied during ECP (+1.8V vs Ag/AgCl) is capable of oxidizing the surface contaminants and clean the electrode. However, in the case of laser irradiation, ORR kinetics are slower on cleaner electrode surfaces. Low power density (≤ 25MW/cm²) laser irradiation cleans the electrode surface, but \( E_{p_1} \) is in fact more negative than on conventionally polished electrode. When the power density is increased, e.g., >40MW/cm², \( E_{p_1} \) becomes even more negative, suggesting that the surface is less favorable for oxygen reduction. It is possible that high power laser irradiation can modify the carbon surface via local melting due to the extreme high temperature generated. STM has shown that 3 pulses of 70MW/cm² laser irradiation causes severe structural damage to the GC electrode, especially along the polishing scratches (72). The partially melted electrode might possess an electronic feature similar to HOPG basal plane which is much less active for electron transfer. Hence the overpotential for ORR increases with increasing laser power density. However, the low power laser irradiation does not change the surface microstructure. The more negative \( E_{p_1} \) observed with low power laser treated electrodes suggests that oxygen reaction is slower on cleaner surfaces. Therefore, the faster kinetics on ECP electrode is
unlikely due to surface cleanliness, but instead due to the surface catalysis by $\text{C-OH}$
type oxides.

Among all the different ORR results observed after electrode pretreatment, the
most intriguing ones perhaps are those on fractured electrodes. The fractured surfaces are
unusual in the way they are prepared. The electrode surface is created in situ by breaking
the GC post. There is no intentional impurity adsorption and the electrode is inherently
clean. XPS found lower O/C ratio on fractured electrodes than polished electrode (18).
However, ORR kinetics are quite fast on fractured surfaces. $E_p$ is 37mV more positive
than on polished electrode in KOH solution (Figure 8). This enhanced kinetics can not be
explained by surface cleanliness, as the laser irradiated electrodes have shown slower ORR
kinetics on cleaner surfaces. It can be, though, that the faster kinetics on fractured
electrode is due to the surface roughness. The active surface area of these electrodes,
measured by chronoamperometry of $\text{Fe(CN)}_6^{3/-4}$, is usually higher than their geometric
area. But a more probable cause to this enhanced kinetics is the catalysis by surface
oxides. This will be discussed later.

In addition to being strongly dependent on the electrode pretreatment, ORR
kinetics are also dependent on the cations in the electrolyte. Figure 15 shows that $E_p$ is
more positive in the order of the alkaline solutions $\text{LiOH} > \text{NaOH} > \text{KOH} > \text{TEAOH}$.
This indicates that cations participate in the reduction mechanism and smaller (non-
hydrated radii) cations shift $E_p$ to more positive potentials. Jaworski et al (181), reported
that cations interact with glassy carbon electrodes in the above order. The potential of
zero charge (PZC) of a given system was dependent of the cations.
Another interesting phenomenon to oxygen reduction in alkaline solutions carried out in this study is the strong H/D isotope effect. Table 2 shows that ORR becomes slower in KO\textsubscript{D}/D\textsubscript{2}O solution than in KO\textsubscript{H}/H\textsubscript{2}O solution. The H/D isotope effect is more significant on oxide-rich surface than on low oxide surface. For example, the difference in \( \Delta E_{p_1} \) is 33.9mV on ECP surface as compared to 16.9mV on fractured-in-argon surface. The changes in \( E_{p_1} \) after deuterium substitution implies that a proton is involved in the rate determining steps under these circumstances. Due to the higher mass of D vs H, the reduction kinetics becomes slower in KO\textsubscript{D}/D\textsubscript{2}O solution.

The above discussion has presented the experimental observations that are important for deriving a working model. A summarization of the facts include:

1. ORR is strongly dependent of the electrode pretreatment. More positive \( E_{p_1} \) is observed on ECP electrodes and fractured electrode while more negative \( E_{p_1} \) is observed on low power laser irradiated electrode;
2. A quasi-reversible \( O_2/O_2^- \) reaction can be obtained in TEAOH solutions with an average \( E_{1/2} = -0.31 \text{V} \) and apparent \( k^o = 0.005 \text{cm/s} \);
3. The \( O_2/O_2^- \) reaction proceeds via an outer-sphere mechanism since intentional surface contamination using \( \beta \)-carotene and BHT do not significantly affect the reaction kinetics;
4. The surface \( C = O \) oxides such as carbonyls are unlikely to be the active sites since they can not explain the great peak shift between ECP electrode and polished electrode. Other type of oxides must be responsible for the enhanced
kinetics;

(5) ORR is subjected to strong cation effect and H/D isotope effect. Smaller cations (non-hydrated radii) shift $E_{p_1}$ to more positive potentials. H/D effect is more evident on oxide rich surfaces.

A mechanism deduced for ORR in alkaline solutions must be consistent with these observations. Yeager et al, proposed a quinone mediated reaction process for oxygen reduction (172) based on the result that adsorbed 9,10-phenanthrenequinone (PQ) activates ORR on HOPG basal plane and the activity of the electrode tracks the concentration of (PQ$^-$). We also observed higher activities of polished electrodes with adsorbed PQ and anthraquinone-2,6-disulfonic acid, disodium salt (AQDS), as shown in Figure 18. However, benzoquinone treated electrode has no effect on $E_{p_1}$.

Although certain kind of adsorbed quinones can catalyze oxygen reduction, Nagaoka et al, found that quinones of electrochemically treated electrodes can not serve as mediators (62). Our current data are also against a mediation mechanism, because:

1. ORR kinetics is dependent of different cations (Figure 15) and is subjected to a H/D isotope effect (Table 2). There is no reason for such an effect if mediation via surface quinone groups determines the kinetics;

2. The quinone redox peaks (PQ or AQDS) is almost 200mV more negative than $E_{p_1}$ of ORR (Figure 18). Very little semiquinone anions can be expected at the onset potential of ORR ($\sim -0.25V$).

3. DNPH treatment does not greatly affect $E_{p_1}$ (Figure 15) although DNPH is known to bind to the $\overset{\varphi}{C} = O$ groups.
(4) ORR kinetics is fast on fractured GC electrode yet there is no background quinone redox peaks observed (Figure 19). The fractured electrode exhibits extremely low background currents, thus allowing the best possibility of observing surface quinone peaks. The waves at about -0.3V is from residual O$_2$ reduction and is not the quinone redox peak.

(5) If quinones mediate O$_2$ reduction, then adsorption with monolayer of PQ or AQDS should enhance the kinetics much more than the fractured electrode. The fractured surface should have only small surface quinone coverage. Table 2 shows the opposite. Ep$_1$ on fractured surface is more positive than the quinone adsorbed surfaces. Therefore, if quinone mediation occurs at all, it must be minor under these circumstances.

In order to deduce a mechanism that is consistent with current results, we propose that {s}-OH type of surface oxides (e.g., phenol or alcohol, {s} represents surface) are the dominant active species in catalyzing oxygen reduction in base. Since both carbonyl and phenol type of oxides are increased after ECP (63) and carbonyls do not have significant effect on the kinetics after they have been converted to hydrozone form ($\langle C = N - N - R\rangle$), it is most likely that the phenol groups are responsible for the enhanced kinetics seen with ECP electrodes.

The proposal of surface catalysis via {s}-OH is consistent with the observation of the cation effect. In 1M base, these {s}-OH groups would be deprotonated to become {s}-O$^-$ which can ion-pair with the cations in the supporting electrolyte in the following fashion:
Figure 18  Background NOT corrected cyclic voltammograms of $O_2$ reduction on quinone (PQ and AQDS) adsorbed polished GC electrodes in 1M KOH. Scan rate = 50mV/s. [AQDS] = 0.3mM, [PQ] = saturated, approximately 1mM.
Figure 19  Background voltammograms on fractured GC electrodes in 1M KOH. Scan rate = 50mV/s.
Oxygen reduction can then be facilitated through these ion-pair bridges. The smaller the cations, the more efficient the ion-pairing, and the faster the ORR kinetics. This is shown in Figure 15 where $E_p$ is the most positive with LiOH and the most negative with TEAOH. Instead of the ion-pairing possibility proposed here, Meyer et al. suggested a proton assisted electron transfer mechanism on oxidatively activated glassy carbon electrodes through the semiquinone groups for couples such as catechol, $(\text{bpy})_2(\text{H}_2\text{O})\text{Ru(OH)}^{2+}$ and $(\text{NH}_3)_2\text{Ru(OH)}^{2+}$ in acidic media (63).

The faster kinetics seen with fractured electrodes can also be explained with the $\{s\}$-$O^-$ catalysis mechanism. In preparing the fractured electrode, when the GC post is broken, some unsaturated valences can be created. These unsaturated valences can then be quenched either with each other or by the solvent, or they can form surface oxide with dissolved oxygen and/or the surrounding electrolyte. Kelemen, Freund and Mims (182) reported that large number of broken bonds were created when a carbon surface is subjected to ion bombardment. These type of surfaces were active toward $\text{H}_2\text{O}$ adsorption and dissociation, e.g., exposure to $\text{H}_2\text{O}$ vapor at 30°C produced saturation oxygen coverage after $10^2$ torr-s on a glassy carbon surface. The dissociative adsorption of $\text{H}_2\text{O}$ produce hydroxyls and/or oxygen species on the surface. Somorjai et al (183), also reported that the physical wetting of clean graphite by liquid $\text{H}_2\text{O}$ favored the formation of
alcohol or ether species. The following cartoon can be used to illustrate the fracturing process:

![Fracturing Process Cartoon]

Depending on the fracturing environment, the type and the amount of oxides formed might be different. For example, if fracturing is performed in oxygen saturated solution, then the broken bonds can react with both the dissolved O_2 and the electrolyte to yield phenol, quinone and carbonyl type of oxides (above cartoon). If fracturing is performed in argon saturated solution, then the broken bonds can react with the electrolyte and most likely to yield phenol or alcohol type of oxides as suggested by Kelemen (182) and Somorjai (183):

![Fracturing Process Cartoon]

In either case, \{s\}-OH type of oxides can be expected. These groups then serve as the active sites for oxygen reduction, which result in the more positive E_{p1} on fractured electrodes. However, since the \{s\}-OH concentration generated via the unsaturated
valences is probably much lower than those on ECP electrodes, the fractured GC is not as active for ORR as ECP electrode. Ep₁ on fractured electrode is -0.289V relative to -0.234V on ECP electrode.

As for laser irradiated electrodes, because the surface layer that contains the oxides is thermally desorbed, the {s}-OH concentration may be lower than on conventionally polished electrode. Therefore, Ep₁ on laser irradiated electrode is more negative than the Ep₁ on polished electrode due to a lack of {s}-O⁻ catalysis.

The above hypothesis is consistent with the observation that Ep₁ is more positive on more oxidized surfaces and it is subjected to a cation effect. However, it does not explain the H/D isotope effect or how the surface {s}-O⁻ groups affect the reduction kinetics. Since the first electron transfer (O₂ + e⁻ ⇌ O₂⁻) does not involve protons, the H/D effect must come from subsequent reactions where protons are involved. The greater isotope effect on more oxidized surface indicates that the proton transfer reaction has become the rate determining step on the oxidized surface. Stated differently, the first electron transfer reaction, O₂ + e⁻ ⇌ O₂⁻, must be reasonably fast on oxidized surfaces such that the subsequent reaction becomes rds in the mechanism. If the reaction of O₂ + e⁻ ⇌ O₂⁻ is slow, then this reaction is the rate-determining step and the overall kinetics should have little influenced from the subsequent reactions.

Since the only likely proton source in base is H₂O, the reaction followed by O₂⁻ is most probably:

\[ O₂ + H₂O \rightarrow HO₂ + OH^- \]  [2.26]
Based on a pKₐ for HO₂ of 4.8 (76), the equilibrium constant Kₑq for this reaction is calculated to be $6.3 \times 10^{-10}$. After the proton transfer, HO₂ can either be reduced via step [2.29]:

$$\ce{HO2 + e^- \rightleftharpoons HO2^-}$$ \hspace{1cm} \(E^\circ = 0.342 \text{V vs Ag/AgCl}\) \hspace{1cm} [2.29]

or it can be disproportionated as in step [2.27]:

$$\ce{2HO2 + OH^- \rightleftharpoons HO2^- + H2O + O2}$$ \hspace{1cm} [2.27]

with a Kₑq calculated from $\Delta G^\circ$ of $2 \times 10^{15}$ (76) and $k_f$ of $1 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ (177). Whether HO₂ is reduced or disproportionated, the reaction following step [2.26] is fast given the negative potential of $E_p$ (~ -0.3 V) and should have little effect on the overall kinetics.

A commercial digital simulation program (BioAnalytical Systems, DigiSim™ 1.0) was used to assess the influence of the electron transfer kinetics $k_i^e$ and the proton transfer reaction on the voltammetry based on the following mechanism. Simulation based on the disproportionation step [2.27] will be discussed later.

$$\ce{O2 + e^- \rightleftharpoons O2^-}$$ \hspace{1cm} \(E^\circ_1 = -0.311 \text{ V}\) \hspace{1cm} [2.24]

$$\ce{O2^- + H_2O \rightleftharpoons HO2 + OH^-}$$ \hspace{1cm} \(K_{eq}\) \hspace{1cm} [2.26]

$$\ce{HO2 + e^- \rightleftharpoons HO2^-}$$ \hspace{1cm} \(E^\circ_2 = 0.342 \text{ V}\) \hspace{1cm} [2.30]
The following parameters were used in the simulation:

\[
k_1^p = 0.005 \text{ cm/s}, \quad k_2^p = 0.01 \text{ cm/s}
\]

\[
D_{O_2} = 1.65 \times 10^{-5} \text{ cm}^2/\text{s}, \quad [O_2] = 1.2 \text{ mM}, \quad \nu = 0.05 \text{ V/s}, \quad \text{and } T = 298 \text{K}
\]

First assuming the reverse rate for step [2.26] is diffusion controlled \((k_b = 10^{10} \text{ M}^{-1} \text{s}^{-1})\) such that the largest forward rate \(k_f\) is 6.3 \text{ M}^{-1} \text{s}^{-1}. The predicted peak one current density \((i_{p1})\) and \(E_{p1}\) are shown in Figure 20A. Note that \(E_{p1}\) is nearly independent of the magnitude of \(K_{eq}\) indicating that reaction [2.26] has little effect on the peak potentials because reaction [2.24] is relatively slow \((k_1^p = 0.005 \text{cm/s})\). The peak current density at \(K_{eq} < 10^8\) is 0.27 mA/cm\(^2\), corresponds to a reversible 1e\(^-\) reduction. But at \(K_{eq} \geq 10^4\), \(i_{p1} = 0.49 \text{mA/cm}^2\), similar to the experimental peak current density of \(\sim 0.47 \text{mA/cm}^2\) in both Figure 8 and Figure 11. This value also corresponds to an irreversible 2e\(^-\) reduction process, as estimated from the following equation (184):

\[
\text{Current Density} = \frac{i_p}{A} = (2.99 \times 10^5) \times n \times (\alpha n_a)^{1/2} \times D_0^{1/2} \times \nu^{1/2} \times C_0^* \quad [2.33]
\]

Giving \(n=2, \alpha=0.52, n_a=1, D_0=1.65 \times 10^{-5} \text{cm}^2/\text{s}, \nu=0.05 \text{ V/s} \) and \(C_0^* = 1.2 \text{ mM}\), the calculated current density is 0.47 mA/cm\(^2\).

While the trend of \(i_{p1}\) increasing with higher \(K_{eq}\) because step [2.26] makes the follow up reaction possible, the value of \(K_{eq} = 10^4\) is unreasonably large given the known \(pK_a\) for HO\(_2\) of 4.8. Such a discrepancy is in part due to the assumption that there is no
adsorption involved in the reaction (DigiSim™ 1.0 can not incorporate the effect of adsorption into the simulation). The no-adsorption assumption is probably not valid since it has been widely agreed that oxygen reduction involves the adsorption of intermediates. A much larger $K_{eq}$ would be possible if the actual $pK_a$ for $HO_2$ under the experimental conditions is higher due to some kind of interaction of $O_2^-$ with the electrode. For example, if $O_2^-$ is adsorbed to a surface radical sites to become $\{s\}$-C-O-O' moiety, the $pK_a$ for $HO_2$ should be larger than when $O_2^-$ is a free ion. Using Figure 20A as a guide, we should predict that $K_{eq}$ might be $\geq 10^{-4}$ (thus $pK_a$ for $\{s\}$-C-O-O' is $\sim 10$ instead of 4.8) to yield a peak current that corresponds to $2e^-$ reduction.

Figure 20B shows the simulated $ip_1$ and $E_{p1}$ for $K_{eq} = 1\times10^{-4}$ and various $k_f$. Again the peak potentials are quite independent of $k_f$ and the peak current density reaches the values of $2e^-$ reduction only for $k_f \geq 100 \text{ M}^{-1}\text{s}^{-1}$.

The slight changes of $E_{p1}$ in the above simulation is in contradiction to the experimental observations. Both Figure 8 and Figure 11 show that the peak potentials in fact change dramatically with the pretreatment while the current densities stay about the same. The observed changes in $E_{p1}$ can not be explained by varying the equilibrium constant ($K_{eq}$) or the forward rate constant ($k_f$) for the proton transfer reaction. Therefore, the electrode pretreatment does not seem to enhance ORR kinetics by affecting the chemical reaction step. Further more, the simulated current densities correspond to $2e^-$ reduction only with large $K_{eq}$ and $k_f$, indicating that the reaction following the $O_2^-$ formation must be fast to yield a peak current correlates with the experimental results.
Figure 20A and 20B also demonstrate that $k_\circ$ of 0.005 cm/s is slow enough even a fast follow up reaction have little effect on $E_{p_1}$. However, changes in $k_\circ$ can dramatically affect $E_{p_1}$, as shown by the simulation results in Figure 20C where $K_{eq} = 1 \times 10^{-4}$ and $k_f = 100$ are used. For the range $k_\circ^* = 10^{-6}$ to $k_\circ^* = 10^{-3}$ cm/s, the peak current density is nearly constant, but $E_{p_1}$ shifts linearly from -0.764 V to -0.422 V. The increase in peak current at $k_\circ^* > 10^{-3}$ cm/s is cause by rapid protonation of O$_2^-$. The current increase for rapid chemical steps following fast electron transfer has long been recognized (77).

Figure 20C simulates a trend that is consistent with the experimental results. Unfortunately, even with $k_\circ$ of 0.1 cm/s, the simulated $E_{p_1}$ is still -0.304 V, much more negative than $E_{p_1}$ observed on ECP surface (-0.233 V). In order to obtain a $E_{p_1}$ of -0.23 V, the simulation predicts a $k_f$ of $10^5$ M$^{-1}$s$^{-1}$ using $k_\circ$ of 0.1 cm/s. This is unreasonably high. However, the more positive $E_{p_1}$ observed than predicted can result from the ion-paring effect which provides a bridge to facilitate the reaction, e.g., through a bridging mechanism. Simulation can not take this into account and results in more negative peak potentials than the observed values.

Although the above digital simulations rely on various assumptions, they do suggest that more positive $E_{p_1}$ correspond to larger $k_\circ$, e.g., the ECP surface possesses larger $k_\circ^*$ than the polished surface. When $k_\circ^*$ is large, i.e., the first electron reduction step [2.24] is not rate limiting, the proton transfer step [2.26] would be subjected to H/D isotope effect since it becomes the rate limiting step. On the other hand, if $k_\circ^*$ is small, the first electron reduction step [2.24] is rate limiting and the subsequent proton transfer step
Figure 20 Digital simulation of ORR peak one potentials ($E_{p1}$) and current densities ($i_{p1}$).

For all simulations, $E_1^o = -0.311\, \text{V}$, $E_2^o = 0.342\, \text{V}$ (vs Ag/AgCl) and $k_2^o = 0.01\, \text{cm/s}$ (see text): (A) $k_1^o = 0.005\, \text{cm/s}$, $k_t = 6.3$, vary $K_{eq}$; (B) $k_1^o = 0.005\, \text{cm/s}$, $K_{eq} = 10^{-4}$, vary $k_t$; (C) $K_{eq} = 10^{-4}$, $k_t = 100$, vary $k_1^o$. 
Figure 20 (Continued)
[2.26] would have little H/D isotope effect. This is illustrated in Figure 21 for two values of $k_i^\circ$. When $k_i^\circ = 0.005 \text{cm/s}$, which corresponds to a slow first electron reduction, a change in $k_f$ by a factor of 6 (typical value for a reaction constant change due to H/D substitution) has no apparent effect on both $E_{p_1}$ and $i_{p_1}$. But if $k_i^\circ = 0.1 \text{cm/s}$, which corresponds to a fast first electron reduction, a change in $k_f$ by a factor of 6 shifts $E_{p_1}$ $21 \text{mV}$ negative while maintaining $i_{p_1}$ the same. In both cases, the second electron reduction step [20] is assumed to be fast, as would be expected given the positive value of $E_2^\circ$. These results qualitatively correlate to the H/D effect found experimentally where a larger $\Delta_{D-H}$ occurs for more positive $E_{p_1}$ (Table 2).

Based on the simulations, three working models that are consistent with current data can be proposed:

Model 1: the first electron reduction kinetics is fast because the surface possesses catalytic sites, mainly of $\{s\}$-OH type. The subsequent chemical reaction becomes the rate determining step and the overall reaction subjects to strong H/D effect. This is the case with ECP electrode and the fractured electrode.

Model 2: the first electron reduction kinetics is slow because the surface lacks catalytic sites. Since step [2.24] is the rate determining step, subsequent chemical reaction is not subjected to H/D isotope effect. This is the case with the laser treated electrode.

Model 3: the first electron reduction kinetics is moderately fast and the overall reaction experiences a fair amount of isotope effect. The surface possesses oxides but is low in $\{s\}$-OH concentration. This is the case with the polished electrode.
Figure 21 Simulated ORR voltammograms at two $k_1^\circ$ values and two $k_f$ values to show the kinetics effect and the H/D isotope effect.
Hence, the different electrode pretreatments appear to affect the first electron transfer kinetics of step [2.24]. It has been reported by various workers that step [2.24] is the rds in oxygen reduction. Current results agree with them in that when the surface is low in catalytic sites such as the polished electrode, the first electron reduction is the rds. However, on ECP or fractured electrodes, the first electron transfer reaction is no longer the dominating rate limiting step. Instead, the chemical reaction following the formation of \( \text{O}_2^- \) becomes the limiting factor in determining the overall kinetics. The enhanced first electron transfer kinetics on ECP or fractured surface is due to the ion-paring effect between the \( \{\text{s}\} - \text{O}^- \) group and the cations in the bulk electrolyte that provides a bridge to facilitate the reaction. In addition, these ion pairs may also accelerate the proton transfer reaction by providing sites for \( \text{O}_2^- \) to adsorb. As a result, ORR kinetics is significantly increased, evidenced by the positive \( \Delta E_p \) shift on ECP and fractured electrode relative to conventionally polished GC electrode.

\( \text{O}_2 \) reduction is the first redox process we have observed which is kinetically slower on the laser treated surface than on the fractured or polished surfaces. This evidence indicates that surface oxides are the catalysts for \( \text{O}_2 \) reduction, and perhaps laser treatment reduces the \( \{\text{s}\} - \text{OH} \) density on the surface. The fact that fracturing a GC electrode in \( \text{O}_2 \) saturated solution yielded more positive \( \Delta E_p \) (by \( \sim 10 \text{mV} \)) than fracturing in Ar saturated solution supports the possibility that catalytic oxides are formed following fracturing. A study by XPS will be able to provide a direct measurement of the surface oxide densities following fracturing.
It is necessary to point out that the mechanism proposed above may not be the only one. In fact, simulation based on step [2.24], [2.26] and a disproportionation step [2.27] can also yield similar results as those in Figure 20 and 21. Under these circumstances, $K_{eq}$ is found to be $\geq 10^{-5}$ and $k_f$ is found to be $\geq 10$ M$^2$s$^{-1}$. However, even with $k_i^0 = 0.1$cm/s, $k_f = 10^4$ M$^{-1}$s$^{-1}$ for the proton transfer step and $k_f = 10^4$ M$^{-2}$s$^{-1}$ for the disproportionation step, the simulated $E_{p1}$ is still -0.29V, much more negative than the $E_{p1}$ on ECP electrode (-0.23V). This suggests that even though there is no direct evidence to rule out the disproportionation reaction after the proton transfer step, it is unlikely that the disproportionation reaction is as important as a second electron reduction. Therefore, the most probable reaction mechanism still consists of step [2.24], [2.26] and [2.27].

