Novel Approach to Non-Precious Metal Catalysts

Final Report

Cooperative Agreement No. DE-FC36-03GO13106

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Prepared for:

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Foreword and Acknowledgements

This report documents the work performed by 3M Company under Cooperative Agreement No. DE-FC36-03GO13106, “Novel Approach to Non-Precious Metal Catalysts.” The period of performance for this contract was September 1, 2003 to August 31, 2007.

Catalyst and MEA materials fabrication and process development work were carried out by 3M Company at the 3M Center in St. Paul, Minnesota. The 3M team included primarily members from the Fuel Cell Components Program, Corporate Research Materials Laboratory, and Corporate Research Process Laboratory, but significant assistance was received from the Corporate Research Analytical Laboratory. Dr. Radoslav Atanasoski was the Principal Investigator and Technical Team Leader, Dr. Judith Hartmann the Program Manager, and Mr. Steven Kays of 3M’s Government Research and Development Center the Contract Administrator.

Dalhousie University (Halifax, Nova Scotia, Canada) served as a subcontractor for the program. The research team included Drs. Ruizhi Yang, E. Bradley Easton, Arman Bonakdarpour, and Arnd Garsuch and the effort was led by Professor Jeff Dahn.

Collaborations were established with Dr. X.-Q. Yang and Dr. W.-S. Yoon at Brookhaven National Lab, Professor David Wieliczka at University of Missouri – Kansas City, and Professor J-P Dodelet of INRS-Energie, Matériaux et Télécommunications, (Varenes, Quebec, Canada).

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Executive Summary

This report details the work performed by 3M Company under 3M/DOE Cooperative Agreement No. DE-FC36-03GO13106, “Novel Approach to Non-Precious Metal Catalysts.” The technical work in this report covers the period from September 1, 2003 to August 31, 2007.

This project was directed at reducing the dependence of PEM fuel cell catalysts on precious metals. The primary motivation was to reduce the cost of the fuel cell stack as well as the overall system cost without loss of performance or durability. Platinum is currently the catalyst of choice for both the anode and the cathode. However, the oxygen reduction reaction (ORR) which takes place on the cathode is an inherently slower reaction compared to the hydrogen oxidation reaction (HOR) which takes place on the anode. Therefore, more platinum is needed on the cathode than on the anode to achieve suitable fuel cell performance. As a result, developing a replacement for platinum on the cathode side will have a larger impact on overall stack cost.

The drawbacks of using platinum as an ORR catalyst include its price, scarcity, and susceptibility to forming oxides at voltages of interest for efficient fuel cell operation. The price of platinum has more than doubled during the time period between the drafting of the proposal for this project and its completion. The monthly average price in the beginning of 2003 was \$620/troy oz and the present price is \$1450/troy oz. At these numbers and the 2010 DOE targets of 0.2 g Pt/kW and \$30/kW, the cost of fuel cell stack would be over 30% due to platinum. Thus, the specific objectives of the project, as stated in the solicitation, were to produce non-precious metal (NPM) cathode catalysts which reduce dependence on precious metals (especially Pt), perform as well as conventional precious metal catalysts currently in use in MEAs, cost 50% less compared to a target of 0.2 g Pt/peak kW, and demonstrate durability of greater than 2000 hours with less than 10% power degradation. During the term of the project, DOE refined its targets for NPM catalyst activity to encompass volumetric current density. The DOE Multi-Year RD&D Plan (2005) volumetric current density targets for 2010 and 2015 are greater than 130 A/cm³ and 300 A/cm³ at 800 mV (IR-free) respectively.

The initial approach to achieve these targets was to use vacuum deposition techniques to deposit transition metal, carbon and nitrogen moieties onto 3M’s nanostructured thin film (NSTF) catalyst support. While this approach yielded compounds with similar physicochemical characteristics as catalysts reported by others as active for ORR, the activity of these vacuum deposited catalysts was not satisfactory. In order to enhance catalytic activity additional process steps were introduced, the most successful of which was a thermal treatment. To withstand high temperatures (~900 °C), alternative supports to NSTF were introduced. A variety of carbon fabrics were tested for this purpose. Vacuum deposited materials were used as precursors and physicochemically transformed via thermal treatment to produce substantially better catalytic activity. This activity was further amplified by increasing the surface area of the carbon fabrics which lead to significant gains in fuel cell performance.

The second synthetic approach was based on 3M nanotechnology and involves depositing precursor catalytic materials on high surface area supports, initially carbon. These materials were subsequently thermally treated in a nitrogen-containing gas atmosphere. While this approach is similar to others reported in the literature, we exploited 3M's nanotechnology platform and our expertise in the areas of synthesis and application of the precursor on the substrate. ORR activity proved higher for the materials produced via this approach. In fact, to our knowledge, the performance achieved from this effort exceeded the best previously reported for any NPM catalyst. With 4-nitroaniline as a precursor, the volumetric current density of our material achieved 19 A/cm^3 at 800 mV (using a Tafel slope extrapolation, see section 4.C), exceeding the value reported by DOE as the 2005 status (8 A/cm^3) by a factor of more than two. We emphasize a unique feature of this project was that all measurements were done in real PEM fuel cells using 50-cm^2 MEAs, therefore rendering credibility to the data for practical projection to a fuel cell stack application. In addition, the price of the precursor nitroaniline is only $\$1.5 \text{ kg}^{-1}$ on the commodity market, which enables reducing the DOE requirement of the cost of the catalyst by a factor of two.

A drawback of high-performing catalysts on carbon supports is their poor durability. Therefore, in the last stage of this project the focus shifted towards improving the stability of the NPM catalyst. For that purpose alternative supports to carbon were introduced. The best catalyst synthesis methods remained practically the same for the new supports. Consequently, catalysts were made that were stable up to 1.4 V and one such material ran for over 1000 hours in a 50-cm^2 fuel cell with no significant performance loss.

Throughout the project, a close interaction with Dalhousie University as a subcontractor helped define the area of stability and activity of the Fe (and Co)-C-N material systems. Detailed XAS and UPS studies performed using synchrotron facilities at Brookhaven National Lab and the University of Wisconsin, identified significant changes that took place in the catalysts upon thermal treatment. Finally, modeling work guided and verified the results coming from both the vacuum and nanotechnology approaches. The modeling was performed in a feedback mode with the experimental findings.

In conclusion, by using precursor materials that are commodity items this project achieved the best performing and the most durable NPM catalyst reported thus far in PEM fuel cells. The knowledge base in the area of NPMC has been substantially increased and a solid platform for reaching the 2010 and 2015 targets of the DOE Multi-Year RD&D Plan has been established.

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Appendix 1 – Copies of Publications

List of Abbreviations

AC	Alternating current
CCB	Catalyst coated backing
CV	Cyclic voltammograms
DC	Direct current
ESCA	Electron spectroscopy for chemical analysis
EXAFS	Extended x-ray absorption fine structure
FC	Fuel cell
GDE	Gas diffusion electrode
GDL	Gas diffusion layer
HOR	Hydrogen oxidation reaction
MEA	Membrane electrode assembly
NPM	Non-precious metal
NSTF	Nanostructured thin film
OCV	Open circuit voltage
ORR	Oxygen reduction reaction
PEM	Proton exchange membrane
PEMFC	Proton exchange membrane fuel cell
RDE	Rotating disk electrode
RF	Radio frequency
RRDE	Rotating ring disk electrode
SEM	Scanning electron microscopy
SHE	Standard hydrogen electrode
SIMS	Secondary ion emission spectroscopy
TM	Transition metal
UPS	Ultra-violet photoelectron spectroscopy
UV	Ultra-violet
XANES	X-ray absorption near edge structure
XAS	X-ray absorption spectroscopy
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
XRF	X-ray fluorescence

1. Overview and Objectives

1.A Introduction

This report details the work performed by 3M Company under 3M/DOE Cooperative Agreement No. DE-FC36-03GO13106, “Novel Approach to Non-Precious Metal Catalysts.” The technical work in this report covers the period from September 1, 2003 to August 31, 2007. The end date of the project had been amended from the original end date (August 31, 2006) by a modification to the Cooperative Agreement that was processed in April 2006.

Replacing platinum as a catalyst in fuel cells in general and in PEM fuel cells in particular has long been an industry goal. Well-known drawbacks of using platinum as a catalyst are its price and scarcity. An additional, fundamental limitation is that platinum reacts with water or with oxygen at high voltages producing an oxide layer that inhibits its catalytic activity in the oxygen reduction reaction (ORR) [1;2]. This oxide renders the platinum catalyst less efficient. Developing a suitable replacement could contribute significantly to fuel cells becoming widely accepted.

This project was directed at reducing the dependence of PEM fuel cells catalysts on precious metals in order to reduce the cost of the fuel cell stack as well as the overall system cost without loss of performance or durability. To achieve these objectives, the project focused on developing non-precious metal (NPM) catalysts that should:

- exhibit high inherent catalytic activity for oxygen reduction;
- have high volumetric concentration of active catalyst centers at the catalyst/membrane interface;
- demonstrate high stability with respect to reversible and irreversible processes such as corrosion;
- be fabricated by processes compatible with high-volume manufacturability;
- take into account that the total cost of the catalysts include the processing costs for their synthesis and integration into a membrane electrode assembly.

The specific objectives of the project, as stipulated in the DOE solicitation, were to produce NPM catalysts which would reduce dependence on precious metals (especially Pt), perform as well as conventional precious metal catalysts currently in use in MEAs, cost 50% less compared to a target of 0.2 g Pt/peak kW, and demonstrate durability of greater than 2000 hours with less than 10% power degradation.

Updated Department of Energy targets as introduced in the DOE Multi-Year Research, Development and Demonstration Plan in 2005, lists non-Pt catalyst activity per volume of supported catalyst as the performance metric. This metric takes into account that even if a catalyst that costs nothing were developed, there would still be implications as to the overall size of the stack based on electrode layer thickness. That is, one wants to minimize electrode layer thickness (to reduce stack size) while maximizing catalyst performance (for details see [3]). The DOE Multi-Year RD&D Plan (2005) lists the 2005 volumetric current density status in a single cell at 8 A/cm³ at 800 mV (IR-free) and the targets for 2010 and 2015 as > 130 A/cm³ and 300 A/cm³ at 800 mV (IR-free) respectively.

1.B Technical Background

The idea to eliminate the use of noble metals, in particular platinum and platinum group metals, for hydrogen – oxygen fuel cell electrocatalysis has existed even before the term electrocatalysis was coined. Platinum, with its unique electronic structure and chemical stability, has kept its position as a catalyst of choice in spite of the fundamental changes in technology that have taken place during the last several decades. The changes in fuel cell technology have been dominated by the electrolyte and have gone from alkaline to phosphoric acid and finally to polymer electrolyte membrane fuel cells (PEMFC). The amount of platinum used has significantly dropped over the last decade and is presently $\sim 0.4 - 0.6 \text{ mg/cm}^2$ for each electrode. However, because of the scarcity and high price of platinum, a large volume market penetration of the PEMFC would benefit from a further substantial reduction or, preferably, from a complete substitution with non-precious metal catalyst.

At present, platinum is the most commonly used electrocatalyst for both the hydrogen oxidation reaction (HOR) on the anode side and for the ORR on the cathode side. However, there is a fundamental difference in the mechanisms of the two reactions as well as their performance in operating fuel cells. The catalytic activity of platinum for the HOR, expressed through the exchange current density, is 6-10 orders of magnitude higher than that for the ORR. Because of these phenomena, there are two important consequences that impact the successful commercialization of fuel cells for stationary and automotive applications: a) The platinum loading on the cathode has to be higher than on the anode side (assuming hydrogen operation only); b) Even with typical higher platinum loadings, the cathode over-potential or energy penalty for driving the ORR at acceptable rates is such that an energy efficiency (electrical) of higher than 75% is not attainable. Thus, from an economic point of view the priority is on the elimination of platinum on the cathode side. This will have a large impact on the fuel cell performance as well as advantages in the cost and abundance issues associated with platinum and platinum recycling.

Early reports of non-precious metal catalysts for replacement of Pt focused on transition-metal macrocyclics. These materials have obtained attention ever since they were introduced forty years ago not only because of a theoretical interest but also due to evidence that thermally treated forms of these compounds exhibit improved activity for ORR. Notably, these compounds are also stable in acid environments and have the potential for lower cost. The transition metal elements are usually centrally coordinated by a macrocyclic molecule, and the elements of interest include iron, cobalt, chromium, nickel, and others. The macrocyclics typically include phthalocyanines and porphyrins. Numerous review articles exist where the mechanisms of ORR on these complex compounds are proposed along with their chemical and electronic structure [4;5]. Multiple metal center macrocyclics have been researched [6] with the approach of adjusting the metal-metal distance in order to facilitate the first step in the ORR mechanism, the adsorption of molecular oxygen (see [7] for an ORR mechanism overview).

From a technological point of view, only the metal-macrocyclic-like active centers formed with simple precursors such as iron hydroxide, acetate, etc. that have undergone further

thermal treatment appear to have enough potential to eventually replace platinum. (Note: other promising macrocyclics and compounds that contain precious metals such as ruthenium were not considered.) While numerous reports in the literature show evidence of improved catalytic activity and stability upon heat treatment, conclusive data as to the nature of the active sites formed after thermal transformation of the precursors are still lacking. A significant number of literature references point to the stabilization of the original metal - N₄ moiety of the chelate in the macrocyclics, which is centrally disposed and acts as a catalytic site [8]. Even if the synthesis of complex molecules such as the metal-macrocyclics demonstrated acceptable performance, they would not be of practical interest due to the cost of these compounds. Therefore, early on attempts were made to reproduce a similar type of catalytic activity by using much simpler transition metal precursors such as their common salts.

In the last several years, experimental evidence of the nature of the functional group that constitutes the active centers of these catalysts and the processes yielding their creation has been proposed. The topic was recently reviewed by Dodelet [9].

Lefevre et al. have documented most convincingly that with or without the use of macrocyclics as precursors, at temperatures higher than 800 °C, Fe—N₂—C entities are responsible for the catalytic activity [10]. The simultaneous presence of iron and nitrogen from components different than macrocyclics in a synthetic process carried out at 1000 °C was documented by Lalande et al. [11]. These researchers started with polyvinylferrocene as the iron precursor and acetonitrile as the nitrogen source and have demonstrated stable performance of their catalyst in PEMFC for 300 hours. Process conditions were optimized and new compositions were identified by adding carbon to the mix. Carbon can be introduced from the substrate or from the pyrolyzing gas and processing at temperatures higher than 800 °C resulting in nitrogen containing groups on the carbon substrate [12]. Besides producing the best catalyst in terms of activity and stability, the temperature of the heat treatment has been attributed as a factor in forming the structure of the Fe-N₂-C entities. Okada et al. [13] point out the “amorphous nature” of the compounds formed out of the iron, nitrogen and carbon mixtures, a feature that is important for our approach in the catalyst preparation. It also seems that the pyrolysis temperature is a factor in lowering the activation energy of the catalyst for the ORR [14].

In conclusion, forty years ago macrocyclic catalysts were identified as possible ORR catalysts and have evolved to the point that the active species can be produced without using macrocyclics at all. In addition, a partial knowledge of the nature of the active species, most likely identified as TM-N₂-C, opens up the space for new, more effective approaches to their synthesis, which were explored as part of this project.

1.C Approach and Tasks

Technical motivation

Among the model catalyst active center put forward thus far, the one supported the best by experimental evidence was proposed by Dodelet's group and is shown here in Figure 1.C-1.

Dodelet proposed that there are four requirements for catalytic activity: (1) a transition metal, such as Fe or Co, (2) a nitrogen source, either incorporated as a nitrogen-containing gas during the pyrolysis or a nitrogen groups as part of the starting carbon or transition metal source, (3) a carbon source, and (4) a high temperature treatment [12]. The initial approach 3M proposed was to incorporate elements (1) – (3) in a vacuum deposition process on 3M's unique nanostructured thin film (NSTF) catalyst support. The effect of the high temperature, as the fourth requirement, was meant to be substituted by the high energetics of the vacuum deposited elements. The NSTF substrate has been shown to have enhanced specific activities for Pt-based materials and be high volume roll-good manufacturability capable. Further, 3M has previously successfully vacuum deposited high activity PtTM cathode catalysts. Two types of vacuum deposition were identified: reactive sputter deposition and pulsed cathodic arc deposition.

Figure 1.C-1. The model catalyst active site as proposed by Dodelet's group.

In parallel, a nanotechnology-based synthesis approach was adopted which deposited precursor catalytic materials on high surface area supports. Initially the support was carbon and was subsequently thermally treated in a nitrogen-containing gas atmosphere. Two major directions in this part of the effort were (i) the deposition of combinations of variety of nanoparticles on high surface area substrates and (ii) the transition metal assisted polymerization of suitable monomers, both of which were followed by pyrolysis in nitrogen containing gasses.

To achieve the project objectives, new NPM catalysts were developed utilizing the infrastructure for, and understanding of, catalysts generated by previous and concurrent 3M/DOE cooperative agreements and 3M's commercial program. This included, in particular, high transition metal (TM)/low Pt catalysts, 3M's nanostructured thin film (NSTF) substrate [15], 3M nanotechnologies, and processes compatible with high volume manufacturability.

The work was divided into two principal tasks. The first task was focused on development of new materials through extensive catalyst fabrication and performance screening. The intent was to establish correlations between the various process parameters, the material composition and structure characteristics and the measured electrochemical properties. The second task was to focus on scale-up of the materials and processes to demonstrate the feasibility for high volume production. An objective of this task was to generate large area

MEA's for PEM fuel cell stack testing. The Task 2 effort was replaced by extended Task 1 activities in a modification to the Cooperative Agreement that was processed in April 2006.

Task 1. Research and Development of Transition Metal Based Catalysts

The objective of Task 1 was to develop the technology for producing non-precious metal catalysts that have catalytically active transition metal centers of high inherent ORR activity, are stable to fuel cell conditions, have sufficiently high interfacial concentration and can be processed using high volume compatible methods. A full array of materials characterization techniques, catalyst testing and fuel cell testing were used to select the best performing catalyst. These methods were necessary to provide feedback for modifications and new directions in the synthetic process. It has been pointed out by us and others during the last four years that the role of the transition metals as a key part of the catalytically active centers has been questioned. Their role may only be as participants or catalysts in the process of generating the active centers. This has to be kept in mind when we refer to the active centers generically as TM – N – C.

Subtask 1.1 Development and/or modification of equipment for catalyst syntheses

The basic vacuum deposition equipment facilities for producing the new TM-N-C type catalysts already existed at 3M. For both types of vacuum deposition (reactive sputtering and cathodic arc deposition), operational equipment was available. However, some modification to the coaters and added instrumentation for process control were necessary. Modifications to allow control of the process parameters identified in Subtask 1.2 below were the focus of these improvements. Since all of these modifications were done on existing 3M equipment, all of the material cost of these modifications was covered by 3M funds.

Subtask 1.2 Process development for catalyst syntheses

The objective of Subtask 1.2 was to develop synthesis and coating processes for the new TM-N-C based catalysts. The two main areas of development under this subtask were based on vacuum technology and on nano-technology. As illustrated in Fig. C-1, the two approaches were run interactively and were complementary to each other.

The two vacuum processes used, reactive sputtering and cathodic arc, had similar issues with respect to identifying the critical process parameters, calibration and control of those parameters, and establishment of databases correlating process parameters with the resulting material properties. Process parameters that were explored include source material compositions, gas compositions and flow rates, target power densities, plasma discharge characteristics, deposition rates, substrate characteristics and temperatures. The sequence of steps in the process method was also an important tool to effect different film properties, such as the degree of intermixing or alloying of multi-component elements. Composition of the nitrogen and Fe in the carbon films as well as the structure and morphology of the resulting deposits on the nanostructured support particles were also areas of study.

The nanotechnology approach was introduced to allow us to pursue the most promising technical directions to achieve the objectives of the contract outlined in Section 1.A by taking

advantage of the catalysts dispersed on high surface area supports. Both carbon and non-carbon based supports were investigated.

Variety of pre- and post-processing conditions, such as substrate modifications and thermal treatments, were also extensively explored. The next most important effect after the precursors/target materials were the processing conditions, both in the catalytic activity and the durability of the fabricated catalysts.

Initial efforts were focused on exploring new ways of fabricating Fe-N-C moieties as “model catalysts”. Once sufficient understanding was gained on the model catalysts, the effort was expanded to the development of new catalyst constructions and synthetic methods. Molecular modeling work as well as knowledge garnered from industry news and other 3M projects directed the synthesis of new compounds that were potentially active. Advances made in one area were used to improve and expand research in the other synthesis areas.

Figure 1.C-1. Overall synthetic and characterization approach.

Structural and electrochemical characterization in Subtasks 1.3 and 1.4 were used to identify the process conditions that produce the optimal TM-C-N catalytic site properties.

Extensive physicochemical characterization took place. Some of the techniques used are highlighted in Figure 1.C-1. Specifics of the measurement method are outlined in Section 2.A. Modeling was used to guide and verify the synthetic effort.

Functional characterization was performed chiefly in a 50-cm² fuel cell and was supplemented by other techniques, such as the segmented cell, gas diffusion electrode, and rotating-ring disk electrode (RRDE). Details of these measurement techniques can be found in Section 2.C. We are emphasizing throughout this report that most of the catalytic activity and catalyst durability testing took place in 50 cm² PEM fuel cells, an accepted test standard.

Subtask 1.3 New catalyst materials characterization

There were two principal objectives or activities for Subtask 1.3. One focused on the electrochemical screening and in-depth characterization of the materials fabricated under Subtask 1.2. The purpose of this work was to identify the sample fabrication process conditions that correlate best with the desired electrochemical properties necessary for good fuel cell performance. The second focused on chemical and structural characterization of the best performing materials. The purpose here was to correlate those material characteristics with both the desired electrochemical properties and the process conditions used to make them. In this way, continuous progress towards the desired catalyst performance was obtained.

Subtask 1.4 MEA formation and fuel cell evaluation of selected catalysts

This subtask was directed at fabrication of membrane electrode assemblies and their testing in 50 cm² sized single cells. 3M's experience with fabrication and testing of well over 10,000 MEAs during the life of the fuel cell project has resulted in key insights into the subtleties and science of forming effective interfaces between the catalyst electrode layers and the ion exchange membranes to which they are attached. Matching of the gas diffusion layers to those catalyst coated membranes, the influence of operating conditions for proper water management, and the application of a wide host of *in-situ* characterization tools are just some of the significant aspects necessary to learn how to fabricate effective MEAs when incorporating new-to-the-world materials.

Task 2. Scale-up, Fabrication, and Stack Testing

The objective of Task 2 was to scale-up the process and quantities of materials down-selected from Task 1. The goal of this task was to produce adequate quantities of catalysts and MEAs for testing in a 1-2 kW sized fuel cell stack having > 200 cm² active areas, while demonstrating the feasibility of the catalyst and MEA fabrication process costs meeting the goal of at least 50% less as compared to a target of 0.2 g Pt/peak kW. The Task 2 effort was replaced by extended Task 1 activities in a modification to the Cooperative Agreement that was processed in April 2006.

Project Timeline

The project timeline presented here is in its final version. Due to the exploratory nature of the R&D work, Task 1 was projected to run throughout the duration of the contract. Within Task 1, subtask 1.1 was extended in order to follow the new developments in the catalyst synthesis (subtask 1.2).

Project Timeline

9/03

8/07

1. R&D of NPM Catalysts

1.1. Dev/mod catalyst synthesis **equipment**

1.2. Process development & catalyst **synthesis**

1.3. New catalyst materials **characterization**

1.4. **MEA** formation & fuel cell **evaluation** of selected catalysts

Task 2 replaced by
extended activity in
Task 1 in April 2006

Go/No Go Decision for Task 2 ♦

2. Scale-Up, Fabr, & Stack Testing

2.1. Downselected process – facilities upgrades

2.2. Pilot scale coating process

2.3. Web-coated catalyst & CCM fabrication

2.4. Short stack testing

1.D Accomplishments

- Today, 3M's catalysts are among the best performing and most durable NPMC tested in a real PEM fuel cell environment.
- *Performance* expressed as volumetric current density of 19 A/cm³ at 800 mV was achieved, approaching the DOE 2010 target of 130 A/cm³ by a factor of less than 7 but exceeding the best value reported by DOE (8 A/cm³) by a factor of more than two.
- *Durability* of the catalysts made on non-carbon support of over 1000 hours in a 50-cm² fuel cell and in the useful voltage range above 0.6 V with no significant performance loss was accomplished vs. 2000 hours required in the solicitation for this project.
- *Costs* of 50% less compared to a target of 0.2 g Pt/peak kW can easily be achieved since the price of nitroaniline as a catalyst precursor for the most active catalyst at the commodity market is only \$1.5/ kg.
- Overall, the project established new synthetic approaches and opened new avenues for further development in the NPMC world.
- Strong interactive advanced characterization and modeling complemented the synthetic effort.
- Strong, fully-integrated collaborations supplemented 3M expertise and lead to fundamental understanding of catalyst.

- 19 publications, 20 presentations (9 *invited: plenary, key note or seminars*), and 5 patent applications were produced.
- Among the peer NPMC projects that were awarded by the 2003 DOE solicitation, the 3M Project was the highest ranked in all four years with an average score of 3.1 compared to the DOE fuel cell projects average of 2.8.

1.E Overview of the Report

To ensure cohesiveness, this report will be organized by topic rather than the tasks outlined in section 1.C. Section 2 will provide a background of both the physicochemical and electrochemical characterization techniques that were used during the project. Section 3 discusses the results obtained from the vacuum processing approach. Section 4 summarizes the highlights from the nanotechnology approach. In both sections emphasis will be given to the major breakthroughs, to the processes that produced the best catalytic activity and durability. The appendix lists all the publications that resulted from this projects. The publications provide a more thorough account of the approaches, details of the experiments as well as more in-depth discussion on particular topics. Copies of these publications are included and as such should be considered as an integral part of this report.

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2. Physicochemical and Functional Characterization

2.A. Physicochemical methods

X-ray photoelectron spectroscopy (XPS)

XPS, also known as electron spectroscopy for chemical analysis (ESCA), is used to measure near surface (~100 Angstrom) composition and provides chemical information by measuring core level binding energies. XPS measurements were performed using a Phi 5000 series ESCA system with a Mg source; survey composition measurements were made using a pass energy of 90 eV and the high resolution core level spectra were obtained using a pass energy of 20 eV. This technique has been used extensively to characterize the model catalyst. For this class of catalysts, high resolution spectra of the N1s peak often reveals two major components. The higher binding energy component at 400 eV is attributed to nitrogen substituting into sp²-bonded graphene rings. There is some disagreement regarding the lower binding energy component at about 398.5 eV. Some researchers attribute this peak to nitrogen bonded to sp³ carbon while others assign it to “pyridinic nitrogen” [1]. Jaouen et al. found that the oxygen activity in the model catalyst correlated with the N1s XPS intensity of the 398.5 eV component [2]. They also found that the binding energy of this component shifted to slightly higher binding energy as the Fe content increased, a result that was confirmed in our study.

X-ray absorption spectroscopy (XAS)

While XPS spectra of the vacuum deposited and model catalysts were similar, the fuel cell performance was not. More sensitive techniques were employed to attempt to resolve this disparity. In collaboration with scientists at Brookhaven National Lab, XANES (X-ray Absorption Near Edge Structure), which provides information about changes in the iron valence electrons such as local symmetry and electronic structure, and EXAFS (Extended X-ray Absorption Fine Structure), which provides information about the iron atoms coordination number and nearest-neighbor distances, were used to characterize catalyst materials.

Ultra-violet photoelectron spectroscopy (UPS)

UPS is a surface technique more sensitive to the changes in the valence electronic structure than XPS since the photon energies are used (20-80 eV) where the emission intensity of valence electrons is greatest, these energies also provide high surface sensitivity since the penetration depth is only about 3 nm (vs. over 10 nm for XPS). Valence photoemission spectra were taken with photon energies varying from 40 eV up to 70 eV where the Fe 3p-3d resonance occurs. Resonance enhances emission intensity from Fe 3d states and therefore can be used to locate valence d-states in Fe-based catalysts. For our studies, the spectra were obtained near the maximum of the Fe3d resonance at a photon energy of 55 eV [3]. To our knowledge, this project was the first time UPS was used for characterization of catalysts similar to ours. This experimental work was done in collaboration with Prof. D. Wieliczka, University of Missouri – Kansas City at the Synchrotron Radiation Center at the University of Wisconsin, Madison.

Secondary ion emission spectroscopy (SIMS)

Lefevre et al. used time-of-flight SIMS to study the model catalyst materials and learned that fragments containing multiples of FeN_2 and FeN_4 structures were common [4]. Correlating the oxygen activity with the FeN_2/C and FeN_4/C signals, they proposed that such structures are responsible for the catalytic activity with the FeN_2/C structure more active for ORR than FeN_4/C . Time-of-flight SIMS was performed on select vacuum deposited materials to determine if species containing iron, carbon and nitrogen were present and if any of these species has similar N to C ratios as the model catalyst. See [5] for an example of the SIMS data.

X-ray fluorescence (XRF)

XRF was used for elemental analysis. Samples were analyzed qualitatively for most elements in the periodic table (from carbon to uranium) using a Rigaku/MSX-100E wavelength dispersive x-ray fluorescence spectrometer equipped with a rhodium x-ray source, a vacuum atmosphere and a 20 mm diameter measurement area. Specifically, XRF could be used to measure the total amount of transition metal in the catalyst in powder or catalyst coated backing (CCB) form.

X-ray diffraction (XRD)

XRD was used to determine crystallinity, particle size, and nanostructure.

Scanning electron microscopy (SEM)

SEM was used in the initial phases of the project to assess the suitability of the nanostructured thin film (NSTF) supports before and after catalyst coating. For example, SEM was used to examine the effect of depositing very thick films of nitrogenated carbon on NSTF. This determined the thickest coating that could be used with the NSTF substrate. Later, SEM was used to study the alternative supports identified for the vacuum approach.

Ellipsometry

Coating thickness (on flat substrates) was calibrated to vacuum deposition parameters using ellipsometry.

Surface resistivity

The vacuum deposited samples were analyzed for surface resistivity. Measurements were performed according to ASTM D257 using a Keithley 8009 resistivity test fixture.

Acid soak

In order to determine the catalyst's stability in acid, an acid soak test was employed. In this test, the catalyst is placed in dilute acid (e.g. 0.5M H_2SO_4) at a set temperature (e.g. room temperature, 80°C) for a set length of time (e.g. 1 week) (for an example of the procedure see [6]). Electron microprobe was used to measure composition before and after acid soaking. If some material remains after the soaking, the catalyst is deemed acid stable.

2.B. Modeling

The first objective of modeling was to understand the thermodynamics interaction of carbon, nitrogen, and iron atoms as well as the catalytic site proposed by Lefèvre et al [7]. The second objective of modeling was to understand the effect of substrate temperature and presence or absence of hydrogen on the structures formed during the cathodic arc deposition process. Both of these objectives were studied using *ab initio* methods. The key “assumptions” of the modeling studies were the use of projector augmented waves [8] and density functional theory [9]. These theories formed the basis for the calculations and were used as implemented in Vienna Ab Initio Simulation - VASP Package [10] and have been tested extensively for various systems in the literature. The version of this commercial code used for the calculations was 4.6.25. A detailed summary of the techniques used as well as the specific validation studies performed for the Fe-C-N system can be found in [11].

2.C. Functional characterization

50-cm² fuel cell

The 50-cm² fuel cell was by far the most utilized functional characterization method. The major advantage of this technique is that it is the end-use environment of the catalyst – eliminating potentially irrelevant or spurious effects that might be seen with other methods. In general, the catalyst material would be incorporated into a membrane electrode assembly (MEA) with a dispersed Pt/C catalyst as the anode catalyst (0.3 – 0.4 mg Pt/cm²) and a Nafion™ membrane. This MEA would be placed into a 50-cm² test cell (Fuel Cell Technologies) and run on a test stand. The test stand has capabilities to regulate gas flow, temperature, back pressure, and humidity as well as control voltage and current. The catalysts were tested for performance, durability (once performance reached an acceptable level), and voltage stability (if an alternative rather than carbon support was used).

In general, performance testing consisted of:

1. AC (alternating current) impedance to determine coating resistance
2. Cyclic voltammetry under nitrogen to characterize the surface of the catalyst and serve as a baseline for oxygen activity
3. Current-voltage measurement under oxygen for catalytic activity.

In order to obtain more representative data and/or to establish reproducibility, this sequence was repeated usually twice a day for four to seven days. The cell was cooled down between the two testing periods and the gasses were shut off.

A total of 364 50-cm² MEAs were tested during the duration of the project. To accommodate the testing requirement, the number of test stations dedicated to the project has increased from one at the start of the project to four during the third year. The demand for test station time increased substantially with the durability testing.

Durability testing consisted of potentiostatic polarization at fixed voltage under air at 75°C. Every five hours, a polarization curve would be taken to assess performance. The

potentiostatic hold and polarization curves measurements were continuously repeated. Periodically, AC impedance and CVs under nitrogen were performed to assess the state of the catalyst.

Voltage stability testing was performed by holding the cell at high voltage (≥ 1.2 V) under nitrogen. Performance, CVs under nitrogen, and AC impedance were measured before and after each high voltage step.

A Solarton 1470 multi-channel potentiostat controlled by CorWare™ software (Scribner Associates) was used for all the testing.

Segmented fuel cell

The segmented fuel cell was originally developed under 3M/DOE Cooperative Agreement #DE-FC02-99EE50582 and further modified under 3M/DOE Cooperative Agreement # DE-FC36-02AL67621. In short, a standard 50-cm² fuel cell was modified to have eight segments that are electrically isolated from each other. The MEA was made such that catalyst was only present on the active segment area of the cell. This allows for eight different catalyst materials to be assessed simultaneously. This technique is effective when there are large performance variations among the catalysts. However, tests using 50-cm² fuel cells are more effective at pinpointing small variations in catalyst performance. Approximately 20 segmented cells allowing for the screening of over 80 catalysts were assembled during the project.

Dalhousie University used its 64-channel segmented cell to assess many of the composition spread materials. Similar to the 3M segmented cell in design, the Dalhousie cell has 64 electrically isolated segments allowing for performance screening of a wide range of compositions. Further details of the 64-channel cell construction can be found in [12].

Gas diffusion electrode

Due to the large number of samples prepared on carbon paper or fabric supports and long duration of fuel cell testing, the gas diffusion electrode (GDE) technique was employed to complement the fuel cell testing. In this technique, the catalyst material (deposited on a backing made of carbon or other conducting material which is permeable to gas) is placed in contact with an acid electrolyte (0.5M H₂SO₄) solution. To measure performance, oxygen is bubbled through the catalyst and into the solution while the cell is polarized. A Pt wire serves as counter electrode and a mercury-mercury sulfate or saturated calomel reference electrodes were used. Figure 2.C-1 is a schematic representation of this test cell set-up. In this method, the entire volume of the catalyzed GDL is exposed to the liquid electrolyte in contrast to only the surface in contact with the PEM in a fuel cell. The GDE is a more corrosive environment than is usually seen in a fuel cell due to the presence of liquid acid. Catalyst materials that are not acid-stable will dissolve. During the project, over 60 samples were tested using the GDE technique. While the results of the GDE were often similar to those obtained the fuel cell, there were some discrepancies. Overall, while the technique may have utility as a rapid-screening method, it is not best suited for careful catalyst characterization.

Figure 2.C-1. Schematic representation of Gas Diffusion Electrode test cell.

Rotating-ring disk electrode (RRDE)

RRDE measurements were performed to gain fundamental knowledge about the catalytic activity. In general, the catalyst is coated onto a glassy carbon disk, which is immersed into an acid electrolyte solution. Activity is measured by monitoring voltage and current in an oxygen-saturated solution. The amount of peroxide formed (from incomplete oxygen reduction to water) can be detected by setting the ring at a high voltage (~ 1.2 V vs. SHE) and measuring the oxidation current. The RRDE measurements were performed in collaboration with Professor Jeff Dahn's group at Dalhousie University. For further information on these measurements, see [13].

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3. Catalyst Development – Vacuum Approach

3.A Introduction

The initial phase of the project focused on fabricating baseline TM-C-N materials using vacuum processing. The aim was to reproduce $\text{Fe-N}_2\text{-C}_x$ as a model active center, as described in papers by J.-P. Dodelet [1,2]. These new, vacuum deposited, NPM catalysts utilized 3M's unique nanostructured thin film (NSTF) substrate [3], and processes compatible with high-volume manufacturability. See Section 1 for a complete discussion of the approach.

In order to synthesize the NPM catalytic sites, several different sets of vacuum equipment were used. All three elements of the model catalyst (C, N, TM) could be deposited in one-step. Alternatively, highly nitrogenated carbon could be produced as a precursor for subsequent deposition of transition metals and conversion to catalytic sites (two-step process). These two synthetic routes are illustrated in Figure 3.A-1.

Figure 3.A-1. Schematic presentation of the two synthesis paths.

Initial work focused onto deposition onto 3M's NSTF substrate. Later, due to the higher impedance observed with the NSTF support and the inability to use the NSTF at high (~900

°C) temperatures, carbon fabric was used as a substrate. As the project matured, modifications to the carbon fabric which increased surface area were explored.

3.B Vacuum deposition techniques and systems

During the course of this contract, three different vacuum deposition techniques utilizing six different vacuum systems were employed to produce catalyst material.

The first technique, pulsed cathodic arc plasma deposition, uses high power and large capacitors to deliver an energetic pulse to the tip of a pressed carbon rod (for C) or carbon rod with embedded Fe wires (for C-Fe). This ionizes the tip of the rod leading to deposition of a film of the material on a substrate (for more information on the cathodic arc technique see [4]). Thickness and film uniformity can be precisely controlled as well as the composition of the final film. Purity of the film is obtained by using high quality starting materials. The vacuum system was pumped to the low 10^{-6} Torr range. This technique has been shown to produce highly nitrogenated carbon (CN_x) materials [5]. CN_xFe could be fabricated using a composite C-Fe target and a flow of nitrogen or ammonia to the chamber [6].

Sputter deposition was the second technique utilized. Both RF and DC magnetron systems were used at various points in the project. It has previously been shown that Fe-N compositions can be made with sputter deposition using RF magnetron sputtering and a N₂/Ar atmosphere [7;8]. The first sputtering system used to produce Fe-C-N materials on this project was a Perkin-Elmer Randex RF sputtering system. An RF power supply and matching automatic impedance network were used to sputter Fe on to our substrates. Base pressure was in the low 10^{-6} Torr range. Reproducible results were difficult to achieve when only sputtering was used for catalyst synthesis.

The second sputtering system that replaced the Randex had the capability for either DC or RF magnetron deposition, although only the DC magnetron sputtering capability was used during this project. This drum-based system can be pumped down to the 10^{-7} Torr range and has three magnetron based target positions including one with specially made enhanced magnet assembly. While DC sputtering is generally difficult with magnetic materials, iron could be sputtered using a thin target and the enhanced magnet setup. Reactive gasses could be added during the deposition. The drum system is a cryopump-based system inherently cleaner than other systems. A drum heater was also available for use. Control of the pressure ratio of the gases, reactivity of the gases (e.g. ammonia), sputter deposition rates, and substrate morphology are all important process parameters that can be controlled to obtain the desired material catalyst properties.

The third technique, thermal evaporation used resistive heating to evaporate Fe, C and N-containing organics in a controlled fashion. No working gas is needed. The system is pumped to 10^{-7} Torr and the material was added through a load lock and evaporated. No special care was taken not to expose this material to atmosphere.

For samples thermally treated, post-treatments were performed in a quartz tube furnace. Later in the project, a resistive heater was added to the cathodic arc system for in-process heating. This heater had the capability to reach approximately 650 °C.

We are pointing out that while several different vacuum systems were used, in the future it would be possible to combine several of these techniques (e.g., cathodic arc, sputtering, and thermal treatment) in one vacuum system leading to a simple, one-step manufacturing process.

3.C Catalyst characterization

Physicochemical characterization of initial depositions of TM-C-N

As previously noted, the initial phase of the project was directed at vacuum depositing TM-C-N materials on NSTF support for fuel cell testing and Si wafers or glass slides for analytical characterization. This was done in one step via the pulsed cathodic arc process. Alternatively, nitrogenated carbon would be made by the cathodic arc process followed by a subsequent sputter deposition of Fe to make the catalyst.

XPS spectra from the nitrogenated carbon (C-N_x) showed a nitrogen content of 10 to 12 atomic %, which is approximately five times higher than that of the model catalyst. Carbon content of these coatings was 85 to 88%. Similar to the model catalyst, high resolution spectra of the N1s peak had a higher binding energy component at about 400 eV and a lower binding energy component at 398.5 eV. The carbon 1s peak was also found to be similar to the model catalyst. Specifically, the C1s spectra has an asymmetric peak due to three or four components. The major peak component, due to C-C bonds, has a binding energy of about 284.5 eV. Nitrogen incorporation adds a small C1s component at about 288.8 eV.

This C-N_x material was transferred into another vacuum system for deposition of transition metals (Fe and Fe alloys). XPS analyses of the initial materials show that about 10% transition metal is added to the near surface region, probably on top of the C-N_x coating. The oxygen content after the first step was generally between 1 and 3 at %, similar to the levels reported for the model NPM catalysts. However, after the second step, the near surface region had significant oxygen content. The high oxygen content detected in these samples may be caused by oxidation during transfer of the samples between systems.

From a processing point of view, the preferred way to make the catalyst would be in one step using one set of equipment. To accomplish this, new targets containing both carbon and iron needed to be fabricated. In collaboration with Dalhousie University, several Fe/C targets with Fe content varying from 5 to 25 % by weight were produced. However, these targets lacked the mechanical integrity to withstand the arc deposition process (this was especially true for the cathodic arc process). The effort with Dalhousie alerted us to the need for uniformity and the proper particle size for the composite targets.

In order to produce a composite target appropriate for cathodic arc deposition, iron wires were pressed into the graphite cathode. This allowed for successful deposition of C-N-Fe all

in one step in one piece of equipment. Analysis of the XPS spectra show a change in the intensity and binding energy of the nitrogen 398.5 eV component with Fe content. Figure 3.C-1a shows XPS spectra of the N1s core level in a nitrogenated carbon sample (lower spectrum) and a vacuum deposited CNxFe (7%) sample (upper spectrum). Peak fitting shows 2 main components near 398.5 eV and 400.3 eV. As the Fe content increases, the component at approximately 398.5 eV shifts to higher binding energy. Figure 3.C-1b plots the relative intensity of the 398.5 eV component (peak 1) relative to the ~ 400 eV component (peak 2) as a function of the Fe content. More “pyridinic”-type nitrogen (398.5 eV component) is seen as Fe content increases [6].

Figure 3.C-1. (A) Comparison of XPS spectra for CNx (bottom) and CNxFe (top). Note the shift to higher binding energy of the component at about 398.5 eV with the addition of Fe. (B) Ratio of peak at 398.5 eV to the ~ 400 eV component. Note that more “pyridinic”-type nitrogen is produced as the Fe content increases.

Electrochemical performance of initial TM-C-N catalysts

The catalysts made on NSTF substrate were transferred via hot roll lamination to a Nafion™ membrane, made into an MEA, and tested in a 50-cm² fuel cell according to the procedure outlined in section 2.C. In general, these materials were found to perform poorly. It was postulated that the poor performance was due in part to the high impedance of these catalysts. The first interim milestone of the project was set as understanding and overcoming this high impedance issue.

To understand better the nature of the high impedance, the materials characterization efforts were expanded to include resistivity and thickness measurements. It is well known that the total resistance of a thin film decreases as the film thickness increases and that only after a threshold thickness does the dependence become linear. Measurements of the film resistivities on flat substrates indicated that, for a given thickness, the nitrogenated carbon coatings deposited by the cathodic arc process are about three orders of magnitude less resistive than pure carbon coatings. However, when applied on NSTF whiskers as substrate, the impedance remained high even for thicker C-Nx deposits. In order to prove that the C-Nx deposit resistivity was the cause for the high impedance, a gold underlayer on top of the

NSTF but beneath the C-N_x catalyst was deposited. This was found to dramatically reduce AC impedance, which indicated that the C-N_x coatings were not sufficiently conductive for fuel cell applications.

Vacuum-deposited TM-C-N on carbon fabric substrate

Due to the high impedance of NSTF, carbon fabric was identified as alternative support. After initial screening, Freudenberg H23-15 (Freudenberg GmbH, Germany) was selected for this purpose. This material has the additional benefit of being thermally stable. In order to form an MEA, the catalyst deposited on carbon fabric was put in contact with the membrane on the cathode side. The catalyst coated on the carbon fabric served as both catalyst and gas diffusion layer (GDL). AC impedance (total ohms/fuel cell) on an identical coating on NSTF, carbon fabric, and carbon fabric subsequently thermally post-treated are presented in Figure 3.C-2a.

Figure 3.C-2. Effect of substrate and thermal post-treatment of vacuum-synthesized catalyst on (A) AC impedance and (B) oxygen polarization curves.

Impedance values were found to be strongly dependent on substrate type. The carbon fabric substrate gave lower impedance values than the NSTF whiskers. The post-process thermal treatment of the coated carbon fabric decreased the impedance further. Oxygen response

increased as the impedance decreased (Figure 3.C-2b). However, the decrease in impedance cannot fully account for the increase in activity. By identifying a methodology to improve the impedance to an acceptable level and by improving the understanding of its origin, one of the interim milestones of the project was fulfilled.

Thermal treatment effects

To better understand thermal treatment effects, a systematic study was undertaken to determine the thermal treatment conditions required for optimum catalytic activity. Segments of the same lot of catalyst (coated in the same process run) were taken and thermally treated to three different temperatures under two different firing gases. Figure 3.C-3 details the results of this study. Higher temperature thermal treatments are better with ammonia a superior thermal treatment gas to nitrogen.

Figure 3.C-3. Performance at 0.6V in a 50-cm² for an identical catalyst treated to 400 °C, 600 °C, or 800 °C in an ammonia or nitrogen atmosphere.

Thermal treatment is clearly needed to activate the catalyst material. However, thermal post-treatment requires that the sample be transported between two different systems (deposition system and furnace), which may be cumbersome and is not ideally suited for high volume manufacturability. Heating the sample during deposition can be an easier and quicker way of achieving the same catalytic activity. For this reason, the cathodic arc system was modified to have a resistive heater so that the samples could be heated during the deposition process. Figure 3.C-4 compares the polarization curves of a catalyst heated during the deposition

(~625 °C/NH₃) with a catalyst that was deposited and subsequently thermally post-treated (600 °C/NH₃). For reference, the performance of the catalyst without heat treatment is also presented. Heating during the deposition clearly enhances performance. What is remarkable is that the performance achieved via heating during the deposition is very similar to that achieved with a post-deposition thermal treatment. This correspondence points to a potential processing advantage.

Figure 3.C-4. Fuel cell performance of CN_xFe catalysts as-deposited at ambient temperature (no thermal treatment), thermally post-treated in a tube furnace to 600 °C in ammonia (post-treated), and heated during the deposition to 625 °C in an ammonia atmosphere (in-process treatment).

High throughput approach – Dalhousie University

Simultaneously and in collaboration with the work at 3M, Dalhousie University used its rapid screening techniques to map the region of the C-N-Fe phase diagram that was stable in an acidic environment. Following the 3M experience with thermal treatment for activating the vacuum deposited catalysts, a thermal treatment step was added to the synthetic process. The acid soak test as described in section 2.A was used to determine acid stability. Figure 3.C-5 gives an example of the results from the acid soaking. The glass slide at the far left is an example of a film as deposited. The carbon and iron contents vary across the slides. The arrows indicate the direction of the variation. The second slide from left has not been

subjected to thermal treatment, but was subjected to the acid soak test (immersion in 0.5M H_2SO_4 for 7 days). The two slides at right were each thermally treated to temperatures T_a and T_b ($T_b > T_a$) respectively in an argon atmosphere and subsequently tested for acid stability. Note that the bare area near the bottom of the slides is due to the film flaking off the glass (due to the film being very thick). The amount of material remaining on the slide increases as the thermal treatment temperature increases. This would indicate that higher temperature thermal treatments yield greater acid stability.

Figure 3.C-5. Stability of a range of compositions sputtered on a glass slide (left) and tested for acid stability (right three slides) after sputtering (second from left) and after thermal treatment to T_a (600 °C) and T_b (800 °C).

RRDE studies were performed to assess the ORR activity. The area of the Fe-C-N phase diagram that is both stable in acid and ORR active was defined. This area is depicted as the shaded area in Figure 3.C-6. More detailed results from these studies can be found in [9]. Similar studies were undertaken with Co-C-N [10;11].

Figure 3.C-6. Region of acid stability (determined by acid soak test) and activity (determined by RRDE measurements) of Fe-C-N catalysts. Same symbols belong to same run of a single compositional spread. The black star indicated by the black arrow represents a sample with high cobalt content.

Figure 3C-7 displays the disk CVs obtained under oxygen for Fe-C-N libraries annealed to 700, 800, and 1000 °C. Compositional spreads that were not annealed (not shown) were not active toward oxygen reduction. For comparison, the activity reported by Dodelet's group for their 0.2% Fe acetate catalyst on a high surface area carbon support (total Brunauer-Emmett-Teller (BET) surface area = 370 m²/g) is also shown in Fig. 3.C-7. Reasonably good activity has been achieved, although the activity is less than that reported by Dodelet [2]. However, our catalyst libraries are thin films that most likely have a significantly smaller electrochemical surface area.

Looking at trends across the libraries, catalytic activity increases with increased Fe content for libraries that were annealed at 700 and 1000 °C. However, the library annealed at 800 °C exhibited increased activity with decreasing Fe content. For each individual disk, activity typically improved upon increasing the annealing temperature from 700 to 800 °C. However, further increasing the annealing temperature from 800 to 1000 °C decreased the catalytic activity.

Figure 3.C-7. Disk current densities for sputtered compositional spreads annealed at 700, 800, and 1000 °C. Measurements: 5 mV/s in O₂-saturated 0.1 M HClO₄ at room temperature. Average composition on each disk indicated on the plot. Activity reported by Dodelet's group for 0.2% Fe acetate (900 °C) at 100 rpm (dashed line) are for comparison.

Further insight into the genesis of the active centers can be obtained by simultaneously following the compositional, structural and morphological changes and by correlating these changes with the ORR catalytic currents at different stages of the thermal treatment. As illustrated in figure 3C-8 (left panel), the loss of nitrogen at a given temperature (> 700 °C) coincides with the onset of the ORR current. The right panel illustrates how the effects of the temperature on the morphological changes and correlates the increase in the heterogeneity of the deposit with the increase in the ORR catalytic activity.

In conclusion, annealing sputtered TM-C-N films was demonstrated to increase catalytic activity dramatically. The onset of catalytic activity for ORR coincides with a transformation from a homogenous amorphous TM-C-N film to a heterogeneous mixture of partially graphitized carbon and Fe₃C or Co, as observed by XRD and SEM. The onset of this transformation occurs both as a function of TM content and temperature. Catalyst activity for ORR is at its maximum partway through this transformation. If this transformation goes to completion, almost all N is lost from the film for the case of Fe and the catalytic activity severely drops. Maximum catalytic activity with TM-C-N libraries is achieved at an annealing temperature of 800 °C for both Fe and Co. The Co-C-N libraries retain their

catalytic activity when annealed up to 1000 °C, and perhaps beyond, because they retained an appreciable quantity of nitrogen even at 1000 °C.

The **loss of nitrogen** is accompanied by a transition from **homogeneity to heterogeneity** in the material structure which is reflected on ORR activity as measured by RDE.

Figure 3.C-8 Nitrogen loss, morphological changes and ORR activity with temperature of the thermal treatment. Left panel, from top: Co content, nitrogen content, Co particle size, ORR onset potential, and ORR current at 0.7 V as a function of heat-treatment temperature. Right panels: Changes in heterogeneity and corresponding RDE (900 rpm; 5mV/s) polarization curves at different heat-treatment temperatures.

Comparison of thermally treated materials to the Fe – Nx – C model catalyst

Synchrotron UPS and XAS were employed to further probe the thermal treatment effects. One of the challenges in the interpretation of the UPS and XAS data was the lack of a reference compound. Therefore, an interaction was initiated with Professor J.-P. Dodelet (INRS-Energie, Matériaux et Télécommunications, Varennes, Quebec, Canada). Professor Dodelet supplied three variations of the model catalyst to be used as reference compounds for the UPS and XAS studies.

Both techniques revealed electronic and structural changes from post-treatment of the catalysts. Figure 3.C-7a shows EXAFS k3-weighted Fourier transform magnitudes for the Fe K-edge for vacuum deposited catalysts and Figure 3.C-7b shows the same for the model catalysts. These transforms are not phase-corrected, therefore there is a shift in the x-axis from real values. Examination of Figure 3.C-7a shows that the thermal post-treatment

produces a rearrangement of atoms around the iron and this is consistent with changes in the near-edge structure (not shown). EXAFS revealed the Fe nearest neighbor distance decreases approximately 0.15 Å with thermal post-treatment, and the atomic order of the catalysts is increased. This data is discussed in detail in [6]. Comparison of Figure 3.C-7a with 3.C-7b shows that model catalysts (with higher ORR activity) have a different Fe coordination with two well-resolved coordination shells visible. The vacuum deposited sample without a post-treatment (as-deposited) seems more disordered since the main peak is broader and the other peaks are not well resolved.

Figure 3.C-7. The k^3 -weighted Fourier transform magnitudes of the Fe K-edge (the transforms are not phase-corrected); a) vacuum deposited catalyst before and after the thermal post-treatment, b) three Fe acetate-derived catalysts.

Figure 3.C-8 summarizes the UPS spectra taken for a variety of samples. The spectra (a), (b) and (c) are all without Fe; a tetrahedral amorphous carbon, a carbon powder (graphitic) and a vacuum deposited nitrogenated (~14% at.) carbon. Spectra (d) and (e) are as-deposited catalyst materials with different amounts of Fe, 1 % at. and 7 % at., respectively. The spectrum (f) was taken from the sample used for the (e) spectrum, but after the post-treatment. Spectrum (g) was obtained from a model catalyst. The spectra (c) and (d) show an intensity increase near the Fermi level at a binding energy of about 0.5 eV and also between 5 to 6 eV binding energy. The spectra (e) changes significantly since the sample was subjected to a thermal post-treatment; the valence band peak near -6 eV becomes more pronounced and shifts to deeper binding energy. In addition, the intensity near the Fermi level is significantly reduced. The fact that the post-treatment causes significant changes to the valence electrons is consistent with the XANES and EXAFS results and suggests that thermal treatment causes significant atomic rearrangement. The valence-band spectra for the model catalyst (the same material as in the EXAFS spectra in Figure 3.C-7b) are very similar to that for the carbon powder that was used as the carbon support for the model catalyst.

Their similarity only illustrates the very low nitrogen and iron content in these catalyst materials.

Figure 3.C-8. UV valence photoelectron spectra ($h\nu = 55$ eV) from a) amorphous carbon, b) carbon powder, c) vacuum deposited nitrogenated carbon (~14 %), d) vacuum deposited C-N_x-Fe (1 %), e) vacuum deposited C-N_x-Fe (7 %), f) same as (e) but with post-treatment and g) a model catalyst.

Both UPS and XAS unambiguously confirmed that the structural changes due to the post-treatment are playing a crucial role in the improvement of the inherent catalytic activity of the vacuum deposited materials.

Modified substrates: Increased surface area

Despite the fact that activity improved substantially with thermal treatment, it still lagged far behind that of Pt and even behind that of the model catalyst. While the carbon fabric is a conductive and thermally and acid-stable support, the surface area is quite low. Modifying the carbon fabric to increase the geometric surface area would increase the number of active sites per unit area leading to an increased ORR response in the fuel cell environment.

Several such substrates have been fabricated. An example of the characteristics of one of these new substrates is depicted in Figure 3.C-9. Figure 3.C-9a shows CVs under nitrogen for an unmodified carbon fabric substrate and this same material after deposition of nanoporous carbon film (new substrate A). Substrate A exhibits a surface area enhancement of several orders of magnitude relative to the unmodified substrate. Polarization curves of performance under oxygen at various points in the synthetic process (bare substrate A, Substrate A modified with iron) and the finished catalyst (substrate A modified with iron and subsequently thermally treated) are presented in Figure 3.C-9b. Performance of this finished catalyst is over an order of magnitude better than the previous best vacuum sample.

Figure 3.C-9. (A) Cyclic voltammograms under nitrogen for an unmodified carbon fabric substrate and new substrate A with nonporous carbon film on the same carbon fabric. (B) Polarization curves obtained at various points in the synthetic process (substrate A and substrate A with vacuum-deposited Fe) and the finished catalyst (substrate A with vacuum-deposited Fe and thermally post-treated).

The best performance was achieved with substrate C which was produced via proprietary 3M process. Figure 3.C-10a shows the surface area enhancement of substrate C relative to substrate A. Figure 3.C-10b compares the oxygen response of similar catalysts deposited on substrate A and substrate C. The oxygen response shown in Figure 3.C-10b for substrate C is the best performance measured on this contract for the vacuum approach. While this is still lower than the best performing model catalysts, it represents significant progress since the beginning of the contract.

Figure 3.C-10. Characteristics of nominally identical catalysts deposited on substrate A and Substrate C; (A) CVs under nitrogen and (B) ORR performance.

3.D Modeling of vacuum deposited TM-C-N

In order to understand the thermodynamics of the model catalytic site (see fig. 1.C-1) proposed by Lefèvre et al. [1], calculations to elucidate the energetics of the proposed structure were performed. Lowest energy configurations for incorporation of nitrogen in bulk of graphene sheet as well as on edge were determined. The substitution of nitrogen in bulk graphene is endothermic. The substitution of nitrogen on the graphene edge was exothermic only if hydrogen is present and remains endothermic in the absence of hydrogen. Next, the energies of various configurations for the incorporation of iron on the edge of the nitrated graphene sheet were examined. It was found that in the absence of hydrogen, iron prefers to bond with nitrogen and a carbon atom (Figure 3.D-1 c). However, in the presence of hydrogen, iron was found to prefer bonding to two nitrogen atoms on the graphene edge (Figure 3.D-1 b). This lowest energy structure is similar to the catalytic site proposed by Lefèvre et al. Secondary Mass Ion Spectroscopy (SIMS) results (Figure 3.D-1 a) of the vacuum deposited films showed a $\text{Fe}(\text{CN})_2$ moiety – rather than the one seen by Lefèvre et al. The SIMS results are not in agreement with this simplistic computational model which showed that the proposed catalytic site is indeed the most stable structure in the presence of hydrogen. The density of states of the Fe containing structures showed a peak near the Fermi level, which was attributed to Fe d states. These states were speculated to be important for electrocatalysis. Much of the information has been summarized in [12].

Figure 3.C-1: a) SIMS data of the vacuum deposited films showing the abundance of $\text{Fe}(\text{CN})_2$ moiety and absence of fragments indicating structure proposed by Lefèvre et al. [1];
 b) Lowest energy configuration in the presence of H (same as the catalytic site proposed by Lefèvre et al.);
 c) Lowest energy configuration in the absence of H.

Figure 3.D-2: The calculated partial radial distribution functions around the Fe atom. The green curve corresponds to Fe-N, red to Fe-C and blue to Fe-H. The various panels indicate the substrate temperature of the simulations as well as presence or absence of H atoms in the system.

