Electrocatalysis of Oxygen Reduction in Acidic Media with Non-platinum Group Metal Catalysts and a Study of Anion Poisoning

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Dissertation directed by

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Professor of Chemistry and Chemical Biology
Dedication

I would like to dedicate my dissertation work to my father, for patiently allowing me to follow my own path and never giving up on me.
Acknowledgements

First and foremost, I would like to thank my parents Graydon and Sandra Strickland for their generous love and support. I have tested their patience and faith, but they have always been my strongest advocates. I thank my father for showing me how to work hard and I thank my mother for showing me how to push myself beyond my limits.

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Abstract of Dissertation

Concerns of climate change and depleting fossil fuel resources have encouraged researchers to develop a replacement for the internal combustion engine in automotive transportation. The Hydrogen/air polymer electrolyte fuel cell (PEMFC) is a promising technology, but it suffers from several technical challenges. One of the most critical of these challenges is the high production cost of the fuel cell stack. A significant portion of the cost of the system can be attributed to the use of platinum as the catalyst material in both the anode and cathode. The slow kinetics of the oxygen reduction reaction (ORR) at the cathode requires more platinum than the more facile hydrogen oxidation at the anode, and therefore finding a non-platinum group metal (non-PGM) catalyst with high ORR activity would have the greatest payoff. Traditional platinum based electrocatalyst also suffer poisoning effects from various anions that further inhibit ORR. Anion adsorption is structure dependent and it has been shown that some Pt-alloys exhibit a heightened tolerance to poisoning. Additionally, fuel cell lifetime has been shown to be limited by factors such as Pt-particle dissolution and particle agglomeration.

Significant performance advancements have been made with non-PGM catalysts in the last several years, but the structure of the active site and the resulting ORR mechanism are still heavily debated. The current state of the art non-PGM catalysts are made by mixing and heat-treating a metal and nitrogen precursors on a carbon support. The heat treatment step has led to improvement of the durability and performance, but the composite nature of the derived catalyst material imposes significant challenges in its characterization.

This dissertation focuses on the synthesis and characterization of two novel types of non-PGM cathode electrocatalysts for use in acidic media. Chapter 1 introduces the electrochemical...
and spectroscopic methods that are used in Chapter 2-5 to investigate the ORR activity and stability of the electrocatalysts. A Co-based non-PGM is introduced in Chapter 2, and the rotating ring disk electrode (RRDE) technique was used to determine the reactivity and selectivity of the material towards the individual steps of ORR. Synchrotron based X-ray absorption spectroscopy (XAS) analysis of the electronic and structural properties of the cobalt after heat treatment. Chapter 3 introduces a Fe-based non-PGM that is very active for ORR in alkaline and acidic media and lacks the Fe-Nₓ coordination that has been heavily debated as the active site of non-PGMs. The combination of ex situ and in situ characterization techniques reveal the Fe is present as Fe/FeₓC particles subsurface to a carbon overlayer. The lack of Fe-Nₓ coordination and isolation of the Fe-particles allows us to attribute the ORR activity to the nitrogen-doped carbon. Chapter 4-5 further probes the Fe-based non-PGM introduced in Chapter 3. The traditional Pt-based catalysts are poisoned by the phosphate anion and Chapter 4 investigates the effect of anion poisoning on the Fe-based catalyst. Electrochemical measurements combined with a subtractive technique, ‘Δµ’, provided insight into the site specific adsorption and the electrocatalytic pathways. Durability of non-PGMs is a significant issue so fuel cell durability of the most active material was also investigated in Chapter 5 using the above mentioned techniques. Correlation of catalyst degradation with electrochemical oxidation of the carbon is obtained. In situ XAS revealed that the Fe is stable during normal fuel cell operating conditions, eliminating concerns of any Fenton type process related to onset of peroxide induced free radical formation. Chapter 6 summarizes the findings and future directions.
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<tr>
<td>α</td>
<td>Charge transfer coefficient</td>
</tr>
<tr>
<td>δ(k)</td>
<td>Central atom phase shift</td>
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<tr>
<td>ΔE₀</td>
<td>Absorption edge energy shift</td>
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<tr>
<td>ΔG</td>
<td>Gibbs free energy</td>
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<tr>
<td>ΔG₀</td>
<td>Standard Gibbs energy</td>
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<tr>
<td>Δμ</td>
<td>XANES difference, delta mu</td>
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<td>λ(k)</td>
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<td>μ</td>
<td>Absorption coefficient</td>
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<tr>
<td>ν</td>
<td>Kinematic viscosity or scan rate</td>
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<td>η</td>
<td>Overpotential</td>
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<tr>
<td>θ</td>
<td>Angle</td>
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<tr>
<td>σ²</td>
<td>Mean-square radial disorder</td>
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<tr>
<td>χ(k)</td>
<td>EXAFS equation</td>
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<tr>
<td>ω</td>
<td>Rotation rate</td>
</tr>
<tr>
<td>Å</td>
<td>1 × 10⁻¹⁰ meters</td>
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<tr>
<td>AFC</td>
<td>Alkaline fuel cells</td>
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<tr>
<td>BET</td>
<td>Brunauer-emmet teller</td>
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<tr>
<td>C</td>
<td>Coulomb</td>
</tr>
<tr>
<td>CN</td>
<td>Coordination number</td>
</tr>
<tr>
<td>CNT</td>
<td>Carbon nanotube</td>
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<tr>
<td>Co</td>
<td>Concentration of oxygen</td>
</tr>
<tr>
<td>Co₂bpbp</td>
<td>([\text{Co}^{\text{III}}_2(bpbp)-(\text{O}_2)]\text{2bdc}(\text{PF}_6))</td>
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<td>CV</td>
<td>Cyclic voltammetry</td>
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<td>D</td>
<td>Diffusion coefficient</td>
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<td>DFT</td>
<td>Density functional theory</td>
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<td>DOE</td>
<td>U.S. Department of Energy</td>
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<td>e⁻</td>
<td>Electron</td>
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<td>E</td>
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<td>Eᵣing</td>
<td>Potential of ring electrode</td>
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<td>FEG</td>
<td>Field emission gun</td>
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<tr>
<td>f(k)</td>
<td>Scattering amplitude function</td>
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<tr>
<td>F-Kₑ₆₀₀</td>
<td>Functionalized Ketjanblack EC-600JD</td>
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<td>FT</td>
<td>Fourier transform</td>
</tr>
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<td>FTIR</td>
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<td>Abbreviation</td>
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</tr>
<tr>
<td>GC</td>
<td>Glassy carbon</td>
</tr>
<tr>
<td>GDL</td>
<td>Gas diffusion layer</td>
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<tr>
<td>h</td>
<td>Planck’s constant</td>
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<td>HF</td>
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<td>Hbpbp</td>
<td>2,6-Bis[(bis(2-pyridylmethyl)amino)methyl]-4-tert-butylphenol</td>
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<td>Hydrogen nuclear magnetic resonance</td>
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<td>HFR</td>
<td>High-frequency resistance</td>
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<td>HR-TEM</td>
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<td>H_upd</td>
<td>Hydrogen underpotential deposition</td>
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<tr>
<td>i</td>
<td>Current density</td>
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<tr>
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<td>Intensity of incident x-ray beam</td>
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<td>Diffusion limiting current</td>
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<td>Isomer shift</td>
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<td>[O]/[R]</td>
<td>Activities ratio</td>
</tr>
<tr>
<td>ORR</td>
<td>Oxygen reduction reaction</td>
</tr>
<tr>
<td>PAFC</td>
<td>Phosphoric acid fuel cell</td>
</tr>
<tr>
<td>PEMFC</td>
<td>Proton exchange membrane fuel cell</td>
</tr>
<tr>
<td>PBI</td>
<td>polybenzimidazole</td>
</tr>
<tr>
<td>PFSA</td>
<td>perfluorosulfonic acid</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>QS</td>
<td>Quadrupole splitting</td>
</tr>
<tr>
<td>R</td>
<td>Reduced reactant, distance of neighboring atom</td>
</tr>
<tr>
<td>$R$</td>
<td>Gas constant</td>
</tr>
<tr>
<td>RDE</td>
<td>Rotating disk electrode</td>
</tr>
<tr>
<td>RH</td>
<td>Relative humidity</td>
</tr>
<tr>
<td>RHE</td>
<td>Reversible hydrogen electrode</td>
</tr>
<tr>
<td>rpm</td>
<td>rotation per minute</td>
</tr>
<tr>
<td>RRDE</td>
<td>Rotating ring disk electrode</td>
</tr>
<tr>
<td>RT</td>
<td>Room-temperature</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>$t$</td>
<td>sample thickness</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric analysis</td>
</tr>
<tr>
<td>UV-Vis</td>
<td>Ultraviolet-visible</td>
</tr>
<tr>
<td>V</td>
<td>Volts</td>
</tr>
<tr>
<td>XANES</td>
<td>X-ray absorption near edge structure</td>
</tr>
<tr>
<td>XAS</td>
<td>X-ray absorption spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>$Z$</td>
<td>Atomic number</td>
</tr>
</tbody>
</table>
Chapter 1

Introduction to Fuel Cells and Non-PGM Electrocatalysts

1.1 Need for Renewable Energy

Development of our nation has relied heavily on the use of fossil fuels, but our natural resource supply will not sustain the future demands. In addition to the dwindling reserve of this finite resource, we also have to face the environmental repercussions due to fossil fuel emissions. Burning of fossil fuels releases carbon dioxide (CO$_2$) into the atmosphere and increased CO$_2$ levels have been recognized as a factor that has caused climate change, such as rising temperatures. Even those who don’t believe the global warming theory cannot argue that fossil fuels such as natural gas, petroleum, coal etc. are a finite resource that is decreasing while the human population and industrial nation’s needs are increasing. The U.S. Department of Energy (DOE) has recognized the need to create an economy that can be sustained with renewable and clean energy technologies and research in this area has grown. Electrochemical energy conversion devices, such as fuel cell and batteries, have the potential to be integrated into markets as diverse as transportation to mobile devices to large scale energy storage. Batteries have already become heavily integrated into the market, but are already functioning at their maximum potential. However, fuel cells have the potential to supply more power and can theoretically run uninterrupted with no need to recharge. Therefore this chapter will introduce the fundamental principles behind the fuel cell technology and the techniques used to study them.

1.2 Electrochemical Energy Conversion

Electrochemistry is a branch of chemistry that studies chemical reactions that take place at an electrode-electrolyte interface. Electrochemistry is a vast field that deals with a variety of devices and technologies, but this thesis will focus primarily on fuel cell technologies in which the
chemical energy of a fuel is converted into electrical energy that powers an application. Fuel cells operate much like an internal combustion engine, in that they are not consumed as they take the chemical energy stored in a fuel and convert it into electrical and mechanical energy. In theory, as long as the fuel is provided the fuel cell will continuously produce electricity, which is one of the main advantages of a fuel cell over a battery.

There are five major types of fuel cells and they all function on the same principles but are classified by the electrolyte, which will also determine the operating temperature. Currently the most studied device is the Proton Exchange Membrane fuel cell (PEMFC) that operates around 80 °C. Alkaline fuel cells (AFC) also operate at lower temperatures, below 100 °C, however the performance still lags behind PEM cells due to challenges with the membrane electrolyte. Phosphoric acid fuel cells (PAFC) operate at mid-level temperature, 150-200 °C, and are the only fuel cell technology that has been successfully commercialized. PAFCs are used for stationary power and the higher operating temperature allows for utilization of the heat produced, which increase the overall efficiency of the technology. Molten Carbonate and Solid Oxide fuel cells operate at the highest temperatures, 600-1,000 °C, and are predominantly used for stationary power. The main focus of this thesis will be on the PEMFC technology with a small section on the PAFC technology.

1.2.1 Proton Exchange Membrane Fuel Cells (PEMFC)

The simple design of the PEMFC is illustrated in Figure 1.1. In a single cell the electrons are conducted through two porous electrodes (anode and cathode) that are separated by the solid polymer membrane (the electrolyte) that conducts the ions. Reactant gases are humidified and fed into the cell; fuel to the anode and oxidant to the cathode. The fuel (hydrogen) is oxidized at the anode to generate protons and electrons following equation 1.1.
The protons then migrate, due to the electrical potential gradient, through the membrane to the cathode where they are recombined with the electrons that flow through an external circuit. The oxidant (atmospheric oxygen) is fed to the cathode and combines with the electrons and protons to produce water, following equation 1.2.

Anode: \[ \text{H}_2 \leftrightarrow 2\text{H}^+ + 2e^- \quad \text{E}^\circ=0.00 \text{ V vs SHE} \quad (1.1) \]

Cathode: \[ \frac{1}{2}\text{O}_2 + 2\text{H}^+ + 2e^- \leftrightarrow \text{H}_2\text{O} \quad \text{E}^\circ=1.23 \text{ V vs SHE} \quad (1.2) \]

Combination of the two electrochemical half reactions produces the overall cell reaction (\(E_{\text{Cell}} = E_{\text{Cathode}} - E_{\text{Anode}}\)) in which the combustion of hydrogen and oxygen produce water, heat and electricity.

Overall: \[ \text{H}_2 + \frac{1}{2}\text{O}_2 \leftrightarrow \text{H}_2\text{O} \quad \text{E}_{\text{Cell}}=1.23 \text{ V} \quad (1.3) \]
Due to the involvement of protons in the overall reaction, PEM fuel cells are operated under acidic conditions. The electrolyte, which acts as a separator of the anode and cathode compartments, is an important component of the fuel cell in that it transports the protons (H\(^+\)). Invention of a perfluorosulfonic acid (PFSA) proton conducting membrane (Nafion®) in the late 1960s revolutionized PEM fuel cell technology, surpassing all other fuel cell technologies by increasing the power density and extending the lifetime. The chemical structure of Nafion® (Figure 1.2) involves a tetrafluoroethylene (Teflon) backbone that incorporates perfluorovinyl ether groups terminated with sulfonate groups in which the protons on the sulfonic acid hop from acid site to acid site.

![Figure 1.2: Perfluorinated Sulfonic Acid Proton Exchange Membrane (Nafion®). Chemical structure of perfluorinated sulfonic acid proton exchange membrane (Nafion®).](image)

1.2.2 Phosphoric Acid Fuel Cells (PAFC)

The PAFC technology was developed in the mid-1960s and was the first fuel cell technology to be commercialized successfully. PAFCs are used for stationary distributive power plants and on-site cogeneration energy systems. The PAFC design is very similar to the PEMFC design in Figure 1.1, but the primary difference is the electrolyte is liquid phosphoric acid (H\(_3\)PO\(_4\)).
addition to similar design, the PAFC also oxidizes hydrogen at the anode and reduces oxygen at
the cathode resulting in the same overall cell reaction as Equation 1.3.

In order to achieve higher cell performance the cells operate at 150-200 °C, therefore the acid
electrolyte has to be highly concentrated (85-100% H₃PO₄). The higher operating temperatures
allow the expelled water to be used for heat generation as well. Combining heat and power
generation allows these fuel cells to operate at 80 to 85% efficiency. PAFC systems generate 40
kW up to 11 MW, but pressurization is needed to achieve the higher performance.

PAFC technology has several disadvantages when compared with PEM.
1.) Phosphoric acid electrolyte is highly corrosive and requires the use of more expensive
cell components.
2.) Electrolyte anions adsorb to the electrocatalyst and increase overpotential.
3.) The phosphoric acid electrolyte has lower ionic conductivity, especially at lower
temperatures.
4.) Cell stacks have a maximum lifetime of approximately 40,000 hours before performance
loss.
5.) Lower power density of the cell.

1.3 Electro catalysis of the Oxygen Reduction Reaction

The rate of the electrochemical reactions described above will dictate the current output
of the fuel cell; therefore electrocatalysts are used to increase the rate of the half-cell reactions.
The hydrogen oxidation reaction (HOR) is thermodynamically reversible¹ and suffers minimal
kinetic losses, but the oxygen reduction reaction (ORR) is irreversible and the slow kinetics are
responsible for the majority of fuel cell voltage loss². In aqueous alkaline and acidic media ORR


is a complex multi-electron process that precedes through two pathways with several reaction intermediates:

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Pathway</th>
<th>Reactions</th>
<th>Thermodynamic electrode potential at standard conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acidic Media</td>
<td>Direct 4 electron</td>
<td>O₂ + 4H⁺ + 4e⁻ → 2H₂O</td>
<td>E₀ = 1.229 V</td>
</tr>
<tr>
<td></td>
<td>Peroxide</td>
<td>O₂ + 2H⁺ + 2e⁻ → H₂O₂</td>
<td>E₀ = 0.67 V</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H₂O₂ + 2H⁺ + 2e⁻ → 2H₂O</td>
<td>E₀ = 1.77 V</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H₂O₂ → 2H₂O + O₂</td>
<td></td>
</tr>
<tr>
<td>Alkaline Media</td>
<td>Direct 4 electron</td>
<td>O₂ + 2H₂O + 4e⁻ → 4OH⁻</td>
<td>E₀ = 0.401 V</td>
</tr>
<tr>
<td></td>
<td>Peroxide</td>
<td>O₂ + H₂O + 2e⁻ → HO₂⁻ + OH⁻</td>
<td>E₀ = -0.065 V</td>
</tr>
<tr>
<td></td>
<td></td>
<td>HO₂⁻ + H₂O + 2e⁻ → 3OH⁻</td>
<td>E₀ = 0.867 V</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2HO₂⁻ → 2OH⁻ + O₂</td>
<td></td>
</tr>
</tbody>
</table>

Table 1.1: Oxygen Reduction Pathways. Oxygen Reduction in Acidic and Alkaline Media.

The reduction pathway preferred depends on the application, but for the scope of this dissertation the full 4e⁻ reduction to water is preferred. An overall 4 e⁻ reduction can be achieved by either the direct pathway or a series of the 2 reduction reactions of the peroxide pathway. Much of this dissertation will focus on electrocatalysis of ORR in acidic media, but alkaline media will be utilized to further understand the nature of the catalyst. The remainder of this chapter will offer a brief introduction into the fundamental principles and techniques that will be used throughout this thesis to study ORR electrocatalyst materials.

1.3.1 Electrochemistry Fundamentals
Electrochemistry is a branch of chemistry that studies heterogeneous chemical reactions occurring at the interface of an electronic conductor (electrode) and ionic conductor (electrolyte) that produce or are caused by electrical energy. Electrochemical reactions that involve the movement of electrons from one element to another are called oxidation-reduction (redox) reactions.

\[
O + ne^- \leftrightarrow R \tag{1.4}
\]

When electrons \((ne^-)\) are gained the oxidation state decreases and the species \((O)\) is oxidized. Conversely, when electrons are lost the oxidation state increases and the species \((R)\) is reduced. Equation (1.4) represents a half-reaction (reduction) and the potential of the half cell \((E)\) can be related to the concentration of the redox couple \((O/R)\) with the Nernst equation:

\[
E = E^{o'} + \left(\frac{RT}{nF}\right) \ln(C_{O^*}/C_{R^*}) \tag{1.5}
\]

where \(E^{o'}\) is the formal potential, \(R\) is the universal gas constant \((8.314 \text{ J/K mol})\), \(T\) is the Kelvin temperature, \(n\) is the number of moles of electrons transferred in the reaction, \(F\) is the Faraday constant \((96,485 \text{ C/mol})\) and \((C_{O^*}/C_{R^*})\) represents the ratio of the bulk concentrations of \(O\) and \(R\). The formal potential \((E^{o'})\) precludes the use of activity coefficients and can be related to the standard reduction potential with the following equation:

\[
E^{o'} = E^o + \left(\frac{RT}{nF}\right) \ln([O]/[R]) \tag{1.6}
\]

where \([O]/[R]\) denotes the ratio of activities of \(O\) and \(R\).

