Nitrogen Containing Carbon Nanofibers as Non-Noble Metal Cathode Catalysts in PEM and Direct Methanol Fuel Cells

Dissertation

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

By

Elizabeth Joyce Biddinger, B.S.ChE

Graduate Program in Chemical Engineering

* * * *

The Ohio State University

2010

Dissertation Committee:

Professor Umit S. Ozkan, Advisor

Professor Jeffrey Chalmers

Professor Stuart Cooper
ABSTRACT

PEM and direct methanol fuel cells (DMFC) have great potential for use as alternative fuel energy conversion devices. Before this potential can be realized, however, performance improvements must be made and material costs need to be reduced. The limiting reaction in the PEMFCs and DMFCs is the oxygen reduction reaction (ORR), which occurs at the cathode. In an attempt to improve the reaction kinetics, substantial loadings of Pt catalysts are required on the cathode. This significantly increases the overall cost of the fuel cell. Also, in DMFCs, methanol crossover from the anode allows for competing reactions at the cathode catalyst to occur, reducing the power output of the fuel cell further. As the demand for fuel cells increase, the demand for Pt will far outpace the supply of Pt.

Replacements studied for Pt cathode catalysts include Pt alloys, other noble metals, chalcogenides and nitrogen-containing carbons. Nitrogen-containing carbons made from simple precursors can provide an economical replacement to Pt catalysts. Before this can be realized, improvements in the activity and selectivity of the nitrogen-containing carbons need to occur.
The work presented here involves the study of nitrogen-containing carbon nanostructures (CNx) as ORR catalysts for PEMFCs and DMFCs. Improving the ORR catalytic performance in both activity and selectivity for CNx catalysts, while gaining a better understanding of the catalyst materials and the way they are evaluated were the major driving forces behind this research.

CNx catalyst performance was studied by incorporating heteroatoms beyond nitrogen and surface functional groups into the catalyst. Boron and sulfur heteroatoms were studied along with oxygen functional groups. It was found that the methods to introduce boron into the nanostructure had a large impact on the ORR performance. Sulfur did not have an effect on the ORR performance, but was successfully used as a CNx growth promoter in the form of thiophene during acetonitrile pyrolysis. An increase in oxygen functional groups on the surface of CNx catalysts improved the ORR selectivity to water formation.

The role CNx catalyst nanostructure plays in ORR activity was studied using model nanofiber systems with both high levels of graphitic edge plane exposure and low levels of graphitic edge plane exposure. Experiments showed that un-doped graphitic edge planes were not the ORR active site. Incorporation of nitrogen into the graphitic edge planes significantly improved ORR activity compared to the nitrogen-free nanofibers.

The use of electrochemical half cell methods have been evaluated and reported here. Rotating Ring Disk Electrode (RRDE) testing is commonly used to measure the
ORR activity and selectivity of a catalyst. The factors affecting catalyst selectivity reporting including catalyst loading and RRDE catalyst ink aging were studied.

In addition to these studies, the performance of CN$_x$ catalysts developed in the laboratory for use as cathode catalysts in DMFCs were evaluated. It was found that CN$_x$ catalysts are both methanol tolerant and inactive towards the methanol oxidation reaction, making them favorable potential DMFC catalysts.

Throughout the studies, materials developed and evaluated were characterized using classic heterogeneous catalysis techniques to gain a better understanding of the systems being analyzed. These techniques include, X-Ray Photoelectron Spectroscopy (XPS), Transmission Electron Microscopy (TEM), Temperature Programmed Oxidation (TPO) and Desorption (TPD) studies and Thermogravimetric Analysis, among others.
DEDICATION

To Josh, Miracle and Merlin for all of your love and support
ACKNOWLEDGMENTS

I gratefully acknowledge the assistance and camaraderie I have received in the laboratory from the many members of the HCRG both past and present.

I am especially indebted to those who laid the ground work for this project: Paul Matter, PhD, and his undergraduate assistants Ling Zhang, Eugenia Wang and Maria Arias.

Thank you to those who have more recently worked on the “PEM Team:” undergraduates Doug Knapke, Jesaiah King, Katie Luthman and Hilary Marsh along with high school student Kate Baker, and of course, fellow graduate students Deepika Singh and Dieter von Deak, who ideas are bounced off of on nearly a daily basis.

This group would not be possible without the guidance and dedication of my advisor Professor Umit S. Ozkan.

I acknowledge the financial assistance provided to this project through NSF, DOE-BES, and Ohio Department of Development Wright Center for Innovation.

Finally, a deep thanks to my family and friends, especially my husband Josh, for supporting me in my endeavors as a graduate student.
VITA

November 6, 1982 .................. Born, Ashland, Ohio

June 2001 ......................... H.S. Diploma, Mapleton High School, Ashland, Ohio

Summer 2003 ...................... Chemical Engineering Co-Op, Cooper Tire & Rubber Company, Findlay, Ohio

Summer 2004 ...................... Chemical Engineering Co-Op, Cooper Avon Tyres, Melksham, England

Winter 2004-Spring 2005......... Undergraduate Research Assistant, Ohio University, Athens, Ohio

June 2005 .......................... B.S. Chemical Engineering, Ohio University, Athens, Ohio

2005-Present ...................... Graduate Research Associate, Ohio State University, Columbus Ohio
Book Chapter


Invited Papers


Journal Articles


**FIELDS OF STUDY**

Major Field: Chemical Engineering

Area of Interest: Heterogeneous Catalysis
<table>
<thead>
<tr>
<th>CHAPTER</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Introduction</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>Research Objectives</td>
<td>10</td>
</tr>
<tr>
<td>3</td>
<td>Literature Review of Carbon-Nitrogen ORR Catalysts and Related Materials</td>
<td>12</td>
</tr>
<tr>
<td>3.1</td>
<td>Carbon-Nitrogen ORR Catalysts</td>
<td>12</td>
</tr>
<tr>
<td>3.1.1</td>
<td>Non-Pyrolyzed Macrocycles as ORR Catalysts</td>
<td>12</td>
</tr>
<tr>
<td>3.1.2</td>
<td>Pyrolyzed Macrocycles as ORR Catalysts</td>
<td>14</td>
</tr>
<tr>
<td>3.1.3.a</td>
<td>ORR C-N Catalysts Derived from Simple Precursors</td>
<td>15</td>
</tr>
<tr>
<td>3.1.3.b</td>
<td>Characteristics of C-N ORR Catalysts</td>
<td>19</td>
</tr>
<tr>
<td>3.1.4</td>
<td>Active Site Debate in C-N ORR Catalysts</td>
<td>25</td>
</tr>
<tr>
<td>3.2</td>
<td>Other Heteroatom-Containing and Functionalized Carbon Nanostructures</td>
<td>30</td>
</tr>
<tr>
<td>3.2.1</td>
<td>Types of Carbon Nanostructure and their Growth Characteristics</td>
<td>30</td>
</tr>
<tr>
<td>3.2.2</td>
<td>Nitrogen-Containing Carbon Nanostructures</td>
<td>34</td>
</tr>
<tr>
<td>3.2.3</td>
<td>Sulfur-Containing Carbon Nanostructures</td>
<td>35</td>
</tr>
<tr>
<td>3.2.4</td>
<td>Boron-Containing Carbon Nanostructures</td>
<td>36</td>
</tr>
</tbody>
</table>
4.2.6 Temperature Programmed Desorption-Temperature Programmed Oxidation (TPD-TPO) Experiments .......................................................... 64
4.3 Electrochemical Testing and Related Studies ........................................... 65
4.3.1 Rotating Ring Disk Electrode (RRDE) Testing ...................................... 66
4.3.2 Methanol Tolerance and Methanol Oxidation Activity Testing .................. 70
4.3.3 RRDE Studies to Examine the Effect of Catalyst Loading ......................... 71
4.3.4 Catalyst Layer Thickness Determination .................................................. 72
4.3.5 RRDE Catalyst Ink Aging Studies .............................................................. 72
4.3.6 Electrochemical Reduction and Oxidation of Hydrogen Peroxide ............... 73

CHAPTER 5. Effect of Sulfur as a Growth Promoter for CNx Nanostructures as PEM and DMFC ORR Catalysts ................................................................. 75

5.1 Motivation for Studying Sulfur as a Growth Promoter .................................. 75
5.2 Results & Discussion .................................................................................... 77
5.2.1 Thiophene as a Growth Promoter ............................................................... 77
5.2.2 Catalyst Morphology .................................................................................. 78
5.2.3 Activity and Selectivity Testing ................................................................. 81
5.2.4 Hydrophobicity Testing ............................................................................ 83
5.2.5 Surface Species Characterization ............................................................... 84
5.2.6 Stability of Sulfur in CNx Nanostructures .................................................. 92
5.3 Thiophene Usage as a Growth Promoter Concluding Remarks ..................... 99

CHAPTER 6. Impact of Oxygen Functional Groups on CNx ORR Catalysts ............ 102

6.1 Oxygen Functional Groups on Carbon and their Potential Role in ORR .......... 102
6.2 Results & Discussion .................................................................................... 104
6.2.1 CNx Treated with HNO3 .......................................................................... 104
6.2.2 Additional Oxygen Functional Group Observations ................................. 109
6.3 Conclusions for Oxygen Functional Groups in ORR .................................... 110

CHAPTER 7. Role of Graphitic Edge-Plane Exposure in Carbon Nanostructures for Oxygen Reduction Reaction .......................................................... 112

7.1 Motivation in Studying Role of Graphitic Edge-Plane Exposure ..................... 112
7.2 Results and Discussion ................................................................................ 113
7.2.1 Synthesis and Physical Characterization ............................................................ 113
7.2.2 Chemical Characterization ................................................................................. 121
7.2.2.a X-Ray Photoelectron Spectroscopy ................................................................. 121
7.2.2.b Temperature-Programmed Oxidation Experiments ........................................ 131
7.2.3 Activity and Selectivity Testing ......................................................................... 135
7.3 Conclusions to Investigation of Role of Graphitic Edge Plane Exposure ............. 140

CHAPTER 8. Effect of Ammonia Treatment on CN\textsubscript{x} Catalysts ......................... 142
8.1 Background into CN\textsubscript{x} Catalysts Treated with Ammonia .............................. 142
8.2 Results & Discussion ............................................................................................ 143
8.2.1 Ammonia Treatment Process Observations on CN\textsubscript{x} Materials ................. 143
8.2.2 Surface Species Analysis of Treated CN\textsubscript{x} ................................................. 146
8.2.3 Activity and Selectivity Observations for CN\textsubscript{x} Oxidized and Treated with Ammonia ............................ 148
8.3 Conclusions to Studies on CN\textsubscript{x} Treated with Ammonia ............................... 151

CHAPTER 9. Use of Boron and Phosphorus in CN\textsubscript{x} Catalysts .......................... 152
9.1 Overview of Purpose of Using Boron and Phosphorus in CN\textsubscript{x} Catalysts .......... 152
9.2 Graphitic Site Blocking of CN\textsubscript{x} .................................................................. 154
9.3 Boron Incorporation into CN\textsubscript{x} ................................................................. 156
9.3.1 Surface Species Analysis on Boron Incorporated CN\textsubscript{x} .............................. 157
9.3.2 Surface Area and Pore Volume of Boron Incorporated CN\textsubscript{x} ....................... 160
9.3.3 Activity of Boron-Incorporated CN\textsubscript{x} ...................................................... 161
9.3.4 Acid Treatment of Boron-Incorporated CN\textsubscript{x} .......................................... 162
9.4 Conclusions for Graphitic Site Blocking and Boron Incorporation into CN\textsubscript{x} .... 164

CHAPTER 10. Evaluation of RRDE Testing Methods and their Impact on Reported ORR Catalyst Results ........................................................................................................ 166
10.1 Background on RRDE Testing ............................................................................ 166
10.2 Examination of Catalyst Loading Effects on the Selectivity of CN\textsubscript{x} and Pt/VC ORR Catalysts using RRDE ................................................................. 168
10.2.1 Effect of Catalyst Loading on Selectivity ........................................................ 170
10.2.2 RRDE Catalyst Layer Thickness Observations .............................................. 176
10.2.3 Electroreduction of H₂O₂ by CNₓ Catalysts ......................................................... 182
10.3 RRDE Catalyst Ink Aging Effects on Selectivity to Water Formation in ORR . 184
10.3.1 RRDE Results with Ink Aging ......................................................................... 185
10.3.2 Role of Ethanol in Ink Aging ........................................................................... 188
10.4 Summary of RRDE Method Examinations ......................................................... 190
CHAPTER 11. Methanol Tolerance of CNₓ Oxygen Reduction Catalysts ............... 192
  11.1 Introduction to Direct Methanol Fuel Cell Cathode Catalysts ......................... 192
  11.2 MOR Activity and Effect of Methanol on ORR with Pt and Pt/Ru Catalysts .... 194
  11.3 MOR Activity and Effect of Methanol on ORR with CNₓ Catalysts ............... 198
CHAPTER 12. Conclusions ....................................................................................... 206
CHAPTER 13. Recommendations for Future Work ................................................... 209
CHAPTER 14. Glossary of Acronyms .................................................................... 214
REFERENCES ......................................................................................................... 217
LIST OF FIGURES

Figure 1. PEM fuel cell schematic. Drawing by Paul Matter. .................................................. 4

Figure 2. Typical fuel cell polarization curve displaying the types of performance losses and power density. ........................................................................................................ 6

Figure 3. Monthly average Pt and Ru prices July 1992-March 2010\textsuperscript{11} ..................... 8

Figure 4. Examples of macrocycles used as catalysts for ORR. As published in\textsuperscript{31} ...... 14

Figure 5. Types of nitrogen groups in carbon and their binding energy positions in XPS. As published in\textsuperscript{199} ........................................................................................................ 20

Figure 6. FeN\textsubscript{2}-type site. As illustrated in\textsuperscript{31} .................................................. 22

Figure 7. Proposed FeN\textsubscript{2+2} active site from Dodelet group. Illustration courtesy of Dieter von Deak. ........................................................................................................ 23

Figure 8. Examples of carbon nanostructures. As published in\textsuperscript{199} ......................... 31

Figure 9. Illustration of electrical conductivity within and between graphitic planes..... 33

Figure 10. Armchair and zigzag graphitic edge planes......................................................... 39

Figure 11. Oxygen functional group locations on graphite. .................................................. 40

Figure 12. Acetonitrile pyrolysis treatment conditions....................................................... 51

Figure 13. Stacked platelet nanofiber. ............................................................................... 52

Figure 14. Setup for Rotating Ring Disk Electrode. Figure courtesy of Dieter von Deak. ........................................................................................................................................... 66

Figure 15. Typical RRDE activity results. (Catalyst: CN\textsubscript{x} on 2\%Fe/MgO-HCl washed). 69
Figure 16. Sample comparison of ring current corrected for collection efficiency to absolute disk current using the RRDE method (Catalyst: CN$_x$ on 2%Fe/MgO-HCl washed). ................................................................. 70

Figure 17. Weight gain during pyrolysis of catalysts made with thiophene:acetonitrile combinations (y1 axis, circles) and the BET surface area of those materials (y2 axis, triangles) *as published in*$^{325}$ ................................................................. 78

Figure 18. TEM images of a) CN$_x$- no thiophene, b) CN$_x$-1.8% thiophene, c) CN$_x$-7.3% thiophene, d) CS$_y$-100% thiophene. *As published in*$^{325}$ ................................................... 80

Figure 19. Onset of activity comparison for thiophene containing catalysts. Inset: Activity comparison of the linear scan at 1000 rpm in oxygen saturated 0.5M H$_2$SO$_4$ for CN$_x$-8.9% thiophene and 100% thiophene catalysts. *As published in*$^{325}$ ...................... 82

Figure 20. Hydrophobicity comparison of CN$_x$, CN$_x$(8.9%) and CS$_y$ catalysts showing their dispersion in water. *As published in*$^{325}$ ................................................................. 84

Figure 21. XPS S 2p region for selected CN$_x$-thiophene catalysts (labels are mol% thiophene in acetonitrile solution) deconvoluted using two doublets, b) XPS S 2p region deconvoluted using three doublets for CN$_x$-8.9%thiophene. *As published in*$^{325}$ ............ 87

Figure 22. XPS N 1s region deconvoluted for select CN$_x$-thiophene catalysts (labels are mol% thiophene in acetonitrile solution). *As published in*$^{325}$ ................................................................. 89

Figure 23. XPS O1s region deconvoluted for select CN$_x$-thiophene catalysts (labels are mol% thiophene in acetonitrile solution). *As published in*$^{325}$ ................................................................. 91

Figure 24. Locations of possible oxygen functional groups by XPS binding energy. *As published in*$^{325}$ ................................................................. 92

Figure 25. a) Selectivity, n, (number of electrons transferred per oxygen molecule) from RRDE as a function of normalized oxygen surface content. Inset: Visual comparison of disk (absolute current) to ring (after adjustment for theoretical collection efficiency) currents at 100rpm in oxygen saturated 0.5M H$_2$SO$_4$ for CN$_x$-8.9%thiophene. b) Comparison of ring to disk currents used in determination of selectivity from RRDE. System is oxygen-saturated 0.5M H$_2$SO$_4$ with background currents subtracted for both ring and disk. *As published in*$^{325}$ ................................................................. 95
Figure 26. TPOs ran in 10%O2/He a) TG signal, b) Mass signals for 44 (CO2), 30 (x50) (NOx), and 64 (x150 for CNx-1.8%, 3.6%, 5.5% and 8.9% thiophene; x10 for 100% thiophene catalyst) (SO2). As published in325. ................................................................. 96

Figure 27. TPD-TPO experiment for CNx-3.6% thiophene a) TPD in He showing mass signals 18 (H2O), 44 (CO2) and 64 (SO2), b) TPO in 5%O2/He showing mass signals 30 (NOx), 44 (CO2) and 64 (SO2). As published in325. ................................................................. 98

Figure 28. Wet-TPD-TPO experiment for CNx-3.6% thiophene a) wet-TPD in 10%H2O/He showing mass signals 44 (CO2) and 64 (SO2), b) TPO in 5%O2/He showing mass signals 30 (NOx), 44 (CO2) and 64 (SO2). As published in325. ................................................................. 101

Figure 29. TEM images of a) and b) CNx grown on Fe/MgO, and c) and d) CNx-HNO3. As published in199. ........................................................................................................... 105

Figure 30. O 1s XPS spectra for CNx and CNx-HNO3. ................................................ 107

Figure 31. Comparison of ORR activity for CNx and CNx-HNO3 measured using RRDE at 1000 rpm. Inset: Selectivity of CNx and CNx-HNO3 .................................................. 108

Figure 32. TEM images of stacked platelets-HCl washed. Inset to a): Illustration of graphite sheet orientation in stacked platelets. Box in a) refers to region where b) was taken. As submitted to338. ........................................................................................................... 115

Figure 33. TEM images of nanofibers with basal plane exposure after HCl washing. Insets represent the lower-magnification images of the same nanofibers. As submitted to338. ........................................................................................................... 117

Figure 34. TEM images of a) stacked platelets and b) nanofibers with basal plane exposure after acid oxidation and ammonia treatment at 900°C for 19.5h. As submitted to338. ........................................................................................................... 121

Figure 35. N 1s region of the X-ray photoelectron spectra comparing stacked platelets after oxidation and ammonia treatments. Signal intensities were magnified where noted for comparison. As submitted to338 ........................................................................................................... 124

Figure 36. O 1s region of the X-ray photoelectron spectra comparing stacked platelets after oxidation and ammonia treatments. Signal intensities were magnified where noted, for comparison. As submitted to338 ........................................................................................................... 126
Figure 37. S 2p region of the X-ray photoelectron spectra for stacked platelets-HCl-HNO₃:H₂SO₄. *As submitted to*³³⁸ ................................................................. 128

Figure 38. O 1s region of the X-ray photoelectron spectra comparing nanofibers with basal plane exposure after oxidation and ammonia treatments. Signal intensities were magnified where noted for comparison. *As submitted to*³³⁸ ........................................... 130

Figure 39. Temperature programmed oxidation profiles for stacked platelets after oxidation and ammonia treatments. Gray is m/z=44 (CO₂), pink is (m/z=30) x50 (NOₓ), green is m/z=64 (SO₂) x500 for all treatments except “HCl-HNO₃:H₂SO₄” which is x100. *As submitted to*³³⁸ ........................................................................................................... 133

Figure 40. Temperature programmed oxidation profiles for nanofibers with basal plane exposure after oxidation and ammonia treatments. Gray is m/z=44 (CO₂), pink is (m/z=30) x50 (NOₓ), green is m/z=64 (SO₂) x500 for all treatments except “HCl-HNO₃:H₂SO₄” which is x100. *As submitted to*³³⁸ .......................................................................................... 135

Figure 41. a) ORR RRDE results of stacked platelets after oxidation and ammonia treatments at 1000rpm in oxygen saturated electrolyte after background subtraction. b) Selectivity results. *As submitted to*³³⁸ ................................................................. 137

Figure 42. ORR RRDE results of nanofibers with basal plane exposure after oxidation and ammonia treatments at 1000rpm in oxygen saturated electrolyte after background subtraction. *As submitted to*³³⁸ ....................................................................................... 138

Figure 43. TEM images of broken nanofibers on CNₓ-conc HNO₃-900°C NH₃. ......... 145

Figure 44. TEM images of CNₓ-conc HNO₃ treated. .................................................... 145

Figure 45. N1s spectra for ammonia treated CNₓ. ......................................................... 148

Figure 46. RRDE comparison for ammonia and nitric acid treated CNₓ. (top) Activity comparison on disk, (bottom) Selectivity comparison from ring results. ....................... 150

Figure 47. Site blocking on graphitic edges by boron and phosphorus groups. *Illustration courtesy of Paul Matter.* ........................................................................................................... 153

Figure 48. RRDE activity results for site-blocked CNₓ. ................................................ 155

Figure 49. B 1s spectra for boron incorporated CNₓ. ..................................................... 158

Figure 50. Atomic ratios of surface elements on boron incorporated CNₓ. ............... 160
Figure 51. RRDE activity for boron-incorporated CNx .................................................. 162

Figure 52. B 1s spectra from XPS for CNx-B:C=0.10 washed with 5M HCl ............... 163

Figure 53. ORR activity for B-CNx catalysts before and after 5M HCl treatment........... 164

Figure 54. Select catalyst disk loadings for activity testing from literature. Authors listed are first authors44,122,126,167,296,356-359,362 ........................................................................... 169

Figure 55. Example comparison of ring current (top) to disk current (bottom) in oxygen-saturated 0.5M H2SO4 at 1000rpm after background subtraction for a CNx catalyst with 142 μg/cm² loading, which had the lowest selectivity to water formation out of all tests performed. Inset: Absolute current comparison of ring to disk after adjustment for theoretical collection efficiency................................................................. 172

Figure 56. Selectivity as a function of catalyst loading on disk. Selectivity is taken at 0.5 V vs. NHE. Theoretical collection efficiency of N=0.22 was used. a) CNx catalyst, b) Pt/VC catalyst ......................................................................................................................................... 174

Figure 57. SEM top view images showing the distribution of catalyst on a model aluminum rod with same geometric area as the glassy carbon electrode. a) for 142 μg/cm² CNx catalyst loading and b) 1420 μg/cm² CNx catalyst loading.................. 178

Figure 58. Example SEM side-view images of CNx catalyst loadings on aluminum rods. a) 142 μg/cm² loading. Thickness indicated in image is 17.8 μm. b) 426μg/cm² loading. Thickness indicated in image is 52.1 μm. c) 1420 μg/cm² loading. Thicknesses indicated in image are 207 μm and 424 μm. .................................................................................. 179

Figure 59. Average CNx catalyst thickness as a function of catalyst loading on the disk. Error bars show 1 standard deviation................................................................. 180

Figure 60. Selectivity as a function of average CNx catalyst thickness. Selectivity values taken at 0.5V vs. NHE. .................................................................................. 181

Figure 61. (Top) ORR activity on CNx as a function of rotation rate in oxygen saturated electrolyte, (bottom) hydrogen peroxide reduction activity as a function of rotation rate in 6.25 mM H2O2 ................................................................................................. 183

Figure 62. a) Ring (top) and disk (bottom) currents for RRDE tests on CNx catalysts exposed to different ink aging periods. (Measurements in oxygen-saturated 0.5M H2SO4 at 100rpm with 142 μg/cm² of catalyst loading on the disk). (b) Resulting oxygen
reduction reaction selectivity as a function of age of the RRDE ink used. *As accepted in*\textsuperscript{353}.*  

Figure 63. ORR selectivity as a function of RRDE catalyst ink age for Pt/VC catalyst with a 426 µg/cm\(^2\) loading on the disk at 100rpm. *As accepted in*\textsuperscript{353}.*  

Figure 64. ORR selectivity results for CN\(_x\) treated with ethanol (Catalyst loading on disk: 426 µg/cm\(^2\)). *As accepted in*\textsuperscript{353}.*  

Figure 65. Cyclic voltammetric scan for 20%Pt/VC from 1.2 to 0.2 to 1.2V vs. NHE in 0.5M H\(_2\)SO\(_4\) saturated with oxygen at 0 rpm showing both 1.0M methanol and methanol-free systems.  

Figure 66. Reduction sweep voltammogram for 20%Pt/VC in 0.5M H\(_2\)SO\(_4\) solutions at 1000 rpm showing both 1.0M methanol and methanol-free systems.  

Figure 67. Reduction sweep voltammogram for Pt:Ru/VC in 0.5M H\(_2\)SO\(_4\) solutions at 1000 rpm showing both 1.0M methanol and methanol-free systems.  

Figure 68. Cyclic voltammetric scan for CN\(_x\) grown on Fe/Al\(_2\)O\(_3\) from 1.2 to 0.0 to 1.2V vs. NHE in 0.5M H\(_2\)SO\(_4\) saturated with oxygen at 0 rpm showing both 1.0M methanol and methanol-free systems.  

Figure 69. Cyclic voltammetric scan for CN\(_x\) grown on Ni/Al\(_2\)O\(_3\) from 1.2 to 0.0 to 1.2V vs. NHE in 0.5M H\(_2\)SO\(_4\) saturated with oxygen at 0 rpm showing both 1.0M methanol and methanol-free systems.  

Figure 70. Reduction sweep voltammogram for CN\(_x\) grown on Co/SiO\(_2\) in 0.5M H\(_2\)SO\(_4\) solutions at 1000 rpm showing both 1.0M methanol and methanol-free systems.  

Figure 71. Cyclic voltammetric scan for CN\(_x\) grown on Fe/Al\(_2\)O\(_3\) from 1.2 to 0.0 to 1.2V vs. NHE in 0.5M H\(_2\)SO\(_4\) saturated with oxygen at 0 rpm shown both 3.0M methanol and methanol-free systems.  

xx
LIST OF TABLES

Table 1. Types of fuel cells and their features ............................................................... 2
Table 2. Surface composition of catalysts from XPS as published in \textsuperscript{325} .................. 85
Table 3. Surface species (atomic \%) on CN\textsubscript{x} and CN\textsubscript{x}-HNO\textsubscript{3} from XPS analysis. \textit{As published in} \textsuperscript{199} .................................................................................................................. 107
Table 4. Mass loss during ammonia treatment. \textit{As submitted to} \textsuperscript{338} .................. 120
Table 5. Surface species concentrations from XPS analysis on stacked platelets after oxidation and ammonia treatments. \textit{As submitted to} \textsuperscript{338} .................................................. 122
Table 6. Surface species concentrations from XPS analysis on nanofibers with basal plane exposure after oxidation and ammonia treatments. \textit{As submitted to} \textsuperscript{338} .......... 129
Table 7. Mass losses during heat treatment of CN\textsubscript{x} catalysts. ................................ 144
Table 8. Surface species composition (atomic\%) from XPS on CN\textsubscript{x} after ammonia treatments .................................................................................................................. 147
Table 9. Surface chemical species (atomic\%) composition for boron incorporated CN\textsubscript{x} catalysts .......................................................................................................................... 159
Table 10. Surface area and pore volume for select Boron incorporated CN\textsubscript{x} .......... 161
Table 11. CN\textsubscript{x} catalysts tested in 1.0M Methanol+0.5M H\textsubscript{2}SO\textsubscript{4} solution \textsuperscript{368} .......... 203
CHAPTER 1. Introduction

As demands for energy increase and pollution regulations become stricter, new fuel sources and alternative energy conversion devices are needed. The fuel cell has been promoted as an energy conversion device that can use alternative fuels such as hydrogen and methanol, as well as more traditional fuel sources such as methane and diesel, depending upon the type. Fuel cells are attractive because of their varied fuel sources, increased fuel efficiency and less polluting exhaust. Fuel cells types are divided by their operating temperature, component materials and fuel. Some of the more common fuel cell types and their unique features are listed in Table 1. The direct methanol fuel cell (DMFC) is actually a sub-type of the proton exchange membrane fuel cell (PEMFC), where very little is changed in the system beyond the fuel source and the electrolyte thickness.

PEMFCs and DMFCs have the most promise for mobile applications such as cell phones, laptops and automobiles, because of their low operating temperature (60-80°C) and relatively fast start-up time compared to higher operating temperature fuel cells. Their solid polymer electrolyte also aids in the manufacturability and lifetime of the fuel cell because corrosive electrolyte leaks are eliminated.
Table 1. Types of fuel cells and their features

<table>
<thead>
<tr>
<th>Type of Fuel Cell</th>
<th>Fuel</th>
<th>Identifying Components</th>
<th>Operating Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid Oxide (SOFC)</td>
<td>Variety; hydrogen, diesel, methane, coal gas and more</td>
<td>All components ceramic</td>
<td>800°C-1000°C</td>
</tr>
<tr>
<td>Molten Carbonate (MCFC)</td>
<td>Hydrogen</td>
<td>Carbonate salt electrolyte</td>
<td>650°C</td>
</tr>
<tr>
<td>Phosphoric Acid (PAFC)</td>
<td>Hydrogen</td>
<td>Liquid phosphoric acid electrolyte</td>
<td>150°C-200°C</td>
</tr>
<tr>
<td>Alkaline (AFC)</td>
<td>Hydrogen</td>
<td>Liquid alkaline electrolyte</td>
<td>90°C-100°C</td>
</tr>
<tr>
<td>Proton Exchange Membrane or Polymer Electrolyte Membrane (PEMFC)</td>
<td>Hydrogen</td>
<td>Solid polymer electrolyte</td>
<td>80°C</td>
</tr>
<tr>
<td>Direct Methanol Fuel Cell (DMFC)</td>
<td>Aqueous methanol</td>
<td>Solid polymer electrolyte</td>
<td>60°C</td>
</tr>
</tbody>
</table>

Today, there are limited PEMFC and DMFC systems available on the market. Most systems seen are exploratory in nature. The first emerging market for DMFCs appears to be that of battery replacements for laptops as high energy density is required and the systems are small enough for cost to not be as significant of an issue. All of the major auto companies have fuel cell prototypes, but each one reportedly cost over $1 million to produce because of the economy of scale, raw material expenses and engineering time put into them. The city of San Francisco, as well as a few European cities, have partnered with fuel cell companies to operate PEM fuel cell buses for actual use. Pilot test facilities have also been installed for PEM fuel cell operated fork lift
operations in warehouses\textsuperscript{1-3}. The military has made some investments in fuel cell research in hopes of reducing the battery weight carried by soldiers in the field. These examples illustrate the interest in fuel cells for many applications and in some cases, the acceptance of their use by the general public. Significant advances are still needed, however, before fuel cells can move out of such niche trial markets.