Calculations were undertaken to study the more realistic structures formed during the vacuum deposition of iron-containing nitrogenated carbon films. To study the effect of temperature and presence or absence of hydrogen in deposition of these films, *ab initio* molecular dynamics studies were performed. These studies used the *liquid quenching* [13] method to generate structures representing the vacuum deposited films. It was found that the overall structure of iron-containing nitrogenated carbon films is similar to the structure of nitrogenated carbon films without iron. At the deposition densities of interest (2.5 g/cc), most of the carbon atoms were sp^2 hybridized. Addition of hydrogen atoms to the system as well as lowering the substrate temperature increased the carbon sp^3 content in the structures. Nitrogen atoms were found to be equally sp^2 or sp^3 like. The iron radial distribution functions (Figure 3D-2) showed that the iron atoms had 4-5 carbon atoms and one nitrogen atom as first nearest neighbors. Direct comparison of the radial distribution functions around the Fe atom with the EXAFS data, however, could not be made because of the lack of phase correction in the EXAFS data. The presence or absence of hydrogen had no effect on the local bonding around the iron atoms. Substrate temperature also did not make a difference in the bonding around the Fe atom. The density of states (DOS) as shown in figure also showed a peak near the Fermi level. A peak at the same energy has not been seen in the experimental

UPS of nitrogenated carbon films (not containing any iron). This peak was, therefore, associated with the iron in the system and speculated to be important for electro-catalysis.

Figure 3.D-3: The calculated total density of states of the various systems. The legend indicates the substrate temperature of the simulations as well as presence or absence of H atoms in the system.

Overall, the density of states agrees well with the UPS spectra before thermal treatment. The UPS spectra showed significant changes upon post-thermal treatment of the samples. The calculated DOS, however, does not change significantly upon increasing the substrate temperatures. The reason for this discrepancy can be attributed to several factors. During the experimental post-thermal treatment, there is significant nitrogen loss and changes in density of the deposited films. The calculations do not account for these changes. Also, as the film thickness becomes smaller (due to loss of material) upon thermal treatment, there may be some substrate effects in the UPS spectra. Further studies (both experimental as well as computational) are needed to resolve these differences better. Further details of this study can be found in [14].

3.E Summary

TM-C-N catalysts made via vacuum deposition were found to have higher nitrogen and pyridinic nitrogen contents than the model catalyst [1]. However, the fuel cell performance

of the initial vacuum deposited materials lagged behind (by several orders of the magnitude) that of the model catalyst. Performance of the vacuum deposited catalysts improved with thermal treatment, but was still below that of the model catalyst. Therefore, extensive XAS and UPS measurements were undertaken to compare the vacuum deposited materials with the model catalyst. These studies pointed to potential differences between the two catalyst systems.

The high throughput approach revealed that the onset of catalytic activity for ORR coincides with a transformation from a homogenous amorphous TM–C–N film to a heterogeneous mixture of partially graphitized carbon and TM. The onset of this transformation occurs both as a function of TM content and temperature. Maximum catalytic activity with TM–C–N compositional spreads is achieved at an annealing temperature of 800 °C.

Improvements in fuel cell performance were obtained when the number of active sites per geometric unit area was increased with the introduction of higher surface area, thermally stable modified carbon fabric substrates. Catalysts deposited on these substrates showed much improved oxygen response to those prepared on unmodified carbon fabric.

Ab initio calculations for the structure of the model catalytic site [1] showed that the proposed structure was most stable only in the presence of hydrogen. First principles simulations of the structure of vacuum deposited Fe–C–N films showed that overall structure was similar to nitrogenated carbon films without iron. However, the calculated electronic properties agreed well only with the results of the UPS measurements of films before thermal treatment.

The catalyst found to have the best performance could easily be scaled-up and manufactured in a roll-to-roll process. However, further improvements in catalytic activity are required before it would be prudent to undertake any scale-up.

3.F References

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4. Catalyst Development – Nanotechnology Approach

4.A Introduction

As noted in the previous section, the original intent of the project was to reproduce the active site of the model catalyst using a new fabrication technique, namely vacuum deposition. Due to the low surface area of the substrate and lack of adequate thermal treatment the initial fabrications of the vacuum deposited NPM catalysts exhibited low activity. Therefore, supplementary approaches were initiated to improve the catalytic activity and to gain further insight into the C-N-Metal material system.

In order to probe the nature of the active sites in non-precious metal catalysts based on the C-N-metal system, catalyst test samples were prepared using synthetic methods based on modification of each of the catalyst site components. A flow chart for this approach is shown in figure 4.A-1.

Initially, catalysts were prepared on a carbon substrate in fabric or particle form. Catalysts precursors (vide infra) were deposited onto the carbon substrate and nitrogen sources were introduced followed by a variety of thermal treatment procedures.

Figure 4.A-1 A flow chart of the synthetic methods based on modification of the catalyst site components.

The initial studies on the synthesis of active sites through variation of the carbon, nitrogen and metal precursors led to an understanding of the criticality of incorporating high nitrogen content into the catalyst structure. The nitrogen must be in combination with the metal precursor prior to thermal processing. Thermal treatments, even when carried out in a nitrogen-containing atmosphere, resulted in expulsion of nitrogen from the precursor mixture. Thus, the focus of our efforts became the search for a precursor that had high a nitrogen content in an aromatic structure that is in intimate contact with the activating metal species. The synthetic efforts were directed towards forming aromatic, high nitrogen content chars containing a homogeneous distribution of an activating metal. The materials that were found to exhibit the desired characteristics were poly(quinoxaline)-like chars described by Errede *et al* [1].

In this approach, a nitro- and/or amino-functional aromatic molecules such as nitroaniline are used as the nitrogen-rich aromatic precursor molecule. These molecules can be thermally polymerized in the presence of an acid catalyst and with release of water will generate a highly-nitrogenated, conductive carbon char. The chars developed through the polymerization of these types of molecules in the presence of an acidic metal halide are part of a general class of materials that was developed at 3M. The materials have been used as sorbents and oxidation catalysts by Errede *et al.* [1]. To our knowledge, this class of materials has not been previously used as a precursor for ORR catalysts.

Because of the very high activity of the catalyst materials produced by using these nitro- and/or amino-functional aromatic molecules as sources of both carbon and nitrogen, these materials are described separately in the characterization section. Of particular note is the high activity in combination with durability that was achieved when the polymerization of 4-nitroaniline was carried out using anhydrous ferrous chloride as a catalyst in the presence of nanoparticulate titanium carbide.

4.B Catalysts Components

Carbon

Carbon precursors that were examined include the following:

- Carbon particles (C55 carbon particles (99.99% purity carbon, 82 M²/g, Chevron Phillips Chemical Company, TX) and Vulcan XC-72 carbon particles (210 M²/g, Cabot Corporation, Boston, MA);
- Modified carbon particles (surfaces were modified by nitrating with nitric acid or nitric acid/sulfuric acid mixtures, by adsorption of surface active species including stearic acid, hydroxyl and carboxylate-functional polymers, functionalized aromatic molecules, or by heat treating carbon particles in an ammonia/N₂ atmosphere);
- Carbon fibers in fabric form (Freudenberg H23-15; Freudenberg GmbH, Germany);
- Modified carbon fabric (modified by nitrating with nitric acid, by deposition of (CN)_x or (CN)_xFe via vacuum deposition processes, by heat treatment in an ammonia/N₂ atmosphere, or by treatment with phenolics);
- High nitrogen carbons produced by polymerization of an aromatic, nitro- and/or amine-functional molecule (see list 4.A-2-4);
- Metal carbides, nitrides and silicides (nanoparticulate TiC, WC, W₂C, TiN, and SiC).

Nitrogen

Nitrogen was incorporated into the catalyst through the following methods:

- Introduction of nitrogen by heating the carbon component in ammonia and/or N₂;
- Introduction of nitrogen through inclusion of nitrogen containing aromatic molecules (1, 10-Phenanthroline, phthalocyanines, naphthalocyanine, pyridine, polyaniline, or polyvinylpyridine);
- Introduction of nitrogen by heating in a vapor of a nitrogen containing hydrocarbon (acetonitrile or pyridine) or hydrazine.
- Introduction of nitrogen by polymerization of an aromatic, nitrogen-containing, nitro- and/or amine-functional molecule (the primary polymer precursor molecules examined were 2-nitroaniline, 3-nitroaniline and 4-nitroaniline). Other materials that were included as primary precursor molecules or that were added as modifiers in the nitroaniline polymerization include; 3-nitrophthalimide, p-phenylazophenol, 29H, 31 H-phthalocyanine, 6-quinolinecarboxylic acid, 6-nitrobenzimidazole, 5-amino-6-nitroquinoline, 2, 3-naphthalocyanine, 4, 4'-azoxydibenzoic acid, 2-amino-5-nitropyrimidine, 4,4'-azodianiline, hematin, 4,4'-azo-bis-(cyanovaleric acid), haematoporphyrin dihydrochloride, polyaniline (MW ca. 65,000), 4-(4-nitrophenylazo)catechol, and 4, 6-dihydroxypyrimidine. A series of nitrogen-containing, non-aromatic molecules were also examined in the formation of these catalyst precursor chars. Although non-aromatic in the monomer state, after thermal polymerization these molecules form aromatic chars. These molecules were synthesized by the method of Johnson *et al* [2]. They include the nitrophenyl, the benzoic acid, the p-pyridyl, and the m-pyridyl derivatives of diaminomaleonitrile).

Metal containing component

The metal component was provided through the use of the following catalyst site inducers:

- Ferrous and ferric salts (acetate, formate, chloride, gluconate, sulfate); cobalt chloride, alkaline earth tungstates, silicates and heterometallates, chromium acetate, manganese chloride, iron oxy-chloride, cerium acetate, zinc chloride, and zirconium acetate;
- Metal complexes (phthalocyanine and 1, 10-phenanthroline complexes of iron with halide, gluconate or tungstate counterions), pyridine-2,6-dicarboxylic acid complexes of iron, picolinate complexes of iron, tripyridyltriazine complexes of iron and nicotinamide complexes of iron;
- Nanoparticle sols (metal oxides and oxy-hydroxides of iron, manganese, cobalt, tungsten, copper, chromium, nickel, gallium, and combinations of these metals as well as combinations of different oxidation states (e.g., Fe⁺³ in combination with Fe²⁺, Mn²⁺ in combination with Fe³⁺, etc.), iron phosphate, Fe metal supported on silica, colloidal, amorphous titania, amorphous silica, tin oxide, and ceria);
- Surface modified nanoparticle sols (sols modified by reaction with gluconic acid, amino acids, ammonium tungstate, polyvinyl alcohol, or polyacrylic acid).

Support materials

Support materials included:

- ❖ Carbon particles (C55 carbon particles (99.99% purity carbon, 82 m²/g, Chevron Phillips Chemical Company, TX) and Vulcan XC-72 carbon particles (210 m²/g, Cabot Corporation, Boston, MA);
- ❖ Modified carbon particles (surfaces were modified by nitrating with nitric acid or nitric acid/sulfuric acid mixtures, by adsorption of nitrogen-containing aromatic molecules (e.g., phthalocyanine), or by heat treating carbon particles in an ammonia/N₂ atmosphere);
- ❖ Metal carbides (nanoparticulate titanium carbide, tungsten carbide and silicon carbide);
- ❖ Nanoparticulate titanium nitride and titanium silicide.

4.C Synthetic techniques and equipment

Supporting metal component on carbon component

The interaction between the metal component and the carbon component was induced using the following methods:

- 1) The metal compound was milled with the carbon component to provide a homogeneous mixture. In the case of metal oxide and oxy-hydroxide sols, the milling was performed using zirconia mill media in polypropylene containers and a Sweco Model M 18/5 vibro-grinding mill.
- 2) The metal salt was hydrolyzed by the addition of a base (either ammonium hydroxide or sodium hydroxide) during introduction into a rapidly agitated dispersion of the carbon component.
- 3) The nanoparticle sol was adsorbed onto the carbon component by wetting followed by washing.
- 4) The nanoparticle sol was electrolytically coated onto the carbon fabric by putting a potential on the carbon fabric using a D.C. power source while having the fabric immersed in the nanoparticle sol. Iron gauze was used as the counter-electrode.
- 5) The metal complex was precipitated onto the carbon component by introduction of a non-solvent for the metal complex in the presence of the carbon component.

Synthesis of metal-oxy nanoparticles

Nanoparticle dispersions in water or water-alcohol comprising iron oxy-hydroxide doped with hetero-metal ions (Cr³⁺, Mn³⁺, Co²⁺, Ni²⁺, Ga³⁺) or with mixed valent iron were prepared according to the general procedure of Spiro et al. [3]. This process involves the addition of a sub-stoichiometric amount of base to a mixture of metal salts followed by dialysis to stabilize the small particles that are formed. The resulting sols were ultrasonically dispersed prior to combining with the carbon component.

Amorphous titania particles were prepared by hydrolysis of titanium tetra-isopropoxide with a nitric acid water mixture. The resulting slightly turbid sol was dialyzed to remove nitric acid and isopropyl alcohol and was treated with ultrasonic energy prior to combination with the carbon component.

Thermal treatment of C-N-Metal precursors

A gas handling manifold was constructed to enable introduction and independent flow control of H₂, NH₃, N₂, and oxygen into a 4' furnace fitted with a 4" flow-through tube reactor. A separate bubbler was attached to allow introduction of acetonitrile, pyridine, hydrazine, or water vapor in nitrogen carrier gas. Typical heat treatment involved heating to 400 °C in a flow of nitrogen, an optional hold at 400 °C in nitrogen or nitrogen/hydrogen, heating to 600 °C and holding for 1 hour in a flow of NH₃/N₂, and heat treating to the target temperature in a flow of NH₃/N₂.

4. C-4 Polymerization of the nitrogen-containing aromatic molecules

The catalyst preparation consisted of four to five major steps:

- a) mixing and heating the nitroaniline and the iron salt under an inert atmosphere to form a metal-containing polymer in the presence of carbon;
- b) activating the metal-containing polymer by heating in the presence of ammonia to form a metal-containing fuel cell cathode catalyst;
- c) milling the catalyst to maximize surface area;
- d) optionally, repeating the heating, step b), after milling;
- e) washing the metal-containing fuel cell cathode catalyst with an acid to remove the leachable metal.

In a typical preparation, the anhydrous metal salt (generally an iron chloride) was mixed with nitroaniline in a molar ratio of ~ 1:4 as dry powders, sometimes with additional metal salts or organic additives. Substrate material, e.g., finely divided carbon or metal carbide [17] powder, was blended into the dry mixture. This mixture is milled to a consistent color. The mixture was transferred to a thick-walled glass vessel fitted with gas inlet and outlet. The vessel was first purged with nitrogen, and then, with nitrogen flowing, the dry mixture was heated while being stirred to 150 – 170 °C to allow melting of the nitroaniline and further homogenizing the reagents. The mixture was heated to slightly above 200 °C at which point the mixture began to polymerize with the evolution of gas. After the gas evolution subsided, the mixture was heated to ~ 300 °C to ensure complete polymerization. The resulting material was then heated according to the thermal treatment described earlier.

4.D Catalyst characterization: Nano-particles on carbon support

In order to prepare MEAs from samples received in powder form, one must first make a catalyst ink. Briefly, this is made by mixing catalyst powder with an aqueous Nafion™ solution. This ink is brushed onto a gas diffusion layer to form a catalyst coated backing (CCB). An MEA is then prepared by sandwiching a PEM between the anode (Pt/C) and cathode (NPM) CCBs and bonding the assembly together in a static press.

Surface characterization and performance

Initial work on the synthesis of the catalyst was the systematic variation of the catalyst site precursors. This work revealed that active materials could be prepared by thermal treatment of the product of the hydrolysis of the metal salt or salt mixture in the presence of ammonia and a suitable carbon component. It was found that the addition of nitrogen containing aromatic ligands such as 1, 10- phenanthroline would enhance the activity. In addition, it was noted that certain metals were clearly more activating in a given system. Thus, an effort was made to optimize the activity of the nanoparticle materials through changes in the identity of the metal cations in the nanoparticle metal precursor. At the same, an effort was made to examine using metal complexes containing nitrogen containing aromatic ligands. From these studies it was found that in general iron was more activating than cobalt and that mixtures of iron with manganese could be more active than iron alone.

Because forming the complex of the metal with nitrogen-containing aromatic ligands altered the hydrolysis behavior of the metal, a study was initiated to develop methods of controlled precipitation of metal mixtures in the presence of these coordinating ligands. It was discovered that in certain cases tungstate or molybdate anions could be used to enhance the deposition of the hydrolyzed metal complexes onto the carbon substrate. Surprisingly, a study of the activities of the resulting materials showed that the presence of the hetero-metal introduced as a metallate anion in the precursor could dramatically enhance the activity of the resulting catalyst. An example of a strong synergistic effect is seen in the catalysts made using the hydrolysis of Fe^{2+} in the presence of meta-tungstate anion to form the active site.

Electrochemically, the CVs under nitrogen for the combination Fe/W/C catalysts appear additive of the individual components as if no interaction between the two has taken place (Figure 4.D-1a; S2 is W). However, careful UPS studies reveal some interaction between the components in the form of mixed W/Fe d-states and p-states (Figure 4.D-1b). This interaction of Fe with W manifested itself in the oxygen performance measurements. The oxygen reduction current of the Fe/W/C catalysts is orders of magnitude enhanced relative to the single component baselines (Figure 4.D-1c).

Figure 4.D-1. Characterization of two-component catalyst made via nanotechnology approach; example given for Fe and W as second component (S2): A) CVs (under nitrogen); B) UPS spectra; C) Oxygen reduction polarization curves.

The effect of catalyst loading for the Fe/W/C system was also investigated. A linear relationship was found between the loading of catalysts, determined by weight basis, and the current density at 0.6V (Figure 4.D-2). Loadings were subsequently confirmed by XRF measurements. Evidence of the increased loading was seen both by the CVs under nitrogen and the impedance under hydrogen. As expected, the high-frequency component of the impedance (R_s) increased due to the thicker coating (thicker coatings are generally more resistive), while the polarization resistance (R_p) decreased with increased catalyst loading due to the increase in activity (Figure 4.D-2).

Figure 4.D-2. Effect of catalyst loading on performance (squares, left axis) and both high frequency (circles, right axis) and polarization (stars, right axis) resistances.

In addition to the synergistic effect of combinations of iron and tungsten in the active site, it was discovered that very active catalysts could be prepared by forming the nanoparticle metal component separate from the carbon component. The pre-formed nanoparticle can then be combined with the carbon component and thermally treated in the presence of ammonia or acetonitrile. In this work, nanoparticle oxy-hydroxides formed from mixtures of Fe^{2+} , Fe^{3+} and Mn^{2+} were found to induce the highest catalytic activity. In addition, it was found that thermally treating these materials in the presence of acetonitrile produced higher activity than thermal

treatment in the presence of ammonia alone. The use of acetonitrile, however, in some cases led to the formation of carbon nanotubes in the final product. The materials containing carbon nanotubes formed in this fashion showed lower activity than samples without these features.

Acid leaching

One of the major features seen in the CVs under nitrogen shown thus far is the prominent $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox couple (reduction peak at ~ 0.72 V and oxidation peak at ~ 0.8 V). In order to eliminate this Fe redox, the catalyst powder was subjected to an acid leaching step. Comparing the nitrogen CVs of the sample before and after acid leaching (Figure 4.D-3a), shows the Fe redox is virtually eliminated after acid leaching. XRF confirms that the amount of Fe left in the catalyst is greatly reduced after acid leaching (250 kilocounts Fe/second before acid leaching vs. 72 kilocounts Fe/second after acid leaching). While the acid leaching improves the high frequency AC impedance, the performance is essentially unaffected (Figure 4.D-3b). This would indicate that the excess surface Fe does not aid in oxygen reduction catalysis.

Figure 4.D-3. Effect of acid leaching on (A) CVs under nitrogen and (B) ORR response.

Thermal treatment effects

Several studies were undertaken to assess the effects of different thermal treatment routines on catalyst performance. The results of one such study are shown in Figure 4.D-4. Plotted in this figure are the thermal treatment temperature, Fe content as measured by XRF, Fe content as measured by the intensity of oxidation peak of the $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox couple, and fuel cell performance (under oxygen) at 0.6 V. It should be noted that the starting material came from the same batch and the thermal treatment should be the only difference between the samples. There

are two correlations. First, as expected, the Fe redox intensity closely maps to the Fe content (kilocounts/second) as measured by XRF. The Fe content is at a maximum at 700 °C. This could indicate that temperature influences how strongly Fe is retained the catalyst structure. Second, the oxygen performance increases with thermal treatment temperature.

The thermal treatment studies showed that in the absence of nitrogen in the firing atmosphere, all the materials are unstable with respect to thermal loss of nitrogen. The presence of ammonia in the firing atmosphere provided a reducing environment, retarded the loss of nitrogen, and produced a higher surface area product (as shown by charging of the sample during CV's under N₂). It is believed that the ammonia etches the carbon at higher temperatures through reaction with the carbon substrates to form volatile, small molecule hydrocarbons. In addition and most importantly, the presence of the active metal (iron most active, cobalt also active), the ammonia can insert into the graphite structure to provide the correct (CN)_x structure that is required for the ORR activity.

Figure 4.D-4. Effect of thermal treatment temperature on Fe retention and performance.

4.E Polymerization derived catalysts

The performance of catalysts improved dramatically with the introduction of a new class of samples based on a carbon and nitrogen-containing polymer made from nitro and/or amine-functional aromatic molecules. Of particular importance are the chars derived from polymers synthesized by the polymerization of isomers of nitroaniline. Based on the reaction mechanism of the polymerization process, possible structures of these two polymers derived from two isomers of nitroaniline are depicted in Figure 4.E-1. Note that the repeating subunits in the polymers are quinoxaline containing pyrazinic rather than pyridinic nitrogen. Figure 4.E-2a shows the CVs under nitrogen for catalysts derived from two structurally related isomers, 2-nitroaniline (X) and 4-nitroaniline (Y), and a mixture of the 2-nitroaniline and 4-nitroaniline (X + Y). In this case ferrous chloride was used as the acid catalyst for the polymerization.

Figure 4.E-1 Possible polymer structures derived from thermal polymerization of 2-nitroaniline (a) and 4-nitroaniline (b).

The polarization curves under oxygen are shown in Figure 4.E-2b. Their performance scales with the apparent surface area determined from the charge of the CVs recorded under nitrogen and the content of the more active component. What is remarkable is that even after a high temperature ($>800\text{ }^{\circ}\text{C}$) firing, the structure of the precursor appears to influence the ORR performance. The performance of the sample based on 4-nitroaniline fulfilled the project's second interim milestone (0.08 A/cm^2 at 0.6 V).

Figure 4.E-2. Characterization of catalyst derived from two structurally related isomers, precursors 2-nitroaniline (X) and 4-nitroaniline (Y), and a mixture of the two (X+Y). A) CVs under nitrogen at 50 mV/s and B) polarization curves under oxygen. Note that the activity of the catalyst follows the content of 4-nitroaniline.

Because of these results, 4-nitroaniline was used as the starting point for the synthesis of an entire family of catalysts. The CVs under nitrogen (a) and ORR activity (b) of this family are presented in Figure 4.E-3. The different markers represent variations in the chemistry used to synthesize the catalysts. The open and closed markers of the same color and shape represent identical samples with the distinction that the open markers have been subjected to a physical post-treatment. Iron content of the post-treated catalysts (measured by XRF) was approximately

Figure 4.E-3. N₂ CVs (A) and Performance (B) of a family of catalysts derived from 4-nitroaniline. The open markers represent catalysts have been subjected to a further post-treatment.

10 $\mu\text{g}/\text{cm}^2$. Note that the onset voltage of the best-performing catalysts is greater than 0.9 V and the Tafel slope is similar to that of Pt (~ 70 mV/decade). Interestingly, while the surface area decreased with post-treatment, the ORR activity increased. This may indicate that the active

sites formed during the post-treatment are more catalytically active. This family showed the highest performance on the project to date and several samples fulfilled the project's third interim milestone (0.1 A/cm^2 at 0.7 V) indicating a large processing window. It is also interesting to note that the Fe content of these high performing samples is quite low, between $4 - 12 \text{ } \mu\text{g/cm}^2$. This may indicate that Fe is not present in the active site, but merely needed as a precursor (or catalyst) to produce the active site upon thermal treatment.

Comparison with DOE goals

Figure 4.E-4 compares the results of the best performing catalyst to DOE's targets (as outlined in the Multi-Year Research, Development, and Demonstration Plan). Using a Tafel slope extrapolation, the volumetric current density of the 3M sample at 800 mV is 19 mA/cm^3 . This value is over twice as high as the 2005 status reported by DOE (8 A/cm^3). Assuming the same electrode layer thickness, the performance that would be needed to fulfill the DOE 2010 and 2015 goals are noted in the figure. For reference, the performance of pure Pt is also plotted. It may be possible to further increase the volumetric current density by optimizing the ink and coating processes. If performance could be retained using a thinner electrode layer, the volumetric current density would increase.

Figure 4.E-4. Polarization curve from the best performing nanotechnology catalyst as compared to state-of-the-art Pt [4]. DOE targets for non-platinum catalyst activity are calculated assuming an electrode layer thickness equal to that of the NPM catalyst presented in the figure.

On the nature of the catalytic sites

It has been proposed by the Dodelet group that the limiting step in the creation of the catalytically active sites is the small concentration of surface pyridinic nitrogen as coordination sites for the iron. Therefore, it is illustrative to compare the nitrogen and iron contents in these two materials. The approximately $6 \mu\text{g iron cm}^{-2}$ that is measured in our highest performing catalysts after acid washing is the same as reported by Dodelet's group for their most active catalysts [5]. The major difference in the composition of the catalysts is the content of the surface nitrogen, which at 4 % for the nitroaniline derived catalyst is almost a factor of two higher than the highest ever reported by Dodelet's group. The same is true for the XPS N1s component with a binding energy of $\sim 398.5 \text{ eV}$, assigned as pyridinic by Dodelet's group [6;7;8], which accounts for $\sim 32\%$ of the nitrogen for both catalysts. (It is important to note that observation of a N1s binding energy at 398.5 eV is not necessarily indicative of the presence of a pyridinic nitrogen. For possible assignments of the 398.5 eV binding energy to functionalities different than pyridinic nitrogen, see [9] and [10]. Clearly, these two Fe-derived catalyst materials contain different amounts of the 398.5 eV binding energy nitrogen and total nitrogen. Since the amount of iron in both materials is about the same, one may surmise that catalytically active sites exist that do not contain iron. A conclusion that can be drawn from the present work

A previous study of the thermally-driven, acid-catalyzed polymerization of nitro-anilines described the resulting materials as poly-quinoxalines [1]. Quinoxalines contain aromatic nitrogen in a pyrazinic rather than a pyradinic configuration (figure 4.E-1). Pyrazinic nitrogen is known to have a much lower affinity for protons than the pyradinic nitrogens (the protonated form of pyrazine has a pK_a of 0.67; the protonated form of pyridine has a pK_a of ~ 5.2). It is suspected that basic structure of the starting polymer, having been formed at greater than 220°C , survives the high temperature treatment in the presence of ammonia. As a result, the finished catalyst comprises aromatic rings having nitrogen in pyrazinic sites (more than one nitrogen per graphite ring). The lower basicity of the pyrazinic nitrogens in the poly-quinoxaline-generated chars results in a catalyst surface that is much less likely to be protonated in the strongly acidic environment of the PEM fuel cell. Protonation at the nitrogen sites is expected to be detrimental as it blocks the lone pair of electrons on the nitrogens to binding and reaction with oxygen.

4.F Catalysts Durability

Carbon support

Durability testing under air according to the protocol described in section 2.C was conducted on the higher performing catalysts. Many of these catalysts were not very robust. Figure 4.F-1 shows performance degradation at 0.6 V over time for the same catalysts whose performance characteristics are shown in Figure 4.E-2. The results of fuel cell testing with varied amount of catalyst indicated that increasing the loading might improve durability [11]. After 30 hours, a sample with approximately 1 mg/cm^2 of catalyst decayed to about 45% of its initial performance at 0.6 V . Using twice as much of the same catalyst ink, the performance decays to 65% of the initial value after 30 hours. Three times the loading of catalyst retains approximately 80% of the initial performance after the same amount of time.

Figure 4.F-1. Performance change over time for the highest performing family of catalysts.

Titanium carbide support

In an effort to develop greater durability in our high activity catalysts, conductive, fine particle carbides and nitrides were examined as supports for the polymerization of the nitroaniline-derived materials. Materials that were examined include titanium nitride, silicon carbide, tungsten carbide, titanium silicide, and titanium carbide.

The introduction of titanium carbide as a substitute for particulate carbon gave rise to a striking increase in durability as shown in Figure 4.F-2. This figure shows the durability of four samples on carbon supports (same as those in Figure 4.F-1) versus a catalyst with similar composition and processing history on nanoparticle titanium carbide as a support (purple hexagons). The TiC-supported sample has a lower initial performance, but after around 66 hours of operation the performance exceeds that of the four carbon supported materials. The performance of the sample on the new support remains steady for over 1000 hours. This is remarkable due to the relatively high (for a NPM catalyst) performance. Researchers at Los Alamos National Lab (LANL) recently reported in Nature [12] on a high performing NPM catalyst that had 100 hours of durability. Under similar test conditions, the performance of the 3M, highly durable NPM catalyst after 1000 hours matches that of the initial LANL catalyst performance (see Figure 4.F-3).

Figure 4.F-2. Performance change over time for five catalysts: four on dispersed carbon substrate (diamond, triangle, star, and circle) and one on nanoparticle TiC (purple hexagons).

In order to elucidate the role and potentially the contribution of the TiC itself to the catalytic activity towards ORR, a sample of TiC underwent the same preparation procedure and thermal treatment as used for making the catalyst, however, without the catalyst precursor and the iron chloride. The results are presented in Figure 4.F-4. The cyclic voltammograms obtained while the catalyst side is under nitrogen are an indication of the surface area of the catalysts. The first observation is that in the double layer region, the current on the catalyst covered TiC is larger by a factor of three to four than on bare TiC. However, while TiC has a rather appreciable catalytic activity towards ORR, its activity contributes approximately less than 1% to the total activity of catalyst coated TiC, which is three to four orders of magnitude higher.

Figure 4.F-3. Performance of 3M's highly durable catalyst after 1000 hours as compared to initial performance of LANL "high durability" catalyst [12].

Figure 4.F-4 Cyclic voltammograms and ORR polarization curves of uncatalyzed TiC support and three 4-NA catalyzed catalyzed TiC;
 Left: CVs under nitrogen (50 mV/s); Right: ORR polarization curves.

Further data reduction indicates that there may be a correlation between the hydrogen evolution peak (in the nitrogen CVs) and the durability of the sample. It was generally found that the performance loss decreased with an increase in intensity of the hydrogen evolution peak. Figure 4.F-5 plots the performance loss (zero would indicate a very durable catalyst) fifty hours after the performance was at a maximum versus the intensity of the hydrogen evolution peak. There appears to be a clear correlation between the two quantities. Because the hydrogen evolution peak is characteristic of platinum, this might be indicating that catalysts with surface properties

similar to platinum are more durable. If one could pinpoint this surface property and find materials that exhibit it, then one might be able to design a more durable catalyst.

Figure 4.F-5. Durability versus intensity of hydrogen evolution peak.

Voltage stability of non-carbon supports

As discussed above, the biggest breakthrough in durability came with the introduction of a new support which is an alternative to carbon. Properties of a good support include acid and thermal stability and electrical conductivity. An additional property of a durable support is that it is stable against oxidation in the (acidic) fuel cell environment. Often, less stable carbon supports experience oxidation at voltages greater than about 1.2 V. While this is outside of the normal operating range of a fuel cell, this voltage can be experienced during start-up and shut-down. Carbon oxidation leads to performance degradation [13;14]. An alternate support to carbon can have applicability in both non-precious and Pt-based fuel cell catalysts.

Voltage stability studies as described in Section 2.C were performed on materials that were identified as possible alternatives to carbon supports. Many of these supports were found to be stable to up to 1.4 V. In Figure 4.F-6 the results of exposure of uncatalyzed TiSi, as a substrate

material, up to 1.5 V are presented. TiSi – is stable up to 1.4 V. Only after second exposure at 1.5 V, for a total of 20 minutes, considerable surface area effect is observed. At higher voltages, a quinone-hydroquinone redox couple was seen in the N₂ CVs. Because there is no carbon present in the new support, this may indicate that the GDL (or GDL microlayer) is being oxidized.

Figure 4.F-6 the results of exposure of uncatalyzed TiSi as a substrate material up to 1.5 V under nitrogen;

Left: Potentiostatic hold at 1.2V, 1.4V, and 1.5V for 10 minutes; then repeated (1.2V, 1.4V, 1.5V); 75°C, N₂, 132%/132%RH.

Right: CVs under nitrogen (50 mV/s) – Initial, After 1.2V, 1.4V, and 1.5V for 10 min and after additional 10 min at 1.2V, 1.4V, and 1.5V.

4.G Summary

The introduction of the nanotechnology approach brought many advances in performance and durability of the NPM catalyst. Catalyst performance exceeded the best reported in the literature for NPM catalysts. The best volumetric current density measured (19 A/cm^3 at 800 mV) exceeds the 2005 status (8 A/cm^3 at 800 mV) reported by DOE in the 2006 Multi-Year Research, Development, and Demonstration Plant.

Systematic alterations of the catalyst components and the processing conditions resulted in a better understanding of the (CN)_x-metal catalyst. The presence of transition metals promoted nitrogen retention in the carbon structure when heating to temperatures high enough to char the carbon and produce a conductive substrate. Nitrogen-containing precursors in the form of aromatic polymers in the presence of iron or cobalt cations produced very active catalysts. In these polymers, the nitrogen was mainly pyrazinic rather than pyradinic in structure. Better activity was measured for these systems when the transition metal was iron rather than cobalt. Iron in the form of ferrous cations was found to be more activating than ferric cations. The activity of the final catalyst changed little after removal of the vast majority of the activating metal by acid washing. These observations point to a mechanism in which the activating metal cations are required to only form the catalytic sites rather than to act as ORR catalyst themselves.

A highly durable material based on using nanoparticulate titanium carbide as a support for the non-precious metal catalyst was fabricated. This material ran for over 1000 hours

without significant loss of activity. Future work focusing on the mechanism of the stabilization of the non-precious metal fuel cell catalysts through interaction with non-carbon supports as well as expanding the understanding of the catalyst site in the new NPM catalysts may enable the development of a commercially viable, inexpensive and high performing NPM fuel cell catalyst.

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Publications

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13. R. Atanasoski: "Can Platinum Be Replaced in PEM Fuel Cells? And When?", International Conference on "Polymer Batteries-Fuel Cells, PBFC-2007" in occasion of Professor Scrosati's 70th Birthday, Rome, Italy, June 11-15, 2007 (*Invited*).
14. R. Atanasoski: "Low platinum and non-precious metal catalysts for PEM fuel cell application", 233rd Am. Chem. Soc. Meeting, Nanoscale Inorganic Catalysis Session, Chicago, March 2007. (*Invited*)
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Patent Applications

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2. 61952US002 “Method for Making Oxygen-Reducing Catalyst Layers”, O’Brien, Dennis P.; Schmoeckel, Alison K.; Vernstrom, George D.; Atanasoski, Radoslav; Wood, Thomas E.; O’Neill, David G. (Published)
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5. 63073US002 “High Performance, High Durability Non-precious Metal Fuel Cell Catalysts”, Wood, Thomas E.; Atanasoski, Radoslav; Schmoeckel, Alison K. (Pending)

Appendix 1: Copies of Publications

1. R. Atanasoski: “Novel Approach to Non-Precious Metal Catalysts”, DOE Hydrogen Program Annual progress reports: *FY 2003*, IV-253. Available online at:
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Publication #6:

David G. O'Neill, Alison K. Schmoedel, George D. Vernstrom, Dennis P. O'Brien, Manish Jain, Thomas E. Wood and Radoslav Atanasoski, “Material Characterization of Vacuum Deposited Non-Precious Metal Catalysts for PEM Fuel Cells”, Submitted to *J. Material Sci.* (Nov., 2007)

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Abstract: Characterization of non-precious metal catalysts has failed to identify a unique fingerprint for catalysis of the oxygen-reduction reaction (ORR) thereby making it more difficult to optimize processes and material structures. This paper describes the use of element-specific analytical techniques, not normally applied to NPMC materials. This paper also describes the use of energetic vapor deposition processes used to make the potential catalyst materials used for study. The element-specific techniques (NEXAS, EXAFS and resonant photoemission) show process dependent variations not seen with conventional techniques such as ESCA and Auger.

Material Characterization of Vacuum Deposited Non-Precious Metal Catalysts for PEM Fuel Cells

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Characterization of non-precious metal catalysts has failed to identify a unique fingerprint for catalysis of the oxygen-reduction reaction (ORR) thereby making it more difficult to optimize processes and material structures. This paper describes the use of element-specific analytical techniques, not normally applied to NPMC materials. This paper also describes the use of energetic vapor deposition processes used to make the potential catalyst materials used for study. The element-specific techniques (NEXAS, EXAFS and resonant photoemission) show process dependent variations not seen with conventional techniques such as ESCA and Auger.

INTRODUCTION

Current PEM fuel cell technology uses platinum as a catalyst. More platinum is generally required on the cathode than on the anode due the slow kinetics of the oxygen reduction reaction (ORR). Despite a variety of attempts to find an alternative to Pt, none have shown a level of oxygen reduction activity that could be exploited in a commercial fuel cell. A large body of work involves ORR catalysts produced using nitrogen coordinated transition metal compounds, such as Fe porphyrins or Fe phthalocyanine [1, 2, 3]. Traditionally, these catalysts are made by first applying an appropriate solution of transition metal compound onto carbon support particles and then heating to temperatures of up to 950°C in a reducing and/or nitrogen-containing atmosphere. Unfortunately, ORR activity of these catalysts has not been as high as has been obtained from Pt catalysts. Attempts to increase the oxygen activity, for example by increasing the Fe content, have not been successful. The activity saturates at a fairly low Fe content (~ 0.2 wt%). The upper limit to the catalytic activity has stimulated many materials characterization studies to help understand the structure and function of these catalysts with the hope that higher performing catalysts are possible. The review article by Dodelet [4] provides an excellent summary of these studies.

In order to elucidate the nature of the active site, many groups have systematically pursued a variety of methods and techniques that will be briefly discussed. Lefevre et al. used TOF-SIMS to study these materials and learned that fragments containing multiples of FeN₂ and FeN₄ structures were common [5]. Correlating the oxygen activity with the FeN₂/C and FeN₄/C signals, they proposed that such structures are the sites responsible for the catalytic activity with the FeN₂/C structure more active for ORR than FeN₄/C.

X-ray Photoelectron Spectroscopy (XPS) has been used to determine the chemical state of the nitrogen and iron in the near-surface region of pyrolyzed, Fe-derived catalysts (generally XPS has a probe depth of about 100Å). Measurements of the near-surface composition for pyrolyzed Fe-derived catalysts show that only carbon, nitrogen and iron remain. Nitrogen contents are typically between 2-3 at%, while the Fe contents are very low, about 0.05 at%.

Deconvolution of the N1s core level showed two major components; one with a binding energy (B.E.) of about 400 eV and another with a B.E. of 398.5 eV.

Jaouen et al. found that the oxygen activity in Fe-derived catalysts correlated with the XPS intensity of the 398.5 eV N1s component [6]. They also found that the binding energy of this component shifted to slightly higher binding energy as the Fe content increased. Faubert et al. have pointed out that a binding energy of 398.5 eV is consistent with the presence of 'pyridinic nitrogen' [7].

The analytical work by Dodelet's group, including TOF-SIMS, XPS and other techniques, led to their proposal that a pyridinic structure is required for good oxygen activity. They proposed the structure shown in Figure 1, where an Fe atom is bonded to two nitrogen atoms that have substituted for two surface carbon atoms in a graphene structure. The model has lately been further refined to include the relevance of the microporous structure of the carbon substrate [8].

Figure 1. Structure proposed by Jaouen et al. [6] for the species required for ORR catalytic activity.

Despite years of analytical work on Fe-based catalysts that were made using a variety of Fe containing molecules including various thermal processing histories, we still do not have a technique that tells us the identity and mechanism for Fe-based catalysts. The TOF measurements mentioned earlier tell us what elements were present, but not how they were attached in the functioning catalyst. The detected molecular fragments have been broken off from the original catalyst material. As a result, we do not have a measurement that we can use in materials synthesis for process optimization studies. This paper describes the results from analytical techniques that probe the local environment around specific atoms, e.g. Fe atoms, since many believe it to be central to ORR catalysis.

The atom-specific analytical techniques described herein were used to study potential ORR catalyst materials made with a new approach, using vacuum deposition techniques. Vacuum deposition was used to create a vapor (or plasma) of the three elements believed to be required for ORR catalysis (a transition metal, carbon, and nitrogen)[9,10] and condense them as a coating onto carbon surfaces. ~~Previous reports have described these techniques and shown that despite having XPS spectra consistent with good catalyst materials, their catalytic activity~~

The atom-specific vacuum techniques used include two x-ray absorption spectroscopies (XAS), focusing on the Fe k-edge, and resonant ultraviolet photoelectron spectroscopy (UPS) to measure the valence electronic structure around Fe atoms. Both techniques take advantage of intense, tunable synchrotron radiation. The XAS techniques we used were XANES (X-ray Absorption Near Edge Structure), which provides information about changes in the iron valence electrons, and EXAFS (Extended X-ray Absorption Fine Structure), which provides information about the iron atoms coordination number and nearest-neighbor distances. For the photoelectron

spectroscopy studies, ultraviolet photons, 40 to 80 eV, were to prove the catalyst's valence electronic structure. Resonant photoemission techniques were used to highlight emission from Fe-derived valence d-states.

The ability to focus on the structural and electronic environment around Fe atoms provides insight into role of Fe in these catalysts. These local analytical probes reveal differences between catalysts that otherwise would appear identical when using non-local or non element-specific probes.

EXPERIMENTAL DESCRIPTION

The vacuum deposited samples described in this paper were produced using pulsed cathodic arc plasma techniques that allow simultaneous deposition of carbon and iron, optionally in a nitrogen containing gas. The base pressure of the system used was in the low 10^{-6} Torr range. Heating was used both during and after deposition (post-treatment) to activate the catalyst. To heat the base substrate during deposition, a resistive sample heater was used that was capable of heating up to 650°C. Heating the materials after deposition was done in a separate tube furnace which required the potential catalysts to be exposed to atmosphere between deposition and the thermal treatment. The coating and carbon substrate is heat treated in a tube furnace under a flowing nitrogen (75%) – ammonia (25%) gas mixture to 800 – 1000 °C which increases the materials ORR catalytic activity.

A carbon non-woven fabric was used as the substrate. Although the carbon fabric provided a chemically and thermally stable substrate, it has a much lower surface area than dispersed carbon powders, which reduced the total ORR current we could expect. Silicon wafers were also used as a substrate when smooth surfaces were needed for certain analytical techniques.

The pulsed arc equipment is similar to that described by Tochitsky et al. [11] where the electrical current to the arc discharge is supplied by a charged capacitor bank. The 1480 microfarad capacitor bank was charged to 250 volts and discharged at a frequency between 4 and 8 Hz. Nitrogenated carbon was deposited by using a high purity graphite rod from Poco Graphite, as the cathode with nitrogen gas flowing into the vacuum deposition system while operating the pulsed arc plasma source. The nitrogen flow was controlled to maintain a system pressure of between 1 and 3 milli-Torr. The graphite rod was modified by inserting iron wires, 1.2 mm diameter, into the graphite rod and parallel to the axis to produce C-Nx:Fe coatings. The cathode arc spot would then travel across both the graphite and iron vaporizing both and generating a carbon/iron vapor/plasma stream directed towards the substrate to be coated.

To measure the catalytic activity for the oxygen-reduction reaction (ORR), the catalysts were built into membrane electrode assemblies (MEAs) for testing as 50-cm² fuel cells. The catalysts deposited on nonwoven carbon fabric were simply placed in contact with test fixture's polymer electrolyte membrane. A dispersed Pt/C catalyst (0.3 – 0.4 mg Pt/cm²) was used as the anode and as the reference electrode. The MEA was characterized first by measuring the response under nitrogen to determine stability and serve as a baseline for oxygen activity. Polarization curves were then measured under oxygen to determine catalytic activity. Finally, AC impedance measurements were performed to determine the coating and interfacial resistance [12].

Standard analytical techniques, such as scanning electron microscopy (SEM), x-ray fluorescence (XRF), Auger and XPS, were used to characterize vapor deposited Fe-based

catalysts and allow comparison with published analytical studies. The XPS measurements were made using a Phi 5000 series ESCA system with a Mg source; composition measurements were made using a pass energy of 90 eV and the high resolution core level spectra were obtained using a pass energy of 20 eV. The XAS Fe k-edge measurements were done at Brookhaven National Laboratory and the UPS measurements were done at the Alladin Light Source (Madison, Wisconsin). Resonant photoemission studies of the Fe 3p core level required synchronously changing both the photon energy and the electron detection energy so that photoelectron emission always came from the same energy below the Fermi level (known as “constant initial state, or CIS, measurements). For comparison purpose and because of the lack of “standards”, we applied some of the same techniques to the “state-of-the-art” non-precious metal catalysts, which, in our opinion, are those produced by Prof. Dodelet’s group. These samples were derived from Fe acetate applied on dispersed carbon and pyrolyzed at 900°C in an ammonia/hydrogen gas mixture and will be referred heretofore as Fe-Ac derived catalysts.

RESULTS

Surface composition measurements by XPS showed that the nitrogen and iron content of vapor deposited coatings can be larger than is possible for catalysts made with molecular pyrolysis methods. Typically, the nitrogen content of as-deposited C-N_x:Fe coatings using the pulsed arc process was between 10 to 15 at% and the iron content could be varied between 0.5 and 7 at% (nitrogenated carbon coatings also had between 10 to 15 at% nitrogen). When comparing surface composition measurements by XPS it is important to point out that the iron in pyrolyzed catalysts is likely to be just on the surface, not uniformly distributed throughout the probe depth as is the case with vapor deposited coatings. Indeed, measuring the composition vs. depth by Auger depth profiling showed that the Fe and nitrogen contents remained approximately constant throughout the C-N_x:Fe coating. The oxygen content was usually between 1-2 at% and increased slightly to 1-7 at% for C-N_x:Fe coatings.

High resolution XPS spectra of the N1s core level was compared with published spectra obtained from other Fe-derived catalysts. The N1s core level in vapor deposited C-N_x:Fe coatings has the same doublet structure with a strong component at 398.5 eV similar to that reported for pyrolyzed Fe-derived catalyst materials, recall that the 398.5 eV component has been identified as being due to pyridinic nitrogen. [6]. Figure 2 shows the N1s background-subtracted spectra of a nitrogenated carbon and a C-N_x:Fe coating, both deposited with the pulsed arc process. The solid lines show the results of peak fitting calculations, where only two components were used to fit to the XPS spectrum. While fitting the calculated curve to the experimental data could be slightly improved by adding one or two additional components at high binding energy, between 401 and 404 eV, these had very low intensity and did not alter the behavior of the major components. In C-N_x carbo-nitride, the component near 398.5 eV contributed 48% to the total N1s intensity.

The addition of iron (in C-N_x:Fe, 3.8wt%) causes the intensity of the 398.5 eV component to increase to 75% of the N1s signal and the binding energy increased by about 1eV. The fact that a small amount of iron has such an effect on the nitrogen core level suggests that they are near each other instead of being uniformly dispersed. The inset to Figure 2 contains a graph plotting the intensity ratio (398.5 / 400.5) of the two components plotted as a function of the Fe content. This shows that the intensity of the N1s component near 398.5 eV increases as the Fe content increases, simultaneously the binding energy of this component shifts to deeper binding

energy. The shift to deeper binding energy is similar to findings by Dodelet's group for pyrolyzed Fe-derived catalysts, although in those materials the shift is smaller [5].

Figure 2. XPS (ESCA) spectra of the N1s core level in a nitrogenated carbon sample (lower spectrum) and an iron-containing sample (C-Nx:Fe(7%), upper spectrum). Peak fitting shows 2 main components near 398.5 eV and 400.3 eV. The inset plots the relative intensity of the 398.5 eV component as a function of the Fe content.

Analysis of the Fe core level shows that the Fe atoms are not clustered to form metallic iron nor are they oxidized since the binding energy of the Fe 2p^{3/2} core level is about 710 eV. For comparison, the binding energy in metallic iron is 707 eV, about 709 eV in FeO and 711 eV in Fe₂O₃. As mentioned, the oxygen content varied between 1-7 at% and the O1s core level has 2 components at binding energies of 532 and 533 eV, neither of which is close to the binding energy of 530 eV for Fe₂O₃. Additional work is needed to distinguish between an iron carbide vs. an iron nitride.

Figure 3 shows the fuel cell performance of a vacuum deposited C-Nx:Fe catalysts, the same catalyst after thermal post-treatment to 600°C in a the nitrogen/ammonia gas mixture, and a compositionally identical catalyst deposited onto a heated substrate (~625°C) in a nitrogen/ammonia gas mixture. While the catalyst deposited near room-temperature shows some catalytic response, it is clear that the thermal post-treatment greatly enhances activity. Heating the sample during deposition is an easier and quicker method of activation. Similar performance is obtained when the thermal activation is performed during deposition, allowing fewer process steps. AC impedance measurements show that the thermal treatment also lowers the coatings contact resistance. However, the lower resistance does not fully account for the increased catalytic activity. It is difficult to compare the catalytic activity of these vacuum deposited samples with other catalyst materials dried onto carbon powders because, in this case, the surface

area is much less. Modifying the carbon fabric to produce a higher surface area support has been shown to increase the activity [13]. However, even accounting for the lower surface area, the vacuum deposited catalysts appear to be less active than the Fe-acetate materials.

Figure 3. Fuel cell performance of C-Nx:Fe catalysts as-deposited at ambient temperature (no thermal treatment), thermally post-treated in a tube furnace to 600°C in ammonia (post-treated), and heated during the deposition to 625°C in an ammonia atmosphere (in-process treatment).

Comparing published reports characterizing pyrolyzed Fe-derived catalyst materials, reports containing similar SEM, ESCA and Auger studies, with those for vapor deposited coatings do not show significant differences. However, there are differences in their electrochemical performance. Therefore, the analytical techniques that have been proposed to uniquely identify catalytically active materials are not unique analytical probes. It is still a worthwhile goal to develop analytical techniques that may provide the unique fingerprint of ORR catalytic activity to speed development of Pt replacement catalysts. Therefore we selected analytical techniques that provide information about the local environment around Fe atoms such as XANES and EXAFS.

X-ray absorption spectroscopies, XANES and EXAFS, of the Fe k-edge spectra, being sensitive to the local environment around Fe atoms do show differences between C-Nx:Fe materials with different processing histories. Spectra from two sets of samples are shown, one each from an as-deposited sample and another after a thermal post-treatment. Examination of the near-edge region in the x-ray absorption spectra, Figure 4a, show changes that occur due to a

thermal annealing step done after deposition. Specifically, both samples that received a thermal post-treatment have increased intensity at the absorption edge. The near-edge region is associated with transitions involving valence electrons and suggests that changes occur in the valence electronic structure due to the post-treatment. The XANES spectra in Figure 4b, used for comparison, were obtained from 3 different pyrolyzed, FeAc-derived catalysts. These do not show a shoulder in the near-edge region as seen in the vacuum deposited and heated materials.

Figure 4. Fe k-edge XANES spectra of C-N-Fe catalyst materials; a) vacuum deposited C-N_x:Fe catalysts as-deposited (black and green) and after post-treatment (red and blue) b) 3 different FeAc-derived catalyst materials.

Figure 5a shows EXAFS Fourier transforms for vacuum deposited catalysts and Figure 5b shows the same for FeAc-derived catalysts. These transforms are not phase-corrected, therefore the x-axis can only be used for relative positions because the values are shifted relative to the real-world values. Examination of Figure 5a shows that the thermal post-treatment produces a rearrangement of atoms around the iron and this is consistent with changes in the near-edge structure observed in Figure 4a. The thermal treatment causes one peak in the transform to split into two peaks suggesting a change in the atomic nearest neighbors around Fe atoms. Comparison of Figure 5a with 5b shows that FeAc-derived catalysts (with higher ORR activity) have a different Fe coordination with two well-resolved coordination shells visible. The individual spectra in Fig. 5b were obtained from catalysts with different levels of ORR activity, however the heights of the two prominent features in 5b are not correlated with ORR activity. The vacuum deposited sample without a post-treatment (as-deposited) seems more disordered since the main peak is broader and the other peaks are not well resolved. Not a surprising result since there is less thermal energy available to facilitate atomic ordering.

Figure 5. The k^3 -weighted Fourier transform magnitudes of the Fe K-edge (the transforms are not phase-corrected); a) vacuum deposited catalyst before and after the thermal post-treatment, b) three FeAc-derived catalysts.

Changes in the valence electronic structure are more easily, and more directly, observed using photoelectron spectroscopy especially when done at a synchrotron where the photon energy can also be varied. A complete set of valence photoemission spectra were taken with photon energies varying from 40 eV up to 70 eV, an energy range that spans the Fe 3p-3d resonance. Resonance enhances emission intensity from Fe 3d states and therefore can be used to identify Fe-derived valence d-states. Figure 6 shows valence band spectra obtained from various vacuum deposited coatings using a photon energy of 55 eV. This photon energy was selected because it is near the Fe3d resonance where emission from Fe 3d states is maximized. The intensities are all normalized to the incident photon flux as measured by the photocurrent from a gold mesh placed in the light beam. The spectra are plotted after removing the contribution from secondary electrons by subtracting the background intensity (a Shirley background calculation was used). The samples for spectra (a) and (b) were without Fe, a tetrahedral amorphous carbon and a nitrogenated (~14 at%) carbon. Spectra (c) and (d) are as-deposited catalyst materials with different amounts of Fe, 1 at% and 7 at%, respectively. The spectrum (e) was taken from the sample used for the (d) spectrum, but after a post thermal-treatment.

The spectra (a) and (b) in Figure 6, both without Fe, are shown for comparison with the Fe containing samples (c) – (e). The spectra (c) and (d) show an intensity increase near the Fermi level at a binding energy of about 0.5 eV and also between 5 to 6 eV binding energy. In addition, the spectrum (e) changes significantly after being subjected to a thermal post-treatment; the valence band peak near -6 eV becomes more pronounced and shifts to deeper binding energy. Furthermore, the intensity near E_f is significantly reduced. The fact that the post-treatment causes significant changes to the valence electrons is consistent with the XANES and EXAFS results shown in Fig. 4a and suggests that a thermal treatment causes significant atomic rearrangement.

Figure 6. UV valence photoelectron spectra ($h\nu=55$ eV) from a) amorphous carbon, b) nitrogenated carbon ($\sim 14\%$ N), c) vacuum deposited C-Nx:Fe(1%), d) vacuum deposited C-Nx:Fe(7%) and e) same as (d) but with post thermal treatment.

Figure 7 shows two valence band spectra, without the background intensity subtracted, taken with photon energies of 50 and 55 eV and a ‘difference curve’ for pulsed arc deposited C-Nx:Fe(7%) coating (vacuum deposition), but without a thermal treatment. The ‘difference curve’ is obtained by subtracting the 50 eV spectrum from the 55 eV spectrum. The 55 eV spectrum is taken just above the resonance where d-state emission is near a maximum, whereas the 50 eV spectrum is taken just below the resonance where d-state emission is depressed. Therefore, the difference curve highlights emission from Fe d-states. Emission from Fe d-states is seen in a fairly narrow peak at 0.5 eV binding energy and also in a broad feature between about -4 eV to -12 eV binding energy. The shape of the resonance curve (intensity vs. photon energy) for electronic states with 0.5 eV binding energy indicate that it has almost pure iron character, meaning that those d-states have not hybridized with carbon p-states. In contrast, the resonance curve for states below -4 eV are more complicated due to hybridization with either carbon or nitrogen p-states. Unfortunately, a similar analysis of the same coating after a post thermal treatment was not completed due to insufficient beam time at the synchrotron (the thermal treatment reduces the Fe content and therefore requires even longer data acquisition times). Attempts to use resonant photoemission to highlight emission from d-states in FeAc-derived catalysts also could not be done for the same reason.

Figure 7. Photoelectron spectra from pulsed arc deposited C-Nx:Fe(7%) taken with 50 eV and 55 eV photon energy. The ‘difference curve’ was obtained by subtracting the 50 eV spectrum from the 55 eV spectrum, thereby highlighting emission from Fe d-states. For comparison, the graph inset shows a calculated Fe d partial density of states for several configurations, as discussed elsewhere [15].

CONCLUSIONS

Vacuum deposited carbon-nitrogen-iron coatings by pulsed cathodic arc were characterized before and after thermal treatment and were compared with Fe-based catalysts formed by high temperature pyrolysis. Although measurements with conventional techniques such as XPS imply such coatings are similar, analytical techniques such as EXAFS and UPS show process-dependent differences as well as differences between similarly processed FeAc-derived materials. Clearly XANES and EXAFS as well as valence band electronic structure measurements by UPS are able to detect differences between Fe-based catalysts that more conventional techniques such as XPS and electron microscopy images cannot. These local, element-specific probes may be useful in identifying or understanding the bonding environments responsible for ORR catalytic activity.

Electrochemical studies have shown that a post-treatment step increases ORR activity even though the iron and nitrogen contents are reduced. The low Fe content of pyrolyzed materials and the extremely low content in materials made by pyrolysis of Fe compounds makes analytical techniques very difficult due to the resultant low count rates. The local probes used in this study, XAS and resonant photoemission can increase signal intensities and may allow more to be learned about the role of iron and nitrogen in their ORR catalysis. Additional XAS and XPS work is needed before more definitive statements can be made about the nature of Fe in these materials. Nevertheless, the fact that these techniques are able to distinguish between materials with different process histories and ORR activities is encouraging.

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Abstract: The cost of platinum is one of the major obstacles in the commercialization of proton exchange membrane fuel cells. Non-precious metal catalysts (NPMC) as an inexpensive substitute for platinum have been viewed as the only long-term solution to the problem. In this paper, we introduce new precursors used to synthesize NPMC active sites through metal-assisted polymerization of nitrogen-containing, aromatic molecules. Results of electrochemical characterization, which was performed in a real fuel cell environment, with emphasis on the activity of the catalyst are presented. Catalytic activity among the highest in the NPMC area was obtained when using 4- nitroaniline as a precursor.

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Non-precious metal oxygen reduction catalyst for PEM fuel cells based on nitroaniline precursor

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Dedicated to Professor Bruno Scrosati on the occasion of his 70th birthday.
Based on Invited talk at the “Polymer Batteries – Fuel Cells, PBFC - 2007” International Conference, Rome, June 2007

Abstract

The cost of platinum is one of the major obstacles in the commercialization of proton exchange membrane fuel cells. Non-precious metal catalysts (NPMC) as an inexpensive substitute for platinum have been viewed as the only long-term solution to the problem. In this paper, we introduce new precursors used to synthesize NPMC active sites through metal-assisted polymerization of nitrogen-containing, aromatic molecules. Results of electrochemical characterization, which was performed in a real fuel cell environment, with emphasis on the activity of the catalyst are presented. Catalytic activity among the highest in the NPMC area was obtained when using 4- nitroaniline as a precursor.

