Non-Precious Metal Electrocatalysts for the Oxygen Reduction Reaction in Proton Exchange Membrane (PEM) Fuel Cells

DISSERTATION

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By

Deepika Singh, M.S

Graduate Program in Chemical and Biomolecular Engineering

The Ohio State University

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Dissertation Committee:

Professor Umit S. Ozkan, Advisor
Professor Aravind Astagiri
Professor Jeffrey Chalmers
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ABSTRACT

Increasing concern about CO$_2$ emissions, together with the limited availability of fossil fuels have provided a great impetus towards development efficient energy conversion devices. Proton Exchange Membrane (PEM) fuel cells, that use hydrogen as a fuel and generate energy while producing water as the only by-product are among such efficient energy conversion devices. Commercial PEM fuel cells use platinum supported on carbon as the anode and cathode catalyst. The Hydrogen Oxidation Reaction on the anode exhibits relatively fast reaction kinetics and, therefore, low loadings of platinum are sufficient to catalyze the reaction. However, the Oxygen Reduction Reaction (ORR) is a kinetically slow reaction that requires high loadings of platinum on the cathode, thereby significantly increasing the cost of a PEM fuel cell. The associated high cost and limited platinum availability have motivated research towards development of non-precious metal catalysts (NPMCs) for the ORR in PEM fuel cells.

A number of NPMCs have been widely studied, including transition metal-nitrogen-carbon-coordinated complexes, nitrogen-doped carbon nanostructures (CN$_x$), heat-treated macrocycles, transition metal carbides, nitrides, oxy-nitrides, N-graphene, to name a few. However, one of the significant challenges has been to develop catalysts

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which can withstand sustained fuel-cell operation, as most of these catalysts are seen to lose much of their activity over time. The reason for their degradation is not known, since there is much debate regarding the active site of these materials. It is unclear if the transition metal, in conjunction with surface nitrogen groups catalyzes the reaction, or merely acts as a catalyst for generation of nitrogen-containing active sites. The studies undertaken in this work are aimed at elucidating the active sites in two specific ORR catalysts, namely, nitrogen-doped carbon nanostructures (CN$_x$) and iron-nitrogen catalysts supported on carbon (Fe-N-C).

The growth process of nitrogen-doped carbon nano-structures (CN$_x$) was studied using in-situ and ex-situ characterization techniques. CN$_x$ nano-structures were grown on two different Co-doped substrates: Vulcan carbon and MgO, and CN$_x$ formation was achieved by pyrolyzing a C- and N-containing compound, CH$_3$CN, at high temperatures. It was found that the Co phase was seen to go through different transformations during the pyrolysis process, depending on the growth substrate used. The Co species, which started in an acetate matrix prior to pyrolysis, became partially reduced with heating and with CH$_3$CN treatment. CN$_x$ fibers that formed were acid-washed, and the structure of CN$_x$ obtained as well as the nitrogen content was significantly different on the two substrates, which led to activity differences as shown by RRDE.

CN$_x$ and Fe-N-C as two classes of catalysts were studied and compared for activity towards oxygen reduction in acidic medium. The effect of exposure to acidic media was also studied. While FeNC exhibited a much higher initial activity than CN$_x$, it was seen to degrade rapidly in both half-cell and fuel cell environments, while CN$_x$
retained much of its initial activity. The results discussed clarified some of the ambiguity in the role of the transition metal in these two catalysts, and help establish that they are indeed two different materials with different active sites that catalyze ORR.

Different stages of preparation of Fe-N-C catalysts were also studied, to evaluate the role of the transition metal and effect of the inert and ammonia heat-treatments on the catalyst. It was found that even in the absence of a transition-metal, when the nitrogen-carbon precursors were heat-treated either in an inert atmosphere, or with a subsequent NH$_3$ treatment, the ORR activity was significantly better than when the catalyst precursor contained a transition-metal without any heat-treatment. However, superior activity was achieved in the presence of both the transition metal as well as a high temperature heat-treatment.

H$_2$S poisoning of Fe-N-C catalysts was undertaken in order to selectively poison specific Fe-sites in these catalysts. It was seen that Fe-N-C-Argon treated only and Fe-N-C-Ar-NH$_3$ treated catalysts exhibited significant differences in behavior after H$_2$S poisoning, indicating that that the two catalysts might involve different active sites in catalyzing ORR. Differences were also observed depending on whether the H$_2$S treatment was a final step or an intermediate heat-treatment during the preparation of the catalysts. However, in all cases, the catalysts that showed poor ORR activity after H$_2$S poisoning also suffered from lower nitrogen incorporation. This implies that the H$_2$S treatment impeded formation of nitrogen moieties on carbon which help catalyze ORR.
Operando X-ray Absorption Spectroscopy (XAS) experiments using electrochemical techniques were also conducted at the Advanced Photon Source of Argonne National Laboratory. XAS, along with other characterization techniques such as X-ray Photoelectron Spectroscopy (XPS), X-ray Diffraction (XRD), Transmission Electron Microscopy (TEM), Temperature Programmed Oxidation (TPO), Temperature Programmed Desorption (TPD), etc. have been used to gain insight into the active site of these materials.
DEDICATION

For Ma and Papa
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VITA

July 2003 ...................................................  Higher Secondary Certificate Exam, D. G.
                                               Ruparel College of Science,
                                               Matunga, Mumbai

December 2006 .................................  Intern at Larsen and Toubro, Mumbai

July 2007 ...................................................  B. Engg, Chemical Engineering,
                                                   University of Mumbai

September 2007-August 2009 ..............  Graduate Research Assistant,
                                           Electrochemical Engineering Research
                                           Laboratory (EERL), Ohio University,
                                           Athens, OH

December 2009 ..........................................  M. S, Chemical Engineering, Ohio
                                                   University, Athens, OH

2009- Present ...........................................  Graduate Research Associate,
                                                   The Ohio State University, Columbus
                                                   OH
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PUBLICATIONS


FIELDS OF STUDY

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CHAPTER 1. Introduction

With the ever-increasing demand of energy along with diminishing fossil fuel resources, there has been a widespread interest in developing technologies that utilize renewable sources of energy such as wind, solar, biomass or energy carriers such as hydrogen. Hydrogen, as an energy carrier has a distinct advantage of having zero carbon-emissions (when produced via renewable energy sources) and being energy efficient when used in electrochemical energy conversion devices such as fuel cells. Due to this, fuel cell technology holds tremendous potential to power stationary and automotive devices in the near future.

Fuel cells are electrochemical energy conversion devices in which gaseous fuels supplied to the anode (negative electrode) react with an oxidant, usually oxygen from air at the cathode (positive electrode), generating an electrical current[1]. There are a few different types of fuel cells being investigated currently, based on the type of electrolyte used, and they are classified as 1. Polymer Electrolyte or Proton Exchange Membrane Fuel Cell (PEMFC) 2. Alkaline Fuel Cell (AFC) 3. Phosphoric Acid Fuel Cell (PAFC) 4. Molten Carbonate Fuel Cell (MCFC) 5. Solid Oxide Fuel Cell (SOFC). The approximate operating temperatures for these are as follows: 80°C for PEMFC, 100°C for AFC, 200°C for PAFC, 650°C for MCFC and 800°C for SOFC. The operating temperature dictates the type of fuel that can be used in a fuel cell. Low temperature fuel cells are constrained to
the usage of hydrogen as a fuel, whereas in the high temperature fuel cells such as SOFCs, CO and CH$_4$ can be used as fuels due to their rapid electrode kinetics and lesser requirement for high catalytic activity at such high temperatures[2].

1.1 Proton Exchange Membrane Fuel Cells (PEMFCs)

PEMFCs consist of the catalyst layers of the anode and cathode separated by an ion exchange membrane (Nafion). The reactions taking place on the anode and cathode respectively are:

\[ H_2 \leftrightarrow 4H^+ + 4e^- \quad 0V \quad \text{(Anode)} \quad \text{Hydrogen Oxidation Reaction} \quad (1) \]

\[ O_2 + 4H^+ + 4e^- \leftrightarrow 2H_2O \quad 1.23V \quad \text{(Cathode)} \quad \text{Oxygen Reduction Reaction} \quad (2) \]

The membrane allows the conduction of protons (H$^+$ ions) through it from the anode to the cathode, while resisting the flow of electrons. The electrodes are sandwiched by electrically conducting backing layers from the outside along with bipolar plates that deliver the fuel and oxidant to the gas diffusion layers, and then the catalytic active sites. The components of a PEMFC are shown in Figure 1. The fuel (hydrogen) and and the oxidant (oxygen) flow in and out of the end-plates through the graphite serpentine channel, while the gas diffusion electrode (GDE) consisting of carbon paper in contact with the catalyst layer allows contact between the gases and the catalysts.
The anode and cathode catalyst (typically a precious or non-precious metal supported on high surface area carbon) are hot-pressed with the Nafion membrane to form a sandwich structure called the Membrane Electrode Assembly (MEA), which forms the heart of the fuel cell. The features of the Nafion membrane are multi-fold. It is:

- **Chemically resistant.**
- **Mechanically strong, hence can be made into thin films**
- **Acidic**
- Absorb large quantities of water
- The $\text{H}^+$ ions move freely within the membrane when hydrated, i.e., they are proton conductors.

When this entire assembly, complete with the gaskets is bolted and pressed together with compression force, and when humidified gases are flown across the anode and cathode respectively, an open circuit voltage (OCV) of 1.23V (theoretically), is generated. The actual generated OCV is much lower, (~0.9V), and the reasons for lower efficiency will be covered in the following sections.

1.2 Overview of PEMFC

1.2.1 Electrodes

The current commercial catalyst for both the anode and cathode is platinum supported on carbon black. In order to prepare the gas diffusion electrodes, the catalyst in the form of an ink with the electrolyte material (Nafion in aliphatic alcohol) and ethanol, is dispersed uniformly onto a porous and conductive material such as carbon fiber paper or carbon cloth. The carbon conductive material not only provides structural integrity to the catalyst, but also permits diffusion of gases through it to make contact with the catalyst particles. The gas diffusion electrodes are then hot pressed at 140°C at high pressure for about three minutes to yield a complete MEA. The electrolyte is mixed with the ink while dispersing it onto the gas diffusion layer, promotes the “three phase contact” between the reactant gas, electrolyte and electrode catalyst, by spreading out over the catalyst.
1.2.2 Bipolar Plates

Bipolar plates in PEMFCs are responsible for uniformly distributing fuel and oxidant to the MEA, conduction of electrical current across the cell, heat removal and leakage prevention of the gases and coolant. Careful material selection and design consideration is employed towards manufacture of bipolar plates. Serpentine channels like the one shown in Figure 2. are often employed to ensure movement of reactants along all possible pathways within the channel. The grooves in the flow field are less than a mm in length and height, and the system is arranged such that the pressure drop along each channel is greater than the surface tension holding each water droplet in place. This way if the gas flow is obstructed by the formation of a water droplet, there is sufficient pressure to move the droplet and have the gases moving again.

Figure 2. Parallel serpentine flow field pattern in a PEMFC [1]
The material of construction used commonly is either graphite, or graphite with injection/compression moulded polymer resins to retain the conductivity of graphite while providing mechanical strength due to inclusion of polymers[4].

**1.2.3 Water Management in a PEMFC**

In order for proton conduction to take place, the polymer electrolyte membrane should be sufficiently hydrated, but not so much so as to cause flooding on the electrodes bonded to the electrolyte. Hence, water management is a critical issue for PEMFCs.

During the operation of a PEMFC, the H\(^+\) ions migrate from the anode to the cathode through the electrolyte, pulling water molecules within the electrolyte with them, by a process called electro-osmotic drag. This could lead to drying out of the anode, even if the cathode is hydrated. Hence in order to maintain the humidity on the fuel and air side to 80-100\%, external humidifiers are employed.

**1.3 Efficiency of a fuel cell compared to heat engines**

The ideal standard voltage for a PEMFC in which H\(_2\) and O\(_2\) participate in the reaction is 1.229V. However, the actual cell voltage is less than the ideal cell voltage due to losses associated with polarization, internal resistance and mass transfer (discussed below).
1.3.1 Losses in a PEMFC

The actual cell potential in a fuel cell deviates significantly from its ideal theoretical value, due to losses that can be distinguished as polarization losses arising from (1) activation polarization (2) ohmic polarization and (3) concentration polarization as shown in Figure 3.

![Graph showing theoretical and actual fuel cell current-voltage characteristics](image)

Figure 3. Theoretical and Actual Fuel Cell Current-Voltage Characteristics
1.) **Activation Polarization Losses:** This is most dominant at low current densities, and occurs due to the sluggish kinetics associated with the rate of an electrochemical reaction on an electrode surface. Processes such as those involving absorption of reactant species, transfer of electrons through the electrical double layer and desorption of product species, all contribute to activation polarization. Activation polarization may be overcome by:

- Using a more effective catalyst to catalyze the reaction.
- Increasing the roughness of porous electrodes, which translates to an increase in its actual surface area.
- Increasing reactant concentration, by using pure oxygen instead of air. This leads to a more efficient occupancy of the catalytic active sites.

2.) **Ohmic Polarization:** These losses occur due to resistance to the flow of ions through the electrolyte and resistance to the flow of electrons through the electrode. The following measures can be taken to reduce the ohmic losses of the cell:

- Use of electrodes with best possible conductivity.
- Appropriate design for the materials for the bipolar plates or cell connections.
- Employing the use of the thinnest possible electrolyte layers.

3.) **Concentration Polarization:** With the consumption of reactants (oxygen or hydrogen), a concentration gradient occurs on the surface of the electrode, on which the reactant molecules are consumed faster than they can migrate from the bulk to the surface. This results in a drop in pressure of the reactants on the surface which leads to a
reduction in voltage. Concentration polarization may be caused by a number of factors such as slow diffusion rate of the gas phase through the electrode pores, or solution/dissolution of the reactants and products in and out of the electrolyte. Concentration polarization becomes important when hydrogen is directly supplied from a reformer, such that the rate of its supply cannot be increased spontaneously in response to its demand. On the oxidant side, if air is used instead of pure oxygen, there could be a build-up of nitrogen caused by consumption of oxygen, leading to mass transport problems. Similarly a build-up of water as a by-product is also commonly observed as a cause of concentration polarization. Innovative engineering design is required to overcome these challenges associated with polarization losses that decrease the power density over time in PEM fuel cells

### 1.4 Catalysis in PEMFCs

Platinum is currently the commercial catalyst of choice for both the anode and cathode of a PEMFC stack. Based on a 2012 analysis of the US Department of Energy, the cost of platinum in an 80kW PEMFC stack on a mass production scale is approximated to be about 17% of the total cost[5]. In 2009, a signed memorandum of understanding was released by seven leading automotive manufacturers: Daimler, Ford, General Motors, Honda, Hyundai, Nissan, and Toyota, expressing intent to release a significant number of commercial fuel cell vehicles by 2015[6]. As a result, the fuel cell industry has seen a renewed interest in active research and development. Much of this R&D is focused towards overall cost reduction, as a typical fuel cell vehicle (as disclosed by Toyota) still has a target sales price of $50,000[7]. Hence reducing the platinum usage
by increasing the overall efficiency of a PEMFC stack is currently one of the most active areas of research in fuel cells at this point.

1.4.1 Reasons for Platinum as the Electro-catalyst

For a heterogeneous catalytic reaction to occur on the surface of a metal, an ideal catalyst must adsorb species strongly enough to allow chemical bonds to break, allowing for, at the same time, the products to be released when the reaction has occurred. Based on the Sabatier principle, if the interaction between the catalyst and the reactant is too weak, the reactant will adsorb weakly on the catalyst and the reaction occurs very slowly or not at all. On the other hand, if the binding interaction is too strong, the catalytic surface becomes blocked by the bound substrate, intermediate or product, hindering the reaction. On the basis of this principle, volcano plots have been created for both the Hydrogen Oxidation Reaction (HOR) and Oxygen Reduction Reaction (ORR), plotting the catalyst activity against adsorption energy for a given reaction[8] (Figure 4 and Figure 5), and platinum lies at the top of the volcano plot, indicating highest activity for both the reactions out of all the bulk metals.
Figure 4. The logarithm of exchange current densities (log $i_0$) for cathodic hydrogen evolution vs. the bonding adsorption strength of intermediate metal-hydrogen bond formed during the reaction itself [9]

Since the HOR is a kinetically fast reaction, it generally requires low loadings of platinum. But the ORR suffers from sluggish reaction kinetics and necessitates high loadings of platinum, raising the overall cost of a PEMFC stack, and as a result, is the subject of intense research, to either lower cathode loadings for platinum or replace it altogether with non-noble metal catalysts.
1.5 Non-Precious Metal Cathode Catalysts (NPMCs)

1.5.1 Macrocycles

The first NPMCs reported in literature consisted of unpyrolyzed macrocycles used as fuel cell cathode catalysts in alkaline conditions in the mid 1960’s[11, 12].

Macrocycles are molecules with rings of nine or more atoms, often coordinated to a metal center, with an example shown in Figure 6. Out of all macrocyclic structures, the metal-N$_4$ complexes, such as metal porphyrins and phthalocyanines have shown the highest activity for ORR[13].
Some of the factors that affect the activity and stability of these macrocyclic complexes for ORR are (a) the transition metal used and (b) for a given transition metal, ORR activity varies with the nature of substituents on the macrocyclic ligand, due to differences in the electronic densities that they induce on the transition metal ion. These macrocyclic complexes were inspired by naturally occurring copper laccase enzymes consisting of four copper atoms in their active site, that have shown a natural propensity to reduce oxygen to water[16].

The electroreduction of oxygen to water can proceed via two pathways: (1) Direct $4e^-$ reduction to $\text{H}_2\text{O}$ or (2) $2e^-$ reduction via an $\text{H}_2\text{O}_2$ intermediate. The two electron pathway is undesirable as $\text{H}_2\text{O}_2$ is a highly oxidizing intermediate that could corrode the
internal components of a fuel cell, and releases about half of the free energy compared to the four electron pathway, leading to lower efficiency of the fuel cell. Hence it is essential for a catalyst to show selectivity towards complete reduction to water, rather than proceeding via the $\text{H}_2\text{O}_2$ intermediate. It has been shown that the ORR activity and mechanism for macrocyclic complexes are highly pH-dependent, owing to which, certain complexes can catalyze the reaction via the 4 electron pathway within a particular pH range, outside of which, exclusive 2 electron reduction occurs[17]. Fe phthalocyanines reduce oxygen via the 4 electron pathway in alkaline conditions, with the 2 electron pathway dominating under acidic conditions, with the reverse being true for Co phthalocyanines[15].

The overall catalytic activity of metal macrocycles is also linked to the redox potential: Metal (III)/(II) of the complexes, i.e., the more positive the redox potential is, higher the activity. However, the metal-N$_4$ chelates require a conducting support, and long term stability is still a challenge with these catalysts. Inert heat treatments, however, increase both their stability and activity, and one of the reasons attributed for this improvement is a shift in the positive direction of the Metal (III)/(II) redox potential[18, 19]

Overall, most N$_4$-metallomacrocyclic complexes rarely achieve oxygen reduction via the four electron direct pathway without forming significant amounts of $\text{H}_2\text{O}_2$, which has perhaps hindered their development as efficient ORR catalysts in recent years. But considering that they were first NPMCs reported for ORR and are closely linked to the naturally occurring heme-like structures that catalyze the biological oxygen reduction
reaction, they serve as building blocks for development of more active and selective ORR catalysts.

1.5.2 Pyrolyzed N₄-Macrocycles

A few decades later from the discovery of macrocycles as ORR catalysts, it was found that a heat-treatment step imparted stability to these macrocycles in acidic media, possibly through formation of isolated metallic sites coordinated by thermally-modified ligands that retained the inner metal-N₄ macrocyclic structure[20]. This hypothesis was counter-argued by Yeager, who proposed that macrocycles such as heat-treated tetramethoxyphenylporphyrins (TMPP) do not require the presence of a transition metal center within the complex to be active for ORR (rather, the transition metal could be present as an impurity in carbon, or added separately), and that the heat-treatment in the range of 450-900°C destroys the metal-N₄ centers in these complexes[21]. Subsequently, Wiesener performed a similar study with heat-treated and untreated macrocycles, in which he concluded that the catalyst without the metal was active for ORR, and active sites consisted of highly-active carbon with surface functional groups[22]. Their conclusion was supported by the fact that they did not see a significant degradation of catalytic activity after the metal was dissolved out of the catalyst in an acidic medium. However, the transition metal participated in the formation of the catalytically active centers upon thermal activation.

Dodelet and coworkers, who have made significant contributions towards development and characterization of various types of non-precious metal catalysts
(NNMC), had similar observations as Yeager and Wiesener about destruction of the Me-N₄ centers in metal-complexes, but they attributed activity to metallic particles consisting of clusters of the order of 20 Å, whereas larger clusters forming at higher temperatures led to a decrease in activity[23]. In a series of control experiments to observe the effect of pre-treatment of carbon black supports on activity of Fe-containing catalysts, they pre-treated the carbon support Vulcan Carbon XC-72 with HNO₃, NH₃, or a combination of both. Their most-active catalysts with pre-treated supports contained iron and the control experiments did not, but still showed significant activity for ORR[24]. They later revised the metallic active-site model, claiming that the active site in these materials was a FeN₄/C-type configuration, lying between two adjacent graphitic planes, and this site was present within the micropores of the catalyst[25, 26].

Scherson and co-workers have done substantial work with both pyrolyzed and unpyrolyzed macrocycles for ORR. Upon comparison between heat-treated tetramethylporphyrin (TMPP) versus Cobalt-containing TMPP, they discovered an improvement in activity with heat-treatment, and upon addition of the transition metal[27]. For the first time, they provided direct spectroscopic evidence by conducting in-situ X-ray Absorption Near Edge Spectroscopy (XANES) experiments, that a Fe-porphyrin macrocycle itself undergoes reduction in solution as the potential is scanned to more negative potentials[28]. They also showed that upon bubbling CO gas through the electrolyte in which an iron porphyrin adsorbed on carbon is the catalyst, there is a formation of an iron macrocycle-CO adduct, providing indirect evidence that CO
adsorption on the macrocycle could block the active site rendering it inactive for ORR[29].

Gojkovic et al. conducted extensive studies on the characterization and kinetics of ORR of heat-treated iron(III) tetramethoxyphenyl porphyrin chloride catalyst supported on carbon[30, 31]. They established using the kinetic and limiting currents obtained from the Rotating Ring Disk Electrode (RRDE) set-up, that O₂ reduction obeyed first order kinetics, and that the Tafel slope in the range of –(60-80) mV/decade was attributed to the transfer of the first electron as a rate determining step[31]. This has been viewed as a benchmark for analyzing ORR kinetics for NNMCs in the recent past.

1.5.3 Conducting Polymers

Conducting polymers such as cobalt polypyrrole (Co-PPy) and polyacrylonitrile (PANI) have been used successfully as both carbon and nitrogen precursors for Metal-Nitrogen-Carbon (Me-Nₓ/C) catalysts for ORR[32-34]. Heat treatment of these polymeric compounds was also seen to increase their activity, possibly due to the formation of catalytically active nitrogen functionalities such as pyrrolic and quarternary nitrogen groups. In a noteworthy article from Los Alamos National Laboratory, Zelenay’s group used pyrolyzed PANI/C doped with Fe and/or Co, and observed that ORR activity was significantly improved by combining both the metals with the polymer in the preparation method[35]. Doping the polymer with the transition metal also made it more selective to water production (99.6% H₂O produced at 0.4V vs. RHE, in comparison with 84% H₂O produced by the pyrolyzed undoped PANI/C). In addition, the catalyst was seen to be
highly stable, losing only 2% of its activity over 450 hours of fuel cell operation. This was attributed to the aromatic nature of PANI, which facilitated stronger interactions with the metal ion centers, and formation of more ordered graphitic structures. With further optimization, a maximum power density of 550 mA/cm$^2$ and 700 hours of operational stability have been seen at 0.4V[36].

1.5.4 Fe-N-C Materials

After an extensive research on pyrolyzed and un-pyrolyzed macrocycles, researchers began exploring alternatives to these expensive starting materials in the late nineties[36-40]. This was concomitant with investigations on nitrogen-doped carbon materials which were not necessarily used as ORR catalysts, and it was seen that a high temperature treatment of a nitrogen-containing starting material would yield nitrogen functional groups of different kinds that transformed from one type to another, depending on the temperature of the treatment[41, 42].

Dodelet’s group began investigating “activation” of their transition metal precursors by heat-treating them at above 1000°C in the presence of a nitrogen containing source; acetonitrile, to yield ORR-active materials[37]. It was following these investigations, that the researchers realized that nitrogen was an important component of transition metal catalysts for ORR[38, 43]. They have experimented with numerous starting materials such as perylene tetracarboxylic dianhydride (PTCDA)[44], heat treated in inert Ar or N$_2$ atmospheres or with NH$_3$ and H$_2$.[45] and claimed that the active site for their Fe-based catalysts were FeN$_2$/C or FeN$_4$/C structures[45]. Over the years, as
mentioned earlier, they revisited their active sites by claiming that simple Fe-N-C catalysts prepared by impregnation of an iron acetate salt on carbon black, are activated by an ammonia treatment, which leads to etching of the carbon support, forming micropores that host the Fe-N active sites[46, 47]. These studies were validated by a number of their collaborators who performed cross-laboratory experiments using different metal, N and C precursors that were characterized using X-ray Photoelectron Spectroscopy (XPS), porosimetry, Mossbauer, (Extended X-ray Absorption Fine Structure) EXAFS and neutron activation[48-53]. Over a period of time, the distinction between the active sites of heat-treated macrocycles supported on high surface area carbon, and those catalytic materials starting with inorganic metal precursors with external nitrogen sources, seems to have merged.