Fuel cells are electrochemical devices that allow for conversion of chemical energy directly into electrical energy by avoiding the restricting heat generating Carnot cycle. Fuel cells differ from batteries in that they are continuous systems rather than batch. A fuel cell is made up of two electrodes, an electrolyte material that separates the electrodes, and the circuit that connects the two electrodes. At the anode, fuel oxidation occurs. At the cathode, oxidant reduction occurs. The electrolyte separates the electrodes so that a short circuit does not occur and the fuel and oxidant do not mix, while still allowing for the transport of selected ions to the opposite electrode. The electrons that are not able to pass through the electrolyte are forced through an external circuit, producing useable electricity.

In a PEM fuel cell, hydrogen is the fuel fed to the anode. It is oxidized in the following reaction:

\[ \text{H}_2 \rightleftharpoons 2e^- + 2\text{H}^+ \quad 0.00 \text{ V vs. NHE} \quad \text{(HOR)}^4 \]

Where all potentials are at the standard temperature of 25°C. A schematic of a PEM fuel cell is shown in Figure 1. The electrons move through the circuit to the cathode, while the protons move through the ion selective membrane, commercially perfluorosulfonic
acid (Nafion), to the cathode to participate in the following reaction when oxygen or air is fed to the cathode:

\[
\text{O}_2 + 4\text{H}^+ + 4e^- \rightleftharpoons 2\text{H}_2\text{O} \quad 1.23 \text{ V vs. NHE} \quad (\text{ORR})^4
\]

The overall reaction for a PEM fuel cell is:

\[
\text{H}_2 + \frac{1}{2} \text{O}_2 \rightleftharpoons \text{H}_2\text{O} \quad 1.23 \text{ V vs. NHE}
\]

PEM fuel cells operate at about 80°C. Operation much above this level is limited by the degradation of the Nafion membrane.

![PEM fuel cell schematic. Drawing by Paul Matter.](image)

**Figure 1.** PEM fuel cell schematic. *Drawing by Paul Matter.*

In a DMFC, the feed to the anode is 0.5-2M aqueous methanol⁵. Methanol is oxidized by the reaction:
CH$_3$OH + H$_2$O $\rightleftharpoons$ CO$_2$ + 6H$^+$ + 6e$^-$ 0.02 V vs. NHE  (MOR)$^6$

The cathode reaction remains the same in the DMFC. Normally the membrane is also Nafion. The overall DMFC reaction is:

CH$_3$OH + 3/2O$_2$ $\rightleftharpoons$ CO$_2$ + 2H$_2$O  1.21 V vs. NHE

Typical operating temperatures for DMFCs are about 60°C, because of the desire to keep methanol in the liquid state. The MOR is irreversible, meaning the deviation in potential at which the reaction begins is far from the theoretical potential. This causes power output losses (Figure 2 shows how power is a function of current and potential). The advantage of DMFCs is the convenience of liquid fuel handling, opposed to compressed hydrogen gas.

There are three main types of performance losses in fuel cells: kinetic losses, ohmic losses and mass transfer losses. Kinetic losses in a fuel cell are observed by the initial drop from the theoretical operating voltage as shown in part A in the fuel cell polarization curve in Figure 2. Kinetic losses are typically due to deviations from the thermodynamic potentials of the reactions. These kinetic losses are related to the catalysts present at the anode and cathode. Ohmic losses are observed in section B of the fuel cell operation curve. Ohmic losses are due to resistances in the fuel cell. These can be due to membrane resistances and poor electrical conductivity in the catalyst layers. Mass transfer losses are observed by the drop in potential in section C. Water formation blocking the active sites of the catalyst is a main cause of mass transfer losses.
While research needs to be continued on all components that cause performance losses in fuel cells, the oxygen reduction reaction (ORR) is one of the largest contributors to fuel cell performance losses in PEM and DM fuel cells. The ORR in acidic media, which both the PEMFC and DMFC are, is highly irreversible. The ORR is the limiting reaction in the PEM and direct methanol fuel cells. The best catalysts developed allow for the ORR to occur at 0.9V vs. NHE. That is an overvoltage of 0.3V. This means that the performance of a PEM fuel cell is automatically dropped by at least 0.3V before any current is ever drawn.

![Figure 2. Typical fuel cell polarization curve displaying the types of performance losses and power density.](image)
The commercial catalyst used in today’s PEM and DM fuel cells is Pt supported on Vulcan carbon, a type of carbon black. Due to the high overvoltages at the cathode, the cathode is loaded with significantly more Pt than the anode. State-of-the-art Pt loadings on the anode are 0.05 mg/cm², while the cathode has 0.4 mg/cm². Pt is an expensive noble metal. Using the current catalyst loadings, the Pt costs would be prohibitively high for use in an automobile fuel cell system. For an 85 kW fuel cell system that could be used in 75 kW (100 hp) vehicle, the Pt costs alone would be $3200-$4500 using March 2010 Pt US market prices. For most standard automobiles today, the catalyst costs in a fuel cell system would be much higher due to their higher power demands. The platinum market price has fluctuated widely in the past decade with an overall upward trend, slowed by the recent global economy, as seen in Figure 3. If this 75 kW system was priced at the peak of the market in March 2008, the system would have cost an additional $2000.

Pt is also available in only a few regions of the world. The largest reserves of Pt are located in South Africa and the Ural Mountain regions of Russia. Political instability in these regions could cause disruptions in the Pt supplies for fuel cell production. The supply is limited as well. Some estimate that with the current catalyst loadings, there would only be enough Pt to outfit 10-20% of the cars produced annually with fuel cells.
Cost and availability are not the only disadvantages that Pt catalysts have. Pt is known to sinter during fuel cell operation, where the nano-sized Pt particles agglomerate into larger particles, therefore reducing the active surface area of the catalyst. In DMFCs, methanol crossover, where methanol leaches through the membrane to the cathode, is a problem. When methanol reaches the cathode, the Pt reacts with the methanol, taking away active sites for ORR in a competing reaction, causing a mixed potential. The mixed potential causes coulombic losses in the fuel cell. The operating potentials are required to be below 0.5V vs. NHE to have favorable ORR, which drops the efficiency of the fuel cell significantly.
Selectivity of the cathode catalyst is also a major concern. Oxygen can be reduced to form either water or hydrogen peroxide. The formation of hydrogen peroxide occurs in the undesirable side reaction:

$$\text{O}_2 + 2\text{H}^+ + 2e^- \leftrightarrow \text{H}_2\text{O}_2 \quad 0.695 \text{ V vs. NHE}$$

With only two electrons being transferred in this process, there is a drop in the current. More importantly, hydrogen peroxide degrades the components of the fuel cell and can significantly reduce the overall lifetime of the fuel cell\textsuperscript{16}.

To reduce the cost, increase current, reduce the overpotential, improve selectivity, and provide methanol resistance, many catalyst alternatives to Pt/VC have been studied. These include Pt-alloys, chalcogenides, other noble metal transition metal catalysts, and non-noble metal catalysts. The difficulty in finding ORR catalyst replacements to Pt for fuel cells are increased due to the acidic and oxidizing fuel cell environment.

Among the Pt-free catalysts, the chalcogenide and non-noble metal C-N catalysts have been the subject of most of the non-Pt ORR studies. Chalcogenide ORR catalysts have especially been studied as DMFC ORR catalysts due to their inactivity for methanol oxidation\textsuperscript{6,17-23}. In general, the most active ORR chalcogenide catalysts are ruthenium containing. Ruthenium containing catalysts are also subject to wide fluctuations in price and are much higher in cost in recent years due to the increased demand for catalyst materials. Figure 3 illustrates the price climb in both Pt and Ru since 1992. With the flexibility in precursors, C-N catalysts do not have to be subject to the high costs similar to the noble-metal markets.
CHAPTER 2. Research Objectives

The overall objective of this research is to study nitrogen-containing carbon nanostructures (CNₓ) as catalysts for the oxygen reduction reaction (ORR) in acidic media for use in PEM and direct methanol fuel cells (DMFCs). This area of research addresses two main needs:

- **Improving ORR activity and selectivity.** Currently, these catalysts underperform compared to the commercial Pt-based catalysts. Improvements in current density and overpotential are needed before these catalysts can become viable replacements to platinum.

- **Understanding the nature of activity.** There is much debate in the field on what makes these types of catalysts active. Some believe that an iron stabilized by nitrogen supported on carbon is the source of activity. Others believe that a transition metal is not part of the active site and that nitrogen incorporated into the graphitic matrix of the carbon may be the cause of activity.

These two needs go hand-in-hand with each other. In order to design better performing catalysts, the active site should be well understood.
To address these needs, the research program had multiple focal points. The role that heteroatoms and surface functional groups beyond nitrogen plays in these CN$_x$ catalysts have been studied using sulfur and boron heteroatoms and oxygen functional groups. Nanostructure of the carbon has been suggested to play a role in ORR activity. The role of graphitic edge plane exposure in ORR activity has been investigated. The way the electrochemical testing methods are performed can also have an impact on the results reported. Electrochemical half cell testing methods have been investigated and the role that the catalyst treatment plays in these tests has been studied. In addition to these studies, it is also important to understand what environments these CN$_x$ materials can perform in. Testing of catalyst performance for ORR in the presence of methanol has also been studied.
CHAPTER 3. Literature Review of Carbon-Nitrogen ORR Catalysts and Related Materials

3.1 Carbon-Nitrogen ORR Catalysts

The high costs and limited availabilities associated with noble-metal based ORR catalysts have prompted research on catalysts that are free of noble metals. The materials that can be studied as ORR catalysts for PEM and direct methanol fuel cells is limited due to the acidic and oxidizing environment of the fuel cell. Obtaining materials that are able to remain stable in this environment is difficult. Carbon-nitrogen (C-N) materials are the most studied class of non-noble metal ORR catalysts. Three generations of these catalysts have been studied in the literature based upon their starting materials and treatment conditions: non-pyrolyzed macrocycles, pyrolyzed macrocycles and non-macrocycle-based catalysts.

3.1.1 Non-Pyrolyzed Macrocycles as ORR Catalysts

Carbon-based materials have been studied as ORR catalysts for nearly five decades. The first of such catalysts were transition-metal-containing macrocycles
supported on high surface area carbons\textsuperscript{24,25}. Generally macrocycles are large molecules with a cyclic ring. Inside these rings, metal ions can be stabilized. For these purposes, there were metal ions stabilized by the central nitrogen groups such as shown in the examples of Figure 4. Macrocycles were selected for study as a model to the nature-inspired hemoglobin-type active site for oxygen reduction. Jasinski first reported on these materials as ORR catalysts in alkaline media using cobalt phthalocyanine in 1964\textsuperscript{24,25}. While the macrocycles showed substantial activity for the electroreduction of oxygen, they proved to be unstable in the fuel cell acidic environment that is required for PEM and phosphoric acid fuel cells\textsuperscript{26}. For this reason, macrocycles supported on carbon without further treatment have not been studied much in the last thirty years. Several reviews have gone in-depth into the history of these untreated macrocycles used as ORR catalysts\textsuperscript{26-30}. 
3.1.2 Pyrolyzed Macrocycles as ORR Catalysts

Beginning in the 1970’s, Jahkne\textsuperscript{27} and others\textsuperscript{26,28-36} found that heat treating the macrocycles on carbon support in an inert environment, or pyrolyzing, produced an ORR catalyst that still was active, but now had a greater stability in the fuel cell environment. Several reviews have covered these catalysts in detail as well\textsuperscript{26,28-31,37,38}. It was observed that this pyrolysis step could be as low as 400°C and as high as 1000°C\textsuperscript{26-28,32-36,39-41}, to increase stability while maintaining activity. The majority of the materials studied showed that treatment temperatures closer to 1000°C were more desirable for stability, however\textsuperscript{27,41}.

A variety of metal ions have been used in the pyrolyzed macrocycle catalysts. The metal ions used in the pyrolyzed macrocycles have included iron\textsuperscript{26,28,36,39,40,42-74}, cobalt\textsuperscript{27,33,34,41,46,49,62,65-68,70,73,75-101}, nickel\textsuperscript{49,67,73} and copper\textsuperscript{68,73}, among others. Iron- and

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure4.png}
\caption{Examples of macrocycles used as catalysts for ORR. \textit{As published in}\textsuperscript{31}.}
\end{figure}
cobalt-centered macrocycles have been studied the most. This is due to their higher activity compared to the other metal-containing macrocycle systems. The types of macrocycles used in these heat-treated studies include porphyrins\textsuperscript{33,39,45,52,54-62,66,67,70,72,74,81,84-87,98,99} (including tetraphenylporphyrins (TPP) and tetramethoxyphenyl porphyrins (TMPP)), phthalocyanines (Pc)\textsuperscript{36,40,44,49-51,53,64,75,91-97} and dihydrodibenzotetraazaannulenes (TAA)\textsuperscript{34,76-78} most commonly, with other macrocycle derivatives on occasion. In addition to transition-metal-containing macrocycles, non-metal macrocycles have been pyrolyzed to form ORR catalysts\textsuperscript{34,65,76,90,102}. While these catalysts were not as active as the iron- and cobalt-containing catalysts, they still had substantial ORR activity.

While the early work in pyrolyzed macrocycles as ORR catalysts focused on creating an ORR active catalyst that would maintain adequate stability by studying different macrocycles and treatment temperatures, use of pyrolyzed macrocycle catalysts more recently has been focused in two main areas—studying of the active site and altering the preparation methods such as carbon treatment\textsuperscript{46,49,89,103-105}. The active site discussions will be covered in a later section of this literature review.

\subsection{3.1.3 ORR C-N Catalysts Derived from Simple Precursors}

While the pyrolyzed macrocycles showed improved stability in acidic media and were active for ORR, the macrocycle precursors did not prove to be an economical solution. The cost of macrocycles is still very high. Gupta, \textit{et al.} were among the first to report using precursors other than macrocycles to get similar C-N ORR catalysts\textsuperscript{106}.
They heat treated polyacrylonitrile supported on a carbon black mixed with an iron or cobalt salt. This heat-treated mixture resulted in an ORR active catalyst. Since this time, pyrolysis of a variety of simple sources of carbon, nitrogen and transition metals together has successfully been used as ORR catalysts in acidic electrolytes. Reviews of these non-macrocycle ORR catalysts have been published\textsuperscript{31,37,107-110}, including a review from our research group\textsuperscript{31}. Recently, a cross-laboratory study was published on C-N catalysts using multiple preparation techniques and precursors also\textsuperscript{111}.

3.1.3.a Materials and Preparation of C-N Catalysts Derived from Simple Precursors

Primarily iron\textsuperscript{63,111-164} and cobalt\textsuperscript{82,111,113,144,145,151-157,165-182} have been used as the metals in these non-macrocycle C-N ORR catalysts, but nickel\textsuperscript{140-142,144,145,151,152} and other metals have also been used with less success. Catalysts made with iron or cobalt have shown the most ORR activity. While those made with nickel have been less active. The source of the iron or cobalt is usually a salt like acetate\textsuperscript{116,119,141-145}, hydroxide\textsuperscript{63,114}, chloride\textsuperscript{63,164} or sulfate\textsuperscript{183}. These transition metal salts are normally supported on a type of carbon black. Typical metal loadings range from 50 ppm to 10wt\%\textsuperscript{119,144}. A maxima in loading typically occurs, but the concentration depends upon the metal precursor, support and heat treatment. In addition, ORR C-N catalysts have been made in the absence of a transition metal\textsuperscript{140-142,144,145,184-187}. These catalysts have had measurable ORR activity, but are frequently less active than the Fe- and Co-containing C-N catalysts. Some have cited the ORR activity for these transition-metal free C-N ORR catalysts being due to contamination of the support with iron or other metals\textsuperscript{26,121}. 
Many types of supports have been studied for the C-N catalysts, with the majority being various types of carbon black. The commercial ORR platinum catalyst carbon black support is Vulcan carbon XC-72 and has been used frequently as a support to the transition metals in C-N catalysts. The Dodelet research group has done extensive work examining the role that carbon black type plays in the ORR performance. Early on, they found that carbons with more amorphous structures were more reactive to the nitrogen-containing treatments resulting in better performing catalysts. More recently, they have found that supports with high microporosity have better performance. Others have examined non-carbon black supports with some success. These supports include activated carbons, carbon nanotubes and oxides. In our research group at Ohio State, we have shown that a carbon-based support is not necessary as long as a carbon source is introduced into the heat treatment step of the catalyst development. In place of the carbon support, oxide supports of alumina, silica and magnesia have been used. These oxide supports were used so that the role of carbon black could be removed from the study. Additionally, the oxide supports can be removed with acidic or basic washes to make a more concentrated catalyst with higher electrical conductivity (compared to when the oxide is still present).

When a macrocycle is not being used in the preparation of the C-N catalyst, the nitrogen source is commonly introduced in the gas phase at an elevated temperature over the transition metal supported material. Ammonia treatments over transition metal supported carbon blacks at temperatures similar to macrocycle pyrolysis temperatures have successfully produced active ORR catalysts. The ammonia
concentration, duration, type of carbon black and carbon pretreatments all play a role in the success of the resulting material as an ORR catalyst, in addition to the transition metal used. Higher temperatures and ammonia concentrations along with increased treatment durations tend to improve ORR activity. Carbon blacks that are more amorphous and have more microporosity also respond better to ammonia treatments. An additional carbon oxidizing pretreatment also has increased the success of ammonia treatments on creating ORR-active catalysts. Acetonitrile (CH$_3$CN) introduced in the gas phase at elevated temperature over transition metal supported catalysts is also commonly used creating C-N ORR catalysts. The acetonitrile can serve as both the carbon and nitrogen source as well. In our group, we have used acetonitrile as the only source of nitrogen and carbon when producing nitrogen-containing carbon nanostructured (CN$_x$) catalysts over oxide supports.

Nitrogen-containing polymers have also been used as the carbon and nitrogen source in C-N ORR catalysts, as related back to the early work of Gupta, et al. heat-treating polyacrylonitrile with a transition metal over a carbon support. Polymers used include poly(4-vinylpyridine), polyaniline, polypyrrole, poly(3-methylthiophene) and poly-o-phenylenediamine. Typically, a metal is still mixed in the polymer matrix as a cobalt or iron support prior to heat treatment.

In 2006, Bashyam and Zelenay reported on the preparation of a C-N ORR catalyst from synthesizing a cobalt polypyrrole without a heat treatment step. Unlike the non-heat treated macrocycles studied decades ago, this catalyst showed remarkable stability in fuel cell testing. After 100 hours of fuel cell operation, no substantial activity was lost.
The stability results for the new cobalt polypyrrole catalyst were considered better than the pyrolyzed marcocycles and related heat-treated non-macrocycle C-N catalysts. ORR activity of these catalysts was also substantial and comparable to other C-N catalysts.

While Bashyam and Zelenay created what they called a “new class” of ORR C-N catalysts, nearly all of the work published in the four years since has been on the heat-treated C-N materials prepared using both simple and macrocycle precursors.

3.1.3.b Characteristics of C-N ORR Catalysts

Much of the work on C-N ORR catalysts derived from simple precursors have used similar precursors. The differences in the studies have involved investigating the treatment conditions and developing a better understanding of these C-N materials. Three main characteristic areas have been the focus of much of the attention: surface species, microporosity and nanostructure. Much of the understanding developed is also transferable to the pyrolyzed macrocycle catalysts.

The concentrations and types of carbon, nitrogen and transition metal have been extensively examined on the C-N catalysts. To a lesser degree, oxygen has been examined. X-Ray photoelectron spectroscopy (XPS) studies are typically used for identification of surface species and surface concentrations. Carbon is the major component of all C-N ORR catalysts. It appears to be largely graphitic in nature after treatment. Some broadening of the graphitic peak in XPS has been reported with introduction of nitrogen. Because the graphitic peak is so dominant, other carbon species are not frequently identified.
In most reports, pyridinic-nitrogen, located as a substituted heteroatom on the graphitic edge plane, and quarternary-nitrogen, a substituted nitrogen deeper in the graphitic plane bonded to at least three carbons, are identified. Figure 5 is an illustration of the possible types of nitrogen located in graphitic carbons. Other nitrogens including pyrrolic-nitrogen have also been identified in some catalysts. Typical total nitrogen surface concentrations are in the 1 to 9 atomic% range.

Pyridinic-N has commonly been cited as a required species for ORR activity. It is thought that the pyridinic-N species are the groups required to stabilize iron- or cobalt-ions. Others, including our research group, have hypothesized that pyridinic-N alone may be contributing to the ORR activity. In both cases, the
observation was that catalysts with increased pyridinic-N content had improved ORR activity. More recently, some have observed increases in quarternary-N content with ORR activity\textsuperscript{98,186}.

In some cases, XPS has been used in identification and quantification of iron (or cobalt) species in the C-N ORR catalysts. The small quantities of iron used limit the usefulness of XPS, as high resolution and very long scan times are required to even observe any iron at the typical concentrations. Iron is thought to bond to or be stabilized by nitrogens\textsuperscript{119,120,146,147,149,195}. Some have reported a macrocycle-like center with iron being stabilized by four nitrogens\textsuperscript{120}. Others have reported iron being stabilized by two nitrogens, as shown in Figure 6\textsuperscript{119,120}. Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) has also been used in identifying Fe-N type species\textsuperscript{115,120}. As the iron content increases to percent levels, metallic iron has been identified to form\textsuperscript{43}. Activity has not been shown to increase with metallic iron, resulting in the observation that a maxima with iron content occurs\textsuperscript{119,120}. 

21
Oxygen functionalities have been studied less, but are commonly reported as part of XPS analysis on C-N catalysts. Generally, only overall oxygen content is reported. From most studies, it is unclear if oxygen plays a role in ORR performance on C-N catalysts. Any carbon-based catalyst exposed to air will have some oxygen functionalities on the surface because of oxygen species adsorption at room temperature\textsuperscript{200-202}. Later sections of this chapter will cover oxygen functional groups in more depth.

Recently, the porous structure of C-N catalysts has been analyzed more closely using nitrogen physisorption techniques\textsuperscript{125,128,138,187,203,204}. Depending upon the carbon support used, heat treatment conditions and post-pyrolysis treatments, the porosity of the resulting C-N catalysts can be different. Researchers in the Dodelet group have shown that microporosity plays an important role in ORR catalyst activity\textsuperscript{125,128,138,203}. Catalysts with a significant proportion of the pores being of diameters less than 2 nm have shown to
improve the ORR activity of their catalysts\textsuperscript{125,128,138,203}. They have hypothesized that two Fe-N\textsubscript{2} sites are located across from each other in the micropores, forming a pseudo Fe-N\textsubscript{4} type active site, illustrated in Figure 7.

![Figure 7](image-url)

\textbf{Figure 7.} Proposed FeN\textsubscript{2+2} active site from Dodelet group. \textit{Illustration courtesy of Dieter von Deak.}

Work coming out of Oakridge National Laboratories recently has shown active ORR catalysts using nitrogen-containing mesoporous carbons\textsuperscript{187,204} that contrasts to the microporous work from Dodelet. These carbons had a large quantity of mesopores, and very little micropores\textsuperscript{187,204}. The quantity of micropores decreased when carbon was grown on mesoporous silica supports\textsuperscript{204}.

The carbon nanostructures produced when C-N ORR catalysts are pyrolyzed have been discussed less frequently than many other characteristics of the C-N catalysts.
However, in our research group\textsuperscript{140-142,144,145} and others\textsuperscript{205} observations have been made that carbon nanostructure may play a role in creating active ORR catalysts. We have found that catalysts that are mostly composed of stacked cup nanofibers with high graphitic edge plane exposure are more active towards ORR than catalysts composed mostly of nanotubes\textsuperscript{140,141,144,145}. Several other observations are paired with the nanostructures that may merely make the nanostructure observation happenstance rather than a direct correlation to ORR activity. The first of these is that catalysts with mostly stacked cup nanostructures also have more pyridinic-N content, which is located on the graphitic edge plane. The second is that the catalysts with the most high-edge plane exposure nanofibers were made with iron- and cobalt-containing supports using acetonitrile pyrolysis, while those with little edge plane exposure were made with nickel-containing supports\textsuperscript{140-142,144,145}. These observations leave the door open to pyridinic-N playing a role but not the nanostructure and the metals used being more significant than nanostructure. Further studies of this were performed and are included in a later chapter.

While the C-N ORR catalysts have shown substantial activity towards ORR in acidic media, they still are not as high of performing as the Pt/VC commercial catalysts. Recent strives toward improved ORR activity have been published by the Dodelet group in \textit{Science}\textsuperscript{138} and discussed by Gasteiger as a promising material\textsuperscript{206}. Gasteiger’s comments are significant, as he previously declared C-N catalysts had little chance, if any, of becoming viable commercial catalysts\textsuperscript{8}. In the \textit{Science} article from the Dodelet group, they show that their most recent generation of Fe-N-C catalysts had turnover frequencies (TOF) comparable to that of Pt/VC ORR catalysts\textsuperscript{138}. This can be exciting news, but high turnover frequency of a catalyst is not enough. A catalyst with a low
active site density can have a high TOF but still be a low performing material overall because of the amount of material that would be needed. Additionally, determination of an active site concentration to predict a TOF is difficult and has even been acknowledged by the Dodelet group. In addition, the active site is still being debated in the literature and will be discussed further in a later section of this chapter.

This problem of lower concentration of active sites on C-N ORR catalysts becomes a challenge when full fuel cell testing is performed. For most studies, ORR catalysts are first studied for activity and selectivity using the electrochemical half cell techniques of rotating disk electrode (RDE) and rotating ring disk electrode (RRDE). The better catalysts are then manufactured into membrane electrode assemblies (MEA) to be tested in full fuel cells. In a half cell thin-film method such as RDE and RRDE, mass transfer effects are not significant. In a full fuel cell, mass transfer plays an important role in the operation of the fuel cell. Substantial increases in the thickness of the cathode catalyst layer can increase the mass transfer losses, thereby reducing the performance of the fuel cell.

3.1.4 Active Site Debate in C-N ORR Catalysts

While C-N ORR catalysts continue to improve, there is still more improvement necessary for them to become viable commercial catalysts. One key to developing better catalysts is to increase the active site density on the materials. This will require a better understanding of the nature of the active sites on C-N ORR catalysts and the ORR mechanism which occurs on these materials.
Much debate has occurred in the literature on the nature of the active site in both the pyrolyzed macrocycles and the C-N non-macrocycle catalysts. In general, it is thought that the active site for both these types of catalysts is the same or similar. The argument in the literature is on what the active site looks like. Metal (Fe,Co)-nitrogen active sites are argued by one side, while non-metal active sites are argued by the other.

Researchers involved in the active site debate have studied both pyrolyzed macrocycle- and non-macrocycle-based C-N ORR catalysts to support their arguments. Before the early work in simple precursors began, people were already questioning what the active site of the ORR C-N catalysts was. Some believed that the macrocycle center remained intact after pyrolysis treatment. Others made observations that as the temperature of pyrolysis increased above 600°C or 700°C, the macrocycle center decomposed. Additionally, when transition metal-free macrocycles were pyrolyzed on a carbon support, ORR activity was still observed. Some believed that transition metal contamination in the carbon black was the source of the non-metal macrocycle ORR activity, as it had previously been shown that a transition metal like iron or cobalt could be mixed with a non-metal centered macrocycle prior to heat treatment and the resulting pyrolyzed material was ORR active.

The use of non-macrocycle precursors further elevated the active site debate for C-N ORR catalysts. While the pyrolysis treatment of a metal, nitrogen source and carbon...
source together could result in a macrocycle-like metal-nitrogen coordination, it was more difficult to argue this than if the material originally had a macrocycle in it.

For about the last decade, the leading voice in support of the Fe-centered active site has come from the Dodelet research group. Early on, Dodelet and others argued that the iron center bound to two or four nitrogens was the active site for ORR (as shown in Figure 6)\textsuperscript{26,119,120}. This theory was supported by ToF-SIMS measurements, which showed the presence of FeN\textsubscript{2} groups\textsuperscript{119,120} and FeN\textsubscript{4} groups\textsuperscript{120}. The iron ions needed to be dilute enough to not separate into metallic iron, which they observed to reduce the ORR activity of the catalyst\textsuperscript{119}. More recently, Dodelet has expanded upon this active site model to suggest that the true active site is the combination of two FeN\textsubscript{2} active sites in near proximity to each other in carbon micropores to form a pseudo-FeN\textsubscript{4} site (labeled an FeN\textsubscript{2+2} site) similar to the intact macrocycle, as illustrated in Figure 7\textsuperscript{125,128,138,203}. A comparison of FeN\textsubscript{2+2} to FeN\textsubscript{4} revealed a much more active FeN\textsubscript{2+2} site in acidic media\textsuperscript{203}.

Several German research groups have worked together and separately in support of the metal-N active site\textsuperscript{45,47,69,71,193}. \textsuperscript{57}Fe Mössbauer has been used in several occasions by these researchers to examine their C-N catalyssts. Schulenburg, \textit{et al.} concluded that a 6-fold coordinated Fe\textsuperscript{3+} was part of the active site\textsuperscript{72}. They suggested the site was an FeN\textsubscript{4}-type coordinated with two additional bonds to either oxygen or carbon\textsuperscript{72}. Koslowski, \textit{et al.} reported observing two active sites through Mössbauer analysis; an FeN\textsubscript{4} and an CFeN\textsubscript{2} site\textsuperscript{45}. They found that the CFeN\textsubscript{2} site degraded in the presence of H\textsubscript{2}O\textsubscript{2}, suggesting that the FeN\textsubscript{4} site was more stable\textsuperscript{45}. 
A large contingent of Japanese researchers have been actively involved in the ORR C-N active site debate. For the most part, they have reported evidence of a metal-free active site\textsuperscript{88,172,185,186}. Some of the research has involved X-Ray Absorption (XAS) experiments to study the activity of nitrogen species\textsuperscript{88}. Others have been involved in using non-carbon black carbon precursors to eliminate metal contamination in their studies\textsuperscript{185,186}. Maruyama has been the most vocal in support of heme-type active sites from this contingent\textsuperscript{146,147,149,195}. The work supporting the Fe-N type sites coming from this research group have also included unconventional precursors including bovine hemoglobin\textsuperscript{149} and amino acids\textsuperscript{147}.