Keywords: Fuel cell, Non-precious metal, catalyst, oxygen reduction, polymer precursor

1. Introduction

Replacing platinum as a catalyst in hydrogen – air fuel cells, particularly in proton–exchange membrane (PEM) fuel cells (FC), has long been an industry goal. Well-known drawbacks of using platinum as a catalyst are its price and scarcity. An additional, fundamental limitation is that the use of platinum makes the fuel cell operation energy inefficient. At high voltages platinum reacts with water and oxygen [1,2] producing a surface oxide layer that inhibits catalysis of the oxygen reduction reaction (ORR). To compensate for this drawback, much higher loadings of platinum are needed on the cathode side, where the reduction of oxygen (from air) takes place. With this consideration, developing a suitable replacement for platinum as a catalyst for the ORR could contribute significantly to fuel cells becoming commercially viable.

From an application point of view, a successful PEM fuel cell catalyst should satisfy three essential requirements: performance, durability and cost. This report will focus on the performance of a non-precious metal catalyst (NPMC) based on nitroaniline precursors. Catalyst performance is determined by the site-specific catalytic activity for ORR and by the surface density of these active catalyst centers at the catalyst – membrane (electrolyte) interface. For platinum, every surface platinum atom is potentially a catalytically active site. In the case of non-precious metal catalysts, the catalytic sites of interest are believed to be multi-atomic entities rather than single atoms, the structure of which is not certain. This implies that the surface packing density of multi-atomic catalytic centers will play a crucial role in the total activity of NPMCs.

Numerous articles have been published discussing ORR catalysis by transition metal compounds, including an excellent review by Dodelet [3] where both the developments leading to and the work most relevant to our own approach are summarized in a comprehensive way. In the last several years, Dodelet's group produced time-of-flight secondary ion mass spectroscopy (SIMS) data and x-ray photoelectron spectroscopy (XPS) spectra from which they proposed that the composition of the most catalytically active functional group is $Fe-N_2-C_x$ [4]. The two nitrogen atoms to which iron is coordinated are claimed to be pyridinic in nature and can be either in a phenanthroline

configuration or can be located at the edges of the opposite walls of the carbon micropores [5]. Based on their model, Dodelet's group has postulated that the key to achieving higher activity is to increase the amount of nitrogen-coordinated iron by first increasing the surface concentration of pyridinic nitrogen.

3M approach. As part of a broader effort to develop more efficient NPMC for ORR, we adopted three strategic directions. One approach is based on vacuum deposition processes [6 – 8], a second approach is focused on synthesis of metal-containing nanoparticles finely dispersed on carbon substrates [9], and the third approach generates active sites through metal-assisted polymerization of nitrogen-containing aromatic molecules [10]. In this paper we present the results of the third approach where nitroaniline is used as the nitrogen rich aromatic precursor molecule. Nitroaniline is part of a general class of materials that was developed at 3M as sorbents and oxidation catalysts by Errede *et al.* [11] and to our knowledge it has not been previously used as a precursor for ORR catalysts. Based on the reaction mechanism of the polymerization process, possible structures of the polymers derived from nitroaniline are depicted in Figure 1. Note in Figure 1 that the repeating subunits in the polymers are quinoxaline containing pyrazinic rather than pyridinic nitrogen.

We discovered that the polymerization of nitroaniline in combination with certain anhydrous metal salts, followed by a thermal treatment could be used to create NPMCs with greater activity than obtained with other precursor materials. While the details of the synthesis are given in section 2, the three basic process steps can be described as follows:

1. The transition metal (iron) is intimately mixed with the monomer during polymerization.
2. The product is pyrolyzed at 800 – 1000 °C in a nitrogen-containing atmosphere to develop active sites.
3. The leachable metal is removed in an acid bath.

Dozens of catalyst samples derived from the nitroaniline precursor have been synthesized and tested. This paper presents examples of the electrochemical results measured on these materials. A unique aspect of our work is that all catalysts are tested by incorporation

into a 50-cm² PEM fuel cell, which is considered the smallest size acceptable for reliable projections of activity in full size fuel cell stacks. Since this is application driven research, the catalytic activity results are also presented in a form convenient for automotive use, volumetric current densities [12]. The measured volumetric current densities are compared to the US Department of Energy (DOE) goals [13].

2. Experimental

Catalyst synthesis. The catalyst preparation consists of four to five major steps:

- a) mixing and heating the nitroaniline and the iron salt under an inert atmosphere to form a metal-containing polymer in the presence of carbon;
- b) activating the metal-containing polymer by firing in the presence of ammonia to form a metal-containing fuel cell cathode catalyst;
- c) milling the catalyst to maximize surface area;
- d) optionally, repeating the firing, step *b*), after milling;
- e) washing the metal-containing fuel cell cathode catalyst with an acid to remove the leachable metal.

In a typical preparation, the anhydrous metal salt (generally an iron chloride) is mixed with nitroaniline in a molar ratio of ~ 1:4 as dry powders, sometimes with additional metal salts or organic additives. Substrate material, e.g., finely divided carbon is blended into the dry mixture. This mixture is milled to a consistent color. The mixture is transferred to a thick-walled glass vessel fitted with gas inlet and outlet. The vessel is first purged with nitrogen, and then with nitrogen flowing, the dry mixture is heated to 150 – 170 °C while being stirred allowing the nitroaniline to melt and further homogenizing the reagents. The mixture is heated to slightly above 200 °C at which point it begins to polymerize with evolution of gas. After the gas evolution subsides, the mixture is heated to ~ 300 °C to ensure complete polymerization.

The active catalyst is formed from the polymerized mixture in a tube furnace under flowing nitrogen (75%) – ammonia (25%) gas mixture at 800 – 1000 °C. The catalyst is ball-milled to break apart agglomerates formed during the thermal processing and to

comminute the catalyst. The milled catalyst is then acid washed (2 M sulfuric acid) to remove the leachable portion of transition metals.

The results presented here were all obtained on catalysts deposited on Cabot C55 carbon powder (Cabot Corporation; surface area $\sim 55 \text{ m}^2 \text{ g}^{-1}$). Cabot's C55 carbon is chosen on the basis of its enhanced electrochemical stability relative to other higher surface area carbons.

Catalyst ink, MEA and FC assembly. A dispersion of the catalyst particles is prepared by mixing approximately 10 grams of 10 – 13 % (by weight) aqueous Nafion[®] dispersion with 1.5 to 2.5 grams of the catalyst particles and approximately 10 grams of deionized - water. The catalyst ink dispersion is hand-brushed onto a 50-cm² coupon of a carbon paper support which is previously treated for hydrophobicity and coated with a gas diffusion microlayer. The catalyst loading on the final catalyst-coated-backing (CCB) is approximately 1 mg cm⁻². The CCB is vacuum-dried at 110 °C for ~20 minutes. The CCB serves as the cathode catalyst and gas diffusion layer (GDL) of the test membrane electrode assembly (MEA).

The anode catalyst layer is a platinum/carbon-dispersed ink similarly coated on a carbon-paper gas diffusion layer. The anode catalyst platinum loading is between 0.3 - 0.4 mg Pt cm⁻². Gaskets are selected for 25% to 30% compression on both the anode and the cathode. Using a static press, the anode and cathode catalysts are bonded to a pair of cast Nafion[®] membranes (each 30 μm thick, 1000 EW) at ~ 135 °C for 10 minutes. The resulting MEA is tested in a standard 50-cm² fuel cell test fixture with quad serpentine flow fields (from Fuel Cell Technologies).

Electrochemical and fuel cell testing. Using the 50-cm² test cell described above, cyclic voltammograms with nitrogen flowing to the cathode are obtained to provide insight about the surface of the catalyst. Polarization curves under oxygen are then recorded. The anode under hydrogen is used as a quasi-reference hydrogen electrode and all the voltages presented are the cell voltages without any corrections. Due to the relatively low current densities, the high platinum loading on the anode, and hydrogen flow rates well

over stoichiometric, it is reasonable to assume that the anode voltage is close to the reversible hydrogen potential at all times. A Solarton 1470 potentiostat controlled by CorWare™ software (Scribner Associates) was used for all the testing.

3. Results and discussion

In this section we present data showing the performance of NPM catalysts derived from two nitroaniline precursors and the processing steps leading to the most active catalysts. We also present data describing the effect of catalyst loading on the key performance characteristics as well as data related to the catalyst ORR selectivity. Finally, fuel cell performance of our most active NPM catalyst will be compared with the best activity reported for similar NPMC as well as with the state-of-the-art performance of a platinum catalyst.

Precursor and processing. Initially, two nitroaniline isomers were studied to determine the most appropriate precursor for NPMC. Depicted in Figure 2 are the cyclic voltammograms under nitrogen and polarization curves for catalysts derived from both 2- and 4- nitroaniline precursors and a mixture (1:1 mole ratio) of the two precursors. In spite of the fact that the two isomers are structurally related and that the polymers derived from these isomers are thermally treated in ammonia to high temperatures, a large difference in the electrochemical behavior is observed. Figure 2A shows the cyclic voltammograms recorded under nitrogen. These voltammograms are the result of the double layer charging with addition of the charge related to the presence of surface redox groups. All three voltammograms are rather featureless except for the slightly pronounced peaks between 0.57 - 0.59 V coinciding with voltage for the quinone – hydroquinone redox couple. Assuming that similar surface species are present, the integrated area (charge) of the cyclic voltammograms can be taken as a relative measure of surface area. Using this approach, the surface area of the catalyst derived from 2-nitroaniline is about half that of to 4- nitroaniline derived material.

Figure 2B shows the catalytic activity of the nitroaniline derived catalyst materials. It can be seen that the catalysts' activity in the kinetic region is even more dependent on the

precursor isomer. At the relatively small current density of 1 mA cm^{-2} , the catalyst derived from 4- nitroaniline is more active by about 70 mV , indicating possibly even an order of magnitude higher activity than for the 2- nitroaniline derived catalyst. Both the surface area and the catalytic activity of the material made from the mixture of the two isomers fall in between that measured for catalysts derived from each precursor separately as if each precursor has kept its own features, i.e. as if their properties are additive. These observations provide a notable example of where small changes in the structure of a precursor molecule produce marked differences in the electrochemical properties of the resulting catalysts despite the fact that the catalysts are derived from a high temperature pyrolysis in a reactive gas.

After establishing that 4- nitroaniline is the precursor of choice, a variety of modifications in the synthetic procedure were evaluated in order to determine their effect on catalyst activity. The most beneficial is the additional firing step after the milling of the catalyst (step *(d)* in section 2 – Catalyst synthesis). This step increases fuel cell performance 30 mV to over 100 mV throughout the polarization curves. The difference is most pronounced in the kinetic region as illustrated in Figure 3A. The second firing generates a catalyst that under the applied testing conditions produces extremely high catalytic activity with ORR starting at unusually high voltage of 0.97 V. This activity is maintained throughout a large linear Tafel region extending over two decades, with a slope of $70 \text{ mV decade}^{-1}$.

From practical point of view, the fuel cell performance of the best performing catalysts can be better appreciated by observing the full polarization curves shown in a linear scale, see the inset in Figure 3A. The fuel cell performance is recorded for voltages that are above 0.6 V, a range that is useful for energy efficient FC operation.

Simultaneously with the increased catalytic activity, the second heating step decreases the iron content in the catalyst. Even though also washed in acid, the catalysts after the first firing very often exhibit a redox peak at approximately 0.78 V that can clearly be ascribed to ferrous – ferric redox couple due to the presence of iron as a remnant from the polymerization of the nitroaniline. The $\text{Fe}^{2+}/\text{Fe}^{3+}$ peaks are persistent throughout the

performance testing in the fuel cell, which usually takes between three to seven days, indicating that the iron is in a form that is not readily soluble in the PEM FC environment. After the second firing at 800 – 1000 °C, in most cases the redox peaks disappear (Figure 3B). Since the second firing step takes place after the milling, it can be assumed that more iron, which during the first firing is probably “blocked” within the polymer, is accessible to the gasses flowing during the heat treatment. As a result, more iron is accessible for dissolution during the acid washing step (*e*) leading to lower iron content in the finished catalyst. In the group of highest performing catalysts, the estimated amount of iron in the catalyst layer as determined by x-ray fluorescence is between 4 – 12 $\mu\text{g cm}^{-2}$ of geometric area of the fuel cell.

Catalyst loading and selectivity. Since the cost of NPMC is not prohibitive, we have explored the effect of higher catalyst loading on the FC performance. For this purpose, fuel cells with different catalyst loadings (approximately 1, 2 and 2.8 mg cm^{-2}) were prepared and tested. Because the exact nature of the active sites is unknown, catalyst loading refers to the total mass of powder upon which the catalyst was deposited per geometric area.

Although the current at a given voltage increases with loading, there is not a 1:1 relationship. To gain insight into the relationship between catalyst loading and fuel cell performance, we have also examined the dependence of the surface area and the durability of NPM catalyst on the loading. Figure 4 shows the cyclic voltammograms recorded under nitrogen for the three different catalyst loadings. The voltammograms exhibit the same features for all the loadings and the current responses seems to be proportional to the catalyst loading. Because the catalyst for all three FCs has come from the same batch, a comparison of the charge of the CVs gives a measure of the relative surface area. Figure 5 shows the values for the surface area normalized to the lowest loading and that the proportionality factor is less than one, 0.89. This could indicate that there might be some agglomeration in the thicker catalyst layers. Figure 5 also shows that catalyst performance increases by only 0.68 as the loading is increased. While the reasons for these findings were not explored further, a different ratio of catalyst to

ionomer in the catalyst ink might be required in order to avoid agglomeration and to access all the catalyst sites in the thicker catalyst layer.

The most interesting dependence on the catalyst loading presented in Figure 5 is durability. The normalization for the durability was done with respect to the initial performance of each of the fuel cells tested. In the first forty hours of continuous operation the cell with a catalyst loading of 1 mg cm^{-2} loses two-thirds of its original performance. This finding is typical of the samples that were tested. It is generally accepted that the generation of peroxide is the most probable cause for the loss of performance in NPM catalysts [3]. Rotating ring – disk electrode (RRDE) testing of our catalyst showed a rather substantial amount of peroxide, approximately 10%. In order to explain the improved stability with a thicker catalyst layer, two things can be considered. First, at a given voltage, the volumetric current density for the thicker catalyst layer is lower since the current increase with the catalyst loading is by a factor of 0.68. Therefore, the concentration of peroxide in the catalyst layer should be smaller. However, this concentration is still relatively high compared to that measured for a platinum based catalyst.

Second, recent platinum loading RRDE studies provide another possible explanation for increased durability. Studies showed that the amount of peroxide formed is related to the amount of the catalyst deposited on the disk; the amount of peroxide decreases as the amount of catalyst on the disk increases [14, 15]. In a thicker catalyst layer the peroxide generated during the ORR has more opportunities to be further reduced or decompose to water, thus decreasing the chances of the peroxide attacking the catalytically active sites.

The selectivity of the catalyst towards ORR plays an important role in the performance of a fuel cell. In a hydrogen – oxygen (air) fuel cell, the gasses from one electrode can diffuse through the membrane to the other electrode area (cross-over effect) lowering the performance of the respective electrodes. Since this NMPC is meant to be used on the cathode side, it is of interest to know what would be the reactivity of hydrogen diffusing through the membrane on this catalyst. A fuel cell with the usual construction, NPMC on the cathode and platinum on the anode side, was run with hydrogen on the anode and

nitrogen on the cathode side. The voltage is potentiostatically controlled at 0.6 V and the current response is measured. For comparison purposes, the polarity of the imposed voltage and the gasses are reversed. The current due to the oxidation of hydrogen crossing over is presented in Figure 6. Since at 0.6 V hydrogen is almost completely oxidized when it reaches platinum, three orders of magnitude lower current is observed when nitrogen is flowing over NPMC. This indicates that nitroaniline derived NPMCs are very selective in a PEM FC, i.e. active only for ORR.

Catalytic activity comparison. Among the many NPM catalysts with similar final compositions, mostly carbon, some nitrogen and much less Fe, the ORR activity of these catalysts can vary significantly depending on the precursors and the synthesis methods. We will compare the activity of the nitroaniline-derived catalyst with the best performance of a recently published NPM catalyst in the C – N – Fe category from Dodelet's group [16]. The current densities in the catalytic region are over three times higher for the nitroaniline-derived catalyst than that measured by Ruggeri and Dodelet: 32 mA cm^{-2} (see Figure 3A) vs. 10 mA cm^{-2} [16] at 0.8 V. It is important to point out that the fuel cell testing conditions, with the exception of the fuel cell size (1.13 cm^2 vs. 50 cm^2), used by Dodelet's group and in this work are very similar: the temperature (80°C) is the same and the relative humidity and oxygen partial pressure are similar. In addition, the amount of catalyst used is also approximately the same, 1 mg cm^{-2} . In order to explain the difference in the catalytic activity, we will look next to the composition of the two catalysts.

Dodelet's group has proposed that the limiting step in the creation of the catalytically active sites is the small concentration of surface pyridinic nitrogen as coordination sites for the iron. Therefore, it is instructive to compare the nitrogen and iron contents in these two materials. The approximately $6 \mu\text{g iron cm}^{-2}$ in our highest performing catalyst is the same as reported by Dodelet's group for their most active catalyst [16]. The major difference in the composition of the catalysts is the content of the surface nitrogen, which at 4 % for the nitroaniline derived catalyst is almost by a factor of two higher than the highest ever reported by Dodelet's group. The same is true for the XPS N1s component with a binding energy of $\sim 398.5 \text{ eV}$, assigned as pyridinic by Dodelet's group [3,4],

which accounts for ~32% of the nitrogen for both catalysts. (For possible assignments of the 398.5 eV binding energy to functionalities different than pyridinic nitrogen, see [11, 2004] and [13]). Clearly, these two Fe-derived catalyst materials contain different amounts of total surface nitrogen as well as the 398.5 eV nitrogen component. Since the amount of iron in both materials is about the same but the activity differs, one may ask if catalytically active sites exist that do not contain iron. Indeed, it was recently proposed that nitrogen-rich carbon with no detectable transition metal at the surface can be very active for ORR in PEM fuel cells [17].

The main goal of this NPMC synthesis project was to achieve DOE performance targets for volumetric current density, which measured at 0.8 V under hydrogen – oxygen are 130 A cm^{-3} for year 2010 and 300 A cm^{-3} in 2015. Figure 7 compares the polarization curve of the most active nitroaniline-derived NPM catalyst, as presented in Figure 3A, with a state-of-the-art platinum catalyst [12]. Comparisons of NPMC catalysts with platinum are frequently uninformative because they are done with inferior Pt-based fuel cell. In contrast, the comparison presented here is more credible for several reasons. Our data is obtained from a 50 cm^2 fuel cell, an accepted test standard. Second, the calculated volumetric current density is based on the measured thickness of the coated catalyst layer. Finally, the platinum data used in the comparison was obtained from an independent source.

From electrochemical point of view this particular comparison can be seen to be valid because the two curves have the same Tafel slope allowing comparison at any current density or voltage. The extended linear Tafel region on the NPMC allows the inherent activity of the catalyst to be revealed by accurate extrapolation that encompasses all the necessary corrections for IR drop and diffusion polarization. Although the catalyst activity reported here is still far from the performance attained using platinum, the activity of the 4- nitroaniline derived NPM catalyst, 19 A cm^{-3} at 0.8 V, is only a factor of seven lower than the DOE 2010 goal of 130 A cm^{-3} . We believe that with further research, partly by optimization of the catalyst ink but mostly by improving the inherent catalytic activity, this class of catalyst materials may approach US DOE performance goals.

4. Conclusion

In summary, a highly active ORR NPM catalyst based on a new precursor, 4-nitroaniline, has been synthesized and characterized. Catalysts based on this material show unusually high ORR onset voltages, above 0.9 V, and Tafel slopes of 70 mV decade⁻¹. We believe that with further process improvements catalyst performance can be increased and that by substituting the carbon support we will obtain a more durable 4-nitroaniline derived catalyst, one that shows promise to achieve the near-term goals as a substitute for platinum. In addition, since the price of nitroaniline on the commodity market is around \$1.5 kg⁻¹, the criterion for a catalyst to be acceptable for a large scale application, its cost, is also satisfied. A potential drawback in developing a process based on nitroaniline could be its high toxicity. For this reason, we are in the process of developing new, non-toxic analogs for inexpensive and safe NPMC production.

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Figure captions

Figure 1. Possible polymer structures derived from 2- nitroaniline (upper) and 4-nitroaniline (lower). Note that the nitrogen in the quinoxaline repeating subunits is pyrazinic rather than pyridinic.

Figure 2A. Cyclic voltammograms characterizing the catalysts made from 2-nitroaniline, 4-nitroaniline and a combination of 2- & 4-nitroaniline precursors. CVs are taken at 50 mV s^{-1} under hydrogen/nitrogen at 75°C with 132%RH.

Figure 2B. Polarizations curves of the catalysts in Figure 2A measured at 80°C with saturated hydrogen (180 sccm) and oxygen (335 sccm) with 300 kPa backpressure on anode and 430 kPa backpressure on cathode. Voltage scan rate: 5 mV s^{-1} .

Figure 3A. Polarization curves of the 4-nitroaniline precursor - based catalyst after the first firing (circles) and after the second firing (squares); test conditions are the same as in Figure 2B. The straight line slope is 70 mV per decade. Inset: Polarization curves on a linear scale.

Figure 3B. Cyclic voltammograms of the catalysts in Figure 3A; test conditions are the same as in Figure 2A.

Figure 4. Cyclic voltammograms showing the effect of catalyst loading on surface area. “1x” catalyst loading is approximately 1 mg cm^{-2} ; “2x” is approximately 2 mg cm^{-2} ; “3x” is approximately 2.8 mg cm^{-2} . CVs taken under the same conditions as in Figure 2A.

Figure 5. Three normalized FC properties, surface area, ORR current, and durability, in relation to loading of the 4-nitroaniline derived catalyst. Surface area (stars) assessed from CVs in Figure 4 and normalized to the value for 1 mg cm^{-2} catalyst loading; ORR performance is the current at 0.8 V (circles) normalized to the value for 1 mg cm^{-2} catalyst loading under the conditions noted in Figure 2B; Durability (triangles) represents the fraction of the initial ORR performance after 40 hours running potentiostatically at 0.6 V at 75°C with saturated hydrogen and air at approximately 300 kPa backpressure on both anode and cathode.

Figure 6. NPM catalyst response to hydrogen cross-over. Fuel cell at 80 °C, 300 kPa/430 kPa backpressure, 180 sccm hydrogen/335 sccm nitrogen, saturated gas streams, at 0.6 V potentiostatic hold. The cell is first run with nitrogen on the NPM catalyst side of the cell (hydrogen on Pt side) and then reversed (both gases and polarity), with nitrogen on the Pt catalyst side of cell (hydrogen on NPM catalyst side).

Figure 7. Polarization curves comparing of highest activity NPM catalyst to platinum and DOE targets. Both tests under hydrogen – oxygen at 80 °C, 100% relative humidity. Oxygen pressure: 430 kPa for 3M catalyst and 150 kPa for GM Pt. Detailed test conditions: 3M catalyst as in Figure 3B; GM Pt as in ref. [12,13].

From: 2 - nitroaniline

From: 4 - nitroaniline

Figure 1

Figure 2A

Figure 2B

Figure 3A

Figure 3B

Figure 4

Figure 5

Figure 6

Figure 7

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Preparation and characterization of sputtered $\text{Fe}_{1-x}\text{N}_x$ films

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Abstract

Iron nitride films have been prepared by reactive DC magnetron sputtering. The composition of $\text{Fe}_{1-x}\text{N}_x$ was varied over a range of $0 \leq x \leq 0.5$ by controlling the nitrogen flow rate during sputtering. These films were characterized using powder X-ray diffraction (XRD), thermogravimetric and electron microprobe analysis. We found that the nitrogen content in the films increased with nitrogen gas partial pressure. XRD experiments revealed an evolution through the $\alpha\text{-Fe}$, $\gamma'\text{-Fe}_4\text{N}$, $\epsilon\text{-Fe}_{2+z}\text{N}$, $\zeta\text{-Fe}_2\text{N}$, $\gamma'''\text{-FeN}$ and $\gamma''\text{-FeN}$ phases, when the nitrogen gas mole percentage was increased from 0% up to 70%. Above 70%, only the $\gamma'''\text{-FeN}$ phase was formed despite a measurable increase in the nitrogen content of the film with nitrogen gas partial pressure. Rietveld analysis of powder X-ray diffraction patterns revealed that this behavior is due to an increase in the nitrogen site occupation factor within the lattice.

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Keywords: Iron nitride; Sputtered films; Reactive sputtering; Nitrides

1. Introduction

Iron nitrides have attracted considerable attention due to their interesting magnetic properties and corrosion resistance [1,2]. Nitride coatings have also been shown to improve wear resistance and enhance hardness of iron or steel [3]. Thin films of iron nitride have been prepared by numerous techniques including vapor deposition [4], molecular beam epitaxy [5], laser nitriding [6] and reactive sputtering [1,2,7–10]. In addition, recent work by Dodelet's group [11–15] has shown that Fe-C-N containing materials show catalytic activity for the oxygen reduction reaction in polymer electrolyte membrane fuel cells. Deng and Dignam [16,17] found that sputtered Co-C-N materials showed activity for the oxygen reduction reaction in alkaline fuel cells as well. As a first step in combinatorial studies of the catalytic activity of sputtered Fe-C-N materials, we report here the characterization of binary $\text{Fe}_{1-x}\text{N}_x$ materials prepared by sputtering.

Most previous reports of sputtered iron nitrides concentrate only on a very narrow region of the iron–nitrogen phase diagram due to interest in a particular iron nitride

phase. Here we report the preparation of $\text{Fe}_{1-x}\text{N}_x$ thin films by reactive DC magnetron sputtering over the entire compositional range of the iron–nitrogen phase diagram ($0 \leq x \leq 0.5$). The nitrogen content of these films was varied by controlling the concentration of nitrogen in the plasma during sputtering. Film composition was determined using electron microprobe analysis, powder X-ray diffraction, and thermogravimetric analysis (TGA). When the mole percentage of nitrogen gas is above 70%, only the $\gamma''\text{-FeN}$ crystal phase is present. However, the nitrogen content of the films continues to increase with the mole percentage and partial pressure of nitrogen gas. Rietveld refinement of XRD patterns was performed and accounts for this increase in terms of the N site occupation factor within the lattice.

2. Experimental details

2.1. Film deposition

Samples were prepared by magnetron sputtering using a Corona Vacuum Coater's (Vancouver, British Columbia, Canada) V3T system, which is described in detail elsewhere [18]. Briefly, the system holds up to five targets, is

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turbopumped, and reaches a base pressure of 6×10^{-6} Pa. A thin (1.3 mm) sheet of low carbon steel (Grade 1008, <0.1 wt.% Carbon) was cut into a 2-in. diameter disc and was used as the iron target. Films were deposited at ambient temperature using a dc power supply that provided a constant power of 60 W in all cases. Ultra high purity argon (99.999%) was supplied at a constant rate of 7.50 sccm, while the flow rate of ultra high purity nitrogen (99.999%) was varied between 0 and 50 sccm. Gas flows were independently controlled using mass flow controllers. This corresponds to mole percentages of nitrogen between 0% and 87% and chamber pressures between 0.24–1.67 Pa (1.8–12.5 mTorr) during sputtering. The sputtering conditions for each film are summarized in Table 1. Films were deposited onto room temperature substrates, which included pre-weighed 1.3 cm diameter Al disks, (111) oriented Silicon wafers, and 10 × 10 cm glass slides. The deposited mass was obtained by weighing the Al disks before and after film deposition using a precision Cahn 29 microbalance that has a resolution of 1×10^{-7} g.

Sputtered films were also deposited onto 10 × 10 cm glass slides that were pre-coated with a thin layer (3 μm) of photoresist. Shipley SPR220-3.0 Megaposit photoresist was spin-coated onto the glass slides. The coated glass slides were then heated to 110 °C for 30 s to remove solvents. After sputtering, these substrates were soaked in acetone, which completely dissolves the photoresist layer and separates the sputtered material from the substrate. The sputtered material was then collected via suction filtration and washed thoroughly with acetone.

2.2. Film characterization

Powder X-ray diffraction patterns were collected using a Siemens D5000 diffractometer utilizing Cu–K_α radiation

and equipped with a graphite secondary monochromator. Data was collected over a scattering angle range of 20–80° in 0.05° intervals. The count time was 15 s per point, giving total scan times of 5 h. Rietveld refinement of diffraction patterns was performed using the program WinPlotR [19].

For rapid analysis of numerous Fe_{1-x}N_x films deposited on Si wafers, an INEL CPS120 curved position sensitive detector coupled to an X-ray generator equipped with a Cu target X-ray tube was used. There is a monochromator in the incident beam path that limits the wavelengths striking the sample to Cu–K_α. The system is equipped with an automated x–y motion stage for analyzing numerous samples. The size of the X-ray beam spot on the specimen is about 1 by 1 mm.

Composition analysis of the films was made using a JEOL JXA-8200 Superprobe equipped with one energy dispersive spectrometer, five wavelength dispersive (WDS) spectrometers, and an automated motion stage. Silicon nitride was used as the nitrogen standard while magnetite was used as the iron standard. Reuter's method for thin films analysis, which corrects for the excitation of the back-scattered electrons caused by the substrate, was employed [20]. All elemental compositions were determined using the WDS detectors and have an estimated uncertainty of ±0.3%.

Thermogravimetric analysis (TGA) was performed using TA instruments 910 TGA. Samples were heated from room temperature up to 600 °C at a rate of 5 °C/min under a flow of extra dry air. Compositions calculated from TGA analysis have an estimated uncertainty of ±0.3%.

3. Results and discussion

3.1. Compositional analysis

Fig. 1 shows the variation in film composition as a function of the nitrogen flow rate, as determined by WDS analysis. Between 0–10 sccm, the nitrogen content (x) rapidly increased with the nitrogen flow rate. Above a flow rate of 10 sccm, only a small change in composition occurred, which approaches x=0.50. To verify these results, iron nitride samples were also characterized using TGA. Upon heating to 600 °C in air, all iron nitrides are converted to Fe₃O₄ (confirmed by XRD). The transformation of several iron nitrides sputtered at various nitrogen flow rates are displayed in Fig. 2. The nitrogen content of the starting materials was determined from the mass gain during TGA assuming the reaction:

and is plotted as a function of the nitrogen flow rate in Fig. 1. Good agreement between the TGA and WDS data was obtained.

Table 1
Summary of sputtering conditions used to produce Fe_{1-x}N_x films

Ar flow (sccm)	N ₂ flow (sccm)	N ₂ mole percent	Total Pressure (Pa)	N ₂ partial pressure (Pa)
7.5	0	0.0%	0.237	0.000
7.5	1.0	11.8%	0.261	0.024
7.5	2.0	21.1%	0.277	0.040
7.5	3.0	28.6%	0.340	0.103
7.5	4.0	34.8%	0.353	0.123
7.5	5.0	40.0%	0.413	0.176
7.5	6.0	44.4%	0.485	0.248
7.5	7.0	48.3%	0.495	0.257
7.5	8.0	51.6%	0.508	0.263
7.5	10.0	57.1%	0.549	0.312
7.5	12.5	62.5%	0.665	0.428
7.5	15.0	66.7%	0.711	0.473
7.5	20.0	72.7%	0.819	0.581
7.5	25.0	76.9%	1.016	0.779
7.5	30.0	80.0%	1.171	0.933
7.5	35.0	82.4%	1.345	1.108
7.5	40.0	84.2%	1.477	1.240
7.5	50.0	87.0%	1.660	1.423

The iron target was sputtered at a constant power of 60 W in all cases.

Fig. 1. Variation of the nitrogen content (x in $\text{Fe}_{1-x}\text{N}_x$) as determined by WDS analysis as a function of the nitrogen gas flow rate during sputtering.

3.2. XRD

Diffraction patterns of $\text{Fe}_{1-x}\text{N}_x$ films deposited onto Si wafers were analyzed using the Inel X-ray detector. The diffraction patterns obtained at various N_2 flow rates are displayed in Fig. 3. The diffraction patterns were found to vary greatly below a nitrogen flow rate of 20 sccm. Above 20 sccm, very little change in the diffraction pattern with flow rate was observed and they mainly consisted of only 1 strong peak at a scattering angle of about 36° . We attribute this to the (111) peak of FeN, crystallizing in a sphalerite structure (SG F-43 m), which is known to preferentially orient along the (111) plane [2].

To obtain higher quality powder XRD patterns suitable for structural analysis, films were sputtered onto 10×10 cm glass slides. The material was then scraped off the slide to

Fig. 2. Transformation of $\text{Fe}_{1-x}\text{N}_x$ to Fe_3O_4 during heating by TGA analysis. The nitrogen flow rate used during sputtering is noted.

Fig. 3. X-ray diffraction patterns of $\text{Fe}_{1-x}\text{N}_x$ films deposited on Si wafer at different nitrogen flow rates.

obtain a powder that could be studied by powder XRD without the effect of preferential orientation. The obtained diffraction patterns are shown in Fig. 4. In the absence of nitrogen flow, pure α -Fe was obtained. As the nitrogen flow was increased up to 10 sccm, a rapid evolution of iron nitride phases from α -Fe, γ' - Fe_4N , ϵ - $\text{Fe}_{2+\epsilon}\text{N}$, ζ - Fe_2N , γ''' -FeN and γ'' -FeN, was observed and identified [21–24] using the JCPDS database. At nitrogen flow rates greater than 20 sccm (greater than 70 mol% N_2), only fcc γ'' -FeN was obtained, similar to that reported by Rissanen et al. [7]. In addition, the γ'' -FeN powder XRD pattern displayed all expected Bragg-reflections for this phase.

Fig. 4. Powder X-ray diffraction patterns of $\text{Fe}_{1-x}\text{N}_x$ sputtered at different nitrogen flow rates onto glass substrates.

Table 2

Crystallographic data obtained from Rietveld refinement of XRD patterns shown in Fig. 4

N ₂ flow [sccm]	Phase	wt. %	Lattice parameter			GoF			
			a/Å	b/Å	c/Å	occ.	S.G.	Bragg R-factor	χ^2
50	γ'' -FeN	100	4.3006(5)			0.87(8)	F-43 m	3.7	2.3
40	γ'' -FeN	100	4.3004(18)			0.79(7)	F-43 m	3.2	3.1
30	γ'' -FeN	100	4.3004(21)			0.78(4)	F-43 m	2.7	2.6
20	γ'' -FeN	100	4.3199(20)			0.69(3)	F-43 m	5.2	1.6
10	γ'' -FeN	77(5)	4.325(5)			*	F-43 m	14.2*	2.1
10	γ''' -FeN	16(3)	4.501(6)			*	Fm3m	23.1*	2.1
10	ζ -Fe ₂ N _{0.94}	7(2)	4.1950	5.6727	4.95(8)	*	Pbcn	41.9*	2.1
8	γ'' -FeN	35(7)	4.32(3)			*	F-43m	14.5*	2.7
8	γ''' -FeN	30(5)	4.49(3)			*	Fm3m	32.4*	2.7
8	ζ -Fe ₂ N _{0.94}	18(4)	4.4299	5.5705	4.7646	*	Pbcn	28	2.7
8	ϵ -Fe _{2+z} N	17(5)	4.8151(6)		4.4381(7)	*	P312	19.9*	2.7
4	ϵ -Fe _{2+z} N	92	4.80559(7)		4.4377(1)	*	P6322	14.5	2.5
4	γ''' -FeN	8	4.436(3)	5.575(6)	4.786(5)	*	Fm-3m	14	2.5
0	α -Fe	100	2.8683(4)			*	Im3-m	6	3

The lattice parameters for samples containing only the γ'' -FeN phase (nitrogen flow rates greater than 20 sccm) were extracted using Rietveld refinement and are compiled in Table 2. The Rietveld refinement obtained for the sample prepared using a nitrogen flow rate of 50 sccm is displayed

in Fig. 5a. The lattice parameter did not significantly change with the nitrogen flow rate and is in excellent agreement with the value of 4.307 Å reported by Suzuki et al. [24]. However, the N site occupation factor within the γ'' -FeN phase was found to increase with nitrogen flow rate. The different nitrogen partial pressures appear to change the nitrogen content of the γ'' -FeN phase while the lattice itself is invariant and most likely stabilized by the unchanged iron

Fig. 5. The Rietveld refinement obtained for (a) γ'' -FeN prepared at a nitrogen flow rate of 50 sccm deposited onto bare glass, (b) a mixture of γ'' -FeN, γ''' -FeN and ζ -Fe₂N deposited onto photoresist coated glass at a nitrogen flow rate of 10 sccm, and (c) ϵ -Fe_{2+z}N deposited onto photoresist coated glass at a nitrogen flow rate of 5 sccm.

Fig. 6. Powder X-ray diffraction patterns of Fe_{1-x}N_x sputtered at different nitrogen flow rates onto photoresist coated glass substrates.

Fig. 7. Comparison of the powder X-ray diffraction patterns of $\text{Fe}_{1-x}\text{N}_x$ sputtered onto bare glass and photoresist coated glass prepared at a nitrogen flow rate of (a) 15 sccm (b) 10 sccm (c) 4 sccm.

sublattice of this sphalerite-type structure. Using these occupation factors (listed in Table 2), the atomic composition (x in $\text{Fe}_{1-x}\text{N}_x$) of these sputtered γ'' -FeN films were calculated and are plotted as a function of nitrogen flow rate in Fig. 1. These values agree with those determined by WDS and TGA within experimental error [25].

Sputtering with a nitrogen flow rate less than 20 sccm produced films that contained a mixture of iron nitride phases. Using Rietveld analysis, we have determined the amount of each identified iron nitride phase present in the films. These values are listed in Table 2.

To further improve the quality of our XRD patterns, particularly for samples prepared at nitrogen flow rates below 20 sccm, films were sputter deposited onto 10×10 cm glass slides that were pre-coated with a thin layer of photoresist. After sputtering, the photoresist layer was dissolved using acetone to free the sputtered film from the substrate. This method greatly increased the yield of sputtered material collected from the substrate. Powder diffraction patterns for all materials sputtered onto photoresist-coated glass are displayed in Fig. 6. These patterns are very similar to those obtained with material sputtered onto bare glass and are of much higher quality. Since these films are of high purity and are insoluble in acetone, it is extremely unlikely that exposure to acetone had any effect on our films. The main reason for the increased pattern quality is due to the larger mass of material harvested from the photoresist-coated glass. Fig. 7 overlays diffraction patterns collected for materials sputtered onto glass and Photoresist coated glass substrates at a nitrogen flow rate of 4, 10 and 15 sccm. From this we see that the diffraction patterns are nearly identical for materials sputtered at 4 and 15 sccm. However, there was a noticeable difference in the patterns obtained for materials prepared at nitrogen flow rates of around 10 sccm. In this region, films are composed of a mixture of ζ - Fe_2N , γ''' -FeN and γ'' -FeN phases. [γ''' -FeN is isostructural to rocksalt (NaCl) and γ'' -FeN is isostructural to sphalerite (ZnS).] Materials sputtered onto

Table 3

Crystallographic data obtained from the Rietveld refinement of XRD patterns of films deposited onto photoresist-coated glass

N_2 flow [sccm]	phase	wt.%	Lattice parameter			S.G.	Bragg R -factor	GoF χ^2
			$a/\text{\AA}$	$b/\text{\AA}$	$c/\text{\AA}$			
50	γ'' -FeN	100	4.3033(1)			F-43 m	8	13
15	γ''' -FeN	99(6)	4.316(1)			F-43 m	3	4
15	γ'' -FeN	1	4.483(7)			Fm-3 m	6	
10	γ'' -FeN	52(6)	4.33(1)			F-43 m	7*	20
10	γ''' -FeN	30(3)	4.50(1)			Fm-3 m	7*	
10	ζ - $\text{Fe}_2\text{N}_{0.94}$	18(2)	4.21(4)	5.7(2)	4.9(2)	Pbcn	20*	
8	γ'' -FeN	38(8)	4.32(2)			F-43 m	11*	38
8	γ''' -FeN	31(4)	4.49(2)			Fm-3 m	7*	
8	ζ - $\text{Fe}_2\text{N}_{0.94}$	31(7)	4.217(5)	5.66(7)	4.88(4)	Pbcn	20*	
6	γ'' -FeN	11(2)	4.308			F-43 m	43*	90
6	γ''' -FeN	4(1)	4.499			Fm-3 m	43*	
6	ζ - $\text{Fe}_2\text{N}_{0.94}$	2(1)	4.437	5.541	4.843	Pbcn	34*	
6	ϵ - Fe_{2+z}N	83(9)	2.763		4.434	P-3m1	26*	
5	ϵ - Fe_{2+z}N	100	4.7961(1)		4.4296(1)	P6322	9.5	7
4	ϵ - Fe_{2+z}N	100	4.7929(2)		4.4269(2)	P6322	21	24
3	ϵ - Fe_{2+z}N	100	4.7979(1)		4.4106(1)	P6322	10	4
2	ϵ - Fe_{2+z}N	75(9)	4.6967(5)		4.3837(3)	P6322	17	14
2	γ' - Fe_4N	25(7)	3.829(8)			Fm-3 m	14	
1	α' - $\text{FeN}_{0.088}$	100	2.88(1)		3.07(2)	I4/mmm	3	3

The space groups (S.G.) of the individual phases are included for clarity. Values marked by an asterisk are not meaningful since an additional unidentified contribution is present. All errors are listed with estimated standard deviations (E.S.D.) [25].

photoresist-coated glass have an increased presence of the γ'' -FeN phase. For example, if we compare the phase fraction of γ'' -FeN (calculated from our Rietveld refinements in Table 3) for films sputtered directly on glass at a nitrogen flow rate of 10 sccm, γ'' -FeN represents only 17% of all Fe–N phases on glass. However, γ'' -FeN represents 37% of all Fe–N phases deposited on photoresist-coated glass at the same nitrogen flow rate. We speculate that the decreased presence of the γ'' -FeN phase on bare glass is due to a substrate effect. The photoresist layer is much more compliant than bare glass; and hence films deposited on the two substrates will have differing stress. It is possible that the presence or absence of stress during deposition may favor the formation of the γ'' - or γ' -FeN phases.

Rietveld refinement of the diffraction patterns obtained with materials deposited onto photoresist-coated glass was performed and the results are compiled in Table 3. Fig. 5b and c display samples of these Rietveld fits. Based on these refinements, we are able to calculate the fraction of each iron nitride phase present in each film. Fig. 8a and b display the fraction of each phase present in the films as a function of increasing nitrogen flow rate during sputtering and atomic percent nitrogen in the film, respectively. Upon first addition of nitrogen into the sputtering gas, the substoichiometric α' -FeN_{0.088} phase (tetragonal, I4/mmm space group) was observed and unambiguously identified. Upon increasing the nitrogen flow rate to 2 sccm, we observe a mixture of the γ' -Fe₄N (25%) and ϵ -Fe_{2+z}N (75%). Between a nitrogen flow rate of 3–5 sccm exists a region where only the pure ϵ -Fe_{2+z}N phase exists. Within this region, the lattice parameter of the ϵ -Fe_{2+z}N phase increases

Fig. 9. The phase diagram for sputtered iron nitride films. The solid and dashed lines come from the work in references [26] and [27]. Data from this work is indicated by the individual data points as designated in the legend. All data from this work was obtained at 298 K, however the data points are offset for clarity.

with nitrogen flow rate (and at.% N) before leveling off, as depicted in Fig. 8c and d. This is expected based on an increase in the amount of nitrogen incorporated into the lattice. At nitrogen flow rates between 6 and 8 sccm, a mixture of ϵ -Fe_{2+z}N, ζ -Fe₂N, γ'' -FeN and γ'' -FeN phases is formed. The amount of ζ -Fe₂N is largest at 8 sccm and its

Fig. 8. Variation in iron nitride phase compositions parameters as a function of (a) nitrogen flow rate during sputtering and (b) nitrogen content in the films. Variation in iron nitride lattice parameters as a function of (c) nitrogen flow rate during sputtering and (d) nitrogen content in the films.

lattice parameter decreases with nitrogen flow rate. Surprisingly, the largest phase fraction of ζ -Fe₂N occurs when the atomic concentration of nitrogen in the film is near 42%, as shown in Fig. 8b. This may be a result of the fact that phases formed during sputtering are not necessarily equilibrium compositions and are a mixture of phases. The amount of both FeN phases continues to increase between flow rates of 6–10 sccm. At 8–10 sccm, the amount of the γ'' -FeN phase is at its maximum (at approx. 30%) and is not found in patterns obtained at nitrogen flow rates higher than 15 sccm where only the pure γ'' -FeN is formed. The lattice parameters of both FeN phases do not show a significant trend with nitrogen flow rate.

The diffraction patterns obtained at nitrogen flow rates of 6, 8 and 10 sccm contain additional reflections that we cannot yet attribute to an established phase. Obviously the parameters describing the quality of fit (Bragg R -factors, and χ^2) of our refinements are influenced by this fact, resulting in somewhat high but tolerable values. Further investigations into the source of these reflections are ongoing. Possible sources include impurities, a superstructure or a currently unknown phase.

Based upon our XRD analysis, we can create the phase diagram shown in Fig. 9, which is based upon the low temperature extensions proposed by Boerma and co-workers [26,27]. The main difference between our phase diagram and that proposed by Boerma is that we have much more detail between 33–50% nitrogen at room temperature. Also, we have shown that the γ'' -FeN phase begins to form in sputtered films when the atomic percentage of nitrogen is as low as 40%, a region where only γ''' -FeN was previously shown to form.

4. Conclusions

Fe_{1-x}N_x films have been deposited on various substrates using reactive DC magnetron sputtering. By varying the concentration of N₂ in the plasma, the nitrogen content and phase composition within the film can be varied. The γ'' -FeN phase first begins to form at a nitrogen flow rate of 6 sccm and is exclusively formed at flow rates greater than 15 sccm. However, a measurable increase in nitrogen content in the film (45–50 at.%) is observed upon further increasing the nitrogen gas concentration. This increase is attributed to an increase in the nitrogen site occupation factor within the lattice. Between 0 and 15 sccm, an evolution of iron nitride phases was observed that was consistent with those expected from the Fe–N phase diagram. Curiously, we found that a polymer coating on the substrate has a strong influence on the γ'' -FeN to γ''' -FeN ratio. A more pliable surface may promote the formation of the more symmetric γ''' -FeN structure.

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In Search for Structure of Active Site in Iron-Based Oxygen Reduction Electrocatalysts

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Calculations to elucidate the structure of Fe-based electrocatalysts were performed. Lowest energy configurations for incorporation of nitrogen in bulk of graphene sheet as well as on edge were determined. Substitution of nitrogen in bulk graphene is endothermic, while on the edge it can be either exothermic, if hydrogen is present, or endothermic. Energies of various configurations for the incorporation of iron on the edge of the nitrated graphene sheet were also examined. In the absence of hydrogen, iron prefers to bond with nitrogen and a carbon atom. In the presence of hydrogen, however, iron was found to prefer bonding to two nitrogen atoms on the graphene edge.

I. Introduction

Fuel cells are devices that transform chemical reaction energy into electrical energy. They have attracted much interest in the context of distributed global energy needs as well as localized power sources for appliances such as laptop computers. A critical but complex cathodic process in a functioning proton-exchange membrane fuel cell is the electrochemical reduction of oxygen (eq 1)

Much effort has been devoted to elucidating the mechanism of this reaction, which is incompletely understood even on seemingly simple platinum single-crystal surfaces.¹ Another more practically and economically driven aspect of oxygen reduction reaction (ORR) electrochemistry has been a search for less expensive yet effective substitutes for platinum, currently the electrode material of choice. One, centered on iron, was of interest because we considered that the fundamental chemistry might be carried out using continuous, vacuum sputtering deposition process technology.² The progress in this nonprecious metal ORR catalysts area during the past 10 years can be followed through the effort by Dodelet's group.³ For example, Lefèvre and co-workers⁴ prepared oxygen reduction electrode materials by pyrolyzing perylenetetracarboxylic dianhydride combined with various Fe and N precursors. From secondary ion mass spectrometric (SIMS) studies, the authors proposed that the ion fragment FeN_2C_4^+ might be a signature of the most active catalytic site. This result has led to the suggestion that the active site might correspond to a graphene lattice into which Fe and N had been substituted and in which the nitrogen atoms act as ligands that provide binding sites for iron.

In the literature, there have been several studies—both experimental and theoretical—of incorporation of nitrogen atoms in carbon solid-state structures.^{5–13} Merchant et al.⁵ have considered structures generated by cathodic arc deposition of nitrated carbon films. Stafstrom⁶ has examined incorporation of nitrogen atoms into fullerene-like structures. Jungnickel et al.⁹ have studied doping of nitrogen in sp^2 forms of carbon. Dos Santos and Alvarez¹⁴ investigated the structural evolution

of a graphene sheet as increasing amounts of nitrogen were substituted. A transition from planar to corrugated topology was calculated to occur at relative atomic concentration $[\text{N}]/[\text{C}] > 20\%$. In this study, the purpose is to examine the ORR catalyst system as proposed by Dodelet⁴ using graphene sheets containing small amounts of nitrogen. Experimentally, these low levels of nitrogen were usually introduced in a high-temperature pyrolysis reaction of the catalyst precursor in the presence of ammonia.

Synthesis of catalytic materials using continuous vacuum sputtering processes² can be achieved in both the presence and absence of hydrogen. Nitrogen gas can serve as the source of nitrogen as opposed to ammonia. The role of hydrogen in these materials has not been studied.

The high-temperature synthesis condition in Dodelet's work and others in this area¹⁵ raises the possibility that the system may be under thermodynamic control. While kinetics might play an important role in growth of nitrated graphene, it will not be considered in this study. To gain understanding of Fe–C–N ORR electrocatalysts, we first examined energetics of incorporation of nitrogen in planar graphene sheets. All studies were undertaken in both the presence and absence of hydrogen. One of the goals of this study was to identify sites that two nitrogen atoms could occupy—edge sites or interior positions. It was of interest to find out whether nitrogen edge site substitution is preferred than graphene interior site substitution. It was also of interest to identify the lowest energy substitution sites that two nitrogen atoms would prefer—adjacent positions (with N–N bonds) or ortho, meta, or para positions relative to each other.

Subsequently, we also investigated the interaction of a single iron atom with the various graphene edge structures, with two carbon atoms on the edge substituted by two nitrogen atoms. The purpose was to identify most energetically favorable FeN_2C_4 ORR catalyst structure and compare its energy of formation to the structure proposed by Dodelet and co-workers.⁴

II. Computational Methods

To calculate the stability of various configurations of nitrogen and iron atoms in graphite, total energy calculations using the density functional theory (DFT) method with periodic boundary conditions were performed. The ab initio calculations within DFT were carried out using generalized gradient approximation

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Figure 1. Graphene edge considered in the calculations. A row of atoms is eight atoms along the edge.

Figure 2. Isomers of diazines: (a) 1,2-diazine (ortho), (b) 1,3-diazine (meta), and (c) 1,4-diazine (para).

of Perdew and Wang (PW91)¹⁶ for the exchange correlation functional. This was used as implemented via the Vienna ab-initio simulation package (VASP).^{17–19} Projector augmented waves (PAW)²⁰ were used to represent the valence electrons of carbon, nitrogen, and iron. The interaction between the basal planes of graphite is of weak van der Waals type. It is poorly described within DFT and was completely ignored in this calculation. Calculations were performed for graphene sheets within the supercell geometry with a spacing of 10 Å between sheets. This spacing ensured that there was negligible interaction between the layers. Four points were sampled in the Brillouin zone to properly account for the metallic nature of graphene. The results did not change significantly upon going to a higher k point sampling. The dimensions of the sheet were 19.1 Å by 16.54 Å. This amounted to 128 atoms in the system. All atoms were allowed to relax to their minimum-energy positions such that the force on any atom was less than 0.01 eV/Å.

To model an edge of graphite, the graphene sheets were cut along an armchair edge so that there were 80 atoms in the system (as shown in Figure 1). Within the periodic DFT code, two k points were sampled in the Brillouin zone along the continuous direction to account for the metallicity of graphene in that direction. Several rows of atoms from the edge were allowed to relax to their equilibrium positions. Forces on the relaxed atoms in all cases were minimized to less than 0.01 eV/Å.

To examine the suitability of the PAW potentials, structural properties of pure graphite were calculated. The carbon–carbon bond distance corresponding to lowest energy was 1.41 Å. This is in good agreement with the experimental value²¹ of 1.42 Å. The interlayer spacing was calculated to be 3.31 Å compared to 3.35 Å in experiment. While interlayer spacing is close to the experimental value, the inadequacy of present density functionals to describe the van der Waals interactions is well-known. These calculations agree with other density functional calculations²² on graphite.

To further test the potentials within DFT, the relative stabilities of the three C₄H₄N₂ diazine isomers were examined (shown in Figure 2). This calculation was done in a large

TABLE 1: Relative Stability of Diazines As Calculated Using DFT

compound	relative energy (DFT) (eV)	experimental ²⁴ relative stability (eV)
1,3-diazine	0.0	0.0
1,4-diazine	0.16	0.001
1,2-diazine	0.91	0.85

supercell of size 20 Å in each direction. Only the gamma point was sampled for these calculations.

Upon relaxation of the armchair edge of graphene, without hydrogen atoms passivating the surface, bond lengths between atoms at the edge decrease. Because the atoms at the edge are 2-fold coordinated, they shorten their other bonds to reduce their energy. The bond lengths between two such 2-fold coordinated atoms contracts to 1.24 Å forming a triple bond as compared to 1.41 Å in the bulk. Their bonds with 3-fold carbon atoms also shorten, and their bond length contracts to 1.34 Å. This is in good agreement with previous calculations.²³

In the presence of hydrogen, it was found that the system lowers its energy by acquiring hydrogen atoms at the edge. This is in accordance with the expectation that absent the passivating effect of C–H bond formation, the graphene edge has dangling bonds on the surface, which make it highly reactive.

High-resolution transmission electron microscopy¹³ (HREM) revealed that amorphous CN_x films contain buckled and curved basal planes. However, dos Santos et al.¹⁴ have established that the nitrogen-substituted carbon clusters in graphite-like structures are planar for nitrogen concentrations up to [N]/[C] ~ 20%. The models employed in this study have [N]/[C] ratios which are far smaller than this concentration, and therefore it is reasonable to use planar conformations.

III. Results

Incorporation of Nitrogen in Graphene (in Bulk as Well as on Edge). Table 1 shows the relative stability of diazine isomers. The values are in good agreement with the calculated values available in the literature.²⁴ For the isomeric diazines, it was found that 1,3-diazine is the most stable isomer. The isomer in which the nitrogen atoms are in the 1,2-position (i.e., adjacent) is higher in energy by 0.91 eV. The 1,4 isomer is also higher in energy with respect to the 1,3 isomer—although only by 0.16 eV. The results from this study are in good qualitative agreement with the experimental trends in the heats of formation of these compounds.²⁴

To assess the thermodynamic stability of nitrogen-substituted carbon in a solid-state environment, the incorporation of nitrogen in a graphene sheet was studied. It was found that the energetics of substituting carbon with nitrogen in the bulk of graphene are unfavorable. On substituting one carbon in graphene by nitrogen, the change in energy corresponding to the reaction (ΔE) shown in eq 2 is 0.71 eV.

The energy of substitution is given as

$$\Delta E = E(\text{N-substituted system}) - E(\text{N-unsubstituted system}) + E(\text{C}) - 0.5E(\text{N}_2) \quad (3)$$

where $E(\text{C})$ is the energy per carbon atom in a graphene sheet. Since this reaction is endothermic, such a substitution is unlikely to happen.

Upon introducing two nitrogen atoms in the bulk, ΔE according to eq 3 becomes position dependent and is given as

$$\Delta E = E(\text{N-substituted system}) - E(\text{N-unsubstituted system}) + 2E(\text{C}) - E(\text{N}_2) \quad (4)$$

Table 2 shows both the relative energies and the energies of substitution for various configurations. The energy is lowest when two nitrogen atoms are far apart and not in the same ring (as configuration a–e shown in Figure 3). It is highest (least favorable) when the nitrogen atoms are adjacent to each other. This calculated trend of energetics for two nitrogen substitutions in a graphene sheet is similar to that found in diazine isomers. As the nitrogen atoms move further apart (from first-nearest neighbors to second-nearest neighbors), the energy of substitution becomes lower. The structure when two nitrogen atoms are in the 1,4-position within the six-membered ring (configuration a–d in Figure 3) is close in energy to the one when nitrogen atoms are far apart (configuration a–e in Figure 3). This indicates that the nitrogen atoms do not interact with each other strongly once they are beyond second-nearest neighbors. It also appears that the interaction between them is repulsive.

The interaction between two nitrogen atoms within a graphene sheet can be examined using the nitrogen 2s partial density of states (DOS) (Figure 4). The splitting of the s level into bonding and antibonding states decreases from 3.25 eV (configuration a–b) to zero (configuration a–e) as the nitrogen atoms are moved away from each other. When they are in the para position in a six-membered ring (configuration a–d), the splitting is less than 1 eV. In all two-nitrogen-atom models considered (for substitution in the bulk), the energy of substitution (ΔE) is endothermic. This type of substitution is not preferred.

Figure 4 compares the partial nitrogen DOS of 2p states for the various graphene models with two nitrogen atoms in the interior sites. It is evident from the figure that nitrogen 2p DOS is not very sensitive to the variation of the nitrogen atoms substitution sites. There is a peak at about 9 eV below the Fermi level. The nitrogen p states in the bulk are delocalized due to hybridization with carbon p states. From Figure 4, one can conclude that the nitrogen substitution site preference is only weakly dependent on the nitrogen 2p states. The nitrogen 2s states, however, are affected strongly by the proximity of the nitrogen atoms.

Figure 5 shows the various configurations when two nitrogen atoms have been substituted at the edge of a graphene sheet. The calculations were done both with and without hydrogen atoms passivating the graphene edge. When the edge is terminated with hydrogen, there are two options. While the carbon atoms on the edge are always passivated by hydrogen atoms, the nitrogen atoms on the edge may or may not be passivated. To assess whether that is the case, we considered the following reaction:

The ΔE for the reaction can be written as

$$\Delta E = E(\text{C:N-H}) - E(\text{C:N}) - E(\text{H}_2) \quad (6)$$

All configurations with different number of hydrogen atoms were compared in this manner. The heat of formation of hydrogen molecule was calculated to be -4.55 eV, which agrees well with the experimental value.³² It was found that the configurations that have nitrogen atoms passivated by the hydrogen atoms are always lower in energy than their counterparts, where the nitrogen atoms were left unpassivated. This agrees well with experimental data of Bouchet-Fabre et al.³⁵

Figure 3. Position of nitrogen atoms in the bulk graphene.

Figure 4. Nitrogen partial density of states for nitrogen substituted in bulk graphene.

TABLE 2: Relative Energies and Heats of Substitution for Two Nitrogen Atoms in the Bulk of a Graphene Sheet (See Figure 3)

positions	relative energy (DFT) (eV)	heat of substitution (DFT) (eV)
a–b	0.0	2.71
a–c	−0.82	1.89
a–d	−1.13	1.58
a–e	−1.17	1.54

The authors³⁵ there found that, upon incorporating nitrogen in amorphous CN_xH , C–H vibrations are replaced by N–H vibrations. The heats of reaction for various configurations as calculated according to eq 6 are -0.55 to -0.7 eV. This binding of hydrogen to nitrogen is opposite to the case of pyridine.³³ In pyridine, there is a loss of resonance energy due to the formation of the N–H bond. As the system size becomes large, this resonance energy loss becomes smaller and the penalty for the loss of aromaticity becomes smaller.³⁴

In the absence of hydrogen atoms, the graphene sheet undergoes significant relaxation. Figure 6 shows the convergence of total energy as rows of carbon atoms from the graphene edge were relaxed in the absence of hydrogen. Relaxation of atoms in this case extends up to the fourth row of atoms from the edge. The total energy of the system does not decrease significantly beyond that. Table 3 shows the relative stability and energies of substitution of nitrogen atoms for various configurations on the edge of a graphene sheet in both the presence and absence of hydrogen (as calculated using eq 3). In addition to the configurations shown in Figure 5, other configurations—where one of the nitrogen atoms was in a 3-fold

Figure 5. (i) Positions of nitrogen atoms on the edge of graphene. (ii) Shows the attachment of hydrogen atoms to the nitrogen atoms.