Atanassov’s group from University of New Mexico has conducted extensive XPS characterization of Co porphyrin based catalysts supported on mesoporous silica heat-treated at temperatures from 200-1000°C. They showed these catalysts to possess Co\(^{2+}\)-N\(^4\)-centers with about 50% distribution, with the remaining 50% existing as inactive metallic crystallites coated with a layer of cobalt[54]. These sites, however, catalyzed ORR via 2 electron reduction to hydrogen peroxide first[55].

1.5.5 Chalcogenides, transition metal oxides and carbides

Transition metal chalcogenides consisting \(M^{(a)}_{2}M^{(b)}_{3}X_{4}\) thiospinels where \(M^{(a)}=\) Mn, Fe, Co, \(M^{(b)}=\) Ti, V, Cr, Fe, Co or Ni and \(X=\) S, Se or Te synthesized at 400°C-450°C have displayed significant ORR activity with OCVs \(\sim 800\text{mV}\) vs. RHE[56-59].
However, the catalysts degrade rapidly over time. These studies were followed up by theoretical investigations by Sidik and Anderson to explain the activity of Co sulfide species[60]. They determined that Co$_{0}$S$_{8}$ (202) with a partially covered surface with OH groups would be active for ORR, whereas when S was replaced by Se in a Co$_{9}$Se$_{8}$ type structure, the resulting catalyst exhibited lower activity than its sulfide counterpart, which tied in well with experimental observations. Other synthesis methods have been investigated: using FeS$_{2}$ and Fe/CoS$_{2}$ thin films, supported Co$_{3}$S$_{4}$ and CoSe$_{2}$ chalcogenides, W-Co-Se catalysts[36, 61, 62].

1.5.6 Metal Oxides

Figure 7. Summary of progress over recent years with respect to transition metal oxide, carbide and nitride based materials as ORR Electrocatalysts [36].
Non-precious metal oxides have exhibited limited activity in acidic media, possibly due to the inherently large band gap (low conductivity of these materials). As a result, they are not seen as very promising catalysts for ORR in PEM fuel cells. Nevertheless, quite a large number of studies have been conducted to study metal oxide composites as ORR catalysts such as ZrO$_x$, Co$_3$O$_{4-x}$, TiO$_{2-x}$, SnO$_{2-x}$, NbO$_{5-x}$, WO$_x$ and M$_x$WO$_3$ as well as Tantalum Oxides as shown in Figure 7[63-66].

1.5.7 Metal carbides, nitrides, oxynitrides and carbonitrides

Out of all metal carbides, tungsten carbide is seen to possess similar electronic structure to that of platinum[67], resulting in several investigations towards ORR activities of these materials. Tantalum, when incorporated into WC materials exhibited enhanced activity and stability towards ORR, attributed to the formation of a W-Ta alloy phase[68]. Sputtered Ni-Ta-C compounds have also shown reasonable stability in acidic media, owing to the formation of a TaO protective film[69].

Transition metal nitrides have exhibited better stability in acidic media than carbides and oxides, and show promise as suitable ORR catalysts[70]. Carbon supported tungsten nitride (W$_2$N/C), although possessed low activity (~0.6V vs. RHE), showed significant stability after 100 hours of operation[71]. Molybdenum nitrides have also been studied, either as they are, or after heat treatment. Nitridation using ammonia has been studied for a variety of metals such as Niobium, as well as Co-W supported on
carbon to obtain an onset potential of 0.75V vs. RHE and a current density of -0.158 mA/cm$^2$ for the most active catalyst.

Metal oxynitrides are essentially metal oxides doped with substitution nitrogen to reduce the inherently high band gap of the oxides. This led to enhanced electronic conductivity of these materials, and Tantulum oxynitrides have subsequently shown activity up to onset potentials of 0.8V vs. RHE[72].

Metal carbonitrides that have been investigated are those first synthesized by thin film magnetron sputtering such as Co$_x$C$_{1-x}$N$_y$[73]. Fe and Co carbonitrides were also synthesized using a similar method and the ORR activity of these materials was found to be affected by the total nitrogen content up to 3 atomic % N[74]. Partial oxidation of transition metals such as Ta, Zr and Nb also had a positive effect on their catalytic ORR activity, and onset potentials as high as 0.97, 0.9 and 0.89V vs. RHE have been observed for partially oxidized ZrCN, TaCN and NbCN respectively[75, 76]. Hence metal carbonitrides have been regarded as one of the most promising candidates for ORR catalyst materials.

1.5.8 Doped Carbon Materials

In addition to the above mentioned compounds, nitrogen-doping of carbon support has been viewed as an effective method to prepare NNMCs. This method of preparation eliminated the use of expensive macrocyclic compounds, instead, simple precursors such as acetonitrile, phenanthroline, ammonia, along with a transition metal
salt (Fe or Co acetate) and a high surface area support when heat treated together, yield very active ORR materials.

Nitrogen doping in carbon nanotubes (CNTs), nanofibers (CNFs), and more recently fullerenes and graphene has been extensively studied, due to the superior electronic properties imparted by incorporation of nitrogen in the carbon framework. From a theoretical standpoint, the somewhat metallic conductive properties of N-doped CNTs (N-CNT) can be explained by the bonding of nitrogen with two carbons in the pyridinic site, giving rise to an electron donor state due to the lone pair of electrons[77]. Structurally, N-doping has been shown to produce relatively long, bamboo-like MWCNTs (100-500nm). N-doping has also been shown to impart chemical reactivity to otherwise inert CNTs, thereby, opening up opportunities for many applications such as ORR in fuel cells[78] and batteries[79].

1.5.9 Nitrogen-doped carbon prepared with a transition metal as ORR catalysts

From 2004 onwards, there appeared independent reports of significant ORR activity of carbon nanofibers containing nitrogen, prepared with a transition metal precursor which may or may not be responsible for activity towards ORR in acid or alkaline media[80-82]. Stevenson’s research group was among the first to report the use of carbon nanofibers as electrodes for ORR in alkaline medium. The CNFs prepared via pyrolysis of iron phthalocyanine on nickel mesh supports showed activity for ORR at neutral and high pH values[80]. They proposed that oxygen reduction occurred via the two electron, $\text{H}_2\text{O}_2$-intermediate pathway. This was in agreement with an earlier
observation by Yang and McCreery on glassy carbon electrode surfaces covered with methylphenyl at pH values >10 [83]. In another noteworthy publication, Stevenson’s group prepared nitrogen-doped carbon nanofibers by chemical vapor deposition (CVD) of ferrocene and xylene or pyridine, which showed a 100-fold enhancement for hydroperoxide decomposition in neutral to basic pH solutions [84]. They attributed this superior activity to N-doping, which increased the basicity of graphitic carbon through strong π electron delocalization. This was in agreement with a study carried out by Strelko et al. which suggested that delocalized π electrons imparted Lewis basicity to carbon and increased its resistance towards oxidation, thereby, catalyzing reduction reactions without the irreversible formation of oxygen functionalities.[85, 86] Stevenson and coworkers also acknowledged that the presence of pyridinic nitrogen groups would make an extra lone pair of electrons available on the nitrogen atom, which in turn would increase the electron density of the carbon’s edge planes[81]. This edge plane exposure of graphitic carbon could possibly be responsible for increased ORR activity due to the increased electron density from the presence of pyridinic groups. They have reported subtle but significant structural differences between non-doped and N-doped CNFs as seen in Figure 8 [84]. Both the CNFs had similar morphologies in terms of hollow interiors, 20-40 nm diameters and >10 μm lengths. However, the N-doped CNFs had sidewall structures that seemed more compartmentalized and disordered compared to the non-doped CNFs, and also contained more dislocations and disruptions in the stacked graphitic planes. This was in agreement with the observation of Sjostrom et al. who reported that incorporation of nitrogen led to pentagonal defects in graphene sheets, with buckling and an irregular curvature of graphene layers in N-doped carbon materials[87].
Bao and co-workers have also studied N-doped graphene and carbon nanotubes for ORR in alkaline media and made some interesting observations about structural effects in facilitating ORR[88, 89]. The size of crystals of graphene nano-sheets was correlated to activity for ORR, such that higher activity was seen for smaller crystalline sizes. Theoretical calculations pointed towards origin of activity from the zig-zag edges of N-graphene. A computational study, targeted specifically towards study of the interaction of the Fe with carbon nanotubes stated that Fe bonds more strongly with the outer wall of a CNT than the inner wall, with a higher distribution of electrons on the outer wall. This change in the electronic charge on the surface of CNTs facilitated by Fe,
could influence the chemical reactivities of gas molecules upon interaction with the CNTs[90].

At OSU, Ozkan and co-workers have reported the use of nitrogen-containing carbon nano-structures for ORR in acidic media since 2005. Their early work has focused on developing N-containing nanostructured carbon catalysts (CN$_x$) that are formed during the decomposition of a carbon and nitrogen source (e.g., acetonitrile) over a substrate (e.g., Vulcan carbon or an oxide support such as Al$_2$O$_3$, SiO$_2$, or MgO) doped with a transition metal (Fe, Co, or Ni) at high temperatures[82, 91-94]. The resulting carbon nano-structures were washed with strong acids and/or bases to eliminate the oxide support and any exposed metal. Regardless of the support or the transition metal used, the best ORR activity was achieved when the carbon nanostructures had high-edge plane exposure (Figure 9) and, as a result, high pyridinic nitrogen content. The best-performing CN$_x$ catalysts, prepared with 2 wt% Fe on alumina showed only a 100 mV overpotential as compared to Platinum. Also, carbon nanostructures that were grown on a pure alumina support without any transition metal doping had significant ORR activity, as long as nano-geometries (e.g., stacked-cups, platelets, or herring bone structures) that led to high edge plane exposure and high pyridinic nitrogen content were attained[82, 91, 92, 94-97]. The samples prepared with nickel as a transition metal resulted in tube-like structures, with significantly less activity than the more active samples with edge plane exposure.
Characterization of the carbon nanostructures after acid washing showed the transition metal particles encased in carbon. When Mössbauer characterization of carbon nanostructures grown on Fe-doped supports was performed at different stages of preparation (e.g., before and after acid/base washing), the results showed iron to be present either in the form of a cementite phase, confirming that the carbon growth mechanism catalyzed by the metal particles involved a carbide intermediate, or as a
paramagnetic phase ($\gamma$-Fe), confirming that Fe left behind after washing is encased in graphite. Acid washing of the pyrolyzed product removed a significant amount of the carbide and oxidized phases, leaving behind metallic Fe. There was also no correlation observed between the activity and any of the Fe phases present.

Later on, Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy studies also confirmed that the Fe-K edge of CN$_x$ catalysts grown on Fe-MgO, bore striking similarities to the iron carbide reference[98]. These studies showed no evidence of a N-stabilized metal center. These results suggested that the role of iron in these materials is to catalyze the formation of ORR-active carbon nanostructures with increased edge plane exposure and nitrogen functional groups, without directly participating in the reaction itself.

In one study, an attempt was made to compare the activity differences in CN$_x$ catalysts prepared with a high degree of edge plane exposure, versus CN$_x$ prepared with minimal edge plane exposure[96]. It was found that CN$_x$ with a larger extent of edge plane exposure was not a marker of ORR activity in itself, rather, the edge planes facilitated the incorporation of nitrogen functional groups at the appropriate locations within the graphitic matrix.

More recently, we have shown that CN$_x$ catalysts subjected to known catalytic poisons such as H$_2$S, CO, and cyanide retained their ORR activity and, in the case of H$_2$S treatment, showed improved catalytic activity after treatment[99]. This supported the assertion that the iron present in CN$_x$ catalysts after acid washing remained encased in
carbon and was inaccessible to molecules smaller than O₂, thereby not participating in the oxygen reduction reaction.

The effect of other dopants on the ORR activity of CNₓ catalysts has also been studied. The use of sulfur as a growth promoter for CNₓ catalysts with no negative effect on ORR activity was reported[100]. Phosphorus was incorporated within the growth media of CNₓ catalysts prepared on Fe-MgO, with different ratios of P/Fe. Lower ratios of P/Fe (<1) was seen to increase the ORR activity of CNₓ catalysts drastically with improved selectivity towards water formation[101, 102]. The increase in activity could not be attributed to extent of structural defects of graphite, as seen by Raman spectroscopy, as the P-doped and undoped CNₓ catalysts exhibited approximately the same D-band intensities. However, temperature programmed oxidation experiments indicated that CO₂ evolution was shifted to higher temperatures with higher phosphorus levels, which could be an indicator of increased stability. Computational studies modeling carbon catalysts with a phosphinate (>O(=O)OH) moiety demonstrated their catalytic activity for ORR in acidic conditions for both 2 and 4 electron reduction[101]. CNₓ catalysts have also been evaluated for their carbon corrosion characteristics as carbon is known to oxidize in sulfuric acid at high potentials and form intermediate hydroquinone/quinone species during corrosion[103]. CNₓ catalysts have shown good resistance to carbon corrosion in comparison with bare Vulcan carbon with chronoamperometric potential holds at high potential values, possibly due to surface stabilization of the functional groups during ORR, in the process of which most of the electrochemically active quinone/hydroquinone species appeared to have been consumed.
It should be noted that these catalysts are not as active as Pt catalysts or as the new generation of Fe- or Co-N-C catalysts. However, their stability as well as their tolerance to methanol and inactivity for methanol oxidation suggests some potential for application[104].

Popov and coworkers are another research group that began investigating transition-metal based carbon catalysts for ORR in acidic media from around 2006 onwards[105, 106]. They worked with a transition metal-nitrogen chelate complex catalysts that were acid-leached post pyrolysis[107]. Their EXAFS analysis indicated that the Me-N bonds were not stable at temperatures greater than 800°C, as the EXAFS spectra indicated presence of Co-Co metallic bonds. From XPS, they did not detect any metallic species from the catalyst after leaching, indicating that no metal was present on the surface after leaching, although pyridinic nitrogen was incorporated on the surface, leading to high activity and selectivity of these catalysts. Stability tests performed on metal-N catalysts that were base and acid washed after pyrolysis demonstrated that catalysts with pyrolysis conducted at a higher temperature for a longer duration (1000°C, 10h) were significantly more stable than those heat-treated at a lower temperature for a shorter duration (800°C, 3h)[108]. The authors brought up an interesting correlation between the nitrogen content and stability of these catalysts. After the stability test, both the catalysts showed similar N 1s peaks. The authors hypothesized that the pyridinic nitrogen, which is bonded to two carbon atoms and has a basic lone pair of electrons that are not delocalized in the aromatic π-system, can be protonated to pyridinic N-H in the acidic conditions of the PEM fuel cell(Figure 13). They also demonstrated that pyridinic-
N-H is difficult to be distinguished from quaternary-nitrogen in terms of binding energies, hence after the stability test, the peak at 401.4eV could be attributed to either quaternary-N or pyridinic N-H. The NNMC-1000°C-10h, which contained mainly quaternary-nitrogen atoms, showed a lesser degree of degradation, as a quaternary-N is bonded to three carbon atoms in the carbon plane without a lone pair of electrons, hence it cannot be easily protonated.

These findings are in contradiction from those reported by Dodelet and coworkers, in which they acknowledge that it is the anion binding of the basic protonated nitrogen species in Fe-N-C catalysts that manifests itself to cause long-term stability and performance loss in PEM fuel cells, instead of metal leaching from the catalyst[109]. And in fact, protonated pyridinic-N groups are essential for the conduction of protons to the active Fe site to catalyze the ORR. The role of pyridinic nitrogen in catalyzing ORR in carbon catalysts that were initially prepared with transition metal precursors has been asserted by a number of researchers including Ozaki[110], Muhler[111], Anderson[112], Tammeveski[113, 114] and Ozkan[94-97, 104].

In 2006, Ozaki and coworkers used a carbonized mixture of ferrocene and poly(furfuryl alcohol) that was acid washed in H₂SO₄ with no observed decrease in activity[110]. They found a correlation between electrochemical activity and crystallinity of the carbon in acidic media, which was in turn related to increased conductivity and distribution of mesopores. Ultimately, the activity was attributed to the structure of the carbon materials since the sample was not prepared with any nitrogen containing precursors and iron removal left activity unaffected. They have also studied BN-doped
carbon prepared through carbonization of a mixture of melamine & BF$_3$-MeOH complex, and its activity in acidic media[115]. In similar study, they have demonstrated a 4-5 fold improvement in activity for B- and N-doped and 20 fold for BN-doped carbons. Correlation was found between edge-N and B-N-C moieties and ORR activity.

In 2009, Lyth et al. reported preparation of N-doped Ketjen black (KB) through carbonization of a mixture of Co(II) Cl and poly(4-vinylpyridine) at 1000°C followed by acid wash in HCl to remove the Co[116]. They attributed the ORR activity to the growth of nanoshells and introduction of nitrogen and not to Co as it was undetected by XPS. They have also shown improved ORR activity for graphitic- carbon nitride catalysts, whose surface area was significantly improved by addition of carbon black, and it resulted an improved performance in acidic media. This was an example of a metal-free ORR catalyst, as no transition metal precursor was used in its preparation[117].

More recently, Zhongwei Chen and coworkers have reported work on nitrogen-doped CNTs prepared from ferrocene and ethylene-diamine or pyridine as the nitrogen source. They have shown that higher nitrogen content is strongly correlated with high ORR activity in alkaline media[36, 118, 119]. In some cases, their catalysts have even outperformed Pt/C[120].

Muhler and coworkers initially worked on synthesizing carbon nanotubes with iron as a catalyst, and functionalized the CNTs using either nitric acid or oxygen plasma and examined their surface-functional groups[121]. They further investigated the use of CNTs in ORR in acid media, prepared by pyrolysis of acetonitrile over a cobalt precursor.
on silica support at two temperatures- 550°C and 750°C, which underwent two leaching steps: one in KOH to leach out the silica, and another in concentrated HCl to dissolve the metal[111]. They observed that the N-CNTs prepared at a lower temperature had a higher concentration of pyridinic groups, with higher edge plane exposure, which was seen due to transformation of pyridinic nitrogen to the more stable quaternary nitrogen at higher temperatures. They attributed the high kinetic current in their N-CNTs to increase in resistance of their carbon structures to oxidation, and to an increased basicity of the graphite structure due to nitrogen incorporation.

Liming Dai and coworkers, who have pioneered the application of metal-free nitrogen-doped carbon materials including vertically aligned N-CNT, N-graphene, and N-quantum dots for alkaline fuel cells[122-124], recently used vertically aligned nitrogen-doped carbon nanotubes (VA-N-CNTs) grown on silicon wafer via pyrolysis in the presence of Ar, H₂ and NH₃ on an iron (II) phthalocyanine catalyst, for ORR in PEM fuel cells[125]. Without delving into the possible mechanism of reactions, they have shown superior activity to Pt/C, when these VA-NCNTs were supported on a platinum mesh in an air saturated H₂SO₄ solution.

Kurak and Anderson have performed theoretical calculations on N-doped graphite and ORR on their pyridinic-edge sites[112]. They concluded that with the absence of a direct four-electron pathway, it was likely that (i) there could be another catalytic structure involving substituent N (ii) the 2 electron-H₂O₂ pathway was predominant, or (iii) transition metals were aiding the direct 4 electron reduction.
1.5.10 Nitrogen-doped carbon materials prepared without a metal

Most of the studies mentioned in the previous section had a metal used in the preparation of the carbon materials, which still leaves the role of metal in ORR activity as an open question. There are also several studies that focus on N-doped carbon materials prepared without a metal. Notwithstanding a large body of literature that exists on metal-free nitrogen-doped carbon materials for ORR in alkaline media for alkaline fuel cells and batteries[118, 126, 127] there is still significant work devoted towards such materials for applications in PEM fuel cells, as this would lead to a more significant economic impact in long term commercialization in place of the internal combustion engine in automobiles.

One of the first studies on ORR in acidic medium on metal-free nitrogen-doped carbon catalysts was from Sidik et al. in which they conducted an experimental and theoretical study of nitrided Ketjen Black which was pre-washed with HCl and HNO₃ to remove trace metals and then heat-treated in ammonia. The highest ORR activity in acidic medium was found in the NH₃-treated carbon, followed by the one that was HCl and HNO₃-treated, followed by untreated carbon black, and the least active was the HCl-treated carbon black. From rotating ring disk electrode (RRDE) and theoretical studies, they concluded that edge of graphite sheets or nitrided graphite basal planes are active for the 2 electron reduction of oxygen, activated by radical carbon sites next to substituted nitrogen atoms in the graphite sheet[105]. There were concurrent studies from our group at OSU which demonstrated that carbon nanostructures grown over pure alumina, without
any transition metal incorporation, still showed significant activity for ORR, albeit lesser than CNx prepared with a transition metal[82].

In another study in 2009, Subramanian et al. synthesized similar catalysts as above, using Ketjen Black which was pre-washed with concentrated acid, followed by adsorption of nitrogen-containing precursors such as formaldehydes of urea, melamine or selenourea in a polymerization reaction, followed by a heat treatment step in the range of 400-1000°C in N₂[128]. Their most active catalysts were obtained at 800°C, the temperature at which a significant amount of pyridinic nitrogen was observed on the surface, which was then transformed to graphitic nitrogen at 1000°C. Their X-ray Diffraction (XRD) patterns also revealed an increased degree of graphitization for the heat-treated carbons. On the basis of these experiments, the authors concluded that pyridinic nitrogen-enriched carbon without the presence of metal was the active site for ORR, indicating that the doped carbons turned into strong Lewis bases and thus catalyzed the adsorption-reduction reaction of oxygen, without getting oxidized themselves.

Sheng Dai and coworkers, who have contributed significantly to synthesis and characterization of mesoporous carbon materials and graphene[129, 130] recently carried out a study on ORR activity of nitrogen doping of 2D hexagonal ordered mesoporous carbon (N-O-MC) by heat treatment in ammonia at high temperatures. The catalyst heat-treated at a temperature of 1050°C demonstrated an onset potential of 720 mV vs. NHE, which, although lower than Pt/C catalyst, was still on the higher side of metal-free nitrogen-doped carbon catalysts[131]. This catalyst also showed superior stability in
comparison with Pt/C, losing only ~30% of their activity in comparison with Pt/C which showed an activity loss of about 80%.

Theoretical methods have helped to predict the role of nitrogen in various nitrogen containing carbon materials for ORR. Ikeda et al. have conducted molecular dynamics simulations to analyze the possible oxygen adsorption and reduction sites on nitrogen-doped carbon materials[132]. It was found that certain N sites enhanced catalytic activity without requiring metal catalysts: specifically, they prepared 8 different model structures in which N replaced sp\(^2\) carbon atoms. This produced 3 different configurations of atoms on the exposed surface- basal plane, zigzag edge, and armchair edge. It appears that an oxygen molecule would be preferentially adsorbed at C-sites on graphene like zig-zag edges if graphitic-N is nearby. These findings were supported by experimental results in which carbon polymers were carbonized along with their nitrogen precursors and a transition metal containing compound[115]. As a result of this synthesis procedure, the materials consisted of nanoshells of sp\(^2\) carbon, and their catalytic activity towards ORR was enhanced by increasing nitrogen concentration or codoping with boron.

In another study involving first principles calculations, pyridinic-N was found to be the most stable nitrogen species in a graphene cluster[133]. According to the researchers, pyridinic nitrogen stabilizes the zig-zag edges of graphene, aiding their growth in the synthesis process. However, for a given zig-zag edge, pyridinic nitrogen may not be favorable for ORR. Rather, N-doped at the site next to zig-zag edges can activate neighboring edge-carbons, but this configuration was not found to be
energetically favorable. However, co-doping with B and N may counteract the energetic limitations of ORR at these sites and EXAFS analysis of the N1s region found that catalysts with larger amounts of “graphite-like” nitrogen exhibited higher ORR activity. Hard X-ray photoemission spectroscopy (HXPES) experiments of N-doped carbon catalysts were conducted, namely (i) nitrogen-doped carbon synthesized from melamine and poly furfuryl alcohol, (ii) nitrogen-doped onto carbon black using 50% and 90% ammonia gas at 600°C, and (iii) nanoshell carbon from pyrolyzed cobalt phthalocyanine and phenolic resin, acid washed with HCl after pyrolysis to remove cobalt[134]. In the nanoshell carbon sample, it was found that the cobalt concentration was only 0.03% within the probing depth of photoelectrons, most of which was metallic cobalt. Since metallic cobalt is known to be inactive for ORR, the activity of the nanoshell carbon was not attributed to cobalt.

1.6 Active Site Debate

One of the most widely researched topics in the NNMC community is to determine the active sites in these nitrogen-doped carbon or Fe-N-C catalysts.