An electrochemical device is a cell that is able to produce an electric current from the combination of two half-cells. The half-cell where oxidation occurs is the anode and the half-cell where reduction takes place is the cathode. The difference in potential energy of the anode and cathode will determine the direction of electrons flow.
The difference in potential energy of the two electrodes, known as the cell potential ($E_{\text{cell}}$), is measured in volts (V) and it takes one volt to produce a charge of 1 coulomb (C) from 1 joule (J) of energy. The potential difference of the cell can be associated to the amount of work it can perform with Gibbs free energy ($\Delta G^o$) equation:

$$\Delta G^o = -nFE_{\text{cell}}$$

where a positive value of $E_{\text{cell}}$ gives a negative change in Gibbs free energy and signifies a spontaneous reaction that can be used to generate electricity. However, the experimentally observed reduction potential is often different than the thermodynamically determined reduction potential. The additional potential that is needed to drive the reaction is known as overpotential ($\eta$).

Several factors will govern the overall electrode reaction (1.4) when measuring current as a function of potential ($i$-$E$ curves):

1. Mass transfer (O transported from bulk solution to electrode surface)
2. Charge transfer between O and the electrode surface
3. Chemical reactions (homogeneous or heterogeneous) preceding or following electron transfer.
4. Surface reactions (adsorption, desorption, etc.).

In the absence of mass-transport limitations the relationship between current and applied potential is modeled by the fundamental relation known as the Butler-Volmer equation:

$$i = i_0 \left[ \exp(-\alpha f \eta) - \exp((1-\alpha)f \eta) \right]$$
where \( i \) is the current density, \( i_0 \) is the exchange current density, \( \alpha \) is the charge transfer coefficient, \( \eta \) is the overpotential and \( f = F/RT \). In the high overpotential region (\( \eta \gg 50 \text{ mV} \)) the second half of (1.9) can be neglected and is simplified to the Tafel equation:

\[
\eta = \left[ \frac{RT}{\alpha F} \ln(i_0) - \frac{RT}{\alpha F} \ln(i) \right]
\]  

(1.10)

A plot of \( \eta \) vs. \( \ln(i) \), known as a Tafel plot, allows extraction of important kinetic parameters, such as \( i_0 \), \( \alpha \) and the Tafel slope (-2.3RT/\( \alpha F \)) which are very useful for evaluating the performance of electrocatalysts for redox reactions.

Cyclic Voltammetry (CV) is the technique most commonly used for the initial characterization studies of an electrocatalyst in an electrolyte solution. A CV is collected by ramping the potential linearly versus time on a stationary electrode to a set potential and then reversing the direction to the original potential. A CV plot (Fig. 1.3) provides valuable information about the properties and characteristics of the electrochemical process, such as location of redox potentials of the electroactive species, as well as coupled chemical reactions or adsorption processes.
As an illustrative example, Figure 1.3 shows a typical CV of platinum supported on high surface area carbon black in acidic media that is saturated with either argon (inert) or oxygen (reactive) gases. Characteristics of the platinum surface can be studied when the electrolyte is saturated with an inert gas, such as hydrogen adsorption/desorption below 0.4 V and water oxidation above 0.7 V forming Pt-OH species. No charge transfer between the electrode and electrolyte is observed between 0.4 and 0.7 V and the detected current is from the capacitive charging of the electrolyte double layer. Once the electrolyte is purged with oxygen gas a new cathodic peak is introduced from the oxygen reduction reaction (ORR) on the Pt catalyst.

Figure 1.3: Cyclic Voltammetry of Pt/C. Cyclic Voltammetry of Pt/C electrocatalyst in 0.1 M HClO₄. Scan rate 20 mV/s.
1.3.2 Rotating Ring Disk Electrode Technique

The Rotating Ring Disk Electrode (RRDE) technique allows investigation into the kinetics of ORR$^3$. Shown in Figure 1.4 is a schematic of a RRDE electrode that employs two working electrodes; a disk composed of glassy carbon surrounded by a ring (usually gold or platinum). Rotation of the electrode allows the convective transport of the dissolved oxygen in the electrolyte solution to the electrode surface, thereby increasing the transport of oxygen and allowing one to obtain a current that is limited by mass transport.

![Figure 1.4: Rotating Ring Disk Electrode. Schematic of Rotating Ring Disk Electrode.](image)

Additionally, use of the ring electrode allows products that are produced at the disk to be detected as they are swept past the ring. An insulation layer between the disk and ring electrode
allow the potential of each to be controlled independently. An electrocatalyst that is deposited on the disk electrode will catalyze ORR and any peroxide intermediate that is formed during ORR at the disk will be detected at the ring electrode that is set at a suitable potential for oxidation of the peroxide species. A typical rotating disk electrode (RDE) profile is made up of three regions; (1) diffusion controlled region, (2) mixed diffusion-kinetic region and (3) the kinetic region. In the kinetic control region ORR is limited by the reaction kinetics and in the diffusion controlled region ORR is limited by the mass transport of dissolved O$_2$ to the electrode surface from the bulk electrolyte. The diffusion limiting current is described by the Levich equation:

$$i_{\text{lim}}=0.62nFD^{2/3} \nu^{-1/6}C_0^\omega^{1/2}$$

(1.11)

where $n$ is the number of moles of electrons transferred, $F$ is the Faraday constant, $D$ is the diffusion coefficient of O$_2$ in the electrolyte, $\nu$ is the kinematic viscosity, $C_0$ is the concentration of O$_2$ in the electrolyte and $\omega$ is the rotation rate (radian/s). Here, $i_{\text{lim}}$ is the current which can be generated when limited by the rate at which O$_2$ can be supplied to the electrode by convection created by the rotation of the electrode. The total current density ($i$) can be written as the sum of the reciprocals of the diffusion limited current ($i_{\text{lim}}$) and the kinetic current ($i_k$) as shown below:

$$1/i = 1/i_{\text{lim}} + 1/i_k$$

(1.12)

The kinetic current density can be obtained from the total current density using the following equation:

$$i_k = (i_{\text{lim}}/i) / (i_{\text{lim}} - i)$$

(1.13).
**Figure 1.5: RRDE Polarization Curves.** RRDE polarization curves collected at 20 mV/s in argon saturated 0.1 M NaClO$_4$ with 20 mM K$_3$(Fe(CN)$_6$ at room temperature. The RRDE was a 5.61 mm glassy carbon slug with a gold ring.
The ferrocyanide/ferricyanide half reaction is a simple single-electron reversible redox reaction that is commonly used to characterize the collection efficiency of an RRDE system (Fig. 1.5). The diffusion limiting current is designated as the plateau region that is obtained at high overpotentials, and the magnitude of the current increases with the rotation rate following Eq. 1.11. As the ferricyanide is reduced at the disk, the ferrocyanide generated is swept away from the disk to the ring electrode, which is held constant at an oxidizing potential. Only some of the ferrocyanide generated at the disk travels close enough to the ring to be oxidized back to ferricyanide. The ratio of the limiting anodic current of the ring to the limiting cathodic current of the disk is the collection efficiency.

1.3.3 Non-Platinum Group Metal (non-PGM) Electrocatalysts

The rate of the electrochemical reactions described above will dictate the current output of the fuel cell; therefore electrocatalysts are used to increase the rate of the half-cell reactions. Over a century of effort has been dedicated to identifying an effective electrocatalyst to reduce the significant overpotential for ORR in order to reach an acceptable performance output. The current state-of-the-art electrocatalysts for H₂/O₂ fuel cells that operate in the acidic environment are based on precious metals, most commonly platinum. However, the scarcity of platinum and the accompanying high price prohibit mass production of PEM fuel cells for transportation applications. The cost issue of platinum has encouraged researchers to explore transition-metal based electrocatalysts, non-PGMs. Non-PGMs can be generally classified into precursors with nitrogen-coordinated sites (macrocycles) and individual carbon, nitrogen and metal precursors (non-macrocyclic precursors, Fig. 1.6), both of which are subjected to a heat treatment to improve stability and activity.
Jasinski was the first to demonstrate that a metal-N₄ molecule could reduce oxygen in 1964 and by 1978 it was determined that heat treatment is essential to improve the stability and activity of non-PGMs in the acidic environment of the PEMFC. The active site of non-PGMs has been heavily debated with one side claiming a nitrogen-coordinated metal (Me-Nₓ) site and others claiming the metal is only needed to catalyze the carbon-based active site. It is widely accepted that a transition metal (Fe or Co) must be present during the synthesis to form the most active non-PGMs and this requirement has prevented the resolution of this debate.

1.4 X-ray Absorption Spectroscopy (XAS)

X-ray Absorption Spectroscopy (XAS) is an element specific core level spectroscopy that uses x-rays to excite the core level electrons of the element of interest into higher energy electron orbitals. Experiments are usually conducted at synchrotron radiation sources that produce high intensity tunable x-rays. XAS provides structural information of the atomic environment and is helpful for identifying chemical speciation of heterogeneous materials. This technique is widely used under ex situ conditions to determine the local geometry and/or electronic nature of the element of interest. XAS can be further broken down into x-ray absorption near edge structure (XANES) that provides information about the valence state and local geometry, and the extended
x-ray absorption fine structure (EXAFS) that provides information about the local molecular structure.

Our XAS experiments were performed at Brookhaven National Laboratory’s National Synchrotron Light Source, a particle accelerator built in 1978 that became operational in 1984. As the electrons orbit, changes in their angular momentum cause emission of photons as polychromatic “white light.” The white light then travels through various optical devices to obtain a single fixed wavelength at the beamline endstation, or hutch. A schematic of our in situ experiment is shown in Figure 1.7, where a specially designed spectro-electrochemical cell is used to study the electrode material of interest. The spectro-electrochemical cell is unique to our research and allows us to collect data on electrocatalyst materials under simulated fuel cell conditions as a function of applied potential and reactant gas. Three gas ionization detectors are used to measure the incident ($I_0$), transmission ($I_t$) and reference ($I_r$) x-ray intensities. The sample

![Image of synchrotron-based in situ XAS experiment.](image)

**Figure 1.7: Synchrotron-based In Situ XAS Experiment.** Schematic of synchrotron based in situ XAS experiment.
is placed between \( I_0 \) and \( I_t \) and a reference foil of the same element of interest is placed between \( I_t \) and \( I_r \).

A spectrum is collected from approximately 200 electron volts (eV) below the absorption edge and approximately 1000 eV above the edge. A typical XAS spectrum taken at the Fe K-edge absorption edge energy\( (E_0 = 7112 \text{ eV}) \) is shown in Figure 1.8, and can be divided into three regions, (1) pre-edge \( (E < E_0) \), (2) XANES \( (E = E_0 \text{ up to } 50 \text{ eV above the edge}) \) and (3) EXAFS \( (50 \text{ eV up to } 1000 \text{ eV above the edge}) \). The absorption of x-rays by a material is governed by the following equation:

\[
I_t = I_0 e^{-\mu t} \tag{1.14}
\]
where $I_t$ and $I_0$ are the intensities of the transmitted and incident x-rays, $\mu$ is the absorption coefficient and $t$ is the sample thickness. The absorption coefficient is dependent on the types of atoms and the density of the material. When the energy of the incident photons excites the core electrons into empty states near the Fermi level a sharp increase in the absorption coefficient is observed, known as the absorption edge. The electron that is ejected is known as a photoelectron and it carries the energy of the incident photon minus the binding energy. As the energy of the x-ray is increased above the absorption edge the excess energy propels the photoelectron outside the absorbing atom where it interacts with the surrounding atoms. The photoelectron wave is backscattered by the surrounding atoms and there will be constructive and destructive interference as the backscattered wave interacts with the photoelectron wave. The wave interferences create the oscillations in the EXAFS region that provide information about the nature and the distance of the surrounding atoms. The EXAFS spectrum can be described as the sum of the contribution of all scattering paths of the photoelectron by the EXAFS equation:

$$\chi(k) = \sum_j N_j f_j(k)e^{-2k^2\sigma_j^2} \sin[2kR_j + \delta_j(k)]$$  \hspace{1cm} (1.15)

where $f(k)$ and $\delta(k)$ are scattering properties of the neighboring atoms, $N$ is the number of neighboring atoms, $R$ is the distance to the neighboring atom, and $\sigma^2$ is the disorder in the neighboring atoms. By knowing the scattering amplitude $f(k)$ and phase shift $\delta(k)$ Eq. 1.15 allows us to determine $N$, $R$ and $\sigma^2$. The scattering factors are also sensitive to the atomic number $(Z)$ of the neighboring atom, which allows us to determine the atomic species.

Whereas the EXAFS region provides information about the structural properties of the absorber atom, the XANES region provides information about the electronic properties, such as the valence state and bonding symmetry. Subtle changes in the XANES occur when adsorbate
species form on the surface of the absorber atom. In order to accentuate these subtle changes, Ramaker et al \cite{ramaker2008, ramaker2009} developed the XANES difference ($\Delta \mu$) method in which the XANES spectrum of a clean surface is subtracted from the XANES spectrum with adsorbates. Using FEFF8 code \cite{feff8}, we can generate theoretical XANES spectra from models and compare the theoretical $\Delta \mu$ signatures to the experimental XANES collected \textit{in situ}. The $\Delta \mu$ method is extremely useful understanding the surface-adsorbate interactions by overcoming the bulk averaging nature of XAS.

1.5 Scope of Dissertation

This dissertation deals with the development of non-PGM electrocatalyst for ORR in acidic media. Chapter two focuses on the development of a cobalt-based non-PGM using a combination of catalyst synthesis, physicochemical and electrochemical characterization to understand the role of the cobalt moieties in the ORR mechanism of a PEMFC. Chapter three focuses on the characterization of an iron-based non-PGM electrocatalyst using the same techniques as Chapter two, but focuses on identifying the role of iron in the active site. Chapter four probes the effect of poisoning the Fe-based non-PGM electrocatalyst with electrolyte anions present in a PAFC. Finally, Chapter 5 explores the durability of the Fe-based non-PGM in a PEMFC and uses a combination of electrochemical measurements coupled with \textit{in situ} XAS to propose degradation mechanisms.
1.6 Chapter 1 References


Chapter 2

Cobalt Dinuclear Non-PGM Electrocatalyst for Oxygen Reduction Reaction

2.1 Introduction

Effective activation of molecular oxygen by the complete four-electron four-proton conversion to water is an essential aspect for improving renewable energy conversion technologies, such as fuel cells. The polymer electrolyte fuel cell (PEMFC) has received considerable attention as a possible replacement of the internal combustion engine. In the acidic medium of the PEMFC platinum-based electrocatalysts are very efficient for catalyzing the oxidation of hydrogen at the anode, but the kinetics of the oxygen reduction reaction (ORR) at the cathode are sluggish and inhibit the overall efficiency of the cell. To increase the kinetics of ORR, increased loadings of Pt are used and account for approximately 90% of the Pt content of the cell\(^1\). Pt is a precious metal of limited supply and the cost of the electrocatalyst material currently contributes significantly to the overall fuel cell cost\(^2\). In order to successfully commercialize the PEMFC technology it is essential to develop an alternative cathode material that is inexpensive but still able to maintain the current ORR activity that is produced by Pt.

Proteins are very efficient for catalyzing the reduction of oxygen to water with porphyrin-based active sites. Scientists have tried to mimic this model when developing non-platinum group metal (Non-PGM) electrocatalysts for ORR\(^3\). Jasinski\(^4\) was the first to report ORR catalytic activity using cobalt phthalocyanine, but these materials were only able to catalyze the \(2e^-\) reduction of oxygen to hydrogen peroxide. Collman and Anson\(^5\) believed that mononuclear complexes were incapable of delivering four electrons and developed a binucleating ligand that oriented two cobalt centers in a face-to-face coordination. They proposed a mechanism in which
each metal center would transfer 2 e\textsuperscript{-} and together the binuclear catalyst would carry out the full 4e\textsuperscript{-} reduction of oxygen. However, they found that the function of these binuclear catalysts were extremely sensitive to the geometry of the Co centers. Amide bridges of different linkages were used to prepare binuclear oxygen reduction catalysts with an interporphyrin distance between 4-7 Å, and the dimer linked at 4 Å was the most efficient at the full 4e\textsuperscript{-} reduction of oxygen. The following two decades focused on the structural aspects of these binuclear oxygen reduction catalysts. More recently, Nocera et al\textsuperscript{6} developed a material that allowed them to investigate the effect of the electronic environment and found that targeted proton delivery was essential for the 4e\textsuperscript{-} reduction pathway.

Despite the promising results initially obtained with Co-based non-PGMs, most of the recent progress of non-PGMs in acidic media has been made with Fe-based materials. Even though the activity of Fe-based non-PGMs has approached that of Pt-based materials, stability is still an issue and some work has shown that adding Co enhances the stability\textsuperscript{7}. Despite the growing literature on non-PGM electrocatalysts, very few publications have focused on Co-based electrocatalysts. Another benefit of Co-based catalysts is addressing the concern of the Fe ions participating in a Fenton type process that culminates in peroxide initiated free radical formation that would severely inhibit the lifetime of the device.

This work aims to develop a binuclear Co-catalyst by investigating the effect of heat treatment temperature and Co-coordination on ORR activity in the acidic media. Synthesis of the desired structure was confirmed with hydrogen nuclear magnetic resonance (\textsuperscript{1}H NMR) and X-ray diffraction (XRD). Thermogravimetric analysis (TGA) was used to observe the effect of high temperature on degradation of the material and based on these results a window of heat treatment temperatures was chosen. Structural changes were observed at each distinct heat treatment
temperature and changes to the Co-coordination were observed with X-ray absorption spectroscopy (XAS). ORR activity was tested using the rotating ring disk electrode technique that allowed simultaneous observation of ORR activity with the production of the undesired peroxide intermediate. The most active catalyst was then chosen for further studies that observed the effect of loading and pH to better understand the ORR mechanism.

2.2 Experimental Methods

2.2.1 Catalyst Synthesis

The synthesis of the cobalt dinuclear electrocatalyst was comprised of several steps: (1) organic synthesis of the 2,6-Bis[{bis(2-pyridylmethyl)amino]methyl}-4-tert-butylphenol (Hbpbp) ligand, (2) inorganic synthesis of {[Co^{III}[2(bpbp)-(O_2)]2bdc}(PF_6) (Co_2bpbp), (3) ball milling of Co_2bpbp with a functionalized carbon support and (4) heat treatment of the Co_2bpbp/Carbon mixture.

Hbpbp was synthesized according to a method previously reported^8. p-formaldehyde (1.55 g, 0.0517 moles (mol)) and 4-tert-Butylphenol (1.994 g, 0.0133 mol) were dissolved in ethanol (25 mL) at room temperature with stirring in flask A. In flask B a solution of N,N-bis(2-pyridylmethyl)amine (10 g, 0.0503 mol) was added to water (50 mL) at room temperature. Flask B was added to Flask A and stirred at reflux temperature (82 °C) for 3 days. The two-phase reaction mixture was cooled to room temperature and separated between water (100 mL) and dichloromethane (CH_2Cl_2; 200 mL) in a separatory funnel. The aqueous phase (yellow and opaque) separated from the organic phase (brown and transparent) that settled at the bottom of the funnel. The organic phase was removed and the aqueous phase was extracted with dichloromethane (3x50 mL). The combined organic phase was dried with anhydrous sodium
sulfate. Solvent was isolated with a vacuum filter and removed with a rotary evaporator to isolate a brown-oil. The brown-oil was chromatographed on a silica gel column using acetone as the eluent to afford the crude product after removing solvent with rotary evaporator (yellow solid; 5.91 g, 78% yield). Crude product was recrystallized with diethyl ether and petroleum ether (700 mL) to afford Hbpbp (white crystals; 3.93 g, 57% relative to the crude product). $^1$H NMR (250 MHz): $\delta$ 1.27 (s, 9 H), 3.82 (s, 4 H), 3.90 (s, 8 H), 7.08 (m, 1H), 7.19 (s, 2 H), 7.48-7.61 (m, 8 H), 8.52 (m, 4 H), 10.80 (s, 1H).