So far the effect of electrode pretreatment on the first two electron reduction for ORR on GC electrodes have been discussed. As mentioned earlier, it would be desirable to utilize the 4e$^-$ reduction potentials. However, since the third and fourth electron reduction does not occur until about -1.0V vs Ag/AgCl, it is less important for possible fuel cell applications due to this negative potential. Typically, the HO$_2^-$ is catalytically disproportionated rather than further reduced to avoid their build up. Although the HO$_2^-$ /H$_2$O redox has been studied in much less detail, a few observations are available from current results. Table 4 summarizes the peak potentials obtained on various electrodes.

First, peak two is only observed on ECP and fractured surfaces in KOH solution. $E_{p2}$ is almost the same on these two surfaces. The peak on polished electrode is negligible. Second, in KOD/D$_2$O solutions, peak two is also distinctive on polished electrode. $E_{p2}$ on
ECP electrode is not subjected to H/D isotope effect while Ep₂ shifts negative by about 40mV on fractured surfaces with deuterium substitution. Third, Ep₂ on ECP electrode is pH dependent but Ep₁ is not. Ep₂ moves +134mV from pH 14 to 12. Fourth, peak two remains negligible on laser treated surfaces. Although there is a broad wave at about -0.8V on laser irradiated electrode in KOH solutions, it does not appear consistently. Finally, peak two appearance on the basal plane of HOPG strongly depends on the quality of the surface. On a near defect-free surface, there is no second reduction peak can be observed (Figure 7F). If the surface becomes slightly defective (Figure 7E), peak two starts to emerge but its potential varies drastically with the surface double layer capacitance (C').

Although a clear conclusion to the \( \text{HO}_2/\text{H}_2\text{O} \) reaction is not available from these observations, it is evident that this reaction is also dependent of the electrode pretreatment and is catalyzed by surface oxides. The facts that Ep₂ shifts with pH and has little H/D effect on ECP electrodes suggest that the reduction kinetics are still governed by some kind of electron transfer process rather than a proton transfer reaction.

\( \text{O}_2 \) reduction reaction on glassy carbon electrodes are discussed above. As pointed out earlier, GC is structurally very different from HOPG, e.g., the microcrystallite sizes on glassy carbon is around 25Å but it can be over 1μm on HOPG basal plane. Due to the large microcrystallite sizes, it is conceptually possible to prepare a "perfect" HOPG electrode that consists only of the six member rings. In reality, small amount of defects such as step edges are always introduced. These defects can serve as the adsorption sites.
Table 4  ORR peak two potentials after various electrode pretreatment

<table>
<thead>
<tr>
<th></th>
<th>KOH/H₂O (mV)</th>
<th>KOD/D₂O (mV)</th>
<th>ΔEp (D-H) (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polished</td>
<td>negligible</td>
<td>-1037</td>
<td>N/A</td>
</tr>
<tr>
<td>LA-25</td>
<td>none</td>
<td>small</td>
<td>N/A</td>
</tr>
<tr>
<td>Fracture-O₂</td>
<td>-957</td>
<td>-996</td>
<td>-39</td>
</tr>
<tr>
<td>Fracture-Ar</td>
<td>-980</td>
<td>-1023</td>
<td>-43</td>
</tr>
<tr>
<td>ECP-pH14</td>
<td>-971</td>
<td>-967</td>
<td>+4</td>
</tr>
<tr>
<td>ECP-pH13</td>
<td>-896</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ECP-pH12</td>
<td>-837</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HOPG</td>
<td>varies with C°</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note: All potentials are vs Ag/AgCl reference (E°=0.203V) and is obtained from 50mV/s scans.
for O$_2^-$ or the reaction intermediates. Oxygen reduction has a much facile kinetics when defects are present on the HOPG surface.

However, the basal plane of HOPG is electronically not favorable for electron transfer. This is mainly due to a small energy overlap between the conduction band and the valance band (172) of the material which requires extremely high activation energy for the electron transfer. But when the surface electronic structure is disturbed by defects, the energy overlap can quickly increase such that the electron transfer becomes easier. This is demonstrated in Figure 7E and 7F where two basal plane surfaces were used for O$_2$ reduction. In Figure 7E, the electrode surface has a C° of 4.8 $\mu$F/cm$^2$, which is considered to be slightly "defective" (70). Two reduction peaks are observed. Peak one appears at -0.45V while peak two appears at -0.77V. Note that $E_{p1}$ is still over 100mV more negative than $E_{p1}$ on polished surfaces. When C° decreases to 1.1 $\mu$F/cm$^2$, peak one shifts to almost -1.2V and peak two disappears (Figure 7F). These results show that the material's electronic structure has dramatic effect on O$_2$ reduction kinetics. Because the overpotential is quite high and the peak current density is very small on HOPG basal plane, this material is not suitable for fuel cell electrocatalysis.

Finally, the influence of the electrode pretreatment on HO$_2^-$ oxidation was investigated on polished, fractured and ECP electrodes. It has been shown above that these electrodes have significantly different activities toward oxygen reduction. However, they yield quite similar results for HO$_2^-$ oxidation, as shown in Figure 16. The oxidation peak occurs at about 0.6V on all electrodes, indicating a compatible surface catalysis for HO$_2^-$ oxidation. When the electrodes are treated with Ba$^{2+}$ by sonicating them in
BaCl\textsubscript{2}-2H\textsubscript{2}O solution, HO\textsuperscript{2-} oxidation becomes much easier. The oxidation peak shifts negative by more than 150mV for all electrodes (Table 3). In contrast, oxygen reduction kinetics is not affected by Ba\textsuperscript{2+} treatment.

The HO\textsuperscript{2-} oxidation is also subjected to H/D isotope effect, e.g., the peak potentials are more positive in KOD/D\textsubscript{2}O than in KOD/D\textsubscript{2}O solution (Table 3). The degree of peak potential shift with deuterium substitution depends on the electrode, but the H/D effect appears to be more significant for HO\textsuperscript{2-} oxidation than for O\textsubscript{2} reduction. The Ba\textsuperscript{2+} effect, the H/D effect, and the similar oxidation peak potentials observed on all three electrodes for HO\textsuperscript{2-} oxidation suggest that either surface oxides are not important or different kind of oxide is involved in the HO\textsuperscript{2-} oxidation. Clearly, Ba\textsuperscript{2+} has great influence on the HO\textsuperscript{2-} oxidation kinetics. It is possible that Ba\textsuperscript{2+} ions bind to the surface, presumably to some oxide sites, to form bridges such that the oxidation becomes facilitated.

**CONCLUSION**

Oxygen reduction is an important reaction in many technological and biological processes. This reduction involves multiple electrons and multiple protons and its mechanism is not well understood. On carbon electrode, the reduction occurs to the first two electron step under most practical potentials and there exists controversial conclusions with respect to its mechanism.

In this chapter, oxygen reduction reaction was investigated on four well defined carbon electrodes in both KOH/H\textsubscript{2}O solution and KOD/D\textsubscript{2}O solution. The effect of the
electrode pretreatment was discussed. It is found that surface oxide, in particular, the phenol-like groups, plays a major role in determining the reaction kinetics. In alkaline solutions, these phenol-like groups are deprotonated to form anions, which can then ion-pair with the cations in the supporting electrolyte. Oxygen reduction is significantly enhanced by these ion-pairs since they may serve as the bridge between the oxygen species and the electrode surface.

The electrode pretreatment alters the reduction mechanism by changing the first electron transfer kinetics ($k_1^o$). Both ECP and fracturing increase $k_1^o$, but laser irradiation decreases $k_1^o$. When $k_1^o$ is large, e.g., on ECP electrodes, the reduction is subject to strong H/D isotope effect which results from the subsequent proton transfer reaction. If $k_1^o$ is small, e.g., on laser treated electrodes, then the first electron reduction is the rate determining step and the reaction has little H/D isotope effect.

The changes in the chemical reaction after the formation of $O_2^-$ have minimal influence on the overall kinetics. Simulation using BAS DigiSim™ 1.0 indicates that only slight variation in $Ep_1$ is introduced when either the equilibrium constant or the forward reaction constant is dramatically changed. The different electrode pretreatment tends to affect the interaction between the oxygen species and the electrode surface rather than the chemical reaction. In addition, electrode modification with $\beta$-carotene, BHT or DNPH only results in small changes in the peak potentials, indicating that the first electron reduction proceeds via an outer-sphere mechanism.
The enhanced electrode activities on ECP and fractured surfaces can not be explained by a surface quinone mediated mechanism. The most likely mechanism that is consistent with current observations include a first electron reduction step:

\[ \text{O}_2 + e^- \rightleftharpoons \text{O}_2^\cdot \]

followed by a proton transfer step:

\[ \text{O}_2^\cdot + \text{H}_2\text{O} \rightleftharpoons \text{HO}_2 + \text{OH}^- \],

and a second electron reduction reaction:

\[ \text{HO}_2 + e^- \rightleftharpoons \text{HO}_2^\cdot \].

Although there is no direct evidence to rule out a disproportionation step for the \( \text{HO}_2 \) species, it appears to be less important since the simulation based on a disproportionation step is not capable of yielding a \( E_{p1} \) as positive as the experimentally observed values even with unreasonably high reaction constants.

HOPG basal plane is structurally different from glassy carbon. Oxygen reduction on HOPG basal plane strongly depends on the surface preparation. On a near perfect basal plane surface, the reduction is extremely slow. Once the surface is perturbed by defects, the reduction kinetics increases drastically, but they are still slower than on glassy carbon surfaces. The material electronic properties are dominant in determining the reaction kinetics on HOPG.

Although pretreated GC electrodes have quite different activities for oxygen reduction, they yield similar catalysis for \( \text{H}_2\text{O}_2 \) oxidation. Modifying the surface with \( \text{Ba}^{+2} \) has no apparent effect for oxygen reduction but it considerably improves the kinetics for \( \text{H}_2\text{O}_2 \) oxidation. In \( \text{O}_2 \) reduction, there are second reduction peaks observed on oxide rich surfaces. This peak is found to correlate with the further reduction of \( \text{HO}_2^\cdot \) to \( \text{OH}^- \) in alkaline solution and it is a process catalyzed by surface oxides.
Glassy carbon is quite active for oxygen reduction in alkaline solutions, especially when they are properly treated. However, the material itself has generally low surface area and produces less than 0.5mA/cm² peak current density at 50mV/s. This is apparently very inefficient for fuel cells applications. It is possible to increase the electrode activity by introducing certain type of active species onto the surface such as superficially chemically modified electrodes (CMEs). However, CMEs suffer from mechanical instability and surface irreproducibility. In order to prepare an oxygen electrode that can be used for energy conversion devices, the active electrode surface area must be dramatically increased and efficient catalysts must be incorporated into the carbon structure. This will be discussed in the next chapter with doped glassy carbon materials.
CHAPTER III

STRUCTURE AND ACTIVITY OF NANOSCALE PLATINUM CLUSTERS IN A SYNTHETIC GLASSY CARBON MATRIX

INTRODUCTION

Glassy carbon is one of the most commonly used electrode materials in modern electrochemistry. It was first synthesized by Yamada and Sato in 1962 using phenolic resins (78). Since then, a host of other precursors have been developed, including polyacrylonitrile (PAN), polyvinyl chloride (PVC), polyphenylene oxide, polyphenylene sulfide, cellulose, furfuryl alcohol resin and phenolformaldehyde polymers (79).

Commercially, glassy carbon is made by careful thermal degradation of the above precursors. During the heat treatment, small molecules of foreign atoms are gasified and leave a material that consists of over 99.5% carbon. This result is independent of the precursors (80). Because of the out-gassing process, the thermal treatment process must be very slow (i.e., <0.1°C/min) and the resulting glassy carbon material is limited to about 5mm in thickness.

Glassy carbon has many useful properties, e.g., it is electrically conductive, chemically inert, thermally stable and mechanically hard. It can be applied to a wide potential range with little background interference. Glassy carbon possesses rich
functionalities (Figure 3) which make it amenable for surface modifications. Because of these, glassy carbon has become an attractive electrode material for decades.

The activity of GC material depends on their microstructures which in turn depend on the final temperature of thermal treatment. A temperature of 1800°C produces a GC material that has satisfactory physical properties for most applications (2). Raman spectroscopy has been extensively used to probe the carbon microstructures since the sp\(^2\)-hybridized graphite material has relatively high Raman cross section. Figure 2 shows the typical Raman Spectra obtained on three grades of GC materials, namely, GC10, GC20 and GC30, which have been heat treated to 1000°C, 2000°C and 3000°C, respectively. The Raman bands at 1360cm\(^{-1}\) and 1580cm\(^{-1}\) are characteristic of GC materials. Their intensity ratio as well as the peak resolution have been related to the degree of graphitization (26). Higher \(I_{1360}/I_{1580}\) ratio and better peak separation correspond to more graphitic structure. The appearance of second order bands in the region of 2400cm\(^{-1}\) to 3000cm\(^{-1}\) also indicate a higher crosslinked GC formation.

Despite its unique electrochemical properties, glassy carbon itself has very low catalytic activities for many reactions. The main cause for this low activity is that the material contains less than 0.5% of any foreign elements other than carbon due to the extremely high temperature used in the manufacturing. In order to increase its activity, glassy carbon is often pretreated electrochemically such as those discussed in Chapter II, or modified chemically by introducing active centers to the electrode surface.

As shown in Chapter I, there are several ways of preparing chemically modified electrodes (CMEs, Figure 4). The most common reagents that are adsorbed onto
electrode surfaces are transition metal macrocyclics such as iron porphyrins and cobalt porphyrins. Numerous reports can be found in the literature regarding oxygen reduction on porphyrin adsorbed GC electrodes (19-21, 81-85). Although the activity of CMEs depends on the type of porphyrin and how they are adsorbed, O$_2$ reduction kinetics are greatly enhanced in most cases. However, in practice, many surface-modified electrodes have limited applicability for electrocatalysis due to the mechanical instability of the films and the difficulty of regenerating the films in a convenient and reproducible fashion.

An alternative way of improving the activity of glassy carbon material involves the bulk modification of its structure by incorporating other elements that might serve as catalytic centers. Ingersoll and Huskisson prepared molybdenum and tungsten doped carbon films which exhibited different electrochemical responses in H$_2$SO$_4$ solution (23). Wang et al. prepared metal-dispersed (Pt, Pd and Ru) carbon paste electrodes and found improved activities for several redox species including hydrogen peroxide (24). We have developed a new approach to the preparation of doped glassy carbon (DGC) materials (27-29) through diacetylenic polymer precursors (Figure 5). It was found that the incorporation of dopants at the molecular level in the poly(arylenediacetylene) precursor, followed by thermal treatment at relatively low temperature (<600°C), results in a conductive, dimensionally stable carbon matrix that not only looks but behaves like commercial glassy carbon. Several kinds of dopants have been incorporated including Pt, Fe and halogen. Since relatively low temperature (<600°C) is required, these dopants can survive the heat treatment and become homogeneously doped in the carbon matrix at fairly high levels (>15 atom%).
The advantages of bulk modification relative to superficial modification are many folds. For example, when the electrode becomes deactivated, its activity can be renewed with an easy procedure such as polishing. Since the material's structure is altered entirely rather than just the surface layer, the user has much better control over its long term activity and stability.

Among all doped glassy carbons that have been synthesized, platinum doped material (Pt-DGC) is a special case in that nanoscale platinum clusters are homogeneously incorporated in the carbon structure. Because of the dimension of the clusters (~20-30Å, measured by TEM), the expensive platinum is very efficiently utilized in these catalysts.

The goal of this chapter is to investigate the structure and activity of the Pt-DGC materials and then apply them for polymer electrolyte membrane (PEM) fuel cell applications. The initial studies will be carried out on thin film electrodes. With the information and understanding gathered from the thin film electrodes, the Pt-DGC material will then be applied to the PEM fuel cells. Finally, their catalytic activities will be related to the catalyst's structures by extended x-ray absorption fine structure (EXAFS) spectroscopy and transmission electron microscopy (TEM).

EXPERIMENTAL

Precursor Synthesis

The detailed synthetic chemistry for platinum doped glassy carbon precursor material was given elsewhere (86) and is represented schematically in Figure 5. Briefly, 1,3-dibromobenzene is first converted to 1,3-bis[(trimethylsilyl)ethynyl] benzene by
reaction with trimethylsilyl-acetylene using palladium and copper catalysts. The protective trimethylsilyl group is then removed by reaction with catalytic amount of KOH in aqueous methanol to yield 1,3-diethynylbenzene. Oligomerization of 1,3-diethynylbenzene with phenylacetylene as an end caping group using CuCl catalyst and O₂ gives poly(1,3-butadiynylene-1,3-phenylene). This oligomer is then react with ethylene bis-(triphenylphosphine) platinum (0) and the result is an oligomeric material where platinum becomes an appendage to the backbone structure (the precursor). The precursor can be precipitated to become a light yellow powder that is subsequently soluble in toluene, acetone and tetrahydrofuran.

Preparation of Thin Film Pt-DGC Electrodes on GC-25 Substrate

A 1.5cm diameter glassy carbon disk (GC25, Atomergic, Chemetals Corp., Farmingdale, NY ) was washed with acetone and distilled water and then sonicated in distilled water for 5 min. The disk was dried in a vacuum oven at 65°C and then affixed to a photoresist spinner. A saturated solution of the Pt-DGC precursor in toluene was added dropwise to the glassy carbon disk (rotating at a rate of 200 rpm) until the disk was completely covered with the solution. Spinning was continued at a constant rate until evaporation of the toluene was complete (5min). This procedure provided reproducible and homogeneous films with thickness in the range of 2-5 μm.

Three types of Pt-DGC precursors were used, designated as 1:2, 1:6 and 1:10. The different ratios reflect slightly different precursor structures. For example, the 1:2 material has one platinum triphenylphosphine unit per two diacetylene units in its precursor struc-
ture while the 1:6 precursor has one platinum triphenylphosphine unit per six diacetylene units in its precursor structure, and so on. These different precursor structures can be achieved by varying the stoichiometry of the reaction between poly(1,3-butadiynylene-1,3-phenylene) and ethylene bis-(triphenylphosphine) platinum (0). This is an important feature of the current synthetic scheme since a wide spectrum of precursors with different Pt content can be easily synthesized. Because the three precursors have quite different Pt loading, care has been taken to ensure that the resulting thin film electrodes have comparable platinum concentration. The air dried thin film was subsequently pyrolyzed.

Preparation of Pt-DGC on Toray Carbon "Felt"

In addition to the conventional GC25 substrate, a porous carbon "felt" material made from carbon fibers (TGP-090, Toray Industries, Inc., Shiga, Japan) was also used to disperse the Pt-DGC precursor solution. The carbon fibers were synthesized from polyacrylonitrile and the porous "felt" was made by a papermaking technique which used binders. These binders were subsequently graphitized. The "felt" is about 0.27mm in thickness.

Different concentrations of precursor solutions were made from the 1:2 type Pt-DGC material. The solution was applied to both sides of the "felt" using a micro-syringe until the Pt loading reached the desired level. The "felt" was air-dried followed by thermal pyrolysis.
**General Pyrolysis Procedures**

The thin film electrodes and the Pt-DGC treated "felt" were pyrolyzed in a quartz tube according to the following schemes:

- **Room Temperature** → **1°C/min. Ramp Up** → **Final Temperature** → **Dwell 6 hours at Final Temperature** → **5-10°C/min. Ramp Down** → **Room Temperature**

The system was maintained under argon flow (pre-purified) or 0.005 torr (using mechanical pump) during the entire thermal treatment. A final temperature of 600°C was typically used to produce well graphitized carbon matrix. For Raman analysis, the final temperature varies from 200°C to 600°C. After dwelling at final temperature for 6 hours, the sample was cooled down at 5-10°C/min until it reached room temperature. The pyrolyzed film on GC25 substrate was dark and highly reflective, while the doped carbon "felt" became darker compared to the undoped portion.

**Raman Spectroscopy**

All Raman measurements were obtained on a SPEX 1403 Spectrometer with double monochromator and a water cooled photomultiplier tube (PMT) detector. The 514.5nm laser line from a Coherent Innova 90 argon ion laser provided the excitation. The monochromator slits were set to achieve a 10cm⁻¹ spectral resolution. The laser power was 100mW at the laser head, but approximately 40mW at the sample. An integration time of one second per wavenumber was used during spectral acquisition.
**Cyclic Voltammetry**

Cyclic voltammetry was performed in a custom-designed three-electrode cell immediately after heat treatment. The thin film electrode was housed in a Teflon cell with its area defined by an O-ring. Electrode area was measured using chronoamperometry of Fe(CN)$_6^{3-/4-}$. The reference electrode was Ag/AgCl and the auxiliary electrode was a platinum wire. A triangular waveform triggered by a personal computer was delivered to the electrocell through a conventional three-electrode potentiostat with a RC setting according to $n_{RC}<4mV$ criteria (186). Electrolyte was purged either with argon (Linde Gas, pre-purified, for background measurement) or oxygen (Linde Gas, ultra high purity) for 20 minutes prior to experiment under ambient temperature and pressure. During data acquisition, the system was maintained under the designated gas atmosphere. In between scans, electrolyte was further degassed for one minute. Due to the much higher currents resulting from the hydrogen evolution reaction, a Princeton Applied Research (PAR) model 173 potentiostat was used.

**Preparation of Carbon Supported Fuel Cell Catalyst**

To prepare the supported fuel cell catalyst, Pt-DGC precursor was first dissolved in small volume of toluene and THF solvent (typically, 2 mls. of toluene plus 1 ml. of THF per 30mg precursor) followed by sonication for 5 min. to completely dissolve the precursor. High surface area carbon powder was added to the above solution. After further sonicating for 40 min and stirring for 1 hour, the solvent was evaporated. The dry powder was then heat treated under ultra-pure argon atmosphere or high vacuum.
environment (10^6 torr) to a final temperature of either 600°C or 400°C in a quartz tube furnace according to the general pyrolysis procedures. When heat treatment was performed under ultra-pure argon, the system was monitored for O_2 concentration using a TM-1B oxygen analyzer (AMETEK). O_2 was not detected at system temperature above 100°C.

The commercial ETEK catalyst (20% Pt on XC72, from E-TEK Inc., Natick, MA) was first mixed with Vulcan XC72 carbon powder (Cabot, Waltham, MA) at 1:1 weight ratio in isopropanol by means of sonication and stirring before use. Pt black (80% Pt on XC72, from E-TEK, Inc.) was used as received. No heat treatment was necessary for both commercial catalysts.

Preparation of Fuel Cell Ink

The supported fuel cell catalysts were ground and then mixed with Nafion solution (Solution Technology) at a weight ratio of 1:1 or 5:2 (dry Nafion weight). Such processed catalysts can be directly packed onto the solid polymer electrolyte gas diffusion backing (SPE, 3.8mg/cm^2 carbon loading on the active side, from E-TEK, Inc.) to make the fuel cell electrode, or they can be further mixed with other components to make an ink then paint the ink to make fuel cell electrode.

Two types of inks have been used in the study. Type One ink was made by simply mixing the pyrolyzed catalyst powder with Nafion solution at 1:1 weight ratio. No other ingredient was added to the ink. The ink was stirred overnight before use. Type Two ink was made by first mixing the pyrolyzed powder with Nafion solution at 5:2 weight ratio.
The mix was stirred for 2 hours, then glycerol (Ultrapure, >99%, Alfa Products) was added at 1.2 times the amount of Nafion solution followed by another 2 hours of stirring. Finally, for every 500mg of the Nafion solution used, 24.44mg of Tetrabutylammonium hydroxide (TBAOH) (1M, dissolved in methanol, from Janssen Chemical) solution was added and the ink was stirred overnight before use.