Professor Dodelet compared the potentials for onset of ORR activity by different researchers in a recent review[135]. The comparison indicates that the overall average onset potential value for all N-doped catalysts prepared without a transition metal (namely Fe or Co) is about 0.56 V vs. RHE. Whereas the overall average onset potential value for the catalysts prepared with either Fe or Co is 0.74V vs. RHE and that for the carbon supports without any doped nitrogen is reported as ~0.20V. It is likely that the
catalysts that show a high onset potential for N-doped carbon without any transition metal, is due to the presence of pyridinic or graphitic nitrogens in these materials. Graphene edge planes also play an important role in facilitating better interaction with O\textsubscript{2} atoms than carbon atoms located at the basal planes. But it is difficult to isolate the effect of pyridinic nitrogen groups from graphitic edge planes, because pyridinic-N groups are only found on graphene sites with higher edge plane exposure.

Catalyst characterization techniques such as Time of Flight- Secondary Ion Mass Spectrometer, Mossbauer Spectroscopy, Scanning Transmission Electron Microscopy (STEM) and Electron Energy Loss Spectroscopy (EELS) have been used recently to corroborate the existence of Fe-N\textsubscript{x} sites in Fe-N-C materials. Out of these, Mossbauer Spectroscopy has been the most insightful\textsuperscript{51}. Based on the technique, the FeN\textsubscript{4} sites that possess an unfilled 3d\textsuperscript{2} orbitals with only one electron present, as well as those Fe sites that have no electrons in the 3d\textsuperscript{2} are both seen to interact readily with O\textsubscript{2} resulting in active sites. This iron\textsuperscript{II} site is present in a high spin state\textsuperscript{53, 136}. The role of the pyridinic nitrogen is that when this is present in the vicinity of an FeN/C site, and is protonable, it acts as an agent to quickly transfer the protons to the iron ion\textsuperscript{109}. However, in the presence of the fuel cell ionomer, the sulfonate group binds to the protonated pyridinic nitrogen groups, leading to an active site blockage over time, which translates to activity losses over a period of time. For the mechanism of O\textsubscript{2} reduction on Fe-N-C catalysts, though there are many plausible reaction pathways explored, one point of agreement between researchers is the first electron transfer being the rate limiting step in the O\textsubscript{2} reduction reaction in acidic medium.
Oxygen reduction on N-doped carbons is relatively harder to understand than the easier interaction between O$_2$ and Fe catalytic sites. In an acidic environment, O$_2$ adsorbs H$^+$ to form H$^+$-O-O which is reduced at the electrode to form water. This reaction occurs only on N-doped graphene as the (highest occupied molecular orbital- lowest occupied molecular orbital) HOMO-LUMO gap for graphene is lower by a factor of 2 compared to pure graphene[137]. This leads to an improvement in the chemical reactivity of N-doped graphene, since electrons can more easily get transferred from the valence to the conduction band. Nitrogen doping also introduces unpaired electron in the matrix which causes spin and charge densities to be introduced in the graphene layer, resulting in their transformation into catalytic sites for ORR.

While some researchers still believe that the ORR activity in transition metal-based N doped carbon materials is partly attributable to trace amounts of transition metal being involved in the reaction, there is another group, including ours, that believes in the existence of nitrogen-functionalized carbons as the catalytic active site[138].
CHAPTER 2. Research Objectives

The scope of this research has been multi-fold: *operando, in-situ and ex-situ* characterization techniques have been used to reveal differences in the transition metal present in carbon nanostructures (CN\textsubscript{x}) catalysts over different supports, during the different stages of carbon growth process on these catalysts. This provided some crucial insight into the role of the transition metal in CN\textsubscript{x} catalysts.

Also, while there is ambiguity about the role of the transition metal in the Me-N\textsubscript{x}-C and CN\textsubscript{x} catalysts for ORR, the results from our research group over the years have led us to believe that in nitrogen-doped carbon nanostructured (CN\textsubscript{x}) catalysts, the active sites consist of a synergy of graphitic edge planes along with pyridinic nitrogen groups present on these edge planes. Another objective of this research has been to achieve a better understanding of the active site in these materials, and differentiate between the two materials. The experimental methods and characterization techniques used to accomplish this goal, along with catalyst synthesis and activity testing parameters have been outlined in Chapter 3.
**In-situ** characterization of carbon nanostructures using Extended X-ray Absorption Fine Structure Spectroscopy (EXAFS) has been used to analyze the changes in the transition metal phase as a function of increasing temperature and durations of acetonitrile treatments (carbon growth), and this study is the subject of Chapter 4.

Furthermore, we synthesized and compared the two types of catalysts debated in the literature, namely, CN\textsubscript{x} and FeNC catalysts, and compared their performance in terms of activity and long term stability tests in an electrolytic half-cell and a PEM fuel cell. These differences in activity have been correlated with compositional and structural characteristics of these two materials which allow for a better understanding of the existing differences and similarities between them. This is described in Chapter 5. The stages of preparation of FeNC catalysts have been evaluated for ORR activity in Chapter 6. This study elucidated the role of the transition in FeNC catalysts, as well as the effect of the heat-treatments.

Sulfur treatment and targeting the active sites of FeNC catalysts has been attempted using H\textsubscript{2}S as a sulfur source, and its effect on the activity of the catalysts has been evaluated. This study incorporated sulfur treatments of FeNC catalysts at various stages of their preparation to isolate the effect of sulfur as a probe molecule. This is the subject of Chapter 7.

**Operando** half-cell and fuel cell experiments using EXAFS performed under actual fuel cell conditions have been described in Chapter 8 with conclusions and future recommendations in Chapter 9.
CHAPTER 3. Experimental Methods

3.1 Materials Synthesis

3.1.1 CNₓ catalysts

The carbon nanostructured (CNₓ) catalysts investigated for various studies performed were grown over a transition metal salt (cobalt or iron acetate) over a magnesium oxide or Vulcan carbon precursor. For in-situ characterization studies, the metal loading was increased to 10\% from a typical loading of 2\% by weight of the metal on the support, for ease of detection during X-ray Absorption spectroscopy and X-ray diffraction experiments.

The carbon growth substrates for in-situ characterization were prepared by incipient wetness impregnation of 10wt.\%Co onto a nano-powder magnesia support (Sigma-Aldrich) or Vulcan carbon XC-72 using an aqueous solution of cobalt acetate (Sigma-Aldrich) followed by drying of the growth substrate overnight at 110°C in an air oven.
1 gram of the growth substrate was weighed into a quartz calcination boat and placed inside a quartz tube in a high temperature furnace. The calcination tube was purged with nitrogen at 65 mL/min for 30mins at room temperature and then heated to 800°C at 10°C/min, at which time acetonitrile- (CH$_3$CN, Fisher, Optima grade) saturated nitrogen gas at 65 mL/min was streamed over the cobalt-impregnated growth substrate for 2h. During this 2h period, acetonitrile decomposed over the growth substrate depositing a carbonaceous material. Following this step, the system was cooled to room temperature under nitrogen. The carbonaceous material grown over magnesia or Vulcan carbon was then acid washed in 1M HCl at 60°C for 1h, rinsed thoroughly with DI water, and dried overnight in an air oven at 110°C. The resulting catalyst was denoted as nitrogen-containing carbon nanostructures (CN$_x$).

The catalysts grown on two difference growth substrates have been characterized at different stages of heat treatment, acetonitrile decomposition, as well as before and after acid washing. For ease of identification, we have established a nomenclature for the catalysts studied, described in Chapter 4.

CN$_x$ grown on 2 wt.% iron-impregnated magnesia or Vulcan carbon were prepared by the procedure outlined above, with the use of iron acetate instead of cobalt acetate as the transition metal salt. CN$_x$ was deposited onto the support by flowing acetonitrile over the growth substrate at a higher temperature (900°C) for 2h, after which the CN$_x$ and support were removed from the quartz tube and acid washed in 250 mL of 1M HCl for 1h. After acid-washing, it is vacuum filtered, rinsed with 1 L DI water and dried overnight in an oven at 110 °C. Samples were also prepared by acid-leaching for a
longer duration of 2 days and 1 week, and are referred to as CN\textsubscript{x}-AW-48h and CN\textsubscript{x}-AW-1week.

### 3.1.2 Fe-N-C Catalysts

Fe-N-C catalyst precursor was prepared via a wet-impregnation technique by dissolving 1,10-phenanthroline (phen) in a 150 mL solution of 2:1 deionized water: ethanol (Fisher Scientific). Next, 31 mg iron(II) acetate was added to this solution, which was stirred until it achieved a deep red color indicative of the formation of [Fe(phen)\textsubscript{3}]\textsuperscript{2+} complex. Black Pearls 2000 (Cabot Corp.) was added to this solution such that the ratio of 50:50 phen:BP2000 was achieved. The mixture was stirred at 80 °C until about 50 mL remained. The solution was then placed overnight in a drying oven at 90 °C. The residue obtained after drying was ball-milled for 3h in a rotary ball-mill at 200 rpm. This catalyst precursor is called FeNC-prec-NoHT. The resulting fine powder was then weighed into a quartz boat which was placed at the end of a long quartz tube in a pyrolysis furnace, such that the quartz boat itself was outside the furnace. The furnace was heated to 1050 °C with argon gas flowing at 300 mL/min, and upon reaching the set-point, the quartz boat was inserted in the furnace by means of a magnet-containing glass-rod directed by an external horseshoe magnet. The catalyst was then treated in argon for 1h, and removed from the furnace upon completion of the treatment time. This catalyst is called- FeNC-Ar. A portion of the catalyst was then subjected to a second heat treatment in NH\textsubscript{3} at 950 °C for 20 min, following the same procedure outlined above, and the catalyst is called- FeNC-Ar-NH\textsubscript{3}. For acid-washed (AW) samples, the NH\textsubscript{3} treated catalyst was leached in 1M HCl for 1h, 2 days or 1 week following the same procedure adopted for acid washing
of CN$_x$. These Fe-N-C catalysts are denoted as FeNC, FeNC-AW-1h, FeNC-AW-48h and FeNC-AW-1w. Some of the catalysts used for experiments were acid-washed in 1M HCl right after the Argon treatment step, and they are called FeNC-Ar-AW-1h.

While comparing the two classes of catalyst: CN$_x$ and FeNC, we are comparing them in their most active form, which is CN$_x$-washed in HCl for 1h and FeNC unwashed. Hence for the sake of clarity the nomenclature CN$_x$-washed/ unwashed and FeNC-washed/unwashed are used to compare the two catalysts in Chapter 5 and the effect of acid washing on them, unless otherwise specified.

In order to evaluate the effect of transition-metal incorporation in FeNC catalysts, and the effect of heat-treatments on them, control catalysts were prepared as follows: Phenanthroline was dissolved in a mixture of DI H2O and ethanol in a 2:1 ratio, to which Black Pearls 2000 was added. Care was taken to ensure there was no Fe contamination in the solution. When the solution reduced to approximately 1/3$^{rd}$ of its volume, it was placed overnight in an oven and dried. This precursor was called BP-Phen-NoHT. The dried powder was hand-ground to avoid Fe contamination from stainless-steel balls used in ball-milling, and was then heat-treated in Ar at 1050°C for 1h. This catalyst is called BP-Phen-Ar. There was a subsequent NH$_3$ treatment incorporated at 950°C for 20mins and the catalyst is called BP-Phen-Ar-NH$_3$.

3.2 Catalyst Characterization

A number of analytical techniques have been used to gain a better understanding of the structure, morphology, and composition of the catalysts used for ORR, to be able
to identify the features that distinguish a good catalyst from a bad one. Most experiments described below such as temperature programmed oxidation, desorption, pulsed chemisorption, as well as all electrochemical tests using a half cell and fuel cell were performed in the Heterogeneous Catalysis Research Laboratory. The X-ray diffraction and X-ray photoelectron spectroscopy (XPS) experiments were performed in the Department of Chemistry. Transmission electron microscopy (TEM) experiments were performed at the Campus Electron Optics Facility in the Department of Materials Science and X-ray absorption fine structure spectroscopy (EXAFS) experiments were performed at the Argonne National Laboratory.

3.2.1 Extended X-ray Absorption Fine Structure (EXAFS)

EXAFS (also known as XAFS, or just X-ray Absorption Spectroscopy (XAS)) provides detailed information about the local bonding environment and coordination state of an element of interest. The principle behind this technique is based on creation of photoelectrons by the photoelectric effect. The central atom is bombarded with X-rays which are tuned to the excitation energy of the atom of interest, creating photoelectrons. These photoelectrons are ejected and undergo interference with the electron waves of the neighboring atoms. If the interference is constructive, it results in the formation of a fine structure of the X-ray absorption spectrum. The frequency of the EXAFS spectrum contains information about the interatomic distances between the absorbing and the neighboring atoms, and the amplitude gives information about the number, type and order of the neighboring atoms. EXAFS is a versatile tool that can be used for doing a number of in-situ catalyst characterization at high temperatures and under reaction conditions,
which is otherwise not possible with lower energy X-ray techniques. However, access to high energy sources can only be found at synchrotron facilities away from traditional lab facilities.

EXAFS Spectra were collected for the Co K-edge (7709 eV) at the bending magnet beamline (5BM-D) of the Dow-Northwestern-DuPont Collaborative Access Team (DND-CAT) of the Advanced Photon Source, Argonne National Laboratory. The measurements were made in transmission mode with the Si(111) monochromator detuned by 30% to eliminate the higher order harmonics in the beam. 10% Co-VC or Co-MgO catalysts were mixed with SiO₂ in a weight ratio of 1:3 and finely ground to obtain a homogeneous mixture. Approximately 10 mg of the mixture was then pelletized and placed inside a 5cm-long quartz tube (6.5 mm ID) and supported with quartz wool plugs. The sample was then centered in a 45×2 cm controlled-atmosphere XAFS chamber that was fitted with Kapton® windows. The XAFS reactor set-up allowed continuous flow of the reactants as well as atmospheric isolation of the catalyst sample. Carbon deposition was observed on the pelletized support upon introduction of acetonitrile at elevated temperature in the XAFS reactor setup.

Spectra were collected under in-situ conditions, with the pelletized Co-VC or Co-MgO: (1) at room temperature, (2) heated to 800°C in nitrogen, (3) in nitrogen-saturated acetonitrile at 800°C for 30 mins and (4) for 2h. Spectra of samples after acid washing were collected ex-situ for both Co-VC and Co-MgO samples.
Spectra for the Fe k-edge were collected under identical conditions as outlined above, by tuning the monochromator to 7112 keV. The *ex-situ* spectra were collected by making thick pellets of the samples and loading them into sample holders of 1.3mm diameter each.

### 3.2.2 X-ray Diffraction (XRD)

XRD relies on the principle that crystal structures consist of planes formed by repetitive arrangements of atoms, that are capable of diffracting X-rays[139]. The diffraction is caused by the elastic scattering of X-ray photons by atoms in a periodic lattice. The scattered monochromatic X-rays that are in phase produce constructive interference. A detector scans the intensity of the diffracted radiation as a function of the angle $2\theta$, which is the angle between the incoming and the diffracted beams. With the angle $2\theta$, one can determine the lattice spacings within a crystal based on the Bragg relationship:

$$n\lambda = 2d \sin\theta$$

The diffraction pattern obtained from these lattice spacings are characteristic of every compound or element, and allows for differentiation of various structures within a catalyst.

The XRD patterns were collected on a Bruker D8 Advance X-ray diffractometer with a monochromatically isolated Cu K$_{\alpha1}$ radiation source and a Braun position sensitive detector (operated at 50mA and 40 kV). Diffraction patterns were collected *in-situ* or *ex-situ* in a polyethylene sample holder, with the catalyst powder firmly pressed onto the holder. *In-situ* XRD high temperature experiments were conducted using an Anton Paar
HTK 1200 controlled-atmosphere oven where the catalyst growth precursor (Co-VC or Co-MgO) were heat treated in N\textsubscript{2} atmosphere to 800°C. Spectra were collected every 100°C. The diffraction patterns were collected in the 20°-80° range of Bragg angle with a step size of 0.0106°.

3.2.3 Transmission Electron Microscopy (TEM)

In a TEM, a primary electron beam of high energy and high intensity passes through a set of magnetic lenses to produce parallel rays that impinge on the sample. The beams are attenuated and depending on the density and thickness of the sample, they form a two-dimensional projection of the sample, which is subsequently magnified by electron optics to produce a bright field image. An FEI Tecnai F20 XT TEM was used at 200 keV for imaging of the carbon nanostructures. Sampled were dispersed in ethanol before being loaded onto lacey formvar carbon supported by a 200 mesh copper grid.

3.2.4 X-ray Photoelectron Spectroscopy (XPS)

XPS provides critical information about the elemental composition and oxidation state of the surface of a catalyst. XPS is based on the photoelectric effect in which an atom absorbs a photon of energy hv. Following this event, a core or a valence electron with binding energy E\textsubscript{b} is ejected with kinetic energy=

\[ E_k = h\nu - E_b - \varphi \]

Where \( E_k \) = kinetic energy of the photoelectron

\( h \) = Planck’s constant

\( \nu \) = frequency of exciting radiation

\( \varphi \) = work function of the spectrometer
These binding energies are not only specific to elements, but also contain information about oxidation states, as the energy levels of core electrons somewhat depend on the chemical state of the atom. Chemical shifts seen typically are in the range of 0 to 3eV.

X-ray photon spectroscopy was used to analyze the composition of the surface species present on the carbon growth substrates and acid-washed catalysts. The samples were prepared according to the procedure outlined in the catalyst preparation section. A Kratos Ultra Axis spectrometer was used with a monochromated aluminum anode source operated at 12 kV and 10mA. An initial survey scan was collected with a pass energy of 80 eV. Subsequently, individual scans were collected with a pass energy of 20 eV and the regions scanned were Co 2p, Fe 2p, Mg 1s, O1s, N 1s, C 1s, S 2p for the different samples that were characterized.

3.2.5 Temperature Programmed Oxidation (TPO)

Temperature-programmed oxidation (TPO) experiments are typically used to determine the different types of elemental species present in a sample that are capable of undergoing oxidation. Since the catalysts are primarily carbon-based, TPO studies are a useful tool to examine the different types of carbon present, based on the degree of graphitization and defects present in the sample. Depending on the nature of graphitization, the different carbon species present in the catalyst oxidize at different temperatures. The same phenomenon is observed for nitrogen and sulfur species, if present in the catalyst, as the surface species would get oxidized at a lower temperature as
compared to those embedded within the carbon matrix, that would evolve as oxidation products at a higher temperature.

TPO experiments were performed for CN₅ and Fe-N-C catalysts using an Autochem 2010 under 10% O₂/He gas at a flowrate of 30 ccm. 30 milligrams of the catalyst was packed in a U-tube quartz reactor and held in a high-temperature furnace. The sample temperature was first allowed to equilibrate to 50 °C for 15 min, then the temperature was ramped to 850 °C at 5°C/min and held there for 20 min. The TPO product stream was fed to an MKS Cirrus benchtop residual gas analyzer with mass signals of 1-100 monitored throughout the experiment.

TPO experiments using an external furnace

Temperature-programmed oxidation (TPO) experiments were performed using 7 mg of catalyst loaded into a 4 mm-ID quartz reactor with a quartz frit, heated in a Carbolite, MTF 10/15/30 furnace under 5% O₂/He at 30 ccm, with a linear temperature program ramp rate of 10°C/min up to 900°C. The TPO product stream was fed to an MKS Cirrus benchtop residual gas analyzer with mass signals of 1-100 monitored throughout the experiment.

3.2.6 Temperature Programmed Desorption (TPD)

TPD experiments were performed to analyze the surface species that desorbed from catalysts under the flow of inert gas (Helium) while ramping temperature to 950°C. Temperature-programmed desorption (TPD) experiments were performed using 7 mg of catalyst loaded into a 4 mm-ID quartz reactor with a quartz frit, heated in a Carbolite,
MTF 10/15/30 furnace under pure He at 30 ccm, with a linear temperature program ramp rate of 10°C/min up to 900°C. The TPD product stream was fed to an MKS Cirrus benchtop residual gas analyzer with mass signals of 1-100 monitored throughout the experiment.

3.2.7 Superconducting Quantum Conducting Device (SQUID) Magnetometry

Magnetization was measured as a function of field using a Superconducting Quantum Interference Device (SQUID) magnetometer (Quantum Design MPMS XL) at 300 K. The applied field was varied from -30000 Oe to +30000 Oe and then back to -30000 Oe. A total of 100 data points were collected for each sample. These data were then fitted to the Langevin function (Equation 3) and the values for saturation magnetization and average iron particle size (assuming a spherical shape) were determined.

\[
\frac{M}{M_{sat}} = L\left(\frac{M_s V H}{k_B T}\right) \quad \text{where}
\]

\(M\) is the magnetization (emu/g)

\(M_{sat}\) is the saturation magnetization (emu/g)

\(Ms\) is the spontaneous magnetization (emu/cm\(^3\))

\(V\) is the volume of particle (cm\(^3\))

\(H\) is the applied field (Oe)

\(K_b\) is the Boltzmann Constant (cm\(^2\)gs\(^{-2}\)K\(^{-1}\))

\(T\) is the temperature (K)

\(L(x) = \coth(x) - \frac{1}{x}\) is the Langevin function for superparamagnetic particles.
3.2.8 Inductive Coupled Plasma Optical Emission Spectrometer (ICP-OES)

Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) is an analytical tool to determine the concentration of elements in a sample. The limitation of the technique is that solid samples require acid digestion so that the analytes can be present dissolved in solution. The liquid or gaseous sample is converted to aerosol and channeled into the center of plasma chamber. The inductively coupled plasma is at a temperature of about 10000 K, as a result the aerosol is quickly vaporized. The analytes are then liberated as free atoms in gaseous form. The atoms are also provided with additional energy to promote them to excited states by the collisional excitation within the plasma, while simultaneously converting them to ions, which too are promoted to excited states. Both the excited atoms and ions relax to ground state with the emission of photons, which have characteristic wavelength finger prints that are used to identify and quantify the elements from which they originated.

ICP-OES was performed on the samples for Fe analysis using a Perkin Elmer Optima 3000 Fe samples were diluted 2x with deionized water and data was acquired for wavelengths of 234, 238, 239 and 259 nm. Calibration standards equivalent to 0, 2, 10 and 20 ppm in the original samples were prepared. The standards were prepared using single element standards purchased from High Purity Standards and diluted with 2% v/v ultrapure HCl in deionized water. Calibration blanks were 2% v/v ultrapure HCl in deionized water.
3.3 Electrochemical Characterization

Electrochemical activity and stability characterization for the catalysts was implemented using an electrolytic half-cell, as well as a single fuel cell. The half-cell consists of a glass container with 0.5M H₂SO₄ (pH=1) which provides the protons for the reaction in Equation 2, in the absence of hydrogen gas, while oxygen gas is bubbled through the solution to provide an excess of reactant. The set-up used in this experiment consists of a rotating disk or rotating ring-disk electrode (RDE or RRDE), which is essentially a two working electrode system: 1. The glassy carbon disk on which the catalyst ink is applied and where ORR occurs. 2. The platinum ring surrounding the disk which detects the H₂O₂ generated in the reaction, thus determining whether the reaction proceeds via the 4 electron or 2 electron mechanism. The fuel cell experiments are conducted as explained in Chapter 1. However, the process of fabrication of an MEA requires expertise and a considerable amount of time to complete testing a single MEA. Due to this, catalysts are first screened using the simpler RDE or RRDE technique, and those catalysts that show significantly high activity are then used for fuel cell tests.

3.3.1 Rotating Ring Disk Electrode (RRDE)

The electrochemical activity of the catalysts was first tested using rotating ring disk electrode (RRDE) technique, fitted with a glassy carbon disk and platinum ring, in an oxygen-saturated 0.5 M H₂SO₄ aqueous solution. Catalyst ink was prepared by mixing 10 mg catalyst, 95µl Nafion (5wt% in aliphatic alcohols), and 350µl ethanol. The ink
suspension was sonicated for ~1h, following which 2 aliquots of 9 µl of the ink were pipetted onto a clean glassy carbon disk electrode of surface area 0.2472 cm², amounting to a catalyst-loading of 1.6 mg/cm². All measurements were performed in a 0.5M H₂SO₄ solution with platinum counter electrode and Ag/AgCl reference electrode. RRDE measurements were performed by collecting CVs at the disk in a potential range of 1.2 to 0.0 V vs. RHE with scan rates of 10 mV/s at 1000 or 1600rpm, while the ring was held at a constant potential of 1.2V vs. RHE. Cyclic Voltammetry was conducted in argon-saturated H₂SO₄ at 10 mV/s from 1.2 to 0.0V vs. RHE V vs. Ag/AgCl to subtract the capacitive current. The conversion from Ag/AgCl to RHE scale was made by measuring the potential difference between Ag/AgCl and a Pt foil in the same electrolyte saturated with hydrogen. ORR activity is reported as the onset potential, which is defined as the potential at which the current in oxygen-saturated electrolyte becomes 10% greater than the current in the argon-saturated electrolyte.