Co$_2$bpbp was synthesized according to previously reported method$^9$. The Hbpbp (102 mg, 0.18 mmol) was dissolved in acetone (25 mL) in beaker A. Cobalt(II) nitrate (103 mg, 0.32 mmol) was dissolved in water (5 mL) in beaker B. Beaker B was added to beaker A to form a red-brown solution. Sodium 1,4-benzenedicarboxylate (19 mg, 0.10 mmol) was dissolved in water (3 mL) then added to the reaction mixture to form a dark-brown solution. Ammonium hexafluorophosphate (59 mg, 0.36 mol) was dissolved in water (2 mL) and added to the reaction mixture. The reaction mixture was left on the benchtop to slowly evaporate in air at room temperature to yield Co$_2$bpbp (black crystals; 0.14 g, 65% yield) that were isolated by vacuum filtration.

The commercial carbon (Ketjanblack EC-600JD (K$_{600}$), Akzo Nobel) was purified and functionalized prior to catalyst synthesis. In order to remove any metallic impurities, K$_{600}$ was combined with 6 M hydrochloric acid and allowed to stir for 24 hours at room temperature. The acid washed K$_{600}$ was isolated by vacuum filtration and washed with copious amounts of water. Following a previously published method to functionalize the carbon support$^{10}$, the acid washed K$_{600}$ was combined with 70% nitric acid and stirred for 24 hours at reflux temperature (80 °C).
The functionalized K600 (F-K\textsubscript{600}) was isolated by vacuum filtration, washed with copious amounts of water and dried in a vacuum oven for 24 hours at 80 °C.

The catalyst precursor was generated by mixing Co\textsubscript{2}bpbp with F-K\textsubscript{600} in the mass ratio 1:1 and ball milling for 30 minutes (Co\textsubscript{2}bpbp/F-K\textsubscript{600}). The resulting powder was subjected to one heat treatment in argon at various temperatures (300-900 °C) with a 2 hour dwell time.

2.2.2 Rotating Ring Disk Electrode (RRDE) Measurements

Perchloric acid electrolyte (0.1 M) was prepared using double-distilled 70% perchloric acid (GFS Chemicals), sulfuric acid electrolyte (0.5 M) was prepared using double-distilled 98% sulfuric acid (GFS Chemicals) and potassium hydroxide electrolyte (0.1 M) was prepared using pellets (Alfa Aesar). Electrochemical measurements were carried out on glassy carbon (GC) disk (5.61 mm diameter, Pine Instruments) that was polished with 0.05-micron alumina paste (Buehler, Lake Bluff, IL) and then sonicated in distilled water and isopropyl alcohol. Catalysts inks were prepared by dispersing the catalyst in a volume of 1:1 Millipore water:isopropyl alcohol with 10 vol% of 5 wt% Nafion® as a binder. The ink solution was then sonicated approximately 60 minutes to get a uniform suspension. A small volume of the catalyst ink was deposited on the GC substrate to obtain a non-PGM loading of approximately 200-600 µg/cm\textsuperscript{2}. All electrochemical measurements were carried out at room temperature (20-25 °C) in a standard electrochemical cell (Chemglass) with an acid or base electrolyte using a rotating disk electrode (RDE) setup from Pine Instrument Company connected to an Autolab bipotentiostat (PGSTAT302N). Cyclic voltammetry was run on non-PGM catalysts in 0.1 M perchloric acid (HClO\textsubscript{4}), 0.5 M sulfuric acid (H\textsubscript{2}SO\textsubscript{4}) and 0.1M potassium hydroxide (KOH) bubbled with argon. ORR was investigated by the RDE technique after bubbling oxygen in the electrolyte.
solution followed with rotations at 100, 400, 900, 1600 and 2500 rpm. The ring electrode was
held at 1.3 V vs RHE in acidic electrolyte and 1.1 V vs RHE in alkaline electrolyte. Scans were
recorded at 20 mV/s and all potentials are referenced to a reversible hydrogen electrode (RHE)
scale made from the same solution as the electrolyte. The percentage of $\text{H}_2\text{O}_2$ was calculated by
\[
\%\text{H}_2\text{O}_2 = 200 \times \frac{(N \times I_{\text{ring}})}{(I_{\text{disk}} + (N \times I_{\text{ring}}))}
\]
(2.1)
where $N$ is the collection efficiency of the ring electrode, 37.5%, measured according to a
previously reported method$^{11}$.

2.2.3 Physicochemical Characterization

X-ray diffraction was performed on a Rigaku (model Ultima-IV) diffractometer with Cu
Kα radiation ($\lambda=1.5418$ Å) at 40 kV and 40 mA. The scan speed was 2-20 seconds and the step
size was 0.1°. Thermogravimetric analyses (TGA) were performed on TA Instruments SDT
Analyzer Q600 from 22-1100°C with a ramp rate of 5°C/min and dwelling for 5min at maximum
temperature. All studies were conducted under argon atmosphere, with a flow rate of
100mL/min. Scanning electron microscopy was performed on a Hitachi S-4900 FSEM
instrument with an accelerating voltage of 3-5 keV with samples mounted on a carbon adhesive
stub attached to an aluminum sample stage. Elemental composition was collected by Energy
Dispersive X-ray Analysis (EDAX) Genesis with Hitachi S-4900 FSEM at an accelerating
voltage of 15 keV.

2.2.4 X-ray Absorption Spectroscopy (XAS) Measurements

The XAS studies at the Co K-edge (7709 eV) were performed at X3B beamline of
National Synchrotron Light Source (NSLS, Brookhaven National Laboratory, NY). The
electrode inks for the EXAFS electrodes were composed of 1:1 (wt%) 18.2 MΩ purity deionized water (Millipore) and 2-propanol (HPLC-grade, Aldrich), a 5 wt% Nafion solution (Aldrich), and the catalyst powder. The composition was chosen to give a final electrode with a dry Nafion loading of 5 wt%. The ink was hand-painted onto a Zoltek® carbon cloth and dried for 15 minutes in a 65°C vacuum oven between coats. The final cobalt geometric loadings were chosen to give 0.05 edge heights at the Co K–edge. A specially designed spectro-electrochemical cell was utilized and has been described previously. The Co K-edge spectra were collected in fluorescence mode with a 32-element Ge solid state detector as a function of potential in the range 0.1 – 0.9 V vs. RHE. Data were collected in fluorescence mode with a Co reference foil positioned between I_2 and I_3 as a reference. The voltage cycling limits were 0.05 to 1.10 V vs. RHE. Data collection was performed at the chosen potentials held during anodic sweeps. A pseudo steady-state was established by holding the cell for approximately 5 minutes before collecting the spectra. The electrolyte, 0.1 M HClO_4, was saturated with either argon or oxygen. Athena and Artemis programs were used to process and fit the data. IFEFFIT suite was used to calibrate, align and normalize the scans. FEFF6 code was used to calculate scattering paths to model the χ(R) transforms.

2.3 Results and Discussions

2.3.1 Physicochemical Characterization
The dinucleating ligand Hbpbp was synthesized according to a previously published method\textsuperscript{8} and its structure was confirmed by $^1$H NMR (Fig. 2.1). The combination of Co(NO)$_3$ with Hbpbp in a mixture of acetone and water allowed the formation of a dinuclear unit with two Co$^{III}$ centers coordinated by two pyridyl and one amine nitrogen from the bpbp$^-$ ligand. Addition of sodium 1,4-benzenedicarboxylate (Na$_2$bdc) and ammonium hexafluorophosphate (NH$_4$PF$_6$) promoted the formation of a tetranuclear complex cation, where two of the dinuclear units were bridged by the coordination of the carboxylate O atoms from the bdc$^{2-}$ ligand with the Co$^{III}$ centers (Fig. 2.2, inset).
Figure 2.2: XRD Confirmation of Co₂(bpbp). Powder pattern of [Co₄(O₂)₂(bpbp)₂(BDC)](PF₆)₄ synthesized (a) compared to published pattern (b).
A metal-organic host material formed from the edge-to-face interactions between one of the pyridyl rings of the bpbp ligand of one cation with the bdc$^{2-}$ ligand on an adjacent cation, resulting in parallel chains that stack in zigzag layers alternating with counteranions (PF$_6^-$). A comparison of the powder XRD pattern of the material synthesized in our lab, [Co$_4$(O$_2$)$_2$(bpbp)$_2$(BDC)](PF$_6$)$_4$ (Co$_2$(bpbp)), with the published pattern (Fig. 2.2) confirmed formation of the metal organic host material.

![Figure 2.3: Thermogravimetric Analysis of Co$_2$(bpbp)](image)

Following synthesis of Co$_2$(bpbp), a high-temperature heat treatment was employed to create a viable catalyst by surmounting the inherently insulating nature of the material. Determining an optimum heat treatment temperature is an integral first step in developing a new non-PGM electrocatalyst for ORR. TGA was performed on Co$_2$(bpbp) under nitrogen flow from...
ambient temperature up to 1100 °C to mimic the conditions of the high-temperature heat treatment step. The TGA trace revealed an initial mass loss below 200 °C due to removal of guest species (water and oxygen). Around 300 °C a small mass loss is observed and corresponds with the melting point of the ammonium hexafluorophospahte salt. A steep drop around 400 °C accounts for most of the mass loss of the material and could signify decomposition of the metal organic host material. There is a final drop from 700-900 °C, resulting in an overall mass loss of ~45 wt%. Previous non-PGM reports have shown that the best heat treatment temperature to form active non-PGM electrocatalysts can range from 500-1000 °C, but it is dependent on the precursor material utilized. Based on the TGA results it was apparent that the significant transitions took place at three distinct temperatures (300, 400 and 900 °C), which led us to generate electrocatalysts at various temperatures in the range of 300-900 °C.
Co$_2$(bpbp) was mixed with a functionalized carbon black support (Co$_2$(bpbp)/F-K$_{600}$) and heat treated under an argon flow with a 2 hour dwell at the respective temperatures. Changes in elemental composition were monitored by EDAX as a function of heat treatment temperature (Table 2.1). Heat treatment at the lowest temperature, 300 °C, produced a 30% mass loss mostly due to evaporation of the adsorbed water and oxygen. Following the first heat treatment at 300 °C, fluorine was no longer detected, confirming the TGA results that the hexafluorophosphate anion decomposed around 300 °C. Increasing the heat treatment temperature to 400 °C produced very little changes in the elemental composition or mass loss. An additional increase of heat treatment temperature up to 600 °C induced degradation that accounted for 17% of the overall mass loss and oxygen was no longer detected. Combining these results with our TGA we believe

<table>
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<th>%O</th>
<th>%F</th>
<th>%P</th>
<th>% Co</th>
<th>% mass loss</th>
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<td>3</td>
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Table 2.1: Elemental Analysis of Co$_2$(bpbp). Quantification of elemental components of [Co$_4$(O$_2$)$_2$(bpbp)$_2$(BDC)](PF$_6$)$_4$ mixed with functionalized carbon black and as a function of heat treatment temperature. Measurements were taken with an accelerating voltage of 15 kEV on multiple on 5 different areas of sample and quantities are an average.
the tetranuclear cation decomposes above 400 °C and the resulting material is predominantly comprised of carbon, phosphorus and cobalt. Increasing the heat treatment temperature up to 800 °C and 900 °C produced very little changes in the elemental composition, but promoted further material degradation that accounted for 16% of the overall mass loss. Heat treatment up to 900 °C produced an overall mass loss of ~45%, but the Co was stable throughout the heat treatment of Co₂(bpbp)/F-K₆₀₀ as evidenced by the increase in the Co wt%.

Figure 2.4: XRD Monitoring Effect of Heat Treatment Temperature. Powder patterns comparison of Co₂(bpbp) mixed with functionalized carbon black, after heat treatment at specified temperature and diffraction pattern of cobalt phosphide standard.
XRD analysis was employed to monitor phase changes to the crystalline structure at the different heat treatment temperatures. The XRD pattern of \(\text{Co}_2(\text{bpbp})/\text{F-K}_600\) (Fig. 2.4) matches the pattern of \(\text{Co}_2(\text{bpbp})\) alone, indicating the ball milling with the functionalized carbon does not disturb the structure of the metal-organic host material. Following heat treatment at 300 °C, the powder pattern of the catalyst no longer shows any evidence of the original crystal structure and is instead characterized by diffraction lines of graphite. The higher heat treatment temperatures led to the formation of several new diffraction lines that indicate the formation of a new cobalt phase (cobalt phosphide-\(\text{Co}_2\text{P}\) \((\text{Pnma}(62))\). These results are supported by the EDAX analysis that shows phosphorus and cobalt are stable in the entire heat treatment temperature range investigated.

![Figure 2.5: XAS Monitoring Effect of Heat Treatment Temperature](image)

**Figure 2.5: XAS Monitoring Effect of Heat Treatment Temperature.** Fourier transform EXAFS and XANES of \(\text{Co}_2(\text{bpbp})\) mixed with functionalized carbon black and after heat treatment at specified temperature compared with reference Co foil.

XAS was used to further probe the local coordination of the cobalt before and after the various heat treatment temperatures. Fourier transform (FT) of the extended X-ray absorption fine structure spectra (EXAFS) of the Co K-edge is shown in Figure 2.5, left. The FT-EXAFS of \(\text{Co}_2(\text{bpbp})/\text{F-K}_600\) before heat treatment is characterized by a peak at \(~1.5\ \text{Å}\) due to Co-N/O
scattering. After heat treatment at 300 °C the Co-N/O peaks shifts to higher radial distances and continues to shift as the heat treatment temperature is increased. At 600 °C it appears the Co-N/O structure starts to degrade and evidence of a Co-Co structure appears. Heat treatment of Co$_2$(bpbp)/F-K$_{600}$ at 800 and 900 °C produces a peak at ~2.0 Å, as well as displaying long range order. The multi-component nature of heat treated of Co$_2$(bpbp)/F-K$_{600}$ makes the EXAFS fitting impossible, but a qualitative comparison with the FT-EXAFS of the Co foil indicate the peak at ~2.0 Å is due to Co-Co scattering. The FT-EXAFS results indicate that Co-N/O structure is decomposed and most of the cobalt ions are converted to metallic cobalt at the higher heat treatment temperatures. X-ray absorption near-edge structure (XANES) spectra (Fig. 2.5 b) also confirm the transformation of the Co-N/O structure to a Co-Co/O structure as evidenced by the XANES of Co$_2$(bpbp)/F-K$_{600}$ heat treated at 800 and 900 °C is very similar to the XANES of the Co foil.

2.3.2 Electrochemical Performance
The electrocatalytic activity for the oxygen reduction reaction (ORR) of Co$_2$(bpbp)/F-K$_{600}$ catalyst was studied using the RRDE technique. Reduction of oxygen can proceed through either a 4e$^-$ or 2e$^-$ path, and a second working electrode allowed us to monitor the production of

**Figure 2.6: RRDE Catalyst Heat Treatment Study.** Disk- and string-currents measured during ORR on Co$_2$(bpbp)/F-K$_{600}$ catalyst at various heat treatment temperatures in O$_2$ saturated 0.5 M H$_2$SO$_4$ electrolyte at 20 mV/s with rotation rate of 900 rpm at room temperature. $E_{\text{ring}}=1.3$ V vs RHE.
peroxide from the undesirable $2e^-$ path. The RDE polarization curves in oxygen saturated acidic electrolyte (0.5 M H$_2$SO$_4$) and corresponding ring response of the Co$_2$(bpbp)/F-K$_{600}$ catalyst is shown in Figure 2.7. Without heat treatment Co$_2$(bpbp) shows no activity for ORR over what is achieved with the functionalized carbon black support. Following heat treatment Co$_2$(bpbp) shows activity for ORR, but for all the tested electrocatalyst no clear diffusion limited current was achieved. The diffusion limiting current ($i_{\text{lim}}$) is defined by the Levich equation:

$$i_{\text{lim}}=0.62nFD^{2/3}v^{-1/6}C_0$$

(2.2)

where $n$ is the number of moles of electrons transferred, $F$ is the Faraday constant, $D$ is the diffusion coefficient of O$_2$, $v$ is the kinematic viscosity and $Co$ is the concentration of O$_2$ in the electrolyte. Lack of a clear diffusion limiting current indicates that the reaction is under kinetic control possibly due to poor distribution of active sites$^{16}$. As the heat treatment temperature is increased from 300 to 600 °C the electrocatalyst performance is correspondingly increased as evidenced by the steady improvement of the half-wave potential ($E_{\text{1/2}}$) (0.49 vs 0.64 V). For the catalyst generated in this temperature range (300 to 600 °C), the onset of peroxide oxidation detected at the ring electrode coincides with the onset of ORR at the disk electrode indicating that peroxide intermediate that is formed is not stabilized by Co$_2$(bpbp)/F-K$_{600}$ . When the heat treatment temperature is further increased to 800 °C the electrocatalyst performance degrades slightly and the $E_{\text{1/2}}$ shifts cathodically (0.63 vs 0.64 V). After heat treatment at 900 °C the electrocatalyst performance degrades more severely, which interestingly coincides with the material degradation witnessed with the TGA analysis. The ORR activity of F-K$_{600}$ heat treated at 800 °C indicates that the ORR activity of Co$_2$(bpbp)/F-K$_{600}$ stems from the presence of Co.
Based on these original performance results presented above, Co$_2$(bpbp)/F-K$_{600}$-800 was selected for further study. The porosity and thickness of an electrode will determine the current-

**Figure 2.7: RRDE Catalyst Loading Study.** Disk- and ring-currents measured during oxygen reduction reaction (ORR) on Co$_2$(bpbp)/F-K$_{600}$-800 in O$_2$ saturated 0.5 M H$_2$SO$_4$ electrolyte at 20 mV/s with rotation rate of 1600 rpm at room temperature. $E_{ring}$=1.3 V vs RHE.
potential behavior in a RDE system\textsuperscript{17}. Due to the porous nature of Co\textsubscript{2}(bpbp)/F-K\textsubscript{600-800} it was important to work with the optimal catalyst loading. Shown in Figure 2.8 are the RRDE polarization curves at 1600 rpm in oxygen saturated acidic electrolyte (0.5 M H\textsubscript{2}SO\textsubscript{4}) with catalyst loadings ranging from 100 to 500 µg/cm\textsuperscript{2}. An increase in the reduction current is observed when the loading is increased from 100 to 200 µg/cm\textsuperscript{2}, but further increases in the loading did not produce a higher reduction current. However, the peroxide oxidation at the ring showed more variation with increased loading. Increasing the loading from 100 to 200 µg/cm\textsuperscript{2} caused an increase in the peroxide detected, which is most likely due to the increase in the amount of O\textsubscript{2} reduced. When the loading was further increased from 200 to 500 µg/cm\textsuperscript{2}, the magnitude of the reduction current remained the same while the amount of peroxide detected at the ring decreased. These results indicate that above a loading of 200 µg/cm\textsuperscript{2} the amount of peroxide released from the catalyst layer decreased. Since all the other parameters remain constant it can be concluded that the increased catalyst layer thickness changes the diffusion path for the H\textsubscript{2}O\textsubscript{2} product and allows the H\textsubscript{2}O\textsubscript{2} molecules to further react either electrochemically or chemically. Co\textsubscript{2}(bpbp)/F-K\textsubscript{600-800} may contain catalytic sites that electrochemically reduce the peroxide according to the following equation:

\[ \text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow 2\text{H}_2\text{O} \]  \hspace{1cm} (2.3)

