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DEGRADATION MECHANISMS OF CARBON-BASED
ELECTROCATALYST SUPPORT MATERIALS AND
DEVELOPMENT OF AN ADVANCED SUPPORT BASED ON
ELECTRICALLY CONDUCTING DIAMOND

presented by

ANNE ELIZABETH FISCHER

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of the requirements for the

Ph.D. degree in Chemistry


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DEGRADATION MECHANISMS OF CARBON-BASED ELECTROCATALYST
SUPPORT MATERIALS AND DEVELOPMENT OF AN ADVANCED SUPPORT
BASED ON ELECTRICALLY CONDUCTING DIAMOND

By

Anne Elizabeth Fischer

A DISSERTATION

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

2005

ABSTRACT

DEGRADATION MECHANISMS OF CARBON-BASED ELECTROCATALYST SUPPORT MATERIALS AND DEVELOPMENT OF AN ADVANCED SUPPORT BASED ON ELECTRICALLY CONDUCTING DIAMOND

By

Anne Elizabeth Fischer

In this dissertation, the degradation mechanisms of sp^2 -bonded carbon electrocatalyst supports were studied under potential and temperature conditions relevant to the polymer electrolyte membrane fuel cell (PEMFC). In addition, an alternative support was fabricated in two forms: electrically conducting diamond powder and paper to overcome current material stability issues in the PEMFC.

Two structurally well-characterized sp^2 -bonded carbon powders, graphite (structurally well-ordered) and glassy carbon (GC, structurally disordered) were studied under potentiostatic polarization from 1.0 to 1.6 V vs. Ag/AgCl at 25, 50, and 80 °C. Characterization of the surface oxidation and microstructural changes (i.e., increase in the exposed edge plane density) provided evidence for the so-called order/disorder mechanism where structurally disordered carbons corrode more severely because of oxidation and gasification of the exposed edge plane. Microstructural changes for graphite were heterogeneously distributed across the electrode surface. This is indicative of a nucleation and growth process, where disordered regions and defects serve as active sites for electrochemical corrosion, while other, more structurally ordered regions do not corrode. Preliminary results for a high-surface-area carbon black, Vulcan XC-72, are presented that show changes in the surface oxide content and also discuss the effect of polarization potential on Pt activity.

The physical and electrochemical properties of two commercial boron-doped diamond thin-film electrodes were compared with microcrystalline and nanocrystalline boron-doped diamond thin film deposited in our laboratory. The electrochemical response for $\text{Fe}(\text{CN})_6^{3-/4-}$, $\text{Ru}(\text{NH}_3)_6^{3+/2+}$, $\text{IrCl}_6^{2-/3-}$, 4-methylcatechol, and $\text{Fe}^{3+/2+}$ was quite reproducible from electrode type-to-type and from film-to-film for a given type. ΔE_p , i_p^{ox} , and i_p^{red} values for $\text{Fe}(\text{CN})_6^{3-/4-}$, $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ on all electrodes were relatively unaffected by pH.

Electrically conducting diamond powder was prepared by coating insulating diamond powder (8-12 μm diam) with a thin boron-doped diamond layer using microwave-assisted chemical vapor deposition (CVD). Increases in the electrical conductivity after growth confirmed that a conductive diamond overlayer formed. The charge passed during anodic polarization at 1.6 V vs. Ag/AgCl and 25 °C for 1 h was largest for GC powder (0.88 C/cm²) and smallest for conductive diamond powder (0.18 C/cm²), illustrating the dimensional stability of diamond powder compared to sp^2 -bonded carbon powder.

Boron-doped nanocrystalline diamond (BND) was coated on Toray[®] carbon paper (TCP) via microwave-assisted CVD. Pt nanoparticles were deposited on TCP and BND using a pulsed galvanostatic method. The stability of the bare TCP and BND substrates and the composite Pt/TCP and Pt/BND electrodes were studied using potentiostatic polarization in 0.1 M HClO_4 . The BND electrode exhibited superior morphological and microstructural stability over TCP at 1.6 V vs. Ag/AgCl. Evidence was found for dissolution and redeposition of Pt on composite electrodes, particularly for Pt/TCP.

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In memory of
Jennifer Ruth White,
friend and inspiration.
November 5, 1977 – February 6, 2001

ACKNOWLEDGEMENTS

So many people have touched my life throughout my time and Michigan State University. I would first and foremost like to thank my advisor, Dr. Greg Swain, for his guidance, support, and encouragement over the last few years. Thanks to my committee members, Dr. Gary Blanchard, Dr. Jim McCusker, and Dr. Michael Mackay, for your helpful comments about my research. I would also like to thank Dr. Simon Garrett and Dr. Kathryn Severin for their support and mentoring.

Where would I be without the fun, support, friendships, and frustrations that come with being a Swain group member? Thanks to all along the way who helped shape the scientist and the person that I have become. As Luther would say, 'thank-ye' (alphabetically, of course) to Audrey, Doug, Elizabeth, Gloria, Grace, Hua, the Jasons, Jesse, Jinwoo, Luther, Martin, Show, Veronika, Yang, and Yingrui.

I have been fortunate to have a wonderful group of friends at Michigan State, without whom, I am not sure I would have survived. Words alone cannot express my gratefulness to have friends like Amber, Audrey, Bennett, Carl, Elizabeth, Heather, Mark, Melissa (a.k.a., Melita and Phyllis), and Prerna. You guys are the best.

Not to be forgotten are the non-chemistry (a.k.a. sane) people in my life that saw me through the process. Allison, Katie, and Nick, your love and support were invaluable. You helped me keep a healthy perspective (sometimes, at least) about what life is really all about. Thanks so much. I would also like to extend a very special thanks to Katie for all of her support during these last 5 years. I truly could not have done this without you.

Finally, and most importantly, I would like to say thank you to my parents. I would not be where I am today without your encouragement, your love, and your support. Thank you for always being there for me.

-Anne

TABLE OF CONTENTS

List of Tables	x
List of Figures	xiii
<u>CHAPTER 1 – INTRODUCTION</u>	1
1.1 Background	1
1.2 Fuel Cell Materials and Operation	4
1.3 Carbon Corrosion in Fuel Cells	8
1.4 sp^2 -Bonded Carbon Structure	12
1.5 Boron-Doped Diamond	17
1.6 Chemical Vapor Deposition (CVD) of Diamond	20
1.6.1 Microcrystalline Diamond Growth Mechanism	22
1.6.2 Nanocrystalline Diamond Growth Mechanism	24
1.7 Research Goals and Objectives	26
1.8 Dissertation Outline	30
1.9 References	32
<u>CHAPTER 2 – EXPERIMENTAL METHODS</u>	37
2.1 Diamond Thin Film Growth	37
2.2 Material Characterization	42
2.2.1 Scanning Electron Microscopy (SEM)	42
2.2.2 X-Ray Diffraction Spectroscopy (XRD)	42
2.2.3 Raman Spectroscopy	42
2.2.4 Electrical Resistance	43
2.3 Electrochemical Characterization	44
2.3.1 Electrode Preparation and Experimental Setup	45
2.3.1.1 Diamond Thin-Film Electrodes on Si	45
2.3.1.2 Carbon Powder Electrodes	46
2.3.1.3 Carbon Paper Electrodes	48
2.3.2 Electrochemical Kinetics	49
2.3.3 Polarization Studies	50
2.3.4 Pt Electrodeposition	51
2.4 Reagents	51
2.5 References	53
<u>CHAPTER 3 – STUDY OF THE DEGRADATION MECHANISMS OF SP^2-BONDED CARBON POWDERS DURING ELECTROCHEMICAL POLARIZATION</u>	54
Abstract	54
3.1 Introduction	56
3.2 Results and Discussion	60
3.2.1 Anodic Polarization of Graphite and Glassy Carbon (GC) Powders	60
3.2.2 Evaluation of the Extent of Surface Oxide in Terms of Electroactive Oxide Formation	66

3.2.3 Evaluation of Microstructural Changes	69
3.3 Anodic Polarization of Carbon Black, Vulcan XC-72	75
3.4 Conclusions	84
3.5 References	85
<u>CHAPTER 4 – THE ELECTROCHEMICAL PERFORMANCE OF DIAMOND THIN-FILM ELECTRODES FROM DIFFERENT COMMERCIAL SOURCES</u>	88
Abstract	88
4.1 Introduction	90
4.2 Results and Discussion	91
4.2.1 Material Characterization	91
4.2.2 Electrochemical Characterization	96
4.2.3 pH Effects on Voltammetric Response	107
4.3 Conclusions	109
4.4 References	111
<u>CHAPTER 5 – PREPARATION AND CHARACTERIZATION OF BORON-DOPED DIAMOND POWDER: A POSSIBLE DIMENSIONALLY STABLE ELECTROCATALYST SUPPORT MATERIAL</u>	115
Abstract	115
5.1 Introduction	117
5.2 Results and Discussion	119
5.2.1 Material Characterization and Electrical Measurements	119
5.2.2 Electrochemical Characterization	127
5.2.3 Morphological and Microstructural Stability	137
5.3 Conclusions	140
5.4 References	142
<u>CHAPTER 6 – PREPARATION AND CHARACTERIZATION OF BORON-DOPED DIAMOND PAPER WITH PT NANOPARTICLES</u>	144
Abstract	144
6.1 Introduction	146
6.2 Results and Discussion	149
6.2.1 Nanocrystalline Diamond Deposition on Carbon Paper	149
6.2.1.1 Morphology and Microstructure	149
6.2.1.2 Electrochemical Characterization	153
6.2.2 Electrodeposition of Pt on TCP and BND	155
6.2.3 Evaluation of Pt/TCP and Pt/BND Stability	165
6.3 Conclusions	174
6.4 References	176
<u>CHAPTER 7 – FUTURE RESEARCH DIRECTIONS</u>	178

LIST OF TABLES

Table 1.1	Crystallite width (L_a) and interlayer spacing (d_{002}) for some common sp^2 -bonded carbons.	16
Table 2.1	Growth conditions for microcrystalline and nanocrystalline boron-doped diamond thin film deposited on Si.	39
Table 2.2	Film thickness, resistivity, carrier concentration, and carrier mobility for typical microcrystalline and nanocrystalline boron-doped diamond thin film.	39
Table 2.3	Growth conditions for coating insulating diamond powder with a conducting diamond overlayer.	40
Table 2.4	Growth conditions for coating carbon paper with boron-doped nanocrystalline diamond.	41
Table 3.1	Charge passed during the 1 h potentiostatic polarization of graphite and GC powders at 1.0 and 1.6 V vs. Ag/AgCl (25 °C).	64
Table 3.2	Charge passed (mC/cm^2) during the 1 h potentiostatic polarization of graphite powder from 1.0 to 1.6 V vs. Ag/AgCl at 25, 50, and 80 °C.	65
Table 3.3	Charge passed (mC/cm^2) during the 1 h potentiostatic polarization of GC powder from 1.0 to 1.6 V vs. Ag/AgCl at 25, 50, and 80 °C.	66
Table 3.4	Change in current density (ΔJ , $\mu\text{A}/\text{cm}^2$) for surface oxide reduction before and after polarization on graphite powder as a function of the polarization potential and temperature in 0.1 M HClO_4 for 1 h.	69
Table 3.5	Change in current density (ΔJ , $\mu\text{A}/\text{cm}^2$) for surface oxide reduction before and after polarization on GC powder as a function of the polarization potential and temperature in 0.1 M HClO_4 for 1 h.	69
Table 3.6	Ratio ($n=6$) of the D/E_{2g} Raman modes for graphite powder electrodes at different polarization potentials and temperatures.	73
Table 3.7	Ratio ($n=6$) of the D/E_{2g} Raman modes for GC powder electrodes at different polarization potentials and temperatures.	74
Table 3.8	Percent Pt lost ($\%_{\text{Lost}}$) as a result of potentiostatic polarization of Pt-loaded (20 wt. %) Vulcan XC-72 in 0.1 M HClO_4 at different polarization potentials and temperatures.	83

Table 4.1	Cyclic voltammetric and heterogeneous electron-transfer rate constant data for five redox systems at MSUMicro, Condias, Sumitomo, and MSUNano boron-doped diamond thin-film electrodes.	103
Table 4.2	Cyclic voltammetric and heterogeneous electron-transfer rate constant data for $\text{Fe}(\text{CN})_6^{3-/4-}$ and $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ at MSUMicro, Condias, Sumitomo, and MSUNano boron-doped diamond thin-film electrodes, as a function of the solution pH.	108
Table 5.1	Bulk conductivity values of graphite and CVD diamond powder before (as-grown) and after (cleaned) washing in warm aqua regia (30 min) and warm 30% H_2O_2 (30 min).	125
Table 5.2	Cyclic voltammetric ΔE_p values (mV) for 1 mM $\text{Fe}(\text{CN})_6^{3-/4-}$ at conductive diamond powder, graphite powder, GC powder, and a planar microcrystalline boron-doped diamond thin-film electrodes at three different scan rates.	132
Table 6.1	Two different (A and B) current and charge conditions for the pulsed galvanostatic deposition of Pt metal on carbon paper (TCP) and boron-doped nanocrystalline diamond deposited on carbon paper (BND) including the solution-exposed and actual surface area (SA).	157
Table 6.2	Electrode and Pt surface areas (SA) calculated for the Pt/carbon composite electrodes (Pt/TCP-A, Pt/BND-A, Pt/TCP-B, and Pt/BND-B) with the metal phase formed by pulsed galvanostatic conditions A (0.146 mA/cm^2 or 0.0047 C/cm^2) and B (1.25 mA/cm^2 or 0.040 C/cm^2) with the corresponding surface enhancement factor, SEF.	160
Table 6.3	Estimated specific surface area of Pt on Pt/TCP-A, Pt/BND-A, Pt/TCP-B, and Pt/BND-B formed using pulsed galvanostatic deposition conditions A (0.146 mA/cm^2 or 0.0047 C/cm^2) and B (1.25 mA/cm^2 or 0.040 C/cm^2) assuming 100% deposition efficiency.	162
Table 6.4	Peak position ($E_{p/2}$) and approximate limiting current (i_{lim}) for the oxygen reduction reaction on Pt/TCP-A, Pt/BND-A, Pt/TCP-B, and Pt/BND-B in oxygen-saturated 0.1 M HClO_4 at 1 mV/s normalized to the surface enhancement factor ($i_{lim, SEF}$, $\mu\text{A}/\text{SEF}$) and to the mass of Pt ($i_{lim, mass}$, $\text{mA}/\text{mg}_{\text{Pt}}$).	164

Table 6.5	Charge density (mC/cm^2), change in faradaic current density for electroactive surface-oxygen functional groups (ΔI), and Raman D/E_{2g} ratio for bare carbon paper (TCP) and nanocrystalline diamond deposited on carbon paper (BND) after polarization at different potentials in 0.1 M HClO_4 at 25 °C for 1 h.	168
Table 6.6	Electrochemically-active Pt surface area (Pt/TCP-B and Pt/BND-B) before and after anodic polarization at 1.4 V vs Ag/AgCl and 25 °C in 0.1 M HClO_4 for 1 h.	172
Table 6.7	Half-peak position ($E_{p/2}$) and current (i_{lim}) for the oxygen reduction reaction on Pt/TCP-B and Pt/BND-B in oxygen-saturated 0.1 M HClO_4 after anodic polarization at 1.4 V vs. Ag/AgCl and 25 °C in 0.1 M HClO_4 for 1 h. The scan rate was 1 mV/s and the current was normalized to the surface enhancement factor ($i_{lim, SEF}$, $\mu\text{A}/\text{SEF}$).	174

LIST OF FIGURES

Figure 1.1	History and projections of world energy use in British thermal units (BTU).	2
Figure 1.2	(A) Schematic and (B) picture of a PEMFC.	5
Figure 1.3	Schematic of the triple phase boundary at the electrocatalyst/ electrocatalyst support/ionomer interface in a PEMFC.	8
Figure 1.4	Microstructures of (A) graphite, (B) GC, and (C) carbon black.	14
Figure 1.5	Schematic of proposed surface oxides on sp^2 -bonded carbons.	16
Figure 1.6	Schematic of the bonding arrangement in sp^3 -bonded diamond.	18
Figure 1.7	Input, deposition process, reactor design, and internal variables that affect output variables for CVD.	22
Figure 1.8	Simplified CVD scheme showing plasma composition, major reactive components, and the primary reaction pathway for microcrystalline diamond deposition.	24
Figure 1.9	Proposed mechanism for nanocrystalline diamond growth by insertion of a C_2 dimer into the diamond lattice.	26
Figure 2.1	Schematic microwave plasma-assisted CVD reactor used to grow microcrystalline and nanocrystalline boron-doped diamond thin-film electrodes.	37
Figure 2.2	Schematic of the apparatus used to measure i - V curves for the powder samples. This same general scheme was used to measure the powder resistance with an ohmmeter, simply by removing the power supply and ammeter.	44
Figure 2.3	Design of the single compartment, glass, three-electrode electrochemical cell.	46
Figure 2.4	Carbon paper electrode preparation schematic.	48
Figure 3.1	Schematic of the oxidation of graphitic carbons including intercalation and exfoliation of the graphite lattice, oxidation of new exposed edge plane, and gasification (corrosion) to CO and CO_2 .	59

Figure 3.2	Amperometric <i>i-t</i> curves for graphite and GC powders during a 1 h polarization at 1.0 and 1.6 V vs. Ag/AgCl in 0.1 M HClO ₄ at 25 °C. The top curve (A) is a plot of current and the bottom curve (B) is a plot of the logarithm of the current.	62
Figure 3.3	Background cyclic voltammetric <i>i-E</i> curves for (A) graphite and (B) GC in 0.1 M HClO ₄ at 0.1 V/s before and after polarization at 1 V vs. Ag/AgCl and 25 °C for 1 h.	68
Figure 3.4	Raman spectra for graphite and GC before anodic polarization showing the E _{2g} mode (~1580 cm ⁻¹) and D band (~1360 cm ⁻¹).	71
Figure 3.5	Charge density vs. polarization potential for Vulcan XC-72 as a function of the temperature.	77
Figure 3.6	Change in faradaic current density for surface oxide reduction of Vulcan XC-72 before and after polarization as a function of the polarization potential and temperature in 0.1 M HClO ₄ for 1 h.	78
Figure 3.7	Background cyclic voltammetric <i>i-E</i> curve for Pt-loaded (20 wt. %) Vulcan XC-72 in 0.1 M HClO ₄ at 0.005 V/s. Current is normalized to the estimated Pt surface area.	80
Figure 3.8	Charge density vs. polarization potential for Pt-loaded (20 wt. %) Vulcan XC-72 as a function of the temperature.	81
Figure 3.9	Background cyclic voltammetric <i>i-E</i> curves for Pt-loaded (20 wt. %) Vulcan XC-72 in 0.1 M HClO ₄ at 0.005 V/s before and after polarization from 0.8 to 1.4 V vs. Ag/AgCl at 25 °C. Current is normalized to the estimated Pt surface area before polarization.	83
Figure 4.1	Scanning electron micrographs of (A) MSUMicro, (B) Condias, (C) Sumitomo, and (D) MSUNano diamond thin films.	93
Figure 4.2	Raman spectra for MSUMicro, Condias, Sumitomo, and MSUNano diamond thin films.	95
Figure 4.3	Cyclic voltammetric <i>i-E</i> curves for all four diamond types in 0.1 M HClO ₄ at 0.1 V/s (geometric area = 0.2 cm ²).	97
Figure 4.4	Cyclic voltammetric <i>i-E</i> curves for all four diamond types in (A) 0.1 mM Fe(CN) ₆ ^{3-/4-} , (B) 0.1 mM Ru(NH ₃) ₆ ^{3+/2+} and (C) 0.1 mM IrCl ₆ ^{2-/3-} , all in 1 M KCl, and (D) 4-methylcatechol and (E) Fe ^{3+/2+} in 0.1 M HClO ₄ . Curves for scan rates of 0.1 and 1 V/s are shown (geometric area = 0.2 cm ²).	101

Figure 4.5	Experimental and simulated (DigiSim [®] 3.03) cyclic voltammetric <i>i-E</i> curves for (A) 0.1 mM Fe(CN) ₆ ^{3-/4-} in 1 M KCl at the Sumitomo diamond electrode (0.1 V/s) and (B) 0.1 mM IrCl ₆ ^{2-/3-} in 1 M KCl at the MSUMicro diamond electrode (50 V/s). The experimental voltammograms contain both the background and faradaic currents while the simulated voltammograms contain just the faradaic current.	106
Figure 5.1	Deposition scheme for coating insulating diamond powder with a conductive, boron-doped diamond overlayer showing both full and partial grain coverage as well as fusion of neighboring grains. The shaded areas represent the conducting diamond overlayer.	119
Figure 5.2	Scanning electron micrographs of (A) bare diamond powder and conductive diamond powder after (B) 1, (C) 2, and (D) 4 h coating times.	120
Figure 5.3	X-ray diffraction spectrum of a 4 h growth diamond powder sample.	122
Figure 5.4	Raman spectra of bare diamond powder and conductive diamond powder after coating times of 1, 2, 4, and 6 h.	124
Figure 5.5	Scanning electron micrographs of a 4 h growth conductive diamond powder (A) as-grown and (B) after acid washing.	126
Figure 5.6	<i>I-V</i> curves for a 4 h growth conductive diamond powder, graphite powder, and a boron-doped diamond thin film over a ±10 V range.	127
Figure 5.7	(A) Background cyclic voltammetric <i>i-E</i> curves for conductive diamond powder electrodes (2, 4, and 6 h deposition times) in 0.1 M HClO ₄ at 100 mV/s. (B) Enlarged view of an 800 mV region. Current is normalized to the diamond powder surface area exposed to solution.	129
Figure 5.8	(A) Cyclic voltammetric <i>i-E</i> curves for a conductive diamond powder electrode (4 h coating time) in 1 mM Fe(CN) ₆ ^{3-/4-} at scan rates between 10 and 500 mV/s and (B) a plot of the oxidation peak current versus the scan rate ^{1/2} .	134
Figure 5.9	Cyclic voltammetric <i>i-E</i> curves for 1 mM Ru(NH ₃) ₆ ^{3+/2+} for a conductive diamond powder electrode (4 h coating time) at scan rates between 10 and 300 mV/s with (A) 10 wt. % PTFE binder and (B) 5 wt. % PTFE binder.	136

Figure 5.10	Chronoamperometric <i>i-t</i> curves for the 4 h conductive diamond powder, graphite powder, and glassy carbon powder electrodes recorded during potentiostatic polarization at 1.6 V vs. Ag/AgCl and 25 °C for 1 h.	139
Figure 5.11	Scanning electron micrographs of a conductive diamond-coated diamond powder electrode (4 h coating time) (A) before and (B) after and GC powder electrode (C) before and (D) after constant potential polarization of 1.6 V vs. Ag/AgCl for 1 h in 0.1 M HClO ₄ .	139
Figure 6.1	Scanning electron micrographs of (A) bare carbon paper (TCP), (B) an individual bare carbon fiber within the paper, (C) boron-doped nanocrystalline diamond deposited on the carbon paper (BND), and (D) a cross-section of a nanocrystalline diamond-coated carbon fiber.	150
Figure 6.2	X-ray diffraction spectra of bare (TCP) and boron-doped nanocrystalline diamond-coated carbon paper (BND).	151
Figure 6.3	Raman spectra for the bare (TCP) and boron-doped nanocrystalline diamond-coated carbon paper (BND).	152
Figure 6.4	Background cyclic voltammetric <i>i-E</i> curves for bare (TCP) and boron-doped nanocrystalline diamond-coated carbon paper (BND) in 0.1 M HClO ₄ at 100 mV/s. The current is normalized to the electrode area estimated to be in contact with the solution.	154
Figure 6.5	Scanning electron micrographs of Pt/carbon composite electrodes (Pt/TCP-A, Pt/BND-A, Pt/TCP-B, and Pt/BND-B) under two different pulsed galvanostatic deposition conditions A (0.146 mA/cm ² or 0.0047 C/cm ²) and B (1.25 mA/cm ² or 0.040 C/cm ²).	158
Figure 6.6	Cyclic voltammetric <i>i-E</i> curves of Pt/carbon composite electrodes Pt/TCP-A, Pt/BND-A, Pt/TCP-B and Pt/BND-B deposited by pulsed galvanostatic deposition (A = 0.146 mA/cm ² or 0.0047 C/cm ² and B = 1.25 mA/cm ² or 0.040 C/cm ²) in 0.1 M HClO ₄ at 50 mV/s. Currents are normalized to the carbon electrode surface area.	161
Figure 6.7	Linear sweep voltammetric <i>i-E</i> curves for the oxygen reduction reaction at Pt/TCP-A, Pt/BND-A, Pt/TCP-B, and Pt/BND-B in oxygen-saturated 0.1 M HClO ₄ at 1 mV/s. Current is normalized to the surface enhancement factor (SEF).	165

Figure 6.8	Scanning electron micrographs of (A) BND and (B) TCP after potentiostatic polarization at 1.6 V vs. Ag/AgCl at 25 °C for 1 h.	167
Figure 6.9	Raman spectra of BND before and after potentiostatic polarization at 1.6 V vs. Ag/AgCl in 0.1 M HClO ₄ at 25 °C for 1 h.	169
Figure 6.10	Scanning electron micrographs of Pt/TCP-B and Pt/BND-B before and after potentiostatic polarization at 1.4 V vs. Ag/AgCl and 25 °C in 0.1 M HClO ₄ for 1 h.	171
Figure 6.11	Cyclic voltammetric <i>i</i> - <i>E</i> curves for Pt/TCP-B and Pt/BND-B in 0.1 M HClO ₄ , recorded at 50 mV/s normalized to the electrode surface enhancement factor (SEF), before and after a 1 h polarization at 1.4 V vs. Ag/AgCl at 25 °C.	172
Figure 6.12	Linear sweep voltammetric <i>i</i> - <i>E</i> curves for the oxygen reduction reaction at Pt/TCP-B and Pt/BND-B in oxygen-saturated 0.1 M HClO ₄ before and after polarization at 1.4 V vs. Ag/AgCl at 25 °C in 0.1 M HClO ₄ for 1 h. Curves were recorded at 1 mV/s and are normalized to the electrode surface enhancement factor (SEF).	173

Chapter 1

Introduction

1.1 Background

Energy use in the United States and abroad is increasing at an alarming rate. As a result, the production of energy from fossil fuels, such as oil and coal, and renewable sources, such as water and wind, is being outpaced by demand. Each year, the Energy Information Administration of the U.S. Department of Energy releases the International Energy Outlook report, which details various aspects of the world energy market. Figure 1.1, adapted from the 2005 report, illustrates world energy use (by fuel type) from 1970 to 2004, as well as energy demand projections until 2025.¹ As evident, world energy consumption is expected to rise almost 70% by the year 2020 due to population growth and emerging industrialized economies.² Considering that the main source of world energy is fossil fuels, this rise in consumption will lead to a 50% increase in the amount of CO₂ released into the environment each year.² The atmospheric CO₂ concentration has already increased from 280 to 370 parts per million (ppm) during the last 150 years.³ If this trend continues, the atmospheric CO₂ concentration is expected to rise to over 550 ppm during the next 100 years.³ This prediction has detrimental environmental implications in terms of global warming.⁴ In addition, oil production worldwide is expected to peak within the next few decades.³ Although supplies will remain for some time afterward, prices will soar. To minimize these monetary and environmental costs, as well as to ensure that world energy supply can meet growing energy demand, it is imperative that alternative energy sources be developed and utilized in the near term.

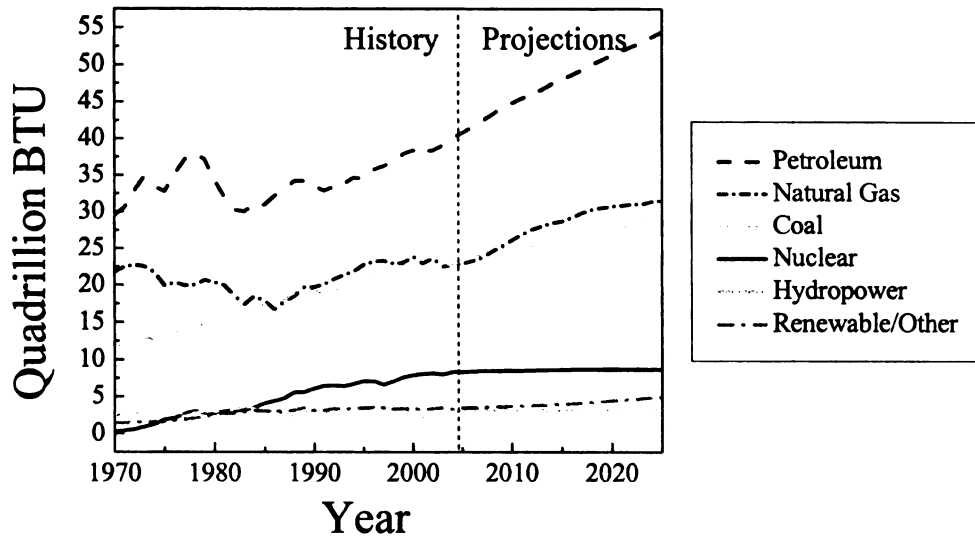


Figure 1.1 History and projections of world energy use in British thermal units (BTU). (Adapted from ref 1)

Hydrogen has received much attention in recent years as a clean, plentiful source of energy that may serve as an alternative to commonly used fossil fuels.⁵ The principal hydrogen energy conversion device used today, the polymer electrolyte membrane fuel cell (PEMFC), is analogous to a combustion engine that burns gasoline. However, the PEMFC converts the chemical energy of hydrogen directly into electrical energy, instead of into heat as in the combustion engine. This direct conversion significantly reduces the amount of energy lost during the conversion cycle. In fact, the theoretical efficiency of a fuel cell is 100%, while the combustion engine has only 40% efficiency under ideal operating conditions and is reduced to about 25% in practice. From an environmental perspective, the use of hydrogen would eliminate harmful emissions like CO₂, NO_x, and SO_x. Hydrogen could also be beneficial economically and militarily by reducing U.S. dependence on foreign oil.

Despite the attractiveness of hydrogen as an environmentally-friendly, domestically-available energy source, there are remaining problems to be overcome before it will be a viable energy alternative. These include production, transport, and storage of the hydrogen fuel, in addition to significant technical issues that must be solved with the PEMFC in terms of cost, efficiency, and operational lifetime.^{3,5} A considerable amount of research has been done to address some of these problems. For example, a survey of the literature using the SciFinder Scholar[®] search engine reveals that over 20,000 articles have been published on fuel cell science and technology since 1970. The interested reader is referred to two reviews on the major advances in fuel cell technologies from 1960 to 2000 by Costamagna and Srinivasan.^{6,7}

A global research effort is now focused on almost every aspect of PEMFC development to improve and advance the so-called "hydrogen economy." The Office of Science of the U.S. Department of Energy published a report in February 2004 entitled "Basic Research Needs for the Hydrogen Economy," which outlined 11 high-priority research directions for the hydrogen fuel and the PEMFC.⁵ One of the key research needs identified is the development of low-cost, highly-active, and durable electrodes (electrocatalyst, carbon electrocatalyst support, and ionomer) for the PEMFC. Studies of automotive PEMFC performance degradation have shown that voltage losses of $>50 \mu\text{V/h}$ occur during operation, while target losses of less than $10 \mu\text{V/h}$ have been proposed for a 5,000 h operating lifetime.⁵ These voltage losses are caused by degradation of the electrode components, but the specific mechanisms of the degradation are not well-understood. Thus, studies of the conditions under which these voltage losses occur, as

well as of the mechanisms involved in the electrode performance degradation are important for the development of more durable electrode materials.

The research presented in this dissertation was conducted to address part of the multifaceted electrode stability issue and specifically focused on corrosion of the carbon electrocatalyst support. This chapter presents background information and provides a context for the current work, including a description of PEMFC operating principles and electrode materials, specific stability criteria for electrocatalyst supports in PEMFCs, and a description of current corrosion issues. The details of a proposed dimensionally stable electrocatalyst support, electrically conducting diamond, including material properties, established stability, and growth mechanisms are then presented. Next, the specific research questions addressed in each chapter are given, followed by an outline of the dissertation.

1.2 Fuel Cell Materials and Operation

Although there are several types of fuel cells that are typically classified by the specific electrolyte employed, the discussion in this chapter and the research presented in **this** dissertation will focus on the hydrogen-powered PEMFC. The PEMFC is a low-**temperature** (~80 to 100 °C) energy conversion device that is being investigated for **transportation** and decentralized stationary power systems. As shown in the simplified **schematic** and picture in Figure 1.2A and B, respectively, the PEMFC consists of two **electrodes** that contain an electrocatalyst (e.g., Pt) dispersed on a high-surface-area **support** (e.g., carbon black). The electrodes are connected through an external circuit and **separated** by a hydrated solid polymer electrolyte membrane, which is typically a ~10-30

μm thick perfluorosulfonic acid polymer, such as Nafion[®],
 $(\text{CF}_2\text{CF}_2)_x[\text{CF}(\text{OR}_i\text{SO}_3\text{H})\text{CF}_2]_y$.

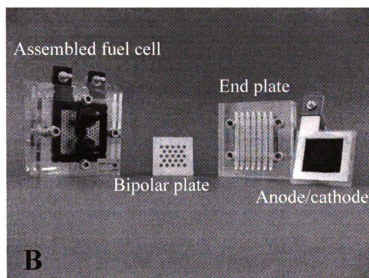
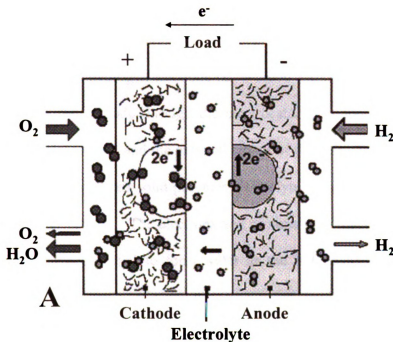


Figure 1.2 (A) Schematic (Adapted from ref 8) and (B) picture of a PEMFC.

In the PEMFC, hydrogen is directed into the fuel cell through a gas diffusion layer (e.g., carbon paper), enters the anode, and reacts on an electrocatalyst to produce two protons and two electrons, as shown in Equation 1.1:



where SHE is the standard hydrogen electrode ($E^\circ = 0.000 \text{ V}$). The electrons travel from the electrocatalyst to the cathode through the electrocatalyst support material, bipolar plate (e.g., Ti or stainless steel), and the external circuit of the cell. The protons travel to the cathode through the hydrated solid polymer electrolyte (an ionomer) that is present near the surface of the catalyst. The electrons and protons then react with oxygen from either air or a pure gaseous feed to form water as the only byproduct, according to Equation 1.2:



The overall cell reaction ($E_{\text{Cell}} = E_{\text{Cathode}} - E_{\text{Anode}}$), shown in Equation 1.3, has a standard potential of 1.229 V vs. SHE.



Much research has been directed toward the improvement of fuel cell electrode materials in terms of efficiency, stability, and cost. Fuel cell electrodes generally consist of nanometer-sized electrocatalyst particles, such as Pt, that are highly dispersed onto a high-surface-area ($\sim 100 \text{ m}^2/\text{g}$), sp^2 -bonded carbon powder support. Finely dispersed electrocatalyst particles on a stable and conductive support increase the number of electrocatalytically-active atoms available for the fuel cell reactions, thereby reducing the loading requirements of expensive metallic catalysts.^{9,10} Although high-surface-area graphitic carbons offer greater chemical stability and mechanical strength as

electrocatalyst supports, graphitization decreases the number of active sites for electrocatalyst attachment. Instead, high-surface-area carbon blacks, such as Vulcan XC-72, are typically used as the electrocatalyst support. To form the electrode, a catalyst-loaded carbon black ink is sprayed or painted onto a hydrophobic carbon paper gas diffusion electrode. Two of these layers are then hot-pressed under pressure into each side of a Nafion[®] membrane to form the so-called membrane electrode assembly (MEA). The interested reader is referred in an excellent review by Antolini that discusses the recent advances in electrode preparation and materials for PEMFCs.¹¹

Regardless of the manner in which the MEA is formed, the most important factor in determining the electrochemical performance and lifetime of a fuel cell is the stability of the interface where the fuel, electrocatalyst, and ionomer are all in direct contact. This is so-called triple phase boundary (TPB). Figure 1.3 shows a simplified schematic of this interface at the anode, where the dark circles represent the carbon support and the small light circles represent the electrocatalyst particles. Only those electrocatalyst particles that are in direct contact with the support material and with the polymer electrolyte will be active for the hydrogen oxidation or the oxygen reduction reaction at the anode and cathode, respectively. Considering this, it is not surprising that the morphological and microstructural stability of the materials at this interface affect device performance, possibly more than any other fuel cell component. Issues, such as overpotential limitations and resistance effects (electronic and ionic), within the TPB strongly influence fuel cell efficiency. Materials research to reduce the resistance (mass transport, kinetic, and ohmic) at the TPB has focused on optimization of the properties of the conductive polymer membrane electrolyte, reduction of the electrocatalyst loading, and improved

electrocatalyst utilization.^{8,9,12,13} However, the long-term chemical stability of all components in the MEA is a critical problem that requires a more focused research effort.

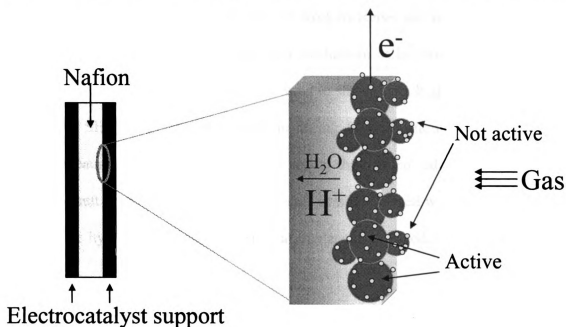


Figure 1.3 Schematic of the triple phase boundary at the electrocatalyst/electrocatalyst support/ionomer interface in a PEMFC.

1.3 Carbon Corrosion in Fuel Cells

Although the thermodynamic potential for the fuel cell reaction is 1.23 V vs. SHE, in practice, fuel cells operate at *ca.* 0.7 V vs. SHE, primarily because of sluggish kinetics for the oxygen reduction reaction at the cathode. During start-up and shut-down, however, the materials in the MEA are subject to potentials as high as 1.2 to 1.5 V vs. SHE.¹⁴ In the presence of liquid water and oxygen, as well as low pH (<1) and high temperature (~80 °C), carbon corrosion is especially favorable at the fuel cell cathode at these high potentials. Some work has been done to study the conditions that lead to corrosive environments in a fuel cell. For example, it has been shown that flooding of the

MEA, caused by factors such as insufficient operating temperature, result in non-uniform current distribution through the MEA.¹⁵ This creates potential "hot spots" and may lead to high, localized corrosive potentials. Recent work by Reiser and co-workers has shown that high potentials may be due, in part, to a mechanism called reverse-current decay.¹⁶ In this work, a one-dimensional model was used to show that a high interfacial potential (1.44 V vs. SHE) is present at the anode during PEMFC startup.¹⁶ This potential develops because at some locations on the anode, the oxygen reduction reaction takes place as a result of the presence of air that leaked in when the cell was off, while at others locations, the hydrogen oxidation reaction takes place after introduction of the hydrogen fuel.¹⁶

Research has shown that stability issues with both the metal electrocatalyst and the carbon support, particularly at the cathode in the presence of oxygen, exist at these high potentials. Specifically, degradation of the carbon electrocatalyst support has been shown to lead to loss of electrocatalyst activity, increased ohmic resistance, reduced operational efficiency of PEMFCs, and eventually complete electrode failure.^{9,17-21} Mathais and co-workers published an excellent review of the current issues with fuel cell commercialization including both cost and stability limitations.¹⁴ In this work, production goals and benchmark stability targets were proposed. For use in automotive applications, fuel cells are predicted to undergo *ca.* 30,000 on/off cycles. With a targeted lifetime performance loss of less than 30 mV for a PEMFC operating at 1.5 A/cm² over 10 y and 5,500 h of operation, materials used in the MEA must be stable to potentials as high as 1.5 V vs. SHE for up to ~100 h.¹⁴

It is important to develop an understanding of the mechanisms by which current sp^2 -bonded supports degrade and corrode in a working-PEMFC environment. Many of the early reports on the microstructural degradation and corrosion of sp^2 -bonded carbons were carried out in both alkaline and acidic media, typically at high temperatures (>100 °C).^{9,21-26} Consideration of these studies is useful for gaining insight into carbon corrosion mechanisms. In acidic media, potential-dependent corrosion of sp^2 -bonded carbon materials occurs according Equation 1.4.⁹



Kinoshita and Bett measured the corrosion current and CO_2 evolved from a high-surface-area carbon black ($1000 \text{ m}^2/\text{g}$) in 96% H_3PO_4 under potentiostatic conditions (0.7 to 1 V vs. SHE) at 135 °C.²⁴ They found that electrochemical corrosion proceeded through two independent processes, surface oxide formation and carbon gasification to CO_2 .²⁴ Unlike high temperature gas-phase oxidation of carbon in which the surface oxide layer reduces the active surface area and slows the rate of gasification, electrochemical formation of surface carbon oxides does not inhibit the carbon gasification.²⁴ In fact, a positive correlation has been found between the percentage of surface oxides and the corrosion of carbon black materials, perhaps because the oxygen atoms serve as nucleation sites for degradation.²¹ Antonucci and co-workers reported an increase in the corrosion current recorded at 1 V vs. SHE from *ca.* 0.03 mA/mg to 0.3 mA/mg when the O/C ratio was raised from 2 to 14.²¹

Other work has related the graphitic nature of the carbon support to the extent of corrosion. For example, Stonehart postulated that disordered regions of the carbon, such as edge plane and defect sites, were oxidized first, followed by slow attack of the more

ordered graphene sheets.²⁵ In addition, heat-treated carbons (i.e., graphitized) were found to be more resistant to corrosion than were the as-received materials, further supporting the belief that the degree of microstructural order is critical for corrosion resistance.²⁵ Similarly, Antonucci and co-workers found that as the d_{002} -spacing of the carbon increased, (i.e., as the material became less ordered), the corrosion current increased due to the so-called order/disorder dependence.²¹ More detailed kinetic and mechanistic studies of carbon black oxidation in aqueous ozone have shown that oxidative degradation proceeds through a three-stage process: 1) the formation of chemical functional groups on the surface resulting in degradation products (e.g., polyphenols), 2) oxidation of disordered carbon to CO₂, and 3) further oxidation of the more ordered (i.e., graphitic) carbon to CO₂.²⁷ Regardless of the reagents used to study oxidative degradation of carbon blacks, results have shown that the microstructure strongly influences the extent of corrosion. The less-ordered portions of the material degrade first and more severely, followed by degradation of graphite-like regions during prolonged exposure to harsh conditions.²³

Appleby studied the corrosion of graphitized carbon black, graphite, and various other carbon blacks in a phosphoric acid fuel cell environment.⁹ Corrosion of these carbon supports, as measured by the corrosion current, was found to depend on the carbon microstructure and increased with increasing potential, temperature, and pressure. Operating at 1 atm, 190 °C, and 0.7 V vs. SHE in 98 % H₃PO₄, the corrosion rate of all carbons was initially high, falling off to a pseudo-steady state level after about 100 hours. The total mass loss of graphitized carbon black, graphite, and carbon black was approximately 40, 50, and 75%, respectively. These differences were attributed to

structure-dependent corrosion rates. The more disordered regions are characterized by a higher free energy and, hence, a higher reactivity.⁹

Recent work has focused on lower temperature systems (50 to 90 °C) to study sp^2 -bonded carbon oxidation/corrosion in an environment more similar to that in a PEMFC.^{17-19,28} Kangasniemi and co-workers studied the electrochemical surface oxidation of a carbon black, Vulcan XC-72, after polarization from 0.6 to 1.2 V vs. SHE at both room temperature and 65 °C.¹⁷ They found evidence for surface oxidation at 0.8 V vs. SHE at 65 °C and at 1.0 V vs. SHE at room temperature.¹⁷ Roen and co-workers examined the effect of Pt on sp^2 -bonded carbon support corrosion and found that CO₂ evolution increased as the Pt mass fraction increased, suggesting that Pt accelerated the rate of carbon corrosion.¹⁹ Maja and co-workers evaluated the lifetimes of carbon blacks by monitoring the voltage stability under a constant current load of 200 mA/cm².²⁹ Vulcan XC-72 outperformed Black Pearls 3700 and Shawinigan Black AB50 (acetylene black) with a constant potential output over 1000 h, while the others failed after *ca.* 50 h and 400 h, respectively.²⁹ More recently, Stevens and Dahn showed that combustion of the cathode carbon support was enhanced when impregnated with Pt in a PEMFC.³⁰ At 125 °C, a carbon support containing 57% Pt lost some 40% of its mass due to corrosion, while the mass of the carbon support with no Pt was relatively unchanged.³⁰

1.4 sp^2 -Bonded Carbon Structure

It is obvious from the above discussion that corrosion of sp^2 -bonded carbon electrocatalyst support materials is a problem in fuel cells. However, until quite recently, many researchers believed that these carbons were stable under PEMFC conditions

because of the low temperature (<100 °C) and operating potential (~0.7 V vs. SHE). The mechanism of degradation is still not well-understood, especially with regard to new and ongoing MEA and electrocatalyst development. It is important to gain a better fundamental understanding of the chemical and electrochemical processes that occur under PEMFC operating conditions, especially to aid in the development of an advanced electrocatalyst support material that will provide enhanced stability with respect to sp^2 -bonded carbons. This understanding must be based on consideration of important structural factors (e.g., edge plane density and surface oxide content) that affect the chemical, physical, and electrochemical properties of carbons.