Selectivity (n) is determined as the number of electrons transferred per oxygen molecule at the disk by comparing the disk and ring currents during ORR activity tests. The reactions occurring during the complete and partial reduction of oxygen to water or H₂O₂ respectively, are as follows:

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

\[
O_2 + 2e^- + 2H^+ \rightarrow H_2O_2 \quad 0.695V \text{ vs. RHE} \quad (5)
\]

Selectivity was determined by comparing the ring and the disk current obtained in the O₂ saturated solution, by the following formula:
\[ n = \frac{4I_D}{I_D + \frac{I_R}{N}} \]  

Where \( n \) is the number of electrons transferred per oxygen molecule, \( I_D \) is disk current, \( I_R \) is ring current and \( N \) is the collection efficiency of the ring (equal to 37% as determined by the manufacturer). An \( n \) value of 4 corresponds to a complete reduction of oxygen to water, whereas an \( n \) value of 2 is equivalent to a complete formation of hydrogen peroxide. The ring was held at 1.2V vs. RHE, at a potential where ORR current is negligible and oxidation of \( \text{H}_2\text{O}_2 \) to oxygen would be mass transfer limited.

### 3.3.2 Accelerated Durability Tests

Accelerated durability tests (ADTs) were performed by first collecting initial activity data as described above. The electrode was then cycled between 1.2V to 0.0V to 1.2V vs. R/NHE at 100 mV/s for several hundred cycles, with a hold at 1.2V for 5 seconds after each cycle. Activity data was collected after 100, 500 and 1000 cycles.

### 3.3.3 Fuel Cell Activity and Stability Tests

Membrane Electrode Assemblies (MEAs) were prepared by the following method. Anode comprised of commercial 20 wt % Pt/C from E-TEK (Pt loading 0.5 mg/cm\(^2\)). The ink for the cathode catalyst was prepared by using 10 mg catalyst, 326 \( \mu \)L 5 wt% Nafion in aliphatic alcohols solution, 163 \( \mu \)L ethanol and 136 \( \mu \)L deionized water. The ink was sonicated in an ice bath until the catalyst was well-dispersed. An aliquot of 71 \( \mu \)L was spread uniformly on a gas diffusion layer of carbon paper with surface area of
1.14 cm$^2$, to achieve a catalyst loading of 1 mg/cm$^2$. After drying, the electrodes were hot-pressed at 140 °C with a Nafion 115 membrane in between them.

Fuel cell tests were performed using an Arbin Fuel Cell Test Stand at a cell temperature of 80 °C, flow rates of O$_2$ and H$_2$ at 300 ccm with a back-pressure of 15 psig and dew-point temperature of 85 °C. Polarization curves were obtained by scanning the cell potential from open circuit voltage (OCV) to 0V at a scan rate of 0.5 mV/s. For stability tests, the first polarization curve was recorded once the temperature and pressures reached a steady-state. The cell was then held at a potential of 0.5V for 1h, before measuring a second polarization curve. Following this polarization curve, the cell was held at 0.5V for 100h before finally recording a third polarization curve.
CHAPTER 4. In-situ characterization of the growth of CN$_x$ carbon nano-structures as oxygen reduction reaction catalysts

As published in *Journal of Catalysis* [140]

4.1 Motivation

In our earlier studies, CN$_x$ catalysts were characterized ex-situ to reveal differences in their nitrogen contents based on graphitic edge-plane exposure and these differences were correlated to ORR activity of these catalysts. However, the role of cobalt over magnesia and Vulcan carbon precursors for ORR not been studied before and this is the first report of an *in-situ* characterization study undertaken for these catalysts to observe changes in the transition metal during the growth process of carbon nanostructures, by acetonitrile pyrolysis at 800°C.

The growth process of nitrogen-doped carbon nano-structures (CN$_x$) was characterized using *in-situ* (XANES, EXAFS, XRD), and *ex-situ* (XPS, TEM) techniques. CN$_x$ nano-structures were grown on two different Co-doped substrates: Vulcan carbon and MgO. CN$_x$ formation was achieved by pyrolyzing a C- and N-containing compound, CH$_3$CN, at high temperatures. The Co phase was seen to go through different transformations during the pyrolysis process, depending on the growth substrate used. The Co species, which started in an acetate matrix prior to pyrolysis, became partially reduced with heating and with CH$_3$CN treatment. CN$_x$ fibers that
formed were acid-washed, and the Co phase left behind was primarily metallic, regardless of the growth substrate used. The structure of CN$_x$ obtained as well as the nitrogen content was significantly different on the two substrates, which led to activity differences as shown by RRDE.

4.2 Results and Discussion

The catalysts grown on two different growth substrates have been characterized at different stages of heat treatment, acetonitrile decomposition, as well as before and after acid washing. The method of preparation is outlined in the experimental methods, in Chapter 2. For ease of identification, we have established a nomenclature for the catalysts studied, which is presented in Table 1 below.
Table 1. Nomenclature for identification of CN$_x$ growth catalysts on Vulcan carbon and MgO.

<table>
<thead>
<tr>
<th>Sample Description</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>A. Growth substrate: Co-VC</td>
<td>Vulcan carbon doped with 10%Co</td>
</tr>
<tr>
<td>A.1. Co-VC-RT</td>
<td>Co-VC at room temperature</td>
</tr>
<tr>
<td>A.2. Co-VC-800-N$_2$</td>
<td>Co-VC heated in nitrogen at 800°C</td>
</tr>
<tr>
<td>A.3. Co-VC-800-CH$_3$CN-30m</td>
<td>Co-VC treated with acetonitrile-saturated nitrogen at 800°C for 30 minutes</td>
</tr>
<tr>
<td>A.4. Co-VC-800-CH$_3$CN-2h</td>
<td>Co-VC treated with acetonitrile-saturated nitrogen at 800°C for 2h</td>
</tr>
<tr>
<td>A.5. CN$_x$-Co-VC-800-CH$_3$CN-2h-AW</td>
<td>Sample A.4. washed in 1M HCl for 1h</td>
</tr>
<tr>
<td>B. Growth substrate: Co-MgO</td>
<td>MgO doped with 10%Co</td>
</tr>
<tr>
<td>B.1. Co-MgO-RT</td>
<td>Co-MgO at room temperature</td>
</tr>
<tr>
<td>B.2. Co-MgO-800-N$_2$</td>
<td>Co-MgO heated in nitrogen at 800°C</td>
</tr>
<tr>
<td>B.3. Co-MgO-800-CH$_3$CN-30m</td>
<td>Co-MgO treated with acetonitrile-saturated nitrogen at 800°C for 30 minutes</td>
</tr>
<tr>
<td>B.4. Co-MgO-800-CH$_3$CN-2h</td>
<td>Co-MgO treated with acetonitrile-saturated nitrogen at 800°C for 2h</td>
</tr>
<tr>
<td>B.5. CN$_x$-Co-MgO-800-CH$_3$CN-2h-AW</td>
<td>Sample B. 4. washed in 1M HCl for 1h</td>
</tr>
</tbody>
</table>

4.2.1 In-situ X-ray Absorption Spectroscopy

10wt%Co-VC and 10wt%Co-MgO substrates were characterized using in-situ XAFS during different stages of heat treatment and pyrolysis. Figure 10a shows the timeline used during pyrolysis and spectra acquisition. Figure 10b and c show a photograph of the furnace/reactor assembly inside the XAS hutch and a schematic of the in-situ system used for data acquisition and carbon growth, respectively. Figure 10d shows a photograph of carbon nano-structures grown over the pelletized Co/MgO substrate in the
beam path, where the carbon growth is visibly protruding from the opening in the quartz reactor.

**In-situ X-ray absorption near edge structure (XANES)**

The ease of reduction and coordination environment of 10%Co-VC and Co-MgO were studied using *in-situ* XANES. Cobalt acetate, CoO, and Co foil were used as reference compounds for linear combination X-ray absorption near-edge structure (LC-XANES) fits. The results of fits are tabulated in Table 2 for Co-VC. From LC-XANES analysis of the Co-VC spectra at room temperature (Figure 11a), cobalt species were seen to exist as cobalt acetate prior to any heat treatment. Under nitrogen at 800°C, the sample reduced to a mostly metallic form (Figure 11b) and remained in this state even after introduction of acetonitrile for 30mins and 2h (Figure 11c and d).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Percentage of Co in different phases (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cobalt acetate</td>
</tr>
<tr>
<td>Co-VC-RT</td>
<td>100</td>
</tr>
<tr>
<td>Co-VC-800-N₂</td>
<td>-</td>
</tr>
<tr>
<td>Co-VC-800-CH₃CN-30m</td>
<td>-</td>
</tr>
<tr>
<td>Co-VC-800-CH₃CN-2h</td>
<td>-</td>
</tr>
</tbody>
</table>
The LC-XANES fits for the Co-MgO samples showed more oxidized states for cobalt (Table 3), which could be explained by the presence of the oxide support. At room temperature, Co in Co-MgO substrate exists in the Co$^{2+}$ form (Figure 12a). Up to 40% reduction was observed at 800°C under nitrogen (Figure 12b). Metallic cobalt became more evident upon introduction of acetonitrile for 30mins (Figure 12c) and persisted with the same weighted percentage contribution after 2h of acetonitrile treatment (Figure 12d). Co over MgO appeared to be less reduced at the end of CH$_3$CN treatment compared to Co in the Co-VC substrate.
Figure 10. Set-up for in-situ XAS at APS for growth of CNx a) Time-line used during pyrolysis and spectra acquisition, b) photograph of the furnace/reactor assembly inside the XAS hutch, c) a schematic of the operando system for data acquisition and carbon growth, d) a photograph of carbon nano-structures grown over the pelletized Co/MgO substrate in the beam path.
Table 3. Results of XANES FITS for Co-MgO Samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Percentage of Co in different phases (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cobalt acetate</td>
</tr>
<tr>
<td>Co-MgO-RT</td>
<td>17</td>
</tr>
<tr>
<td>Co-MgO-800-N₂</td>
<td>-</td>
</tr>
<tr>
<td>Co-MgO-800-CH₃CN-30m</td>
<td>-</td>
</tr>
<tr>
<td>Co-MgO-800-CH₂CN-2h</td>
<td>-</td>
</tr>
</tbody>
</table>

XANES spectra were collected ex-situ for CNₓ samples after acid washing (Figure 13). The LC-XANES fits for these samples are tabulated in Table 4. Acid-washed CNₓ grown on Co-VC showed that cobalt maintained its mostly-metallic form (>90% Co⁰) even after acid washing (Figure 13a). CNₓ formed on MgO after acid washing also showed >90% metallic Co. (Figure 13b). This result is significant in demonstrating that, although the type and abundance of cobalt phases that exist at the end of the acetonitrile pyrolysis may be different over the two growth substrates, once washed in acid, the cobalt phase left behind in the CNₓ materials is the same regardless of the growth substrate used.
Figure 11. Normalized in-situ XANES spectra of Co K-edge taken during the growth of CNx over Co-Vulcan Carbon growth substrate at different stages of pyrolysis. a) room temperature, b) after treatment in N₂ at 800°C, c) after 30 minutes of CH₃CN pyrolysis, d) after 2 h of CH₃CN pyrolysis (Spectra for Co acetate, CoO and Co are shown as reference).

Table 4. Results of XANES fits for CNx grown on Co-VC and Co-MgO after acid washing

<table>
<thead>
<tr>
<th>Sample</th>
<th>Percentage Fraction of components (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cobalt acetate</td>
</tr>
<tr>
<td>CNₓ-Co-VC-800-CH₃CN-2h-AW</td>
<td>-</td>
</tr>
<tr>
<td>CNₓ-Co-MgO-800-CH₃CN-2h-AW</td>
<td>-</td>
</tr>
</tbody>
</table>
Figure 12. Normalized in-situ XANES spectra of Co K-edge taken during the growth of CNx over Co-MgO substrate at different stages of pyrolysis a) room temperature, b) after treatment in N\textsubscript{2} at 800°C, c) after 30 minutes of CH\textsubscript{3}CN pyrolysis, d) after 2 h of CH\textsubscript{3}CN pyrolysis.
Figure 13. Normalized ex-situ XANES Co K-edge spectra of acid-washed CNx grown on a) Co-VC and b) Co-MgO

Extended X-ray absorption fine structure (EXAFS)

The extended X-ray absorption fine structure (EXAFS) spectroscopy technique provides information about the coordination environment of the samples. The magnitudes of the $k^2$ weighted Fourier Transform of the Co K-edge EXAFS spectra for Co-VC samples are shown in Figure 14a. At room temperature, the peak at the uncorrected R-value of 1.59 Å can be attributed to the Co-O peak present in Co-acetate. After nitrogen treatment at 800°C, the Co-O peak disappeared with a concurrent appearance of the Co-Co peak at 2.1 Å in the uncorrected FT-magnitude. This Co-Co peak persisted in both of the spectra taken 30 min and 2h after acetonitrile introduction. EXAFS fits were carried out using the same experimental standards used in XANES fits. The coordination parameters for Co-Co, Co-O and Co-O-Co, were obtained by isolation of the respective
shells from the EXAFS spectrum using the method outlined in Miller et al[141]. The coordination numbers (CN) obtained by fitting the isolated shells were divided by the fraction of the given component obtained from XANES to calculate the actual CN values. The Debye-Waller factors for Co species were calibrated in the 200-800 °C temperature range with known standards assuming a linear correlation with temperature[142]. The EXAFS fits are reported in Table 5. After heat treatment in N₂ only, and even after acetonitrile introduction for 30 mins, the cobalt particle size under in-situ conditions was very similar to that of bulk metallic cobalt, as indicated by the calculated CN values of 11.2 and 10.9 respectively.

Table 5. Results of EXAFS fits for Co-VC

<table>
<thead>
<tr>
<th>Sample</th>
<th>Component</th>
<th>CN</th>
<th>CN calculated</th>
<th>R</th>
<th>σ2</th>
<th>E₀ shift</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-VC-RT</td>
<td>Co-O from</td>
<td>4.7</td>
<td>4.7</td>
<td>2.10</td>
<td>0.00</td>
<td>-1.39</td>
</tr>
<tr>
<td></td>
<td>Co-Ac</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co-VC-800-N₂</td>
<td>Co-Co from</td>
<td>10.3</td>
<td>11.2</td>
<td>2.47</td>
<td>0.01</td>
<td>3.07</td>
</tr>
<tr>
<td></td>
<td>Co foil</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co-VC-800-CH₃CN-30m</td>
<td>Co-Co from</td>
<td>10.0</td>
<td>10.9</td>
<td>2.49</td>
<td>0.01</td>
<td>1.12</td>
</tr>
<tr>
<td></td>
<td>Co foil</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 14. Magnitudes of $k^2$-weighted Fourier transforms of in-situ cobalt K-edge EXAFS spectra of (a) Co-VC and (b) Co-MgO growth substrates during different stages of pyrolysis.
Figure 14b shows the FT-magnitudes acquired over the Co-MgO substrate at four different stages during pyrolysis. At room temperature, there exists a peak at 1.59Å, which could correspond to the Co-O bond in CoO. At 800°C in nitrogen, a smaller peak appeared at 1.4 Å along with a peak at 2.6 Å, which could be due to the Co-O and Co-O-Co interactions, respectively. After reduction under acetonitrile atmosphere, the intensity of the peak at 1.59Å decreased, with the simultaneous occurrence of a broad peak at 2.27 Å (uncorrected), which could be due to the conjunction of Co-Co with the Co-O-Co bond contributions. EXAFS fits carried out for the Co-MgO-RT, Co-MgO-N₂-800, and Co-MgO-CH₃CN-800-30m samples are tabulated in Table 6. References used are shown in Figure 15a. The fits provided further verification that the ratios of cobalt acetate, cobalt oxide, and metallic cobalt obtained for the different sample compositions were accurate.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Components</th>
<th>CN Calculated</th>
<th>R</th>
<th>σ²</th>
<th>E₀ shift</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-MgO-RT</td>
<td>Co-O from Co-Ac</td>
<td>1.02</td>
<td>6</td>
<td>2.15</td>
<td>-9.01</td>
</tr>
<tr>
<td></td>
<td>Co-O from CoO</td>
<td>3.9</td>
<td>4.7</td>
<td>2.05</td>
<td>4.99</td>
</tr>
<tr>
<td>Co-MgO-800-N₂</td>
<td>Co-Co from Co foil</td>
<td>4.8</td>
<td>12</td>
<td>2.57</td>
<td>8.62</td>
</tr>
<tr>
<td></td>
<td>Co-O-Co from CoO</td>
<td>7.2</td>
<td>12</td>
<td>3.08</td>
<td>0.09</td>
</tr>
<tr>
<td>Co-MgO-800-CH₃CN-30m</td>
<td>Co-Co from Co foil</td>
<td>6.0</td>
<td>9.1</td>
<td>2.53</td>
<td>7.2</td>
</tr>
<tr>
<td></td>
<td>Co-O-Co from CoO</td>
<td>4.2</td>
<td>12.3</td>
<td>3.08</td>
<td>-4.6</td>
</tr>
</tbody>
</table>
The EXAFS results are in agreement with XANES, where it was observed that Co on VC support was reduced almost completely to metallic cobalt upon heat treatment in nitrogen, with no significant difference observed after acetonitrile introduction. However, Co on MgO support was not as easily reducible even upon acetonitrile introduction. After acid washing, however, both CNₓ catalysts grown on VC and MgO had identical Co-Co peak contributions from metallic cobalt (Figure 15b).
Figure 15. Magnitudes of $k^2$-weighted Fourier transforms of cobalt K-edge EXAFS spectra of a) references of CoO and Co metal and b) acid-washed CN$_x$ grown on Co-VC and Co-MgO substrates
4.2.2 *In-situ* and *ex-situ* X-Ray Diffraction (XRD)

X-ray diffraction patterns acquired on the Co-VC substrate at different stages of pyrolysis are shown in Figure 16. All three diffraction patterns exhibit a broad graphitic peak at 2Θ values of 26° for the (002) plane of hexagonal graphite (ICDD#41-1487). At room temperature (Figure 16a), Co-VC did not show any crystalline peaks attributable to a Co-phase, since Co was in an amorphous CoAc phase after the impregnation process prior to any heating. After acetonitrile pyrolysis for 30min and 2h (Figure 16b and c), metallic Co peaks appeared at 2Θ values of 44°, 51°, and 76° corresponding to the (111), (200), and (220) planes, respectively (ICDD #89-4307). This result is consistent with the *in-situ* XANES and XAFS data indicating metallic character of Co in the Co-VC substrate following acetonitrile pyrolysis.
Figure 16. XRD patterns of growth substrate Co-VC at different stages of pyrolysis a) at RT, b) after CH3CN pyrolysis for 30mins, c) after CH3CN pyrolysis for 2h

For the Co-MgO substrates, the distinction between magnesia and cobalt crystalline peaks was not very clear. To further elucidate the differences between magnesia and cobalt-impregnated magnesia, the bare MgO support was heat-treated in nitrogen while *in-situ* XRD patterns were collected. Magnesia support at room temperature, shown in Figure 17, showed diffraction lines for cubic MgO (ICDD# 89-248) at 43°, 62°, 74°, and 78° corresponding to the (200), (220), (311), and (222) planes, and weakly resolved peaks corresponding to Mg(OH)₂ at 38°, 51°, and 58° for the (101), (102), and (110) planes (ICDD #7-239), due to formation of Mg(OH)₂ upon reaction with atmospheric moisture. After heating in nitrogen, the Mg(OH)₂ peaks disappeared at
300°C, due to its dissociation to MgO [143], and only those diffraction lines at 2θ values of 37°, 43° and 62°, 74° and 78°, of cubic MgO are seen, corresponding to the (111), (200), (220), (311), 222), respectively. The shift seen between the patterns taken at 800°C and after cooling to room temperature was due to the unit cell expansion/contraction with temperature.

In Figure 18a, for Co-MgO-RT, only the weakly-resolved peaks attributed to the Mg(OH)₂ were visible at 38°, 51°, and 58°(ICDD #7-239), corresponding to the (101), (102), and (110) planes, respectively. Diffraction lines from the MgO phase were not present, since the interaction of MgO with water during the impregnation procedure is likely to convert the oxide to the hydroxide phase. Also, as seen in the case of VC support, there is no Co-associated crystalline phase present since the acetate phase is amorphous. After treatment in acetonitrile for 30 mins and 2h, (Figure 18b and c), the diffraction lines of cubic MgO at of 37°, 43° and 62°, 74° and 78°, corresponding to the (111), (200), (220), (311), and (222) planes appeared, similar to those seen in Figure 17. These peaks coincide with diffraction lines from possible CoO phases (ICDD# 78-431) that could exist in the system, making it difficult to distinguish between the cobalt oxide and magnesia peaks. Even after CH₃CN pyrolysis at 800°C, the presence of metallic Co could not be detected over this substrate.
XRD patterns acquired for acid washed CNₓ grown on Co-MgO and Co-VC are presented in Figure 19. Both samples have identical diffraction lines that can be assigned to metallic cobalt (ICDD #89-4307), and coincide with the peaks observed in Co-VC during different stages of pyrolysis (Figure 16). None of the diffraction lines for the MgO support could be detected, showing that the oxide support had been eliminated. The graphitic peak of Co-VC samples at 26° was sharper for acid washed samples than for the unwashed samples, indicating the presence of a more ordered, graphitic carbon phase.
Figure 18. XRD patterns of growth substrate Co-MgO at different stages of pyrolysis a) at RT, b) after CH$_3$CN pyrolysis for 30mins, c) after CH$_3$CN pyrolysis for 2h
The XRD results are in agreement with XANES and EXAFS spectra implying that, although phase transformations in the metal-phase occur to different extents over the two supports, the Co phase left in the final product after acid washing is mostly metallic in both cases.

4.2.3 X-Ray Photon Spectroscopy (XPS)

X-ray photon spectroscopy analysis was carried out to analyze the surface species over the Co-VC and Co-MgO substrates at different stages during the CN\textsubscript{x} growth process. Figure 20 shows the C1s spectra acquired over cobalt acetate (Figure 20a) along with the Co-MgO samples at RT, after 30 min and 2 h of CH\textsubscript{3}CN pyrolysis (Figure 20 b-d, respectively). The peak at 288.5 eV may be due to sp\textsuperscript{2} hybrid orbital of carbon in the
acetate molecule. This peak, which is present in pure Co acetate as well as MgO doped with Co acetate, grew weaker and eventually disappeared after 2h of acetonitrile treatment. The peak at 284.6 eV may correspond to adventitious carbon in spectra shown in Figure 20 a-c. After 2h of CH$_3$CN treatment, this peak became much stronger and sharper, which may signal the growth of a graphitic carbon phase (Figure 20d). At this stage of pyrolysis, a broad shoulder at lower binding energies 283.8-282.2 eV was also observed and has been attributed to transition-metal carbide formation [144-146]. This observation is in agreement with our earlier Mössbauer studies of CN$_x$ materials grown over Fe-doped substrates[98], which showed the presence of a cementite phase suggesting a carbon growth mechanism involving a carbide intermediate. The C1s spectra taken over Co-VC substrate at different stages of pyrolysis (data not shown) exhibited a strong peak at 284.6 eV, which can be attributed to the Vulcan carbon support present in all samples and would obscure any contribution from other carbonaceous species.
Figure 20. C 1s XPS spectra of a) Cobalt Acetate, b) Co-MgO-RT, c) Co-MgO-800-CH$_3$CN-30m, d) Co-MgO-800-CH$_3$CN-2h
C1s spectra taken over acid-washed CN$_x$ samples grown on VC or MgO are shown in Figure 21a and b, respectively. After acid washing, there was only one major peak seen in these spectra at 284.6 eV corresponding to graphitic carbon. This suggested that any metal carbide phase was leached out through the acid washing process.

The Co 2p region of X-ray photoelectron spectra for the Co-MgO samples during different stages of pyrolysis is shown in Figure 22. Spectrum of pure Co-acetate is also shown (Figure 22a) for comparison. The spectrum taken over Co-MgO before pyrolysis was very similar to that of pure Co-acetate, with the 2p$^{3/2}$ binding energy appearing at 780.9 eV. The presence of shake-up lines at 785.9 eV verified the oxidation state of Co as 2$^+$. After CH$_3$CN pyrolysis at 800°C for 30 minutes, the spectrum did not change much. However, after 2 hours of CH$_3$CN pyrolysis a shift in the Co 2p$^{3/2}$ peak to 780.6
eV was seen, accompanied by a lower-binding-energy-shoulder. At this stage, Co is likely to exist in multiple phases, including a mixture of sub-oxides, as suggested by the persisting presence of shake-up lines[54, 147, 148] and metallic Co. This is supported by the bulk composition of the same catalysts, as seen by XANES, where Co$^{2+}$ and Co$^0$ oxidation states co-existed even after heat treatment in acetonitrile.

Figure 22. Co 2p region of XPS spectra taken over a) Cobalt acetate b) Co-MgO-RT c) Co-MgO-800-CH$_3$CN-30m d) Co-MgO-800-CH$_3$CN-2h
The presence of the oxide phase may be due to oxygen contributions from the oxide support itself. The contribution from the oxide phase appears to be stronger in XPS than that observed in XAFS, which showed significant reduction to metallic cobalt in the bulk species. XPS being a surface-sensitive technique, it is possible that the majority of cobalt exposed on the surface would get oxidized in contact with atmosphere, leading to a stronger contribution from the oxide phase. This phenomenon has also been reported by Lalande et al. [149], where they observed that the Co\textsuperscript{2+} signal to arise “from a very superficial oxidation of Co\textsuperscript{0} surrounded by graphite” in their tetracarboxylic cobalt phthalocyanine adsorbed on carbon black-supported catalyst.