Figure 6. Total energy relaxation vs number of rows of graphene allowed to relax for various configurations of two nitrogen atoms on the edge of graphene, as shown in Figure 5(i).

TABLE 3: Relative Energies and Heats of Substitution for Two Nitrogen Atoms on the Edge of Graphene Sheet (See Figure 5)^a

positions	relative energy (eV)	heat of substitution (eV)
a-b	0.0 (0.0)	-2.64 (+1.06)
a-c	+0.07 (-0.75)	-2.58 (+0.31)
a-d	-0.01 (-0.88)	-2.66 (+0.18)

^a The numbers in parentheses are in the presence of hydrogen and others in the absence of hydrogen.

coordination—were also considered. Such configurations were always found to be higher in energy compared to the ones shown in Figure 5 (for in both the presence and absence of hydrogen atoms). The energies associated with nitrogen substitutions in all configurations (as shown in Figure 5(i)) in the absence of hydrogen passivation are exothermic. There is also no repulsive

Figure 7. Nitrogen partial density of states for nitrogen substituted on the edge of graphene.

interaction for nitrogen substitution on the edge in this case in contrast to substitutions in the interior. The energies of nitrogen substitution on graphene edge in the presence of hydrogen are endothermic, although the magnitude of endothermicity is small—especially for the lower energy configuration (a-c and a-d). Because these calculations are done at 0 K and entropic effects are not taken into account, this endothermic reaction could be exothermic at room temperature.

It is evident from Tables 2 and 3 that substitution of nitrogen in carbon in the bulk of the graphene sheet is endothermic. On the edge, however, the result depends on the presence or absence of hydrogen. While in the absence of hydrogen the substitution is exothermic, in the presence the substitution is endothermic. In both cases, the nitrogen on edge substitutions would be preferable to the nitrogen substitution in interior. A conclusion from this study is that majority of added nitrogen atoms on graphene sheet are likely to reside at edges, rather interior sites on graphene. Such nitrogen-enriched graphene edges make bonding to iron possible, as proposed by Dodelet and co-workers.⁴

Figure 7 shows the partial DOS for the nitrogen states. For the configurations with no hydrogen passivation, the 2s states are closer to the Fermi level by ~ 2 eV. When the nitrogen atoms are farther than second-nearest neighbor, they do not interact with each other, and the 2s states show little or no splitting. In the a-b configuration in the absence of hydrogen passivation, the antibonding 2s states hybridize with the carbon s states and delocalize in energy, while the DOS for same configuration in the presence of hydrogen is similar to the a-b configuration in Figure 3.

The nitrogen 2p DOS for hydrogen-passivated configurations have peaks between ~ 14 and ~ 8 eV below the Fermi level. This is similar to the peaks of nitrogen 2p in Figure 4. This is very different from the case when the edge is unpassivated. In those configurations, the peaks are closer to the Fermi level at ~ 3.5 eV below it. In both cases, the DOS curves for a-c and a-d configurations are similar, indicating that once the nitrogen atoms are beyond second-nearest neighbors, they do not interact with each other. In configuration a-b with no passivation, the nitrogen p states show a peak very close to the Fermi energy.

Figure 8. Positions of Fe atoms on the edge of nitrogenated graphene: (i) Fe bond sites a, b, c; (ii) models of nitrated graphene edge being passivated by hydrogen atoms and bonded with Fe. Here Fe is coordinated with three NH_3 ligands.

The ultraviolet photoemission spectroscopy (UPS) of amorphous CN_x materials have been studied by several groups.^{14,25–29} Electron energy loss spectra (EELS) for hydrogenated CN_x were measured by Silva and co-workers.³⁰ From this study, it was found that the 2p DOS of nitrogen has peaks within 5 eV of the Fermi level. When the nitrogen atoms are within the bulk of graphene sheet, the 2p densities of states showed peaks right at the Fermi level, as shown in Figure 4. When the two nitrogen atoms are on the edge of graphene sheet, the 2p densities of states of nitrogen atoms show peaks at 1 or 3.5 eV from the Fermi level, as shown in Figure 7. Souta²⁵ found that as the concentration of N increases in the sample increases, the UPS peaks at 4.5, 7.1, and 9.5 eV increase, while peaks at 3.6 and 7.7 eV decrease. The peak at 4.5 eV was attributed to the nitrogen lone pair electrons. This assignment is consistent with our DOS results as shown in Figure 7. Santos et al.¹⁴ calculated the DOS for nitrogen-substituted carbon clusters. Their DOS for CN_x clusters also showed a N lone pair peak at ~ 5.0 eV. Zhao and co-workers²⁷ also found that for their a- CN_x sample, as the nitrogen content increased, the UPS peaks at regions 2–7 and 20–30 eV increase. Overall, the DOSs determined for two nitrogen atoms substitution in graphene sheet from this work are in good correspondence with experimental observed UPS data.

Incorporation of Iron on the Edge of Nitrogen-Containing Graphene. The lowest energy configurations from the nitrogen substitution on the edge were chosen, and arrangements of Fe atoms around those configurations were studied. It was assumed that Fe atom would bond on configurations that were thermodynamically the most stable ones. Figure 8 shows the various configurations that were considered. Some other configurations were also considered but were found to be much higher in energy. As shown in Figure 8(i), for the cases considered, the Fe atom was bonded only to two atoms. The effect of ligands on the other side of the Fe atom would be considered separately later.

In the absence of hydrogen atoms passivating the edge, the Fe atom causes substantial relaxation in the graphene sheet. Figure 9 shows the convergence of the total energy in the absence of hydrogen passivation as a function of the numbers

Figure 9. Total energy relaxation vs number of rows of graphene allowed to move for various configurations of Fe and two nitrogen atoms on the edge of graphene, in the absence of hydrogen passivation.

TABLE 4: Relative Energies Position of Fe Atom on the Edge of Nitrated Graphene Sheet (See Figure 8)^a

positions	relative energy (eV)	relative energy (eV) with ammonia ligands
a	0.00 (0.00)	0.00 (0.00)
b	-0.12 (+2.01)	+0.51(+2.53)
c	-0.99 (+0.33)	-0.73(+0.61)

^a The values in parentheses are ones in the presence of hydrogen and others without.

of rows of carbon atoms from graphene edge that were relaxed. Table 4 shows the relative stability of three different arrangements of Fe atom on the edge of graphene containing nitrogen atoms. From Table 4, it can be seen that the most stable structure in the absence of hydrogen passivation is the one with Fe attached to a nitrogen atom on the edge and a carbon (site c in Figure 8(i)). This energetically most stable structure (site c in Figure 8(i)) differs from the catalytic site model proposed by Dodelet et al.⁴

In the presence of hydrogen passivation, however, the ordering of configurations according to stability is not the same. Hydrogen atoms can passivate the edge atoms in several different configurations. For each of the configuration in Figure 8(i) several possibilities were considered. It was found that when the nitrogen atoms are not connected to the Fe atom, it is always energetically favorable for the hydrogen atoms to passivate them. This is consistent with the finding above for nitrogen substitution on the edge. In contrast to the relative energetics in the absence of hydrogen passivation, it was found that for the lowest energy configuration the Fe atom was attached to two nitrogen atoms (Figure 8(i), site a).

Figure 10 shows the partial densities of states for the iron in the various configurations in the presence and absence of hydrogen. As can be seen from the figure, Fe s states hybridize to some extent with the valence band. However, in all cases there is also a peak above the Fermi level, indicating that it is partially occupied. The Fe d states have a peak at the Fermi level and are partially occupied. These d states probably play a role in electrocatalysis just as they do in homogeneous catalysis.

It is known that iron is seldom, if ever, just 2-fold coordinated. The relative stability ordering (as shown in Table 4) could change if the coordination number of the iron were higher. Experimentally, electrocatalysts are prepared in a strongly

Figure 10. Fe partial density of states for configurations shown in Figure 8.

Figure 11. Fe partial density of states for configurations shown in Figure 8.

reducing environment provided by ammonia at high temperature. The Fe atom is not expected to be 2-fold coordinated under such conditions. To assess the role of coordination around the iron atom, we examined the relative energies of the all the configurations by coordinating the Fe atom with three NH_3 ligands in a pyramidal structure,³¹ as shown in Figure 8(ii). Ammonia is a ligand that binds strongly to both 0 and +1 iron. In the absence of hydrogen passivation, the configuration c was still found to be lowest in energy (as shown in Table 4). However, configuration b was now found to be higher in energy than configuration a. In the presence of passivation, the configuration a was found to be the lowest in energy.

Figure 11 shows the DOS for the configurations in Figure 8 with ammonia ligands. As can be seen from the figure, the states near the Fermi energy have little Fe s character upon this bonding interaction NH_3 . These states now are completely hybridized with the valence band. However, the Fe d states are still close to the Fermi energy and available to participate in catalysis.

These results suggest that the most stable linkages near the catalytic site in the absence of hydrogen are the iron atom bonded to a carbon atom and a nitrogen atom. In more realistic, higher coordination number structures, coordinating of iron by NH_3 groups does not change the relative ordering of stability—the lowest energy structure still contains iron bonded to both nitrogen and carbon. In the presence of hydrogen, however, the catalytic site as proposed by Dodelet⁴ and co-workers seems to be the lowest in energy.

IV. Conclusions

Substitution of nitrogen in bulk graphene is energetically endothermic, while on the edge it is exothermic when there is no hydrogen passivation and endothermic in the presence of hydrogen. The energy of substitution becomes less unfavorable as the nitrogen atoms get farther apart in the bulk. In the presence of hydrogen, the energetics of substitution of two nitrogen atoms on the edge are similar within ± 0.1 eV (see Table 3). In the presence of hydrogen, the energy of substitution becomes less endothermic as the nitrogen atoms get farther apart on the edge. Nitrogen 2s peaks are a good indicator of the distance between the nitrogen atoms in the bulk. We also show some of the minimum-energy configurations for the incorporation of Fe on the edge of the nitrated graphene sheets. Energetically, when there is no hydrogen passivation on the graphene edge, iron prefers to bond with nitrogen and a carbon atom. When the nitrated graphene edge is passivated by hydrogen, iron prefers to bond with two nitrogen atoms (as shown in Figure 8(i), site a), as proposed by Dodelet et al.⁴

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Fe-C-N Oxygen Reduction Catalysts Prepared by Combinatorial Sputter Deposition

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Thin-film libraries of $\text{Fe}_x\text{C}_{1-x-y}\text{N}_y$ libraries ($0 < x < 0.12$; $0 < y < 0.5$) have been prepared by combinatorial sputter deposition. The libraries were subsequently annealed at 700, 800, and 1000°C to induce structural and compositional changes. Respectable catalytic activity was achieved with libraries having $0 < x < 0.035$ and $0.01 < y < 0.16$ that were annealed at 800°C. This is explained in terms of nitrogen content and the degree of graphitization of the annealed catalysts.
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The proton exchange membrane fuel cell (PEMFC) is an emerging technology that could help meet the energy demands of the 21st century. However, several issues must be overcome before fuel cells are a commercially viable technology. One such issue is the activity and cost of the cathode catalyst. Pt and Pt alloys are the most active catalysts for the oxygen reduction reaction (ORR) and can be stable in the acidic environment of a PEMFC. Pt is both expensive and in limited supply; therefore, there are significant ongoing efforts to reduce the required Pt loading without performance losses. The development of carbon-supported Pt catalysts and optimization of the electrode structure¹⁻³ have led to a significant reduction in Pt loadings without performance loss. In spite of this, a significant further reduction in Pt loading is still required to make fuel cells commercially viable.

Consequently, there is a great desire to replace Pt with an inexpensive, non-noble metal-based electrocatalyst. Transition metal N_4 -macrocycles (Fe, Co) are promising candidates that have been widely studied. Traditional methods for preparing these catalysts involve the pyrolysis of different Fe (or Co) and nitrogen-containing precursors deposited onto various carbons.^{4,5} Dodelet's group claims that their most active catalysts contain a significant number of FeN_2/C or FeN_4/C active sites, or both, which are believed to be Fe coordinated to pyridinic-type and pyrrolic-type nitrogen sites that are embedded into the carbon support.⁶

An alternative, simpler, and potentially less expensive processing approach to fabricating transition metal-C-N nonprecious metal catalysts is to use physical vapor methods to deposit the three components of Dodelet's model catalyst. Dignam and Deng have previously prepared Co-C-N catalysts via sputter deposition, which were active for ORR in alkaline conditions but, because of the very high concentration of Co, unstable in acid.^{7,8}

By focusing on the compositional range close to the one reported by Dodelet's group, researchers at 3M Company used a variety of vacuum deposition processes to make transition metal-C-N catalysts on high surface area substrates to form acid stable, catalytically active materials.⁹⁻¹¹ Jain et al. have also explored theoretical aspects of the Fe-C-N active sites.¹²

In order to efficiently and systematically explore the Fe-N-C compositional space of interest, combinatorial methods¹³ were used here to prepare sputtered $\text{Fe}_x\text{C}_{1-x-y}\text{N}_y$ libraries with a composition gradient across the film ($0 < x < 0.12$; $0 < y < 0.5$). After deposition, catalyst libraries were heat treated to induce structural and compositional changes. The catalytic activity of the libraries as a function of composition and annealing temperature has been measured and is discussed.

Experimental

Film deposition.— Samples were prepared by magnetron sputtering using a Corona Vacuum Coaters' (Vancouver, B.C., Canada) V3T system, which is described in detail elsewhere.¹³ Briefly, the system holds up to five targets, has a rotating substrate table, is turbopumped, and reaches a base pressure of 6.7×10^{-6} Pa (5×10^{-8} Torr).

Two-inch-diameter targets of carbon (graphite) and iron (grade 1008 low carbon steel, less than 0.08% C by weight, balance Fe) were used. Fe and C were sputtered using MDX-1k dc power supplies that provided a constant power of 15 and 150 W, respectively. Specially designed masks were positioned in front of each target to produce a linear deposition profile of Fe and a constant deposition profile of C within a 76 mm track when the substrate table is rotated.⁹ Nitrogen was incorporated into the libraries by sputtering in an Ar/N_2 gas mixture.¹⁴ Gas flows were independently controlled using mass flow controllers (MKS Instruments, Wilmington, MA). Ultra-high-purity Ar (99.999%) and N_2 (99.999%) were supplied at constant flow rates of 7.5 and 2.0 sccm, respectively. This corresponds to total pressure of 0.277 Pa (2.1 mTorr) and a N_2 partial pressure of 0.058 Pa (0.44 mTorr) during sputtering. Films were deposited at room temperature onto four 10×2.5 cm quartz strips, a 10×2.5 cm (100) oriented silicon wafer, 6 preweighed 1.3 cm diameter Al disks, and 15 glassy carbon disks (diameter = 5 mm, Tokai Carbon Co.). Glassy carbon disks were evenly spaced and mounted as three sets of 5 disks within the 75 mm sputtering track. Within each set, disks are numbered from 1–5 in order of increasing Fe content. A schematic diagram illustrating the substrate table layout and iron composition gradient is shown in Fig. 1.

Film thickness.— The thickness of the library sputtered onto a Si wafer was determined using a Dektak 8 advanced development profilometer (Veeco Instruments Inc.). Film thickness was found to linearly increase across the library from 100 to 220 nm with increasing Fe content. The strong increase in film thickness with Fe content is because the N content in the film increases as the Fe content increases, as is shown in Fig. 2.

Heat treatment.— Films deposited on quartz substrates and glassy carbon disks were annealed at 700, 800, or 1000°C using a Modular Process Technology RTP-600S rapid thermal processor (RTP). Films were heated under flowing argon (2 L/min) at a rate of 5°C/s up to the annealing temperature, where it was held for 60 s.

Library compositions.— The compositions of sputtered libraries were determined using a JEOL JXA-8200 Superprobe equipped with one energy dispersive (EDS) spectrometer, five wavelength dispersive (WDS) spectrometers, and an automated motion stage. Using the automated motion stage, compositions were measured as a function of position across the library. All elemental compositions were determined using the WDS detectors.

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Figure 1. Schematic diagram illustrating the layout of the rotating substrate table. Projections of the Fe and C targets and the masks that create the composition spread are also shown.

Grazing incidence X-ray diffraction (GIXRD).—X-ray diffraction patterns were collected using a Siemens D5000 diffractometer equipped with a grazing incidence attachment. Cu K α radiation was used at an incidence angle of 0.5° and with divergence slits set to 0.1°. Such conditions lead to an illuminated spot of 40 × 12 mm in the Fe-rich end of the 76 × 15 mm library. A Soller slit box in front of the detector was used to ensure that the scattered X-rays from this large illuminated sample area that entered the detector all had the same scattering angle. Data were collected over a scattering angle range of 10–70° in 0.05° intervals. Total scan times varied between 2 and 10 h.

Electrochemical characterization.—The electrocatalytic activity of each deposited film was determined by performing cyclic voltammetry (CV) with a rotating ring-disk electrode (RRDE). The RRDE electrode consisted of a catalyst-coated glassy carbon disk (5 mm diameter) surrounded by a Pt ring (7.5 and 8.5 mm inside and outside diameters, respectively). Measurements were performed in a three-electrode, one-compartment cell, equipped with a Pt wire counter electrode and a Hg/Hg₂SO₄ reference electrode. The potential of the Hg/Hg₂SO₄ reference electrode was calibrated vs the reversible hydrogen electrode (RHE). All data presented in this work have been corrected to the RHE potential. Measurements were made at room temperature using 0.1 M HClO₄ (aq) as the electrolyte. The electrolyte solution was prepared from doubly distilled high-purity HClO₄ (GFS Chemicals, Inc.) and 18 M Ω Barnstead nanopure water.

RRDE measurements were made using a Pine Instruments AFCBP1 bipotentiostat controlled using PineChem software. CVs were collected by scanning the disk potential between 0.9 and 0.05 V vs RHE at a sweep rate of 5 mV/s. For all electrochemical measurements, the ring potential was held at 1.2 V vs RHE to oxidize any hydrogen peroxide that was produced.¹⁵ For each catalyst tested, CVs were first collected in Ar-purged electrolyte in the potential range of 0–1.0 V (vs RHE) at 100 mV/s. During these Ar CVs, corrosion of Fe was observed for some films. If corrosion of Fe was observed, Ar CVs were continued until a steady-state CV was achieved (i.e., no further corrosion was observed). A final CV in Ar-purged electrolyte was then collected to determine the nonfaradaic current. For subsequent CVs, the electrolyte was saturated with

Figure 2. Variation of atom % N as a function of atom % Fe for Fe-C-N libraries (a) before annealing and after annealing at (b) 700°C, (c) 800°C, and (d) 1000°C. The balance of the composition is carbon. The compositions of several different libraries are shown (where available) to illustrate reproducibility. Also shown are the positions of the glassy carbon disks studied by RDE.

O₂ and the electrode was rotated at 900 rpm. The faradaic current was determined by subtracting the Ar-purged CV from those obtained under O₂.

The %H₂O₂ produced was calculated from the following equation¹⁵⁻¹⁷

$$\%H_2O_2 = \frac{200I_R}{NI_D + I_R} \quad [1]$$

where I_D is the faradaic current at the disk, I_R is the faradaic current at the ring, and $N = 0.2$ is the RRDE collection efficiency.

Results and Discussion

Library compositions.—Figure 2 shows the nitrogen content as a function of iron content for libraries annealed at different temperatures. This representation was chosen because only a small region of the entire Fe-C-N Gibbs' triangle studied in numerous experiments is discussed in the experiments reported in this paper. It was observed that the nitrogen content of the as-sputtered library increases with iron content. Annealing these libraries resulted in a significant decrease in nitrogen content, which decreased further with increased annealing temperature. In addition, nitrogen was lost first at lower temperatures from regions of higher Fe content.

RRDE results.—Figure 3 displays the disk CVs obtained under oxygen for Fe-C-N libraries annealed to 700, 800, and 1000°C. Libraries that were not annealed (not shown) were not active toward oxygen reduction. For comparison, the activity reported by Dodelt's group for their $\Pi(0.2)\text{FeAc}(900)$ catalyst on a high surface area

Figure 3. Disk current densities for sputtered libraries annealed at 700, 800, and 1000°C. Measurements were made at a sweep rate of 5 mV/s in O₂-saturated 0.1 M HClO₄ at room temperature. The average composition on each disk is indicated on the plot. Also shown in each panel is the activity reported by Dodelet's group for Fe(0.2)FeAc(900) at 100 rpm (dashed line).¹⁸

carbon support [total Brunauer-Emmett-Teller (BET) surface area = 370 m²/g]¹⁸ is also shown in Fig. 3.⁴ Reasonably good activity has been achieved, although the activity is less than that reported by Dodelet. However, our catalyst libraries are thin films that most likely have a significantly smaller electrochemical surface area.

Looking at trends across the libraries, catalytic activity increases with increased Fe content for libraries that were annealed at 700 and 1000°C. However, the library annealed at 800°C exhibited increased activity with decreasing Fe content. For each individual disk, activity typically improved upon increasing the annealing temperature from 700 to 800°C. However, further increasing the annealing temperature from 800 to 1000°C decreased the catalytic activity.

Figure 4 displays the %H₂O₂ produced as a function of disk potential for Fe-C-N libraries annealed at 700, 800, and 1000°C. H₂O₂ production typically increases with both Fe content and with annealing temperature. The catalysts with the highest onset potential for ORR also produce the least amount of peroxide.

Dodelet's group has shown that catalytic activity increases with increased nitrogen content.^{4,6,17} In the Fe-C-N libraries presented here, the library annealed at 800°C displayed the highest activity but corresponds to neither a maximum nor a minimum in nitrogen content. CN_x sputtered at room temperature forms amorphous films. Hellgren and co-workers have found that when sputtered CN_x films are annealed above 500°C, progressive graphitization and nitrogen loss occurs.¹⁹ They have also found that above 800°C, there is a preferential loss of pyridinic nitrogen. Based on this, we infer that films annealed at 700°C are not graphitized to a large enough extent to form a significant number of active sites, and therefore have poor activity. Despite the fact that films annealed at 1000°C have been adequately graphitized, they contain very little pyridinic nitrogen (or any other form of nitrogen), and therefore do not form a significant number of active sites. Therefore, we conclude that annealing at

Figure 4. Percent H₂O₂ produced as a function disk potential for sputtered libraries annealed at 700, 800, and 1000°C. Measurements were made at a sweep rate of 5 mV/s in O₂-saturated 0.1 M HClO₄ at room temperature. The average composition on each disk is indicated in the plot.

Figure 5. GIXRD patterns for the Fe-C-N library as-sputtered, and after annealing at 800 and 1000°C.

800°C induces sufficient graphitization and retains a significant quantity of N to form a substantial number of active sites.

To confirm this hypothesis, GIXRD was performed on as-sputtered and annealed libraries, as shown in Fig. 5. Prior to heating, the library was amorphous. After annealing at 800°C, a peak at 26.3°, which is attributed to the graphite (002) Bragg peak, begins to form. This peak became more intense when the library was annealed at 1000°C. While this experiment does confirm the formation of graphitic carbon, it is not the ideal experiment for combinatorial libraries. The spot size of the X-ray beam used was 40 mm, which illuminated a signal from over half of the 76 mm library within which there is a significant composition gradient. However, in order to obtain an XRD pattern with a high signal-to-background ratio from these thin films (100–220 nm), GIXRD was essential. GIXRD is an ideal experiment for single-composition thin films, and we have recently used this method to follow the thermal evolution of the XRD pattern of sputtered single-composition Fe-C-N and Co-C-N thin films.²⁰

To assess the corrosion stability of these catalysts, a library annealed at 800°C on a quartz substrate was subsequently immersed in 0.5 M H₂SO₄ for 7 days. The composition across the library was measured before and after acid treatment and is shown in Fig. 6. Little change in composition was observed across the first 35 mm of the library (ca. 0–3.5 atom % Fe). Near 35 mm, Fe begins to corrode. Beyond 40 mm, the Fe content drops from an initial range of 4–10 atom % to less than 1 atom %. The loss of Fe from this region of the library may account for lower catalytic activity.

Conclusions

Fe-C-N catalysts for oxygen reduction in acid have been prepared by magnetron sputtering. Maximum activity was achieved when the libraries were annealed at 800°C. Annealing below 800°C apparently did not result in sufficient structural changes (i.e., graphitization) to induce high catalytic activity. Libraries annealed at 1000°C displayed lower catalytic activity than those annealed at 800°C, which is attributed to a significant decrease in nitrogen content. Films annealed at 800°C were stable against corrosion when the Fe content was below ca. 3.5 atom %. Efforts to further improve (and understand) catalytic activity and corrosion stability by varying the sputtering parameters are ongoing.

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Figure 6. Composition as a function of position for the library annealed at 800°C before (solid symbols) and after acid treatment (open symbols). Also shown are the positions of the glassy carbon disks studied by RDE.

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Thermal Evolution of the Structure and Activity of Magnetron-Sputtered TM–C–N (TM = Fe, Co) Oxygen Reduction Catalysts

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Thin-film libraries of $\text{TM}_x\text{C}_{1-x-y}\text{N}_y$ (TM = Fe, Co; $0 < x < 0.09$; $0 < y < 0.5$) have been prepared by combinatorial sputter deposition. The libraries were subsequently annealed at 700–1000°C to induce structural and compositional changes. Using grazing-incidence X-ray diffraction and scanning electron microscopy, structural changes were followed as a function of annealing temperature. At temperatures above 700°C, the previously homogeneous and amorphous thin films became a heterogeneous mixture of (partially) graphitized nitrogen-containing carbon and either Fe_3C or $\beta\text{-Co}$. The onset of this transformation is accompanied by a rapid decrease in N content and occurs as a function of both transition metal content and temperature. Catalytic activity for oxygen reduction is at its maximum partway through this transformation.
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Due to both cost and supply issues, there is a great desire to replace the Pt-based oxygen reduction electrocatalysts employed in proton exchange membrane fuel cell cathodes with a less expensive and more abundant material. One promising catalyst is based on the transition metal (TM)–C–N systems (TM = Fe, Co). Traditional methods for preparing these catalysts involve the heat-treatment of a TM precursor, carbon powder, and a source of nitrogen at 600–1000°C.^{1–3} The heat-treatment can be performed in either an inert atmosphere or in the presence of ammonia.

Physical vapor deposition methods have also been used to prepare TM–C–N catalysts.^{4–8} Our group has recently reported combinatorial libraries of $\text{Fe}_x\text{C}_{1-x-y}\text{N}_y$ ⁹ and $\text{Co}_x\text{C}_{1-x-y}\text{N}_y$ ¹⁰ libraries prepared by magnetron sputtering.

The exact nature and structure of the active catalytic sites is still not well understood. The Dodelet group has proposed the existence of two active sites, FeN_2/C and FeN_4/C , which are believed to be Fe coordinated to pyridinic-type and pyrrolic-type nitrogen sites that are embedded into the carbon support.^{11,12} Recently, Dodelet's group proposed that these sites exist in micropores, with a $\text{FeN}_{2+2}/\text{C}$ molecular assembly bridging the pore walls.^{13,14}

Here we report the changes in the catalytic activity toward the oxygen reduction reaction (ORR) with annealing temperature for TM–C–N libraries prepared by combinatorial magnetron sputtering. Grazing incidence X-ray diffraction (GI-XRD) and scanning electron microscopy (SEM) were used to monitor how the film structure and morphology changed with annealing temperature. Changes in catalytic activity are also explained in terms of film heterogeneity, the phases formed, and N content.

Experimental

Film deposition.—Samples were prepared by magnetron sputtering using a Corona Vacuum Coaters' (Vancouver, British Columbia, Canada) V3T system, which is described in detail elsewhere.¹⁵ Briefly, the system holds up to five targets, has a rotating substrate table, is turbopumped, and reaches a base pressure of 2.7×10^{-7} Pa (2×10^{-7} Torr).

Two-inch diameter targets of carbon (graphite, Kurt J. Lesker Co., Clairton, PA), Co (Williams Advanced Materials, Buffalo, NY), iron (grade 1008 low carbon steel, less than 0.08% C by weight, balance Fe) were used. TM and C were sputtered using Advanced Energy MDX-1 k dc power supplies that provided a constant power of 15 and 150 W, respectively.

Combinatorial libraries were prepared by positioning specially designed masks in front of each target to produce a linear deposition profile of TM and a constant deposition profile of C within a 76 mm track when the substrate table is rotated.⁹ Nitrogen was incorporated into the libraries by sputtering in an Ar/N_2 gas mixture.¹⁶ Gas flows were independently controlled using mass flow controllers (MKS Instruments, Wilmington, MA). Ultrahigh-purity Ar (99.999%) and N_2 (99.999%) were supplied at constant flow rates of 4.5 and 3.0 sccm, respectively. This corresponds to total pressure of 0.216 Pa (1.6 mTorr) and an N_2 partial pressure of 0.086 Pa (0.65 mTorr) during sputtering. Uniform composition films of both Fe–C–N and Co–C–N were prepared using the same sputtering conditions, except that constant deposition profile masks were positioned in front of both Fe (or Co) and C targets.

Films were deposited onto a linear array of 1.3 cm diam pre-weighed Al foil disks for determining the mass per unit area of the deposited film, 80 × 10 mm Si(100) wafer strips for electron microprobe analysis and film thickness determination, 80 × 10 mm quartz substrates for heat-treatment and corrosion testing, and 5 mm diam glassy carbon disks (Tokai Carbon Co.) for rotating disk electrode (RDE) measurements. Three sets of five glassy carbon disks equally spaced within the 76 mm wide range of composition variation were mounted onto the substrate table. Within each set, disks are numbered from 1 to 5 with increasing TM content.

Film thickness.—The thickness of films deposited on a Si wafer was determined using a Dektak 8 advanced development profilometer (Veeco Instruments, Inc.). Film thickness was found to linearly increase across the libraries from 354 to 422 nm and 289 to 408 nm with increasing TM content for Fe and Co, respectively. The single-composition Fe–C–N and Co–C–N films were 1.25 and 1.46 μm thick, respectively.

Heat-treatment.—Films deposited on various substrates were annealed at temperatures between 700 and 1000°C using a Modular Process Technology RTP-600S rapid thermal processor (RTP). Films were heated under flowing Ar or N_2 (2 L/min) at a rate of 5°C/s up to the annealing temperature, where it was held for 300 s.

Electron microprobe analysis and scanning electron microscopy.—The compositions of sputtered libraries and single-composition films were determined using a JEOL JXA-8200 Superprobe equipped with one energy-dispersive (EDS) spectrometer, five wavelength-dispersive (WDS) spectrometers, and an automated motion stage. Using the automated motion stage, compositions were measured as a function of position across the library. All elemental compositions were determined using the WDS detectors. Silicon nitride (Si_3N_4) was used as the N standard, MnCo alloy (Mn/Co = 30:70 weight ratio) was used as the Co standard, magne-

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tite was used as the Fe standard, and pyrolytic graphite was used as the C standard. In the case of Co–C–N, the overlap of the $N(K_{\alpha})$ and $Co[L_{\beta}(2)]$ lines was carefully considered and accommodated. Reuter's method for thin-film analysis, which corrects for the excitation of the backscattered electrons caused by the substrate, was employed.¹⁷

High-resolution images of the sputtered films on glassy carbon disks were taken using a cold-field-emission Hitachi S-4700 scanning electron microscope (SEM).

Grazing incidence X-ray diffraction.—XRD patterns were collected using a Siemens D5000 diffractometer equipped with a grazing incidence attachment. $Cu K\alpha$ radiation was used at an incidence angle of 0.5° and with divergence slits set to 0.1° . Such conditions lead to an illuminated spot of 40×12 mm in the center of the 76×1.5 mm constant-composition specimen. A Soller slit box in front of the detector was used to ensure that the scattered X-rays from this large illuminated sample area that entered the detector all had the same scattering angle. Data was collected over a scattering angle range of 10 – 70° in 0.05° intervals. Total scan times varied between 4 and 10 h.

Electrochemical characterization.—The electrocatalytic activity of each film deposited on a 5 mm diam glassy carbon disk determined by performing cyclic voltammetry (CV) with an RDE. Measurements were performed in a three-electrode, one-compartment cell, equipped with a Pt wire counter electrode and either a Hg/Hg_2SO_4 or a $Ag/AgCl$ reference electrode. The potential of each reference electrode was calibrated vs the reversible hydrogen electrode (RHE). All data presented in this work have been corrected to the RHE potential. Measurements were made at room temperature using 0.1 M $HClO_4(aq)$ as the electrolyte. The electrolyte was prepared from doubly distilled high-purity $HClO_4$ (GFS Chemicals, Inc.) and 18 M Ω Barnstead nanopure water.

RDE measurements were made using a Pine Instruments AFCBP1 bipotentiostat controlled using PineChem software. CVs were collected by scanning the disk potential between 0.9 to 0.05 V vs RHE at a sweep rate of 5 mV/s. For each catalyst tested, a CV was first collected using Ar-purged electrolyte to determine the non-faradaic current. For subsequent CVs, the electrolyte was saturated with O_2 and the electrode was rotated at 900 rpm. The faradaic current was determined by subtracting the Ar-purged CV from those obtained under O_2 .

Results

Library compositions.—Figure 1 shows the nitrogen content as a function of TM content for libraries annealed at different temperatures. The nitrogen content of the as-sputtered libraries increases with both Fe or Co content. Annealing these libraries resulted in a significant decrease in nitrogen content, which decreased further with increased annealing temperature.

Libraries annealed at $800^{\circ}C$ or higher displayed a knee-shaped point where the N content of the library began to rapidly decrease. At higher annealing temperatures, this “knee-point” occurred at lower TM contents. Beyond this knee-point, the N content decreases less rapidly with TM content. The Co–C–N library annealed at $700^{\circ}C$ did not display a sharp knee point and retained most of the original N content.

Catalytic activity.—Figure 2 compares the CVs obtained under oxygen for the Fe–C–N and Co–C–N libraries annealed at $800^{\circ}C$. In both cases, activity increased with TM content. Figure 3 compares SEM images of catalytic films on disks 1, 3, and 5 for both Fe–C–N and Co–C–N. It can be seen that on disk 1, the films are relatively homogenous on the nanometer scale. Films deposited on disk 3 have a more heterogeneous appearance, with a surface decorated with nanoparticles and nanotube structures. Further increasing the TM content resulted in films with a very heterogeneous appearance. A large number of nanoparticles and nanotubes are present in the film. This increase in heterogeneity correlates with the increase in TM

Figure 1. (Color online) Variation of atom % N as a function of atom % TM for (a) Fe–C–N libraries and (b) Co–C–N libraries annealed at various temperatures. Also shown are the positions of the glassy carbon disks (hollow circles) studied by RDE.

content and also the increase in catalytic activity observed in Fig. 2. Both catalyst systems display similarly high onset potentials (near 0.8 V vs RHE) for ORR. The Co–C–N library displays two separate waves for the ORR, indicating the presence of two (or more) catalytically active species. More details about the electrochemical behavior of these catalysts are reported elsewhere.^{10,18}

Film heterogeneity was also found to vary with temperature. Figure 4 displays SEM images and disk CVs obtained under oxygen for the Co–C–N library on disk 3 annealed at 700, 800, and $1000^{\circ}C$. As the annealing temperature was increased from 700 to $1000^{\circ}C$, the film became more heterogeneous, displaying more discrete regions of nanoparticles and nanotubes. The catalytic activity of this film increased significantly between 700 and $800^{\circ}C$, coinciding with the onset of heterogeneity. The catalyst remained active, although the onset potential decreased slightly after heating to $1000^{\circ}C$. It is possible that more active catalysts could be prepared at a heating temperature between 800 and $1000^{\circ}C$, but we have not yet carefully explored this temperature range in small increments.

Also shown in Fig. 4 is the variation in catalytic activity of disk 5 of the Fe–C–N library with annealing temperature. Much like the Co–C–N library, maximum activity was achieved at $800^{\circ}C$ and the activity decreased at higher annealing temperatures. However, the activity at $1000^{\circ}C$ is significantly lower for Fe–C–N than the Co–C–N. This is attributed to the fact that at $1000^{\circ}C$, there is no N remaining in the Fe–C–N library.

GI-XRD (single composition study).—In order to identify the species formed during the film transformation from homogeneous to heterogeneous, GI-XRD measurements were performed on single-composition Fe–C–N and Co–C–N films annealed at various temperatures. Figure 5 shows the diffraction patterns collected after the films had been heated to the temperatures indicated. Prior to heating, the as-sputtered Fe–C–N and Co–C–N films were amorphous (not shown) and contained ca. 4 atom % Fe or ca. 7 atom % Co. As the temperature was increased an evolution from an amorphous XRD pattern to one containing peaks corresponding to crystalline phases was observed in both cases. The peak at ca. 26.3° was present in both samples and can be attributed to the carbon (002) Bragg peak which is indicative of graphitic species and is often observed for carbon nanotubes.¹⁹ The other observed peaks can be attributed to the formation of either Fe_3C ²⁰ or $\beta-Co$.²¹ At $1000^{\circ}C$, Fe_3C is the

Figure 2. (Color online) Disk current densities for sputtered (a) Fe-C-N and (b) Co-C-N libraries annealed at 800°C. Measurements were made at a sweep rate of 5 mV/s in O₂-saturated 0.1 M HClO₄ at room temperature while the electrode was rotated at 900 rpm. The average composition of each disk is indicated in each panel.

only iron-carbide predicted to be stable by the phase diagram.²² Higher carbides such as Fe₂C are metastable and are not stable above 550°C.²³ Dodelet's group has reported XRD measurements that may contain Fe₃C, though they were unable to unambiguously identify it due to a poor signal-to-background ratio.^{24,25} The presence of Fe₃C in heat-treated Fe-C-N catalysts has been previously observed using Mössbauer spectroscopy.²⁶ The presence of β-Co has been previously observed by XRD,²⁷ but the presence of other Co-containing phases could not be ruled out.

The homogeneous-heterogeneous transformation was also followed by SEM. Figure 6 displays SEM images of the Fe-C-N constant-composition film annealed at 750, 800, and 850°C. Figure 6 shows that heterogeneity and nanotube formation does not occur at

800°C for this sample. Images were taken near film cracks to show a "natural cross section" and that no tube growth occurred below the surface at 750 and 800°C.

Figures 5 and 6 show that phase formation and heterogeneity begins to occur between 825 and 850°C and corresponds to the onset of the rapid decrease in N content from the film, as shown in Fig. 7. Also shown in Fig. 7 is the change in N content with temperature for a position in the Fe-C-N library of similar initial composition. Rapid N loss occurred at a slightly higher temperature for the constant composition film, which could be attributed to the fact that the constant composition film is ca. three times thicker than the library (1250 nm vs 400 nm).

The degree of heterogeneity is related to both the heat-treatment temperature and the TM content (i.e., samples annealed at higher temperatures require less TM to undergo this transformation). This suggests that the "knee-point" observed in Fig. 1 for the Fe-C-N libraries occurs at the minimum Fe content required to initiate this transformation at a particular temperature.

Discussion

The thermal evolution of sputtered TM-C-N films can be summarized as follows:

1. As-sputtered TM-C-N films are amorphous by XRD. The appearance of the film in SEM is homogeneous on the nanoscale, consistent with an amorphous structure.
2. Upon heating these materials in an inert atmosphere, TM-catalyzed graphitization occurs.
3. The temperature at which this occurs is dependent upon the TM content of the film.
4. During graphitization, the N content rapidly decreases.
5. When Fe is the catalyst, Fe₃C begins to form. When Co is the catalyst, β-Co begins to form.
6. At higher temperatures (e.g., 1000°C), the N content of the Fe-C-N films is extremely small and the main species remaining are graphitic carbon and Fe₃C.

The most catalytically active materials contain some Fe₃C or β-Co, as evidenced by the onset of heterogeneity. However, Schulenberg et al. have shown that the Fe₃C initially present in their catalysts is not stable in acid and not responsible for catalytic activity.²⁶ Also, Lalande et al. have shown that metallic Co has

Figure 3. (Color online) SEM images of (a) Fe-C-N disk 1, (b) Fe-C-N disk 3, (c) Fe-C-N disk 5, (d) Co-C-N disk 1, (e) Co-C-N disk 3, and (f) Co-C-N disk 5 films deposited on glassy carbon disk electrodes and annealed at 800°C. The scale bar indicates a distance of 500 nm. Images were taken after electrochemical measurements.

Figure 4. (Color online) SEM images of Co-C-N catalyst on disk 3 heated at (a) 700, (b) 800, and (c) 1000°C. Images were taken after RDE measurements. The scale bar indicates a distance of 500 nm. Disk current densities of Co-C-N catalyst on disk 3 heated at (d) 700, (e) 800, and (f) 1000°C and Fe-C-N on disk 5 at (g) 800, (h) 900, and (i) 1000°C. Measurements were made at a sweep rate of 5 mV/s in O_2 -saturated 0.1 M HClO_4 at room temperature while the electrode was rotated at 900 rpm.

practically no activity toward the ORR.²⁸ For the case of our sputtered TM-C-N materials, acid stability measurements show that when more Fe_3C or $\beta\text{-Co}$ is initially present, less Fe or Co remains in the film after acid exposure.^{9,10,18} Although Fe_3C and $\beta\text{-Co}$ are not the active catalytic species, the presence of these species does not preclude the presence of a high number of TM- and N-containing active sites, provided that the N content of the film remains high. Furthermore, a certain quantity of Fe_3C or $\beta\text{-Co}$ may need to form as a consequence of inducing sufficient graphitization to produce the maximum number of catalytically active sites. In the case of Fe-C-N at 1000°C (or higher), there is almost no N remaining in the film and most Fe is in the form of inactive Fe_3C . In the

case of Co-C-N at 1000°C, while there is a large presence of $\beta\text{-Co}$, there is still an appreciable amount of N remaining in the film; hence, good catalytic activity was still achieved.

Conclusions

Annealing sputtered TM-C-N films has been shown to increase catalytic activity dramatically. This onset of catalytic activity coincides with a transformation from a homogenous amorphous TM-C-N film to a heterogeneous mixture of (partially) graphitized carbon and Fe_3C or $\beta\text{-Co}$, as observed by XRD and SEM. The onset of this transformation occurs both as a function of TM content and temperature. Catalyst activity for ORR is at its maximum partway through this transformation. If this transformation goes to completion, almost all N is lost from the film for the case of Fe and the catalytic activity severely drops. Maximum catalytic activity with TM-C-N libraries was achieved at an annealing temperature of 800°C for both Fe and Co. The Co-C-N libraries retain their catalytic activity when annealed up to 1000°C, and perhaps beyond, because they retained an appreciable quantity of N even at 1000°C.

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Figure 5. (Color online) GI-XRD patterns for (a) single-composition Fe-C-N film annealed at 750, 800, 825, 850, and 1000°C and (b) single-composition Co-C-N film annealed at 700, 725, 735, 800, and 1000°C.

Figure 6. (Color online) SEM images for a single-composition Fe-C-N film deposited on a glassy carbon disk after annealing (a) 750, (b) 800, and (c) 850°C. The scale bar indicates a distance of 500 nm.

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Figure 7. (Color online) Variation in N content with heat-treatment temperature for both the constant-composition Fe-C-N film and the Fe-C-N library at a position of similar initial composition.

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Thermally Treated Fe-C-N Oxygen Reduction Catalysts Prepared by Vacuum Deposition

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Vacuum deposition techniques were used to prepare combinatorial libraries of thin film Fe-C-N catalysts. After deposition, catalyst films were thermally treated to induced structural and composition changes. Catalytic activity was found to be at its largest when the films were annealed at ca. 800°C. At this temperature, partial graphitization of the film occurred but it still contained a significant amount of nitrogen, which is required to have an active site. Above 800°C, a significant quantity of Fe₃C, which is inactive and not stable in acid, was formed. Single composition thin films were also prepared, thermally treated, and tested in a 50-cm² fuel cell. After thermal treatment of the catalyst, the fuel cell performance was significantly improved.

Introduction

The replacement of the expensive Pt catalyst (\$40,000/kg) used in fuel cell cathodes with a cheaper, but equally effective catalyst, is a major challenge for both the fuel cell industry and the scientific community. Fe-C-N and Co-C-N materials are promising candidates that have been widely studied. Traditional methods for preparing these catalysts involve the pyrolysis of various combinations of Fe (or Co), carbon and nitrogen containing precursors [1,2]. Catalytic activity has been correlated with higher surface nitrogen content in the post-pyrolysis material [3]. Surface pyridinic and pyrrolic-type nitrogen embedded into the carbon support are believed to co-ordinate Fe (or Co) to form active sites, which Dodelet's group commonly refer to as of FeN₂/C and FeN₄/C sites, respectively [4].

As an alternative to traditional methods, we have fabricated transition metal (TM)-C-N (TM = Fe, Co) catalysts using vacuum deposition techniques [5-8]. Thin films are prepared by co-depositing TM and C in a N₂/Ar plasma. One major advantage of this method is that the resulting materials can contain a large atomic fraction (up to ca. 50 at %) of N. This is substantially more N than the most effective traditional method, heating in the presence of ammonia, which has resulted in maximum N contents approaching only 3 at% [9].

However, as-sputtered TM-C-N thin films are amorphous and have very poor catalytic activity towards the oxygen reduction reaction (ORR). They do show excellent

activity after annealing above 700°C to 800°C (depending on TM content) under an inert atmosphere. During the annealing process, partial graphitization of the CN_x type material occurs. During graphitization, a significant portion of the N content is lost and either Fe₃C or β-Co has been shown to form [10]. Our approach to increasing the amount of N retained in the film after annealing has been to sputter the films using a higher concentration of N₂ in the plasma [6,11]. Here we have prepared combinatorial libraries of Fe-C-N catalysts that were sputtered in a 40% N₂/Ar plasma. The catalytic activity and acid stability as a function of both composition and annealing temperature is discussed.

Thermal treatment in ammonia has been shown to produce more active catalysts [16]. Fuel cell performance for a single composition Fe-C-N catalyst thermally treated in ammonia is also presented.

Experimental

Film Deposition

Samples were prepared by magnetron sputtering using a Corona Vacuum Coaters' (Vancouver, British Columbia, Canada) V3T system, which is described in detail elsewhere [12]. Two-inch diameter targets of carbon (graphite, Kurt J. Lesker Co., Clairton, PA) and iron (grade 1008 low carbon steel, less than 0.08% C by weight, balance Fe) were used. Fe and C were sputtered using Advanced Energy MDX-1k DC power supplies that provided a constant power of 15 W and 150 W, respectively.

Combinatorial libraries were prepared by positioning specially designed masks in front of each target to produce a linear deposition profile of Fe and a constant deposition profile of C within a 76 mm track when the substrate table is rotated [8]. Nitrogen was incorporated into the libraries by sputtering in an Ar/N₂ gas mixture [13]. Gas flows were independently controlled using mass flow controllers (MKS Instruments, Wilmington, MA). Ultra high purity Ar (99.999%) and N₂ (99.999%) were supplied at constant flow rates of 4.5 sccm and 3.0 sccm, respectively. This corresponds to total pressure of 0.216 Pa (1.6 mTorr), an N₂ partial pressure of 0.086 Pa (0.65 mTorr) and a 40% N₂/Ar gas mixture during sputtering.

Films were deposited onto: a linear array of 1.3 cm diameter pre-weighed Al foil disks for determining the mass per unit area of the deposited film; 80 × 10 mm Si (100) wafer strips for electron microprobe analysis and film thickness determination; 80 × 10 mm quartz substrates for heat-treatment and corrosion testing; 5 mm diameter glassy carbon discs (Tokai Carbon Co.) for rotating disc electrode (RDE) measurements. Three sets of five glassy carbon discs equally spaced within the 76 mm wide range of composition variation were mounted onto the substrate table. Within each set, discs are numbered from 1 to 5 with increasing Fe content.

Heat Treatment

Films deposited on various substrates were annealed at temperatures between 800 and 1000°C using a Modular Process Technology RTP-600S Rapid Thermal Processor (RTP). Films were heated under flowing Ar (2 L/min) at a rate of 5°C/s up to the annealing temperature, where they were held for 300s.

Physical and Surface Characterization

The compositions of sputtered libraries on quartz strips were determined using a JEOL JXA-8200 Superprobe equipped with one energy dispersive (EDS) spectrometer,

five wavelength dispersive (WDS) spectrometers and an automated motion stage. Using the automated motion stage, compositions were measured as a function of position across the library. All elemental compositions were determined using the WDS detectors.

Electrochemical Measurements

The electrocatalytic activity of each deposited film was determined by performing cyclic voltammetry (CV) with a rotating ring-disc electrode (RRDE). The RRDE electrode consisted of a catalyst-coated glassy carbon disc (5 mm diameter) surrounded by a Pt ring (7.5 mm and 8.5 mm inside and outside diameters respectively). Measurements were performed in a three-electrode, one compartment cell, equipped with a Pt wire counter electrode and a Ag/AgCl reference electrode. The potential of the Ag/AgCl reference electrode was calibrated versus the reversible hydrogen electrode (RHE). All data presented in this work have been corrected to the RHE potential. Measurements were made at room temperature using high purity 0.1M HClO₄ (aq) (GFS Chemicals, Inc.) as the electrolyte.

RRDE measurements were made using a Pine Instruments AFCBP1 bi-potentiostat controlled using PineChem software. CVs were collected by scanning the disc potential between 0.9 to 0.05V vs. RHE at a sweep rate of 5 mV/s. For all electrochemical measurements, the ring potential was held at 1.2V vs. RHE in order to oxidize any hydrogen peroxide that was produced [14]. For each catalyst tested, CVs were first collected in Ar-purged electrolyte in the potential range of 0 - 1.0 V (versus RHE) at 100 mV/s. During these Ar CVs, corrosion of Fe was observed for some of the films. If corrosion of Fe was observed, Ar CVs were continued until a steady state CV was achieved (i.e. no further corrosion was observed). A final CV in Ar-purged electrolyte was then collected to determine the non-Faradaic current. For subsequent CVs, the electrolyte was saturated with O₂ and the electrode was rotated at 900 RPM. The Faradaic current was determined by subtracting the Ar-purged CV from those obtained under O₂.

Fuel Cell Measurements

Iron was vacuum deposited in the presence of nitrogen onto a carbon fabric substrate that had been modified to increase its surface area. After deposition, the catalyst was thermally treated in a quartz tube furnace. In general, the temperature increased 6°C/minute and was held at the set point for 15 minutes.

The treated catalyst material was die-cut into 50-cm² coupons and assembled with two Nafion™ 112 membranes and a dispersed Pt/C (0.3 – 0.4 mg Pt/cm²) coated onto a carbon paper gas diffusion layer as anode catalyst into a membrane electrode assembly (MEA). The MEA was assembled in a 50-cm² test cell (Fuel Cell Technologies). The fuel cell was tested using a Solartron 1470 potentiostat with Solartron SI1250 frequency response analyzer controlled by CorrWare and ZPlot software (Scribner Associates).

Results and Discussion

RDE Results

Figure 1 shows the RDE CVs obtained under oxygen for catalyst libraries annealed at 800, 900 and 1000°C. Also shown in Figure 1 is the activity reported by Dodelet's group for Fe-based catalysts prepared by traditional methods, which are two of the most active Fe-based catalysts reported in the literature to date [3,15]. Our most active thin film

catalyst (disc 5 annealed at 800°C) displayed comparable activity despite having a significantly smaller electrochemical surface area.

For samples annealed at 800°C, we see that activity increased with Fe content. Samples annealed at 900°C displayed higher current but lower onset potentials with increasing Fe content. The activity at 1000°C decreased with increasing Fe content. Also apparent in Figure 1 is the similarity of the RDE curves and Fe-content of disc 4 and 5 annealed at 800 and 900°C. Closer examination of the curves reveals that lower activity was achieved at 900°C which can be attributed to the lower N content.

Figure 2 displays the percentage of hydrogen peroxide produced by catalyst libraries annealed at 800, 900 and 1000°C. The best catalysts prepared here produce between 20-30% peroxide. Hydrogen peroxide production increased with increased annealing temperature, which can be attributed to a decrease in N-content.

Acid Stability

In order to assess the acid stability of the catalysts, libraries deposited on quartz strips were immersed in 0.5M H₂SO₄ at room temperature for 7 days. Figure 3 displays the Fe content as a function of library position before and after acid exposure. Also shown in Figure 3 are the corresponding positions of each glassy carbon disc. From this it can be seen that the position at which Fe corrosion began shifted to lower Fe content when the annealing temperature was increased. Furthermore, the amount of that Fe corroded from the library increased with annealing temperature. This loss is attributed to the corrosion of Fe₃C that we have shown to form when Fe-C-N films are annealed above ca. 800°C [10]. As the annealing temperature was increased, more N was lost from the film and more Fe₃C formed, which subsequently corroded from the film upon acid exposure [11]. The Fe that remains in the film after acid exposure is most likely Fe that is present in active sites. The library annealed at 800°C retained more Fe after acid exposure; therefore it is inferred to have more active sites, which would explain why it had the highest catalytic activity.

Single Composition Fuel Cell Tests

The ORR activities of the base carbon substrate, the catalyst deposited on the substrate, and the catalyst after thermal treatment are shown in Figure 4. In this instance, the thermal treatment consisted of 900°C in ammonia. It has been found that thermal treatment in ammonia atmosphere yields better performing catalysts than those treated in nitrogen [16]. While some activity is seen with the substrate alone and the substrate with iron deposited before the thermal treatment, it is clear that thermal treatment is required for best performance.

The activity of this best performing catalyst when measured in a 50-cm² fuel cell is still lower than the best non-precious metal catalysts prepared by traditional methods and several orders of magnitude lower than state-of-the-art platinum MEAs. However, the support used for the fuel cell measurements of the vacuum deposited, thermally treated catalysts (carbon fabric) is orders of magnitude lower in surface area than the carbon blacks used as supports for both the traditional method of preparing non-precious metal catalysts and state-of-the-art Pt.

Conclusions

Fe-C-N based catalysts have been prepared by combinatorial sputter deposition. Using RRDE, high catalytic activity towards ORR that approached the best reported in scientific literature for Fe-based catalysts, was measured. Fe_3C also forms upon annealing these films, which is inactive towards ORR and corrodes in acid. The amount of Fe_3C present in the libraries increased with annealing temperature. Maximum catalytic activity was achieved when the library was annealed at 800°C , where active sites have formed and presumably only a small portion of Fe present was in the form of Fe_3C .

Measurements in a 50-cm^2 fuel cell did not show activity as high as those reported for traditional non-precious metal catalyst preparations. This is believed to be partially due to the lower surface area of the support. Thermal treatment of the catalyst significantly improved fuel cell performance.

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Figure 1. Rotating disc voltammograms obtained for sputtered libraries annealed at 800, 900, and 1000°C. The average composition of each disc is indicated in each panel. Measurements were made at a sweep rate of 5 mV/s in O_2 -saturated 0.1M HClO_4 at room temperature. Also shown in each panel is the activity of reported by Dodelet's group for $\text{II}(\text{O}.2)\text{FeAc}(900)$ at 100 RPM and $\text{ClFeTMPP}/\text{RC1}$ at 1500 RPM [3,15].

Figure 2. Hydrogen peroxide production as a function disc potential for sputtered libraries annealed at 800, 900, and 1000°C. The average composition of each disk is indicated in each panel.

Figure 3. Fe-content as a function of position across the film for libraries annealed at 800, 800, and 1000°C.

Figure 4. Fuel cell performance of a vacuum deposited Fe-C-N catalyst at various points in the synthetic process [5].

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Co-C-N Oxygen Reduction Catalysts Prepared by Combinatorial Magnetron Sputter Deposition

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Abstract

Thin film libraries of $\text{Co}_x\text{C}_{1-x-y}\text{N}_y$ ($0 < x < 0.107$, $0.003 < y < 0.389$) were prepared by combinatorial magnetron sputter deposition in an Ar/N₂ gas mixture followed by subsequent heat-treatment at 700, 800 or 1000°C in N₂ atmosphere. By increasing the nitrogen partial pressure during sputtering, the nitrogen content was increased significantly in the as-sputtered libraries and more nitrogen remained in the libraries after heat-treatment. The catalytic activities of the libraries towards the oxygen reduction reaction (ORR) were studied using the rotating ring-disk electrode (RRDE) technique. $\text{Co}_x\text{C}_{1-x-y}\text{N}_y$ libraries heat-treated at 800°C with $0.004 < x < 0.105$ and $0.026 < y < 0.097$ showed good catalytic activities towards ORR in 0.1M HClO₄ solution at room temperature. The heating temperature that induces the onset of catalytic activity coincides with the temperature at which both substantial nitrogen release from the originally amorphous films and the formation of graphitic carbon and β -Co occurs. This

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temperature varies significantly with both the Co and N content in the films. The production of H_2O_2 and the corrosion stability of the libraries are also discussed.

Introduction

Polymer electrolyte membrane fuel cells (PEMFC), have attracted attention due to their high energy densities, low operating temperatures and lack of emissions [1-3]. The high cost of PEMFC is one of the barriers to their commercialization. The replacement of Pt by non-noble metal catalysts could lead to significant cost reduction and is desirable, provided that similar area-specific activity can be obtained [4].

The electrochemical activity of transition metal macrocycles towards the oxygen reduction reaction (ORR) was first explored in 1964 [5] and then improved by heat-treatment in an inert atmosphere in 1976 [6]. Since then, non-noble metal catalysts based on pyrolyzed carbon-supported N_4 -metal macrocycles (where the metal is usually Fe or Co) [7-13] have been widely studied. Later, it was reported that active ORR catalysts can also be prepared by heat treating carbon-supported organometallic (Fe or Co) complexes [14,15] or even Fe or Co salts [16, 17] in ammonia or acetonitrile vapor. For the active sites of the catalysts, Dodelet and coworkers proposed that two active sites (FeN_2/C and FeN_4/C) exist in the Fe-based catalysts [18] and that one active site (CoN_4/C) exists in the Co-based catalysts [19] based on the time-of-flight secondary ion mass spectrometry (TOF SIMS) results.

Other methods have been used to prepare Co-based catalysts. Deng and Dignam reported that thin films of Co-C-N co-sputtered in vacuum showed good catalytic activity for ORR in alkaline solution but the films were not stable in acid solution due to dissolution [20, 21]. More recently, Sirk *et. al.* reported that sol-derived [Co, N, C, O]-based catalysts after heat-treatment showed promising activity towards ORR [22].

Our work focuses on the preparation of active catalysts for ORR by combinatorial magnetron sputter deposition. Active Fe-C-N oxygen reduction catalysts have been prepared using our combinatorial infrastructure [23]. In this paper, studies of thin film libraries of $\text{Co}_x\text{C}_{1-x-y}\text{N}_y$ ($0 < x < 0.107$, $0.003 < y < 0.389$) prepared combinatorially by magnetron sputter deposition followed by subsequent heat-treatment in N_2 atmosphere are reported. The impacts of the heat-treatment temperature and the initial composition on the structure, morphology, corrosion stability and catalytic activity of the libraries were studied.