The catalytic sites can also chemically decompose the peroxide product according to the following equation:

\[ 2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2 \]  \hspace{1cm} (2.4)

The chemical decomposition of peroxide will produce water as well as oxygen, and the oxygen can be electrochemically reduced back to peroxide according to the following equation:
$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$  \hspace{1cm} (2.5)

With lower catalyst loadings the catalyst layer is thinner and most of the $H_2O_2$ is produced near the electrolyte bulk, enhancing the possibility of the $H_2O_2$ diffusing and being oxidized at the ring electrode. Based on these results a loading of 200 $\mu$g/cm$^2$ was used for the following studies into the ORR mechanism.
Co\textsubscript{2}(bpbp)/F-K\textsubscript{600-800} was used for our RRDE studies and compared to Pt/C to estimate electrocatalytic activity for ORR. Pt/C is the benchmark cathode catalyst and is known to

**Figure 2.8: RRDE ORR Mechanism Study.** Disk- and ring-currents measured during oxygen reduction reaction (ORR) on Tanka Pt/C and Co\textsubscript{2}(bpbp)/F-K\textsubscript{600-800} in O\textsubscript{2} saturated 0.1 M KOH and 0.5 M H\textsubscript{2}SO\textsubscript{4} electrolyte at 20 mV/s with rotation rate of 1600 rpm at room temperature. Alkaline E\textsubscript{ring}=1.1 V vs RHE. Acid E\textsubscript{ring}=1.3 V vs RHE.
proceed principally through the 4 e⁻ path in both alkaline and acidic media, as long as the surface is free of poisonous adsorbates. The ORR polarization plots of Co₂(bpbp)/F-K₆₀₀-800 and Pt/C in acidic and alkaline media are shown in Figure 2.9. In alkaline media Co₂(bpbp)/F-K₆₀₀-800 had an onset potential of 0.84 V and the oxidation of the super peroxide anion intermediate (HO₂⁻) detected at the ring electrode corresponds with generation of reduction current at the disk. Unlike the catalyst tested in acidic media, Co₂(bpbp)/F-K₆₀₀-800 established a well-defined limiting current in alkaline media that was higher in magnitude than what was produced in acid. Despite the different pH range of the electrolyte tested, the diffusion and concentration of oxygen in the electrolyte are expected to remain constant. Therefore the changes in the diffusion limiting current indicate an increase in the number of electrons transferred in the reaction. It could be possible the primary active site of Co₂(bpbp)/F-K₆₀₀-800 produces the peroxide intermediate, but the peroxide is further reduced by a secondary active site and ORR proceeds through a series of two 2e⁻ reductions resulting in an overall 4e⁻ reduction. Conversely, Pt/C had an onset of ~1 V and the onset of oxidation of the peroxide intermediate was not detected until ~0.45 V. Peroxide oxidation at 0.45 V observed on Pt/C electrocatalyst has been attributed to 2e⁻ reduction of oxygen by the quinone functionalities of the carbon support. Therefore, the active sites of Pt/C are able to stabilize the peroxide intermediate more effectively than Co₂(bpbp)/F-K₆₀₀-800. When the same experiment was conducted in acidic media Co₂(bpbp)/F-K₆₀₀-800 displayed poorer performance in the low pH environment. The onset of ORR on Co₂(bpbp)/F-K₆₀₀-800 was shifted cathodically by 60 mV (0.78 vs 0.84 V) when compared with its performance in alkaline media. The peroxide intermediate becomes a neutral species (H₂O₂) when switching to the low pH environment, decreasing its stability on metal-ion active sites (Co-N₄), such as those resembling the poryphyrin active sites of proteins. The onset of peroxide
oxidation detected at the ring in acidic media still coincides with the Co$_2$(bpbp)/F-K$_{600-800}$ catalyzed ORR detected at the disk. However, the magnitude of the ring current is very similar in alkaline and acidic media, despite the difference in magnitude of the disk current. These results indicate that the primary active site of Co$_2$(bpbp)/F-K$_{600-800}$ still produces the peroxide intermediate in acidic media, but the peroxide is not further reduced by a secondary active site.

2.3.3 Investigation of a Secondary Active Site

The high temperature heat treatment of Co$_2$(bpbp)/F-K$_{600}$ generated cobalt metal, which is known to be thermodynamically unstable in the low pH environment. However, if the metallic moieties are protected they could survive the acidic environment. Co$_2$(bpbp)/F-K$_{600-800}$ was subjected to an acid wash to investigate the stability of the metallic moieties present after the high temperature heat treatment.
Shown in Figure 2.6 are the FT-EXAFS of fresh Co$_2$(bpbp)/F-K$_{600}$-800 and Co$_2$(bpbp)/F-K$_{600}$-800 after the acid wash. It can be seen that the peak at ~2.4 Å completely disappears and the peak at ~2.0 Å shows a decrease in intensity. Some of the Co NPs that are created at the higher heat treatment temperatures appear to be protected, while the metallic Co-moieties that are not protected are spontaneously oxidized when exposed to air. The Co-Co-O scattering of the oxidized Co NPs contribute the peak at 2.4 Å. The lack of protection around these moieties makes them vulnerable in the low pH environment and they are completely removed when

**Figure 2.9: Stability of Cobalt Moieties in Acid.** Fourier transform of fresh Co$_2$(bpbp)/F-K$_{600}$-800 catalyst and acid washed Co$_2$(bpbp)/F-K$_{600}$-800 catalyst.
washed in acid. However, some of the Co NP moieties are stable during the acid wash and their Co-Co scattering contribute to the peak at 2.0 Å.

**Figure 2.10: RRDE Effect of Acid Wash on ORR Mechanism.** Disk- and ring-currents measured during oxygen reduction reaction (ORR) on fresh and acid washed Co₂(bpbp)/F-K₆₀₀-₈₀₀ in O₂ saturated 0.1 M KOH and 0.5 M H₂SO₄ electrolyte at 20 mV/s with rotation rate of 1600 rpm at room temperature. Alkaline E<sub>ring</sub>=1.1 V vs RHE. Acid E<sub>ring</sub>=1.3 V vs RHE.

Based on these XAS results, we investigated the effect of the acid wash of Co₂(bpbp)/F-K₆₀₀-₈₀₀ on the ORR activity to better understand the involvement of the Co NPs in the ORR mechanism. RRDE measurements were taken on fresh Co₂(bpbp)/F-K₆₀₀-₈₀₀ and catalyst that had been acid washed (Co₂(bpbp)/F-K₆₀₀-₈₀₀-AW). Shown in Figure 2.10 are the ORR polarization plots and corresponding ring responses in acidic and alkaline media. The removal of
Co NPs reduces ORR activity in acidic media as witnessed by a 20 mV increase in overpotential for ORR (0.76 vs 0.78 V). This potential loss is maintained throughout entire potential range and shifts the $E_{1/2}$ cathodically by 20 mV (0.59 V vs 0.61 V). Production of the peroxide intermediate still commences with the onset of ORR and removal of Co NPs has no effect on the amount of peroxide produced in the low pH environment. However, in alkaline media the removal of Co NPs has a very different effect on the ORR activity. Despite an improvement in the onset potential by 40 mV (0.88 V vs 0.84 V), the $E_{1/2}$ shifts cathodically by 10 mV (0.78 V vs 0.79 V) and the diffusion limiting current is reduced by 10% (4.6 vs 5.1 mA/cm$^2$). The most drastic change due to the removal of Co NPs is the substantial increase in the amount of peroxide intermediate detected at the ring (20% vs 7.7%). It appears in alkaline media a secondary active site is able to further reduce the peroxide intermediate to yield the 4e$^-$ reduction of oxygen. The Co-N moieties could initiate $O_2$ adsorption and complete the 2e$^-$ reduction to $HO_2^-$, but the Co NPs act as a second active site that further reduce the peroxide intermediate to water. However, in acidic media of Co$_2$(bpbp)/F-K$_{600-800}$ is only capable of the 2e- reduction of oxygen since the peroxide intermediate formed by the Co-N moieties is not stabilized well enough to be further reduced. Although, the loading studies suggest that the Co NPs would still function as a secondary active site capable of further reducing peroxide if the peroxide pathway was altered by high-loadings.

2.4 Conclusions

In this work we generated a Co-based non-PGM electrocatalyst by subjecting a tetranuclear cobalt cation to a high temperature heat treatment in inert atmosphere. Catalyst heat treated above 600 °C were the most active for ORR and were comprised of Co-N and Co NP moieties. Co$_2$(bpbp)/F-K$_{600-800}$ is an effective catalyst for the 2e$^-$ reduction of oxygen in acidic
electrolyte and enhanced stability of the peroxide intermediate in alkaline media allowed the Co NPs to act as a secondary active site that allowed a series of two \(2e^-\) reductions, resulting in an overall \(4e^-\) reduction of oxygen to water in alkaline media. In acidic media the Co NPs moieties can still act as a second active site if high enough loadings are used to allow further reduction of the peroxide before it is released into the electrolyte.

### 2.5 Acknowledgements

The authors deeply appreciate financial assistance from the U.S. Department of Energy, EERE (DE-EE-0000459). Use of the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory (BNL), was supported by the U.S. Department of Energy, Office of Basic Energy Sciences. Synchrotron spectroscopy in this publication was made possible by the Center for Synchrotron Biosciences grant, P30-EB-009998, from the National Institute of Biomedical Imaging and Bioengineering (NIBIB). Support from beamline personnel Dr. Erik Farquhar and Mark Chance (X3B) are gratefully acknowledged. Dr. Qingying Jia is acknowledged for his assistance in the collection and analysis of the XAS data.
2.6 Chapter 2 References


Chapter 3

Metal-Nₓ Free Electrocatalyst with High Activity for the Oxygen Reduction Reaction

3.1 Introduction

Replacement of noble metal electrocatalysts such as those used in the oxygen reduction reaction (ORR), especially as a consequence of the “stability criterion” in low pH environment is a holy grail for electrochemists involved in the low and medium temperature proton-conducting membrane fuel cells. The high efficiency and theoretical energy density of the H₂/air fuel cell technology makes it a potential alternative for the replacement of internal combustion engine based power sources in applications such as transportation, and decentralized power.

Three decades of effort towards engendering non-platinum group metal (non-PGM) electrocatalyst has seen a slow but promising evolution of activity for ORR as well as our general understanding of the catalytic active site. Most of these prior efforts have relied on the presence of nitrogen-coordinated sites with or without a transition metal, such as Fe. Despite making progress, especially those achieved in the recent past, the current state of the art non-PGM electrocatalyst has yet to achieve the catalytic activity of platinum and thus remains an important research area.

Among the key breakthroughs in this arena were those by Jasinski¹ et al., who were the first to report the oxygen reduction capabilities of cobalt phthalocyanine in basic media. This was followed with that of Jahnke² et al., who reviewed the activity of various N₄-metal chelates and recognized the necessity of heat treatments which resulted in improvement of stability in basic media and significant enhancement of activity and stability in acidic media. Heat treatment of an existing metal-nitrogen (Me-Nₓ) coordinated macrocycle dominated the early research of
non-PGMs, but Yeager and coworkers\textsuperscript{3} caused a principle shift resulting in a significant jump in activity by transitioning to non-macrocyclic precursor materials. More recently Zelenay\textsuperscript{4,5} \textit{et al.} and Dodelet\textsuperscript{6,7} \textit{et al.} have demonstrated significant enhancement using the non-macrocyclic precursor based active-site evolution route. The generally accepted notion of active sites for ORR, formed as a result of a series of heat treatment and etching steps, involved some form of Me-N\textsubscript{x} sites\textsuperscript{8,9}. In addition, the presence of some type of transition metal/metal oxides (those involving some degree of metal-metal bonds) are also typically reported especially for materials heat-treated at temperatures >800 °C\textsuperscript{10}. It was generally believed that these moieties were catalytically inactive due to their thermodynamic instability in low pH environment, or their inaccessibility to oxygen if isolated/protected from the electrochemical environment by layers of carbon\textsuperscript{11,12}. More recently their direct involvement in acidic media is reported in a cascade of 2e\textsuperscript{-} reduction steps via a peroxide intermediate\textsuperscript{13-15}.

The role of transition metal/metal oxides has however been debated. For example, Kramm \textit{et al.},\textsuperscript{16} claimed that the formation of metal/metal oxides was detrimental to the overall activity of their non-PGM electrocatalyst. Using Mössbauer spectroscopy they investigated iron-based non-PGMs and identified five different types of iron species present, but attributed activity to only two types of the iron, both of which were coordinated to nitrogen. They claimed the addition of sulfur had a beneficial effect on ORR activity by inhibiting the formation of iron carbides (Fe\textsubscript{3}C) which they believed were responsible for destroying the active Fe-N\textsubscript{4} centers\textsuperscript{17}.

While most of the recent non-PGM literature has focused on a metal-based active sites there have been several reports of nitrogen-doped (N-doped) carbons with “metal-free” active sites\textsuperscript{18,19}. Stevenson \textit{et al.},\textsuperscript{20} elucidated the ORR pathway in neutral and basic media and found nitrogen doping enhanced ORR activity due to improved adsorption of O\textsubscript{2} and decomposition of
peroxide intermediate. Ozkan et al.,\textsuperscript{21} were the first to demonstrate that N-doped carbons have ORR activity in acidic media and attributed this activity to the increased edge planes of the graphite with pyridinic nitrogen. Dai et al.,\textsuperscript{22} investigated a N-doped graphene in alkaline media and provided further proof of these “metal free” active sites. Deng et al.,\textsuperscript{23} reported a material consisting of FeNPs encapsulated in carbon nanotubes (CNT) that was shown to effectively catalyze ORR in the acidic environment of a proton exchange membrane fuel cell (PEMFC). Their density functional theory (DFT) calculations revealed that the interaction between the Fe and the C, in the wall of the CNT, significantly enhanced the activity of the CNTs for ORR catalysis. Hu et al.,\textsuperscript{24} reported a material with Fe\textsubscript{3}C nanoparticles encased by graphitic layers that is also an effective ORR electrocatalyst in acidic media. The Fe\textsubscript{3}C nanoparticles are protected from the acidic environment by the graphitic layers, but are believed to activate the carbon for ORR.

The previous examples constitute a small sample from the literature of a growing consensus that there are “metal-free” active sites present in non-PGMs. However, the synthesis procedure for all of previously reported electrocatalysts invariably involve a metal component (typically iron) and the final electrocatalyst cannot be declared completely devoid of iron nanoparticles (FeNPs) and/or iron carbides (Fe\textsubscript{3}C)\textsuperscript{4,25,26}. Since these moieties are present in the electrocatalyst, their role in ORR cannot be ruled out without \textit{in-situ} evidence. As per the original active site theory proposed by Yeager\textsuperscript{27-29}, the formation of Me-N\textsubscript{x} sites resulted from the dissolution of exposed metal/metal oxides in acidic electrolyte and their eventual adsorption on nitrogen sites coordinated to the carbon. This work \textit{via} our unique spectroscopic evidence and the use of metal organic framework (MOF) as a template to form active sites with and without
transition elements provide for the first time irrefutable evidence of creation of metal-free active sites for ORR with no involvement of active Fe-Nx sites.

In this chapter an iron-based non-PGM ORR electrocatalyst is introduced that utilizes a MOF as the source for embedding Fe-based sites. In order to achieve this, a MOF based on Zn (ZIF-8) is used as an encapsulator for Fe-chelated with a nitrogen complex. The MOF support was chosen in order to take advantage of the porosity and high surface area, which are features known to improve the catalytic activity. Also, encapsulation of the chelated iron complex in the pores was employed in an effort to obtain equal distribution and high density of active sites. ORR was investigated in alkaline and acidic media to better understand the reduction mechanism of the studied electrocatalyst. The synthetic approach featuring chemical encapsulation is an important distinction to another reported approach with the same MOF structure that used ball milling for extended periods\(^7\). The derived catalyst in this work is referred to as “FePhen@MOF”. The corresponding MOF procured commercially (BASF) has a trade name of “Basolite®”. MOF based structures with and without incorporation of iron precursor were heat treated and etched to form the active electrocatalyst, hereby referred to as “FePhen@MOF-ArNH\(_3\)” and “Basolite®-ArNH\(_3\)” respectively. The most critical advantage however was that this approach enabled proper comparison with samples derived wherein no Fe was chelated, everything else remaining the same. This is in contrast to previous reports where a complete absence of Fe cannot be claimed\(^{20-24}\). By combining electrochemical and spectroscopic methods we are able to show that while the derived Fe containing non-PGM catalysts exhibits one of the best-reported ORR activities, the coordination environment for Fe is predominantly Fe/Fe\(_x\)C particulate in nature. Using \textit{in situ} X-ray absorption spectroscopy (XAS) we are able to characterize the iron coordination of the electrocatalyst (FePhen@MOF-ArNH\(_3\)) under actual
simulated operating conditions of a PEM fuel cell and are unable to detect any direct Fe-N\textsubscript{x} coordinated sites present in the non-PGM electrocatalyst. To our knowledge this is the first definitive report of a non-PGM electrocatalyst without the presence of Fe-N\textsubscript{x} sites exhibiting one of the highest reported activities for ORR in acidic media. The electrochemical performance (both RRDE and PEM fuel cell polarization) is correlated with active site function determined using \textit{in situ} synchrotron XAS and aided by \textit{ex situ} physicochemical methods such as X-ray diffraction (XRD) and high-resolution transmission electron microscopy (HR-TEM). In addition to the absence of direct Fe-N\textsubscript{x} coordination, we also show the complete absence of any direct involvement of the Fe in the electrocatalytic pathway as a result of its presence subsurface to the carbo-nitrided fibers and hence its important implication in avoidance of any Fenton type process related to onset of peroxide induced free radical formation as detailed earlier\textsuperscript{30}.

3.2 Experimental Methods

3.2.1 Catalyst Synthesis and Electrochemical Measurements

The commercial Pt/C (46\%) electrocatalyst used as a standard in this study is obtained from Tanaka Kikinzoku International KK (Japan). For the synthesis of FePhen@MOF 2-methylimidazole (5.90g, 0.072mol, 160 equivalents (eq)) was dissolved in methanol (20mL) at room temperature with stirring in flask A. In flask B, zinc(II) nitrate \(\chi\)-hydrate (10.80g, 0.036mol, 80eq) and 1,10-phenanthroline monohydrate (12.96g, 0.072mol, 160eq) were dissolved in methanol (30mL) and water (45mL) at room temperature with stirring. Once both flasks’ contents were fully dissolved, flask B was added to flask A. Iron(II) acetate (0.081g, 4.66 \(x\) 10\textsuperscript{-3}mol, 1eq) was added to the reaction, and this was stirred at room temperature for 24h. A second reaction identical to the aforementioned vessel was assembled, and the two separate
reactions progressed in tandem. Before addition of iron(II) acetate, the reaction began to turn slightly milky white/turbid in appearance. This intensified over the course of the reaction, resulting in a fine suspension turbid and pale orange in color. The two reaction vessels were then combined in 6x50mL centrifuge tubes and centrifuged at 4000 rpm for 25min, washed 3 times with methanol (6x40mL each time), centrifuging at 3700 rotation per minute (rpm) for 17 minutes in between each washing. The resulting orange/white solid was dried in a vacuum oven for 6-12 hours at 60-70°C and afforded formation of the desired FePhen@MOF, a light tan powder (typically 4.5-5.5g total yield from the two combined reaction vessels). The dried powder was then subjected to either one or two heat-treatments, i.e., in argon at 1050 °C with a 1 hour dwell time (FePhen@MOF-Ar) and ammonia at 1050 °C with an 18 minute dwell time (FePhen@MOF-ArNH₃) respectively. The weight percent of Fe used in the synthesis of FePhen@MOF and its retention throughout the heat treatment process (FePhen@MOF-Ar and FePhen@MOF-ArNH₃) was quantified using ICP-MS and is listed Table 3.1.