In our own research group at Ohio State, we have contributed to the active site debate by creating CN\textsubscript{x} catalysts grown by pyrolyzing acetonitrile over sol-gel alumina supports made with less than 1ppm transition metals contamination\textsuperscript{140}. This catalyst showed substantial ORR activity. After an HF wash to remove the alumina support, the catalyst was within 200 mV of the commercial Pt/VC catalyst, indicating significant ORR activity without the presence of a transition metal\textsuperscript{140}. It was also observed that pyrolysis over an iron-containing alumina support created catalysts with even more activity, while pyrolysis over nickel-containing alumina had less ORR activity compared to the transition-metal free catalyst\textsuperscript{140,141}. Several trends were observed with these catalysts. It was found that ORR activity increased with pyridinic-nitrogen content and as well as with graphitic edge plane exposure of the nanostructures\textsuperscript{140,141}. These trends were also observed when Vulcan carbon\textsuperscript{142}, silica\textsuperscript{144,145} and magnesia\textsuperscript{144,145} were used as catalyst supports. It was hypothesized that iron and cobalt acted as catalysts for the creation of active sites during pyrolysis rather than directly participating in the ORR.
activity. While this hypothesis may be true, the studies were unable to rule out the possibility of two active sites being present – one that was transition metal free and one that was a metal-nitrogen site.

To illustrate how uncertain this debate on the ORR active site of C-N catalysts is, several researchers have published conflicting papers themselves. The majority of these researchers once argued for an Fe-N or Co-N type active site, but more recently have argued for a metal-free active site\textsuperscript{100,178}. This small shift in no way settles the debate, however. There are still many papers being published arguing for each side.

In addition to investigations of the active site experimentally, there have been a small number of studies examining the C-N catalyst active site debate using computational techniques. Metal-N active sites have been modeled recently for electron donation properties by in the Anderson group\textsuperscript{210-212}. Titov, \textit{et al.} used DFT to model FeN\textsubscript{x} sites on carbon nanotubes paired with EXAFS simulation calculations to show activity towards FeN\textsubscript{x} sites\textsuperscript{161}. Metal-free active sites have also been proposed for ORR activity \textsuperscript{35,57,64,101,205}. Preliminary modeling of carbon-nitrogen systems for electron donation properties has been performed by several groups\textsuperscript{197,213-217}, which might provide some insight into the possible active sites for ORR on C-N type catalysts. At this point, there still is no definitive answer to what the active site in the CN\textsubscript{x} catalysts is. This makes it more difficult to improve the catalysts as the desired active site properties are unknown.
3.2 Other Heteroatom-Containing and Functionalized Carbon Nanostructures

Nanostructured carbons do not only have potential for applications as fuel cell catalysts. Carbon nanofibers (CNFs) are known for their high surface areas and conductive properties\textsuperscript{218,219}. CNFs have recently been investigated for use as catalyst supports\textsuperscript{218-231}, in lithium ion batteries\textsuperscript{219,232,233} and in hydrogen storage devices\textsuperscript{234-236}. Carbon nanofibers can have many different geometries and properties. They can also be heteroatom-doped or surface-functionalized to further alter the properties of the nanofibers.

3.2.1 Types of Carbon Nanostructure and their Growth Characteristics

The properties of carbon nanofibers are dictated by the geometry of the structure, degree of edge-plane exposure, fiber diameter, fiber length, degree of graphitization, and orientation of the graphite planes. Nanostructure is dependent upon the starting materials, catalysts and growth temperatures. Examples of some carbon nanostructures are shown in Figure 8. The structures in this figure vary greatly in the edge plane exposure and orientation of the graphite planes.
Figure 8. Examples of carbon nanostructures. As published in\textsuperscript{199}.

Single-walled and multi-walled nanotubes (SWNT and MWNT, respectively) are the most widely used and well characterized nanofibers. These nanotubes are composed of graphitic sheets that are rolled into a tube. The graphitic edge plane exposure is minimal, as edge planes are only located at the ends of the tubes, which are up to microns in length\textsuperscript{219}. Multiple graphite sheet layers compose the tube in MWNTs, while SWNTs are only 1 graphite layer thick. MWNTs and SWNTs have been made by a variety of methods including chemical vapor deposition (CVD) using natural gas and xylene\textsuperscript{237}, and toluene vapors\textsuperscript{238} as the carbon sources. The catalysts have included many metal systems such as cobalt supported on silica materials\textsuperscript{239}, and bi-metalics like cobalt-molybdenum and iron-molybdneum\textsuperscript{238}. Both MWNTs and SWNTs can have metallic properties\textsuperscript{219}. SWNTs with a certain chirality and diameter can also behave as a semiconductor\textsuperscript{219}. One drawback of using MWNTs or SWNTs is that most uses require high purity levels of the nanotube type\textsuperscript{239,240}. Purification to one type of nanotube is still a challenge\textsuperscript{239,240}. 
Herringbone nanofibers, also known as fishbone nanofibers, are composed of graphitic sheets oriented at an angle to the longitudinal axis of the nanofiber. This orientation leaves a large amount of graphitic edge plane exposure revealed with very little basal plane exposure. Herringbone nanofibers have been reported to be made by decomposition of ethylene and hydrogen over a bimetallic copper-nickel catalyst. They have been used in demonstration for use in lithium ion batteries, hydrogen storage and as catalyst supports.

Stacked platelet nanofibers are nanofibers with graphitic planes stacked on one another oriented perpendicular to the longitudinal axis. Once again, they have a large amount of graphitic edge plane exposure with a smaller amount of basal planes. Stacked platelets have been made by decomposition of CO-H₂ gas streams over iron and iron-copper catalysts. Stacked platelets have shown to be useful as platinum and nickel catalyst supports because the facets of the metal can be controlled and well-adhered to the carbon edge planes.

Ribbon nanofibers are an analog of stacked platelet nanofibers. In ribbon nanofibers, the stacked graphitic sheets are oriented parallel to the longitudinal axis. This gives the nanofiber high edge plane exposure with increased electrical conductivity compared to stacked platelets. This is because electrical conductivity is high within the graphitic sheet, but low between graphitic sheets as illustrated in Figure 9. Ribbons have been made from the decomposition of CO-H₂ streams over iron-based catalysts. It has been observed that the temperature of decomposition has the greatest effect on
determining if a stacked platelet or a ribbon nanofiber is formed\textsuperscript{242}. Ribbons were also shown to be useful as a catalyst support\textsuperscript{227}.

![High conductivity](image)

**Figure 9.** Illustration of electrical conductivity within and between graphitic planes.

Stacked cup nanofibers are nanofibers that are similar to herringbone nanofibers except that there are hollow spaces between groups of graphitic sheets in the interior of the nanofiber. Stacked cup nanofibers also have some edge plane exposure. They also have been called “bamboo” nanofibers in the literature. Stacked cup nanofibers have been made with nickel and sulfur catalysts when decomposing natural gas and xylene\textsuperscript{237}. Stacked cup nanostructures are commonly grown over iron-containing catalysts when nitrogen precursors are used\textsuperscript{191,243-246}, as will be discussed later in this chapter.

Many other nanofiber types have been reported in the literature, but the ones discussed above are a good illustration of the varieties. In addition to nanofibers, carbon can also form into other non-nanofiber nanostructures. This includes the nano-onions
that are illustrated in Figure 8 and nanocubes that formed with acetonitrile pyrolysis over magnesia, as observed in our own research group\cite{144,145}. The body of literature on such non-nanofiber carbon nanostructures is much smaller.

Extensive work has been done on carbon nanofibers. The discussions above are considered a very brief overview. For more in-depth investigations into non-nanotube nanofibers, Baker and Rodriguez have published extensively in the area\cite{218,225-230,232,234,235,241,242,247,259}. Nanotube reviews are prevalent and include\cite{231,260-262}.

3.2.2 Nitrogen-Containing Carbon Nanostructures

Strelko, et al. have modeled carbons doped with nitrogen, phosphorus and boron and found them all to have significant electron donation properties\cite{216}, which may be why there are so many areas in which C-N materials are being researched.

Many researchers have worked on developing C-N nanostructures for uses beyond ORR catalysts. A variety of preparation techniques can be used. Depending upon the technique, the resulting C-N nanofiber properties will vary including nanostructure, nitrogen content and type, and graphitic nature of the carbon. Nitrogen can be introduced during carbon nanofiber growth\cite{191,243-246,263-270} or in a post treatment step as discussed in earlier sections with ammonia treatment\cite{88,118,123,125,135,137,138,159,187}. C-N precursors that have been used during the growth of carbon nanostructures include acetonitrile\cite{191,245,263,265,267,268}, melamine\cite{243,246,264} and pyridine\cite{245,266,268-270}. Ammonia also
can be introduced at low levels during carbon growth with hydrocarbon type materials \textsuperscript{244,266}.

Because of the wide variety of treatment conditions that can be used to obtain nitrogen containing carbon nanostructures, only a few will be outlined here.

Kvon, et al. observed nanofibers with high degree of edge exposure while using a system of methane/hydrogen/pyridine for carbon deposition over Ni-Cu catalysts \textsuperscript{269}. Nakajima, et al. made fibers with less edge exposure using system of acetonitrile/nitrogen for carbon fiber growth over Ni catalysts \textsuperscript{268}. When iron was used as the nanofiber growth catalyst and a carbon-nitrogen precursor was used for growth, stacked cup nanofibers were commonly observed \textsuperscript{191,243-246,264}.

3.2.3 Sulfur-Containing Carbon Nanostructures

Just as nitrogen can act as an electron donor, in the graphitic carbon structure, sulfur has the potential to act as an electron donor. Sulfur has been used in the growth of carbon nanostructures \textsuperscript{253,257,271-274}. In these studies, sulfur has been reported as a fiber growth-promoter. These literature reports do not indicate, however, if the presence of sulfur alters the structure of the fibers or if sulfur is incorporated into the final product. H\textsubscript{2}S and thiophene are the two primary sulfur precursors that have been used in the growth of carbon nanofibers. Examples of sulfur-carbon systems that have been reported for the growth of carbon nanostructures include H\textsubscript{2}S with hydrogen/ethylene over unsupported Co \textsuperscript{253}, thiophene with benzene/hydrogen catalyzed by ferrocene \textsuperscript{271-274}, H\textsubscript{2}S
with ethane/steam catalyzed by Fe-Ni\textsuperscript{257}, and H\textsubscript{2}S with natural gas/air/ammonia catalyzed by iron pentacarbonyl (Applied Scientific as referenced in\textsuperscript{237}).

Pretreatment of catalysts with sulfur before carbon fiber growth has also been reported\textsuperscript{253}. Kim, et al. has studied the growth of carbon fibers by the decomposition of ethylene over an H\textsubscript{2}S treated Co catalyst\textsuperscript{253}. They observed that low level H\textsubscript{2}S treatments (up to 100 ppm) to the catalyst promoted growth of the carbon nanofibers and concentrations above 100 ppm acted as a poison in the growth of carbon nanofibers.

3.2.4 Boron-Containing Carbon Nanostructures

The introduction of boron into carbon nanostructures can create high electrical conducting nanotubes\textsuperscript{275,276}, ceramic nanostructures\textsuperscript{277}, carbon oxidation resistant materials\textsuperscript{278-282}, as well as, increase the degree of graphitization of the carbon\textsuperscript{283-285}. Not all of these properties co-exist in the nanostructures. The properties the nanostructure possesses is dependent upon the boron-to-carbon ratio, preparation methods and nanostructure.

It is possible to have boron-carbon materials in two possible forms – boron carbides and boron-doped carbons. Boron is the main component in boron carbides, while carbon is the predominant component in boron-doped carbons. Boron carbides are ceramic materials with atomic compositions between B\textsubscript{10.5}C and B\textsubscript{4}C\textsuperscript{277}. Many B-doped carbon studies have involved nanostructures (SWNTs\textsuperscript{286} and MWNTs\textsuperscript{275,276,284-289}). These nanotubes can be made by arc discharge\textsuperscript{276,284,285,287,288}, laser ablation\textsuperscript{286}, CVD
Intermediate concentrations of B can cause isolated B-rich particles to form. *In situ* boron-introduction systems have included boron trichloride\(^ {275,283,290}\) and diborane\(^ {291}\). Post treatment conditions to introduce boron into CNFs have included high temperature treatments of B\(_2\)O\(_3\)\(^ {289,292,293}\).

When boron is introduced into nanotube growth systems, boron tends to build up in higher concentrations at the ends of the nanotubes. Hsu, *et al.* reported BC\(_3\) forming at the tips of the tubes\(^ {284}\). These exposed ends preferentially are formed to be the zigzag type\(^ {284,285}\). Few armchair tipped nanotubes have been observed in the presence of boron\(^ {285}\). The zigzag and armchair configurations of graphite are shown in Figure 10. The presence of boron on the zigzag tips is thought to prevent the closure of the nanotube end\(^ {284,285}\). This causes the nanofibers to continue to grow. Some B-doped MWNTs have been observed to have lengths ranging from ~5 to 100 \(\mu\)m\(^ {285}\).

Studies have shown that boron-doped MWNTs have increased electrical conductivity compared to non-doped MWNTs\(^ {275,276}\). Non-doped MWNTs were found to have electrical resistances one order of magnitude\(^ {276}\) and two orders of magnitude\(^ {275}\) smaller than the B-doped MWNTs. The increased conductivity may be due to the increase in tube length and not due to any change in the electron-donation properties of the carbon, however.

When boron is heat treated with amorphous carbons, it is known to increase the graphitization properties of the carbon\(^ {294}\). Increased crystallinity of carbon nanostructures has also been observed with the introduction of boron\(^ {283-285}\).
Boron and nitrogen have been doped together into carbons, as well\textsuperscript{290-293,295-298}. It has been suggested that nitrogen changes the electronic properties for SWNTs, but not the physical dimensions of the SWNTs, while boron changes the physical dimensions\textsuperscript{296}. The methods used for B-N doped nanocarbons are very similar to those listed above for boron-only doped carbons. The boron and nitrogen atoms can substitutionally replace carbon in the graphite planes, however, this only occurs at low levels of doping (levels less than 10 atomic\% Boron\textsuperscript{292,295}). At higher levels of doping, separate phases of BN and C are formed. This phenomenon was observed when BC\textsubscript{2}N nanostructures via pyrolysis of CH\textsubscript{3}CN-BCl\textsubscript{3} were made over cobalt catalysts at 1000°C\textsuperscript{290}. These BC\textsubscript{2}N nanostructures produced “stacked cup cone” structures with thick graphitized walls. Using High-Resolution TEM and Electron Energy Loss Spectroscopy (EELS), it was determined that the nanostructure layers alternated between BN and C. This phase separation was said to be more stable than the incorporation of B and N into the C phase. It was hypothesized that the phase separation occurs during the initial growth of the carbon nanofibers and was not a product of diffusion once the fiber was grown\textsuperscript{290}.

The introduction of B and N into carbon nanotubes was shown to increase graphitization\textsuperscript{297}. Redlich, \textit{et al.} found that the degree of graphitization increased compared to undoped samples by XRD. These doped CNTs also had a ten-fold increase in length when compared to the non-doped CNTs\textsuperscript{297}. The effect of boron on the nanotube tip morphology may also be the cause of the increased length in B-N doped carbon nanotubes, as Stephan, \textit{et al.} reported “tube ends that were ill formed and not closed”\textsuperscript{295}.

38
3.2.5 Oxygen Functional Groups on Carbon

Carbon commonly has oxygen functional groups located on its surface because of its exposure to air\textsuperscript{200-202}. Carbon is intentionally functionalized with oxygen for many reasons including to change their hydrophilic properties\textsuperscript{299}, increase their reactivity\textsuperscript{300} and to create anchoring sites for other functional groups or metals to be added to\textsuperscript{169,301-304}. The type of oxygen functional groups added to carbon depends upon the type of carbon and oxidation treatment. These oxygen functional groups include carbonyls, phenols, carboxyls, quinones, carboxylic anhydrides, lactones, lactols, hydroxyls, and ethers\textsuperscript{200,305}. 

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{figure10.png}
\caption{Armchair and zigzag graphitic edge planes}
\end{figure}
Figure 11 illustrates the location of some of the types of oxygen functional groups that can be present on carbon.

Rivin has reported a carbon oxidation pathway where the type of functional group progresses with treatment, ultimately oxidizing into CO$_2$:\(^{306}\):

\[
\text{C—H} \xrightarrow{[O]} \text{C—OH} \xrightarrow{[O]} \text{C=O} \xrightarrow{[O]} \text{C—OH} \xrightarrow{[O]} \text{H}
\]
Gaseous treatments, chemical treatments, electrochemical treatments and, plasma treatments all can be used to oxidize carbon. Gaseous treatments to oxidize carbon include exposure to air at room or elevated temperatures\textsuperscript{299,302,307-309}, treatment in oxygen\textsuperscript{307} and N\textsubscript{2}O\textsuperscript{308}. Chemical oxidation can occur by suspending the carbon in an oxidizing solution. The chemical species, concentration of the chemical, temperature and duration of the treatment can have a significant impact on the degree of oxidation and the functional groups added to the carbon surface\textsuperscript{118,307,309,310}. Chemicals used for oxidizing carbon include: nitric acid\textsuperscript{118,169,202,299,300,303,304,307-312}, nitric acid/sulfuric acid combinations\textsuperscript{299,302,303,307}, hydrogen peroxide\textsuperscript{299,304,308,311}, phosphoric acid\textsuperscript{309}, potassium permanganate\textsuperscript{299,303}, hydrochloric acid\textsuperscript{313}, ruthenium tetraoxide\textsuperscript{303} and acetic acid\textsuperscript{309}. The electrolyte and the charge passed through the electrolyte in the presence of the carbon controls the degree of oxidation by electrochemical means\textsuperscript{314}. Electrolytes used for electrochemical oxidation of carbons include ammonium bicarbonate\textsuperscript{314} hydrochloric acid\textsuperscript{313} and, potassium nitrate\textsuperscript{315}. Oxidation of carbon through plasma treatments requires quick exposure of the carbon to plasmas containing oxygen in a dry environment\textsuperscript{316,317}. With all of these treatment techniques the oxidation length, concentration of the oxidant and temperature play a significant role in the degree of oxidation, types of functional groups, and the structural effects to the carbon\textsuperscript{118,307,309,310,314,315}.

Further treatment to the carbon after oxidation may be required. Depending upon the method, amorphous carbon residues\textsuperscript{310} and chemical residues\textsuperscript{299} may require additional washing and treatments. Other functional groups, such as nitrogen groups
from the oxidation treatment with nitric acid$^{312}$ and sulfur from sulfuric acid treatments$^{318}$ can be added to the carbon as well.

A wide variety of carbons have been studied after oxidation. They include carbon blacks$^{118,202,300,309}$, activated carbons$^{302,304,308,311}$, carbon fibers$^{309,310,313-315,319,320}$ and, carbon nanofibers$^{299,303,307,309,312,321}$. The types of carbon also control the functional group species that are present. The defects, edge plane exposure, pore size and surface area can control the type and quantity of oxygen functional groups added to carbon surfaces in comparable treatments. Functional groups already present on the surface of the carbon also can play a role in further oxidation treatments.

No one analysis technique can completely characterize the oxygen functional groups present on carbon. Combinations of complementary techniques are needed to gain a good understanding of the functional groups present. Exposure to air may also alter the type and quantity of functional groups present on carbon$^{200-202,314}$. The most common characterization techniques used for oxidized carbons are XPS, temperature programmed desorption (TPD) experiments, titration methods and infrared methods. Other techniques that have also been used to a lesser degree in the characterization of oxygen functionalized carbons include: Electron Spin Resonance spectroscopy, ToF-SIMS, isotopic labeling, dye adsorption, and chemical reaction and adsorption probing. Structural changes to the carbon are commonly monitored through electron microscopy, surface area and pore volume analysis, and Raman spectroscopy.

XPS and IR techniques, including transmission FTIR and DRIFTS, can provide qualitative examinations of oxidized carbons. Sensitivity and deconvolution of the
spectra can add challenges to the analysis of these techniques\textsuperscript{201,313,314}. Deconvolution of the C 1s spectra to identify the carbon-oxygen species tends to be easier than identification of the oxygen species in the O 1s spectra of XPS\textsuperscript{315}. Carbons must be heavily functionalized or very diluted for practical IR spectra to be obtained due to the black-body like absorption abilities of many carbons\textsuperscript{201,308}. TPD and titration experiments are considered more quantitative techniques for identification of oxygen functional groups on carbon. In TPD experiments, the oxidized carbon is exposed to an inert atmosphere (or a vacuum) and the desorption gases are monitored while the temperature is ramping. The temperature of the desorption and gaseous species (water, carbon monoxide or carbon dioxide) can indicate the type of functional groups present\textsuperscript{307,308}. Deconvolution methods of TPD spectra can be difficult, but there have been several methods presented in the literature on deconvolution techniques to identify the oxygen functional groups\textsuperscript{307,308}. Titration experiments, particularly Boehm titrations\textsuperscript{200,322}, can be used to detect acidic and basic functional groups on the carbon surface\textsuperscript{310}. The strength of the acidic or basic functional group and concentration can dictate the accuracy of the titration method\textsuperscript{311}. Also if the functional groups are located in small pores on the carbon surface, the titrant may not be able to reach the species, causing an underestimate of the surface species\textsuperscript{311}.

3.2.5.a Oxygen Functional Groups in ORR

Controlling oxygen functional groups on carbon supports has aided in the preparation of platinum-based ORR catalysts for PEM fuel cells\textsuperscript{301,302}. The anchoring and particle dispersion properties that oxygen functional groups lend to carbon supports
have aided in the increase in ORR activity for Pt-based ORR catalysts\textsuperscript{301,302}. The role of oxygen functional groups in non-noble metal ORR catalysts has also been studied to a smaller extent\textsuperscript{118,121,169,300,323}. These studies have shown that carbon blacks containing oxygen functional groups improve ORR activity over non-functionalized carbon blacks\textsuperscript{118,121,169,300,323}. The Popov and Dodelet groups have concluded that the role of the oxygen functional groups were not to improve ORR activity themselves, but to provide a better support medium for the active sites\textsuperscript{118,121,169,323}. Nabae, \textit{et al.} concluded that oxygen functional groups were the active site and that copper added to the catalyst created an oxygen adsorption site\textsuperscript{300}. The Popov group studied ORR catalysts composed of a cobalt ethylene diamine chelate supported on oxidized and un-oxidized carbon blacks that were then heat treated in inert atmospheres\textsuperscript{169,323}. They also investigated un-oxidized carbon blacks, oxidized carbon blacks and the cobalt-free chelate supported on un-oxidized and oxidized carbon blacks for comparison. It was observed that even the oxidized carbon black had a 100 mV improved activity over pristine carbon black. The addition of the nitrogen-containing chelate improved the activity even more. The cobalt catalyst on the oxidized carbon performed the best for ORR. It was found that the cobalt particle size was significantly reduced when the cobalt chelate was dispersed on an oxidized carbon black. Popov cited the acidity of the quinone groups on the carbon surface as an effective dispersant of the basic cobalt chelate. The presence of the quinone groups was verified through the observation of the quinone/hydroquinone redox couple at 0.55V vs. NHE during cyclic voltammetry testing.
The Dodelet group also studied the effect of the pretreatment of carbon blacks on their Fe-N-C ORR catalysts. The oxidized carbons were heat treated in ammonia, then an iron salt was added to the carbon and heat treated. It was found that the presence of oxygen functional groups on the carbon black increased the nitrogen content of the support after ammonia treatment. Even when the nitrogen and iron were not added to the oxidized carbon, the oxidized carbon had superior activity to pristine carbon black. The Fe-N-C catalysts prepared on oxidized supports showed higher ORR activity than those prepared on pristine supports. In a separate study of 19 different carbon supports, the Dodelet group also found that if the catalyst did not contain any nitrogen, then the ORR activity was proportional to oxygen content. Once nitrogen was introduced to the catalyst, the ORR activity was controlled by the nitrogen species.

While both Popov and Dodelet attribute the presence of oxygen functional groups as important in the preparation of metal-supported catalysts, Nabae, et al. believe that the oxygen functional groups play a more pivotal role during oxygen reduction. They studied modified carbon blacks with and without copper. The carbon blacks were modified by mixing with HNO₃ and NH₄H₂PO₄ and then heat treating in inert atmosphere at 823K. The carbon was oxidized to create quinone/hydroquinone oxygen functional groups that were shown to participate in ORR. The phosphorous groups were added to the carbon to increase the proton mobility in the electrocatalyst. While the ORR activity improved when copper was added to the catalyst, the catalyst had significant activity without it. The authors hypothesized copper added an oxygen adsorption site for the catalyst and was not part of the active site. They hypothesized the quinone/hydroquinone redox couple to be the active site for ORR on their catalyst.
The Savy group also observed less sintering of the catalyst when they studied the oxygen content on carbon supports used for Co-macrocycle pyrolysis\textsuperscript{76}. They found that the presence of oxygen on the carbon increased the selectivity of the catalyst to water formation. It was also observed that during high temperature pyrolysis, the cobalt was converted to cobalt oxides instead of metallic cobalt when higher amounts of oxygen were present on the carbon support\textsuperscript{76}. 
CHAPTER 4. Experimental Methods

4.1 Catalyst Preparation

Several types of nitrogen containing carbon nanostructured (CN$_x$) catalyst materials were studied to investigate the role of nanostructure, heteroatom species and other properties. Development of CN$_x$ ORR catalysts involves the growth and treatment of carbon nanostructures. These nanostructures are grown by flowing carbon-containing (and possibly other heteroatom-containing) reactant gas streams over fiber-growth catalysts at elevated temperatures (usually 600°C to 900°C). The resulting nanostructure and chemical composition depends upon the treatment temperature, duration, reactant gas and growth catalyst.

4.1.1 Magnesia Supported CN$_x$ Catalysts

The magnesia (MgO) supported CN$_x$ catalysts were used as a baseline for comparison and a basic material for modification. This material was selected because of
the ability to remove the growth support (compared to Vulcan carbon\textsuperscript{142} also previously studied in the research group) and the ease of preparation (compared to alumina\textsuperscript{140,141} and silica\textsuperscript{144,145} catalysts also previously studied in the research group) while still maintaining a high level of activity and selectivity\textsuperscript{144,145}. In most cases the CN\textsubscript{x} was grown over 2\%Fe/MgO growth catalyst using acetonitrile pyrolysis which was then washed to remove the exposed MgO and Fe.

Catalysts were prepared using high-surface area magnesia nanopowder from Sigma Aldrich as the support. The MgO was left as-received or impregnated with metal salts. Incipient wetness impregnation (IWI) technique was used for the doping of the metal salts into the support. The IWI method was used to evenly spread the metal over the support and within the support pores. In the IWI technique, the MgO support is weighed out first. Then the total volume of the pores based upon the mass of support desired to impregnate and the measured BJH pore volume is calculated. An aqueous solution with a total volume equal to the total volume of the pores is made with the metal salt to give the desired metal loading on the support. The aqueous metal salt solution is then slowly mixed with the support to evenly distribute the metal on the support material. The metal salt precursors used for impregnation were iron (II) acetate, cobalt (II) acetate and nickel (II) acetate. Typical metal loadings for the prepared fiber growth catalyst were two weight percent. Impregnated supports were dried at 110°C. These impregnated supports served as the nanofiber growth catalysts.

Acetontirle (CH\textsubscript{3}CN) pyrolysis to form the CN\textsubscript{x} catalyst was performed by placing 2g of the MgO support as received or the dried metal-impregnated MgO support
into a quartz catalyst reactor boat loaded in a quartz calcination tube in a high-temperature furnace. The calcination tube with the nanofiber growth catalyst was purged with nitrogen (N$_2$) at 150 mL/min for 30 minutes before any treatment was started to eliminate any oxygen in the reactor system. The acetonitrile bubbler used in the nanofiber growth was also purged with N$_2$ to remove any oxygen in the system. The gases from the acetonitrile purge prior to nanofiber growth were set to bypass the reactor system so as not to introduce any acetonitrile before the desired temperature. After purging the system, N$_2$ was flowed through the calcination tube over the nanofiber growth catalyst while heating the furnace at 10°C/min to 900°C. Once 900°C was reached, the N$_2$ stream was flowed through an acetonitrile bubbler at room temperature and then to the furnace held at 900°C for two hours to grow the nitrogen-containing carbon nanostructures (CN$_x$). The CN$_x$ materials were cooled back to room temperature in nitrogen (See Figure 12 of pyrolysis growth procedures for a visual depiction).

After fiber growth, approximately 1.5g of CN$_x$ grown over MgO was washed with 250 mL of 1M HCl at 60°C for 1 hour while stirring with a magnetic stirbar. This acid wash was performed to remove any exposed metals and the magnesia support itself. After washing, the CN$_x$ was vacuum filtered with about 1L excess DI water. The CN$_x$ was collected into a beaker by rinsing the material off of the filter paper. These final CN$_x$ catalysts were dried in air in a 110°C oven for 24 hours.

The weight gain of CN$_x$ materials during fiber growth was calculated using the following equation:
Where the final CN\textsubscript{x} weight was the mass of CN\textsubscript{x} recovered after pyrolysis and adjusted initial precursor weight was the mass of the precursor (metal/support) loaded into the sample boat adjusted for the mass loss found to occur during heating at 10°C/min in N\textsubscript{2} to 900°C. For 2%Fe/MgO, the precursor was found to lose 41.8% of its mass during heating. Typical weight gains were 20-30% for CN\textsubscript{x} grown over 2wt% Fe/MgO. Mass losses of 70-80% were typical after HCl washing.
4.1.2 Stacked Platelet Nanofibers

Stacked platelets were prepared to examine the role of edge plane exposure. Stacked platelets are nanofibers with graphite sheets stacked upon one another perpendicular to the longitudinal axis of the nanofiber (see Figure 13). As prepared, they contained no nitrogen, but were later treated to contain nitrogen if desired.

Figure 12. Acetonitrile pyrolysis treatment conditions.
To prepare the stacked platelet nanofibers, a procedure following the outline of a patent by Rodriguez and Baker was used\textsuperscript{324}. An unsupported 95:5 atomic ratio iron:copper (Fe:Cu) nanofiber growth catalyst was prepared for the creation of stacked platelet nanofibers. This 95:5 Fe:Cu catalyst was prepared using a co-precipitation method. In this method, the respective nitrate salts were made into 1M solutions and combined to form the 95:5 Fe:Cu ratio. A small amount of ammonium carbonate (0.5M) was added to a beaker and the nitrate solution was slowly added while stirring. Additional ammonium carbonate was added during the nitrate addition process to maintain a pH between 8.1 and 8.4. After all of the nitrate solution was added, the co-precipitation catalyst was vacuum filtered with excess DI water and allowed to dry at
110°C. The dried 95:5 Fe:Cu catalyst was calcined at 350°C for 2 hours while exposed to air.

To grow the stacked platelets, 200mg of the calcined 95:5 Fe:Cu catalyst was loaded into a quartz sample boat in a quartz calcination tube in a high temperature furnace. The unsupported metal catalyst was reduced in 10% H_2 in He at 600°C for 12 hours before stacked platelet growth. Immediately following the reduction step without cooling, the calcination tube and sample was purged with He to remove any hydrogen from the system. Stacked platelets were grown over the reduced catalyst after the purge using a 4:1 CO:H_2 reactant stream with a balance of He (88 ml/min CO, 22 ml/min H_2 and 21 ml/min He). This was performed at 600°C for 2 hours before being cooled under He. About 1.3g – 1.4g of nanofibers and growth catalyst were collected after carbon deposition.