In addition to oxide and metallic species, there may also be a carbidic phase formed following CH\textsubscript{3}CN pyrolysis for 2h. Since binding energies of 778.9 eV[150] and 780.3[151] have been reported for cobalt carbide, it is possible that the broad peak observed at 780.6 eV has contributions from a carbide phase. This possibility is supported by the presence of a carbide peak observed in the C1s spectra, as discussed earlier.

Figure 23a shows a comparison of Co 2p spectra of CN\textsubscript{x} grown over Co-MgO before and after acid washing. After acid washing of CN\textsubscript{x} grown on Co-MgO, most surface cobalt oxide species seemed to have been washed away (Figure 23a ii). A sharp metallic cobalt peak was seen at 778.5 eV[148], which could be due to cobalt bound to the carbon grown over the support. This supports our findings from XANES spectra of
the acid washed CN$_x$ catalysts, which showed that the bulk of cobalt species existed as metallic cobalt encased within carbon nanostructures grown during acetonitrile pyrolysis.

Figure 23. Co 2p spectra of cobalt on a) MgO, b)Vulcan Carbon treated with CH$_3$CN 2h. i. Unwashed ii. Washed

A similar comparison is presented for the CN$_x$ grown over Co-VC in Figure 23b. The Co phase in this sample seemed to be more metallic even before acid washing (Figure 23b-i), although the signal is quite weak. After acid washing, the only feature seen was the peak at 778.5 eV (Figure 23b ii), but with a diminished intensity in comparison with acid washed CN$_x$ grown on Co-MgO. This is somewhat expected, since acid washing leaches away all or most of the MgO, leaving behind only CN$_x$ structures with cobalt particles encased in them. Whereas, in the Vulcan carbon support, most of the
support remains unleached, as a result of which, the net concentration of cobalt in this
catalyst is lower than that on MgO, giving rise to a lower intensity metallic peak.

The N1s spectra of the acid washed CN$x$ grown on Co-VC and Co-MgO substrates are shown in Figure 24a and b, respectively. There are three types of nitrogen species identified based on a detailed XPS analysis of nitrogen species formed during high temperature pyrolysis[152]. Quarternary or “graphitic” nitrogen, which consists of nitrogen within a graphite plane bonded to three carbon atoms has a characteristic peak at 401.3± 0.3 eV. Pyridinic nitrogen is bonded to two carbon atoms on the edge of the graphite planes, and has a characteristic binding energy of 398.6 ± 0.3 eV. There is also reported a nitrogen species with a high binding energy in the range of 402-405 eV, which is identified as a type of oxidized pyridinic nitrogen (N$^+\cdot$-O$^-$) [153, 154].

In the acid washed CN$x$ samples, quarternary nitrogen has been identified at 401.2 eV, pyridinic nitrogen at 398.8 eV for both samples, and oxidized nitrogen species at 403.8 eV for CN$x$ on VC, and 405 eV for CN$x$ on MgO. The percentage composition of the nitrogen species in the two catalysts is given in Table 7. From the species comparison, we saw that CN$x$ grown on Co-MgO had a higher pyridinic nitrogen content than CN$x$ grown on Co-VC. Pyridinic nitrogen content has been identified as a marker for edge plane exposure or for ORR activity by many researchers[32, 107, 155], and as seen from the activity results in the next section, CN$x$ grown on Co-MgO did indeed show higher activity than CN$x$ grown on Co-VC, which could be partly attributed to the pyridinic nitrogen content differences between the two catalysts.
Figure 24. N1s XPS spectra of acid washed CNx grown on a) Co-VC and b) Co-MgO substrates

Table 7. Percent distribution of nitrogen species obtained from XPS N 1s region analysis

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pyridinic-N%</th>
<th>Quarternary-N%</th>
<th>Pyridinic N⁺-O⁻%</th>
<th>Total N%</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNₓ-Co-VC-800-CH₃CN-2h-AW</td>
<td>20</td>
<td>56</td>
<td>24</td>
<td>1.1</td>
</tr>
<tr>
<td>CNₓ-Co-MgO-800-CH₃CN-2h-AW</td>
<td>24</td>
<td>46</td>
<td>30</td>
<td>4.0</td>
</tr>
</tbody>
</table>
4.2.4 Transmission Electron Microscopy (TEM)

Transmission electron microscopy imaging helped characterize the growth of acid-washed carbon nanostructures formed upon acetonitrile pyrolysis over Co-VC and Co-MgO substrates. As seen in Figure 25a-d, after acid washing, the carbon nanostructures grown over Co-VC are in the form of stacked cups, but with less order as compared to the CN\textsubscript{x} grown on Co-MgO (Figure 25e-h). Carbon nanostructures are less abundant in the CN\textsubscript{x} grown over the VC support due to the majority of growth medium (i.e., Vulcan carbon) remaining after acid washing. The fibers are thick-walled (wall thickness~10nm), with relatively large cobalt particles encased within the carbon shell, with a diameter of approximately 25nm (Figure 25c-d).

CN\textsubscript{x} nano-structures grown over the Co-MgO, on the other hand, are more-ordered and better-defined stacked cups, as shown in Figure 25e, f, and g. They are more abundant because the oxide support is washed away with acid leaching, leaving only the carbon nanostructures behind. Cobalt also appeared to be encased within the nanostructures, and the particle size and wall thickness were smaller than those seen in CN\textsubscript{x} grown over Co-VC, as is the diameter of the stacked cups (Figure 25d and h). This could be another reason for the higher abundance of surface cobalt species detected in XPS for the acid washed CN\textsubscript{x} grown on Co-MgO, as compared to CN\textsubscript{x} grown on Co-VC. The thickness of the walls encasing the cobalt particles in the case of CN\textsubscript{x}-VC may be
larger than the penetration depth for XPS, thus, making it more difficult to detect the photoelectron signal.

Figure 25. TEM images of acid-washed CNx grown on Co-Vulcan Carbon (a-d) and Co-MgO (e-h)

The stacked-cup nanostructures observed in this study are consistent with CNx grown on 2 wt% Fe-MgO or Co-MgO substrates that we have reported earlier[92, 94, 95, 98]. This implies that the CNx catalysts grown over substrates with 10wt%Co loading are representative of CNx grown over substrates with a lower metal content, although higher metal loading is not optimum for the ORR activity.
4.2.5 Rotating Ring Disk Electrode ORR Activity Tests

Electrochemical activity tests for washed and unwashed CN\textsubscript{x} grown over Co-VC and Co-magnesia were performed using RRDE technique. Figure 26a shows the polarization curves for the washed and unwashed samples grown over the two different growth substrates. Figure 26 b shows the Tafel plots constructed using the same data set. It should be noted that the catalysts used for this study are not the best-performing ones among CN\textsubscript{x} catalysts, since the growth substrates used are not the ones optimized for best activity/selectivity, but rather those that would lend themselves to characterization of the growth substrate during pyrolysis. The unwashed magnesia supported catalyst was mixed with 5mg of Vulcan carbon to counteract any impeded conductivity that could be attributed to the non-conductive oxide present in the unwashed catalyst. In both cases, the activity improved significantly after washing.

The Tafel plots in Figure 26b show the differences in activity more clearly in the kinetically controlled region. When washed samples were compared, the CN\textsubscript{x} catalysts grown over Co-MgO were seen to be more active towards ORR than CN\textsubscript{x} grown over Co-VC. There was a difference of 50 mV between the onset potentials observed over these two washed catalysts. This finding is in agreement with our previous results, which showed CN\textsubscript{x} catalysts grown on 2% Fe-MgO to outperform those grown on other supports [94, 97]. It was also noted that the catalyst with the superior ORR performance had a higher pyridinic nitrogen content (pyridinic N and pyridinic N-O). This result is also consistent with our previous studies, which showed a correlation between the ORR activity and the pyridinic N content[82, 91, 94, 96, 97]. The selectivities of the unwashed
catalysts were both around 3.7. Acid washing did not change the selectivity of the catalyst grown on Co/VC whereas the selectivity of the catalyst grown on Co/MgO increased noticeably by acid washing (Table 8).

Figure 26. Rotating ring disk electrode (RRDE) ORR activity tests of washed and unwashed CNx catalysts grown on Co-Vulcan Carbon and Co-Magnesia in O2-saturated 0.5M H2SO4 at 25°C; rotation rate: 2500 rpm; scan rate 10 mV/s; scan direction: cathodic; catalyst loading 1.6 mg/cm²; geometric area: 0.2472 cm². a) Polarization curves, b) Tafel plots.
Carbon corrosion is a significant concern with cathode catalysts in PEM fuel cells, in the higher potential ranges, especially during the start/stop operation or fuel starvation.[156, 157] We have previously evaluated CN_x catalysts for their carbon corrosion characteristics [103]. Carbon is known to oxidize in sulfuric acid, at higher potentials, and form intermediate hydroquinone/quinone species during corrosion.[158-160]. We have evaluated the extent of hydroquinone-quinone formation by performing chronoamperometric potential holds at 1.2V versus RHE for a duration of 48h, and subsequently collecting oxygen reduction CVs in 0.5 M H_2SO_4. It was seen that the hydroquinone/quinone species formation was much more evident on Vulcan carbon than CN_x grown on Vulcan carbon or magnesia over time. ORR onset potentials for CN_x did not change after the prolonged potential hold, and in fact, it exhibited an improvement in selectivity from ~3.7 to 3.9. This superior resistance of carbon corrosion of CN_x over Vulcan carbon was attributed to possible surface stabilization during ORR, in the process of which most of the electrochemically active quinone/ hydroquinone species appeared to have been consumed. Hence, CN_x catalysts prepared on both Vulcan Carbon and magnesia supports have been seen to outperform Vulcan Carbon support by itself in terms of their corrosion resistance characteristics. Additional stability studies with CN_x catalysts are currently underway.
Table 8. Selectivity values at 0.5V vs. RHE from RRDE

<table>
<thead>
<tr>
<th></th>
<th>Selectivity (n) at 0.5V</th>
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<tbody>
<tr>
<td>CN$_x$-Co-VC</td>
<td></td>
</tr>
<tr>
<td>Washed</td>
<td>3.7</td>
</tr>
<tr>
<td>Unwashed</td>
<td>3.7</td>
</tr>
<tr>
<td>CN$_x$-Co-MgO</td>
<td></td>
</tr>
<tr>
<td>Washed</td>
<td>3.8</td>
</tr>
<tr>
<td>Unwashed</td>
<td>3.7</td>
</tr>
</tbody>
</table>

4.3 Conclusions

Vulcan carbon and magnesia supports doped with cobalt were used as growth substrates for the formation of N-doped carbon nano-structures (CN$_x$) during the pyrolysis of a carbon- and nitrogen-containing precursor, i.e., acetonitrile. The changes that took place in the transition metal during the growth process were examined using in-situ and ex-situ characterization techniques. In-situ XANES and EXAFS revealed a change in the oxidation state of cobalt from Co$^{2+}$ to a more reduced form after heat treatment. Cobalt on Vulcan carbon was seen to reduce in the inert atmosphere even before acetonitrile pyrolysis, whereas, cobalt on the magnesia support showed a gradual reduction from Co$^{2+}$ to Co$^0$. While in-situ XRD showed similar results for the Co-VC substrate, the XRD patterns obtained for the Co-MgO substrates were more difficult to
interpret due to the changes taking place in the crystal structure of the MgO support during pyrolysis. XPS data showed the coordination environment of Co to change from that of an acetate to a mixture of sub-oxides during the pyrolysis. C 1s spectra suggested the formation of a carbide phase during acetonitrile pyrolysis.

Regardless of the different stages that the cobalt phase went through during the pyrolysis process depending on the support used, once the final yield of CN\textsubscript{x} materials were washed with acid, the transition metal left behind was primarily in a metallic phase, as shown by XAFS, XRD and XPS data. TEM images showed formation of stacked-cup structures, with cobalt particles visibly encased in the carbon nano-structures. The stacked-cup nano-geometry was more prevalent and more orderly for the CN\textsubscript{x} grown on MgO substrates, whereas CN\textsubscript{x} grown on VC showed more irregularity.

N1s region of the X-ray photoelectron spectra also showed differences between the two CN\textsubscript{x} samples grown on the two different substrates. Those grown on Co-MgO had a higher nitrogen content, as well as a higher fraction of pyridinic nitrogen and oxidized pyridinic nitrogen compared to their counterparts grown on Co-VC. This difference also manifested itself in the superior performance of the former, while acid washing led to improved performance for both. These results are consistent with previous findings that showed a correlation between the pyridinic N content and ORR activity, regardless of how the CN\textsubscript{x} nano-structures were grown.
Acknowledgements

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CHAPTER 5. A comparison of nitrogen containing carbon nano-structures (CN$_x$) with carbon-supported iron-nitrogen coordinated (Fe-N-C) catalysts for the Oxygen Reduction Reaction in Acidic Media

Submitted to *Journal of Catalysis*

5.1 Motivation

Over the years, the active site of non-precious metal catalysts has been a topic of debate for many researchers, especially the role of the transition metal[135]. Only recently, it has come to light that the two types of catalysts discussed in Chapter 1 might indeed be different materials[161]: (1) Fe-N-C catalysts that are prepared by supporting a macrocycle on a carbon support that do have a metal center. During pyrolysis in an inert or nitrogen-containing environment, there is no washing step in their preparation to leach out the metal, hence it is expected that a metal center still remains in these materials, although its exact nature may not yet be fully understood. (2) CN$_x$, on the other hand, prepared by decomposition of a nitrogen-carbon source on a metal-impregnated support, undergoes an acid-digestion step to leach away the surface metal; any remaining metal is encased in carbon and does not participate in ORR. This has been corroborated further when a number of reports of nitrogen-doped carbonaceous materials prepared with or
without a transition metal growth precursor, such as N-graphene have shown very high ORR activity in alkaline media \([118, 120, 123, 124, 162, 163]\).

In this current work, we have attempted to distinguish between Fe-N-C and CN\(_x\) catalysts, in terms of their possible active sites and degradation mechanisms, by means of extended durability tests in a fuel cell and half-cell. The catalysts were prepared as described in the Experimental Methods section and have been characterized using X-ray photoelectron spectroscopy (XPS), X-ray absorption near edge spectroscopy (XANES), Extended X-ray absorption fine structure (EXAFS), Superconducting quantum interference device (SQUID) magnetometry, inductive-couple plasma optical emission spectrometry (ICP-OES) and temperature-programmed oxidation (TPO). The results show significant differences in the activity, stability and compositional characteristics of these materials, shedding light on their inherent differences in catalyzing ORR.

While comparing the two classes of catalyst, CN\(_x\) and FeNC, we are comparing them in their most active form, which is CN\(_x\)-washed in HCl for 1h and FeNC unwashed. Hence for the sake of clarity the nomenclature CN\(_x\)-washed/ unwashed and FeNC-washed/unwashed are used to compare the two catalysts and the effect of acid washing on them, unless otherwise specified.
5.2 Results and Discussion

5.2.1 Differences in ORR Activity and Stability between CNx and FeNC
Rotating (Ring) Disk Electrode Tests

The RRDE activity tests for FeNC (unwashed and washed) and CNx (unwashed and washed) are shown in Figure 27(a) and (b). Between the two catalysts, FeNC is clearly more active than CNx, with an onset potential of 0.87V (unwashed), versus the onset potential of CNx, which is 0.78V (washed). The effect of acid washing is markedly different on the two catalysts. While CNx showed a dramatic improvement in activity (Figure 27b) after acid washing, FeNC, on the other hand showed a slight decrease in its activity, to an onset potential of (0.83V), for the washed catalyst. This trend is a first evidence of the inherent differences in the catalytic active sites of both the catalysts. Acid washing possibly leaches away Fe from the active Fe-Nx sites in FeNC, leading to an activity loss, while in the case of CNx, the effect of acid washing is to eliminate the inactive iron species from the catalyst surface, along with the oxide support. The product after acid washing of CNx, which does not have exposed iron species, and consists of carbon nanostructures with Fe embedded within the graphitic matrix, exhibits significantly high ORR activity.

Selectivity of the catalysts was evaluated using RRDE. For both FeNC -unwashed and – washed, the selectivity at 0.5V was 3.9 and 4.0 respectively, indicating that the selectivity to water formation for both the catalysts was very similar. CNx-washed exhibited a selectivity of 3.8, and was much higher than the unwashed-CNx, with a selectivity of 3.2. It should also be noted however, that in two independent studies[164, 165], it has been
observed that the selectivity of both CN₃ and FeNC catalysts is highly dependent on the catalyst loading. For both catalysts, the selectivity was seen to increase with increased loading levels, suggesting a mechanism proceeding via an H₂O₂ intermediate, where the H₂O₂ molecules may have sufficient time to undergo further reduction to water while diffusing out of a thicker catalyst layer.
Figure 27. Comparison of ORR RRDE results for unwashed and acid washed catalysts at 1000 rpm in 0.5M H$_2$SO$_4$ oxygen-saturated solution. (a) FeNC and (b) CNx
Accelerated Durability Tests using RDE

Accelerated durability tests were also conducted on CN$_x$ as well as FeNC. Figure 28(a) shows performance losses by ADTs in FeNC-unwashed. In these ADTs for FeNC, we observed that there was a continued deterioration of performance with repeated cycles, and a significant loss between 100 and 1000 cycles. The carbon support in FeNC catalysts itself may be susceptible to corrosion, as seen previously by other researchers, leading to a continued degradation in performance [158, 160, 166, 167].

In contrast to FeNC, which showed a steady loss of activity with increasing cycles, it was observed that CN$_x$ demonstrated the highest activity loss during the first 100 cycles of repeated CVs (Figure 28b). It reached a pseudo-steady state thereafter, as there was no significant activity loss between cycles 100, 500 and 1000. As reported by Ozkan and co-workers previously, CN$_x$ grown on MgO has been seen to not undergo carbon corrosion as severely as pure Vulcan carbon support, as seen by our research group previously[103], and this could be an additional factor responsible for its prolonged stability.
Figure 28. Accelerated durability tests on the two most active catalysts. (a) FeNC-unwashed and (b) CN\textsubscript{x}-washed
**Fuel Cell Activity and Stability Tests**

iR-free polarization curves obtained before and after a 100-hour potential hold at 0.5V are shown in Figure 29(a) for CN₅ and FeNC. While CN₅ performed worse than FeNC, it exhibited better retention of initial activity over the full range of current. The activity after the 100h potential hold was more similar for the two catalysts, than before the potential hold. It is worth noting that although CN₅ exhibited lower activity than FeNC catalysts, it also showed significantly less degradation over time.

We also compared activities of acid-washed and unwashed FeNC catalysts. Figure 29(b) shows polarization curves of FeNC with and without an acid-wash. Although, the unwashed FeNC catalyst possessed a higher initial activity, after the potential hold, it is apparent that both the catalysts deactivated to almost the same level. This observation is significant in showing that the activity loss due to acid washing is similar in magnitude to the activity loss suffered by the catalyst during the potential hold.

Although the mechanism of deactivation is not yet fully understood, a clear distinction that emerges between FeNC and CN₅ catalysts is that CN₅ catalyst have a higher degree of stability than FeNC. This also suggests that the activity loss in FeNC catalysts is directly linked to the Fe sites, and CN₅ catalysts, in which iron does not play a catalytic role, is not affected by this mode of deactivation.
Figure 29. Fuel-cell polarization curves before (solid lines) and after (dashed lines) 100h potential hold at 0.5V for (a) FeNC-unwashed and CN$_x$-washed (b) FeNC-unwashed and FeNC-washed
5.2.2 Surface species characterization

X-ray Photoelectron Spectroscopy

\textit{N 1s:} XPS spectra of the CN\textsubscript{x} and FeNC catalysts revealed differences in the specific nitrogen content (Figure 30). The N 1s region was deconvoluted into three different nitrogen species, identified as pyridinic N (398.0-398.9 eV)[152, 168], quaternary-N (401-402 eV)[152, 169], and oxygenated pyridinic-N groups (N\textsuperscript{+}-O\textsuperscript{-}) at binding energies higher than 402 eV[95-97].

Spectra for CN\textsubscript{x} (unwashed and washed) are shown in Figure 30 (a-b), and their compositions are tabulated in Table 9. The fraction of N in pyridinic form was the same in CN\textsubscript{x} catalyst before and after washing, suggesting that washing, which leaches out the oxide support and the exposed metal, does not affect the nitrogen species.

In the case of FeNC (Figure 30 (c-d)), there was a significant increase in the pyridinic-N content, from 25\% to 36\%, after washing. A possible explanation for this increase in pyridinic-N content could be that Fe-species that were coordinated to edge-nitrogen species on two graphite planes were washed away, leaving behind more exposed edge-nitrogen and subsequently increasing the percentage of pyridinic nitrogen in FeNC.

The highest contribution was from quaternary-N species at 401-402 eV[96], which was consistently over half of the total nitrogen in both in FeNC and CN\textsubscript{x} catalysts.
Table 9. XPS N 1s content for FeNC and CN$_x$ catalysts.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pyridinic (eV) (%fraction)</th>
<th>Quarternary (eV) (%fraction)</th>
<th>Pyridinic N-O (eV) (%fraction)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeNC</td>
<td>398.6 25</td>
<td>401 57</td>
<td>405.4 18</td>
</tr>
<tr>
<td>FeNC-W-1h</td>
<td>398.9 36</td>
<td>401 48</td>
<td>405.9 16</td>
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<tr>
<td>CN$_x$</td>
<td>398.4 27</td>
<td>401 51</td>
<td>405.3 22</td>
</tr>
<tr>
<td>CN$_x$-UW</td>
<td>398.4 27</td>
<td>400.8 66</td>
<td>402.4 7</td>
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</tbody>
</table>

It is possible that the leaching of iron during acid washing of the FeNC catalysts led to lower initial activity, with the non-leachable iron remaining behind in the acid-washed catalysts[109]. There are two hypotheses in literature about the mechanism of deactivation of Me-N$_x$ type materials. Popov’s group proposes that the protonation of pyridinic nitrogen groups in the acidic fuel cell environment, leads to a decrease in activity of these catalysts over time[108]. Whereas in a recent study by Dodelet’s group, mentioned that the basic nitrogen (pyridinic) groups (next to the coordinated Fe active sites) that are protonable in an acidic fuel cell environment, act as a pathway for quick transfer of protons to the Fe-active site, thus drastically improving the turnover frequency for these composite sites[109, 135]. Rather, the protonated NH$^+$ group appears to be neutralized by the presence of an anion (sulfonate group of the proton exchange
membrane), which leads to its long-term activity loss. However, between FeNC and CNx, clearly CNx showed a higher degree of stability than FeNC. Hence it is speculated that possibility of iron leaching or protonation/anion-binding of pyridinic N has a more detrimental effect on long term stability of FeNC catalysts, than for CNx, in which Fe does not play a catalytic role.

Figure 30. N 1s XPS spectra of unwashed and washed (a) (b)FeNC and (c) (d) CNx respectively
We have seen in this study that the higher pyridinic nitrogen content for both acid-washed FeNC catalysts and CNₓ catalysts does not necessarily translate to lower stability. In fact, these catalysts showed higher stability than unwashed FeNC. Hence, one hypothesis that could explain this phenomenon is that protonation of pyridinic nitrogen or its anion binding does cause activity degradation, but is not the only source of activity loss. It is possible, however, that the unwashed FeNC catalysts exhibit a loss in activity over time due to a coupled effect of the iron from the active sites being leached out, in addition to protonation effects/and-or anion binding of the already-protonated pyridinic nitrogen.

The effect of acid-washing of FeNC could also be two-fold: gain of pyridinic-N species, at the expense of some Fe active sites that are leached out in the process. While the loss of Fe active sites may be leading to reduced activity, this effect might be counter-balanced with the gain in pyridinic-N species which could be contributing to activity. It is difficult to decouple the effect of the iron and nitrogen and the changes therein brought about by extended durability tests or acid-washing, especially since the surface iron sites are low in concentration and harder to analyze using surface spectroscopic techniques.

**Temperature Programmed Oxidation (TPO)**

Temperature-programmed oxidation was conducted on all CNₓ and FeNC samples and precursors in 10% O₂/He. M/z signals of 28 (CO), 30 (NO), 44 (CO₂) and 46 (NO₂) were recorded in a Cirrus mass-spectrometer (MS) and are reported here. Figure
Figure 31 shows the comparison of TPO spectra for FeNC and CN$_x$ respectively for (a) and (b) unwashed, (c) and (d) washed for 1h (e) and (f) washed-1week.

It is known that iron catalyzes the oxidation of carbon. As a result, the onset of oxidation temperature is nearly identical for both FeNC and CN$_x$ unwashed catalysts (Figure 31(a) and (b), due to the presence of surface iron. After acid washing for one hour for FeNC, there was an increase in the oxidation onset temperature by only ~30°C for
FeNC, indicating that iron was still left behind in the carbon matrix. For CN$_x$, however, after acid washing, the onset of oxidation temperature increased by \(~100^\circ\text{C}\). This clearly indicates that the surface iron that was present before acid washing, was leached away.