<table>
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<tr>
<th>SAMPLE</th>
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<th>%Zn</th>
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<tr>
<td>FePhen@MOF</td>
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<td>21.85</td>
</tr>
<tr>
<td>FePhen@MOF-Ar</td>
<td>2.5</td>
<td>0.56</td>
</tr>
<tr>
<td>FePhen@MOF-ArNH₃</td>
<td>3.1</td>
<td>0.13</td>
</tr>
<tr>
<td>Basolite</td>
<td>-</td>
<td>25</td>
</tr>
</tbody>
</table>

**Table 3.1: Metallic Composition of MOF Catalysts.** Quantification of Fe and Zn in non-PGM materials based on ICP-MS measurements (0.012 gm/L limit of detection).

Perchloric acid electrolyte (0.1 M) was prepared using double-distilled 70% perchloric acid (GFS Chemicals) and potassium hydroxide electrolyte (0.1 M) was prepared using pellets (Alfa Aesar). Electrochemical measurements were carried out on glassy carbon (GC) disk (5.61 mm diameter, Pine Instruments) that was polished with 0.05-micron alumina paste (Buehler, Lake Bluff, IL) and then sonicated in distilled water and isopropyl alcohol. Catalysts inks were
prepared by dispersing the catalyst in a volume of 1:1 Millipore water:isopropyl alcohol with 10 vol% of 5 wt% Nafion® as a binder. The ink solution was then sonicated approximately 60 minutes to get a uniform suspension. A small volume of the catalyst ink was deposited on the GC substrate to obtain a platinum metal loading of 15 µg/cm² and a non-PGM loading of approximately 600 µg/cm². All electrochemical measurements were carried out at room temperature (20-25 °C) in a standard electrochemical cell (Chemglass) with an acid or base electrolyte using a rotating disk electrode (RDE) setup from Pine Instrument Company connected to an Autolab bipotentiostat (PGSTAT302N). Cyclic voltammetry was run on both Pt and non-Pt catalysts in 0.1 M perchloric acid (HClO₄) and 0.1M potassium hydroxide (KOH) bubbled with argon. ORR was investigated by the RDE technique after bubbling oxygen in the electrolyte solution followed with rotations at 100, 400, 900, 1600 and 2500 rpm. Scans were recorded at 20 mV/s and all potentials are referenced to a reversible hydrogen electrode (RHE) scale made from the same solution as the electrolyte. Carbon corrosion treatment of FePhen@MOF-ArNH₃ was performed in argon saturated 0.1M HClO₄ by cycling 1-1.5 V vs RHE at 100 mV/s and 1600 rpm rotation speed for 7,500 cycles.

Membrane electrode assemblies (MEAs) for fuel cell testing were prepared using a FePhen@MOF-ArNH₃ cathode on Gas Diffusion Layer (Sigracet BC25 GDL), Pt/C (Tanaka, 46%) anodes on GDL (Sigracet BC25), Nafion 5wt% ionomer solution, and Nafion 211 ionomer membrane. To prepare the cathode, a catalyst ink composed of FePhen@MOF-ArNH₃ dispersed in a water-alcohol mixture with the requisite amount of ionomer (Nafion 5wt%) was sprayed on a gas diffusion layer (Sigracet, BC25). Typical cathode loading consisted of 0.2 mg/cm² with an ionomer content of 60% by weight of the catalyst. After drying the cathodes, a layer of interfacial ionomer was sprayed to achieve a loading of 0.4mgNafion/cm². Anodes were prepared
with commercial Pt/C (Tanka, 46%) in the same manner as the cathode. Electrodes for the Pt-based cathode MEA were supplied by industry. Hot pressing of the electrodes together with a Nafion 211 membrane was carried out at 130 °C and 1,000 psi. for duration of 5 minutes. MEAs were then assembled in a fuel cell consisting of 5 cm² serpentine flow fields. Humidification of the MEA was performed for 60 minutes by flowing N₂ (100% relative humidity, RH) at a cell temperature of 80 °C. The operating temperature of the fuel cell was 80 °C and the cell was activated with H₂/O₂ (inlet temperatures 85 °C, 100% RH, 22 psi back pressure). Durability cycling followed protocols from Nissan Technical Center North America (NTCNA) designed to simulate accelerated drive cycle conditions based on transitions between open circuit voltage and idling in automobile operation. Durability was tested at 80 °C with N₂ flowing on the cathode while stepping potential from 0.6 to 1.0 V vs. RHE with 3s hold at each potential step.

3.2.2 Physicochemical Characterization

X-ray diffraction was performed on a Rigaku (model Ultima-IV) diffractometer with Cu Kα radiation (λ=1.5418 Å) at 40 kV and 40 mA. The scan speed was 2-20 seconds and the step size was 0.1°. N₂ sorption analysis was performed on a Quantachrome NOVA 2200e at 77 K. Total surface area was determined by the Brunauer-Emmett-Teller (BET) method and pore size distribution was determined using Non-Local Density Functional Theory (NLDFT) split pore method from the NovaWin software. Thermogravimetric analyses (TGA) were performed on a TA Instruments SDT Analyzer Q600 from 22-1100°C with a ramp rate of 5°C/min and dwelling for 5min at maximum temperature. All studies were conducted under an argon atmosphere, with a flow rate of 100mL/min. Ultraviolet-visible (UV-Vis) spectroscopy quantification performed on Thermo-Fisher UV-Vis spectrophotometer collecting absorbance spectra from 190-700 nm. A calibration curve was generated from 12.5-100.0 µM 1,10-phenanthroline monohydrate
dissolved in 1 M HCl. 300 µM solutions of FePhen@MOF and Basolite Z1200© standard dissolved in 1 M HCl were run under the same conditions. Scanning electron microscopy was performed on a Hitachi S-4900 FSEM instrument with an accelerating voltage of 3-5 keV with samples mounted on a carbon adhesive stub attached to an aluminum sample stage. High-resolution transmission electron microscopy images were taken on a JEOL 2010 field emission gun (FEG) TEM at 200 kV with samples deposited on a holey carbon film on a 300 mesh copper grid.

$^{57}$Fe Mössbauer spectroscopy was measured with a $^{57}$Co source embedded in a rhodium matrix. The measurement was performed keeping the source and absorber at room temperature. The spectrometer was operated with a triangular velocity waveform, and a gas filled proportional counter was used for the detection of the $\gamma$-rays. Velocity calibration was performed with an $\alpha$-Fe foil. The spectra were fitted with a combination of Lorentzian lines. In this way, spectral parameters such as the isomer shift (IS), the electric quadrupole splitting (QS), the linewidth at half maximum (LW), the hyperfine fields (HF) and the absorption spectral areas of the various spectral components were determined. No constraints were applied to the fitting parameters except on the IS of the singlet assigned to $\gamma$-Fe, fixed at -0.08 mm s$^{-1}$ on the basis of previous experimental studies on Fe-N-C catalysts showing the presence of the ubiquitous singlet assigned to $\gamma$-Fe.

The *in situ* XAS studies at the Fe K-edge (7112 eV) were performed at X3B beamline of National Synchrotron Light Source (NSLS, Brookhaven National Laboratory, NY). A specially designed spectro-electrochemical was utilized and has been described previously $^{31}$. The Fe K-edge spectra were collected in fluorescence mode with a 32-element Ge solid state detector as a function of potential in the range 1.0 – 0.1 V. A pseudo steady-state was established by holding
the cell for approximately 5 minutes before collecting the spectra. The electrolyte, 0.1 M HClO₄, was saturated with either argon or oxygen. Athena$^{32}$ and Artemis$^{33}$ programs were used to process and fit the data. IFEFFIT suite$^{32}$ was used to calibrate, align and normalize the scans. FEFF6 code$^{34}$ was used to calculate scattering paths to model the $\chi(R)$ transforms.

3.3 Results and Discussion

3.3.1 Physicochemical Characterization

![XRD Confirmation of Encapsulation](image)

Figure 3.1: XRD Confirmation of Encapsulation. Powder pattern comparison of non-heat treated Basolite Z1200®, FePhen@MOF and 1,10-phenanthroline to confirm formation of MOF structure with encapsulation synthesis of FePhen@MOF and absence of crystalline 1,10-phenanthroline.
The 2θ values and symmetry of the powder XRD of FePhen@MOF (prior to heat treatment) as compared with the as purchased Basolite® (Sigma, Basolite Z1200) confirm the formation of the crystalline MOF structure (Fig. 3.1).

**Figure 3.2: XRD of Encapsulation vs. Ball Milling.** Powder pattern comparison of two samples: ZIF-8 MOF mixed with FePhen complex (MOFw/FePhen) and FePhen@MOF from encapsulation synthesis. First peak of FePhen@MOF compared to MOFw/FePhen (inset) shows diminished intensity and positive shift due to encapsulation.

The concomitant diminished intensity of the signal from FePhen@MOF (Fig. 3.2, inset) is indicative of the presence of guest molecules within the MOF structure as a result of encapsulation, this is in agreement with similar observations reported earlier. In addition the absence of the diffraction lines characteristic of 1,10-phenanthroline (Fig. 3.1) (N-chelating agent for Fe) imply that it is not present as a separate entity in crystalline form.
However, ultraviolet-visible (UV-Vis) spectroscopy (Table 3.2) confirmed retention of 1,10-phenanthroline in the FePhen@MOF and thermogravimetric analysis (TGA) indicated its enhanced thermal stability as a result of the encapsulation (Fig. 3.3).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Imax (nm)</th>
<th>A</th>
<th>%wt phenanthroline</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,10-phenanthroline</td>
<td>287</td>
<td>0.114-1.467</td>
<td>n/A</td>
</tr>
<tr>
<td>Basolite Z1200©</td>
<td>203</td>
<td>0.044</td>
<td>0</td>
</tr>
<tr>
<td>FePhen@MOF</td>
<td>286</td>
<td>0.274</td>
<td>4.26</td>
</tr>
</tbody>
</table>

Table 3.2: UV-Vis Quantification of Phenanthroline. Quantification of 1,10-phenanthroline in non-heat treated Basolite Z1200© and FePhen@MOF to confirm retention after encapsulation synthesis.
Figure 3.3: Thermogravimetric Analysis of Encapsulation. Thermogravimetric analysis of 1,10 Phenanthroline precursor, Basolite Z1200©, FePhen precursors mixed with Basolite Z1200© (MOFw/FePhen), and non-heat treated FePhen@MOF. Thermal stability of 1,10-phenanthroline is enhanced due to encapsulation in FePhen@MOF. All measurements were run under argon with 100 mL/min flow rate. Samples were heated at ramp rate of 5 °C/min.
Further, FePhen@MOF exhibited a much smaller Brunauer-Emmet-Teller (BET) (Fig. 3.7) surface area than the commercial analogous Basolite® (424 m²/g vs. 1813 m²/g) which is likely attributable to the encapsulation of the chelated iron complex within the MOF-pore reducing the overall pore volume (Fig. 3.4).

Figure 3.4: Effect of Encapsulation on Pore Size Distribution. Pore size distribution of Basolite Z1200© and FePhen@MOF determined from Non-Local Density Functional Theory (NLDFT) model of nitrogen adsorption data. The pore volume of FePhen@MOF is less than Basolite Z1200© due to encapsulation of FePhen in the pores.
The FePhen@MOF material was subjected to an initial heat treatment (1050 °C) in an Ar atmosphere (FePhen@MOF-Ar) for a tailored breakdown of the MOF structure and removal of Zn nodes via sublimation resulting in an initial rendering of a carbonaceous material with significant electronic conductivity. The XRD powder pattern (Fig. 3.5 a) shows emergence of an

![Figure 3.5: XRD of FePhen@MOF-ArNH₃. (a) X-ray diffraction pattern of FePhen@MOF-ArNH₃ and iron-free Basolite-ArNH₃. (b) diffraction patterns of iron, iron carbide, and iron nitride.](image)

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elevated baseline typical for presence of an amorphous material as well as diffraction lines of graphite and several iron phases (Fig. 3.5 b) (iron-Fe (Im-3m) and iron carbide-Fe$_3$C$_2$ (C2/c)). We were not able to accurately determine the exact stoichiometry of the iron carbide and believe we have mixture (Fe$_x$C).

An additional heat treatment (900 °C) in ammonia (FePhen@MOF-ArNH$_3$) led to the formation of several new diffraction lines (Fig. 3.6) that indicate the incorporation of nitrogen into the carbon scaffold in the vicinity of the iron. These new diffraction lines post NH$_3$ heat treatment show emergence of Fe-nitrides (Fe$_3$N$_{1.59}$ (P6322) and Fe$_2$N (P-31m(162))); however

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**Figure 3.6: XRD of Ammonia Heat Treatment Effect.** Powder pattern comparison of effect of heat treatment of FePhen@MOF in argon alone or argon followed by ammonia. Subsequent heat treatment in ammonia shows emergence iron nitride diffraction lines indicating incorporation of nitrogen functionalities.
XRD alone could not unambiguously determine the exact nitrogen content. Comparing these XRD results with those obtained from Basolite®-ArNH₃ (subjected to the same heat treatments as FePhen@MOF-ArNH₃) led us to believe that in the latter case the iron is converted to its metallic form during the initial argon heat treatment and subsequently acts as a catalyst that graphitizes the vicinal carbon-nitrogens from the MOF precursor. The second heat treatment in ammonia thus is effective in etching a portion of the remaining amorphous carbon³⁶ and introducing nitrogen functionalities into the carbon scaffold.

![Figure 3.7: Surface Area Change with Catalyst Synthesis.](image)

**Figure 3.7: Surface Area Change with Catalyst Synthesis.** Brunauer-Emmett-Teller (BET) surface area of non-heat treated Basolite Z1200®, FePhen@MOF, FePhen@MOF-Ar and FePhen@MOF-ArNH₃. Encapsulation synthesis of FePhen@MOF results in diminished surfaced area, but a high surface area is recovered from heat treatments.

The BET surface area increased with each heat-treatment (Fig. 3.7) resulting in FePhen@MOF-ArNH₃ exhibiting a surface area of 1200 m²/g, comparable to that of the original
Basolite® (no heat treatment). Basolite® and FePhen@MOF are originally microporous (<20 Å) materials, however the microporosity is increased with each heat-treatment and mesopores (20-40 Å) are introduced (Fig. 3.8) to FePhen@MOF-ArNH₃.
Figure 3.8: Pore size distribution. Pore sized distribution of non-heat treated FePhen@MOF compared to FePhen@MOF-ArNH₃, determined from Non-Local Density Functional Theory (NLDFT) model of nitrogen adsorption data. Heat treatment introduces mesopores (20-40 Å) and new micropores (<20 Å).
X-ray absorption spectroscopy (XAS) was used to further probe the local coordination of the iron present after heat treatment. Fourier transform (FT) of the extended X-ray absorption fine structure spectra (EXAFS) of the Fe K-edge (Fig. 3.9) measured on the electrode in situ (held at 0.3 V, free of adsorbates) was dominated by a peak at ~2.2 Å, which corresponds well with the known Fe-Fe bond length in bulk iron (2.49 Å) and/or iron carbide (2.48 Å).

Figure 3.9: In Situ Fourier Transform EXAFS of Iron Non-PGMs. FePhen@MOF-ArNH₃, FeTPP pyrolyzed at 800 °C and PVAG-Fe in N₂ saturated 0.1M HClO₄.
The qualitative comparison of the FePhen@MOF-ArNH₃ spectrum with the spectra of the standard metallic iron foil (Fe foil) and a Fe₃C standard (Fig. 3.10) suggests that the iron is predominantly converted to its metallic state with a minor carbide phase. However it should be noted that an inherent limitation of XAS is the inability to differentiate between C, N and O.
neighbors. Visual examination of the EXAFS data cannot rule out the presence of small amount of Fe-N$_x$ species by itself, especially considering the normal uncertainties of EXAFS fits (usually <1 for coordination number). In this work EXAFS is only used as additional evidence of the absence of Fe-N$_x$ species. Therefore we cannot use FT-EXAFS to conclusively identify the presence or absence of Fe nitrides or carbides in the final catalyst.

![57Fe Mössbauer spectrum of FePhen@MOF-ArNH$_3$.](image)

**Figure 3.11:** $^{57}$Fe Mössbauer spectrum of FePhen@MOF-ArNH$_3$. $^{57}$Fe Mössbauer spectrum of FePhen@MOF-ArNH$_3$ measured at room temperature.

In order to further investigate the different iron coordination environments in FePhen@MOF-ArNH$_3$ and to unambiguously confirm the absence of FeN$_x$C$_y$ moieties, the sample was examined with *ex situ* $^{57}$Fe Mössbauer spectroscopy (Fig. 3.11). The absorption
spectrum measured at room-temperature (RT) was fitted with four components and their parameters are reported in Table 3.2.

<table>
<thead>
<tr>
<th></th>
<th>γ-Fe</th>
<th>α-Fe</th>
<th>Doublet</th>
<th>Fe$_3$C</th>
</tr>
</thead>
<tbody>
<tr>
<td>IS$^{(1)}$ / mm s$^{-1}$</td>
<td>-0.08$^{(2)}$</td>
<td>-0.03</td>
<td>0.16</td>
<td>0.19</td>
</tr>
<tr>
<td>QS / mm s$^{-1}$</td>
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<td>0.00</td>
<td>0.50</td>
<td>0.00</td>
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<tr>
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<td>HF / Tesla</td>
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<td>33.2</td>
<td>0.00</td>
<td>20.7</td>
</tr>
<tr>
<td>% Area</td>
<td>13</td>
<td>6</td>
<td>45</td>
<td>36</td>
</tr>
</tbody>
</table>

**Table 3.3: Table of fitted Mössbauer parameters for the catalyst FePhen@MOF-ArNH$_3$.**

Fitted spectral parameters for the four components used to fit the $^{57}$Fe Mössbauer spectrum of FePhen@MOF-Ar-NH$_3$. The isomer shift (IS), quadrupole splitting (QS), linewidth, (LW) and hyperfine field (HF) are given as well as the relative absorption area corresponding to each component (% Area).

$^{(1)}$ Relative to a calibration performed with an α-Fe foil.

$^{(2)}$ Fixed spectral parameter, on the basis of previous studies on Fe-N-C catalysts.