The resulting stacked platelet nanofibers were washed with 1M HCl as described in the MgO supported CN_x catalyst preparation section to remove any exposed copper or iron.

4.1.3 Nanofibers with Basal Plane Exposure

As a comparison to the stacked platelet nanofibers, nanofibers with low graphitic edge-plane exposure, or high basal plane exposure, were prepared. The preparation of the nanofibers with basal plane exposure followed the same outline as the stacked platelet nanofibers. For the nanofibers with basal plane exposure, a 6:4 Fe:Cu nanofiber growth
catalyst was prepared and calcined. To grow the nanofibers with basal plane exposure, 100 mg of 6:4 Fe:Cu catalyst was reduced in hydrogen at 600°C before nanofiber growth in 4:1 CO:H₂, balance He stream at 675°C for 2 hours. After cooling in He, the nanofibers with basal plane exposure were also washed in HCl as described in the magnesia supported CNₓ preparation section.

4.1.4 Nanofiber Acid Oxidation

Nanofibers were oxidized with acid to add oxygen functional groups to the carbon surface. There were two reasons that oxygen functional groups were added to the nanofiber surface. The first was to study the role of oxygen functionalities on carbon and nitrogen-containing carbon ORR performance. The second was to create sites for nitrogen to incorporate into the carbon nanostructure during high temperature ammonia treatment. Two types of acid oxidation were used; concentrated nitric acid oxidation and concentrated nitric and sulfuric acid oxidation. It was found that the more severe concentrated nitric and sulfuric acid combination was required prior to ammonia treatment on highly graphitic stacked platelet nanofibers and nanofibers with basal plane exposure. Less severe nitric acid treatments were used on CNₓ catalysts.

4.1.4.a Nanofiber Acid Oxidation Using Nitric and Sulfuric Acid

Nanofibers were oxidized to add oxygen functional groups to the carbon surface prior to high temperature ammonia treatment using nitric and sulfuric acid. A concentrated solution of 1:1 by volume HNO₃ (69 mass%) : H₂SO₄ (97 mass%) was prepared as the
oxidation medium. Nanofibers were suspended in 200 ml of the concentrated acid solution at 60°C under constant stirring using a magnetic stir bar for 3 hours, before allowing to cool 1 hour. The nanofiber-acid suspension was slowly added to excess DI water for dilution before vacuum filtering the nanofibers with additional excess DI water. The collected nanofibers were dried in air at 110°C for 24 hours.

4.1.4.b CN\textsubscript{x} Acid Oxidation Using Nitric Acid Only

CN\textsubscript{x} catalysts were oxidized to add oxygen functional groups to the carbon surface using nitric acid. A concentrated solution 69 mass% HNO\textsubscript{3} was used as the oxidation medium. CN\textsubscript{x} nanofibers were suspended in 250 ml of the concentrated acid solution at 60°C under constant stirring using a magnetic stir bar for 3 hours, before allowing to cool 1 hour. The nanofiber-acid solution was slowly, and carefully, vacuum filtered with excess DI water. The collected nanofibers were dried in air at 110°C for 24 hours.

4.1.5 Ammonia Treatments on Nanofibers

Ammonia treatments at elevated temperatures were performed on a variety of nanofibers and CN\textsubscript{x} catalysts to alter the nitrogen content in them.

4.1.5.a Ammonia-Treated Stacked Platelets and Nanofibers with Basal Plane Exposure

Ammonia was used to introduce nitrogen into the stacked platelet nanofibers and nanofibers with basal plane exposure after HNO\textsubscript{3}:H\textsubscript{2}SO\textsubscript{4} acid oxidation. Nanofibers
(approximately 0.2-0.3g) were placed in a quartz sample boat and purged with He. After purging, 72% NH₃ in He was introduced into the reactor and the furnace was ramped at 10°C/min to 600 or 900°C. Ammonia treatment durations were 4 hours at 600 or 900°C and 19.5 hours at 900°C, before cooling in He for the acid oxidized stacked platelets. The acid oxidized nanofibers with basal plane exposure were treated at 900°C for 19.5 hours in ammonia for comparison.

4.1.5.b Ammonia-Treated CNₓ Catalysts

Ammonia treatments were performed on CNₓ catalysts grown over 2%Fe/MgO and HCl washed. Approximately 200 mg of the CNₓ catalyst was loaded into a quartz calcination boat. A stream of 38% ammonia in helium (total flowrate of 57ml/min) was flown over the CNₓ material while heating at 10°C/min. The temperature of the furnace was brought to either 600°C or 900°C and held for 4 hours in the ammonia stream. The catalyst was cooled under helium.

Additional batches of CNₓ catalyst were treated with ammonia after concentrated nitric acid oxidation.

4.1.6 Ethanol-Treated CNₓ

To probe the solvent effect on ink aging, CNₓ was treated in an ethanol soak or left as prepared to examine the effects of ethanol on the catalyst. CNₓ catalyst was soaked in 100% ethanol in a ratio of 1:100 catalyst:ethanol by mass in two closed vials at room temperature for 1 week. One uncapped vial was placed directly in a drying oven at
110°C to dry. This catalyst was labeled “CNₓ-ethanol soaked”. The contents of the other vial was vacuum filtered with 1L excess DI water before being collected and dried at 110°C. This catalyst was labeled “CNₓ-ethanol soaked, DI water rinsed”.

4.1.7 Other Heteroatom Incorporation into Carbon Nanofibers

Incorporation of other heteratoms into the graphitic nanostructure can also alter the electronic structure of the CNₓ catalyst. Heteroatoms were incorporated into the nanostructure both during fiber growth and through post treatment of the CNₓ catalysts.

4.1.7.a Sulfur as a Growth Promoter in CNₓ

Sulfur was used as a CNₓ growth promoter during acetonitrile pyrolysis. The 2%Fe/MgO fiber growth catalyst described above was used for these studies. The acetonitrile pyrolysis technique described in the magnesia-supported CNₓ catalyst section was modified by using a range of mixtures of thiophene and acetonitrile in the organic precursor bubbler. Before treatment, the organic bubbler was purged with nitrogen for exactly 15 minutes to keep the conditions consistent while removing any oxygen from the system. All other conditions for the preparation remained the same. Thiophene (C₄H₄S) was added to the acetonitrile bubbler at levels of 1.8, 3.6, 5.5, 7.3, 8.9, 11.5 mol% as a growth promoter. For comparison, carbon nanostructures were also formed by pyrolyzing 100 mol% thiophene over the same fiber growth catalysts. All catalysts in this study are reported using the mol% thiophene in the acetonitrile solution, e.g.,
CN_x(7.3) denotes CN_x catalysts prepared from a 7.3% thiophene in acetonitrile mixture. CS_y refers to the carbon nanostructures grown using thiophene only.

All carbon nanostructures were washed in 2.4M HCl at 60°C, vacuum filtered with excess deionized and distilled water and dried in an atmospheric oven at 110°C to remove the magnesia support and any exposed iron.

4.1.7.b Boron-Incorporated CN_x Catalysts

Boron was incorporated into CN_x catalysts using a wet impregnation technique followed by a heat treatment. 2%Fe/MgO supported CN_x catalysts were prepared and HCl washed as described above. A solution of 6 mL DI water and an appropriate amount of ammonium pentaborate ((NH_4)_2B_{10}O_{16} \cdot 8H_2O) was made. B:C atomic ratios equaling 0.025, 0.05, 0.10, and 0.25 were used when the CN_x catalyst was assumed to be all carbon for the calculation. This solution was mixed into 200 mg of CN_x while stirring in a vial suspended in a 90°C water bath for twenty minutes. The slurry was dried at 110°C before being heat treated. The dried B-CN_x material was heat-treated at 900°C for 4 hours in N_2 flowing at 150 mL/min. Materials developed using this method were identified by the B:C atomic ratio of the ammonium pentaborate – CN_x slurry before heat treatment. For this ratio, it was assumed that the CN_x catalyst was 100% carbon.

4.1.8 Graphitic Site Blocking on CN_x

Park and Baker have reported on blocking the armchair and zigzag graphitic edge planes on carbon nanofibers^{230}. Attempts were made to determine the location of the
CN_x active site by selective blocking of the armchair and zigzag edge planes. CN_x grown on 2%Fe/MgO-HCl washed and stacked platelets following oxidation and ammonia treatments were used in this study. The zigzag graphitic edge can be blocked by boron groups while the armchair edge can be blocked by phosphorus groups.

The starting catalyst material was wet impregnated with methylphosphonic acid or ammonium pentaborate to add the blocking materials. To do this, approximately 0.25g of carbon catalyst was added to a small vial and 2 ml of DI water containing enough boron or phosphorus precursor to make 5wt% additive on the carbon was mixed with the carbon while stirring at 90°C. The solution container was rinsed into the catalyst paste with a small amount of excess DI water. The catalyst was stirred for about 45 minutes until the observable liquid was gone. The catalyst and precursor were then dried overnight in air at 110°C.

To create the materials with site blocking, the wet-impregnated material was heat-treated for three hours at 450°C in 10%O_2 in 80 ml/min of flow. After heat treatment, some of the boron or phosphorus groups should be bound to the carbon. Any residual material not bound to the carbon was removed through a wash with 1.0M HCl as described in the CN_x preparation section.

As a comparison, a “blank-blocked” CN_x was also prepared that went through the entire site-blocking treatment process in the absence of the methylphosphonic acid or ammonium pentaborate.
4.1.9 Commercial Catalysts

Commercial catalysts were used throughout the study as a comparison to those created in the laboratory. The most common commercial catalyst used as a comparison was 20% Pt/Vulcan Carbon (VC). This catalyst was obtained from Electrochem, Inc. and manufactured by E-Tek. From the same manufacturers, 20%Pt-10%Ru on Vulcan carbon was also used.

4.2 Catalyst Characterization

Catalysts were characterized throughout the entire process from preparation through end-of-use to gain a better understanding of the positive and negative features of the catalyst for future catalyst development. Both physical and chemical characterizations were performed on the catalysts. Characterization instrumentation used for the described work is available in the research group laboratories, the Campus Electron Optics Facility, and the Chemistry Department’s Surface Analysis Facility.

4.2.1 Nitrogen Physisorption

Nitrogen physisorption was performed on catalyst materials to determine the BET (Brunauer, Emmett and Teller) surface area and BJH (Barrett, Joyner and Halenda) cumulative desorption pore volume and pore size distribution. Greater surface area can
increase the quantity of active sites on a catalyst, though with increased surface area, electrical contact resistance is increased. The distribution of the volume of the pores also can be used in understanding of the transport of water to and from the catalyst during fuel cell operation. A Micromeritics ASAP 2010 was used for this analysis.

To perform the analysis, a quartz analysis tube was evacuated and then filled with nitrogen. The tube was weighed filled with nitrogen and then 100-200mg of catalyst was placed in the tube. The sample was evacuated and then heated at 130°C overnight while continuing to degass. The sample was removed from the system after backfill with nitrogen and weighed. The sample weight after pretreatment was used in the surface area and pore volume analysis. The analysis was performed at liquid nitrogen temperatures.

4.2.2 X-Ray Photoelectron Spectroscopy (XPS)

XPS was used to study the chemical surface species on the catalysts. A Kratos Ultra Axis Spectrometer was used with a monochromated aluminum anode source set at 13 kV and 10 mA. Catalyst samples were prepared into pellets in stainless steel disk sample holders. They were prepared using pellets to eliminate the carbon signal coming from carbon tape that is commonly used for XPS sample preparation. A survey scan was collected with an 80 eV pass energy. Individual regions were scanned with a 20 eV pass energy and included Mg 1s, Fe 2p, O 1s, N 1s, C 1s, B 1s, Cl 2p, S 2p, and Mg 2p, depending upon the sample.
Sensitivity factors reported for the anode and position by the manufacturer were used in the calculation of species contents in the catalysts. The spectra baselines were determined using a Shirley-type background fitting. Spectra were fitted using Lorentzian-Gaussian combination peaks. The concentrations of surface species above about 1% are able to be detected by the instrument more easily. From the information gained by XPS, the type of nitrogen present and surface composition can be determined. Other dopant species can also be investigated by XPS.

4.2.3 Transmission Electron Microscopy (TEM)

Morphological characterization of the catalysts was done using a FEI Tecnai F20 XT TEM in imaging mode set at 200kV. Catalysts were prepared for imaging by suspending catalyst in ethanol, sonicating and then depositing the catalyst suspension on lacey-formvar carbon supported on 200 mesh copper TEM grids.

4.2.4 Hydrophobicity Testing

The relative hydrophobicity of the CN_x catalysts was examined by suspending 1mg of catalyst in 5mL of DI water. The suspensions were sonicated for 30 minutes and then visually compared. Photographs were taken of the suspended catalysts side-by-side on a white backdrop to study the hydrophobicity.
4.2.5 Temperature Programmed Oxidation (TPO) Experiments

Temperature programmed oxidation (TPO) experiments can be used in determining types of carbon, degree of graphitization, edge plane exposure and the nature of chemical species present in the carbon. Depending on the degree of graphitization, the edge plane exposure and amount of defects, the carbon will oxidize at different temperatures. By connecting the product gas line to a residual gas analyzer, the chemical composition of what is oxidizing can be monitored. TPO experiments can be run using several different set-ups, including in conjunction with thermogravimetric experiments. Several TPO experimental set-ups have been used in the study of CNₓ materials.

4.2.5.a Temperature Programmed Oxidation – Thermogravimetric Analysis (TPO-TGA) Experiments

The types of carbon present in the CNₓ were studied through the use of Temperature programmed oxidation (TPO) experiments ran on a thermogravimetric analyzer (TGA). The mass loss observed during oxidation can aid in determining the relative amounts of carbon types as well as the effectiveness of washing. Approximately 5-10 mg of the catalyst studied was placed in a Setaram TGA-DSC 111 instrument using platinum crucibles. The reactant gas was 60 ml/min 10% O₂/He. Temperatures were ramped at 5°C/min to 750°C for the experiment. Blank experiments with the same temperature profile and gases were run with empty crucibles to subtract any mass changes due to buoyancy effects. The TPO-TGA experiments were also paired for product gas analysis by connecting the exit gas to a Cirrus residual mass analyzer. Mass
signals from 1-100 were scanned during these experiments to aid in the determination of components of a particular carbon.

4.2.5.b Temperature Programmed Oxidation (TPO) Experiments Using an External Reactor System

Temperature programmed oxidation (TPO) experiments were performed using an external reactor system when oxidation temperatures of the materials approached 750°C, the maximum operating temperature of the TGA, or when more than 5 to 10 mg of material needed to be oxidized to identify a species being studied through oxidation. The external reactor used was a fritted quartz bulb reactor that was positioned vertically in an upright high temperature furnace. Approximately 25 mg of the catalyst to be studied was loaded into the reactor for study. The reactant gas was 50 ml/min 10% O₂/He. Temperatures were ramped at 5°C/min to 900°C for the experiment. The product gas was monitored using Cirrus residual mass analyzer. Mass signals from 1-100 were scanned during these experiments to aid in the determination of components of a particular carbon and the temperature at which oxidation occurred.

4.2.6 Temperature Programmed Desorption-Temperature Programmed Oxidation (TPD-TPO) Experiments

Temperature programmed desorption (TPD) – temperature programmed oxidation (TPO) coupled experiments were performed using a Micromeritics Autochem II system coupled to a MKS Cirrus residual gas analyzer to study the CNₓ catalyst surface and bulk
species, as well as the stability of the catalyst species. TPD-TPO experiments were performed with approximately 25 mg of catalyst. A helium gas stream was flowed over the catalyst bed while heating at 5°C/min to 900°C and cooling using forced convection back to room temperature for the TPD portion of the experiment to detect any desorbed species. Following the TPD, a TPO was immediately ran in 5%O₂/He at 5°C/min to 750°C to characterize the catalyst material remaining after the TPD. The product gas mass signals of the entire experiment were monitored from 1-100.

To study the effect of the presence of water on the catalyst, 10mol% water vapor was introduced into the TPD temperature ramp to 900°C. The catalyst bed was cooled in He and then a TPO was performed as described above for the dry TPD-TPO experiment. The experiments involving water during the TPD are named wet TPD-TPO experiments.

4.3 Electrochemical Testing and Related Studies

Electrochemical testing methods were used on the CNₓ catalysts to study their behavior as fuel cell materials using electrochemical half cell methods. Additional phenomena studies were also performed.
4.3.1 Rotating Ring Disk Electrode (RRDE) Testing

Activity testing of the ORR catalyst was performed using the half-cell electrochemical technique known as Rotating Ring Disk Electrode (RRDE) testing. Figure 14 is a schematic of the set-up for RRDE testing. Inks for RRDE testing were prepared fresh for each test using a composition of 1:10:160 (by mass) catalyst: 5% Nafion in aliphatic alcohols: ethanol. The inks were sonicated for 30 min. Three-5μL aliquots of ink were applied to the glassy carbon disk electrode with an area of 0.1642 cm² to coat the disk without covering the Teflon casing or the Pt ring.

![Figure 14. Setup for Rotating Ring Disk Electrode. Figure courtesy of Dieter von Deak.](image-url)
All tests were performed in a half cell containing a 0.5M sulfuric acid (H$_2$SO$_4$) electrolyte. A PAR Bistat connected to a model 636 RRDE setup was used. An Ag/AgCl(sat KCl) reference electrode and a Pt wire counter electrode were used in the system. All RRDE tests were performed using cyclic voltammogram sweeps. For CN$_x$ catalysts, the sweeps were from 1.2V to 0.0V to 1.2V vs. Normal Hydrogen Electrode (NHE). Materials containing Pt were cycled from 1.2V to 0.2V to 1.2V vs. NHE to avoid H$_2$ production, occurring at 0.0V vs. NHE.

To begin RRDE testing, the electrolyte was saturated with oxygen. A CV was run at 10 mV/s to remove any gaseous oxygen from the CN$_x$ pores and fully wet the catalyst. The solution was then purged with Ar. In the Ar purged system, CVs at 50 mV/s were run on the disk paired with the ring set at a constant 1.2V vs. NHE until steady-state curves were obtained in each. Then a CV at 10 mV/s rotating at 100 rpm was completed with the ring set at a constant 1.2 V to obtain a background current for both the ring and disk. The solution was then saturated with oxygen. Steady-state CVs at 50 mV/s were run paired with the ring held at 1.2V. The disk (at 10 mV/s) and ring (1.2 V) were run while rotating at 100 rpm to obtain the H$_2$O$_2$ production rates at the ring. CVs at 10 mV/s were also run for the disk in oxygen at 0 rpm and 1000 rpm. Later studies also collected the ring data during the 1000rpm scan in oxygen.

The ORR activity, identified as the onset of activity, was quantified as the potential at which the current obtained in O$_2$-saturated solution at 0 rpm is 10% higher.
than the Ar background. For more active samples this separation occurs at higher values, closer to the theoretical potential of 1.2 V. Figure 15 is a set of typical reduction scans for activity testing. While the onset of activity is actually calculated using 0rpm data, as seen from this figure, the onset at all rotations will occur at the same potential. Selectivity of the catalyst is determined by a pairing of the glassy carbon disk with the platinum ring at 100 or 1000 rpm. The ring detects H₂O₂ production formed from the following reaction at the ring:

\[ \text{H}_2\text{O}_2 \rightarrow \text{O}_2 + 2\text{H}^+ + 2e^- \quad 0.695 \text{ V vs.NHE} \]

The number of electrons transferred, \( n \), equals 4, if only H₂O is formed during ORR. If only H₂O₂ is formed, then \( n \) equals 2. The value of \( n \) is calculated from the ring and disk current measurements by:

\[
n = \frac{4I_D}{I_D + \left(\frac{I_R}{N}\right)}
\]

and the selectivity to water formation is calculated by:

\[
\text{H}_2\text{O Selectivity} = \frac{I_D - \frac{I_R}{N}}{I_D + \frac{I_R}{N}} \times 100
\]

Where \( I_D \) is the disk current, \( I_R \) is the ring current, and \( N \) is the ring collection efficiency.

The manufacturer reports \( N \) for this instrument as 0.20, indicating that 20% of all H₂O₂
passing closely by the ring in laminar flow at the ring potential held will be detected.

Figure 16 is a representative comparison of the ring to the disk.

In recent work, we have found that the ring may perform at its optimum levels if it is conditioned before testing and not held at a constant potential excessively. To accomplish this, the ring is no longer held at a constant potential during disk scans that are performed merely to get a consistent scan. Prior to each 10 mV/sec scan of the disk where the ring is also normally paired (as noted above), the ring is conditioned. Prior to the first Argon background collection scan, the ring was conditioned by performing 20 - 100 mV/sec CVs from -0.1V to 1.8V to -0.1V vs. NHE. Subsequent ring conditionings were run for only 10 CVs.

Figure 15. Typical RRDE activity results. (Catalyst: CNₓ on 2%Fe/MgO-HCl washed).
The inactivity of the ORR catalysts to the oxidation of methanol and tolerance to the presence of methanol during ORR were studied using the RRDE setup. CN$_x$ ORR catalysts developed in the HCRG studied for methanol tolerance and inactivity included CN$_x$ grown over the following supports: 2%Fe/Al$_2$O$_3$-HF washed, 2%Ni/Al$_2$O$_3$-HF washed, 2%Fe/SiO$_2$-KOH-HCl washed, 2%Co/SiO$_2$-KOH-HCl washed, 2%Ni/SiO$_2$-
KOH-HCl washed, 2%Fe/MgO-HCl washed, 2%Co/MgO-HCl washed and 2%Ni/MgO-HCl washed. Commercial catalysts used were 20%Pt/Vulcan Carbon (VC) and 20:10 Pt:Ru/VC both from E-Tek.

To study ORR catalysts in the presence of methanol, RRDE testing was first performed as described above. Once the methanol-free tests were completed, the half cell solution was changed to 1.0 M methanol + 0.5 M H₂SO₄ or 3.0 M methanol + 0.5 M H₂SO₄ without disturbing the catalyst thin film on the disk. The fresh solution was purged with Ar for 30 min. Then steady-state CVs and a disk and ring background were taken as described above. The methanol solution was then saturated with oxygen. The steady-state CVs, disk and ring at 100 rpm and disk only at 0 rpm and 1000 rpm were run as described above.

4.3.3 RRDE Studies to Examine the Effect of Catalyst Loading

When comparing work done by the HCRG to other researchers, it was noticed that the catalyst loadings used in RRDE testing varied significantly. A study was completed to investigate the effect of catalyst loading using both commercial 20%Pt/VC (E-Tek) and CNₓ grown over 2%Fe/MgO-HCl washed.

RRDE testing procedures were followed as described above, except that the amount of ink loaded on the glassy carbon disk varied. Ink levels studied were based upon aliquot applications. Each one-5μL aliquot is equivalent to 142 μg/cm² loading on the glassy carbon RRDE disk when assuming 100% dispersion of the catalyst in the ink.
Loading levels studied include 1 aliquot (142 μg/cm$^2$), 2 aliquots (284 μg/cm$^2$), 3 aliquots (426 μg/cm$^2$), 4 aliquots (568 μg/cm$^2$), 6 aliquots (852 μg/cm$^2$), 8 aliquots (1136 μg/cm$^2$) and 10 aliquots (1420 μg/cm$^2$). Testing was randomized to eliminate any experimental drift effects.

4.3.4 Catalyst Layer Thickness Determination

Film thickness and surface roughness of the catalyst films were studied with a Sirion FEG Scanning Electron Microscope (SEM). In this study, aluminum rods with the same diameters as the RRDE glassy carbon disk were used as “model” electrodes for applying the catalyst ink. Films were prepared by depositing 5 μL aliquots of catalyst inks onto the ends of aluminum rods in the same manner and at the same loadings as described in the RRDE catalyst loading studies. For SEM observation, the aluminum rods were placed horizontally so that the sides of the films were exposed directly to the SEM detector. The rods were tilted when necessary to give a clear observation of the film thickness and surface details. Film thicknesses were measured at a minimum of five locations along the disk for each loading. The average and standard deviations of the thicknesses were calculated.

4.3.5 RRDE Catalyst Ink Aging Studies

It has also been observed that the age of the RRDE ink has an effect on the selectivity results. To study this, RRDE procedures were followed as described above,
with the 20%Pt/VC and CN$_x$ on 2%Fe/MgO-HCl washed catalyst inks being prepared and aged.

Catalyst inks for RRDE testing were prepared using 1:10:160 (by mass) catalyst: 5% Nafion in aliphatic alcohols: ethanol. The capped ink vial was sonicated in a low energy sonicator water bath for 30 min prior to use. Catalyst ink sonicated for 30 minutes immediately following preparation was considered fresh. After the immediate use, the ink was allowed to sit capped until Day 1 use, 24 hours later. Prior to each use, the ink was sonicated for 30 min to maintain good dispersion of the catalyst in the ink suspension. Catalyst inks were used fresh and after 1, 2, 3, 4 and 11 days of aging.

Catalyst was applied to the glassy carbon disk working electrode in 5µL-aliquot increments. Catalyst loadings used on the disk were 142 µg/cm$^2$ and 426 µg/cm$^2$ assuming 100% dispersion of the catalyst in the ink.

4.3.6 Electrochemical Reduction and Oxidation of Hydrogen Peroxide

Changes in hydrogen peroxide detected at the ring with catalyst loading may suggest that ORR catalysts participate in a two-step mechanism where oxygen is first electrochemically reduced to hydrogen peroxide and then further electrochemically reduced to water. If this is the case, CN$_x$ catalysts should have some electrochemical reduction activity towards hydrogen peroxide. A series of experiments were performed to analyze the electrochemical activity towards hydrogen peroxide reduction and oxidation.
To have a direct comparison, RRDE testing was performed as described above using CNx grown over 2%Fe/MgO-HCl washed at a loading of 426 µg/cm² in 100.0 mL of fresh 0.5M H₂SO₄ as the electrolyte. Immediately following the RRDE measurements, hydrogen peroxide reduction and oxidation experiments were performed following a similar method to that reported by Jaouen and Dodelet¹³⁷.

Background linear voltamogram scans were collected in argon-purged electrolyte. The reduction scan was from +0.65V to 0.0V vs. NHE at 10 mV/sec, while the oxidation scan was from +0.65V to +1.1V vs. NHE at 10 mV/sec. Both were collected at a rotation of 100rpm.

After the backgrounds were collected, a known amount of 30% H₂O₂ was added to the 100.0 mL of H₂SO₄ in the electrochemical half cell to make a concentration of either 6.25 mM H₂O₂ or 1.3 mM H₂O₂. The volume added to the half cell was considered minimal so that 100 mL was considered the total volume of the solution.

Following the introduction of hydrogen peroxide, reduction scans were run all together before any oxidation scans were performed. This is to eliminate any oxygen noise interference produced from hydrogen peroxide oxidation. Also during scans, the electrolyte was continuously purged with argon to keep any oxygen out of the system as well. Reduction scans were collected at the following rotation rates: 100 rpm, 500 rpm, 1000rpm, 2000 rpm and 3000rpm. Rotation rates were randomized during experiments. Once the reduction scans were complete, oxidation scans were performed in the half cell at the same rotation rates as listed for the reduction scans.
CHAPTER 5. Effect of Sulfur as a Growth Promoter for CN\textsubscript{x} Nanostructures as PEM and DMFC ORR Catalysts

As published in *Applied Catalysis B: Environmental*\textsuperscript{325}

5.1 Motivation for Studying Sulfur as a Growth Promoter

As the activity of C-N catalysts continues to improve, manufacturing issues will have to be considered. If nanostructured carbons are to be used as fuel cell catalysts, then it is likely that their yield will have to be increased using a growth promoter in the energy-intensive manufacturing process. Sulfur has been reported as a growth promoter in the production of carbon nanofibers\textsuperscript{253,257,271-274}. While reports discuss the benefits of low-levels of sulfur during the nanofiber growth-process, significant discussion on the presence of sulfur in the carbon nanostructures after production has not occurred. From these reports, it is unclear if sulfur remains in the carbon nanostructure and if so, whether it has an impact on the behavior of the nanostructure, especially in catalytic systems. The incorporation of sulfur into the graphitic nanostructure of carbon could alter the electronic behavior of the carbon, thereby changing the performance of carbon
nanostructures used in electrochemical systems, such as ORR catalysts for PEMFCs and DMFCs. Sulfur could also become a contaminant to different components of fuel cells if it were not well adhered to the catalyst.

In this study, we have investigated the use of thiophene as a growth promoter for the production of CN_x catalysts from acetonitrile pyrolysis and its impact on the catalyst behavior for the oxygen reduction reaction in a PEM or DMFC environment. It should be noted that, in this study, there was no effort made to optimize the catalyst formulation or the testing protocols to get the best performance since the focus of the study is an understanding of the nature of the sulfur species incorporated during nanofiber growth and their impact on the ORR activity and selectivity.

The detailed preparation of CN_x catalysts made with thiophene as a growth promoter is described in the Experimental Methods Chapter. CN_x catalysts were made through acetonitrile pyrolysis at 900°C over a 2wt%Fe/MgO nanofiber growth catalyst. Thiophene was mixed with the acetonitrile before introduction to the pyrolysis furnace in levels of 1.8, 3.6, 5.5, 7.3, 8.9 and 11.5mol% thiophene in acetonitrile. For comparison, a catalyst was also made using 100% thiophene as the carbon precursor. All catalysts were washed with HCl to remove the exposed MgO and Fe.
5.2 Results & Discussion

5.2.1 Thiophene as a Growth Promoter

The addition of thiophene into the acetonitrile pyrolysis feed stream did promote the deposition of carbon. At all thiophene growth promoter levels studied, sample weight gain during pyrolysis was greater than acetonitrile-only pyrolysis. As shown in Figure 17, carbon deposition during pyrolysis goes through a maximum with increasing thiophene % in the feed mixture and the maximum occurs at 7.3% thiophene concentration. This shows that sulfur, in the form of thiophene, can act as a growth promoter when the feed stream contains both carbon and nitrogen in the form of acetonitrile. Previous studies using thiophene and other sulfur-containing growth promoters have been for non-heteroatom containing carbon nanostructures. Even when thiophene was used as the only carbon precursor, significant amounts of carbon deposition occurred, indicating that thiophene does not inhibit the carbon deposition process even at high levels.

Interestingly, there was an inverse relationship between the amount of carbon deposition and the BET surface area of the catalysts, also shown in Figure 17. This decrease in surface area could be caused by several reasons including the carbon nanostructure changing with growth promoter concentration or carbon depositing on itself reducing the amount of exposed surface.
5.2.2 Catalyst Morphology

To determine the impact of the use of thiophene as a growth promoter on the morphology of the CN$_x$ catalysts, TEM imaging was performed. CN$_x$ catalysts made with no sulfur growth promoters grown over 2wt%Fe/MgO produce mainly stacked cup nanofibers with varying diameters as shown in Figure 18a. These stacked cup nanofibers have graphite edge planes exposed at an acute angle to the longitudinal axis. Also, as previously reported, all CN$_x$ catalysts grown using a magnesia support contained some
nanocubes, regardless of the metal on the support\textsuperscript{144,145}. This observation held for these CN\textsubscript{x} catalysts as well, though there were significantly more nanofibers than nanocubes.