Experimental

Deposition of Thin-Film Libraries

A Co sputtering-target (2.00 in. diameter, 0.250 in. thick and 99.95% pure) was obtained from Williams Advanced Materials (Buffalo, NY). A C sputtering-target (2.00 in. diameter, 0.250 in. thick, and 99.999% pure) was obtained from Kurt J. Lesker Co. (Clairton, PA). Co and C were sputtered using MDX-1K DC (Advanced Energy) power supplies with powers of 15 W and 150 W, respectively. Specially designed masks were positioned in front of each target to produce a linear composition variation when the substrate table was rotated. More details about the production of binary and pseudobinary libraries using our equipment can be found elsewhere [24].

Nitrogen was incorporated into the libraries by sputtering in an Ar/N_2 gas mixture [23]. Gas flows were independently controlled using MKS mass flow controllers. Ultra high purity Ar (99.999%) and N_2 (99.999%) were supplied at constant flow rates during

the sputtering. Two libraries and two films of constant composition were produced in this work. Library 1 was sputtered under 7.5 sccm Ar and 2.0 sccm N₂, which corresponds to a total pressure of 0.277 Pa (2.1 mTorr) and a N₂ partial pressure of 0.058 Pa (0.44 mTorr) (i.e. N₂/Ar =20/80). Library 2 was sputtered under 4.5 sccm Ar and 3.0 sccm N₂, which corresponds to a total pressure of 0.224 Pa (1.7 mTorr) and a N₂ partial pressure of 0.090 Pa (0.68 mTorr) (i.e. N₂/Ar =40/60).

Films were deposited onto: a linear array of 1.3 cm diameter pre-weighed Al foil disks for determining the mass per unit area of the deposited film; 80 × 10 mm Si (100) wafer strips for electron microprobe analysis and film thickness determination; 80 × 10 mm quartz substrates for heat-treatment and corrosion testing; glassy carbon (GC) disks with a diameter of 5 mm (Tokai Carbon Co.) for electrochemical measurements using the rotating ring-disk electrode (RRDE) technique. Three sets of five GC disks equally spaced within the 76 mm wide range of composition variation were mounted onto the substrate table. Within each set, disks are numbered from 1 to 5 with increasing Co content. Figure 1 shows the various substrates mounted on the substrate table as well as a projection of the targets and their associated masks on the substrate table.

The constant composition films were prepared for grazing incidence X-ray diffraction measurements versus heat-treatment temperature. The films of constant composition were sputtered using constant masks over both Co and C targets and using the same sputtering gas pressures as Library 2. The films were sputtered onto Si(100) wafer strips 80 mm in length and 15 mm in width. These wafers had a 500 nm layer of SiO₂ on their polished surface. The SiO₂ layer prevented reaction of the Co in the film with the Si substrate during the heat treatments. The compositions prepared were

$\text{Co}_{0.5}\text{C}_{66.8}\text{N}_{32.7}$ and $\text{Co}_{4.7}\text{C}_{51.7}\text{N}_{43.6}$ in the as-sputtered films. These compositions are same as the compositions of the films sputtered on glassy carbon disks #1 and #5, respectively for Library 2.

Films deposited on quartz substrates and three sets of GC disks were heat-treated at 700°C, 800°C and 1000°C in N_2 using a Modular Process Technology RTP-600S Rapid Thermal Processor (RTP). The samples were heated at a heating rate of $5^\circ\text{C}\cdot\text{s}^{-1}$ in flowing N_2 ($2\text{ L}\cdot\text{min}^{-1}$) and held at the target temperature for 5 minutes before cooling.

Thickness of the Thin-Film libraries

The thickness of the thin-film library sputtered on a Si wafer was determined using a Dektak 8 Advanced Development Profilometer (Veeco Instruments Inc.). Film thickness before heat-treatment was found to linearly increase across the library from about 90 nm to 200 nm with increasing Co content for Library 1 and from about 289 nm to 408 nm with increasing Co content for Library 2. One reason for the large increase in film thickness with Co-content is that the nitrogen content in the film increases strongly with Co content as will be shown below.

Composition of the Thin-Film Libraries

The composition as a function of position in the library was obtained using a JEOL JXA-8200 superprobe electron microprobe system equipped with one energy dispersive (EDS) spectrometer and five wavelength dispersive (WDS) spectrometers. Silicon nitride (Si_3N_4) was used as the N standard, MnCo alloy (Mn:Co=30:70, weight ratio) was used as the Co standard and pyrolytic graphite was used as the C standard. The overlap of the

N(K_{α}) and Co($L_{\beta}(2)$) lines was carefully considered and accommodated. Reuter's method for thin films analysis, which corrects for the excitation of the backscattered electrons caused by the substrate, was employed [25]. Co, N and C atomic compositions were all determined by WDS detectors. The analysis spot size was 50 μm . Typically the composition was measured every 2 mm along the 76 mm-long libraries.

Grazing Incidence X-ray Diffraction

X-ray diffraction patterns were collected using a Siemens D5000 diffractometer equipped with a grazing incidence attachment. Cu- K_{α} radiation was used at an incidence angle of 0.5° and with divergence slits set to 0.1° . Such conditions lead to an illuminated spot of 40 x 12 mm in the center of the 80 mm x 15 mm constant-composition specimen. A Soller slit box in front of the detector was used to ensure that the scattered X-rays from this large illuminated sample area that entered the detector all had the same scattering angle. Data was collected over a scattering angle range of 10 - 80° in 0.05° intervals. Total scan times varied between 8-12 hours.

Surface Analysis

The surfaces of the samples on the GC disks were characterized by X-ray Photoelectron Spectroscopy (XPS). XPS was performed with a VG Microtech Multilab XPS system (Thermo Electron Corporation) equipped with a CLAM-4 hemispherical analyzer and using a Mg K_{α} (15 kV, 20 mA) source with a 600 μm diameter illumination spot. The measurement parameters were as follows: 20 eV pass energy, 200 ms dwell time, 0.05 eV energy increments, 5 mm analyzer slit. The measurements were performed on the samples on the GC disks after RRDE experiments. Charging, if present on the

sample, was corrected using the carbon C_{1s} peaks, which are, at least partially due to the presence of the adventitious carbon on the samples. The binding energy of adventitious carbon is reported to be in the range of 284.5 to 285.0 eV in the literature [26]. If the observed C_{1s} peak was higher than 285.0 eV by an amount, δE , due to charging, then the measured data were shifted to lower binding energy by δE . For peak fitting, a mixed Gaussian-Lorentzian shape and Shirley background were used. Similar shape parameters were used for all peaks. The peak broadening was constrained to a maximum of 2.0 eV.

SEM Images of the Films

High-resolution images of the as-sputtered and heat-treated films on glassy carbon disks were taken using a cold field emission Hitachi S-4700 scanning electron microscope (SEM).

Corrosion testing

Thin film libraries of Co_xC_{1-x-y}N_y on quartz strips heated at 700°C, 800°C and 1000°C were immersed in 0.5 M H₂SO₄ (reagent, analytical grade) acid solution at 25°C for one week. After treatment, the samples were rinsed with nanopure water and dried in air for further study. Normally, the composition as a function of position on the library was measured and compared to the composition at the same spots measured before acid treatment.

Electrochemical Characterization

The electrocatalytic activity for the oxygen reduction reaction of the films deposited on the GC disks was studied with the rotating ring-disk electrode (RRDE) technique using a Pine Electrochemical system (AFMSRX rotator, and AFCBP1 bipotentiostat). The RRDE electrode consisted of a catalyst film-coated GC disk (5 mm diameter) surrounded by a Pt ring (7.5 mm inner diameter and 8.5 mm outer diameter). The electrochemical measurements were conducted in a one-compartment cell. A Pt-wire counter electrode and Koslow Hg/Hg₂SO₄ (MMS) reference electrode were used for the measurement. The electrolyte was 0.1M HClO₄ solution prepared from double-distilled HClO₄ (GFS Chemicals Inc.) and 18 M Ω Barnstead nanopure water. The potential of the Hg/Hg₂SO₄ reference electrode was calibrated versus the reversible hydrogen electrode (RHE). The potentials reported in this study all refer to that of the RHE potential.

The films on the GC disks were first electrochemically cleaned by sweeping the potential in the range between 0 - 1.0 V (vs. RHE) at 50 mV·s⁻¹ in an Ar-saturated 0.1 M HClO₄ solution until steady state cyclic voltammograms (CV) were obtained. For each catalyst tested, a CV was first collected in Ar-saturated 0.1 M HClO₄ solution from 1.0 to 0.05 V at 5 mV·s⁻¹ to determine the non-Faradaic current. The CVs during oxygen reduction were performed in O₂-saturated 0.1 M HClO₄ solution from 1.0 to 0.05 V at 5 mV·s⁻¹ with the electrode stationary and with the electrode rotated at 900 rpm and O₂ gas purged into the solution at a rate of 1 L·min⁻¹. The Faradaic current was determined by subtracting the CV in Ar-saturated 0.1 M HClO₄ solution from that obtained in O₂-saturated 0.1 M HClO₄ solution. For all the measurements, the ring potential was held at

1.2 V vs. RHE in order to oxidize any H_2O_2 that was produced [27]. The % H_2O_2 produced was calculated with the following equation [13,27,28]

$$\%H_2O_2 = 100 \frac{2I_R / N}{I_D + (I_R / N)} \quad (1)$$

where I_D is the Faradaic current at the disk, I_R is the Faradaic current at the ring, and $N = 0.2$ is the RRDE collection efficiency.

Results and Discussion

Composition of the Thin-Film libraries

The N content versus Co content in the two as-sputtered libraries and those heat-treated subsequently at 700°C, 800°C or 1000°C is shown in Figure 2. The atomic fraction of N ranges from 0.184 to 0.320 in as-sputtered Library 1 (sputtered at a lower nitrogen partial pressure, $N_2/Ar = 20/80$), while the atomic fraction of N ranges from 0.302 to 0.441 in as-sputtered Library 2 (sputtered at a higher nitrogen partial pressure, $N_2/Ar = 40/60$). The N content of the as-sputtered libraries increases with the nitrogen partial pressure used during sputtering. The variation of N content with heat-treatment temperature in the two libraries shows some similar trends. First, the N content is reduced with heat-treatment temperature. Second, the N content decreases sharply at a particular Co content, about 1.2 % for Library 1 heated to 700°C and about 1.5 % for Library 2 heated to 800°C. There are also significant differences between the libraries. For example, Library 2 does not lose much nitrogen at all when heated to 700°C unlike Library 1. Library 2 also retains more nitrogen at all Co-C compositions when heated to

800 or 1000°C. Grazing incidence XRD and SEM imaging of the heated libraries were used to understand the processes that occur during nitrogen loss.

Grazing Incidence XRD and SEM imaging of the Heated Libraries

Figure 3 shows the XRD patterns of the as-sputtered constant-composition samples $\text{Co}_{0.5}\text{C}_{66.8}\text{N}_{32.7}$ and $\text{Co}_{4.7}\text{C}_{51.7}\text{N}_{43.6}$ after heat-treatment to various temperatures in N_2 . The compositions match those of glassy carbon disks 1 and 5 for Library 2. The trends observed in both samples are similar. At low temperatures, the samples are amorphous by XRD. At a critical temperature, about $885 \pm 15^\circ\text{C}$ for $\text{Co}_{0.5}\text{C}_{66.8}\text{N}_{32.7}$ and at $730 \pm 5^\circ\text{C}$ for $\text{Co}_{4.7}\text{C}_{51.7}\text{N}_{43.6}$, the samples transform to primarily a nanoscale mixture of N-containing partially graphitic carbon and $\beta\text{-Co}$. This critical temperature presumably coincides with a strong release of nitrogen. Note that the sample corresponding to disk 1 for Library 2 has not released substantial N by 800°C in Figure 2, corresponding to the amorphous XRD pattern seen for this sample in Figure 3. By 1000°C this sample has lost almost all of its N (Figure 2) and the XRD pattern shows graphitic carbon and $\beta\text{-Co}$. Similarly, the sample corresponding to disk 5 for Library 2 has not released substantial N by 700°C in Figure 2 and its corresponding XRD pattern is amorphous in Figure 3. By 800°C, this sample has released substantial N (Figure 2) and the corresponding XRD pattern shows graphitic carbon and $\beta\text{-Co}$.

Figure 4 shows SEM images of the samples on glassy carbon disks 5 for both Library 1 and Library 2 after heat treatment to various temperatures. Figure 4a shows the homogeneous amorphous appearance of the as-sputtered disk 5 of Library 1 sample. After heat treatment to 700°C, the film appears heterogeneous as shown in Figure 4b,

presumably because of N-loss and the formation of nanoparticles of N-containing graphitic carbon and β -Co. Substantial N loss has occurred for disk 5 of Library 1 heated to 700°C (Figure 2). The degree of heterogeneity increases with increasing heating temperature (Figure 4c and 4d), presumably because of an increase in the size of the N-containing graphitic carbon and β -Co.

Figures 4e and 4f show that the film sputtered on disk 5 of Library 2 remains homogeneous and amorphous in appearance when heated to 700°C, in agreement with the XRD patterns in the top panel of Figure 3. When this sample is heated to 800°C (Figure 4g), the SEM image shows that the sample is heterogeneous on the nanometer scale and evidence for carbon nanotubes is observed. According to the XRD pattern in the top panel of Figure 3, the sample at 800°C should be a mixture of N-containing graphitic carbon and β -Co. Upon heating to 1000°C, the sample remains heterogeneous.

XPS measurements

The XPS measurements were performed on the samples on GC disks after RRDE experiments. Figure 5 shows N_{1s} core level spectra obtained on the samples on disks 1, 3 and 5 heat-treated at 800°C for both Library 1 and Library 2. Figure 6 shows N_{1s} core level spectra for the samples on disk 3 heat-treated at 700°C, 800°C and 1000°C for both Library 1 and Library 2. All N_{1s} spectra in Fig. 5 were deconvoluted into three components except for the spectrum from disk 3 in Library 2 heat-treated at 700°C that was deconvoluted into only two components. Unlike most reports of XPS results on transition-metal carbon nitrogen catalysts in the literature, here we report the actual raw counts of the XPS spectrum, unnormalized. Since the spectra have been collected on thin

film combinatorial libraries where sample preparation conditions are identical for all library members, the raw counts are directly proportional to the N content at the surface.

The three peaks in Figures 5 and 6 with binding energies of 398.5-398.6 eV, 400.4-401.1 eV and 402.2 –403.7eV were assigned to pyridinic-type N, pyrrolic-type N, and highly coordinated N atoms (N atoms bound to three C atoms within a graphene layer), respectively [29,30]. The pyridinic-type N and pyrrolic-type N are the two main components of the N_{1s} peak and the highly coordinated N represents only a small contribution. Figure 5 shows that the area under the pyridinic-type N and pyrrolic-type N peaks decreases as the Co content increases for Libraries 1 and 2 heat-treated at 800°C, in qualitative agreement with the total N content as shown in Figure 2.

Figure 7 shows the bulk N content, as determined by WDS, plotted versus the integrated area of the N_{1s} XPS peak for those 10 samples where both measurements are available. There is a good correlation between the techniques. Most interesting is that the surface N content appears to increase more strongly than the bulk N content at low N concentrations. It was not possible to determine an accurate surface nitrogen atomic percentage due to the presence of adventitious carbon and its contribution to the integrated area of the carbon peak.

Figures 5 and 6 show that there is a dramatic reduction in the relative size of the pyridinic peak when the samples transform from the amorphous phase to the heterogeneous structure consisting of nanoscale regions of N-containing graphitic carbon and β -Co. As an example, the intensity of the pyridinic peak for disk 3 of Library 2 decreases significantly (Figure 6) when the sample changes from amorphous (700°C) to heterogeneous (800°C). Another example is shown in Figure 5, where disk 1 of Library 2

is amorphous at 800°C and has a strong pyridinic peak while disk 3 is heterogeneous and has a pyridinic peak about the same intensity as the pyrrolic peak. It is interesting that this dramatic structural change hardly affects the positions of the N_{1s} spectral components at all, although it does affect their relative intensities.

Electrocatalytic characterization using RRDE

Figure 8 shows the CVs of the samples of Libraries 1 and 2 on the glassy carbon (GC) disks heat-treated to 700, 800 and 1000°C measured in O_2 -saturated 0.1M $HClO_4$ at 25°C. The CV of the film on GC disk1 of Library 1 heated at 800°C measured in argon-saturated 0.1M $HClO_4$ solution is shown in the first panel of the second row in Fig. 8 (dotted line). The CVs of the other film samples in Ar-saturated solution are similar and are not shown in the figure. Compared to the CV under Ar, it is clear that the reduction currents observed in the CVs under O_2 for all the samples can be attributed to the ORR. The unheated libraries showed no activity for ORR.

Trends in the variation of the onset potential for the ORR with composition, surface composition, structure and heat-treatment temperature are summarized in Figure 9. Figure 9 plots the onset potential versus the bulk nitrogen content by WDS (top panel) and versus N_{1s} peak area by XPS (bottom panel) of the heated samples and also distinguishes those samples that are amorphous (by XRD and SEM) from those that are heterogeneous. All samples that are amorphous have low onset potentials. This explains one feature of Figure 8. The samples of Library 2 heated to 700°C show lower onset potentials than those of Library 1, even though Library 2 samples contain more nitrogen. This is because the Library 2 samples are still amorphous at 700°C and the Library 1

samples (apart from disk 1) are not. In all cases where samples from both Library 1 and Library 2 are heterogeneous, consisting of N-containing graphitic carbon and β -Co, the onset potential of Library 2 samples is higher than Library 1 samples containing the same amount of Co (within the same panel of Figure 5). We believe this is because the Library 2 samples contain more N than the Library 1 samples.

Possible correlations between the variation of the onset potential for the heterogeneous samples and the ratio of the intensities of the pyridinic and pyrrolic N_{1s} spectral components were examined. We could find no correlation between increased activity and the pyridinic:pyrrolic peak intensity ratio. The best correlation we could find was to the total nitrogen content as shown in Figure 9.

The lines drawn as guides to the eye in the top panel of Figure 9 show that the onset potential of heterogeneous samples having the same bulk nitrogen content increases with the heat-treatment temperature. This provides a strategy for preparing materials with even further improved catalytic performance: increase the nitrogen content and increase the heat-treatment temperature. The challenge to overcome is that the nitrogen content of samples having a fixed cobalt content always decreases with heat treatment temperature.

The activity for ORR of a heated carbon black-supported cobalt ethylene diamine (CoEDA) catalyst reported recently by N. P. Subramanian *et. al.* [31], which is the most active Co-C-N catalyst reported in the literature, is shown in the fifth panel of the second row (dotted line) of Figure 8 for comparison. The onset potential of $Co_{8.4}C_{85.7}N_{5.9}$ in this work ($E_{onset} = 0.81$ V versus RHE, measured in 0.1M $HClO_4$, 900 rpm, $5\text{ mV}\cdot\text{s}^{-1}$) is close to the activity of the CoEDA catalyst ($E_{onset} = 0.82$ V versus RHE, measured in 0.5M

H₂SO₄, 900 rpm, 5 mV·s⁻¹) [31]. Our thin film catalysts certainly have a significantly smaller surface area than N. P. Subramanian's catalysts which are adsorbed on a carbon black (Ketjen Black EC300J, BET surface area = 886 m²/g).

The CV curves for the active catalysts in Figure 8 show two steep reduction waves, which indicates that there may be two active sites for ORR in these samples. The identification of the active sites in the heat-treated Co_xC_{1-x-y}N_y thin-film libraries is a goal for our future work. There is no well-defined diffusion limiting current plateau in our samples (which should be about -4.5 mA/cm² at 900 rpm based on measurements on pure Pt films). This could be caused by a number of factors but is thought to be related to low reaction rate for the catalytic sites [32]. Understanding this is another goal of future research.

Figure 10 shows the percentage of H₂O₂ (%H₂O₂) produced at the disk electrode versus the disk potential for the same samples as shown in Fig. 8. For Library 1 heat-treated at different temperatures, the %H₂O₂ produced on the samples is between 60 and 90% at 0.65-0.45 V (vs.RHE) and then decreases with disk potential. For Library 2 heat-treated at 700°C, the %H₂O₂ produced on disks is higher than that in Library 1 treated at the same temperature. Recall that Library 2 samples were amorphous at 700°C. For Library 2 heat-treated at 800°C, the %H₂O₂ produced on the disks between 0.70-0.40 V (vs.RHE) is much less than in Library 1 heat-treated at the same temperature. Library 2 samples contain more N than Library 1 samples and this may be a factor in the decreased H₂O₂ production. However, further work is needed to understand the factors that govern H₂O versus H₂O₂ production by these catalysts.

Corrosion stability of film libraries

Figure 11 shows the Co content of the heat-treated $\text{Co}_x\text{C}_{1-x-y}\text{N}_y$ libraries before and after exposure to 0.5M H_2SO_4 solution at 25°C for one week. Co is dissolved from the films when the Co concentration is relatively high in the two libraries and the libraries with low Co content show relatively good stability with respect to Co dissolution. The Co content is reduced to a maximum of about 3.5, 2.0 and 1.0 atomic % for Library 1 heated at 700, 800 and 1000°C, respectively. The Co content is reduced to a maximum of about 4.6, 3.1 and 1.6 atomic % for Library 2 heated at 700, 800 and 1000°C, respectively. It would have been very interesting to measure the catalytic activity of the samples after acid exposure to see if the dissolution of Co (presumably mostly from grains of β -Co) had any impact on the catalytic activity. This will be a focus of our future work.

Conclusions

Highly active thin film $\text{Co}_x\text{C}_{1-x-y}\text{N}_y$ libraries ($0 < x < 0.107$, $0.003 < y < 0.389$) towards ORR have been prepared by combinatorial magnetron sputtering deposition and subsequent heat-treatment. As-sputtered libraries were amorphous and showed no catalytic activity. Upon heating above a critical temperature, the amorphous materials transformed into a nanoscale mixture of N-containing graphitic carbon and β -Co and then catalytic activity was observed. The results in Figure 9 showed that the most active catalysts are those prepared at the highest heating temperatures and with the highest

nitrogen content. The challenge to further improve the catalytic performance of these materials is that the N content is reduced as the temperature increases. We showed that the nitrogen content remaining after heat treatment could be increased by incorporating more nitrogen in the as-sputtered film. This was accomplished by sputtering at higher N_2 partial pressures.

XPS studies of the N_{1s} core level spectra of these materials showed that the surface N content was increased with the bulk N content. However, the spectra showed little change to the individual spectral components for catalytically active and inactive materials, apart from a decrease in the intensity of the pyridinic peak relative to the pyrrolic peak

The ORR proceeds on heat-treated $Co_xC_{1-x-y}N_y$ libraries with a large fraction of H_2O_2 product. In order for such catalysts to be commercially viable, the fraction of H_2O_2 produced must be reduced. On the positive side, heat-treated $Co_xC_{1-x-y}N_y$ libraries with low Co content show relatively good stability in 0.5M H_2SO_4 solution at 25°C.

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Figure Captions:

Figure 1: The layout of the substrate table with various substrates indicated and a projection of the targets and associated masks on the substrate table.

Figure 2: Atomic % N versus atomic % Co for $\text{Co}_x\text{C}_{1-x-y}\text{N}_y$ Library 1 [panel a)] and 2 [panel b)] before and after heat-treatment at 700, 800, and 1000°C. The balance of the composition is carbon. The open circles indicate the compositions of the five glassy carbon (GC) disks at each heating temperature. GC disk number increases from 1 to 5 moving to the right.

Figure 3. Grazing incidence x-ray diffraction measurements showing intensity versus scattering angle for heat-treated $\text{Co}_{0.5}\text{C}_{66.8}\text{N}_{32.7}$ (same composition as the sample on disk 1 of Library 2) and $\text{Co}_{4.7}\text{C}_{51.7}\text{N}_{43.6}$ (same composition as the sample on disk 5 of Library 2) samples. The heat-treatment was done in flowing N_2 and the heat-treatment temperature is indicated next to each curve. The major Bragg peaks of the phases present are indicated. Note that the compositions listed are the starting compositions and that the compositions change as N is lost during the heating.

Figure 4. SEM images of disk 5 of Library 1 unheated (a), heated at 700°C (b), 800°C(c) and 1000°C (d) and of disk 5 of Library 2 unheated (e), heated at 700°C (f), 800°C(g) and 1000°C (h).

Figure 5: XPS spectra for the N_{1s} peak the $Co_xC_{1-x-y}N_y$ Libraries 1 and 2 on GC disks 1, 3 and 5 heat-treated at 800°C.

Figure 6. XPS spectra for the N_{1s} peak the $Co_xC_{1-x-y}N_y$ Libraries 1 and 2 on GC disk 3 heat-treated at 700°C, 800°C and 1000°C.

Figure 7. Bulk nitrogen content measured by WDS plotted versus the integrated area of the N_{1s} XPS peak, proportional to the surface N content, for the 10 samples studied in Figures 5 and 6.

Figure 8: Disk current densities for samples of $Co_xC_{1-x-y}N_y$ libraries 1 (grey lines) and 2 (black lines) on glassy carbon disks heat-treated at 700, 800, and 1000°C measured in O_2 -saturated 0.1M $HClO_4$ at 25°C. The five samples are equally spaced along the libraries as indicated in Figures 1 and 2. The sweep rate is $5\text{ mV}\cdot\text{s}^{-1}$ and the rotation speed is 900 rpm. The average composition of the film on each disk is indicated in each panel. The dotted line in the first panel of the second row indicates the disk current density for disk1 of Library 1 heat-treated at 800°C measured in Ar-saturated 0.1M $HClO_4$ solution at 25°C. The dotted line in the fifth panel of the second row shows the current density of a carbon black-supported cobalt ethylene diamine (CoEDA) catalyst heat-treated at 800°C measured in O_2 -saturated 0.5M H_2SO_4 solution with a rotation speed of 900 rpm and a sweep rate of $5\text{ mV}\cdot\text{s}^{-1}$ from Figure 4b of reference [31] reported by N. P. Subramanian *et al.*

Figure 9. (Top panel) Onset potential for the catalysts in Figure 8 plotted versus their N content. (Bottom panel) Onset potential for the catalysts in Figure 8 plotted versus the integrated area of the N_{1s} XPS peak, proportional to the surface N content. Diamond-shaped data points indicate samples that show a nanoscale mixture of N-containing graphitic carbon and β -Co while square data points represent amorphous samples. The heat-treatment temperatures of the samples are indicated in the Figure and the solid lines are guides to the eye.

Figure 10: % H_2O_2 produced as a function of disk potential for samples in $Co_xC_{1-x-y}N_y$ Libraries 1 and 2 heat-treated at 700°C, 800°C and 1000°C. Measurements were made at a sweep rate of $5\text{ mV}\cdot\text{s}^{-1}$ in O_2 -saturated 0.1M $HClO_4$ at 25°C. The average composition of each disk is indicated in each panel. The samples are the same as those reported in Figure 8.

Figure 11: The atomic fraction of Co versus position in the $Co_xC_{1-x-y}N_y$ Libraries 1 and 2 heat-treated at 700°C, 800°C, 1000°C before and after soaking in 0.5M H_2SO_4 at 25°C for one week.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11

Publication #14:

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Vacuum Deposited Non-Precious Metal Catalysts for PEM Fuel Cells

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Alison K. Schmoeckel, Alison K. Schmoeckel, George D.
Vernstrom, Dennis P. O'Brien, Dr. Manish Jain, Dr. Thomas E.
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Current PEM fuel cell technology uses platinum as a catalyst. A large body of work seeking to find a Pt replacement involves Oxygen Reduction Reaction (ORR) catalysts produced using nitrogen coordinated transition metal compounds, such as Fe porphyrins or Fe phthalocyanine.^{1,2,3} Traditionally, these catalysts are made by pyrolyzing transition metal compounds dried onto carbon support particles at temperatures up to 950 °C in reducing and/or nitrogen-containing atmosphere. Unfortunately, ORR activity of these catalysts has not been enough and attempts to increase the oxygen activity, for example by increasing the Fe content, have not been successful.⁴ Analytical work by Dodelet's group, including TOF-SIMS, XPS and other techniques, led to their proposal that a pyridinic structure is required for good oxygen activity.^{5,6}

Figure 1. Structure proposed by Dodelet's group⁶ for the species required for ORR catalytic activity.

A new, alternative process to make non-precious ORR metal catalysts for the oxygen reduction reaction is to use vacuum deposition techniques to combine the three elements believed to be required (a transition metal, carbon, and nitrogen).^{7,8} Processes including pulsed arc plasma deposition, sputter deposition, evaporation and combinations thereof have been used to produce a variety of materials whose catalytic activity was determined by assembling and measuring the oxygen generated electrical current in 50 cm² fuel cells. The pulsed arc process is well suited to deposit carbon/Fe based catalysts because it can produce a carbon/iron plasma by erosion of a high-purity graphite cathode containing Fe wires.⁹ The plan is to vary deposition processes and conditions over a wide range while checking their catalytic activity in a 50 cm² test fuel cell fixture.^{10,11} However, solely relying on fuel cell testing does not provide clues to process changes that would be most beneficial, but an analytical technique has not been identified that uniquely qualifies catalytic behavior. Nevertheless, an ability to measure a material characteristic that is known to relate to ORR catalysis would significantly improve process R&D.

Therefore, we began using local, element-specific, analytical probes that have the ability to differentiate between Fe-based catalyst materials that have had different process histories but similar compositions. Vacuum deposited C-N_x:Fe catalysts were analyzed using Extended X-ray Absorption Fine Structure (EXAFS) analyses of the Fe k-edge and resonant ultraviolet photoelectron spectroscopy (UPS) to measure the valence electronic structure around Fe atoms. Both techniques show significant differences between samples that received and those that did not, receive thermal treatment.

Results

Carbon-nitrogen-iron coatings were deposited onto either a carbon non-woven cloth or Si wafers, depending on the analytical technique to be used, and processed either with or without a thermal treatment. Surface composition measurements by XPS showed that the nitrogen and iron content could be varied between 1–5 at. % for nitrogen and between 0.1 to 7 at. % for iron. This range is much larger than can be obtained with molecular pyrolysis methods (2–3 at. % nitrogen and 0.05 at. % Fe). Analysis of the Fe core level indicates that the iron in these coatings is neither metallic nor an oxide; however some carbide phase cannot be ruled out. High resolution XPS shows that the N 1S core level in vapor deposited C-N_x:Fe coatings has the same doublet structure with a component at 398.5 eV, identified as pyridinic nitrogen, that has been reported for pyrolyzed Fe-derived catalyst materials.⁶ The fact that the nitrogen exhibits the same XPS fingerprint as pyrolyzed Fe catalysts combined with the fact that the nitrogen and iron content is much higher than in pyrolyzed Fe catalysts suggested that the catalytic currents would be higher. However, our electrochemical fuel cell testing showed the opposite to be true. Although a direct comparison is difficult, after correcting for large differences in surface area, the ORR catalytic activity of vapor deposited coatings is lower than that of pyrolyzed Fe catalysts. Although a thermal treatment above 650 °C, either during or after deposition, significantly increased catalytic activity the level was still below that of pyrolyzed molecular compounds.

The similarity of vacuum deposited coatings based on XPS spectra and the difference in their electrochemical behavior suggests that more detailed materials characterization is needed. Detailed analyses of the N 1S core-level shows that the intensity and binding energy of the 398.5 eV component, the component normally associated with pyridinic nitrogen, changes with iron content. For example, in C-N_x:Fe(7 at. %) the intensity is 75% of the total N 1S intensity, whereas in a nitrogenated carbon (i.e. without iron) the intensity is only 45% of the total. Indeed, the pyridinic component intensity steadily increases as the Fe content increases, as shown by the graph in **Figure 2**. In addition, the pyridinic components binding energy increases with increasing iron content. The shift to deeper binding energy is similar to findings by Dodelet's group for pyrolyzed Fe-derived catalysts, although in those materials the shift is much less.⁶ The fact that a small amount of iron has such an effect on the nitrogen core level binding energy suggests that Fe and N atoms are near each other instead of being uniformly dispersed.

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Figure 2. Relative intensity of the N 1S peak at 398.5 eV associated with pyridinic nitrogen as a function of Fe content.

Figure 3. The k^3 -weighted Fourier transform magnitudes of the Fe K-edge of a vacuum deposited catalyst before and after the thermal post-treatment. The transforms are not phase-corrected.

Figure 3 shows EXAFS Fourier transforms for vacuum deposited catalysts. These transforms are not phase-corrected and therefore they have a small shift in the x-axis from real values. Examination of Figure 3 shows that the unheated material has a single main peak while the heated sample has two well-resolved peaks. This indicates that the as-deposited material is fairly disordered and that heating increases atomic order (narrower peaks) with the introduction of a second coordination shell around Fe atoms. Photoelectron spectroscopy is another technique that has the potential to identify unique aspects of $C-N_x$:Fe materials because it directly probes valence electrons that are involved in bonding, and many believe catalysis. Photoemission is not, in general, element specific, however, element specific information can be obtained by utilizing resonant photoemission. In resonant photoemission, large intensity variations occur with small changes in the exciting photon energy and this can be used to detect where Fe d-states are located in the valence density-of-states.¹² The role of Fe and its importance for catalytic behavior, many believe, is key to understanding Fe-based catalysts. We have successfully used photoemission to study $C-N_x$:Fe materials including the use of resonant techniques to detect valence Fe d-states. These studies, to be published, show that metallic Fe d-states exist near the Fermi level in as-deposited coatings as well as hybridized d-states between 4 to 10 eV below the Fermi level. Photoemission studies combined with *ab initio* density functional theory simulations, using VASP,^{12,13} has the potential to provide new insights into bonding in ORR Fe-based catalysts.

Conclusions

Vacuum deposited carbon-nitrogen-iron coatings deposited by pulsed cathodic arc plasma deposition were characterized and the effects of a high temperature thermal treatment were evaluated. Characterization by XPS shows that the iron is not metallic iron and that the N 1S core level matches that found in pyrolyzed Fe-based catalysts. High resolution XPS studies of the N 1S core level vs. Fe content shows that Fe atoms cause the N 1S core level component at about 398.5 eV, also associated with pyridinic nitrogen, to increase in intensity and to shift to deeper binding energy. Clearly, Fe atoms must be near nitrogen atoms in order to change N 1S binding energies.

Subjecting the vapor deposited catalysts to a thermal treatment, either during or after deposition, significantly increases the catalytic activity of these materials. However, comparison of these materials, with and without a thermal treatment, using high resolution XPS does not show significant differences. EXAFS studies of the Fe k-edge show that atomic rearrangements occur after high temperature treatments, thermal treatments that also increase ORR catalytic currents. The thermal treatment increases atomic order and introduces a second coordination shell around Fe atoms. Resonant UV photoemission techniques show that Fe d-electrons are located in two energy regions of the electronic density of states. There are metallic Fe d-states located near the Fermi level and hybridized Fe d-states, most likely with ligand p-states, located between 4 to 12 eV below the Fermi level. More work is needed with different materials before more conclusive statements can be made.

Element specific techniques such as EXAFS and resonant photoemission show promise in being able to detect changes around given atoms, e.g. iron, in a ternary compound such as the $C-N_x$:Fe materials that exhibit catalytic activity for the oxygen-reduction reaction. Changes that are associated with better catalytic activity. Although the vapor deposited materials made so far have not exhibited significant ORR catalytic activity, future developments and improved understanding of these materials could allow vapor deposition to be a viable process for economical catalyst production.

Acknowledgments

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	Rod	diam. 6.3 mm	99.98	266213-30G 266213-150G	101.50 395.50
Graphite	Rod	length 150 mm, diam. 3 mm, low density	99.999	496537-43.5G	53.60
		length 150 mm, diam. 3 mm, high density	99.995	496545-60G	65.50
		length 150 mm, diam. 6 mm, low density	99.999	496553-180.7G	49.50
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Publication #15:

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Co–C–N Oxygen Reduction Catalysts Prepared by Combinatorial Magnetron Sputter Deposition

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Thin-film libraries of $\text{Co}_x\text{C}_{1-x-y}\text{N}_y$ ($0 < x < 0.107$, $0.003 < y < 0.389$) were prepared by combinatorial magnetron sputter deposition in an Ar/N_2 gas mixture followed by subsequent heat-treatment at 700, 800, or 1000°C in N_2 atmosphere. By increasing the nitrogen partial pressure during sputtering, the nitrogen content was increased significantly in the as-sputtered libraries and more nitrogen remained in the libraries after heat-treatment. The catalytic activities of the libraries towards the oxygen reduction reaction (ORR) were studied using the rotating ring-disk electrode (RRDE) technique. $\text{Co}_x\text{C}_{1-x-y}\text{N}_y$ libraries heat-treated at 800°C with $0.004 < x < 0.105$ and $0.026 < y < 0.097$ showed good catalytic activities towards ORR in 0.1 M HClO_4 solution at room temperature. The heating temperature that induces the onset of catalytic activity coincides with the temperature at which both substantial nitrogen release from the originally amorphous films and the formation of graphitic carbon and β -Co occurs. This temperature varies significantly with both the Co and N content in the films. The production of H_2O_2 and the corrosion stability of the libraries are also discussed.

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Polymer electrolyte membrane fuel cells (PEMFCs) have attracted attention due to their high energy densities, low operating temperatures, and lack of emissions.^{1–3} The high cost of PEMFCs is one of the barriers to their commercialization. The replacement of Pt by nonnoble metal catalysts could lead to significant cost reduction and is desirable, provided that similar area-specific activity can be obtained.⁴

The electrochemical activity of transition-metal macrocycles towards the oxygen reduction reaction (ORR) was first explored in 1964⁵ and then improved by heat-treatment in an inert atmosphere in 1976.⁶ Since then, nonnoble metal catalysts based on pyrolyzed carbon-supported N_4 -metal macrocycles (where the metal is usually Fe or Co)^{7–13} have been widely studied. Later, it was reported that active ORR catalysts can also be prepared by heat-treating carbon-supported organometallic (Fe or Co) complexes^{14,15} or even Fe or Co salts^{16,17} in ammonia or acetonitrile vapor. For the active sites of the catalysts, Dodelet and co-workers proposed that two active sites (FeN_2/C and FeN_4/C) exist in the Fe-based catalysts¹⁸ and that one active site (CoN_4/C) exists in the Co-based catalysts¹⁹ based on the time-of-flight secondary ion mass spectrometry (TOF SIMS) results. Ozkan et al.^{20,21} and Stevenson et al.²² proposed that the active sites for the ORR are located on the edge planes of nitrogen-containing carbon that do not contain any metal. Ozkan et al. suggested that the metal site is not needed for the ORR and, instead, that the metal may be acting as a catalyst for the formation of active sites.

Other methods have been used to prepare Co-based catalysts. Deng and Dignam reported that thin films of Co–C–N cosputtered in vacuum showed good catalytic activity for ORR in alkaline solution but the films were not stable in acid solution due to dissolution.^{23,24} Recently, Sirk et al. reported that sol-derived [Co, N, C, O]-based catalysts after heat-treatment showed promising activity towards ORR.²⁵

Our work focuses on the preparation of active catalysts for ORR by combinatorial magnetron sputter deposition. Active Fe–C–N oxygen reduction catalysts have been prepared using our combinatorial infrastructure.²⁶ In this paper, studies of thin-film libraries of $\text{Co}_x\text{C}_{1-x-y}\text{N}_y$ ($0 < x < 0.107$, $0.003 < y < 0.389$) prepared combinatorially by magnetron sputter deposition followed by subsequent heat-treatment in N_2 atmosphere are reported. The impacts of the

heat-treatment temperature and the initial composition on the structure, morphology, corrosion stability, and catalytic activity of the libraries were studied.

Experimental

Deposition of thin-film libraries.— A Co sputtering-target (2.00 in. diam, 0.250 in. thick, and 99.95% pure) was obtained from Williams Advanced Materials (Buffalo, NY). A C sputtering-target (2.00 in. diam, 0.250 in. thick, and 99.999% pure) was obtained from Kurt J. Lesker Co. (Clairton, PA). Co and C were sputtered using MDX-1K dc (Advanced Energy) power supplies with powers of 15 and 150 W, respectively. Specially designed masks were positioned in front of each target to produce a linear composition variation when the substrate table was rotated. More details about the production of binary and pseudobinary libraries using our equipment can be found elsewhere.²⁷

Nitrogen was incorporated into the libraries by sputtering in an Ar/N_2 gas mixture.²⁶ Gas flows were independently controlled using meter-kilogram-second mass flow controllers. Ultrahigh-purity Ar (99.999%) and N_2 (99.999%) were supplied at constant flow rates during the sputtering. Two libraries and two films of constant composition were produced in this work. Library 1 was sputtered under 7.5 sccm Ar and 2.0 sccm N_2 , which corresponds to a total pressure of 0.277 Pa (2.1 mTorr) and a N_2 partial pressure of 0.058 Pa (0.44 mTorr) (i.e., $\text{N}_2/\text{Ar} = 20:80$). Library 2 was sputtered under 4.5 sccm Ar and 3.0 sccm N_2 , which corresponds to a total pressure of 0.224 Pa (1.7 mTorr) and a N_2 partial pressure of 0.090 Pa (0.68 mTorr) (i.e., $\text{N}_2/\text{Ar} = 40:60$).

Films were deposited onto a linear array of 1.3 cm diameter preweighed Al foil disks for determining the mass per unit area of the deposited film, 80 × 10 mm Si(100) wafer strips for electron microprobe analysis and film thickness determination, 80 × 10 mm quartz substrates for heat-treatment and corrosion testing, any glassy carbon (GC) disks with a diameter of 5 mm (Tokai Carbon Co.) for electrochemical measurements using the rotating ring-disk electrode (RRDE) technique. Three sets of five GC disks equally spaced within the 76 mm wide range of composition variation were mounted onto the substrate table. Within each set, disks are numbered from 1 to 5 with increasing Co content. Figure 1 shows the various substrates mounted on the substrate table as well as a projection of the targets and their associated masks on the substrate table.

The constant composition films were prepared for grazing-incidence X-ray diffraction (XRD) measurements vs heat-treatment

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Figure 1. (Color online) The layout of the substrate table with various substrates indicated and a projection of the targets and associated masks on the substrate table.

temperature. The films of constant composition were sputtered using constant masks over both Co and C targets and using the same sputtering gas pressures as Library 2. The films were sputtered onto Si(100) wafer strips 80 mm in length and 15 mm in width. These wafers had a 500 nm layer of SiO₂ on their polished surface. The SiO₂ layer prevented reaction of the Co in the film with the Si substrate during the heat treatments. The compositions prepared were Co_{0.5}C_{66.8}N_{32.7} and Co_{4.7}C_{51.7}N_{43.6} in the as-sputtered films. These compositions are the same as the compositions of the films sputtered on GC disks no. 1 and no. 5, respectively, for Library 2.

Films deposited on quartz substrates and three sets of GC disks were heat-treated at 700, 800, and 1000°C in N₂ using a Modular Process Technology RTP-600S rapid thermal processor (RTP). The samples were heated at a heating rate of 5°C s⁻¹ in flowing N₂ (2 L min⁻¹) and held at the target temperature for 5 min before cooling.

Thickness of the thin-film libraries.— The thickness of the thin-film library sputtered on a Si wafer was determined using a Dektak 8 Advanced Development Profilometer (Veeco Instruments Inc.). Film thickness before heat-treatment was found to linearly increase across the library from about 90 to 200 nm with increasing Co content for Library 1 and from about 289 to 408 nm with increasing Co content for Library 2. One reason for the large increase in film thickness with Co content is that the nitrogen content in the film increases strongly with Co content, as is shown below.

Composition of the thin-film libraries.— The composition as a function of position in the library was obtained using a JEOL JXA-8200 superprobe electron microprobe system equipped with one energy dispersive (EDS) spectrometer and five wavelength dispersive (WDS) spectrometers. Silicon nitride (Si₃N₄) was used as the N standard, a MnCo alloy (Mn/Co = 30:70, weight ratio) was used as the Co standard, and pyrolytic graphite was used as the C standard. The overlap of the N(Kα) and Co(L_β(2)) lines was carefully considered and accommodated. Reuter's method for thin-film analysis, which corrects for the excitation of the backscattered electrons caused by the substrate, was employed.²⁸ Co, N, and C atomic compositions were all determined by WDS detectors. The analysis spot size was 50 μm. Typically the composition was measured every 2 mm along the 76 mm long libraries.

Grazing incidence XRD.— XRD patterns were collected using a Siemens D5000 diffractometer equipped with a grazing incidence attachment. Cu Kα radiation was used at an incidence angle of 0.5° and with divergence slits set to 0.1°. Such conditions lead to an

illuminated spot of 40 × 12 mm in the center of the 80 × 15 mm constant-composition specimen. A Soller slit box in front of the detector was used to ensure that the scattered X-rays from this large illuminated sample area that entered the detector all had the same scattering angle. Data was collected over a scattering angle range of 10–80° in 0.05° intervals. Total scan times varied between 8 and 12 h.

Surface analysis.— The surfaces of the samples on the GC disks were characterized by X-ray photoelectron spectroscopy (XPS). XPS was performed with a VG Microtech Multilab XPS system (Thermo Electron Corporation) equipped with a CLAM-4 hemispherical analyzer and using a Mg Kα (15 kV, 20 mA) source with a 600 μm diameter illumination spot. The measurement parameters were as follows: 20 eV pass energy, 200 ms dwell time, 0.05 eV energy increments, and 5 mm analyzer slit. The measurements were performed on the samples on the GC disks after RRDE experiments. Charging, if present on the sample, was corrected using the carbon C_{1s} peaks, which are at least partially due to the presence of the adventitious carbon on the samples. The binding energy of adventitious carbon is reported to be in the range of 284.5–285.0 eV in the literature.²⁹ If the observed C_{1s} peak was higher than 285.0 eV by an amount, δE, due to charging, then the measured data were shifted to lower binding energy by δE. For peak fitting, a mixed Gaussian–Lorentzian shape and Shirley background were used. Similar shape parameters were used for all peaks. The peak broadening was constrained to a maximum of 2.0 eV.

Scanning electron microscope images of the films.— High-resolution images of the as-sputtered and heat-treated films on GC disks were taken using a cold field emission Hitachi S-4700 (SEM).

Corrosion testing.— Thin-film libraries of Co_xC_{1-x-y}N_y on quartz strips heated at 700, 800, and 1000°C were immersed in 0.5 M H₂SO₄ (reagent, analytical grade) acid solution at 25°C for 1 week. After treatment, the samples were rinsed with nanopure water and dried in air for further study. Normally, the composition as a function of position on the library was measured and compared to the composition at the same spots measured before acid treatment.

Electrochemical characterization.— The electrocatalytic activity for the ORR of the films deposited on the GC disks was studied with the RRDE technique using a Pine Electrochemical system (AFM-SRX rotator and AFCBP1 bipotentiostat). The RRDE electrode consisted of a catalyst film-coated GC disk (5 mm diam) surrounded by a Pt ring (7.5 mm inner diam and 8.5 mm outer diam). The electrochemical measurements were conducted in a one-compartment cell. A Pt-wire counter electrode and Koslow Hg/Hg₂SO₄ reference electrode were used for the measurement. The electrolyte was 0.1 M HClO₄ solution prepared from double-distilled HClO₄ (GFS Chemicals Inc.) and 18 MΩ Barnstead nanopure water. The potential of the Hg/Hg₂SO₄ reference electrode was calibrated vs the reversible hydrogen electrode (RHE). The potentials reported in this study all refer to that of the RHE potential.

The films on the GC disks were first electrochemically cleaned by sweeping the potential in the range between 0–1.0 V (vs RHE) at 50 mV s⁻¹ in an Ar-saturated 0.1 M HClO₄ solution until steady-state cyclic voltammograms (CVs) were obtained. For each catalyst tested, a CV was first collected in Ar-saturated 0.1 M HClO₄ solution from 1.0 to 0.05 V at 5 mV s⁻¹ to determine the non-faradaic current. The CVs during oxygen reduction were performed in O₂-saturated 0.1 M HClO₄ solution from 1.0 to 0.05 V at 5 mV s⁻¹ with the electrode stationary and with the electrode rotated at 900 rpm and O₂ gas purged into the solution at a rate of 1 L min⁻¹. The faradaic current was determined by subtracting the CV in Ar-saturated 0.1 M HClO₄ solution from that obtained in O₂-saturated 0.1 M HClO₄ solution. The onset potential, at which the current for oxygen reduction is first observed,³⁰ was determined by the point of intersection of two tangent lines, one drawn parallel to the baseline (i.e., from 0.9 to approx 0.8 V) and the second parallel to the in-

Figure 2. (Color online) Atom % N vs atom % Co for $\text{Co}_x\text{C}_{1-x}\text{N}_y$ Library 1 (panel a) and 2 (panel b) before and after heat-treatment at 700, 800, and 1000°C. The balance of the composition is carbon. The star-shaped data points indicate the compositions of the five GC disks at each heating temperature. GC disk number increases from 1 to 5 moving to the right.

creasing current signal. For all the measurements, the ring potential was held at 1.2 V vs RHE in order to oxidize any H_2O_2 that was produced.³¹ The percentage of H_2O_2 produced was calculated with the following equation^{13,31,32}

$$\% \text{H}_2\text{O}_2 = 100 \frac{2I_R/N}{I_D + (I_R/N)} \quad [1]$$

where I_D is the faradaic current at the disk, I_R is the faradaic current at the ring, and $N = 0.2$ is the RRDE collection efficiency.

Results and Discussion

Composition of the thin-film libraries.— The N content vs Co content in the two as-sputtered libraries and those heat-treated subsequently at 700, 800, or 1000°C is shown in Fig. 2. The atomic fraction of N ranges from 0.184 to 0.320 in as-sputtered Library 1 (sputtered at a lower nitrogen partial pressure, $\text{N}_2/\text{Ar} = 20:80$), while the atomic fraction of N ranges from 0.302 to 0.441 in as-sputtered Library 2 (sputtered at a higher nitrogen partial pressure, $\text{N}_2/\text{Ar} = 40:60$). The N content of the as-sputtered libraries increases with the nitrogen partial pressure used during sputtering. The variation of N content with heat-treatment temperature in the two libraries shows some similar trends. First, the N content is reduced with the heat-treatment temperature. Second, the N content decreases sharply at a particular Co content, about 1.2% for Library

1 heated to 700°C and about 1.5% for Library 2 heated to 800°C. There are also significant differences between the libraries. For example, Library 2 does not lose much nitrogen at all when heated to 700°C, unlike Library 1. Library 2 also retains more nitrogen at all Co–C compositions when heated to 800 or 1000°C. The compositions of the samples on the five GC disks at heating temperatures of 700, 800, and 1000°C for Libraries 1 and 2 as indicated by the star-shaped data points in Fig. 2 are shown in Table I. Grazing-incidence XRD and SEM imaging of the heated libraries were used to understand the processes that occur during nitrogen loss.

Grazing-incidence XRD and SEM imaging of the heated libraries.— Figure 3 shows the XRD patterns of the as-sputtered constant-composition samples $\text{Co}_{0.5}\text{C}_{66.8}\text{N}_{32.7}$ and $\text{Co}_{4.7}\text{C}_{51.7}\text{N}_{43.6}$ after heat-treatment to various temperatures in N_2 . The compositions match those of GC disks 1 and 5 for Library 2. The trends observed in both samples are similar. At low temperatures, the samples are amorphous by XRD. At a critical temperature, about $885 \pm 15^\circ\text{C}$ for $\text{Co}_{0.5}\text{C}_{66.8}\text{N}_{32.7}$ and $730 \pm 5^\circ\text{C}$ for $\text{Co}_{4.7}\text{C}_{51.7}\text{N}_{43.6}$, the samples transform to primarily a nanoscale mixture of N-containing partially graphitic carbon and β -Co. This critical temperature presumably coincides with a strong release of nitrogen. Note that the sample corresponding to disk 1 for Library 2 has not released substantial N by 800°C in Fig. 2, corresponding to the amorphous XRD pattern seen for this sample in Fig. 3. By 1000°C this sample has lost almost all of its N (Fig. 2) and the XRD pattern shows graphitic carbon and β -Co. Similarly, the sample corresponding to disk 5 for Library 2 has not released substantial N by 700°C in Fig. 2 and its corresponding XRD pattern is amorphous in Fig. 3. By 800°C, this sample has released substantial N (Fig. 2) and the corresponding XRD pattern shows graphitic carbon and β -Co.

Figure 4 shows SEM images of the samples on GC disks 5 for both Libraries 1 and 2 after heat-treatment to various temperatures. Figure 4a shows the homogeneous amorphous appearance of the as-sputtered disk 5 of the Library 1 sample. After heat-treatment to 700°C, the film appears heterogeneous as shown in Fig. 4b, presumably because of N loss and the formation of nanoparticles of N-containing graphitic carbon and β -Co. Substantial N loss has occurred for disk 5 of Library 1 heated to 700°C (Fig. 2). The degree of heterogeneity increases with increasing heating temperature (Fig. 4c and d), presumably because of an increase in the size of the N-containing graphitic carbon and β -Co.

Figure 4e and f show that the film sputtered on disk 5 of Library 2 remains homogeneous and amorphous in appearance when heated to 700°C, in agreement with the XRD patterns in the top panel of Fig. 3. When this sample is heated to 800°C (Fig. 4g), the SEM image shows that the sample is heterogeneous on the nanometer scale and evidence for carbon nanotubes is observed. According to the XRD pattern in the top panel of Fig. 3, the sample at 800°C should be a mixture of N-containing graphitic carbon and β -Co. Upon heating to 1000°C, the sample remains heterogeneous.

Table I. Compositions of the samples on the five GC disks in the as-sputtered condition and at heating temperatures of 700, 800, and 1000°C for Libraries 1 and 2 as indicated by the star-shaped data points in Fig. 2.

Library	Heating temperature (°C)	Compositions				
		Disk 1	Disk 2	Disk 3	Disk 4	Disk 5
1	As-sputtered	$\text{Co}_{0.5}\text{C}_{79.6}\text{N}_{19.9}$	$\text{Co}_{1.4}\text{C}_{75.0}\text{N}_{23.6}$	$\text{Co}_{2.6}\text{C}_{72.9}\text{N}_{24.5}$	$\text{Co}_{3.8}\text{C}_{67.2}\text{N}_{29.0}$	$\text{Co}_{6.0}\text{C}_{62.7}\text{N}_{31.3}$
	700	$\text{Co}_{0.8}\text{C}_{82.2}\text{N}_{17.0}$	$\text{Co}_{2.1}\text{C}_{84.4}\text{N}_{13.5}$	$\text{Co}_{4.3}\text{C}_{83.0}\text{N}_{12.7}$	$\text{Co}_{6.6}\text{C}_{82.6}\text{N}_{10.8}$	$\text{Co}_{9.9}\text{C}_{80.7}\text{N}_{9.4}$
	800	$\text{Co}_{0.9}\text{C}_{92.4}\text{N}_{6.7}$	$\text{Co}_{2.3}\text{C}_{93.5}\text{N}_{4.2}$	$\text{Co}_{4.5}\text{C}_{91.6}\text{N}_{3.9}$	$\text{Co}_{6.7}\text{C}_{90.1}\text{N}_{3.2}$	$\text{Co}_{10.0}\text{C}_{87.3}\text{N}_{2.7}$
	1000	$\text{Co}_{1.1}\text{C}_{97.4}\text{N}_{1.5}$	$\text{Co}_{2.5}\text{C}_{96.3}\text{N}_{1.2}$	$\text{Co}_{4.9}\text{C}_{94.1}\text{N}_{1.0}$	$\text{Co}_{6.8}\text{C}_{92.7}\text{N}_{0.5}$	$\text{Co}_{9.9}\text{C}_{89.8}\text{N}_{0.3}$
2	As-sputtered	$\text{Co}_{0.5}\text{C}_{66.8}\text{N}_{32.7}$	$\text{Co}_{1.1}\text{C}_{63.9}\text{N}_{35.0}$	$\text{Co}_{2.0}\text{C}_{61.8}\text{N}_{36.2}$	$\text{Co}_{3.1}\text{C}_{58.3}\text{N}_{38.7}$	$\text{Co}_{4.7}\text{C}_{51.7}\text{N}_{43.6}$
	700	$\text{Co}_{0.7}\text{C}_{70.9}\text{N}_{28.4}$	$\text{Co}_{1.9}\text{C}_{66.8}\text{N}_{31.3}$	$\text{Co}_{3.4}\text{C}_{66.1}\text{N}_{30.5}$	$\text{Co}_{5.5}\text{C}_{61.1}\text{N}_{33.4}$	$\text{Co}_{7.8}\text{C}_{54.3}\text{N}_{37.9}$
	800	$\text{Co}_{0.9}\text{C}_{78.4}\text{N}_{20.7}$	$\text{Co}_{2.1}\text{C}_{91.0}\text{N}_{6.9}$	$\text{Co}_{3.6}\text{C}_{89.4}\text{N}_{7.0}$	$\text{Co}_{5.2}\text{C}_{88.3}\text{N}_{6.5}$	$\text{Co}_{8.4}\text{C}_{85.7}\text{N}_{5.9}$
	1000	$\text{Co}_{1.1}\text{C}_{96.2}\text{N}_{2.7}$	$\text{Co}_{2.2}\text{C}_{95.5}\text{N}_{2.3}$	$\text{Co}_{3.7}\text{C}_{93.9}\text{N}_{2.4}$	$\text{Co}_{5.5}\text{C}_{92.6}\text{N}_{1.9}$	$\text{Co}_{8.2}\text{C}_{90.2}\text{N}_{1.6}$

Figure 3. Grazing-incidence XRD measurements showing intensity vs scattering angle for heat-treated $\text{Co}_{0.5}\text{C}_{66.8}\text{N}_{32.7}$ (same composition as the sample on disk 1 of Library 2) and $\text{Co}_{4.7}\text{C}_{51.7}\text{N}_{43.6}$ (same composition as the sample on disk 5 of Library 2) samples. The heat-treatment was done in flowing N_2 and the heat-treatment temperature is indicated next to each curve. The major Bragg peaks of the phases present are indicated. Note that the compositions listed are the starting compositions and that the compositions change as N is lost during the heating.

XPS measurements.—The XPS measurements were performed on the samples on GC disks after RRDE experiments. Figure 5 shows N_{1s} core-level spectra obtained on the samples on disks 1, 3, and 5 heat-treated at 800°C for both Libraries 1 and 2. Figure 6 shows N_{1s} core-level spectra for the samples on disk 3 heat-treated at 700, 800, and 1000°C for both Libraries 1 and 2. All N_{1s} spectra in Fig. 5 and 6 were deconvoluted into three components, except for the spectrum from disk 3 in Library 2 heat-treated at 700°C (Fig. 6) that was deconvoluted into only two components. Unlike most reports of XPS results on transition-metal carbon nitrogen catalysts in the literature, here we report the actual raw counts of the XPS spectrum, unnormalized. Because the spectra have been collected on thin-film combinatorial libraries where sample preparation conditions are identical for all library members, the raw counts are directly proportional to the N content at the surface.

The three peaks in Fig. 5 and 6 with binding energies of 398.5–398.6, 400.4–401.1, and 402.2–403.7 eV were assigned to pyridinic-type N, pyrrolic-type N, and highly coordinated N atoms (N atoms bound to three C atoms within a graphene layer), respectively.^{33,34} The pyridinic-type N and pyrrolic-type N are the two main components of the N_{1s} peak and the highly coordinated N represents only a small contribution. Figure 5 shows that the area

Figure 4. (Color online) SEM images of disk 5 of Library 1 (a) unheated and heated at (b) 700, (c) 800, and (d) 1000°C and of disk 5 of Library 2 (e) unheated and heated at (f) 700, (g) 800, and (h) 1000°C.

under the pyridinic-type N and pyrrolic-type N peaks decreases as the Co content increases for Libraries 1 and 2 heat-treated at 800°C, in qualitative agreement with the total N content as shown in Fig. 2.