Figure 1.4 shows the microstructure of model sp^2 -bonded carbon materials: graphite, glassy carbon (GC), and carbon black. All structures are composed of six-membered carbon rings in which each carbon atom is trigonally bonded to three others. This bonding arrangement creates a planar honeycomb array called the basal plane, as seen on the face of graphite in Figure 1.4A. The carbon-carbon bond distance in the basal plane for all sp^2 -bonded carbons is 1.42 Å.³¹ Graphite has the most well-ordered sp^2 -bonded carbon microstructure, characterized by a stacking of the graphene sheets in an *ABAB...* sequence. The first structural model of GC, shown in Figure 1.4B, was published by Jenkins and Kawamura in 1971.³² They proposed that the GC structure consisted of tangled graphitic ribbons, connected by highly-strained carbon-carbon covalent bonds, which resemble the polymer precursor backbone.³² More recent work by Harris has suggested that GC is actually composed of imperfect, multilayered, porous fullerene-related nanoparticles (i.e., structures with non-six-membered rings).³³ Carbon black microstructure strongly depends on the powder preparation conditions, including

temperature, feedstock composition (i.e., impurities), and speed of the synthesis reaction.³⁴ However, in general, carbon blacks are turbostratic in nature, composed of a bidimensional organization of stacked, graphitic planes that are arbitrarily rotated with respect to one another, as shown in Figure 1.4C.²³ High-resolution transmission electron microscopy measurements have shown that carbon blacks are composed of small spherical particles that join together to form agglomerates.³⁴ The agglomerates coalesce as a result of Van der Waals forces to form larger particles, called aggregates.³⁴

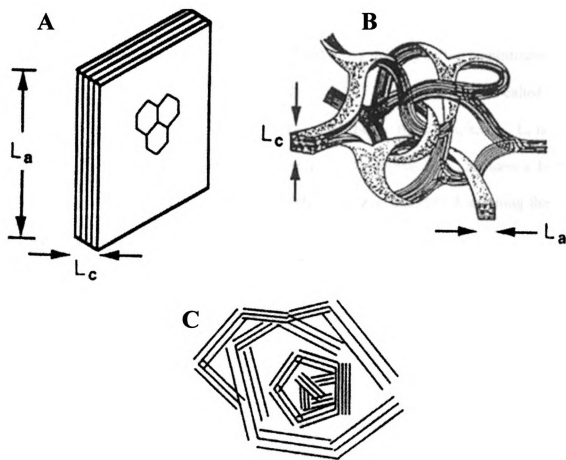


Figure 1.4 Microstructures of (A) graphite, (B) GC, and (C) carbon black. Note: drawings not to scale. (Adapted from ref 35)

sp^2 -bonded carbons are typically characterized by the dimensions of the crystallite lattice determined from X-ray diffraction (XRD) measurements. In this characterization scheme, L_c is the crystallite stacking height perpendicular to the graphene sheets, L_a is the crystallite width, and d_{002} is the interlayer spacing. Comparative d_{002} and L_a values for highly oriented pyrolytic graphite (HOPG), polycrystalline graphite, GC, and carbon black are listed in Table 1.1. HOPG, analogous to a single crystal metal, is a benchmark model carbon to which the structural properties (L_c , L_a , and d_{002}) of other carbons are typically compared. For example, the d_{002} -spacing is commonly used to quantify the "graphitic nature" of sp^2 -bonded carbons; carbon microstructures with d_{002} near that of HOPG (3.354 Å) are more "graphitic" than those with larger layer plane spacing. Carbon blacks can be treated at high temperatures (~2000 °C), a process called graphitization, to reduce the d_{002} spacing closer to that of HOPG. GC, in contrast, is a so-called non-graphitizing carbon because heat treatment does not change the d_{002} spacing. L_a is also an important parameter because carbons with a smaller crystallite width have a higher proportion of edge plane density. L_a for HOPG is greater than 10^4 Å meaning that the basal plane density in this material is high, while the edge plane density is low. L_a for GC and carbon black are significantly smaller, resulting in more disordered microstructures with a higher edge plane density and thus, a higher electrochemical and chemical reactivity.

The electrical and chemical properties of sp^2 -bonded carbons are anisotropic because of the difference in bonding perpendicular and parallel to the basal plane. For example, electrical conduction parallel to the basal plane in sp^2 -bonded carbons is high because three of the four carbon valence electrons are occupied within the extended π -

electron ring system. In contrast, electrical conduction perpendicular to the basal plane, across the so-called edge plane, is lower because bonding between the layer planes is a result of weak Van der Waals interactions. The resistivities of the basal and edge plane of HOPG are 0.17 and $4 \times 10^{-5} \Omega\text{-cm}$, respectively.³⁵ The chemical reactivity of the respective graphitic planes also varies. Atoms in the basal plane have saturated valencies and are typically unreactive, while the unsaturated edge plane atoms are active sites for chemisorption of heteroatoms, such as oxygen. As seen in Figure 1.5, the edge plane of sp^2 -bonded carbon typically contains several types of oxides such as hydroxyls, ketones, and quinones. The coverage and type of functional group depends on the type of sp^2 -bonded carbon and its past history.

Table 1.1 Crystallite width (L_a) and interlayer spacing (d_{002}) for some common sp^2 -bonded carbons.^{31,32,35}

Carbon Material	d_{002} (Å)	L_a (Å)
HOPG	3.354	$>10^4$
Polycrystalline graphite	3.355	>100
GC	3.48	~ 50
Carbon black	3.43-3.57	~ 20

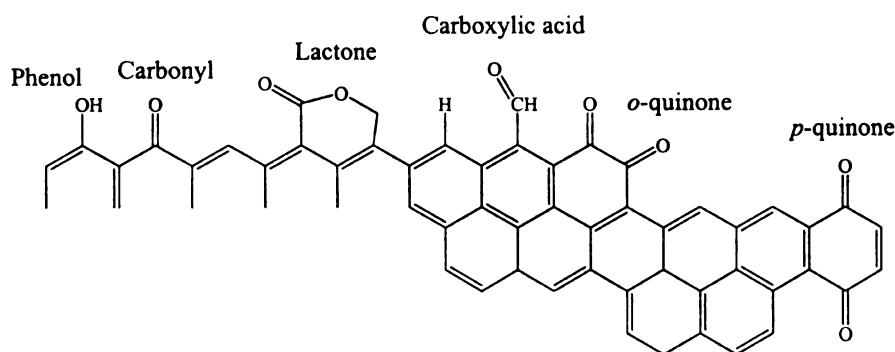


Figure 1.5 Schematic of proposed surface oxides on sp^2 -bonded carbons.

1.5 Boron-Doped Diamond

An ideal PEMFC electrocatalyst support material should have (i) electrical conductivity ($>10 \text{ S/cm}^2$), (ii) high-surface-area ($\sim 100 \text{ m}^2/\text{g}$), (iii) mechanical strength, (iv) chemical resistance in aqueous environments, (v) thermal stability (0 to 150°C), and (vi) microstructural stability at high potentials (e.g., $>1 \text{ V}$ vs. SHE) and current densities.³⁶ Carbon blacks commonly used in fuel cells, such as Vulcan XC-72, possess many of these characteristics. However, as discussed above, these carbons are susceptible to microstructural and morphological degradation under typical fuel cell operating conditions and this affects the operational efficiency and electrode lifetime. It is our supposition that boron-doped diamond can function as a dimensionally stable support material, outperforming currently used sp^2 -bonded carbon materials.

Diamond is a technologically important material because of its unique properties, such as extreme hardness, high electrical resistance, chemical inertness, high electron and hole mobility, high thermal conductivity, and optical transparency.^{37,38} Unlike the three-fold bonding arrangement in graphite, carbon atoms in diamond are bonded in a tetrahedral arrangement forming six-membered rings in a chair conformation, as shown in Figure 1.6. Natural diamond is an electrical insulator with a band gap of $\sim 5.5 \text{ eV}$ and a resistivity greater than $10^{12} \Omega\text{-cm}$.^{39,40} However, synthetic diamond can be grown via chemical vapor deposition (CVD) and made electrically conductive by doping with boron. Boron-doped diamond (BDD) single crystals and polycrystalline thin films can be prepared with resistivities as low as *ca.* $0.005 \Omega\text{-cm}$.^{39,40} Both high-quality microcrystalline and nanocrystalline thin films can be produced by CVD methods.

Diamond thin films that are hydrogen-terminated, hydrophobic, and conductive have been used for numerous electrochemical applications.⁴⁰⁻⁴³

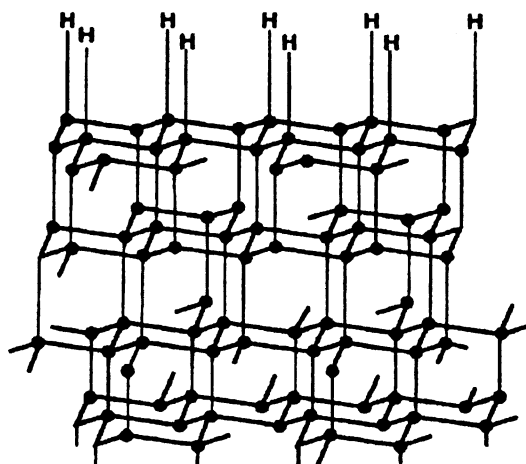


Figure 1.6 Schematic of the bonding arrangement in sp^3 -bonded diamond.

BDD has many advantageous properties that make it an attractive candidate as an electrocatalyst support including mechanical strength, chemical and thermal stability, and corrosion resistance.^{40-42,44} For example, Swain compared the morphological, microstructural, and electrochemical stability of BDD electrodes with that of HOPG and GC in acidic fluoride media.⁴⁴ In this study, each electrode was exposed to potentiodynamic cycling in 1.0 M HNO_3 + 0.1 M NaF at 50 °C for 2 h,⁴⁴ conditions known to cause severe corrosion of HOPG and Grafoil®.⁴⁵⁻⁴⁷ It was found that structural degradation, including delamination and fracturing of the HOPG graphene sheets, as well as severe pitting of GC resulted, while the diamond microstructure was unaffected. The potential window for BDD after potential cycling was larger than before with an

unchanging voltammetric background current, suggesting the surface had simply been cleaned of nondiamond carbon impurity. In contrast, the background current for both HOPG and GC increased significantly with evidence for redox-active surface oxide formation at the edge plane sites. Similar results were found during the anodic polarization of BDD thin-films, HOPG, GC, and Grafoil® in acidic chloride media.⁴⁸ Each electrode was exposed to 1.0 M HNO₃ + 2.0 M NaCl at constant current densities of 0.05 or 0.5 A/cm². Severe structural and electrochemical degradation were observed for the *sp*²-bonded carbon electrodes, while excellent stability was seen for BDD.⁴⁸

As a first step towards the development of diamond as a new electrocatalyst support material, Pt/diamond composite electrodes were prepared using planar microcrystalline and nanocrystalline boron-doped diamond thin films.⁴⁹⁻⁵² Work is ongoing to understand the metal nucleation and growth on diamond so that the electrocatalyst deposition can be optimized in terms of catalyst particle size and distribution.⁴⁹⁻⁵² The Pt/diamond composite electrodes are active for the oxygen reduction reaction, a prerequisite for possible use in PEMFCs.^{49,51} Moreover, the Pt/diamond composite electrode exhibited superior stability in hot concentrated phosphoric acid compared to an *sp*²-bonded carbon cloth electrode impregnated with Pt.⁵² In this study, the electrodes were exposed to anodic polarization in 85% H₃PO₄ at 170 °C and 0.1 A/cm² for two 1-h periods. Severe morphological and microstructural degradation were observed for the *sp*²-bonded carbon electrode, while no damage or loss of catalyst activity was observed for the Pt/diamond composite electrode.⁵²

Despite the advantages of diamond in terms of its morphological and microstructural stability, the surface area of the thin-film electrodes does not approach

the value necessary for a viable support material (10-100 m²/g). In addition, the solid, planar thin-film geometry is not suitable for use in PEMFCs because it is not gas permeable. Research and development of high-surface-area, gas permeable (i.e., powder) forms of conducting diamond is presented in this dissertation.

1.6 Chemical Vapor Deposition (CVD) of Diamond

sp^3 -bonded diamond is the thermodynamically stable form of carbon at high temperature and high pressure, while sp^2 -bonded graphite is the stable form under ambient conditions.⁵³ Early efforts to synthetically produce diamond involved the costly production from graphite, or other sp^2 -bonded carbon precursors, in the presence of molten metal catalysts under both high pressure (7 to 10 GPa) and high temperature (1700 to 2000 K).⁵³ Diamond is, in fact, metastable with respect to graphite at low temperature and pressure as the free energy difference between the two materials at 298 K and 1 atm is only 2.900 kJ/mol (~0.03 eV per atom).^{54,55} Thus, in theory, diamond growth can be achieved in the metastable region of the carbon phase diagram as long as graphite formation is suppressed.⁵³

Low pressure diamond synthesis via CVD dates back to the 1950s and 60s when research was conducted in both the former Soviet Union and the United States.^{55,56} Since then, developments in CVD technology have enabled the production of diamond for a number of applications, such as optical windows, wear-resistant coatings for cutting tools, thermistors, and electrodes.⁵³ Several CVD growth methods exist for producing diamond, all of which utilize a carbon-containing reactant source gas (e.g., methane and hydrogen), an energy source to promote reactant dissociation (e.g., microwave, hot-

filament, or DC discharge), and a substrate (e.g., Si, W, Mo). High-quality (i.e., low defect density and low nondiamond carbon impurity content) CVD diamond is typically produced at low pressure (10 to 500 Torr), high gas temperature ($>1700\text{ }^{\circ}\text{C}$), high substrate temperature (700 to $800\text{ }^{\circ}\text{C}$), and low carbon concentration in the source gas (e.g., 0.5%) with an energy source for gas dissociation and radical formation.⁵³⁻⁵⁵

The morphology, microstructure, and properties of the thin-film CVD diamond are controlled by the method (e.g., excitation source, reactor design, and substrate variables) and deposition conditions (e.g., source gas composition, temperature, and pressure).^{53,55-57} In general, the factors that affect CVD reactor performance and the resultant diamond film properties can be divided into four main categories: input, reactor design, deposition process, and internal variables. The pertinent control parameters of each category and the affected reactor output variables are shown in Figure 1.7. Although the discussion of each variable is beyond the scope of this work, a number of reports have been published that examine various CVD conditions and the resultant film characteristics and growth mechanisms.^{37,53,55-61}

Microwave plasma-assisted chemical vapor deposition (PACVD) is a common deposition method that was utilized for all diamond growth presented in this dissertation. In PACVD, microwave energy is coupled into a deposition chamber, causing the source gas components to dissociate into reactive species (radicals). Both microcrystalline (grain size $\sim 1\text{-}3\text{ }\mu\text{m}$) and nanocrystalline (grain size $\sim 10\text{-}15\text{ nm}$) diamond thin films can be grown via PACVD by selection of the appropriate source gas composition, pressure, and microwave power. These parameters control the relative nucleation rate and subsequent crystallite size of the polycrystalline thin films. A brief introduction to the

growth mechanisms for microcrystalline and nanocrystalline thin films is provided below. Details of the morphology and microstructure of these two diamond types will be discussed in Chapter 4.

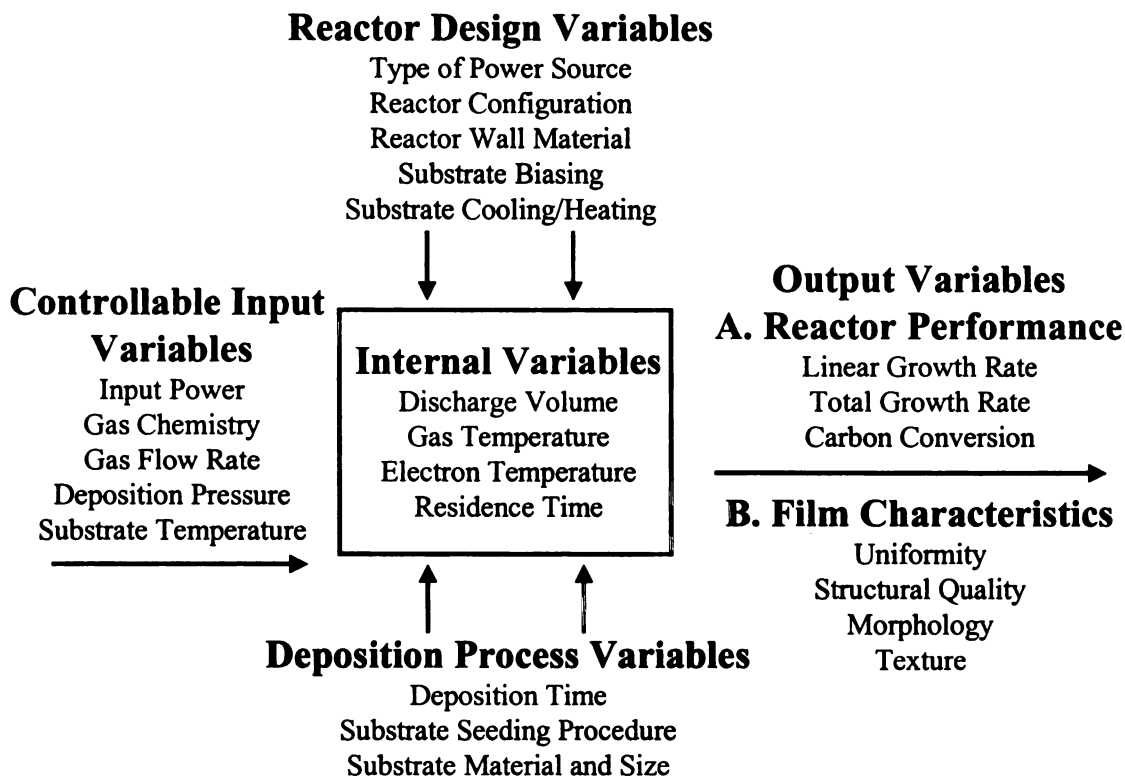


Figure 1.7 Input, deposition process, reactor design, and internal variables that affect output variables for CVD. (Adapted from ref 53)

1.6.1 Microcrystalline Diamond Growth Mechanism

Many reports have been published on the CVD growth mechanism of microcrystalline diamond.^{37,55-58,60-62} This discussion will be limited to microcrystalline diamond deposited in a hydrogen-rich plasma with a low concentration of gas-phase hydrocarbon (< 1%), such as methane. Increases in the CH₄/H₂ ratio are known to

increase the defect density and nondiamond carbon impurity content in CVD diamond films.⁵³ Under conditions of low CH_4/H_2 , the primary reactive species in the plasma are atomic hydrogen and carbon-containing radicals. These species undergo a variety of complex processes during diamond growth that include surface adsorption, diffusion, reaction resulting in diamond nucleation, suppression of nondiamond carbon growth, and eventually, growth of a diamond film.⁶² Figure 1.8 shows a simplified schematic of these processes that includes the main steps for diamond deposition: 1) hydrogen abstraction from gas-phase CH_4 by atomic hydrogen to form methyl radicals, 2) reaction of these radicals with the substrate, and 3) propagation of diamond growth by abstraction of a surface hydrogen and reaction with another methyl radical.^{53-55,57,62} The presence of a high concentration of atomic hydrogen at the surface is important because it stabilizes the diamond lattice during growth, maintains the presence of carbon radical reactive species by hydrogen abstraction, reduces the number of defects in the diamond lattice, and suppresses the formation of graphite on the substrate surface.^{53,54,56,57,60} More detailed information including the distribution of reactive species in the plasma, the effect of temperature and pressure on diamond growth, and the effect of diamond crystallographic orientation on growth rate can be found elsewhere.^{37,53,55,59-62}

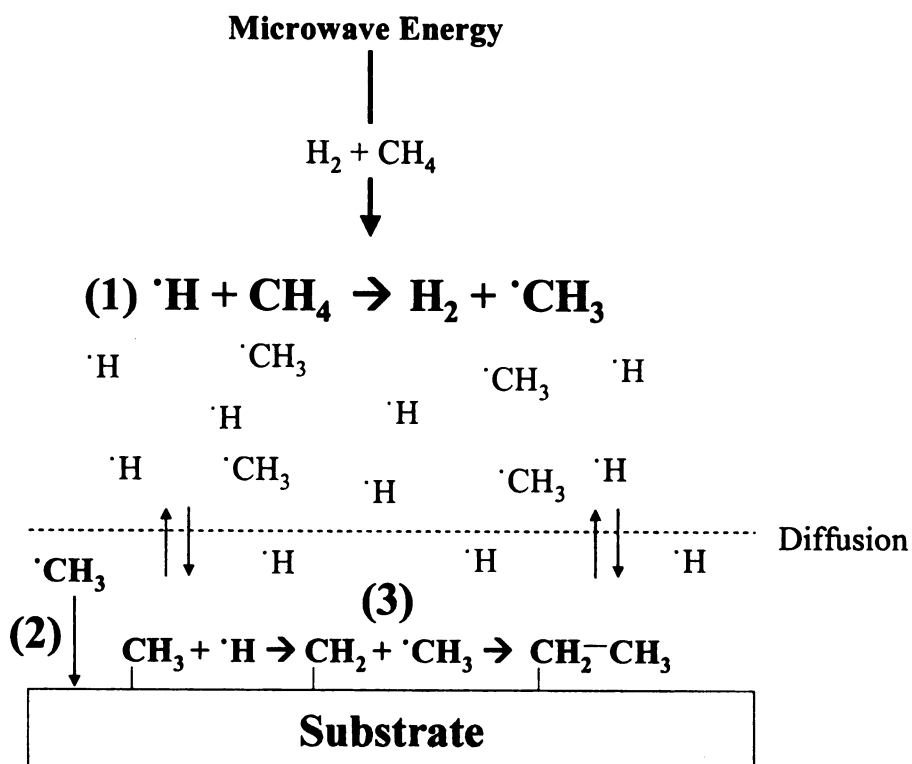


Figure 1.8 Simplified CVD scheme showing plasma composition, major reactive components, and the primary reaction pathway for microcrystalline diamond deposition. (Adapted from ref 62)

1.6.2 Nanocrystalline Diamond Growth Mechanism

Deposition of nanocrystalline diamond thin films is a relatively new field of CVD technology, developed throughout the mid-1990s. In contrast to the H_2 -rich atmosphere in which microcrystalline diamond is grown, nanocrystalline diamond is produced in an Ar/CH_4 plasma with little or no added H_2 . The gas composition (i.e., amount of added H_2) used for nanocrystalline diamond deposition directly affects structural properties including surface morphology, film roughness, and grain size.^{63,64} The discussion presented here will consider data from both experimental and theoretical studies of the

simplest mechanistic case, nanocrystalline diamond deposition from an Ar/CH₄ plasma.⁶⁴⁻⁶⁷ Unlike microcrystalline diamond deposition in which methane radicals are the primary growth species, insertion of the carbon dimer radical (C₂) into the growing diamond lattice is thought to be the major mechanistic pathway for growth of nanocrystalline films.⁶⁴⁻⁶⁷ C₂ insertion into a diamond lattice is shown schematically in Figure 1.9. In this scheme, hydrogen abstraction of surface C-H bonds is not required. Rather, it is thought that growth proceeds through 1) C₂ insertion into a C-H surface site, 2) rotation and insertion of the other C atom into an adjacent C-H site, 3) insertion and 4) rotation of a second C₂ molecule into an nearby surface site, and 5) single bond formation between adjacent C₂ dimers within the carbon lattice.⁶⁸ This process is, in fact, energetically more favorable than the hydrogen abstraction reaction required for CH₄/H₂ plasmas. The activation energy was calculated to be ~5 kcal/mol for insertion of the C₂ dimer into a diamond (110) lattice,⁶⁵ while hydrogen abstraction requires ~25 kcal/mol.⁵³ Details of nanocrystalline diamond growth, including the effect of source gas composition on film morphology and measurement of C₂ plasma density, can be found elsewhere.⁶⁴⁻⁷¹

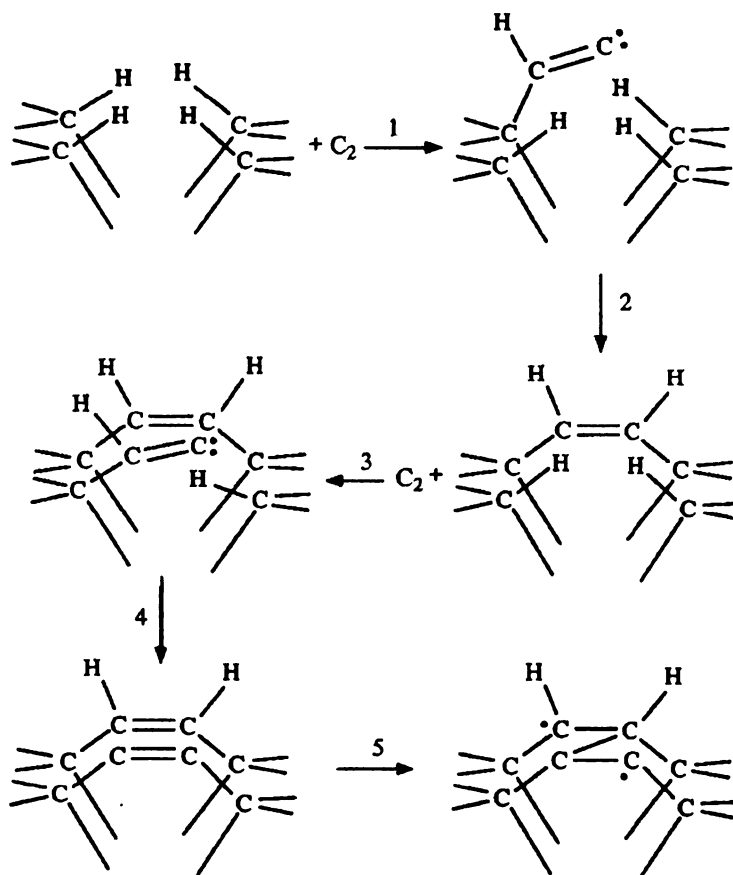


Figure 1.9 Proposed mechanism for nanocrystalline diamond growth by insertion of a C_2 dimer into the diamond lattice.⁶⁸

1.7 Research Goals and Objectives

Understanding the mechanisms by which the microstructure of current sp^2 -bonded carbon support materials degrade (i.e., changes in surface chemistry, mass, and microstructure) is one of the many technological challenges in modern fuel cell research. Morphological and microstructural degradation of carbon electrocatalyst supports leads to reduced fuel cell efficiency, reduced electrode lifetime, and eventually, complete electrode failure. There is still much to be learned in terms of how sp^2 -bonded carbon

supports degrade and, in particular, the structural and chemical property changes that lead to decreased fuel cell performance. The research presented in this dissertation was focused on developing a better understanding of the condition-specific limitations, as well as the structural factors, that lead to carbon degradation and corrosion in PEMFCs. In addition, work on an advanced material was undertaken to create a more stable support. The following research questions are addressed in the following chapters of this dissertation.

Chapter 3: Study of the Degradation Mechanisms of sp^2 -Bonded Carbon Powders During Electrochemical Polarization

- 1) Under what conditions (potential and temperature) do sp^2 -bonded carbon electrocatalyst support materials commonly used in PEMFCs undergo microstructural degradation and corrosion?
 - The morphological and microstructural degradation of structurally well-characterized sp^2 -bonded carbon powders (graphite and GC) were tested under controlled potential and temperature using chronoamperometry.
 - The carbon powders were studied by cyclic voltammetry, Raman spectroscopy, scanning electron microscopy (SEM), and XRD before and after potentiodynamic polarization to more fully understand the nature of the degradation.

2) What influence do microstructural degradation and corrosion have on the electrocatalyst activity and what influence does the electrocatalyst have on the carbon support degradation?

- The morphological and microstructural degradation of a PEMFC-relevant carbon black, Vulcan XC-72, with and without Pt, was investigated under controlled potential and temperature conditions using chronoamperometry.
- The bare and Pt-loaded Vulcan XC-72 powders were also fully characterized by cyclic voltammetry, Raman spectroscopy, and SEM before and after potentiodynamic polarization to better understand the influence of carbon structure and Pt on the degradation.

Chapter 4: The Electrochemical Performance of Diamond Thin-Film Electrodes from Different Commercial Sources

1) Is electrically conducting diamond a viable alternative material for fuel cell electrocatalyst supports in terms of the commercial availability of the material?

- The physical, chemical, and electrochemical properties of two commercial boron-doped diamond electrodes were compared with those of two electrodes (microcrystalline and nanocrystalline) grown in our laboratory.

Chapter 5: Preparation and Characterization of Boron-Doped Diamond Powder: A Possible Dimensionally Stable Electrocatalyst Support Material

and

Chapter 6: Preparation and Characterization of Boron-Doped Diamond Paper with Pt Nanoparticles

- 1) Can a high-surface-area advanced electrocatalyst support material be made based on electrically conducting diamond?
 - Microcrystalline conductive diamond powder and nanocrystalline diamond-coated carbon paper were grown via microwave plasma-assisted chemical vapor deposition.
- 2) What are the physical, chemical, and electrochemical properties and stability of these new materials with respect to sp^2 -bonded carbons?
 - The new diamond materials were studied using cyclic voltammetry, SEM, Raman spectroscopy, and XRD.
 - The long-term physical and electrochemical properties of these new sp^3 -bonded materials were compared to sp^2 -bonded carbon supports, under a variety of controlled potential and temperature conditions.
- 3) How does the electrodeposition of Pt on the new sp^3 -bonded carbon paper electrocatalyst support compare to electrodeposition on sp^2 -bonded carbon paper in terms of the electrochemical activity of the catalyst as well as particle density and size?

- Pt was electrodeposited onto diamond-coated carbon paper and bare carbon paper using pulsed galvanostatic deposition.
 - The physical and electrochemical properties of the metallized electrodes were evaluated using cyclic voltammetry, SEM, and Raman spectroscopy.
- 4) Are the composite sp^2 - and sp^3 -bonded paper electrodes stable during potentiostatic polarization?
- The Pt/diamond and Pt/carbon paper electrodes were subject to polarization at 1.6 and 1.8 V vs. SHE.
 - The physical and electrochemical properties of the electrodes were then studied using cyclic voltammetry, SEM, and Raman spectroscopy.

1.8 Dissertation Outline

This dissertation describes studies of the degradation and corrosion of sp^2 -bonded carbon support materials under controlled potential and temperature conditions, as well as the development of a new material based on electrically conducting diamond that may serve as an advanced electrocatalyst support material in fuel cells. In Chapter 2, the experimental parameters of the work in this dissertation including materials, instrumentation, and methods are presented. Evaluation of the morphological and microstructural stability of two model carbon materials, graphite and GC, with that of a high-surface-area carbon black, with and without Pt electrocatalyst, is presented Chapter 3. Chapter 4 establishes that high-quality boron-doped diamond electrodes are commercially available with reproducible properties. In this chapter, the physical,

chemical, and electrochemical properties of two commercial microcrystalline boron-doped diamond thin films, and microcrystalline and nanocrystalline boron-doped diamond thin film from our laboratory are compared. The fabrication and physical and electrochemical characterization of a boron-doped diamond powder is described in Chapter 5. The stability of this new material is compared to that of graphite and GC powders under controlled potential. Chapter 6 presents work on the fabrication of diamond-coated carbon paper to serve as a possible electrocatalyst support material. In this chapter, the electrodeposition of Pt on bare and diamond-coated carbon paper is described. The morphological and microstructural stability of this new diamond material is compared with that of uncoated carbon paper, with and without Pt. Finally, future directions for this research are proposed in Chapter 7.

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Chapter 2

Experimental Methods

2.1 Diamond Thin Film Growth

Conductive diamond thin film was grown on all substrates by microwave plasma-assisted chemical vapor deposition (CVD, 1.5 kW, ASTeX Inc., Lowell, MA). A block diagram of a typical reactor system is shown in Figure 2.1. Briefly, the source gases (e.g., Ar, H₂, CH₄, and B₂H₆) enter the chamber at controlled rates regulated by mass flow controllers. Microwave energy is focused into the quartz cavity and ignites a plasma. The plasma, which is in close proximity to the substrate, contains the reactive species important for growth. The chamber pressure is maintained by a throttle exhaust valve and rotary pump that is operated continuously during film growth.

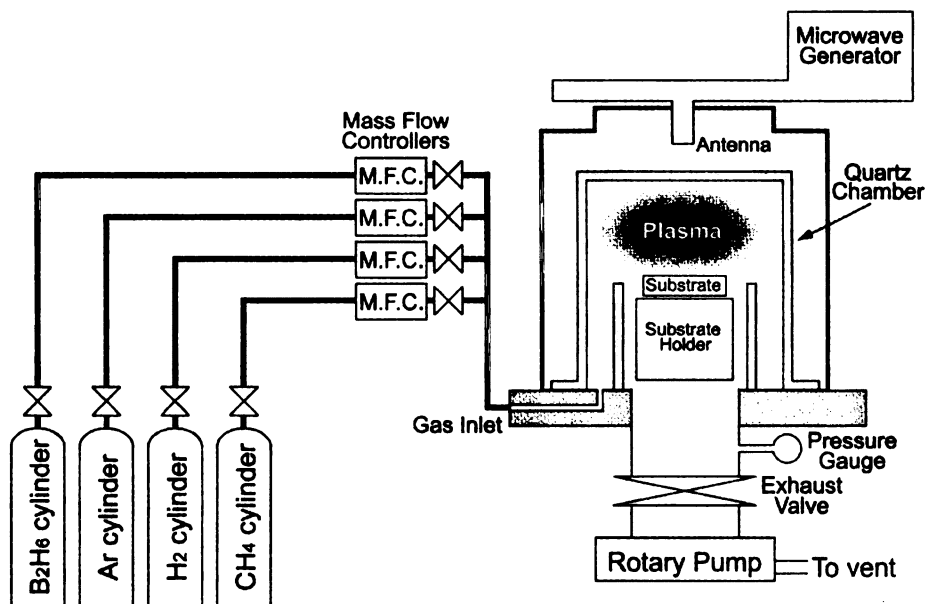


Figure 2.1 Schematic microwave plasma-assisted CVD reactor used to grow microcrystalline and nanocrystalline boron-doped diamond thin-film electrodes.¹

Microcrystalline and nanocrystalline diamond thin films were grown on *p-type* Si (111) (0.05 cm thick x 1 cm² in area, $\sim 10^{-3}$ Ω -cm, Virginia Semiconductor Inc., Fredricksburg, VA). The substrates were pretreated by mechanically scratching with 0-0.1 μ m diameter diamond powder (GE Superabrasives, Worthington, OH) on a felt polishing pad for 5 min. The scratched substrates were then washed sequentially with ultrapure water, isopropyl alcohol (IPA), acetone, IPA, and ultrapure water to remove polishing debris from the surface. Embedded diamond powder, as well as the defects introduced by the scratching, served as the initial nucleation sites.

The specific deposition conditions used for the growth of each diamond type on Si are listed in Table 2.1. All source gases were ultrahigh purity (99.999%). At the end of the deposition period, the CH₄ and B₂H₆ gas flows were stopped and the films remained exposed to a H₂ (microcrystalline) or an Ar/H₂ (nanocrystalline) plasma for an additional 10 min. The plasma power and pressure were slowly reduced over a 15 min period to cool the samples in the presence of atomic hydrogen to a temperature below 400 °C. The plasma power was then turned off and the films were cooled to room temperature under a flow of H₂ (microcrystalline) or Ar/H₂ (nanocrystalline). Typical diamond film thickness, resistivity, carrier concentration, and carrier mobility are listed in Table 2.2.

Boron-doped microcrystalline diamond thin film, deposited on conducting Si, was also purchased from CONDIAS GmbH (DIACHEM[®], 0.01 cm thick x 1 cm², Germany) and Sumitomo Electric Industries, Ltd. (0.5 cm thick x 7.3 cm² in area, #SHMF-16128-1, Japan). The exact deposition conditions were not disclosed.

Table 2.1 Growth conditions for microcrystalline and nanocrystalline boron-doped diamond thin film deposited on Si.

	Microcrystalline	Nanocrystalline
Microwave Power	1000 W	800 W
Chamber Pressure	45 Torr	140 Torr
Gas Mixture	CH ₄ /H ₂ /B ₂ H ₆	Ar/H ₂ /CH ₄ /B ₂ H ₆
Methane Concentration	0.5% CH ₄	1% CH ₄
Dopant	10 ppm B ₂ H ₆	10 ppm B ₂ H ₆
Total Gas Flow	200 sccm	100 sccm
Substrate Temperature	~800 °C	~800 °C
Growth Time	10 h	2 h

Table 2.2 Film thickness, resistivity, carrier concentration, and carrier mobility for typical microcrystalline and nanocrystalline boron-doped diamond thin film.¹⁻³

Type	Film Thickness (μm)	Resistivity (Ω-cm)	Carrier Concentration (cm ⁻³)	Carrier Mobility (cm ² /V-s)
Microcrystalline	~5-7 μm	0.01 – 0.1	~10 ²⁰	10-40
Nanocrystalline	~4 μm	0.2	~10 ²⁰	90

The diamond powder (8-12 μm diam [$\sim 2 \text{ m}^2/\text{g}$], GE Micron Products) was prepared for deposition by sequential cleaning in warm aqua regia (30 min) and warm 30% hydrogen peroxide (30 min) to remove nondiamond sp^2 -bonded carbon and metallic impurities. The clean powder was then copiously rinsed with ultrapure water, IPA, and acetone, filtered, and dried. A portion of the clean powder (*ca.* 15 mg) was thinly spread over the surface of an undoped Si (100) wafer (Virginia Semiconductor Inc., Fredricksburg, VA) and placed in the CVD reactor. The deposition conditions are listed

in Table 2.3. At the end of deposition period the CH₄ and B₂H₆ gas flows were stopped and the powder remained exposed to a H₂ plasma for an additional 10 min. The plasma power and pressure were slowly reduced over a 15 min period to cool the samples (< 400 °C) in the presence of atomic hydrogen. The plasma power was then turned off, and the powder was cooled to room temperature under a flow of H₂.