When the lowest level of thiophene growth promoter was used, 1.8\% (Figure 18b), the morphology of the CN\textsubscript{x} catalyst still remained mostly stacked cup nanofibers. There were more of the larger, less organized nanofibers and more nanocubes were also found compared to the thiophene-free catalyst. At the highest levels of growth promotion (7.3\% thiophene), the catalyst morphology was no longer dominated by the stacked cup nanofibers (Figure 18c). There were many more of the large, disordered nanofibers and a significant amount of nanocubes. Only a few stacked cup nanofibers were found. The change in morphology distribution along with the maximum growth promotion for the catalyst made with 7.3\% thiophene may signify a change in the growth mechanism of the carbon deposition with higher thiophene contents. In comparison, the catalyst made with thiophene only (Figure 18d) was composed of only nanocubes, indicating that acetonitrile was the precursor required to form stacked cup nanofibers over 2wt\%Fe/MgO fiber growth catalysts. Others have also observed changes in morphology with increased growth promoter concentration, as well, though the sulfur source and treatment conditions dictated whether changes observed were desirable or undesirable for the specific application\textsuperscript{253,271,273}. 


Figure 18. TEM images of a) CNₓ- no thiophene, b) CNₓ-1.8% thiophene, c) CNₓ-7.3% thiophene, d) CS₅-100% thiophene. As published in\textsuperscript{325}. 
5.2.3 Activity and Selectivity Testing

Activity and selectivity testing using the Rotating Ring Disk Electrode (RRDE) technique was performed on the CN$_x$ catalysts manufactured using the growth promoter to determine if the use of thiophene had an impact on the catalyst performance for ORR. The catalyst made with acetonitrile only had an onset of activity at 760 mV vs. NHE. All catalysts made with pyrolyzing thiophene and acetonitrile combined had onsets of activity within a very tight range, near to that of the catalyst prepared with acetonitrile only, as shown in Figure 19. The deviations in onset of activity measurements for these catalysts are not considered significant enough to distinguish differences in ORR activity. When thiophene was used as the only feedstock for the carbon growth, the ORR activity was very low. The onset of activity for the CS$_y$ catalyst was 510 mV vs. NHE, which would be considered a very poor catalyst for ORR. The inset to Figure 19 illustrates the significant difference with a voltammogram comparison of the CS$_y$ catalyst (no acetonitrile) to CN$_x$(8.9). From the activity testing, it appears that as long as the catalyst precursor contained some amount of acetonitrile, the ORR activity could remain unchanged. Selectivity calculations obtained from RRDE testing found the selectivity of the CN$_x$-thiophene catalysts to range from an average of 3.6 to 3.9 electrons transferred per oxygen molecule. No trend in the selectivity of the catalysts with thiophene precursor content was observed.
There have been studies in the literature about the reliability of the RRDE technique for selectivity measurements. It has been reported in the literature and demonstrated in our laboratory (presented in a later chapter on RRDE methods) that selectivity determined by RRDE is dependent upon the catalyst loading on the electrode disk. In this study, the catalyst loading was kept constant at 426µg/cm².

To verify the selectivity results obtained by the RRDE technique, additional analysis using the Koutecky-Levich (K-L) Equation was performed on some of the catalysts. K-L analysis results were comparable to those obtained by the RRDE, (n= 3.7
from K-L analysis as compared to a selectivity of $n=3.63$ from RRDE measurements). It should be noted that the Koutecky-Levich analysis is not without its own shortcomings\textsuperscript{71,331-333}, but the comparison between the two methods provides additional confidence in the reported selectivity values.

Factors affecting selectivity of the CN$_x$-thiophene catalysts will be discussed further in Section 5.2.5.

5.2.4 Hydrophobicity Testing

Relative hydrophobicity tests were performed by dispersing the catalysts in water with sonication. The use of thiophene as a growth promoter did not change the hydrophobicity/philicity properties of the catalysts as long as acetonitrile was still in the feed stream. An example of the hydrophobicity differences between catalysts made with acetonitrile and with thiophene-only is shown in Figure 20. Carbon nanostructures grown using thiophene only are considerably more hydrophobic as can be seen from the lack of dispersion in water. This observation is consistent with the lack of edge planes observed over these materials (as confirmed through TEM) and could be linked to the differences in the activity of CN$_x$ catalysts grown with or without the sulfur growth promoter and the CS$_y$ materials.
5.2.5 Surface Species Characterization

X-Ray Photoelectron Spectroscopy (XPS) was used to characterize the surface species on the catalysts produced. The S 2p region was scanned to determine if there was any detectable sulfur, and if so, what type of sulfur species were present on the surface of the CNₓ catalysts using thiophene as a growth promoter. Previous reports in the literature focus on the growth promotion effects of sulfur, but do not extensively discuss the sulfur that could be incorporated into the product carbon nanofibers²⁵³,²⁵⁷,²⁷¹-²⁷⁴. The impact of the presence of sulfur in the nanofiber could be significant depending upon the application. XPS analysis showed that there was a significant amount of sulfur on the nanostructure surfaces. Surface sulfur content for the CNₓ-thiophene catalysts ranged from 0.7 to 1.6 atomic%, as shown in Table 2. The catalyst prepared using 100% thiophene (CSₓ) had 3.6% sulfur on its surface. Figure 21a shows the S 2p region for a
representative group of the CNₓ-thiophene and CSₓ catalysts. Up to three types of sulfur can be identified in these catalysts. The peak at 168.3 eV was attributed to sulfate species. The literature has some discrepancies in the assignment of sulfur species in the 163-164 eV region. Figure 21a shows one doublet being fitted to the 163-164 eV envelope. S-C species can be identified at 163.5 eV. The peak at 164.1 eV was assigned to elemental sulfur. The assignment of C-S is less certain, as some have identified C-S at 163 eV, while others attributed 163.6 eV peak to possibly S-S or S-C and 163.6 eV to only S-S. Figure 6b is an example of when two doublet peaks are fitted in the 163-164 eV envelope. Both fits are reasonably good and possible. It is possible that both elemental S and S-C species are present in the thiophene-CNₓ catalysts with excess elemental sulfur being present on the surface of the catalyst. The sulfate percentage of the catalysts from XPS as published in Table 2. Surface composition of catalysts from XPS as published in. 

<table>
<thead>
<tr>
<th>%Thiophene in acetonitrile</th>
<th>0%</th>
<th>1.8%</th>
<th>3.6%</th>
<th>5.5%</th>
<th>8.9%</th>
<th>11.5%</th>
<th>100%</th>
</tr>
</thead>
<tbody>
<tr>
<td>O 1s</td>
<td>1.9</td>
<td>10.0</td>
<td>8.6</td>
<td>5.4</td>
<td>15.4</td>
<td>6.1</td>
<td>8.0</td>
</tr>
<tr>
<td>N 1s total</td>
<td>9.3</td>
<td>7.6</td>
<td>7.4</td>
<td>8.3</td>
<td>7.7</td>
<td>7.2</td>
<td>0.0</td>
</tr>
<tr>
<td>Pyridinic</td>
<td>26.1</td>
<td>26.7</td>
<td>27.3</td>
<td>23.7</td>
<td>31.4</td>
<td>23.7</td>
<td>0.0</td>
</tr>
<tr>
<td>Quartenary</td>
<td>47.8</td>
<td>47.9</td>
<td>47.8</td>
<td>49.4</td>
<td>45.6</td>
<td>48.6</td>
<td>0.0</td>
</tr>
<tr>
<td>Pyridinic-O</td>
<td>26.1</td>
<td>25.4</td>
<td>24.9</td>
<td>27.0</td>
<td>23.0</td>
<td>27.8</td>
<td>0.0</td>
</tr>
<tr>
<td>C 1s</td>
<td>88.8</td>
<td>81.7</td>
<td>82.7</td>
<td>85.4</td>
<td>75.2</td>
<td>85.9</td>
<td>88.9</td>
</tr>
<tr>
<td>S 2p</td>
<td>0.0</td>
<td>0.7</td>
<td>1.4</td>
<td>1.0</td>
<td>1.6</td>
<td>0.9</td>
<td>3.1</td>
</tr>
</tbody>
</table>
identified could have been elemental sulfur that, when exposed to air, reacted to form sulfate. This is possible, as the samples are exposed to air after they are synthesized. Interestingly, the fitting of the CNₓ(1.8%) catalysts required an additional lower binding energy doublet. This species has not been identified at this time, but sulfides are commonly found in this region.
Figure 21. XPS S 2p region for selected CN$_x$-thiophene catalysts (labels are mol\% thiophene in acetonitrile solution) deconvoluted using two doublets, b) XPS S 2p region deconvoluted using three doublets for CN$_x$-8.9\%thiophene. *As published in*\textsuperscript{325}.

X-ray photoelectron spectra of the N 1s region for the CN$_x$-thiophene catalysts were examined to determine if the introduction of sulfur led to significant changes in the
nature or the quantity of the detected surface nitrogen species (Figure 22). CNₓ catalysts grown with acetonitrile only over 2wt%Fe/MgO contained 9.3% nitrogen with the nitrogen content being split into 26.1% pyridinic-N (located on the graphitic edge planes), 47.8% quarternary-N (located inside the graphitic plane), and 26.1% pyridinic-N-O, as shown in Table 2. These results are similar to what has previously been observed in our research for CNₓ catalysts grown over Fe/MgO supports¹⁴⁵. When thiophene was used as a growth promoter, the nitrogen level dropped to between 7 and 8 atomic%. The breakdown of the nitrogen species changed little with the introduction of thiophene into the pyrolysis feed stream, as shown in Table 2 and in Figure 22. This relatively high amount of nitrogen and limited change to the nitrogen species most likely contributes to why no significant change in ORR activity for these catalysts was observed. It also suggests that the presence of thiophene does not alter the mechanism for incorporation of nitrogen into the graphite structure through acetonitrile pyrolysis. The absence of any detectable nitrogen in the CSᵧ may also explain why it was relatively inactive for ORR.

XPS analysis showed that the oxygen content increased significantly with the use of thiophene as a growth promoter. Oxygen content went from under 2 atomic% of the surface when no thiophene was used to more than 15% when 8.9% thiophene was introduced into the feed stream. While some of the oxygen content can be attributed to the sulfate species formation, the contribution from sulfate in the O 1s region does not account for all of the oxygen increase. It appears that the presence of sulfur may promote
Figure 22. XPS N 1s region deconvoluted for select CN$_x$-thiophene catalysts (labels are mol% thiophene in acetonitrile solution). As published in$^{325}$. 

the addition of oxygen species onto the carbon. Five types of oxygen were identified from the O 1s spectra, as deconvoluted on representative catalysts in Figure 23. These species can be identified as physically adsorbed oxygen at 530.1 eV$^{336}$; carbonyls and
quinones at 531.0 eV; sulfur-oxygen compounds at 531.6 eV; ethers, and C=O in anhydrides or lactones at 532.3 eV; and ether oxygens in anhydrides or lactones at 533.3 eV. A peak fit with fewer curves fails to recognize oxygen-sulfur species and quinone species, although we have evidence of their presence from XPS (S 2p region) and electrochemistry testing, respectively. The FWHM of the peaks remains reasonable at about 1 eV on all of the fits using five curves and have peak locations that match multiple literature reports well. The typical oxygen species found in graphite and their binding energy assignments are shown in Figure 24. The composition fractions changed little with sulfur content, with each component making up 15-25% of the oxygen spectra, this may also be due to the combination of oxygen species identified in the literature at each binding energy.

While no trend in selectivity with thiophene concentration or resulting sulfur content of the catalysts was observed, a trend in selectivity with oxygen surface content was observed. Selectivity of the catalysts increased with oxygen content as shown in Figure 25a where the oxygen content was normalized for the surface area of the catalysts. The inset to Figure 25a is a visual comparison of the ring current (corrected for collection efficiency) to the absolute disk current. A series of curves used in the calculation of the selectivity of the catalyst from RRDE testing is shown in Figure 25b. Due to the fairly even distribution of types of oxygen species on the catalyst surface, no one type of oxygen (from XPS results) was found to control the selectivity trend with oxygen functionalization. The presence of oxygen may contribute to the complete formation to
water. This was also observed on the CNₙ catalysts in a separate study when they were treated with nitric acid to add oxygen functional groups. Some researchers have

Figure 23. XPS O1s region deconvoluted for select CNₓ-thiophene catalysts (labels are mol% thiophene in acetonitrile solution). As published in.\textsuperscript{323}
Figure 24. Locations of possible oxygen functional groups by XPS binding energy. As published in \textsuperscript{225}.

hypothesized that the quinone/hydroquione groups play a role in oxygen reduction \textsuperscript{169,300}, though no clear trend in our study was observed with the quinone groups when comparing them to the selectivity of the catalysts found.

5.2.6 Stability of Sulfur in CN\textsubscript{x} Nanostructures

Once it was determined that thiophene could be used as a growth promoter for CN\textsubscript{x} and that the ORR activity was not affected by the presence of sulfur in the final CN\textsubscript{x} product, further studies were performed to examine if sulfur species might elute under conditions that would be relevant to an actual fuel cell environment. RRDE testing does not readily reveal the ability of a catalyst to withstand the fuel cell environment for long durations without activity loss, material degradation, or leaching of the catalyst components into other parts of the fuel cell. To address the preliminary concerns of degradation and leaching, temperature programmed oxidation (TPO) and temperature
programmed desorption (TPD) experiments were performed. In addition, desorption tests were also performed in the presence of water to mimic the humidified conditions of a fuel cell environment better.

The temperature at which significant oxidation of carbon materials begins can be a marker for the orderliness of the material and can imply what the oxidation resistance over long periods of time may be for the material. In addition, the chemical species that are evolved during oxidation indicates the chemical composition of the material. TPO experiments were performed in a TGA-DSC instrument connected to a mass spectrometer for product analysis. It was found that all CNₙ-thiophene catalysts had similar oxidation properties to CNₙ made without thiophene, as shown by the TG signal in Figure 26a. Significant oxidation of these catalysts began at about 485°C. While the largest mass loss occurred for the CSₙ catalyst at the same temperature as the CNₙ-thiophene catalysts, an initial mass loss of 18% was observed beginning at about 220°C. From the mass spectrometry data collected at the outlet of the reaction, a significant SO₂ peak was observed for the CSₙ catalyst during the 18% mass loss region (Figure 26b). The other catalysts made with varying levels of thiophene also had SO₂ evolved at this temperature, but with signal intensities more than an order of magnitude smaller than the 100% thiophene catalyst. This small amount of SO₂ evolution on the CNₙ-thiophene catalysts did not cause significant mass loss due to the minimal amount evolved. During the oxidation period beginning at about 485°C, carbon oxidation, nitrogen oxidation and sulfur oxidation products were observed in the product gas analysis. It was observed that CO₂ evolved earlier than the NOₓ and SO₂ during the final oxidation stage. Carbon that
was less graphitized or contained more defects may begin the oxidation process before the more ordered carbon\textsuperscript{305}. From the product analysis, it appears that the nitrogen and sulfur imbedded in the carbon came more from the latter type of carbon. Overall, the TPO results suggest that there are two-types of sulfur in the CN\textsubscript{x}-thiophene and CS\textsubscript{y} catalysts – sulfur that was easily evolved from the surface and sulfur that was incorporated into the carbon matrix.
**Figure 25.** a) Selectivity, $n$, (number of electrons transferred per oxygen molecule) from RRDE as a function of normalized oxygen surface content. Inset: Visual comparison of disk (absolute current) to ring (after adjustment for theoretical collection efficiency) currents at 100rpm in oxygen saturated 0.5M H$_2$SO$_4$ for CN$_x$-8.9%thiophene. b) Comparison of ring to disk currents used in determination of selectivity from RRDE. System is oxygen-saturated 0.5M H$_2$SO$_4$ with background currents subtracted for both ring and disk. *As published in* \textsuperscript{325}. 
Figure 26. TPOs ran in 10%O₂/He a) TG signal, b) Mass signals for 44 (CO₂), 30 (x50) (NOₓ), and 64 (x150 for CNₓ-1.8%, 3.6%, 5.5% and 8.9% thiophene; x10 for 100% thiophene catalyst) (SO₂). *As published in*\textsuperscript{325}. 
To further study the two types of sulfur observed and to evaluate the desorption properties of the catalysts, TPD experiments were performed on the CN\textsubscript{x}-thiophene catalysts that were immediately followed by TPOs. From these TPD experiments where the temperature was ramped in He to 900°C before cooling under the same atmosphere, an SO\textsubscript{2} desorption peak was observed that began at about 175°C and ended about one hundred degrees later (an illustration of this is shown for the CN\textsubscript{x}-3.6% thiophene catalyst experiment in Figure 27a). This peak corresponds well to the sulfur peak observed during the TGA-TPO experiments discussed above, suggesting that the early sulfur evolution in the TPOs was due to the desorption of adsorbed sulfur on the surface of the catalyst. The TPO experiments that immediately followed the TPD also showed sulfur oxidation during the carbon oxidation (Figure 27b). The information gained from the TGA-TPO and TPD-TPO experiments support the sulfur species identified by XPS, namely elemental sulfur, S-O and S-C. The S-O sulfur would be desorbed at lower temperatures and the sulfur which was incorporated into the graphite matrix, i.e., S-C, was only released during the carbon oxidation.

While TPD-TPO experiments were useful in verifying the types of sulfur species present in the CN\textsubscript{x}-thiophene catalysts and the temperatures at which sulfur began to evolve from the surface of the catalyst, the impact of the high-humidity fuel cell environment may alter these properties, especially the desorption temperatures. To address this, TPD experiments were repeated by introducing 10% water into the He feed stream during temperature ramping to 900°C (labeled “wet TPD”). Wet TPD
Figure 27. TPD-TPO experiment for CN$_x$-3.6% thiophene a) TPD in He showing mass signals 18 (H$_2$O), 44 (CO$_2$) and 64 (SO$_2$), b) TPO in 5%O$_2$/He showing mass signals 30 (NO$_x$), 44 (CO$_2$) and 64 (SO$_2$). As published in$^{325}$.

Experiments were followed by TPO after the catalyst was cooled in He. It was found that sulfur desorption was not significantly affected by the presence of water. As shown in Figure 28a, the desorption of sulfur began at about the same temperature as when it did in
dry conditions. Also, to be noted from the wet-TPD was that water began to oxidize the CNₓ catalysts at about 700°C. The TPO immediately following the TPD (shown in Figure 28b) also did not show any early sulfur desorption, indicating that all adsorbed sulfur on the surface of the catalyst was removed during the initial heat ramp. During the carbon oxidation stage, small quantities of SO₂ were still observed. The temperature of the sulfur desorption and carbon oxidation in both the presence of water and the presence of oxygen are significantly higher than the operating temperatures for PEM and DMFC of 60-80°C. This should limit the amount of sulfur desorption into the fuel cell and carbon oxidation during operation. Pretreatments of the catalyst could also be performed to reduce the risk of any sulfur contamination.

5.3 Thiophene Usage as a Growth Promoter Concluding Remarks

It was shown that thiophene can be used as a growth promoter in the acetonitrile pyrolysis production of CNₓ catalysts for the oxygen reduction reaction. Low levels (2-5mol%) of thiophene promote carbon deposition without significantly altering the carbon nanostructure. Even though sulfur was incorporated into the CNₓ both as adsorbed elemental sulfur and its oxides or S-C, the ORR activity was not impacted. Selectivity of the catalyst to water formation was not a function of thiophene used as a growth promoter, but rather a function of the amount of oxygen functional groups present on the
CN$_x$ surface. The use of thiophene did increase the amount of oxygen functional groups present.

If the CN$_x$-thiophene catalysts were pretreated in an inert atmosphere at 250-300°C, the adsorbed sulfur could be removed from the surface of the catalyst, significantly reducing the possibility of sulfur leaching into the fuel cell.
Figure 28. Wet-TPD-TPO experiment for CN$_x$-3.6% thiophene a) wet-TPD in 10%H$_2$O/He showing mass signals 44 (CO$_2$) and 64 (SO$_2$), b) TPO in 5%O$_2$/He showing mass signals 30 (NO$_x$), 44 (CO$_2$) and 64 (SO$_2$). As published in$^{325}$. 
CHAPTER 6. Impact of Oxygen Functional Groups on CN$_x$ ORR Catalysts

Published in part in *Topics in Catalysis*\textsuperscript{199}

6.1 Oxygen Functional Groups on Carbon and their Potential Role in ORR

Several important questions remain about the CN$_x$ nanostructures and their performance as ORR catalysts. While previous studies in the research group showed a correlation between the pyridinic-N content and ORR activity\textsuperscript{140,142,145}, it may still be possible to functionalize the graphite surface further through different treatments. There is a large volume of literature on surface functionalization of carbon\textsuperscript{76,118,121,169,202,299-304,308-310,312} and it may be possible to tailor the surface composition of CN$_x$ materials through such techniques. It is also important to examine the stability of these materials through various treatments in different media.

Carbons are oxidized to change their hydrophilic properties\textsuperscript{299}, increase their reactivity\textsuperscript{300} and to create anchoring sites for other functional groups or metals\textsuperscript{169,301-304}. 
A wide variety of oxygen functional groups can be found on the surface of carbons, depending upon the type of carbon and oxidation treatments. Nitric acid treatments have been used to oxidize carbon. While nitric acid treatments on carbon have shown an increase in oxygen functional groups, they also led to the addition of more surface nitrogen. Researchers investigating ORR activity for PEM and DMFC ORR catalysts also found that oxidizing carbon-containing catalysts aided in the improvement of activity. Some of these researchers state that the addition of the oxygen groups to the surface aided in cobalt or iron dispersion for the metal-N-C catalysts being studied. ORR activity was found to be proportional to the oxygen content when nitrogen was not present in the carbon catalyst. When nitrogen and oxygen groups were present on the catalyst surface, they found that nitrogen controlled the ORR activity. It has also been shown that nitrogen incorporation through ammonia treatment on carbon black is much more effective when the carbon has been oxidized with nitric acid first. While some researchers believe that oxygen groups contribute to higher ORR activity through better incorporation of nitrogen and metal particles, some have attributed the ORR activity to quinone/hydroquinone oxygen groups in catalysts which are oxidized carbons containing copper. In these catalysts it is believed that the copper acts as an adsorption site for the oxygen during ORR, but the quinone/hydroquinone site is the actual active site.
6.2 Results & Discussion

6.2.1 CN\textsubscript{x} Treated with HNO\textsubscript{3}

With the above findings about oxygen functional groups in mind, nitric acid treatments were studied using CN\textsubscript{x} grown over Fe/MgO that had been washed with HCl to remove the magnesia and exposed iron. These nitric acid-treated catalysts were labeled CN\textsubscript{x}-HNO\textsubscript{3} in this study. After three hours of treatment in concentrated nitric acid, the suspension containing the CN\textsubscript{x} and nitric acid was amber in color, suggesting partial removal of carbon tars and amorphous carbons from CN\textsubscript{x}. While some carbon was removed, it was not a significant portion. Greater than 90\% of the CN\textsubscript{x} catalyst mass was collected through the vacuum filtration process.

Significant change to the CN\textsubscript{x} nanostructures was not observed when the pre- and post-treated catalysts were studied with TEM. At low magnifications (as shown in Figure 29a and c), the nanostructure appeared to be consistently stacked cup nanofibers and nanocubes for both the CN\textsubscript{x} and CN\textsubscript{x} – HNO\textsubscript{3} samples, as expected with CN\textsubscript{x} catalysts grown over Fe/MgO. The graphitic planes did not appear to be affected either, as shown in the high-resolution images of Figure 29b and d.
Figure 29. TEM images of a) and b) CN$_x$ grown on Fe/MgO, and c) and d) CN$_x$-HNO$_3$. 
*As published in$^{199}$.*

While the nanostructure of the CN$_x$ remained intact, the surface species were altered with the nitric acid treatment. Table 3 lists the surface composition of both
catalysts as analyzed with XPS. A four-fold increase was observed in oxygen content on the surface of the CN_x-HNO_3 catalyst. This is consistent with other studies involving surface oxidation with nitric acid. The O 1s region spectra did not change appreciably with the nitric acid treatment (as shown in Figure 30), suggesting that CN_x catalysts already contain a similar distribution of oxygen species compared to CN_x treated with HNO_3. The types of oxygen present in both materials and their XPS binding energy included physisorbed oxygen (530.1 eV)^{336}, quinones and carbonyls (531.0 eV)^{308,318}, C=O in anhydrides or lactones and ethers (532.3 eV)^{308,318} and ether oxygens in lactones or anhydrides (533.3 eV)^{308,318}. The nitric acid treatment only appeared to increase the quantity of oxygen on the surface. While the table indicates that the portion of the surface attributed to nitrogen decreases slightly with nitric acid treatment, the ratio of N to C remains constant. This indicates that the nitrogen content most likely did not change significantly but is reduced because of the large oxygen surface coverage. The pyridinic-N component of the N 1s region increased from 24.1% to 28.8% with nitric acid treatment. The acid treatment may be incorporating small amounts of nitrogen into the graphitic edges from the HNO_3 source, but this is still unclear.
Table 3. Surface species (atomic %) on CN$_x$ and CN$_x$-HNO$_3$ from XPS analysis. As published in$^{199}$

<table>
<thead>
<tr>
<th></th>
<th>CN$_x$</th>
<th>CN$_x$-HNO$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>O 1s</td>
<td>1.5</td>
<td>6.5</td>
</tr>
<tr>
<td>N 1s (total)</td>
<td>7.7</td>
<td>7.2</td>
</tr>
<tr>
<td>Pyridinic (portion of N)</td>
<td>24.1</td>
<td>28.8</td>
</tr>
<tr>
<td>C 1s</td>
<td>90.8</td>
<td>86.3</td>
</tr>
</tbody>
</table>

Figure 30. O 1s XPS spectra for CN$_x$ and CN$_x$-HNO$_3$. 

107
The combined retention of nanostructure, increase in oxygen surface content, and increase in pyridinic-N, appeared to result in an overall increase in the catalytic performance of the CN$_x$-HNO$_3$ catalyst. As shown in Figure 31, the ORR activity for CN$_x$-HNO$_3$ increased both in onset of activity and current density. In addition, the selectivity, as illustrated in the inset to Figure 31, significantly improved as well. Further treatments and characterization of the CN$_x$-HNO$_3$ catalyst are required to better determine the impact of each effect on the improved activity and selectivity as well as any synergetic effects.

Figure 31. Comparison of ORR activity for CN$_x$ and CN$_x$-HNO$_3$ measured using RRDE at 1000 rpm. Inset: Selectivity of CN$_x$ and CN$_x$-HNO$_3$. 

108
6.2.2 Additional Oxygen Functional Group Observations

In addition to directly studying the oxygen functional groups, several of the studies reported in other chapters and published elsewhere have suggested that oxygen functional groups play several roles.

Oxygen functional groups can be added to nitrogen-free carbon nanostructures, such as the case with nanofibers with basal plane exposure and stacked platelet nanofibers reported in another chapter of this volume, as a processing step before nitrogen introduction. While the intent was to create locations on the graphitic nanofibers where ammonia could incorporate nitrogen at high temperature through HNO₃:H₂SO₄ acid oxidations, a significant amount of oxygen was added. For the stacked platelet nanofibers, 15.4 atomic% oxygen was found to be on the surface after acid oxidation. Prior to this oxidation step only 1.5% oxygen was located on the surface. Similar increases were observed with nanofibers with basal plane exposure treatment, except at lower levels due to the low graphitic edge plane exposure. Acid oxidation pretreatments proved to be important in being able to incorporate nitrogen into the carbon nanostructure through high temperature ammonia treatment. Without the oxygen functional groups present first, the ammonia treatment was not as successful in incorporating nitrogen.
Activity testing showed that addition of oxygen functional groups alone on these nanofibers did not have a significant impact on ORR activity or selectivity.

In a separate study examining the impact of thiophene as a growth promoter in CN\textsubscript{x} catalysts (also in a separate chapter and published in *Applied Catalysis B: Environmental*\textsuperscript{325}), it was found that use of thiophene increased the affinity for surface oxygen to be present on the CN\textsubscript{x} catalysts produced. The use of thiophene in the growth process allowed for surface oxygen to increase to 15.4\% of the surface compared to only 1.9\% surface coverage for CN\textsubscript{x} catalysts grown in the absence of the thiophene growth promoter. While changes in oxygen functional group concentration was not found to alter the ORR activity, selectivity to water formation was observed to increase with total oxygen surface content. There was no trend in any one type of oxygen functional group as identified by XPS fitting, suggesting that there may be multiple types of oxygen playing a role and that further investigation is needed to identify the types.

### 6.3 Conclusions for Oxygen Functional Groups in ORR

Preliminary observations on the role of oxygen functional groups in ORR performance were made on several systems. It was found that HNO\textsubscript{3} treatments to CN\textsubscript{x} materials improved both ORR activity and selectivity. HNO\textsubscript{3} treatments significantly increased the oxygen surface content of the catalyst, suggesting that oxygen content had a role in improved ORR performance. CN\textsubscript{x} materials produced with thiophene as a growth
promoter supported this observation that increased oxygen groups improved ORR performance. When thiophene was used as a growth promoter, the oxygen surface content increased as did the ORR selectivity of the catalyst. Oxygen functional group impact was not apparent when there was no nitrogen incorporated into the carbon nanostructure, as was the case with nanofibers with basal plane exposure and stacked platelet nanofibers.
CHAPTER 7. Role of Graphitic Edge-Plane Exposure in Carbon Nanostructures for Oxygen Reduction Reaction

As submitted to Journal of Physical Chemistry C

7.1 Motivation in Studying Role of Graphitic Edge-Plane Exposure

From work in our research group\textsuperscript{140,142,145} and others\textsuperscript{205}, carbon nanostructure has been proposed to have a role in carbon-based ORR catalyst performance. We have previously reported that nitrogen-containing carbon catalysts with higher graphitic edge plane exposure, such as stacked cups compared to nanotubes, have higher ORR activity\textsuperscript{140,142,145}.

Graphitic plane orientation and edge plane exposure of nanostructures can be controlled by altering the nanofiber growth conditions\textsuperscript{237,255,339}. Changes to the growth temperature, medium and fiber growth catalyst can significantly alter the resulting carbon nanostructures produced\textsuperscript{255}. Stacked platelets, stacked cups and herringbone nanofibers
are commonly used when high edge-plane exposure is desired\textsuperscript{220,229,242,340}. Nanotubes are commonly the nanofiber of choice when minimal edge plane exposure is desired\textsuperscript{242,341}.

The intent of work discussed in this chapter was to study the role of carbon nanostructure in ORR carbon-based catalysts by comparing nanofibers with high graphitic edge-plane exposure (stacked platelets) to nanofibers with very little edge-plane exposure (nanofibers with basal plane exposure) as model structures. These nanofibers have been grown and treated to incorporate nitrogen into the nanostructure. The objective of this study is not to develop high performance catalyst materials, but rather probe the role of nanostructure using these model systems.