The singlet with an isomer shift (IS) of -0.08 mm s$^{-1}$ is ubiquitous in pyrolyzed Fe-N-C catalysts and assigned to paramagnetic γ-Fe$^{37-40}$. While α-Fe nanoparticles could also result at RT in a singlet with similar parameters, it would turn into a sextet at 5 K due to a super-paramagnetic transition. The Mössbauer spectrum of FePhen@MOF-Ar-NH$_3$ measured at 5 K (not shown) still showed the singlet, thereby foreboding its assignment to α-Fe nanoparticles. Next, the most intense sextet in Fig. 3.11 with an IS of 0.19 mm s$^{-1}$ and a hyperfine field (HF) of 20.7 T corresponds to ferromagnetic Fe$_3$C$^{40}$. The minor sextet with an IS-value close to zero and a larger hyperfine field of 33.2 T is unambiguously assigned to ferromagnetic α-Fe. The last component is a doublet with an IS of 0.16 mm s$^{-1}$ and a quadrupole splitting (QS) of 0.50 mm s$^{-1}$. It may not be assigned to iron-rich nitrides such as ε-Fe$_3$N and γ'-Fe$_4$N, but can be assigned to
either paramagnetic amorphous iron carbide, Fe₃C⁴¹,⁴² or nitrogen-rich iron nitrides⁴³. On the basis of the experimental X-ray diffraction pattern (Fig. 3.6a) and doublet’s Mössbauer parameters (especially QS), the doublet is assigned to ξ-Fe₂N or ε-Fe₂+xN with x = 0.1, featuring an interstitial binary nitride with Fe atoms defining a hexagonal close-packed structure⁴³. Its presence after a pyrolysis at 1050°C in pure NH₃ is in agreement with the Fe-N phase diagram and actually expected since the pyrolysis conditions are typically those employed for producing Fe₂N⁴⁴,⁴⁵.

Thus, the analysis of the Mössbauer spectrum of FePhen@MOF-ArNH₃ demonstrates the absence of the doublets D1 and D2 that had been identified in all Fe-N-C catalysts investigated with Mössbauer spectroscopy thus far. D1 and D2 have been assigned to FeₙCₙ moieties covalently integrated in graphene sheets, with the ferrous ion in low- and medium-spin state, respectively⁴⁶. Their Mössbauer spectral parameters resemble those of Fe(II)-phthalo cyanine adsorbed on carbon (D1) and crystalline iron phthalocyanine (D2). The IS and QS values of D1 typically range from 0.26-0.39 mm s⁻¹ and 0.90-1.16 mm s⁻¹, respectively⁴⁸,⁴⁷. For D2, the typical range of IS and QS values are 0.36-0.37 mm s⁻¹ and 2.40-2.65 mm s⁻¹, respectively. The doublet D observed here with IS and QS values of 0.16 and 0.50 mm s⁻¹ is fundamentally different and cannot be assigned to any FeₙCₙ moiety integrated in a graphene sheet. Thus, the doublet D observed in the present work can be confidently and entirely assigned to a nitrogen-rich iron nitride crystalline structure. Hence, it is concluded that FeₙCₙ moieties integrated in graphene sheets are absent in the sample FePhen@MOF-ArNH₃.
The surface morphology of FePhen@MOF-ArNH₃ (Fig. 3.12 b) was probed with scanning electron microscopy (SEM) and revealed that the heat treatment produces a heterogeneous material that is comprised of several different carbon morphologies. The MOF framework decomposed during the heat treatment forming a porous carbon framework. Additionally, some of the Fe agglomerated into FeNPs that catalyzed the growth of carbon nanotubes (CNTs) of varying sizes and possessed distinct bamboo-like joints, which are characteristic of N-doped carbon\textsuperscript{20,48}. High-resolution transmission electron microscopy (HR-TEM) revealed that Fe/Fe₃C particles were contained within the compartments of the CNTs (Fig. 3.12 c and d) and the compartment wall thickness varied with the size of the Fe/Fe₃C particles. Conversely, the surface morphology of Basolite®-ArNH₃ (Fig. 3.12 a) had no CNTs present, which suggests the iron present in FePhen@MOF primarily acts as a catalyst for the graphitization of carbon.

3.3.2 Electrochemical Performance
Basolite® (Basolite-ArNH$_3$) was subjected to the same heat treatment as FePhen@MOF-ArNH$_3$ (i.e., Ar followed with NH$_3$ at 1050 and 1050 °C respectively) to be used as a reference for an iron-free catalyst in our RRDE studies. Typically, Pt/C is known to proceed predominantly through the 4 e$^-$ path in both alkaline and acidic media, as long as the surface is free of poisonous adsorbates$^{29}$.

**Figure 3.13: RRDE Polarization Plots in Alkaline Media.** Disk- and ring-currents measured during ORR on Tanaka Pt/C, Basolite-ArNH$_3$ and FePhen@MOF-ArNH$_3$ in O$_2$ saturated 0.1M KOH electrolyte at 20 mV/s with rotation rate of 1600 rpm at room temperature. $E_{\text{ring}}$=1.1 V vs RHE. Ring-current due to peroxide oxidation coincides with onset of reduction at the disk or Pt/C and Basolite-ArNH$_3$, however with FePhen@MOF-ArNH$_3$ oxidation of peroxide is shifted cathodically and is attributed to ORR by the quinone functionalities on the carbon.

However, in alkaline media it has been shown that specifically adsorbed hydroxyl species non-covalently interact with solvated oxygen molecules and the reduction proceeds through a 2e$^-$ outer sphere charge transfer process producing the super peroxide anion intermediate (HO$_2^-$), (as detected at the ring electrode of RRDE at ~0.8 V$^{49}$ (Fig. 3.13)) followed with an additional concerted 2e$^-$ reduction step to water. The same report showed that in contrast to this a non-PGM catalyst derived from heat treated Fe-tetraphenylporphyrin (Fe-TPP)$^{49}$ exhibits an
exclusive inner sphere concerted $4e^-$ reduction in alkaline media due to direct adsorption of $O_2$ and the kinetically favored hydrogen peroxide reduction reaction (HPRR)\textsuperscript{49}. Central to this mechanism was its correlation with Fe-N\textsubscript{4} (predominant four coordination) active sites formed in the divacant defects in the carbon basal plane\textsuperscript{49}.

In alkaline media Basolite®-ArNH\textsubscript{3} has an onset potential of 0.97 V (Fig. 3.14) and the oxidation of the peroxide intermediate detected at the ring electrode coincides with the onset of reduction at the disk (Fig. 3.13). This indicates that the peroxide is not stabilized on the active-site and ORR proceeds predominantly through a $2e^-$ reduction pathway. However, the presence of the iron in FePhen@MOF-ArNH\textsubscript{3} provides a 60mV improvement (w.r.to Basolite®-ArNH\textsubscript{3})

**Figure 3.14: ORR Polarization Comparison.** ORR polarization plots collected with FePhen@MOF-ArNH\textsubscript{3}, Basolite-ArNH\textsubscript{3} and Tanaka Pt/C in $O_2$ saturated electrolyte (0.1M HClO\textsubscript{4} and 0.1M KOH) at 20 mV/s with rotation rate of 1600 rpm at room temperature.
in the onset potential (1.03 V vs 0.97 V) as well as a 40 mV improvement in half-wave potential (E_{1/2}) (0.86 V vs 0.82 V) (Fig.3.14). In addition, the onset of the peroxy peak at the ring electrode is shifted cathodically to ~0.45 V (Fig. 3.13). Peroxy oxidation at 0.45 V is also observed on Pt/C electrocatalyst (Fig. 3.13) and has been attributed to 2e\(^-\) reduction of oxygen by the quinone functionalities of the carbon support\(^{49}\).

![Figure 3.15: RDE Investigation of Hydrogen Peroxide Reduction.](image)

However, FePhen@MOF-ArNH\(_3\) did not demonstrate enhanced HPRR activity (Fig. 3.15) and therefore this increase in activity cannot be attributed to peroxy specific Fe-N\(_x\) sites. These electrochemical results suggest incorporation of iron moieties in FePhen@MOF-ArNH\(_3\) in a different coordination environment as compared to classical Fe-N\(_x\) active site based electrocatalyst (as exemplified by Fe-TPP). Considering the XRD, SEM and TEM results presented above, it can be conjectured that Fe is present in the form Fe/Fe\(_3\)C, sub-surface to the N-doped carbon overlayer. As shown later in this chapter based on in situ element specific XAS spectroscopy results, subsurface Fe/Fe\(_3\)C are inactive towards O\(_2\) adsorption, and the ORR
activity predominantly appears to arise from the N-doped carbon surface. It appears the presence of the subsurface Fe/Fe$_3$C acts to stabilize the peroxide intermediate on the active-site in the alkaline medium.

When the same experiment was conducted in acidic media, FePhen@MOF-ArNH$_3$ exhibited a 90 mV improvement in $E_{\text{1/2}}$ (0.77 V vs 0.68 V) for ORR when compared with Basolite®-ArNH$_3$ (Fig. 3.14). This is evidenced by the higher onset potential ($E=0.93$ V vs. $E=0.89$ V) of FePhen@MOF-ArNH$_3$ vs. Basolite®-ArNH$_3$ in oxygen saturated 0.1M HClO$_4$. More interestingly, the onset of peroxide oxidation for both of the non-PGM electrocatalysts in acidic media now coincides with the onset of ORR (Fig. 3.16).

**Figure 3.16: RRDE Polarization Plots in Acidic Media.** Disk- and ring-currents measured on Tanaka Pt/C, Basolite-ArNH$_3$ and FePhen@MOF-ArNH$_3$ in O$_2$ saturated 0.1M HClO$_4$ electrolyte at 20 mV/s with rotation rate of 1600 rpm at room temperature. $E_{\text{ring}}=1.3$ V vs RHE. Ring-current due to peroxide oxidation coincides with onset of oxygen reduction at the disk for all catalysts, indicating peroxide intermediate is not stable in acidic media. However, the magnitude of the ring-current for Basolite-ArNH$_3$ is an order of magnitude higher than FePhen@MOF-ArNH$_3$ indicating the presence of Fe promotes the selectivity for the 4e- ORR pathway on FePhen@MOF-ArNH$_3$. 

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When switching to the low pH environment the peroxide intermediate is no longer present as an anion, but as a neutral species (H₂O₂) that has been shown to desorb more easily into the bulk electrolyte due to the absence of intermediate stabilization on the active site⁴⁹. Our results confirm this finding, but we also find that the oxidative ring current of Basolite®-ArNH₃ is an order of magnitude higher than FePhen@MOF-ArNH₃. This suggests that the presence of the iron moieties in FePhen@MOF-ArNH₃ still promotes the selectivity toward the 4e⁻ ORR pathway in acidic media. As mentioned above in our discussions on alkaline media results, subsurface Fe appears to be critical in the electrocatalysis in close concert with the synergistic effect of N-doped carbon (Fig. 3.12 c and d). This hypothesis is supported by the DFT calculations from Deng et al., ⁲³ in which the electronic properties of the carbon are enhanced by the interaction with nitrogen and Fe, enabling easier adsorption of O₂ and reduction to H₂O.
The inherent ORR activity exhibited by RRDE measurements of FePhen@MOF-ArNH₃ in acidic media (Fig. 3.14) are corroborated by single PEM fuel cell measurements. Polarization and durability curves were collected, on a membrane electrode assembly (MEA) employing a FePhen@MOF-ArNH₃ cathode, under the U.S. Department of Energy (DOE) suggested testing conditions of 80 °C, 100% relative humidity, 1 bar partial pressure of H₂/O₂ (1.5 bar total pressure) and/or 0.4 bar partial pressure of O₂ in H₂/air (2.5 bar total pressure). In a H₂/O₂ fuel cell FePhenMOF-ArNH₃ MEA generated a kinetic current density of more than 100 mA/cm² at 0.8 V_{ir-free} (Fig. 3.17), ranking it as one of the most active non-PGM cathodes reported to date.
with no FeN₆ moieties. Non-PGM cathodes require higher catalyst loadings (3 mg/cm² compared to 0.4 mgPt/cm² for Pt/C) that traditionally introduces mass-transport limitations, however FePhen@MOF-ArNH₃ was able to reach 75% of the power density of a state-of-the-art Pt/C cathode run under the same conditions. Although microporosity is a prerequisite for good catalytic activity in non-PGM’s, mesopores are essential for effective mass-transport, and we believe the increase in mesoporosity upon heat-treatment imparted superior mass-transport properties that result in the enhanced activity.

**Figure 3.18: H₂/Air Fuel Cell Polarization Curve.** H₂/air fuel cell polarization curve and corresponding power density curve for same MEA from a. A Pt/C (0.4 mgPt/cm² loading) cathode reference was used for comparison.

Upon switching to air as the oxidant the FePhen@MOF-ArNH₃ MEA (Fig. 3.18) reached a kinetic current density of 50 mA/cm² at 0.8 V_{non-iR corrected} and a peak power density of 0.38
W/cm² at 0.4 V (or a current density of 1 A/cm², the current DOE performance target), approximately 60% the power density reached by the Pt-based cathode under the same operating conditions. To our knowledge this is the highest reported H₂/Air activity to date by a non-PGM cathode containing no direct Fe-Nₓ coordination (as detailed in subsequent sections).

### 3.3.3 Identification of Fe-coordination

Earlier observations of heat treated Fe-TPP⁴⁹ (heat treatment of an existing macrocycle) and PVAG-Fe¹⁴ (Fe-based catalysts prepared from precursors using a reactive polymer approach), clearly indicated the presence of Fe-Nₓ active sites in addition to relatively small but stable Fe NPs in both electrocatalysts despite the different precursors/synthetic routes used. They also represent different types of defect structures on the carbon and hence Fe spin states. Among the key features associated with ORR on such Fe-Nₓ containing electrocatalyst elucidated using *in situ* XAS are (a) The Fe²⁺-N₄ active site undergoes a redox transition to (H)O-Fe³⁺-N₄ between 0.7 and 0.9 V vs. RHE, which correlates with an edge shift of the X-ray absorption near-edge spectra (XANES) characteristic of such a change in oxidation state with increasing potential (Fig. 3.19 a and b) and (b) a concomitant increase in the magnitude of the FT peak at ~1.6 Å (associated with Fe-N/O scattering) in the same corresponding potential showing oxide formation on the Fe in oxidation state 3 (Fig. 3.20 b). Fe³⁺-Nₓ (OH) formation close to 0.9 V vs. RHE is clearly indicated by the forward FT at the Fe K-edge (Fig. 3.20 b) also means that the onset of oxygen reduction is intimately related to such a redox transition (this is also supported by redox peaks in alkaline and acidic media). In contrast to these observations on non-PGM catalysts containing Fe-Nₓ coordination, the Fe K edge FT of the EXAFS for FePhen@MOF-ArNH₃ does not contain the characteristic Fe-N/O peak at 1.6 Å (indicative of Fe-N interaction at and below 0.7 V and an additional Fe-O(H) interaction at higher potentials) and is characterized
instead by a peak at ~2.2 Å coinciding with Fe-Fe scattering as seen by comparison with characteristic corresponding peaks from metallic Fe and Fe₃C standards.

Figure 3.19: *In situ* XAS Investigation of Fe-based Non-PGMs. Potential dependent normalized Fe K-edge XANES of FeTPP, PVAG-Fe, FePhen@MOF-ArNH₃ and carbon corroded Fe-Phen@MOF-ArNH₃ collected in N₂ saturated 0.1M HClO₄, inset Δµ = µ (0.9 V) - µ (0.3 V). (d) Potential dependent FT-EXAFS of same electrocatalysts in b collected in O₂ saturated 0.1M HClO₄.

However, *in situ* XANES is much more sensitive than EXAFS at detecting the presence of FeNₓ species and as the potential is increased the Fe K-edge XANES energy of
FePhen@MOF-ArNH₃ remains unchanged. These results also clearly point towards the fact that since FePhen@MOF-ArNH₃ consists of subsurface Fe/Fe₃C type moieties and their role in any Fenton’s type peroxide induced free radical formation is unlikely. This is a very critical distinction from the Fe-Nₓ based non-PGM electrocatalysts.

3.4 Conclusions

In this work, we introduced a Fe-based non-PGM ORR electrocatalyst, FePhen@MOF-ArNH₃, which utilizes a MOF-support that acts as a host for the Fe-based sites. Orderly dispersion of the Fe-chelates is achieved with the encapsulation synthesis and gives rise to an electrocatalyst with a distinct active site. In addition, FePhen@MOF-ArNH₃ exhibits one of the highest reported activities for ORR in acidic media and outperforms the benchmark Pt/C catalyst in alkaline media. The exceptional ORR activity measured using a RRDE setup in acid translated to the superior PEM fuel cell performance where FePhen@MOF-ArNH₃ showed excellent mass-transport properties and stability that has not been demonstrated by previous non-PGM cathodes. Characterization techniques revealed the Fe is present as Fe/Fe₃C nanoparticles that are subsurface to a N-doped carbon overlayer; however, they seem to play an important role in the electrocatalysis by imparting a synergistic effect on the N-doped carbon that allows stabilization of the peroxide intermediate and enables the full 4e⁻ reduction of oxygen to water. What sets this work apart from others is the definitive proof that this exceptionally active non-PGM electrocatalysts lacks direct Fe-Nₓ coordination when studied using in situ synchrotron XAS at the Fe K-edge under simulated conditions of an operating PEM cell. All previous reports in the literature have been obtained under ex situ conditions that cannot account for catalyst structure changes at the catalyst-electrolyte interface with an applied potential. This is the first Fe-based non-PGM catalyst reported to date that shows no empirical evidence of the Fe-Nₓ coordination
witnessed in the most active materials, but is predominantly comprised of Fe/Fe₃C nanoparticles encapsulated by an N-doped carbon structure. The lack of evidence suggesting the presence of Fe-Nₓ moieties under in situ conditions allows us to conclusively attribute the majority of the ORR activity to the N-doped carbon structure. Based on our results we believe the Fe first acts as a catalyst for the graphitization of N-doped carbon during the heat treatment in which some iron is integrated into the carbon and enhances the electrocatalytic properties enabling the 4 e⁻ reduction of oxygen.

3.5 Acknowledgements

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3.6 Chapter 3 References


31 Arruda, T. M. *et al.* Fundamental aspects of spontaneous cathodic deposition of Ru onto Pt/C electrocatalysts and membranes under direct methanol fuel cell operating conditions:


Chapter 4

Anion Resistant Oxygen Reduction Electrocatalyst in a Phosphoric Acid Fuel Cell

4.1 Introduction

Development of environmentally friendly energy conversion devices is a contemporary challenge facing scientists, and fuel cell technologies are promising candidates due to their high theoretical energy density. Phosphoric acid fuel cells (PAFC) were the first commercially viable fuel cell technology and are currently used for stationary power applications in multiple countries\textsuperscript{1,2}. However, utilizing a membrane electrolyte allows the proton exchange membrane (PEM) fuel cell technology to be lightweight and ideal for mobile/transportation applications. The current state-of-the-art membrane electrolyte (Nafion®) relies on proper humidification for proton conductivity, which limits the operation temperature to well below 100 °C. Operating at lower temperatures introduces complicated heat and water management issues, as well as increasing CO poisoning effects\textsuperscript{3}. The PAFC technology employs a concentrated phosphoric acid (85-100% H\textsubscript{3}PO\textsubscript{4}) electrolyte that allows operation between 150 to 220 °C, which overcomes the aforementioned complications as well as allowing the waste heat to be exploited thereby increasing the overall efficiency of the fuel cell\textsuperscript{2}. High-temperature proton exchange membrane (HT-PEM) technologies, employing polybenzimidazole (PBI) membranes doped with phosphoric acid\textsuperscript{4-6}, have emerged in the last decade in an effort to capitalize on the advantages of both the PEM and PAFC technologies.