There was no significant difference between the oxidation temperatures of CN$_x$ or FeNC catalysts acid washed for 1 hour or 1 week; the same trend was observed for FeNC as well. However, the nitrogen species seemed to evolve at a higher temperature (~550 °C) for CN$_x$ acid washed for 1 week (Figure 31f). The oxidation envelope was also much narrower for CN$_x$ acid washed for 1h. Evidently, CN$_x$ is more resistant to oxidation than FeNC catalysts, even with prolonged acid washing. One of the causes for this may be due to the presence of carbon support in FeNC catalysts, which remains behind within the catalyst matrix even after acid-leaching, but does indeed get etched with time, leading to slightly lower oxidation temperatures. CN$_x$ catalysts have proven to be more resilient to corrosion, since the support (MgO) itself is washed away and only the nanostructures are present in the catalyst [103]. It was also observed that CN$_x$ catalysts emitted significantly higher NO (m/z = 30) than FeNC catalysts, indicating higher concentration of nitrogen in these catalysts, which is in agreement with results from XPS.

5.2.3 Bulk species characterization

X-ray Absorption Near Edge Spectroscopy (XANES)

XANES spectra were collected ex-situ for different CN$_x$ and FeNC catalysts, along with references such as iron foil, iron(II) oxide and iron carbide. Unwashed CN$_x$ (Figure 32a), the Fe-k edge spectra appeared more oxidized, possibly due to oxidation of the iron
species from oxygen contribution of the MgO support. For acid-washed CN\textsubscript{x} (Figure 32b), the features corresponding to the oxide disappeared while the XANES energies showed similarities to the iron carbide as well as the iron foil standard.

Figure 32. XANES spectra of a.) CNx-unwashed b.) CNx-washed c.) FeNC-unwashed d.) FeNC-washed with ref. Fe oxide, Fe foil and Fe carbide respectively
As seen in Figure 32(c) and (d), the XANES spectra of FeNC-unwashed and washed respectively, are shown. Both the spectra are similar to iron carbide. From the XANES spectra of CN\textsubscript{x} and FeNC catalysts, one cannot discern any significant difference between the states of iron in both sets of catalysts. Although the heat treated and acid washed CN\textsubscript{x} and FeNC catalysts showed near-edge features similar to iron carbide, the presence of iron nitride in these catalysts cannot be discounted: indeed its presence is highly likely. Due to the inherent limitation of the technique to distinguish the second scatterers, especially if they are lighter elements such as carbon, nitrogen or sulfur, it is hard to distinguish between iron carbide or nitrides.

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

Since analysis of the XANES spectra showed minor differences in the state of iron, the FT-Magnitudes of the catalysts were compared with standards. The uncorrected values are discussed. FT-magnitudes of CN\textsubscript{x}-unwashed is shown with iron carbide and iron oxide references in Figure 33a. There were two peaks observed: one at a value of 2.7 Å and a smaller peak at about 1.7 Å. This spectrum corresponds very well with the iron oxide reference, and the two peaks are possibly Fe-O and Fe-O-Fe, respectively. For CN\textsubscript{x}-washed, there is a large peak indicative of Fe-Fe bonds at the value of ~2.1 Å. However, there was a shoulder at ~1.5 Å that is evidence of iron carbide; hence the catalysts appear to be either in a metallic or a carbide-like state. Both the catalyst and the iron carbide reference have a shoulder at about 1.5 Å. This is in agreement with our previously reported results from Mossbauer spectroscopy, in which co-existence of a
cementite-type Fe carbide phase was seen with metallic γ-Fe, encased in the carbon structure[98].

This shoulder and the Fe-Fe peak at 2.1 Å were present in the FeNC catalysts too, with and without acid washing (Figure 33c and d), which could be attributed to either an Fe-C_x or an Fe-N_x bond.
Figure 33. FT-Magnitudes of a.) CNx-unwashed b.) CNx-washed c.) FeNC-unwashed, d.) FeNC-washed with ref. and Fe oxide, Fe foil and Fe carbide respectively
5.2.4 Determination of iron concentration

ICP-OES

ICP-OES experiments were performed on both CN_x- and FeNC catalysts that were kept in 250 mL of 1M HCl solution for 48h, and aliquots of the acidic mixture were pipetted out at intervals after 1h and 48h. The solutions were analyzed using ICP-OES for Fe content and the percentage of iron leached out from the initial iron content of the catalysts are tabulated in Table 10. The total concentration of iron leached out from CN_x was greater than Fe-N-C, (78% after 48h for CN_x, versus 35% for FeNC). Another important observation is that in the case of CN_x, most acid leaching took place within the first 1h of immersing in the acid solution, and there was little change in iron concentration after 48h. For FeNC however, iron leaching continued with time, with a change of over 10% (from 24% to 35%) between 1h and 48h. indicating that only about 22% of the initial concentration of iron is encased within the carbon nanostructures, and is unreachable by acid leaching.
Table 10. Percentage of iron leached out in acid obtained from ICP-MS

<table>
<thead>
<tr>
<th>Sample</th>
<th>% iron leached out relative to the amount present before AW</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeNC-washed-1h</td>
<td>24</td>
</tr>
<tr>
<td>FeNC-washed-48h</td>
<td>35</td>
</tr>
<tr>
<td>CN_x-washed-1h</td>
<td>77</td>
</tr>
<tr>
<td>CN_x-washed-48h</td>
<td>78</td>
</tr>
</tbody>
</table>

These results are also significant in showing that, although most of the iron in CN_x catalysts leaches out during the 1-hour washing process, which is a routine step in the preparation procedure, these materials become substantially more active after washing. This observation provides further support to the assertion that Fe left in these materials is not part of the active site. FeNC catalysts, however, show significant activity loss as more and more Fe is lost through leaching. Also, the loss of activity continues, as does the loss of iron, with additional time in the acidic medium. This observation lends support to an active site model where Fe is an integral part of the active center.
5.2.4 Magnetization of iron in CN$_x$ and FeNC

SQUID

Figure 34 shows the magnetization as a function of field at 300K for CN$_x$ and FeNC (washed and unwashed). The data suggests a superparamagnetic behavior for all samples as evident from the negligible hysteresis in the curves[170]. The values of saturation magnetization for various samples as observed in Figure 34 and reported in Table 11 reveal interesting trends. Firstly, acid-washing led to an increase in the saturation magnetization for CN$_x$ sample while it showed the opposite effect for FeNC catalyst.

In our analysis of the characterization of iron-phases in acid-washed CN$_x$ from Mossbauer Spectroscopy, it was seen that majority of the iron in the catalyst is either Fe$^0$ or Fe$_3$C, which is confirmed by the high saturation magnetization values of CN$_x$ obtained from SQUID. Furthermore, after acid-washing, the diamagnetic contribution from the support (magnesia) as well as Fe-O species is eliminated, thereby leading to an increase in the saturation magnetization for acid-washed CN$_x$. On the other hand, in FeNC, acid-washing leaches away some surface iron species, consequently acid-washed FeNC has a lower saturation magnetization than unwashed catalyst. This observation suggests that acid-washed FeNC contains a relatively lower fraction of iron in zero-valent state compared with the unwashed catalyst.

The values of particle diameters of iron for various samples were estimated by fitting Langevin function (Equation 3) to the data and were found to be in the range of 3.5-4.8 nm (reported in Table 11). These values are lower than the critical diameter for iron,
below which superparamagnetic behavior is exhibited[171]. It must be noted that the iron particle sizes reported in these calculations are lower than the particle size observed in TEM; an observation also made by other researchers. This is attributed to the presence of an amorphous, magnetically “dead” layer surrounding the crystalline magnetic core which is not detected in magnetic measurements [172-174].

Figure 34. Magnetization as a function of field at 300 K
Table 11. Saturation magnetization and iron particle diameter for various samples estimated by fitting Langevin function to magnetization vs. field data

<table>
<thead>
<tr>
<th>Sample</th>
<th>$M_{\text{sat}}$ (emu/g of catalyst)</th>
<th>$d$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeNC-unwashed</td>
<td>1.0</td>
<td>4.8</td>
</tr>
<tr>
<td>FeNC-washed</td>
<td>0.20</td>
<td>4.4</td>
</tr>
<tr>
<td>CN$_x$-unwashed</td>
<td>1.4</td>
<td>3.5</td>
</tr>
<tr>
<td>CN$_x$-washed</td>
<td>3.0</td>
<td>4.1</td>
</tr>
</tbody>
</table>

5.3 Conclusions

The results discussed in this article bring to light several differences between FeNC and CN$_x$ materials for ORR. The first prominent difference between CN$_x$ and FeNC was seen in their activity and stability towards ORR. CN$_x$ was less active than FeNC, albeit more stable. CN$_x$ underwent slower degradation in fuel cell stability tests and in ADTs, and attained stability faster while FeNC showed continued activity loss.

Effect of acid washing was strikingly different for both types of catalysts. CN$_x$ gained significant ORR activity after acid washing, and just the reverse was seen in the case of FeNC. Acid-washed FeNC demonstrated a lower initial activity than unwashed catalyst,
but after the 100-hour potential hold, there was no difference in activity between the former and latter. This suggests that the activity loss observed due to acid washing may occur through a similar process to the deactivation that takes place during a potential hold in the fuel cell environment. It was also observed that after a potential hold of 100 hours, CN$_x$ and FeNC catalysts converged to similar activity levels.

A significant insight from ICP-OES experiments was most of the iron in CN$_x$ is leached readily during acid washing and further exposure to acid does not change its iron content. In FeNC, on the other hand, the loss of iron through leaching continues as long as the catalyst is immersed in the acid solution. This result supports the assertion that iron left in CN$_x$ catalyst is encased in carbon and is not accessible while iron in FeNC is more readily accessible.

The causes for loss of activity are somewhat speculative, but a cumulative effect of iron leaching and either the protonation of pyridinic groups or their anion binding may be responsible for losses seen in FeNC catalysts, while iron leaching does not seem to affect ORR activity in CN$_x$ negatively. Whether the pyridinic-N groups in CN$_x$ undergo transformation in the fuel cell or half-cell environment is still unknown, but considering that both the catalysts showed different stability behavior, it is likely that their degradation mechanism is quite different.

XPS results indicated that pyridinic nitrogen was present in both CN$_x$ and FeNC catalysts. CN$_x$ catalysts exhibited a higher pyridinic-nitrogen content. Since pyridinic-nitrogen content was greater in CN$_x$, if protonation or anion binding of pyridinic nitrogen
was the only cause of deterioration of the stability for both these catalysts, it cannot explain the greater stability of \( \text{CN}_x \). Hence, there is clearly another degradation mechanism involved for \( \text{FeNC} \). Another interesting finding from XPS was that the acid-washed \( \text{FeNC} \) catalysts exhibited higher pyridinic-nitrogen content than unwashed \( \text{FeNC} \). This could be attributed to some of the iron centers leaching out, leaving behind exposed edge nitrogen sites. \( \text{CN}_x \) was also seen to be more resistant to oxidation than \( \text{FeNC} \) from TPO experiments.

EXAFS and XANES revealed significant differences in the effect of acid-washing on \( \text{CN}_x \) and \( \text{FeNC} \). In \( \text{CN}_x \), the oxidized Fe species exposed to air after pyrolysis were removed upon washing with acid, with only carbide-like or metallic Fe left behind encased within carbon. Whereas in \( \text{FeNC} \), although the acid-washing leached out a part of Fe from the \( \text{FeNC} \) matrix, the iron left behind still existed in a similar coordination, with or without the washing.

SQUID results indicated major differences in the magnetic properties of \( \text{CN}_x \) and \( \text{FeNC} \), with \( \text{CN}_x \) having the higher saturation magnetization after acid-washing, while \( \text{FeNC} \) showed the opposite trend. This behavior is attributed to the diamagnetic contribution of oxide-species originating from the MgO support in \( \text{CN}_x \) before acid-washing, which lower its overall saturation magnetization in the unwashed state. Whereas in the case of \( \text{FeNC} \), acid-washing leads to a loss of surface Fe species, lowering its saturation magnetization in the acid-washed sample.
With the results discussed above, we have established that CN\textsubscript{x} and FeNC materials are indeed two different classes of NPMC catalysts, with different activities and deactivation behavior towards ORR in acidic media, and evidently different active sites. While iron certainly plays an active role in catalyzing ORR for FeNC, its presence is CN\textsubscript{x} does not manifest itself with higher ORR activity. We believe the findings reported in this article will shed some light on the ambiguity of the role of the transition metal on the active sites of these two materials.
CHAPTER 6. Stages of FeNC catalyst preparation: Effect of transition metal and heat-treatments

Manuscript in Preparation

6. 1 Motivation

There are certain fundamental differences between FeNC and CN\textsubscript{x} catalysts for ORR that have become evident from the studies discussed in Chapter 5. FeNC catalysts are prepared by wet impregnation of an iron precursor and an organic nitrogen-containing pore-filler (Phenanthroline) onto a high surface area carbon black support, and the dried powder is then ball-milled and heat-treated in an inert followed by an ammonia treatment. Since there is typically no acid-washing involved after the heat-treatment, the iron-nitrogen coordinated sites are believed to reside in the micropores of the high surface area carbon support\cite{46}. In order to evaluate the effect of the different stages of treatment steps incorporated in FeNC catalysts, the catalysts have been studied systematically at different steps such as before heat-treatments, and without incorporation of the transition metal. The catalysts have been prepared according to the methods outlined in the experimental methods section. A brief description, along with the nomenclature used is provided in Table 12.
Table 12. Description and nomenclature of catalysts used

<table>
<thead>
<tr>
<th>Catalyst Description</th>
<th>Nomenclature</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. FeNC precursor: wet impregnation (WI) of BP 2000 (BP), phenanthroline (Phen) and iron acetate, followed by drying and ball-milling</td>
<td>FeNC-Prec-NoHT</td>
</tr>
<tr>
<td>2. Metal-free WI of BP and Phen, no heat-treatment</td>
<td>BP-PhenNoHT</td>
</tr>
<tr>
<td>3. Metal-free WI of BP and Phen, dried, hand ground; heat-treated in Argon-1050°C-1h</td>
<td>BP-Phen-Ar</td>
</tr>
<tr>
<td>4. 1%Fe WI of BP and Phen, dried and hand ground; heat-treated in Argon-1050°C-1h</td>
<td>FeNC-Ar</td>
</tr>
<tr>
<td>5. 1%Fe WI of BP and Phen, dried and hand ground; heat-treated in Argon-1050°C-1h; Acid-washed for 1h in 1M HCl</td>
<td>FeNC-Ar-AW-1h</td>
</tr>
<tr>
<td>6. 1%Fe WI of BP and Phenanthroline, dried and hand ground; heat-treated in Argon-1050°C-1h; in NH3-950°C-20mins</td>
<td>FeNC-Ar-NH3</td>
</tr>
<tr>
<td>7. 1%Fe WI of BP 2000 and Phenanthroline, dried and hand ground; heat-treated in Argon-1050°C-1h; in NH3-950°C-20mins; acid washed for 1h in 1M HCl</td>
<td>FeNC-Ar-NH3-AW-1h</td>
</tr>
</tbody>
</table>

6.2 Results and Discussion

6.2.1 Activity Tests (RDE and Fuel Cell), Accelerated Durability Tests (ADTs) and Stability

The ORR activity of FeNC-Ar-NH3 (washed and unwashed) and FeNC-Ar (washed and unwashed) catalysts using RDE in 0.5M H2SO4 is shown in Figure 35(a)
and (b) respectively. Clearly, the effect of acid washing brings about a decrease in activity for both FeNC-Ar and FeNC-Ar-NH₃. For FeNC-Ar-NH₃, a decrease is seen from 0.87V to 0.83V after acid washing whereas in FeNC-Ar, a decrease in onset potential occurs from 0.83V to 0.80V. As seen in Chapter 5, acid leaching of both the FeNC brings about dissolution of active Fe sites into the acid which translates to a loss in ORR activity.

Figure 35. Comparison of ORR RDE results for unwashed and acid washed catalysts. (a) FeNC-Ar-NH₃ and (b) Fe-N-C-Ar at 1000 rpm in 0.5M H₂SO₄ oxygen-saturated solution

Accelerated Durability Tests (ADTs) performed on both FeNC-Ar-NH₃ and FeNC-Ar (unwashed) catalysts revealed that significant activity losses were observed between 100, 500 and 1000 cycles for both the catalysts (Figure 36(a) and (b)). Since the
The purpose of the accelerated durability tests is to keep the catalyst immersed in an acidic environment for a prolonged period of time, the loss in activity in the ADTs appears to be similar to the effect of acid washing in these catalysts.

Figure 36. Accelerated durability tests on (a) FeNC-Ar-unwashed and (b) FeNC-Ar-NH$_3$-unwashed catalysts
This was revalidated using 100h stability tests using a Fuel Cell Test Stand (FCTS). As seen in Figure 37(a), FeNC-Ar-NH$_3$ has a higher initial activity than FeNC-Ar, but after a potential hold at 0.5V, the final activity of both the catalysts is almost identical. Ammonia treatment of the FeNC imparted high ORR activity to the catalyst, but the treatment evidently decreased the stability of the catalyst. The ammonia treatment imparts a higher degree of pyridinic-N or edge-nitrogen functionalities on the surface of the catalyst. It has been speculated that in the harsh acidic environment of the PEM fuel cell, the pyridinic-N functionalities undergo protonation, leading to a site blockage, which results in a degradation of activity[175]. Another possible degradation mechanism discussed previously is attributed to the anion (sulfonate groups arising from the polymer membrane itself) binding of the protonated pyridinic-N functionalities in the fuel-cell leads to a decrease in activity over time[109].

Effect of acid washing on FeNC-Ar-NH$_3$, leads to a decrease in initial activity as seen in Figure 37(b). But after the 100h potential hold, the final activity of both the washed and un-washed catalyst is the same, indicating a better retention of activity for the acid washed catalyst. The same trend was observed regardless of the ammonia treatment for the catalyst. Although FeNC-Ar-AW catalyst had a lower initial activity, the final activities were almost the same for both the catalysts (Figure 37(c)). Hence it appears that the active sites in unwashed catalyst undergo either site blockage over a period of time, or they are lost altogether during prolonged fuel cell operation, leading to a lowering of activity after the stabilization test. However, in the washed catalyst, it
appears that the active sites that are prone to fast degradation are not present to begin with; as a result, the catalyst does not show as significant of an activity loss.

Figure 37. Fuel-cell polarization curves (solid lines) and after (dashed lines) 100h potential hold at 0.5V for (a) FeNC-Ar and FeNC-Ar-NH$_3$ (unwashed) (b) FeNC-Ar-NH$_3$ (washed and unwashed) (c) FeNC-Ar-washed and FeNC-Ar-NH$_3$-washed
We also ran control experiments to observe the effect of the transition metal precursor and heat-treatments on these catalysts. Figure 38 shows the ORR activity of the (a) FeNC precursor (FeNC-prec-NoHT) with no heat treatment, along with (b) Fe-free precursors consisting of BP:Phen heat-treated in Ar, and (c) Ar-NH₃. All three catalysts do not perform as well as the original FeN-C-Ar or FeNC-Ar-NH₃ catalysts, but they exhibited an interesting trend. The Fe-free sample heat-treated in Ar or Ar-NH₃ exhibited an ORR activity of 0.60 V and 0.695V respectively, while the non-heat-treated , FeNC-Prec-NoHT catalyst exhibited at activity of 0.453V. It appears that the heat-treatment of the catalyst using a nitrogen source like ammonia is more essential in imparting ORR activity to the catalyst, than the presence of Fe. However, when both components are present at the same time, the catalyst produced is very active for ORR.
6.2.2 Surface nitrogen species determination

X-ray Photoelectron Spectroscopy (XPS):

XPS spectra of FeNC-Ar-NH$_3$ unwashed and washed are shown Figure 40 (a) and (b), and tabulated in Table 13. There is a sharp increase in the pyridinic nitrogen content (396.6 ±0.3 eV) of the catalyst after acid washing from 25% to 36%. A similar trend was seen for FeNC-Ar unwashed and washed (Figure 39(c) and (d)), with an increase from 16% before washing to 38% after acid washing. FeNC-Ar-NH$_3$ also showed a higher extent of pyridinic N content (25%) to in comparison with FeNC-Ar only (16%). This indicated that the ammonia treatment successfully imparts surface nitrogen functional groups to the catalyst. The increase in pyridinic N functional groups after acid washing
for both FeNC-Ar and FeNC-Ar-NH₃ catalysts is concomitant with our observation that the leaching of Fe from the Fe-N coordinated sites in FeNC, leave behind nitrogen species at the edge of the graphitic layers, which gives rise to an increase in the pyridinic-N species.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pyridinic (eV) (%fraction)</th>
<th>Quartenary (eV) (%fraction)</th>
<th>Pyridinic N-O (eV) (%fraction)</th>
<th>Total Nitrogen Content</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeNC-Ar</td>
<td>398.4</td>
<td>400.8</td>
<td>402.5</td>
<td>1.1%</td>
</tr>
<tr>
<td>FeNC-Ar-NH₃</td>
<td>398.6</td>
<td>401</td>
<td>405.4</td>
<td>1.9%</td>
</tr>
<tr>
<td>FeNC-Ar-AW-1h</td>
<td>398.9</td>
<td>401</td>
<td>404.4</td>
<td>2.8%</td>
</tr>
<tr>
<td>FeNC-Ar-NH₃-AW-1h</td>
<td>398.9</td>
<td>401</td>
<td>405.9</td>
<td>2.5%</td>
</tr>
</tbody>
</table>
Figure 39. XPS spectra for (a) FeNC-Ar-NH$_3$-unwashed (b) FeNC-Ar-NH$_3$-washed (c) FeNC-Ar-unwashed (d) FeNC-Ar-washed

Figure 40 is the XPS spectra of control catalysts for FeNC with (a) FeNC-prec-No HT (b) BP-Phen-No HT (c) BP-Phen-Ar-NH$_3$ and the fraction of nitrogen species is reported in Table 14. A peak appears at 399.1 eV which corresponds to an N-Fe bond (Figure 41a), although there exits some ambiguity in discriminating between N-Fe and pyridinic N species, with their binding energies very close to each other (399.2 eV for Metal-N, and 398.2-399eV for pyridinic N). There is also some extent of pyrrolic nitrogen species at 400.3 eV (assignment 400.0-400.3 eV). BP-Phenanthroline that has undergone no heat-treatment shows a peak at 398.8 eV which corresponds to pyridinic N (Figure 40b). While after undergoing a heat treatment in Ar-NH$_3$, the same catalyst
undergoes transformation to a higher fraction of pyrrolic N at 400.4 eV at about 68%, with the rest being pyridinic-N (Table 14). Hence it appears as though although there is exists a large fraction of Fe-N type species (83%) for FeNC-precursor-BM-No HT, and there is also evidence for presence of pyridinic N species without the metal, in the presence of high temperature Ar-NH$_3$ treatments, both of these by themselves are not sufficient enough to impart high ORR activity to these catalysts. Hence, quite clearly, both the Fe precursor and the high temperature heat treatments need to be present to impart high ORR activity to these catalysts. This is also proven by means of the activity data, in which, although the acid washed catalysts showed higher Pyridinic N, these catalysts performed poorly as compared to unwashed samples. A high quantity of pyridinic N could then possibly be a marker for stability for these catalysts.

Table 14. XPS N1s content of FeNC Precursor and control catalysts

<table>
<thead>
<tr>
<th>Sample</th>
<th>(eV)</th>
<th>(Fraction)</th>
<th>(eV)</th>
<th>(Fraction)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeNC-Prec-NoHT</td>
<td>399.1</td>
<td>83%</td>
<td>400.3</td>
<td>17%</td>
</tr>
<tr>
<td>BP-Phen-NoHT</td>
<td>398.8</td>
<td>100%</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>BP-Phen-Ar-NH$_3$</td>
<td>398.2</td>
<td>32%</td>
<td>400.45</td>
<td>68%</td>
</tr>
</tbody>
</table>
6.2.3 Resistance to oxidation

Temperature Programmed Oxidation (TPOs)

Temperature Programmed Oxidation reactions were also carried out under 10% O₂ in Helium. The spectra shown in Figure 41 are for the CO₂ (m/z=44), CO (m/z=28), NO₂ (m/z=46), NO (m/z=30) signals for the following catalysts (a) FeNC-Prec-No HT (b) FeNC-Ar (c) FeNC-Ar-NH₃ and (d)BP:PHen-Ar-NH₃. It is known that iron catalyzes the oxidation for carbon. Hence the lowest oxidation temperature is seen for FeNC-prec-No HT, with an onset of oxidation at ~295°C. This is expected as this catalyst contains surface iron which would initiate carbon oxidation at a lower temperature. Both FeNC-Ar
and FeNC-Ar-NH$_3$ exhibited slightly higher onset of oxidation temperatures, at $\sim$328°C and $\sim$333°C respectively. It has been seen previously that a heat-treatment step leads to encapsulation of the iron-species within the carbon, hence there is much less iron present on the surface for the heat-treated catalyst, than its non-heat-treated counterpart. This could possibly lead to an increase in the onset of oxidation temperature. However, when no iron was used in the precursor (Figure 41(d), the oxidation onset temperature was significantly higher at $\sim$450°C. It should also be noted that the NO species evolved (m/z=30) was significantly higher for the BP:Phen-Ar-NH$_3$ sample, reinstating that the ammonia treatment itself leads to significant incorporation of nitrogen functionalities.
Figure 41. Temperature Programmed Oxidation (TPO) spectra of (a) FeNC-Prec-No HT (b) FeNC-Ar-NH$_3$ (c) BP:Ph-Ar-NH$_3$

6.2.4 Bulk iron species determination

XANES and EXAFS

XANES and EXAFS on the Fe-K edge were also performed for these catalysts. Figure 42 (a) and (b) show the XANES spectra of FeNC-Ar, FeNC-Ar-NH$_3$, FeNC-Ar-AW and FeNC-Ar-NH$_3$-AW. There was no significant difference in the spectra between these catalysts, and they resembled iron carbide, when compared to the standard
reference. However, the possibility of the existence of Fe-Nₓ cannot be discounted due to similar scattering from all 2p elements. The only significant difference was seen in FeNC-Prec-NoHT (Figure 42(c)), which resembled a mixture of iron (II) acetate and iron (II) oxide. This would be expected since the iron precursor used for the study is iron (II) acetate.