7.2 Results and Discussion

7.2.1 Synthesis and Physical Characterization

The successful preparation and treatment of well controlled carbon nanostructure types is not trivial and must be discussed before any conclusions can be made about their use as model catalyst systems in ORR.

Small changes in Fe:Cu ratio and nanofiber growth temperature can change the carbon nanostructure produced significantly. TEM analysis of the nanofibers produced was performed to verify that stacked platelets with high edge plane exposure were prepared. Figure 32 shows examples of the nanofibers prepared using 95:5 Fe:Cu
catalyst at a 600°C growth temperature after HCl washing. Nanofiber diameters varied from 50nm to 300nm, with the nanofiber shown in Figure 32a exhibiting a typical diameter. Most important for this study are the orientation and exposure of the graphitic edge planes. Under these preparation conditions, graphitic sheets were positioned perpendicular to the longitudinal axis of the nanofiber, allowing for large degrees of graphitic edge plane exposure and minimal basal plane exposure, as illustrated in the inset to Figure 32a. Figure 32b shows the graphitic edge plane exposure for these stacked platelets at a higher magnification. The perpendicular orientation of the graphitic sheets verified that stacked platelet nanofibers were produced. Additionally, all nanofibers studied with TEM using the 95:5 Fe:Cu catalyst had similar shape and perpendicular graphitic edge plane exposure.
Figure 32. TEM images of stacked platelets-HCl washed. Inset to a): Illustration of graphite sheet orientation in stacked platelets. Box in a) refers to region where b) was taken. *As submitted to*.

In contrast, carbon deposition over 6:4 Fe:Cu at 675°C produced a variety of nanofibers, as shown in Figure 33. Two main types of nanofibers were observed; large helical nanofibers (Figure 33a-b) and smaller hollow tubes (Figure 33c). The helical-type nanofibers had diameters of 200nm to 500nm. While the hollow tubes had diameters of 30nm to 100nm. Interestingly, high resolution analysis of both types of nanofibers produced from the 6:4 Fe:Cu growth catalyst showed long graphitic sheets parallel to the longitudinal axis with low levels of edge plane exposure and high levels of graphitic basal plane exposure, even though at lower magnification the nanofibers appeared very different (insets to Figure 33a-c). After the observation that both types of nanofibers grown from 6:4 Fe:Cu at 675°C had mostly graphitic basal plane exposure, these
nanofibers were deemed acceptable as a comparison structure to the stacked platelet nanofibers with high edge plane exposure. These nanofibers with basal plane exposure were preferred to a commercial multi-walled nanotube (MWNT) because the physical dimensions of the nanofibers with basal plane exposure were more similar to the stacked platelets than the very small diameter MWNTs.
Figure 33. TEM images of nanofibers with basal plane exposure after HCl washing. Insets represent the lower-magnification images of the same nanofibers. *As submitted to*\textsuperscript{338}.

It is known that the incorporation of nitrogen into graphitic materials can be difficult\textsuperscript{118}. To aid in the nitrogen incorporation, mild oxidation of the carbon can be
performed. In concentrated acid oxidations, such as the HNO₃ and H₂SO₄ used in this study, defects are created in the graphitic structure providing sites for oxygen functional groups to attach. A constant temperature treatment at 60°C was selected as opposed to refluxing. A nanofiber with basal plane exposure that has a high concentration of surface defects would result in losing the objective of the study to examine the role of graphitic edge plane exposure. While the oxidation temperature was rather mild, oxidation was obviously occurring, as seen through even simple hydrophobicity observations. When both types of nanostructures were suspended in water, they tended to not disperse well, indicating their hydrophobic nature. When the nanofibers were added to the HNO₃:H₂SO₄ solution, they immediately dispersed into the solution and did not settle out even with repeated washings with water. This indicated a change to their hydrophobic nature, indicative of addition of oxygen functional groups on the surface of the nanofibers.

Significant differences in the carbon nanostructure were not observed with oxidation treatment using TEM analysis (images not shown), also verifying that the oxidation procedure was rather mild.

Ammonia treatments at elevated temperatures are known to incorporate nitrogen into carbon matrices. With increased graphitization of the carbon, nitrogen-incorporation becomes more difficult, hence the need to create sites for ammonia attack through oxidation arises. Ammonia is proposed to introduce nitrogen into carbon through a corrosion process where ammonia directly reacts with the carbon to form HCN and H₂ or exchanges with the oxygen functional groups on the carbon.
surface, ultimately incorporating nitrogen into the carbon\textsuperscript{123}. In this study, after a 4-hour ammonia treatment at 600°C, little mass was lost (19\%) from the stacked platelets, as listed in Table 4 of mass losses with ammonia treatment. A 4-hour treatment duration at 900°C in ammonia also saw minimal mass loss. Interestingly, after 19.5 hours at 900°C in an ammonia-rich stream, a significant percentage of the mass (76\%) was lost from the starting acid oxidized stacked platelets. This suggests that not only temperature, but also duration is important for significant ammonia corrosion on the carbon to occur. The oxidation pretreatment was also found to increase the ammonia corrosion. As a comparison, an ammonia treatment on unoxidized stacked platelets for 19.5 hours at 900°C led to a 42\% mass loss only. For the oxidized nanofibers with basal plane exposure treated at 900°C for 19.5 hours in ammonia, a mass loss of 47\% was also observed, suggesting that ammonia was able to successfully corrode carbon and incorporate nitrogen into the nanofibers. However, further analysis was required using XPS and temperature programmed oxidation experiments to verify nitrogen incorporation.
### Table 4. Mass loss during ammonia treatment. As submitted to\textsuperscript{338}.

<table>
<thead>
<tr>
<th>Sample &amp; Treatment</th>
<th>Mass Loss (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stacked platelets -HCl – HNO\textsubscript{3}:H\textsubscript{2}SO\textsubscript{4}– 600°C NH\textsubscript{3} (4 hr)</td>
<td>19</td>
</tr>
<tr>
<td>Stacked platelets -HCl – HNO\textsubscript{3}:H\textsubscript{2}SO\textsubscript{4} – 900°C NH\textsubscript{3} (4 hr)</td>
<td>7</td>
</tr>
<tr>
<td>Stacked platelets - HCl – HNO\textsubscript{3}:H\textsubscript{2}SO\textsubscript{4} – 900°C NH\textsubscript{3} (19.5 hr)</td>
<td>76</td>
</tr>
<tr>
<td>Stacked platelets-HCl-900°C NH\textsubscript{3} (19.5 hr)</td>
<td>42</td>
</tr>
<tr>
<td>Nanofibers with basal plane exposure - HCl – HNO\textsubscript{3}:H\textsubscript{2}SO\textsubscript{4} – 900°C NH\textsubscript{3} (19.5 hr)</td>
<td>47</td>
</tr>
</tbody>
</table>

The significant mass loss during ammonia treatment at 900°C for extended time would suggest that the carbon nanofiber structures may be attacked or altered. TEM analysis did not reveal significant changes in the carbon nanostructure as indicated by examining the graphitic planes of Figure 34.
Figure 34. TEM images of a) stacked platelets and b) nanofibers with basal plane exposure after acid oxidation and ammonia treatment at 900°C for 19.5h. As submitted to 338.

7.2.2 Chemical Characterization

7.2.2.a X-Ray Photoelectron Spectroscopy

Beyond the physical structure of the nanofibers used in this study, it is important to know the chemical composition. X-Ray photoelectron spectroscopy (XPS) was used to analyze the types of surface species on the nanofibers. Table 5 shows surface species content for stacked platelets. As expected, the stacked platelet surface was largely composed of graphitic carbon.
Table 5. Surface species concentrations from XPS analysis on stacked platelets after oxidation and ammonia treatments. As submitted to338.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Species Concentration (atomic %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe 2p</td>
</tr>
<tr>
<td>HCl</td>
<td>0.4</td>
</tr>
<tr>
<td>HCl – HNO$_3$:H$_2$SO$_4$</td>
<td>0.0</td>
</tr>
<tr>
<td>HCl – HNO$_3$:H$_2$SO$_4$ – 600°C NH$_3$ (4 hr)</td>
<td>0.0</td>
</tr>
<tr>
<td>HCl – HNO$_3$:H$_2$SO$_4$ – 900°C NH$_3$ (4 hr)</td>
<td>0.0</td>
</tr>
<tr>
<td>HCl – HNO$_3$:H$_2$SO$_4$ – 900°C NH$_3$ (19.5 hr)</td>
<td>0.0</td>
</tr>
</tbody>
</table>

XPS analysis showed no detectable surface nitrogen in the stacked platelets prior to acid oxidation and ammonia treatments. Figure 35 shows that after acid oxidation and ammonia treatments, nitrogen was present in the stacked platelets. Depending upon the treatment, the nitrogen species and content differed. After acid oxidation treatment on the stacked platelets, 1.6 atomic % nitrogen was observed on the surface of the nanofiber. This nitrogen is residual from the HNO$_3$ used in the oxidation treatment. An assignment of N-O species$^{318}$ aligns with this assumption. The stacked platelets with the highest nitrogen content were the ones treated at 600°C in ammonia. The nitrogen spectra broadened to shift to lower binding energies with this lower temperature ammonia treatment. With increased ammonia treatment temperature and duration, the nitrogen surface content decreased and the species appeared more prevalent at lower binding energies. It is likely that after the 600°C treatment, there was a mix of nitrogen bonded to
the surface oxygen and nitrogen beginning to be incorporated into the graphitic lattice. At higher temperatures, the oxygen functional groups are being removed and at the locations where the oxygen was once attached, nitrogen is being substituted by incorporating into the carbon in the form of pyridinic-N. Typical binding energies for the pyridinic-N are 398.0-398.9 eV\textsuperscript{121,342}. 
Figure 35. N 1s region of the X-ray photoelectron spectra comparing stacked platelets after oxidation and ammonia treatments. Signal intensities were magnified where noted for comparison. As submitted to\textsuperscript{338}.

Oxygen content also follows the discussion of the nitrogen content for stacked platelets. A large amount (15.4\%) of surface oxygen is present immediately following acid oxidation of the stacked platelets. The quantity of surface oxygen diminishes significantly with ammonia treatment. There is a possibility that nitrogen is both
exchanging with surface oxygen (as evidenced by the increase at 600°C in nitrogen content) and desorbing from the surface with temperature as well.

As seen from Figure 36, there was a wide distribution of oxygen species present on the stacked platelets. O 1s oxygen functional group assignments include: physically adsorbed oxygen (530.1 eV)\textsuperscript{336}, quinones and carbonyls (531.0 eV)\textsuperscript{308,318}, sulfur-oxygen functional groups (531.6 eV)\textsuperscript{337}, C=O in anhydrides or lactones and ethers (532.3 eV)\textsuperscript{308,318}, ether oxygens in lactones or anhydrides (533.3 eV)\textsuperscript{308,318} and oxygen atoms in carboxyl groups (534.2 eV)\textsuperscript{308,318}. While there was not a clear trend between treatment used and the nature of the functional groups formed, a few interesting observations were made beyond total oxygen content. The lower binding energy species appeared to be most resilient to ammonia attack or formed most readily when exposed to the atmosphere after treatment. Large quantities of quinone or carbonyl groups were added with acid oxidation and removed or masked any physisorbed oxygen found on the stacked platelets.
Figure 36. O 1s region of the X-ray photoelectron spectra comparing stacked platelets after oxidation and ammonia treatments. Signal intensities were magnified where noted, for comparison. As submitted to\textsuperscript{338}.

If ammonia was incorporating nitrogen into the carbon matrix through an oxygen functional group pathway, the loss of oxygen species with ammonia treatment would be expected. It has been proposed in the literature that ammonia exchanges with C=O
oxygen functionalities on carbon nanostructures to incorporate nitrogen into the carbon. Most of the functionalities that can be identified by XPS have a C=O feature that could participate in the nitrogen exchange with ammonia. This would also explain why the small amount of carboxylic species disappears with ammonia treatments, as did the lactone and anhydride assignment for the stacked platelets after extended duration ammonia treatment at 900°C. The acid-oxidized stacked platelets had a large quantity of carbonyl and quinone-type groups identified, that again, decreased with ammonia treatment. Some of these most likely desorbed from the surface with simple heating, but a portion may have been subject to ammonia attack.

Also a product of the acid oxidation, a small amount of sulfur was detected on the surface of the acid oxidized stacked platelets. This appeared to be a sulfate species located on the carbon surface as seen through the S 2p\text{1/2} assignment of 163.8 eV, shown in Figure 37. The absence of detectable lower binding energy sulfur species indicates that little, if any sulfur was incorporated into the nanostructure. With ammonia treatment, sulfur was no longer detectable in XPS, suggesting it was also part of an oxygen functional group either exchanged with nitrogen or desorbed from the graphitic surface with treatment.
Comparing the surface composition of the nanofibers with basal plane exposure to the stacked platelets, overall there were fewer surface species present on the nanofibers with basal plane exposure after each treatment, as seen in Table 6. Acid oxidation of the nanofibers with basal plane exposure was effective in adding oxygen surface functionalities, however, at a lesser degree than the treatment of stacked platelets. The absence of graphitic edges for the oxygen functional groups to readily adhere to is likely to be the reason behind the reduced amount of surface oxygen after acid oxidation on the nanofibers with basal plane exposure. It has been reported that, during oxygen functionalization of nanotubes, defects in the basal planes are created for the oxygen functional groups to adhere to\textsuperscript{261}. In this study, creation of more defects was not desirable since it would make the nanofibers with basal plane exposure become more and
more like the high-edge-exposure stacked platelets. Some of the oxygen was required, however, to be able to incorporate nitrogen into the nanofibers with basal plane exposure through the oxygen exchange process with ammonia treatment.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Species Concentration (atomic %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe 2p</td>
</tr>
<tr>
<td>HCl</td>
<td>0.0</td>
</tr>
<tr>
<td>HCl – HNO₃:H₂SO₄</td>
<td>0.0</td>
</tr>
<tr>
<td>HCl – HNO₃:H₂SO₄ – 900°C NH₃ (19.5 hr)</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Table 6. Surface species concentrations from XPS analysis on nanofibers with basal plane exposure after oxidation and ammonia treatments. *As submitted to*[^38].

There were several observations that can be made by comparing the oxygen species on the nanofibers with basal plane exposure to the stacked platelets, as seen in Figure 38. The untreated nanofibers with basal plane exposure had less physisorbed oxygen than the stacked platelets. This may be due to the lack of edge planes for the oxygen to adhere to. With acid oxidation, the largest component was again quinones and carbonyls, similar to the spectra taken over stacked platelets. After ammonia treatment at 900°C for 19.5 hours, the nanofibers with basal plane exposure had very little oxygen left. A large component was physisorbed oxygen, which is likely due to exposure to the atmosphere after treatment. It is possible that most of the reactive oxygen was exchanged
during ammonia treatment. Another explanation for the reduced amount of non-physisorbed oxygen species on the surface of the nanofibers with basal plane exposure compared to the stacked platelets, is that oxygen functional groups are likely not as well adhered to the carbon surface on the basal planes. This would allow for more of the oxygen functional groups to desorb from the surface of the carbon with heating.

**Figure 38.** O 1s region of the X-ray photoelectron spectra comparing nanofibers with basal plane exposure after oxidation and ammonia treatments. Signal intensities were magnified where noted for comparison. *As submitted to*.\(^{338}\)
After ammonia treatment of the acid-oxidized nanofibers with basal plane exposure, only a trace amount of nitrogen was observed in XPS and could not be quantified. Oxygen groups were largely evolved off after ammonia treatment as well. Although there was no significant nitrogen incorporation, the mass losses reported above for these nanofibers still suggest that ammonia corrosion was occurring.

7.2.2.b Temperature-Programmed Oxidation Experiments

Temperature-programmed oxidation (TPO) experiments were performed to further study the composition of the nanofibers and the stability of the carbon. The temperature at which carbon oxidizes can be indicative of the type of carbon, degree of graphitization and edge plane exposure.

The TPO profiles for stacked platelets after various treatments are presented in Figure 39. The mass signals for 44 (CO$_2$), 30 (NO$_x$) and 64 (SO$_2$) are shown. As seen from the figure, a shift in the carbon oxidation to higher temperatures with treatment, suggesting a change in the oxidation resistance. As treatment severity increases on the stacked platelets from simple HCl wash to high temperature ammonia treatments, the easily oxidizable carbon continues to be removed, thereby shifting the observed oxidation onset temperature from 430°C to 515°C. For the acid-oxidized stacked platelets, early evolution of nitrogen and sulfur groups is observed prior to carbon oxidation. This suggests that much of the nitrogen and sulfur groups were attached to the surface of the
stacked platelets rather than incorporated into the graphitic matrix, which was also observed in XPS. However, there were small amounts of nitrogen and sulfur that evolved during the carbon oxidation period suggesting that a small amount of the nitrogen and sulfur was incorporated into the graphitic matrix with acid oxidation treatment, even though they were below XPS detection limits.
Figure 39. Temperature programmed oxidation profiles for stacked platelets after oxidation and ammonia treatments. Gray is m/z=44 (CO$_2$), pink is (m/z=30) x50 (NO$_x$), green is m/z=64 (SO$_2$) x500 for all treatments except “HCl-HNO$_3$:H$_2$SO$_4$” which is x100. As submitted to$^{338}$. 
After ammonia treatments, the low temperature surface species evolution during TPO was not observed. Larger quantities of nitrogen were observed to evolve with the carbon oxidation, verifying the observation from XPS of a shift to more pyridinic-type nitrogen with ammonia treatment rather than surface-attached nitrogen. A small amount of sulfur left in the graphite appeared to stay in the carbon matrix even after ammonia treatment, though in lesser quantities with increased ammonia treatment severity.

TPO experiments performed on the nanofibers with basal planes revealed similar trends with treatment compared to the stacked platelet TPO experiments, as seen in Figure 40. The nanofibers with basal plane exposure had a much broader carbon oxidation envelop. This broader envelop may be due to the heterogeneity of the nanofibers with basal plane exposure, with its two types of nano-geometries. Once again, surface nitrogen and sulfur species were observed evolving from the nanofibers at low temperatures after acid oxidation treatments, supporting the XPS findings that nitrogen and sulfur are on the surface rather than incorporated into the graphitic nanostructure. The TPO experiments were able to verify that nitrogen was present in the carbon nanostructure. This finding shows that ammonia treatment was successful in incorporating nitrogen into the graphitic nanostructure, even though the nitrogen content was below quantifiable levels from XPS.
Figure 40. Temperature programmed oxidation profiles for nanofibers with basal plane exposure after oxidation and ammonia treatments. Gray is m/z=44 (CO₂), pink is (m/z=30) x50 (NOₓ), green is m/z=64 (SO₂) x500 for all treatments except “HCl-HNO₃:H₂SO₄” which is x100. As submitted to 338.

7.2.3 Activity and Selectivity Testing

The characterization results discussed above show that nanofibers with low- and high-graphitic edge plane exposure were successfully made and post-treated to incorporate nitrogen. While nitrogen levels were low compared to nitrogen-containing
carbon nanostructures (CNₙ) studied as ORR catalysts in our research group previously¹⁴₀,¹⁴₂,¹⁴₅,³₂₅, they were deemed high enough to investigate further for ORR activity.

Rotating ring disk electrode (RRDE) tests were performed on the nanofibers after each treatment process to study the role of nanostructure and composition on ORR activity and selectivity. The results obtained for the stacked platelets are shown in Figure 41. Untreated stacked platelets showed minimal oxygen reduction activity, with an onset of activity at 0.444 V vs. NHE. Both acid oxidation and ammonia treatment at 600°C on the stacked platelets showed minimal ORR activity as well. Increasing the ammonia treatment temperature on the stacked platelets to 900°C began to produce a material with some ORR activity. By increasing the ammonia treatment duration at 900°C, the activity was improved by another 300mV shift towards better ORR activity compared to the untreated stacked platelets. The additional ammonia treatment duration also saw a significant increase in current density. Selectivity results were shown to trend with ORR activity as illustrated in Figure 41b. The untreated stacked platelets had poor selectivity to water formation, while the stacked platelets treated at 900°C for 19.5 hours in ammonia had a selectivity approaching 3.9 electrons transferred per oxygen molecule, equivalent to 95% selectivity to water formation.
Figure 41. a) ORR RRDE results of stacked platelets after oxidation and ammonia treatments at 1000rpm in oxygen saturated electrolyte after background subtraction. b) Selectivity results. *As submitted to* 338.
In comparison to the stacked platelets, the nanofibers with basal plane exposure had significantly less activity under the same treatment conditions, as shown in Figure 42. Untreated nanofibers with basal plane exposure had even less ORR activity than untreated stacked platelets. Prolonged ammonia treatment at 900°C on nanofibers with basal plane exposure increased the ORR onset of activity, but only by 150 mV to a 0.565 V vs. NHE onset of activity.

**Figure 42.** ORR RRDE results of nanofibers with basal plane exposure after oxidation and ammonia treatments at 1000rpm in oxygen saturated electrolyte after background subtraction. *As submitted to*.338
While none of the materials studied would be considered good ORR catalysts, there is enough activity to use them as model systems to discuss the role that nanostructure and composition play in ORR activity.

High nitrogen contents in carbon-based catalysts are frequently cited as a significant contributor to ORR activity. Observations with the acid-oxidized stacked platelets and the stacked platelets treated with ammonia at 600°C ammonia following acid oxidation showed that gross nitrogen content does not dictate ORR performance. The location of the nitrogen plays an important role in the ORR activity. As the nitrogen species shifted to more pyridinic-N type, the ORR activity increased, even though the overall surface nitrogen content dropped by almost a factor of seven when comparing the stacked platelets treated in ammonia at 900°C to those treated at 600°C. Previous studies in our research group have also seen ORR activity trends with pyridinic-N content\textsuperscript{140,142,145}. From those studies, it was unclear if the pyridinic-N was directly impacting ORR activity or if it was merely acting as a marker for edge plane exposure, as it is located on the edge plane and the most active catalysts had both the highest graphitic edge plane exposure content and highest pyridinic-N content\textsuperscript{140,142,145}. Since the same starting stacked platelet nanofibers were used before and after ammonia treatment for this study, the role that pyridinic-N and edge plane exposure can be better distinguished. These results suggest that pyridinic-N content plays a much stronger role than edge plane exposure. Rather, edge plane exposure provides the appropriate geometry for nitrogen incorporation leading to an active site. Nanofibers with basal plane exposure, on the other hand, did not possess the right geometry for the formation of ORR active sites.
In addition to nanostructure and nitrogen, a few observations about oxygen content may also be made from this study. High oxygen contents on the nanofibers did not substantially improve the ORR activity without the presence of nitrogen incorporated into the nanostructure. A small improvement in ORR activity was observed with increased oxygen content on the nanofibers with basal plane exposure. It is possible that this improvement was due to the increase in graphitic defects created during the acid oxidation process, as current density began to approach that of the acid oxidized stacked platelets.

7.3 Conclusions to Investigation of Role of Graphitic Edge Plane Exposure

Stacked platelet nanofibers and nanofibers with basal plane exposure were successfully grown and characterized after various treatments with acids and/or ammonia. The stacked platelets, with high graphitic edge plane exposure, and nanofibers with basal plane exposure and minimal edge plane exposure, were studied before and after ammonia treatment to probe the role that nanostructure plays in ORR activity. While neither type of nanofiber had large quantities of nitrogen or was highly active for ORR, they were considered useful model systems. It was found that edge plane exposure alone does not promote ORR activity. Rather, carbon nanostructures with high edge plane exposure provide the appropriate locations for nitrogen to incorporate into the
graphitic matrix. The presence of oxygen functionalities alone were also not sufficient to have a significant impact on ORR activity.
CHAPTER 8. Effect of Ammonia Treatment on CNₙ Catalysts

8.1 Background into CNₙ Catalysts Treated with Ammonia

Ammonia treatments at elevated temperatures over carbon have been reported to introduce nitrogen into the carbon structure\(^8\)\(^{,88,118,123,135,137,138,159,187}\). The carbons used in these studies were not normally nitrogen-containing prior to ammonia treatment. Studying the effect of ammonia treatment on carbon-nitrogen materials is of interest.

Ammonia and nitric acid treatments have been studied on CNₙ materials grown over 2%Fe/MgO-HCl washed. This investigation has been undertaken to study the types of nitrogen present in the CNₙ catalysts and also attempt to improve ORR activity by increasing nitrogen content in the catalyst nanostructure.

Studies performed for this set of experiments have involved the treatment of CNₙ with concentrated nitric acid at 60°C for three hours followed by filtering and drying. These acid-oxidized CNₙ materials were treated with ammonia for study. The ammonia treatments were performed at 900°C and 600°C both in 38% NH₃ for 4 hours. Ammonia treatments followed nitric acid treatment, because the literature suggests that pretreating
carbon materials with nitric acid allows for better incorporation of nitrogen into the carbon structure. Villers, et al. proposed that ammonia exchanges with C=O oxygen functionalities on carbon nanostructures to incorporate nitrogen into the carbon. These types of functionalities are frequently present after nitric acid oxidation treatments.

For comparison of the materials several other catalysts have been treated for study including CNx-HNO3 treated at 900°C in He only for 4 hours, and CNx treated at 600°C and 900°C in ammonia without prior HNO3 treatment.

8.2 Results & Discussion

8.2.1 Ammonia Treatment Process Observations on CNx Materials

Since ammonia is known to corrode carbon, examination of the mass loss with treatment is important. Immediate differences were observed for mass loss from the varying treatment levels, as compiled in Table 7. Ammonia treatment at 600°C did not cause a significant mass loss even when the CNx was oxidized first. While it is possible to have mass loss with heat treatment without nitrogen incorporation, it is unlikely that nitrogen incorporation will occur with ammonia treatment without mass loss. This lack of mass loss after ammonia treatment at 600°C suggests that ammonia treatment at this temperature and duration may not be sufficient for significant nitrogen incorporation. When CNx catalysts were treated at 900°C more mass was lost compared to the 600°C
treatments, even when ammonia was not present during treatment. Mass loss at 900°C from the oxidized CN\textsubscript{x} without ammonia is likely due to loss of oxygen functional groups and attached carbon\textsuperscript{307,308}. Ammonia treatment at 900°C had a more significant mass loss over the oxidized CN\textsubscript{x}. This indicates that the temperatures and pretreatment were substantial enough to promote ammonia corrosion and oxygen exchange.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Mass loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>CN\textsubscript{x}-conc HNO\textsubscript{3}-900°C He</td>
<td>12.6%</td>
</tr>
<tr>
<td>CN\textsubscript{x}-conc HNO\textsubscript{3}-600°C NH\textsubscript{3}</td>
<td>7.9%</td>
</tr>
<tr>
<td>CN\textsubscript{x}-conc HNO\textsubscript{3}-900°C NH\textsubscript{3}</td>
<td>36.7%</td>
</tr>
<tr>
<td>CN\textsubscript{x}-600°C NH\textsubscript{3}</td>
<td>3.7%</td>
</tr>
<tr>
<td>CN\textsubscript{x}-900°C NH\textsubscript{3}</td>
<td>12.5%</td>
</tr>
</tbody>
</table>

When the oxidized CN\textsubscript{x} catalyst and the oxidized CN\textsubscript{x} catalyst treated at 900°C with ammonia were analyzed using TEM imaging, it was found that there were many more broken nanofibers in the catalyst after ammonia treatment. Figure 43 shows examples of the broken nanofiber edges in the HNO\textsubscript{3}-900°C NH\textsubscript{3} sample, while Figure 44 are examples of the larger masses of fibers prior to ammonia treatment without evident breakage of the nanofibers. These observations in TEM support the mass loss finding with ammonia treatment at 900°C over oxidized CN\textsubscript{x}. 
**Figure 43.** TEM images of broken nanofibers on CN$_x$-conc HNO$_3$-900°C NH$_3$.

**Figure 44.** TEM images of CN$_x$-conc HNO$_3$ treated.
8.2.2 Surface Species Analysis of Treated CN$_x$

Through XPS analysis, it was found that the types of nitrogen alter as the treatment path progresses. Untreated CN$_x$ materials have N 1s spectra that can be deconvoluted into three types of nitrogen (as seen in Figure 45): edge-plane exposed pyridinic-N at 398.8 eV, graphitic substituted quarternary-N at 401.1 eV and a third type which is still debated, but could be pyridinic-N-O at 402 eV$^{342}$. Similar spectra have been reported previously for CN$_x$ catalysts grown over Fe/MgO from the research group$^{144,145}$. After nitric acid treatment, only two peaks are present: 400.9 eV and 398.6 eV. These are most likely pyrrolic-N and pyridinic-N, respectively$^{342}$.

A much larger oxygen component is also revealed from the O 1s spectra (as listed in Table 8) for the CN$_x$ treated with nitric acid. This is expected, as nitric acid treatment is an oxidizing treatment that adds oxygen functional groups. Ammonia treatment causes a reduction in the amount of oxygen and the reappearance of the three nitrogen peaks seen in the untreated CN$_x$ material. The loss in oxygen content can be expected as part of the ammonia exchange process$^{123}$ and from desorption of surface oxygen species with heat treatment$^{307,308}$. After the 600°C ammonia treatment, there is an intermediate amount of oxygen left and an increase in nitrogen content. This nitrogen could be completely incorporated into the graphitic structure or some could be externally bound to oxygen groups$^{318}$. At this point in time, it is not clear why the nitrogen content decreases on the CN$_x$ that had been oxidized and then ammonia treated at 900°C. One possible reason may include that with the loss of carbon, nitrogen species are evolved from the CN$_x$ as well. This also supports the observation of less pyridinic-nitrogen after ammonia
treatment, as carbon (and nitrogen) will be evolved off of the graphitic edges first. Another is if oxygen and nitrogen groups are bound together at 600°C, then when the oxygen groups desorb, some of the nitrogen could as well.

**Table 8.** Surface species composition (atomic%) from XPS on CNₓ after ammonia treatments.

<table>
<thead>
<tr>
<th></th>
<th>CNₓ</th>
<th>CNₓ- conc HNO₃</th>
<th>CNₓ- conc HNO₃- 600°C NH₃</th>
<th>CNₓ- Conc HNO₃- 900°C NH₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>O 1s</td>
<td>1.5</td>
<td>6.5</td>
<td>1.5</td>
<td>1.3</td>
</tr>
<tr>
<td>N 1s (total)</td>
<td>7.7</td>
<td>7.2</td>
<td>8.9</td>
<td>5.7</td>
</tr>
<tr>
<td>pyridinic</td>
<td>24.1</td>
<td>40.5</td>
<td>34.4</td>
<td>26.6</td>
</tr>
<tr>
<td>C 1s</td>
<td>90.8</td>
<td>86.3</td>
<td>89.6</td>
<td>93.0</td>
</tr>
</tbody>
</table>
8.2.3 Activity and Selectivity Observations for CN$_x$ Oxidized and Treated with Ammonia

Activity and selectivity results from RRDE are shown in Figure 46. Both oxidized CN$_x$ and oxidized CN$_x$ treated at 900°C in ammonia have a promotion effect for ORR while the oxidized CN$_x$ treated at 600°C in ammonia did not. While a decrease in nitrogen is observed in oxidized CN$_x$ treated at 900°C in ammonia, TEM images showed an increase in edge plane exposure from the breakage of the nanofibers treated at 900°C in ammonia. The oxidized CN$_x$ may have improved activity because of the synergistic effects of oxygen on the surface of the catalyst. Oxygen functional groups on carbon...
have been the focus of much study on their own. It has also been observed that increase in oxygen functionality on the surface of C-N catalysts increase ORR activity slightly.