Figure 7 shows the bulk N content, as determined by WDS, plotted vs the integrated area of the N_{1s} XPS peak for those 10 samples where both measurements are available. There is a good correlation between the techniques. Most interesting is that the surface N content appears to increase more strongly than the bulk N content at low N concentrations. It was not possible to determine an

Figure 5. XPS spectra for the N_{1s} peak of $\text{Co}_x\text{C}_{1-x}\text{N}_y$ Libraries 1 and 2 on GC disks 1, 3, and 5 heat-treated at 800°C.

Figure 6. XPS spectra for the N_{1s} peak of $Co_xC_{1-x-y}N_y$ Libraries 1 and 2 on GC disk 3 heat-treated at 700, 800, and 1000°C.

accurate surface-nitrogen atomic percentage due to the presence of adventitious carbon and its contribution to the integrated area of the carbon peak.

Figures 5 and 6 show that there is a dramatic reduction in the relative size of the pyridinic peak when the samples transform from the amorphous phase to the heterogeneous structure consisting of nanoscale regions of N-containing graphitic carbon and β -Co. As an example, the intensity of the pyridinic peak for disk 3 of Library 2 decreases significantly (Fig. 6) when the sample changes from amorphous (700°C) to heterogeneous (800°C). Another example is shown in Fig. 5, where disk 1 of Library 2 is amorphous at 800°C and has a strong pyridinic peak while disk 3 is heterogeneous and has a pyridinic peak about the same intensity as the pyrrolic peak. It

Figure 7. (Color online) Bulk nitrogen content measured by WDS plotted vs the integrated area of the N_{1s} XPS peak, proportional to the surface N content, for the 10 samples studied in Fig. 5 and 6.

is interesting that this dramatic structural change hardly affects the positions of the N_{1s} spectral components at all, although it does affect their relative intensities.

Electrocatalytic characterization using RRDE

Figure 8 shows the CVs of the samples of Libraries 1 and 2 on the GC disks heat-treated to 700, 800, and 1000°C measured in O_2 -saturated 0.1 M $HClO_4$ at 25°C. The CV of the film on GC disk 1 of Library 1 heated at 800°C measured in argon-saturated 0.1 M $HClO_4$ solution is shown in the first panel of the second row in Fig. 8 (dotted line). The CVs of the other film samples in the Ar-saturated solution are similar and are not shown in the figure. Compared to the CV under Ar, it is clear that the reduction currents observed in the CVs under O_2 for all the samples can be attributed to the ORR. The unheated libraries showed no activity for ORR.

Trends in the variation of the onset potential for the ORR with composition, surface composition, structure, and heat-treatment temperature are summarized in Fig. 9. Figure 9 plots the onset potential vs the bulk-nitrogen content by WDS (top panel) and vs N_{1s} peak area by XPS (bottom panel) of the heated samples and also distinguishes those samples that are amorphous (by XRD and SEM) from those that are heterogeneous. All samples that are amorphous have low onset potentials. This explains one feature of Fig. 8. The samples of Library 2 heated to 700°C show lower onset potentials than those of Library 1, even though Library 2 samples contain more nitrogen. This is because the Library 2 samples are still amorphous at 700°C and the Library 1 samples (apart from disk 1) are not. In all cases where samples from both Libraries 1 and 2 are heterogeneous, consisting of N-containing graphitic carbon and β -Co, the onset potential of Library 2 samples is higher than Library 1 samples containing the same amount of Co (within the same panel of Fig. 5). We believe this is because the Library 2 samples contain more N than the Library 1 samples.

Possible correlations between the variation of the onset potential for the heterogeneous samples and the ratio of the intensities of the pyridinic and pyrrolic N_{1s} spectral components were examined. We could find no correlation between increased activity and the pyridinic/pyrrolic peak-intensity ratio. The best correlation we could find was to the total nitrogen content as shown in Fig. 9.

The lines drawn as guides to the eye in the top panel of Fig. 9 show that the onset potential of heterogeneous samples having the same bulk-nitrogen content increases with the heat-treatment temperature. This provides a strategy for preparing materials with even further improved catalytic performance: increase the nitrogen content and increase the heat-treatment temperature. The challenge to overcome is that the nitrogen content of samples having a fixed cobalt content always decreases with heat-treatment temperature.

The activity for ORR of a heated carbon black-supported cobalt ethylene diamine (CoEDA) catalyst reported recently by Subramanian et al.,³⁵ which is the most active Co-C-N catalyst reported in the literature, is shown in the fifth panel of the second row (dotted line) of Fig. 8 for comparison. The onset potential of $Co_{8.4}C_{85.7}N_{5.9}$ in this work ($E_{onset} = 0.81$ V vs RHE, measured in 0.1 M $HClO_4$, 900 rpm, 5 $mV s^{-1}$) is close to the activity of the CoEDA catalyst ($E_{onset} = 0.82$ V vs RHE, measured in 0.5 M H_2SO_4 , 900 rpm, 5 $mV s^{-1}$).³⁵ Our thin-film catalysts certainly have a significantly smaller surface area than Subramanian's catalysts, which are adsorbed on a carbon black (Ketjen Black EC300J, Brunauer-Emmett-Teller surface area = 886 m^2/g).

The CV curves for the active catalysts in Fig. 8 show two steep reduction waves, which indicates that there may be two active sites for ORR in these samples. The identification of the active sites in the heat-treated $Co_xC_{1-x-y}N_y$ thin-film libraries is a goal for our future work. There is no well-defined diffusion-limiting current plateau in our samples (which should be about -4.5 mA/cm^2 at 900 rpm based on measurements on pure Pt films). This could be caused by a number of factors but is thought to be related to a low reaction rate for the catalytic sites.³⁶ Understanding this is another goal of future research.

Figure 8. (Color online) Disk current densities for samples of $\text{Co}_x\text{C}_{1-x-y}\text{N}_y$ Libraries 1 (gray lines) and 2 (black lines) on GC disks heat-treated at 700, 800, and 1000°C measured in O_2 -saturated 0.1 M HClO_4 at 25°C. The five samples are equally spaced along the libraries as indicated in Fig. 1 and 2. The sweep rate is 5 mV s^{-1} and the rotation speed is 900 rpm. The average composition of the film on each disk is indicated in each panel. The dotted line in the first panel of the second row indicates the disk current density for disk 1 of Library 1 heat-treated at 800°C measured in Ar-saturated 0.1 M HClO_4 solution at 25°C. The dotted line in the fifth panel of the second row shows the current density of a carbon black-supported cobalt ethylene diamine catalyst heat-treated at 800°C measured in O_2 -saturated 0.5 M H_2SO_4 solution with a rotation speed of 900 rpm and a sweep rate of 5 mV s^{-1} from Fig. 4b of Ref. 35 reported by Subramanian et al.

Figure 10 shows the percentage of H_2O_2 ($\%\text{H}_2\text{O}_2$) produced at the disk electrode vs the disk potential for the same samples as shown in Fig. 8. For Library 1 heat-treated at different temperatures, the $\%\text{H}_2\text{O}_2$ produced on the samples is between 60 and 90% at 0.65–0.45 V (vs RHE) and then decreases with disk potential. For Library 2 heat-treated at 700°C, the $\%\text{H}_2\text{O}_2$ produced on disks is higher than that in Library 1 treated at the same temperature. Recall that Library 2 samples were amorphous at 700°C. For Library 2 heat-treated at 800°C, the $\%\text{H}_2\text{O}_2$ produced on the disks between 0.70 and 0.40 V (vs RHE) is much less than in Library 1 heat-treated at the same temperature. Library 2 samples contain more N than Library 1 samples and this may be a factor in the decreased H_2O_2 production. However, further work is needed to understand the factors that govern H_2O vs H_2O_2 production by these catalysts.

Corrosion stability of film libraries.—Figure 11 shows the Co content of the heat-treated $\text{Co}_x\text{C}_{1-x-y}\text{N}_y$ libraries before and after exposure to 0.5 M H_2SO_4 solution at 25°C for 1 week. Co is dissolved from the films when the Co concentration is relatively high in the two libraries and the libraries with low Co content show relatively good stability with respect to Co dissolution. The Co content is reduced to a maximum of about 3.5, 2.0, and 1.0 atom % for Library 1 heated at 700, 800, and 1000°C, respectively. The Co content is reduced to a maximum of about 4.6, 3.1, and 1.6 atom % Library 2 heated at 700, 800, and 1000°C, respectively. It would have been very interesting to measure the catalytic activity of the samples after acid exposure to see if the dissolution of Co (presumably mostly from grains of β -Co) had any impact on the catalytic activity. This will be a focus of our future work.

Conclusions

Highly active thin-film $\text{Co}_x\text{C}_{1-x-y}\text{N}_y$ libraries ($0 < x < 0.107$, $0.003 < y < 0.389$) toward ORR have been prepared by combinatorial magnetron sputtering deposition and subsequent heat-treatment. As-sputtered libraries were amorphous and showed no catalytic activity. Upon heating above a critical temperature, the amorphous materials transformed into a nanoscale mixture of N-containing graphitic carbon and β -Co and then catalytic activity was observed. The results in Fig. 9 showed that the most active catalysts are those prepared at the highest heating temperatures and with the highest nitrogen content. The challenge to further improve the catalytic performance of these materials is that the N content is reduced as the temperature increases. We showed that the nitrogen

Figure 9. (Color online) (a) Onset potential for the catalysts in Fig. 8 plotted vs their N content. (b) Onset potential for the catalysts in Fig. 8 plotted vs the integrated area of the N_{1s} XPS peak, proportional to the surface N content. Diamond-shaped data points indicate samples that show a nanoscale mixture of N-containing graphitic carbon and β -Co, while square data points represent amorphous samples. The heat-treatment temperatures of the samples are indicated in the figure and the solid lines are guides to the eye.

Figure 10. (Color online) % H_2O_2 produced as a function of disk potential for samples in $\text{Co}_x\text{C}_{1-x-y}\text{N}_y$ Libraries 1 and 2 heat-treated at 700, 800, and 1000°C. Measurements were made at a sweep rate of 5 mV s^{-1} in O_2 -saturated 0.1 M HClO_4 at 25°C. The average composition of each disk is indicated in each panel. The samples are the same as those reported in Fig. 8.

Figure 11. The atomic fraction of Co vs position in the $\text{Co}_x\text{C}_{1-x-y}\text{N}_y$ Libraries (a) 1 and (b) 2 heat-treated at 700, 800, and 1000°C before and after soaking in 0.5 M H_2SO_4 at 25°C for 1 week.

content remaining after heat-treatment could be increased by incorporating more nitrogen in the as-sputtered film. This was accomplished by sputtering at higher N_2 partial pressures.

XPS studies of the N_{1s} core-level spectra of these materials showed that the surface N content was increased with the bulk N content. However, the spectra showed little change to the individual spectral components for catalytically active and inactive materials, apart from a decrease in the intensity of the pyridinic peak relative to the pyrrolic peak.

The ORR proceeds on heat-treated $\text{Co}_x\text{C}_{1-x-y}\text{N}_y$ libraries with a large fraction of H_2O_2 product. In order for such catalysts to be commercially viable, the fraction of H_2O_2 produced must be reduced. On the positive side, heat-treated $\text{Co}_x\text{C}_{1-x-y}\text{N}_y$ libraries with low Co content show relatively good stability in 0.5 M H_2SO_4 solution at 25°C.

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Dependence of the Activity of Sputtered Co–C–N Oxygen Reduction Electrocatalysts on Heat-Treatment Temperature

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The variations of the structure and the activity of a sputtered Co–C–N sample for the oxygen reduction reaction (ORR) with heat-treatment temperature are studied. The sample begins to show activity for ORR in acidic electrolyte at a critical heat-treatment temperature (T_c) of 725°C, at which both substantial nitrogen release from the originally amorphous films and the transformation to a heterogeneous structure (β -Co + N-containing graphitic carbon) occurs. The sample shows activity in alkaline electrolyte when heated above 500°C, the activity increases substantially near T_c and the highest activity occurs at 850°C. This suggests that active sites, apparently created below T_c , which are active below T_c , are blocked in acidic electrolyte. When N loss, graphitization and formation of β -Co occurs at T_c , sites apparently become available in acidic electrolyte. The variation of the transformation temperature, T_c , with x and y in sputtered $\text{Co}_x\text{C}_{1-x-y}\text{N}_y$ combinatorial libraries was mapped using electron microprobe and X-ray diffraction studies. T_c decreases strongly as the Co content increases since Co is a graphitization catalyst and T_c increases weakly as the N content increases.

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The replacement of Pt by non-noble metal catalysts could lead to significant cost reduction in PEM fuel cells and is desirable, provided that similar area-specific activity can be obtained.^{1,2} The development of non-noble metal catalysts for the oxygen reduction reaction (ORR) is an active area of research. Active non-noble metal ORR catalysts prepared by heat-treating carbon-supported N_4 -metal macrocycles (where the metal is usually Fe or Co),^{3,9} organometallic (Fe, Co) complexes^{10,11} and Fe or Co salts^{12,13} in ammonia or acetonitrile vapor have been widely studied. Based on these studies it was believed that a transition metal, a nitrogen source, a carbon support and heat treatment are required to prepare a highly active catalyst stable in acidic environment. However, Matter et al.^{14–16} and Maldonado and Stevenson¹⁷ prepared active catalysts without any metals and proposed that a metal site is not needed for the oxygen reduction reaction. Recently, a carbon-supported Co-polypyrrole catalyst prepared without heat treatment and showing excellent stability was reported by Bashyam and Zelenay.¹⁸ More recently, Popov¹⁹ prepared highly active nitrogen-containing carbon catalysts that showed very low levels of H_2O_2 production.

The nature of the active sites in all these catalysts is under debate. Lefèvre and co-workers proposed that FeN_2/C and FeN_4/C or CoN_4/C active sites exist in Fe-based²⁰ or Co-based catalysts²¹ based on the time-of-flight secondary ion mass spectrometry results. Matter et al.^{14–16} and Maldonado and Stevenson¹⁷ proposed that the active sites are located on the edge planes of nitrogen-containing carbon that do not contain any metal. Popov¹⁹ proposed that active sites with pyridinic nitrogen are responsible for the catalytic activity for the ORR.

Vacuum deposition methods have also been used to prepare active non-noble metal catalysts. Thin films of Co–C–N co-sputtered in vacuum were reported by Deng and Dignam. The films showed good catalytic activity for ORR in alkaline solution but the films were not stable in acid solution due to dissolution.^{22,23} Researchers at 3M Co. also prepared active catalysts by vacuum deposition followed by heat treatment that were stable, at least for some time, under fuel cell conditions and in acid solution.^{24–26}

Catalysts with a wide range of compositions can be prepared with a composition-spread sputtering system in our lab. Active Fe–C–N and Co–C–N ORR thin-film catalysts showed excellent activity in acid electrolyte after heat treatment in inert gas.^{27–29} It was shown^{27–29} that the onset of activity coincided with the temperature, T_c , at which samples transformed from the amorphous as-sputtered

structure to a heterogeneous nanoscale mixture of N-containing graphitic carbon and either Fe_3C or β -Co. In this paper, the effect of the heat-treatment temperature on the catalytic activity for ORR of a heat-treated Co–C–N thin film sample prepared by magnetron sputter deposition was studied in both acid and alkaline electrolytes. Comparison was made to a sputtered $\text{Co}_{0.23}\text{C}_{0.77}$ sample and to a pure sputtered Co sample. Furthermore, thin film libraries of $\text{Co}_x\text{C}_{1-x-y}\text{N}_y$ with varying cobalt and nitrogen contents were used to determine the dependence of T_c on the Co content, x , and the N content, y , in the initial as-sputtered films.

Experimental

Deposition of thin-film samples.—A Co sputtering-target (2.00 in. diameter, 0.250 in. thick and 99.95% pure) was obtained from Williams Advanced Materials (Buffalo, NY). A C sputtering target (2.00 in. diameter, 0.250 in. thick, and 99.999% pure) was obtained from Kurt J. Lesker Co. (Clairton, PA). Co and C were sputtered using MDX-1K DC (Advanced Energy) power supplies with powers of 15 and 150 W, respectively. Specially designed masks were positioned in front of each target to produce the desired composition variations while the substrate table was rotated. More details about the production of binary and pseudobinary libraries using our equipment can be found elsewhere.³⁰ For the constant composition sample, “constant” masks³⁰ were used in front of both C and Co targets. For the composition-spread libraries produced, a “constant mask” was used for the C target and a “linear out” mask was used for the Co target.³⁰

Nitrogen was incorporated into the libraries by sputtering in an Ar/ N_2 gas mixture.^{27–29} Gas flows were independently controlled using MKS mass flow controllers. Ultrahigh purity Ar (99.999%) and N_2 (99.999%) were supplied at constant flow rates during the sputtering. One Co–C–N sample with a constant composition and four composition-spread libraries of Co–C–N were produced in this work. The constant composition sample was sputtered under 4.5 sccm Ar and 3.0 sccm N_2 , which corresponds to a total pressure of 0.224 Pa (1.7 mTorr) and a N_2 partial pressure of 0.090 Pa (0.68 mTorr) (i.e., $\text{N}_2/\text{Ar} = 40/60$). The composition was $\text{Co}_{9.2}\text{C}_{57.4}\text{N}_{33.4}$. Composition-spread library 1 was sputtered under 7.5 sccm Ar and 2.0 sccm N_2 , which corresponds to a total pressure of 0.277 Pa (2.1 mTorr) and a N_2 partial pressure of 0.058 Pa (0.44 mTorr) (i.e., $\text{N}_2/\text{Ar} = 20/80$). Composition-spread library 2 was sputtered under 4.5 sccm Ar and 3.0 sccm N_2 , which corresponds to a total pressure of 0.224 Pa (1.7 mTorr) and a N_2 partial pressure of 0.090 Pa (0.68 mTorr) (i.e., $\text{N}_2/\text{Ar} = 40/60$). Composition-spread library 3 was sputtered under 3.0 sccm Ar and 4.5 sccm N_2 , which corresponds to a total pressure of 0.216 Pa

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(1.64 mTorr) and a N_2 partial pressure of 0.130 Pa (0.99 mTorr) (i.e., $N_2/Ar = 60/40$). Composition-spread library 4 was sputtered under 9.5 sccm N_2 , which corresponds to a N_2 pressure of 0.224 Pa (1.70 mTorr) (i.e., $N_2/Ar = 100/0$).

To better understand the origin of catalytic activity in the Co–C–N materials, constant composition Co–C and Co films were also prepared. The Co–C sample had an average composition of $Co_{22.7}C_{77.3}$ with 0.7 atom % oxygen as measured by electron microprobe analysis. The constant composition Co–C and Co samples were sputtered under 6.6 sccm Ar, which corresponds to a total pressure of 0.216 Pa (1.64 mTorr).

The constant composition Co–C–N film was deposited onto: (i) a number of 80×15 mm SiO_2 -coated Si(100) wafer strips (500 nm layer of SiO_2) for heat treatment, grazing incidence X-ray diffraction (XRD) measurements, electron microprobe analysis and film thickness determination and (ii) a number of glassy carbon (GC) disks with a diameter of 5 mm (Tokai Carbon Co.) for electrochemical measurements using the rotating ring-disk electrode (RRDE) technique. The composition-spread libraries were only deposited onto 80×15 mm SiO_2 -coated Si(100) wafer strips for heat treatment, XRD measurements, electron microprobe analysis and film thickness determination. More details about the various substrates mounted on the substrate table as well as a projection of the targets and their associated masks on the substrate table can be found elsewhere.²⁹

Films deposited on the SiO_2 -coated Si(100) wafer strips and GC disks were heat treated at different temperatures in Ar using a Modular Process Technology RTP-600S rapid thermal processor (RTP). The samples were heated at a heating rate of $5^\circ C\ s^{-1}$ in flowing Ar (2000 sccm min^{-1}) and held at the target temperature for 5 min before cooling.

Thickness of the sputtered samples.— The thickness of the constant composition samples and the composition-spread libraries sputtered on a Si wafer were determined using a Dektak 8 advanced development profilometer (Veeco Instruments Inc.). The constant composition Co–C–N, Co–C, and Co samples had thicknesses of 390 ± 5 nm, 146 ± 5 nm, and 30 ± 2 nm, respectively. For the composition-spread Co–C–N libraries the film thickness before heat treatment was found to linearly increase across the library from about 450 ± 5 nm to $1.00 \pm 0.01\ \mu m$ with increasing Co content for library 1, from about $1.35 \pm 0.01\ \mu m$ to $1.90 \pm 0.01\ \mu m$ with increasing Co content for library 2, from about $1.50 \pm 0.01\ \mu m$ to $2.10 \pm 0.01\ \mu m$ with increasing Co content for library 3, and from about $1.70 \pm 0.01\ \mu m$ to $2.50 \pm 0.01\ \mu m$ with increasing Co content for library 4. The average thickness increases from library 1 to library 4, even though the Co and C sputtering powers and sputtering time were identical, because more N is incorporated into the films as the N partial pressure increases.

Composition of the sputtered samples.— The composition of the sputtered samples was obtained using a JEOL JXA-8200 superprobe electron microprobe system equipped with one energy dispersive spectrometer and five wavelength dispersive (WDS) spectrometers. Silicon nitride (Si_3N_4) was used as the N standard, a Mn–Co alloy (Mn:Co = 30:70, weight ratio) was used as the Co standard and pyrolytic graphite was used as the C standard. The overlap of the $N(K\alpha)$ and $Co(L\beta(2))$ lines was carefully considered and accommodated. Reuter's method for thin film analysis, which corrects for the excitation of the backscattered electrons caused by the substrate, was employed.³¹ Co, N, and C atomic compositions were all determined by WDS detectors. The analysis spot size was 50 μm . The composition was measured every 2 mm along the 76 mm long composition-spread libraries before and after various heat treatments.

Grazing incidence X-ray diffraction for the constant composition sample.— The crystallographic structure of the constant composition sample after heat treatment to various temperatures was deter-

mined by grazing incidence X-ray diffraction (XRD). Grazing incidence XRD patterns were collected using a Siemens D5000 diffractometer equipped with a grazing incidence attachment. Cu $K\alpha$ radiation was used at an incidence angle of 0.5° and with divergence slits set to 0.1° . Such conditions lead to an illuminated spot of 40×12 mm in the center of the 80×15 mm constant-composition specimen. A Soller slit box in front of the detector was used to ensure that the scattered X-rays from this large illuminated sample area that entered the detector all had the same scattering angle. Data were collected over a scattering angle range of 10 – 80° in 0.05° intervals. Total scan times varied between 8 and 12 h. The average size of Co grains was calculated according to Scherrer formula

$$L = \frac{0.9\lambda_{K\alpha 1}}{B_{(2\theta)} \cos \theta} \quad [1]$$

where L is the diameter of the particle, λ is the wavelength of the X-ray radiation ($\lambda = 0.154$ nm), θ is the Bragg angle and B is the full width at half maximum of the Co(111) Bragg peak of the sample, corrected for instrumental resolution. The Co(111) peak was fitted with a Lorentzian peak shape using least-squares software to extract the full width of the peak. The instrumental resolution at approximately the same scattering angle was determined by a fit of a Lorentzian peak shape to a Bragg peak of a crystalline corundum sample (National Bureau of Standards standard reference material). The parameter, B , used in Eq. 1, was obtained by subtracting the width of the peak from the corundum sample from the measured width of the Co(111) peak.

X-ray diffraction studies of the composition-spread libraries.— The crystallographic structures of the composition-spread libraries were determined using an INEL CPS120 curved position sensitive detector coupled to a Philips 1720 X-ray generator equipped with a Cu target X-ray tube. The X-ray spot has a width of 1 mm in the direction of the composition spread. X-ray diffraction patterns were measured every 2 mm over the 76 mm long libraries. Libraries were heated in the rapid thermal processing station and then diffraction patterns were collected at room temperature. Each individual wafer was only heated to a single temperature and was not reused for heating at a higher temperature.

Electrochemical characterization.— The electrocatalytic activity for the oxygen reduction reaction of the films deposited on the GC disks was studied with the rotating ring-disk electrode (RRDE) technique using a Pine Electrochemical system (AFMSRX rotator, and AFCBP1 bipotentiostat). The RRDE electrode consisted of a catalyst film-coated GC disk (5 mm diameter) surrounded by a Pt ring (7.5 mm inner diameter and 8.5 mm outer diameter). The electrochemical measurements were conducted in a one-compartment cell. The electrolyte was either a 0.1 M $HClO_4$ solution or a 0.1 M KOH solution prepared from double-distilled $HClO_4$ (GFS Chemicals Inc.) or KOH (GFS Chemicals Inc.) and 18 M Ω Barnstead nanopure water. A Pt-wire counter electrode and Koslow Hg/Hg_2SO_4 reference electrode (used in 0.1 M $HClO_4$ solution) or Ag/AgCl reference electrode (Bioanalytical Systems, Inc., used in 0.1 M KOH solution) were used for the measurements. The potential of the Hg/Hg_2SO_4 and Ag/AgCl reference electrodes was calibrated vs the reversible hydrogen electrode (RHE). The potentials reported in this study all refer to that of the RHE potential.

The mass per unit area of the Co–C–N, Co–C, and Co constant-composition films on the GC disks before heat treatment was 0.056, 0.051, and 0.024 $mg\ cm^{-2}$, respectively. The Co mass per unit area of the Co–C–N, Co–C, and Co samples was 0.018, 0.030, and 0.024 $mg\ cm^{-2}$, respectively.

The films on the GC disks were first electrochemically cleaned by sweeping the potential in the range between 0 and 1.0 V (vs RHE) at 50 $mV\ s^{-1}$ in an Ar-saturated 0.1 M $HClO_4$ solution or 0.1 M KOH solution until steady state cyclic voltammograms (CV) were obtained. For each catalyst tested, a CV was first collected in

Figure 1. Grazing incidence X-ray diffraction measurements showing intensity vs scattering angle for the heat-treated $\text{Co}_{9.2}\text{C}_{57.4}\text{N}_{33.4}$ sample. The composition changes with heating temperature as indicated in Fig. 4. The heat treatment was done in flowing Ar and the heat-treatment temperature is indicated next to each curve. The major Bragg peaks of the phases present are indicated.

Ar-saturated 0.1 M HClO_4 solution or 0.1 M KOH solution from 1.0 to 0.05 V at 5 mV s^{-1} to determine the nonfaradaic current. The CVs during oxygen reduction in 0.1 M HClO_4 solution were performed between 1.0 and 0.05 V at 5 mV s^{-1} with the electrode stationary and with the electrode rotated at 900 rpm. O_2 gas was purged into the solution at a rate of 10 sccm min^{-1} . The measurements in alkaline solution were performed at 400, 900, 1600, and 2500 rpm with the same O_2 gas purge rate. The faradaic current was determined by subtracting the CV in Ar-saturated 0.1 M HClO_4 or 0.1 M KOH solution from that obtained in O_2 -saturated 0.1 M HClO_4 or 0.1 M KOH solution. The onset potential, at which the current for oxygen reduction is first observed³² was determined by the point of intersection of two tangent lines, one drawn parallel to the base line (i.e., from 0.9 V to approx. 0.8 V) and the second parallel to the increasing current signal. For all the measurements, the ring potential was held at 1.2 V vs RHE in order to oxidize any H_2O_2 ³³ produced in acid solution and HO_2^- ³⁴ produced in alkaline solution. The % H_2O_2 produced in acid solution (or % HO_2^- produced in alkaline solution) was calculated using the following equation^{9,33,35}

$$\% \text{H}_2\text{O}_2 = 100 \frac{2I_R/N}{I_D + (I_R/N)} \quad [2]$$

where I_D is the faradaic current at the disk, I_R is the faradaic current at the ring, and $N = 0.2$ is the RRDE collection efficiency.

Results and Discussion

Grazing incidence XRD of the constant composition sample heat-treated at different temperatures.— Figure 1 shows the grazing incidence XRD of the as-sputtered $\text{Co}_{9.2}\text{C}_{57.4}\text{N}_{33.4}$ film heat treated at 650, 700, 725, 750, 775, 800, 825, 850, 875, 900, and 1000°C. The sample is amorphous at 650 and 700°C. At a critical temperature, T_c , of about $725^\circ\text{C} \pm 10^\circ\text{C}$, the film transforms to a heterogeneous mixture of β -Co and N-containing graphitic carbon, in agreement with observations in Ref. 28. The intensity of the graphitic carbon peaks increases with the heat-treatment temperature. The widths of

Figure 2. (a) Disk current densities for samples of $\text{Co}_x\text{C}_{1-x-y}\text{N}_y$ (derived from the single composition sputtering experiment) on glassy carbon disks heat treated at different temperatures measured in O_2 -saturated 0.1 M HClO_4 at 25°C . The sweep rate is 5 mV s^{-1} and the rotation speed is 900 rpm. The average composition of the film on each disk is indicated in each panel and in Fig. 4. (b) % H_2O_2 produced as a function of disk potential for samples of $\text{Co}_x\text{C}_{1-x-y}\text{N}_y$ on glassy carbon disks heat treated at different temperatures. Measurements were made at a sweep rate of 5 mV s^{-1} in O_2 -saturated 0.1 M HClO_4 at 25°C . The average composition of each disk is indicated in each panel. The samples are the same as those in (a).

the Bragg peaks from β -Co decrease as the heat-treatment temperature increases, indicating an increase in the size of the Co grains.

Electrocatalytic activity of the constant composition sample heat-treated at different temperatures.— Figure 2a shows the CVs of the constant composition sample on the glassy carbon (GC) disks without heat treatment (i.e., 25°C) and heat treated to 650, 700, 725, 750, 775, 800, 825, 850, 875, 900, and 1000°C measured in O_2 -saturated 0.1 M HClO_4 solution at 25°C . The samples without heat treatment (i.e., 25°C) and heat treated at 650 or 700°C show little or no activity for ORR. The sample begins to show activity as it is heat treated to 725°C , when the film transforms from an amorphous structure to a heterogeneous structure comprised of β -Co and N-containing graphitic carbon as shown in Fig. 1. The activity of the samples for ORR changes with the heat-treatment temperature, which will be considered later below. The CV curves of the active

Figure 3. (Color online) (a) Disk current densities for samples of Co_xC_{1-x-y}N_y (derived from the single composition sputtering experiment) on glassy carbon disks heat treated at different temperatures measured in O₂-saturated 0.1 M KOH at 25°C. The sweep rate is 5 mV s⁻¹ and the rotation speeds are 400, 900, 1600, and 2500 rpm. The average composition of the film on each disk is indicated in each panel and in Fig. 4. (b) % HO₂⁻ produced as a function of disk potential for samples of Co_xC_{1-x-y}N_y on glassy carbon disks heat treated at different temperatures. Measurements were made at a sweep rate of 5 mV s⁻¹ in O₂-saturated 0.1 M KOH at 25°C and the rotation speed is 900 rpm. The average composition of each disk is indicated in each panel. The samples are the same as those in (a).

catalysts show two steep reduction waves except for the sample heat treated at 1000°C. Figure 2b shows the percentage of H₂O₂ produced at the disk electrode vs the disk potential for the same samples as shown in Fig. 2a. The percent peroxide is between 30 and 85% between 0.65 and 0.45 V (vs RHE) and then increases as the disk potential decreases, which correlates to the two steep reduction waves in the CV curves shown in Fig. 2a.

Figure 3 shows the CVs of the constant composition sample on the GC disks without heat treatment (i.e., 25°C) and heat treated to 500, 550, 600, 650, 700, 725, 750, 775, 800, 825, 850, 875, 900, and 1000°C measured in O₂-saturated 0.1 M KOH solution at 25°C. By comparison with the CVs measured in 0.1 M HClO₄ solution, there are two important differences. First, the samples heat treated at 650 and 700°C show significant activity for ORR in 0.1 M KOH solution while they do not in 0.1 M HClO₄ solution, that is, the samples begin to show activity at a lower temperature than in 0.1 M HClO₄ solution. Second, the CVs of the films measured in 0.1 M KOH

solution show relatively well-defined current plateaus while the CVs of the films measured in 0.1 M HClO₄ solution do not. These two observations suggest that the catalytic sites are blocked by adsorbed acidic species until the samples are heat treated above T_c , however this is speculation. Figure 3b shows the percentage of HO₂⁻ (% HO₂⁻) produced at the disk electrode vs the disk potential for the same samples as shown in Fig. 3a. The percentage of HO₂⁻ (% HO₂⁻) is between 30 and 70% between 0.70 and 0.10 V (vs RHE). The peroxide content appears to reduce substantially for the sample heated to 1000°C. This result suggests that higher heating temperatures should be explored as we discuss later, below.

Figure 4 shows the trends with heat-treatment temperature of the Co content, the N content, the Co grain sizes, the onset potential and the current densities at 0.7 V for the ORR. There is a dramatic decrease in the N content at $T_c = 725^\circ\text{C}$. The Co content then increases with heat-treatment temperature due to the decrease in N

Figure 4. The Co content (a), N content (b), Co particle size (c), onset potential (d), and current density at 0.7 V (e) for ORR in 0.1 M HClO₄ and 0.1 M KOH solution vs heat-treatment temperature of the samples. The samples were derived from the constant-composition sample described by Fig. 1-3.

content with the heat-treatment temperature. The size of Co particles in the films heat treated above T_c increases with the heat-treatment temperature. The onset potential for ORR in acid increases with the heat-treatment temperature in the range between 700 and 800°C, as the catalyst becomes active above $T_c = 725^\circ\text{C}$. The onset potential decreases slightly with heat-treatment temperature above 800°C. The onset potential measured in 0.1 M KOH solution increases with heat-treatment temperature in the range between 600 and 1000°C. The current density at 0.7 V in acid electrolyte is strongly dependent on the heat-treatment temperature and is maximum for the sample heat treated at 800°C. The current density at 0.7 V in the alkaline electrolyte increases over the range between 600 and 750°C and then does not change significantly although the maximum occurs for the sample heat treated at 850°C. The increase in activity could be caused by the porosity induced by the N loss at T_c that would increase the surface area. The current density at 0.7 V is always larger

Figure 5. Grazing incidence X-ray diffraction measurements showing intensity vs scattering angle for the Co-C sample without heat treatment (i.e., as sputtered) and heat treated at 800°C under N₂. The major Bragg peaks of the phases present are indicated.

in alkaline electrolyte than in acidic electrolyte, and diffusion-limiting currents are not reached in acid electrolyte suggesting that adsorbed acid may block catalytic sites.

Pourbaix diagrams show³⁶ that Co is passivated by an oxide or hydroxide layer above ~ 0.15 V (vs RHE) in an alkaline solution with pH > 9. Co oxide,³⁷⁻³⁹ Co hydroxide and Co oxyhydroxide⁴⁰ are electro-active for ORR in alkaline solution. The Co-C-N sample heated above T_c contains β -Co, which presumably converts at least partially to oxide, hydroxide or oxyhydroxide upon exposure to aqueous solution. Therefore, to further understand the activity of the sputtered Co-C-N sample, Co-C and Co samples were sputtered for comparison.

Figure 5 shows the grazing incidence XRD patterns of the Co-C sample without heat treatment and after heat treatment at 800°C. A broad peak near 35–48° is observed for the as-sputtered Co-C sample, which might result from Co nanoparticles in a carbon matrix. The width of the peak implies nanoparticles of only 1–2 nm in size. The Co-C samples consists of a mixture of β -Co and graphitic carbon after heating to 800°C, which is similar to Co-C-N heated at 800°C as shown in Fig. 1.

Scanning electron microscopy (SEM) images of the Co-C-N and Co-C samples without heat treatment and heat treated at 800°C are shown in Fig. 6. The as-sputtered Co-C-N (Fig. 6a) and Co-C (Fig. 6c) appear homogeneous and amorphous although a very broad Co peak can be observed in the XRD pattern of Co-C sample. After heat treatment, both Co-C-N and Co-C appear heterogeneous as shown in Fig. 6b and d, as expected since both are mixtures of coexisting β -Co and graphite (or N-containing graphite) phases by XRD.

Figure 7 shows the CVs and % HO₂⁻ produced on the constant composition Co-C-N, Co-C, and Co samples without heat treatment and after heating at 800°C measured in O₂-saturated 0.1 M KOH solution at 25°C. For the as-sputtered samples, the activity for ORR follows: Co > Co-C > Co-C-N. We believe that Co metal (in the form of oxide or hydroxide in the alkaline solution) accounts for the activity for ORR because no Co crystallites or nanoparticles can be detected in the inactive as-sputtered Co-C-N sample. For the samples heat-treated at 800°C, the activity for ORR follows: Co-C-N > Co > Co-C. In this case, crystalline Co exists in all three heated samples and could explain the fact that all are quite active. However, Fig. 4 shows that the Co-C-N samples heat treated below $T_c = 725^\circ\text{C}$ (600–700°C) are still active toward ORR in al-

Figure 6. (Color online) SEM images of Co-C-N unheated (a), heated at 800°C (b), and of Co-C unheated (c), heated at 800°C (d).

kaline solution and no Co metal exists in the samples as shown in Fig. 1. This proves that other sites are active for ORR over this temperature range. Although the activity of the Co-C-N heat treated above T_c for ORR in alkaline solution is complicated due to the activity of the Co metal in the samples, the activity of the samples heat treated below T_c in alkaline solution suggests that the lack of activity of the same samples in acid solution is due to the blocking of adsorbed acid on the catalytic sites.

Figure 8 shows the activity of the Co-C sample before heat treatment and after heating at 800°C measured in acid solution. Neither Co-C sample shows significant activity in acid solution as compared to the Co-C-N sample, which confirms the importance of the N on the ORR activity of the Co-C-N sample. The Co content in the Co-C sample heat treated at 800°C shown in Fig. 7 and 8 was measured on the film heated on a Si wafer substrate. The value measured, 16.6 atom %, is lower than 22.7 atom % measured for the unheated sample. We believe this discrepancy is caused by the reaction of some Co in the film with the Si wafer support during heating. We do not believe the Co content was actually reduced from approximately 22.7 atom % in the samples measured by RDE which were heated on GC disks.

Figure 9 shows the CVs and % HO_2^- produced on the constant composition sample heat treated to 1000, 1100, and 1200°C measured in O_2 -saturated 0.1 M KOH solution at 25°C. The activity of the sample decreases as the heat-treatment temperature increases from 1000 to 1200°C, as can be seen in Fig. 9a. The % HO_2^- pro-

Figure 7. (Color online) Comparison of disk current densities and % HO_2^- produced as a function of disk potential for samples of Co-C-N (derived from the single composition sputtering experiment) (solid line), Co-C (dot-dashed line) and Co (dashed line) on glassy carbon disks without heat treatment and heat treated at 800°C measured in O_2 -saturated 0.1 M KOH at 25°C. The sweep rate was 5 mV s^{-1} and the rotation speed was 900 rpm. The average composition of the film on each disk, inferred from measurements on the same film heated on SiO_2 coated Si wafers, is indicated in each panel.

Figure 8. (Color online) Comparison of disk current densities for samples of Co-C-N (derived from the single composition sputtering experiment) (solid line) and Co-C (dot-dashed line) on glassy carbon disks without heat treatment and heat treated at 800°C measured in O₂-saturated 0.1 M HClO₄ at 25°C. The sweep rate was 5 mV s⁻¹ and the rotation speed was 900 rpm.

duced on the electrode, as shown in Fig. 9b, does not decrease further as the heat-treatment temperature increases to 1100 or 1200°C. Figure 10 shows the CVs and % H₂O₂ produced on the constant composition sample heat treated to 1000, 1100, and 1200°C measured in O₂-saturated 0.1 M HClO₄ solution at 25°C. Figure 10a shows that the activity of the sample in acid solution gets much worse as the heat-treatment temperature increases to 1100 or 1200°C. The % H₂O₂ produced on the samples heat treated at 1000, 1100, and 1200°C are all high. The results show that the activity of the sample in either alkaline solution or acid solution decreases after being heat treated to temperatures higher than 1000°C. The sample reported in Fig. 9 and 10 was sputtered under similar conditions to the sample shown in Fig. 1-4 although the composition was slightly different. The Co content in the sample heat treated at 1100 or 1200°C shown in Fig. 9 and 10 is listed as 4.4 and 3.5 atom %, respectively, due to reaction of Co in the film with the Si substrate used for the WDS measurements. We do not believe the Co content was actually reduced from approximately 12.1 atom % in the samples measured by RDE which were heated on GC disks.

We proposed earlier²⁷⁻²⁹ that the graphitization of the N-containing carbon at T_c plays an important role in the activity of the sputtered samples in acid solution. Above 800°C the activity in acidic solution decreases as the heat-treatment temperature increases. This is perhaps caused by the reduction in the N content with increasing heat-treatment temperature above 800°C shown in Fig. 4. In any event, the activity of sputtered and heat-treated Co-C-N films depends on the heat-treatment temperature in both acid and alkaline electrolytes. In acid electrolyte, the activity improves dramatically after the amorphous-heterogeneous transition at T_c . Therefore we undertook studies to determine the variation of T_c with the composition of the as-sputtered films.

Dependence of T_c on x and y in $\text{Co}_x\text{C}_{1-x-y}\text{N}_y$.—The elemental composition vs position along the co-sputtered composition-spread libraries was measured using electron microprobe. Figure 11 shows the atom % N plotted vs the atom % Co for the four $\text{Co}_x\text{C}_{1-x-y}\text{N}_y$ composition-spread libraries before and after heat treatment to various temperatures. The balance of the composition is carbon. The composition of the as-sputtered (not heated) libraries varies smoothly as shown in Fig. 11a-d for libraries 1-4, respectively. The N content of the as-sputtered libraries increases with the nitrogen partial pressure used during sputtering. The N content across as-sputtered libraries 1-4 varies smoothly from 25.2 to 36.0%, 35.4 to 44.1%, 39.8 to 47.5% and 44.8 to 49.0%, respectively.

After heat treatment, the plots of atom % N vs atom % Co show a place where the N content drops quickly with spatial position across the library. The location of this “knee”^{26,27} can be used to determine the composition that is just undergoing the amorphous-heterogeneous transition at the heat-treatment temperature studied.

Figure 9. (Color online) (a) Disk current densities for samples of $\text{Co}_x\text{C}_{1-x-y}\text{N}_y$ (derived from the single composition sputtering experiment) on glassy carbon disks heat treated at 1000, 1100, and 1200°C measured in O₂-saturated 0.1 M KOH at 25°C. The sweep rate was 5 mV s⁻¹ and the rotation rates were 400, 900, 1600, and 2500 rpm. The average composition of the film on each disk, inferred from measurements on the same film heated on SiO₂ coated Si wafers, is indicated in each panel. (b) % H₂O₂ produced as a function of disk potential for samples of $\text{Co}_x\text{C}_{1-x-y}\text{N}_y$ on glassy carbon disks heated at 1000, 1100, and 1200°C. Measurements were made at 5 mV s⁻¹ and 900 rpm in O₂-saturated 0.1 M KOH at 25°C. The samples are the same as those in (a).

Figure 10. (a) Disk current densities for samples of $\text{Co}_x\text{C}_{1-x-y}\text{N}_y$ (derived from the single composition sputtering experiment) on glassy carbon disks heat treated at 1000, 1100, and 1200°C measured in O₂-saturated 0.1 M HClO₄ at 25°C. The sweep rate was 5 mV s⁻¹ and the rotation speed was 900 rpm. (b) % H₂O₂ produced as a function of disk potential for samples of $\text{Co}_x\text{C}_{1-x-y}\text{N}_y$ on glassy carbon disks heated at 1000, 1100, and 1200°C. Measurements were made at 5 mV s⁻¹ and 900 rpm in O₂-saturated 0.1 M HClO₄. The samples in (a) and (b) are the same as those in Fig. 9.

Figure 11. (Color online) Atom % N vs atom % Co for composition-spread $\text{Co}_x\text{C}_{1-x-y}\text{N}_y$ libraries before and after heat treatment. The balance of the composition is carbon. The $\text{Co}_x\text{C}_{1-x-y}\text{N}_y$ libraries were sputtered under four different conditions: (a) library 1, $\text{N}_2/\text{Ar} = 20/80$; (b) library 2, $\text{N}_2/\text{Ar} = 40/60$; (c) library 3, $\text{N}_2/\text{Ar} = 60/40$; (d) library 4, $\text{N}_2/\text{Ar} = 100/0$.

Figure 12 illustrates the procedure. Figure 12 shows XRD patterns and atom % N measured every 2 mm along library 1 heated to 700°C. It is clear that the N content drops at the same point as the Bragg peaks from β -Co begin to appear. Therefore, positions on the film between 26 and 76 mm have undergone the amorphous-heterogeneous transformation and positions between 0 and 22 mm have not. The composition of as-sputtered library 1 at 24 mm corresponds to the composition that has $T_c = 700^\circ\text{C}$.

The results in Fig. 11 were used to determine the variation of T_c with composition in as-sputtered $\text{Co}_x\text{C}_{1-x-y}\text{N}_y$ materials according to the procedure outlined in Fig. 12. In Fig. 11, library positions to the right of the knee at various temperatures have undergone the amorphous-heterogeneous transition and those to the left of the knee have not. Figure 13 summarizes the variation of T_c with the composition of as-sputtered $\text{Co}_x\text{C}_{1-x-y}\text{N}_y$ materials using a contour map. The value of T_c for a sputtered $\text{Co}_x\text{C}_{1-x-y}\text{N}_y$ material with a particular atom % N and atom % Co can be read directly off Fig. 13. Based on the results in Fig. 4 and in Ref. 28, Fig. 13 indicates the temperature to which a particular as-sputtered $\text{Co}_x\text{C}_{1-x-y}\text{N}_y$ material must be heated to cause catalytic activity for ORR in acid electrolyte.

Figure 13 shows how the amorphous-heterogeneous (β -Co + N-containing graphitic carbon) transition temperature, T_c , depends on

Figure 12. (Color online) (a) XRD patterns measured every 2 mm along $\text{Co}_x\text{C}_{1-x-y}\text{N}_y$ library 1 after heat treatment to 700°C (b). The atom % N vs position (every 2 mm) across the same library after heat treatment to 700°C.

the as-sputtered N and Co contents in the four libraries. First, T_c decreases strongly with Co content at fixed N content, indicating that increased Co content in the sample makes it easier to graphitize, as expected.⁴¹ Second, T_c increases with N content at fixed Co content, indicating that more nitrogen in the as-sputtered amorphous sample makes it more difficult to graphitize.

Conclusions

The activity of the as-sputtered and heat-treated Co-C-N co-sputtered films for ORR in the acid electrolyte is much more strongly dependent on the heat-treatment temperature than that in the alkaline electrolyte. In acid solution, the samples show virtually no activity unless heat treated above T_c , the temperature at which the initially amorphous samples transform to a heterogeneous mixture of β -Co and N-containing graphitic carbon. The N loss that accompanies the transformation at T_c may play a role in helping create active sites for ORR in acid solution. It is possible that small pores created by N loss are too small for the adsorption of acidic species that block catalytic sites. Thus, the sites formed in the pores that remain "clean" are active for ORR. By contrast, the heat-treated (above 500°C) samples show activity in alkaline solution regardless of whether the samples have been heated through T_c or not. We believe this is because sites are not blocked by ions in the alkaline solution. A useful experiment to do on these catalyst systems is a measurement of the ORR activity at various pH, while maintaining constant ionic strength to ensure high solution conductivity.

Careful studies of the structural and compositional changes in a series of $\text{Co}_x\text{C}_{1-x-y}\text{N}_y$ composition-spread libraries heated to various temperatures were used to determine T_c as a function of x and y . This information can be used to select appropriate heat-treatment temperatures for co-sputtered $\text{Co}_x\text{C}_{1-x-y}\text{N}_y$ materials to ensure activity in acid solution.

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Figure 13. (Color online) Contour map of T_c (in $^{\circ}\text{C}$) vs atom % N and atom % Co in the as-sputtered $\text{Co}_x\text{C}_{1-x}\text{N}_y$ libraries. Data derived from the various libraries are indicated with different symbols: $\bullet$ library 1, $\text{N}_2/\text{Ar} = 20/80$; $\blacklozenge$ library 2, $\text{N}_2/\text{Ar} = 40/60$; $\blacktriangle$ library 3, $\text{N}_2/\text{Ar} = 60/40$; $\blacktriangledown$ library 4, $\text{N}_2/\text{Ar} = 100/0$.

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Investigation of Activity of Sputtered Transition-Metal (TM)-C-N (TM = V, Cr, Mn, Co, Ni) Catalysts for Oxygen Reduction Reaction

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Variations with heat-treatment temperature of the structure and the electrocatalytic activity of sputtered transition-metal (TM)-C-N (TM = V, Cr, Mn, Co, and Ni) films for the oxygen reduction reaction (ORR) in acid and alkaline electrolytes were studied. The films prepared were all originally amorphous. At a critical heat-treatment temperature (T_c , different for each composition) substantial nitrogen release occurred and the films transformed to a heterogeneous N-containing carbon structure with either Cr_3C_2 , Co, Ni, V_3C_7 , or Mn_7C_3 , depending on the TM used. In acid electrolyte, heat-treated $\text{Cr}_x\text{C}_{1-x-y}\text{N}_y$, $\text{Co}_x\text{C}_{1-x-y}\text{N}_y$, and $\text{Ni}_x\text{C}_{1-x-y}\text{N}_y$ films began to show oxygen reduction activity at T_c , while $\text{V}_x\text{C}_{1-x-y}\text{N}_y$ and $\text{Mn}_x\text{C}_{1-x-y}\text{N}_y$ films showed little or no activity for ORR in acid electrolyte for all temperatures studied. However, all of the heat-treated $\text{TM}_x\text{C}_{1-x-y}\text{N}_y$ (TM = V, Cr, Mn, Co, and Ni) films showed oxygen reduction activity in alkaline electrolyte even when heated to temperatures below T_c . Because all the $\text{TM}_x\text{C}_{1-x-y}\text{N}_y$ films heated above T_c contained N-containing carbon, the activity of heat-treated sputtered C_{1-x}N_x and C films, as well as graphite powder, were studied for comparison. Their activities were much lower in acid electrolyte than those of the $\text{Cr}_x\text{C}_{1-x-y}\text{N}_y$, $\text{Co}_x\text{C}_{1-x-y}\text{N}_y$, and $\text{Ni}_x\text{C}_{1-x-y}\text{N}_y$ films heat-treated at the same temperatures. C_{1-x}N_x films, C films, and graphite powder all showed activity in alkaline electrolyte but were less active than some heated $\text{Co}_x\text{C}_{1-x-y}\text{N}_y$ and $\text{Ni}_x\text{C}_{1-x-y}\text{N}_y$ films. The choice of TM and the heat-treatment temperature played important roles in determining the activity of the sputtered $\text{TM}_x\text{C}_{1-x-y}\text{N}_y$ films for ORR in acid and alkaline electrolytes. The corrosion stability of the heat-treated $\text{TM}_x\text{C}_{1-x-y}\text{N}_y$ libraries was studied as well. Heat-treated $\text{Cr}_x\text{C}_{1-x-y}\text{N}_y$ libraries showed good passivation against corrosion.
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The increasing need for polymer electrolyte membrane fuel cells (PEMFCs) as power sources for residential and transportation applications has intensified research on the oxygen reduction catalysts used in these cells. So far, Pt and Pt-alloy catalysts are the best electrocatalysts for the oxygen reduction reaction (ORR) due to their ability to reduce oxygen efficiently to water in a four-electron reduction. However, Pt is expensive and of limited availability. The replacement of Pt by non-noble metal catalysts could lead to significant cost reduction in PEMFCs and is desirable, provided that similar area-specific catalytic activity can be obtained.^{1,2}

Comprehensive reviews on the development of non-noble catalysts for PEMFCs have been published recently.²⁻⁴ Heat-treating carbon-supported transition-metal (TM) and nitrogen-containing complexes⁵⁻¹³ or TM salts¹⁴⁻¹⁶ in inert gas, ammonia, or acetonitrile vapor has led to promising ORR electrocatalysts. Dodelet and co-workers proposed that FeN_2/C and FeN_4/C or CoN_4/C active sites exist in Fe-based¹⁷ and Co-based catalysts,¹⁸ based on time-of-flight secondary ion mass spectrometry (TOF SIMS) results. Recently, Ozkan et al.¹⁹⁻²¹ and Stevenson et al.²² proposed that a metal site is not needed for ORR and that the active sites are located on the edge planes of nitrogen-containing carbon. Popov et al.²³ proposed that active sites with pyridinic nitrogen are responsible for the catalytic ORR activity. Although the nature of the active sites for ORR is not yet clear, the choice of TM, the nitrogen content, the carbon type, and the preparation method are all believed to influence the formation of the active sites and thus the activity of the catalysts.

The influence of the central metal ion of N_4 -phthalocyanines on ORR activity was reported to vary as $\text{Fe} > \text{Co} > \text{Ni} > \text{Cu} \approx \text{Mn}$.²⁴ Chu and Jiang investigated the ORR catalytic activity of a series of heat-treated TM (V, Mn, Fe, Co, Ni, Cu, and Zn) tetraphenylporphyrin (TPP) and binary TM TPP (V/Fe, Co/Fe, Ni/Fe, and Cu/Fe). All of these heat-treated TM TPP showed high activity except for metal-free TPP and ZnTPP. Heat-treated FeTPP/CoTPP was shown to be the best ORR catalyst.²⁵ Dodelet et al. studied the ORR activity of Ti, V, Cr, Mn, Fe, Co, Ni, Cu, and Mo-based catalysts prepared by adsorbing various TM hydroxides or acetates on carbon blacks or perylenetetracarboxylic dihydride (PTCDA) followed by

pyrolysis in acetonitrile vapor or ammonia at elevated temperature.²⁶ The activity of Cr, Mn, Fe, and Co-based catalysts decreased according to the following sequence: $\text{Fe} > \text{Co} > \text{Cr} > \text{Mn}$. The other metal-based materials showed little activity.^{26,27} Recently, carbon-supported Ru-chelate and Ru-based bimetallic electrocatalysts that produced only 2–3% H_2O_2 were reported by Popov and co-workers, which suggests that the central metal plays an important role in the catalytic activity.^{28,29}

Active Fe-C-N and Co-C-N thin-film electrocatalysts prepared by combinatorial magnetron sputter deposition method in our lab showed excellent ORR activity in acid electrolyte after heat-treatment in inert gas.³⁰⁻³³ In our previous work,³⁰⁻³³ the effect of heat-treatment temperature on the composition, structure, and ORR catalytic activity of sputtered Fe-C-N (acid electrolyte) and Co-C-N (acid and alkaline electrolyte) was studied in detail. In this paper, the effect of TM choice and heat-treatment temperature on the catalytic activity in acid and alkaline electrolytes and corrosion stability of sputtered TM-C-N (TM = V, Cr, Mn, Co, and Ni) films are reported. Results for TM = Fe are not included here because the sputtered Fe-C-N and Co-C-N catalysts showed similar trends in the variation of the ORR activity with the metal (Fe or Co) content and the heat-treatment temperature, which was reported in a previous paper.³¹ Comparisons to the activities of sputtered $\text{Co}_x\text{C}_{1-x}\text{N}_x$, and C films, as well as powdered graphite, are made as well in this paper.

Experimental

Deposition of thin-film samples.—The V, Cr, Mn, and Co sputtering targets (2.00 in. diameter, 0.250 in. thick, and 99.95% pure) were obtained from Williams Advanced Materials (Buffalo, NY). The Ni target (2.00 in. diameter, 0.039 in. thick, and 99.99% pure) was obtained from Advent Research Materials (Eyansham, Oxford, U.K.). The C sputtering target (2.00 in. diameter, 0.250 in. thick, and 99.999% pure) was obtained from Kurt J. Lesker Co. (Clairton, PA). All targets, with the exception of Ni, were mounted on 0.125 in. thick copper backing plates using SilverTech PT-1 silver epoxy from Williams Advanced Materials. The Ni target was held in place on the copper backing plate by the magnetic field from the magnetron itself. V, Cr, Mn, Co, Ni, and C were sputtered using MDX-1K DC (Advanced Energy) power supplies with powers of 41, 33, 15, 15, 15, and 150 W, respectively. Specially designed

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Table I. The composition and film thickness of the as-sputtered composition spreads and the constant-composition samples.

	As-sputtered composition spreads					
	V-C-N		Cr-C-N		Mn-C-N	
	Minimum	Maximum	Minimum	Maximum	Minimum	Maximum
Composition Thickness (nm)	$V_{0.6}C_{75.7}N_{23.7}$ 170 ± 2	$V_{6.1}C_{51.1}N_{42.8}$ 350 ± 2	$Cr_{0.4}C_{77.1}N_{22.5}$ 169 ± 2	$Cr_{7.0}C_{46.9}N_{46.1}$ 380 ± 2	$Mn_{0.3}C_{74.3}N_{25.4}$ 173 ± 2	$Mn_{6.4}C_{49.3}N_{44.3}$ 383 ± 2
As-sputtered constant composition samples						
Composition Thickness (nm)	$V_{9.4}C_{47.4}N_{43.2}$ 421 ± 2	$Cr_{11.4}C_{47.2}N_{41.3}$ 408 ± 2	$Mn_{9.7}C_{52.7}N_{37.6}$ 463 ± 2	$Co_{9.2}C_{57.3}N_{33.5}$ 390 ± 2	$Ni_{10.1}C_{50.5}N_{39.4}$ 403 ± 2	$Co_{6.1}N_{38.9}$ 135 ± 2
						$C_{61.1}N_{38.9}$ 72 ± 2
						$Ni_{7.4}C_{57.3}N_{35.3}$ 288 ± 2

masks were positioned in front of each target to produce the desired composition variations, while the substrate table was rotated. More details about the production of binary and pseudo-binary composition spreads using our equipment can be found elsewhere.³⁴ For the constant composition samples, “constant” masks³⁴ were used in front of both C and TM targets. For the composition spread libraries produced, a constant mask was used for the carbon target and a “linear out” mask was used for the TM target.³⁴

Nitrogen was incorporated into the libraries by sputtering in an Ar/N₂ gas mixture.³⁰⁻³³ Gas flows were independently controlled using MKS mass-flow controllers. Ultrahigh-purity Ar (99.999%) and N₂ (99.999%) were supplied at constant flow rates during the sputtering. One composition spread and one constant composition sputtering run was completed for each TM-C-N system. The composition-spread run for each TM-C-N system was sputtered under 7.5 sccm Ar and 2.0 sccm N₂, which corresponds to a total pressure of 0.277 Pa (2.10 mTorr) with N₂/Ar = 20:80. The constant composition run for each TM-C-N system was sputtered under 4.5 sccm Ar and 3.0 sccm N₂, which corresponds to a total pressure of 0.224 Pa (1.70 mTorr) with N₂/Ar = 40:60.

The constant composition C_{1-x}N_x film was sputtered under 4.5 sccm Ar and 3.0 sccm N₂. The constant composition C film was sputtered under 7.2 sccm Ar, which corresponds to a total pressure of 0.224 Pa (1.70 mTorr). For the purpose of comparison of activities in alkaline solution, a constant composition Co film was also sputtered under 6.6 sccm Ar, which corresponds to a total pressure of 0.216 Pa (1.64 mTorr).