Membrane and Electrode (M&E) Assembly

The single PEM fuel cell electrode consists of an anode, a cathode and a Nafion membrane. The anode was made by painting an ink made from the as received ETEK catalyst (20% Pt on XC72) with Nafion solution either onto the SPE backing or onto a Teflon decal, depending on the application. The anode has a typical Pt loading of 0.12mg/cm² and they are termed "standard anode" hereafter unless otherwise indicated. The cathode (oxygen electrode) can be prepared by one of the following three methods:

Method One: the Nafion processed catalyst powder was directly pressed onto a SPE backing which has an area defined by electrical tapes. Typical Pt loading was 1-2mg/cm². M&E assembly was done by hot press the cathode and the anode separated by a protonated Nafion type 115 membrane (DuPont) at 125°C and 600psi for 90 seconds.

Method Two: the fuel cell ink (either type) was painted directly onto a SPE backing to reach a Pt loading of about 0.1mg/cm². Subsequent M&E assembly depends on the type of ink. If Type One ink was used, then protonated Nafion type 115 membrane was used and hot press was done at 125°C and 600psi for 90 seconds. If Type Two ink was used, then Na⁺-form membrane "C" (Chlorine Engineering, LTD, Tokyo, Japan) was
used and the hot press was done at 210°C and 500psi for two minutes for a 5cm² electrode. The pressure is set to 100psi/cm² electrode area.

**Method Three: Type Two** ink only was painted onto a Teflon decal (5cm²) to form a thin film catalyst layer. The catalyst layer was then transferred to membrane "C" by means of hot press at 210°C and 500psi for two minutes. Catalyzed membrane "C" was subsequently boiled in 0.5M H₂SO₄ for 1 hour followed by soaking in deionized water for overnight before use.

A typical M&E assembly is illustrated in Figure 22. The standard assembly shows the membrane, the SPE backing with painted-on catalyst or Teflon decal with thin catalyst layer, and the Teflon gasket. The M&E&G assembly also included an edge protecting thin Teflon gasket with a cut out to determine the active electrode area. This becomes handy when smaller electrode sizes are desired.

**Fuel Cell Construction**

The above M&E assembly can be tested only after it has been properly attached to the fuel cell hardware. To assemble a fuel cell, a 1/2" thick steel end plate with 1/4" (type 28) bolts facing up (Figure 23) was laid out. A Teflon insulation was placed over the end plate followed by the anode current collector. Next place the anode graphite block. A Teflon mask was then added on top of the graphite block. This Teflon mask has a cut-out the size of the backing (see Figure 24 for clarity). Next add 1/8" diameter reference electrode followed by the M&E assembly, then another Teflon mask. Place cathode graphite block face down. The above single cell hardware assembly (shown clearer in
Figure 24) was guided by 1/8" diameter Teflon pins. Next add cathode current collector followed by Teflon insulator and other end plate. Attach bolts with flat washers and torque alternately in steps of 15 oz to a total of 90 oz. Both gas inlets used 1/8" Teflon tubing. Gas outlet tubings are 1/8" for hydrogen and 1/4" for air/oxygen.

The important parameters in the cell assembly are the Teflon gas mask thickness and the pressure. It is important that the total gas mask thickness is 0.1 to 0.15mm thinner than the thickness of the electrode in M&E assembly to assure adequate pressure applied to the electrode.

**Fuel Cell Operation**

The complete PEM fuel cell can be operated via the front panel (Figure 25). Data acquisition used a Macintosh LC II with a custom-written control program. The standard operating conditions are: cell temperature = 80°C, water reservoir temperature for H₂ gas = 105°C, water reservoir temperature for air/O₂ = 90°C, back pressure for H₂ = 30 psi, back pressure for air/O₂ = 60 psi, H₂ flow rate = 200 ml/min., and air/O₂ flow rate = 1700 ml/min. Three performance curves are measured simultaneously: the current-voltage curve, the reference-anode curve and high frequency resistance curve. An iR-corrected current-voltage curve was obtained after proper mathematical calculation.

**Elemental Analysis**

Elemental analysis was performed on the precursor, the pyrolyzed catalyst powder
Figure 22 Illustration of the membrane and electrode (M&E) assembly in making polymer electrolyte membrane (PEM) fuel cell electrodes. The thickness of the materials is: electrode - 0.46mm, Teflon gasket - 0.20mm, edge protecting thin Teflon gasket: 0.05mm, Nafion 115 membrane - 0.13mm.
Figure 23  Illustration of the polymer electrolyte membrane (PEM) fuel assembly.
Figure 24 Illustration of the single cell hardware in a polymer electrolyte membrane (PEM) fuel cell assembly.
Figure 25 Illustration of the details of a polymer electrolyte membrane (PEM) fuel cell front panel control system.
and the actual fuel cell electrode to obtain an accurate platinum concentrations. These analyses were done by Galbraith Laboratory Inc, Knoxville, TN, using Inductively Coupled Plasma (ICP) Emission Spectroscopy. The materials were first boiled in concentrated H₂SO₄ to dissolve any residual organic species. They were then thoroughly digested in Aqua Regia to prepare sample solutions for ICP. All analyses were calibrated against standard compounds. The accuracy of the analysis is 95%.

**Transmission Electron Microscopy (TEM)**

TEM was performed on most Pt-DGC catalysts to study the Pt cluster sizes and their distribution. The catalyst powder was sonicated in deionized H₂O to break the clumps. The suspension was allowed to decant for 10-15 minutes. A drop of the top layer solution was pipetted onto a carbon grid substrate. TEM was done on a high resolution Hitachi H9000 NAR electron microscope operated at 300keV with a resolution of approximately 1.8 Å.

**Extended X-ray Absorption Fine Structure (EXAFS) Spectroscopy**

All EXAFS measurements were done at Stanford Synchrotron Radiation Laboratory (SSRL) beam line 2-3. Pt L₃ EXAFS were measured at 80K using Si[220] monochromator crystals detuned ca. 50% with respect to the crystal orientation (θ) to reduce the beam harmonic content. All spectra were collected in the transmission mode under dedicated operating conditions at 3.0GeV and ca. 60mA. After taking the measurements of the cured materials, the liquid nitrogen in the cryostat was evaporated by
heating the sample compartment and in situ reduction was accomplished by heating the
samples at 180°C for 5 minutes in the presence of 0.08 atm H₂. Liquid nitrogen was then
refilled and the sample holder was allowed to equilibrate to 80K before EXAFS
measurements of the reduced samples were taken. For in situ oxidation, the samples were
heated to 180°C for 5 minutes in air. Three scans were collected at each stage over a total
time of about 45 minutes.

EXAFS data reduction and data analysis were done on VAXstation 3100 at Los
Alamos National Laboratory using standard procedures (87). The ionization threshold for
Pt L₃ edge was defined as 11580 eV, and the first inflection point in the adsorption of the
metal foil was defined as 11572.2 eV. The data were normalized by setting the difference
between the polynomial extrapolated from the pre-edge region and the one through the
EXAFS region to unity at the ionization threshold. A four region polynomial spline
background was used to fit the EXAFS region and extract the raw EXAFS data. Fourier-
transform of the k³-weighted data was calculated from k = 2.5-13.0Å⁻¹ and subsequent
back-transform was done from R = 1-3.5Å using Gaussian window functions of 0.5Å⁻¹
and 0.5Å, respectively. Nonlinear least-square curve fits were performed on the filtered
EXAFS data over the range of k= 3.0-13Å⁻¹ using theoretical phase and amplitude
functions derived from the program FEFF (169).

RESULTS AND DISCUSSION

In this section, results from four aspects that relate to the structure and activity of
Pt-DGC catalyst will be presented and discussed. They include the glassy carbon
formation, the catalysis on thin film material, PEM fuel cell applications on the supported Pt-DGC, and the structural analysis by TEM and EXAFS.

Carbon Matrix Formation

Raman spectroscopy has been used to study the sp\(^2\)-hybridized carbon structure formation of the 600°C pyrolyzed Pt-DGC catalyst. Raman spectra of Pt-DGC and an undoped, low temperature synthesized glassy carbon material (GC6) are compared to a commercial GC10 in Figure 26. The characteristic graphite bands at 1360cm\(^{-1}\) and 1580cm\(^{-1}\) were observed on all electrodes. GC6 and GC10 materials have similar Raman features. The peak width, peak separation and I\(_{1360}/I_{1580}\) ratio are almost identical, suggesting that the carbon microstructure formed at 600°C by the low temperature synthetic route is very similar to those made at 1000°C by conventional procedures. There is a small second order band appears at about 2700cm\(^{-1}\) on GC6, indicating that GC6 might be slightly more graphitic than GC10. Pt-DGC, however, has a broader 1360cm\(^{-1}\) band and a lower I\(_{1360}/I_{1580}\) ratio. Tuinstra and Koenig (26) related this ratio to the graphite lattice parameter L\(_a\) as measured by X-ray diffraction. Higher I\(_{1360}/I_{1580}\) ratio corresponds to higher degree of graphitization (Figure 2). Thus the Pt-DGC material is less graphitic than GC6 and GC10. This is probably due to the incorporated platinum that affects the crosslinking process during heat treatment. However, the similarity in the Raman features indicates that the DGC materials have attained a microstructure that is comparable to the commercial GC material when they were heat treated to 600°C.

Alsmeyer (88) has investigated the Raman features of Pt-DGC material as a function of
Figure 26  Raman Spectra of platinum doped glassy carbon (Pt-DGC) in comparison with the low temperature synthesized GC6 and commercial GC10 material.
curing temperature. He found that the 1360 cm\(^{-1}\) band was not observable on the 200°C cured material but this peak gradually developed with increasing temperature.

Other physical and chemical properties of Pt-DGC have also been measured. Table 5 summarizes the results from earlier works (5, 27, 88). The apparent density, the Young's modulus, the heterogeneous electron transfer constant (k\(^0\)) for Fe(CN)\(_6\)\(^{3/-4}\) and the lattice parameters (L\(_a\), L\(_c\)) are all similar for the four materials. The electrical conductivity of GC6 is about 300 times lower than the commercial glassy carbon materials. However, GC6 has sufficient conductivity to be used as electrode material. These properties together with the Raman characteristics have ensured that a sp\(^2\)-hybridized carbon lattice has been formed in the doped glassy carbon material after 600°C heat treatment.

**Thin Film Material Catalysis**

Thin film Pt-DGC catalysts, either cast on GC25 disks or supported on Toray carbon "felt", were applied to the oxygen reduction and hydrogen evolution reactions in order to investigate their catalytic activities.

Figure 27 compares the oxygen reduction cyclic voltammograms on three Pt-DGC thin film electrodes with that on polycrystalline platinum in 1M HClO\(_4\) solution at 50mV/s. The DGC thin film electrodes were cycled at 50mV/s for 3-5 times before the data acquisition. These Pt-DGC electrodes were subjected to surface elemental analysis by X-ray Photoelectron Spectroscopy. The results in Table 6 show that the dominant species on the Pt-DGC electrodes was carbon and only residual phosphorus was present. Based on the high resolution scans of the Pt(4f), C(1s) and O(1s) peaks, Hutton (109) found that
the 1:2 electrode had a Pt loading of 1.4 atom% and the 1:6 electrode had a Pt loading of 1.1 atom%. The 1:10 electrode had a Pt loading of only 0.2 atom%.

These DGC electrodes have quite different catalytic activities for oxygen reduction reaction. The ORR peak potentials in 1M HClO₄ are 0.472V, 0.417V and 0.121V vs Ag/AgCl on the 1:6, 1:2 and 1:10 electrodes, respectively. The reduction occurs at 0.41V on polycrystalline Pt electrode. It is apparent from Figure 27 that the 1:2 electrode has slightly better activity than the polycrystalline Pt while the 1:6 electrode exhibits higher activity than both the 1:2 electrode and the polycrystalline Pt (more positive potential and higher current density). The 1:10 material, however, has very low activities. It gives a broad reduction peak with about half of the current density. The peak potential is ~300mV more negative than that on polycrystalline Pt electrode.

These results suggest that certain type of Pt-DGC material can have higher catalytic activities for oxygen reduction than polycrystalline Pt. The major difference in these DGC materials is their precursor structures, which ultimately affects the platinum cluster sizes and distribution after pyrolysis. For example, the average particle size, measured by TEM, is 21±7Å and 14±6Å for the 1:2 and the 1:6 material, respectively. The higher activity given by the 1:6 material is probably due to its smaller Pt particles which, in this case, are capable of giving about 50% more active Pt surface area for the same loading. For the 1:10 catalyst, its poor activity can be related to the precursor structure. Since every platinum triphenylphosphine group is separated by 10 diacetylene units in the precursor backbone, the initial Pt concentration in the precursor is low. Since the Pt atoms are so far separated, the chance of forming Pt clusters during pyrolysis is
Figure 27 Background corrected voltammograms of $O_2$ reduction on thin film Pt-DGC electrodes in 1M HClO$_4$. Scan rate = 50mV/s.
<table>
<thead>
<tr>
<th>Carbon Type</th>
<th>Apparent Density (g/cm³)</th>
<th>Young's Modulus (MN/m²)</th>
<th>Conductivity (S/cm)</th>
<th>k° for Fe(CN)₆⁻³⁻⁴ (cm/s)</th>
<th>Lₐ (Å)</th>
<th>Lₐ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GC6</td>
<td>1.5</td>
<td>28,500</td>
<td>0.7</td>
<td>0.024</td>
<td>~12</td>
<td>~5</td>
</tr>
<tr>
<td>GC10</td>
<td>1.5</td>
<td>30,900</td>
<td>222</td>
<td>0.027</td>
<td>20</td>
<td>~10</td>
</tr>
<tr>
<td>GC20</td>
<td>1.5</td>
<td>30,900</td>
<td>238</td>
<td>0.100</td>
<td>25</td>
<td>12</td>
</tr>
<tr>
<td>GC30</td>
<td>1.5</td>
<td>23,100</td>
<td>270</td>
<td>0.172</td>
<td>55</td>
<td>70</td>
</tr>
</tbody>
</table>
Table 6  XPS analysis of Pt-DGC thin film electrodes

<table>
<thead>
<tr>
<th>Electrode</th>
<th>1:2</th>
<th>1:6</th>
<th>1:10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>97.3 atom%</td>
<td>97.8 atom%</td>
<td>92.2 atom%</td>
</tr>
<tr>
<td>Platinum</td>
<td>1.4%</td>
<td>1.1%</td>
<td>0.2%</td>
</tr>
<tr>
<td>Oxygen</td>
<td>1.1%</td>
<td>0.8%</td>
<td>5.3%</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>0.3%</td>
<td>0.3%</td>
<td>0.2%</td>
</tr>
</tbody>
</table>
small and the result is that fewer but maybe very small Pt particles are formed which gives a Pt loading of only 0.2 atom%. Because these Pt particles are extremely small (e.g., <5Å), their activities toward oxygen reduction are in fact decreased, as observed by Kinoshita (89).

Nevertheless, the above catalysis data on thin film Pt-DGC electrodes have shown that a properly design Pt-DGC material is capable of delivering higher catalytic activity than polycrystalline Pt for the oxygen reduction reaction. This is the first important fact that justifies their subsequent use in fuel cell applications.

In addition to being a good catalyst for the oxygen reduction, Pt-DGC was also found to be very effective for hydrogen evolution reaction (HER). Figure 28 shows the evolution curves obtained on Pt-DGC electrodes that were supported on Toray carbon "felt". For comparison, the evolution curves on a polycrystalline Pt electrode and a undoped "felt" were also given.

As expected, the undoped "felt" was totally inactive while the polycrystalline Pt was highly active. Remarkable activities were noted on the Pt-DGC electrodes. At a Pt loading of only 0.11μg/cm² (geometric area, same for all subsequent Pt loading data), the "felt" already shows dramatically enhanced activity than the undoped electrode. The activity increased with higher Pt loading. The curve obtained with 5.5μg/cm² loading closely resembled the one obtained on polycrystalline Pt electrode. The difference between them was mainly caused by the lower conductivity of the DGC material compared to polycrystalline Pt (Table 5). For example, at a current density of 50mA/cm² and assuming
the DGC film is 5µm thick, the iR drop would be 36mV using the conductivity of GC6 as 0.7 S/cm. The observed potential difference at 50mA/cm² between the polycrystalline Pt curve and the 5.5µg/cm² Pt loaded DGC curve is 47mV. So most of the difference between the two electrodes can be attributed to the lower electrical conductivity of the DGC material. Note that the activity of a 80µg/cm² Pt doped "felt" was similar to the one with 5.5µg/cm² Pt loading, except at potentials positive than -50mV vs NHE where the 80µg/cm² Pt doped "felt" showed slightly higher current response.

Figure 29 shows the effect of the Pt loading level on the current densities obtained at -100mV vs NHE at 20mV/s scan rate. At loading less than 0.1µg/cm², only negligible activity was observed. There was a sharp increase in current densities at between 0.1µg/cm² and 5µg/cm² Pt loading. Above 5µg/cm² the curve levels off. This plot demonstrates that only 5-10µg/cm² of Pt loading is necessary to make an effective DGC electrode for hydrogen evolution reaction.

Due to the small platinum cluster sizes, the HER mechanism on Pt-DGC was found to be different from that on polycrystalline platinum electrode (86, 88). The reaction appears to be dependent on two transferred electrons and one proton. A larger portion of corner site atoms in smaller clusters were believed to cause the mechanism difference.

From Figure 27 and 28, it is concluded that the platinum doped glassy carbon material is an efficient catalyst for both the oxygen reduction and hydrogen evolution reactions. These properties have resulted in the further investigation of Pt-DGC materials in Polymer Electrolyte Membrane (PEM) fuel cells through a collaboration with Los Alamos National Laboratory. The fuel cell performance data were obtained under the
Figure 28 Hydrogen evolution curves on Toray "felt" supported Pt-DGC electrodes in comparison with the curves on polycrystalline Pt and undoped "felt" electrodes. Scan rate = 50mV/s.
Figure 29 Current densities of hydrogen evolution reaction at -100mV vs NHE on Toray "felt" supported Pt-DGC electrodes as a function of platinum loading level.
normal operating conditions as described in the experimental section. Except where
indicated otherwise, the Pt-DGC precursor was mixed with the high surface area carbon
substrate at 1:1 weight ratio to make the supported catalyst. Factors such as the substrate,
the membrane and electrode (M&E) assembly, the ink preparation, the pyrolysis
environment and the catalyst structure dramatically affect the catalyst's activity. Their
influence was investigated.

Effect of Carbon Substrate

The first Pt-DGC catalyst tested on the PEM fuel cells was made with pure
precursor without dispersing onto any substrate. The cured catalyst was ground and mixed
with Nafion solution to make an ink then the ink was painted directly onto a Solid
Polymer Electrolyte (SPE) gas diffusion backing. The Pt loading for this electrode was
1.23mg/cm². The M&E assembly used a standard anode (see experimental section) and a
Nafion type 115 membrane. Unfortunately, no activity was observed for this electrode
(Figure 30A). The current was below the instrument detection limit (10mA) over the
entire cell potential range. Therefore, this catalyst appears to be totally inactive for PEM
fuel cells.

However, we have detected significant amount of platinum in this material by
various techniques including TEM and EXAFS. The reason for such a low activity is not
because there was no platinum particles incorporated. Instead, it is because that almost all
the Pt particles formed were inside the GC matrix and were not accessible to the reactant
molecules (O₂). The high energy X-ray source in EXAFS (3GeV) was capable of
penetrating through the GC matrix and detecting the platinum clusters inside the carbon structure. In order to make this material into an useful catalyst, it is necessary to expose these platinum particles to the reactants. This can be accomplished by dispersing the precursor solution onto a high surface area carbon support before pyrolysis. Figure 31 illustrates the dispersion process. Effectively, the precursor solution was coated onto the surface of the support as thin films. Because the support has high surface area, it is possible to make the catalyst film thin enough that nearly all the platinum particles formed can be exposed.

Depending on the BET area of the carbon substrate, the supported Pt-DGC catalysts exhibit different activities for oxygen reduction. Figure 30A shows that almost no activity was gained by dispersing the precursor onto a 325 mesh graphite powder. The catalyst remains extremely poor. This graphite powder has a BET area of ~10m²/g.

Assuming homogeneous dispersion of the precursor solution, at 1:1 weight ratio, the catalyst layer formed on the graphite surface can be calculated to be 670Å thick, using the density of the precursor material as 1.5g/cm³:

\[
\text{1 gram of substrate } \Rightarrow \text{ surface area } = 10 \text{ m}^2
\]

\[
\text{1 gram of Pt-DGC precursor dispersed onto } 10 \text{ m}^2 \text{ area}
\]

\[
\Rightarrow \text{ film thickness } = \frac{1 \text{ gram of precursor}}{10 \text{ m}^2 \times \text{density of precursor}} = \frac{1 \text{ gram of precursor}}{10 \times 10^4 \text{ cm}^2 \times 1.5 \text{ g/cm}^3}
\]

\[
= 6.7 \times 10^{-6} \text{ cm} = 670\text{Å}
\]
The typical Pt cluster sizes are in the order of 10-50 Å, as measured by TEM of previous study (29). Under this circumstance, the majority of the platinum particles are still buried inside the GC matrix and are not accessible to the reactant molecules. Hence this catalyst has low activity and it behaves similarly to the non-dispersed catalyst.

However, dramatic performance improvement was observed when the precursor was dispersed onto Vulcan XC72 carbon powder. XC72 has a BET area of ~250 m²/g. Again assuming homogeneous dispersion, at 1:1 weight ratio, the catalyst layer formed averages 27 Å thick. This is in the order of the platinum particle sizes, which means that the majority of the Pt clusters are now exposed and become the catalytic centers for oxygen reduction. As a result, the catalyst shows much higher activity than those unsupported ones.

The Pt-DGC precursor was further dispersed onto black pearls (BP), another high surface area carbon substrate that has a BET area of ~1250 m²/g. Theoretically, the catalyst layer thickness is only 5 Å. With such a thin film, all Pt particles formed should reside on the surface and the material should have much higher activity compared to those supported with XC72. However, this was not the case (Figure 30A). With XC72, the current density obtained at 0.5 V cell potential was 380 mA/cm². With black pearls, the current density was 530 mA/cm². The DGC/XC72 catalyst has a Pt loading of 0.072 mg/cm² while the DGC/BP catalyst has a Pt loading of 0.10 mg/cm². After correcting for the difference in Pt loading, the normalized current density becomes 5277 mA/mgPt with XC72 and 5300 mA/mgPt with black pearls. These two catalysts in fact have the same activities in air fuel cells. However, in oxygen fuel cells (pure O₂ as the oxidant instead of
air, Figure 30B), the normalized current density at 0.5V cell potential was 11000mA/mgPt with XC72, whereas it was only 7700mA/mgPt with black pearls. Clearly, the Pt-DGC catalyst dispersed onto XC72 has a much higher activity than those dispersed onto black pearls in O₂ fuel cell. Table 7 summarizes the results.

The main reason that Black Pearl supported Pt-DGC does not give the expected high activity is that much of the catalyzed surface area is tied up in the extremely small pores that are not easily accessed by the electrolyte and/or reactant. Black pearls are known to be very porous. The majority of its BET area comes from the inside of its porous structure, e.g., the inner pores. The actual catalyst film coated is probably much thicker than the calculated 5Å and some Pt clusters might not be exposed. Another possible cause that BP supported catalyst gives lower than expected activity is a weak platinum-carbon interaction with black pearls. Since the catalyst dispersion is strongly affected by the interaction between the Pt atoms and the carbon support (187-189), a weak interaction will result in poor dispersion of the Pt catalyst which in turn decreases the material's activity. In fact, the role of the carbon support was identified as a key component in improving the mass transport properties and preventing the agglomeration of platinum particles (189-191).