Table 2.3 Growth conditions for coating insulating diamond powder with a conducting diamond overlayer.

Diamond Powder	
Microwave Power	1000 W
Chamber Pressure	45 Torr
Gas Mixture	CH ₄ /H ₂ /B ₂ H ₆
Methane Concentration	1% CH ₄
Dopant	20 ppm B ₂ H ₆
Total Gas Flow	200 sccm
Substrate Temperature	~800 °C
Growth Time	1,2,4, or 6 h

While this approach led to both full and partial coating of the powder particles, it was not the most ideal because of the difficulty ensuring uniform plasma/gas contact with the entire particle surface. Additionally, the variable height of the powder particles in the plasma led to temperature variations during film growth, which caused differences in overlayer thickness and microstructural quality. Particles that experienced higher temperatures had more nondiamond carbon impurity content.

Carbon paper (Toray TGP-H, 0.19 mm thick, ElectroChem, Inc., Woburn, MA) was cut into *ca.* 1x1 cm² squares and seeded for growth by sonication in a slurry

containing 2 mg of 0-0.1 μm diameter diamond powder (GE Superabrasives, Worthington, OH) in 100 mL ethanol, for 10 min. The substrates were then dried and placed in the CVD reactor. The deposition conditions used to coat the carbon paper are presented in Table 2.4. At the end of deposition period the CH_4 and B_2H_6 gas flows were stopped and the paper remained exposed to an Ar/H_2 plasma for an additional 10 min. The plasma power and pressure were slowly reduced over a 15 min period to cool the samples in the presence of atomic hydrogen to a temperature below 400 $^\circ\text{C}$. The plasma power was then turned off, and the paper was cooled to room temperature under a flow of Ar/H_2 . After growth on one side, the substrate was removed from the CVD reactor, reseeded by sonication in the diamond/ethanol slurry for an additional 10 min, and placed back in the CVD reactor. Growth was then completed on the backside using the same deposition conditions. The same cool-down procedure was used after the second growth.

Table 2.4 Growth conditions for coating carbon paper with boron-doped nanocrystalline diamond.

Carbon Paper	
Microwave Power	800 W
Chamber Pressure	140 Torr
Gas Mixture	$\text{Ar}/\text{CH}_4/\text{H}_2/\text{B}_2\text{H}_6$
Methane Concentration	1% CH_4
Dopant	10 ppm B_2H_6
Total Gas Flow	100 sccm
Substrate Temperature	$\sim 800^\circ\text{C}$
Growth Time	2 h

2.2 Material Characterization

A number of analytical methods were used to characterize the diamond properties, including crystallinity (X-ray diffraction), microstructure (Raman), morphology (scanning electron microscopy), and electrical conductivity (current-voltage curves). These same methods were also employed to assess the chemical and physical changes of the sp^2 - and sp^3 -bonded carbon samples before and after applied potential.

2.2.1 Scanning Electron Microscopy (SEM)

Sample morphology was probed by SEM using a JEOL-6400F microscope (JEOL Ltd., Tokyo, Japan) with a 20 kV accelerating voltage and a working distance of 15 mm. The diamond thin film on Si and the carbon paper samples were mounted on aluminum subs with conductive carbon tape. Carbon powder samples (on glass or Si) were attached to aluminum stubs with conductive carbon tape and coated with a thin layer of gold to reduce surface charging effects and to improve the SEM image quality.

2.2.2 X-Ray Diffraction Spectroscopy (XRD)

Crystallinity of diamond (powder and paper) was studied by XRD. Spectra were obtained by scanning 2θ from 20 to 100 on a Rikagu Rotaflex RTP300 RC instrument. X-rays were produced at 1.540 Å from a Cu anode.

2.2.3 Raman Spectroscopy

Microstructure of the carbons was evaluated using Raman spectroscopy. Spectra were acquired at room temperature, using a RAMAN 2000 spectrograph (Chromex, Inc.,

Albuquerque, NM) consisting of a diode-pumped, frequency-doubled CW Nd:YAG laser (500 mW at 532 nm, COHERENT), with a holographic grating ($f/4$, 600 grooves/mm), and a thermoelectrically cooled 1024x256 element charge-coupled device (CCD) detector (ANDOR Tech., Ltd.). Spectra were collected with an incident power density of ca. 500 kW/cm² (100 mW at the sample and 5 μ m diameter spot size) and a 10 s integration time. A white-light spectrum was collected under the same conditions and served as the background spectrum to which the spectra were referenced. The Raman instrument was calibrated using a high-pressure, high-temperature (HPHT), single crystal diamond sample (first-order phonon position = 1332 cm⁻¹).

2.2.4 Electrical Resistance

Four-point probe measurements were used to evaluate the resistivity of the planar diamond thin film. Electrical measurements were used to evaluate the resistance of the conductive diamond powders and were made by placing a fixed quantity of the powder (ca. 20 mg) between a metal plate (bottom) and a metal rod (top), and measuring the contact-to-contact resistance with an ohmmeter. The powder resistance was also measured from i - V curves recorded between ± 10 V. The current was measured in series with the resistive powder as a function of the applied dc voltage, as shown in Figure 2.2. The plate-to-plate distance with the powder sample was ca. 2 mm. A 200 g weight was placed on the top metal rod contact to ensure that a constant force was applied during a measurement. The short-circuit resistance between the two plates was measured first and was always near 0 Ω .

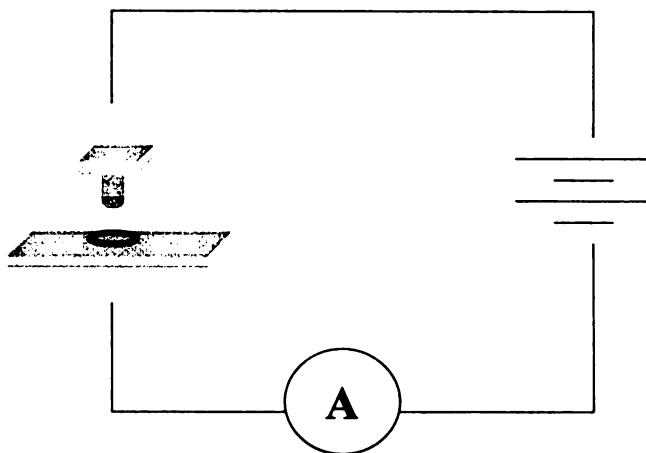


Figure 2.2 Schematic of the apparatus used to measure i - V curves for the powder samples. This same general scheme was used to measure the powder resistance with an ohmmeter, simply by removing the power supply and ammeter.

2.3 *Electrochemical Characterization*

Electrochemical measurements were at the core of the material characterization performed on the electrodes. Cyclic voltammetry was used to 1) assess the electrochemical reaction kinetics for several redox systems at diamond thin films deposited on Si, 2) probe the electrochemical properties of conductive diamond powder and diamond-coated carbon paper, 3) evaluate the microstructural stability of diamond and commercial carbon powders, and 4) study the electrochemical properties of Pt nanoparticles electrodeposited on carbon paper and diamond-coated carbon paper. The morphological and microstructural stability of several sp^2 - and sp^3 -bonded carbon powders was studied at PEMFC-relevant potentials and temperatures using chronoamperometry. Finally, pulsed galvanostatic electrodeposition of Pt was used to deposit the electrocatalyst on bare and diamond-coated carbon paper. Basic theory and

operating principles of the electrochemical techniques used in this work can be found elsewhere.⁴⁻⁷

All of the electrochemical measurements, except Pt deposition, were performed using a CHI650a computerized potentiostat (CH Instruments Inc., Austin, TX) with a graphite rod counter electrode and a Ag/AgCl reference electrode (3 M NaCl, $E^{\circ'} = -45$ mV vs. SCE). All measurements were made at room temperature (25 ± 1 °C), unless otherwise noted, and all solutions were deoxygenated with N₂ for at least 20 min prior to a measurement and blanketed with the gas during the measurement. Details of the electrode preparation procedures and the electrochemical cells used for each electrode morphology are provided below. This is followed with a description of the experimental approaches for assessing electrode reaction kinetics, morphological and microstructural stability, and electrocatalytic activity.

2.3.1 Electrode Preparation and Experimental Setup

2.3.1.1 Diamond Thin-Film Electrodes on Si

The diamond thin film electrodes on Si (~0.2 cm² area) were sealed against the bottom of a single-compartment electrochemical cell with a Viton[®] o-ring, as shown in Figure 2.3.³ The backside of the Si substrate was scratched, cleaned, and coated with graphite in order to ensure good ohmic contact with a metal current collector plate. All electrodes were used after a 20 min soak in distilled isopropyl alcohol.^{2,8}

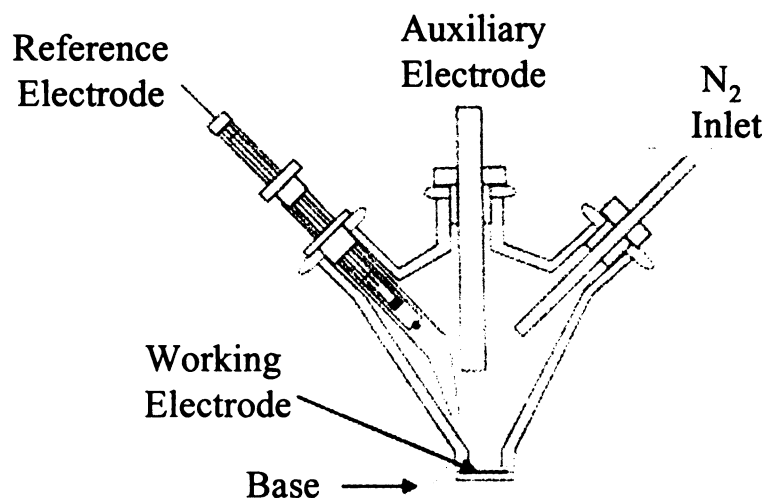


Figure 2.3 Design of the single compartment, glass, three-electrode electrochemical cell. (Adapted from ref 3)

2.3.1.2 Carbon Powder Electrodes

Conductive diamond, graphite (Superior Graphite Co., Bedford Park, IL), glassy carbon (GC) powder (SIGRADUR[®] G, HTW GmBH, Germany), and carbon black (Vulcan XC-72, Electrochem, Inc, Woburn, MA), with and without Pt (20 wt. %), were thoroughly mixed with a (10 wt. %) polytetrafluoroethylene (PTFE, 60 wt. % in H₂O, Aldrich) binder and a few mL of distilled isopropyl alcohol. Each electrode contained ~10 mg carbon powder. The diamond, graphite, and GC slurries were cast on a clean glass slide using a pipet and dried overnight in air. The Vulcan XC-72 slurry was spread over a microcrystalline diamond thin film (0.5 % CH₄ in H₂, 10 ppm B₂H₆, 6 h deposition). During the solvent evaporation, the slurry was smoothed and spread over the diamond electrode with successive passes of a Teflon-coated razor blade. This was necessary to limit agglomeration of the carbon black particles and produce a thin, crack-free film. In terms of preparation of powder electrode with a binder, the Vulcan powder

was the most challenging to work with, requiring extreme care during electrode fabrication. After the initial solvent evaporation in air, all electrodes were heated in an oven (air atmosphere) for 30 min at 280 °C and for 30 min at 350 °C. This final heat treatment was found to be necessary to mechanically strengthen the electrodes.

The powder electrodes, mounted on glass slides, were pressed against a Viton[®] o-ring (~0.2 cm² area) at the bottom of a single compartment glass electrochemical cell. Electrical contact was made to the diamond, graphite, and GC powders by pressing copper foil against the surface of the powder outside the o-ring. Electrical contact with the Vulcan XC-72 powder was made through the microcrystalline diamond thin-film electrode. The electrode area in contact with the solution was estimated from the cyclic voltammetric background current according to Equation 2.1:

$$A = \frac{i_{ch}}{C_{dl}\nu} \quad (2.1)$$

where A is the electrode area in cm², i_{ch} is the anodic current at 800 mV in μ A, C_{dl} is the capacitance of the electrode (~5 μ F/cm² for diamond, ~35 μ F/cm² for graphite, GC, and Vulcan XC-72),⁹ and ν is the scan rate in V/s. 800 mV was chosen because it was the flattest region of the background cyclic voltammetric i - E curve for all carbon powders and the only region in which the measured current could be assumed to be all capacitive in nature. Note: The background current for the microcrystalline boron-doped diamond thin-film electrode was not subtracted from that of the Vulcan XC-72 because it was *ca.* 3 orders lower in magnitude and did not significantly contribute to the electrochemical signal.

2.3.1.3 Carbon Paper Electrodes

Conductive epoxy (Chemtronics, Kennesaw, GA) was used to seal a Cu wire (Aldrich) to the bare and diamond-coated carbon paper. The epoxy was cured by heating at 80 °C for 20 min in an oven. The bare Cu wire was wrapped in Teflon tape (Aldrich) and the entire wire and epoxy section was coated with nail polish, as shown in Figure 2.4. For the solutions used in this work, the nail polish was stable and electrically insulated this section from solution contact. The sealed electrodes were fully immersed in electrolyte contained in a beaker for electrochemical measurements. Unless otherwise noted, the electrode area in contact with solution was estimated from the anodic current at 0 mV using Equation 2.2, as described for the carbon powder electrodes above.

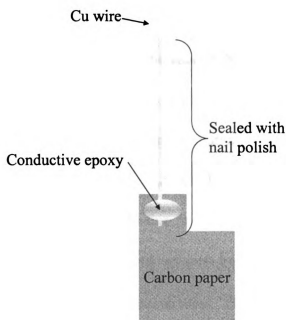


Figure 2.4 Carbon paper electrode preparation schematic.

2.3.2 Electrochemical Kinetics

The electrochemical kinetics for a number of redox systems on microcrystalline and nanocrystalline boron-doped diamond thin-film electrodes are described in Chapter 4. The apparent heterogeneous electron-transfer rate constant, k_{app}^o , for $\text{Fe}(\text{CN})_6^{3-/4-}$, $\text{Ru}(\text{NH}_3)_6^{3+/2+}$, and $\text{IrCl}_6^{2-/3-}$ was determined from cyclic voltammetric data (ΔE_p - ν dependence) using the method developed by Nicholson.⁷ According to theory, ΔE_p for an electrochemical reaction is dependent on the scan rate (ν , V/s), transfer coefficient (α), and heterogeneous electron-transfer rate constant (k^o , cm/s). The behavior of quasireversible reactions can be described by the Equation 2.2:

$$\psi = \frac{(\frac{D_{ox}}{D_{red}})^{\alpha/2} k^o}{(\pi D_{ox} f \nu)^{1/2}} \quad (2.2)$$

where D_{ox} and D_{red} are the diffusion coefficients of the oxidized and reduced species (cm^2/s), respectively, f is the Faraday constant divided by the ideal gas constant and temperature (F/RT), and Ψ is a dimensionless parameter. Nicholson derived an experimental relationship between Ψ and ΔE_p such that k^o can be calculated from the above equation at different scan rates. In this research, ΔE_p varied over the scan rate range tested and the apparent heterogeneous electron-transfer rate constant, k_{app}^o , was statistically determined from data at several scan rates. The rate constants are referred to as apparent, because no correction for any electric double layer effects was made. k_{app}^o was additionally determined through digital simulation of the cyclic voltammetric i - E curves, using DigiSim[®] 3.03 (Bioanalytical Systems, Inc., W. Lafayette, IN). In all cases,

the simulated ΔE_p for a given k_{app}^o value differed from the experimental value by 9 mV, or less, at scan rates up to 50 V/s. The following diffusion coefficients were used for the redox couples, assuming $D_{ox}=D_{red}$: $\text{Fe}(\text{CN})_6^{3-/4-}$, ($7.6 \times 10^{-6} \text{ cm}^2/\text{s}$), $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ ($5.5 \times 10^{-6} \text{ cm}^2/\text{s}$), $\text{IrCl}_6^{2-/3-}$ ($6.8 \times 10^{-6} \text{ cm}^2/\text{s}$), 4-MC ($6.0 \times 10^{-6} \text{ cm}^2/\text{s}$), and $\text{Fe}^{3+/2+}$ ($9.0 \times 10^{-6} \text{ cm}^2/\text{s}$).^{10,11}

2.3.3 Polarization Studies

Carbon powder and paper electrodes were subjected to applied potentials from 1.0 to 1.6 V vs. Ag/AgCl at 25, 50, and 80 °C in 0.1 M HClO_4 for 1 h periods. The measurements were performed in the chronoamperometric mode with the current (hence, charge) being recorded as a function of time. The single compartment glass electrochemical cell was wrapped with heating tape powered by a Variac for temperature control. The solution temperature was measured before and after the polarization and remained constant (± 5 °C). The reference electrode temperature was not directly controlled and was likely between that of room temperature and solution temperature. The recorded current-time profiles were integrated to determine the charge passed at a given potential. For a faradaic process, the charge passed is related to the number of moles electrolyzed according to Equation 2.3:

$$Q = nFN \quad (2.3)$$

where Q is the integrated charge (Coulombs), n is the number of electrons involved per reaction, F is the Faraday constant, and N is the number of moles electrolyzed.

2.3.4 Pt Electrodeposition

Electrocatalytic Pt particles were deposited on diamond-coated and bare carbon paper electrodes from a solution of 1 mM potassium hexachloroplatinate(IV) dissolved in 0.1 M HClO₄. A pulsed galvanostatic method was employed for deposition, as discussed in Chapter 6. A homemade galvanostat, constructed with an OMNI 90 potentiostat (Cypress Systems, Inc., Lawrence, KS), was interfaced with a PCI-6034E controller and data acquisition board (National Instruments, Austin, TX). LabVIEW software (version 6.0, National Instruments) was used to control the pulse generation, which was performed at 1 Hz with a 25% duty cycle, resulting in an on-time of 200 ms and an off-time of 800 ms per pulse. Cyclic voltammograms were recorded before and after Pt electrodeposition to assess the presence of Pt on the electrode surface. The Pt surface area was determined by integrating the cyclic voltammetric charge (cathodic cycle) between 0.15 to -0.2 V vs. Ag/AgCl, which is associated with H adsorption. This calculation assumes a 1H:1Pt surface interaction and a surface charge of 210 $\mu\text{C}/\text{cm}^2$ for hydrogen adsorption on an atomically flat Pt(111) surface.^{12,13}

2.4 Reagents

All chemicals were analytical-grade quality, or better, and were used without additional purification. Solutions of 0.1 mM potassium ferrocyanide (Aldrich), potassium hexachloroiridate (IV) (Aldrich), hexaammineruthenium (III) chloride (Aldrich) in 1 M potassium chloride (Spectrum), and 0.1 mM ferric sulfate (Matheson, Coleman, and Bell) and 0.1 mM 4-methylcatechol (Aldrich) in 0.1 M perchloric acid (redistilled 99.999%, Aldrich) were made. Solutions of 1 M potassium phosphate buffer

with 0.1 mM potassium ferrocyanide and 0.1 mM hexaammineruthenium (III) chloride at pH values of 1.90 and 7.35 were prepared using the appropriate molar ratios of phosphoric acid (Aldrich), sodium phosphate dibasic (Columbus Chemical Industries, Inc.), and sodium phosphate (Columbus Chemical Industries, Inc.). The appropriate amount of potassium hexachloroplatinate(IV) (98%, Aldrich) was dissolved in 0.1 M HClO_4 to make a 1 mM solution. All redox analyte solutions were prepared daily using ultrapure water ($>18 \text{ M}\Omega\text{-cm}$) from an E-pure water purification system (Barnstead) in glassware that was cleaned by a three-step process: ethanol/KOH bath, alconox/ultrapure water solution, and an ultrapure water rinse.

2.5 *References*

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Chapter 3

Study of the Degradation Mechanisms of sp^2 -Bonded Carbon Powders During Electrochemical Polarization

Abstract

Two microstructurally well-characterized carbon powders, graphite and glassy carbon (GC), were studied under potentiostatic polarization using conditions that mimic those of a polymer electrolyte membrane fuel cell (0.8 to 1.6 V vs. Ag/AgCl and 25, 50, and 80 °C). Electrochemical (cyclic voltammetry) and spectroscopic (Raman) characterizations were completed before and after polarization to determine the extent of carbon oxidation and microstructural degradation. Several important results may provide insight on the degradation mechanisms of sp^2 -bonded carbon electrocatalyst supports (e.g., carbon blacks). First, there was evidence of oxidation of graphite and GC at low potential (1.0 V) and temperature (25 °C), caused by oxidation of exposed edge plane. The extent of surface oxidation was larger for GC, a material with a higher edge plane density. Second, as the potential and temperature were raised, the edge plane density for graphite heterogeneously increased across the electrode surface, likely because of intercalation and fracturing of the graphite lattice. The heterogeneity of this corrosion is indicative of a nucleation and growth process, where disordered regions and defects serve as the active sites for electrochemical corrosion, while other, more structurally ordered regions do not corrode. Third, increases in the graphite edge plane density correlated well with changes in the surface carbon-oxygen content, suggesting that fracturing of the

graphite lattice, perhaps as a result of intercalation, exposed additional carbon edge plane. Fourth, the charge passed during potentiostatic polarization, as well as the increase in surface oxide coverage was always larger for GC than for graphite. Moreover, there were no noticeable changes in the GC microstructure after polarization at most potentials and temperatures. These results provide evidence for the so-called order/disorder mechanism where structurally disordered carbons corrode more severely because of oxidation and gasification of the exposed edge plane. Preliminary results for the potentiostatic polarization (0.8 to 1.4 V vs. Ag/AgCl at 25, 50, and 80 °C) of a carbon black commonly used in fuel cells, Vulcan XC-72, show that the charge passed is not sensitive to cell temperature, but changes as a function of the applied potential. Oxidation of Vulcan XC-72 seemed to play a major role in the corrosion, with evidence for possible gasification at higher potentials (1.4 V). The charge recorded as a function of polarization potential and temperature under similar conditions for a Pt-loaded (20 wt. %) Vulcan XC-72 showed similar behavior. Significant Pt surface area was lost (>30%) after polarization at 1.2 V and all temperatures. This could possibly be due to corrosion of the carbon support and subsequent loss of electrocatalyst, as well as electrocatalyst corrosion. Changes in the cyclic voltammetric *i*-*E* curve, including a decrease in the current for Pt-oxide formation, as well as for hydrogen adsorption/desorption on Pt were noted after polarization at 50 and 80 °C. The curves were also characterized by significant electrode resistance after 1.2 and 1.4 V at 80 °C, likely because of severe support gasification.

3.1 Introduction

The electrochemical corrosion of sp^2 -bonded carbon electrocatalyst supports (e.g., carbon black) in the phosphoric acid fuel cell environment (PAFC, 96% H_3PO_4 , $>100\text{ }^\circ\text{C}$) is well studied.¹⁻⁸ Although it was originally thought that corrosion of these same materials was not a problem at the low operating temperature ($\sim 80\text{ }^\circ\text{C}$) and potential ($\sim 0.7\text{ V}$ vs. SHE) of the PEMFC, it has recently been recognized that some of the performance degradation of PEMFCs is due to corrosion of the sp^2 -bonded carbon electrocatalyst support when the cell is subject to potentials above the normal operating voltage.⁹⁻¹³ Kangasniemi and co-workers studied the electrochemical surface oxidation of a common carbon electrocatalyst support in fuel cells, Vulcan XC-72, during potentiostatic polarization from 0.8 to 1.2 V vs. SHE for 16, 60, and 120 h, without the Pt electrocatalyst.¹⁰ Most of the experiments in this report were done at $25\text{ }^\circ\text{C}$, although polarization carried out at $65\text{ }^\circ\text{C}$ was also briefly discussed.¹⁰ Using cyclic voltammetry, X-ray photoelectron spectroscopy, and thermal gravimetric analysis coupled with on-line mass spectrometry, they provided evidence for carbon oxidation at potentials $\geq 1.0\text{ V}$ vs. SHE at $25\text{ }^\circ\text{C}$ and $\geq 0.8\text{ V}$ vs. SHE at $65\text{ }^\circ\text{C}$.¹⁰ Roen and co-workers studied the influence of Pt on carbon corrosion, utilizing cyclic voltammetric measurements with on-line mass spectrometry.¹¹ In this study, CO_2 generation increased as the Pt mass fraction increased (0, 10, and 39%).¹¹ In addition, studies at 30, 50, and $70\text{ }^\circ\text{C}$ showed a lower apparent activation energy for gasification of Vulcan XC-72 with Pt as compared to the bare carbon.¹¹ Dahn and co-workers have studied the thermal degradation of two carbon blacks, Vulcan XC-72 and BP2000, with and without Pt, in dry and humidified air, and at high temperatures (125 to $195\text{ }^\circ\text{C}$).^{12,13} In these studies, it was shown that increasing

mass fraction of Pt, humidity, and higher carbon surface areas all increased the carbon corrosion.^{12,13}

Although these reports have presented some useful data about the conditions that cause support corrosion, they do not investigate the fundamental structural and microstructural causes of carbon corrosion. The early PAFC corrosion work showed that carbon black corrosion proceeds through a two-step process, which includes oxidation of carbon edge plane and defect sites and gasification of surface oxides to CO₂.⁵ Corrosion of the structurally disordered regions occurs first, but the more graphitic regions are also susceptible to corrosion during prolonged exposure harsh conditions.⁴ It is unclear if this same process, the so-called order/disorder mechanism, occurs in the PEMFC. The extent of degradation (i.e., surface oxidation or carbon gasification) is also unclear. Elucidation of the degradation mechanism and the effect that electrocatalyst support degradation has on the activity of the electrocatalyst is an important task, not only to better understand the conditions that cause support degradation, but also to enable the systematic development an advanced material that will exhibit superior stability in a PEMFC.

An extensive amount of research has been published about the electrochemical corrosion of *sp*²-bonded carbons such as highly-oriented pyrolytic graphite (HOPG) and glassy carbon (GC). It would be advantageous to utilize this large body of literature and draw parallels between the carbon electrochemical literature and the electrochemical corrosion of carbon in PEMFCs to more fully elucidate the carbon degradation mechanism. It is well known in the electrochemical community that the electrochemical nature of *sp*²-bonded carbons, including the electron-transfer rate and dimensional stability, depends strongly on microstructure, surface roughness, and the presence of

physi- and chemisorbed species.¹⁴⁻¹⁸ McCreery and co-workers systematically studied the electrochemical reaction kinetics for common redox analytes on sp^2 -bonded carbons of varying microstructure (i.e., differences in edge to basal plane ratio) and electrode pretreatment (e.g., laser activation and polishing) to elucidate the relationship between carbon type and electrochemical reactivity and stability.^{15-17,19-21} Of specific importance to the fuel cell community, two reports paired electrochemical methods with Raman spectroscopic investigations to yield a wealth of information about the dependence of the electron-transfer rate on the presence of carbon edge plane.^{19,21} Carbon electrodes with a higher edge plane density (e.g., GC with respect to HOPG) exhibited orders of magnitude higher heterogeneous electron-transfer rate constants for redox systems such as $\text{Fe}(\text{CN})_6^{3-/4-}$.²¹ McCreery and co-workers also showed that the electron-transfer rate for electrodes that did not have a significant edge plane density (e.g., HOPG) could be increased by fracturing the graphite plane via electrochemical pretreatment (i.e., holding the electrode at anodic potentials) or by laser activation.¹⁹ In this study, parallel Raman spectroscopic investigations revealed that both laser activation and electrochemical pretreatment at potentials >1.6 V vs. Ag/AgCl increased the edge plane density of HOPG.¹⁹

Detailed studies of the HOPG degradation mechanism during electrochemical pretreatment using Raman spectroscopy, atomic force microscopy, optical microscopy, and scanning electron microscopy have shown that intercalation plays a significant role in damage of the sp^2 -bonded carbon lattice.^{20,22} From Raman spectroscopic analysis of short (2 min) potential steps up to 2.0 V vs. the sodium saturated calomel electrode, Alsmeyer and McCreery showed that (1) anion intercalation always preceded lattice

damage and (2) intercalation did not necessarily result in lattice damage.²⁰ For example, there was no increase in the edge plane density (i.e., lattice damage) for intercalation in 1 M NaClO₄, while potential excursions in 1 M HClO₄, HNO₃, and H₂SO₄ resulted in lattice damage.²⁰ Damage of the graphite lattice is thought to occur because of strain caused by the formation of oxides after intercalation.²⁰ From this, a general mechanism of corrosion and oxidation for graphitic carbons can be proposed, which is shown in Figure 3.1. This mechanism includes: (i) anion intercalation between the graphite layers which causes distortion in the graphene layer d_{002} spacing, (ii) exfoliation of the layers creating new edge plane density, (iii) oxidation of new edge plane sites, and (iv) gasification of surface oxides to CO and CO₂.

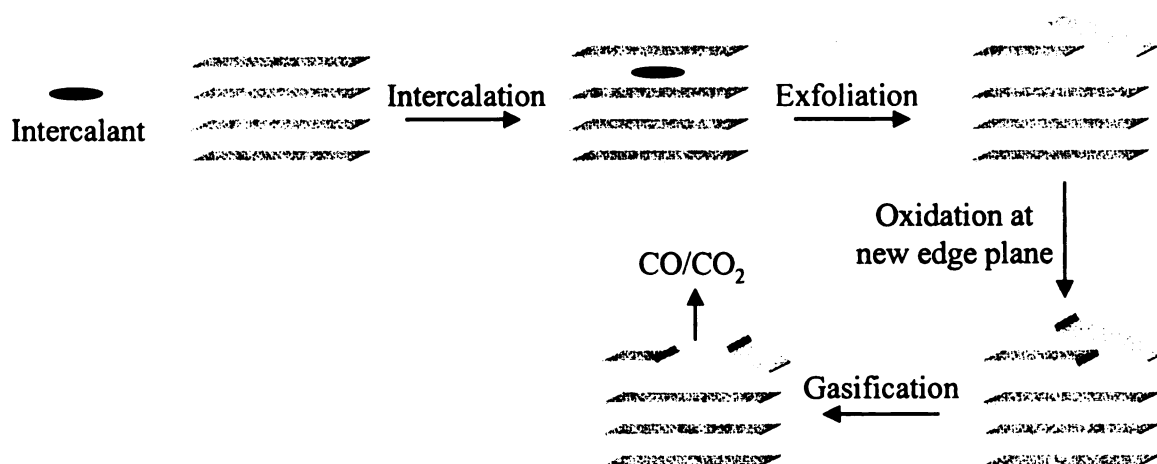


Figure 3.1 Schematic of the oxidation of graphitic carbons including intercalation and exfoliation of the graphite lattice, oxidation of new exposed edge plane, and gasification (corrosion) to CO and CO₂.

This chapter presents a first step towards elucidation of the mechanism of carbon corrosion in PEMFCs. In this work, the electrochemical (cyclic voltammetry) and spectroscopic (Raman) changes for two structurally well-characterized sp^2 -bonded carbon

powders, graphite (structurally well-ordered) and GC (structurally disordered), were compared under different PEMFC-relevant potential and temperature conditions. Comparisons are drawn from the well-known electrochemical and Raman spectroscopic literature of sp^2 -bonded carbons studied by McCreery and co-workers to propose a degradation mechanism. Data were also collected for a structurally disordered sp^2 -bonded carbon commonly used in PEMFCs, Vulcan XC-72 (with and without Pt electrocatalyst), under similar potential and temperature conditions. Preliminary results from these experiments will be discussed.

3.2 Results and Discussion

3.2.1 Anodic Polarization of Graphite and Glassy Carbon (GC) Powders

Chronoamperometric i - t curves for graphite and GC powder electrodes recorded in 0.1 M HClO₄ during potentiostatic polarization at 1.0 and 1.6 V vs. Ag/AgCl (25 °C) are shown in Figure 3.2. The curves are plotted against current (A) and log current (B) to more clearly show the differences for the carbons at different polarization potentials. All currents, unless otherwise noted, are normalized to the apparent electrode area in contact with the solution, as described in Chapter 2. 1.0 and 1.6 V were selected as an initial comparison because 1.0 V vs. Ag/AgCl is equal to *ca.* 1.2 V vs. SHE (the PEMFC E°) and 1.6 V vs. Ag/AgCl represents an extreme potential value. The current density for all curves increases sharply at short times due to charging of the electrical double layer (nonfaradaic), followed by an initial rapid decrease. The current recorded for graphite and GC at 1.0 V quickly reaches a relatively steady-state value of *ca.* 0.02 and 0.07 $\mu\text{A}/\text{cm}^2$, respectively. In contrast, the current for graphite and GC at 1.6 V increases over

the 1 h period, after the initial decay of nonfaradaic current. Importantly, the current for GC is significantly higher during polarization at 1.6 V than that for graphite at the same potential.

Current recorded in a chronoamperometric experiment, in the absence of an electroactive surface or solution species (i.e., nonfaradaic), is expected to decay with e^{-t} behavior, quickly reaching a non-zero, steady-state value. The magnitude of this steady-state current depends on experimental variables such as the electrode capacitance. Thus, the increase in current for graphite and GC electrodes anodically polarized at 1.6 V relative to the current recorded during polarization at 1.0 V may provide evidence for faradaic electrochemical reactions occurring at the electrode surface. Surface electrochemical reactions such as oxidation of the carbon edge plane, carbon gasification to CO_2 , and intercalation of solvent molecules are common in acidic solutions at these potentials.^{2,6,14,20-23} However, it is also possible that the increase in current is a result of delamination of the polytetrafluoroethylene binder which would expose additional electrode area to the solution. In fact, it is difficult to determine the nature of the current in a chronoamperometric experiment solely from the $i-t$ profile. Other electrochemical (cyclic voltammetry) and spectroscopic (Raman) experiments are necessary in the case of these carbon powders to confirm surface oxidation and microstructural degradation, respectively, and will be presented later.

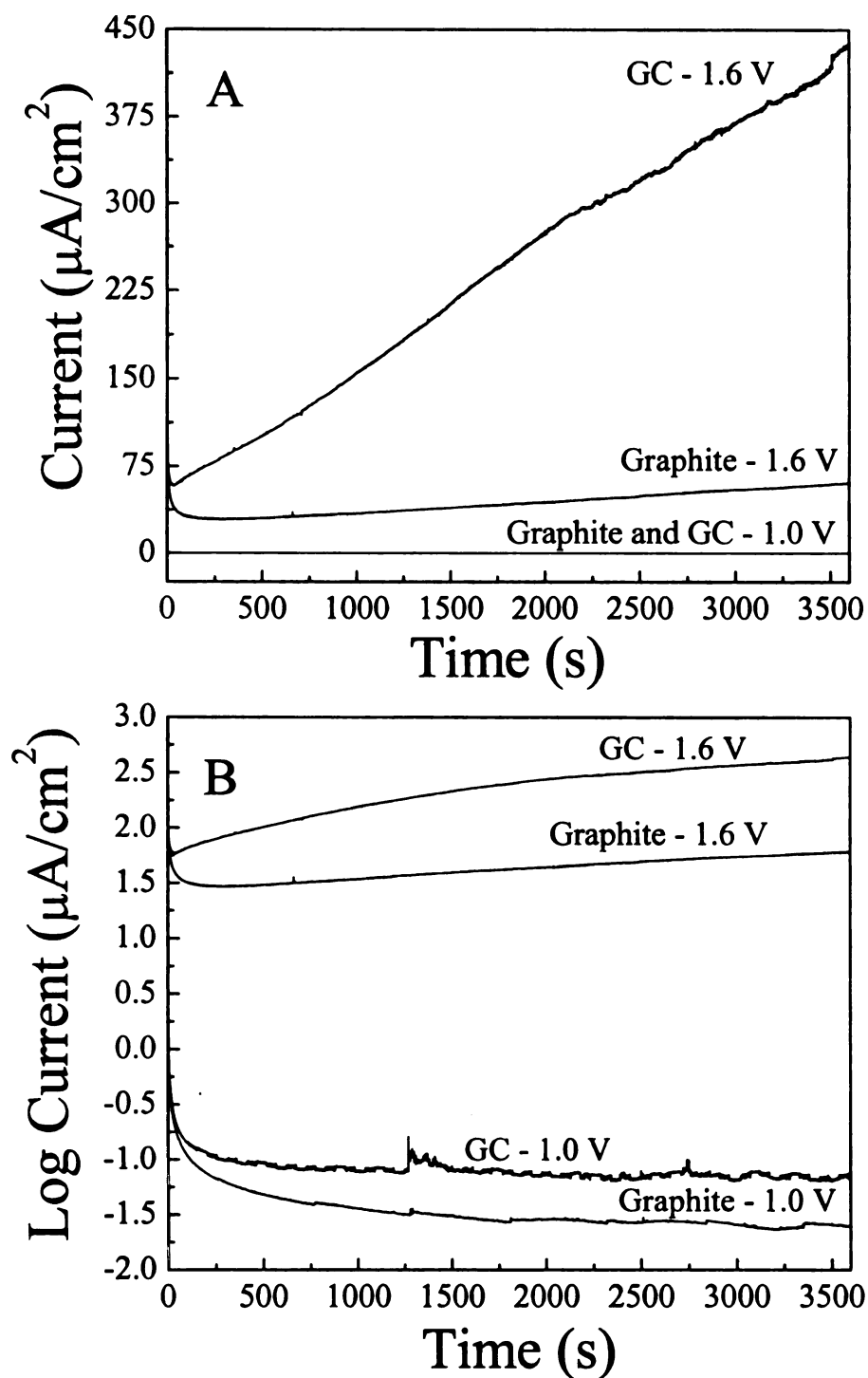


Figure 3.2 Amperometric $i-t$ curves for graphite and GC powders during a 1 h polarization at 1.0 and 1.6 V vs. Ag/AgCl in 0.1 M HClO₄ at 25 °C. The top curve (A) is a plot of current and the bottom curve (B) is a plot of the logarithm of the current.

Integration of the i - t curve yields the charge passed during polarization, which is a sum of the charge to form the electric double layer, the charge for formation of surface carbon-oxygen functionalities, and the charge due to gasification of the carbon. Thus, this value can provide a gauge of the relative reactivity of graphite and GC at the different potentials. The charge recorded for a faradaic electrochemical reaction is proportional to the number of moles electrolyzed according to Equation 3.1:

$$Q = nFN \quad 3.1$$

where Q is the charge passed (Coulombs), n is the number of electrons transferred in the reaction, F is the Faraday constant, and N is the number of moles electrolyzed. Table 3.1 presents the charge density passed during anodic polarization of the two powders at 1.0 and 1.6 V. The charge density at 1.0 V is 0.14 and 0.15 mC/cm² for graphite and GC, respectively. A significant increase and difference in the charge density arises at 1.6 V, as values of 460 and 880 mC/cm² are seen for graphite and GC, respectively. The larger charge for GC is likely a reflection of a greater degree of oxidative reactivity and is expected due to the greater microstructural disorder. Many early works on the electrochemical corrosion of carbon blacks in phosphoric acid at high temperatures (>100 °C) found a correlation between the d -spacing, or graphitic nature, of the carbon and the extent of electrochemical oxidation.^{1,4,6} In this so-called order/disorder mechanism, less-ordered regions of the material oxidize and/or degrade first, followed by reaction of the more graphitic regions during prolonged exposure to harsh conditions.⁴ Considering the higher proportion of exposed edge plane density for GC with respect to graphite, the difference in charge passed provides evidence for the order/disorder mechanism.

Table 3.1 Charge passed during the 1 h potentiostatic polarization of graphite and GC powders at 1.0 and 1.6 V vs. Ag/AgCl (25 °C).

Carbon Type	Potential (V vs. Ag/AgCl)	Charge Density (mC/cm²)
Graphite	1.0	0.14
Glassy Carbon	1.0	0.15
Graphite	1.6	460
Glassy Carbon	1.6	880

The charge density passed during a 1 h potentiostatic polarization in 0.1 M HClO₄ for graphite and GC powder electrodes at 1.0, 1.2, 1.4, and 1.6 V (25, 50, and 80 °C) are presented in Table 3.2 and 3.3, respectively. Potentiostatic polarization was also completed at 0.8 V. However, no detectable changes in surface oxidation or microstructure were observed so these data are omitted for clarity. A few important trends can be seen in the charge density measurements. First, the charge passed during polarization increases as the polarization potential is increased for both graphite and GC. If oxidation and gasification of the carbon surface is taking place, the extent of these processes would be expected to grow at higher potentials. Second, the charge passed increases at any given potential as the temperature is raised. This is important considering that fuel cells operate at higher temperatures (~80 °C) for maximum efficiency. Third, the charge passed for GC is always higher than that for graphite, except for polarization at 1.6 V and 80 °C. The increased reactivity of GC compared to that of graphite is again attributed to the higher edge plane density of GC, which are the active sites for oxidation and subsequent structural degradation. GC electrodes anodically polarized at 1.6 V at and 80 °C, as well as at higher potentials at all

temperatures, failed (i.e., began to break apart). The charge passed for graphite at polarization potentials >1.6 V continued to increase as the potential and temperature were increased up to 2.2 V (the upper potential limit studied). We suppose that carbon gasification becomes the major degradation process at high potentials and temperatures for GC, causing the electrode to fail. Support gasification would be very detrimental to fuel cell operating efficiency and lifetime. In contrast, the major process for the graphite electrodes is probably anion intercalation and fracturing of the graphite lattice which exposes additional surface area for oxidation. These processes are expected to increase as the potential increases and likely cause the large increases in charge density passed at 1.6 V for both materials. Future work will focus on analyses of the gases evolved (e.g., CO and CO₂) as a function of potential and temperature to more fully characterize the carbon gasification as well as *in situ* Raman spectroscopic investigations to more fully characterize anion intercalation and lattice damage.

Table 3.2 Charge passed (mC/cm²) during the 1 h potentiostatic polarization of graphite powder from 1.0 to 1.6 V vs. Ag/AgCl at 25, 50, and 80 °C.