Another benefit of high operating temperatures is increased reaction kinetics of the hydrogen oxidation reaction (HOR) and oxygen reduction reaction (ORR) on the anode and cathode respectively\textsuperscript{7}. The gold standard for electrocatalysis in acidic media is platinum
supported on carbon (Pt/C). However, Pt-based electrocatalysts suffer from poisoning effects in phosphoric acid electrolyte due to adsorption of molecular and ionic species on the catalyst surface that leads to loss of catalytic activity. This activity loss is most detrimental on the cathode, where the slow kinetics of ORR introduces an overpotential that accounts for most of the voltage loss of the fuel cell\textsuperscript{8}. Extensive studies have been conducted in the past to understand the sources of electrocatalytic activity loss in an effort to improve catalysts. Zeleney\textsuperscript{9} et al. conducted a radiotracer/Fourier transform infrared spectroscopy (FTIR) study on Pt-based electrodes and found that the potential dependence of H\textsubscript{3}PO\textsubscript{4} adsorption was governed by water displacement and oxide formation, which resulted in adsorption well above the potential of zero charge (pzc). Most cathodic fuel cell reactions are initiated above the pzc and oxygen must compete with adsorbed species for access to the active site. Tanaka\textsuperscript{10} et al. found that Pt catalyzed ORR in concentrated phosphoric acid exhibits a structural sensitivity that originates from the 3-fold adsorption of the phosphate anion (H\textsubscript{2}PO\textsubscript{4}\textsuperscript{−}) on the Pt(111) surface, but only a one- or two-fold adsorption on Pt(100) and Pt(110) surfaces. Their findings were corroborated by He\textsuperscript{11} et al., who showed ORR on Pt single crystals was most severely poisoned on Pt(111) due to the abundance of 3-fold surface sites for phosphate anion adsorption. However, they found that poisoning was diminished when Pt(111) was alloyed with Sn by virtue of the steps and defects introduced on the PtSn(111) surface. A follow up study was conducted on a PtNi alloy in an attempt to mitigate phosphate anion poisoning by surface engineering\textsuperscript{12}. Electrochemical and X-ray absorption spectroscopic (XAS) measurements determined poisoning of ORR was less severe on PtNi/C than Pt/C due to the phosphate anions remaining adsorbed on PtNi/C at a higher potential as compared to Pt/C. It was concluded that the presence of phosphate anions on
PtNi/C at the higher voltages prevented OH adsorption (known to hinder ORR), thereby freeing more ORR active sites.

Despite the poisoning issue, Pt-based electrocatalysts still represent the benchmark for ORR activity and durability in acid-based fuel cell technologies. However, for the last several decades extensive research has been dedicated to the development of non-platinum group metal (non-PGM) electrocatalysts to replace Pt-based cathode electrocatalysts. Recent progress in this field has produced PEM cell activity and durability that rivals that of Pt-based materials. Additionally, researchers have shown preliminary results that suggest the ORR activity of Fe-based non-PGMs is resistant to anion poisoning in a variety of electrolytes. A new non-PGM study specific to phosphate poisoning used electrochemical measurements conducted at room temperature to show improved phosphate tolerance of a Fe-based electrocatalysts when compared to Pt/C. However, the source of phosphate anion tolerance on Fe-based non-PGM electrocatalysts and their ability to withstand the operation temperature and environment of HT-PEM fuel cells has not been addressed.

This study will investigate the use of the MOF-supported Fe-based non-PGM (FePhen@MOF-ArNH3), introduced in Chapter 3, as an alternative ORR electrocatalyst in HT-PEM fuel cells. Preliminary tests of FePhen@MOF-ArNH3 showed very little activity loss in the presence of phosphoric acid when compared with its Pt-based counterpart. Physical characterization elucidates the make-up and morphology of the material and electrochemical testing monitors the kinetics of ORR in the presence of varied concentrations of phosphoric acid. In addition, in situ XAS is used to monitor how the electronic and structural properties of the Fe present in FePhen@MOF-ArNH3 are changed under the operating electrochemical environment with and without the presence of phosphoric acid. The Δμ technique is applied to investigate
changes in adsorbate coverage as a function of potential in an effort to understand the interaction of the phosphate anions with the active surface of FePhen@MOF-ArNH$_3$.

4.2 Experimental Methods

4.2.1 Catalyst Synthesis

The commercial Pt/C (46%) electrocatalyst is produced and obtained from Tanaka Kikinzoku International KK. For the synthesis of FePhen@MOF 2-methylimidazole (5.90g, 0.072mol, 160eq) was dissolved in methanol (20mL) at room temperature with stirring in flask A. In flask B, zinc(II) nitrate $\chi$-hydrate (10.80g, 0.036mol, 80eq) and 1,10-phenanthroline monohydrate (12.96g, 0.072mol, 160eq) were dissolved in methanol (30mL) and water (45mL) at room temperature with stirring. Once both flasks’ contents were fully dissolved, flask B was added to flask A. Iron(II) acetate (0.081g, 4.66 x 10$^{-4}$mol, 1eq) was added to the reaction, and this was stirred at room temperature for 24h. A second reaction identical to the aforementioned vessel was assembled, and the two separate reactions progressed in tandem. Before addition of iron(II) acetate, the reaction began to turn slightly milky white/turbid in appearance. This intensified over the course of the reaction, resulting in a fine suspension turbid and pale orange in color. The two reaction vessels were then combined in 6x50mL centrifuge tubes and centrifuged at 4000 rpm for 25min, washed 3 times with methanol (6x40mL each time), centrifuging at 3700 rpm for 17 minutes in between each washing. The resulting orange/white solid was dried in a vacuum oven for 6-12 hours at 60-70°C and afforded formation of the desired FePhen@MOF, a light tan powder (typically 4.5-5.5g total yield from the two combined reaction vessels). The dried powder was then subjected to either one or two heat-treatments, i.e., in argon at 1050 °C with a 1 hour dwell time (FePhen@MOF-Ar) and ammonia at 1050 °C with
an 18 minute dwell time (FePhen@MOF-ArNH$_3$) respectively. Perchloric acid electrolyte was prepared using double-distilled 70% perchloric acid (GFS Chemicals). The phosphoric acid (H$_3$PO$_4$, 85%, Alfa Aesar) was purified following a standard procedure described in the literature$^{34}$.

### 4.2.2 Electrochemical Characterization

Electrochemical measurements were carried out on glassy carbon (GC) disk (5.61 mm diameter, Pine Instruments) that was polished with 0.05-micron alumina paste (Buehler, Lake Bluff, IL) and then sonicated in distilled water and Isopropyl alcohol. Catalysts inks were prepared by dispersing the catalyst in a volume of 1:1 Millipore water:Isopropyl alcohol with 10vol% of 5wt% Nafion® as a binder. The ink solution was then sonicated approximately 30 minutes to get a uniform suspension. A small volume of the catalyst ink was deposited on the GC substrate to obtain a platinum metal loading of 15 µg/cm$^2$ and a NPMC loading of 600 µg/cm$^2$. All electrochemical measurements were carried out at room temperature (20-25 °C) in a standard electrochemical cell (Chemglass) with an acid electrolyte using a rotating disk electrode (RDE) setup from Pine Instrument Company connected to an Autolab bipotentiostat (PGSTAT302N). Cyclic voltammetry was run on both Pt and non-Pt catalysts in 0.1 M perchloric acid (HClO$_4$) bubbled with argon. ORR was investigated by the RDE technique after bubbling oxygen in the 0.1 M HClO$_4$ solution followed with incremental addition of 1mM, 10 mM and 100 mM phosphoric acid (H$_3$PO$_4$). Scans were recorded at 20 mV/s and all potentials are referenced to a reversible hydrogen electrode (RHE) scale made from the same solution as the electrolyte.

### 4.2.3 Physicochemical Characterization
X-ray diffraction was performed on a Rigaku (model Ultima-IV) diffractometer with Cu Kα radiation (λ=1.5418 Å) at 40 kV and 40 mA. The scan speed was 2-20 seconds and the step size was 0.1°. N₂ sorption analysis was performed on a Quantachrome NOVA 2200e at 77 K. Total surface area was determined by the Brunauer-Emmett-Teller (BET) method and pore size distribution was determined using Non-Local Density Functional Theory (NLDFT) split pore method from the NovaWin software. Thermogravimetric analyses (TGA) were performed on TA Instruments SDT Analyzer Q600 from 22-1100°C with a ramp rate of 5°C/min and dwelling for 5min at maximum temperature. All studies were conducted under argon atmosphere, with a flow rate of 100mL/min. Scanning electron microscopy was performed on a Hitachi S-4900 FSEM instrument with an accelerating voltage of 3-5 keV with samples mounted on a carbon adhesive stub attached to an aluminum sample stage. High-resolution transmission electron microscopy images were taken on a JEOL 2010 field emission gun (FEG) TEM at 200 kV with samples deposited on a holey carbon film on a 300 mesh copper grid.

4.2.4 X-ray Absorption Spectroscopy (XAS) Measurements

The in situ XAS studies at the Fe K-edge (7112 eV) were performed at X3B beamline of National Synchrotron Light Source (NSLS, Brookhaven National Laboratory, NY). A specially designed spectro-electrochemical cell was utilized and has been described previously. The Fe K-edge spectra were collected in fluorescence mode with a 32-element Ge solid state detector as a function of potential in the range 0.1 – 0.9 V vs. RHE. A pseudo steady-state was established by holding the cell for approximately 5 minutes before collecting the spectra. The electrolyte, 0.1 M HClO₄, was saturated with either argon or oxygen. Athena³⁶ and Artemis³⁷ programs were used to process and fit the data. IFEFFIT suite³⁶ was used to calibrate, align and normalize the scans. FEFF6 code³⁸ was used to calculate scattering paths to model the χ(R) transforms. Delta-
Mu (Δµ) analysis of the Fe K-edge followed specific normalization procedures that are described in the literature\textsuperscript{35}. Difference spectra were obtained by utilizing the equation (3) where µ(V, Ar 100 mM H3PO4) represents the XANES of the catalyst at various potentials in Ar saturated 0.1 M HClO\textsubscript{4} electrolyte doped with 100 mM H\textsubscript{3}PO\textsubscript{4} and µ(0.3V, Ar) is the XANES at 0.3V in Ar-saturated 0.1 M HClO\textsubscript{4} electrolyte without doping H\textsubscript{3}PO\textsubscript{4} used as the reference due to the absence of adsorbates on the surface of the catalyst. FEFF8 code\textsuperscript{39} was used to generate theoretical delta mu curves (Δµt) using the relationship

\[ Δµt = \mu(PO_4^{ads-Fe_6}) - \mu(Fe_6) \]  

(4.1)

where the adsorbate is in a specific binding site on Fe.

4.3 Results and Discussion

4.3.1 Electrochemical Performance
A commercially available Pt/C electrocatalyst (Tanaka Kikinzoku International KK (Japan), average particle size 15 Å) was used as a reference material in this study to estimate the poisoning effect of phosphoric acid on FePhen@MOF-ArNH₃. As mentioned previously, Pt/C is the gold standard for ORR electrocatalysis in acidic media despite previous reports that have
shown that adsorption of phosphate anions on surface active sites severely inhibits the electrocatalytic activity\textsuperscript{11,12}. In order to determine the effect of phosphate poisoning on the kinetic parameters of ORR, the rotating disk electrode (RDE) technique was performed in 0.1M HClO\textsubscript{4} with incremental dosing of phosphoric acid (0-100 mM H\textsubscript{3}PO\textsubscript{4})(Fig. 4.1).
Phosphoric acid is polyprotic in nature, but based on the dissociation constants the predominant species at pH 1 is H$_2$PO$_4^-$ (concentration of HPO$_4^{2-}$ is six orders of magnitude less than H$_2$PO$_4^-$ at room temperature). The RDE profiles collected at 1600 rpm for Pt/C and
FePhen@MOF-ArNH$_3$ in 0.1 M HClO$_4$ are shown in Figure 4.2a. Each RDE profile can be broken down into three regions: (1) diffusion controlled region (<0.7 V), (2) mixed diffusion-kinetic region (0.7 V to 0.9 V for Pt/C and 0.7 V to 0.8 V for FePhen@MOF-ArNH$_3$) and (3) the kinetic region (>0.9 V for Pt/C and >0.8 V for FePhen@MOF-ArNH$_3$). As can be seen in the kinetic region of Pt/C (Fig 4.2a) in 0 mM H$_3$PO$_4$ the on-set of ORR is ~1.0 V vs RHE, and a well-defined limiting current is established in the diffusion controlled region. The diffusion limiting current ($i_{\text{lim}}$) is defined by the Levich equation:

$$i_{\text{lim}}=0.62nFD^{2/3}v^{-1/6}C_o$$  

(4.2)

where $n$ is the number of mole of electrons transferred, $F$ is the Faraday constant, $D$ is the diffusion coefficient of O$_2$ in 0.1 M HClO$_4$, $v$ is the kinematic viscosity and $C_o$ is the concentration of O$_2$ in the electrolyte. Introduction of just 10 mM H$_3$PO$_4$ into the electrolyte causes a slight decrease in the magnitude of the limiting current, which indicates that O$_2$ is being inhibited from reaching the electrode surface. To further illustrate the effect of phosphate adsorption on platinum, cyclic voltammograms (CV) with increasing concentrations of phosphoric acid are shown in Figure 4.3. The solid black line represents the signature features of polycrystalline platinum in clean perchloric acid$^{40}$; Pt-O[H] formation and reduction at high potentials (0.7 and 0.8 V vs. RHE respectively) and symmetric peaks associated with hydrogen underpotential deposition (H$_{\text{upd}}$) below 0.4 V vs. RHE. As phosphoric acid is introduced to the electrolyte a reduction in the Pt-O[H] and H$_{\text{upd}}$ peak are observed. Additionally, new peaks around 0.55 V vs. RHE appear that have been attributed to the adsorption/desorption of phosphate anions$^{10,11}$. The electrochemical surface area of platinum, can be calculated from the charge density of the H$_{\text{upd}}$ peak$^{41}$, continually decreased (59 to 39 m$^2$/g$_{\text{Pt}}$ for 0 vs. 100 mM H$_3$PO$_4$ in 0.1M HClO$_4$) with increasing concentration of phosphoric acid. The reduction in magnitude of
the limiting current density observed in Figure 4.2 a might be attributable to the blocking of platinum active sites.

**Figure 4.3: Phosphate Anion Poisoning of Pt/C.** Cyclic Voltammogram of Tanaka Pt/C in argon saturated 0.1 M HClO₄ electrolyte at 20 mV/s at room temperature with incremental addition of 1-100 mM H₃PO₄.

Furthermore, when compared with the profile in the absence of H₃PO₄ the half-wave potential (E₁/₂), a parameter that is characteristic of capacity for ORR catalysis, is shifted cathodically ~150 mV (0.87 vs 0.72 V). To further probe the kinetic effect of adsorption of the phosphate anion Tafel plots were extracted from the ORR polarization curves in order to evaluate the Tafel slope. This allowed us to only consider the interfacial dynamics of the system since the Tafel slope is determined by the transfer coefficient and the number of electrons transferred in the rate limiting step. Two Tafel slopes are usually observed for ORR kinetics on
Pt surfaces, a smaller slope at low overpotentials is attributed to ORR on the oxide covered Pt-surface and the Tafel slope increases at higher overpotentials when the surface is free of oxides\textsuperscript{10,42}. The ORR polarization curves were corrected for mass transport by applying the equation

\[ i_k = i_{\text{lim}} \times \frac{i}{i_{\text{lim}} - i} \]  

(4.3)

where \( i_k \) represents the kinetic current density, \( i_{\text{lim}} \) is the diffusion limiting current density from eqn (4.2) and \( i \) is the current measured from ORR. As can be seen in Figure 4.2b, the shape is changed (0 vs. 10 mM H\textsubscript{3}PO\textsubscript{4}) indicating the ORR rate limiting step on Pt/C is different in the presence of phosphoric acid. In contrast, when the same experiment was performed with FePhen@MOF-ArNH\textsubscript{3} the RDE profile of 0 vs 10 mM H\textsubscript{3}PO\textsubscript{4} (Fig. 4.2a) are virtually identical. FePhen@MOF-ArNH\textsubscript{3} was able to reach approximately the same limiting current density and only a 10mV shift in \( E_{1/2} \) was observed when 10 mM H\textsubscript{3}PO\textsubscript{4} was added to the electrolyte. Also, the two Tafel plots (0 vs. 10 mM H\textsubscript{3}PO\textsubscript{4}, Fig. 4.2 b) overlay almost perfectly and show no change in reaction mechanism due to the presence of phosphoric acid. These results clearly show that the active sites of FePhen@MOF-ArNH\textsubscript{3} are not poisoned by phosphoric acid.
The natural tolerance of FePhen@MOF-ArNH₃ to phosphate anion poisoning exhibited by RDE measurements (Fig. 4.2a) was substantiated by single HT-PEM fuel cell measurements.
Polarization curves were collected at 180 °C and 1.5 bar pressure H₂/O₂ on a membrane electrode assembly (MEA) fabricated using a phosphoric acid doped polymeric membrane sandwiched between a FePhen@MOF-ArNH₃ cathode and Pt/C anode. For comparison, a duplicate MEA substituting Pt/C for FePhen@MOF-ArNH₃ on the cathode was run under identical conditions. The FePhen@MOF-ArNH₃-based MEA generated a kinetic current density of approximately 160 mA/cm² at 0.8 V_{irr-free} (Fig. 4.4b); outperforming the Pt/C-based MEA in the low current density region (Fig. 4.3b). In the high current density region it can be seen that FePhen@MOF-ArNH₃ suffers from some mass-transport limitations that were not as detrimental on the Pt/C MEA (Fig. 4.4a). The mass transport losses witnessed could be an effect of the electrode layer thickness. Non-PGM cathodes require a higher catalyst loading than Pt/C cathodes, and are generally an order of magnitude thicker (100 µm vs. 10 µm). However, these outstanding preliminary results embolden the opportunity to replace Pt/C catalysts in HT-PEM technologies utilizing phosphoric acid electrolyte and compels further understanding of the source of ORR activity with FePhen@MOF-ArNH₃ in phosphoric acid.

4.3.2 Physicochemical Characterization

The as synthesized FePhen@MOF material was subjected to two heat treatments, first in argon at 1050 °C followed by ammonia at 1050 °C, to engender electrical conductivity and ORR activity. Thermogravimetric analysis (TGA) performed on FePhen@MOF (Fig. 4.5) reveals a gradual weight loss (35-350 °C) due to loss of guest species (H₂O < 100 °C and MeOH >100 °C) followed by a small mass loss above 350 °C possibly due to the decomposition of some free 1,10-phenanthroline.
The mass loss plateaus until 550 °C is reached and a steep drop signifies the decomposition of the MOF framework and eventual evaporation of Zn around 900 °C. The TGA conditions simulate the heat treatment in argon, hence we believe the resultant catalyst is a porous graphitic framework formed from the decomposition of the MOF support in which the Fe is retained and the Zn is lost through evaporation. The additional heat treatment in ammonia is known to introduce nitrogen functionalities and etch the amorphous carbon.

Figure 4.5: Thermogravimetric Analysis of FePhen@MOF. TGA of FePhen@MOF with inset of derivative plot. Measurements was run under argon with 100 mL/min flow rate. Sample was heated at ramp rate of 5 °C/min.
An additional TGA analysis of the final electrocatalyst, FePhen@MOF-ArNH₃ (Fig. 4.6), revealed remarkable thermal stability at the elevated temperatures that is required for operation of HT-PEM fuel cells. FePhen@MOF-ArNH₃ shows a small drop in mass below 100 °C due to evaporation of water followed by a long plateau from 100-900 °C. The TGA trace of Pt/C is also characterized by water evaporation below 100 °C, but is followed by a drop in mass from 200-250 °C that is not witnessed with FePhen@MOF-ArNH₃. A possible source of mass loss at this temperature range could be attributed to the degradation of the O functional groups on the carbon⁴⁵ or from carbon combustion catalyzed by the Pt particles⁴⁶. FePhen@MOF-ArNH₃ compared to Pt/C displayed exceptional thermostability and maintained 90% of its original mass.