So for Pt-DGC, it appears that Vulcan XC72 carbon powder is the most effective substrate. Significantly higher activities were observed on the XC72 supported catalyst than on those non-dispersed or the thin film electrodes. The current density with XC72 in Figure 30A is over 400 times higher than the current density on the thin film 1:2 electrode in Figure 27, despite that the latter has much higher Pt loading than the supported catalyst.
Figure 30 Effect of high surface area carbon substrate on the fuel cell performance of supported Pt-DGC catalysts. (A) H₂/air fuel cell; (B) H₂/O₂ fuel cell.
Figure 31 Illustration of dispersing the Pt-DGC precursor onto a high surface area carbon substrate.
Table 7  Summary of the effect of high surface area carbon support

<table>
<thead>
<tr>
<th>Substrate</th>
<th>BET Area</th>
<th>Pt Loading</th>
<th>Normalized Current Density in H₂/Air Fuel Cell</th>
<th>Normalized Current Density in H₂/O₂ Fuel Cell</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>—</td>
<td>1.23 mg/cm²</td>
<td>7.7 mA/mgPt</td>
<td>—</td>
</tr>
<tr>
<td>Graphite</td>
<td>10 m²/g</td>
<td>0.12</td>
<td>42</td>
<td>—</td>
</tr>
<tr>
<td>XC72</td>
<td>250</td>
<td>0.072</td>
<td>5277</td>
<td>11000 mA/mgPt</td>
</tr>
<tr>
<td>Black Pearls</td>
<td>1250</td>
<td>0.10</td>
<td>5300</td>
<td>7700</td>
</tr>
</tbody>
</table>
Effect of Membrane and Electrode (M&E) Assembly

The most effective carbon support for the Pt-DGC catalyst was determined above. However, there are many other factors that influence the catalyst's performance. One of them is the M&E assembly. The influence of M&E assembly comes from three areas: the ink composition, the ink transfer method and the type of membrane.

It might seem simple that mixing the pyrolyzed powder with Nafion solution will make the ink. To some extent, this is correct. But for fuel cell inks, there are much more to it. Fuel cell electrodes made with the simply mixed ink often suffer from catalyst layer cracking. An electrode with cracked catalyst layer might not perform as well because the reactant gases can pass through the cracks before they have a chance to react and because stagnant water might be trapped in these cracks and cover portion of the catalyst. The cause of the catalyst layer crack comes from the ink itself since the simply mixed ink has very low thermal and mechanical flexibility. To avoid this problem, two very important ingredients, glycerol and tetrabutylammonium hydroxide (TBAOH), must be added to the ink.

The purpose of using glycerol include: (1) to increase the ink viscosity so that stirring may be more effective in breaking up big particles due to an increased sheer force; (2) to increase the boiling point (b.p.) of the solvent (isopropanol b.p.=82.4°C, glycerol b.p.=182°C) so that when painting the ink onto electrode or membrane, the solvent will not evaporate as quickly, leaving an uneven thickness of catalyst layer; and (3) to increase the catalyst layer thermal flexibility. Glycerol behaves like a plasticizer which increases the catalyst layer's thermal elasticity upon subsequent hot press. TBAOH also serves as an
internal plasticizer (90, 91). Moore, Cable and Croley (91) added stoichiometric amount of TBAOH to neutralize the \(-H^+SO_3^-\) ions that are present in Nafion backbone. These covalently attached \(-H^+SO_3^-\) side groups aggregate into ion-rich domains which act as electrostatic crosslinks that make the material not thermally flexible. By adding TBAOH, TBA\(^+\) ions form weak ion pair dipoles with \(-H^+SO_3^-\) groups that reduces or eliminates the electrostatic crosslinking and the material does not suffer from cracks when subjected to hot press. For fuel cells, it is important that the ink is thermally flexible since they will be subjected to hot press in the M&E assembly. Both TEAOH and glycerol are thus very important ingredients. Based on the Nafion used (1100 equivalent weight), it was calculated that 24.44 mg of 1M TBAOH in methanol is needed to reach a stoichiometric neutralization of 500mg of 5% Nafion solution.

The ink transfer method is another important factor in the M&E assembly. The ink can be painted directly onto the SPE backing, or they can be painted onto a Teflon decal then transfer to the membrane. The first method relies on the subsequent hot press to make the contact between the membrane and the catalyst layer. The catalyst remains on the SPE backing and the contact between the membrane and the catalyst layer is relatively poor. The second method, however, allows a direct contact between the membrane and the catalyst since the catalyst layer can be quantitatively transferred from the decal directly to the membrane at hot press. This intimate membrane-catalyst contact results in an improved activity so the second ink transfer method is preferred.

The third factor that influence the M&E assembly is the membrane itself. Nafion membrane comes with different thickness and equivalent weight. For example, Nafion 115
membrane has 1100 equivalent weight and is 127\textmu m thick (dry) while membrane "C" has 900 equivalent weight and about is 152.4\textmu m thick. These different equivalent weight and thickness have dramatic effect on the proton conductivity and the water diffusion coefficient through the membranes. For example, membrane "C" has \textasciitilde 20\% lower equivalent weight relative to Nafion membrane 115 thus it has \textasciitilde 20\% higher H^+ conductivity per equivalent weight. In the mean time, membrane "C" is thinner than Nafion 115, which results in smaller membrane resistivity. These two properties, together with the different water diffusion coefficient, can have dramatic effect on the water transport profile across the membrane. As the current through the cell increases, water is dragged away from the anode. The anode begins to dry out and the cell resistance increases. The cell starts to lose its performance due to the ohmic loss. All These can be minimized by using a thinner membrane that offers higher proton conductivity and higher water diffusion coefficient (92). Since the PEM fuel cells are operated with different gas pressure where cathode has higher pressure than the anode, when thinner membrane with higher water diffusion coefficient is used, H_2O can be back-diffused to the anode side to prevent the cell dry-out. Because membrane "C" is thinner and provides higher proton conductivity and water diffusion coefficient than Nafion membrane 115, it is used for all subsequent studies.

With the understanding of these non-catalyst related technical problems, a more efficient fuel cell electrode was made. Figure 32 compares the air fuel cell performance on two electrodes. One was made with type one ink and membrane 115 where the ink was painted directly onto the SPE backing. The other was made with type two ink (with
Figure 32 Effect of the ink composition, the membrane and electrode (M&E) assembly and the ink painting method on the catalytic activities of supported Pt-DGC catalysts in H₂/air fuel cells.
TBAOH and glycerol added) and membrane "C" where the ink was painted first onto a Teflon decal then quantitatively transferred to the membrane. Clearly, the second electrode exhibits much higher activity than the first one. Stability test also shows that the second electrode gives more stable performance than the first one.

**Effect of Catalyst**

The above activity enhancement due to different M&E assembly is not directly related to the catalyst itself. However, there is no doubt that the influence of the catalyst dominates any other factors. The following section will demonstrate the dramatic influence of the pyrolysis environment and the curing temperature on the Pt-DGC's catalytic activity. Both factors change the catalyst’s structure.

Figure 33 compares both the air and O$_2$ fuel cell performance of three Pt-DGC catalysts. Normally, the catalyst is cured under argon atmosphere to 600°C and remain at 600°C for 6 hours. This catalyst exhibits a gradual current density drop over the entire cell potentials. If the catalyst is not held at 600°C for 6 hours, then the resulting catalyst has much lower activity in air fuel cells but comparable activity in O$_2$ fuel cells. When the material is cured under $10^{-6}$ torr vacuum to 600°C and remain at 600°C for 6 hours, its activity become mixed. In air fuel cell, it shows better performance than the normal catalyst at $E_{cell} > 0.5$V but its performance drops quickly at lower cell potentials. In O$_2$ fuel cell, however, the $10^{-6}$ torr vacuum cured catalyst shows consistently higher activity than the normal catalyst.
The influence of final curing temperature on the catalyst's performance is shown in Figure 34. In both air and O₂ fuel cells, the 600°C cured catalyst has significantly higher activity than the 400°C cured catalyst. The current density at 0.5V cell potential is 4.6 times (in air) and 3.5 times (in O₂) higher with the 600°C catalyst than with the 400°C catalyst.

The difference in the above catalyst's activities can be related to their structures as determined by transmission electron microscopy (TEM). Figure 35 shows the TEM micrographs of all four catalysts. Very small Pt clusters, ~20-30Å in sizes, are formed in the catalyst cured under argon for 6 hours (A). These particles have narrow size distribution and are homogeneously dispersed throughout the carbon matrix. The carbon support is relatively amorphous, as the graphite fringes are not well structured. In the high vacuum cured catalyst (B), the Pt clusters are much bigger, ~20-50Å, and have a wider size distribution than the normal catalyst. The particles are not as homogeneously dispersed, with some regions more heavily populated than others. The carbon matrix appears to be more graphitic, evidenced by the visible graphite fringes. In the catalyst that was cured under argon but was not held at 600°C (C), very few platinum clusters are observed and they are scarcely distributed, indicating that the 6 hour dwelling at 600°C is very important to form the platinum clusters. For the 400°C cured catalyst (D), significantly bigger Pt particles are observed compared to either the normal catalyst in A or the high vacuum cured catalyst in B. These particles are randomly distributed and have a wide size distribution (~10-60Å). The carbon matrix along the edges appears to be more graphitic than those in the middle. Raman study shows that the carbon matrix formed at
Figure 33 Effect of the pyrolysis environment on the fuel cell performance of supported Pt-DGC catalysts. (A) H₂/air fuel cell; (B) H₂/O₂ fuel cell.
Figure 34 Effect of the final curing temperature on the fuel cell performance of supported Pt-DGC catalysts. (A) $\text{H}_2$/air fuel cell; (B) $\text{H}_2$/O$_2$ fuel cell.
Figure 35  Transmission electron micrographs of Pt-DGC fuel cell catalysts.
(A) cured at 600°C for 6 hours under flowing argon;
(B) cured at 600°C for 6 hours under 10^{-6} torr vacuum;
(C) cured at 600°C under flowing argon but not held at 600°C;
(D) cured at 400°C for 6 hours under flowing argon.
Figure 35  (Continued)
400°C is much less graphitic than that formed at 600°C (88).

The catalyst performance can be related to the Pt particle sizes and their dispersion. For example, the Pt particles in the catalyst cured under argon for 6 hours are smaller and more homogeneously dispersed than the catalyst that was not held at 600°C or cured at 400°C. Correspondingly, the 600°C/6 hour argon cured catalyst has much higher activities than the other two. The high vacuum cured catalyst is an exception. It gives higher activity than the normal catalyst in O₂ fuel cell despite its bigger Pt particles and poorer distribution. This probably is due to an enhanced interaction between the Pt particles and the carbon matrix for this catalyst. For the 600°C/6 hour argon cured catalyst, its higher activity may also result from the reaction of the trace O₂ in the argon stream with the Pt clusters which reduces particle agglomeration during cell operation.

**Effect of Dispersion**

All the fuel cell catalysts studied above were prepared with 1:1 (w/w) precursor to substrate ratio. If this ratio is increased to 2:1, then the catalyst starts to lose its activity. Figure 36 compares the fuel cell performance curves of such two catalysts. They show similar performance at $E_{\text{cell}} > 0.7$V. But the current densities on the 2:1 catalyst degrades drastically at potentials below 0.7V. This decrease is in part due to the thicker catalyst film formed on the 2:1 catalyst. As shown in Figure 31, the precursor solution is coated onto the carbon support to form a thin film. When the amount of precursor increases, e.g., changing from 1:1 weight ratio to 2:1 weight ratio, the film coated becomes thicker. As a result, some of the platinum clusters are not exposed to the reactants and the catalyst
becomes less active.

Comparison With Commercial Catalysts

After investigating the factors that change the Pt-DGC catalyst's activity, it is
determined that the most appropriate conditions in preparing the supported Pt-DGC fuel
cell catalyst are as follow: the Pt-DGC precursor is first mixed with XC72 carbon powder
at 1:1 weight ratio followed by heat treatment to 600°C under argon atmosphere and
maintain at 600°C for 6 hours. This pyrolyzed catalyst is then mixed with Nafion solution
at 5:2 weight ratio with TBAOH and glycerol added to make the ink. The ink is painted
onto a Teflon decal and then transferred to membrane "C" by means of hot press at 210°C
and 500psi for two minutes.

The fuel cell performance of a Pt-DGC electrode made with the above described
method is compared to two other electrodes that were made with the commercial ETEK
catalyst and platinum black by the same method. Both of these two commercial catalysts
are obtained from E-TEK Inc. (Natick, MA) and have been studied (93). Figure 37 shows
the current-voltage curves obtained under the standard operating conditions. The Pt black
electrode has slightly higher current response than the ETEK electrode in air fuel cell but
they are quite similar in O₂ fuel cell. The Pt loading level on the Pt black electrode are
about 10 times as high as the ETEK electrode. This is necessary because the Pt particles in
Pt black catalyst are much bigger than those in ETEK catalyst. To ensure a fair
comparison, it is calculated that a loading level of 10 times higher for Pt black catalyst is
needed for the two electrodes to have comparable active Pt surface area. Although the
Figure 36 Effect of the precursor dispersion on the fuel cell performance of supported Pt-DGC catalysts. (A) H₂/air fuel cell; (B) H₂/O₂ fuel cell. The weight ratio is that of precursor to carbon substrate.
Figure 37 Comparison of the Pt-DGC catalyst with commercial ETEK and Pt black catalysts for $\text{H}_2/\text{air}$ (A) and $\text{H}_2/\text{O}_2$ (B) fuel cell applications.
platinum black catalyst is capable of delivering high current densities similar to the ETEK catalyst, it uses 10 times as much Pt as the ETEK catalyst and would be less economical for industrial application.

The Pt-DGC electrode, on the other hand, seems to give inferior performance than the ETEK electrode in Figure 37. However, this is not the case if the difference in Pt loading is taken into account. The loading level on the Pt-DGC electrode is 0.062mg/cm², only 48% of that on the ETEK electrode. The current densities obtained at 0.5V cell potential are 770 and 1240mA/cm² in air fuel cell and 1200 and 1710mA/cm² in O₂ fuel cell, for Pt-DGC electrode and ETEK electrode, respectively. With less than half of the Pt loading, the Pt-DGC electrode produced 62% and 70% of the current densities in H₂/air and H₂/O₂ fuel cell relative to the ETEK electrode. This holds consistent through the entire cell potential range.

The difference in the catalytic activities between the Pt-DGC catalyst and the ETEK catalyst can be related to the Pt cluster sizes and distribution. Figure 38 shows the TEM micrograph of ETEK catalyst. The platinum particles are ~ 40-50Å in sizes and they are very homogeneously dispersed. These particles are relatively small such that the ETEK catalyst exhibit high catalytic activities. However, the Pt particles in Pt-DGC catalyst are even smaller (~20-30Å) than those in ETEK catalyst, causing the former to be slightly more active than the latter at the same Pt loading level. Although the carbon support seems to be more graphitic in ETEK than in Pt-DGC, the platinum clusters are the dominant factor in determining the catalyst's activity.
Figure 38  Transmission electron micrographs of ETEK catalyst.
Figure 39  Stability test of the Pt-DGC and commercial ETEK catalysts for (A) H₂/air and (B) H₂/O₂ fuel cells. Current density values are obtained at 0.5V cell potential.
All useful catalysts should have good activity, good selectivity and good stability. The Pt-DGC catalyst has demonstrated unusually high activity for PEM fuel cells. Figure 39 shows the stability test on both the Pt-DGC catalyst and the ETEK catalyst. The current densities obtained at 0.5V cell potential are plotted as a function of test days. Clearly, both catalysts are able to maintain a consistent performance over the test period. The ETEK catalyst has been subjected to >4000 hour lifetime test and only slight decrease (<10%) in activity was observed (94). The Pt-DGC catalyst has not been exhaustibly tested due to a limitation in resources.

The XC72 supported Pt-DGC catalyst has shown to be a viable PEM fuel cell catalyst. The normalized activity is 12.4A/mgPt in air fuel cell and 19.3A/mgPt in O2 fuel cell, both at 0.5V cell potential, under the standard operating conditions (Figure 37). Although currently the Pt-DGC electrode in Figure 37 does not produce a current density high enough for practical application (e.g., ≥1A/cm2 at 0.5V), this is mainly due to the low platinum loading in the precursor material which results in low Pt concentration in the catalyst layer. However, it is possible to increase the precursor Pt density by varying the stoichiometry in the synthesis steps. Another advantage of Pt-DGC material compared to the commercial catalysts is that they are easily processable. Since the precursor can be made into a solution, different shape and thickness of electrodes can be fabricated by casting the solution onto the appropriate substrates. When making supported fuel cell catalysts, the concentration of the precursor solution can be varied such that different platinum loading can be easily achieved. This is a very attractive feature of the doped glassy carbon material that may have important applications for other purposes.
**Structural analysis by EXAFS**

With all the high activity and stability observed on Pt-DGC catalyst, it is desirable to investigate the material's local atomic and electronic structure such that their activities can be related to the catalyst's structure at the atomic level. When a better understanding of the structural parameters has been reached, the catalyst's activity and lifetime may be further improved. Extended X-ray absorption fine structure (EXAFS) spectroscopy was used to examine the catalyst.

Figure 40 illustrates the basic principles of EXAFS and the data analysis procedures. Platinum atom in the Pt-DGC catalyst absorbs the incident X-ray photons (with proper energy) and a core electron is ejected which produces the outgoing photoelectron wave. The photoelectron waves travel through the material and are backscattered by the neighboring atoms (Figure 40A). The outgoing and the backscattered photoelectron waves interfere with each other and produce the oscillatory structure in the absorption coefficient (Figure 40B). Subtracting the pre-edge and the post-edge background gives the normalized spectrum in Figure 40C. Then a polynomial spline through the EXAFS region is subtracted out to give the raw EXAFS data ($k^2$-weight, Figure 40D). Fourier transform of a selected region of the raw data (defined by the two dashed lines) results in the FT modulus in Figure 40E. Back transform of the peaks of interest gives a filtered data (solid line, Figure 40F) which is subsequently fitted to reveal information such as ligands, coordination numbers, bond distances and local disorder (dashed line, Figure 40F).
Figure 40 Illustration of the basic principles of EXAFS and typical data analysis procedures.
EXAFS has been widely used in studying supported fuel cell catalysts due to their ability to probe the short range order structure of selected elements (95-98). It differs from classical surface techniques such as ellipsometry, UV-Vis reflectance, IR spectroscopy, XPS and XRD in that EXAFS measures the bulk properties of the material rather than just the surface properties. It is the preferred technique when dealing with amorphous materials or components of a composite structure and has become a common tool in the field of dispersed metal catalysts characterization.

Non-supported Pt-DGC precursor was cured under argon atmosphere to various final temperatures and the resulting materials were subjected to EXAFS measurement. Figure 41 shows the raw $k^3$-weighted EXAFS spectra of the precursor material and three Pt-DGCs that have been heat treated to 200°C, 400°C and 600°C, respectively, together with the reference compounds Pt metal and PtO$_2$ (the amplitude on Pt metal has been reduced 3 times for easy comparison). On Pt metal, the amplitude of the EXAFS increases at higher $k$ region, while on PtO$_2$ the oscillatory pattern extended throughout the whole $k$ region at about the same amplitude. In contrast, there are essentially no features observed at $k > 12$ Å$^{-1}$ on the precursor sample. After heat treated to 200°C, some structure starts to appear at high $k$ region which indicates a gradual transformation of the atomic platinum to the metallic state. When heated to 400°C, the structure at high $k$ region further increases. Finally, at 600°C, the oscillatory pattern at high $k$ region reaches a similar amplitude as the low $k$ region.

Figure 42 compares the Fourier Transform (FT) moduli of the above samples (the amplitude for Pt metal is reduced 3 times). These FT moduli are not phase-shift corrected.
and all peaks appear at a lower $R$ value than their actual bond distances. The major peak observed on the precursor is at 1.9Å with an amplitude of 13.7. There is another peak appears at 4Å on the precursor which corresponds to some kind of long range bonding. This peak decreases and splits into two after 200°C heat treatment, but the major peak for the 200°C material appears at 1.7Å with an amplitude of 7.8. Additional side peaks around the major peak also appear on this material. Upon 400°C heat treatment, the peaks at ~ 4.0Å disappear, and the major peak shifts to 1.8Å with an amplitude of 6.7. In the meantime, one small peak appears at 2.6Å. Its position corresponds to the Pt-Pt bonding (compare to the strongest peak on Pt foil). On the 600°C material, two equally distinctive peaks, one at 1.9Å and one at 2.6Å, were observed, each with an amplitude of 6.8. For platinum foil, the peak at 2.6Å corresponds to the well ordered shell of 12 first nearest neighbor atoms. The side lobe at 2.2Å results from the complex amplitude envelope of the Pt backscatterer and does not correspond to a shorter Pt-Pt bond. However, the peaks at higher $R$ values correspond to more distant shells of nearest neighbors.

The development of platinum clusters in Pt-DGC can be qualitatively seen from these FT moduli. There is no detectable Pt-Pt bonding in the 200°C and the raw material. There is a very small Pt-Pt peak observed for the 400°C material but that peak grows significantly by going from 400°C treatment to 600°C treatment. The exact identities of these peaks and their coordinations can be obtained from non-linear curve fit of the filtered data (back transformed data). Table 8 summarizes the results.

On the precursor material, there are Pt-P and Pt-C bonds. The coordination of 2 for both bonds correlate exactly to the precursor structure (Figure 5). At 200°C, the Pt-P
contribution decreased significantly to a coordination of 0.55. This decrease indicates that less Pt is bonded to P at 200°C, consistent with the heat treatment procedure (the triphenylphosphine group gasified upon heat treatment). In the mean time, the coordination for Pt-C increased to 3, indicating that the carbon matrix starts to form. No Pt-Pt bonds are found at this temperature. At 400°C, all the Pt-P contribution disappears but small amount of Pt-Pt peaks are formed with N_{Pt}=0.5. The coordination of Pt-C peak is further increased to 3.3. Then at 600°C, much more Pt clusters are formed, evidenced by the five fold increased in Pt-Pt coordination (0.5 to 2.6). These curve fit results not only show the development in carbon matrix and platinum clusters during thermal treatment, they also provide structural support to explain the activity difference between a 400°C cured and a 600°C cured catalyst. The latter material has formed more platinum clusters than the former material. A coordination number of 2.58 (the first shell Pt neighbor atoms) corresponds to an average Pt particle size <10Å, which is the main reason that Pt-DGC catalyst has extremely high catalytic activity when the Pt particles are exposed, e.g., supported catalyst. The EXAFS curve fit results confirm the assumption that nanoscale platinum clusters are formed within the GC matrix.

The Pt-DGC catalysts were also subjected to in situ gas phase reduction and oxidation because such treatments have been found to introduce significant changes to the Pt clusters structure (192). Since only the 600°C cured material shows appreciable amount of Pt-Pt peaks, in situ gas phase reduction and oxidation was done on this catalyst only. Figure 43 demonstrate the difference in the FT moduli after the reduction and oxidation
Figure 41 Raw $k^3$-weighted Pt EXAFS of Pt metal (top), PtO$_2$ (bottom) and Pt-DGC samples that have been heat treated to different temperatures.
Figure 42  Comparison of Fourier Transform (FT) moduli of Pt-DGC materials cured at different temperatures to the FT modulus of Pt metal.
Figure 43  Comparison of the FT moduli of a 600°C cured Pt-DGC catalyst after gas phase reduction (with H₂) and oxidation (with O₂).
Table 8  EXAFS least-square curve fit results

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Bond Distance (Å)</th>
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<tbody>
<tr>
<td>Pt-P</td>
<td>2.382</td>
<td>2.195</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pt-C</td>
<td>2</td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pt-Pt</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>200°C</td>
<td>Bond Distance (Å)</td>
<td>2.479</td>
<td>2.117</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Coordination Number</td>
<td>0.552</td>
<td>3.01</td>
<td></td>
</tr>
<tr>
<td>400°C</td>
<td>Bond Distance (Å)</td>
<td>2.124</td>
<td>2.671</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Coordination Number</td>
<td>3.27</td>
<td>0.49</td>
<td></td>
</tr>
<tr>
<td>600°C</td>
<td>Bond Distance (Å)</td>
<td>2.182</td>
<td>2.785</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Coordination Number</td>
<td>2.84</td>
<td>2.58</td>
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step. It can be seen that the Pt-Pt peak height is the biggest on the reduced material and the smallest on the as-made material. An increase in the peak height indicates either more clusters are formed or the clusters have grown bigger with the reduction treatment. Subsequently oxidized material has a smaller Pt-Pt peak height than the reduced sample but it has bigger peak height than the as-made material. These changes, however, are very small, suggesting that the platinum clusters can not be easily reduced or oxidized. Note in this case that the 600°C cured Pt-DGC catalyst used for these EXAFS studies were not supported on any substrate. The small change in the Pt-Pt intensity indicates that platinum clusters formed inside the GC matrix are not accessible to H₂ or O₂ gas, which explains why the non-supported DGC catalysts have low activity for PEM fuel cells.