Potential (V vs. Ag/AgCl)	25 °C	50 °C	80 °C
1.0	0.14	0.25	0.61
1.2	0.84	0.82	4.1
1.4	6.5	13	20
1.6	460	1300	4200

Table 3.3 Charge passed (mC/cm^2) during the 1 h potentiostatic polarization of GC powder from 1.0 to 1.6 V vs. Ag/AgCl at 25, 50, and 80 °C.

Potential (V vs. Ag/AgCl)	25 °C	50 °C	80 °C
1.0	0.15	0.32	0.82
1.2	1.1	1.1	4.2
1.4	9.1	15	40
1.6	880	2600	3000

3.2.2 Evaluation of the Extent of Surface Oxidation in Terms of Electroactive Oxide Formation

Cyclic voltammetry was used to assess the correlation between the charge passed during anodic polarization and the extent of surface oxidation of the two powders. Background cyclic voltammograms of sp^2 -bonded carbons are characterized by faradaic current arising from the electroactive quinone/hydroquinone surface functionality terminating the edge plane and defect sites.^{24,25} The magnitude of this current can be used as a measure of the relative extent of surface oxidation of a carbon during anodic polarization. Background cyclic voltammograms for graphite and GC powder in 0.1 M HClO_4 at 0.1 V/s before and after polarization at 1.0 V for 1 h are shown in Figure 3.3A and B, respectively. The background cyclic voltammograms for both powder types recorded before anodic polarization have a nonfaradaic background current of approximately 2 to 3 $\mu\text{A}/\text{cm}^2$. Faradaic current due to the electroactive quinone/hydroquinone surface carbon-oxygen functionality is also present, as indicated by the arrows, centered *ca.* 350 mV for both carbon types. After polarization, the cyclic voltammetric faradaic and nonfaradaic current increased for both carbons, with much

larger changes noted after polarization at higher potentials (e.g., 1.6 V) and temperatures. Nonfaradaic, or capacitive, current in an electrochemical measurement is a result of charging of the electric double layer and can be described by Equation 3.2:

$$i_c = AC\nu \quad (3.2)$$

where i_c is the capacitive background current (A), A is the electrode area (cm^2), C is the electrode capacitance (F/cm^2), and ν is the scan rate (V/s). Because the electrode capacitance and scan rate do not change during a measurement, changes in the nonfaradaic background cyclic voltammetric current noted here results from increases in the electrode surface area exposed to solution. This increase could result from microstructural changes (e.g., fracturing of the graphite basal plane to expose additional edge plane density), corrosion (i.e., carbon gasification), or delamination of the binder. Microstructural changes to graphite and GC as a result of anodic polarization were probed using Raman spectroscopy and will be discussed in the following section.

There are also increases in the faradaic current for oxidation and reduction of the quinone/hydroquinone surface oxygen functionality after anodic polarization at potentials as low as 1.0 V and 25 °C. This provides evidence for the oxidation of the electrode surface. In fact, comparison of the faradaic current density for this surface redox reaction provides a measure of the extent of oxidation, specifically the electroactive oxygen content, after polarization. Equation 3.3 was used to assess the increase in the surface oxide content for graphite and GC after polarization:

$$\Delta J = j_{f,after} - j_{f,before} \quad (3.3)$$

where ΔJ is the change in current density ($\mu\text{A}/\text{cm}^2$), $j_{f,after}$ is the faradaic current density ($\mu\text{A}/\text{cm}^2$) of the reduction peak after polarization, and $j_{f,before}$ is the faradaic

current density ($\mu\text{A}/\text{cm}^2$) of the reduction peak before polarization. As shown in Table 3.4 (graphite) and 3.5 (GC), ΔJ follows the same trend as the measured polarization charge, increasing with the applied potential and temperature. There is also a large increase in ΔJ for both graphite and GC at 1.6 V. The similar trends between the charge passed and electrode oxidation provides evidence that at least some of the charge passed during anodic polarization, even at the thermodynamic PEMFC operating potential, is due to oxidation of the graphite and GC surfaces. Importantly, ΔJ for GC is always higher than that for graphite, especially at 80 °C. Considering the order/disorder mechanism proposed for carbon blacks and the relationships found between edge plane density and electrochemical reactivity of carbon,^{4,19-21,26} the higher edge plane density of GC leads to a significantly higher proportion of surface oxides.

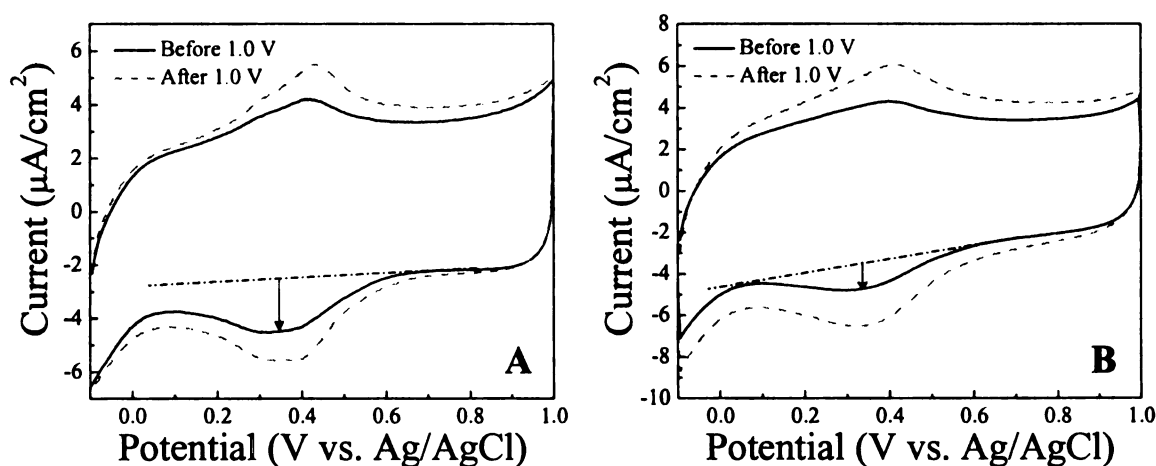


Figure 3.3 Background cyclic voltammetric i - E curves for (A) graphite and (B) GC in 0.1 M HClO_4 at 0.1 V/s before and after polarization at 1 V vs. Ag/AgCl and 25 °C for 1 h.

Table 3.4 Change in current density (ΔJ , $\mu\text{A}/\text{cm}^2$) for surface oxide reduction before and after polarization on graphite powder as a function of the polarization potential and temperature in 0.1 M HClO_4 for 1 h.

Potential (V vs. Ag/AgCl)	25 °C	50 °C	80 °C
1.0	0.38	0.53	1.8
1.2	0.95	1.5	4.7
1.4	3.9	9.0	14
1.6	89	230	460

Table 3.5 Change in current density (ΔJ , $\mu\text{A}/\text{cm}^2$) for surface oxide reduction before and after polarization on GC powder as a function of the polarization potential and temperature in 0.1 M HClO_4 for 1 h.

Potential (V vs. Ag/AgCl)	25 °C	50 °C	80 °C
1.0	0.67	0.76	9.0
1.2	2.2	3.5	10
1.4	11	25	62
1.6	590	1900	2100

3.2.3 Evaluation of Microstructural Changes

Raman spectroscopy is a useful tool to characterize sp^2 -bonded carbon materials because the Raman spectral features are dependent on microstructural characteristics such as L_a , L_c , and the interplanar d_{002} spacing.²⁷ A number of reports have been published on the Raman spectra of sp^2 -bonded carbons to determine the origin of the spectral features.²⁷⁻³¹ The primary Raman line at 1582 cm^{-1} , as shown in Figure 3.4 for graphite and GC before anodic polarization, is a result of the E_{2g} vibrational mode which consists of the in-plane stretching of the carbon atoms within the graphite lattice. The origin of a

second first-order mode that arises at 1360 cm^{-1} (the so-called disorder, or D band) in carbons with $L_a > 1000\text{ Å}$ was the subject of debate for some time.²⁷ It is now generally accepted that this mode is associated with edge plane density in carbons; the intensity of the D band is inversely proportional to L_a .³¹ Small D band scattering intensity can be seen in the Raman spectrum for graphite before anodic polarization in Figure 3.4, while that for GC is much more intense because of the higher proportion of edge plane density.

McCreery and co-workers used the carbon D to E_{2g} ratio (D/E_{2g}) to track the edge plane density and "disorder" (with respect to a graphite single crystal), correlating carbon structural elements with the electrochemical behavior of carbon electrodes.^{19-21,26} Importantly, by studying various pretreatment procedures such as laser irradiation and anodic polarization on planar HOPG electrodes, the relationship between D/E_{2g} and corrosion (i.e., damage of the graphite lattice) became more clear.^{19,21} For example, evidence was presented suggesting that both oxidative (anodic polarization) and non-oxidative (laser irradiation) treatment resulted in increases in D/E_{2g} , caused by fracturing of the graphite lattice.²¹ Although surface oxide formation was not required to note differences in D/E_{2g} (i.e., during laser irradiation), oxidation of HOPG caused by anodic polarization caused strain on the carbon lattice and resulted in lattice damage, increasing the amount of exposed edge plane.²¹ Important spatial information was also gained which showed that anodization at potentials, such as 1.85 V, caused heterogeneous changes in the edge plane density, while higher potentials led to a more uniform disorder across the HOPG surface.¹⁹ This finding supports a nucleation and growth process of the order/disorder mechanism for carbon corrosion at potentials such as 1.85 V, where disordered or defect sites may serve as nuclei for fracturing of the graphite planes.¹⁹

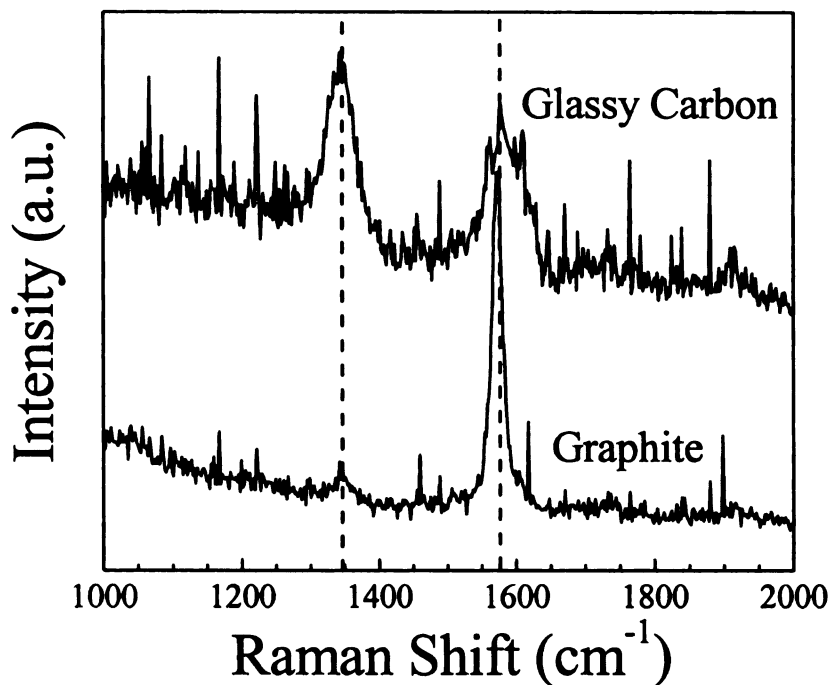


Figure 3.4 Raman spectra for graphite and GC before anodic polarization showing the E_{2g} mode ($\sim 1580\text{ cm}^{-1}$) and D band ($\sim 1360\text{ cm}^{-1}$).

To characterize microstructural changes in carbon powder electrodes and gain a better understanding of the degradation mechanism of carbons in the PEMFC, Raman spectra were taken at 6 different locations on the graphite and GC powder electrode surfaces before and after anodic polarization in 0.1 M HClO_4 (1.0 to 1.6 V at 25, 50, and 80 °C). Although these data alone cannot verify microstructural degradation because of the large standard deviation in the measurements, when considered with the other characterization data presented in this chapter, they provide evidence that the carbon microstructure is affected by polarization. Average D/E_{2g} and standard deviation from these measurements are presented in Table 3.6 (graphite) and Table 3.7 (GC). The first row in each column corresponds to electrodes that were subjected to 0.1 M HClO_4 at each respective temperature for 1 h, with no applied potential. These samples will be referred

to as the controls. Comparison of D/E_{2g} on the control samples shows that the temperature and acidic environment alone did not cause microstructural changes in either graphite or GC.

A few trends can be seen in Table 3.6 for graphite powder electrodes. First, at 25 °C, D/E_{2g} decreases slightly after polarization at all potentials with respect to that of the control. The graphite powder used in these experiments was not pristine HOPG, which has little to no defect density (i.e., no 1360 cm^{-1} scattering intensity). Rather, the Raman spectrum of graphite powder before polarization, shown in Figure 3.4, has small scattering intensity $\sim 1360\text{ cm}^{-1}$. As discussed above, the order/disorder mechanism predicts that disordered regions with a high fraction of edge plane density will be more reactive towards electrochemical corrosion. Thus, the decrease in D/E_{2g} is likely a result of selective corrosion of disordered regions (i.e., regions with higher edge plane density), which are more susceptible to microstructural degradation than the more well-ordered regions. This same trend is seen for graphite powders subject to anodic polarization at 1.0 and 1.2 V and 50 °C. However, at 1.4 and 1.6 V and 50 °C, D/E_{2g} increases, suggesting that at these potentials and temperature, well-ordered portions of the graphite plane are beginning to fracture, perhaps due to anion intercalation, exposing additional edge plane density. It is interesting to note the correlation between the large increase in surface oxygen content for graphite at 50 °C that occurs at 1.4 V (Table 3.4) and the increase in D/E_{2g} under these same conditions. This suggests that oxidation of the graphite lattice induces strain which results in lattice damage, as reported by Alsmeyer and McCreery.²⁰ Table 3.4 also shows that the oxidation of graphite is higher at all potentials during anodic polarization at 80 °C, than at 25 and 50 °C. This finding

correlates well with the noticeable increase in D/E_{2g} as the potential is increased at 80 °C. Importantly, the standard deviation for D/E_{2g} was usually quite high, ranging from *ca.* 6 to over 100%. This large deviation suggests that the graphite lattice is damaged heterogeneously across the electrode surface by a nucleation and growth process. This finding agrees well with work on the anodic polarization of planar HOPG electrodes.¹⁹

Table 3.6 Ratio (n=6) of the D/E_{2g} Raman modes for graphite powder electrodes at different polarization potentials and temperatures.

Potential (V vs. Ag/AgCl)	25 °C	50 °C	80 °C
None	0.15 ± 0.03	0.14 ± 0.03	0.15 ± 0.01
1.0	0.11 ± 0.04	0.14 ± 0.05	0.2 ± 0.1
1.2	0.1 ± 0.1	0.08 ± 0.05	0.23 ± 0.07
1.4	0.08 ± 0.09	0.14 ± 0.02	0.25 ± 0.02
1.6	0.11 ± 0.06	0.24 ± 0.03	0.3 ± 0.1

In contrast to the trends in the graphite Raman spectra with potential and temperature, there is relatively little change in D/E_{2g} for GC until the electrode material is subject to potentiostatic polarization of 1.6 V at 50 and 80 °C. Because GC does not have large, well-ordered regions of basal plane like graphite, anion intercalation and fracturing of the lattice are not expected. Rather, the high proportion of exposed edge plane is oxidized and gasified, without increases in the edge plane density that are seen for graphite.

Table 3.7 Ratio (n=6) of the D/E_{2g} Raman modes for GC powder electrodes at different polarization potentials and temperatures.

Potential (V vs. Ag/AgCl)	25 °C	50 °C	80 °C
None	1.1 ± 0.1	1.0 ± 0.1	1.2 ± 0.1
1.0	1.2 ± 0.1	1.3 ± 0.2	1.1 ± 0.1
1.2	1.2 ± 0.1	1.1 ± 0.1	1.0 ± 0.1
1.4	1.2 ± 0.2	1.3 ± 0.2	1.2 ± 0.07
1.6	1.3 ± 0.1	1.6 ± 0.09	1.6 ± 0.1

Several important results from the electrochemical (cyclic voltammetric) and spectroscopic (Raman) data presented above may provide insight on the degradation mechanisms of *sp*²-bonded carbon electrocatalyst supports (e.g., carbon blacks). First, increases in the surface oxide content at low temperature (25 °C) and potential (1.0 V) were caused by oxidation of exposed edge plane for both graphite and GC. Second, as the potential and temperature were raised, there was evidence for increases in the exposed edge plane density for graphite, likely because of intercalation and fracturing of the graphite lattice. The heterogeneity of this corrosion is indicative of a nucleation and growth process, where disordered regions and defects serve as active sites for electrochemical corrosion, while other, more structurally ordered regions do not corrode. Third, increases in the graphite edge plane density (i.e., increased D/E_{2g}) correlated well with changes in the surface carbon-oxide content, suggesting that fracturing of the graphite lattice, perhaps as a result of intercalation, exposed additional carbon edge plane. Fourth, the charge passed during potentiostatic polarization, as well as the increase in surface oxide coverage was always larger for GC than for graphite, as long as the GC

electrode did not fail (e.g., 1.6 V at 80 °C). Moreover, there were no noticeable changes in the GC microstructure at most potentials and temperatures. These results provide evidence for the so-called order/disorder mechanism where structurally disordered carbons corrode more severely because of oxidation and gasification of the exposed edge plane. Although this result is not surprising, it has important implications in terms of the stability of current carbon electrocatalyst supports in fuel cells (e.g., Vulcan XC-72) and the directions for development of an advanced support material.

3.3 Anodic Polarization of Carbon Black, Vulcan XC-72

Potentiostatic polarization was also carried out on Vulcan XC-72, a high-surface-area ($\sim 250 \text{ m}^2/\text{g}$) carbon black commonly used in fuel cells, followed by subsequent electrochemical characterization using cyclic voltammetry. These measurements were done with both bare and Pt-loaded (20 wt. %) Vulcan XC-72 and may serve as a preliminary comparison of the corrosion behavior of a structurally disordered carbon material and the effect that the corrosion has on the Pt electrocatalyst. However, more detailed experiments should be carried out to more fully evaluate the behavior of Vulcan XC-72 exposed to potentiostatic polarization. All of the data presented in this section were from single measurements such that statistical reproducibility of the data cannot be evaluated.

The charge passed during potentiostatic polarization of bare Vulcan XC-72 powder from 0.8 to 1.4 V at 25, 50, and 80 °C is presented in Figure 3.5. Surprisingly, the charge density passed for these samples was much lower than that for graphite and GC powders. We expected the charge for Vulcan XC-72 to be higher than that for

graphite or GC because of a higher edge plane density and suppose that this disparity may be a function of the manner in which the data were normalized. The surface area, calculated from the background cyclic voltammetric current before polarization, was two orders of magnitude higher for Vulcan XC-72 than for graphite or GC. For this normalization method, it is difficult to numerically compare the charge for carbons with significantly different surface areas, but the trends are still important. It is clear from Figure 3.5 that the charge passed increases as the polarization potential is increased. It is unclear at this point why the temperature does not have a significant affect on the recorded charge. It should be noted that, aside from polarization at 1.4 V, the charge passed did increase slightly at each potential as the temperature was increased, although the increase was not nearly as large as seen for graphite or GC. We suspect that the electrodes exposed to potential polarization at 1.4 V at 50 and 80 °C may have begun to fail due to extensive carbon gasification or binder delamination under such harsh conditions, as discussed for GC at potentials above 1.6 V. Data were not collected for potentiostatic polarization at 1.6 V because the Vulcan XC-72 electrodes were not stable at this potential.

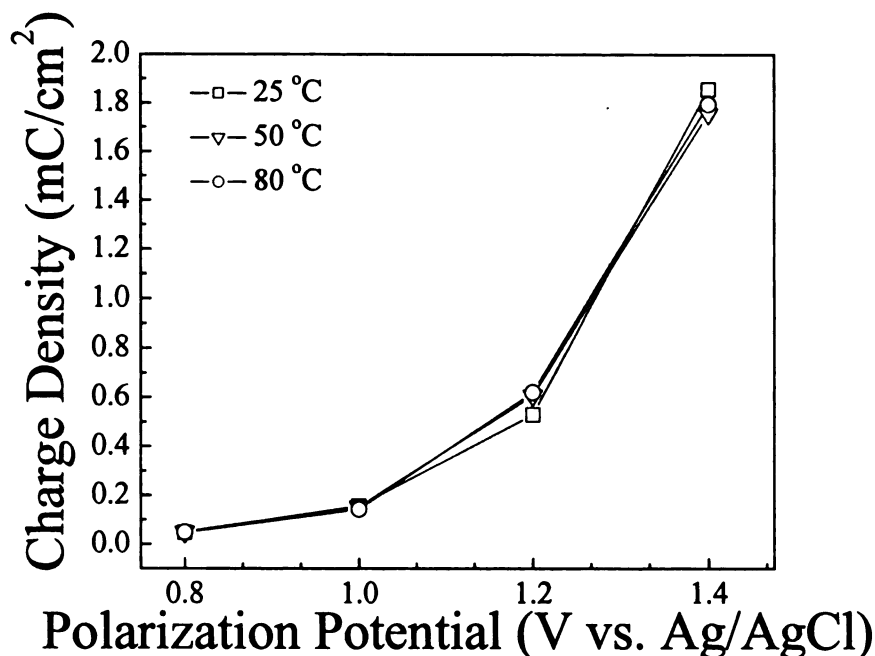


Figure 3.5 Charge density vs. polarization potential for Vulcan XC-72 as a function of the temperature.

Evaluation of Vulcan XC-72 electrode oxidation, presented in Figure 3.6, was done by analysis of the change in the faradaic reduction current associated with surface carbon-oxygen functional groups (ΔJ), as discussed above for graphite and GC. There is evidence for carbon oxidation at 0.8 V at all temperatures, while oxidation was not noted for graphite or GC until 1.0 V. The extent of Vulcan XC-72 oxidation increases significantly for polarizations at 80 °C until 1.4 V, where it decreases. This deviation is attributed to electrode failure as a result of carbon gasification or binder delamination. The electrochemical oxidation follows a more linear trend than the charge measurements, suggesting that carbon oxidation plays a more significant role in the corrosion current as the potential is increased. Although there is not much of a difference in ΔJ between 25 and 50 °C, ΔJ increases for polarization at 80 °C, especially for 1.0 and 1.2 V.

Kangasniemi and co-workers found evidence for surface oxidation of bare Vulcan XR-72 after potentiostatic polarization at 1.0 V vs. SHE and 25 °C (~0.8 V vs. Ag/AgCl), as well as at 0.8 V vs. SHE and 65 °C, (~1.0 V vs. Ag/AgCl) for 16 h.¹⁰ However, the extent of oxidation at the higher temperature was not quantified such that the extent of increase in surface oxidation cannot be compared.

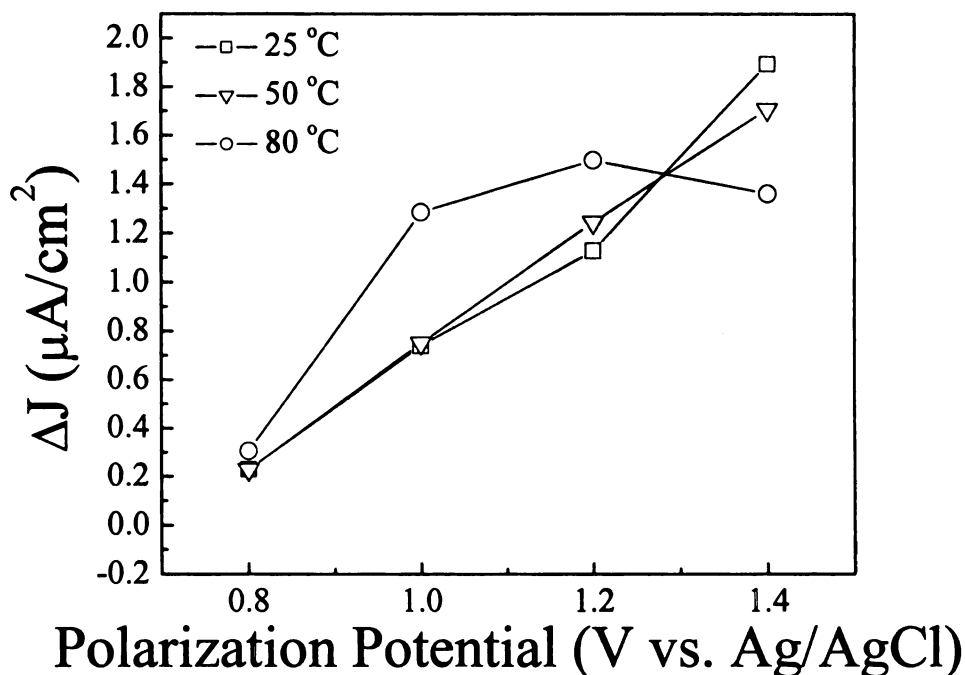


Figure 3.6 Change in faradaic current density for surface oxide reduction of Vulcan XC-72 before and after polarization as a function of the polarization potential and temperature in 0.1 M HClO₄ for 1 h.

Carbon corrosion in a PEMFC environment has been well-established.¹⁰⁻¹³ In addition to the importance of understanding the corrosion mechanism so that an advanced support can be developed, it is also important to understand the influence of carbon corrosion on electrocatalyst activity. As a first step towards this goal, Pt-loaded (20 wt.

%) Vulcan XC-72 electrodes were polarized from 0.8 to 1.4 V at 25, 50, and 80 °C. Figure 3.7 is a representative background cyclic voltammetric *i-E* curve of a Pt-loaded (20 wt. %) Vulcan XC-72 electrode in 0.1 M HClO₄ at 0.005 V/s (cycle 10). Voltammetric features consistent with those expected for polycrystalline Pt, including anodic current from Pt-oxide formation between *ca.* 0.6 and 1.0 V, a cathodic Pt-oxide reduction peak at 0.5 V, and anodic and cathodic current resulting from hydrogen adsorption and desorption, respectively, on Pt between *ca.* 0.1 V and -0.2 V were observed after *ca.* 3 cycles. These features became more well-defined as the electrode was cycled from -0.2 to 1.0 V vs. Ag/AgCl at 0.05 mV/s, however, the background cyclic voltammetric *i-E* signal (i.e., peak shape and magnitude) for the Pt-loaded (20 wt. %) Vulcan XC-72 electrodes was constant after *ca.* 10 cycles. The nonfaradaic background charging current observed at all potentials is a combination of capacitive and pseudocapacitive current arising from both the carbon and the Pt metal nanoparticles. Because these signals cannot be easily or reliably separated, the surface area of carbon exposed to solution cannot be determined from the voltammogram. However, the Pt electrocatalyst surface area, to which the charge density data presented below was normalized, can be calculated by integrating the cyclic voltammetric charge (anodic cycle) between 0.15 to -0.2 V vs. Ag/AgCl, which is associated with H desorption, as shown in the shaded region of Figure 3.7. This calculation assumes a 1H:1Pt surface interaction and a surface charge of 210 $\mu\text{C}/\text{cm}^2$ for hydrogen adsorption on an atomically flat Pt(111) surface.^{32,33}

The charge density passed during potentiostatic polarization, normalized to the Pt electrocatalyst surface area, is plotted as a function of potential and temperature in Figure

3.8. Considering the difference in normalization procedures (i.e., normalization to carbon surface area vs. normalization to Pt surface area), the charge density passed during potentiostatic polarization cannot be directly (i.e., quantitatively) compared to that of the bare carbon powder. However, the trend of increasing charge passed as the potential is raised is similar to that of the bare Vulcan XC-72 powder. There also seems to be little change in charge density with temperature, although the charge passed at 80 °C is higher for polarization at 0.8, 1.0, and 1.2 V, than that at 25 or 50 °C. The difference in temperature dependence for Pt-loaded Vulcan XC-72 (Figure 3.8) compared to bare Vulcan XC-72 (Figure 3.5) may be a result of increased corrosion in the presence of Pt that has been reported by others.¹¹ Electrodes polarized at 1.4 V at 50 and 80 °C visibly failed, presumably due to gasification of the carbon support or binder delamination.

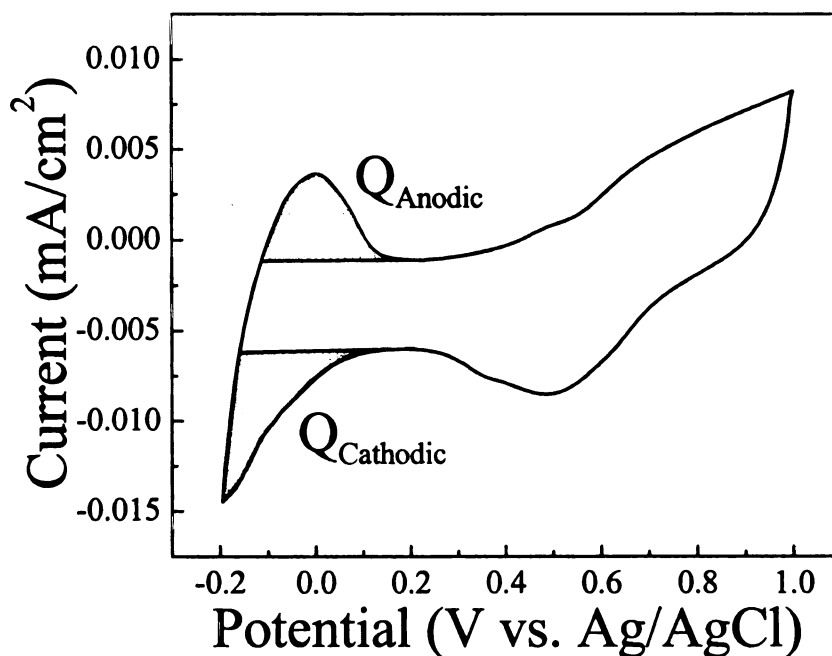


Figure 3.7 Background cyclic voltammetric *i-E* curve for Pt-loaded (20 wt. %) Vulcan XC-72 in 0.1 M HClO₄ at 0.005 V/s. Current is normalized to the estimated Pt surface area.

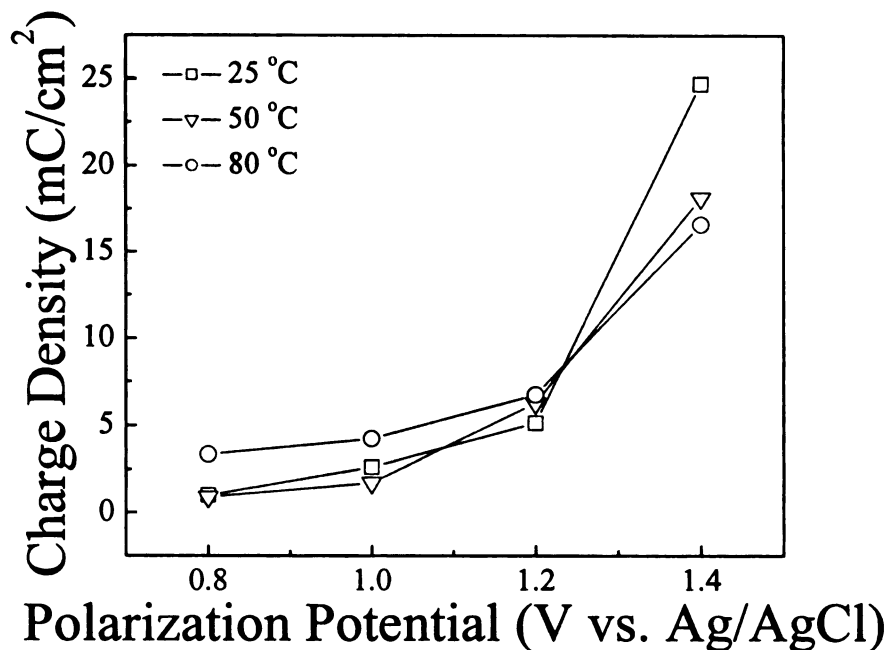


Figure 3.8 Charge density vs. polarization potential as a function of temperature for Pt-loaded (20 wt. %) Vulcan XC-72 as a function of the temperature.

Background cyclic voltammetric i - E curves recorded before and after potentiostatic polarization of Pt-loaded (20 wt. %) Vulcan XC-72 from 0.8 to 1.4 V at 25 °C recorded in 0.1 M HClO₄ at 0.005 V/s are shown in Figure 3.9. Although there is a slight downward shift of the current below *ca.* 0.2 V after polarization at 1.4 V, presumably due to the presence of oxygen in the solution, there is little change in the curve shape after polarization. At 50 and 80 °C, the Pt-oxide reduction peak and the hydrogen adsorption/desorption peaks become less well-defined at 1.2 and 1.4 V. In addition, resistive behavior, as indicated by a sloping curve, is observed after potentiostatic polarization at 80 °C, particularly at 1.2 and 1.4 V. To assess whether potentiostatic polarization affected the electrocatalytic activity, the surface area of Pt was compared before and after polarization. Reduction of Pt surface area in these

experiments could be due to corrosion of both carbon and Pt, but is a useful gauge of the effect of potential and temperature on the electrocatalytic activity. Table 3.8 presents the percentage of Pt surface area lost ($\%_{Lost}$) as a result of potentiostatic polarization according to Equation 3.4

$$\%_{Lost} = \left(\frac{A_{Pt,before} - A_{Pt,after}}{A_{Pt,before}} \right) * 100 \quad (3.4)$$

where $A_{Pt,before}$ is the area (cm^2) of Pt before polarization and $A_{Pt,after}$ is the area (cm^2) of Pt after polarization, calculated from the charge of the hydrogen desorption reaction as described above. The active Pt surface area decreased at all potentials and temperatures, except for that at 0.8 V and 25 °C. It is likely that additional Pt surface area was exposed during this 1 h polarization, possibly as a result of cleaning of the Pt surface or because of particle roughening, as reported by others.³⁴ The $\%_{Lost}$ increased as a function of both potential and temperature, except for potentiostatic polarization at 80 °C, where it seems the Pt area was rather constant at 0.8 and 1.0 V. However, it should be noted that, as mentioned above, the cyclic voltammetric i - E curves for electrodes exposed to polarization at 80 °C exhibited resistive behavior after polarization (i.e., sloping curve), such that determination of the Pt surface area was difficult. In fact, a reliable measurement could not be done for $A_{Pt,after}$ on the 1.4 V, 80 °C sample. The decrease in Pt surface area would have detrimental consequences for a fuel cell, especially at higher potentials, such as 1.2 or 1.4 V, where a large amount (>30%) of the Pt surface area was lost at all temperatures. Future work should include methods to more fully characterize the causes and consequences of support corrosion with Pt, in addition to the studying the loss of electrocatalyst surface area in more detail.

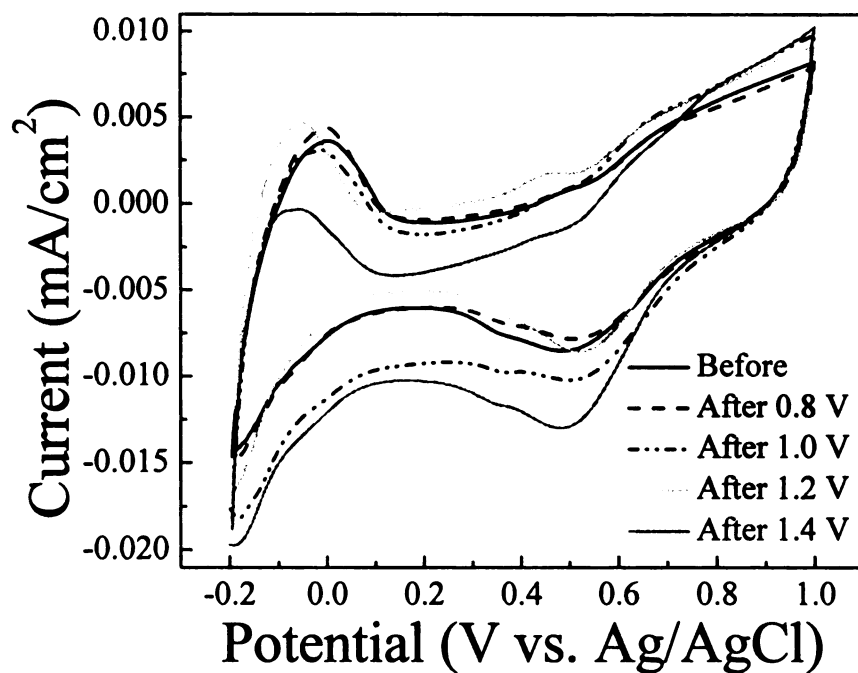


Figure 3.9 Background cyclic voltammetric i - E curves for Pt-loaded (20 wt. %) Vulcan XC-72 in 0.1 M HClO_4 at 0.005 V/s before and after polarization from 0.8 to 1.4 V vs. Ag/AgCl at 25 °C. Current is normalized to the estimated Pt surface area before polarization.

Table 3.8 Percent Pt lost ($\%_{\text{Lost}}$) as a result of potentiostatic polarization of Pt-loaded (20 wt. %) Vulcan XC-72 in 0.1 M HClO_4 at different polarization potentials and temperatures.

Potential (V vs. Ag/AgCl)	25 °C	50 °C	80 °C
0.8	-6.04	9.11	5.4
1.0	4.3	13.6	3.4
1.2	31.5	32.3	58.6
1.4	46.7	88.9	--

3.4 Conclusions

Potentiostatic polarization of two structurally well-characterized carbons, graphite and GC provided evidence for an order/disorder mechanism of carbon degradation/corrosion under PEMFC conditions. The extent of surface oxidation increased for both materials as potential and temperature increased. Microstructural changes evaluated by Raman spectroscopy indicated that intercalation followed by lattice damage may be the prevalent mechanism for graphite corrosion, while oxidation of existing edge plane density is the major process for degradation of GC. The corrosion charge recorded during anodic polarization of a carbon black commonly used in fuel cells, Vulcan XC-72, increased as the potential increased, but temperature had little effect. Cyclic voltammetric analysis provided evidence for oxidation of Vulcan XC-72 at 0.8 V and 25 °C, the extent of which increased somewhat linearly as the potential and temperature were raised. Initial results for the potentiostatic polarization of Pt-loaded (20 wt. %) Vulcan XC-72 showed electrocatalyst surface area was lost during at all potentials and temperatures, except for 0.8 V and 25 °C. Background cyclic voltammograms after polarization showed evidence for loss of Pt as well as for increased electrode resistance.

3.4 References

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Chapter 4

The Electrochemical Performance of Diamond Thin-Film Electrodes from Different Commercial Sources

Abstract

The electrochemical properties of two commercial (Condias and Sumitomo) boron-doped diamond thin-film electrodes were compared with two types of boron-doped diamond thin film deposited in our laboratory (microcrystalline and nanocrystalline). Scanning electron microscopy and Raman spectroscopy were used to characterize the electrode morphology and microstructure, respectively. Cyclic voltammetry was used to study the electrochemical response, with five different redox systems serving as probes ($\text{Fe}(\text{CN})_6^{3-/4-}$, $\text{Ru}(\text{NH}_3)_6^{3+/2+}$, $\text{IrCl}_6^{2-/3-}$, 4-methylcatechol, and $\text{Fe}^{3+/2+}$). The response for the different systems was quite reproducible from electrode type-to-type and from film-to-film for a given type. For all five redox systems, the forward reaction peak current varied linearly with the square root of the scan rate ($\nu^{1/2}$), indicative of electrode-reaction kinetics controlled by mass transport (semi-infinite linear diffusion) of the reactant. The apparent heterogeneous electron transfer rate constant, k_{app}^o , for all five redox systems was determined from ΔE_p - ν experimental data, according to the method described by Nicholson.¹ The rate constant was also verified through digital simulation (DigiSim[®] 3.03) of the voltammetric i - E curves at different scan rates. Good fits between the experimental and simulated voltammograms were found for ν up to 50 V/s. k_{app}^o values

of 0.05 to 0.5 cm/s were observed for $\text{Fe}(\text{CN})_6^{3-/4-}$, $\text{Ru}(\text{NH}_3)_6^{3+/2+}$, and $\text{IrCl}_6^{2-/3-}$ without extensive electrode pretreatment (e.g., polishing). Lower k_{app}^o values of 10^{-4} to 10^{-6} cm/s were found for 4-methylcatechol and $\text{Fe}^{3+/2+}$. The voltammetric responses for $\text{Fe}(\text{CN})_6^{3-/4-}$ and $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ were also examined at all four electrode types at two different solution pH values (1.90 and 7.35). The ΔE_p , i_p^{ox} , and i_p^{red} values for the two systems were relatively unaffected by solution pH because hydrogen-terminated diamond surfaces contain few, if any, ionizable carbon-oxygen functionalities (e.g., carboxylic acid, $\text{pK}_a \sim 4.5$). This is in contrast to the typical behavior of oxygenated, sp^2 -bonded carbon electrodes, such as glassy carbon.

4.1 Introduction

Chemical vapor deposited (CVD) diamond electrodes have attracted considerable interest in recent years due to their versatility and excellent electrochemical properties.²⁻¹² The material can be used in electroanalysis to provide low detection limits for analytes with superb precision and stability, for high-current density electrolysis (1-10 A/cm²) in aggressive solution environments without any microstructural or morphological degradation, as a corrosion resistant electrocatalyst support, and as an optically transparent electrode (OTE) for spectroelectrochemical measurements.¹³⁻¹⁷ The research presented in this dissertation is focused on the development of a more stable and robust electrocatalyst support material for fuel cells using high surface area, electrically conducting diamond. The first step toward development of this new material was to establish that the diamond electrodes sold commercially have reproducible physical, chemical, and electrochemical properties, similar to those of laboratory-grown films.