The presence of additional oxygen functional groups on the CN\textsubscript{x} surface after acid oxidation has improved selectivity according to the RRDE results. This observation has been observed on other treated CN\textsubscript{x} catalysts reported in other chapters. Ammonia treatments on the CN\textsubscript{x} also improved the selectivity towards water formation compared to untreated CN\textsubscript{x}.
Figure 46. RRDE comparison for ammonia and nitric acid treated CN$_x$. (top) Activity comparison on disk, (bottom) Selectivity comparison from ring results.
8.3 Conclusions to Studies on CN₃ Treated with Ammonia

CN₃ catalysts were oxidized with nitric acid and then treated with ammonia at either 600°C or 900°C. It was found that ammonia treatment did not increase nitrogen content with mass loss as expected. ORR activity was improved for both the oxidized catalyst and the oxidized catalyst treated at 900°C with ammonia. More extensive study of these ammonia and nitric acid treated catalysts are needed to better understand the impact of these treatments for PEM & DMFC catalysts.
9.1 Overview of Purpose of Using Boron and Phosphorus in CN_x Catalysts

Boron and phosphorus can be used in multiple ways when studying carbon nanostructures. Boron and phosphorus groups can be used as graphitic edge site blockers. They also can become heteroatom dopants to the carbon, which can alter the electronic structure of the nanostructures among other properties.

Graphitic edge site blocking can be used to probe active site locations and bondings of other species to carbon. Park and Baker have reported on a method where a boron oxide functional group can block the zigzag graphitic edge and a phosphorus oxide functional group can block the armchair graphitic edge\textsuperscript{230}. An illustration of such blocking is shown in Figure 47. Typically one graphitic edge type is blocked at a time and then the performance of the nanofiber is analyzed. When there is a significant drop in performance with site blocking, the site that was blocked can be concluded to have the active site located on it.
Boron\textsuperscript{288,343-348} and phosphorus\textsuperscript{264,347-350} have both been doped into carbon nanostructures for various purposes. The introduction treatments and type of nanofibers dictate the properties that these doped nanofibers can have. Ozaki, \textit{et al.} have shown that low levels of boron doping into nitrogen-containing carbon can improve ORR activity\textsuperscript{345,346}. Strelko, \textit{et al.}\textsuperscript{216} and Huang, \textit{et al}\textsuperscript{217} both also have shown with modeling improved electron donation properties of boron-doped carbons. In contrast Garsuch, \textit{et al.} have shown a negative impact on ORR when carbon-nitrogen thin films were doped with boron\textsuperscript{153}. This suggests that preparation and boron concentrations and types may have a significant impact on the ORR performance.
In this chapter, results at attempting to use site blocking in CN\textsubscript{x} to study ORR are discussed, as well as attempts to dope CN\textsubscript{x} catalysts with boron for improved ORR activity.

\subsection*{9.2 Graphitic Site Blocking of CN\textsubscript{x}}

It an attempt to determine the ORR active site location, CN\textsubscript{x} grown over 2\%Fe/MgO-HCl washed was site blocked using a modified procedure by Park and Baker\textsuperscript{230} that used phosphorus and boron groups to block the armchair and zigzag graphitic edge planes, respectively. CN\textsubscript{x} grown over 2\%Fe/MgO-HCl washed should be an appropriate candidate for site blocking, as it has a large proportion of stacked cup nanofibers with high edge plane exposure. To block the CN\textsubscript{x} edges, ammonium pentaborate or methyl phosphonic acid was introduced into the CN\textsubscript{x} using a wet impregnation technique. The resulting material was then calcined at 450\textdegree C to adhere the boron or phosphorus functional groups to the graphitic edge. Unattached boron or phosphorus was removed through a 1M HCl wash following calcination.

It is expected that the untreated catalyst would have the highest ORR activity and the catalyst with the active edge blocked would have the lowest ORR activity. From RRDE results of these site-blocked CN\textsubscript{x} catalysts, the expected observations were not made (Figure 48). After using boron to site block the zigzag edge, the ORR catalyst activity significantly improved compared to the untreated CN\textsubscript{x}. Site blocking with
phosphorus resulted in a catalyst that was less active than the untreated \( \text{CN}_x \), but comparable to the \( \text{CN}_x \) that had gone through a site blocking procedure without the active boron or phosphorus precursors (“Blank-Blocked \( \text{CN}_x \)”). This suggests that site blocking itself may not have been successful, but rather, boron may be promoting ORR activity on the \( \text{CN}_x \) catalyst. A second possibility is that the ammonium component of the boron precursor did not completely evolve off of the catalyst during heat treatment and it instead increased the nitrogen content of the catalyst. Further analysis is required to support or disprove this second possibility. Further study on the use of boron in \( \text{CN}_x \) catalysts is discussed in the next section of this chapter.

**Figure 48.** RRDE activity results for site-blocked \( \text{CN}_x \).
9.3 Boron Incorporation into CN\textsubscript{x}

After observing ORR activity promoting results with boron site blocking attempts on CN\textsubscript{x}, it was desired to study boron incorporation directly into CN\textsubscript{x} catalysts. Also, incorporation of low levels of boron into C-N catalysts has been reported in the literature to have a positive effect on ORR as recently reported by Ozaki\textsuperscript{345,346}. In contrast, researchers in the Dahn group observed a loss of ORR activity with thin film sputtered carbon-nitrogen catalysts containing boron\textsuperscript{153}. Higher levels of boron can cause phase separation instead of incorporation into the graphitic structure, so boron concentrations and preparation methods may be key\textsuperscript{290}.

Preliminary attempts have been made to incorporate boron into the graphitic structure of CN\textsubscript{x} catalysts grown over 2\%Fe/MgO-HCl washed. Others have incorporated boron into carbon at low levels through methods as easy as piling carbon fiber bundles onto a mound of boron oxide and heat treating in an inert\textsuperscript{289}. Preliminary attempts involved a wet impregnation technique where DI water and ammonium pentaborate precursor were made into a solution that was then added to CN\textsubscript{x} grown over 2\%Fe/MgO-HCl washed at a temperature of 90\degree C while stirring. The appropriate amount of ammonium pentaborate precursor was added to the water to make B:C atomic ratios equaling 0.025, 0.05, 0.10, and 0.25 when the CN\textsubscript{x} catalyst was assumed to be all
carbon for the calculation. A catalyst sample was also prepared using wet impregnation methods with water only to study the effect of the treatment conditions on CN<sub>x</sub>. After drying the wet-impregnated B-CN<sub>x</sub>, it was heat treated in nitrogen at 900°C for 4 hours to incorporate the boron into the nanostructure. It was believed that at some B:C level, phase separation would occur, but it was unknown at which precursor loading, as reports have shown significantly more boron has to be added than what actually is incorporated<sup>290</sup>. To continue the study, some of the prepared boron-CN<sub>x</sub> catalysts were treated with HCl to try and remove any excess boron not bound to carbon.

9.3.1 Surface Species Analysis on Boron Incorporated CN<sub>x</sub>

The effectiveness of incorporating boron was analyzed using XPS. It was found that boron oxide, B-C, and possibly B-N were in the catalysts (see Figure 49). The higher binding energy peaks are attributed to boron oxides and the two lower peaks are due to B-C and B-N species<sup>298,346,351,352</sup>.
Table 9 is a compilation of the surface composition for the boron-incorporated CN$_x$. The boron oxide was formed either by incomplete high temperature treatment or through reactions when exposed to air after treatment. At this point, it is unknown if the boron also has been incorporated into the graphitic structure or has phase separated to graphite and boron nitride. A substantial amount of oxygen was also found on the surface of the B-CN$_x$ catalysts, further verifying the boron oxide phase identification.
When comparing the atomic ratios of the surface species, as in Figure 50, it can be seen that the amount of boron compared to carbon increased with each increase in boron addition. This is not clearly seen in Table 9, because of the oxygen surface content variability. This oxygen surface content variability is not easily explained and further testing is required. While the nitrogen content of the catalyst surface appeared to change significantly when tabulated, less change in nitrogen content when compared to the carbon present at the surface is observed.

After the blank treatment on CN\textsubscript{x} (B:C = 0.00), the oxygen and nitrogen surface groups are decreased. After heat treatment in inert at 900°C, it can be expected that surface oxygen and some nitrogen may desorb from the surface\textsuperscript{307,308}, explaining the drop.

<table>
<thead>
<tr>
<th>Table 9. Surface chemical species (atomic%) composition for boron incorporated CN\textsubscript{x} catalysts</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
</tr>
<tr>
<td>O 1s</td>
</tr>
<tr>
<td>N 1s (total)</td>
</tr>
<tr>
<td>pyridinic</td>
</tr>
<tr>
<td>C 1s</td>
</tr>
<tr>
<td>B 1s</td>
</tr>
</tbody>
</table>
9.3.2 Surface Area and Pore Volume of Boron Incorporated CN$_x$

Through nitrogen physisorption experiments, it was observed that the addition of boron into CN$_x$ at high levels significantly reduced the surface area and pore volume (see Table 10). This suggests that the boron oxide material was coating the surface of the CN$_x$ catalyst, which is also supported through XPS studies. The blank treatment on CN$_x$ also saw a significant increase in surface area with treatment. This also complements the observations from XPS on this catalyst. If surface area is gained, it is possible that some
of the graphitic edges were attacked during heat treatment. This could cause a loss in pyridinic-nitrogen content, as well.

| Table 10. Surface area and pore volume for select Boron incorporated CNₓ |
|-----------------|------------------|------------------|
|                | BET Surface Area (m²/g) | BJH Desorption Pore Volume (cm³/g) |
| CNₓ            | 252.4             | 0.92             |
| B:C=0.00       | 284.6             | 1.00             |
| B:C=0.025      | 179.7             | 0.70             |
| B:C=0.25       | 61.9              | 0.30             |

9.3.3 Activity of Boron-Incorporated CNₓ

The addition of boron at these levels and in this method did not significantly alter the onset of ORR activity for the catalyst as indicated by RRDE testing (Figure 51). Current densities and voltammogram slopes did change with treatment. The blank treated catalyst had the biggest increase in current density. An increase in surface area could increase the current density, if the exposed species were active. The catalysts with the two highest boron levels had reduced slopes before reaching a limiting current. This may suggest a change in catalyst behavior in ORR, but it is difficult to verify this.
9.3.4 Acid Treatment of Boron-Incorporated CN\textsubscript{x}

In an attempt to remove the boron oxide from the surface of the CN\textsubscript{x} and retain the boron-nitrogen and boron-carbon species, the CN\textsubscript{x}-B:C=0.25 and CN\textsubscript{x}-B:C=0.10 were post-treated with 5M HCl at 60°C before filtering with excess DI water. In the graphitic site blocking method, Park and Baker suggested that an acid wash would remove unattached boron\textsuperscript{230}.

XPS analysis of these HCl treated B-CN\textsubscript{x} catalysts showed that the HCl treatment was not successful in removing the boron oxide layer from the catalyst. Interestingly, the B-C and B-N species identified previously, as seen in Figure 49, were not observed after

\textbf{Figure 51.} RRDE activity for boron-incorporated CN\textsubscript{x}
HCl treatment (as seen for the CN$_x$-B:C=0.10 catalyst in Figure 52). After HCl treatment, the boron oxide peak was the only observed peak and was strong.

![Figure 52. B 1s spectra from XPS for CN$_x$-B:C=0.10 washed with 5M HCl.](image)

When the catalysts that were HCl post-treated were tested using RRDE, the current density of the catalysts was observed to improve with the HCl treatment, as seen in Figure 53. The onset of activity for these catalysts did not appreciably change. It is not clear why the current density would increase with HCl treatment on the B-CN$_x$
catalysts. Further analysis is required. Some possible reasons could include an increase in catalyst surface area and an increase in the exposure of graphitic edge planes.

**Figure 53.** ORR activity for B-CNₙ catalysts before and after 5M HCl treatment.

9.4 Conclusions for Graphitic Site Blocking and Boron Incorporation into CNₙ

Techniques were used to both selectively block the graphitic edges on CNₙ and to incorporate boron into the graphitic matrix of CNₙ. Results showed that graphitic site
blocking methods using boron and phosphorus groups did not prevent the CN$_x$ catalyst from being ORR active. Rather, after attempting to block the zigzag graphitic edge plane with boron, the ORR activity of the catalyst improved. This suggests that boron may act as a promoter to ORR activity. After this observation, CN$_x$ catalysts were doped with boron intentionally. The methods used resulted in catalysts coated in a boron oxide film, rather than incorporation into the graphitic matrix. ORR activity was also not significantly improved with boron-doping attempts. A 5M HCl treatment was used on some of the boron-doped CN$_x$ catalysts to remove some of the boron oxide layer. This treatment was successful in making a minor improvement in ORR activity, even though the boron oxide species were still very prevalent from XPS analysis. Other boron treatment methods may need to be investigated to determine the right concentration and treatment for improved ORR activity on CN$_x$ catalysts.
CHAPTER 10. Evaluation of RRDE Testing Methods and their Impact on Reported ORR Catalyst Results

In part accepted to *Electrochemical and Solid-State Letters*\textsuperscript{353} and in part in preparation for submission to the *Journal of the Electrochemical Society*.

10.1 Background on RRDE Testing

Typical ORR catalyst research involves a path where catalysts are first screened for ORR activity and selectivity for water formation in the rotating ring disk electrode (RRDE) half cell environment. Then the best performing RRDE catalysts (and sometimes a few poor ones for comparison) are manufactured into membrane electrode assemblies (MEAs) and tested in full fuel cells.

The RRDE half cell technique is generally regarded as the best method for simultaneously testing the ORR activity and selectivity of the catalysts directly. In this technique, a cyclic voltammogram (CV) on a catalyst-coated disk is performed to
monitor the activity of the catalyst, while a ring (typically Pt) surrounding the disk is held at a constant potential where hydrogen peroxide can be detected in an acidic environment to simulate the cathode side on the PEM or DM fuel cell. The reactions that may occur at the disk are the desired complete reduction to water:\(^4\):

\[
O_2 + 4e^- + 4H^+ \rightarrow 2H_2O \quad 1.23\text{V vs. NHE}
\]

And the undesired incomplete reduction to hydrogen peroxide\(^4\):

\[
O_2 + 2e^- + 2H^+ \rightarrow H_2O_2 \quad 0.695\text{V vs. NHE}
\]

Hydrogen peroxide is an undesired product not only because it leads to a loss in efficiency due to the decreased number of electrons transferred per \(O_2\) molecule, but more importantly, because of its ability to degrade the components of the fuel cell\(^354\).

A technique related to RRDE is the rotating disk electrode (RDE) technique. The RDE system does not have a ring used for the direct determination of selectivity. Commonly used, the Koutecky-Levich technique allows for the calculation of selectivity to water formation from the RDE experimental data.

Just as in any experimental method, these electrochemical half cell techniques have their limitations. Alterations to the experimental methodology have the potential to alter the experimental results. In this chapter, the results of two investigations involving the RRDE technique are discussed. The effect of catalyst loading on the selectivity towards water formation has been studied, as well as the effect of RRDE catalyst ink aging on the selectivity results.
10.2 Examination of Catalyst Loading Effects on the Selectivity of CNx and Pt/VC ORR Catalysts using RRDE

While RDE has been used to study ORR for quite some time, there have been reports in the literature that the technique may not always give comparable results for selectivity\textsuperscript{30,71,326,327}. Recently, letters have also been published reporting on the observation that the selectivity of the catalyst changed with loading level on the disk of an RRDE setup for several ORR catalysts: carbon-nitrogen, Pt-based and chalcogenide catalysts\textsuperscript{328-330,355}. Interestingly, researchers have recently reported that this observation of selectivity changes with catalyst loading level is dependent upon the generation of catalyst used from the same laboratory\textsuperscript{137}.

A survey of the literature shows that the catalyst loadings vary widely for both carbon-nitrogen and Pt-based catalysts using the RRDE technique. While catalyst loadings as different as 70 μg/cm\textsuperscript{2}\textsuperscript{356} and 4370 μg/cm\textsuperscript{2}\textsuperscript{144} have been reported, majority of the studies fall in the 100 μg/cm\textsuperscript{2} to 1100 μg/cm\textsuperscript{2} range\textsuperscript{44,125,345,357-361}. An illustration of the distribution can be seen in Figure 54.
In this section, a study of the effect of catalyst loading on the ORR activity-selectivity measurements using RRDE technique for CN$_x$ and Pt/VC catalysts as well as the variation of the experimentally determined collection efficiency with catalyst loading is presented. The possibility of a two-step mechanism through an H$_2$O$_2$ reduction step has been probed. SEM characterization of model electrodes with different loadings is also presented.
10.2.1 Effect of Catalyst Loading on Selectivity

When catalysts are tested for activity and selectivity using RRDE techniques, activity is determined from the cyclic voltammogram (CV) performed on the catalyst-coated disk. Selectivity is determined by comparing the current produced at the catalyst-coated disk to the current at the ring. As mentioned in the Experimental Methods Chapter, the disk current is a result of the reduction reactions taking place at the disk, namely formation of H$_2$O and H$_2$O$_2$ from O$_2$. The ring catalyzes the oxidation of H$_2$O$_2$ formed over the disk and the ring current is a result of this reaction. Since only a portion of H$_2$O$_2$ formed at the disk reaches and/or is oxidized at the ring, the current measured at the ring represents only a fraction of the total H$_2$O$_2$ produced. This fraction is the collection efficiency, $N$, of the RRDE system. For results reported and discussed in this section, the theoretical collection efficiency as reported by the manufacturer for the setup used in the study will be used. This is a value of $N_{\text{tho}}=0.22$, implying that for the system studied, 22% of the H$_2$O$_2$ produced at the disk is assumed to reach the ring and be oxidized.

An example comparison of the ring current to the disk current in an ORR half cell test is shown in Figure 55. This is a comparison for CN$_x$ catalyst studied with 142 μg/cm$^2$ loading on the disk in an oxygen-saturated electrolyte. A substantial amount of hydrogen peroxide was detected at the ring, shown from the relatively large ring current. The selectivity of CN$_x$ loaded at 142 μg/cm$^2$ was $n = 3.47$, which is equivalent to 73% selectivity to water formation. The inset to Figure 55 shows the comparison of the disk current to the ring current after the ring current has been adjusted for the collection
efficiency of $N_{\text{theo}}=0.22$. If the catalyst had been 100% selective to water formation, the ring current would have been zero. If the catalyst formed only $\text{H}_2\text{O}_2$, then the ring current and disk currents would have been the same after adjustment for collection efficiency. In addition, Figure 55 can also be used to represent the ORR activity of the catalyst from the disk. The onset of activity can be reported as 770 mV vs. NHE for the CN$_x$ catalyst shown. As a reference, the same experiment ran on the blank glassy carbon disk electrode has been added to the Figure 55 graphs. It is easily seen that that the activity is due to the CN$_x$ catalyst and not the underlying glassy carbon. The glassy carbon had an onset of activity at about 400 mV vs. NHE. Current was minimal in this material, as well, because of the low surface area of the polished disk.
Figure 55. Example comparison of ring current (top) to disk current (bottom) in oxygen-saturated 0.5M H₂SO₄ at 1000rpm after background subtraction for a CNₓ catalyst with 142 μg/cm² loading, which had the lowest selectivity to water formation out of all tests performed. Inset: Absolute current comparison of ring to disk after adjustment for theoretical collection efficiency.
RRDE tests were performed on the CNₓ materials, by varying the catalyst loading on the disk from 142 μg/cm² to 1420 μg/cm². A substantial increase in selectivity to water with catalyst loading was observed as shown in Figure 56a. The impact of catalyst loading on selectivity was the most dramatic at low loadings. This phenomenon has also been recently observed by other catalyst loading studies.³²⁸

There have been reports in the literature which suggest that CNₓ-type catalysts participate in a two-step ORR mechanism with H₂O₂ being formed first and further reacting to form H₂O²⁸,³⁶³, while Pt-based catalysts have been hypothesized to participate in a complete reduction to water without an H₂O₂ intermediate step³⁶⁴. There are other studies which suggest that H₂O₂ intermediates could be possible in both types of catalysts²⁸,³⁶⁵. The impact of catalyst loading on commercial Pt/VC catalysts were also studied to better understand if the observed catalyst loading effect was specific to the type of catalyst used.
Figure 56. Selectivity as a function of catalyst loading on disk. Selectivity is taken at 0.5 V vs. NHE. Theoretical collection efficiency of N=0.22 was used. a) CNₓ catalyst, b) Pt/VC catalyst.

It was observed (as in Figure 56b) that Pt catalyst selectivity also increased with catalyst loading, albeit the trend was much less pronounced compared to CNₓ. The selectivity achieved with 142 μg/cm² of catalyst loading was significantly higher for the
Pt catalyst than it was for the CN\textsubscript{x} test catalysts at the same catalyst loading (n=3.78 versus n= 3.47), which would mean that there was less room for improvement of ORR selectivity with increased loading for the Pt catalyst. At higher loading levels, the selectivities achieved for the two catalysts were comparable. Selectivity increases with catalyst loading was also observed by Bonakdarpour, et al., using 3M Pt nanoparticles\textsuperscript{329}. In that literature report, however, the observed selectivities were closer to n=3.0. The authors used catalyst loadings which were significantly lower than used in our study, which can explain the selectivity differences. As catalyst loading increased, they also observed marked improvement in selectivity to water formation\textsuperscript{329}. In general, the Pt-based catalysts produce ORR current densities higher than that of CN\textsubscript{x} catalysts. This may be due to a higher active site density on the Pt catalysts compared to many CN\textsubscript{x} catalysts reported to date in the literature. Pt catalysts may have higher selectivities at the same loadings as CN\textsubscript{x} because of the higher current densities\textsuperscript{206}. With higher active site densities, a reaction that occurs in a two-step mechanism may have a higher probability to reach completion within the same catalyst layer thickness. This would result in an observation that selectivity to water formation would be higher at lower catalyst loadings than a catalyst with fewer active sites. It is possible that when the Pt catalyst is so dispersed that the active site density is significantly reduced that the two steps cannot occur as readily, thereby lowering the catalyst selectivity, which would explain the observation of n~3.0 by Bonakdarpour, et al. on Pt catalysts\textsuperscript{329}. Adzic has also suggested that a two-step process with \textsubscript{2}H\textsubscript{2}O\textsubscript{2} as an intermediate and a complete four-electron
transfer process without an $\text{H}_2\text{O}_2$ intermediate would be indistinguishable with RRDE if the $\text{H}_2\text{O}_2$ intermediate was given sufficient time to completely react to water$^{365}$.

It should also be noted that, throughout this study, onset of activities of the catalysts tested were monitored. Any variations in onset of activities with catalyst loading were statistically insignificant, which points to the reliability of the technique in comparing activities of different catalysts, independent of any catalyst loading.

### 10.2.2 RRDE Catalyst Layer Thickness Observations

If collection efficiency is not a significant factor in the trend of selectivity with catalyst loading observed in this report, electrocatalyst loading must contribute to selectivity differences beyond fluid dynamics. If the hypothesized two-step process occurs in ORR catalysts, additional catalyst layer thickness should improve the probability of the second step being completed.

A closer examination of the catalyst layer thickness was performed to determine if any trends in catalyst layer thickness to selectivity could be obtained. Aluminum rods with the same diameter as the RRDE disk were coated with CN$_x$ catalyst at the same loading levels and using the same ink application method as studied for selectivity and collection efficiency measurements. The catalyst layers on the aluminum rods were then examined with SEM to obtain approximate measurements of catalyst layer thicknesses for each catalyst loading. While the catalyst ink may disperse slightly differently on
aluminum than glassy carbon, the model appeared to be representative of the behavior observed on the RRDE electrodes.

Figure 57 and Figure 58 are example SEM images obtained through this procedure. From Figure 57 (angled views of the top of the disk), it can be seen that the catalyst layer was able to disperse across the aluminum rod tip, further supporting the assumption that the aluminum rods could be used as a model. The catalyst layer showed areas of catalyst particle agglomeration at 142 μg/cm² (Figure 57a), but still nearly completely covered the rod tip. As the amount of catalyst increased on the aluminum rod tip (Figure 57b), more catalyst began accumulating in the center and less at the edges. This can be attributed to the application process where the drop from the pipet tip is deposited at the center of the disk. Visual observations of the RRDE glassy carbon disk after application of catalyst inks also supported the SEM images similar to the disk-top views shown in Figure 57. Side-view SEM images allowed for measurement of the catalyst layer thickness (examples shown in Figure 58). With 142 μg/cm² catalyst loading, the average catalyst layer thickness was 21.1 μm and was fairly evenly distributed (a standard deviation of ±1.8 μm). When the catalyst loading reached 1420 μg/cm², a large, cracked mound of catalyst was observed on the rod tip. The thickness varied significantly with an average thickness being 230 μm with a standard deviation of ±160 μm for the 1420 μg/cm² sample. Figure 59 is a plot of the average film thickness with catalyst loading. As expected, the average and standard deviation increased with catalyst loading. Roughness of the catalyst layer could also play a role in the fluid
dynamics of the system. The catalyst layers were deemed rough, but were not quantified for a roughness factor.

Figure 57. SEM top view images showing the distribution of catalyst on a model aluminum rod with same geometric area as the glassy carbon electrode. a) for 142 μg/cm² CN_x catalyst loading and b) 1420 μg/cm² CN_x catalyst loading.
Figure 58. Example SEM side-view images of CN₅ catalyst loadings on aluminum rods. a) 142 μg/cm² loading. Thickness indicated in image is 17.8 μm. b) 426μg/cm² loading. Thickness indicated in image is 52.1 μm. c) 1420 μg/cm² loading. Thicknesses indicated in image are 207 μm and 424 μm.
The RRDE method was developed for an electrode disk with a surface level with the ring height\textsuperscript{366}. The thicknesses observed through SEM have potential to alter the fluid dynamics of what was initially intended for the method. If the thicknesses were too large to fit the model, then the collection efficiency experiments should have been significantly different from the theoretical collection efficiency, which was not the case (data not shown here). The use of experimental collection efficiency did not make up for the differences in selectivity with loading. This suggests that the catalyst layer thickness must play another role beyond RRDE fluid dynamics. Figure 60 shows the variation of selectivity with the catalyst layer thickness. As expected, the trend is very similar to that
observed when selectivity was plotted against catalyst loading (Figure 56a). If a multi-step mechanism with a hydrogen peroxide intermediate is occurring at the cathode, then an increased catalyst layer thickness would improve the probability of the mechanism going to completion forming the final product of water. This was suggested by Bonakdarpour, et al. also\textsuperscript{328}. The work in this paper also suggests that as the catalyst layer is thickened, more oxygen is fully reduced to form water, thereby supporting a multi-step mechanism for both CN\textsubscript{x} and Pt type ORR catalysts.

![Selectivity as a function of average CN\textsubscript{x} catalyst thickness. Selectivity values taken at 0.5V vs. NHE.](image)

**Figure 60.** Selectivity as a function of average CN\textsubscript{x} catalyst thickness. Selectivity values taken at 0.5V vs. NHE.
10.2.3 Electroreduction of H₂O₂ by CNₓ Catalysts

Changes in hydrogen peroxide detected at the ring with catalyst loading may suggest that ORR catalysts participate in a two-step mechanism where oxygen is first electrochemically reduced to hydrogen peroxide and then further electrochemically reduced to water. If this is the case, CNₓ catalysts should have some electrochemical reduction activity towards hydrogen peroxide. A series of experiments were performed to analyze the electrochemical activity towards hydrogen peroxide reduction and oxidation.

Figure 61a shows a comparison of ORR activity as a function of rotation rate in oxygen-saturated 0.5M H₂SO₄. Currents continue to increase with rotation rate with the maximum current at 3000rpm being just under -6 mA/cm². When hydrogen peroxide is being reduced, the currents are lower, but still increase with rotation, showing there is indeed activity towards hydrogen peroxide reduction. It should be noted, that 6.25mM H₂O₂ is greater than the concentration generally accepted for saturated oxygen in 0.5M H₂SO₄. The higher current in the less concentrated oxygen-saturated electrolyte means that CNₓ catalysts are more active towards oxygen reduction than they are towards hydrogen peroxide reduction alone. This does not mean, though that the CNₓ catalysts cannot participate in a two-step process in ORR. The reduction of hydrogen peroxide to water may be the limiting reaction. Further studies at 1.3 mM H₂O₂ in 0.5M H₂SO₄ are needed to draw any additional conclusions about these hydrogen peroxide reduction results.
Figure 61. (Top) ORR activity on CN$_x$ as a function of rotation rate in oxygen saturated electrolyte, (bottom) hydrogen peroxide reduction activity as a function of rotation rate in 6.25 mM H$_2$O$_2$. 
The results of this study point to the difficulty of comparing selectivities from separate experiments. This challenge is even bigger when selectivities of different catalysts are compared, especially when the nanostructures of the catalysts are quite different as in the case of CNₓ and Pt/VC catalysts. If film thickness plays such a pivotal role in determining the selectivity of ORR catalysts, it raises the question whether comparisons should be made on an equal mass loading per geometric area or they should be made on an equal film thickness basis. For practical purposes, it is much easier to perform RRDE tests on an equal mass per geometric area basis, but variations due to catalyst film thickness should be taken into consideration.

10.3 RRDE Catalyst Ink Aging Effects on Selectivity to Water Formation in ORR

Preliminary observations in our laboratory at Ohio State have shown that catalyst loading may not be the only contributing factor to changes in oxygen reduction reaction (ORR) selectivity measurements when using RRDE. This section will focus on the observation that RRDE catalyst ink preparation technique can play a significant role in the selectivities observed for both commercial Pt/VC and nitrogen-containing carbon nanostructured (CNₓ) catalysts.
10.3.1 RRDE Results with Ink Aging

In an attempt to better understand the possible variables in RRDE testing beyond catalyst loading, catalyst inks were allowed to age for up to 11 days to determine the ink aging effect on RRDE results obtained. An example comparison of the ring to the disk currents for different ink aging periods is shown in Figure 62a. As seen in the figure, there is a dramatic decrease in the ring current with ink aging coupled by a more modest increase in the disk current. The onset of activity does not appear to change with ink aging. Figure 62b shows the corresponding selectivity, n, the number of electrons transferred per oxygen molecule, calculated from the ring and disk currents. To be able to observe greater changes in selectivity due to catalyst aging, a low catalyst loading on the RRDE disk was chosen, as catalysts with lower disk loadings give lower selectivity measurements\textsuperscript{328-330,355}. Over the span of 11 days, the catalyst selectivity increased from 3.46 to 3.80 electrons. Even in just the span of 24 hours, catalyst selectivity increased appreciably, indicating that aging of catalyst ink can have a significant impact even in a short period of time. When similar experiments were run at higher CN\textsubscript{x} loadings on the RRDE disk (426µg/cm²), ink aging was again seen to improve selectivity, resulting in a change of n from 3.67 to 3.83 in 11 days. The change was less pronounced, but still significant, since the starting selectivity at Day 0 was much higher at this loading.
Figure 62.  a) Ring (top) and disk (bottom) currents for RRDE tests on CN₅ catalysts exposed to different ink aging periods. (Measurements in oxygen-saturated 0.5M H₂SO₄ at 100rpm with 142 μg/cm² of catalyst loading on the disk). (b) Resulting oxygen reduction reaction selectivity as a function of age of the RRDE ink used. As accepted in [353].
Similarly, the results reported in Figure 62 were also observed for commercial Pt/VC catalysts. Figure 63 shows the selectivity increase with ink aging for a commercial Pt/VC catalyst when the catalyst loading on the RRDE disk is 426 µg/cm². The increase in selectivity is smaller, and requires a longer aging period in order to be observed, but nevertheless, the trend remains.