CONCLUSIONS

A low temperature synthetic route to the preparation of homogeneously doped glassy carbon materials has been evaluated for use in electrocatalysis. This new synthetic scheme allows the incorporation of a variety of foreign atoms into the GC matrix in a user-controllable fashion. The manufactured material was characterized by various techniques for their structural formation and catalytic activities.

Raman spectroscopy was used to probe the carbon matrix creation. It was found that a 600°C heat treated DGC material possesses a graphite microstructure similar to the commercial high temperature synthesized GC. Comparison of other properties such as the electron transfer kinetics and conductivity with commercial GC material further confirm
that a glassy carbon matrix has been formed at relatively low temperature using the current approach.

The platinum doped glassy carbon (Pt-DGC) material has remarkable catalytic activities for the oxygen reduction and hydrogen evolution reactions. On thin film electrodes supported on GC25 disk, very high catalytic activity for ORR was observed with either the 1:2 or 1:6 type material. On Toray carbon "felt" supported Pt-DGC catalyst, compatible activity for hydrogen evolution reaction was obtained on a polycrystalline platinum electrode and a Pt-DGC electrode with only 5.5μg/cm² Pt loading.

Due to these unusually high catalytic activities of the Pt-DGC materials, further investigation of their structure and properties were carried out in polymer electrolyte membrane fuel cells. It was found that many factors can influence the catalyst's performance. In order to give good activity for the fuel cell application, the Pt-DGC material must be supported on high surface area substrate, then heat treated under argon atmosphere to 600°C for 6 hours. The pyrolyzed catalyst was then mixed with Nafion solution, TBAOH and glycerol to make an ink which was painted onto a Teflon decal and subsequently transferred to membrane "C". Fuel cell electrodes made with such a method exhibit excellent catalytic activities. An optimized Pt-DGC catalyst performs slightly better than the commercial ETEK catalyst at the same Pt loading level. Both of them are capable of delivering stable performance.

The catalytic activities of the Pt-DGC catalyst were related to their structure by TEM and EXAFS. TEM shows that the Pt-DGC catalyst prepared using the most
appropriate conditions has homogeneously distributed platinum clusters which are smaller than those in the commercial ETEK catalyst. The carbon support seems to have significant influence on the catalyst's activity. EXAFS was utilized to investigate the local atomic and electronic structure of the Pt-DGC material. The results establish that a thermal treatment of \(~600^\circ C\) is required for the Pt cluster formation.

Supported Pt-DGC materials have been demonstrated to be viable fuel cell catalysts. Currently the limited availability of this material has prevented wider scale investigation and applications. However, the low temperature synthetic scheme has provided a brand new technique to make high efficiency catalyst where nanoscale platinum clusters (and other species as well) are incorporated in a glassy carbon matrix. These new classes of materials might find use in the energy conversion devices in the future.
CHAPTER IV
SYNTHESIS, CHARACTERIZATION AND ELECTROCHEMICAL ACTIVITIES OF HALOGEN DOPED AND IRON DOPED GLASSY CARBON

INTRODUCTION

This chapter reports work done on two distinctive doped glassy carbon materials, namely, halogen doped glassy carbon and iron doped glassy. It has been pointed out in previous chapters that the low temperature synthetic route to the preparation of glassy carbon materials allows the incorporation of a variety of dopants. The materials investigated in this chapter are just two more examples of the wide variety of DGCs we are capable of synthesizing using the low temperature approach. Due to the difference in the ability of the dopants to interact with the reactants, these DGCs are expected to possess different electrochemical activities.

The platinum doped glassy carbon material presented in Chapter III has demonstrated unusually high catalytic activities for the oxygen reduction reaction and the hydrogen evolution reaction because of the nanoscale platinum clusters. In this chapter, we shall see how the physical and electrochemical properties of glassy carbon can be altered with the incorporation of either halogen or iron. Since the two dopants are significantly different from each other, their influence on the material's properties shall be discussed separately.
Halogenated Carbon Materials

The halogen-DGC investigation originated from a collaboration with Dr. Howard D. Hutton. The interest in pursuing halogen doped glassy carbon is based on the unique properties that halogen elements may provide. For example, the ionization energies for H, Cl and F are 315.0, 300.3 and 403.3 kcal/mol., respectively (99, 100). The very high ionization energy for F prevents it from easily forming electron deficient species on the electrode surface compared to H and Cl. Therefore, the surface adsorption energetics of the materials can be dramatically affected by the incorporation of halogens through a change in the polarity and surface energies. Other factors can also change the material's properties. They include electronegativity, bond strength and lone ion pairs.

Carbon fluoride materials have been made by a high temperature reaction of graphite with fluorine gas (101). This fluorinated material consists of both covalent C-F bonds and intercalated C-F compounds. By varying the temperature and reaction time, different stoichiometry of CF_x compounds were obtained. These materials have significantly different graphite structures, e.g., a material with CF_{1.6} stoichiometry does not have graphitic planes but just arrays of cyclohexane molecules in a chair conformation. Depending on the degree of fluorination, the interplanar distances of the graphitic planes varies from 3.35Å to 6-9Å. In the intercalated C-F compounds, the graphite planes remain intact and the fluorine is directly bonded to the carbon. These fluorines significantly increase the interplanar distance thus decrease the electrical conductivity of intercalated graphite to about half of that on regular graphite. Fluorinated carbon materials have found major use as high temperature lubricants and lithium battery cathodes. They were shown
to possess excellent lubrication functions at high temperatures relative to undoped graphite (102) and they have been used in lithium batteries since 1969 (103).

Similar to fluorine doping, structure and property alterations can also occur with chlorine doping. Because of these halogen's ability to change the electrode surface adsorption properties, they may be used to selectively catalyze certain electrochemical reactions.

The low temperature synthetic route to the preparation of fluorine and chlorine doped glassy carbon material is the first ever reported that allows a homogeneous halogen incorporation to the GC matrix. This novel technique disperses the dopants at an atomic level as opposed to physical mixing of the components. It offers a unique opportunity for the investigation of bulk halogen modified carbon materials for electrocatalysis purpose.

The potential advantages that these halogen doped GC and the excellent catalytic activities already observed on platinum doped GC have led us to the synthesis and investigation of a fluorine and platinum doped glassy carbon material. We studied the effect of fluorine doping on the catalyst's activity toward the oxygen reduction and the hydrogen evolution reactions.

Iron Modified Carbon and Related Oxygen Reduction Reaction

Carbon has been an essential electrode material for electrocatalysis in fuel cell technologies due to two of its useful properties: high electrical conductivity and high corrosion resistance. The latter is critical in alkaline fuel cells and phosphoric acid fuel cells since both are operated at elevated temperatures (~200°C). The relatively low cost
and easy fabrication of carbon electrodes have made them very attractive for
electrochemical applications. However, since carbon itself has very low catalytic activity
for oxygen reduction reaction, the most important and the most difficult one in fuel cells, it
has been used mainly as a support. In order to utilize their inherent advantages, carbon
materials have been commonly modified with cobalt, ruthenium or iron-containing species
(19, 21, 22, 81-83, 85,113-124) to enhance their activity.

The preparation of superficially Fe modified GC electrodes usually involves the
adsorption of some Fe-N4 macrocyclics onto carbon support. The most frequently used N4
chelates are porphyrins (19, 21, 22, 85, 113-119) and phthalocyanines (Pc) (81-83, 120).
Catalytic properties of these superficially modified electrodes depend on the central Fe
oxidation state, the N4 ligands, the ring substituents, the type of carbon support, and the
electrolyte used. When applied for ORR, direct 4e⁻ reduction or parallel 2e⁻ reduction
involving H2O2 intermediate has been observed. However, electrodes with adsorbed Fe-N4
catalyst present poor reproducibility and stability. The electroactive components undergo
desorption, demetallation or decomposition, resulting in the catalytic property loss of such
electrodes. Although it was later found that pyrolysis of these iron N4-chelates
significantly improved their electrocatalytic activity and stability for oxygen reduction
(121-125), these surface modified GC electrodes are still fragile and suffer from
decomposition of the electroactive component. Recovering the electrode activity requires
cleaning and re-adsorbing the active component and the reproducibility is often poor and
tedious. Other approaches include entrapment of the active species in a porous polymer
film or dispersing the catalyst as small particles and make efficient use of them. A number
of methods have been described and this topic has been reviewed (104).

Although iron porphyrin modified GC electrodes show enhanced activity for oxygen reduction, they are generally impractical for fuel cell use due to their short lifetime. As an alternative, iron oxide and metallic iron (or steel) have been used to catalyze a number of reactions. For example, iron oxide is used in the high temperature CO shift conversion and metallic iron is used in ammonia synthesis (105). Lyons and Burke studied O2 evolution on an activated iron electrode in alkaline solutions (106). They reported that a thick surface oxide film was formed on the electrode surface which consisted of an anhydrous thin inner oxide layer and a porous, extensively hydrated and much thicker outer layer. O2 evolution was considerably enhanced by this oxide layer.

Oxygen reduction on iron electrode has not been very well studied despite of its practical importance in the field of metallic corrosion. Okuyama and Haruyama studied ORR on a passivated Fe-18%Cr alloy in a neutral solution (107). They found that H2O2 was not directly involved in O2 reduction mechanism on the passivated Fe-Cr alloy. The reaction most likely involved the adsorbed species with the reaction:

\[ O_2^- + H^+ \rightleftharpoons HO_2(ads) \]  \[ [4.1] \]

as the rate determining step. They proposed that a chemical reaction on the electrode controlled the overall mechanism and the semiconductivity feature of the passivated iron oxide film strongly affected the surface reaction.
Another ORR mechanistic study on steel was carried out by Wroblowa and Qaderi (108). In their RDE measurements, two waves were obtained. One was in the region between 1.0 and 0.4V vs reversible hydrogen electrode (RHE, in 1M NaOH), the other was in the region between 0.4 and -0.1V vs RHE (in 1M NaOH). At more negative potentials, hydrogen starts to evolve on the bare metal surface. The study found that a direct four electron reduction and the re-oxidation/chemical decomposition of peroxyl ions were absent. In the first region, the only product was HO\textsuperscript{2}. In the second region, the reaction followed a sequential 2+2 electron pathway, with HO\textsuperscript{2}/OH\textsuperscript{-} reduction started at ~0.4V vs RHE (in 1M NaOH). At potentials more negative than the RHE potential, the only product of oxygen reduction was OH\textsuperscript{-} generated via the sequential steps.

It is not the purpose of this work to investigate oxygen reduction mechanism on the low temperature formed Fe-DGC materials. Instead, we will demonstrate a brand new approach to the synthesis of homogeneously iron doped glassy carbon material which shows quite different catalytic activities for oxygen reduction relative to either undoped GC or bulk iron. The Fe-DGC material presents a case where two catalysts are intimately mixed at the molecular level. They serve to enhance each other's activity, and are not just the simple addition of two independent components.

**EXPERIMENTAL**

**Synthesis of the F-DGC, Cl-DGC, F-Pt-DGC and Fe-DGC Precursors**

Detailed synthetic chemistry of the above mentioned materials (precursors) is given
elsewhere (109, 110) and is schematically illustrated in Figure 44 and Figure 45. In Figure 44, F-DGC or Cl-DGC precursor was synthesized from 1,2,3,5-tetrafluorobenzene or 1,2,3,5-tetrachlorobenzene. The starting material was first reacted with KI and periodic acid in concentrated H$_2$SO$_4$ to give 1,2,3,5-tetrafluoro-4,6-diiodobenzene or 1,2,3,5-tetrachloro-4,6-diiodobenzene. Selective reaction of the aryliodides with trimethylsilylacetylene using palladium and copper catalysts followed by removal of the trimethylsilyl groups with KOH in methanol gave 1,2,3,5-tetrafluoro-4,6-diethylbenzene or 1,2,3,5-tetrachloro-4,6-diethylbenzene. Oligomerization with pentafluororoethylbenzene or pentachloroethylbenzene under O$_2$ and CuI catalyst gave poly(1,3-butadiynylene-tetrafluoro-1,3-phenylene) or poly(1,3-butadiynylenetetrachloro-1,3-phenylene) which can be precipitated to become a powdery F-DGC or Cl-DGC precursor. These precursors can be subsequently dissolved in toluene to make solutions for casting thin film electrodes on GC disks. The F-Pt-DGC precursor was prepared by further reacting the F-DGC precursor with 1,3-diacetylene bis(triphenylphosphine) platinum (0) in a way similar to the preparation of Pt-DGC precursor (see Figure 5).

Figure 45 illustrates the synthetic schemes for Fe-DGC precursor. 3,5-dibromiodobenzene was first reacted with ethynylferrocene using palladium and copper catalysts to give [(3,5-dibromophenyl)ethynyl]ferrocene. This is then reacted with trimethylsilylacetylene followed by removal of the trimethylsilyl groups to give [(3,5-diethynylphenyl)ethynyl]ferrocene monomer. Reaction of this monomer with phenylacetylene under O$_2$ and CuI catalyst produced the Fe-DGC precursor. This
Figure 44  Illustration of the synthetic schemes to the preparation of F-DGC, Cl-DGC and F-Pt-DGC precursors.
Figure 45 Illustration of the synthetic schemes to the preparation of iron doped glassy carbon (Fe-DGC) precursor.
precursor can be precipitated as powder which can be subsequently dissolved in toluene to make solutions.

All the above precursor materials are stable to air and moisture, either as solid powder or in solution.

**General Procedures for Preparing Thin Film DGC Electrodes and Raman Spectroscopy**

The halogen doped glassy carbon or iron doped glassy carbon precursor was dissolved in toluene to make a saturated solution. Thin film electrodes were made by first casting the precursor solution onto GC25 disks using the method described in Chapter III, followed by pyrolyzing the sample in a quartz tube furnace to a typical final temperature of 600°C under either flowing argon or a dynamic vacuum that is equipped with a mechanical pump, a liquid nitrogen cold trap and a diffusion pump. This vacuum system is capable of achieving $10^{-6}$ torr pressure. The thickness of the thin films are typically 1-5μm.

**Raman Spectroscopy** procedures are the same as those described in Chapter III. In most cases, Raman measurements were done immediately after the samples have been heat treated. In some cases where electrochemical measurements are of priority, Raman measurements were done afterwards. Under these circumstances, the electrode was first rinsed with copious amount of NANOpure H$_2$O and air dried before performing the Raman measurement.

**General Procedures for Cyclic Voltammetry**

All electrochemical experiments were performed on thin film electrodes
immediately after removal from curing. The electrode was housed in a Teflon cell that has the standard three electrode design (13). The reference electrode is Ag/AgCl (BAS, in 3M KCl, $E^\circ = 0.203\text{V} \text{ vs NHE}$) and the auxiliary electrode is a platinum wire. Cyclic voltammetry was performed with a triangle wave generator and a personal computer as described elsewhere (144). The active electrode area was determined by a Teflon washer and is approximately $0.1\text{cm}^2$. Each electrode area is separately determined by chronoamperometry of $\text{Fe(CN)}_6^{3/-4}$. Solutions were degassed for at least 20 minutes before measurements. During data acquisition, the gas stream was maintained over the solution. The pure iron disk electrode was prepared by imbedding an iron wire (Johnson Matthey, 99.9985%, 20mm diameter) in Eccobond epoxy similar to preparing a GC electrode for fracturing (18). All potentials are reported against Ag/AgCl reference.

RESULTS AND DISCUSSION

This section will be presented in two parts. Part I concerns the halogen doped glassy carbon including F-Pt-DGC. Part II concerns the iron doped glassy carbon.

Part I  F-DGC, Cl-DGC and F-Pt-DGC

The halogen doped glassy carbon materials were first subjected to Raman investigation for the $sp^2$-hybridized carbon structure formation. Since carbon material has relatively large polarizability due to its conjugated structure, they are suitable for Raman studies. Figure 46 shows the Raman spectra of the 600°C cured halogen doped materials in comparison to a variety of other DGC materials and a conventionally prepared GC10.
Figure 46 Raman spectra of various doped glassy carbon materials cured to 600°C for 6 hours under argon atmosphere in comparison with a conventional GC10 - effect of dopants on the GC lattice formation.
The characteristic graphite bands at 1360 and 1580 cm⁻¹ can be clearly seen on all materials. The spectra obtained on halogen doped materials are very similar to the spectrum obtained on the conventional GC10, suggesting that the halogen species do not affect the carbon lattice formation. In fact, platinum does not affect the carbon lattice formation, either. All halogen-DGCs and Pt-DGCs have similar Raman spectra to that of GC10. The different intensity ratio between the 1360 and 1580 cm⁻¹ bands is due to a slight difference in the carbon microcrystalline sizes. The only exception is the iron doped material which shows significantly higher \( I_{1360}/I_{1580} \) ratio and dramatic overtone bands at about 2700 cm⁻¹. As will be discussed later in part II, this is caused by the iron dopant which catalyzes carbon lattice formation.

Despite the presence of the dopants, Raman measurements have shown that a sp²-hybridized carbon lattice was formed on all doped glassy carbon materials upon 600°C heat treatment. Because this process appears to be independent of the halogen dopants, it is interesting to know where these dopants end up. Thus XPS was performed to determine the fate of the halogens. Shown in Figure 47 are the XPS spectra on F-DGC and Cl-DGC thin film electrodes. The Cl(2p) peak was found at 201.1 eV and the F(1s) peak was found at 686.5 eV. Integrating these halogen peaks and compared them to the C(1s) peak at 284.6 eV (as internal standard) gives the halogen concentration on the surface as ~20 wt% for Cl and ~15 wt% for F. The halogen doped glassy carbon thus contains large amount of Cl or F. Clearly, this benefits from the low temperature synthesis where the halogen species can survive the heat treatment. Through a careful analysis of the peak binding energies, Hutton (109) has determined that the halogen was bonded to the edge of the
Figure 47  X-ray photoelectron spectra of thin film Cl-GC6 and F-GC6 electrodes.
graphite planes.

Exhaustive efforts have been spent on determining the physical properties of the halogen doped materials. Table 9 summarizes the results (109). These physical properties show the difference as well as the similarity between conventional GC and the low temperature manufactured GC. For example, incorporation of F significantly increases the contact angle but significantly decreases the surface energy, density, elastic moduli and the conductivity relative to GC10, while incorporation of Cl slightly decreases the contact angle and surface energy but substantially decreases the density, elastic moduli and the conductivity.

The electrochemical activities of the halogen doped glassy carbon was studied using Fe(CN)$_6^{3/-4}$ with thin film electrodes supported on GC25 disks. The thin films have sufficiently high conductivity for electrochemical measurement without significant ohmic loss (iR drop). Figure 48 shows the cyclic voltammograms obtained at 10mV/s in 1mM Fe(CN)$_6^{3/-4}$ solution. A low, flat background was observed on both the GC6 electrode and the F-DGC electrode, implying that these electrodes are non-porous and relatively free from oxides. The background on Cl-DGC is much higher, but this difference did not occur reliably. The background current strongly depends on the electrode preparation.

The halogen doped material was found to have anomalously low anthraquinone 2,6-disulphonate (AQDS) adsorption. AQDS has been known to adsorb strongly and readily onto a glassy carbon surface and reach a saturation coverage of about 200 picomole/cm$^2$ (70). On F-DGC electrode, however, no adsorption can be detected after 90 minutes in 5mM AQDS/1M HClO$_4$ solution. This extremely low AQDS adsorption may be a result
of contaminants introduced during the heat treatment. A possibility of the contaminant source is the pump oil vapor from the mechanical pump.

To test this, a polished GC20 electrode was heat treated under exactly the same conditions as pyrolyzing the halogen doped DGCs. Cyclic voltammetry in 50μm AQDS solution was performed immediately upon removal of the electrode from the vacuum chamber. Figure 49 compares the voltammograms before and after additional laser irradiation. On the heat treated electrode, there is no apparent AQDS adsorption. However, after 5 pulses of 25MW/cm² laser irradiation, the adsorption peaks were observed at about -0.13V vs Ag/AgCl (labeled with a "*"). Since laser irradiation at low power density is believed to desorb the surface contaminants, the above results suggest that the heat treated GC20 electrode suffers from some type of impurity adsorption. Because the curing conditions were the same, the halogen doped thin film electrodes might also suffer from similar contaminant adsorption.

Another possibility for the low AQDS adsorption is related to the halogen doping. Since halogens are more hydrophobic than carbon or oxygen, a F-DGC or Cl-DGC electrode surface would be more hydrophobic than conventional GC electrode thus preventing AQDS from adsorbing onto it. Consequently, the heterogeneous electron transfer constant k° for Fe(CN)₆³⁻/⁴ is lower on the halogen doped material than on conventional GC. k° calculated from the peak separation in Figure 48 is 0.005cm/s for F-DGC and 0.001 for Cl-DGC. Unfortunately, because of the complications from the contamination, it is impossible to conclude whether F-DGC is different from Cl-DGC in their electrochemical properties, except to say that halogen doping appears to have
Table 9  Selected physical properties of GC6, GC10 and halogen doped glassy carbon.

<table>
<thead>
<tr>
<th>Carbon Type</th>
<th>Heat Treatment Temperature</th>
<th>Contact Angles (in H₂O)</th>
<th>Surface Energy (dynes/cm)</th>
<th>Density (g/cm³)</th>
<th>Young's Modulus (MN/m²)</th>
<th>Conductivity (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GC6</td>
<td>600°C</td>
<td>82.5°</td>
<td>31.3</td>
<td>1.50</td>
<td>28,500</td>
<td>0.7</td>
</tr>
<tr>
<td>GC10</td>
<td>1000°C</td>
<td>84.8°</td>
<td>31.5</td>
<td>1.50</td>
<td>30,900</td>
<td>222</td>
</tr>
<tr>
<td>F-DGC</td>
<td>600°C</td>
<td>95.7°</td>
<td>27.3</td>
<td>1.22</td>
<td>19,100</td>
<td>0.2</td>
</tr>
<tr>
<td>Cl-DGC</td>
<td>600°C</td>
<td>83.7°</td>
<td>29.9</td>
<td>1.35</td>
<td>7,270</td>
<td>0.1</td>
</tr>
</tbody>
</table>
Figure 48  Cyclic voltammograms of 1mM Fe(CN)$_6^{3/-4}$ on thin film Cl-GC6, F-GC6 and GC6 electrodes with background. Scan rate = 10mV/s
Vacuum heat treated plus laser irradiation

Figure 49 Cyclic voltammograms of a heat treated GC20 electrode ($10^{-6}$ torr vacuum) in 50μM AQDS without and with additional 5 pulses 25MW/cm$^2$ laser irradiation. Scan rate = 200mV/s. CVs are background corrected.
minimal effect on the electron transfer kinetics of $\text{Fe(CN)}_6^{3-4}$ system under current conditions.

The effect of vacuum pressure on the material's electrochemical properties was also investigated. Two thin film electrodes, one cured under $10^{-6}$ torr and the other cured under $10^{-3}$ torr, were studied for the electron transfer kinetics of $\text{Fe(CN)}_6^{3-4}$. It was found that $k^0$ obtained on both electrodes was similar (~0.005 cm/s). However, the electrode cured under $10^{-3}$ torr vacuum has much higher background response, indicating a higher porosity and perhaps higher concentration of the surface oxides. The slightly higher $O_2$ concentration present during thermal treatment under $10^{-3}$ torr is presumably responsible for this difference. XPS study found a decreased $F$ concentration and an increased $O$ concentration on the $10^{-3}$ torr cured film. These changes, however, were observed only on the electrode surface. The bulk property of the material such as density and elastic moduli were unchanged with different vacuum treatment.

The above discussion has shown that the halogen doped glassy carbon has quite different surface physical properties than commercial GC (e.g., surface energy and wettability), therefore they might find applications for certain electrochemical reactions. As an example, a fluorine doped catalyst would be desirable for fuel cell cathode (the oxygen electrode) since the addition of fluorine can potentially minimize the electrode "flooding" (a phenomenon where water accumulates in the porous electrode structure) by increasing the electrode's hydrophobicity (2). Since platinum doped glassy carbon has been shown to be an effective catalyst for oxygen reduction in PEM fuel cells (Chapter III), and since the synthetic process to prepare fluorine-platinum doped glassy carbon is readily
available, we have thus created a F-Pt-DGC material using the process illustrated in Figure 44. Thin film electrodes made of this precursor were used to study the oxygen reduction and hydrogen evolution reactions.