At least four commercial units now market electrically conducting diamond thin-film electrodes. Because the specific substrate pretreatment and film deposition conditions are typically not disclosed, these products are presumably grown using different methods and process variables. As discussed in Chapter 1, variables such as substrate pretreatment prior to growth, source gas composition, growth temperature, and chamber pressure can all affect the resultant film properties, thereby affecting the electrochemical behavior. Several factors influence the diamond thin-film electrode response (i.e., electrode reaction kinetics): (i) potential-dependent density of electronic states, which is affected by the doping type, level, and distribution, (ii) surface chemistry, (iii) morphology and microstructure, (iv) defect density, (v) nondiamond carbon impurity

content, and (vi) double layer structure.^{3,4,7,9,13} The extent to which any of these factors influence the electrode response depends greatly on the reaction mechanism for the particular redox system for both sp^2 - and sp^3 -bonded carbons.^{7,9,13,18-24}

In this chapter, a comparison of the physical, chemical, and electrochemical properties of two commercially-available (Condias and Sumitomo) boron-doped diamond thin-film electrodes is made with two types of diamond produced in our laboratory (microcrystalline, MSUMicro, and nanocrystalline, MSUNano). Electrode morphology and microstructure were characterized using scanning electron microscopy (SEM) and Raman spectroscopy. Cyclic voltammetry was used to study the electrochemical response, with five different redox systems serving as probes: $\text{Fe}(\text{CN})_6^{3-/4-}$, $\text{Ru}(\text{NH}_3)_6^{3+/2+}$, $\text{IrCl}_6^{2-/3-}$, 4-methylcatechol, and $\text{Fe}^{3+/2+}$. Additionally, the voltammetric responses for $\text{Fe}(\text{CN})_6^{3-/4-}$ and $\text{Ru}(\text{NH}_3)_6^{2+/3+}$ were recorded at different pH (1.90 and 7.35), in order to demonstrate the absence of electrostatic double-layer effects. Such effects are commonly observed for sp^2 -bonded carbon electrodes, like glassy carbon, because of the presence of ionizable surface carbon-oxygen functional groups (e.g., carboxylic acid functionalities).

4.2 Results and Discussion

4.2.1 Material Characterization

Scanning electron micrographs for MSUMicro, Condias, Sumitomo, and MSUNano boron-doped diamond thin-film electrodes are presented in Figure 4.1A-D, respectively. All films are polycrystalline and uniformly coat the substrate with no visible cracks, pinholes, or voids. The MSUMicro, Condias, and Sumitomo films contain well-faceted crystallites with a nominal diameter of *ca.* 1, 5 and 2 μm , respectively. The

crystallites of the MSUMicro, Condias, and Sumitomo films possess significant triangular (111) faceting with an abundance of multiply twinned crystals (e.g., decahedral shapes with five-fold symmetry). Twins are a common defect in diamond polycrystalline diamond, particularly ones with a more octahedral morphology, resulting when two or more intergrown crystals form in a symmetric fashion. The Condias film has a large number of re-entrant grooves (i.e., corners) and stacking faults. The re-entrant corners have a higher growth rate than other regions because chemisorbed growth precursors (e.g., methyl radicals) in the grooves are more stable against H attack than moieties attached to the more open, planar surface.²⁵ The MSUNano film, in contrast, possesses a much smoother texture with feature sizes on the order of ~ 100 nm.⁹ Previously reported TEM data revealed that these features consist of aggregates of randomly-oriented grains of diamond with a nominal diameter of ca. 15 nm.⁹ The nanocrystalline film is grown under conditions of high rates of re-nucleation, which leads to the small grain size and smooth texture.²⁶⁻³²

Raman spectroscopy is an excellent tool for probing the microstructure of carbon materials. For diamond, the Raman spectral features, including band positions, line widths, and relative peak intensities, are quite sensitive to the bulk crystal structure, boron-doping level, internal stress (intrinsic and thermal), defect density, and presence of sp^2 -bonded nondiamond carbon impurity.^{18,33-43} As shown in Figure 4.2, spectral analysis revealed that the first-order phonon line for diamond, expected at 1332 cm^{-1} , is most intense, narrow, and symmetric for the Condias film. In contrast, this line is downshifted to ca. 1304 cm^{-1} , attenuated, broadened, and asymmetric, with an upward shift in scattering intensity on the high-wavenumber side, for the Sumitomo and MSUMicro

films. This so-called Fano shift is induced by quantum-mechanical interference between the discrete phonon state and an electronic continuum that occurs particularly with heavy boron doping.^{18,39,41} Two additional peaks emerge near 1200 and 500 cm^{-1} for the Sumitomo and MSUMicro films which are also consistent with heavy boron doping.^{18,38-40} It is important to note that minimal scattering intensity is seen in the 1500-1600 cm^{-1} region, which is associated with the presence of nondiamond, sp^2 -bonded carbon. Considering that the scattering efficiency for graphite is about 50 times that of diamond, the nondiamond impurity content in these films is low.³⁶

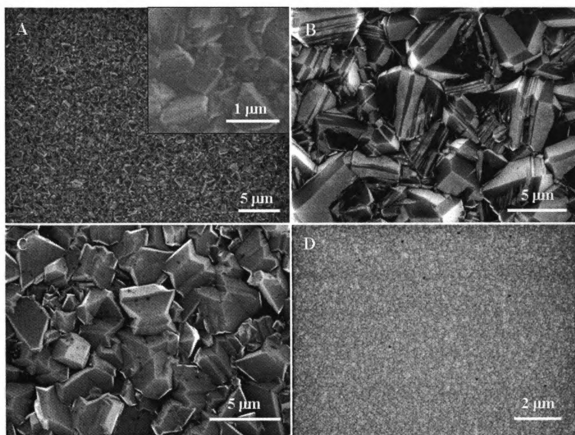


Figure 4.1 Scanning electron micrographs of (A) MSUMicro, (B) Condias, (C) Sumitomo, and (D) MSUNano diamond thin films.

The Raman spectrum of the MSUNano film is characterized by broad peaks at 1150, 1333, 1470, and 1550 cm^{-1} , consistent with Raman spectra previously reported for high-quality nanocrystalline diamond.^{9,35,37,42-44} In nanocrystalline diamond, small clusters of sp^3 -bonded diamond grains are connected by grain boundary carbon in an sp^2 -bonded configuration.^{9,26-32} The one-phonon diamond line at 1332 cm^{-1} is obscured by a large background signal and is considerably broader than for the microcrystalline films, 140 versus 10 cm^{-1} . Two different explanations exist for the line-broadening in nanocrystalline diamond films. The first, so-called confinement model, states that the smaller the domain size, the larger the range of phonon modes (with different q vectors and energies) that are allowed to participate in the Raman process.³⁷ In other words, the line width results from the spread in phonon energy. The second attributes broadening to phonon scattering by impurities and defects (i.e., grain boundaries).³⁷ The scattering event shortens the lifetime of the phonons and thus broadens the Raman line.

The peak at 1150 cm^{-1} is often used as a signature for high-quality nanocrystalline diamond.³⁵ Prawer and coworkers, through the study of clean nanocrystalline diamond particles (~5 nm diam.), have attributed this peak to a surface phonon mode of diamond.⁴² On the other hand, Ferrari and Robertson assert that this peak is associated with sp^2 -bonded carbon, specifically transpolyacetylene segments at the grain boundaries.⁴³ Their assignment of sp^2 - rather than sp^3 -bonded carbon, as has often been proposed, is based on the observations that the peak position changes with excitation energy, the peak intensity decreases with increasing excitation energy, and the peak is always accompanied by another peak at ~1450 cm^{-1} , which behaves similarly with excitation energy.³⁵ Recent work by Birrell and co-workers confirmed this finding.⁴⁴ In

their study, the amount of hydrogen in a nanocrystalline diamond deposition plasma was varied, which resulted in transitions from nanocrystalline to more microcrystalline morphologies at high hydrogen content (~10-20%).⁴⁴ These microstructural changes correlated well with the presence of carbon-hydrogen bonds (i.e., amorphous carbon) in the nanocrystalline diamond grain boundaries.⁴⁴

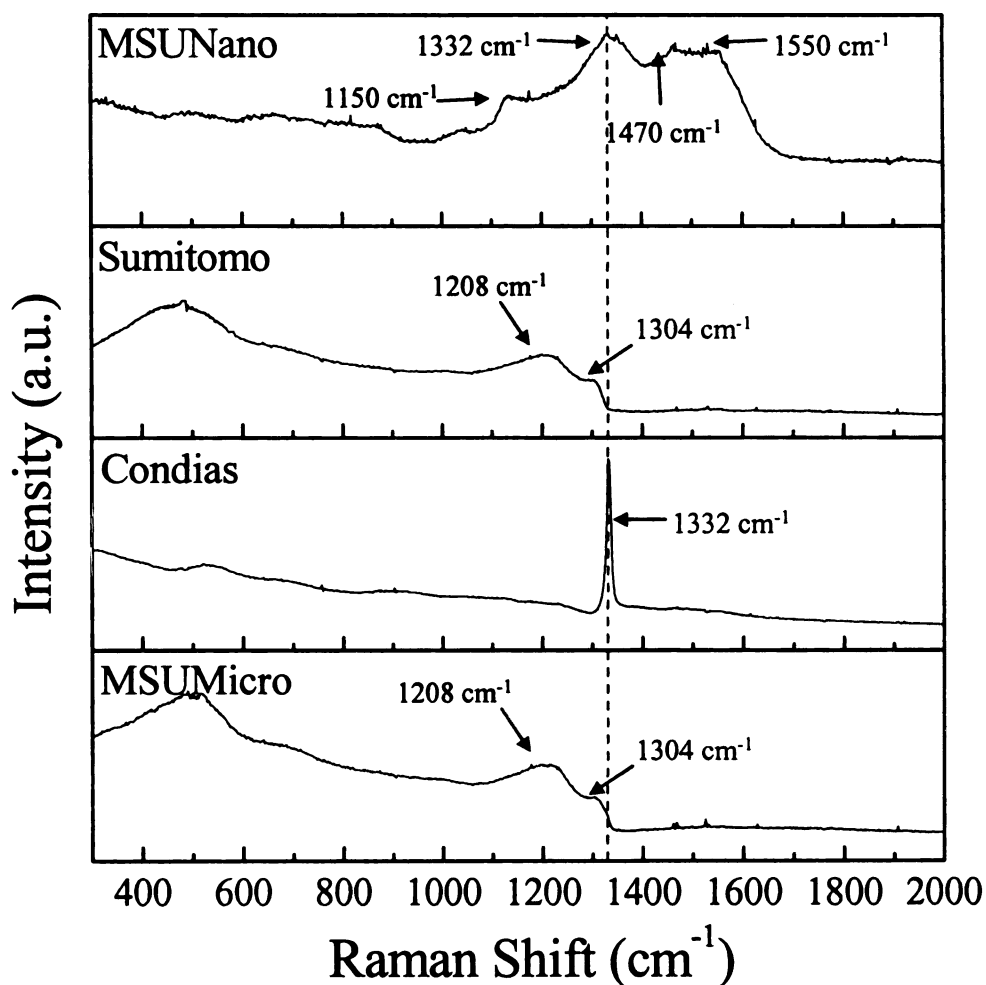


Figure 4.2 Raman spectra for MSUMicro, Condias, Sumitomo, and MSUNano diamond thin films.

4.2.2 Electrochemical Characterization

Background cyclic voltammetric i - E curves can be very informative about the boron-doped diamond film quality (i.e., presence of nondiamond carbon impurity at the surface) and electrical conductivity. Figure 4.3 shows cyclic voltammetric i - E curves for MSUMicro, Condias, Sumitomo, and MSUNano, as well as that for glassy carbon (same geometric area in each case) in 0.1 M HClO₄. The voltammetric curves for the four diamond types are mostly flat and featureless with a low background current that results from (i) a reduced pseudocapacitance because of the absence of redox active and/or ionizable surface carbon-oxygen functional groups and (ii) a reduced capacitance due to a slightly lower internal charge carrier concentration. In contrast, the background current for glassy carbon is approximately a factor of 10 higher with faradaic current evident due to a redox couple (pseudocapacitance) centered at *ca.* 400 mV (acidic pH). This faradaic current is associated with redox-active surface carbon-oxygen functional groups terminating the edge plane and defect sites (e.g., quinone/hydroquinone).^{45,46} These peaks are typically absent in the background cyclic voltammograms for high-quality, hydrogen-terminated boron-doped diamond because the surface is devoid of such functional groups. However, close inspection of the background cyclic voltammograms for the Condias and Sumitomo films shows very weak peaks centered at *ca.* 500 mV. At this point, it is unclear if these peaks are associated with surface carbon-oxygen functional groups.

Cyclic voltammetry was used to study the electrode response for Fe(CN)₆^{3-/4-}, Ru(NH₃)₆^{3+/2+}, IrCl₆^{2-/3-}, 4-MC, and Fe^{3+/2+}. The effects of a number of variables including surface morphology, substrate pretreatment, and surface termination on the

electrode response of sp^2 -bonded carbon and sp^3 -bonded diamond for these analytes has been studied extensively.^{7,9,13,19-24} It is important to note that the extent to which any of these factors influence the electrode response depends on the mechanistic aspects for the particular redox analyte.^{7,9,13,19-24}

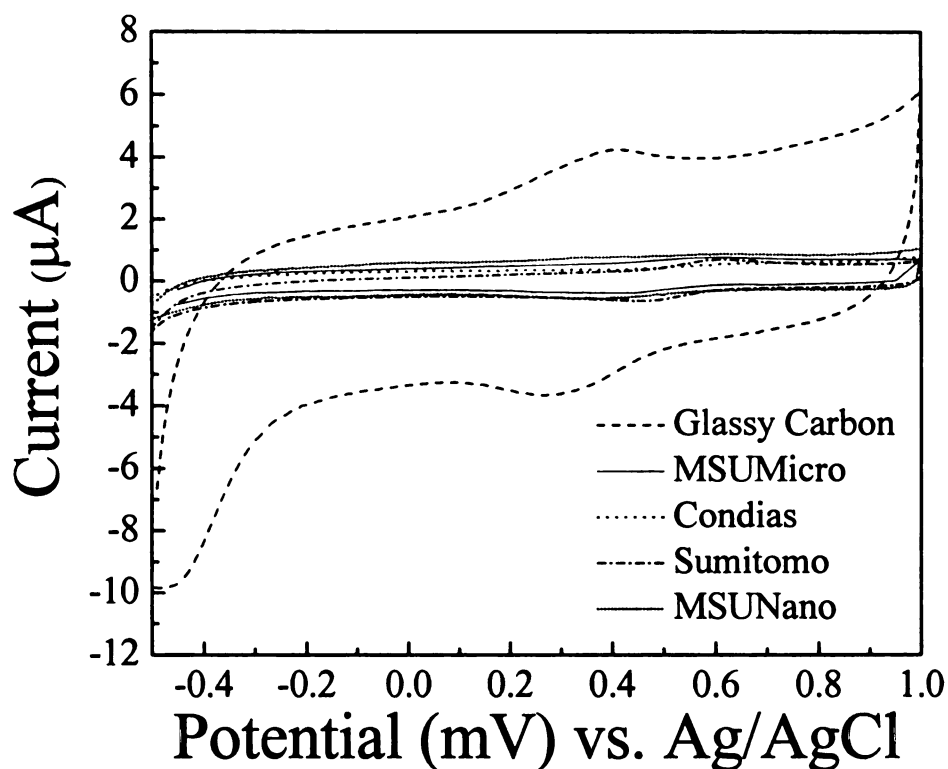


Figure 4.3 Cyclic voltammetric i - E curves for all four diamond types in 0.1 M HClO_4 at 0.1 V/s (geometric area = 0.2 cm^2).

Heterogeneous electron-transfer reactions can be broadly categorized as two types. The first, so-called outer-sphere reactions, proceed by simple mass transport of the analyte to the electrode-solution interface, with the electrode serving solely as a source or sink for electrons. The electrode kinetics for this type of reaction are relatively

insensitive to factors such as the surface chemistry and microstructure, but very sensitive to the density of electronic states near the formal potential of the reaction. The second, so-called inner-sphere reactions, includes those that occur via some specific interaction with the electrode surface. For example, reactions that proceed through an adsorbed state or involve some specific surface site would be categorized as inner-sphere electrochemical reactions. The electrode kinetics for this type of reaction tend to be quite sensitive to surface chemistry and microstructure as well as the density of electronic states near the formal potential. On boron-doped diamond electrodes, $\text{Ru}(\text{NH}_3)_6^{3+/2+}$, methyl viologen, $\text{IrCl}_6^{2-/3-}$, $\text{Ru}(\text{bpy})_3^{3+/2+}$, and chlorpromazine proceed by an outer-sphere electron-transfer pathway with the electrode kinetics being relatively insensitive to the physicochemical properties of diamond.^{7,9,13,47,48} Apparent heterogeneous electron-transfer rate constants, k_{app}^0 , between 0.01 and 0.2 cm/s are commonly observed for conducting polycrystalline films (both microcrystalline or nanocrystalline) without extensive pretreatment.^{7,9,13,47,48} In contrast, extensive pretreatment is required to activate sp^2 -bonded carbon and metal electrodes for charge-transfer.

$\text{Fe}(\text{CN})_6^{3-/4-}$ proceeds through a more inner-sphere electron-transfer pathway on boron-doped diamond, with the electrode kinetics being highly sensitive to the diamond surface termination.^{7,9,13,47-50} Specifically, the reaction appears to proceed through a specific surface site that is blocked by oxygen. k_{app}^0 values from 0.01 to 0.1 cm/s are commonly observed for clean, hydrogen-terminated films, but the rate constants decrease by over two orders of magnitude for oxygen-terminated films.^{7,9,13,47-50} $\text{Fe}^{3+/2+}$ is also of the inner-sphere type with k_{app}^0 being very sensitive to the surface carbon-oxygen functionalities on sp^2 -bonded carbon electrodes, specifically carbonyl functional

groups.⁵¹ In this system, carbonyl groups serve to lower the large energy barrier for reorganizing the solvation sphere around the $\text{Fe}^{3+/2+}$ redox center following electron transfer, apparently by forming a bridging complex with the reactant at the electrode surface.⁵¹ These functional groups are absent on hydrogen-terminated diamond and presumably this is the reason k_{app}^o is low, in the range of 10^{-4} to 10^{-6} cm/s.^{7,9,13,47,48} The more complicated organic systems, like dopamine, 4-MC, and 4-*tert*-butylcatechol, are all of the inner-sphere type with k_{app}^o from 10^{-4} to 10^{-6} cm/s at hydrogen-terminated diamond. It is thought that the slow kinetics for these polar aromatic analytes result from weak adsorption on the diamond surface.^{20,47,48} Strong adsorption of these compounds on sp^2 -bonded carbon electrodes results from π - π interactions between the molecule and the electrode. Diamond electrodes contain little π -electron density and any that exists is highly localized in grain boundaries. Recent work by our group has shown that ΔE_p for dopamine decreases with increasing levels of nondiamond sp^2 -bonded carbon impurity.⁵² Further work is needed to fully understand the structure-function relationships for such inner-sphere redox systems at diamond.

Cyclic voltammetric i - E curves for all five redox systems (0.1 and 1 V/s data) are presented for all four diamond types in Figure 4.4A-E. It is evident that the electrochemical response for all four diamond types is similar toward $\text{Fe}(\text{CN})_6^{3-/4-}$, $\text{Ru}(\text{NH}_3)_6^{3+/2+}$, $\text{IrCl}_6^{2-/3-}$, and 4MC, with the largest response variance seen for $\text{Fe}^{3+/2+}$. The electrode response, in terms of ΔE_p and i_p^{ox} , was very reproducible from film type-to-type and from film-to-film for a give type. The response reproducibility for our MSUMicro and MSUNano films is routinely 2-4% from film-to-film. Additionally, over the years we have studied boron-doped diamond films from various well-regarded

laboratories around the world (e.g., the U.S. Naval Research Laboratory and the National Institute for Materials Science in Japan) and have found the response for these hydrogen-terminated films is very similar to the response for the films reported herein.

In general, all four film types exhibit relatively low ΔE_p values for $\text{Fe}(\text{CN})_6^{3-/4-}$, $\text{Ru}(\text{NH}_3)_6^{3+/2+}$, $\text{IrCl}_6^{2-/3-}$, with larger values for 4-MC and $\text{Fe}^{3+/2+}$. In all cases, the forward reaction peak currents varied linearly with $\nu^{1/2}$, indicating that the electrode kinetics are controlled by mass transfer (semi-infinite linear diffusion) of the reactant to the electrode surface. All four diamond thin-film types exhibit active responses for $\text{Fe}(\text{CN})_6^{3-/4-}$, $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ and $\text{IrCl}_6^{2-/3-}$ without any conventional pretreatment. Time-consuming pretreatment is almost always required to activate sp^2 -bonded carbon and metal electrodes for electron-transfer. Pretreatment often improves the electrode kinetics for redox analytes, but can cause significant variability in electrode surface microstructure and chemistry depending on the pretreatment procedure. These differences can lead to significant response variability for the inner-sphere systems.⁵³ The larger ΔE_p values for 4-MC and $\text{Fe}^{3+/2+}$ are not attributable to an unclean surface, but rather, result from the nature of the reaction mechanism at the non-polar, hydrogen-terminated diamond surface.

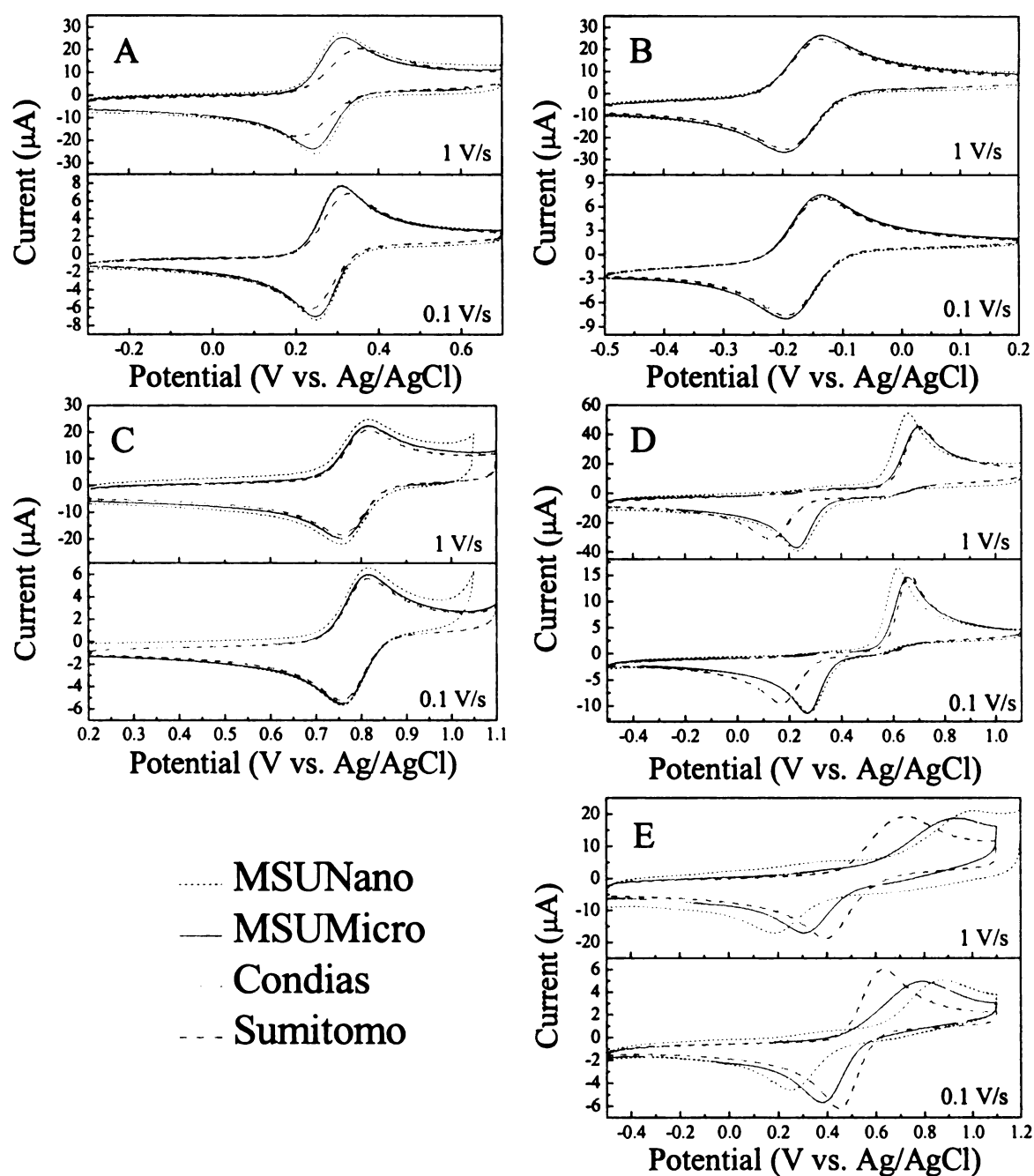


Figure 4.4 Cyclic voltammetric i - E curves for all four diamond types in (A) 0.1 mM $\text{Fe}(\text{CN})_6^{3-/4-}$, (B) 0.1 mM $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ and (C) 0.1 mM $\text{IrCl}_6^{2-/3-}$, all in 1 M KCl, and (D) 4-methylcatechol and (E) $\text{Fe}^{3+/2+}$ in 0.1 M HClO_4 . Curves for scan rates of 0.1 and 1 V/s are shown (geometric area = 0.2 cm²).

A summary of the cyclic voltammetric data for all the diamond thin-film types is presented in Table 4.1. ΔE_p and i_p^{ox}/i_p^{red} values are presented for a single scan rate. k_{app}^o was calculated from the variation of ΔE_p with scan rate, as described in Chapter 2. k_{app}^o values are listed, as well as the range of scan rates over which they were determined. Finally, some comparison rate constant data for glassy carbon are given.

For $\text{Fe}(\text{CN})_6^{3-/4-}$, $\text{Ru}(\text{NH}_3)_6^{3+/2+}$, and $\text{IrCl}_6^{2-/3-}$, ΔE_p is approximately the same for all four electrode types excluding $\text{Fe}(\text{CN})_6^{3-/4-}$ at the Sumitomo electrode, as ΔE_p is 174 mV rather than *ca.* 80 mV. For $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ and $\text{IrCl}_6^{2-/3-}$, relatively low ΔE_p values are seen even for moderately fast scan rates of 20-30 V/s, while for $\text{Fe}(\text{CN})_6^{3-/4-}$, relatively low ΔE_p values are observed only at scan rates below 2 V/s. The i_p^{ox}/i_p^{red} peak current ratio for all three redox systems is near 1, as expected. Standard deviations in k_{app}^o of less than 10% are seen and, importantly, the deviation does not depend on the scan rate. This indicates that the ΔE_p values, hence k_{app}^o , are not significantly affected by uncompensated ohmic resistance (both the solution and electrode) within the cell. k_{app}^o for $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ and $\text{IrCl}_6^{2-/3-}$ is in the low 10^{-1} cm/s range, which is close to the highest values reported for freshly activated glassy carbon.^{19-24,47,48} k_{app}^o for $\text{Fe}(\text{CN})_6^{3-/4-}$ is a factor of 5 lower in the mid 10^{-2} cm/s range. The electrode kinetics for $\text{Fe}(\text{CN})_6^{3-/4-}$ are a little more sluggish at the Sumitomo electrode, possibly due to low levels of surface oxygen. Surface carbon-oxygen functionalities are known to inhibit the electrode kinetics for $\text{Fe}(\text{CN})_6^{3-/4-}$ at diamond.^{49,50} Although the presence of such functional groups was not experimentally verified, the $\text{Fe}^{3+/2+}$ data presented below give credibility to this supposition.

Table 4.1 Cyclic voltammetric and heterogeneous electron-transfer rate constant data for five redox systems at MSUMicro, Condias, Sumitomo, and MSUNano boron-doped diamond thin-film electrodes.^a

Analyte	Electrode	ΔE_p (mV) at (Scan Rate (V/s))	I_p^{ox}/I_p^{red} at 0.1 V/s	Scan Range for k_{app}^o (V/s)	k_{app}^o (cm/s)	k_{app}^o (cm/s) for GC ^b
Fe(CN)₆^{3-/4-} $\alpha = 0.5$	MSUMicro	77 (2)	1.00	0.7-10	0.066 ± 0.005	0.10 ± 0.02
	Condias	83 (2)	1.01	0.3-5.0	0.056 ± 0.005	
	Sumitomo	174 (2)	1.01	0.1-2.0	0.0077 ± 0.0006	
	MSUNano	81 (2)	1.01	1.0-3.5	0.053 ± 0.004	
Ru(NH₃)₆^{3+/2+} $\alpha = 0.5$	MSUMicro	88 (20)	1.01	5.0-29	0.107 ± 0.009	0.24 ± 0.07
	Condias	90 (1)	0.94	0.3-1.5	0.0213 ± 0.0007	
	Sumitomo	97 (20)	0.95	6.0-20	0.082 ± 0.007	
	MSUNano	88 (20)	.93	4.0-30	0.102 ± 0.008	
IrCl₆^{2-/3-} $\alpha = 0.5$	MSUMicro	81 (30)	1.09	15-50	0.19 ± 0.04	0.50 ± 0.06
	Condias	80 (30)	1.08	12-30	0.27 ± 0.05	
	Sumitomo	85 (30)	1.08	15-30	0.18 ± 0.03	
	MSUNano	89 (30)	1.09	15-40	0.14 ± 0.02	
4-MC $\alpha = 0.45$	MSUMicro	360 (0.1)	1.81	0.1-1.0	1.0 x 10 ⁻⁵	-----
	Condias	473 (0.1)	1.61	0.1-1.0	1.0 x 10 ⁻⁶	
	Sumitomo	510 (0.1)	1.58	0.1-1.0	5.0 x 10 ⁻⁷	
	MSUNano	365 (0.1)	1.66	0.1-1.0	8.5 x 10 ⁻⁶	
Fe^{3+/2+} $\alpha = 0.65$	MSUMicro	393 (0.1)	1.00	0.1-1.0	3.0 x 10 ⁻⁴	(2.5 ± 0.3) x 10 ⁻³
	Condias	683 (0.1)	0.87	0.1-1.0	2.0 x 10 ⁻⁵	
	Sumitomo	614 (0.1)	1.08	0.1-1.0	2.0 x 10 ⁻⁴	
	MSUNano	529 (0.1)	1.21	0.1-1.0	8.0 x 10 ⁻⁵	

^a The supporting electrolyte for 0.1 mM solutions of Fe(CN)₆^{3-/4-}, Ru(NH₃)₆^{3+/2+}, and IrCl₆^{2-/3-} was 1 M KCl, while 0.1 mM solutions of 4-MC and Fe^{3+/2+} were prepared in 0.1 M HClO₄. Heterogeneous electron-transfer rate constants for Fe(CN)₆^{3-/4-}, Ru(NH₃)₆^{3+/2+}, and IrCl₆^{2-/3-} were determined from ΔE_p - ν trends, while the rate constants for 4-MC and Fe^{3+/2+}, as well as all α values, were determined by digital simulations (DigiSim 3.03).

^b GC heterogeneous electron-transfer rate constants from ref 44.

Consistent with previous observations, k_{app}^o for 4-MC and $\text{Fe}^{3+/2+}$ is several orders of magnitude lower than the values for the other redox systems.^{7,9,13} As mentioned above, these two redox systems proceed through an inner-sphere mechanism and thus the kinetics of the reaction are very sensitive to the physicochemical properties of the diamond thin-film electrode. The largest rate constant for 4-MC is observed for the MSUMicro electrode (10^{-5} cm/s), while the lowest (10^{-7} cm/s) is seen for the Sumitomo electrode. We suppose that the relatively slow kinetics for this redox system on diamond result from the lack of adsorption on the non-polar, hydrogen-terminated surface. Research with glassy carbon has shown that the electrode kinetics for 4-MC are relatively insensitive to the presence of surface oxides, and that adsorption to the surface is necessary for rapid electron transfer.²⁴ For example, Hunt-DuVall and McCreery demonstrated that removing surface impurities to increase adsorption sites on glassy carbon resulted in an increase in the electron-transfer rate for catechols.²⁴ Their work demonstrates the vital role adsorption plays in the electron-transfer process, effects that may involve changes in the reorganization energy. Anything that inhibits the adsorption (e.g., chemical modification) of catechols also inhibits the electrode kinetics. As mentioned above, related work in our group has shown that the adsorption of dopamine on high-quality, hydrogen-terminated diamond can be promoted by the introduction of nondiamond sp^2 -bonded carbon impurity, which can be controllably incorporated during the deposition.⁵² At this preliminary stage, there appears to be a direct correlation between a reduction in ΔE_p and an increase in the surface coverage and the nondiamond carbon content.

The rate constant for $\text{Fe}^{3+/2+}$ is in the 10^{-4} to 10^{-5} cm/s range for all four electrode types. One of the largest k_{app}^o is observed for the Sumitomo diamond thin film, which also exhibits the smallest k_{app}^o for $\text{Fe}(\text{CN})_6^{3-/4-}$. As mentioned, surface oxygen inhibits the $\text{Fe}(\text{CN})_6^{3-/4-}$ and promotes the $\text{Fe}^{3+/2+}$ electrode kinetics on boron-doped diamond thin-film electrodes. Considering this, it is possible that this diamond thin-film type has some unintentional surface carbon-oxygen functional groups, likely of the carbonyl type.

The k_{app}^o values were additionally verified by digital simulation (DigiSim[®] 3.03). All simulated cyclic voltammetric i - E curves consisted of only faradaic current for the redox system. k_{app}^o values and transfer coefficients, α , were varied to match the simulated ΔE_p and voltammetric i - E curve shape with the experimental curves. In all cases for the experimentally determined k_{app}^o , the difference between the experimental and simulated ΔE_p values was 9 mV or less. Figure 4.5A and B show two examples of simulated and experimental i - E curves for $\text{Fe}(\text{CN})_6^{3-/4-}$ (0.1 V/s) at the Sumitomo electrode and $\text{IrCl}_6^{2-/3-}$ (50 V/s) at the MSUMicro electrode. The agreement of the ΔE_p and shape of the experimental and simulated voltammetric curves is excellent, even with the absence of background current, which is most prominent for the higher scan rate. α values of 0.5 for $\text{Fe}(\text{CN})_6^{3-/4-}$, $\text{Ru}(\text{NH}_3)_6^{3+/2+}$, and $\text{IrCl}_6^{2-/3-}$, 0.45 for 4-MC and 0.65 for $\text{Fe}^{3+/2+}$ were determined, consistent with previously reported values for diamond thin film.⁷

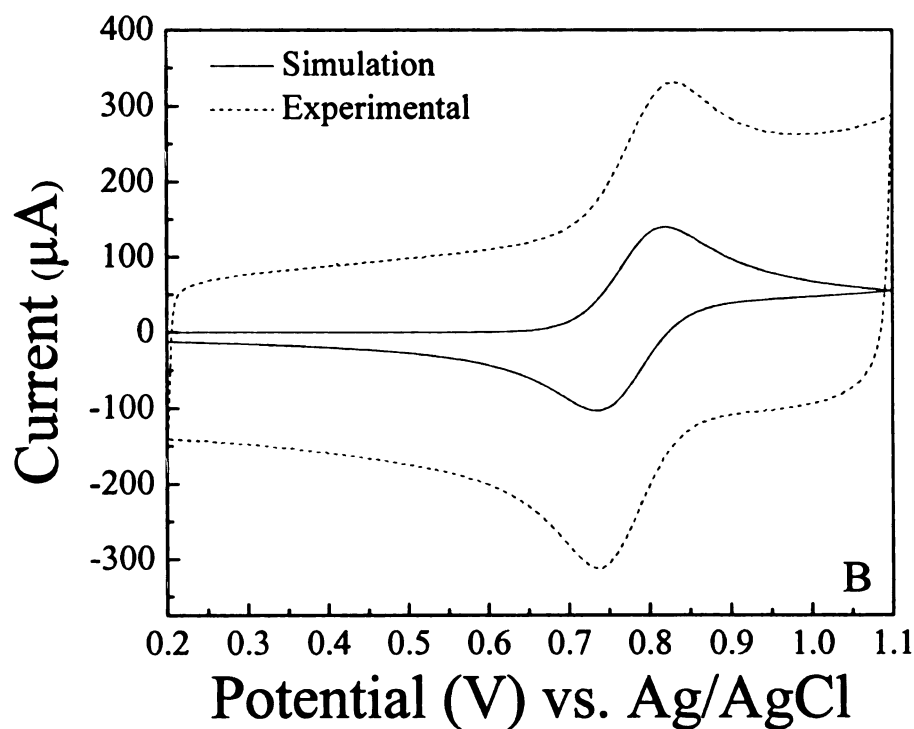
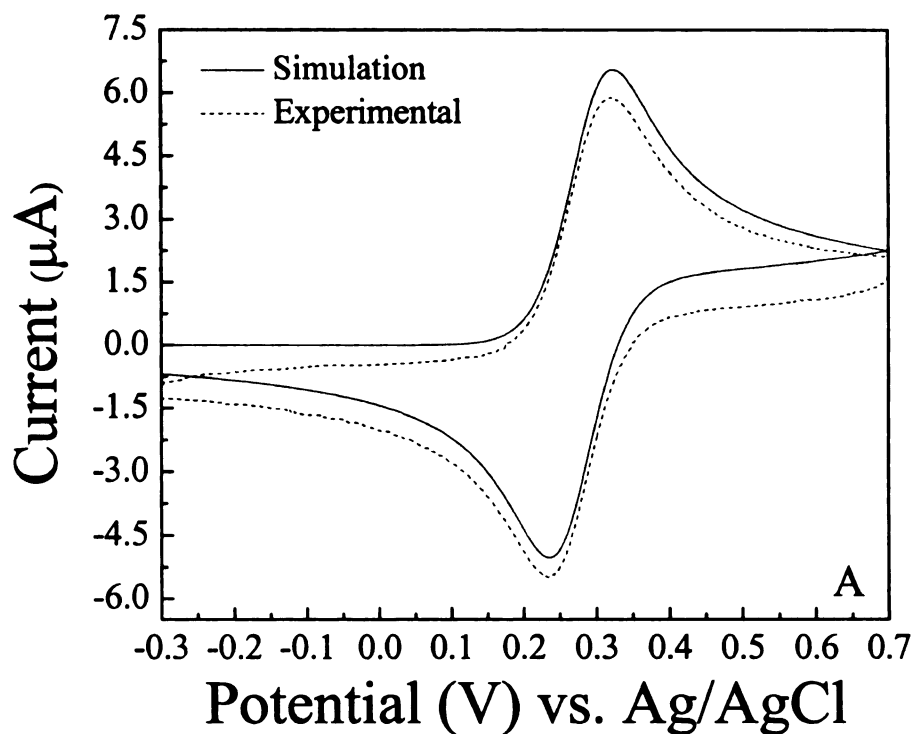


Figure 4.5 Experimental and simulated (DigiSim® 3.03) cyclic voltammetric *i-E* curves for (A) 0.1 mM $\text{Fe}(\text{CN})_6^{3-/4-}$ in 1 M KCl at the Sumitomo diamond electrode (0.1 V/s) and (B) 0.1 mM $\text{IrCl}_6^{2-/3-}$ in 1 M KCl at the MSUMicro diamond electrode (50 V/s). The experimental voltammograms contain both the background and faradaic currents while the simulated voltammograms contain just the faradaic current.

4.2.3 pH Effects on Voltammetric Response

Oxides of varying type and coverage exist on sp^2 -bonded carbon electrode surfaces, terminating the edge plane and defect sites of the microstructure. They form naturally during exposure to the atmosphere (air/H₂O), and are also introduced during pretreatment (e.g., mechanical polishing or anodic polarization). Surface oxides influence the chemical and electrochemical properties of the carbon and they can have a profound effect on the electric double-layer structure and the extent of analyte adsorption. Carboxylic acid functional groups are common on oxygen-containing glassy carbon surfaces with a pK_a near 4.5.^{45,54} Therefore, depending on the solution pH, these groups can either be protonated (uncharged) or deprotonated (negatively charged). Highly charged redox systems can be affected by the presence of these ionizable functional groups (e.g., excess surface charge). For example, ΔE_p for an anionic redox system, such as $Fe(CN)_6^{3-/4-}$ or $IrCl_6^{2-/3-}$, becomes strongly pH dependent, increasing significantly when these functional groups are deprotonated. On the other hand, ΔE_p for a cationic redox system, such as $Ru(NH_3)_6^{3+/2+}$, is reduced when these functional groups are deprotonated. For instance, Deakin et al. observed that k_{app}^o for $Fe(CN)_6^{3-/4-}$ or $IrCl_6^{2-/3-}$ decreases with increasing pH from 2 to 8, while k_{app}^o for $Ru(NH_3)_6^{3+/2+}$ increases.⁵⁴ The larger ΔE_p for $Fe(CN)_6^{3-/4-}$ and smaller value for $Ru(NH_3)_6^{3+/2+}$, when there is excess negative surface charge, reflects more sluggish and more rapid electrode kinetics, respectively, because of electrostatic repulsion and attraction (e.g., electric double-layer effects). Electrostatic repulsion of $Fe(CN)_6^{3-/4-}$ leads to a greater electron tunneling distance and more sluggish electrode kinetics. The opposite trend holds true for $Ru(NH_3)_6^{3+/2+}$.

The response for charged redox analytes at hydrogen-terminated diamond thin-film electrodes should be unaffected by solution pH because of the absence of ionizable surface oxides. To test this, the cyclic voltammetric responses for $\text{Fe}(\text{CN})_6^{3-/4-}$ and $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ were examined at pH 1.90 and 7.35 – below and above the expected pK_a of the carboxylic acid functional groups. Table 4.2 presents a summary of the results for all four electrode types. Generally speaking, there is minimal effect of solution pH on the ΔE_p and k_{app}^o values for these two redox systems. k_{app}^o for $\text{Fe}(\text{CN})_6^{3-/4-}$ and $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ differs by a factor of 2, or less, at both pH values, at all four diamond thin-film types, consistent with a low oxide, hydrogen-terminated electrode surface.