The composition-spread and constant composition samples for each TM-C-N system were deposited onto a number of 80 × 15 mm SiO₂-coated Si(100) wafer strips (500 nm thick layer of SiO₂) for heat-treatment, grazing incidence X-ray diffraction (XRD) measurements (constant composition sample only), electron microprobe analysis, and film thickness determination and a number of 5 mm diameter glassy carbon (GC) disks (Tokai Carbon Co.) for electrochemical measurements using the rotating ring-disk electrode (RRDE) technique. Similar sputtering-table layouts were used for the C_{1-x}N_x, C, and Co films. The TM-C-N composition spread was also deposited onto 80 × 10 mm quartz substrates for heat-treatment and corrosion testing. More details about the various substrates mounted on the substrate table as well as a projection of the targets and their associated masks on the substrate table can be found elsewhere.³²

The TM_xC_{1-x-y}N_y, C_{1-x}N_x, and C films deposited on the SiO₂-coated Si(100) wafer strips, GC disks, and quartz substrates were heat-treated at different temperatures in Ar using a Modular Process Technology RTP-600S rapid thermal processor (RTP). The samples were heated at 5°C s⁻¹ in flowing Ar (2 L min⁻¹) and held at the target temperature for 5 min before cooling.

Composition of the sputtered samples.— The composition of the sputtered samples was measured using a JEOL JXA-8200 superprobe electron microprobe system equipped with one energy dispersive (EDS) spectrometer and five wavelength dispersive (WDS) spectrometers. The standards used were: Silicon nitride (Si₃N₄) for N; V, Cr, and Ni metals for V, Cr, and Ni, respectively; MnO₂ for Mn; a Mn-Co alloy (Mn:Co = 30:70 by weight) for Co; and pyrolytic graphite for C. Overlap of the N(Kα) and Co[L_β(2)] lines was carefully considered and accommodated. TM (V, Cr, Mn, Co, and Ni), N, and C atomic compositions were all determined by WDS detectors. An accelerating voltage of 3 kV was employed to eliminate the effect of the substrate on the measurement. The analysis spot size was 50 μm. The composition was measured every 2 mm along the 76 mm long composition-spread samples before and after various heat-treatments. The composition of the as-sputtered composition-spread and constant composition samples are reported in Table I.

Thickness of the sputtered samples.— The thickness of the composition-spread and constant composition samples sputtered on Si

AQ: #1

170 wafers was determined using a Dektak 8 Advanced Development
171 Profilometer (Veeco Instruments Inc.). The film thickness was found
172 to increase linearly with increasing TM content across the
173 $\text{TM}_x\text{C}_{1-x-y}\text{N}_y$ (TM = V, Cr, Mn, Co, and Ni) films. The thicknesses
174 of the composition-spread and constant composition samples are
175 reported in Table I.

176 *Grazing incidence XRD for the constant composition sample.*—
177 The crystallographic structure of the constant composition films af-
178 ter heat-treatment to various temperatures was determined by graz-
179 ing incidence XRD using a Siemens D5000 diffractometer equipped
180 with a grazing incidence attachment. Cu K α radiation was used at
181 an incidence angle of 0.5° and with divergence slits set to 0.1°. Such
182 conditions lead to an illuminated spot of 40 × 12 mm in the center
183 of the 80 × 15 mm constant-composition specimen. A Soller slit
184 box in front of the detector was used to ensure that the scattered
185 X-rays from this large illuminated sample area that entered the de-
186 tector all had the same scattering angle. Data were collected over a
187 scattering angle range of 10–80° at 0.05° intervals. Total scan times
188 varied from 8 to 12 h.

189 *Electrochemical characterization.*— The $\text{TM}_x\text{C}_{1-x-y}\text{N}_y$ (TM =
191 V, Cr, Mn, Co, and Ni), C_{1-x}N_x , C, and Co films were sputtered
192 directly on GC disks as described in the Deposition of thin-film
193 samples section. The loading of $\text{V}_x\text{C}_{1-x-y}\text{N}_y$, $\text{Cr}_x\text{C}_{1-x-y}\text{N}_y$,
194 $\text{Mn}_x\text{C}_{1-x-y}\text{N}_y$, $\text{Co}_x\text{C}_{1-x-y}\text{N}_y$, $\text{Ni}_x\text{C}_{1-x-y}\text{N}_y$, C_{1-x}N_x , C, and Co films
195 on the GC disks were 79, 75, 67, 56, 63, 50, 42, and 24 $\mu\text{g cm}^{-2}$,
196 respectively. The electrochemical properties of a graphite powder
197 sample (Fluka, 50870 graphite) were also measured for comparison.
198 An ink of graphite was prepared by mixing 10 mg of powder, 95 μL
199 of Nafion solution (5% wt from Aldrich), and 350 μL of ethanol,
200 followed by ultrasonication for 40 min. Seven μL of ink was pipet-
201 ted onto a GC disk, resulting in a graphite powder loading of
202 780 $\mu\text{g cm}^{-2}$.

203 The electrocatalytic activity for the ORR of the samples on the
204 GC disks was studied with the RRDE technique using a Pine Elec-
205 trochemical system (AFMSRX rotator and AFCBP1 bipotential
206 stat). The RRDE electrode consisted of a catalyst film-coated GC
207 disk (5 mm diameter) surrounded by a Pt ring (7.5 mm inside diam-
208 eter and 8.5 mm outer diameter). The electrochemical measurements
209 were made in a one-compartment cell. The electrolyte was either a
210 0.1 M HClO_4 solution or a 0.1 M KOH solution prepared from
211 double-distilled HClO_4 (GFS Chemicals Inc.) or KOH (GFS Chemi-
212 cals Inc.) and 18 M Ω Barnstead NANOpure water. A Pt-wire
213 counter electrode and Koslow Hg/ Hg_2SO_4 reference electrode (used
214 in 0.1 M HClO_4 solution) or Ag/AgCl reference electrode (Bioana-
215 lytical Systems, Inc., used in 0.1 M KOH solution) were used for
216 the measurements. The potential of the Hg/ Hg_2SO_4 and Ag/AgCl
217 reference electrodes were calibrated vs the reversible hydrogen elec-
218 trode (RHE). The potentials reported in this study all refer to that of
219 the RHE potential.

220 The samples on the GC disks were first electrochemically
221 cleaned by sweeping the potential between 0 and 1.0 V (vs RHE) at
222 50 mV s^{-1} in an Ar-saturated 0.1 M HClO_4 solution or 0.1 M KOH
223 solution until steady-state cyclic voltammograms (CVs) were ob-
224 tained. For each catalyst tested, a CV was first collected in Ar-
225 saturated 0.1 M HClO_4 solution or 0.1 M KOH solution from
226 1.0 to 0.05 V at 5 mV s^{-1} to determine the nonfaradaic current. The
227 CVs during oxygen reduction in 0.1 M HClO_4 or 0.1 M KOH so-
228 lution were performed between 1.0 and 0.05 V at 5 mV s^{-1} with the
229 electrode stationary and with the electrode rotated at 900 rpm. O_2
230 gas was purged into the solution at a rate of 1 L min^{-1} . The faradaic
231 current was determined by subtracting the CV in Ar-saturated 0.1 M
232 HClO_4 or 0.1 M KOH solution from that obtained in O_2 -saturated
233 0.1 M HClO_4 solution or 0.1 M KOH solution. The onset potential,
234 at which the current for oxygen reduction is first observed,⁴ was
235 determined by the point of intersection of two tangent lines, one
236 drawn parallel to the baseline (i.e., from 0.9 V to approximately
237 0.8 V) and the second parallel to the increasing current signal. For

all the measurements, the ring potential was held at 1.2 V vs RHE in
order to oxidize any H_2O_2 ³⁵ produced in acid solution and HO_2^{36}
produced in alkaline solution. The % H_2O_2 produced in acid solu-
tion (or % HO_2 produced in alkaline solution) was calculated using
the following equation^{11,35,37}

$$\% \text{H}_2\text{O}_2 = 100 \frac{2I_R/N}{I_D + (I_R/N)} \quad [1]$$

where I_D is the faradaic current at the disk, I_R is the faradaic current
at the ring, and $N = 0.2$ is the RRDE collection efficiency.

Corrosion testing.— Thin-film composition-spread samples of
 $\text{TM}_x\text{C}_{1-x-y}\text{N}_y$ (TM = V, Cr, Mn, Co, and Ni) on quartz strips heated
at 700, 800, and 1000°C were immersed in 0.5 M H_2SO_4 (reagent,
analytical grade) at 25°C for 1 week. Separate $\text{Cr}_x\text{C}_{1-x-y}\text{N}_y$
composition-spread films heated at 700, 800, and 1000°C were im-
mersed in 0.5 M H_2SO_4 solution at 80°C for 1 week. After treat-
ment, the samples were rinsed with NANOpure water and dried in
air for further study. The composition as a function of position was
measured and compared to the composition measured before acid
treatment.

Results

*Composition of the thin-film $\text{TM}_x\text{C}_{1-x-y}\text{N}_y$ (TM = V, Cr, Mn,
Co, and Ni) libraries.*— The N content vs TM content in the as-
sputtered $\text{TM}_x\text{C}_{1-x-y}\text{N}_y$ films and those heat-treated subsequently at
700, 800, or 1000°C is shown in Fig. 1. For the as-sputtered
 $\text{TM}_x\text{C}_{1-x-y}\text{N}_y$ films, the atomic fraction of N varies smoothly from
0.186 to 0.406 for $\text{V}_x\text{C}_{1-x-y}\text{N}_y$, from 0.225 to 0.461 for
 $\text{Cr}_x\text{C}_{1-x-y}\text{N}_y$, from 0.254 to 0.445 for $\text{Mn}_x\text{C}_{1-x-y}\text{N}_y$, from 0.184 to
0.320 for $\text{Co}_x\text{C}_{1-x-y}\text{N}_y$, and from 0.189 to 0.362 for $\text{Ni}_x\text{C}_{1-x-y}\text{N}_y$.
The variation of N content with heat-treatment temperature in these
 $\text{TM}_x\text{C}_{1-x-y}\text{N}_y$ films shows one striking feature: the N content de-
creases as heat-treatment temperature increases. However, the
amount of nitrogen lost depends on both the choice of TM and the
heat-treatment temperature.

$\text{V}_x\text{C}_{1-x-y}\text{N}_y$, $\text{Cr}_x\text{C}_{1-x-y}\text{N}_y$, and $\text{Mn}_x\text{C}_{1-x-y}\text{N}_y$ do not lose much
nitrogen when heated to 700°C. The N content decreases sharply at
about 1.2% with respect to Co for $\text{Co}_x\text{C}_{1-x-y}\text{N}_y$ and at about 1.5%
with respect to Ni for $\text{Ni}_x\text{C}_{1-x-y}\text{N}_y$ heated to 700°C. $\text{V}_x\text{C}_{1-x-y}\text{N}_y$
and $\text{Mn}_x\text{C}_{1-x-y}\text{N}_y$ libraries still retain significant nitrogen when
heated to 800°C, with $\text{Mn}_x\text{C}_{1-x-y}\text{N}_y$ retaining more nitrogen than
 $\text{V}_x\text{C}_{1-x-y}\text{N}_y$. $\text{Cr}_x\text{C}_{1-x-y}\text{N}_y$, $\text{Co}_x\text{C}_{1-x-y}\text{N}_y$, and $\text{Ni}_x\text{C}_{1-x-y}\text{N}_y$ lose nitro-
gen, in a “knee-shaped” transition when heated to 800°C, at about
3.8% with respect to Cr for the $\text{Cr}_x\text{C}_{1-x-y}\text{N}_y$ film, 0.7% with respect
to Co for the $\text{Co}_x\text{C}_{1-x-y}\text{N}_y$ film, and about 1.5% with respect to Ni
for the $\text{Ni}_x\text{C}_{1-x-y}\text{N}_y$ film. The thermal stability of the sputtered
 $\text{TM}_x\text{C}_{1-x-y}\text{N}_y$ libraries decreases in the order of $\text{Co} < (\approx) \text{Ni}$
 $< \text{Cr} < \text{V} < \text{Mn}$.

*Electrocatalytic activity of the sample that showed the highest
activity in each $\text{TM}_x\text{C}_{1-x-y}\text{N}_y$ library after heat-treatment.*— Fif-
teen GC disks, as three repeats for five different compositions, were
included in each preparation of the composition-spread
 $\text{TM}_x\text{C}_{1-x-y}\text{N}_y$ libraries. One group of five disks was heated to
700°C, one group of five disks was heated to 800°C, and the final
group of five disks was heated to 1000°C. The activity of the sput-
tered films on all 15 disks (15 disks for each of the five choices of
TM = a total of 75 disks) was measured in acid solution. The com-
position of the most active GC disk sample for a given TM is indi-
cated by circles in Fig. 1.

Figure 2 shows the CVs of the sample on the GC disk that
showed the highest activity in each $\text{TM}_x\text{C}_{1-x-y}\text{N}_y$ film after heat-
treatment measured in O_2 -saturated 0.1 M HClO_4 solution at 25°C.
No other data is shown in order to limit the amount of data pre-
sented in this paper to a manageable level. The TM content (shown
on each panel in Fig. 2) for the most active compositions in the
samples varied only between 10.0 and 11.8%. The heat-treatment

Figure 1. (Color online) Atomic % N vs atomic % TM for $\text{TM}_x\text{C}_{1-x-y}\text{N}_y$ library before and after heat-treatment at 700, 800, and 1000°C. TM = (a) V, (b) Cr, (c) Mn, (d) Co, and (e) Ni. The balance of the composition is carbon. The circle-shaped data points indicate the compositions of the sample that showed the highest activity for ORR in acidic electrolyte in each $\text{TM}_x\text{C}_{1-x-y}\text{N}_y$ library.

temperature for the most active sample was 800°C for $\text{Cr}_x\text{C}_{1-x-y}\text{N}_y$, $\text{Co}_x\text{C}_{1-x-y}\text{N}_y$, and $\text{Ni}_x\text{C}_{1-x-y}\text{N}_y$ and 1000°C for $\text{V}_x\text{C}_{1-x-y}\text{N}_y$ and $\text{Mn}_x\text{C}_{1-x-y}\text{N}_y$. Notice from Fig. 1 that $\text{V}_x\text{C}_{1-x-y}\text{N}_y$ and $\text{Mn}_x\text{C}_{1-x-y}\text{N}_y$ only lose substantial N when heated above 800°C, whereas the Cr, Co, and Ni-based libraries had already lost substantial N when heated to 800°C. For all TMs tested, the most active sample was found to be that with the highest metal content of the disks tested and after heating to a temperature at which substantial N loss had occurred. The activity of the samples toward ORR decreases in the order of $\text{Co} > \text{Cr} > \text{Ni} > \text{Mn} > \text{V}$. $\text{V}_{11.3}\text{C}_{88.6}\text{N}_{0.1}$ shows little or no activity. The onset potential of $\text{Co}_{10.0}\text{C}_{87.3}\text{N}_{2.7}$ is about 0.76 V vs RHE.

In order to investigate the dependence of the activity of the $\text{TM}_x\text{C}_{1-x-y}\text{N}_y$ films on the heat-treatment temperature in detail, constant-composition $\text{TM}_x\text{C}_{1-x-y}\text{N}_y$ films with nominally the same value of x ($x = 0.10$) were prepared and heat-treated at a closely spaced series of temperatures. The atomic TM content, shown in Table I, in the as-sputtered films was measured to lie between 9.2 and 11.4%. Constant-composition C_{1-x}N_x (composition included in Table I) and C films were also prepared for comparison.

Electrocatalytic activity of the constant-composition $\text{TM}_x\text{C}_{1-x-y}\text{N}_y$, C_{1-x}N_x and C samples heat-treated at different temperatures.—Figures 3-7 show the variation with heat-treatment temperature of the N content, onset potentials, and the current densities at fixed potentials (vs RHE) for the ORR measured in O_2 -saturated 0.1 M HClO_4 and/or O_2 -saturated 0.1 M KOH solution at 25°C for the constant composition TM-C-N films. The potentials for comparing the current densities vs heat-treatment temperature were selected to be about 0.1 V below the onset potential of the best sample for each TM.

The data for the constant-composition V-C-N film presented in Fig. 3 shows that there is a dramatic decrease in the N content at $T_c = 825^\circ\text{C}$. The onset potential of the film in alkaline electrolyte does not change significantly with heat-treatment temperature between 650 and 1000°C, although the maximum occurs for the sample heat-treated at 900°C. The current density in alkaline solution at 0.6 V increases slightly between 650 and 825°C (T_c) and then increases significantly above T_c , with the maximum around 900°C. The significant increase in activity above T_c could be caused by the porosity induced by the N loss at T_c that would increase the surface area. The constant-composition V-C-N film shows little or no activity in acid solution before or after heat-treatment.

There is a dramatic decrease in N content at $T_c = 850^\circ\text{C}$ for the Mn-C-N film (Fig. 4). The onset potential in alkaline electrolyte increases with heat-treatment temperature between 600 and 900°C, with the maximum occurring for the sample heat-treated at 900°C. The current density at 0.6 V increases slightly between 600 and 850°C (T_c) and then increases significantly above T_c with the maximum occurring at 900°C. The constant-composition Mn-C-N film shows little or no activity in acid solution before and after heat-treatment, which is similar to the V-C-N film.

For the constant-composition Cr-C-N film (Fig. 5), there is a dramatic decrease in N content at $T_c = 800^\circ\text{C}$. The onset potential for ORR in acid solution increases with the heat-treatment temperature between 775 and 850°C, as the catalyst becomes active above

Figure 2. Disk current densities for the samples on GC disks that showed the highest activity in an acidic environment for ORR in the $\text{TM}_x\text{C}_{1-x-y}\text{N}_y$ libraries. TM = (a) V, (b) Cr, (c) Mn, (d) Co, and (e) Ni. The measurement was performed in O_2 -saturated 0.1 M HClO_4 at 25°C. The sweep rate was 5 mV s^{-1} and the rotation speed was 900 rpm. The average composition of the film on each disk is indicated in each panel.

Figure 3. (a) N content, (b) onset potential, and (c) current density at 0.6 V for ORR in 0.1 M KOH solution vs heat-treatment temperature of the $V_xC_{1-x-y}N_y$ samples. The samples were derived from the constant-composition sample described in Table I.

Figure 4. (a) N content, (b) onset potential, and (c) current density at 0.6 V for ORR in 0.1 M KOH solution vs heat-treatment temperature of the $Mn_xC_{1-x-y}N_y$ samples. The samples were derived from the constant-composition sample described in Table I.

$T_c = 800^\circ\text{C}$. The onset potential decreases slightly with heat-treatment temperature above 850°C . The film begins to show activity at a lower temperature (700°C) in 0.1 M KOH solution than in 0.1 M HClO_4 solution. The onset potential measured in 0.1 M KOH solution increases with heat-treatment temperature between 700 and 800°C and then does not change much, although the maximum occurs for the sample heat-treated at 900°C . The current density at 0.6 V in acid electrolyte is strongly dependent on the heat-treatment temperature, reaching a maximum for the sample heat-treated at 850°C . The current density at 0.6 V in the alkaline electrolyte increases between 700 and 800°C and then does not change significantly, although, as with the testing in acid, the maximum occurs for the sample heat-treated at 900°C .

There is a dramatic decrease in N content at $T_c = 725^\circ\text{C}$ for the constant-composition Co-C-N film (Fig. 6). The onset potential for ORR in acid increases with the heat-treatment temperature between 700 and 800°C , as the catalyst becomes active above $T_c = 725^\circ\text{C}$. The maximum onset potential occurs for the film heat-treated at 800°C . The samples begin to show activity at a lower heat-treatment temperature (650°C) in 0.1 M KOH solution than in 0.1 M HClO_4 solution. The maximum onset potential in alkaline solution occurs for the sample heat-treated at 850°C . The current density at 0.7 V in acid electrolyte is strongly dependent on the heat-treatment temperature, reaching a maximum for the sample heat-treated at 800°C . The maximum current density at 0.7 V in alkaline electrolyte occurs for the sample heat-treated at 850°C . The observation that the Co-C-N film starts to show activity at T_c in acid solution and below T_c in alkaline solution is similar to that seen for the Cr-C-N film.

For the constant-composition Ni-C-N film, there is a dramatic decrease in N content at $T_c = 725^\circ\text{C}$. The onset potential for ORR in acid increases with the heat-treatment temperature between 700 and

850°C , as the catalyst becomes active above $T_c = 725^\circ\text{C}$. The maximum onset potential and current density at 0.5 V in acid solution occurs for the film heat-treated at 850°C . The maximum onset potential and the current density at 0.6 V in alkaline solution occurs for the film heat-treated at 900°C ; however, the film begins to show activity at a lower temperature (650°C), i.e., below T_c , in 0.1 M KOH solution than in 0.1 M HClO_4 solution. In addition, the ORR activity of the film in alkaline solution is much higher than that in acid solution. This is similar to the behavior of the Co-C-N and Cr-C-N films. In our previous work on the activity of sputtered Co-C-N films in acid and alkaline solutions, we noted³³ that there were samples heated to just below T_c that were active in alkaline solution but not in acid solution. We speculated that small pores created by N loss above T_c are too small for the adsorption of acidic species that block catalytic sites, so the films become active above T_c in acid. We further speculated that the sites are not blocked by ions in the alkaline solution regardless of whether or not the samples have been heated through T_c .

The activity for the ORR, the optimum heat-treatment temperature, and the composition of the most active sample in the constant-composition TM-C-N (TM = V, Cr, Mn, Co, and Ni) films in acid and alkaline solution are summarized in Table II. In 0.1 M HClO_4 solution, the activity of the most active heat-treated sample in TM-C-N (TM = Cr, Co, and Ni) follows the order $\text{Co} > \text{Cr} > \text{Ni}$. In 0.1 M KOH solution, the activity of the most active heat-treated sample in TM-C-N (TM = V, Cr, Mn, Co, and Ni) follows the order $\text{Co} > \text{Ni} > \text{Mn} > \text{V} > \text{Cr}$.

Figure 8 shows the CV and the percentage of HO_2^- (% HO_2^-) produced at the disk electrode vs the disk potential for the most active heat-treated V-C-N and Mn-C-N samples, whose compositions are given in Table II, measured in O_2 -saturated 0.1 M KOH

Figure 5. (a) N content, (b) onset potential, and (c) current density at 0.6 V for ORR in 0.1 M HClO₄ and 0.1 M KOH solution vs heat-treatment temperature of the Cr_xC_{1-x-y}N_y samples. The samples were derived from the constant-composition sample described in Table I.

Figure 6. (a) N content, (b) onset potential, and (c) current density at 0.7 V for ORR in 0.1 M HClO₄ and 0.1 M KOH solution vs heat-treatment temperature of the Co_xC_{1-x-y}N_y samples. The samples were derived from the constant-composition sample described in Table I.

418 solution at 25°C. No well-defined diffusion-limited current is
419 reached, although there is a plateau between 0.4 and 0.6 V in the
420 CV curves in both cases. For V-C-N, the percentage of HO₂⁻
421 (% HO₂⁻) first increases as the disk potential decreases and reaches
422 95.0% at 0.60 V and then decreases with the disk potential. For
423 Mn-C-N, the percentage of HO₂⁻ (% HO₂⁻) first increases as the
424 disk potential decreases and reaches about 55% at 0.50 V, and then
425 does not change much with the disk potential. The fraction of per-
426 oxide produced is very large.
427 Figure 9 shows the CVs and the percentage of H₂O₂ (% H₂O₂)
428 (in acid solution) and HO₂⁻ (% HO₂⁻) (in alkaline solution) produced
429 at the disk electrode vs the disk potential for the most active heat-
430 treated Cr-C-N, Co-C-N, and Ni-C-N samples, whose composi-
431 tions are given in Table II, measured in O₂-saturated 0.1 M HClO₄
432 solution and in O₂-saturated 0.1 M KOH solution at 25°C. No well-
433 defined diffusion-limited current is reached for ORR over the poten-
434 tial range measured in the CV curves in acid and alkaline solution
435 for the Cr-C-N, Co-C-N, and Ni-C-N samples. For Cr-C-N, the
436 activity in acid and alkaline solution are similar. The % HO₂⁻ (about
437 85% between 0.6 and 0.3 V) produced in alkaline solution is higher
438 than the % H₂O₂ (about 65% between 0.6 and 0.3 V) produced in
439 acid solution. For Co-C-N, the CV curve in acid solution shows two
440 clear reduction waves. The % H₂O₂ in acid is between 22 and 50%
441 between 0.80 and 0.05 V and increases as the disk potential de-
442 creases, which correlates to the two step reduction waves in the CV
443 curve. The Co-C-N CV curve in alkaline solution shows a relatively
444 well-defined current plateau, which indicates that the activity in al-
445 kaline solution is higher than that in acid solution. The % HO₂⁻
446 increases as the disk potential decreases, reaching 55% at 0.60 V,
447 and then decreases slightly for lower disk potentials. The % HO₂⁻ is

448 between 40 and 55% between 0.70 and 0.05 V, which is slightly
449 higher than the % H₂O₂ produced in acid solution. For Ni-C-N, the
450 activity in alkaline solution is much higher than in acid solution. The
451 onset potentials measured in acid and alkaline solution are 0.60 and
452 0.84 V, respectively. The % HO₂⁻ (about 60–90% between 0.80 and
453 0.05 V) produced in alkaline solution is higher than the % H₂O₂
454 (about 40–55% between 0.60 and 0.05 V) produced in acid solution.
455 All of these thin-film catalysts produce large amounts of peroxide.

456 *Grazing incidence XRD of the constant-composition*
457 *TM_xC_{1-x-y}N_y samples heat-treated at different temperatures.*
458 Figures 10–14 show grazing incidence XRD spectra for the constant-
459 composition TM-C-N films heat-treated to a range of different tem-
460 peratures between 650 and 1000°C. In all the cases, at a critical
461 temperature (*T_c*), the film transforms to a heterogeneous mixture of
462 N-containing carbon and V₈C₇ (Fig. 10), Cr₃C₂ (Fig. 11), Mn₇C₃
463 (Fig. 12), Co (Fig. 13), or Ni (Fig. 14). The observed phases in the
464 XRD pattern of the heat-treated TM-C-N (TM = V, Cr, Mn, Co,
465 Mn, Co, and Ni) binary-phase diagrams³⁸ are summarized in Table
466 III. Previous studies on Co-C-N samples³³ have shown that *T_c* de-
467 creases with TM content and increases with N content in the films.
468 Even though the constant-composition samples were designed to
469 have similar TM and N contents in the as-sputtered state, the varia-
470 tions that exist between the samples (see Table I) make it impossible
471 to rank the five TMs for their effectiveness at catalyzing the trans-
472 formation at *T_c*. The observed phases in the heat-treated TM-C-N
473 samples are in good agreement with equilibrium-phase diagrams,
474 which indicates that heating above *T_c* causes a transformation to a
475 nanocomposite of expected equilibrium phases.
476

Figure 7. (a) N content, (b) onset potential, and (c) current density for ORR at 0.6 V in 0.1 M KOH solution or 0.5 V in 0.1 M HClO₄ vs heat-treatment temperature of the Ni_xC_{1-x-y}N_y samples. The samples were derived from the constant-composition sample described in Table I.

Figure 8. Disk current density and % HO₂⁻ produced for the heat-treated V_xC_{1-x-y}N_y and Mn_xC_{1-x-y}N_y constant-composition samples on the GC disks that showed the highest activity for ORR measured in O₂-saturated 0.1 M KOH. The measurements were performed at 25°C with a sweep rate of 5 mV s⁻¹ and rotation speed of 900 rpm. The average compositions of the films on the disks are indicated.

C_{1-x}N_x and C samples are presented and later compared to the heated TM-C-N and Co films (in alkaline solution) in the Discussion section.

Figure 15 shows the variation with heat-treatment temperature of the N content, the onset potential, and the current densities at 0.3 V for the ORR measured in O₂-saturated 0.1 M HClO₄ and the current densities at 0.6 V (vs RHE) in O₂-saturated 0.1 M KOH solution at 25°C for the constant-composition C_{61.1}N_{38.9} film (the composition shown here is for the as-sputtered sample). The N content decreases as the heat-treatment temperature increases. The onset potential for ORR in acid increases with the heat-treatment temperature in the range between 700 and 900°C and then decreases as it is heated to 1000 and 1100°C. The maximum onset potential and current density at 0.3 V in acid solution occurs for the film heat-treated to 900°C. The film begins to show activity at 400°C in 0.1 M KOH solution. The maximum onset potential and the current density at 0.6 V in alkaline solution occurs for the film heat-treated at 1000°C. The ORR activity of the film in alkaline solution is much higher than that in acid solution.

Figure 16 shows the CVs and the percentages of H₂O₂ (% H₂O₂) (in acid solution) and HO₂⁻ (% HO₂⁻) (in alkaline solution) produced at the disk electrode vs the disk potential for the constant-composition C_{61.1}N_{38.9} sample heat-treated at 900°C (i.e., the most active one in acid solution, the composition is C_{78.6}N_{21.4} after heat-treatment at 900°C) measured in O₂-saturated 0.1 M

Table II. The activity for ORR, the optimum heat-treatment temperature, and the compositions of the most active sample in the constant-composition TM-C-N (TM = V, Cr, Mn, Co, and Ni) samples in acid and alkaline solutions.

	Composition of the as-sputtered sample	T _c (°C)	Electrolyte	Optimum heat-treatment temperature (°C)	Composition of the most activesample after heat-treatment	Onset potential (V vs RHE)
V-C-N	V _{9.4} C _{47.4} N _{43.2}	825	0.1 M KOH	900	V _{13.2} C _{83.1} N _{3.7}	0.79
Cr-C-N	Cr _{11.4} C _{47.2} N _{41.3}	800	0.1 M HClO ₄	850	Cr _{14.2} C _{80.1} N _{5.7}	0.80
			0.1 M KOH	900	Cr _{14.6} C _{82.0} N _{3.4}	0.78
Mn-C-N	Mn _{9.7} C _{52.7} N _{37.6}	850	0.1 M KOH	900	Mn _{13.3} C _{83.7} N _{3.0}	0.82
Co-C-N	Co _{9.2} C _{57.3} N _{33.5}	725	0.1 M HClO ₄	800	Co _{11.5} C _{82.5} N _{6.0}	0.81
			0.1 M KOH	850	Co _{11.9} C _{82.8} N _{5.3}	0.87
Ni-C-N	Ni _{10.1} C _{50.5} N _{39.4}	725	0.1 M HClO ₄	850	Ni _{13.2} C _{82.7} N _{4.1}	0.60
			0.1 M KOH	900	Ni _{13.4} C _{83.2} N _{3.4}	0.84

Figure 9. Disk current density and % H₂O₂ (% HO₂⁻ in 0.1 M KOH) produced for the heat-treated Cr_xC_{1-x-y}N_y, Co_xC_{1-x-y}N_y, and Ni_xC_{1-x-y}N_y constant-composition samples on the GC disks that showed the highest activity for ORR measured in O₂-saturated 0.1 M HClO₄ and in O₂-saturated 0.1 M KOH. The measurements were performed at 25°C with a sweep rate of 5 mV s⁻¹ and rotation speed of 900 rpm. The average compositions of the films on the disks are indicated.

Figure 10. Grazing incidence XRD measurements showing intensity vs scattering angle for the heat-treated constant-composition sample of V-C-N. The heat-treatment was done in flowing N₂ and the heat-treatment temperature is indicated next to each curve. The major Bragg peaks of the phases present are indicated.

Figure 11. Grazing incidence XRD measurements showing intensity vs scattering angle for the heat-treated constant-composition sample of Cr-C-N. The heat-treatment was done in flowing N₂ and the heat-treatment temperature is indicated next to each curve. The major Bragg peaks of the phases present are indicated.

HClO₄ solution at 25°C and heat-treated at 1000°C (i.e., the most active one in alkaline solution, the composition is C_{88.7}N_{11.3} after heat-treatment at 1000°C) measured in O₂-saturated 0.1 M KOH solution at 25°C. The onset potentials measured for the sample heated at 900°C in acid solution and for the sample heated at 1000°C in alkaline solution are 0.40 and 0.83 V, respectively. The % HO₂⁻ (about 30–60% between 0.80 and 0.05 V) produced in alkaline solution for the sample heated at 1000°C is lower than the % H₂O₂ (about 60–77% between 0.40 and 0.05 V) produced in acid solution for the sample heated at 900°C.

Figure 17 shows the variation with heat-treatment temperature of the onset potential and the current densities at 0.6 V (vs RHE) for the ORR measured in O₂-saturated 0.1 M KOH solution at 25°C for the sputtered C film. The onset potential (0.71–0.73 V) does not change much with heat-treatment temperature in the range between 25 and 900°C and then decreases to 0.62 V when it is heated to 1000°C. The current density at 0.6 V increases slightly over the range between 25 and 800°C and then decreases at 900 and 1000°C. The C film shows little or no activity in acid solution before and after heat-treatment. Recall that the C_{1-x}N_x films heated between

Figure 12. Grazing incidence XRD measurements showing intensity vs scattering angle for the heat-treated constant-composition sample of Mn-C-N. The heat-treatment was done in flowing N₂ and the heat-treatment temperature is indicated next to each curve. The major Bragg peaks of the phases present are indicated.

Figure 13. Grazing incidence XRD measurements showing intensity vs scattering angle for the heat-treated constant-composition sample of Co-C-N. The heat-treatment was done in flowing N₂ and the heat-treatment temperature is indicated next to each curve. The major Bragg peaks of the phases present are indicated.

Figure 15. (a) N content, (b) onset potential for ORR, and (c) current density for ORR at 0.6 V in 0.1 M KOH solution or 0.3 V in 0.1 M HClO₄ vs heat-treatment temperature of the C_{1-x}N_x samples. The samples were derived from the constant-composition sample described in Table I.

Figure 14. Grazing incidence XRD measurements showing intensity vs scattering angle for the heat-treated constant-composition sample of Ni-C-N. The heat-treatment was done in flowing N₂ and the heat-treatment temperature is indicated next to each curve. The major Bragg peaks of the phases present are indicated.

Table III. The critical temperature for the phase transformation, the observed phases (from the grazing incidence XRD patterns) in the heat-treated constant-composition samples of TM-C-N (TM = V, Cr, Mn, Co, and Ni), and the equilibrium phases in the TM-C (TM = V, Cr, Mn, Co, and Ni) binary-phase diagrams.³⁶

As-sputtered sample	Critical temperature (T _c) (°C)	Observed phases	Equilibrium phases for TM-C
V _{9.4} C _{47.4} N _{43.2}	825	V ₈ C ₇ , N-carbon	V ₈ C ₇ , carbon
Cr _{11.4} C _{47.2} N _{41.3}	800	Cr ₃ C ₂ , N-carbon	Cr ₃ C ₂ , carbon
Mn _{9.7} C _{52.7} N _{37.6}	850	Mn ₇ C ₃ , N-carbon	Mn ₇ C ₃ , carbon
Co _{9.2} C _{57.3} N _{33.5}	725	Co, N-carbon	Co, carbon
Ni _{10.1} C _{50.5} N _{39.4}	725	Ni, N-carbon	Ni, carbon

heat-treated at 800°C (i.e., the most active one) measured in O₂-saturated 0.1 M KOH solution at 25°C. There are two waves in the CV curve, possibly corresponding to two active sites for the ORR, which is consistent with literature experiments on GC, on the roughened basal plane of graphite⁴³ and on the edge of pyrolytic graphite.^{44,45} The two waves were also observed in the CV curves of the as-sputtered C film and the C films heated at all temperatures up to 1000°C (not shown here). These results suggest that the as-sputtered C film and the C films heated up to 1000°C are disordered,^{42,46} which agrees with the XRD measurements on these films that show no clear Bragg peaks (not shown). The percentage of HO₂⁻ (% HO₂⁻) produced on the C film heat-treated at 800°C is about 60% between 0.60 and 0.05 V.

Figure 16. Disk current density and % H₂O₂ (% HO₂⁻ in 0.1 M KOH) produced for the heat-treated C_{1-x}N_x sample on the GC disk that showed the highest activity for ORR measured in O₂-saturated 0.1 M HClO₄ and in O₂-saturated 0.1 M KOH at 25°C. The sweep rate was 5 mV s⁻¹ and the rotation speed was 900 rpm. The average compositions of the films on the disks are indicated.

Figure 17. (a) Onset potential and (b) current density at 0.6 V for ORR in 0.1 M KOH solution vs heat-treatment temperature of the C samples. The samples were derived from the constant-composition sample.

557 Stability of the $TM_xC_{1-x-y}N_y$ films heat-treated at different tem-
 558 peratures against corrosion in acid.— Figure 19 shows the differ-
 559 ence in the atomic content of TM ($\Delta\%TM = \% \text{ of TM lost}$) before
 560 and after soaking in 0.5 M H_2SO_4 at 25°C for 1 week plotted vs the
 561 initial (before acid) atomic content of TM (%TM) in the
 562 $TM_xC_{1-x-y}N_y$ libraries heat-treated at 700, 800, and 1000°C. The
 563 films with low TM content show relatively good stability with re-
 564 spect to TM dissolution. For initial TM contents, %TM(TM
 565 = V, Mn, Co, Ni) = 1.0–1.2% and % Cr = 6.5%, little or no TM is
 566 dissolved from the films. More TM is dissolved from the films when
 567 the TM concentration is relatively high in the $TM_xC_{1-x-y}N_y$ libraries.
 568 The amount of TM dissolved ($\Delta\%TM$) from the films increases
 569 as the heat-treatment temperature increases. Especially for
 570 $Co_xC_{1-x-y}N_y$ and $Ni_xC_{1-x-y}N_y$ films heat-treated at 1000°C, Co and

Figure 18. Disk current density and % HO_2^- produced for the heat-treated C sample on the GC disk that showed that highest activity for ORR measured in O_2 -saturated 0.1 M KOH. The measurement was performed at 25°C. The sweep rate was 5 mV s^{-1} and the rotation speed was 900 rpm.

Figure 19. (Color online) The change in TM content ($\Delta\%TM = \% \text{ of transition metal lost}$) caused by soaking in 0.5 M H_2SO_4 at 25°C for 1 week vs the initial atomic content of TM (%TM) in the $TM_xC_{1-x-y}N_y$ libraries heat-treated at 700, 800, and 1000°C. TM = (a) V, (b) Cr, (c) Mn, (d) Co, and (e) Ni. The inset in (b) is $\Delta\%Cr$ before and after soaking in 0.5 M H_2SO_4 at 80°C for 1 week vs the initial % Cr in the $Cr_xC_{1-x-y}N_y$ library.

Ni are almost completely dissolved from the films at high Co and Ni
 concentrations as shown in Fig. 19d and e. Interestingly, the
 $Cr_xC_{1-x-y}N_y$ composition spread is much more stable against corrosion
 than the $V_xC_{1-x-y}N_y$, $Mn_xC_{1-x-y}N_y$, $Co_xC_{1-x-y}N_y$, and
 $Ni_xC_{1-x-y}N_y$ spreads. Only about 1.0% Cr was lost, even at high Cr
 concentration (12.1% Cr), after acid treatment at 25°C for 1 week,
 and $\Delta\%Cr$ is only about 1.5% at 12.1% Cr after acid treatment at
 80°C for 1 week, as shown in Fig. 19b. This indicates that Cr com-
 ponent in the heated $Cr_xC_{1-x-y}N_y$ film provides passivation against
 corrosion in acid solution. The stability of heated $Cr_xC_{1-x-y}N_y$ in
 acid may arise from the presence of Cr_3C_2 ⁴⁷⁻⁴⁹ in the film.

Figure 20. Disk current density of (a) sputtered C heated at 900°C, (b) sputtered C-N heated at 900°C, (c) sputtered C-N heated at 1000°C, (d) sputtered C-N heated at 1100°C, (e) graphite, (f) sputtered V-C-N heated at 900°C, (g) sputtered Cr-C-N heated at 900°C, (h) sputtered Mn-C-N heated at 900°C, (i) sputtered Co-C-N heated at 900°C, and (j) sputtered Ni-C-N heated at 900°C on the GC disks for ORR measured in O₂-saturated 0.1 M KOH. The measurement was performed at 25°C. The sweep rate was 5 mV s⁻¹ and the rotation speed was 900 rpm.

Discussion

Activity in acid solution.— The results from the previous section are summarized in this section and comparisons between the different samples are made. Heat-treated V_xC_{1-x-y}N_y and Mn_xC_{1-x-y}N_y films show little or no activity for ORR in acid electrolyte. The heat-treated Cr_xC_{1-x-y}N_y, Co_xC_{1-x-y}N_y, and Ni_xC_{1-x-y}N_y films show activity after heating to T_c and above in acid electrolyte. Heat-treated C_{1-x}N_x films show much lower activity in acid solution than the Cr_xC_{1-x-y}N_y, Co_xC_{1-x-y}N_y, and Ni_xC_{1-x-y}N_y films heat-treated at the same temperatures. The as-sputtered and heated C films show little or no activity in acid electrolyte. Therefore, it is clear that activity in acid solutions appears above T_c and for TM-C-N materials with TM = Cr, Co, and Ni. It has also been shown that active materials are produced when samples with TM = Fe are heated above T_c^{30,31} and the activity of the Fe-C-N is a bit higher than that of Co-C-N. Therefore, the activity for ORR in acid solution follows the order Fe_xC_{1-x-y}N_y > Co_xC_{1-x-y}N_y > Cr_xC_{1-x-y}N_y > Ni_xC_{1-x-y}N_y. The results show that TM plays an important role in the formation of the active site for ORR in acid solution.

Activity in alkaline solution.— All of the heat-treated TM_xC_{1-x-y}N_y (TM = V, Cr, Mn, Co, and Ni) films show activity in alkaline electrolyte when heated to some temperature below T_c. Heat-treated C_{1-x}N_x and as-sputtered or heated C films all show activity in alkaline electrolyte. What is the source of this activity?

The situation in alkaline solution is complicated, because GC,^{41,42} graphite,⁴²⁻⁴⁴ and activated carbon⁵⁰ all show significant activity for ORR. In addition, metallic Co and Ni, which convert to hydroxides or oxides in alkaline solution, also show significant activity for ORR.^{51,52} Because the TM-C-N samples are carbonaceous (though amorphous) before heating and most show evidence of N-containing graphite after heating above T_c, it is possible that their activity in alkaline solution could arise due to their carbon-containing character alone. Because the Co-C-N and Ni-C-N samples clearly contain Co or Ni after heating above T_c, their activity in alkaline solution could arise from the metal content. We acknowledge that it is difficult to be certain which sites (or combinations of sites) are active for ORR in alkaline solution in these samples. Nevertheless, some comparison graphs of the data presented in the Results section are useful.

Figure 20 compares the activities in alkaline solution of sputtered

Figure 21. Disk current density of (a) sputtered Co heated at 900°C, (b) sputtered Co-C-N heated at 900°C and (c) sputtered Co-C-N heated at 900°C and then treated by soaking in 1.0 M H₂SO₄ at 25°C for one month and at 80°C for one month on the GC disks for ORR measured in O₂-saturated 0.1 M KOH. The measurement was performed at 25°C. The sweep rate was 5 mV s⁻¹ and the rotation speed was 900 rpm.

C heated at 900°C, sputtered C_{1-x}N_x heated at 900, 1000, and 1100°C, powdered graphite, and sputtered TM_xC_{1-x-y}N_y (TM = V, Cr, Mn, Co, Ni) heated at 900°C. Results for graphite are included because graphitic carbon appears in the XRD patterns of the sputtered TM_xC_{1-x-y}N_y (TM = V, Cr, Mn, Co, Ni) films after heating above T_c (Fig. 10-14). The onset potentials of sputtered C_{1-x}N_x heated at 900, 1000, and 1100°C (curves b, c, and d in Fig. 20) are higher than that of sputtered C heated at 900°C (curve a in Fig. 20). The onset potentials of C_{1-x}N_x heated at 1000 and 1100°C are also higher than that of graphite (curve e in Fig. 20). These results suggest that N doping can improve the activity of C in alkaline solution as well as in acid solution.

The activity of activated carbon for ORR in alkaline solution reported in Ref. 50 is better than the C_{1-x}N_x samples and comparable to those of the TM-C-N samples. Note that when N is lost from TM_xC_{1-x-y}N_y and C_{1-x}N_x samples during heating, it is likely that some porosity, similar to the porosity in activated carbon, may form. Thus, the correlation of the increased activity with TM type or N content in the heated films may be a result of increased porosity or increased numbers of particular surface functional groups formed on surfaces which become exposed through N loss.

The samples that show the highest activity in Fig. 20 are the Co_xC_{1-x-y}N_y and Ni_xC_{1-x-y}N_y samples (curves i and j) heated to 900°C. These samples contain metallic Co and metallic Ni as shown in Fig. 13 and 14. It is, therefore, extremely important to compare their activity to the activity of the metals alone. Ni hydroxide⁵¹ and Co hydroxide⁵² are electroactive for ORR in alkaline solution. Pourbaix diagrams show⁵³ that Ni and Co are passivated by an oxide or hydroxide layer above ca. 0.20 and 0.15 V (vs RHE) in an alkaline solution having pH > 9, respectively.

Figure 21 shows CVs in oxygen-saturated alkaline solution for a sputtered Co film and for two samples of Co_xC_{1-x-y}N_y. The Co_xC_{1-x-y}N_y samples were a film heated at 900°C (from the constant-composition sample described in Table II) and an identical film (also heated to 900°C) that was soaked in 1.0 M H₂SO₄ at 25°C for 1 month and then at 80°C for another month to dissolve any exposed Co in the film. The activity of the heated Co_xC_{1-x-y}N_y film is higher than that of heated Co film and does not change significantly after the Co is dissolved away, indicating that other active sites account for the improved activity of the heated Co_xC_{1-x-y}N_y film (and the Ni_xC_{1-x-y}N_y film as well).

The results in Fig. 20 show that the onset potentials for ORR in alkaline solution follow the order Co_xC_{1-x-y}N_y > Ni_xC_{1-x-y}N_y > Mn_xC_{1-x-y}N_y > C_{1-x}N_x heated at 1000°C > V_xC_{1-x-y}N_y > Cr_xC_{1-x-y}N_y. The difference between the activity of C_{1-x}N_x and TM_xC_{1-x-y}N_y (TM = V, Cr, Mn, Co, and Ni) suggests that the TM may play a role in the formation of the active site for ORR. Appar-

ently, Co, Ni, and Mn are beneficial while V and Cr are not useful in the formation of active sites for ORR in alkaline solution.

To summarize, the results in this paper and in the literature suggest that the choice of TM is important in the formation of the active sites for ORR both in acid and alkaline solution. As mentioned earlier, the trends in the activities of heat-treated $\text{Cr}_x\text{C}_{1-x-y}\text{N}_y$, $\text{Co}_x\text{C}_{1-x-y}\text{N}_y$, and $\text{Ni}_x\text{C}_{1-x-y}\text{N}_y$ films in acid and alkaline solutions are different from the trends shown by heat-treated $\text{V}_x\text{C}_{1-x-y}\text{N}_y$ and $\text{Mn}_x\text{C}_{1-x-y}\text{N}_y$ films. Heat-treated $\text{Cr}_x\text{C}_{1-x-y}\text{N}_y$, $\text{Co}_x\text{C}_{1-x-y}\text{N}_y$, and $\text{Ni}_x\text{C}_{1-x-y}\text{N}_y$ films begin to show activity at T_c in acid electrolyte and show activity in alkaline electrolyte when heated to a temperature below T_c . Heat-treated $\text{V}_x\text{C}_{1-x-y}\text{N}_y$ and $\text{Mn}_x\text{C}_{1-x-y}\text{N}_y$ films show little or no activity for ORR in acid electrolyte but show activity in alkaline electrolyte when heated.

For noble-metal catalysts, the pH effect for ORR on Pt^{54} and on Ag^{55} is basically attributed to the adsorption of spectator species that either block the active sites required for adsorption of ORR intermediates or that lower the adsorption energy of the reaction intermediates. In our previous work on the activity of sputtered Co–C–N films in acid and alkaline solutions, we noted³³ that there were samples heated to just below T_c that were active in alkaline solution but not in acid solution. We speculated that small pores created by N loss above T_c are too small for the adsorption of acidic species that block catalytic sites, so the films become active above T_c in acid and the sites are not blocked by ions in the alkaline solution regardless of whether the samples have been heated through T_c .

An alternative explanation for the trends observed could be based on the onset of microporosity above T_c . The detailed studies in this work show that carbon, graphite, and CN_x are all active for ORR in the alkaline solution. More active sites appear above T_c for TM–C–N, which increase the activity in alkaline solution. Dodelet and co-workers⁵⁶ argue that microporosity is essential for the formation of MN_x catalytic sites within slit-shaped pores in carbon that are active in acid solution. Therefore, the activity in acid solution above T_c could result from the porosity created by N loss above T_c , i.e., micropores are essential to obtain catalytic activity in acid solution.⁵⁶

Heat-treated $\text{V}_x\text{C}_{1-x-y}\text{N}_y$ and $\text{Mn}_x\text{C}_{1-x-y}\text{N}_y$ films show little or no activity for ORR in acid electrolyte and show activity in alkaline solution. Apparently, V and Mn seem to show little or no ability to create the sites which are active in acid above T_c . These samples behave similarly to the heated carbon films, and it is therefore believed that their activity arises primarily from the carbon in the samples. For carbon catalysts, the pH effect is attributed to the adsorption of ORR intermediates that block the active sites at low pH.⁵⁷

Conclusion

Sputtered $\text{TM}_x\text{C}_{1-x-y}\text{N}_y$ (TM = V, Cr, Mn, Co, and Ni) films transform from an amorphous structure to a nanoscale mixture of N-containing carbon and V_8C_7 , Cr_3C_2 , Mn_7C_3 , Co, or Ni when heated above T_c . The transformation temperature, T_c , of the sputtered $\text{TM}_x\text{C}_{1-x-y}\text{N}_y$ ($x = 0.10$) films increases in the order of $\text{Co} \approx \text{Ni} < \text{Cr} < \text{V} < \text{Mn}$. No obvious structure changes were observed in the XRD patterns measured on C_{1-x}N_x and C films after heat-treatment.

The activity of the heat-treated sputtered $\text{TM}_x\text{C}_{1-x-y}\text{N}_y$, C_{1-x}N_x , and C films for ORR depends on the N doping, TM type, heat-treatment temperature, and electrolyte. Heat-treated $\text{V}_x\text{C}_{1-x-y}\text{N}_y$ and $\text{Mn}_x\text{C}_{1-x-y}\text{N}_y$ films show little or no activity for ORR in acid electrolyte. Heat-treated $\text{Cr}_x\text{C}_{1-x-y}\text{N}_y$, $\text{Co}_x\text{C}_{1-x-y}\text{N}_y$, and $\text{Ni}_x\text{C}_{1-x-y}\text{N}_y$ films begin to show activity in acid electrolyte at T_c . Heat-treated C_{1-x}N_x films show some activity in acid solution but their activities are much lower than that of the $\text{Cr}_x\text{C}_{1-x-y}\text{N}_y$, $\text{Co}_x\text{C}_{1-x-y}\text{N}_y$, and $\text{Ni}_x\text{C}_{1-x-y}\text{N}_y$ films heat-treated at the same temperatures. The as-sputtered and heated C films show little or no activity in acid electrolyte.

All the heat-treated sputtered $\text{TM}_x\text{C}_{1-x-y}\text{N}_y$ (TM = V, Cr, Mn,

Co, and Ni) films show activity in alkaline electrolyte when heated to a temperature below T_c . Heat-treated C_{1-x}N_x and as-sputtered or heated C films all show activity in alkaline electrolyte. Because disordered carbons, graphite, and transition metals all show activity for ORR in alkaline electrolyte, it is difficult to make conclusive statements about the results in alkaline electrolyte. However, heat-treated Co–C–N samples which were acid-etched for 2 months still showed equivalent ORR to fresh heat-treated samples, suggesting the Co metal, formed after heating above T_c , is not involved in the most active sites.

Corrosion-stability experiments on the heat-treated $\text{TM}_x\text{C}_{1-x-y}\text{N}_y$ (TM = V, Cr, Mn, Co, and Ni) libraries showed that the heat-treated $\text{Cr}_x\text{C}_{1-x-y}\text{N}_y$ libraries show good passivation against corrosion, which is believed to be provided by the Cr component. This suggests that combining Cr into $\text{TM}_x\text{C}_{1-x-y}\text{N}_y$ (TM = Fe or Co) films may improve the stability of the films against corrosion and could increase catalyst lifetime in PEMFC applications.

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Fe-C-N Oxygen Reduction Catalysts Prepared by Mechanochemical Reaction

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Abstract

Fe-C-N oxygen reduction catalysts were prepared by mechanochemical reaction of Fe_xN ($x = 2-4$) and graphite under Ar using high-energy ball milling. The activity of the catalyst towards the oxygen reduction reaction (ORR) depends on the ball milling time and on the Fe_xN precursor content. Heat-treatment up to 600°C doesn't significantly affect the activity but the activity strongly decreases as the samples are heat-treated above 800°C in argon. The onset potential of a typical sample ball-milled for 12 hrs is 0.72 V vs.RHE. About 20% of the product of oxygen reduction is H_2O_2 and the other 80% is water. The X-ray diffraction pattern (XRD) of the ball milled material shows the formation of Fe_7C_3 and disordered carbon, which presumably contains nitrogen, since the ball mills are sealed and the nitrogen cannot escape. This work demonstrates that mechanochemical synthesis is a useful technique for the preparation of Fe-C-N ORR catalysts.

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Introduction

The increasing need for polymer electrolyte membrane fuel cells (PEMFCs) as power sources for residential, transportation and portable applications has intensified research on the oxygen reduction catalysts used in these cells. So far Pt and Pt-alloy catalysts are the best electrocatalysts for the oxygen reduction reaction (ORR) due to their ability to reduce oxygen efficiently to water in a four electron reduction. However, Pt is expensive and its availability is limited. Reduction in Pt loading [1] and replacement of Pt by non-noble metal catalysts [1-4] address this issue. Development of low cost, non-noble metal catalysts is desirable and many researchers are active in this area.

Many methods have been used to prepare non-noble metal catalysts. Catalysts based on heat treated transition metal macrocyclic complexes [5, 6], carbon-supported organometallic (Fe or Co) complexes or even Fe or Co salts in inert gas, ammonia or acetonitrile vapor have been widely studied for ORR [7-14]. Vacuum deposition by co-sputtering Co or Fe and carbon in N₂ atmosphere with or without subsequent heat-treatment [15-19], sol-derived synthesis by incorporating N-containing ligands into a Co oxide sol followed by adsorption onto carbon powder and heat-treatment [20] and a simple chemical method by entrapping Co into polypyrrole matrix supported on carbon without resorting to pyrolysis [21] have also been reported in the literature. In addition, Ozkan et al. prepared active nitrogen-containing carbon catalysts without any metals by vapor deposition of acetonitrile [22-24]. Popov et al. prepared highly active catalysts that showed very low levels of H₂O₂ production by introducing oxygen and nitrogen groups on the surface of carbon followed by post heat-treatment and chemical treatment [25].

For the active sites, FeN₂/C and FeN₄/C or CoN₄/C were proposed by Dodelet and coworkers to exist in Fe-based [26] and Co-based catalysts [27] based on time-of-flight secondary ion mass spectrometry (TOF SIMS) results. Recently the active sites have been proposed by the same group to

be hosted in micropores of the carbon support [28]. Ozkan et al. [22-24] and Stevenson et al. [29] proposed that a metal site is not needed for ORR and the active sites are located on the edge planes of nitrogen-containing carbon. Popov et al. [25] proposed that active sites containing pyridinic nitrogen are responsible for the catalytic activity for ORR. The nature of the active sites for ORR is still under debate. Besides the transition metal content, the nitrogen content and the carbon type, it is believed that the synthesis method, and hence the resulting atomic structure of the catalyst site, plays an important role in determining the activity of the catalysts.

In this paper, Fe-C-N oxygen reduction catalysts were prepared by mechanochemical reaction of Fe_xN and graphite under Ar using high-energy ball milling. This method has not been reported before for the synthesis of non-noble metal ORR catalysts. The catalytic activity of ball-milled Fe-C-N samples towards the ORR is reported. The dependences of the activity on the ball-milling time, on the Fe_xN precursor content and on heat-treatment are also described.

Experimental

High-energy ball milling

High-energy ball milling was carried out in a SPEX 8000 mixer mill at room temperature. Hardened stainless steel balls and milling vials were used. Measured amounts of Fe_xN ($x = 2-4$, Alfa Aesar), called Fe_xN subsequently, and graphite (Fluka, 50870 graphite, 99.9%) were sealed into the ball milling vial under an Ar atmosphere in a glove box. The Fe_xN :graphite mole ratio was 3.7:96.3, 7.2:92.8, 10.4:89.6 and 16.2:83.8, respectively, in the series of samples studied. The ball to powder weight ratio was 27:1. The mixture of Fe_xN and graphite was ground for various times in the closed, Ar-filled, vial.

Composition of the ball milled samples

The composition of the ball milled samples spread on copper tape was measured using a JEOL JXA-8200 Superprobe electron microprobe system equipped with one energy dispersive (EDS) spectrometer and five wavelength dispersive (WDS) spectrometers. Silicon nitride (Si_3N_4) was used as the N standard. Fe metal was used as the Fe standard and pyrolytic graphite was used as the C standard. Fe, N and C atomic compositions were all determined using WDS detectors. An accelerating voltage of 3 KV was employed to eliminate the effect of the substrate on the measurement. The analysis spot size was 10 μm .

X-ray diffraction of the ball milled samples

X-ray diffraction patterns of the ball milled samples were collected using a Siemens D5000 diffractometer equipped with a diffracted beam monochromator to eliminate fluorescence radiation from the iron. Cu-K_α radiation was used with divergence and antiscatter slits set to 0.5° . The generator was set at 40 kV and 30 mA. Data was collected over a scattering angle range of $15\text{--}80^\circ$ in 0.05° intervals with 10 seconds counting time at each scattering angle.

Thermogravimetric analysis (TGA) of the ball-milled samples

Thermogravimetric analysis (TGA) of the samples was performed with a TA instruments SDT Q-600 dual-sample thermogravimetric analyzer. TGA was performed in Ar with a flow rate of $50\text{ cm}^3\cdot\text{min}^{-1}$ and a sweep rate of $5^\circ\text{C}\cdot\text{min}^{-1}$.

SEM images of the ball milled samples

High-resolution images of the samples were taken using a cold field emission Hitachi S-4700 scanning electron microscope (SEM).

Specific surface area of the ball milled samples

Single-point Brunauer–Emmett–Teller (BET) surface area measurements were made with a Micromeritics flowsorb II surface area analyzer using a 30% N₂/70% He gas mixture.

Electrochemical characterization

An ink of ball milled sample was prepared by mixing 10 mg of powder, 95 μ L of Nafion solution (5% wt from Aldrich), and 350 μ L of ethanol, followed by ultrasonication for 40 minutes. Seven μ L of ink was pipetted onto a glassy carbon (GC) disk resulting in a powder loading of 780 $\mu\text{g}\cdot\text{cm}^{-2}$.

The electrocatalytic activity for the ORR of the samples on the GC disks was studied with the rotating ring-disk electrode (RRDE) technique using a Pine Electrochemical system (AFMSRX rotator, and AFCBP1 bipotentiostat). The RRDE electrode consisted of a catalyst-coated GC disk (5 mm diameter) surrounded by a Pt ring (7.5 mm inner diameter and 8.5 mm outer diameter). The electrochemical measurements were made in a one-compartment cell. The electrolyte was a 0.1M HClO₄ solution prepared from double-distilled HClO₄ (GFS Chemicals Inc.) and 18 M Ω Barnstead nanopure water. A Pt-wire counter electrode and Koslow Hg/Hg₂SO₄ reference electrode (used in 0.1M HClO₄ solution) were used for the measurements. The potential of the Hg/Hg₂SO₄ reference electrode was calibrated versus the reversible hydrogen electrode (RHE). The potentials reported in this study all refer to that of the RHE potential.