Figure 50 shows the oxygen reduction cyclic voltammograms in both acid (A) and alkaline (B) solutions at 50mV/s. In 1M HClO₄, the Pt-DGC material and polycrystalline material have approximately equal catalytic activities per geometric area, while F-Pt-DGC is slightly less active. The Pt loading on Pt-DGC is 1.4 atom% but the loading on F-Pt-DGC is only 0.5 atom%. TEM analyses find the average platinum particle sizes are 15Å for Pt-DGC (86) and 16Å for F-Pt-DGC (109). The higher Pt loading and smaller particle sizes for Pt-DGC are likely responsible for the higher activities than F-Pt-DGC. Similarly, for oxygen reduction reaction in alkaline solution, F-Pt-DGC (0.59 atom% Pt) did not perform as well as the polycrystalline platinum. The reduction peak occurs at ~ -0.33V vs Ag/AgCl, similar to a polished GC20 electrode (Figure 7B).

As mentioned earlier, these halogen doped thin film electrodes might suffer from surface contaminants during thermal treatment. The lower activity relative to polycrystalline platinum might be due to these surface impurities.

Figure 51 contains the hydrogen evolution curves obtained in 1M HClO₄ at 50mV/s. As expected, the polycrystalline platinum electrode has the highest activity. The results obtained on Pt-DGC and F-Pt-DGC are similar, with F-Pt-DGC gives slightly higher current response. The Pt loading on F-Pt-DGC is 0.6 atom% and the Pt loading on Pt-DGC is 0.4 atom%. The smaller Pt loading on Pt-DGC is probably responsible for the lower activity than that on F-Pt-DGC.
Although no apparent improvement in catalytic activity was gained by incorporating F to the Pt-DGC matrix on thin film electrodes, this material does show higher stability than polycrystalline platinum for hydrogen evolution. Figure 52 compares the current vs time curves obtained in 1M HClO₄ at -44mV vs Ag/AgCl. The F-Pt-DGC electrode has a Pt loading of 0.43 atom%. The current density on polycrystalline platinum decreases from 11mA/cm² to 4.5mA/cm² within 60 minutes, while the current density on F-Pt-DGC electrode decreases from 5.4mA/cm² to 5.1mA/cm². The relative changes are 60% and 5% for Pt and F-Pt-DGC, respectively. The F-Pt-DGC electrode is also much more stable than a Pt-DGC electrode for hydrogen evolution reaction. The latter was found to retain only 75% of its original activity under the same conditions (88).

Part II. Iron Doped Glassy Carbon

This Fe-DGC project was in collaboration with Dr. John K. Pudelski as part of Prof. Callstrom's doped glassy carbon program. We sought the possibility of using a low cost material such as iron as an alternative to the expensive platinum catalyst for fuel cell oxygen electrode. The versatility of the low temperature glassy carbon synthetic route has allowed us to incorporate iron at a molecular level to the carbon matrix in a way similar to synthesizing halogen and platinum doped glassy carbon.

All materials were synthesized by Dr. Pudelski according to the schemes illustrated in Figure 45. Thin film electrodes were cast on GC25 disks from saturated Fe-DGC precursor solutions and were pyrolyzed under 10⁻⁶ torr vacuum. The resulting materials were first subjected to Raman studies to probe the carbon structure creation.
Figure 50  $\text{O}_2$ reduction voltammograms on F-Pt-DGC, Pt-DGC and polycrystalline Pt in 1M $\text{HClO}_4$ (A) and 1M $\text{KOH}$ (B) solutions. CVs are background corrected. Scan rate = 50mV/s.
Figure 51 Hydrogen evolution curves in 1M HClO$_4$ on Pt-DGC, F-Pt-DGC and polycrystalline Pt. Scan rate = 50mV/s.
Figure 52 Comparison of $H_2$ evolution on polycrystalline Pt and F-Pt-DGC. Curves were obtained at -44mV vs Ag/AgCl.
Figure 53 shows the Raman spectra of a series of Fe-DGC films pyrolyzed to different final temperatures. The Raman spectra of polished GC10 and GC20 were included for comparison. Note the trend of the 1360 cm\(^{-1}\) band development. At low pyrolysis temperatures (300–400°C), the 1360 cm\(^{-1}\) band is broad and unresolvable with the 1580 cm\(^{-1}\) band. If pyrolyzed to 500°C, the film bears a similar Raman spectrum to that of GC10. When pyrolyzed to 600°C, Raman spectrum of Fe-DGC exhibits two well resolved bands and their intensity ratio is close to that of GC20. In the meantime the 2700 cm\(^{-1}\) overtone developed into a distinctive peak. This is quite in contrast to other doped glassy carbon as seen in Figure 46. Except for Fe-DGC, all the other DGCs have a \(I_{1360}/I_{1580}\) ratio equal or less than that of GC10. Since this ratio is directly related to the degree of graphitization (26), the 600°C cured Fe-DGC material is thus more graphitic than all other DGCs cured to the same temperature. This is not a surprise given the fact that Omori, Hirai and Yajima (126) have observed that iron accelerated the glassy carbon formation when they heat-treated acetylfierrocene-furfural resin and found glassy carbon was first formed around the iron particles. They concluded that iron promoted the GC formation. Current Raman results on these Fe-DGC films also suggest that the incorporated iron dopants have promoted the glassy carbon microstructure formation. This unique property of Fe-DGC may find application in low temperature synthesis of multi-element doped material such as platinum doped iron promoted glassy carbon. Since 600°C pyrolyzed films exhibit well defined Raman features and distinctive overtones, we conclude that highly graphitic carbon matrix has been formed. All subsequent experiments were conducted on 600°C cured films.
The fate of iron dopants and their chemical state on the thin films were investigated by XPS. Figure 54 shows a representative XPS spectrum. Clearly, iron, oxygen and carbon were all present on the surface. High resolution scans of the Fe(2p), C(1s) and O(1s) regions find a surface composition of 7.2 atom% iron, 12.9 atom% oxygen and 79.8 atom% carbon for the material shown in Figure 54. The iron peaks binding energy at 700-740eV region (724.3eV and 710.2eV) didn't agree with the expected value for Fe(0). Instead, they correlate with the binding energies found on iron oxide (FeO or FeO₂). Since the synthesis of Fe-DGC involves Fe(0) only (ferrocene), oxide formation is not expected. The iron peak binding energies as well as the high concentration of oxygen suggest that the surface iron exists as oxide rather than Fe(0).

The bulk iron, however, is in zero oxidation state. This is demonstrated in Figure 55. The high resolution scans in the 700-740eV region show that immediately after the heat treatment, iron exists in at least two oxidation states. After 12.5 min Ar⁺ sputter cleaning, only one iron species was found, and its binding energy is consistent with a reduced iron species such as Fe(0). Further sputtering didn't change the iron peak position. If the electrode was exposed to atmosphere for one week, again only one iron specie was found. The peak binding energies, however, correspond to oxidized species such as FeO or FeO₂. These series of experiments suggest that the bulk iron is in zero oxidation state. But since Fe(0) has a strong tendency to react with atmospheric O₂ (112, 193), the surface becomes quickly oxidized when exposed, resulting in the formation of iron oxide.

As pointed out earlier, we are interested in using this material as an oxygen reduction catalyst. Figure 56 compares the ORR cyclic voltammograms obtained on three
Figure 53  Effect of the final curing temperature on the carbon lattice formation of iron doped glassy carbon (Fe-DGC) materials.
Figure 54  XPS spectrum of a 600°C vacuum (10^-6 torr) heat treated iron doped glassy carbon electrode.
Figure 55 High resolution XPS scans of the Fe(2p) region on iron doped glassy carbon electrodes after exposure to air for various amount of time.
different electrodes in oxygen saturated 1M KOH solution. All CVs were background corrected at 50mV/s and only the cathodic halves were plotted. The curve on the Fe-DGC electrode (5.9 atom% of Fe) features two reduction peaks in the cathodic scan between 0 and -1.2V. The curves on polished GC20 disk and a polished iron disk electrode show only one reduction peak. The first peak on Fe-DGC is at approximately the potential of the ORR peak on polished GC20, but the second peak does not agree with the ORR peak on an iron electrode. Such a simple comparison suggests that the Fe-DGC material is not the simple addition of GC and Fe, and ORR on Fe-DGC does not occur as two independent processes on carbon and iron. Instead, ORR on Fe-DGC behaves differently from either GC20 or bulk iron.

Although a detailed mechanism of ORR on Fe-DGC is not available with current data, we propose that peak one corresponds to the first two electron reduction of $\text{O}_2$ to $\text{HO}_2^-$ on the carbon matrix while peak two corresponds to the catalyzed reduction of $\text{HO}_2^-$ to OH$^-$ by the incorporated iron. Several lines of evidence support this suggestion.

First, carbon itself is quite active for oxygen reduction in alkaline solution. This has been shown in Chapter II. Since the majority of the surface atoms are carbon and since ORR on bulk Fe occurs at more negative potentials than on carbon (Figure 56), oxygen reduction will occur on the carbon support first. As discussed in Chapter II, the reduction of $\text{O}_2$ on carbon in alkaline solution proceeds to the first 2e$^-$ step according to the following overall reaction:

$$\text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightleftharpoons \text{HO}_2^- + \text{OH}^- \text{ (first peak)}$$

[4.2]
The peak at ~ -0.40V has a current density of 0.48mA/cm², correlates well with a two electron reduction process (Chapter II, discussion). The product of this reaction is hydrogen peroxide. Because carbon is a poor catalyst for hydrogen peroxide reduction or disproportionation, no further reaction was observed on the GC20 electrode (Figure 56, GC curve). However, on Fe-DGC, a second reduction peak was observed at ~ -0.76V. This peak potential corresponds to that of hydrogen peroxide reduction on Fe-DGC, as shown in Figure 57.

Figure 57 contains the HO₂⁻ reduction voltammograms on Fe-DGC and GC20 in argon degassed 1M KOH solution with 11mM H₂O₂ added. The O₂ reduction voltammogram on Fe-DGC was also plotted for comparison. Clearly, HO₂⁻ reduction on GC20 is negligible. However, on Fe-DGC, a strong reduction peak is readily seen at -0.82V. This peak is close to the second reduction peak observed during oxygen reduction on Fe-DGC, suggesting that peak two for ORR on Fe-DGC results from HO₂⁻ further reduction. The current density of HO₂⁻ reduction peak on Fe-DGC is proportional to HO₂⁻ concentration. A four fold increase in HO₂⁻ concentration increases the peak current by four times. Since HO₂⁻ reduction is minimal on glassy carbon but is significant on Fe-DGC, this reduction must be catalyzed by the incorporated Fe dopant. The overall reaction is:

\[
\text{HO}_2^- + \text{H}_2\text{O} + 2\text{e}^- \rightleftharpoons 3\text{OH}^- \text{ (second peak)}
\] [4.3]

One might argue that this peak could be associated with a process that is due to the iron oxide itself, e.g., iron oxide reduction which has a peak at approximately the same
potential. However, no such reduction peak was observed in an argon saturated solution on Fe-DGC without H₂O₂ added.

Further evidence that supports the above proposal is the pH dependence of oxygen reduction reaction. Figure 58 compares the voltammograms on Fe-DGC at several pH values. The first peak potential appears to be independent of the solution pH between 7 and 14 while the second peak shifts positively with decreasing pH. It is known that the first 2e⁻ O₂ reduction on carbon is zero order dependent on [OH⁻] (48, 139, 177). The fact that the first reduction peak on Fe-DGC is independent of pH suggests that it is most likely a process occurring on the carbon matrix.

It is important to note that the first reduction peak on Fe-DGC appears at more negative potential than the reduction peak on GC20. This is not due to a difference in the carbon structure. In fact, the glassy carbon formed by the low temperature route with Fe dopant is very similar to GC20 in terms of graphite microstructure as evidenced by their Raman spectra (Figure 46). The increased overpotential on Fe-DGC is partially due to the higher electrode resistance of DGC material relative to GC20 (Table 9). In addition, it is interesting to note that the second ORR peak on Fe-DGC is more positive than the pure HO₂⁻ reduction peak on the same electrode (Figure 57). The difference is presumably due to the adsorption of the HO₂⁻ intermediate that is generated by the first 2e⁻ reduction. Since Fe and GC are intimately mixed in the Fe-DGC material, the HO₂⁻ product from O₂ reduction on carbon matrix is right at the proximity of the incorporated iron species. These HO₂⁻ might be adsorbed such that their further reduction becomes relatively easier than if HO₂⁻ are free ions in the solution phase.
Figure 56  
$O_2$ reduction voltammogram in 1M KOH on Fe-DGC electrode in comparison with the voltammograms on pure Fe and GC20 electrodes. Scan rate = 50mV/s.
Figure 57 Comparison of the cyclic voltammograms of $\text{HO}_2^-$ reduction on Fe-DGC and GC20 electrodes to the $\text{O}_2$ reduction voltammogram on Fe-DGC electrode in 1M KOH. All CVs are background corrected. Scan rate = 50mV/s.
Figure 58 O₂ reduction voltammograms on Fe-DGC electrodes as a function of solution pH. CVs are background corrected. Scan rate = 50mV/s.
The stability of Fe-DGC for ORR in alkaline solution was tested using long time scale chronoamperometry. The electrode was maintained at -0.95V vs Ag/AgCl for 20 hours. O₂ was maintained above the solution for the entire data acquisition. Figure 59 shows the current-time dependence. The film retains 60% of its catalytic activity for O₂ reduction after the 20-hour continuously polarization, suggesting that the Fe-DGC material is quite active in catalyzing HO₂⁻ reduction or decomposition. CVs obtained before and after the polarization are identical, which indicates that Fe-DGC is very stable in base. The slow deactivation in polarization can be a result of many variables, e.g., impurity adsorption, loss of active sites by HO₂⁻ adsorption, O₂ concentration change, and local pH change.

Although Fe-DGC exhibits high stability in base, it quickly loses its catalytic activity in acidic media. Figure 60 shows the ORR CVs on Fe-DGC in oxygen pre-saturated 1M HClO₄. A reduction peak at ~0.14V was observed during the first scan. However, when the electrode was kept in HClO₄ for 2 minutes, a second scan and all subsequent scans showed no detectable reduction peak. The loss in activity is related to the loss of the surface iron species. When cured Fe-DGC powder was placed in NANOpure water with a small amount of 1,10-phenanthroline, the solution didn't change color for more than 10 hours. However, when two drops of HClO₄ was added, the solution changed to orange color typical of the iron complex with 1,10-phenanthroline within two minutes. This is a strong indication that the surface iron species is quickly dissolved in acidic media. The test can be repeated for many times. Each time the particles were pulverized into smaller ones. When drops of HClO₄ were added, the solution turns
Figure 59  O$_2$ reduction polarization curve on Fe-DGC electrode at -0.95V vs Ag/AgCl.  
The dashed line is the curve fit to the original data.
Figure 60  Cycl voltammograms of $O_2$ reduction on Fe-DGC electrodes in 1M HClO$_4$. CVs are background corrected. Scan rate = 50mV/s.
orange color within two minutes. These simple experiments demonstrate that the surface iron species are unstable in acidic solutions and the iron species in Fe-DGC are deeply incorporated in the GC matrix. When the surface Fe is dissolved, oxygen reduction becomes inhibited and can only occur on the bare carbon support at much more negative potentials (e.g., -0.5V vs Ag/AgCl).

CONCLUSION

A low temperature route (~600°C) to the synthesis of halogen doped and iron doped glassy carbon materials was described. Raman spectroscopy was performed to characterize the sp²-hybridized carbon lattice formation. It was found that iron dopants promoted glassy carbon formation during pyrolysis while halogen (F, Cl) and platinum did not affect the lattice formation. All DGCs possess similar carbon microstructures as the conventional GC10 material.

The halogen doped materials have dramatically different physical properties from GC10. In particular, the surface energy of fluorine doped glassy carbon is much lower than Cl-DGC or GC10. The surface of a halogen doped GC electrode contains more than 15 wt% of halogens. Both F-DGC and Cl-DGC exhibit fair electron transfer kinetics for Fe(CN)₆⁻³/₄ system and they are comparable to commercial GC material. The background response on GC6 or F-DGC electrodes were very small, suggesting that they are non-porous and relatively free from surface oxides. Due to the complication of contaminants from curing environment, this study cannot conclude whether F-DGC is inherently different from Cl-DGC and whether halogen doped material has much different
electrochemical properties than conventional GC material.

Because of the unique properties observed for F-DGC (low surface energy, high hydrophobicity), a fluorine and platinum doped glassy carbon material was developed and its catalytic activity for oxygen reduction and hydrogen evolution was investigated on thin film electrodes. It was found that F-Pt-DGC exhibits slightly lower catalytic activities than polycrystalline platinum for ORR in both acid and alkaline solutions and for HER in acid solution. However, the platinum loading on these electrodes are in the order of ~0.5 atom% and they appear to have higher stability than polycrystalline platinum. Incorporation of fluorine into Pt-DGC matrix did not seem to improve its activity for oxygen reduction reaction.

Iron doped glassy carbon (Fe-DGC) shows quite unique properties for oxygen reduction. Two reduction peaks were observed on Fe-DGC. The first peak corresponds to the first $2e^-$ reduction on the carbon support while the second peak is the further reduction of hydrogen peroxide catalyzed by the incorporated iron species. Because of the intimate mixing (molecular level doping), this material behaves quite differently from either undoped GC or bulk Fe.

The oxidation state of the iron dopants was studied by XPS. It was found that the surface iron exists as iron oxide while the bulk iron remains in its zero oxidation state. Fe-DGC material is stable in basic media, but loses its catalytic activity in acid media due to the dissolution of surface iron species, hence they are not suitable for application in acidic media.
Although the DGCs discussed in this chapter do not have catalytic activities as high as the Pt-DGC materials discussed in Chapter III, they do provide a new approach, for the first time, to prepare Fe and halogen doped glassy carbon. Because the user has control of the dopants (e.g., loading level), it is conceptually possible to synthesize a new class of materials where extremely high catalytic efficiency can be obtained by incorporating the precious metal catalyst at an atomic scale, or by incorporating a combination of catalysts, each having specific activity for certain part of the reaction and together to achieve unsurpassed activity.
APPENDIX A

ELECTRON TRANSFER KINETICS OF Fe(CN)$_6^{3/-4}$ ON LASER ACTIVATED AND CN$^-$ MODIFIED Pt ELECTRODES

The research discussed in this appendix is based on an independent project performed prior to the works that constitute the main body of the dissertation. Platinum microelectrodes were utilized for the entire research and no carbon electrodes of any form were involved. Publication of this research appeared in J. Electroanal. Chem., 1992 (144).

INTRODUCTION

The Fe(CN)$_6^{3/-4}$ redox couple has been used extensively as a benchmark system for studying electrode kinetics and diffusion, and for characterizing electroanalytical techniques (13, 127-136). Considered superficially, Fe(CN)$_6^{3/-4}$ is a quasireversible, well behaved redox system with an $E_{1/2}$ suitable for Pt, Au, and carbon electrodes in aqueous electrolytes such as 1 M KCl. For this reason, it has served as a test system for numerous examinations of solid electrode preparation and modification, most notably Pt (127-130) and glassy carbon (GC) (5, 9, 59). Unfortunately, Fe(CN)$_6^{3/-4}$ is significantly more complex than a superficial examination indicates. The heterogeneous electron transfer rate constant, $k^0$, depends strongly on cation and anion identity and concentration in the electrolyte solution, with the cation effect being more pronounced (136). Peter et al,
attributed the increase in $k^o$ with potassium ion concentration to the involvement of $K^+$ in
the transition state for electron transfer (128). A second complication is the chemisorption
and decomposition of $\text{Fe(CN)}_6^{3/-4}$ on Pt surfaces, indicated by FTIR, radiochemical, UV-
Vis and electrochemical results (127, 129, 131). Galus, et al., noted that $k^o$ can be
increased by adding free CN$^-$ to the electrolyte, preventing $\text{Fe(CN)}_6^{3/-4}$ chemisorption
(127, 130). Goldstein and Van de Mark noted that large $k^o$ values were observed when
halides were chemisorbed onto the surface, and associated this effect with the observed
anion dependence of $k^o$ (136). An additional issue does not directly involve the $\text{Fe(CN)}_6^{3/-4}$
system, but has an important effect on observed $k^o$ values. The largest literature values
for $k^o$ on Pt in 1M KCl are in the range of 0.1-0.24 cm/s, but in many cases, these values
are at or near the upper limit of the instrumental technique employed. Most previous
detailed kinetic examinations were performed with conventionally sized Pt, Au, or carbon
electrodes having areas of ca. 0.05 cm$^2$ or larger, and are subject to ohmic potential errors
under the transient conditions required to measure large $k^o$ values. With the advent of
microelectrodes, these ohmic potential errors can be greatly reduced, such that fast scan
voltammetry can yield more reliable $k^o$ values above 0.2 cm/s. In some cases reported in
the literature, the observed $k^o$ values were acknowledged to be lower limits due to
instrumental limitations (127, 130, 139). When the actual $k^o$ is 0.1 cm/s or greater,
comparisons of various conditions or electrodes are difficult unless microelectrodes are
used.

Several $k^o$ values for $\text{Fe(CN)}_6^{3/-4}$ from the literature are listed in Table 10, for
various electrode materials, pretreatments, and electrolytes. Note the wide variation in $k^o$
Table 10  $k^o$ for Fe(CN)$_6^{3/-4}$ under various conditions

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Pretreatment</th>
<th>Electrolyte</th>
<th>$k^o$/cm s$^{-1}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt</td>
<td>HNO$_3$</td>
<td>1 M KCl</td>
<td>0.02 ± 0.007</td>
<td>136</td>
</tr>
<tr>
<td>Pt</td>
<td>Flame</td>
<td>1 M KCl</td>
<td>0.22 ± 0.01</td>
<td>136</td>
</tr>
<tr>
<td>Pt</td>
<td>HNO$_3$, Flame</td>
<td>1 M KCl</td>
<td>0.23 ± 0.23</td>
<td>136</td>
</tr>
<tr>
<td>Pt</td>
<td>HClO$_4$, red'n in KCl</td>
<td>1 M KCl</td>
<td>0.24</td>
<td>135</td>
</tr>
<tr>
<td>Pt</td>
<td>HClO$_4$ only</td>
<td>1 M KCl</td>
<td>0.028</td>
<td>135</td>
</tr>
<tr>
<td>Pt</td>
<td>potential cycling</td>
<td>1 M KCl</td>
<td>0.1</td>
<td>128</td>
</tr>
<tr>
<td>Pt/CN</td>
<td>potential cycling</td>
<td>1 M KCl/0.01M NaCN</td>
<td>&gt;0.1</td>
<td>127</td>
</tr>
<tr>
<td>Pt/I</td>
<td>potential cycling</td>
<td>1 M KCl</td>
<td>&gt;0.1</td>
<td>127</td>
</tr>
<tr>
<td>Au</td>
<td>potential cycling</td>
<td>1 M KCl</td>
<td>0.1</td>
<td>139</td>
</tr>
<tr>
<td>GC</td>
<td>laser activation</td>
<td>1 M KCl</td>
<td>&gt;0.5</td>
<td>59</td>
</tr>
<tr>
<td>GC</td>
<td>fractured</td>
<td>1 M KCl</td>
<td>0.5</td>
<td>59</td>
</tr>
<tr>
<td>Pt, $r_o$=10μm</td>
<td>Case 1$^a$</td>
<td>1 M KCl</td>
<td>0.24 ± 0.04</td>
<td>this work</td>
</tr>
<tr>
<td>Pt, $r_o$=10μm</td>
<td>Case 2$^b$</td>
<td>1 M KCl/5mM CN$^-$</td>
<td>0.42 ± 0.03</td>
<td>this work</td>
</tr>
<tr>
<td>Pt, $r_o$=10μm</td>
<td>Case 3$^c$</td>
<td>1 M KCl/5mM CN$^-$</td>
<td>0.56 ± 0.07</td>
<td>this work</td>
</tr>
<tr>
<td>Pt, $r_o$=10μm</td>
<td>50 MW/cm$^2$ laser activation</td>
<td>1 M KCl/5mM CN$^-$</td>
<td>0.46</td>
<td>this work</td>
</tr>
</tbody>
</table>

a. polished in a NANOpure water/Al$_2$O$_3$ slurry, sonicated in NANOpure water. Electrolyte contained no KCN.

b. polished in a NANOpure water/Al$_2$O$_3$ slurry, sonicated in NANOpure water. Electrolyte contained 5 mM KCN.

c. polished in 10 mM KCN/Al$_2$O$_3$ slurry, sonicated in 10 mM KCN. Electrolyte contained 5 mM KCN.
on Pt for different pretreatments, with the highest $k^0$ observed on a "macro" electrode in 1 M KCl being 0.22-0.24 cm/s. In our previous work on GC electrodes, we observed $k^0$ values of >0.5 cm/s following laser activation of electrodes with areas of ca. $2 \times 10^{-3}$ cm$^2$ (59). In order to compare $k^0$ on GC with that on Pt, it is necessary to reconsider the Pt rates using fast scan rates and microelectrodes under conditions where the complications of chemisorption and electrolyte effects are removed or controlled. In addition, we sought to evaluate laser activation on Pt to compare with the dramatic effects on GC. These fairly specific objectives not only serve to clarify the suitability of Fe(CN)$_6^{3/-4}$ as a benchmark redox system, but also bear on the broader question of the surface chemistry accompanying Fe(CN)$_6^{3/-4}$ electron transfer on Pt and GC.