Figure 42. XANES spectra of (a) FeNC-Ar and FeNC-Ar-NH₃ (b) FeNC-Ar-washed and FeNC-Ar-NH₃-washed (c) FeNC-Prec-No HT with references iron carbide, iron foil, iron oxide and iron acetate respectively.
The EXAFS spectra are shown in Figure 43(a-c). The FT magnitudes of FeNC-Ar, FeNC-Ar-NH3, FeNC-Ar-AW and FeNC-AR-NH3 acid washed show similarities to iron carbide, with the Fe-Fe peak showing at 2.1Å. Uncorrected values are reported. There is a small shoulder at ~1.7Å that is attributed to an Fe-C\_x or Fe-Nx type scatter. It is harder to distinguish scattering from the 2p elements such as S, O and N, making it difficult to distinguish between an iron carbide or iron nitride species, and this difficulty stems from an inherent drawback of the technique.
Figure 43. EXAFS spectra of (a) FeNC-Ar and FeNC-Ar-NH$_3$ (b) FeNC-Ar-washed and FeNC-Ar-NH$_3$-washed (c) FeNC-Prec-No HT with references iron carbide, iron foil, iron oxide and iron acetate respectively

6.3 Conclusions

Different stages of preparation of FeNC catalysts were also studied to gain more insight into the effect of pyridinic-N and transition metal incorporation. FeNC catalysts prior to the NH$_3$ treatment, Argon treatment as well as without transition metal...
incorporation were studied. FeNC-Ar was less active, albeit more stable than FeNC-Ar-NH₃, and it is speculated that in addition to the dissolution of active Fe species from prolonged operation in a fuel cell, the pyridinic functional groups may be undergoing some change as well: either in the form of protonation themselves, or being bound to sulfonate groups, they prevent charge transfer from occurring, leading to loss in activity. But in both cases, acid-washing diminished the performance of FeNC-Ar and FeNC-Ar-NH₃, but also led to a higher degree of stability.

It was seen that the presence of pyridinic-N functional groups after a heat-treatment imparted higher activity to the catalyst than the presence of transition metal without a heat-treatment. However, it was seen that only the presence of pyridinic functional groups was not sufficient to make very active ORR catalysts, the transition metal was required in addition, in order to achieve high activity. This re-affirms the presence of a metal-Nₓ coordination catalyzing ORR for FeNC catalysts.
CHAPTER 7. Use of H₂S to probe the active sites in Fe-N-C catalysts for the Oxygen Reduction Reaction (ORR) in acidic media

Manuscript in Preparation for Submission to ACS Catalysis

7.1 Motivation

In order to investigate the active sites of FeNC catalysts, several researchers have investigated poisoning of similar materials using CO and CN⁻[176, 177]. The catalysts with Me-Nₓ active centers were not poisoned with CO, but have seen to deactivate significantly in the presence of CN⁻. Nitrogen-doped carbon nanostructured catalysts, however, showed only a reversible deactivation for ORR in the presence of CO, by rapidly regaining their activity once CO was removed from the medium[161]. CNₓ catalysts have also shown no deactivation in the presence of cyanide. In a previous study we also attempted to exclusively poison any metal centers in these catalysts, if existing, by using H₂S as a poison. On the contrary, the sulfur treatment enhanced the activity of these catalysts for ORR, while quickly deactivating platinum upon exposure[99].

In a previous chapter, the differences between Fe-N-C and CNₓ catalysts were highlighted, and we demonstrated that the two are indeed different types of ORR catalysts, with possibly different mechanisms for catalyzing the reaction. FeNC catalysts
contain metal-nitrogen coordination with carbon as their active site, which was clearly different from CN₄ materials which show no existence of a metal containing active site.

We have highlighted this difference by conducting the following study with a systematic poisoning of FeNC ORR catalysts using H₂S as a probe molecule. H₂S has been used as a poisoning gas at various stages of heat treatments for these catalysts. And it is seen that not only do FeNC catalysts show deactivation for ORR in the presence of H₂S, but the effect of H₂S treatment is dependent on the stage at which the treatment was performed. This indicates the possibility of different active sites existing within the class of Fe-N-C catalysts. The FeNC catalysts have been prepared by the method outlined in the experimental method section. Following is a description of introduction of H₂S treatment on these catalysts. As control experiments, the catalysts were subjected to Argon and H₂ at the same temperature and for the same duration as the H₂S treatment, to evaluate the effect of the heat-treatment alone, or a reducing environment (in the presence of H₂).

7.2 Catalyst Description

7.2.1 H₂S, Ar or H₂ treatments of catalysts

For the H₂S or H₂ treatment of FeNC precursor or catalysts, approximately 150 mg of the catalyst was placed in a quartz boat in a high temperature furnace. The furnace was ramped up to 350°C in 35 mL/min N₂. Once the furnace temperature reached 350°C, the flow was switched to 35 mL/min of 500 ppm H₂S/N₂. The catalyst was treated in H₂S or H₂ for 4h, upon which the furnace began to cool down and the gas flow was switched
back to N₂. To differentiate between the poisoning effect of H₂S from its potential reducing effect, similar experiments were performed using 500 ppm H₂/N₂ under identical conditions. The treatments in H₂S or H₂ at 350°C for 4h were employed either as an intermediate or as a terminal treatment. Ar was also used as a treatment gas at 350°C for 4h, as a control to evaluate the effect of heat treatment without a reactive gas. The flow through the quartz tube was kept at Argon throughout the temperature ramp rate, hold time and cool down.

The catalysts prepared for this study are denoted using the following nomenclature in Table 15:
Table 15. Description of H$_2$S, Ar or H$_2$ treatments of FeNC catalysts

<table>
<thead>
<tr>
<th>Nomenclature used</th>
<th>Intermediate heat treatment (350°C, 4h)</th>
<th>Inert heat treatment (1050°C, 1h)</th>
<th>NH$_3$ heat treatment (950°C, 20 min)</th>
<th>Post-ammonia treatment (350°C, 4h)</th>
<th>Second NH$_3$ treatment (950°C, 20 min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeNC precursor</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>FeNC-Ar</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>FeNC-$H_2S$-Ar</td>
<td>H$_2$S</td>
<td>Ar</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>FeNC-Ar-Ar</td>
<td>Ar</td>
<td>Ar</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>FeNC-$H_2$-Ar</td>
<td>H$_2$</td>
<td>Ar</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>FeNC-Ar-NH$_3$</td>
<td>-</td>
<td>Ar</td>
<td>NH$_3$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>FeNC-Ar-NH$_3$-$H_2S$</td>
<td>-</td>
<td>Ar</td>
<td>NH$_3$</td>
<td>H$_2$S</td>
<td>-</td>
</tr>
<tr>
<td>FeNC-Ar-NH$_3$-Ar$H_2$$S$</td>
<td>-</td>
<td>Ar</td>
<td>NH$_3$</td>
<td>Ar</td>
<td>-</td>
</tr>
<tr>
<td>FeNC-Ar-NH$_3$-$H_2$</td>
<td>-</td>
<td>Ar</td>
<td>NH$_3$</td>
<td>H$_2$</td>
<td>-</td>
</tr>
<tr>
<td>FeNC-Ar-NH$_3$-$H_2S$-$NH_3$</td>
<td>-</td>
<td>Ar</td>
<td>NH$_3$</td>
<td>H$_2$S</td>
<td>NH$_3$</td>
</tr>
<tr>
<td>FeNC-$H_2S$-Ar-NH$_3$</td>
<td>H$_2$S</td>
<td>Ar</td>
<td>NH$_3$</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

7.3 Results and Discussion

7.3.1 Rotating Disk Electrode ORR Activity Experiments

ORR RDE scans collected in 0.5M H$_2$SO$_4$ solutions for FeNC-Ar-NH$_3$ (standard Fe-N-C catalyst in its most active form), and the samples that went through H$_2$S, or Ar treatment (FeNC-Ar-NH$_3$-$H_2S$ and FeNC-Ar-NH$_3$-Ar) and are shown in Figure 44(a). The rationale for using the latter treatment was to differentiate between the poisoning
effect of H$_2$S and the effect of a post-ammonia treatment with a non-reacting gas such as Ar. It is evident that while Fe-N-C-Ar-NH$_3$, FeNC-Ar-NH$_3$-$Ar$ have nearly identical onset potentials (0.84V), the onset potential for FeNC-Ar-NH$_3$-$H_2S$ is lower by 30mV. We performed another control experiment using H$_2$ heat treatment in lieu of H$_2$S or Argon, to rule out the possibility of a reduction effect causing a loss in activity of this catalyst, and no difference in activity was observed due to H$_2$ treatment. Fe-N-C catalyst suffers from a pronounced activity loss after H$_2$S treatment, which is not observed by a post-ammonia inert heat treatment effect or a reduction effect.

However, when the poisoned Fe-N-C catalyst (FeNC-Ar-NH$_3$-$H_2S$) was re-treated in NH$_3$ at 950°C, the catalyst regained its activity, as seen in Figure 44(b), indicating that the poisoning effect was a reversible one. The increased limiting current after the second NH$_3$ treatment can be due to an increase in the surface area/ surface functional groups as a result of NH$_3$ etching.
Figure 44. ORR Activity measurements by RDE in 0.5M H$_2$SO$_4$ at 2500rpm (a) Effect of treatment with H$_2$S, H$_2$ or Ar after high-temperature Ar-NH$_3$ treatment, (b) Effect of the second NH$_3$ treatment after H$_2$S-poisoning

We also compared the effect of sulfur treatment on a FeNC-precursor, black pearls impregnated with 1,10-phenanthroline and iron(II) acetate solution and ball-milled prior
to any high-temperature heating. The sample was treated in H₂S/N₂ at 350°C for 4h, followed by Ar treatment at 1050°C for 1 h. The ORR RDE scans for FeNC-\(H₂S\)-Ar and FeNC-Ar are shown in Figure 45(a). There was a pronounced deactivation effect observed with H₂S treatment, such that FeNC-\(H₂S\)-Ar showed a lower onset of activity by 0.4V than the catalyst prepared by treatment in Ar only (FeNC-Ar). This deactivation effect was exclusive to exposure to H₂S. We performed control experiments by using H₂ or Ar instead of H₂S in order to eliminate the effect of a heat-treatment alone, or a reducing environment and saw that the deactivation was not observed with either of the two gases, and was seen with H₂S only.

It is also evident from Figure 45(b) that a third heat-treatment in NH₃ does not re-activate the catalyst; in fact the onset potential of FeNC-H₂S-Ar-NH₃ at 0.79V, is still 30 mV less than what was observed for FeNC-Ar, at 0.82V. It is likely that the sulfur has a propensity to bind to the Fe sites in the catalyst precursor in such a way that it interferes with the formation of active sites in the subsequent heat-treatments.
Figure 45. ORR Activity measurements by RDE in 0.5M H₂SO₄ at 2500rpm (a) Effect of low-temperature-treatment with H₂S, H₂ or Ar before high-temperature Ar treatment (b) Effect of NH₃ treatment on pre-poisoned catalyst
In Figure 46, we compare the ORR activities of FeNC-$H_2S$-Ar-NH$_3$, FeNC-Ar-NH$_3$-$H_2S$ with FeNC-Ar-NH$_3$ catalyst, to evaluate the effect of H$_2$S treatments at different stages, i.e., before any heat treatment and after Ar and NH$_3$ treatments. It is observed regardless of whether the catalyst is exposed to H$_2$S before the heat-treatments or after, exposure to H$_2$S deactivates it to the same extent, and significantly lowers its activity in comparison to standard and most active form of the catalyst, FeNC-Ar-NH$_3$.

It should also be noted that the differences in the limiting current densities could be caused due to changes in the surface functionalities of these catalysts, as a result of varying the sequence of heat-treatments. The surface functionalities could significantly alter the hydrophobicity of the catalysts, causing differences in the three-phase boundary within the pores of the catalyst, which in turn could affect the limiting current densities obtained.
7.3.2 Catalyst Characterization

7.3.3 Sulfur desorption

7.3.4 Temperature Programmed Oxidation (TPO)

TPO experiments were conducted for the regular and H₂S treated FeNC catalysts. Figure 47 shown a comparison of the TPO profiles for samples that have gone through different temperature and/or gas treatments.

One of the most striking features is the change in the oxidation onset temperatures for these samples upon exposure to sulfur. Since iron catalyzes the oxidation of carbon, its presence in FeNC samples is expected to lower the oxidation onset temperature. In Fe-
NC-Ar, oxidation starts at ~320°C as seen with the rise of the (m/z=44) CO₂ signal (Figure 4(a)). An H₂S exposure before Ar treatment raises the oxidation onset temperature by about 90°C (Figure 47(b)). This result is significant in suggesting that the Fe sites poisoned by sulfur can no longer catalyze the oxidation reaction effectively. When the FeNC-H₂S-Ar sample goes through a high-temperature NH₃ treatment, this activity is not recovered and the oxidation onset temperature does not change (Figure 47(c)).

For FeNC-Ar-NH₃, the oxidation onset temperature is seen to be about 335°C (Figure 47(d)). Exposure to H₂S increases the oxidation onset temperature (Figure 4(e)), but the change is not as drastic as it was for the FeNC-H₂S-Ar sample. A second treatment with NH₃ somewhat lowers it, but does not bring it back to pre-sulfur exposure level (Figure 47(f)). This observation suggests that the coordination of sulfur on Fe sites is different depending on whether the sulfur exposure takes places before any heat treatment or after Ar-NH₃ treatment.

In addition to CO₂, there are also nitrogen oxide species (m/z=30) that evolve from the samples during TPO. They appear at higher temperatures than CO₂, suggesting that they are not primarily on the surface coordinated to carbon, but also in the bulk and coordinated to Fe. In sulfur-exposed samples (Figure 47 b and c), emergence of NOₓ species shifts to higher temperatures, following a trend similar to CO₂.

A third group of species that evolve during TPO are the SOₓ species (m/z= 64). They are most pronounced in FeNC-H₂S-Ar (Figure 47(b). They reduce significantly in FeNC-
$H_2S$-Ar-NH$_3$, but do not disappear altogether (Figure 47(c)). FeNC-Ar-NH$_3$-$H_2S$ also shows SO$_x$ species evolving during TPO, but the signal is lower than that seen over the FeNC-$H_2S$-Ar sample. Another difference is that a second NH$_3$ treatment eliminates all of the sulfur species formed during H$_2$S exposure, once again suggesting that different sulfur species are formed over the FeNC precursor if H$_2$S exposure takes place before any heat treatment. NH$_3$ treatment may eliminate some of the sulfur coordinated to surface carbon, but some of the sulfur, especially those coordinated to Fe stays behind and comes out only during high-temperature oxidation. XPS data presented in the next section provides additional support to these assertions.

It is interesting to note that FeNC-Ar catalyst which was not subjected to any prior sulfur treatment, also showed sulfur species evolving together with CO$_2$ (Figure 47(a). This is somewhat expected, as the carbon support itself (Black Pearls 2000) has some extent of sulfur impurities embedded within its matrix.
Figure 47. Temperature Programmed Oxidation profiles for FeNC samples that have gone through different heat and gas treatments.

7.3.5 Bulk iron and sulfur coordination

**Extended X-ray Absorption Fine Structure**

The magnitudes of the $k^2$ weighted Fourier Transforms for $H_2S$ treated FeNC-Ar catalysts were compared with the regular FeNC catalysts and reference compounds. In Figure 48, the Fourier Transform magnitudes of FeNC-$H_2S$-Ar with FeNC-Ar and iron sulfide and carbide are compared. This appears to have Fe-S bonds with a peak observed at 1.7 Å[178].

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Figure 48. EXAFS spectra of (a) FeNC-Ar and FeNC-Ar-H$_2$S and (b) FeNC-Ar and FeNC-H$_2$S-Ar with reference spectra iron sulfide, iron oxide and iron carbide respectively.

In Figure 49 and Figure 50 are shown comparisons for FeNC-Ar-NH$_3$-H$_2$S and FeNC-H$_2$S-Ar-NH$_3$ respectively with the control catalyst FeNC-Ar-NH$_3$ and references, namely iron sulfide, oxide and carbide, respectively. FeNC-Ar-NH$_3$-H$_2$S showed contributions Fe-S or Fe-O at 1.7 Å (Figure 49). This catalyst exhibits a very different coordination state from FeNC-Ar-NH$_3$ which shows predominantly Fe-N$_x$ or Fe-Fe peaks, implying that the sulfur treatment brought about an evident change in the local bonding environment of iron in FeNC-Ar-NH$_3$-H$_2$S.
The local coordination environment of FeNC-$H_2S$-Ar-NH$_3$ was harder to interpret, due to the increased possibility of different contributions from nitride, carbide or sulfide phases. FeNC-$H_2S$-Ar-NH$_3$ (Figure 50) is somewhat similar to FeNC-Ar-NH$_3$, indicating the possibility of Fe-C$_x$ or Fe-N$_x$ contributions. As seen from the XPS data, the sulfur species seem to have desorbed in the subsequent heat treatments if $H_2S$ treatment is incorporated as a pre-treatment for this catalyst. So it is not surprising that the iron coordination environment is not very different from its pristine sample.

It should also be noted that the light scatterers such as oxygen, nitrogen and sulfur as neighbors to the central scattering atom are hard to distinguish between each other, due to their relatively close bond lengths, thus making exact interpretations of EXAFS spectra difficult.
Figure 49. EXAFS spectra of (a) FeNC-Ar-NH$_3$ and FeNC-Ar-NH$_3$-H$_2$S with reference spectra iron sulfide and iron oxide.

Figure 50. EXAFS spectra of FeNC-Ar-NH$_3$ and FeNC-H$_2$S-Ar-NH$_3$ with reference spectra iron sulfide and iron carbide respectively.
7.3.6 Surface nitrogen and sulfur species determination

X-Ray Photoelectron Spectroscopy (XPS)

S 2p

The S 2p region of all the H$_2$S-treated catalysts was scanned to identify detectable surface species. Figure 51 shows the S 2p spectra of FeNC-$H_2S$-Ar, $H_2S$-Ar-NH$_3$ and Ar-NH$_3$-$H_2S$. The raw spectra of FeNC-Ar-NH$_3$-$H_2S$-NH$_3$ is also shown for comparison; no sulfur species were detected for this catalyst.

Three different types of sulfur species have been identified on the surface of the three catalysts. There is some extent of ambiguity in the literature with peak assignments of sulfur species between 163-164 eV. The peaks at 163.8 eV is indicative of S-C species[179]. A peak at 164.1 eV has been previously assigned to elemental sulfur in literature[180, 181]. There is less certainty for identification for S-C species, as they have been assigned to both 163 eV and 163.6 eV, while 163.6 eV has been assigned to only S-S species as well[100, 181]. Hence it is very likely that both S-C and S-S type species exist for these three catalysts: $H_2S$-Ar, Ar-NH$_3$-$H_2S$ and $H_2S$-Ar-NH$_3$. The peaks for FeNC-$H_2S$-Ar-NH$_3$ are smaller, as the two subsequent heat treatments reduces the surface sulfur species drastically. The peaks at 168.6 eV and 168.8 eV for this catalyst corresponds to iron sulfate/sulfite species[182]. It is possible that the elemental sulfur
present on the surface underwent some degree of surface oxidation, reacting with air to form sulfate.

There is also a small peak at 161.7 eV for all three catalysts, which is most likely an Fe-S$_2$/ Fe-S type species[183]. The resolution of the sulfur species was not sufficiently high for data deconvolution.

An inset of the Temperature Programmed Desorption profiles of SO$_2$ species (m/z= 64, respectively) is shown for FeNC-Ar-NH$_3$-H$_2$S, H$_2$S-Ar-NH$_3$, H$_2$S-Ar. All three catalysts indicated significant rise in intensities for the SO$_x$ and SO$_2$ species between the temperatures of 250°C-450°C, confirming the existence of surface sulfur species.
The nitrogen 1s XPS spectra were deconvoluted to reveal differences in the nitrogen surface species as a function of the treatment and are plotted in Figure 52 and tabulated in Table 16.

The three main surface groups found for the catalysts were pyridinic (398.6 ±0.3 eV), quarternary (401.3 ± 0.3 eV), and pyridinic N⁺O⁻ at a higher binding energy between 402-
405 eV[97]. The pyridinic nitrogen content for FeNC-Ar-NH$_3$-$H_2S$ is seen to be significantly lower as compared to that of FeNC-Ar-NH$_3$ (15% versus 25% of the total nitrogen composition), as seen in Figure 52(a) and (b). This could be the explanation for the marked decrease in activity of FeNC-Ar-NH$_3$-$H_2S$ as compared to its control, and this could be attributed to the adsorption of sulfur onto the catalytic sites via a possible substitution mechanism by which sulfur replaces some nitrogen functionalities that impart ORR activity to these catalysts. There was partial recovery of the pyridinic nitrogen species in FeNC-Ar-NH$_3$-$H_2S$-$NH_3$, with the concentration rising to upto 21%.

For both the catalysts FeNC-$H_2S$-Ar and FeNC-$H_2S$-Ar-NH$_3$ surface nitrogen was not detected by XPS. It appears as if $H_2S$ treatment before any heat treatments severely impedes the formation of nitrogen surface species in the subsequent heat treatments. This could possibly be the reason why a detrimental effect of $H_2S$ treatment was seen on ORR activity for both FeNC-$H_2S$-Ar and FeNC-$H_2S$-Ar-NH$_3$. 
Figure 52. N 1s XPS spectra of control and H₂S treated catalysts

Table 16. N1s XPS spectra for H₂S-treated and control FeNC catalysts

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pyridinic (398-398.9eV)</th>
<th>Quartenary (401-402 eV)</th>
<th>Pyridinic N⁺-O⁻ (402-405 eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeNC-Ar</td>
<td>16</td>
<td>51</td>
<td>33</td>
</tr>
<tr>
<td>FeNC-Ar-NH₃</td>
<td>25</td>
<td>57</td>
<td>18</td>
</tr>
<tr>
<td>FeNC-Ar-NH₃-H₂S</td>
<td>15</td>
<td>75</td>
<td>10</td>
</tr>
<tr>
<td>FeNC-Ar-NH₃-H₂S-NH₃</td>
<td>21</td>
<td>65</td>
<td>14</td>
</tr>
</tbody>
</table>
7.4 Conclusions

The H\textsubscript{2}S heat-treatments were employed on FeNC catalysts in two steps: (1) either after the terminal heat-treatment or (2) on the ball-milled precursor prior to any high temperature treatment.

Exposure to H\textsubscript{2}S caused significant deactivation for ORR, when used as a terminal treatment after Ar-NH\textsubscript{3} for FeNC; an effect not observed for H\textsubscript{2} or Ar treatments when used instead of H\textsubscript{2}S. Clearly sulfur binding to or replacing the active sites was the effect of this loss in activity, which was not brought about by a mere inert heat treatment or a reducing heat treatment for the same duration of time. This was verified by catalyst characterization experiments such as TPO, EXAFS and XPS and TPD. Both TPD and TPO profiles indicated the presence of surface sulfur species, and the oxidation of carbon was shifted to a higher temperature, indicating that the Fe sites that catalyze carbon oxidation as well as ORR were rendered inactive with the H\textsubscript{2}S treatment. EXAFS revealed a change in the coordination environment of Fe, after the H\textsubscript{2}S treatment which may have arisen from the formation of Fe-S bonds. XPS helped identify S-S or S-C surface species, along with the possibility of Fe-S type bonds, indicating that the sulfur indeed binds to Fe in this catalyst.
FeNC-Ar-NH$_3$-$H_2S$ also showed a lower incorporation of pyridinic N, than FeNC-Ar-NH$_3$, which could also explain the detrimental effect on ORR activity. However, this activity loss is reversible, because if this catalyst is re-exposed to NH$_3$, it regains its ORR activity with loss of the adsorbed sulfur species and partial restoration of the pyridinic-N species. This leads us to believe that the sulfur incorporation was possibly an adsorption and site blockage effect.