Table 4.2 Cyclic voltammetric and heterogeneous electron-transfer rate constant data for $\text{Fe}(\text{CN})_6^{3-/4-}$ and $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ at MSUMicro, Condias, Sumitomo, and MSUNano boron-doped diamond thin-film electrodes, as a function of the solution pH.^a

Analyte	Electrode	Scan Range for ΔE_p and k_{app}^o (V/s)	ΔE_p Range (mV)		k_{app}^o (cm/s)	
			pH 1.90	pH 7.35	pH 1.90	pH 7.35
$\text{Fe}(\text{CN})_6^{3-/4-}$ $\alpha = 0.5$	MSUMicro	0.7-5.0	69-83	66-76	0.072 ± 0.004	0.112 ± 0.01
	Condias	0.1-1.0	68-89	67-82	0.026 ± 0.002	0.035 ± 0.002
	Sumitomo	0.3-2.0	77-103	77-126	0.024 ± 0.001	0.0141 ± 0.0001
	MSUNano	0.5-5.0	70-92	69-86	0.055 ± 0.003	0.062 ± 0.002
$\text{Ru}(\text{NH}_3)_6^{3+/2+}$ $\alpha = 0.5$	MSUMicro	15-39	78-97	82-99	0.13 ± 0.01	0.104 ± 0.004
	Condias	0.1-1.0	76-113	79-115	0.011 ± 0.001	0.011 ± 0.001
	Sumitomo	3.0-15	77-100	77-96	0.065 ± 0.002	0.071 ± 0.002
	MSUNano	3.0-20	73-95	71-88	0.083 ± 0.002	0.103 ± 0.004

^a The supporting electrolyte for 0.1 mM $\text{Fe}(\text{CN})_6^{3-/4-}$ and $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ was 1 M phosphate buffer at pH 7.35 and 1.90. Heterogeneous electron-transfer rate constants were determined from ΔE_p - ν trends and verified by digital simulation (DigiSim 3.03).

4.3 Conclusions

The electrochemical response of two commercial (Condias and Sumitomo) boron-doped diamond thin-film electrodes was compared with that of two types of boron-doped diamond thin film deposited in our laboratory (microcrystalline and nanocrystalline). The electrode response for all four electrode types, at least for the redox systems probed, was very reproducible from type-to-type and from film-to-film for a given type. The MSUMicro, Condias and Sumitomo films had similar textures, with nominal grain sizes of 1, 5 and 2 μm , respectively. The MSUNano film was much smoother, with 100 nm aggregates of diamond grains. The Raman spectral features for each film type were consistent with high-quality (i.e., low sp^2 -bonded carbon impurity content) boron-doped diamond. All the diamond electrodes exhibited a low and stable background current, about a factor of 10 lower than comparably sized glassy carbon. Apparent heterogeneous electron-transfer rate constants, k_{app}^o , for $\text{Fe}(\text{CN})_6^{3-/4-}$, $\text{Ru}(\text{NH}_3)_6^{3+/2+}$, and $\text{IrCl}_6^{2-/3-}$ were in the mid 10^{-2} to low 10^{-1} cm/s range without extensive electrode pretreatment. k_{app}^o for 4-MC and $\text{Fe}^{3+/2+}$ was much lower, in the range of 10^{-5} to 10^{-7} cm/s. k_{app}^o for $\text{Fe}(\text{CN})_6^{3-/4-}$ and $\text{Ru}(\text{NH}_3)_6^{3+/2+}$, at all four diamond types, was relatively independent of the solution pH. Surface carbon-oxygen functionalities, particularly those that are ionizable (e.g., carboxylic acid, $\text{pK}_a \sim 4.5$), can strongly influence the carbon electrode response. Such effects are routinely observed for glassy carbon, as the surface normally contains carbon-oxygen functionalities. Hydrogen-terminated diamond surfaces contain few, if any, ionizable carbon-oxygen functionalities; therefore, these pH effects are not observed. These results confirm that high-quality boron-doped diamond with reproducible

electrochemical behavior is available commercially, such that production of diamond electrodes as advanced electrocatalyst supports is possible once a suitable geometry is established.

4.4 References

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Chapter 5

Preparation and Characterization of Boron-Doped Diamond Powder: A Possible Dimensionally Stable Electrocatalyst Support Material

Abstract

Electrically conducting diamond powder was prepared by coating insulating diamond powder (8-12 μm diam, $\sim 2 \text{ m}^2/\text{g}$) with a thin boron-doped diamond layer using microwave plasma-assisted chemical vapor deposition. Deposition times from 1 to 6 h were evaluated. Scanning electron microscopy revealed that the diamond powder particles became more faceted with secondary growths developing at longer deposition times. Fusion of neighboring particles was also observed with increasing growth time. The first-order diamond phonon line appeared in the Raman spectrum at ca. 1331 cm^{-1} for deposition times up to 4 h, and was downshifted to as low as 1317 cm^{-1} for some particles after the 6 h growth. Electrical resistance measurements of the bulk powder confirmed that a conductive diamond overlayer formed, as the conductivity increased with deposition time from near zero (insulating, $<10^{-5} \text{ S/cm}$) for the uncoated powder to 1.5 S/cm after the 6 h growth. Ohmic behavior was seen in current-voltage curves recorded for the 4 h powder between $\pm 10 \text{ V}$. Cyclic voltammetric i - E curves for $\text{Fe}(\text{CN})_6^{3-/4-}$ and $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ were recorded to evaluate the electrochemical properties of the conductive powder when mixed with a 10 wt. % polytetrafluoroethylene (PTFE) binder. At scan rates between 10 and 500 mV/s , ΔE_p for $\text{Fe}(\text{CN})_6^{3-/4-}$ ranged from 140 to 350 mV while ΔE_p for $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ was slightly larger. The large ΔE_p reflect 1) ohmic

resistance within the powder/binder electrode because of poor particle-particle connectivity between the hard, jagged powder particles and 2) significant hydrophobicity (i.e., low electrode wetting) at a binder concentration of 10 wt. % PTFE. (ΔE_p for $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ decreased significantly by reducing the binder to 5 wt. %). Anodic polarization at 1.6 V vs. Ag/AgCl and 25 °C for 1 h was performed to compare the morphological and microstructural stability of the conductive diamond, graphite, and glassy carbon (GC) powders. The total charge passed during polarization was largest for the GC powder (0.88 C/cm²) and smallest for conductive diamond powder (0.18 C/cm²). SEM images taken of conductive diamond powder after polarization showed no evidence for degradation while significant morphological changes were seen for GC.

5.1 Introduction

In Chapter 1, the criteria for an ideal polymer electrolyte membrane fuel cell (PEMFC) electrocatalyst support material were outlined. Among other important requirements, high surface area ($\sim 100 \text{ m}^2/\text{g}$) supports are necessary to maximize electrocatalyst dispersion and utilization, while a gas permeable support is needed to allow diffusion of the reactants to the triple phase boundary. Typical sp^2 -bonded carbon-based supports in a powder form, such as Vulcan XC-72, satisfy both of these requirements, but lack long-term stability in PEMFCs. Planar boron-doped diamond films are neither high-surface-area nor gas permeable, but exhibit excellent dimensional stability in harsh environments.^{1,2} Thus, we believe development of high-surface-area, gas permeable, and corrosion resistant diamond electrode architectures will result in a new electrocatalyst support material for PEMFCs. Our first step toward development of an advanced electrocatalyst support was the preparation and characterization of electrically conducting diamond powder.

High-surface-area diamond powder (so-called nanodiamond) is produced in large quantities worldwide via the detonation of explosives. This nanodiamond powder has a nominal particle size of *ca.* 5-10 nm and a specific surface area of 200-600 m^2/g .³ Although it is available commercially and is relatively inexpensive (\$1 to 5/g), nanodiamond powder is not electrically conducting, and thus, cannot be used as an electrocatalyst support. Diamond powder of lower surface area, used as an abrasive, is also available commercially. This diamond powder is produced by high pressure, high temperature synthesis and typically has particle size ranging from *ca.* 0.1 to 100 μm and a specific surface area of *ca.* 5 m^2/g , or lower. However, the commercially-available

abrasive powders are not electrically conducting. To overcome this limitation and to investigate the potential of conducting diamond powder as an electrocatalyst support, we produced electrically conducting diamond powder by coating the diamond abrasive with a thin layer of boron-doped diamond via microwave plasma-assisted chemical vapor deposition (PACVD).

This chapter describes the initial phase of our advanced carbon support development in which the first-known electrically conducting diamond powder was prepared and characterized. The powder was formed by coating insulating abrasive diamond powder with a boron-doped diamond overlayer, as depicted in Figure 5.1. Conductive powders were prepared using deposition times from 1 to 6 h. Although the surface area of this new material ($\sim 2 \text{ m}^2/\text{g}$) is lower than that desired for an ideal support, it is a useful starting point for making electrically conducting diamond powder and evaluating its physical, electrical, and electrochemical properties. The powder morphology and microstructure were characterized before and after conductive diamond growth by scanning electron microscopy (SEM) and Raman spectroscopy. X-ray diffraction (XRD) analysis was used to verify the crystallinity of the coated powder. Bulk electrical measurements were performed to determine the ohmic resistance of the packed powder. Electrodes for electrochemical testing were prepared by mixing the conductive powder with a polytetrafluoroethylene (PTFE) binder, casting a thin layer of the slurry on glass, and curing in an oven. The electrochemical properties of the powder electrode were investigated by cyclic voltammetry using two redox systems: $\text{Fe}(\text{CN})_6^{3-/4-}$ and $\text{Ru}(\text{NH}_3)_6^{3+/2+}$. Finally, potentiostatic measurements were performed in strong acid to evaluate the degradation resistance of the conducting diamond during anodic

polarization. Comparison measurements were made with graphite and glassy carbon (GC) powders.

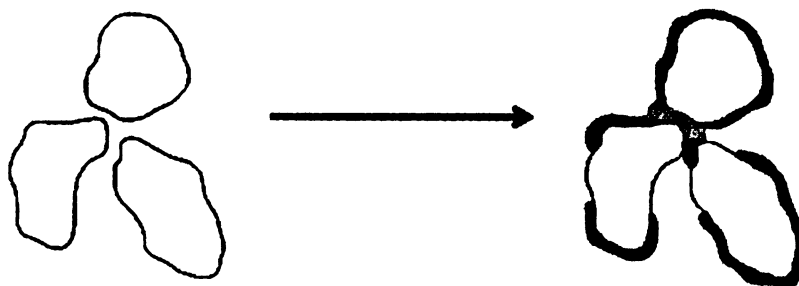


Figure 5.1 Deposition scheme for coating insulating diamond powder with a conductive, boron-doped diamond overlayer showing both full and partial grain coverage as well as fusion of neighboring grains. The shaded areas represent the conducting diamond overlayer.

5.2 Results and Discussion

5.2.1 Material Characterization and Electrical Measurements

According to the scheme in Figure 5.1, the insulating powder is either partially or fully covered with an electrically conducting layer of boron-doped diamond. Scanning electron micrographs of the uncoated (acid-washed) and coated powders after deposition times of 1, 2, and 4 h are shown in Figure 5.2A-D. Although it is difficult to distinguish differences in particle size, changes in the powder morphology are apparent as a function of the deposition time. The uncoated powder particles in Figure 5.2A are irregularly shaped and characterized by jagged edges with little faceting. The particle diameters are in the range of ~8-12 μm . Figure 5.2B shows the powder after a 1 h deposition. The particle edges become smoother and more well-defined faceting develops. Many of the

particle surfaces consist of multiple grooves along the edges of the triangular facets which may be sites of preferential nucleation. For example, carbon atoms may nucleate at these sites with growth continuing laterally across the surface. Pits are also present on the facet surfaces and may result from incomplete coalescence of growth layers across the surface, which begin at different nucleation sites.

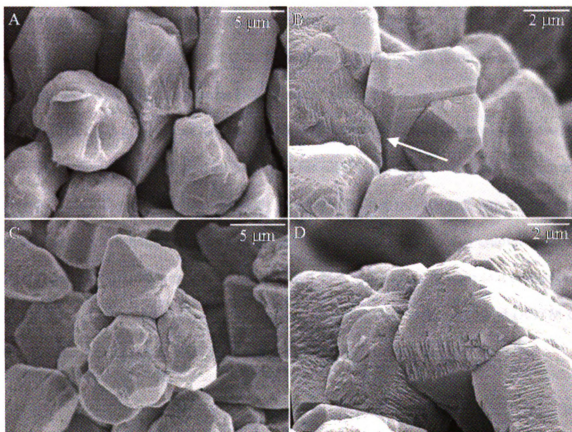


Figure 5.2 Scanning electron micrographs of (A) bare diamond powder and conductive diamond powder after (B) 1, (C) 2, and (D) 4 h coating times.

The most obvious morphological change after diamond deposition is the fusion of neighboring particles, as indicated by the arrow in Figure 5.2B. During the 2 h

deposition, more neighboring particles fused together forming clusters of 4 or 5 grains, as seen in Figure 5.2C. These clusters become larger with longer deposition times. Clusters of ~8 to 10 diamond particles formed during the 4 h deposition and even larger clusters formed during the 6 h period. Ideal growth conditions would produce individually coated diamond particles without the loss of surface area that occurs when neighboring particles fuse together. On the other hand, the particle fusion likely imparts a greater degree of mechanical stability and electrical conductivity to the powder. For this deposition method, shorter growth times of 2 or 4 h seem appropriate to form the conductive diamond overlayer while minimizing the extent of particle fusion.

Figure 5.3 presents an X-ray diffraction (XRD) spectrum of a 4 h growth powder, which is representative of spectra collected for all growth times. The XRD spectrum reveals highly crystalline diamond with no scattering for sp^2 -bonded carbon impurity (graphitic or amorphous carbon) at all the deposition times (e.g., no d_{002} graphite peak at 26.5 degrees).⁴ Intense peaks at 43.9, 75.3, and 91.5 degrees are present that correspond to the (111), (220), and (311) crystallographic orientations of cubic diamond (ASTM 6-0675). The broad peak at 69.5 degrees is from the Si substrate (ASTM 27-1402).

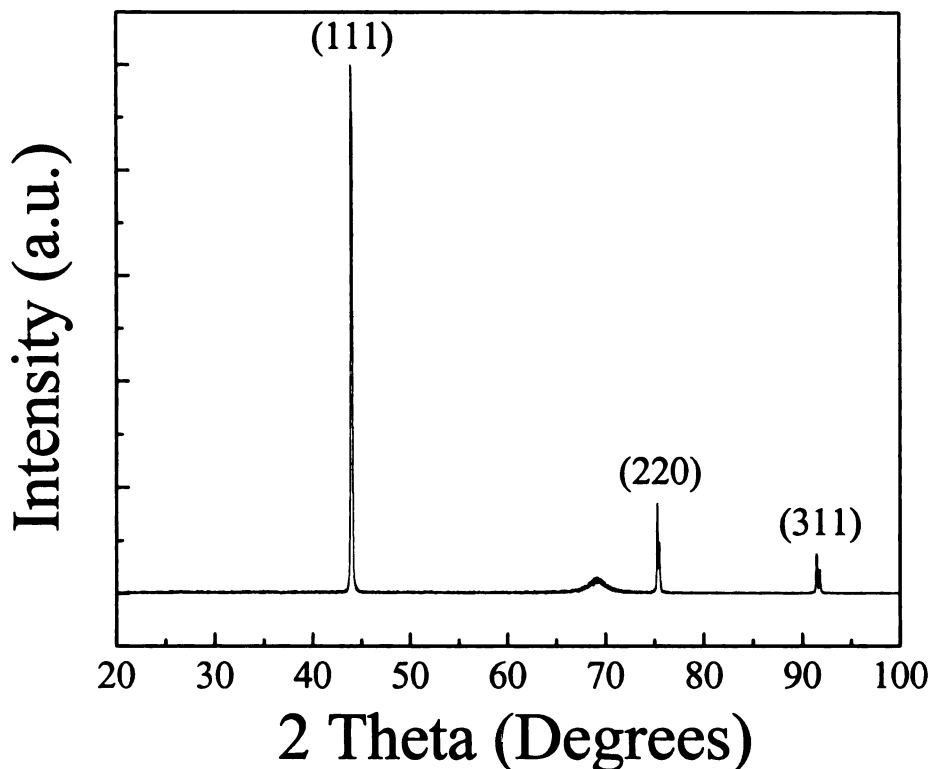


Figure 5.3 X-ray diffraction spectrum of a 4 h growth diamond powder sample.

Raman spectroscopy was also used to evaluate the microstructure of the coated diamond powders. Figure 5.4 presents Raman spectra for the diamond powders after deposition times of 0 (acid washed powder), 1, 2, 4, and 6 h. The first-order diamond phonon line, expected at 1332 cm^{-1} , is present in the spectra for the uncoated and coated powders after the 1, 2, and 4 h periods. The linewidth (FWHM) remains relatively constant, *ca.* 8 cm^{-1} , for all deposition times. For comparison, the measured linewidth for an HPHT reference diamond sample was 7 cm^{-1} . To a first approximation, the linewidth is inversely related to the phonon lifetime and is a measure of the defect density. Thus, the FWHM data suggest that the defect density in the diamond overlayer does not change much from that of the uncoated powder particles. However, a major difference in the

Raman spectrum is seen for the 6 h deposition as the first-order diamond phonon line downshifts by an average of ca. 6 cm^{-1} . In addition, there is a large deviation in the line position for different powder particles in a 6 h growth sample. For example, the diamond line position for about half the particles sampled was 1331 cm^{-1} , while the peak was downshifted for the other half to as low as 1317 cm^{-1} . The diamond line position is known to shift with stress; the degree and direction of which are measures of stress magnitude and type (i.e., tensile or compressive).⁵⁻⁷ Particle fusion in the 6 h growth may cause local tensile stress that is reflected in the downshift in the one-phonon line. In addition to changes in the diamond line position at long deposition times, the spectra also show that the scattering intensity from nondiamond carbon impurity, centered between 1550 and 1580 cm^{-1} , increases with growth time. Some scattering intensity is seen for all the deposition times, but is most intense for the 6 h growth. The nondiamond carbon is not pure graphite but likely consists of a mixture of sp^2 and sp^3 -bonded carbon.

In order to verify that the particles were coated with an electrically conducting overlayer, bulk powder electrical resistance measurements were made and the data are presented as conductivities in Table 5.1. These data provide conclusive evidence that the particles are either partially or fully coated with a conducting overlayer and that a high level of connectivity exists when the powder particles are packed together. Several factors influence the electrical conductivity of the packed powder including (i) the electronic properties of the overlayer (charge carrier concentration and mobility) that are governed primarily by the boron-doping level, (ii) the extent and conformity of the conductive diamond overlayer, (iii) the particle-particle connectivity, and (iv) the nondiamond carbon impurity that might form during deposition. As seen in Table 5.1,

the uncoated powder has poor conductivity (resistance $>40\text{ M}\Omega$). The powder conductivity after the 1 h deposition increases to 0.027 S/cm for the as-deposited (i.e., no post-growth cleaning treatment) powder. The powder conductivity increases further for the as-grown 4 and 6 h depositions to 1.4 and 1.5 S/cm, respectively.

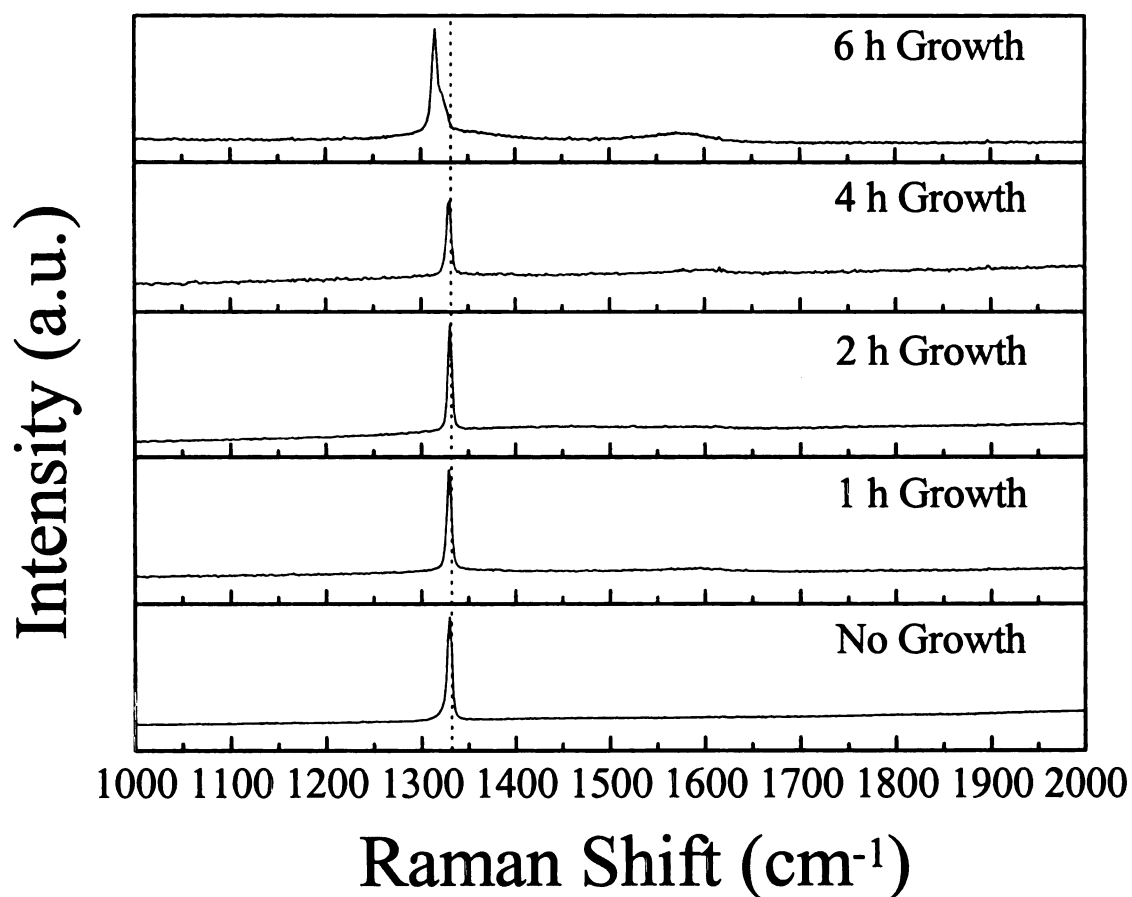


Figure 5.4 Raman spectra of bare diamond powder and conductive diamond powder after coating times of 1, 2, 4, and 6 h.

Table 5.1 Bulk conductivity values of graphite and CVD diamond powder before (as-grown) and after (cleaned) washing in warm aqua regia (30 min) and warm 30% H₂O₂ (30 min).

Sample	Conductance (S/cm)
Graphite powder	1.3
Acid washed diamond powder	0.0

Conductive diamond Powder	As-grown	Cleaned
1 h growth	0.027	4.0×10^{-5}
2 h growth	0.015	0.010
4 h growth	1.4	0.29
6 h growth	1.5	0.30

As indicated by the Raman data, nondiamond carbon impurity forms during the deposition and this will have an influence on the overlayer conductivity. In order to assess the contribution of nondiamond carbon, the conductivity of the powders was also measured after acid washing (i.e., "cleaned"), which has been shown to remove nondiamond carbon and other impurities.⁸ Scanning electron micrographs of a 4 h conductive diamond powder before and after acid washing are presented in Figure 5.5A and B, respectively. There was no evidence of morphological damage to the diamond powder as a result of acid washing, however, the conductivity of the samples changed. For example, Table 5.1 shows that the conductivity of the 1 h powder decreases by 3 orders of magnitude after cleaning, which is consistent with its original conductivity being largely due to the presence of the nondiamond carbon impurity on the surface. After acid washing, the conductivity for the 4 and 6 h growths decreases by only a factor

of 5-7. Therefore, their conductivity is primarily due to the boron-doped overlayer with much less contribution from nondiamond carbon impurity.

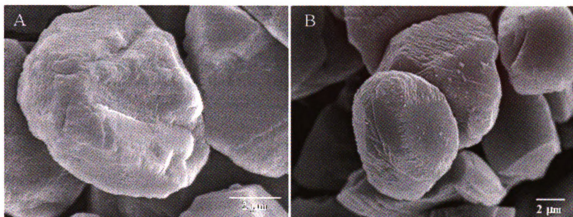


Figure 5.5 Scanning electron micrographs of a 4 h growth conductive diamond powder (A) as-grown and (B) after acid washing.

The data in Table 5.1 were obtained from a simple resistance measurement using an ohmmeter. However, the conductivity of the diamond powder after a 4 h deposition and the graphite powder were also evaluated by measuring i - V curves between ± 10 V. Figure 5.6 shows these data, in addition to that of a boron-doped diamond (BDD) thin-film electrode, for comparison. Ohmic behavior (linear curve) was observed for both powder types and for BDD thin film over the entire voltage range with linear regression correlation coefficients greater than 0.999. The conductivities ($1/R$) of the conductive diamond and graphite powders were calculated from the curve slopes ($V = iR$) and were in agreement with the resistance values obtained by the ohmmeter, 18 and 6 Ω , respectively. These results indicate that the boron-doped powder has high electrical

conductivity exhibiting ohmic behavior between ± 10 V and that good particle-particle contact is achieved when packed as a dry powder.

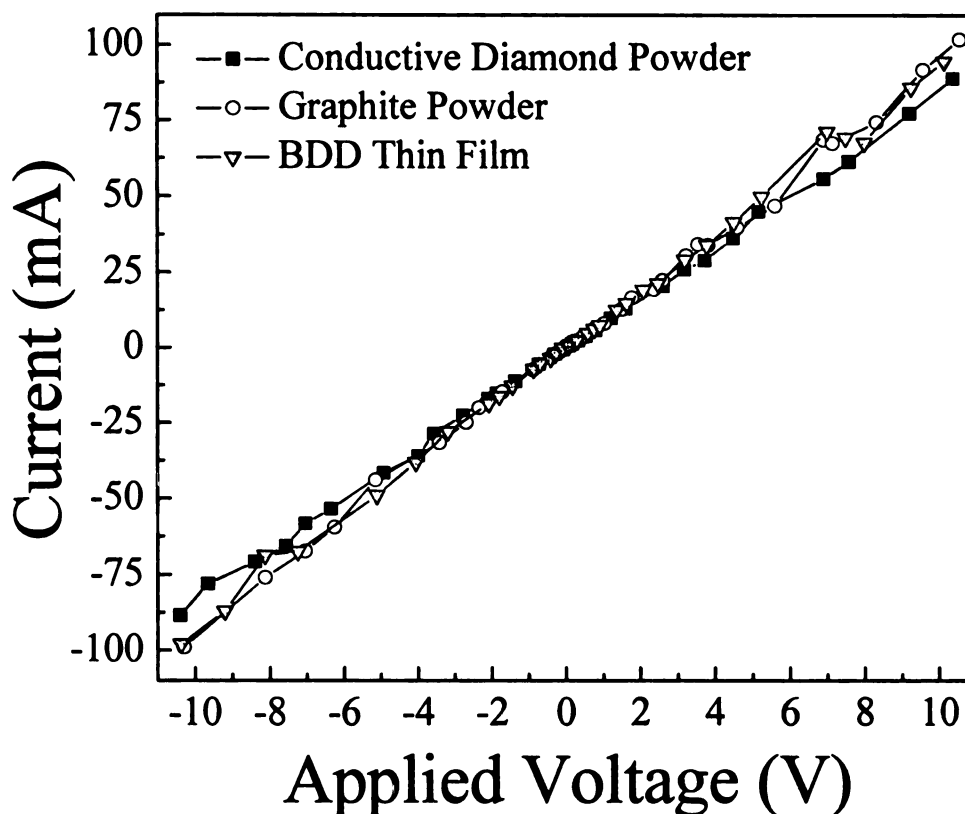


Figure 5.6 I - V curves for a 4 h growth conductive diamond powder, graphite powder, and a boron-doped diamond thin film over a ± 10 V range.

5.2.2 Electrochemical Characterization

Figure 5.7A shows background cyclic voltammetric i - E curves in 0.1 M HClO_4 for the diamond powder electrodes bound with PTFE (10 wt. %) and mounted on glass slides. Curves are shown for powder samples coated with a conductive diamond overlayer for different periods of time. All the powders were used as-grown and not cleaned by acid washing. The curve for the uncoated diamond powder (not shown)

exhibited zero current at all potentials due to its electrically insulating nature. It is important to remember that for sufficient electrical conduction through the powder electrode, the particles must be conformally coated with a conductive diamond overlayer and be in good contact with one another. The network of conductive particles must also be in good electrical contact with the current collector (e.g., copper foil). If poor electrical connectivity exists within the powder network, then the electrical resistance will be high and this resistance will affect the i - E curve by distorting the shape and increasing the ΔE_p value for a redox test system. The curves in Figure 5.7A appear relatively flat and featureless within the working potential window for all deposition times. Close inspection of the curve shapes, however, reveals that small oxidation and reduction peaks develop near ~ 350 mV, as shown in Figure 5.7B, particularly for the 4 and 6 h powders. These peaks are commonly seen for sp^2 -bonded carbon electrodes with a significant fraction of exposed edge plane (e.g., GC) where redox-active surface carbon-oxygen functionalities can form (e.g., quinones).⁹ Since such peaks are not normally seen with high quality, hydrogen-terminated diamond thin films, we attribute these peaks to carbon-oxygen functional groups that form at reactive sites on the nondiamond carbon impurity. The largest background current in this region is seen for the 6 h growth. These electrochemical observations are consistent with the Raman data presented above which revealed increasing nondiamond carbon impurity content for the 4 and 6 h powders.

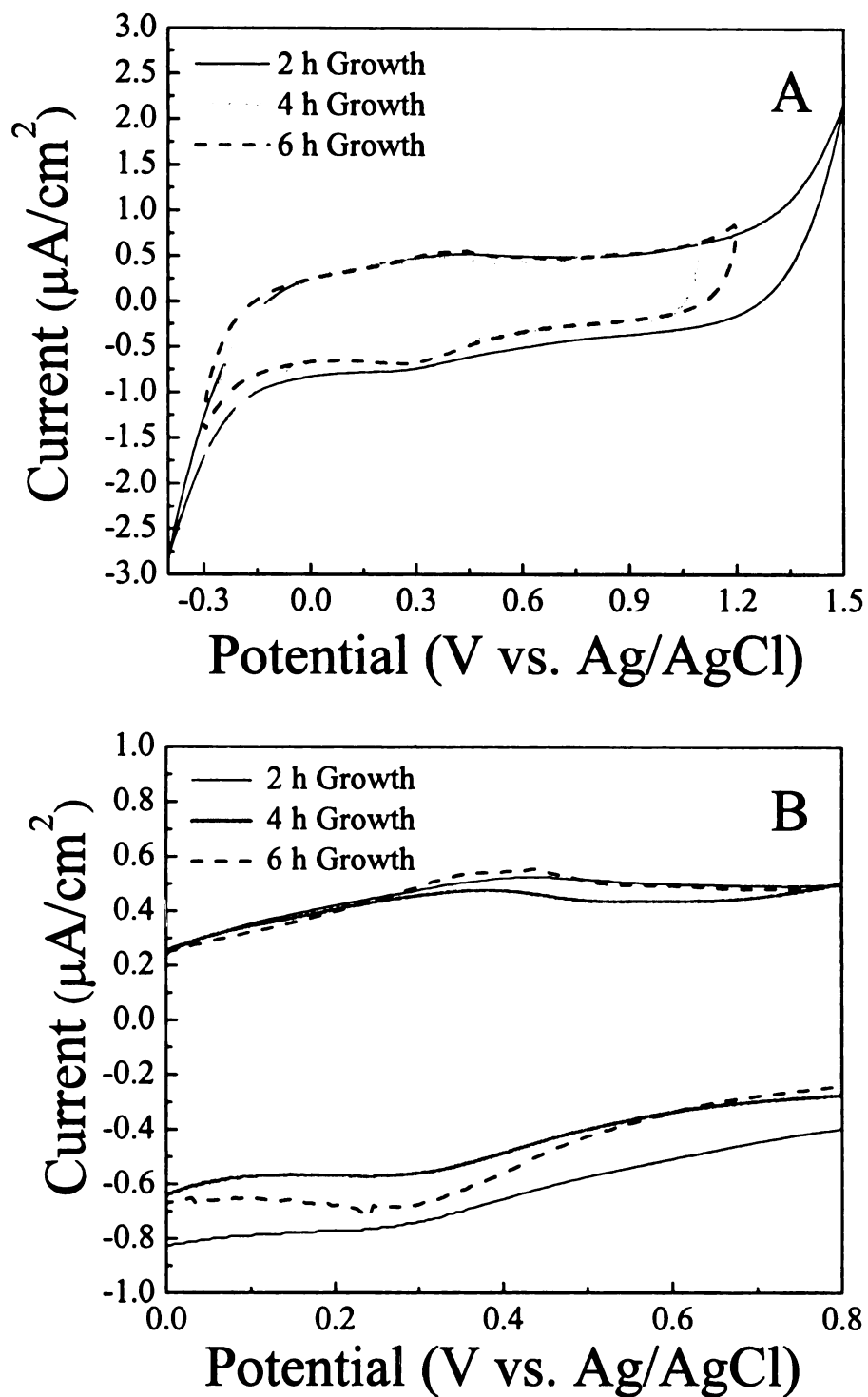


Figure 5.7 (A) Background cyclic voltammetric i - E curves for conductive diamond powder electrodes (2, 4, and 6 h deposition times) in 0.1 M HClO_4 at 100 mV/s. (B) Enlarged view of an 800 mV region. Current is normalized to the diamond powder surface area exposed to solution.

In general, the working potential window (potential range between solvent/electrolyte breakdown) for all the growth times is less than what is commonly observed for high-quality diamond thin films.^{8,10-13} Such diamond thin-film electrodes usually exhibit a flat and featureless voltammetric response over a potential window greater than 3 V in acidic media. The smaller potential window for the conducting powders is also consistent with the presence of nondiamond carbon impurity on the powder surface. A small amount of this impurity is sufficient to cause a reduced potential window, as oxygen and hydrogen evolution are known to occur with lower overpotential on sp^2 -bonded carbon electrodes, such as GC.¹¹ In fact, research with diamond thin-film electrodes containing differing levels of nondiamond carbon impurity has revealed that as the impurity increases, the working potential window decreases.¹⁴

The electrochemical response of the conductive diamond powder (with 10 wt. % PTFE binder) was also probed by cyclic voltammetry using $\text{Fe}(\text{CN})_6^{3-/4-}$ and $\text{Ru}(\text{NH}_3)_6^{3+/2+}$. Both of these redox systems are regularly used to study the electrochemical response of a variety of carbon electrodes, including boron-doped diamond thin film and sp^2 -bonded carbon, such as planar GC, as discussed in Chapter 4.^{8,10,13,15-21} The cyclic voltammetric ΔE_p values and curve shapes for electrochemical redox systems are influenced by a number of variables, including the electron-transfer kinetics and ohmic resistance effects. For example, the density of electronic states in the electrode material near the formal potential of the redox system (i.e., the electrical conductivity) affects the electron-transfer kinetics. Regardless of the mechanism (i.e., inner- or outer-sphere), high rates of electron-transfer can only occur when the electrode has a sufficient density of states available at the energy (i.e., potential) required to accept

electrons from donor states of the analyte or to donate electrons to acceptor states of the analyte.¹⁸ Previous work has shown that highly boron-doped diamond thin film possess a high density of electronic states and supports relatively rapid electron-transfer rates for $\text{Fe}(\text{CN})_6^{3-/4-}$ and $\text{Ru}(\text{NH}_3)_6^{3+/2+}$.^{8,10,13,20-23} Ohmic resistance (solution or electrode) can also significantly affect curve shape, increasing ΔE_p and decreasing the peak current (i_p).

Cyclic voltammetric i - E curves for $\text{Fe}(\text{CN})_6^{3-/4-}$ (10 to 500 mV/s) for a 4 h as-grown diamond powder electrode are shown in Figure 5.8A. Oxidation and reduction peaks are seen for $\text{Fe}(\text{CN})_6^{3-/4-}$ in Figure 5.8A, although the waveform is distorted and ΔE_p is large, ranging from 143 mV at 10 mV/s to 348 mV at 500 mV/s. Table 5.2 lists ΔE_p recorded for $\text{Fe}(\text{CN})_6^{3-/4-}$ for a 4 h conductive diamond powder, graphite powder, GC powder, and boron-doped diamond thin-film electrode at 10, 100, and 500 mV/s. As shown in this table, ΔE_p for $\text{Fe}(\text{CN})_6^{3-/4-}$ for the GC and graphite powder electrodes ranged from 128 to 213 mV, and 102 to 137 mV, respectively, at the same scan rates. The ΔE_p values for all the powders are larger than the typical values seen for this redox system at diamond thin film or a planar GC electrode; ΔE_p values of ~60-70 mV at 100 mV/s are typical for high quality microcrystalline and nanocrystalline boron-doped diamond thin-film electrodes and freshly polished GC.^{8,13} In addition to the large ΔE_p values reported here for $\text{Fe}(\text{CN})_6^{3-/4-}$, it was generally observed the ΔE_p for a given diamond powder electrode increased with usage, apparently due to lessened connectivity between the powder particles. In other words, rinsing the cell between solutions, as well as the turbulence caused by degassing the solution may have weakened the bound particle matrix. It should be noted that there was no visual evidence that the electrodes delaminated or that particles were dislodged from the bound electrode.

Table 5.2 Cyclic voltammetric ΔE_p values (mV) for 1 mM $\text{Fe}(\text{CN})_6^{3-/4-}$ at conductive diamond powder, graphite powder, GC powder, and a planar microcrystalline boron-doped diamond thin-film electrodes at three different scan rates.

Scan Rate (mV/s)	Conductive Diamond Powder	Graphite Powder	GC Powder	Microcrystalline Thin Film
10	140	102	128	60
100	240	137	213	62
500	350	174	329	67

As mentioned, the voltammetric curve shapes can be significantly affected by ohmic resistance either within the solution or the electrode, in addition to electron-transfer rate or density of states effects. Based on what is known about ΔE_p values at diamond thin-film electrodes and the bulk resistance measurements presented earlier which indicated that a well-packed coated diamond powder possesses relatively high electrical conductivity, the large ΔE_p values are attributed mainly to ohmic resistance effects. More specifically, poor particle-particle connectivity within the electrode bound with PTFE limits the electrical conductivity. The connectivity problems could be due to (i) rough particle morphology which would limit the contact area or (ii) uneven distribution of binder through the powder network. SEM images revealed that the diamond particles are irregularly shaped with sharp edges, which may create challenges in achieving good connectivity when a binder is used. To test this hypothesis, a composite electrode was made, consisting of 4 h growth diamond powder mixed with 20 wt. % graphite powder and the 10 wt. % PTFE binder. If the rough diamond particle shape (i.e., low contact area) is responsible for the limited connectivity, the flatter, compressible graphite particles should serve to improve the particle-particle contact,

thereby increasing the electrical connectivity. ΔE_p for $\text{Fe}(\text{CN})_6^{3-/4-}$ at this composite electrode was 86 mV at 10 mV/s, much less than the value for the diamond powder electrode without any added graphite powder. While it is possible that the reduction in ΔE_p is influenced by more facile electron-transfer kinetics at the graphite powder surface, the effect is likely more one of reduced ohmic resistance due to better particle-particle connectivity. This is based on the fact that ΔE_p for the composite electrode was lower than that for the graphite powder alone.

Figure 5.8B shows a plot of the oxidation peak current for $\text{Fe}(\text{CN})_6^{3-/4-}$ versus the scan rate^{1/2}. The peak current increases linearly ($r^2 > 0.99$) up to 100 mV/s indicative of a mass-transport limited response (semi-infinite linear diffusion). However, at scan rates above 100 mV/s, the faradaic current response levels off. Such behavior is not observed for a boron-doped diamond thin film, as the oxidation peak current increases proportionally over the entire scan rate range. In general, current flow through an electrode is limited by the electrical conductivity, specifically the charge carrier concentration and carrier mobility. If the carrier concentration or mobility is limited, the current response may level off as the potential scan rate or analyte concentration is increased (i.e., as more current is passed). The bulk electrical conductivity measurements showed that when the coated powder particles are well packed, relatively high conductivity is seen. This suggests a highly conducting boron-doped diamond layer is formed over most of the powder particle surfaces and that good particle-particle contact can be established so as to not severely restrict the carrier mobility. For example, in the i - V curve measurements between ± 10 V, tens to hundreds of mA flowed through the packed powder, much higher currents than those flowing during the electrochemical

measurement. Therefore, we attribute the limited faradaic current response for $\text{Fe}(\text{CN})_6^{3-/4-}$ at high scan rates to a limited carrier mobility within the conductive diamond powder due to poor particle-particle connectivity when bound with PTFE, rather than to low electrical conductivity of the diamond overlayer.