**EXPERIMENTAL**

A LeCroy 8400-A oscilloscope was used to record voltammograms before transfer to a personal computer with a locally written program. A Tektronix FG 501A 2 MHz function generator was triggered by the computer to output a triangular potential sweep to a three electrode potentiostat. Both the potential sweep and cell current were monitored simultaneously by the digital oscilloscope, then converted to $i$ vs $E$ curves by the computer. A low pass filter (Krohn-hite model 3200) was used to filter out high frequency noise, with the RC set according to the $n\nu RC < 4$ mV criterion (68). Electrodes with radii of 10µm, 25µm and 50µm were made by sealing the same nominal radius Pt wire (Goodfellow Metals) in type 0120 potash soda lead glass (Corning) followed by annealing. A 12.5µm radius electrode was obtained commercially from Electrosynthesis Corporation.
Either polishing/sonicating or in-situ laser activation was employed to prepare the electrode surface. In the first approach, the electrode was immersed in 18M H$_2$SO$_4$ for 30 minutes, then rinsed with NANOpure water (Sybron Barnstead, 16MΩ/cm). After that, the electrode was polished conventionally with 180 grit SiC paper (Buehler) followed by 1.0, 0.3 and 0.05 µm alpha alumina (Buehler) in a slurry with either NANOpure water or 0.01M CN$^-$ solution (as noted below) on a Buehler polishing cloth for 5 minutes in each polishing medium. Immediately after polishing, the electrode was sonicated in either NANOpure water or 0.01M CN$^-$ solution for 5 minutes in order to remove the alumina particles. For laser activation, a Nd:YAG laser (1064nm) was used as described previously (13, 59, 134). A He-Ne pilot beam coincident with the Nd:YAG beam was used to center the laser on the electrode. The Nd:YAG laser beam has a diameter of 6mm and output power densities in the range of 5-100 MW/cm$^2$ at the electrode surface. The electrochemical cell used has been described previously (13). It was constructed from Teflon and was able to accept different size electrodes. The laser beam passed through a quartz window and the solution of interest beforeimpinging on the electrode. Cyclic voltammograms were recorded four times during each trial (3 seconds between each scan) and their average was stored for subsequent data processing.

SEM results were obtained on a Hitachi S-150 scanning electron microscope at an acceleration voltage of 25 KV. Three electrodes were made and polished at the same time proceeding SEM examination. After sonicating, one electrode was laser activated with 3 laser pulses at 75 MW/cm$^2$. Another electrode was activated with 60 laser pulses at
50MW/cm² followed by three pulses of 75MW/cm². All three electrodes were gold-coated before the SEM examination.

KCl, K₄Fe(CN)₆, KI, KBr and KCN were all AR grade obtained from Mallinckrodt and were used without further purification. All solutions were made fresh daily with NANOpure water and were degassed with argon for 10 minutes before experiment. Due to the possibility to toxic HCN formation, neither KCN nor K₄Fe(CN)₆ solutions were exposed to acidic solutions or reagents.

RESULTS

Cyclic voltammograms obtained with a Pt microdisk electrode (r₀=10μm) at 600 V/s in the presence and absence of 5mM CN⁻ are compared in Figure 61. Figure 61A shows background (dashed line) and Fe(CN)₆⁻³/₄ voltammograms (solid line) with CN⁻ present, while 61C is with CN⁻ absent. Note that the background current is higher without CN⁻, with an apparent wave at ca. +0.6 V being attributable to electrode surface oxidation or Fe(CN)₆⁻³/₄ degradation. Figures 61B and 61D show background subtracted voltammograms with CN⁻ present (61B) and absent (61D). Dashed lines show simulated CV's for α = 0.5, T = 21°C, and k° = 0.60 cm/s (61B) and 0.15 cm/s (61D). Note that the agreement of theory and experiment is quite good with CN⁻ present, and that the voltammogram exhibits excess current in the absence of CN⁻ that was not subtracted as background current. Also note that the value for k° of 0.60 cm/s exceeds the previously reported record of 0.24 cm/s for Pt in 1M KCl. As will be discussed later, it is significant that the value of 0.24 cm/s was obtained under conditions conducive to Cl⁻ chemisorption.
Figure 61  CVs of Fe(CN)$_6^{3/-4}$ in 1M KCl at a Pt microdisk ($r_o=10\mu m$) electrode at 600 V/s. (A) signal (solid) and background (dashed) in the presence of 5mM KCN; (B) background corrected CV of (A) (solid) and simulated CV (dashed); (C) signal (solid) and background (dashed) without KCN; (D) background corrected CV of (C) (solid) and simulated CV (dashed). Simulation: $T = 21^\circ C$, $\alpha = 0.5$, $k^o = 0.60cm/s$ (in (B)) and 0.15cm/s (in (D)).
Figure 61 (continued)
$k^o$ values for three different pretreatments and electrolytes are listed in Table 11, for scan rates ranging from 10 to 950 V/s. In the range from 200-1000 V/s, $k^o$ shows no obvious trends, but does exhibit random error. The low values of $k^o$ observed below 200 V/s are probably due to nonplanar diffusion on the microdisk electrode. At 200 V/s, the "p" function (140), defined as $p = (n F r_o^2 v / RT D)^{1/2}$ is 33. As $v$ or $p$ decreases, nonplanar diffusion will significantly distort the CV, and the Nicholson & Shain approach to determining $k^o$ from $\Delta E_p$ will be in error (77). For this reason, all kinetic data reported here were obtained for conditions where $p$ exceeded 33. Note also that $k^o$ for case 3 in Table 11 varies only slightly with $r_o$ ranging from 10 $\mu$m to 50 $\mu$m. Since ohmic potential errors scale linearly with $r_o$, the constant $k^o$ observed with different $r_o$ implies little ohmic error.

The time course of $k^o$ for various conditions is shown in Figure 62. In the absence of added CN$, k^o$ starts at a level comparable to the highest literature values (0.21 cm/s), then decays over a 70 minute period to ca. 0.01 cm/s (curve 62D). An electrode which was polished and sonicated in CN$ solution starts higher (0.43 cm/s), but also decays to less than 0.1 after 70 minutes (curve 62C). Polishing and sonicating in CN$ plus voltammetry in 3mM CN$ yields a large $k^o$ which decays only slightly with an average for 0 to 70 minutes of 0.53 ± 0.06 cm/s (curve 62A). Finally, an electrode polished and sonicated in NANOpure water proceeding voltammetry in 3 mM CN$ and 1M KCl shows a slight increase in $k^o$ with time, and an average of 0.40 ± 0.03 cm/s for the 70 minute period (curve 62B) is obtained.
Table 11  Observed $k^a$ for Fe(CN)$_6^{3/-4}$ under various conditions on Pt microdisk electrode.

<table>
<thead>
<tr>
<th>$v$, V/s</th>
<th>$k^a$/cm s$^{-1}$, $r_o$=10$\mu$m</th>
<th>case 1</th>
<th>case 2</th>
<th>case 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.07</td>
<td></td>
<td></td>
<td>0.24</td>
</tr>
<tr>
<td>40</td>
<td>0.128</td>
<td>0.232</td>
<td>0.248</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>0.144</td>
<td>0.142</td>
<td>0.248</td>
<td></td>
</tr>
<tr>
<td>150</td>
<td>0.16</td>
<td>0.227</td>
<td>0.145</td>
<td></td>
</tr>
<tr>
<td>250</td>
<td>0.186</td>
<td>0.413</td>
<td>0.477</td>
<td></td>
</tr>
<tr>
<td>330</td>
<td>0.235</td>
<td>0.394</td>
<td>0.57</td>
<td></td>
</tr>
<tr>
<td>420</td>
<td>0.17</td>
<td>0.413</td>
<td>0.582</td>
<td></td>
</tr>
<tr>
<td>530</td>
<td>0.28</td>
<td>0.482</td>
<td>0.556</td>
<td></td>
</tr>
<tr>
<td>630</td>
<td>0.258</td>
<td>0.388</td>
<td>0.635</td>
<td></td>
</tr>
<tr>
<td>700</td>
<td>0.243</td>
<td>0.394</td>
<td>0.605</td>
<td></td>
</tr>
<tr>
<td>840</td>
<td>0.267</td>
<td>0.457</td>
<td>0.622</td>
<td></td>
</tr>
<tr>
<td>950</td>
<td>0.258</td>
<td>0.432</td>
<td>0.438</td>
<td></td>
</tr>
</tbody>
</table>

Mean for $250-950$ V/sec

- $0.24 \pm 0.04^b$
- $0.42 \pm 0.03^b$
- $0.56 \pm 0.07^b$

$r_o$ = 12.5$\mu$m, mean for $250-950$ V/s

- $0.56 \pm 0.10^b$

$r_o$ = 25$\mu$m, mean for $250-950$ V/s

- $0.53 \pm 0.08^b$

$r_o$ = 50$\mu$m, mean for $250-950$ V/s

- $0.54 \pm 0.10^b$

$^a$ As defined in Table 10.

$^b$ Standard deviation.
Figure 62  $k^0$ (determined at 600V/s) vs time after exposure of a Pt microdisk ($r_0=10\mu m$) to a 10mM Fe(CN)$_6^{3/-4}$ + 1M KCl solution under various conditions: (A) polished and sonicated in 10mM KCN, voltammetry in 5mM KCN; (B) polished and sonicated in H$_2$O, voltammetry in 5mM KCN; (C) polished and sonicated in 10mM KCN, electrolyte did not contain KCN; (D) polishing, sonication and voltammetry in the absence of CN$^-$. 

215
It is clear from Table 11 and Figure 62 that the largest and most stable $k^0$ values for $\text{Fe(CN)}_6^{3/4-}$ are obtained when CN$^-$ is present during polishing, sonication, and voltammetry. Table 12 shows the dependence of $k^0$ determined at 600 V/s on CN$^-$ concentration in the electrolyte used for voltammetry. Although 3mM yields the highest $k^0$, the random error is significant compared to the changes observed for varying [CN$^-$]. It is sufficient to say that a range of [CN$^-$] from 1-10 mM yields comparable $k^0$ values. The same polishing and sonicating procedure was also carried out with Br$^-$ and I$^-$ instead of CN$^-$, but high and stable $k^0$ values were not obtained. $k^0$ decreased with time for the Br$^-$ and I$^-$ containing electrolytes.

Based on previous experience with GC electrodes, laser activation may provide an attractive alternative to polishing for improving $k^0$ on Pt electrodes. We have shown previously that intense, short (ca. 25 MW/cm$^2$, 9 nsec) Nd:YAG laser pulses delivered to GC in-situ results in large increases in $k^0$ for a variety of redox systems, including $\text{Fe(CN)}_6^{3/4-}$ (13, 59, 134). The technique avoids sometimes tedious polishing and prevents exposure of the electrode to air. Laser activation was attempted for the $\text{Fe(CN)}_6^{3/4-}$ system on Pt in 5mM CN$^-$/1M KCl. The electrodes had been polished and exposed to lab air for several days but were not otherwise pretreated before placing in the laser activation cell. Laser activation at various power densities yielded the results shown in Figure 63. Laser activation was cumulative in this case, with three laser pulses delivered for each power density as power was increased. For power densities from 10 to 50 MW/cm$^2$, the observed $k^0$ was fairly constant with an average of 0.49 ± 0.05 cm/s. Above 50 MW/cm$^2$, $k^0$ increased significantly to 1.19 cm/s at 75MW/cm$^2$. 

Table 12  Effect of CN⁻ concentration on $k^0$ of Fe(CN)$_6^{3/-4}$ determined at 600 V/s

<table>
<thead>
<tr>
<th>Electrode Pretreatment</th>
<th>[CN⁻] in electrolyte (mM)</th>
<th>$k^0$ (cm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polished/sonicated in</td>
<td>0</td>
<td>0.24 ± 0.04</td>
</tr>
<tr>
<td>Polished/sonicated in 0</td>
<td>0.24 ± 0.04</td>
<td></td>
</tr>
<tr>
<td>Polished/sonicated in 0.24 ± 0.04</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polished/sonicated in 0.40 ± 0.03</td>
<td>0.40 ± 0.03</td>
<td></td>
</tr>
<tr>
<td>Polished/sonicated in 0.46 ± 0.05</td>
<td>0.46 ± 0.05</td>
<td></td>
</tr>
<tr>
<td>Polished/sonicated in 0.56 ± 0.07</td>
<td>0.56 ± 0.07</td>
<td></td>
</tr>
<tr>
<td>Polished/sonicated in 0.53 ± 0.08</td>
<td>0.53 ± 0.08</td>
<td></td>
</tr>
<tr>
<td>Polished/sonicated in 0.46 ± 0.09</td>
<td>0.46 ± 0.09</td>
<td></td>
</tr>
<tr>
<td>Polished/sonicated in 0.38 ± 0.08</td>
<td>0.38 ± 0.08</td>
<td></td>
</tr>
<tr>
<td>Polished/sonicated in 50 MW/cm² laser activation</td>
<td>5</td>
<td>0.57</td>
</tr>
<tr>
<td>Polished/sonicated in 60 MW/cm² laser activation</td>
<td>5</td>
<td>1.04</td>
</tr>
<tr>
<td>Polished/sonicated in 75 MW/cm² laser activation</td>
<td>5</td>
<td>1.19</td>
</tr>
<tr>
<td>Polished/sonicated in 50 MW/cm² laser activation</td>
<td>5mM Br⁻</td>
<td>0.25 a</td>
</tr>
<tr>
<td>Polished/sonicated in 50 MW/cm² laser activation</td>
<td>5mM I⁻</td>
<td>0.21 a</td>
</tr>
</tbody>
</table>

a Highest values observed after laser activation, decreased with time.
Figure 63 $k^0$ determined at 600V/s in 5mM KCN + 1M KCl following in-situ laser activation at increasing power densities. These laser pulses were delivered at each power and the activation was cumulative starting at low power.
The time course of $k^o$ following laser activation was also examined for 25, 50 and 75 MW/cm$^2$ pulses, as shown in Figure 64. In all cases, the initial electrode had been partially passivated by long exposure (> 1 day) to lab air proceeding laser activation, and exhibited an initial $k^o$ of less than 0.2 cm/s. In the presence of 5mM CN', $k^o$ was quite stable following laser activation, at least for 70 minutes. The 75 MW/cm$^2$ pulse did not result in a $k^o > 1.0$ cm/s in this case because the activation was not cumulative as in Figure 63 (see below). In the absence of CN' (curve 64D), laser activation did not result in as high a $k^o$ value, and $k^o$ decreased with time for at least 70 minutes.

SEM's of the Pt microdisk before and after laser activation are shown in Figure 65. After polishing the surface exhibits polishing scratches but is otherwise fairly smooth. Three 75 MW/cm$^2$ laser pulses induce some surface roughening but polishing scratches are still visible. Extensive activation (60 pulses at 50 MW/cm$^2$ plus 3 at 75 MW/cm$^2$) caused obvious surface roughness plus some pits and possibly fissures. Higher magnification SEM's of the surface of Figure 65C exhibit small (~ 0.1 μm) globules, apparently solidified from molten Pt. Such globules were absent on the polished surface. Electrodes treated with the same procedure yielding Figure 65C exhibited $k^o$ values of 1.21 ± 0.15 cm/s, comparable to the highest rates in Figure 63.

DISCUSSION

The first conclusion from the current results is quite practical. The $k^o$ values observed here with microdisk electrodes are significantly higher than those reported in the
Figure 64 Plot of $k^o$ versus time for a laser activated electrode following three pulses at laser powers of 50MW/cm$^2$ (curve A), 75MW/cm$^2$ (curve B) and 25MW/cm$^2$ (curve C). The analyte solution is 10mM Fe(CN)$_6^{3/4^-}$ + 5mM CN$^- + 1$M KCl. Curve D is the same as curve A without CN$^-$ present.
Figure 65  Scanning electron micrographs of polished Pt microdisk electrodes following various degrees of laser activation in 1M KCl: (A) initial; (B) after three 75MW/cm² pulses; (C) after sixty 50MW/cm² pulses and three 75MW/cm² pulses.
literature, and require fast voltammetry to determine them with any confidence. Since previous studies use relatively "large" electrodes, the observed k° values are subject to a downward bias due to ohmic potential errors. The constancy of k° with scan rate in the range of 200-1000 V/s and with electrode radius, plus the ability to measure rates of 1.2 cm/s for certain conditions support the conclusion that the k° values of ca. 0.5 cm/s are reliable, and are not just another lower limit. The results indicate that the observed k° values are not instrumentally limited.

Given the previous reports by Galus, et.al.,(127, 130) it is not surprising that CN" stabilizes k° and prevents degradation of electrode performance. Galus proposed that CN" forms a protective layer by occupying chemisorption sites, similar to I', and either CN" or I' treated surfaces yielded k° values for Fe(CN)₆³⁻⁴ above the instrumental limit of 0.1 cm/s. If this model is correct, a small solution concentration of strongly adsorbing I' or CN" will be sufficient to saturate the surface and prevent Fe(CN)₆³⁻⁴ chemisorption. This observation should be considered in light of spectroscopic data indicating formation of a Prussian-blue like film in the absence of CN". In addition, Bocarsly, et.al.,(141, 142) have demonstrated chemisorption of Fe(CN)₆³⁻⁴ onto nickel surfaces, and Wieckowski (129) noted that CN" can be bonded at both ends to yield this chemisorbed species:

\[ \text{Pt} - \text{N} \equiv \text{C} - \text{Fe(CN)}₃^ {-3} \]

All of these reports are consistent with the conclusion that excess CN" in solution can saturate the Pt surface and prevent Fe(CN)₆³⁻⁴ chemisorption. Since 3mM (or less) of free CN" is apparently enough to prevent chemisorption of 10mM Fe(CN)₆³⁻⁴, the equilibrium
constant for CN' adsorption must be significantly higher than that of Fe(CN)₆⁻³/₄. A slight
extension of this model involves events occurring after Fe(CN)₆⁻³/₄ chemisorption. It is
possible that the Fe(CN)₃ (H₂O)³ desorbs, leaving CN' behind, and then reacts with
solution Fe(CN)₆⁻³/₄ to produce Prussian blue or a related material (132, 143). This
reaction leads to a passivated film which eventually impedes electron transfer and
decreases k⁰. Although the current data do not directly test for the presence of
chemisorbed Fe(CN)₆⁻³/₄, it is clear that chemisorbed CN' prevents Fe(CN)₆⁻³/₄
decomposition. By polishing and sonicating the Pt electrode in CN' solution, the
presaturation of the surface may be particularly effective, leading to high, stable k⁰ values.
Even a partially passivated electrode exhibiting a low k⁰ can be reactivated by sonicating in
10 mM KCN.

Below 50 MW/cm², laser activation of Pt in the Fe(CN)₆⁻³/₄/CN'/KCl medium
appears straightforward, resulting in k⁰ values of comparable magnitude and stability to the
polished values. Based on a simple numerical simulation, the peak temperature excursion
for the Pt surface activated by a 50 MW/cm², 9 nsec, 1064 nm laser pulse has an upper
limit of ca. 1260°C (58). Thus the rapid surface heating of the electrode would be
expected to desorb impurities and present an initially clean surface to the solution. With
CN' present, this surface should rapidly saturate with chemisorbed CN' and a high k⁰
should result. The stability of k⁰ following laser activation is presumably attributable to the
same phenomenon which occurs when CN' is present during polishing. After numerous
pulses in the 20-50 MW/cm² range plus several at > 50 MW/cm², the observed k⁰
increases above 1.0 cm/s. SEM's of a similarly treated electrode show significant
roughness and surface damage, perhaps from melting or surface ablation. It is quite likely
that the increase in $k^0$ is a microscopic area effect, implying that the heavily activated
surface has a microscopic area roughly twice that of the initial surface. Without an
independent measure of microscopic area, it would be risky to conclude that the heavily
laser treated surface is inherently more active than the other cases. This uncertainty about
area applies to any solid electrode, so that comparisons of rate constants should be made
for surfaces of comparable roughness when possible. For this reason, our polishing
procedure was conventional with the exception of the presence of CN'.

Table 10 combines several literature values for Fe(CN)$_6^{3/-4}$ in 1 M KCl with
current results. Recognizing that instrumental limitations and surface impurities usually
result in low $k^0$ values, the entries in Table 10 represent lower limits of the true values.
Several points about Table 10 deserve special note. First, the highest $k^0$ values observed
(ignoring the roughened surface) fall in a fairly narrow range from 0.1-0.6 cm/s, even for
quite different electrode surfaces. Second, the Pt/CN' values reported here are comparable
to the highest results obtained on fractured or laser activated GC (59). Based on the
Marcus theory correlating $k^0$ to homogeneous self exchange rates, $k^0$ for Fe(CN)$_6^{3/-4}$
should be in the region of 1-10 cm/s, within an order of magnitude of 0.5cm/s (5, 130).
Third, an inner sphere electron transfer mechanism based on a CN' or K' bridge between
the surface and the Fe(CN)$_6^{3/-4}$ redox center is unlikely given the data of Table 10.
Occupation of Pt surface sites by CN' has a minor effect (a factor of 2) on the initial $k^0$,
before any degradation. If a K' or CN' bridge to the Pt surface (or Pt/Cl surface) were
important to electron transfer, one would expect that intentional CN' chemisorption
should markedly change the observed $k^\circ$. To carry this logic further with reference to Table 10, $k^\circ$ is not greatly different for Pt/Cl, Pt/CN, Pt/I, Au, GC (laser) and GC (fractured). If a K⁺ or CN⁻ bridge were involved in electron transfer to Fe(CN)$_6^{3/4}$, the effect is very insensitive to surface identity. A more likely conclusion is that the electron transfer does not depend on a bridging group, and that the effect of chemisorbed anions (other than to prevent film formation) is quite small, perhaps involving double layer modification or alteration of the distance of closest approach of the redox center. Whatever the effects of anion adsorption on a bridging process, they are very much smaller than the effects of surface cleanliness and instrumental factors. If a bridging mechanism is operative, it's mechanism would have to be compatible with a small effect of anion or electrode identity. The present results do not rule out an inner-sphere mechanism for Fe(CN)$_6^{3/4}$ electron transfer, but they do indicate an insensitivity to electrode surface composition.

CONCLUSION

The heterogeneous electron transfer rate constant, $k^\circ$, for Fe(CN)$_6^{3/4}$ was measured by fast voltammetry at Pt microdisk electrodes with radii from 10 to 50 μm. The observed $k^\circ$ was dependent on electrode pretreatment, but in many cases exceeded the previously reported maximum value of 0.24 cm/s for 1 M KCl electrolyte. When the electrode was polished with alumina in a slurry made with 10 mM KCN, and the 1M KCl also contained 3 mM KCN, $k^\circ$ was invariant with scan rate and electrode radius for the range of 200-1000 V/s and 10-50 μm, with a value of 0.55 ± 0.07 cm/s.
If KCN was absent from the electrolyte, \( k^0 \) decreased with time to below 0.10 cm/s. Laser activation of the Pt electrodes in-situ produced reproducibly high \( k^0 \) values of ca. 0.5 cm/s which varied slightly with laser power density up to 75 MW/cm\(^2\). Above this level \( k^0 \) increased up to ca. 1.2 cm/s, but this increase is attributed to a laser induced increase in microscopic surface area. The observations support a mechanism for electrode passivation based on \( \text{Fe(CN)}_6^{3/-4} \) decomposition to a Prussian blue like film. This process can be prevented by initial saturation of the Pt surface with CN\(^-\), resulting in a high, stable \( k^0 \).
The research described in this appendix results from a collaboration effort with the electronic and device research group (MTL-11) at Los Alamos National Laboratory and Stonehart Associates Inc., Madison, CT. Original EXAFS data were obtained in March of 1992, but data analyses were performed during the period we investigated the PEM fuel cell applications of the Pt-DGC materials, which is present in Chapter III.