However, when the H$_2$S treatment was employed before Ar-NH$_3$ treatments, it lowered the catalyst’s ORR activity. This catalyst (FeNC-$H_2S$-Ar-NH$_3$) indicated presence of a lower degree of sulfur species incorporation in TPOs and XPS, indicating that the two subsequent heat-treatments removed significant amounts of adsorbed sulfur in the catalyst. One noteworthy observation is that no nitrogen species were observed through XPS for FeNC-$H_2S$-Ar-NH$_3$. Hence it is very likely that the H$_2$S treatment prior to the Ar-NH$_3$ treatments interfered with Fe-N$_x$ site formation, which may have adversely affected its activity.

FeNC-$H_2S$-Ar also showed a marked decrease in activity due to the H$_2$S treatment. Although some of the sulfur was desorbed after the Ar treatment, as seen by the TPD, TPO experiments, this intermediate heat treatment impeded the ability of active site formation, as evidenced by the lack of surface nitrogen species in XPS. EXAFS also indicated presence of Fe-S species in this catalyst.

The deactivation of FeNC catalysts seen due to exposure to H$_2$S is a clear indication of the role played by Fe in catalyzing ORR in these catalysts. The mechanism
of deactivation may be different depending on whether the \( \text{H}_2\text{S} \) exposure is performed on the FeNC precursor before the Ar or Ar-NH\(_3\) treatments, or on the FeNC catalyst after the Ar-NH\(_3\) treatment. In the former, \( \text{H}_2\text{S} \) interfered with the formation of catalytically active Fe-N\(_x\) sites in the subsequent high temperature heat-treatments. Whereas in the latter, the sulfur species appear adsorbed on the active Fe-N\(_x\) sites by possible substitution of nitrogen, which are regained upon a second exposure to NH\(_3\).

These results are significant in highlighting the differences between FeNC and CN\(_x\) catalysts in the form of the role of iron in their active sites for ORR. In our previous report, we observed no detrimental effect of \( \text{H}_2\text{S} \) on CN\(_x\), while it deactivated platinum/carbon catalyst for ORR significantly[99]. By demonstrating that \( \text{H}_2\text{S} \) has a negative effect on ORR activity of FeNC catalysts, we provide concrete evidence that while Fe plays a critical role in catalyzing ORR for FeNC, it does not participate in catalyzing ORR in CN\(_x\), thereby proving that the two catalysts are indeed different materials with different active sites for oxygen reduction.
CHAPTER 8. Use of operando fuel cell and half-cell to analyze the Fe- and Co- k edge using X-ray Absorption Spectroscopy (XAS)

8.1 Motivation

As mentioned in the earlier chapters, there has been much debate about the role of transition metal in NPMCs for ORR. One of the main challenges in establishing the role of the transition metal is that it is present in a small mass fraction of the overall catalyst, with the primary composition of the catalysts being carbon, oxygen and smaller quantities of nitrogen.

It has been seen in the past that increasing the transition metal loading beyond (4.5%) does not lead to an overall increase in ORR activity[184]. As a result, most NNMCs prepared using transition metal precursors have a metal loading between 1-3%. The concentration of the metal can decrease further upon acid leaching. This makes it very difficult for most available spectroscopic characterization techniques to detect the transition metal, such as XPS.

EXAFS or XAS is a versatile tool that allows detection of changes in the desired element of interest under true reaction conditions, by the use of specialized flow cells and
systems used at synchrotron sources that would allow the penetration of X-rays through a catalyst surface while reactive gases are being fed over them at the desired temperatures.

The motivation of this study was to develop reaction cells and tools that would enable the use of XAS to measure the changes in the oxidation state and coordination number of the transition metal (Fe or Co) in CNₓ catalysts, with the application of voltage in an electrochemical system. Two electrochemical cells have been designed: (1) an electrolytic half-cell which simulates the PEM fuel cell environment with the help of protons available from sulfuric acid, and (2) a modified home-made PEM fuel cell. Both these cells have been designed to focus the X-ray beam on a carbon electrode containing a catalyst layer (in the half-cell) or on the catalyst of the MEA (in the PEM fuel cell).

The structural modifications used in the designs of these cells have been discussed, along with the results obtained by the use of these cells at APS in Argonne National Laboratory. In this chapter, the experiments performed for the use of the XAS cells are treated independent from the other studies in the previous chapters, and as a result, the theory of XAS and instrumentation has been revisited in this chapter exclusively, for clarity to the reader. The challenges encountered in the use of the cells, as well recommendations to overcome them have been discussed.
8.2 Background

8.2.1 EXAFS

As mentioned in Chapter 3, the principle behind this technique is based on creation of photoelectrons by the photoelectric effect. The central atom is bombarded with X-rays which are tuned to the excitation energy of the atom of interest, creating photoelectrons. These photoelectrons are ejected and undergo interference with the electron waves of the neighboring atoms. If the interference is constructive, it results in the formation of a fine structure of the X-ray absorption spectrum. The frequency of the EXAFS spectrum contains information about the interatomic distances between the absorbing and the neighboring atoms, and the amplitude gives information about the number, type and order of the neighboring atoms. The physical quantity that is measured in XAFS is the X-ray absorption coefficient $\mu (E)$, which provides information about how strongly X-rays are absorbed as a function of X-ray energy $E$. Generally, $\mu (E)$ shows a smooth attenuation with an increase in energy. However, at specific energies that are characteristic of the atoms in the material to which the incident X-ray has been tuned, there appear sudden increases called X-ray absorption edges, and these occur when the X-ray photon has sufficient energy to free electrons from their bound states in the atoms.
The excited photoelectron scatters from the neighboring atoms around the X-ray absorbing atom, creating interferences between the outgoing and the scattered waves of the photoelectron. These interference effects cause an energy dependent variation in the X-ray absorption, and when this variation is decoded using appropriate tools, such as Fourier Transform, we obtain information about the structure, atomic number, structural disorder of the neighboring atoms.

XAFS also requires the use of an X-ray beam of tunable energy, which can be adjusted to the atom of interest. In synchrotron radiation sources, there are electrons moving nearly at the speed of light in an evacuated pipe around a closed pathway of about 100-1000 meter circumference, guided by vertically aligned magnetic fields. When there is a change in the trajectory of motion of the electrons, the electrons accelerate. Upon acceleration, these charged particles emit electromagnetic radiation. Due to speeds approaching the speed of light, the average energy of the X-rays and their total radiated power is increased significantly, making the radiation pattern more directional, hence making the use of X-ray optics such as monochromators much easier.

Beamlines, where the experiments are performed, are large (usually tens of meters in length) and contain complex instruments such as X-ray monochromators, mirrors, slits, ultra high vacuum pumps, valves, gauges, photon shutters, shielding, safety interlocks, detectors, ultra high vacuum chambers, cryostats, furnaces, reaction cells, magnets, movable automated sample stages, goniometers, and data acquisition systems[185].
In a typical EXAFS beamline, an in-situ reactor cell is placed in the path of the X-ray beam. The monochromated X-ray beam is incident upon the catalyst of interest in the reactor cell, and upon transmission, it reaches the X-ray detector. The X-ray absorption spectra is then obtained by a plot of the absorption of the X-rays by the element of interest, as a function of energy.

### 8.2.2 Literature on operando EXAFS electrochemical cells

There have been reports previously on the construction of electrochemical cells for X-ray Absorption Spectroscopy (XAS) to observe changes in platinum on carbon and macrocyclic compounds, pioneered by Scherson et al.[28, 29, 186]. Figure 53 shows the schematic of an electrochemical cell used in the fluorescence mode at Brookhaven National Laboratory. This cell was used to observe CO adduct formation and adsorption on small Pt particles (4-5nm). The authors also conducted similar experiments to observe changes in Fe-k edge spectra using XAS of heat-treated Fe porphyrin adduct absorbed on black pearls[29]. They observed that the onset of the edge of dry, heat treated macrocycle coincided with Fe foil, suggesting that it contained iron in its elemental form. They also saw a reduction in the edge jump by 6% after the electrode was exposed to electrolyte, possibly due to dissolution of iron species, but it could have also been due to absorption of X-rays in the liquid medium, resulting in losing some of their intensity.
Figure 53. Schematic diagram of the electrochemical cell for in-situ Pt-L3-edge XANES measurements of highly dispersed Pt in the fluorescence mode (A) Hydrophobic carbon layer (B) Pt/XC-72R/Teflon electrode (C) Kapton tape (D) Gold wire (E) Glass cell (F) Gas outlet (G) gas inlet (H) Pt fil counter electrode (I) dynamic hydrogen electrode[186]

8.3 Results

8.3.1 Operando Half Cell

The principle behind the construction of an XAS-ready operando electrochemical half-cell was to simulate the half-cell used in our laboratory at OSU to measure ORR activity of catalysts.
The schematic of the electrochemical cell used in laboratory is as shown in Figure 54. It consists of a rotating ring disk electrode consisting of a glassy-carbon disk on which the catalyst of interest is applied. There is also an Ag/AgCl reference electrode against which the potential of the working electrode is measured. The counter electrode (made of platinum or graphite) allows a channel for the flow of electrons, thus completing the circuit. This three electrode set-up is contained in a glass cell containing oxygen-saturated 0.5M sulfuric acid that provides protons to mimic the environment of a PEM fuel cell. The activity scans are collected at different rotation rates of the RRDE, to ensure a constant supply of the reactant (oxygen) onto the surface of the working electrode, so that the reaction is not limited by consumption of oxygen.

Figure 54. Schematic of a glass electrochemical cell used to measure ORR
The Operando electrochemical half-cell used to collect XAS at APS with the application of potential was designed taking into consideration this 3-electrode cell used in laboratory.

The operando electrochemical half-cell is shown in Figure 55 and Figure 56. Figure 56 is a more detailed schematic of Figure 55; the difference between the two schematics is that in the former, the X-ray transparent chamber is made much thinner, in order to have a very thin layer of liquid electrolyte covering the surface of the carbon electrode. This is essential, as liquids absorb X-rays more strongly than gases, reducing their intensity before they reach the catalyst of interest. As a result, no edge jump would be seen for the element to which the X-ray has been tuned to, as they do not have sufficient energy for photoelectron excitation.

The Kapton windows provided on either side of the X-ray chamber provide transparency for the X-rays to pass through, while also providing a good seal with the o-rings provided. There is a small slit at the top to insert the working electrode into the X-ray chamber.
Figure 55. Schematic of the electrolytic half-cell used for electrochemical ORR experiments at Sector 10 ID-B of the Advanced Photon Source
Figure 56 is a more detailed schematic of the electrochemical half-cell. The working electrode consists of CNx catalyst pasted on carbon paper by using polytetrafluoroethylene (PTFE) and Nafion solution. PTFE is a binder that allows the catalyst powder to stick on the electrode surface. Nafion solution provides proton conduction. The electrode assembly is then supported by means of a silver wire that provides electrical contact between the catalyst and leads of the potentiostat. Sulfuric acid is contained in the bulk electrolyte chamber which also houses the Ag/AgCl reference electrode and the platinum counter electrode.
As a simple proof of concept experiment, the cell, containing the electrolyte was mounted on the beamline in the path of the X-ray beam to check if spectra can be collected at all across the working electrode. The spectra obtained is shown in Figure 57.

Figure 57. Normalized EXAFS spectra of Fe-K edge of CNx grown on Fe-MgO in sulfuric acid at OCV.

Although there was an occurrence X-ray absorption through the catalyst, the edge-jump obtained (not shown) in the non-normalized spectra was extremely small (<0.1). Typically, for good XAS spectra, an edge jump =>0.3 is desirable, because the
data analysis involves deconvolution of frequency of oscillations arising from constructive interference of the outgoing and scattered waves of photoelectrons. If the edge jump is not high enough, upon normalization and conversion into frequency domain, it becomes difficult to distinguish actual oscillations from mere noise. This is also partly evident from the attenuating waves (as noise) obtained towards the high energy regions in the scan of Figure 57.

Some of the challenges encountered during the design of this electrochemical half-cell are as follows:

1. The edge jump obtained was not sufficiently high due to 2 reasons:

   There is most likely an inhomogeneous distribution of the transition metal across the bulk of the nanostructures. This is expected, because although the nanostructures themselves are highly ordered, the transition metal impregnated on the support is not. Hence when the nanostructures form over these metal particles, the transition metal is heterogeneously distributed within the structures. As a result, with low loadings of the metal, it is likely that there is not sufficient concentration of the metal coming in the path of the X-ray beam, to give rise to a sufficient edge jump.

   This issue is further aggravated due to the presence of a liquid electrolyte which could be further diffusing the X-ray beam.

2. Since this is a stationery electrode system, there is a strong possibility of concentration gradient of the dissolved oxygen to be significantly high between the bulk of the electrolyte and surface of the catalyst. One way to counter this problem is to use a
diffuser tube that would bubble oxygen across the thin electrolyte layer covering the catalyst surface. But that could potentially give rise to a three-phase situation in the path of the X-ray beam, wherein there exist gas bubbles in the liquid electrolyte that is in contact with the catalyst surface. If this triple phase comes in the path of the X-ray beam, it will significantly affect the absorption phenomenon.

More recently, Gewirth and researchers reported the use of a new XAS cell which was not restricted by Oxygen diffusion limitations on the electrode surface[187]. They reported differences in the metal clusters dependent on both the potential and current. Their cell which uses a thin poly (dimethylsiloxane) membrane for a window material due to its high permeability to oxygen, could be modified for use of characterizing NPMCs in the future.

8.3.2 Operando Fuel Cell

An operando fuel cell system was also constructed, complete with a modified fixture, along with homemade humidifier units and a mobile gas flow system. The entire unit was designed to enable easy assembly and dismantling during transportation to Sector 10 of Argonne for XAS experiments. The schematic of the modified fuel cell fixture is shown in Figure 58.
Figure 58. Schematic of the operando fuel cell fixture used at Sector 10-ID B of Advanced Photon Source.

The modification of the fuel cell fixture involved cutting out the bipolar plates as well as thinning of the graphite block, to enable the passage of X-rays through the fixture. Initially, the plates were thinned according to Figure 58 shown above. But once the fixture was carried to APS for setting up at the beamline, it was observed that a thin slit is not sufficient for the X-ray beams to pass through with sufficient intensity, or to give a good edge jump. As a result, the fixture was modified further once taken to APS.
8.3.2a Platinum

In order to obtain a proof of concept, experiments were designed to collect XAS spectra for both platinum as well as NPMC catalysts. Spectra were collected at room temperature with a fresh Membrane Electrode Assembly (MEA) of the Pt-L₃ edge with platinum on carbon catalyst. The fuel cell fixture was the heated to the fuel cell operating temperature of 80°C, with humidified H₂ and O₂ flowing over the catalyst, and spectra was collected at OCV. Spectra was then collected using an activated MEA while holding them at different potentials: 800mV and 700mV respectively. An activated MEA is one which has undergone several polarization scans until a steady-state polarization scan is obtained.

Over the entire range of X-ray energy, it is harder to see subtle differences in spectra. Hence the data was truncated to show only the spectra near the edge jump: X-ray Absorption Near Edge Spectra (XANES). The differences in the features near the edge jump arise from the valence electron interactions of the X-rays, and as a result, they provide information about the oxidation state of the absorbing atom. The XANES region of the above spectra is shown in the Figure 59 below.
It is evident that the spectra for the Pt cathode catalyst is very different from the platinum foil (Figure 59). Generally, most metallic samples do not exhibit white lines, i.e., there is not much difference in the intensity between the highest point in the peak, and the “tapering-off” line. This trend is also shown by the platinum foil spectra. The experimental spectra are different, in that they contain a wider white line, indicating a more oxidized state. This is expected for the platinum cathode catalyst under the flow of oxygen, at open circuit voltage (OCV). There is not any significant difference observed between the spectra obtained at OCV, 800mV and 700 mV.
This is possible due to the following reason: Since X-ray Absorption Spectroscopy is a bulk technique; it detects the atoms that exist in the bulk of the catalyst. However, catalytic reactions are surface reactions. Hence any change in the catalyst under reaction conditions is most likely to occur on the surface. The only way to ensure that most bulk particles are participating in the catalytic reaction, is to make them small enough (1-5nm) so that there is a large fraction of these particles on the surface. This is also seen in a number of publications previously[187, 188].

For commercial platinum catalyst, like the one used in the above reaction, particle sizes are usually in the order of >50nm. With larger particle sizes it is nearly impossible for the bulk particles to participate in surface reactions. And since XAS detects these bulk particles that do not participate in the reaction, there is no significant change observed in the catalyst at different potentials.

8.3.2b Operando Fuel Cell experiments for CN₅ catalysts

Similar experiments as the ones conducted on Pt-Carbon catalysts were also performed on CN₅ (washed) catalysts (Figure 60). However, due to limited availability of hours at the beamline, accelerated studies were performed to obtain the maximum possible differences in the Fe-K edge of the catalyst used, under ORR conditions with the application of potential. The first scan was obtained at OCV and then at 500mV. This was followed by fast scanning under O₂ flow from OCV to 0V, and back to OCV for 100 cycles, and a third XAS spectra was collected. The spectra obtained are shown in Figure 60.
Figure 60. Normalized Absorption intensities of Fe-CNₓ-MgO (washed) catalyst.

There was not a sufficient edge jump to allow good deconvolution of spectra. However, it can be seen from the comparison in Figure 60 that at OCV, iron appears to be more oxidized than at 500mV, or after 100 cycles. It is a challenge to obtain reasonable spectra for NPMC catalysts, as generally metal concentrations are low, and the metal is not very well dispersed throughout the catalyst.

Significant catalyst design is required to obtain reasonable spectra under ORR conditions both in a half cell and fuel cell. The particle size of the metallic particles should be modulated to make them sufficiently small for the bulk particles to participate in the surface reaction. At the same time, the concentration of the metal would need to be
increased sufficiently to obtain a good edge jump under the X-ray beam. The results reported here are not optimal, but should serve as a good measure or guidelines for improving the cell and catalyst for these operando experiments in the future.
CHAPTER 9. Conclusions, Future Work and Recommendations

9.1 Conclusions

CN$_x$ was grown over substrates cobalt/Vulcan carbon and cobalt/magnesia, and changes oxidation state of the transition metal were monitored using in-situ and ex-situ characterization techniques. Cobalt on Vulcan carbon was seen to reduce in the inert atmosphere even before acetonitrile pyrolysis, whereas cobalt on the magnesia support showed a gradual reduction from Co$^{2+}$ to Co$^0$. XPS data showed the coordination environment of Co to change from that of an acetate to a mixture of sub-oxides during the pyrolysis. Regardless of the different stages that the cobalt phase went through during the pyrolysis process depending on the support used, once the final yield of CN$_x$ materials were washed with acid, the transition metal left behind was primarily in a metallic phase, as shown by XAFS, XRD, and XPS data. There were differences in activity observed between CN$_x$ grown on Vulcan Carbon and magnesia, but they were attributed to the higher pyridinic nitrogen content of CN$_x$ grown on magnesia, and a more ordered structure.
In another study, several differences between FeNC and CN$_x$ materials for ORR were discussed. CN$_x$ was less active than FeNC, albeit more stable. CN$_x$ underwent slower degradation in fuel cell stability tests and in ADTs, and attained stability faster than Fe-N-C catalysts. Effect of acid washing was strikingly different both the types of catalysts. CN$_x$ gained significant ORR activity after acid washing, and just the reverse was seen in the case of FeNC. Acid-washed FeNC demonstrated a lower initial activity than unwashed catalyst, but after the 100 hour stability test, there was no difference in activity between the former and latter. This indicated that the acid-washed Fe-N-C catalysts possess a better retention of activity. The causes for loss of activity are somewhat speculative, but a cumulative effect of iron leaching and either the protonation of pyridinic groups or their anion binding may be responsible for losses seen in FeNC catalysts, while iron leaching does not seem to affect ORR activity in CNx negatively.

Whether its pyridinic-N groups undergo transformation after the stability test is still unknown, but considering that both the catalysts showed different stability behavior, it is likely that their degradation mechanism is quite different. With the results discussed, it was established that CN$_x$ and FeNC materials are indeed two different classes of NPMC catalysts, with different activities and stability towards ORR in acidic media, and evidently different active sites. While iron certainly plays an active role in catalyzing ORR for FeNC, its presence is CN$_x$ does not manifest itself with higher ORR activity. This study provided some significant insights on the ambiguity of the role of the transition metal the active sites of these two materials.
Different stages of preparation of FeNC catalysts were also studied to gain more insight into the effect of pyridinic-N and transition metal incorporation. FeNC catalysts prior to the NH3 treatment, Argon treatment as well as without transition metal incorporation were studied. It was seen that the presence of pyridinic-N functional groups after a heat-treatment imparted higher activity to the catalyst than the presence of transition metal without a heat-treatment. However, it was seen that only the presence of pyridinic functional groups was not sufficient to make very active ORR catalysts, the transition metal was required in addition, in order to achieve high activity. This re-affirms the presence of a metal-Nₓ coordination catalyzing ORR.

The H₂S heat treatments were employed on two FeNC catalysts: FeNC-Ar and FeNC-Ar-NH₃, in two steps: (1) after the terminal heat-treatment (2) prior to any high temperature treatment. The effect of H₂S, or for that matter, any treatment gas- Ar or H₂ (to mimic the reducing environment of H₂S) was seen to be very different for FeNC-Ar versus FeNC-Ar-NH₃ catalysts. H₂S caused significant deactivation for ORR, when used as a terminal treatment after Ar-NH₃ for FeNC; an effect not observed for H₂ or Ar treatments when used in lieu of H₂S. Clearly sulfur binding to or replacing the active sites was the effect of this loss in activity, which was not brought about by a mere inert heat treatment or a reducing heat treatment for the same duration of time. FeNC-Ar-NH₃-H₂S also showed a lower incorporation of pyridinic N, than FeNC-Ar-NH₃, which could also explain the detrimental effect on ORR activity. However, this activity loss is reversible, because if this catalyst is re-exposed to NH₃, it regains its ORR activity, leading us to believe that the sulfur incorporation was possibly an adsorption and site blockage effect.
However, when the H$_2$S treatment was employed \textit{before} Ar-NH$_3$ treatments for this catalyst, it lowered the catalyst’s ORR activity, and the effect on its activity is the same as what is observed for H$_2$ or Ar intermediate treatments at 350°C.

In the case of FeNC-Ar which was heat treated in H$_2$S, H$_2$ or Ar at 350°C as a terminal heat treatment did not show any significant decrease in activity for any of these catalysts. This was in clear contrast with FeNC-$H_2$S-Ar, which showed a marked decrease in activity due to the H$_2$S treatment, as this effect was not seen for FeNC-$H_2$-Ar or FeNC-$Ar$-Ar catalysts. Although some of the sulfur was desorbed after the Ar treatment, as seen by the TPD, TPO experiments, this intermediate heat treatment impeded the ability of active site formation, as evidenced by the lack of surface nitrogen species in XPS. This brings us to the conclusion that H$_2$S has different effects on the activity of these catalysts, bringing to light that the actual ORR mechanism or active sites may be different between the two materials.

9.2 \textbf{Future Work and Recommendations}

Nitrogen-doped carbon materials are progressively being explored as alternative catalysts to platinum in alkaline fuel cells, as they have exhibited performance superior to platinum in alkaline media[162]. The advantages of developing these materials for ORR in alkaline media, stems from the possibility of their use as air cathodes in metal-air batteries (MABs)[189]. Metal-air batteries (MABs), specifically Zinc-air batteries (ZABs) are gaining importance as energy conversion devices due to their high specific energy, environmental friendliness and lower operation risks[79].
N doping of carbon appears to accumulate a high positive charge density on a neighboring carbon atom which serves to weaken the O-O bond, resulting in the 4 electron transfer ORR process[190]. In addition to redistribution of charge density induced due to heteroatom doping, electron spin density also is an important factor influencing ORR on metal-free carbon materials, which strongly affects the formation of intermediate molecules in ORR such as OOH, or O$_2$ adsorption, O-O bond breakage and water formation. As a result, active research has been devoted to the use of N-doped carbons for ORR in alkaline media.

We have initiated work with CN$_x$ and FeNC catalysts in alkaline media to evaluate their suitability for alkaline fuel cells or zinc-air batteries. In preliminary results, it was seen that both the catalysts exhibited superior performance to ORR in 0.5M KOH, comparable to Platinum/carbon catalysts. So far, the tests have been performed in a half-cell cell. It is of interest to see how the catalyst would perform when used either in an alkaline fuel cell or assembled in a zinc-air battery. There are a number of design challenges to be overcome to transform the current PEM fuel cell set-up into an alkaline fuel cell, that would need to be considered.

At the same time, we have recently begun exploring preparation of carbon materials for use as ORR catalysts using alternative carbon sources, such CO and H$_2$, or a mixture of coal gas by the chemical vapor deposition (CVD) technique with a transition metal supported or unsupported catalyst. In a previous report, unsupported Fe:Cu was used for CVD with a 4:1 ratio of CO:H$_2$.[96] The carbon nanostructures obtained had significant edge plane exposure, and were used to evaluate the effect of edge plane
exposure incorporation on ORR. In the future, different ratios of Fe, Cu and Ni will be used to obtain carbon nanostructures with different morphologies from coal gas pyrolysis.

In addition, there is tremendous scope for catalyst characterization using operando EXAFS, as described in Chapter 8. Raman spectroscopy using an in-situ electrochemical cell would also give useful insights into the nature of surface functional groups. Since much attention is being given to study the changes in catalysts under actual reaction conditions, a deeper understanding of these materials will be gained using these in-situ experimental techniques.
References