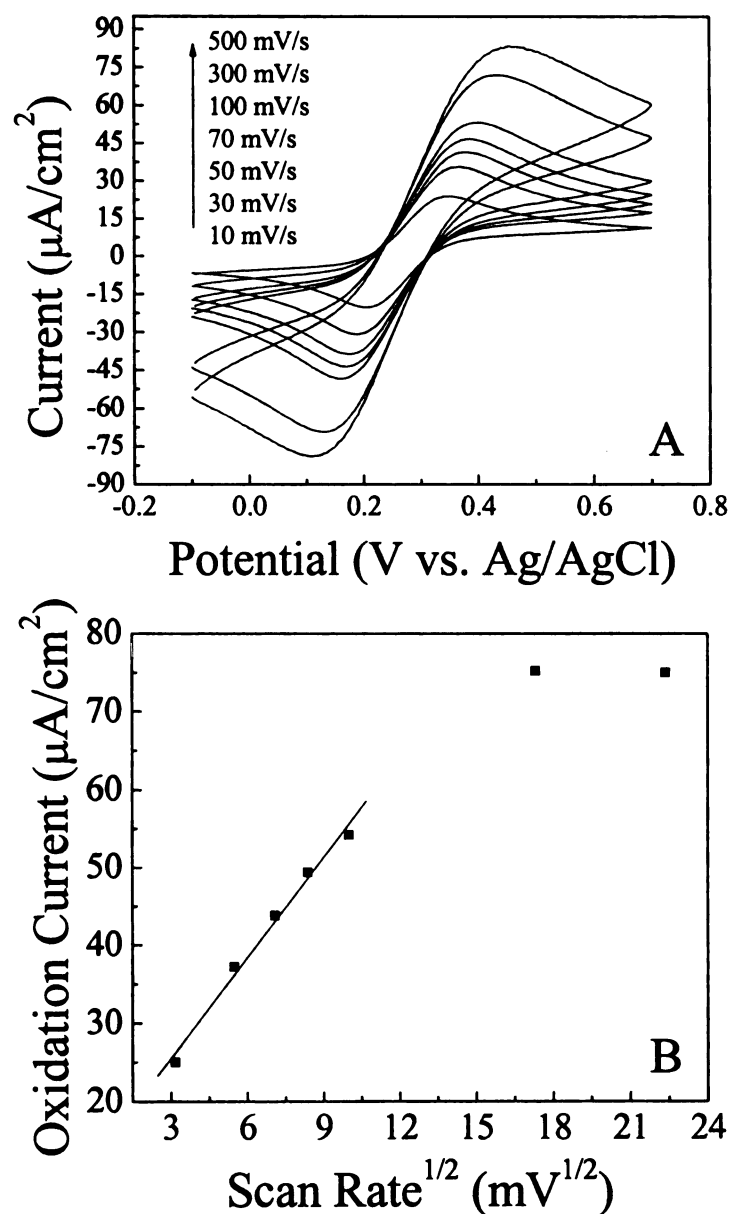


Figure 5.8 (A) Cyclic voltammetric i - E curves for a conductive diamond powder electrode (4 h coating time) in 1 mM $\text{Fe}(\text{CN})_6^{3-/4-}$ at scan rates between 10 and 500 mV/s and (B) a plot of the oxidation peak current versus the scan rate^{1/2}.

More severe distortion of the cyclic voltammetric i - E curves are seen for $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ (10 to 300 mV/s) for a 4 h as-grown diamond power electrode in Figure 5.9A. ΔE_p for $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ is high even at low scan rates, ranging from 220 mV at 10 mV/s to 530 mV at 300 mV/s. ΔE_p values of 112 and 91 mV were observed in comparison measurements of $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ with GC and graphite powder electrodes, respectively, at 10 mV/s. In addition to issues with the ohmic resistance of the diamond powder electrodes discussed above, limited electrode wettability may also influence the ΔE_p recorded for highly charged analytes such as $\text{Fe}(\text{CN})_6^{3-/4-}$ and $\text{Ru}(\text{NH}_3)_6^{3+/2+}$. After diamond growth, the conductive diamond powder is hydrogen terminated. In addition, the powder is bound with a non-polar polymer binder, rendering the electrode quite hydrophobic. To investigate the contribution of electrode hydrophobicity on the cyclic voltammetric curve shape, an electrode was prepared using 4 h conductive diamond powder and only 5 wt. % PTFE, instead of the 10 wt. % used to fabricate all other electrodes. Cyclic voltammetric i - E curves recorded for $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ on this electrode are presented in Figure 5.9B. ΔE_p is significantly reduced, to 117 mV at 10 mV/s and 167 mV at 300 mV/s. These values are comparable to those recorded for graphite and GC powder with 10 wt. % binder, electrode materials that are expected to be more hydrophilic than hydrogen terminated diamond. Thus, it seems that both ohmic resistance as a result of poor particle-particle connectivity and electrode hydrophobicity influence the cyclic voltammetric response for conductive diamond powder when bound with PTFE. Future work will focus on new approaches to fabricate the powder electrodes that will improve the particle-particle connectivity, as well as on the use of different binders to improve electrode wettability.

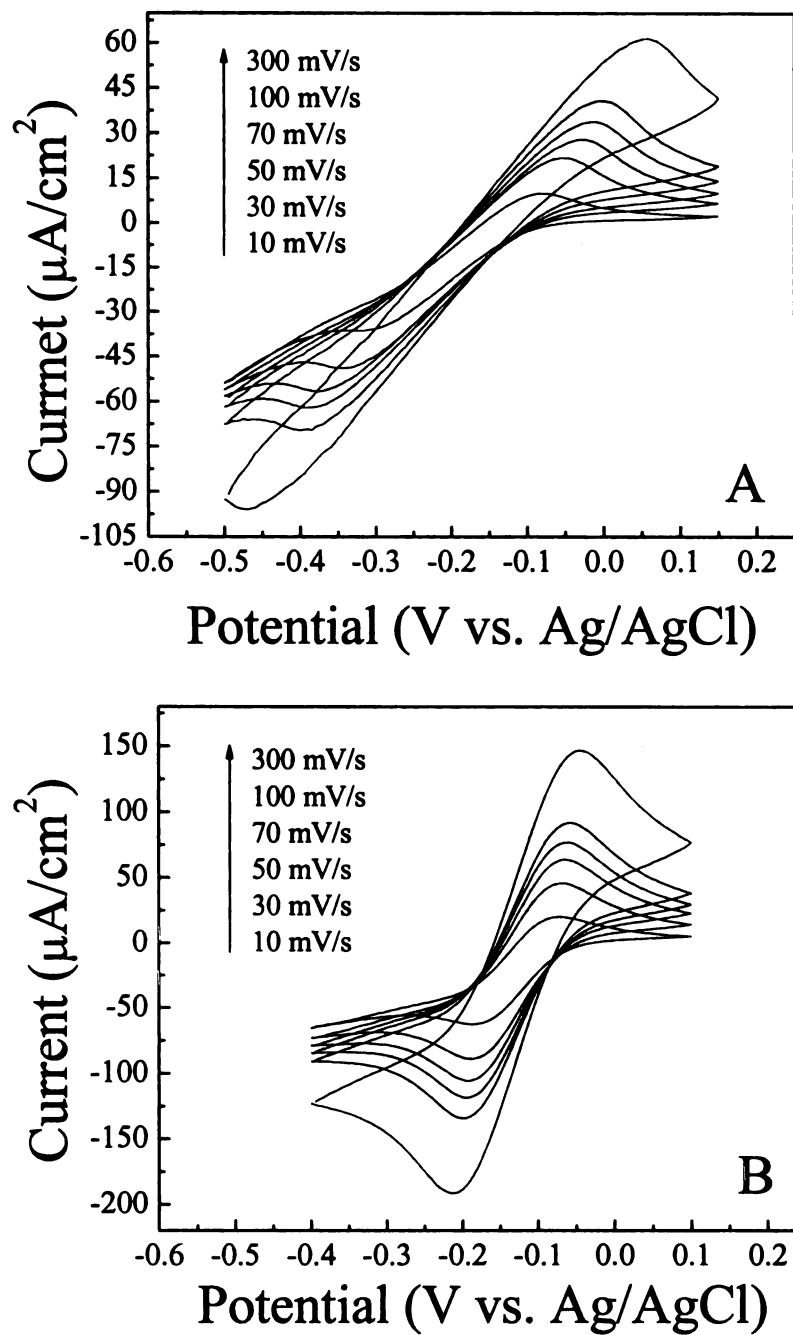


Figure 5.9 Cyclic voltammetric i - E curves for 1 mM $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ for a conductive diamond powder electrode (4 h coating time) at scan rates between 10 and 300 mV/s with (A) 10 wt. % PTFE binder and (B) 5 wt. % PTFE binder.

5.2.3 Morphological and Microstructural Stability

In order to evaluate the morphological and microstructural stability of the conductive diamond powder, the electrodes were anodically polarized at 1.6 V vs. Ag/AgCl and 25 °C for 1 h. Comparison measurements were made with graphite and GC powders. High potentials such as this are possible for short duration in fuel cells during idle operation and can affect the long-term stability and operational lifetime of the device.²⁴ Figure 5.10 shows the chronoamperometric *i-t* curves recorded for each electrode material, normalized to the electrode area calculated from the cyclic voltammetric background current as described in Chapter 2. The total charge passed (i.e., integrated *i-t* curve) is largest for the GC powder (0.88 C/cm²), followed by graphite (0.46 C/cm²) and the conductive diamond powder (0.18 C/cm²). For GC, the current rises and then decreases quickly after the potential step as the electric double layer forms. This is followed by a progressive increase in current over time, which is likely caused by microstructural degradation of GC leading to a continuously increasing exposed surface area. The *i-t* curve for the graphite powder follows the same trend, but the current increase over time is smaller, consistent with less microstructural alterations. This result is not surprising considering that the degradation of carbon materials is known to be related to the degree of microstructural disorder, as presented in Chapter 3. More disordered carbon materials have a higher fraction of exposed edge plane, resulting in more extensive oxidation and corrosion. Clearly, the lowest charge density is passed for the diamond powder consistent with a more microstructurally stable material. There is, however, an increase in current over time.

Figure 5.11 shows scanning electron micrographs of the conductive diamond powder (A) before and (B) after the anodic polarization at 1.6 V vs. Ag/AgCl and 25 °C. Before polarization, the PTFE binder covers some of the particles with a cauliflower-like texture. After polarization, there appears to be much less PTFE covering the grains, although upon close inspection, the polymer still exists between the particles. Magnified images of individual diamond particles showed the same diamond grain morphology and texture before and after anodic polarization. There was no visible morphological or microstructural damage to the conductive diamond powder after polarization under these conditions. Therefore, it is concluded that the increase in the current seen for diamond was caused by exposure of more surface area over time as the PTFE binder delaminated from some of the grains. In contrast, SEM images for GC (C) before and (D) after anodic polarization in Figure 5.11 reveal severe morphological and microstructural degradation of some particles. Degradation of this nature in fuel cells would be catastrophic to the electrode performance because electrocatalyst particles from these areas would be lost and the electrical resistance would increase. The graphite powder particles are flat, irregularly shaped, and not uniform in size. Therefore, SEM images of graphite powder are not presented because the morphology of the particles was such that the degradation was not easily detected.

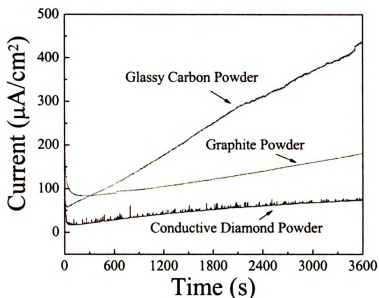


Figure 5.10 Chronoamperometric *i-t* curves for the 4 h conductive diamond powder, graphite powder, and glassy carbon powder electrodes recorded during potentiostatic polarization at 1.6 V vs. Ag/AgCl and 25 °C for 1 h.

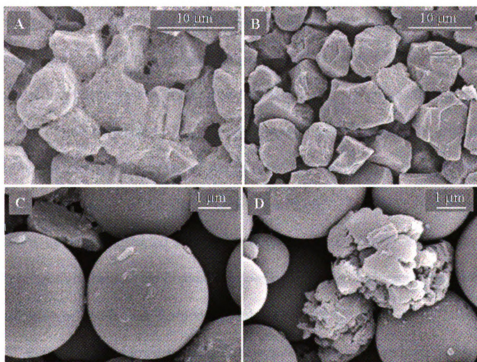


Figure 5.11 Scanning electron micrographs of a conductive diamond-coated diamond powder electrode (4 h coating time) (A) before and (B) after and GC powder electrode (C) before and (D) after constant potential polarization of 1.6 V vs. Ag/AgCl for 1 h in 0.1 M HClO₄.

5.3 Conclusions

The physical, electrical, and electrochemical properties of a boron-doped diamond powder have been described. Even though the surface area and conductivity are lower than that desired for an ideal fuel cell support, these powders represent a first step toward the desired values. The conductive powder was formed by coating a boron-doped overlayer on insulating diamond powder via chemical vapor deposition. SEM, Raman spectroscopy, electrical measurements, and electrochemical tests were used to characterize the material. The results confirm that a boron-doped diamond overlayer was grown on the powder surface with co-deposition of some nondiamond carbon impurity. Stress was also introduced into the powder at long deposition times (6 h) due to the particle fusion. Electrical resistance measurements proved that the powders became electrically conducting after being coated with the boron-doped diamond overlayer. The nondiamond carbon impurity was also shown to contribute some to the conductivity, but its effect was much less for the 4 and 6 h deposition times. i - V curves for the packed, dry powder were ohmic between ± 10 V. Electrochemical tests revealed the presence of the nondiamond carbon at the surface of the powder and that the powder electrodes (with binder) were responsive to $\text{Fe}(\text{CN})_6^{3-/4-}$ and $\text{Ru}(\text{NH}_3)_6^{3+/2+}$. The cyclic voltammetric curves were, however, distorted by ohmic resistance effects attributed to poor particle-particle connectivity within the binder and poor wettability. Amperometric i - t curves for the polarization of conductive diamond, graphite, and GC powders at 1.6 V vs. Ag/AgCl and 25 °C showed that the lowest anodic charge was passed for diamond. SEM images of the diamond powder before and after polarization showed no evidence of morphological

degradation or corrosion. In contrast, significant morphological changes were found for the GC powder.

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Chapter 6

Preparation and Characterization of Boron-Doped Diamond Paper with Pt Nanoparticles

Abstract

Nanocrystalline boron-doped diamond (BND) has been successfully coated on carbon paper (TCP) via microwave plasma-assisted chemical vapor deposition. Scanning electron microscopy revealed that fibers within the first $\sim 100\ \mu\text{m}$ of the TCP surface were fully coated with nanocrystalline diamond (film thickness $\sim 1\ \mu\text{m}$). X-ray diffraction and Raman spectroscopy confirmed that TCP had been coated with a crystalline diamond overlayer. Two different (A and B) currents were used to electrodeposit Pt nanoparticles on bare and diamond-coated TCP using a pulsed galvanostatic method (Pt/TCP and Pt/BND). Under condition A ($0.146\ \text{mA}/\text{cm}^2$ or $0.0047\ \text{C}/\text{cm}^2$), large, widely dispersed Pt particles were deposited on TCP (Pt/TCP-A). Under these same conditions, nanoparticles with a diameter of $177 \pm 39\ \text{nm}$ and a density of $\sim 1.2 \times 10^9\ \text{particles}/\text{cm}^2$ were deposited on BND (Pt/BND-A). Under condition B ($1.25\ \text{mA}/\text{cm}^2$ or $0.040\ \text{C}/\text{cm}^2$) Pt nanoparticles formed on both TCP (Pt/TCP-B, $233 \pm 89\ \text{nm}$ diam and $\sim 2.7 \times 10^8\ \text{particles}/\text{cm}^2$) and BND (Pt/BND-B). The Pt particles on Pt/BND-B were so dense and closely spaced that an accurate measure of the particle size and density could not be obtained. The composite electrode surface enhancement factors (SEF, Pt surface area/electrode surface area) were 0.033, 0.50, 3.3, and 1.7 for Pt/TCP-A, Pt/BND-A, Pt/TCP-B, and Pt/BND-B, respectively. The specific Pt surface areas (S_{Pt} , m^2/g) were 1.4, 21, 16, and 8.2 for Pt/TCP-A, Pt/BND-A, Pt/TCP-B, and Pt/BND-B,

respectively. The oxygen reduction reaction was used to probe the electrocatalytic activity of the composite electrodes. The most active electrode was Pt/BND-A with a half-wave potential, $E_{p/2}$, of 0.583 V vs. Ag/AgCl and a limiting current of *ca.* -1000 $\mu\text{A/SEF}$. The stability of the bare TCP and BND substrates and the composite Pt/TCP and Pt/BND electrodes were studied using potentiostatic polarization at 1.4 and 1.6 V vs. Ag/AgCl (25 °C) in 0.1 M HClO_4 . The BND electrode exhibited superior morphological and microstructural stability over TCP at 1.6 V. Evidence was found for dissolution and redeposition of Pt after polarization of the composite electrodes at 1.4 V, particularly for Pt/TCP.

6.1 Introduction

As discussed in Chapter 1, the hydrogen oxidation and oxygen reduction reactions occur on an electrocatalyst (e.g., Pt), which is supported on high-surface-area carbon within the catalyst layer of the PEMFC. The catalyst layer is sandwiched between two pieces of carbon paper that make up part of the gas diffusion layers (GDLs), through which the reactant gases are distributed evenly into the reactive zone. The first part of our work to develop a dimensionally stable electrocatalyst support material, presented in Chapter 5, focused on the development and characterization of electrically conducting diamond powder as an alternative to Vulcan XC-72 in the catalyst layer. Although the diamond powder exhibited greater dimensional stability with respect to graphite and glassy carbon powders, ohmic resistance of the electrode when using polytetrafluoroethylene as a binder limited evaluation of its properties as an electrocatalyst support. An alternative approach addressed in this chapter focuses on the development of a binderless diamond material that is based on the morphology of the porous GDL.

PEMFC GDLs are typically made of a sp^2 -bonded carbon paper backing layer (BET $\sim 9 \text{ m}^2/\text{g}$), a porous material composed of interconnected carbon fibers. To be effective in the fuel cell, carbon paper GDL materials must be electrically conductive, gas permeable, and thin (~ 0.1 to 0.3 mm), with high mechanical strength. The electrochemical stability requirements for carbon paper in the GDL are not as demanding as those for carbons in the catalyst layer, mainly because the electrocatalytic activity of the fuel cell is not dependent on GDL stability. Thus, corrosion of carbon paper when

used in the GDL is not as detrimental to fuel cell operating efficiency and lifetime as is corrosion of the electrocatalyst support material.

In this second approach to develop high-surface-area diamond as an electrocatalyst support material, we propose to remove the catalyst layer completely and use the porous carbon paper substrate directly as the electrocatalyst support. Used in this manner, the carbon paper stability requirements are similar to those of the catalyst layer itself, discussed in Chapter 1. We showed in Chapters 3 and 5 that sp^2 -bonded carbons corrode under high potentials (1.2 to 1.5 V vs. SHE) present during fuel cell start-up, shut-down, and idle operation. Thus, to increase the corrosion resistance of the porous carbon paper for this application, we have coated the individual carbon fibers of a carbon paper GDL with a nanocrystalline boron-doped diamond overlayer. Used in this way, the diamond coating may not only impart a higher degree of microstructural stability and corrosion resistance to the paper, but the improved support stability may also translate into improved electrocatalytic activity and stability of the metal-coated electrode toward the oxygen reduction reaction.

A number reports have been published recently that discuss the deposition of insulating^{1,2} and electrically conducting (i.e., boron-doped)³⁻⁶ microcrystalline diamond on carbon fibers for a variety of applications. There are a few drawbacks to this method, however, in terms of the development of a material for fuel cell electrodes. First, high atomic hydrogen concentration in microcrystalline diamond deposition plasmas results in significant gasification of the underlying sp^2 -bonded carbon fiber. This alters the carbon paper morphology and increases its brittleness, resulting in decreased mechanical strength. Second, coating the carbon fiber with large ($\sim 1\ \mu\text{m}$), rough microcrystalline

diamond grains would likely decrease the porosity and surface area of the carbon paper. Coating the carbon paper with nanocrystalline boron-doped diamond, however, can potentially overcome both of these issues. The gas composition for nanocrystalline diamond growth has little to no atomic hydrogen, which would should reduce the effects of carbon fiber gasification. Moreover, the smooth texture and small grain size (~10-15 nm) of a nanocrystalline diamond overcoat would maintain the original carbon paper morphology and porosity.

In this chapter, the preparation and characterization of nanocrystalline boron-doped diamond deposited on carbon paper (BND) is described. Although the surface area of this material (BET ~9 m²/g) is lower than that needed for a viable electrocatalyst support, it provides a useful starting point for evaluating the properties of a high-surface-area boron-doped diamond electrocatalyst support material. Scanning electron microscopy, X-ray diffraction, and Raman spectroscopy were used to characterize the morphology, crystallinity, and microstructure of the bare (TCP) and diamond-coated carbon paper. BND and TCP were decorated with Pt nanoparticles by pulsed galvanostatic deposition. Cyclic voltammetry and chronoamperometry were used to evaluate the dimensional stability and corrosion resistance of the bare and diamond-coated carbon paper subjected to potentiostatic polarization, as described in Chapter 3. The electrocatalytic activity of the Pt/carbon composite electrodes towards the oxygen reduction reaction was studied via linear sweep voltammetry in oxygen-saturated 0.1 M HClO₄ before and after potentiostatic polarization.

6.2 Results and Discussion

6.2.1 Nanocrystalline Diamond Deposition on Carbon Paper

6.2.1.1 Morphology and Microstructure

Scanning electron micrographs of the bare (TCP) and diamond-coated carbon paper (BND) are presented in Figure 6.1A-D. As seen in Figure 6.1A and B, TCP is composed of interconnected polyacrylonitrile fibers that form a porous fiber network. The individual fibers are about 5 μm in diameter and each fiber has striations along the longitudinal axis. After nanocrystalline diamond deposition, all fibers within the first ~ 100 μm of the carbon paper surface are fully coated with no evidence of cracks, pinholes, or voids. As shown in Figure 6.1C, BND has a relatively smooth texture with randomly-oriented diamond grains. The linear striations of the TCP substrate have been completely covered by the diamond. The cross-sectional image of a coated carbon fiber, presented in Figure 6.1D, reveals that the diamond coating completely covers the fiber with a thickness of ~ 1 μm . There was little change in the diameter of the carbon fiber, as seen in the center of the cross-section, suggesting that the small amount of atomic hydrogen present during growth did not significantly gasify the TCP substrate.

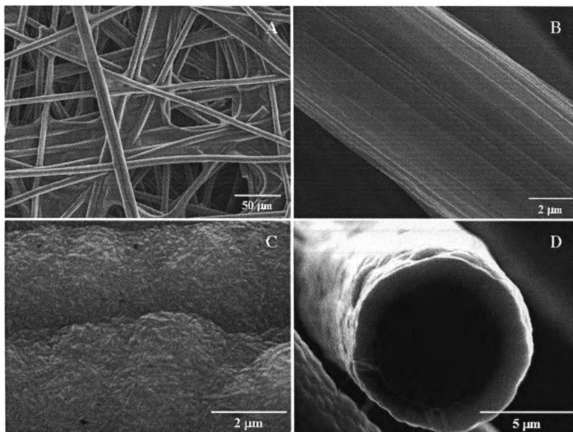


Figure 6.1 Scanning electron micrographs of (A) bare carbon paper, (B) an individual bare carbon fiber within the paper, (C) boron-doped nanocrystalline diamond deposited on the carbon paper, and (D) a cross-section of a nanocrystalline diamond-coated carbon fiber.

X-ray diffraction (XRD) spectra for TCP and BND from 2θ of 10 to 100 degrees are presented in Figure 6.2. The insets show enlarged views of the spectra between 40 and 100 degrees. The XRD spectrum for TCP is characterized by the reflections expected for sp^2 -bonded carbon at ~ 26.5 , 43.2 , 54.4 , 77.7 , and 86.9 degrees, which are assigned to the (002), (100), (004), (110), and (006) crystallographic orientations of graphite, respectively.⁷ These reflections are denoted in Figure 6.2 with a "G". The XRD spectrum for BND also has reflections for cubic diamond (denoted with a "D") at 43.9 ,

75.3, and 91.5 degrees, which are assigned to the (111), (220), and (311) crystallographic orientations (ASTM 6-0675). The diamond spectrum also exhibits the graphite reflections seen for TCP. Since XRD is a bulk technique and only TCP fibers within the top ~100 μm of the paper were coated with diamond, it is not surprising that sp^2 -bonded carbon reflections are also seen for the diamond-coated material.

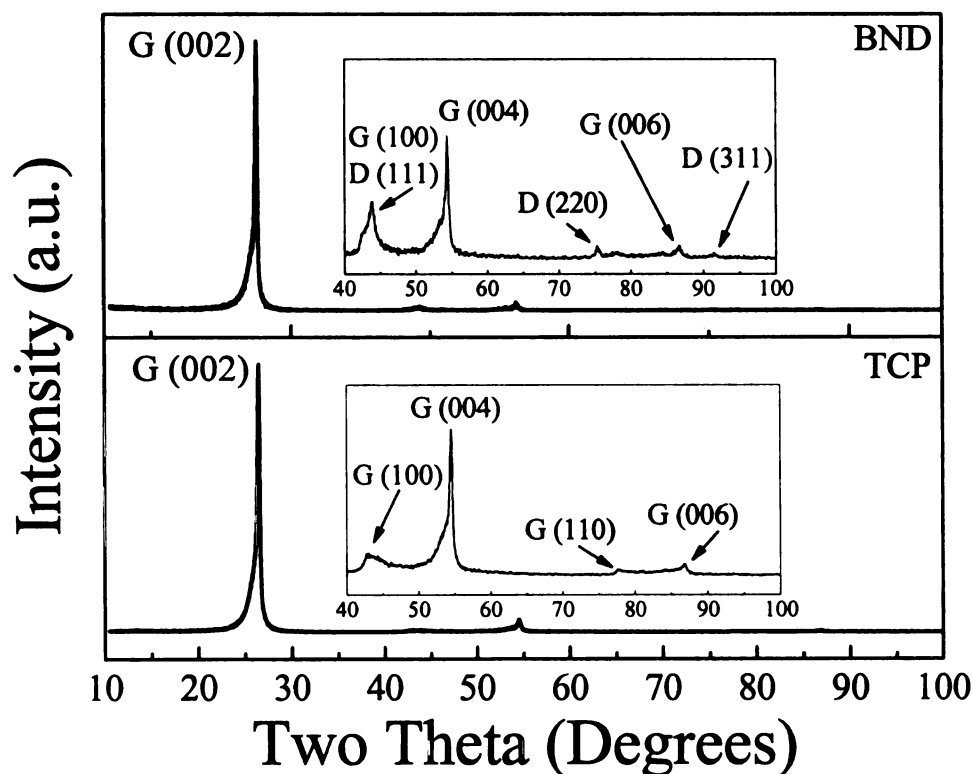


Figure 6.2 X-ray diffraction spectra of bare (TCP) and boron-doped nanocrystalline diamond-coated carbon paper (BND).

As discussed in previous chapters, Raman spectroscopy is a useful tool for studying sp^2 - and sp^3 -bonded carbons because it is sensitive to both short and long-range microstructural order. The Raman spectrum for TCP presented in Figure 6.3 contains two peaks at 1582 cm^{-1} and 1360 cm^{-1} , which correspond to the E_{2g} and D modes of

amorphous sp^2 -bonded carbon, respectively, as discussed in Chapter 3.⁸⁻¹² Briefly, the presence and intensity of the D band suggests that TCP has some microstructural disorder (i.e., some fraction of exposed edge plane density) with respect to crystalline graphite. The Raman spectrum for BND is characterized by broad peaks at 1150, 1333, 1470, and 1550 cm^{-1} , consistent with that for high-quality, nanocrystalline boron-doped diamond.¹³⁻¹⁷ The origin of these peaks was discussed in detail in Chapter 4. The spectrum for BND was similar at different points on the electrode surface with no evidence of sp^2 -bonded carbon.

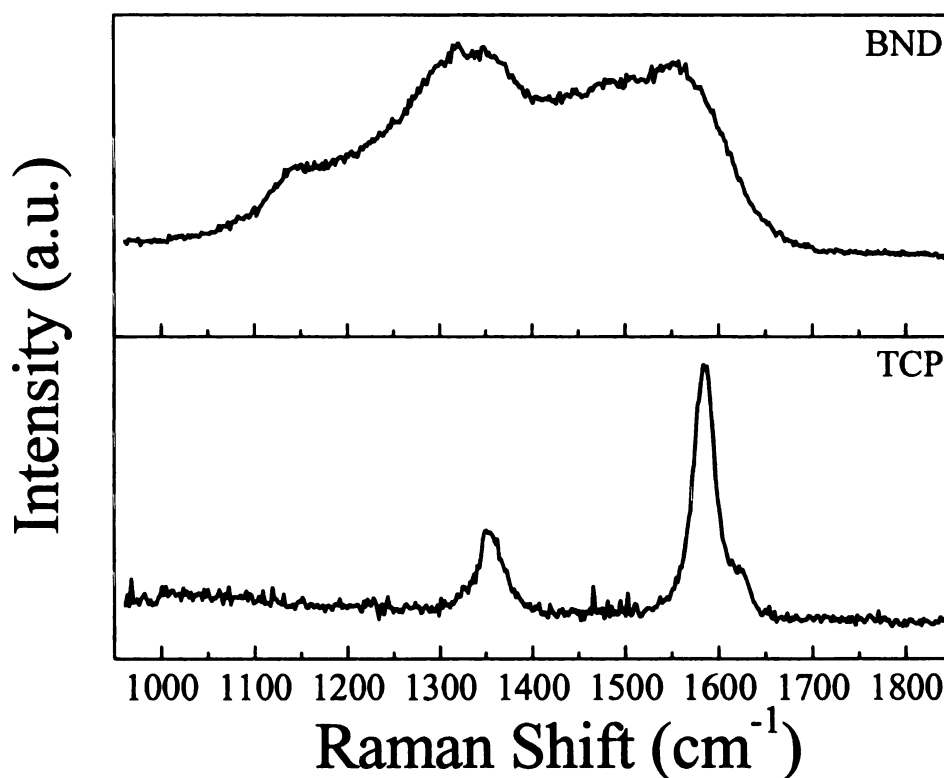


Figure 6.3 Raman spectra for the bare (TCP) and boron-doped nanocrystalline diamond-coated carbon paper (BND).

6.2.1.2 Electrochemical Characterization

Background cyclic voltammetric i - E curves for the TCP and BND electrodes in 0.1 M HClO₄ are presented in Figure 6.4. The current for each electrode was stable with potential cycling between -0.4 and 1.0 V vs. Ag/AgCl (~40 cycles) and is normalized to the solution-exposed electrode area. It is important to note that although the geometric surface areas of TCP and BND were similar, the electrode surface area of TCP exposed to the solution, which was calculated from the background cyclic voltammogram (see Chapter 2), was smaller than that of BND calculated in the same manner. Although the reason for this is not clear at this time, it may be due, in part, to electrode wettability differences. It seems that only the first few layers of carbon fibers in the TCP electrode were contacted by the solution, while the solution penetrated more deeply into the BND electrode. Future work will include strategies to maximize electrode wettability so that the electrode area exposed to solution is more consistent for both materials.

The voltammogram for TCP is characterized by a non-faradaic (i.e., capacitive) background current that is about two times larger than that of BND, after normalization to the exposed electrode surface area. As discussed in Chapter 4, the voltammetric background current is typically smaller for sp^3 -bonded diamond compared to sp^2 -bonded carbon electrodes because of a lower capacitance and less pseudocapacitance from electroactive surface carbon-oxygen functionalities. Faradaic current at *ca.* 400 mV can be seen for the TCP electrode, which is associated with electroactive surface oxygen functional groups at edge plane and defect sites.^{18,19} Faradaic current is also observed for the BND electrode in this region, although the current magnitude is much lower. It is likely that the background current for BND is influenced by both the diamond-coated and

the uncoated fibers in the interior of the carbon paper. Thus, the faradaic current *ca.* 400 mV for BND is likely caused by electroactive surface-oxygen functional groups on the sp^2 -bonded TCP. The cathodic current at ~ -0.4 V vs. Ag/AgCl arises from oxygen reduction on both TCP and BND. Although the solution was degassed with N_2 for 30 min prior to all electrochemical measurements, it is possible that oxygen was still present within the porous electrode. Hydrogen evolution for TCP and BND does not occur until *ca.* -1 V vs. Ag/AgCl.

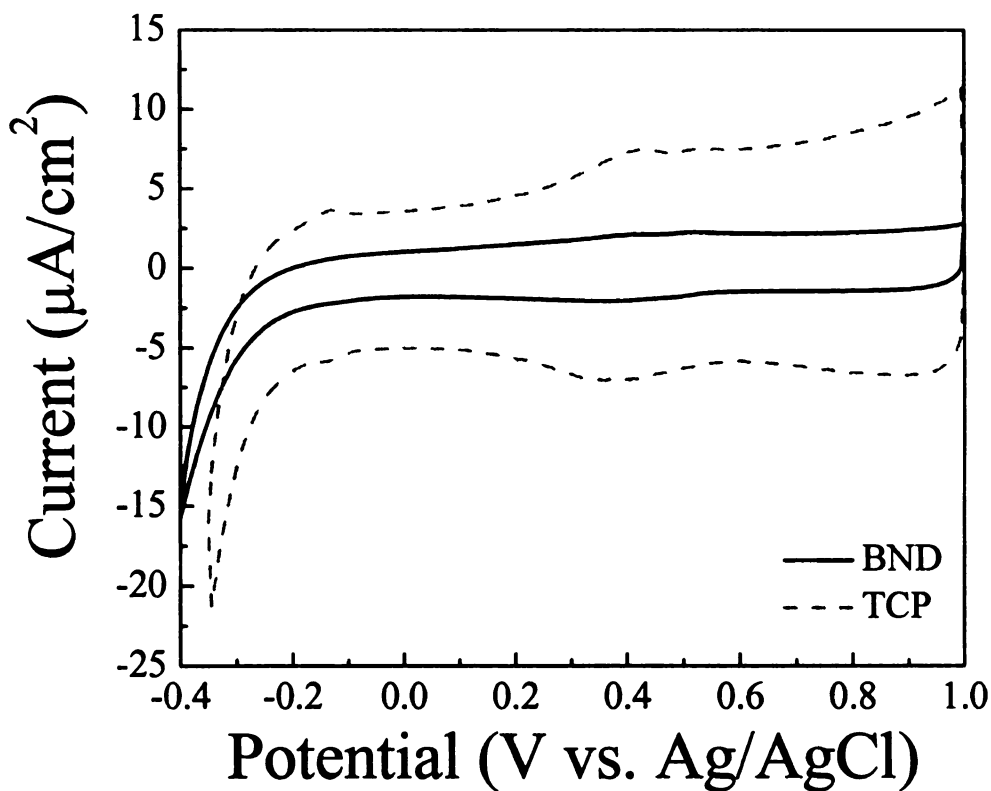


Figure 6.4 Background cyclic voltammetric *i-E* curves for bare (TCP) and boron-doped nanocrystalline diamond-coated carbon paper (BND) in 0.1 M $HClO_4$ at 100 mV/s. The current is normalized to the electrode area estimated to be in contact with the solution.

6.2.2 Electrodeposition of Pt on TCP and BND

Electrodeposition of Pt onto planar boron-doped diamond thin-film electrodes has been accomplished using potentiodynamic, galvanostatic, and pulsed galvanostatic deposition.^{20,21} Pulsed galvanostatic deposition produced Pt nanoparticles with nominal diameters that were an order of magnitude smaller than those deposited by constant potential or current methods.²⁰ Although these Pt/diamond composite electrodes are active for the oxygen reduction reaction, the low surface area of the diamond support renders them impractical for use in fuel cells. Moreover, the planar electrodes are not porous and thus, cannot serve as gas diffusion electrodes. Carbon paper, currently used as a gas diffusion layer in fuel cells is higher in surface area (BET $\sim 9 \text{ m}^2/\text{g}$) than the planar films and is gas permeable. The diamond-coated carbon paper is also both gas permeable and higher in surface area than the planar films (BET $\sim 8.5 \text{ m}^2/\text{g}$). Although the surface area of this material is not as high as that required for fuel cells ($\sim 100 \text{ m}^2/\text{g}$), its fabrication and availability is an important step toward our long-term goal of developing dimensionally stable, high-surface-area, gas diffusion Pt/diamond composite electrodes.

Two different pulsed galvanostatic current/charge conditions (denoted as A and B) were used to electrodeposit Pt on the TCP and BND gas diffusion electrodes, as shown in Table 6.1. To compare the resultant Pt nanoparticles for a given deposition condition, it is important that the same current density be applied to each electrode. Thus, accurate determination of the electrode surface area (TCP or BND) is essential. As discussed above, there were large differences in the TCP and BND surface areas exposed to solution because of possible differences in electrode wettability. Although this surface

area may change slightly throughout the course of the electrochemical characterization (i.e., increased electrode wetting), it is the most accurate means of comparing the electrodes. Electrode geometric area reflects the surface area of the entire electrode, including portions that are not exposed to solution (i.e., portions on which Pt cannot be deposited). Thus, normalization to the electrode geometric area will not provide an accurate comparison of regions on which Pt was deposited. However, comparison of the actual surface area (calculated from the mass of the electrode and the BET surface area) to the solution-exposed surface area is useful to provide some insight into the electrode wettability. Table 6.1 presents the solution-exposed surface area (used for all normalization) that was calculated from the background cyclic voltammetric *i-E* curve, as well as the geometric surface area that was calculated from the mass of the electrode and the electrode BET surface area.

All Pt/carbon composite electrodes (Pt/TCP and Pt/BND) were exposed to 1 s pulses with a 25% duty cycle (i.e., 200 ms on-time and 800 ms off-time). First, 2.5 mA (a total of 0.080 C) was applied to a BND electrode (condition A) to electrodeposit Pt. The normalized current and charge were calculated to be 0.146 mA/cm^2 (a total of 0.0047 C/cm^2), based on the BND solution-exposed surface area. The same normalized current and charge was then applied to a TCP electrode to deposit Pt. These conditions were chosen as a starting point because the total current and charge applied to the BND electrode were similar to values used in previous work for Pt deposition on diamond thin film via pulsed galvanostatic deposition.²⁰ Second, 1.25 mA/cm^2 (a total of 0.040 C/cm^2) was applied to both electrode types (condition B). On planar microcrystalline and nanocrystalline boron-doped diamond thin-film electrodes, this current density resulted in

the most active Pt/diamond composite electrode in terms of particle diameter, coverage, and specific Pt surface area (m^2/g).²⁰

Table 6.1 Two different (A and B) current and charge conditions for the pulsed galvanostatic deposition of Pt metal on carbon paper (TCP) and boron-doped nanocrystalline diamond deposited on carbon paper (BND) including the solution-exposed and actual surface area (SA).

Condition	Current Density (mA/cm^2)	Charge Density (C/cm^2)	Electrode	Solution-Exposed SA (cm^2)	Actual SA (cm^2)	Total Applied Current (mA)	Total Applied Charge (mC)
A	0.146	0.0047	TCP-A	0.452	650	0.066	0.002
			BND-A	16.9	884	2.5	0.08
B	1.25	0.040	TCP-B	1.32	703	1.65	0.05
			BND-B	7.64	935	9.56	0.30

Scanning electron micrographs of the Pt/carbon composite electrodes, Pt/TCP-A, Pt/BND-A, Pt/TCP-B, and Pt/BND-B, deposited under the conditions A and B of Table 6.1, are presented in Figure 6.5. At $0.146 \text{ mA}/\text{cm}^2$ or $0.0047 \text{ C}/\text{cm}^2$, rather large Pt deposits were formed (circled areas) on Pt/TCP-A that were widely dispersed across the electrode surface. Under these same conditions, Pt metal nanoparticles were deposited on the Pt/BND-A electrode with a particle diameter of $177 \pm 39 \text{ nm}$ and density of $\sim 1.2 \times 10^9 \text{ particles}/\text{cm}^2$. The particles were uniformly dispersed across the electrode surface and Pt metal was observed up to a depth of $\sim 100 \mu\text{m}$ (as far as down in the sample as the electron beam could be focused). At $1.25 \text{ mA}/\text{cm}^2$ or $0.040 \text{ C}/\text{cm}^2$, Pt nanoparticles were deposited onto both Pt/TCP-B and Pt/BND-B, as shown in Figure 6.5. Deposition of Pt nanoparticles on Pt/TCP-B was limited to the outermost fibers, presumably because only

these fibers were wetted by the solution. Particle analysis revealed that the Pt/TCP-B nanoparticles were 233 ± 89 nm, with a density of $\sim 2.7 \times 10^8$ particles/cm². Under the same conditions, Pt nanoparticles smaller in size, with a much higher density were deposited onto Pt/BND-B. Although the particle size, coverage, and density look similar for Pt/BND-A and Pt/BND-B on the scale of the SEM presented, Pt/BND-B nanoparticles had a much higher particle density, such that there was little open space between particles. In fact, the particles were so closely spaced that accurate particle analysis could not be completed. The Pt particle size and density on BND under both conditions A and B were superior to that deposited on TCP under condition B.

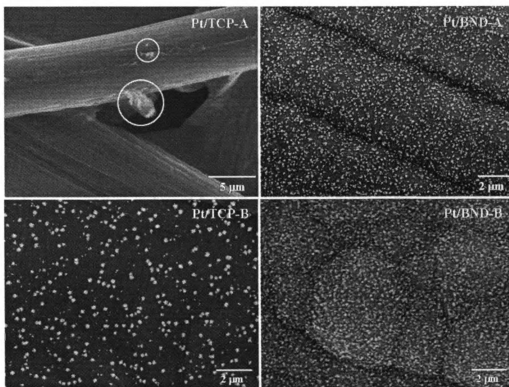


Figure 6.5 Scanning electron micrographs of Pt/carbon composite electrodes (Pt/TCP-A, Pt/BND-A, Pt/TCP-B, and Pt/BND-B) under two different pulsed galvanostatic deposition conditions A (0.146 mA/cm^2 or 0.0047 C/cm^2) and B (1.25 mA/cm^2 or 0.040 C/cm^2).