INTRODUCTION

Highly dispersed, carbon-supported platinum catalysts (Pt/C) are technologically important materials due to their widespread use in various types of fuel cell electrodes (31, 34, 145). It is well known that many of their catalytic properties (i.e., specific activity, sintering) relate to the extent of metal dispersion. One important factor in determining the degree of dispersion is the interaction between the Pt atoms and the carbon support (146-148). For example, the role of the carbon support was identified as a key component in improving the mass transport properties and preventing the agglomeration of platinum particles (148-150).

227
Classical methods used to examine bulk Pt electrode surfaces include ellipsometry (151), UV-Vis reflectance (152) and IR spectroscopy (153). These techniques provide information about the surface adsorbed species and their energetics but typically require special preparation of the electrode surface (i.e., use single crystals). Therefore, they are not suitable for studying complex systems such as Pt/C fuel cell electrodes. In-situ x-ray diffraction (XRD) has been used (154, 155) to investigate the formation of amorphous platinum oxide, and a modification to the Pt lattice structure was observed. However, it is difficult to obtain detailed information regarding short-range order such as surface modifications on small clusters with XRD. These properties are more easily studied using x-ray absorption fine structure (XAFS) spectroscopy.

XAFS is an element-specific technique that directly measures the local structure around any atom. The oscillatory structure observed from 30 to 40 eV up to 1000eV past the absorption edge is known as extended x-ray absorption fine structure (EXAFS) and contains information on the numbers and types of near-neighbors, bond lengths, and local disorder. The structure appearing ~20 ev above and below the adsorption edge is known as x-ray absorption near edge structure (XANES). Much of the XANES arises from bound state electronic transitions and as a consequence gives information about the orbital occupancy at the valence level (e.g., oxidation state). Although the information content of XAFS is similar to crystallography, XAFS does not require long-range order. With the development of intense synchrotron radiation sources, XAFS has become the technique of choice for local structure determination in non-crystalline systems, especially in the field of dispersed metal catalyst characterization.
EXAFS has been widely used to study dispersed catalysts such as Pt/Al$_2$O$_3$ (95, 96, 156, 157), Pt/SiO$_2$ (97, 158), Pt/Zeolite (159, 160), and Pt/C (161-163). Along with EXAFS, there have been numerous XANES studies of the Pt L absorption edges of these materials (164-166). Dexpert et al. (96, 167), observed that the Pt particle growth was related to the structure of the Al$_2$O$_3$ support. At the early stage of reduction, small and unstable clusters (2-3 Pt atoms) were linked to the support and Pt-Pt bond lengths were larger than those in the metallic state. Metallic clusters were formed at longer reduction time. Lytle et al, (97) studied Pt genesis on SiO$_2$ and found that Pt cluster formation was correlated to Pt-O bond breakage and also showed temperature dependence. Maire and coworkers (168) studied the catalytic activity of Pt(PPh$_3$)$_3$ on alumina. They observed that the as-prepared material showed no evidence of cluster formation, and that it was totally inactive. After reduction under hydrogen flow at 300°C, Pt clusters were formed and the material became active.

Although there have been many in-situ EXAFS studies on supported Pt catalysts as discussed above, relatively few have been reported on Pt/C catalysts. In an earlier report, we followed the structural evolution for a series of Pt/C catalysts as they were treated from their as prepared states with H$_2$ or O$_2$ (162). These catalysts generally underwent transformations from nonmetallic molecular complexes in the as prepared forms to dense metallic particles after being treated with H$_2$ or O$_2$. In the current report, we present results of an in-situ EXAFS study of dispersed Pt/C catalysts on different carbon supports as a function of successive gas phase H$_2$ and O$_2$ treatments. The goal was to investigate the effects that structural modifications to the support have on the structure
and reactivity of Pt clusters. The results show that variations in the structure of the carbon support are significant in determining the overall behavior and stability of Pt clusters.

EXPERIMENTAL

The carbon-supported Pt catalysts were obtained from Stonehart Associates, Inc. (Madison, CT). They were prepared by reducing chloroplatinic acid ($\text{H}_2\text{PtCl}_6$) with sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$) using a proprietary process (U.S. Patent 4,956,331). The relative slowness of this process produces dispersed colloidal platinum that is adsorbed onto the carbon support. Subsequent heat treatment at 200°C in reforming gas (10% hydrogen in nitrogen) was used to reduce the non-stoichiometric platinum colloid and activate the catalyst. These Pt/C catalysts were purposely made for polymer electrolyte membrane (PEM) fuel cells. Unlike phosphoric acid fuel cells (PAFC) where the operating temperature is high (e.g., >200°C) and sulfur in the catalyst can be self-cleaned by forming $\text{H}_2\text{S}$ gas, typical PEM fuel cells operate at lower temperatures around 80°C. At this temperature, S in the catalyst can not be readily removed. Instead, it poisons the catalyst by strongly adsorbing onto Pt surface and blocking the active sites. It is also known that S intercalates into the carbon structure. As a result, the Pt/C product (containing $\text{H}_2\text{Pt(S}_2\text{O}_3)_2$) was subjected to extended effort to eliminate sulfur. All samples were analyzed by ICP for their sulfur content, and less than 0.1ppm S was found in the as received samples. Table 13 summarize the composition and selected physical properties four Pt/C catalysts.
Table 13  Summary of the four carbon supported fuel cell catalysts.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pt % wt.</th>
<th>Pt Cryst. Dia.</th>
<th>Carbon Support</th>
<th>Carbon BET</th>
<th>C_d/2</th>
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<td>10C20</td>
<td>17.8</td>
<td>7-12 Å</td>
<td>Consel Carbon</td>
<td>200 m²/g</td>
<td>0.349</td>
</tr>
<tr>
<td>10BH20</td>
<td>19.0</td>
<td>10</td>
<td>Black Pearls</td>
<td>230</td>
<td>0.337</td>
</tr>
<tr>
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<td>18.0</td>
<td>15-20</td>
<td>Acetylene Black</td>
<td>60</td>
<td>0.351</td>
</tr>
<tr>
<td>10G25</td>
<td>27.9</td>
<td>20-25</td>
<td>Furnace Black</td>
<td>100</td>
<td>0.349</td>
</tr>
</tbody>
</table>
The as-received Pt/C catalysts were pressed into pellets of appropriate concentration in order to give and absorption jump of ~1 at the Pt L\textsubscript{3} edge. Pt L\textsubscript{3} XAFS spectra were measured in transmission mode on beam line 4-1 at the Stanford Synchrotron Radiation Laboratory (SSRL). The Si [220] monochromator crystals were detuned 50% with respect to the crystal orientation (θ) to reduce the beam harmonic content. All spectra were collected at 80K using a open cycle liquid nitrogen cryostat. After measuring the as-received (AR) materials, in-situ reduction was accomplished by heating the samples at 100°C in the presence of 0.08 atm. H\textsubscript{2} for 15 minutes. Liquid nitrogen was then refilled and the system was allowed to equilibrate to 80K before XAFS measurements of the reduced samples (RED-1) were taken. For in-situ oxidation, the samples were heated to 100°C in air for 15 minutes, then cooled and spectra were taken at 80K (OX-1). The reduction and oxidation were each performed a second time at 125°C for 15 minutes (RED-2 and OX-2, respectively). Three XAFS scans were collected and averaged at each stage of the treatments.

XAFS data reduction and data analysis were done using standardized procedures (87). The ionization threshold for Pt L\textsubscript{3} edge was defined as 11580 eV, and the first inflection point in the adsorption of the metal foil was defined as 11572.2 eV for calibration. The data were normalized by setting the edge jump equal to unity at the ionization threshold. A 4 region polynomial spline function was used to fit the EXAFS region and extract the raw EXAFS data. Fourier-transform of the k\textsuperscript{2}-weighted data was calculated from k=2.5-15.5 Å\textsuperscript{-1} and subsequent back-transform was done from R= 1-3.5 Å using Gaussian window functions of 0.5 Å\textsuperscript{-1} and 0.05 Å, respectively. Nonlinear least-
square curve fits were performed on the filtered EXAFS data over the range of $k=3.0-15\text{Å}^{-1}$ using theoretical phase and amplitude functions derived from the program FEFF (169).

RESULTS

Figure 66 shows the $k^3$-weighted EXAFS spectra for sample 10K20 as a representative data set together with the reference compounds Pt metal and PtO$_2$. On Pt metal, the amplitude of the EXAFS increases at high $k$, while on PtO$_2$ the oscillatory pattern extended throughout the whole $k$ region at about the same amplitude. In contrast, there are essentially no features observed at $k>10\text{ Å}^{-1}$ on the AR sample. After the first reduction, structure appears at high $k$ which, at this level of analysis, indicates a transformation to the metallic state. After the first oxidation, the overall amplitude is diminished, consistent with a loss of some metallic character. The second reduction dramatically increases the amplitude again, while subsequent oxidation decreases the amplitude.

Figure 67 shows the corresponding Fourier transform (FT) moduli of the spectra in Figure 66. The peaks in the FT appear at lower $R$ value than the true bond distances due to the EXAFS phase shift ($0.2-0.5\text{Å}$). On PtO$_2$ there is one major peak at $1.6\text{ Å}$ which corresponds to Pt-O bonds at ~2.0 Å. The strongest peak on Pt metal is at $2.6\text{ Å}$ which reflects the well-ordered first shell of 12 first nearest neighbors at $2.77\text{ Å}$. The side lobe at $2.2\text{ Å}$ results from the complex amplitude envelope of the Pt backscatterer and does not correspond to a shorter Pt-Pt bond. The peaks at higher $R$ belong to shells of more distant
Figure 66 Raw $k^3$-weighted Pt EXAFS of Pt metal (top), PtO$_2$, and catalyst sample 10K20 after various treatments: AR = as received; RED-1 = first reduction; OX-1 = first oxidation; RED-2 = second reduction; OX-2 = second oxidation.
Figure 67  EXAFS Fourier Transform moduli of Pt metal (top), PtO$_2$, and catalyst sample 10K20 after various treatments: AR = as received; RED-1 = first reduction; OX-1 = first oxidation; RED-2 = second reduction; OX-2 = second oxidation
neighbors. The behavior of the FT moduli demonstrate more clearly the transformation seen in Figure 66. The AR material shows no evidence of the metallic state. The successive treatments show that a metallic phase is formed on reduction and somewhat diminished after oxidation.

In Figure 68, the Pt L₃ absorption edges for 10K20, Pt metal, and PtO₂ are shown. The Pt L₃ absorption peak at ~11580 eV is assigned to the allowed 2p₃/₂ → 5d transition. Its magnitude is known to increase with the electron deficiency of the 5d orbitals (164, 170). Thus, the peak height for PtO₂ is much greater than that of Pt metal. The amplitudes from 10K20 fall between those of PtO₂ and Pt, with the as-received being the most oxidized and RED-2 being the most reduced. The peak height of AR is lower than that of PtO₂, indicating that this sample is only partially oxidized relative to PtO₂. Consistent with the behavior seen in Figure 66 and Figure 67, each reduction brings the Pt state to a level more closely resembling the metal and subsequent oxidation reoxidizes only a fraction of the Pt. Reduction not only decreases the peak height but shifts the peak to lower energy. Since the peak height on RED-2 is still above Pt metal and it appears at higher energy position, it suggests that the Pt clusters formed by reduction still contain a residual amount of oxide.

Figures 69, 70, and 71 show the FT moduli of the samples 10C20, 10BH20, and 10G25 at the different stages of treatment. Two peaks, at R~1.6Å (Pt-O) and 2.0Å (Pt-Cl), can be seen on all AR samples. Their amplitudes decrease after the gas phase treatments and eventually become indistinguishable in the FT moduli. At the same time, a peak at R~2.6Å (Pt-Pt) appears and grows with successive reduction. There are some
Figure 68  Pt L₃ absorption edges of Pt metal (bottom), PtO₂ (top), and catalyst sample 10K20 after various treatments: AR = as received; RED-1 = first reduction; OX-1 = first oxidation, RED-2 = second reduction, OX-2 = second oxidation. From top to bottom, curves are for: PtO₂, AR, OX-1, RED-1, OX-2, RED-2 and Pt metal.
Figure 69 EXAFS Fourier Transform moduli of catalyst sample 10C20 after various treatments: AR = as received; RED-1 = first reduction; OX-1 = first oxidation; RED-2 = second reduction; OX-2 = second oxidation
Figure 70  EXAFS Fourier Transform moduli of catalyst sample 10BH20 after various treatments: AR = as received; RED-1 = first reduction; OX-1 = first oxidation; RED-2 = second reduction; OX-2 = second oxidation
Figure 71  EXAFS Fourier Transform moduli of catalyst sample 10G25 after various treatments: AR = as received; RED-1 = first reduction; OX-1 = first oxidation; RED-2 = second reduction; OX-2 = second oxidation
important differences among the FTs of the 4 samples. For example, no Pt-Pt peak is
detectable on as received 10C20, 10K20 and 10BH20 but a small Pt-Pt peak is found on
10G25. For RED-1, the Pt-Pt peak amplitude is 3.0, 7.4, 13.1 and 56.5 on 10C20,
10BH20, 10K20 and 10G25, respectively. Subsequent oxidation reduces the Pt-Pt peak
amplitude on 10C20, 10BH20 and 10K20 but induces a minor change on 10G25. When
subjected to the second reduction, the Pt-Pt peaks are significantly increased for 10C20,
10BH20 and 10K20, but again little change is observed on 10G25. Finally, at OX-2, the
peak intensities decline noticeably on 10C20, 10BH20 and 10K20 and only slightly on
10G25.

The results of the best least square fits are summarized in Table 14. Determination
of the types of atoms present in the neighboring shells was made on the basis of phase
shifts and bond lengths for analogous compounds. For all samples, the following
parameters were fixed for the oxygen, chlorine, and platinum shells, respectively:
$\Delta E^0=0.5, -1.5$ and $2.7 \text{ eV}$, $\sigma^2=0.006, 0.004$ and $0.005$. Bond distances and coordination
numbers were allowed to float and their results are shown in Table 14. The bond distances
for each sample at all stages of treatment are consistent, averaging to $1.98\pm0.02 \text{ Å}$ for
Pt-O, $2.31\pm0.02 \text{ Å}$ for Pt-Cl, and $2.75\pm0.02\text{Å}$ for Pt-Pt bonds.

In Figure 72, the Fourier filtered experimental data on sample 10K20 is shown
along with the corresponding fit from $k=3-15\text{Å}^{-1}$. The solid lines are the experimental data
and the dashed lines are the best least square fits. Note that the as received spectrum is
well fit with only O and Cl shells (Table 14), confirming that no Pt-Pt bonding exists in the
AR sample. The as received material resembles a simple coordination complex rather than
Figure 72  EXAFS curve fits for catalyst sample 10K20 after various treatments: AR = as received; RED-1 = first reduction; OX-1 = first oxidation; RED-2 = second reduction; OX-2 = second oxidation
Figure 73  EXAFS curve fits for catalyst sample 10K20 after various treatments:
AR = as received; RED-1 = first reduction; OX-1 = first oxidation;
RED-2 = second reduction; OX-2 = second oxidation
Table 14  Curve fitting results for 3-shell fits to Fourier-filtered EXAFS data of dispersed Pt catalyst

<table>
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<tr>
<th></th>
<th>Pt-O</th>
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<th>Pt-Cl</th>
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<th>Pt-Pt</th>
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<td>r(Å)</td>
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<td>r(Å)</td>
<td>N_Cl</td>
<td>r(Å)</td>
<td>N_Pt</td>
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<tr>
<td>AR</td>
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<td>2.74</td>
<td>10</td>
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<tr>
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<tr>
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<td>—</td>
<td>2.763</td>
<td>10.1</td>
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</table>
a dense metallic cluster. Figure 73 shows the quality of the fits in Figure 72 after Fourier transforming into R space. Solid lines are from the experimental data and dashed lines are from the curve-fit data.

DISCUSSION

The Pt structural evolution on the four Pt/C fuel cell catalysts follow a general trend. That is, negligible metallic Pt clusters are detected in the as received samples. When reduced with $H_2$, Pt clusters are formed and they grow with further reduction. Oxidation, on the other hand, loses some of the metallic character by forming surface oxide. This is evidenced by an increased Pt-Pt peak height in the FT moduli after each reduction and a decreased Pt-Pt peak height after each oxidation (Figure 67 and Figures 69-71). The regeneration of surface oxide after oxidation can also be seen from Figure 68 where the peak height on the oxidized sample is higher than on reduced sample. However, due to the difference in the carbon support, the extent of Pt cluster formation and the breakage of Pt-O and Pt-Cl bonds behave differently between samples.

In the as received forms, only Pt-O and Pt-Cl bonding is detected for samples 10K20, 10C20, and 10BH20. However, on 10G25, Pt-Pt bonding is also found. The presence of Pt-Cl is a result of the incomplete reduction of the $H_2PtCl_6$ precursor. Curve-fits confirm the phase-shift corrected bond length is 2.31Å, where Pt-Cl bond distance on $H_2PtCl_6 \cdot 6H_2O$ was found to be 2.32Å (97, 162). The observation of metallic Pt in the AR form of 10G25 may be a result of weaker interaction with the furnace black support and/or the higher Pt loading used in this catalyst. Curve fits found $N_{pt}=1.5$ at $R=2.75$ Å,
in contrast to the long bond length on Pt clusters reported by others (96, 167). The lack of more distant shells in the FTs indicates that these particles are relatively small (5-10 Å diameter) at this stage.

Differences in the extent of cluster formation and the metal-substrate interaction become more apparent after first reduction. On 10G25, the Pt-Pt peak increases most dramatically (Figure 71). The Pt-O and Pt-Cl contribution disappear and the FT modulus closely resembles that of Pt metal with the exception that the peak height at R=2.75Å is smaller than that found on Pt metal. Curve fit gives NPt=10, which corresponds to Pt cluster size of about 30Å (167). Subsequent treatment on 10G25 only slightly change the FT modulus, and the Pt-O and Pt-Cl bonds remain non-detectable. The behavior of the other three samples is different from that observed for 10G25. Evidence for metallic Pt clusters formation is seen on all, but the process occurs more extensively following the trend 10K20>10BH20>10C20, where NPt=4.3, 2.4 and 0.9, respectively. While NCl is slightly reduced in each sample, Pt-O becomes non-detectable on 10K20, and NO decreases from 2.2 to 1.3 for sample 10BH20 and from 2.2 to 1.7 for sample 10C20. This suggests that it is easier to reduce Pt-O bonds than Pt-Cl bonds in these catalyst. The extent to which Pt clusters are formed correlates well with the removal of Pt-O bonds (i.e., O loss follows in the order 10K20>10BH20>10C20).

Subsequent oxidation increases NO and decreases NPt which are consistent with a transformation of Pt-Pt bonds to Pt-O. Evidence for the increased oxygen coordination can also be seen on Figure 68. The oxidized form has a higher peak height than the corresponding reduced form. Using NO as a indication of cluster reactivity, the samples are
more readily reacted with O according to the trend \(10K20 > 10BH20 > 10C20\). However, 10G25 remained essentially inert to the treatment. It must be noted, however, that the results become less quantitative at this point because of the coordination number averaging which is dependent on cluster size. For example, smaller clusters have a larger fraction of surface atoms and will show, on average, a larger change in \(N_O\) than will larger clusters for a monolayer of surface oxide formation.

Upon second reduction, cluster formation is more extensive than after the first reduction, evidenced by the increases in FT peak heights and in \(N_p\). In contrast to the first, the second reduction also introduces peaks that are associated with more distant Pt shells. Except on 10C20 where \(N_{Cl}\) remains detectable, no O or Cl is found on any other samples at this stage. Evidence for metallic Pt clusters is seen on all, but the extent of cluster formation now follows the trend \(10BH20 > 10K20 > 10C20\), where \(N_{Pt} = 12.4, 8.7\) and 5.9, respectively. The second oxidation has nearly the same effect as the first with the total metallic character diminishing for each sample. Monitoring \(N_O\) and \(N_{Pt}\), the reactivity of the clusters follows the trend \(10C20 > 10K20 > 10BH20\). Again, 10G25 was unreactive in each second stage treatment.

There are several different patterns which are present in these data. In the first reduction, the sample reactivities follow in order \(10G25 > 10K20 > 10BH20 > 10C20\) (this order is reversed for the first oxidation). This matches well with the starting crystal diameters shown in Table 13. Although the as-received clusters are not metallic, their initial sizes dictate the observed reactivity at the outset. At this stage in the treatments, sample 10G25 deviates from the rest by remaining inert. This is most likely caused by the
lack of surface sensitivity for large particle sizes that prevail due to the higher Pt loading used on this sample. The only alternative as discussed earlier would be that the furnace black has unusual ability to stabilize the clusters and render them inert. In the second reduction, the reactivities follow $10BH20>10K20>10C20$ (order is reversed for the second oxidation). This order is similar to the first except that $10BH20$ and $10K20$ are now switched. Since we are now several treatments away from the starting materials, the trend from the second stage treatments is probably more representative of the support influence.

Thus it appears that Consel carbon is the most interacting support in terms of its ability to maintain small clusters that continue to readily oxidize or reduce. The furnace black support is the least interacting and particles grow more readily and to larger sizes. The interaction from acetylene black and black pearls apparently falls in the middle. On furnace black, the BET area is low at $100m^2/g$. It can be expected that catalyst dispersion might not be as high on this support than on Consel carbon or black pearls whose BET area is over $200m^2/g$. This possibly explains why larger clusters were present on the as received 10G25 formed. It is interesting to note that the BET area on the proprietary Consel carbon is close to that of black pearls at $200m^2/g$. This Consel carbon is made from an acetylene black precursor but has undergone a surface graphitization and pore opening by steam treatment. The surface functional groups could be expected to be different from other conventional carbon materials.

The catalyst structural genesis observed by in-situ EXAFS could have important implication for their fuel cell applications. A basic requirement for a good fuel cell catalyst
is that it should have high reactivity and be able to maintain such reactivity over a prolonged period of time. This is often achieved by using a highly dispersed catalyst with a maximum active surface area which does not suffer from particle agglomeration (sintering). It is possible to synthesize a Pt/C catalyst that has nanoscale Pt clusters and exhibits high catalytic activity (86). But more often, either the Pt particles are too large and catalyst becomes inefficient, or the small clusters aggregate to form larger particles during cell operation and the catalyst loses its specific activity. For example, 10G25 (with furnace black support) forms large Pt clusters (>30Å), and the catalyst utilization is relatively inefficient. Sample 10C20 (with Consel carbon support) forms small (7-12Å) clusters, and these clusters tend to remain small and are not significantly affected by the treatments. A different condition is found for 10BH20 and 10K20 where particles continue to grow and reach larger sizes. The best case among the four seems to be on 10C20. Catalysts with such properties might be well suited for fuel cell application.

CONCLUSION

Four Pt/C fuel cell catalysts with different carbon supports were studied by in-situ EXAFS. Metallic Pt clusters were formed after gas phase reduction with H₂. Subsequent oxidation loses some of the cluster's metallic character. The structural genesis is related to the carbon support. It is possible that some of these changes are due to the interactions with specific surface functional groups. The catalyst-support interaction is the strongest on Consel carbon and the least on furnace black, with the interaction of black pearls and acetylene black falling in between. Clusters grow larger and more readily on black pearls
and furnace black supports (weak interaction). In contrast, clusters remain small on Consel carbon support (strong interaction). The structural information provides important insight to preparing fuel cell catalysts, where the particle sizes should be small and the active Pt surface area should be maintained (no sintering).
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252


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