The samples on the GC disks were first electrochemically cleaned by sweeping the potential in the range between 0 - 1.0 V (vs. RHE) at 50 mV·s⁻¹ in an Ar-saturated 0.1 M HClO₄ solution until steady state cyclic voltammograms (CV) were obtained. For each catalyst tested, a CV was first collected in Ar-saturated 0.1 M HClO₄ solution from 1.0 to 0.05 V at 5 mV·s⁻¹ to determine the non-Faradaic current. The CVs during oxygen reduction in 0.1 M HClO₄ solution were performed between 1.0 to 0.05 V at 5·mV s⁻¹ with the electrode stationary and with the electrode rotated at 900 rpm. O₂ gas was purged into the solution at a rate of 1 L·min⁻¹. The Faradaic current was determined by subtracting the CV in Ar-saturated 0.1 M HClO₄ solution from that obtained in O₂-saturated 0.1 M HClO₄ solution. The onset potential, at which the current for oxygen reduction is first observed [4], was determined by the point of intersection of two tangent lines, one drawn parallel to the baseline (i.e. from 0.9 V to approx 0.8 V) and the second parallel to the increasing current signal. For all the measurements, the ring potential was held at 1.2 V vs. RHE in order to oxidize any H₂O₂ [30] produced in acid solution. The % H₂O₂ produced in acid solution was calculated using the following equation [30-32].

$$\%H_2O_2 = 100 \frac{2I_R / N}{I_D + (I_R / N)}, \quad (1)$$

where I_D is the Faradaic current at the disk, I_R is the Faradaic current at the ring, and N = 0.2 is the RRDE collection efficiency.

Results and Discussion

Comparison of the electrocatalytic activity of ball milled Fe_xN + graphite with ball milled Fe_xN and ball milled graphite

Figure 1 shows the CVs for samples of ball milled Fe_xN , ball milled graphite and $\text{Fe}_x\text{N} + \text{graphite}$ ($\text{Fe}_x\text{N}:\text{graphite} = 3.7:96.3$ (mole ratio)) ball milled for 12 hrs measured in O_2 -saturated 0.1M HClO_4 at 25°C . Ball milled Fe_xN doesn't show activity for ORR. Ball milled graphite is somewhat active for ORR, the onset potential of which is about 0.53 V. The onset potential of the ball milled $\text{Fe}_x\text{N} + \text{graphite}$ sample is 0.72 V. This suggests that the activity of ball milled $\text{Fe}_x\text{N} + \text{graphite}$ results from Fe-C-N generated from the mechanochemical reaction between Fe_xN and graphite, not from graphite or Fe_xN alone.

The effect of ball milling time and Fe_xN precursor content on the electrocatalytic activity of ball milled $\text{Fe}_x\text{N} + \text{graphite}$

Figure 2a shows the variation of the electrocatalytic activity for the ORR of ball milled $\text{Fe}_x\text{N} + \text{graphite}$ ($\text{Fe}_x\text{N}:\text{graphite} = 3.7:96.3$ (mole ratio)) samples with milling time. Figure 2a indicates that the activity first increases with milling time between 2 and 12 hrs and then decreases with further milling. This suggests that the number of active sites for ORR, which result from the mechanochemical reaction between Fe_xN and graphite, is maximum after 12 hours of milling. Further ball milling apparently adversely affects the active sites already formed and decreases activity.

Figure 2b shows the $\%\text{H}_2\text{O}_2$ produced for samples milled for different times. The $\%\text{H}_2\text{O}_2$ decreases as the ball milling time increases from 2 hrs to 12 hrs and then increases slightly with milling time up to 24 hrs. For the sample milled for 12 hrs, about 20% of the product of oxygen reduction is H_2O_2 and the other 80% is water.

Figure 3 shows XRD patterns of the $\text{Fe}_x\text{N} + \text{graphite}$ ($\text{Fe}_x\text{N}:\text{graphite} = 3.7:96.3$ (mole ratio)) samples milled for different times. Only carbon, Fe_3N and Fe_4N phases, which come from the

precursor phases, can be observed in the samples ball milled for 2 and 4 hrs. Fe_7C_3 is formed in the samples as the ball milling time increases to 8 hrs and up to 24 hrs, which correlates with the appearance of ORR activity over this milling time range (Figure 2). This suggests that the formation of the Fe_7C_3 phase is accompanied by the formation of active sites for the ORR. As the carbide forms, N is released from iron nitride and must be incorporated in N-containing graphite, which presumably contains the active sites according to our experience and also in agreement with hypotheses in the literature. Fe_3N and perhaps Fe_4N phases exist in all the samples ball milled from 2 hrs to 24 hrs but their amount decreases with milling time. The amount of Fe_7C_3 increases with milling time after it appears at 8 hours.

Figure 4 shows the BET surface area versus milling time for a Fe_xN + graphite (Fe_xN :graphite = 3.7:96.3 (mole ratio)) catalyst sample. The BET surface area of control samples of graphite powder and Fe_xN ball milled for 12 hrs are also shown for comparison. The surface area of graphite increases dramatically after milling and the surface area of Fe_xN remains small. The surface area of the catalyst initially increases, presumably due to the increase in carbon surface area, then decreases with extended milling time. The surface area of the milled catalyst at 12 hours is less than that of milled graphite, suggesting that the addition of a small amount of Fe_xN , that leads to Fe_7C_3 and also to catalytic activity, plays a role in the surface area reduction. Catalysts milled for more than 12 hours have a similar onset potential for ORR and similar phase composition by XRD. However, the maximum current density supplied by the catalysts (Figure 2a) drops slightly with milling time beyond 12 hours, which may be related to the gentle reduction in surface area beyond 12 hours of milling. Even though the surface areas of the catalyst samples milled for 2 and 4 hours are quite large (Figure 4), their activity is poor (Figure 2a) because Fe_7C_3 , and the corresponding N-containing graphite, have not yet formed (Figure 3).

Figure 5a shows the variation of the electrocatalytic activity for the ORR of the ball milled Fe_xN + graphite samples with Fe_xN precursor content. Figure 5a shows that the activity of the ball milled Fe_xN + graphite decreases as the Fe_xN precursor content increases from 3.7 mole % to 16.2 mole %, which suggests that Fe_xN contents higher than 3.7 mole % are not beneficial for the formation of active sites and/or extra Fe_xN blocks some active sites already formed. The sample ($\text{Fe}_{10.5}\text{N}_{3.1}\text{C}_{86.4}$) ball milled with 3.7 mole % Fe_xN and 96.3 mole % graphite shows the highest activity.

Figure 5b shows the % H_2O_2 produced for the ball milled Fe_xN + graphite samples prepared with different Fe_xN precursor contents. As the Fe_xN content increases from 3.7 mole % to 10.4 mole %, the % H_2O_2 doesn't vary significantly but remains in the range between 20 and 27% between 0.6 and 0.05V vs.RHE. As the Fe_xN content increases to 16.2 mole %, the % H_2O_2 increases to about 35%. This suggests that too much Fe_xN precursor increases H_2O_2 production, which probably results from less active sites and/or some active sites that are blocked.

Figure 6 shows the XRD patterns of samples of Fe_xN + graphite ball-milled for 12 hrs containing different mole fraction of Fe_xN precursor. The Fe_3N , Fe_4N and Fe_7C_3 phases appear in all the samples. The intensity of the carbon (002) peak decreases as the Fe_xN precursor content increases from 3.7 mole % and almost disappears as the Fe_xN content increases to 16.2 mole %. This suggests that a reduction in the amount of graphitic carbon content in the material might be one of the factors that leads to the reduction in ORR activity as the Fe_xN precursor content increases.

The effect of heat-treatment on the electrocatalytic activity of ball milled Fe_xN + graphite

Figure 7a shows the variation of the electrocatalytic activity for the ORR with the heat-treatment temperature for samples of Fe_xN + graphite (Fe_xN :graphite = 3.7:96.3 (mole ratio)) previously ball milled for 12 hrs. The activity of the sample doesn't change significantly as the heat-

treatment temperature increases to 600°C, but it decreases as the sample is heated above 600°C. The activity is very poor for samples heated to 900°C and 1000°C.

Figure 7b shows the %H₂O₂ produced for the Fe_xN + graphite (Fe_xN :graphite = 3.7:96.3 (mole ratio)) sample ball milled for 12 hrs and then heat-treated at different temperatures. The %H₂O₂ produced (about 14 - 20%) is similar for the as-milled sample and those subsequently heat-treated between 400 and 700°C. The %H₂O₂ produced increases to 50% as the sample is heated to 800°C and it increases further as it is heated to 1000°C.

In order to understand the changes in the activity of the samples as a function of the heat-treatment temperature, the changes induced by heating the sample of Fe_xN + graphite (Fe_xN:graphite = 3.7:96.3 (mole ratio)) ball milled for 12 hrs were investigated through TGA, BET and XRD. Curve "a" in Figure 8 shows the sample mass versus temperature in a TGA experiment. The sample begins to lose mass as it is heated to 480°C and 23 % of its original mass is lost after heating to 1000°C. Curve "b" in Figure 8 shows the N content of the ball-milled sample as a function of the heat treatment temperature as determined by electron microprobe. The N content in the sample is only 2.6 wt. % in the original ball-milled sample and is reduced to 0.5 wt.% after heating to 1000 °C. The 23 % mass loss of the original ball-milled sample is much higher than the N content (2.6 wt. %) in the sample so it is clear that N can not be the only element lost during heat-treatment. This suggests that the as-milled samples contain substantial oxygen incorporated within surface functional groups formed when the samples are exposed to air and that the significant mass loss is from the reaction between carbon and oxygen-containing surface functional groups to form CO₂. This needs to be further studied using techniques like XPS.

Figure 9 shows the variation of BET surface area with the heat-treatment temperature for the sample of Fe_xN + graphite (Fe_xN:graphite = 3.7:96.3 (mole ratio)) ball milled for 12 hrs. The surface

area of the catalyst sample increases after heating above 400°C, which suggests that the reaction between surface functional groups and carbon during heat-treatment creates pores, hence increasing the surface area. The ORR activity of the sample doesn't change significantly as it is heated from room temperature to 600°C even though the surface area increases, suggesting that the reaction between the surface functional groups and carbon is not beneficial for the activity. Above 800°C, a decrease in the surface area occurs, possibly due to sintering at high temperature. The ORR activity drops strongly above 800°C (Figure 7) which coincides with both the loss of surface area (Figure 9) and the loss of nitrogen (Figure 8).

Figure 10 shows the XRD patterns of the samples heat-treated at different temperatures. Carbon, Fe₃N, Fe₄N and Fe₇C₃ phases exist in the as-milled sample and in those heat-treated at 400 and 500°C. As the heat-treatment temperature increases to 600°C and up to 1000°C, Fe₃N and Fe₄N no longer appear and the Fe₇C₃ phase transforms to the Fe₃C phase. As can be seen in Fig.6a, the ORR activity of the sample doesn't change too much as the heat-treatment temperature increases from 400 to 600°C, which suggests that the transformation from the Fe₇C₃ phase to the Fe₃C phase doesn't affect the ORR activity of the sample. This again implies that the active sites are in the N-containing graphite phase.

SEM image of ball milled Fe_xN + graphite (Fe_xN :graphite = 3.7:96.3 (mole ratio))

Figure 11 shows a SEM image of a sample of Fe_xN + graphite (Fe_xN :graphite = 3.7:96.3 (mole ratio)) ball milled for 12hrs. The ball milled material is made of particles between 50 and 300 nm diameter, which indicates that ball milling not only induces the mechanochemical reaction between Fe_xN and graphite but also results in nanoparticles. The BET surface area of this sample is 38.35 m².g⁻¹ as shown in Fig.8. It is notable that a ball milled material with such low surface area shows promising activity for the ORR.

Conclusions

Fe-C-N prepared by the mechanochemical reaction (i.e. high-energy ball milling) of Fe_xN and graphite under Ar is active towards the ORR. Maximum activity was obtained by ball milling Fe_xN and graphite for 12 hrs. Ball milling for less than 12 hrs did not induce sufficient mechanochemical reaction between Fe_xN and graphite, as evidenced by the lack of formation of Fe_7C_3 , and hence the active sites for the ORR were not formed to their full extent. Ball milling beyond 12 hrs under the conditions used here reduces the catalytic activity perhaps due to a reduction in BET surface area. Fe_xN contents higher than 3.7 mole% in the Fe_xN and graphite mixture did not improve catalytic performance. Heat treatment under argon also did not significantly improve the catalysts and heating above 800°C was detrimental. Mechanochemical synthesis is a useful technique for the preparation of Fe-C-N ORR catalysts although the BET surface area of the ball milled material is relatively low. Efforts on further improving the ORR activity of the ball milled Fe-C-N materials by choosing different N, Fe and C precursors are ongoing.

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Figure Captions:

Figure 1. Disk current densities for (a) ball milled Fe_xN ($x=2-4$), (b) ball milled graphite and (c) ball milled Fe_xN ($x=2-4$) + graphite ($\text{Fe}_x\text{N}:\text{graphite} = 3.7:96.3$ (mole ratio), ball milled for 12 hours) samples on GC disks measured in O_2 -saturated 0.1M HClO_4 at 25°C . The sweep rate was $5 \text{ mV}\cdot\text{s}^{-1}$ and the rotation speed was 900 rpm.

Figure 2. (a) Disk current densities and (b) $\%\text{H}_2\text{O}_2$ produced for Fe_xN ($x=2-4$) + graphite ($\text{Fe}_x\text{N}:\text{graphite} = 3.7:96.3$ (mole ratio)) ball milled for different times on GC disks measured in O_2 -saturated 0.1M HClO_4 at 25°C . The sweep rate was $5 \text{ mV}\cdot\text{s}^{-1}$ and the rotation speed was 900 rpm.

Figure 3. XRD patterns of Fe_xN ($x=2-4$) + graphite ($\text{Fe}_x\text{N}:\text{graphite} = 3.7:96.3$ (mole ratio)) ball milled for different times as indicated. Bragg peaks positions for the phases Fe_3N , Fe_4N and Fe_7C_3 have been indicated. Panel b) is an expanded view of the range from 35 to 50° in panel a).

Figure 4. BET surface area of Fe_xN ($x=2-4$) + graphite ($\text{Fe}_x\text{N}:\text{graphite} = 3.7:96.3$ (mole ratio)) as a function of ball-milling time. The BET surface area of control samples of graphite and Fe_xN ($x=2-4$) ball milled for 12hrs are included for comparison.

Figure 5. (a) Disk current densities and (b) $\%\text{H}_2\text{O}_2$ produced for Fe_xN ($x=2-4$) + graphite ball milled with different content of Fe_xN precursor: (A) $\text{Fe}_x\text{N}:\text{graphite} = 3.7:96.3$ (mole ratio), (B) $\text{Fe}_x\text{N}:\text{graphite} = 7.2:92.8$, (C) $\text{Fe}_x\text{N}:\text{graphite} = 10.4:89.6$ and (D) $\text{Fe}_x\text{N}:\text{graphite} = 16.2:83.8$ on GC disks measured in O_2 -saturated 0.1M HClO_4 at 25°C . The sweep rate was $5 \text{ mV}\cdot\text{s}^{-1}$ and the rotation speed was 900 rpm.

Figure 6. XRD patterns of Fe_xN ($x=2-4$) + graphite ball milled with different contents of Fe_xN precursor: (a) $\text{Fe}_x\text{N}:\text{graphite} = 3.7:96.3$, (b) $\text{Fe}_x\text{N}:\text{graphite} = 7.2:92.8$, (c) $\text{Fe}_x\text{N}:\text{graphite} = 10.4:89.6$ and (d) $\text{Fe}_x\text{N}:\text{graphite} = 16.2:83.8$.

Figure 7. (a) Disk current densities and (b) $\%\text{H}_2\text{O}_2$ produced for Fe_xN ($x=2-4$) + graphite ($\text{Fe}_x\text{N}:\text{graphite} = 3.7:96.3$ (mole ratio)) ball milled for 12 hrs and then heat-treated at different temperatures measured in O_2 -saturated 0.1M HClO_4 at 25°C . The sweep rate was $5 \text{ mV}\cdot\text{s}^{-1}$ and the rotation speed was 900 rpm.

Figure 8. (a) TGA curve of Fe_xN ($x=2-4$) + graphite ($\text{Fe}_x\text{N}:\text{graphite} = 3.7:96.3$ (mole ratio)) ball milled for 12 hrs and (b) the N content of the Fe_xN + graphite ball milled for 12 hrs as a function of the heat treatment temperature.

Figure 9. BET surface area of Fe_xN ($x=2-4$) + graphite ($\text{Fe}_x\text{N}:\text{graphite} = 3.7:96.3$ (mole ratio)) ball milled for 12 hrs as a function of heat treatment temperature.

Figure 10. XRD patterns of Fe_xN ($x=2-4$) + graphite ($\text{Fe}_x\text{N}:\text{graphite} = 3.7:96.3$ (mole ratio)) ball milled for 12 hrs and then heat-treated at different temperatures. Panel b) is an expanded view of the range from 35 to 50° in panel a).

Figure 11. SEM image of Fe_xN ($x=2-4$) + graphite ($\text{Fe}_x\text{N}:\text{graphite} = 3.7:96.3$ (mole ratio)) ball milled for 12 hrs.

Figure 1

(a)

(b)

Figure 2

Figure 3

Figure 4

(a)

(b)

Figure 5

Figure 6

(a)

(b)

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11

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Impact of catalyst loading in RRDE experiments: Two or four electron oxygen reduction?

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Abstract

We have investigated the impact of electrocatalyst loading on rotating ring-disk electrode (RRDE) experiments for the oxygen reduction reaction (ORR) in acid medium. In particular, the fraction of H₂O₂ produced as a function of catalyst loading was studied. Two types of electrocatalysts were investigated: 1) non-noble metal electrocatalyst powders based on Fe-N-C and 2) Pt electrocatalysts prepared by sputtering Pt onto 3M's nano-structured thin film (NSTF) support. For both types of electrocatalysts a dramatic increase in H₂O₂ release was observed as the catalyst loading was decreased, confirming some earlier observations by other research groups. For the same non-noble metal catalyst, the fraction of produced H₂O₂ varied between less than 5 % and greater than 95 % depending on the catalyst loading. These observations suggest that oxygen reduction occurs stepwise, via H₂O₂, and if the catalyst is sparsely loaded, the produced H₂O₂ cannot be efficiently reduced to H₂O before it escapes. These studies have important implications for fundamental studies of ORR and also for PEM fuel cell applications.

keywords: O₂ reduction, Pt and non-Pt electrocatalysts, rotating ring-disk electrode, electrocatalyst loading

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Introduction

Polymer Electrolyte Membrane (PEM) fuel cells are currently under intensive research because they are a clean energy conversion device ¹. Electrocatalysts which have high activity for oxygen reduction and show stability in acidic environments are highly desired because a significant fraction (70%) of voltage losses in a fuel cell originates at the cathode where oxygen reduction occurs ^{2,3}. Besides being active and stable, the electrocatalysts must meet other requirements including: immunity against poisoning; ease of preparation; affordable cost and minimum release of H₂O₂. The latter is a particularly important attribute because H₂O₂ is known to decompose into highly reactive intermediates that initiate a chain oxidation starting with the carboxylic groups that then propagates within the Nafion membrane. This membrane breakdown results in the release of F⁻ ions in the effluent water. There are extensive reports on the role of H₂O₂, OH radicals and the degradation of Nafion membranes in the literature ⁴⁻⁶. Furthermore, reduction of oxygen to H₂O₂ is a two electron reaction, thus producing smaller electric current per available oxygen molecule. Thus, minimum production of H₂O₂ and a complete, four electron reduction of oxygen are highly preferred.

Although there are reports of detecting H₂O₂ produced at the electrocatalyst in real operating fuel cells ⁷, the best known method to measure the H₂O₂ yield is still that of the rotating-ring disk electrode (RRDE). By fixing the potential (1.2 to 1.5 V vs. RHE) of the ring during cathodic or anodic sweeps of the disk potential, free H₂O₂, generated at the disk and passing near the ring by

convection, is oxidized and produces a current. By comparing this current to the current produced at the central disk electrode, the percentage of O_2 molecules that are reduced to H_2O_2 can be calculated. Paulus et al. and Schmidt et al. explain the RRDE method applied to carbon-supported ORR electrocatalysts in detail ^{8,9}.

Although there is an extensive literature on RRDE measurements of ORR activity for Pt-based and non-noble metal catalysts ¹⁰⁻¹³, there have been very few reports of the impact of the catalyst loading on H_2O_2 production. By loading it is meant the amount of catalyst that is deposited on the glassy carbon (GC) tip of RRDE assemblies. It may appear logical that the specific activity of the electrocatalyst and the fraction of H_2O_2 it produces are intrinsic properties which should not show any loading dependence; however the results in this paper show otherwise.

During the past two years, the Dalhousie authors studied M-N-C (where M = Ti, Cr, Mn, Cr, Fe, Co and Ni) electrocatalysts prepared combinatorially using magnetron sputtering techniques ¹⁴⁻¹⁶. The initially amorphous and inactive films, prepared on GC disks, have shown, depending on their composition, activity for oxygen reduction when annealed between 700 to 800°C. Some of the better Fe-N-C compositions, as illustrated in Figure 3 of reference ¹⁷ showed activities similar to those of the best reported Fe-N-C electrocatalysts ¹⁸. All the compositions were studied using RRDE and the fraction of H_2O_2 released during the reaction was also measured. A somewhat puzzling fact was that regardless of composition or activity, the amount of H_2O_2 observed was usually high: 40 % or more [e.g. Figure 4 in ¹⁷]. By contrast, there have been reports of non-noble metal catalysts (NNMC) electrocatalysts with very low (<5%) fractions of produced H_2O_2 ^{19,20}.

For NNMC, Bron et al.²¹ have observed a decrease in the number of electrons transferred (i.e. higher H₂O₂ release) during ORR as the electrocatalyst loading on the RRDE glassy carbon tip was decreased. As for Pt-based catalysts, Inaba et al. have studied the effect of loading (and particle size) on Pt/C electrocatalysts in RRDE experiments in more detail²². They reported that the fraction of O₂ molecules that are reduced to H₂O₂ increases as the electrocatalyst loading on the electrode is decreased.

Measurements reported here were made on two types of electrocatalysts: Fe-N-C electrocatalyst powders prepared by solid-state reaction and Pt sputtered on 3M nano-structured thin film (NSTF) support. The NSTF support consists of 3 to 5 billion vertically aligned organic crystalline "whiskers" per cm². Each whisker is about 30 nm x 50 nm in cross-section and about 750 nm in length. For both types of electrocatalysts a monotonic increase in the amount of H₂O₂ released in the electrolyte was observed as the loading of the electrocatalyst on the RRDE tip was decreased.

Experimental Methods

a) Preparation of Fe-N-C non-noble metal catalyst sample

The carbon black (Sid Richardson Carbon Company) used was a furnace black in fluffy form, having a BET surface area of 441 m²/g. The required quantity of iron^{II} acetate, to obtain 0.2 wt % of iron on the carbon (600-700 mg used) was dissolved in 100 ml of d-H₂O. After that, the carbon was added. The mixture was stirred for 2 hours, then dried in an oven (air) overnight. The sample was then heat-treated at 950 °C under NH₃ for 90 min; and the mass loss (due to carbon

reacting with NH_3) during pyrolysis was 46 %wt. The complete description of the pyrolysis procedure is described elsewhere²³.

b) Preparation of sputtered Pt on nanostructured thin film support

The preparation of NSTF support is explained in more detail by Debe²⁴⁻²⁶, as well as procedures for forming catalyst coated membranes for fuel cell testing. Here, Pt electrocatalyst was deposited onto NSTF support using a magnetron sputtering system. The depositions aimed to produce films of $0.15 \text{ mg} \cdot \text{Pt cm}^{-2}$. In order to evaluate the catalyst using RRDE, the catalyst coated NSTF whiskers were carefully brushed off of the original substrate web using a solder brush. Precautions were taken to avoid any contamination of the catalyst with impurities. The procedure for applying the catalyst-coated NSTF to a glassy carbon support for the RRDE measurements is discussed below.

c) Electrochemical Measurements

Rotating ring disk electrode (RRDE) measurements of the Fe-N-C samples were performed both at Dalhousie and INRS using similar testing protocols for inter-laboratory repeatability. The Pt/NSTF samples were studied at Dalhousie only. Both labs used Pine RRDE systems, a Pt-wire counter electrode, and 0.05 M H_2SO_4 as the electrolyte for the NNMC samples. At Dalhousie, a Cl^- -free Koslow $\text{Hg}/\text{Hg}_2\text{SO}_4$ (MMS) reference electrode and at INRS a saturated calomel reference electrode was used. For the Pt/NSTF samples, the measurements (done at Dalhousie) were performed in 0.1 M HClO_4 . All measurements were performed at room temperature (21°C). Extreme care was taken to ensure the cleanliness of the glassware, cell parts, and the samples during

handling. Potentials mentioned in this article are referenced to the reversible hydrogen electrode (RHE) and currents are all normalized by the geometric area of the disk electrode.

The RHE scale for the MMS reference electrode was established by bubbling H₂ in the solution and measuring the open circuit voltage of the cell using both disk (when the Pt/NSTF sample was used) and the ring electrodes. The OCV values of disk (when the Pt/NSTF sample was used) and ring, always within 5 mV or less, were averaged and used as the RHE scale for the measurements. For the NNMC catalysts, the ring measurement alone was used. This reference calibration was performed for each individual disk assembly.

For the NNMC samples, catalyst inks were prepared using a recipe developed at INRS. A given mass of electrocatalyst powder, 95 μL of Nafion (5% by weight in alcohol, from Alfa) and 350 μL of ethanol were mixed to make the catalyst ink. To produce various electrocatalyst loadings on the RRDE glassy carbon tip, the powder content of the ink was adjusted. For example, when 10 mg powder was used in the ink, a deposition of about 800 $\mu\text{g}\cdot\text{cm}^{-2}$ was achieved on the disk. The vial containing the ink was ultrasonicated for 30 minutes, shaken for 15 minutes, followed by 15 minutes of ultrasonication and then 5 minutes of additional shaking. A 7 μL drop was placed on the RRDE tip. The samples were dried in air. Typically, nice crack-free depositions and visually smooth films on the glassy carbon tip were obtained. Electrocatalyst depositions from 40 to 800 $\mu\text{g}\cdot\text{cm}^{-2}$ were measured at Dalhousie and INRS. An extra low loading (20 $\mu\text{g}\cdot\text{cm}^{-2}$) was measured at Dalhousie only (the signal was too noisy at INRS).

For the Pt/NSTF samples, slurries were prepared using only nano-pure water and Pt/NSTF. No Nafion was used. The slurry concentrations were adjusted to provide catalyst mass density loadings of 1.25, 2.5, 5, 10, 20, 40, 60, 80, and 100 $\mu\text{g}\cdot\text{cm}^{-2}$ when a 15 μL drop was placed on a GC disk. The deposited catalyst slurry was dried under air. For all measurements the adhesion of the electrocatalyst to the GC disk was excellent and no loss of electrocatalyst occurred during the measurements as evidenced by an unchanged hydrogen underpotential deposition CV before and after ORR testing.

Details of RRDE experiments for Pt/NSTF are explained elsewhere²⁷. Briefly, we maintained a strict standard of cell setup and cleaning procedures to achieve state-of-the-art values for the ORR activity of standard Pt. Although NNMC are far less sensitive to presence of impurities (unlike Pt-based electrocatalysts), similar cell setups were used. In general, two types of polarization measurements were performed: 1) in Ar-saturated cells and 2) in oxygen saturated cells. The sweep rate for NNMC was 5 $\text{mV}\cdot\text{s}^{-1}$. The sweep rate for Pt/NSTF was 50 $\text{mV}\cdot\text{s}^{-1}$. For the Pt/NSTF samples, enough CVs under argon up to OCV were performed until steady state voltamograms were obtained. Only then were measurements in oxygen made. For both the NNMC and Pt/NSTF samples, the double layer background current, obtained in Ar-saturated cells was subtracted from the ORR currents.

The collection efficiencies of the ring electrodes were obtained by the method explained in⁹. These measurements were performed for different loadings. In general, the collection efficiency was in the range of 15 to 20%. The percentage of H_2O_2 was calculated by:

$$\%H_2O_2 = \frac{200 \times I_{ring}}{(N \times I_{disk}) + I_{ring}} \quad (1)$$

where N is the collection efficiency, measured experimentally for each electrode.

Results and Discussion

Figure 1 shows the disk and ring currents for the NNMC electrocatalyst measured at different loadings at Dalhousie. At all potentials, the reduction current decreases when lower loadings are used. The shape of the reduction wave also changes: only at $800 \mu\text{g}/\text{cm}^2$ is a well-defined mass transfer limited current plateau of $5 \text{ mA}/\text{cm}^2$ reached, indicating that close to 4 electrons are being generated for each oxygen molecule reaching the electrode. The value of the limiting current decreases with decreasing loading and, for the lowest loadings (20 and $40 \mu\text{g}/\text{cm}^2$), the current reached at 0.05 V vs RHE is less than half of $5 \text{ mA}/\text{cm}^2$. Data for a bare glassy carbon disc electrode (no catalyst applied) is also included in Figure 1 to show that the signal from the glassy carbon itself is negligible.

Thus, at high loading, the limiting factor in the oxygen reduction is diffusion of oxygen from the bulk electrolyte to the electrode surface, at medium loading the limiting current plateau decreases because less than four electrons are generated per oxygen molecule reaching the electrode, and at even lower loadings ($\leq 40 \mu\text{g}/\text{cm}^2$) no limiting current plateau is observed and the low value of the currents cannot be solely explained by a 2-electron reduction of oxygen to peroxide. It appears that the intrinsic turn-over frequency of the catalyst is affected by the high concentration of peroxide produced by the electrode. The shape of the curves gives thus information about the availability of catalytic sites.

When compact thin films of Fe-N-C electrocatalysts (low surface area hence a low number of sites) of similar compositions were prepared by magnetron sputtering and measured using RRDE,

reduction current versus potential plots, very similar to those of low-loading data in Figure 1a, were usually observed. Figure 3 in reference (17) shows the reduction currents versus potential for fifteen thin film Fe-N-C samples. Many of these data sets resemble the low loading data in Figure 1a. The samples in (17) have Fe contents ranging from 0.8 to 10.0 at. % and N contents ranging from 0.1 to 18 at. %. For comparison, the NNMC samples studied in Figure 1 contained 0.08 at. % Fe and 1.2 at. % N and had a specific surface area of 980 m²/g.

The ring currents for the Fe-N-C sample measured at different loadings at Dalhousie are plotted in Figure 1b. In Figure 1b, the ring currents have been divided by the collection efficiency, N, so they can be compared to the disk currents more easily. If the disk current and the ring current divided by N are the same, then all the product to the oxygen reduction reaction is H₂O₂. Notice that for the highest catalyst loading the ring current (oxidation of H₂O₂) is low. The increase in the ring currents at high potential, as the loading is reduced, is due to higher yields of H₂O₂, and the subsequent decrease in the ring current is due to the overall smaller disk current. As the loading decreases, however, the magnitude of ring current divided by N gets closer to that of the disk current. Note how the shape of ring current changes. At very low loading, the ring current divided by N mimicks that of the disk, a mirror-like reflection symmetry. As the loading increases, however, the ring current goes through a maximum. INRS measurements, shown in Figures 2a and 2b also convey the same message. The repeatability of the measurements between the two laboratories is very good.

Figure 3 shows that the %H₂O₂ released into the electrolyte after oxygen reduction has taken place on the disk increases as the electrocatalyst loading on the disk is decreased. Data from

Dalhousie (Figure 3a) and INRS (Figure 3b) are in a very good agreement. The shape of the curves are also interesting: when the loading is low there is no significant variation in the fraction of H_2O_2 released vs. potential. However, at higher loadings, the fraction of H_2O_2 released reaches a maximum (around 0.6 V) and then decreases. Figure 4 shows the percentage of H_2O_2 vs. loading for different potentials. This percentage increases as the disk potential increases. The semi-logarithmic nature of the H_2O_2 release vs. loading can be qualitatively understood by the following explanation.

It appears from the experimental results that the catalytic sites of the presently investigated NNMC produce 100 % H_2O_2 if the latter is removed from the catalyst surface (or electrode volume) sufficiently fast; which is the case for thin electrodes. For thick electrodes, H_2O_2 produced inside the electrode must, prior to its release in the bulk electrolyte and subsequent detection by the Pt outer ring, diffuse throughout the electrode. Along this diffusion path, some H_2O_2 molecules produced in the electrode bulk may further react on catalytic sites, either electrochemically to produce only water ($\text{H}_2\text{O}_2 + 2 \text{H}^+ + 2 \text{e}^- \rightarrow 2 \text{H}_2\text{O}$) or chemically to produce water and oxygen; ($2 \text{H}_2 \text{O}_2 \rightarrow 2 \text{H}_2\text{O} + 1 \text{O}_2$, with no exchange of electrons with the disk). When two molecules of peroxide chemically disproportionates, the lone O_2 molecule released by the disproportionation reaction may then again be electrochemically reduced into peroxide ($\text{O}_2 + 2 \text{H}^+ + 2 \text{e}^- \rightarrow \text{H}_2\text{O}_2$), etc. Both processes (either purely electrochemical or chemical / electrochemical) could convert all H_2O_2 molecules produced in the bulk of the electrode to water, resulting in an apparent close-to-four electron reduction reaction path for the ORR. Only the H_2O_2 molecules produced close to the electrolyte bulk would have the possibility to leave the electrode before further reacting with the

catalyst surface. Overall, the above explains why apparent % H₂O₂ decreases with increasing catalyst loading (i.e. electrode thickness).

A simple approach to explain the semi-logarithmic decrease of % H₂O₂ with electrode loading (i.e. electrode thickness) is now proposed. The larger impact of the electrode thickness on the % H₂O₂ measured compared to the impact of the electrode potential (Fig.4) may support the explanation where peroxide produced and desorbed from one catalytic site may react chemically (2 H₂O₂ → 2 H₂O + O₂) on another site. The single oxygen molecule produced from two peroxide molecules could then be electrochemically reduced. Repeating this reaction cycle several times leads to a close-to-four apparent number of electrons per oxygen molecule, as evidenced below when applying this cycle to 100 O₂ molecules.

$$n_{\text{apparent}} = 200/100=2$$

$$n_{\text{apparent}} = (200+100)/100 = 3$$

$$n_{\text{apparent}} = (200+100+50)/100 = 3.5$$

etc.

If one takes as unit length of electrode thickness the value T that corresponds to a loading of 20 μg cm⁻² (loading for which almost 100 % H₂O₂ is measured) and assumes that all peroxide molecules produced in a given slice of the electrode have chemically reacted once after having diffused in the next electrode slice (diffusion length of one unit length, T), then only half of the initially produced

peroxide molecules are still found (owing to line 2 in the above reaction scheme). After a diffusion length of $2T$, the number of peroxide molecules initially produced in the first slice would only be $100/(2^2) = 25\%$. So, for an electrode of thickness T , the H_2O_2 production is 100% . For thickness $2T$, the H_2O_2 production leaving the electrode is the average of peroxide coming from the slice closest to the bulk electrolyte (100%) and from the slice below (50%); that is 75% . For a thickness $3T$, it is the average over 3 slices of 100% (closest to bulk electrolyte) + 50% + 25% (farthest from the bulk electrolyte), that is $175 / 3 = 58.3\%$. etc. The theoretical line corresponding to this approach is represented in Fig.4 and, in view of the simplicity of the model, the shape of the experimental data is fairly well explained. To obtain more meaningful mathematical predictions of H_2O_2 yield, a full physical model including ORR kinetics, peroxide splitting kinetics and O_2 and H_2O_2 diffusion inside a porous electrode must be developed but this is outside the scope of the present paper.

Figure 5 shows the ORR reduction curves and % H_2O_2 released for different loadings of Pt/NSTF catalysts. The trend in both the disk currents and % H_2O_2 are similar to those seen for NNMC: theoretical mass-transfer limited currents ($4.5\text{ mA}\cdot\text{cm}^{-2}$ for 900 rpm) are not reached for low loadings of the electrocatalyst and higher percentages of H_2O_2 are detected. These measurements are in agreement with what Inaba and co-workers²² have observed.

From a fundamental point of view, these results suggest that reduction of O_2 to H_2O takes place through a H_2O_2 intermediate. If a H_2O_2 molecule is not reduced at the site where it is formed, it will diffuse to a neighbouring site and then get reduced to water. All other parameters being fixed,

lowering the electrocatalyst loading is equivalent to reducing the electrode thickness, so H_2O_2 molecules have a higher chance of diffusing away. Hence, a higher percentage of H_2O_2 is observed.

It is worth mentioning that in the case of smooth polycrystalline or single crystals of Pt, little or no H_2O_2 is detected for potentials higher than about 0.6 V (vs. RHE)^{10,28}. On these extended Pt surfaces with high turnover frequency, H_2O_2 molecules have a higher probability of reaching neighbouring catalytic sites and thus being reduced to water. For such samples, H_2O_2 production is only observed during the H_{upd} region where some site blockage occurs. The fraction of H_2O_2 produced also increases when impurities (like Cl^-) block the surface²⁹.

From a more applied point of view, this work emphasizes that % H_2O_2 measured by RRDE experiments are highly dependent on the electrocatalyst loading. We recommend that NNMC researchers examine the behaviour of their catalysts at loadings spanning the range from at least $40 \mu\text{g}\cdot\text{cm}^{-2}$ to $800 \mu\text{g}\cdot\text{cm}^{-2}$ before making conclusions about the 2-electron or 4-electron nature of the oxygen reduction reaction on their particular catalyst. In addition, the goal of reducing electrocatalyst content in PEM fuel cells, both for the Pt-based and NNMC type electrocatalysts, could ultimately lead to higher production of unwanted H_2O_2 .

Conclusions

The percentage of H_2O_2 released into the electrolyte, as measured by RRDE, strongly depends on the amount of electrocatalyst used on the tip of RRDE. As loading of electrocatalyst decreases, the fraction of H_2O_2 observed increases for both Pt and non-noble metal catalysts. Both types of electrocatalysts show very small (Pt: $\sim 0\%$, NNMC $<5\%$) quantities of H_2O_2 when the

loading is high ($\text{Pt} > 60 \mu\text{g}/\text{cm}^2$, $\text{NNMC} \geq 800 \mu\text{g}/\text{cm}^2$). When the catalyst loading is low enough the H_2O_2 molecules have a higher probability of diffusing away into the electrolyte than being reduced to water at a nearby site. Thus, the reduction of oxygen molecules appears to proceed through a H_2O_2 intermediate or desorbed intermediate first, even for Pt. This loading dependence is an important point and researchers must pay attention to it. The ultimate goal of reducing the noble catalyst loading in fuel cells could, in principle, have the undesired effect of releasing more H_2O_2 . NNMC catalysts also need to demonstrate low H_2O_2 yield in fuel cells in order to maximize the current produced and in order not to impair the membrane life time. To what extent this increased production of H_2O_2 at low loadings may matter and what the tolerance level of Nafion really is toward H_2O_2 , are interesting questions which need to be answered.

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Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

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Structure of Iron-containing Nitrogenated Carbon

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We report *ab initio* molecular dynamics simulations of vacuum deposited iron-containing nitrogenated carbon. The study focuses on the effect of substrate temperature and presence or absence of hydrogen on the structure of the deposited films. It is found that carbon and nitrogen atoms in these structures behave similar to those in amorphous nitrogenated carbons. While some Fe atoms bond to the filled π orbitals of carbon-carbon bonds, others bond directly to their carbon and nitrogen neighbors. The Fe atoms increase the cross-linking of amorphous nitrogenated carbon networks. The density of states of the structures shows that there are Fe related states just below the Fermi level, which might be important in electro-catalysis using these films.

61.43.Bn, 71.15.Pd

Introduction

A practical and economically driven aspect of oxygen reduction electrochemistry for fuel cell cathodes has been the search for less expensive yet effective substitute for platinum¹. One of the prominent non-precious metal catalyst system, containing iron, has been extensively studied in the literature^{2 3}. This chemistry might be carried out using continuous, vacuum deposition^{4 5 6 7} instead of the current batch processes^{2 3}. In this study, we focus on this vacuum deposition aspect of this iron based non-precious metal catalyst system, which involves co-deposition of Fe, C and N onto a substrate.

Carbon nitride has been a material of interest since the prediction that its properties would be close to diamond⁸. A separate but related facet of the carbon nitrogen system has been the addition of nitrogen to amorphous carbon. In the literature, there have been several studies – both experimental and theoretical – of incorporation of nitrogen atoms in carbon solid state structures^{9 10 11 12 13 14 15 16 17}. Merchant *et al*⁹ have considered structures generated by cathodic arc deposition of nitrogenated carbon films. Stafstrom¹⁰ has examined incorporation of nitrogen atoms into fullerene-like structures and its affect on the reactivity and planarity of the structures. Fullerene-like carbon nitride films were studied by Hultman *et al*¹¹, who found that nitrogen incorporation promoted a three dimensional cross-linking of the carbon networks - which were hard yet deformed elastically. Jungnickel *et al*¹³ have studied doping of nitrogen in sp^2 forms of carbon. Dos Santos and Alvarez¹⁷ investigated the structural evolution of a graphene sheet as

increasing amounts of nitrogen were substituted. There have, however, been no studies (to the best of our knowledge) of Fe, C and N co-deposition onto substrates.

Vacuum deposition of nitrogenated carbon can be achieved in both the presence and absence of hydrogen. There have been both experimental and theoretical studies examining the role of hydrogen in amorphous carbon¹⁸ and nitrogenated carbons¹⁹. Another aspect of this deposition is the control of substrate temperatures to change the nature of the deposited films. There are, however, no studies looking at the effect of substrate temperature on the structure of the deposited films.

This study will focus on the characterization of structural and electronic properties of iron-containing nitrogenated carbons, via computational methods. We will examine the effect of hydrogen on this system and look at the effect of substrate temperature on the structural and electronic properties of the Fe-C-N system.

Computational Methods

To study the structure and properties of iron-containing nitrogenated carbons, we performed *ab initio* molecular dynamics simulations. The calculations were done within density functional theory (DFT) formalism, using the generalized gradient approximation of Perdew and Wang (PW91)²⁰ for the exchange correlation functional. These were used as implemented via the Vienna *ab-initio* Simulation Package (VASP)^{21 22 23}. Projector

Augmented Waves (PAW)²⁴ were used to represent the valence electrons of carbon, nitrogen and iron. The suitability of the particular PAW potentials chosen for this study has been discussed in detail elsewhere²⁵.

In order to model the amorphous phases formed upon quenching, we used the super-cell approximation with periodic boundary conditions. 128 atoms (104 C, 16 N and 8 Fe) were placed inside this super-cell (labeled as noH in the figures). In case of the hydrogenated structures, 16 atoms of H were added to this structure (labeled as H in the figures). The structures were quenched to three different temperatures: 300K, 1000K, and 1500K. The size of this cubic super-cell was chosen such that the density matched the expected experimental density²⁶ of 2.5 g/cm³. Within the periodic DFT code, gamma point was sampled in the Brillouin zone to construct the charge densities and wave functions.

The calculation of properties of amorphous structures requires construction of ensembles over which properties are averaged. We used the *liquid quench*⁹ method to create amorphous structures for these ensembles. This method has been shown to simulate the formation of structures by cathodic arc deposition⁹, which is of interest^{4,5}. We first randomized each system at 6000K. It was then quenched exponentially in 0.5 ps to the substrate temperature of interest – 1500K, 1000K or 300K. The systems were allowed to equilibrate at that temperature for 0.5 ps. Thereafter, statistics were collected by running the simulation in the canonical ensemble (NVT) for another 2.5 – 3.0 ps. Because cooling rates are high and substrate temperatures low, systems (in particular ones quenched to

300K) are likely to be stuck in local minima. In order to sample more of the phase space, we performed five separate runs for each system. The results were then further averaged over these five systems to give better statistics. In order to assess the variation in these separate runs at the same temperature, we also calculated the standard deviation of the five averages of properties. For most properties, we plot not only the average, but also the $\pm$ standard deviation of the property.

Results

A key measure of the amorphous-state structure is the pair correlation function or the radial-distribution function, $g(r)$. Using the atomic positions for each time step, and averaging the positions over the last 2.5 – 3 ps of the simulation, we obtain $g(r)$ as shown in Figure 1. The peak in the pair correlation function at 1.43-1.45 Å corresponds to the carbon-carbon bond. The first peak in the hydrogen containing structures corresponds to carbon-hydrogen bond. Overall, there is no correlation in the atom positions beyond 4.0 Å. This justifies the use of 128 atom super-cell to study the properties of this system. As the temperature of the substrate is reduced, the peaks become higher, and more localized. This corresponds to a narrower distribution in bond lengths as the temperature is lowered. It is a direct manifestation of the amplitudes of vibration getting smaller as the temperature becomes smaller.

Figure 2 shows the partial radial distribution function around the carbon atom. The carbon-carbon (C-C) pair correlation shows well defined first and second nearest neighbors. The peak position at 1.43-1.45 Å corresponds closely to the experimental nearest neighbor distance in graphite, 1.42 Å. The second nearest neighbor peak in graphite is at 2.46 Å. This distance corresponds well with the second nearest neighbor peak at 2.5 Å in C-C pair correlation function. The corresponding first and second nearest neighbor distances in diamond is at 1.54 Å and 2.51 Å, respectively. Figure 2 also shows the carbon-nitrogen (C-N) pair correlation function. The first peak in the pair correlation is at 1.32 Å. This corresponds well to a pyridine C-N bond (bond order 1.5) of 1.35 Å, and to C-N double bond distance of about 1.30 Å. As the temperature is lowered, there is another peak at 1.2 Å, which corresponds to a C-N triple bond. This is because, upon lowering the temperature, the atoms are not able to diffuse to form lower energy structures and are frozen in meta-stable structures. The peak at 1.2 Å could also be visible because, upon lowering the temperature, the peaks become higher, narrower, and, therefore, prominent. The carbon-hydrogen (C-H) pair correlation shows the C-H bond distance of 1.1 Å.

Figure 3 shows the partial pair correlation functions of carbon (Fe-C), nitrogen (Fe-N) and hydrogen around the iron atoms. Again, as the temperature is lowered, the peaks become higher and distributions become narrower. The first peak for Fe-C pair correlation is at ~1.96 Å. This is in good agreement with than the Fe-C distance in iron-metalloenes as well as in iron carbides. For example, ferrocene²⁷ has a Fe-C distance of 2.01 Å. In cementite²⁸ (Fe₃C) Fe-C bond distances range from 1.90 – 2.1 Å. The Fe-N

pair correlation function has a peak at ~ 1.9 Å. This is also in good agreement with Fe-N bond distances in Fe phthalocyanines²⁹ (1.92 Å) and with Fe-N bond distance in FeN³⁰ (1.87 Å). The Fe-H pair correlation function shows that the H atoms are excluded away from the first nearest neighbor shell around the Fe atoms. The peak in Fe-H pair correlation function at 2.4 Å may be understood as H atoms bonded to the first nearest neighbors of Fe.

Figure 4 shows the average coordination numbers of various atoms around the C atom. These are calculated by integrating the partial radial distribution functions as:

$$C_{\alpha\beta} = \int_0^{R_{cut}} g_{\alpha\beta}(r) * 4\pi r^2 dr$$

The cutoff used for C-C, C-N and C-H radial distribution functions is 1.7 Å. This choice of this distance ensures the inclusion of only the first nearest neighbors for the corresponding atoms. The cutoff used for C-Fe radial distribution function is 2.4 Å, corresponding to the first minima in that radial distribution function. The C-C coordination number is ~ 2.5 . The coordination number for C-C in graphite is 3. Also, the C-C coordination number decreases slightly with increase in temperature. Interestingly, with H in the system, C-C coordination number is smaller indicating some of C atoms are capped by H atoms. One might be tempted to conclude that H atoms only break up the graphite-like C-C network, but as we see later, that is not the case. The C-N, C-Fe and C-H coordination numbers are largely independent of temperature as well as presence or absence of H atoms in the system.

Upon examining the distribution of coordination around the C atoms – table 1 - it is found that ~90% of C atoms have three or four neighbors. As the temperature is lowered, there are more four fold coordinated C and the number of three fold coordinated C atoms decreases proportionally. This is consistent with the C-C coordination number decreasing with increase in temperature. In the presence of H, the percentage of two and three fold coordinated C atoms decreases and the percentage of four fold coordinated C atoms increases. This is consistent with other studies¹⁸ where similar effects were seen upon hydrogenation of amorphous carbon. More than four neighbors for C atoms are found to be extremely rare (< 1%). These distributions suggest that most C atoms are sp^2 hybridized, while a small fraction is sp^3 hybridized. As the one adds hydrogen atoms to the system, while some of them break the amorphous nitrogenated carbon networks, others make the percentage of sp^3 hybridized carbons higher. Among the N atoms, the distribution of neighbors is almost independent of temperature and presence or absence of H in the system. Roughly 50% of the N atoms have two neighbors, 40% have three neighbors, and only 6-8% have one neighbor. At all temperatures, we found N dimers, albeit rarely, in the at least one of the simulations. In agreement with Valladares *et al*³¹, we also found four fold coordinated nitrogen atoms. These were also present in small quantities, and their occurrence increases with the presence of hydrogen. These distributions suggest that N atoms are almost divided equally between sp^2 and sp^3 hybridized with a small number in four fold as well as one fold coordination. These results are in very good agreement with studies of Merchant *et al*⁹ who also studied amorphous nitrogenated carbons.

Figure 5 shows the average coordination numbers of various atoms around the Fe atom. The Fe-C coordination number decreases slightly upon increase in temperature. The coordination number for Fe-N is independent of temperature. Overall the Fe coordination is 4.5 - 5.0 for Fe-C and about 1.0 for Fe-N. Table 2 shows the distribution of coordination of the Fe atom. The distribution shows that most Fe atoms have 5, 6, or 7 neighbors. Few Fe atoms have less than 5 neighbors as well as more than 7 neighbors. Temperature and presence of H do not seem to have any systemic effect on the coordination.

In order to get further structural information, we examined the angular distribution functions. Figure 6 and 7 show the angle distributions around the C atom. From the C-C-C angle distribution, it is clear that most C-C-C bonds are 120° . However, as the temperature is reduced, there is an additional peak at 110° . The peak at 120° indicates that most of the C atoms in the structure are sp^2 hybridized while the peak at 110° appears as temperature is lowered, and it indicates that there are some sp^3 bonded C atoms. This may primarily be due to atoms not getting a chance to rearrange at lower temperatures. The C-C-H angle distribution shows a peak at about 110° indicating that when H atoms add to the C-C bonds, they make the C atoms sp^3 hybridized. The absence of a peak at 120° indicates that the percentage of H atoms breaking the amorphous nitrogenated carbon network is small. Both of the changes in distribution are consistent with the inferences drawn from the change in coordination number distributions around the carbon atoms. The C-C-N angle distribution function also shows peaks at angle of 120° , and as temperature is lowered at 110° . This indicates that even when bonded to N,

the C atoms are largely sp^2 hybridized. The C-N-C bond angle also shows peaks at the same angles. However, the peak at angle 110° appears even at higher temperatures. This indicates that the N atoms are equally likely to be in sp^2 or sp^3 hybridization when bonded to C atoms. This is also consistent with the information from coordination number distribution around the N atom.

To examine the configuration of atoms around the Fe atom, we calculated the C-Fe-C angle distribution function as shown in Figure 8. These show a strong peak at $\sim 40^\circ$ and several peaks between 70° and 145° . The peak at $\sim 40^\circ$ corresponds well to structure of some iron-metallocene compounds – such as Fe bonded to filled π orbitals of ethylene, or in ferrocene²⁷. The presence of several other peaks is due to a diverse bonding environment around the Fe atoms. It also shows that, like the sp^3 bonded C atoms, Fe atoms also cross-link the amorphous nitrogenated carbon networks. While there are some preferred angles at lower temperatures (*e.g.* around 90°), at higher temperatures, the atoms move around and the peaks get washed out. Because few H atoms bond directly to the Fe atom, the presence or absence of H has very little effect to the overall distribution function. The C-Fe-N distribution function shows similar behavior. However, since the coordination number of N atoms around Fe is significantly less than the coordination number of C atoms around Fe, the intensity of C-Fe-N relative to C-Fe-C is low.

The ring statistics of the structures were calculated to assess whether the structures are indeed layered and graphite-like. The rings were calculated according to the shortest path

criterion³². Figure 9 shows the number of rings per atom as a function of the ring size. As can be seen from the figure, the structures contain a large number of 5, 6 and 7 member rings. As the temperature decreases, the number of rings with 10, 11, and 12 members increases. This may be due to the inter-linking of rings via sp^3 C atoms, whose proportion increases as the temperature decreases. Also shown in the figure 9 are the rings containing just C atoms. Because the number of such rings per atom (C only) is small compared to the number with all the atoms, it shows that N and Fe atoms are incorporated in rings. It is also interesting to note that the presence of H atoms does not change the number or distribution of rings. This can be explained as H atoms primarily changing the hybridization of the C atoms that they are connected to – rather than capping off C-C bonds. Also, since H atoms are connected to only one atom, they do not form bridges between layers.

For comparison with experimental ultraviolet photoelectron spectroscopy (UPS) spectra^{17 19 33 34 35 36 37 38 39}, we calculated the density of states of the structures. Figure 10 shows the average density of states of the structures formed. Overall, the density of states (DOS) does not depend on the temperature. There is a broad peak at about 3.5-7 eV below the Fermi level. The presence of H only lowers the peak near the Fermi level and adds some states near the peak to this broad peak. Mansor and Ugolini¹⁹ found that the UPS spectra had a broad peak at about 7 eV below the Fermi level with the leading shoulder at 4 eV below the Fermi level. Souta³⁴ found that at N concentration comparable to the present simulations, the UPS spectra shows peaks at 4.5, 7.1, and 9.5 eV increase. They also found pure amorphous C has peaks at ~7.7 eV and ~3.6 eV below the Fermi level. Zhao

and coworkers³⁵ also found that for their a-CN_x sample, as the nitrogen content increased, the UPS peaks at regions 2 ~ 7 eV and 20 ~ 30 eV increase. The above mentioned studies agree well with the calculated DOS – the difference can be attributed to cross section affects. The cross section of C 2s and 2p are known to be significantly different for low energy photoelectrons¹⁹. Upon comparing with the experimental spectra³³ the peak just below the Fermi level can be attributed to the Fe states present in the system. These are similar to Fe coordinated with graphene sheets²⁵, and it is speculated that these states could be available for electro-catalysis at the surface of these films.

Conclusions

Ab initio molecular dynamic simulations show that the structure of iron-containing nitrogenated carbon is similar to the structure of amorphous nitrogenated carbons without iron. It is found that at the density of 2.5 g/cc, these structures contain mostly sp² carbons. Addition of hydrogen atoms to the system increases the content of sp³ carbon atoms as does lowering of substrate temperatures to room temperature. It is found that nitrogen atoms in this system are almost equally likely to be sp² or sp³ hybridized. On average, the Fe atoms have 4.5 - 5 C atoms around them and one N atom. Presence or absence of hydrogen has no affect on the local bonding of Fe atoms. While some of the Fe atoms bond directly to the neighboring atoms, some also bond to the filled π orbitals of C-C bonds. By bonding to several atoms and being incorporated in the rings, Fe atoms increase the cross-linking in the amorphous nitrogenated carbon network. The density of states of the system shows that there is a peak near the Fermi level which can be

attributed to the presence of Fe atoms in the system. These states could potentially be available for electro-catalysis on the surfaces of Fe-C-N films.

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Tables

Table 1 : Distribution of number of neighboring atoms of C and N atoms

	Carbon Coordination				Nitrogen Coordination			
	2	3	4	5	1	2	3	4
1500K noH	0.10±0.01	0.71±0.04	0.19±0.03	0.01±0.01	0.08±0.06	0.50±0.09	0.40±0.10	0.02±0.02
1000K noH	0.10±0.01	0.69±0.02	0.20±0.02		0.08±0.04	0.53±0.08	0.39±0.06	0.01±0.01
300K noH	0.10±0.03	0.65±0.06	0.24±0.04	0.01±0.01	0.06±0.03	0.52±0.16	0.37±0.12	0.04±0.04
1500K H	0.07±0.02	0.68±0.04	0.24±0.03	0.01±0.01	0.08±0.05	0.45±0.15	0.40±0.07	0.06±0.05
1000K H	0.07±0.01	0.67±0.02	0.24±0.02	0.01±0.01	0.08±0.10	0.49±0.13	0.39±0.08	0.04±0.03
300K H	0.07±0.01	0.62±0.04	0.30±0.05	0.01±0.01	0.06±0.04	0.49±0.15	0.39±0.12	0.06±0.04

Table 2 : Distribution of number of neighboring atoms of Fe atoms

	Iron Coordination						
	3	4	5	6	7	8	9
1500K noH	0.02±0.01	0.14±0.07	0.30±0.04	0.30±0.05	0.17±0.03	0.06±0.02	0.01±0.01
1000K noH	0.02±0.01	0.13±0.05	0.37±0.03	0.30±0.06	0.13±0.03	0.04±0.02	0.01±0.00
300K noH	0.01±0.02	0.06±0.05	0.20±0.09	0.47±0.12	0.19±0.09	0.07±0.10	0.01±0.01
1500K H	0.01±0.00	0.07±0.02	0.21±0.04	0.35±0.03	0.24±0.05	0.08±0.03	0.02±0.01
1000K H	0.01±0.01	0.04±0.02	0.20±0.04	0.31±0.04	0.26±0.05	0.13±0.03	0.03±0.02
300K H		0.04±0.07	0.26±0.05	0.35±0.16	0.29±0.09	0.05±0.03	0.02±0.02

Figure Captions

Figure 1: Total Radial distribution functions.

Figure 2: Partial radial distribution function around the C atoms - $g_{CC}(r)$ in red, $g_{CN}(r)$ in green and $g_{CH}(r)$ in blue.

Figure 3: Partial radial distribution function around the Fe atom – $g_{FeC}(r)$ in red, $g_{FeN}(r)$ in green and $g_{FeH}(r)$ in blue.

Figure 4: Average coordination number around the C atom – C in red, N in green, Fe in dark blue and H in light blue. The square corresponds to structures without H and circles to structures containing H.

Figure 5: Average coordination number around the Fe atom – C in red and N in green and Fe in dark blue and H in light blue. The square corresponds to structures without H and circles to structures containing H.

Figure 6: Angle distribution function around the C atom – C-C-C in green and C-C-H in blue. The C-C-H angle distribution has been multiplied by a factor of 5 to show it on the same scale.

Figure 7: Angle distribution function around the C atom – C-C-N in green and C-N-C in red.

Figure 8: Angle distribution function around the Fe atom – C-Fe-C in green and C-Fe-N in red.

Figure 9: Ring distribution in the structures. Also shown in cyan are the rings containing only C atoms.

Figure 10: Electronic density of states of the structures.

Figure 1.

Figure 2.

Figure 3.

Figure 4.

Figure 5.

Figure 6.

Figure 7.

Figure 8.

Figure 9.

Figure 10.

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