Background cyclic voltammetric *i*-*E* curves of Pt/TCP-A and Pt/BND-A in 0.1 M HClO₄ at 50 mV/s are presented in Figure 6.6A. The corresponding curves for Pt/TCP-B and Pt/BND-B are shown in Figure 6.6B. The voltammograms were stable after *ca.* 10 cycles with cycle number 15 is shown here. All currents are normalized to the solution-exposed area of the original electrode (TCP or BND), presented in Table 6.1. The curves for Pt/BND-A, Pt/TCP-B, and Pt/BND-B exhibit voltammetric features associated with clean, polycrystalline Pt. In contrast, the curve for Pt/TCP-A seems to resemble TCP without Pt metal. Close inspection of the Pt/TCP-A voltammogram does reveal the characteristic Pt voltammetric features. However, the signal for this electrode is dominated by current from the original TCP substrate because the amount of Pt is low. These cyclic voltammetric results, coupled with the SEM images presented in Figure 6.5, show that Pt can be electrodeposited on both TCP and BND, that the Pt nanoparticles are in electrical contact with the carbon substrate, and that the composite electrode is electrochemically active.

From the curves in Figure 6.6B, it seems that the active Pt surface area is larger for Pt/TCP-B than for Pt/BND-B. It should be reemphasized, however, that these curves were normalized to the solution-exposed carbon electrode surface area (TCP or BND) that were presented in Table 6.1. Considering the significant difference in the TCP and BND surface area, a more accurate analysis would be to normalize the Pt surface area to the electrode surface area to give the dimensionless surface enhancement factor (*SEF*),²² as shown in Equation 6.1

$$SEF = \frac{SA_{Pt}}{SA_C} \quad (6.1)$$

where SA_{Pt} is the electrochemically-active Pt surface area (cm^2) and SA_C is the carbon (TCP or BND) substrate surface area (cm^2) exposed to solution. SA_{Pt} can be estimated from the cyclic voltammetric charge associated with the adsorption (cathodic) or desorption (anodic) of H^+ between 0.15 and -0.02 V vs. Ag/AgCl, assuming a 1H:1Pt surface interaction and a charge of $210 \mu\text{C}/\text{cm}^2$ for hydrogen adsorption on a flat Pt (111) surface.^{23,24} Pt surface areas for TCP-A, BND-A, TCP-B, and BND-B, as well as the SEFs are presented in Table 6.2. For condition A, $0.146 \text{ mA}/\text{cm}^2$ or $0.0047 \text{ C}/\text{cm}^2$, the Pt SEF for BND (0.50) is a factor of 10 larger than that for TCP (0.033). In contrast, the Pt SEF for TCP (3.3) and BND (1.7) is more similar under condition B, $1.25 \text{ mA}/\text{cm}^2$ or $0.040 \text{ C}/\text{cm}^2$.

Table 6.2 Electrode and Pt surface areas (SA) calculated for the Pt/carbon composite electrodes (Pt/TCP-A, Pt/BND-A, Pt/TCP-B, and Pt/BND-B) with the metal phase formed by pulsed galvanostatic conditions A ($0.146 \text{ mA}/\text{cm}^2$ or $0.0047 \text{ C}/\text{cm}^2$) and B ($1.25 \text{ mA}/\text{cm}^2$ or $0.040 \text{ C}/\text{cm}^2$) with the corresponding surface enhancement factor, SEF.

Electrode	Electrode SA (cm^2)	Pt SA (cm^2)	SEF
Pt/TCP-A	0.452	0.015	0.033
Pt/BND-A	16.9	8.3	0.50
Pt/TCP-B	1.32	4.3	3.3
Pt/BND-B	7.64	13	1.7

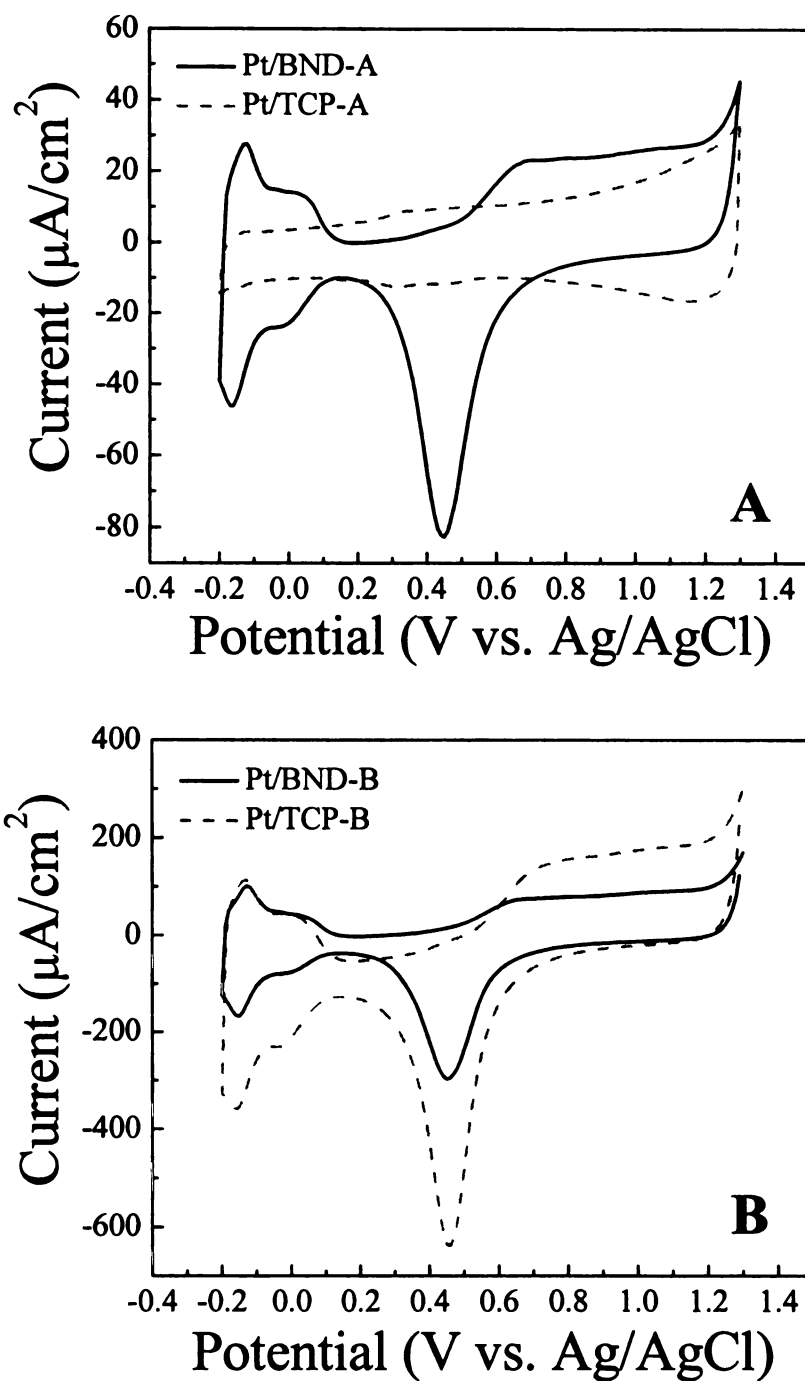


Figure 6.6 Cyclic voltammetric i - E curves of Pt/carbon composite electrodes Pt/TCP-A, Pt/BND-A, Pt/TCP-B and Pt/BND-B deposited by pulsed galvanostatic deposition (A = 0.146 mA/cm² or 0.0047 C/cm² and B = 1.25 mA/cm² or 0.040 C/cm²) in 0.1 M HClO₄ at 50 mV/s. Currents are normalized to the carbon electrode surface area.

The specific surface area of Pt (S_{Pt} , m^2/g_{Pt}) in fuel cell electrodes is an important parameter that affects both the efficiency and cost. S_{Pt} values of $\sim 100 m^2/g$ are typical in PEMFCs.²⁵ The mass of Pt deposited (i.e., loading) can be estimated by assuming a deposition (i.e., coulometric) efficiency of 100% for the 4 electron reduction of Pt^{4+} to Pt^0 according to Reaction 6.1:



The area is determined from the voltammetric charge for H^+ adsorption or desorption. This estimated value of S_{Pt} really represents a lower limit on TCP and BND as the actual loading is likely higher because the efficiency is probably not 100%. Estimated S_{Pt} values for the pulsed galvanostatic deposition of Pt on TCP and BND electrodes, Pt/TCP-A, Pt/BND-A, Pt/TCP-B, and Pt/BND-B, are presented in Table 6.3. The largest S_{Pt} value ($21 m^2/g$) was calculated for Pt/BND-A. Although this is about 5 times less than S_{Pt} in fuel cells, this lower limit may be improved by further optimization of the electrodeposition (i.e., reduction of particle size, increase of particle density, and increase of Pt activity).

Table 6.3 Estimated specific surface area of Pt on Pt/TCP-A, Pt/BND-A, Pt/TCP-B, and Pt/BND-B formed using pulsed galvanostatic deposition conditions A ($0.146 mA/cm^2$ or $0.0047 C/cm^2$) and B ($1.25 mA/cm^2$ or $0.040 C/cm^2$) assuming 100% deposition efficiency.

Electrode	Specific Pt Surface Area (m^2/g)
Pt/TCP-A	1.4
Pt/BND-A	21
Pt/TCP-B	16
Pt/BND-B	8.2

To be viable for fuel cell use, the Pt/carbon composite electrodes must exhibit high activity for the oxygen reduction reaction (ORR), as discussed in Chapter 1. SEF-normalized linear sweep voltammetric i - E curves (first scan) of Pt/TCP-A, Pt/BND-A, Pt/TCP-B, and Pt/BND-B in oxygen-saturated (30 min O₂ bubble) 0.1 M HClO₄ at 1 mV/s are shown in Figures 6.7A and B. The oxygen reduction current recorded for each electrode is only associated with the reduction occurring at Pt sites because both sp^2 - and sp^3 -bonded electrodes are known to have a large overpotentials for this reaction in acidic media. Sigmoidal curve shapes are generally observed for the ORR on bare Pt microelectrodes, indicative of pseudo-steady-state behavior.²⁶⁻²⁹ However, when the concentration of oxygen at the electrode surface is higher than in bulk solution, such as when Pt is coated with a Nafion[®] film that preconcentrates oxygen, a peak is observed in the ORR curve.²⁹ This peak corresponds to the reduction of a high concentration of oxygen and is followed by the typical pseudo-steady-state response as solution oxygen is reduced.²⁹ Thus, we suppose that the peaks in these curves are a result of oxygen preconcentration within the electrode during the 30 min O₂ bubble. It should be noted that a second scan results in the expected pseudo-steady-state behavior without a large reduction peak. Importantly, the onset and half-wave ($E_{p/2}$) potentials for oxygen reduction, as well as the reduction charge, do not change.

$E_{p/2}$ for the ORR (V vs. Ag/AgCl and SHE) as well as the approximate limiting peak current (i.e., pseudo-steady-state), normalized to both SEF (μ A) and mass of Pt (mA/mg_{Pt}), are presented in Table 6.4. As discussed in Chapter 1, the standard potential for oxygen reduction is 1.23 V vs. SHE, or *ca.* 1.0 V vs. Ag/AgCl. If ohmic resistance effects are minimal, as in these experiments, cathodic shifts from this standard potential

are indicative of sluggish electron transfer kinetics. Although the kinetics of the ORR reaction were not studied in detail in these experiments, the shift in $E_{p/2}$ from 0.616 mV vs. Ag/AgCl for Pt/BND-B to 0.567 mV vs. Ag/AgCl for Pt/TCP-B indicates that the electron-transfer rate may be enhanced on the BND electrode. As shown in Table 6.4, there is also a large difference in the SEF and Pt mass-normalized ORR limiting currents (i_{lim}) for the electrodes. Most notably, the Pt/BND-A electrode had a limiting current of *ca.* -1000 $\mu\text{A}/\text{SEF}$ (-11.6 $\text{mA}/\text{mg}_{\text{Pt}}$), while a current for the Pt/TCP-A electrode, deposited under similar conditions, could not be evaluated.

Table 6.4 Peak position ($E_{p/2}$) and approximate limiting current (i_{lim}) for the oxygen reduction reaction on Pt/TCP-A, Pt/BND-A, Pt/TCP-B, and Pt/BND-B in oxygen-saturated 0.1 M HClO_4 at 1 mV/s normalized to the surface enhancement factor ($i_{lim, SEF}$, $\mu\text{A}/\text{SEF}$) and to the mass of Pt ($i_{lim, mass}$, $\text{mA}/\text{mg}_{\text{Pt}}$).

Electrode	$E_{p/2}$ (V vs Ag/AgCl)	$E_{p/2}$ (V vs SHE)	$i_{lim, SEF}$ ($\mu\text{A}/\text{SEF}$)	$i_{lim, mass}$ ($\text{mA}/\text{mg}_{\text{Pt}}$)
Pt/TCP-A	--	--	--	--
Pt/BND-A	0.583	0.780	-1000	-11.6
Pt/TCP-B	0.567	0.764	-130	-2.70
Pt/BND-B	0.616	0.813	-250	-15.1

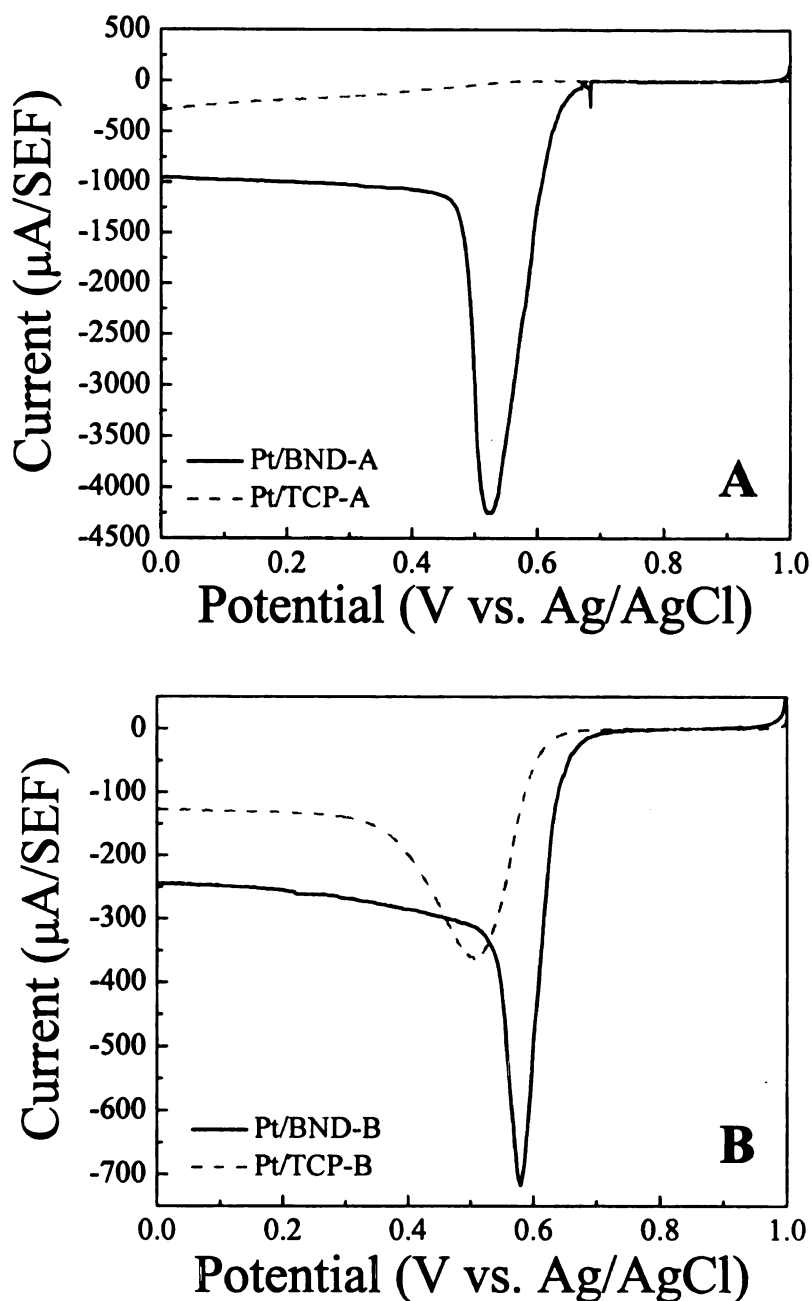


Figure 6.7 Linear sweep voltammetric *i-E* curves for the oxygen reduction reaction at Pt/TCP-A, Pt/BND-A, Pt/TCP-B, and Pt/BND-B in oxygen-saturated 0.1 M HClO₄ at 1 mV/s. Current is normalized to the surface enhancement factor (SEF).

6.2.3 Evaluation of Pt/TCP and Pt/BND Stability

The microstructural stability of the bare and Pt/carbon composite electrodes was evaluated before and after anodic polarization, as presented for the carbon powder

electrodes in Chapter 3. First, chronoamperometric i - t curves were recorded for metal-free TCP and BND held at 1.4 and 1.6 V vs. Ag/AgCl and 25 °C in 0.1 M HClO₄ for 1 h. Polarizations could not be completed at 80 °C because the insulating material was not stable in HClO₄ at this high temperature. Scanning electron micrographs of BND and TCP polarized at 1.6 V are shown in Figure 6.8A and B, respectively. Although no morphological changes were noted after polarization at 1.4 V, severe morphological damage was observed for TCP after polarization at 1.6 V. As shown in Figure 6.8B, individual carbon fibers fractured and separated from the electrode. In contrast, no morphological damage was seen for BND after polarization at 1.6 V.

The charge passed during polarization, change in the faradaic current associated with electroactive surface-oxide functional groups (ΔI), and the Raman D/E_{2g} ratios before and after polarization are presented in Table 6.5. The charge density passed during the 1 h polarization for BND at both potentials was lower than that for TCP under the same conditions. As discussed in Chapter 3, the charge recorded during anodic polarization is associated with reactions at the electrode surface such as oxidation of edge plane and defect sites and gasification of carbon to CO₂, as well as electric double layer formation. In addition, some charge may arise from the oxygen evolution reaction, particularly at the higher polarization potentials. The lower charge for BND is consistent with the material being less reactive under these conditions and more corrosion-resistant. Despite the lower reactivity of BND, it seems that the surface oxide content of both materials increased similarly during polarization at 1.4 V. It should be reemphasized, however, that some fraction of the sp^2 -bonded carbon within the BND electrode is likely exposed to the solution because of incomplete diamond coverage through the interior of

the electrode. It is possible that the charge recorded during polarization, as well as the increase in the fraction of surface oxides, is due to oxidation and/or corrosion of the exposed sp^2 -bonded portions of the electrode.

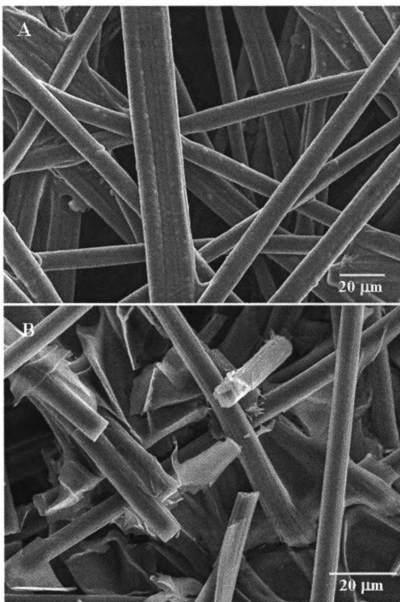


Figure 6.8 Scanning electron micrographs of (A) BND and (B) TCP after potentiostatic polarization at 1.6 V vs. Ag/AgCl at 25 °C for 1 h.

Table 6.5 Charge density (mC/cm^2), change in faradaic current density for electroactive surface-oxygen functional groups (ΔJ), and Raman D/E_{2g} ratio for bare carbon paper (TCP) and nanocrystalline diamond deposited on carbon paper (BND) after polarization at different potentials in 0.1 M HClO_4 at 25 °C for 1 h.

Electrode	Polarization Potential (V vs. Ag/AgCl)	Charge Density (mC/cm^2)	ΔJ ($\mu\text{A}/\text{cm}^2$)	D/E_{2g}
TCP	Untreated	--	--	0.30 ± 0.08
TCP	1.4	3.75	4.15	0.20 ± 0.09
BND	1.4	0.347	3.23	--
TCP	1.6	87.3	51.2	0.4 ± 0.1
BND	1.6	33.7	14.1	--

As discussed in Chapter 3, an increase in the D/E_{2g} ratio is indicative of increases in the microstructural disorder (i.e., edge plane density) of sp^2 -bonded carbons. As shown in Table 6.5, the average D/E_{2g} ratio for TCP decreased slightly after anodic polarization at 1.4 V, from 0.30 ± 0.08 to 0.20 ± 0.09 . According to the order/disorder mechanism presented in Chapter 3, more disordered regions of the carbon will corrode first, leaving a more ordered material under certain conditions. After polarization at 1.6 V, D/E_{2g} increased to 0.4 ± 0.1 , indicative of increases in the carbon edge plane density. This is not surprising considering the severe morphological damage noted for the TCP electrode at 1.6 V. In contrast, there were no microstructural changes observed for BND as shown in the Raman spectra recorded before and after potentiostatic polarization, presented in Figure 6.9.

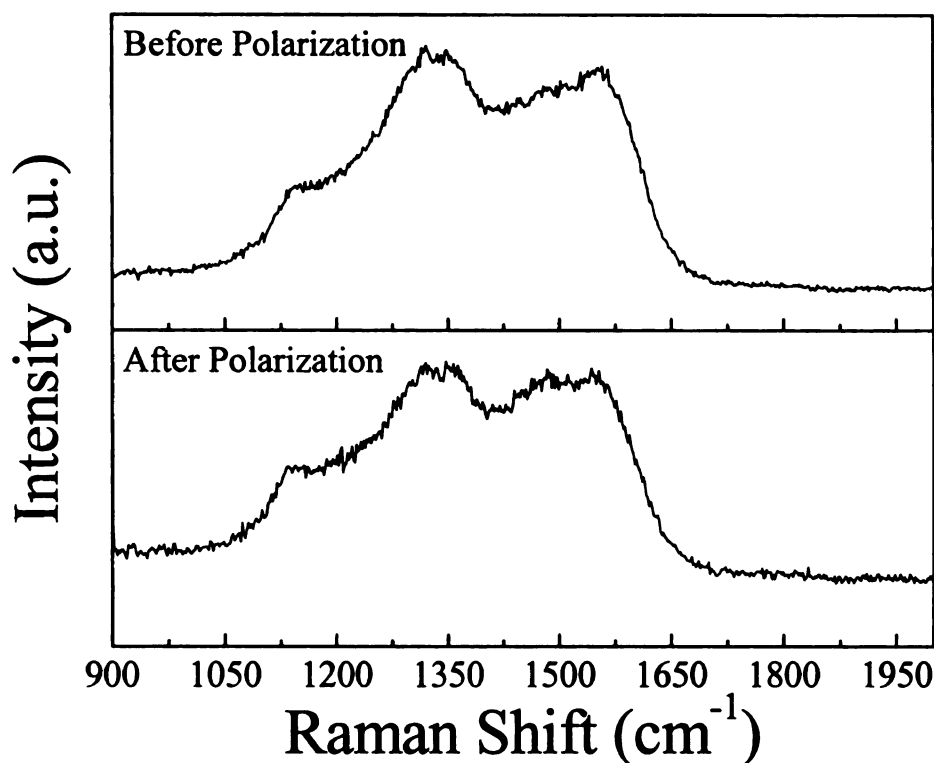


Figure 6.9 Raman spectra of BND before and after potentiostatic polarization at 1.6 V vs. Ag/AgCl in 0.1 M HClO₄ at 25 °C for 1 h.

In addition to the stability requirements of the support material, the stability of the Pt electrocatalyst is also an important concern for maintaining PEMFC efficiency and operational lifetime. The stability of the Pt electrocatalyst over time was first evaluated under conditions similar to those used in phosphoric acid fuel cells (PAFC) and has been attributed to: (i) Pt dissolution/reprecipitation (i.e., an Ostwald ripening process) (ii) Pt nanoparticle migration and coalescence, and (iii) Pt agglomeration resulting from corrosion of the *sp*²-bonded carbon support material.^{30,31, and references therein} In systems where corrosion of the support was not an issue, there was no consensus in these early studies on the mechanism for loss of electrocatalyst surface area. In a recent publication, Ferreira and co-workers studied the mechanism of Pt surface area loss in a PEMFC.³¹

This report provides a detailed discussion of what is known about Pt instability in PAFCs and PEMFCs, as well as a number of relevant references.³¹ In PEMFCs, evidence has been found that loss of Pt electrocatalyst surface area occurs by both Ostwald ripening and by solubilization of Pt (i.e., oxidation), subsequent migration of Pt ions within the ionomer near the cathode, and finally, reduction to Pt metal by H₂ crossover from the anode.³¹

The stability of the Pt/carbon composite electrodes deposited under condition B, as discussed above, was evaluated by potentiostatic polarization at 1.4 V vs. Ag/AgCl and 25 °C in 0.1 M HClO₄ for 1 h. Figure 6.10 shows scanning electron micrographs of Pt/TCP-B and Pt/BND-B before and after anodic polarization. Pt nanoparticles decorate only the first few layers of Pt/BND-B before polarization. However, after the 1 h polarization, Pt nanoparticles can be easily seen at least ~100 μm into the electrode, which suggests that Pt was dissolved and redeposited during polarization (i.e., Ostwald ripening). Changes are more difficult to note for the Pt/BND-B electrode because Pt decorated fibers deep within the electrode before polarization. The Pt particle density on Pt/BND-B after polarization seems to be slightly less than that before polarization on the outermost fibers, suggesting that Pt dissolution and redeposition also occurred on Pt/BND-B.

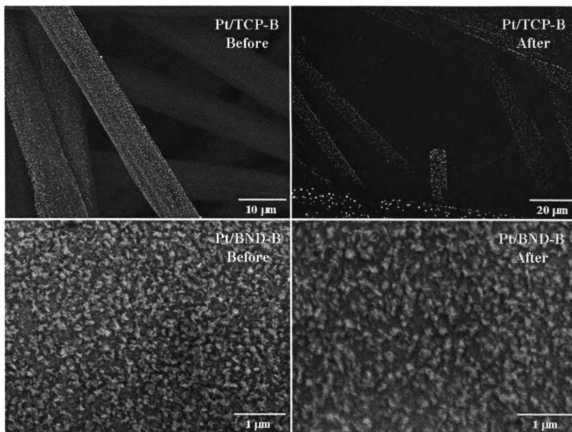


Figure 6.10 Scanning electron micrographs of Pt/TCP-B and Pt/BND-B before and after potentiostatic polarization at 1.4 V vs. Ag/AgCl and 25 °C in 0.1 M HClO₄ for 1 h.

Background cyclic voltammetric *i*-*E* curves recorded in 0.1 M HClO₄ at 50 mV/s before and after anodic polarization of Pt/TCP-B and Pt/BND-B at 1.4 V vs. Ag/AgCl are shown in Figure 6.11. The electrochemically-active Pt surface area, calculated from the hydrogen adsorption charge, is presented in Table 6.6. The curves for Pt/TCP-B and Pt/BND-B look similar before and after polarization and all electrodes exhibit the characteristic Pt signal. Although it seems that the peak current for the Pt-oxide reduction (~450 mV vs. Ag/AgCl) is larger after polarization for Pt/TCP-B, the entire curve is shifted negative below ~600 mV vs. Ag/AgCl, presumably because there is

oxygen present in the electrode after anodic polarization. The electrochemically-active Pt surface area does not change for either electrode after polarization (the measured values were always within 5 %).

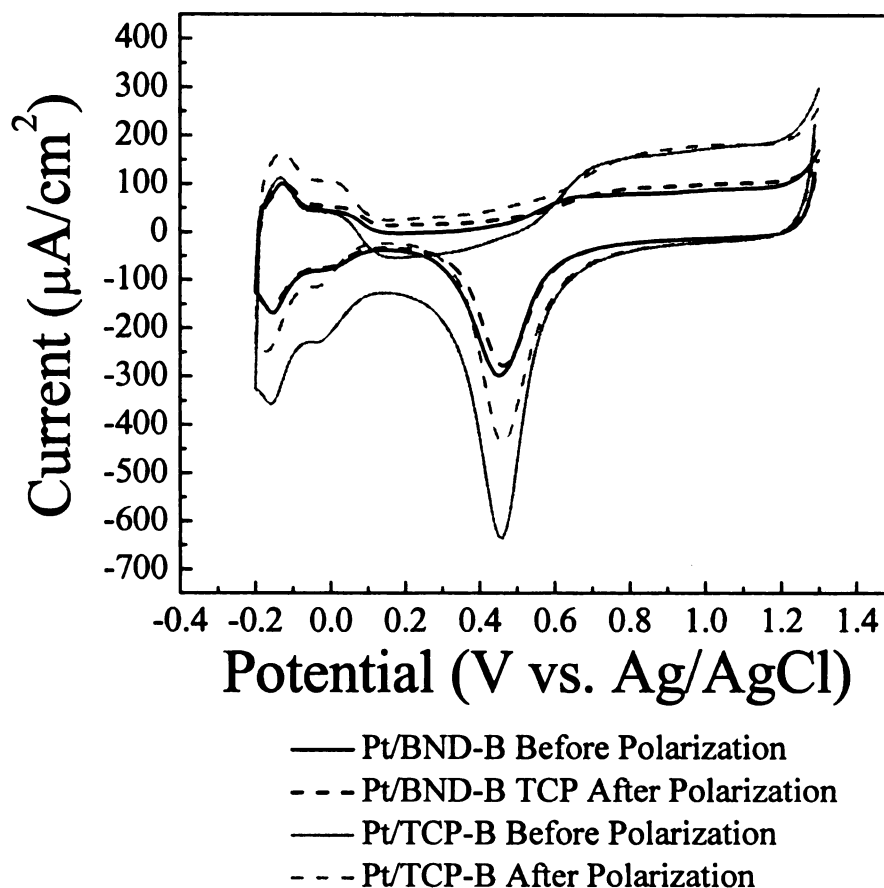


Figure 6.11 Cyclic voltammetric *i*-*E* curves for Pt/TCP-B and Pt/BND-B in 0.1 M HClO₄, recorded at 50 mV/s normalized to the electrode surface enhancement factor (SEF), before and after a 1 h polarization at 1.4 V vs. Ag/AgCl at 25 °C.

Table 6.6 Electrochemically-active Pt surface area (Pt/TCP-B and Pt/BND-B) before and after anodic polarization at 1.4 V vs Ag/AgCl and 25 °C in 0.1 M HClO₄ for 1 h.

Electrode	Pt Surface Area (cm ²) Before Polarization	Pt Surface Area (cm ²) After Polarization
Pt/TCP-B	3.90	3.92
Pt/BND-B	12.2	12.4

Linear sweep voltammetric i - E curves (first scan) for Pt/TCP-B and Pt/BND-B in oxygen-saturated 0.1 M HClO₄ at 1 mV/s, before and after anodic polarization at 1.4 V vs. Ag/AgCl, are presented in Figure 6.12. As shown in Table 6.7, the half-wave potential ($E_{p/2}$) and limiting currents (i_{lim}) normalized to the electrode surface enhancement factor are quite similar before and after polarization, suggesting that Pt mass was not lost as a result of polarization. The only significant difference in the ORR after polarization is the shape of the curves, likely a result of differences in the oxygen concentration within the electrode, as discussed above.

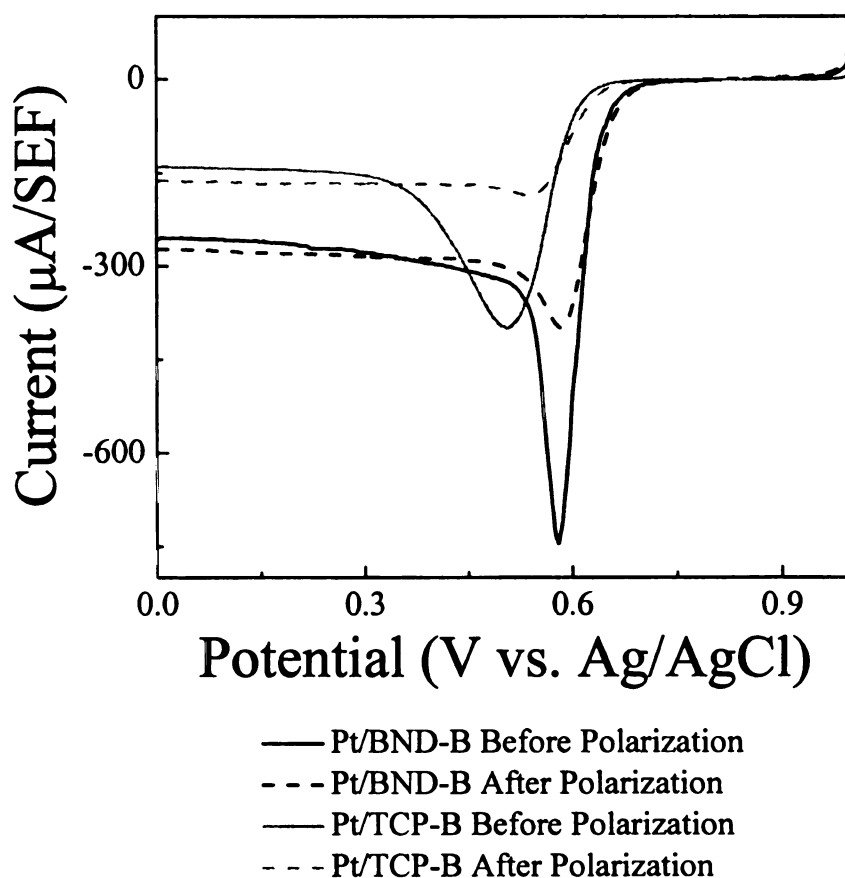


Figure 6.12 Linear sweep voltammetric i - E curves for the oxygen reduction reaction at Pt/TCP-B and Pt/BND-B in oxygen-saturated 0.1 M HClO₄ before and after polarization at 1.4 V vs. Ag/AgCl at 25 °C in 0.1 M HClO₄ for 1 h. Curves were recorded at 1 mV/s and are normalized to the electrode surface enhancement factor (SEF).

Table 6.7 Half-peak position ($E_{p/2}$) and current (i_{lim}) for the oxygen reduction reaction on Pt/TCP-B and Pt/BND-B in oxygen-saturated 0.1 M HClO₄ after anodic polarization at 1.4 V vs. Ag/AgCl and 25 °C in 0.1 M HClO₄ for 1 h. The scan rate was 1 mV/s and the current was normalized to the surface enhancement factor ($i_{lim, SEF}$, $\mu\text{A/SEF}$).

Electrode	$E_{p/2}$ (V) Before Polarization	$E_{p/2}$ (V) After Polarization	$i_{lim, SEF}$ ($\mu\text{A/SEF}$) Before Polarization	$i_{lim, SEF}$ ($\mu\text{A/SEF}$) After Polarization
Pt/TCP-B	0.567	0.602	-130	-160
Pt/BND-B	0.616	0.630	-250	-280

6.3 Conclusions

Carbon paper has been successfully coated with nanocrystalline boron-doped diamond and studied as an electrocatalyst support material. Scanning electron microscopy, XRD, and Raman spectroscopy confirmed that the carbon fibers were fully coated, within the first $\sim 100\ \mu\text{m}$ of the TCP surface, with high-quality, nanocrystalline boron-doped diamond. Pulsed galvanostatic deposition of Pt nanoparticles on TCP and BND was carried out at two different current densities, A ($0.146\ \text{mA/cm}^2$ or $0.0047\ \text{C/cm}^2$) and B ($1.25\ \text{mA/cm}^2$ or $0.040\ \text{C/cm}^2$). Under the best of these two conditions for BND (condition A), $21\ \text{m}^2/\text{g}$ Pt (lower limit estimate) was deposited and an oxygen reduction current of *ca.* $-1000\ \mu\text{A/SEF}$ ($-11.6\ \text{mA/mg}_{\text{Pt}}$) was seen, whereas only $1.4\ \text{m}^2/\text{g}$ Pt was deposited on TCP with no well-defined oxygen-reduction peak. BND exhibited superior structural stability and corrosion resistance during anodic polarization at 1.6 V with no morphological or microstructural damage. In contrast, severe morphological damage was observed for TCP. Anodic polarization of Pt/TCP-B and Pt/BND-B at 1.4 V provided evidence for an Ostwald ripening mechanism where the Pt was dissolved and

redeposited. There were no changes in the morphology of the electrocatalyst supports, Pt/TCP-B or Pt/BND-B, after the polarization.

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Chapter 7

Future Research Directions

Rising energy demands coupled with a limited supply of fossil fuels has led to a significant amount of research and development into alternative energy technologies. For example, the polymer electrolyte membrane fuel cell (PEMFC), an energy conversion device that operates on hydrogen fuel, has received a great deal of attention in recent years because it has a theoretical operating efficiency of 100% with no harmful emissions. However, current PEMFC technologies have a limited operating lifetime and reduced electrical efficiency because of problems with the durability and performance of electrode materials under certain PEMFC operating conditions. Specifically, microstructural degradation and corrosion reactions of the sp^2 -bonded carbon electrocatalyst support under high potentials (1.2 to 1.5 V vs. SHE) during start-up and shut-down, as well as idle operation, is a problem that directly affects PEMFC efficiency. Although the degradation mechanism is not well understood, microstructural damage of the carbon support has been shown to lead to loss of electrocatalytic activity through pathways such as electrocatalyst aggregation and, in extreme cases, complete electrode failure. The research presented in this dissertation focused on the study of sp^2 -bonded carbon degradation mechanisms and the development of a new, dimensionally-stable electrocatalyst support material based on electrically conducting diamond. In this chapter, future work in these two areas is discussed.

Chapter 3: Study of the Degradation Mechanisms of sp^2 -Bonded Carbon Powders During Electrochemical Polarization

The morphology and microstructure of two structurally well-characterized sp^2 -bonded carbon powders, graphite and glassy carbon (GC), were studied under applied potential (0.8 to 1.6 V vs. Ag/AgCl) at 25, 50, and 80 °C. Oxidation of graphite and GC, coupled with heterogeneous microstructural changes across a graphite electrode surface, provided evidence for the order/disorder mechanism of carbon corrosion, with a nucleation and growth process for graphite. Preliminary comparisons were made to a carbon black commonly used in fuel cells, Vulcan XC-72, with and without Pt electrocatalyst.

- 1) These measurements were carried out *ex situ* after short times (1 h) such that no temporal information or conclusions about long-term degradation could be gained. Future work should include *in situ* Raman spectroscopic measurements over longer time periods to gain a better understanding about the nature of degradation.
- 2) Characterization of carbon oxidation and gasification to CO and CO₂ should be done using on-line mass spectrometry. This type of study, coupled with the *in situ* microstructural information, will lead to a better understanding of the processes that occur during carbon degradation.
- 3) Membrane electrode assemblies composed of Vulcan XC-72 with and without Pt electrocatalyst should be studied in a fuel cell at different potentials, temperatures, and time periods. The effect of the Pt electrocatalyst on carbon corrosion, as well

as the consequences of electrocatalyst support corrosion on fuel cell efficiency should be characterized.

Chapter 5: Preparation and Characterization of Boron-Doped Diamond Powder: A Possible Dimensionally Stable Electrocatalyst Support Material

and

Chapter 6: Preparation and Characterization of Boron-Doped Diamond Paper with Pt Nanoparticles

Two high-surface-area electrocatalyst support materials based on electrically conducting diamond were synthesized.

- 1) Future work with conducting diamond powder should include strategies to improve the electrochemical response of the bound electrode.
 - The electrode wetting should be improved by testing different types of binders and by varying the powder/binder ratio.
 - Electrodes fabricated using large (8-12 μm diam) conductive diamond powder particles mixed with a small percentage (e.g., 10-20 wt. %) of smaller (e.g., 0-2 μm) conductive diamond powder particles may reduce electrode ohmic resistance by improving the particle-particle contact.
 - Composite electrodes made by mixing conducting diamond powder with flatter, more compressible powder such as hydrogenated graphite may help to reduce the electrode resistance while still maintaining a significant portion of the corrosion resistance.

- Hot-pressing the powder into a Nafion membrane, as is done with carbon black during MEA fabrication, may reduce the contact resistance. In addition, this electrode geometry could be used directly in a fuel cell.
- 2) The powder surface area should be increased.
- Characterization of detonation nanodiamond powder with different boron doping strategies should continue. This includes conductivity measurements and material characterization such as Raman spectroscopy to assess the nondiamond carbon impurity content.
 - Effective coating strategies should be developed to coat small diameter (nm-sized) abrasive diamond powder with an electrically conducting layer.
- 3) The diamond powder should be tested as an electrocatalyst support material.
- Strategies should be developed to deposit Pt on conducting diamond powder so that its electrocatalytic activity can be addressed. These may include chemical or electrochemical deposition. Durability and performance are key issues.
 - Methods to anchor the Pt electrocatalyst particles to the diamond support should be developed that result in a stable support-catalyst interaction, but do not significantly increase the area of the support or decrease the area of the electrocatalyst.

- 4) The Pt/carbon paper composite electrodes should be further developed as an electrocatalytic electrode.
- A method to accurately assess the carbon paper surface area should be developed so that increases in electrode wetting during electrochemical characterization do not influence the normalized current or charge. This may include strategies to increase electrode wetting at the outset by soaking the carbon paper in a variety of solvents from non-polar to polar.
 - Pt electrodeposition on diamond-coated carbon paper should be optimized in terms of small, uniform particle diameter and high particle density to increase electrocatalytic activity of the Pt/carbon paper electrodes.
 - Carbon paper and diamond-coated carbon paper should be hot-pressed with a Nafion[®] membrane to form a membrane electrode assembly and tested in a fuel cell to address the electrocatalytic activity of the electrodes, as well as their stability over time.

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