Figure 63. ORR selectivity as a function of RRDE catalyst ink age for Pt/VC catalyst with a 426 µg/cm² loading on the disk at 100rpm. As accepted in\textsuperscript{333}. 

187
While the reasons behind these observations of increased selectivity and relatively unchanged overall activity are not yet clear, possible explanations include a change in the physical properties of the catalysts, such as particle size or surface area, due to repeated sonication. Alternative explanations may involve changes in hydrophilicity of the surface\textsuperscript{355,367} and/or additions of surface functional groups, the most likely functional group candidates being the oxygen functional groups\textsuperscript{199,325}.

It is not believed that loss of solvent due to heating during sonication accounts for the increase in selectivity due to an increase in catalyst loading. A solvent heating study found that during sonication, a 6°C increase in ink temperature is observed. In the system used, this is equivalent to a 0.00025 mass% loss in ethanol after each sonication.

10.3.2 Role of Ethanol in Ink Aging

To study the impact of ethanol treatment without the addition of Nafion or repeated sonications on the catalyst, a batch of CN\textsubscript{x} was soaked in excess ethanol for ten days. After ten days, the CN\textsubscript{x} catalyst was either directly dried to remove the excess ethanol or vacuum filtered with DI water before drying. Fresh inks were made of these catalysts and immediately tested at a RRDE catalyst loading of 426 µg/cm\textsuperscript{2}.

Once again, significant changes in ORR activity were not observed, but the selectivity towards water formation did increase with ethanol treatment, as seen in Figure 64. This shows that exposure of CN\textsubscript{x} to ethanol has a major impact on the selectivity of the catalyst. Possible explanations include ethanol imparting oxygen functional groups...
on the catalyst surface; increases in hydrophilicity of the catalyst which would in turn improve the wettability of the catalyst\textsuperscript{367}; and ethanol penetrating the graphitic layers of the carbon, perturbing the nanostructure\textsuperscript{227}. Preliminary XPS results were inconclusive to the role that oxygen functional groups may play. The selectivity increase was more pronounced for the catalyst that was not rinsed with water before drying, an observation which may be in agreement with the hydrophilicity argument. If ethanol molecules are penetrating the graphite layers, as suggested by Baker, et al.\textsuperscript{227}, heating of the CN\textsubscript{x} in ethanol instead of water may also increase the effect. Small changes in nanostructure, supported by the observation that the BET surface area of the ethanol-treated catalysts increased from 148 m\textsuperscript{2}/g for the untreated CN\textsubscript{x} catalyst to 182 m\textsuperscript{2}/g for the CN\textsubscript{x}-ethanol soaked and 188 m\textsuperscript{2}/g for the CN\textsubscript{x}-ethanol soaked-DI water rinsed, which may also contribute to the selectivity differences.
Figure 64. ORR selectivity results for CN$_x$ treated with ethanol (Catalyst loading on disk: 426 $\mu$g/cm$^2$). As accepted in$^{353}$. 

While further study is needed to better understand why RRDE ink aging results in improved selectivity to water formation for ORR catalysts, the observation is reproducible for both CN$_x$ and Pt/VC catalysts.

10.4 Summary of RRDE Method Examinations

An extended study on the effect catalyst loading levels on the ORR selectivity results obtained from RRDE analyses was performed using both CN$_x$ and commercial Pt/VC catalysts. It was found that catalyst loading plays a significant role in the determination of selectivity to water formation. ORR selectivities calculated by RRDE
were observed to increase by as much as 0.35 electrons per oxygen molecule by increasing the catalyst loading. This level of increase in selectivity is significant in determining the viability of a catalyst for commercial applications. SEM images of CN\textsubscript{x} catalyst loadings showed that catalyst thickness increased substantially with loading.

The results suggest that increased catalyst layer thickness increases the selectivity to water formation by increasing the probability that the two-step reaction mechanism to water formation can reach completion. The results discussed in this paper support the need for a uniform standard of catalyst loading or uniform catalyst film thickness be used for RRDE testing. Before any experimental results can be compared to the literature, one must take into consideration the catalyst loading levels used in the studies to be compared.

Catalyst loading on the RRDE disk was found to not be the only factor in the selectivity results reported from the method. Aging of RRDE catalyst inks for both CN\textsubscript{x} and Pt/VC catalysts was found to increase the resulting selectivity to water formation of the catalysts while leaving the activity relatively unchanged. Increases in selectivity were observed to be as high as 0.35 electrons per oxygen molecule after 11 days of aging CN\textsubscript{x} ink. Possibilities for the increase in selectivity with ink age include changes in the physical properties of the catalyst, changes in the hydrophilicity of the catalyst surface and changes in the surface function groups of the catalyst. Further research is required to fully elucidate the reason for selectivity increases with RRDE ink aging.
CHAPTER 11. Methanol Tolerance of CN, Oxygen Reduction Catalysts

As published in Topics in Catalysis368

11.1 Introduction to Direct Methanol Fuel Cell Cathode Catalysts

While DMFCs have advantages in fuel supply and storage, methanol crossover limits the technology currently. Methanol crossover, where the methanol fed to the anode permeates through the membrane to the cathode side, inhibits the Pt-based cathode catalysts369 and causes a reduction in the fuel cell coulombic efficiency14. The methanol oxidation reaction (MOR) occurs at the cathode as a parasitic reaction, reducing the open circuit potential370 and causing a mixed potential15. There is also a possibility that the methanol and MOR intermediates and products could poison the cathode catalyst5.

In an attempt to deal with the methanol crossover, various catalysts have been investigated for the DMFC cathode that can be tolerant to methanol. Platinum is active to both MOR and the oxygen reduction reaction (ORR). The orientation of the Pt crystals
and Pt particle size are known to determine which reaction is favored. There have been studies that focused on developing Pt catalysts with higher selectivity for ORR\textsuperscript{371}. Pt-alloys have also been investigated for use as DMFC cathodes. Alloys studied include those of Co\textsuperscript{6}, Cr\textsuperscript{361,372}, Fe\textsuperscript{6,373,374} and Ni\textsuperscript{375}, among others. Undesired MOR can increase with time on the Pt-alloys if the metal leaches out of the catalyst, leaving MOR active Pt behind\textsuperscript{369}. Macrocycles (both pyrolyzed and non-pyrolyzed) have demonstrated positive results for ORR activity in DMFCs\textsuperscript{42,44,48,60,100}, though the non-pyrolyzed macrocycles had questionable stability\textsuperscript{44}. Pyrolyzed macrocycles have shown inactivity for MOR in both anodic and cathodic sweeps\textsuperscript{42}, as well as in DMFC tests\textsuperscript{42,60} while having little effect of methanol on the ORR activity. Chalcogenide ORR catalysts have also been screened for DMFC cathode catalysts. Chalcogenides tested include compounds of Ru-Mo-Se\textsuperscript{17,18}, Ru-Mo-S\textsuperscript{19,20}, Ru-Mo-Se-O\textsuperscript{17,21}, Rh-Ru-S\textsuperscript{22}, Re-Ru-S\textsuperscript{22}, Rh-S\textsuperscript{376} and Ru-Se\textsuperscript{6,23,376}. The chalcogenides tested in methanol did not demonstrate any methanol catalyst poisoning and were not active for MOR. While studied to a lesser degree, metal oxides have also shown methanol tolerance when used as ORR catalysts in methanol-containing systems, with ZrO\textsubscript{2-x} being the most ORR active\textsuperscript{377}.

Mixed Reactant DMFCs (MRDMFCs) rely on the selectivity of both anode and cathode catalysts for their operation\textsuperscript{6,376,378-380}. MRDMFCs are desirable, because the gas sealing requirements can be relaxed\textsuperscript{378} and the anode and cathode feeds are introduced together\textsuperscript{379}. Selective cathode catalysts that have been studied for MRDMFCs include chalcogenides and macrocycles\textsuperscript{6,376,379}. Compact mixed reactant (CMR) fuel cells take the MRDMFC concept further by removing the bipolar plates and replacing the
membrane with a porous one\textsuperscript{378}. This design reduces the size and cost of the fuel cell as well as increases the active catalyst area\textsuperscript{378}. For MRDMFCs, the tolerance and inactivity of the cathode catalyst for methanol is even more crucial since the exposure of the cathode catalysts to methanol is no longer limited to small quantities that crossover from the anode. On the contrary, cathode catalysts are exposed to much higher concentrations of methanol. Therefore, any activity towards methanol oxidation or any poisoning by methanol over the cathodic active sites would cause much larger coulombic losses.

Some of the CN\textsubscript{x} catalysts grown over metal-impregnated alumina, silica and magnesia supports that were previously studied in the Ozkan group for PEM fuel cell cathodes\textsuperscript{141,143-145}, were examined for their methanol tolerance during ORR. Similar to the Pt-free macrocycles and chalcogenides, the CN\textsubscript{x} catalysts studied were found to be also inactive to MOR.

### 11.2 MOR Activity and Effect of Methanol on ORR with Pt and Pt/Ru Catalysts

To gauge the performance of the CN\textsubscript{x} catalysts, 20 wt\% Pt/VC and Pt:Ru (20:10)/VC were studied for their MOR activity using the RRDE half-cell set-up. The effect of methanol on ORR activity was also examined. Figure 65 shows the cyclic voltammetry scans for 20\%Pt/VC catalyst in methanol-containing electrolyte saturated with O\textsubscript{2}. An ORR voltammogram for the methanol-free system is also included for comparison. As seen in the figure, a significant anodic peak is present during the
reduction sweep from 1.2 V to 0.2 V vs. NHE that is not present in the methanol-free solution. Another anodic peak is present during the sweep from 0.2 V to 1.2 V vs. NHE.

Both of these peaks can be attributed to the oxidation of methanol\textsuperscript{5,15}. CV scans were also

\textbf{Figure 65.} Cyclic voltammetric scan for 20\%Pt/VC from 1.2 to 0.2 to 1.2V vs. NHE in 0.5M H\textsubscript{2}SO\textsubscript{4} saturated with oxygen at 0 rpm showing both 1.0M methanol and methanol-free systems.
taken for the same catalyst at 1000 rpm, for methanol-O₂, and O₂-only systems. Figure 66 shows the reduction sweeps from 1.2 to 0.2 V for these systems. The methanol oxidation feature in methanol-only system becomes prominent between 0.9 and 0.5 V and decreases to zero at more reducing potentials. The anodic peak during the reduction scan in the methanol-O₂ system can be seen to have contributions from both oxygen reduction and methanol oxidation reactions. However, as shown by Paulus et al.¹⁵, in the area where methanol oxidation is dominant, the current is not simply a sum of the oxygen-free methanol oxidation current and the methanol-free oxygen reduction currents.

Figure 66. Reduction sweep voltammogram for 20%Pt/VC in 0.5M H₂SO₄ solutions at 1000 rpm showing both 1.0M methanol and methanol-free systems.
For comparison, we have also tested the PtRu/VC catalysts, which are known for MOR activity\textsuperscript{14}. As presented in Figure 67, PtRu catalysts showed significant activity towards MOR. The MOR was the prevailing reaction in the mixed potential in oxygen-saturated methanol-containing solutions until about 0.55 V at 1000 rpm. ORR currents were comparable to that of Pt/VC catalysts after MOR became limited.

With the occurrence of methanol crossover to the cathode in a DMFC, the mixed potentials shown above illustrate the problem with having Pt-based cathode catalysts in DMFCs. The parasitic MOR at the cathode is likely to lead to significant power loss and cannot be overcome until the system is operating at a potential less than 0.5 V.
Figure 67. Reduction sweep voltammogram for Pt:Ru/VC in 0.5M H₂SO₄ solutions at 1000 rpm showing both 1.0M methanol and methanol-free systems.

11.3 MOR Activity and Effect of Methanol on ORR with CNₓ Catalysts

The methanol oxidation activity and the effect of methanol on ORR activity were tested for CNₓ catalysts, using parameters similar to those used for Pt and PtRu catalysts. Catalysts studied were previously developed and characterized in the PEM-type environment. CNₓ grown over iron-, and nickel-impregnated Vulcan carbon\textsuperscript{142}, alumina\textsuperscript{140,141}, silica\textsuperscript{144,145} and magnesia\textsuperscript{144,145} supports, and cobalt-impregnated silica and magnesia supports\textsuperscript{144,145} were used all after washing to remove the oxide support and exposed metals. Results for two different CNₓ catalysts with different nanostructures and
different ORR performances are presented in Figure 68 and Figure 69. The first catalyst chosen is a highly active CN_x catalyst grown over Fe/Al_2O_3 support (Figure 68). This catalyst consists of mostly stacked cup structures with a high degree of edge plane exposure and a high pyridinic-N content. The second is a catalyst prepared using a Ni/Al_2O_3 substrate (Figure 69). This catalyst, which was characterized by multi-walled nanotube structures, had very low pyridinic-N content and very low ORR activity. The RRDE voltammograms for both catalysts were obtained at 0 rpm and the results for the methanol-free O_2 and the methanol-O_2 systems are plotted in the same figure for comparison. Neither catalyst has any activity for methanol oxidation. There is also no effect of methanol on ORR activity since the curves are essentially the same (differences are well within the experimental error) for the methanol-free system and methanol-O_2 system. These results indicate CN_x catalysts have high methanol tolerance and no activity
**Figure 68.** Cyclic voltammetric scan for CN₅ grown on Fe/Al₂O₃ from 1.2 to 0.0 to 1.2V vs. NHE in 0.5M H₂SO₄ saturated with oxygen at 0 rpm showing both 1.0M methanol and methanol-free systems.

**Figure 69.** Cyclic voltammetric scan for CN₅ grown on Ni/Al₂O₃ from 1.2 to 0.0 to 1.2V vs. NHE in 0.5M H₂SO₄ saturated with oxygen at 0 rpm showing both 1.0M methanol and methanol-free systems.
for MOR regardless of their level of activity for ORR. When mass transfer limitations are reduced, the catalysts still exhibit a high methanol tolerance and a complete lack of any MOR activity. Figure 70 shows CV curves obtained for CN\textsubscript{x} catalysts grown over Co/SiO\textsubscript{2} substrate at 1000 rpm rotation rate. Again, there is no difference between the ORR voltammograms with or without methanol in the system. Similar observations were made when tests were repeated for other CN\textsubscript{x} catalysts. There was no MOR activity or methanol poisoning effect in any of the CN\textsubscript{x} catalysts tested, implying that a change in the pyridinic-N content or nanostructure does not change the behavior towards methanol. The ORR mechanism does not appear to change with addition of methanol, either. With addition of methanol, the calculated n values, obtained using the ring data did not change
Figure 70. Reduction sweep voltammogram for CN$_x$ grown on Co/SiO$_2$ in 0.5M H$_2$SO$_4$ solutions at 1000 rpm showing both 1.0M methanol and methanol-free systems.

(data not shown). Here “$n$” represents the number of electrons that can be harnessed per O$_2$ molecule reduced and is a measure of the ORR selectivity. A value of $n = 4$, represents 100% selectivity for complete reduction of O$_2$ to H$_2$O. Similar observations were also reported by Paulus et al. on Pt catalysts\textsuperscript{15}. Table 11 summarizes the MOR activity and methanol tolerance experiments using the RRDE technique in 1.0 M methanol + 0.5 M H$_2$SO$_4$ solutions. The ORR activity and selectivity to water data that were presented in previous publications are also included in the table.

As reported in methanol ORR studies on macrocyclces and chalcogenides, the active site for MOR is not present without Pt. This has been observed again with the CN$_x$


catalysts. It is also note-worthy that any metal remaining from the metal-doped substrates (e.g., Fe, Co) does not appear to impart any activity for methanol oxidation.

To determine if methanol concentration had an impact on the catalysts, one of the best performing catalysts, CNx on Fe/Al2O3, was tested with the RRDE technique in a 3.0 M methanol, 0.5M H2SO4 solution, using the same method as previously mentioned methanol tolerance and ORR activity tests. Once again, no significant changes were observed in ORR polarization curves with the addition of methanol as seen in Figure 71. The absence of both methanol oxidation and catalyst poisoning at 3.0 M methanol is significant for DMFC and Mixed Reactant Direct Methanol Fuel Cell (MRDMFC) applications. DMFCs generally operate in the range of 0.5-2.0M methanol5. With the crossover methanol, the concentrations at the cathode are likely to be much lower. This
implies that these catalysts can handle methanol concentrations even much higher than what would be encountered at the cathodes of DMFCs.

**Figure 71.** Cyclic voltammetric scan for CN$_x$ grown on Fe/Al$_2$O$_3$ from 1.2 to 0.0 to 1.2V vs. NHE in 0.5M H$_2$SO$_4$ saturated with oxygen at 0 rpm shown both 3.0M methanol and methanol-free systems.

The total inactivity and high tolerance of the CN$_x$ catalysts at high methanol concentrations is even more significant for MRDMFCs and make them a possible candidate as ORR catalysts. MRDMFCs operate under the same methanol concentrations as traditional DMFCs, but instead of a small fraction of the feed methanol transported
across the membrane, the cathode is subjected to the total inlet methanol concentration.
This increased methanol exposure to the cathode requires that the cathode catalyst not be
affected by methanol and be completely inactive towards it in the system. The \( \text{CN}_x \)
catalysts appear to be capable of meeting this requirement.
CHAPTER 12. Conclusions

Modifications to the previously reported CN\textsubscript{x} catalysts were made to study the role of nanostructure and heteroatom incorporation. This was done by modifying CN\textsubscript{x} catalysts grown on 2\%Fe/MgO with ammonia, boron and nitric acid post treatments. Thiophene was introduced as a sulfur source during acetonitrile pyrolysis to both incorporate sulfur into the nanostructure and promote increased growth rates for CN\textsubscript{x} nanofibers. Stacked platelet nanofibers with high edge plane exposure and nanofibers with basal plane exposure were made and treated with ammonia to examine the impact of graphitic edge plane exposure on nitrogen containing carbon catalysts.

Modifications to CN\textsubscript{x} with ammonia after acid oxidation showed that treatments at 900\textdegree{}C could improve ORR activity, and 600\textdegree{}C ammonia treatments were not sufficient. The acid oxidation treatment with HNO\textsubscript{3} on CN\textsubscript{x} alone was able to improve ORR activity and selectivity. It was further found that increases in oxygen functional groups on the surface of CN\textsubscript{x} catalysts could improve ORR selectivity.

It was found that graphitic edge site blocking methods on CN\textsubscript{x} using boron promoted ORR activity rather than blocking an active site. Further treatments to CN\textsubscript{x} to
incorporate boron created boron oxide films on the catalysts, which did not promote ORR activity.

Sulfur, in the form of thiophene, was found to be a successful CN$_x$ growth promoter when introduced at low levels into acetonitrile pyrolysis over 2%Fe/MgO nanofiber growth catalysts. While sulfur was both incorporated into the graphitic structure and accumulated on the surface of CN$_x$, ORR activity was not affected by its presence. Sulfur not incorporated into the CN$_x$ nanostructure could also be removed through mild heat treatment in inert, which may improve the viability of using a growth promoter when creating CN$_x$ materials for use in fuel cells.

Through examination of the role of graphitic edge plane exposure with stacked platelets and nanofibers with basal plane exposure, it was found that graphitic edge planes undoped were not sufficient to catalyze ORR. After nitrogen was incorporated into the graphitic edge planes, even at low concentrations, significant ORR activity was observed. It was also found that the presence of nitrogen alone on nanofibers does not play a significant role in ORR. Rather, nitrogen has to be incorporated into the graphitic matrix for ORR activity to be observed.

In addition to studies on the modification of CN$_x$ and other nanofiber materials, electrochemical studies were performed. It was found that all CN$_x$ catalysts tested were inactive towards methanol oxidation and tolerant to the presence of methanol during ORR testing. The overall ORR activity and selectivity of the CN$_x$ catalysts did not change in the presence of methanol, even when the poor-performing catalysts were
tested. The best CNₙ ORR catalysts had higher ORR activity than the commercial Pt/VC
catalysts in the presence of methanol above 0.5V vs. NHE. Catalyst loading was found to
be a significant variable in the reporting of selectivity from RRDE testing. The aging of
RRDE catalyst inks was also found to have an impact on the selectivity reported by
RRDE.
CHAPTER 13. Recommendations for Future Work

There are still many unanswered questions about CNx materials and their use as ORR catalysts. While there are many directions that could be followed to investigate CNx catalysts, recommendations here are suggestions based upon the work presented in the previous chapters. Suggestions for future work can fall into three categories: investigation of the active site, role of heteroatoms and oxygen functional groups, and evaluation of CNx precursors.

As stated previously, the active site debate is ongoing in the literature. We have contributed in the past to studies that support the argument for a non-metal active site\textsuperscript{140} (which may be acting alone or in tandem with a metal-centered active site). Further investigation into the active site and the role of iron in ORR activity could include poisoning attempts to the iron materials. In traditional heterogeneous catalysis, H\textsubscript{2}S is known to poison iron readily and rapidly, even at low temperatures and concentrations. Treatments to CNx catalysts after preparation, but prior to half cell testing, with H\textsubscript{2}S could poison any iron in the catalyst. If iron is part of the active site, then it is expected that ORR activity would be poor after H\textsubscript{2}S treatment. While in an earlier chapter, it was shown that the use of thiophene as a CNx growth promoter does not inhibit ORR activity,
the sulfur groups formed from that treatment may be too bulky to be located in the pores where iron-based active sites may be located.

The CN₅ active site can also be investigated using the experimental technique X-Ray Absorption Spectroscopy (XAS). Recently, other catalysts in the research group have been analyzed using XAS techniques using the Advanced Photon Source (APS) at Argonne National Laboratories. Investigation of the iron K-edge under electrochemical operating conditions can provide some insight into the coordination and bonding of iron. Results from these studies will not be absolute in determination of the ORR active site because Fe-O, Fe-C and Fe-N bonds are typically undistinguishable from each other. Investigation of the nitrogen edge under operating conditions may give a more clear understanding of the active site. Examination of this edge would allow for identification of the nitrogen species such as pyridinic, quarternary and pyrrolic while under operating conditions. Bonding to iron should also be able to be identified. Any changes to species with operation would help determine the active components of the ORR catalyst. This proposed experiment would be particularly difficult, because many beamlines available are not set to operate in the lowest energy levels where nitrogen is studied. Additionally, nitrogen XAS is typically performed under vacuum because of interference of atmospheric nitrogen.

The use of boron as a CN₅ dopant was discussed briefly in an earlier chapter. It was found that the treatment conditions significantly altered the effect boron had on the resulting CN₅ ORR activity. Use of heat treatments in inert did not prove to be satisfactory in improving ORR activity, however, attempts at using site blocking methods
that involved a calcination step were successful in creating ORR active catalysts. It is recommended that the site blocking method with boron be studied further. Additional treatments using this methodology have the potential to improve ORR activity.

There is significant work that can be pursued in exploring the role of oxygen functional groups in CN_x catalyst activity and selectivity. It was shown in research presented in this volume that addition of oxygen functional groups can improve ORR selectivity towards water formation. In some cases, ORR activity can also be improved. At this time, it is unclear why these results have been observed and what type of oxygen functional groups play a role in the catalyst improvements. There is still significant uncertainty in the assignment of the oxygen functional groups present on the CN_x materials. Further analysis to determine the oxygen functionalities definitively is needed. Several methods including Raman, FTIR, XPS and TPD will most likely need to be used in tandem to determine the oxygen functionalities present. After this determination is made, then studying the techniques to control the oxygen functionalities on CN_x surfaces can be investigated, hopefully leading to an understanding of the role that oxygen functionalities play in ORR catalysts.

As found through the study of stacked platelets and nanofibers with basal plane exposure, carbon nanostructure can play an important role in creating active ORR CN_x catalysts. There are many directions possible for further study in this area. Three areas will be suggested here.
While stacked platelets were found to have the needed graphitic edge plane exposure to create ORR active sites, the electrical conductivity of stacked platelets is poor compared to nanotubes. This is because electrical conductivity is much higher within graphitic planes than between. The orientation of the graphitic sheets in stacked platelets is perpendicular to the longitudinal axis, meaning there will be significant resistances to electrical conductivity down the length of the nanofiber. If the analog to stacked platelets, ribbons, could be used instead, a more active ORR catalyst could be tailored to place active edge sites on the ends. Literature reports are less clear on the preparation of ribbon nanofibers, which should be able to be prepared by slightly tuning the stacked platelet nanofiber preparation conditions.

In earlier publications from the research group, it was shown that catalysts with significant quantities of stacked cup nanostructures had the highest ORR activities\textsuperscript{140,141,144,145}. In these catalysts 60-70% of the nanofibers present were stacked cups. It would be ideal to be able to produce stacked cup nanofibers with 100% concentrations. This would require that magnesia not be used as a support, as it is known to form nanocubes as well. Preliminary results from the group using self-assembled iron nanoparticles on dispersed silicon wafers as the nanofiber growth catalysts during acetonitrile pyrolysis have been able to produce 100% stacked cup nanofibers, but in quantities less than 1 mg per batch (opposed to 300-500 mg per batch for CN\textsubscript{x} grown over 2%Fe/MgO-HCl washed). Investigating high surface area materials to support these iron nanoparticles during acetonitrile pyrolysis would be interesting. The support should be able to keep the nanoparticles from agglomerating without participating in the
nanofiber growth process to produce undesired nanostructures. Mesoporous silica should be investigated as one such support. A non-traditional support like polymethylmethacrylate (PMMA) nanospheres could also be used. In this case, the PMMA support could be burned off before pyrolysis, leaving shells of iron nanoparticles behind.

In addition to the suggested work above, the use of the baseline catalyst CN$_x$ grown over 2%Fe/MgO-HCl washed should be evaluated more closely. While this catalyst may have substantial ORR activity and be easy to produce, some of its other characteristics may make it a less than ideal catalyst for use in an actual fuel cell. The bulk density of the CN$_x$ grown over 2%Fe/MgO-HCl is significantly higher than CN$_x$ grown over VC, Al$_2$O$_3$ and SiO$_2$, as well as, the commercial Pt/VC catalysts. This higher bulk density has the potential to increase mass transfer resistances within a fuel cell significantly. It is also possible that membrane electrode assembly (MEA) preparation could be hindered by the use of thicker catalyst layers to obtain the same activity levels as other catalysts.
CHAPTER 14. Glossary of Acronyms

**BET.** Brunauer, Emmett and Teller. A method for determination of material surface area using a multi-layer adsorption theory.

**CNx.** Nitrogen-Containing Carbon Nanostructure. This is the general carbon-nitrogen catalyst studied in this dissertation.

**CV.** Cyclic Voltammetry or Voltammogram. An electrochemical method where potential is controlled by scanning at a known rate and range in both cathodic and anodic directions while monitoring current.

**DMFC.** Direct Methanol Fuel Cell. A type of low-temperature fuel where fuel fed is 1-3M aqueous methanol and oxidant is oxygen.

**HCRG.** Heterogeneous Catalysis Research Group. The research group of Professor Umit S. Ozkan in the Department of Chemical and Biomolecular Engineering at The Ohio State University.

**HOR.** Hydrogen Oxidation Reaction. In a PEM fuel cell, this reaction occurs at the anode. In an acidic aqueous system at 25°C, the reaction is:
\[ H_2 \rightleftharpoons 2e^- + 2H^+ \quad 0.00 \text{ V vs. NHE} \]

**MEA.** Membrane Electrode Assembly. The interior components of a fuel cell that combines the gas diffusion layers, catalyst layers and membrane electrolyte.

**MOR.** Methanol Oxidation Reaction. In a direct methanol fuel cell, this reaction occurs at the anode. In an acidic aqueous system at 25°C, the reaction is:

\[ CH_3OH + H_2O \rightleftharpoons CO_2 + 6H^+ + 6e^- \quad 0.02 \text{ V vs. NHE} \]

**ORR.** Oxygen Reduction Reaction. The reaction occurring at the cathode in both direct methanol and PEM fuel cells. In an acidic aqueous system at 25°C, the reaction is:

\[ O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O \quad 1.23 \text{ V vs. NHE} \]

**NHE.** Normal Hydrogen Electrode. Standard reference in which electrochemical potentials are reported. It is the potential at which hydrogen oxidizes in an aqueous acidic system at 25°C.

**PEMFC.** Proton Exchange Membrane Fuel Cell. Also known as Polymer Electrolyte Membrane Fuel Cell. This is a low temperature hydrogen fuel cell.

**RRDE.** Rotating Ring Disk Electrode. This is an electrochemical half cell testing method in which one reaction is performed on the disk electrode and its products are monitored on the ring during laminar flow. In the study of ORR catalysts, the disk reduces oxygen and the ring monitors any hydrogen peroxide products.
**SEM.** Scanning Electron Microscope. An electron microscope where electrons are backscattered from sample for detection.

**TEM.** Transmission Electron Microscope. An electron microscope where electrons are transmitted through sample for detection.

**TGA.** Thermogravimetric Analyzer. An instrument in which temperature can be controlled while monitoring mass changes.

**TPO.** Temperature Programmed Oxidation. An experiment where temperature is controlled while flowing an oxidizing gas over a sample. The products are analyzed for characteristic temperatures and species.

**XPS.** X-Ray Photoelectron Spectroscopy. A surface sensitive method in which an X-ray beam is directed at a sample which then photoemits electrons at characteristic binding energies. These characteristic binding energies are based upon the chemical species and chemical bonding of the species.

**XRD.** X-Ray Diffraction. A method in which monochromated X-rays bombard a sample and the reflected X-rays are detected at the scattering angle. The scattering angle at which the rays are reflected are characteristic of the chemical phases for crystalline materials.
REFERENCES


2. In 2007 Ohio Fuel Cell Symposium, Columbus, Ohio, May 23-24, 2007; Columbus, Ohio.


225


362. Faubert, G.; Cote, R.; Guay, D.; Dodelet, J. P.; Denes, G.; Bertrand, P., "Iron catalysts prepared by high-temperature pyrolysis of tetraphenylporphyrins adsorbed on