Figure 4.6: Thermal Stability ORR Electrocatalysts. TGA analysis of heat treated FePhen@MOF-ArNH₃ and Tanaka Pt/C. All measurements were run under argon with 100 mL/min flow rate. Samples were heated at ramp rate of 5 °C/min.
up to 950 °C (Fig. 4.6), as opposed to Pt/C which only maintained 90% of its original mass up to ~200 °C.

Figure 4.7: XRD of FePhen@MOF-ArNH₃. X-ray diffraction pattern (XRD) of FePhen@MOF-ArNH₃ and diffraction patterns of iron, iron carbide and iron nitride.
In order to understand the source of thermal stability X-ray diffraction (XRD) was performed on FePhen@MOF-ArNH₃ to identify crystalline phases that were present following the two heat treatments. The XRD pattern of FePhen@MOF-ArNH₃ (Fig. 4.7) reveals diffraction lines of graphite and several metallic iron phases (iron-Fe (Im-3m), iron carbide-Fe₃C (Pnma) and iron nitride-Fe₂N (P-31m(162)). Scanning electron microscopy (Fig. 4.8 a) revealed numerous bamboo-shaped carbon nanotubes (CNTs) intermingled in a porous carbon network. High-resolution transmission electron microscopy (HR-TEM) confirmed the presence of CNTs with distinct bamboo-like joints (Fig. 4.8 b and c), characteristic of nitrogen-doping in the carbon²⁰,⁴⁷, and revealed particles within some of the CNT compartments that could not be indexed as pure Fe or Fe₃C (Fig. 4.8 c and d). Based on these results we believe the Fe is retained throughout the heat treatments and agglomerates into particles (metallic Fe NPs) in which the dissociated carbon and nitrogen diffuses through to form the witnessed CNTs.
Nitrogen-sorption analysis was performed to monitor the change of surface area and porosity evolution of FePhen@MOF-ArNH$_3$ throughout the synthetic process. Brunauer-Emmet-Teller (BET) surface area of the as synthesized FePhen@MOF was measured and compared with a commercially available ZIF-8 MOF (Sigma, Basolite® Z1200). FePhen@MOF showed a diminished surface area in comparison to Basolite (Fig. 4.9 a) (424 m$^2$/g vs. 1813 m$^2$/g) due to the encapsulation of the iron complex within the pores, causing a substantial reduction in the overall pore volume. However, the surface area increased significantly following the two heat...
treatments in argon and ammonia respectively, engendering FePhen@MOF-ArNH$_3$ with a BET surface area comparable to un-heat treated Basolite® (1200 m$^2$/g vs. 1813 m$^2$/g). Using density functional theory (DFT) split pore method simulation (Fig. 4.9b) the pore size distribution of FePhen@MOF reveals its microporous arrangement (<20 Å) and narrow size distribution. Yet when subjected to the heat treatment process the pore size distribution altered dramatically. The volume and size of micropores in FePhen@MOF-ArNH$_3$ increased in comparison to FePhen@MOF, and mesopores (20-40 Å) that were not originally present in FePhen@MOF were introduced following the heat treatments.

**Figure 4.9: N$_2$ Sorption Analysis.** (a) Bar graph plot of Brunauer-Emmett-Teller (BET) surface area of Basolite®, FePhen@MOF and FePhen@MOF-ArNH$_3$. (b) Pore volume as a function of half pore width of FePhen@MOF and FePhen@MOF-ArNH$_3$ using DFT method of split pore model.

The presence of Fe in the synthesis of non-PGMs is essential to obtain the most active electrocatalysts$^{48}$, but the role of Fe in ORR activity is ambiguous. X-ray absorption spectroscopy (XAS) is an element specific technique that allows us to probe the structural and electronic nature of the Fe in FePhen@MOF-ArNH$_3$. Using a specially designed spectro-electrochemical cell$^{35}$ we are able to collect spectra *in situ*, simulating operating conditions of a
fuel cell, which further enhanced the sensitivity of the technique. Spectra were collected as a function of potential on an electrode in 0.1 M HClO₄ electrolyte saturated with either oxygen or nitrogen. Electrodes held at 0.3 V vs. RHE are considered to be free of adsorbates and are representative of the catalyst structure with a clean surface²². Shown in Figure 4.10 is the Fourier Transform (FT) extended X-ray absorption fine structure spectra (EXAFS). Analysis up to the second shell was applied at the Fe K-edge of FePhen@MOF-ArNH₃ data at 0.3 V (fitting results summarized in Table 4.1). FePhen@MOF-ArNH₃ exhibits one dominant FT peak at ~2.2 Å (without phase correction), which can be fit well with a Fe-Fe scattering path with a bond length of ~2.51 Å. This corresponds well with the known Fe-Fe bond length in bulk iron (2.49 Å) and/or iron carbide (2.48 Å). A small shoulder off the main peak was accounted for with a Fe-C/N scattering path with a bond length of ~1.96 Å. C and N cannot be distinguished by XAS as surrounding atoms, but based on our XRD results we suspect that iron carbide and iron nitride are both present.
Figure 4.10: *In Situ* EXAFS Fit of FePhen@MOF-ArNH₃. EXAFS of FePhen@MOF-ArNH₃ in N₂ saturated 0.1M HClO₄ held at 0.3 V vs. RHE.
X-ray absorption near-edge structure (XANES) spectra are very sensitive to changes in the oxidation state of Fe, and become even more sensitive when coupled with our *in situ* technique. Previous studies of Fe-based non-PGMs (heat treatment of a pre-existing macrocycle FeTPP$^{22}$ and PVAG-Fe$^{23}$ prepared using precursors from a reactive polymer method) identified Fe-N$_x$ active sites in which the Fe-ion is coordinated by nitrogen in the carbon scaffold. These studies revealed that a key feature of ORR occurring on Fe-N$_x$ active sites was that the FeN$_x$ active site undergoes a redox transition when the potential is increased from 0.3 to 0.9 V vs. RHE (Fe$^{2+}$ to Fe$^{3+}$), which causes a XANES edge shift due to the change in oxidation state. As can be seen in Figure 4.11, the Fe K-edge XANES of FePhen@MOF-ArNH$_3$ remains unchanged as the potential is increased from 0.1 to 0.9 V vs. RHE, indicating that the Fe is not redox active and FePhen@MOF-ArNH$_3$ is devoid of FeN$_x$ active sites. The presence of direct Fe-N$_x$

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<th>EXAFS</th>
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<tr>
<td>@ 0.3 V</td>
<td>Fe-C/N/O</td>
</tr>
<tr>
<td>CN</td>
<td>1.2 ± 0.7</td>
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<tr>
<td>R (Å)</td>
<td>1.97 ± 0.06</td>
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<td>Fe-Fe</td>
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<td>6.8 ± 1.2</td>
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<td>2.51 ± 0.01</td>
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Table 4.1: *In Situ* EXAFS Fit Results for FePhen@MOF-ArNH$_3$. EXAFS fit results for FePhen@MOF-ArNH$_3$. Experiments performed at the Fe K-edge (7112 eV) as a function of potential in N$_2$ saturated 0.1M HClO$_4$ electrolyte. Coordination number (CN) and phase-corrected bond length (R) in angstrom are shown.
coordination in non-PGM electrocatalysts introduces stability concerns owing to the possibility of any Fenton type process involving exposed Fe ions producing peroxide generated free radicals\(^{49}\).

\[ \text{Figure 4.11: } \text{In Situ XANES Characterization of FePhen@MOF-ArNH}_3. \text{ Potential dependent normalized Fe K-edge XANES of FeTPP, PVA-G-Fe and FePhen@MOF-ArNH}_3 \text{ collected in N}_2 \text{ saturated 0.1M HClO}_4. \]

Based on our\( \text{ ex situ}\) physicochemical results we believe that during the heat treatment the MOF support will decompose to form a porous graphitic framework and the Fe will agglomerate to form particles of various sizes. As the temperature increases some of the carbon and nitrogen that has dissociated from the precursors diffuses to the Fe nanoparticles (Fe NPs) that catalyze the growth of CNTs. Then as the temperature lowers some of the carbon and/or nitrogen will be trapped in the Fe NPs resulting in Fe/Fe\(_x\)C/Fe\(_x\)N particles that are surrounded by graphitic carbon.
layers doped with nitrogen. Our \textit{in situ} XAS results confirm that FePhen@MOF-ArNH$_3$ is made up of metallic Fe particles and has no detectable Fe-N$_x$ moieties.

4.3.3 Delta Mu Anion Adsorption Investigation

As we mentioned previously, XAS is a bulk averaging technique and requires the use of the spectral subtraction method Delta Mu ($\Delta \mu$) applied to the XANES region in order to remove the bulk structure of the electrocatalyst$^{32,33}$. The Fe K-edge XANES spectra in 0.1M HClO$_4$ collected at 0.3 V was subtracted from a spectrum in the presence of 100 mM H$_3$PO$_4$ (Fig. 4.12) by applying the equation:

$$\Delta \mu = \mu(\text{V, Ar 100 mM H}_3\text{PO}_4) - \mu(0.3 \text{ V, Ar})$$

(4.4)

to study the adsorbate coverage on the electrocatalyst surface. The adsorbate coverage on FePhen@MOF-ArNH$_3$ as a function of potential was monitored and the experimental $\Delta \mu$ spectrum (Fig. 4.12, inset) was compared with theoretical $\Delta \mu$ spectra generated from models (Fig. 4.13) representative of two different modes of phosphate anion adsorption on a Fe$_6$ cluster$^{50}$. However, analysis of the experimental $\Delta \mu$ spectrum of FePhen@MOF-ArNH$_3$ revealed the $\Delta \mu$ amplitude ($|\Delta \mu|$) was within the noise range ($<0.005 |\Delta \mu|$) due to the lack of difference between the XANES spectra with and without H$_3$PO$_4$ (Fig 4.12).
Theoretical models predicted a $|\Delta \mu|$ of approximately 0.2 if the phosphate group was to interact with a Fe cluster. In a previously reported study of Fe-based non-PGMs a $|\Delta \mu|$ of close to 0.4 was observed for changes on the Fe-surface associated with the interaction of the metal with oxygenated adsorbates.23

Figure 4.12: *In Situ* XANES Investigation of Anion Adsorption. Fe K-edge XANES of FePhen@MOF-ArNH$_3$ at 0.3 V vs. RHE in N$_2$ saturated 0.1M HClO$_4$ with and without 100 mM H$_3$PO$_4$, with $\Delta \mu = \mu (0.9 \text{ V}) - \mu (0.3 \text{ V})$ (inset).
The phosphate study mentioned previously conducted with Pt/C and PtNi/C electrocatalyst\textsuperscript{12} found \( \text{H}_2\text{PO}_4^- \) adsorbed on Pt at a 3-fold fcc site for Pt/C, while PtNi/C preferred an atop site. The surface changes observed from the interaction of the phosphate with the

\[ \text{Figure 4.13: Theoretical Models of Anion Adsorption.} \ (a) \text{Theoretical } \Delta \mu \text{ signatures calculated by FEFF8 of illustrated } \text{PO}_4^- \text{ (anion charge was not considered) adsorption on Fe}_6 \text{ cluster.} \ (b) \text{Theoretical } \Delta \mu \text{ signatures calculated by FEFF8 of illustrated } \text{PO}_4 \text{ adsorption on Pt}_6 \text{ cluster.} \]
platinum metal produced a $\Delta\mu$ of 0.2, which is nearly an order of magnitude higher than the reliability threshold of 0.03 set for the Pt L$_3$-edge.$^{51}$

Combining these results with the microscopy imaging we believe the Fe particles are located subsurface to graphitic layers and are protected from contact with electrolyte, therefore preventing phosphate anions to adsorb on the Fe present in FePhen@MOF-ArNH$_3$. This finding further supports our claim from Chapter 3, that the Fe is isolated and does not participate in the ORR pathway directly, but instead catalyzes the graphitization of N-doped carbon that acts as the active site for ORR. The Fe configuration in FePhen@MOF-ArNH$_3$ has important implications for not only anion adsorption, but elimination of potential Fenton processes producing detrimental radical formation. Although electrocatalytic activity is of primary concern, catalyst stability is imperative for successful commercialization of any electrochemical energy conversion technology and the inaccessibility of the Fe to the electrolyte will reduce the potential degradation mechanisms.
4.4 Conclusion

The effect of phosphate anion poisoning on a Fe-based non-PGM, FePhen@MOF-ArNH₃, was investigated electrochemically and spectroscopically. The results were compared with a state-of-the-art Pt-based ORR electrocatalyst using RDE and fuel cell polarization testing. It was discovered that FePhen@MOF-ArNH₃ had enhanced resistance to phosphate anion poisoning of the ORR active site. Based on our *ex situ* physicochemical results we believe that FePhen@MOF-ArNH₃ is made up of Fe/FeₓC/FeₓN particles that are surrounded by graphitic carbon layers doped with nitrogen. Our *in situ* XAS results confirm that the Fe component of FePhen@MOF-ArNH₃ is metallic and there is no change in the oxidation state of Fe with applied potential. Imaging with microscopy confirmed that the Fe particles are isolated from contact with
electrolyte by graphitic layers that ultimately protect the Fe from adsorption of H₂PO₄. This was also confirmed by our poisoning studies using element specific in situ synchrotron XAS coupled with a surface sensitive subtractive technique. Comparison of experimental data with theoretical models revealed that phosphate anions introduced into the electrolyte do not interact with the Fe in FePhen@MOF-ArNH₃. Based on all the above physicochemical characterization results and our electrochemical investigation we believe the Fe present in FePhen@MOF-ArNH₃ primarily act as a catalyst for graphitization of the carbon during the synthesis. The ORR active site appears to be the carbon that is modified by N-doping and possibly Fe, participating through a synergistic effect. The presence of phosphate anions in the electrolyte has no detrimental effect on the ORR mechanism on the carbon-based active site.

4.5 Acknowledgements

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4.6 Chapter 4 References


Chapter 5

Durability of FePhen@MOF-ArNH$_3$ Non-PGM PEM Cathode Electro catalyst

5.1 Introduction

Despite the major advances in renewable energy conversion devices, system cost and lifetime still preclude successful commercialization. Due to the already high price of the current proton exchange membrane fuel cell (PEMFC) technology, mechanisms to enhance durability need to generate similar performance at no additional cost in order to compete with traditional systems. Many efforts have been made to reduce the price of PEM fuel cells, but the traditional platinum based electrocatalyst account for a large fraction of the stack cost and are the most viable material to catalyze the slow kinetics of the oxygen reduction reaction (ORR) in acidic media. Efforts to reduce platinum loading or completely replacing Pt would have the most profound impact, which has encouraged a momentous effort to develop non-platinum group metal (non-PGM) electrocatalyst with high activity for ORR$^{1-12}$. Although significant work has focused on improving the electrocatalytic activity of non-PGMs durability and degradation of these materials has received considerable less attention$^{13-18}$. Extensive work on the durability of Pt supported on carbon has revealed that the lifetime of the electrocatalyst is limited by several degradation mechanisms; such as sintering, dissolution and corrosion of the carbon support$^{19}$. Several theories have been proposed to account for activity loss of non-PGMs: (1) nitrogen protonation$^{16,18}$, (2) high hydrogen peroxide concentration due to 2e$^-\text{ reduction of oxygen}^{20}$ and (3) oxidative corrosion of the carbon support$^{14}$. Dissolution and carbon corrosion are mechanisms that could also degrade non-PGMs, but the identification of the actual degradation mechanisms is complicated by the potential multitude of active sites possible in these materials.
XAS investigations of Fe-based non-PGMs have found that the type of precursors/synthetic route followed\(^8\) to obtain the active catalyst will affect whether the iron will be present as either Fe-N\(_x\) moieties or metallic Fe nanoparticles (NPs). Until now most Fe-based non-PGMs have had both types of Fe-moieties present in varying degrees, but the discovery of an Fe-based non-PGM lacking Fe-N\(_x\) coordination (Chapter 3) provides the unique opportunity to simplify the investigation of degradation mechanisms.

This work aims to determine durability and possible degradation mechanisms of FePhen@MOF-ArNH\(_3\) in the acidic environment of a PEMFC. FePhen@MOF-ArNH\(_3\) is unique in that it lacks FeN\(_x\) moieties and is made up of predominantly Fe/Fe\(_x\)C NPs encased in carbon. The durability was investigated by first testing the stability of the membrane electrode assembly (MEA) with two distinct fuel cell protocols. The first fuel cell cycling protocol was used to determine the electronic stability of FePhen@MOF-ArNH\(_3\) with an inert oxidant gas on the cathode while stepping the potential to simulate the load changes experienced by a fuel cell during automotive application. The chemical stability of FePhen@MOF-ArNH\(_3\) cathode-based MEA was also determined with a fuel cell cycling protocol with a reactive oxidant gas on the cathode while sweeping the potential to simulate drive cycles. Next, the durability of the electrocatalyst during ORR cycling, cycling in the presence of high H\(_2\)O\(_2\) concentrations as well as high voltage cycling was investigated with the rotating ring disk electrode (RRDE) technique. Finally, *in situ* X-ray absorption spectroscopy (XAS) was employed to monitor the stability of the Fe moieties present in FePhen@MOF-ArNH\(_3\), as well as investigate any changes to the electronic and structural properties as a result of the cycling.

### 5.2 Experimental Methods
5.2.1 Catalyst Synthesis

The commercial Pt/C (46%) electrocatalyst used as a standard in this study is obtained from Tanaka Kikinzoku International KK (Japan). The Fe-based non-PGM electrocatalyst (FePhen@MOF-ArNH₃) was the main electrocatalyst being investigated in this work. The detailed synthesis of FePhen@MOF was described in Chapter 3, but in short the MOF linker (2-methyl imidazole) was dissolved in methanol at room temperature and stirred in the reaction flask. In a separate flask the MOF node (zinc(II) nitrate) and the N-chelate (1,10-phenanthroline) were dissolved at room temperature in a 2:3 water/methanol mixture. Once both mixtures were fully dissolved the solution containing the MOF node and N-chelate was combined in the MOF linker solution. Iron(II) acetate was added to the reaction and the mixture was stirred for 24 hours under ambient conditions. This afforded formation of the desired FePhen@MOF. The reaction progressed via selective chelation between iron and 1,10-phenanthroline and zinc and imidazole respectively affording the ZIF-8 MOF with the complexed active site precursors encaged within the MOF pores. The final product was dried in a vacuum oven for 4 hours at 70 °C and then followed by two heat-treatments, argon at 1050 °C and ammonia at 1050 °C (FePhen@MOF-ArNH₃) respectively.

5.2.2 Proton Electrolyte Membrane Fuel Cell Measurements

Membrane electrode assemblies (MEAs) for fuel cell testing were prepared using FePhen@MOF-ArNH₃ cathode on Gas Diffusion Layer (Sigracet BC25 GDL), Pt/C (Tanaka, 46%) anodes on GDL (Sigracet BC25), Nafion 5wt% ionomer solution, and Nafion 211 ionomer membrane. To prepare the cathode, a catalyst ink composed of FePhen@MOF-ArNH₃ dispersed in a water-alcohol mixture with the requisite amount of ionomer (Nafion 5wt%) was sprayed on
gas diffusion layer (Sigracet, BC25). Cathode loading consisted of 0.2 mg/cm² with an ionomer content of 60% by weight of the catalyst. After drying the cathodes, a layer of interfacial ionomer was sprayed to achieve a loading of 0.4mg Nafton/cm². Anodes were prepared with commercial Pt/C (Tanka, 46%) in the same manner as the cathode and served as the reference, reversible hydrogen electrode (RHE). Hot pressing of the electrodes together with a Nafton 211 membrane was carried out at 130 °C and 1,000 lbs. for duration of 5 minutes. MEAs were then assembled in a fuel cell consisting of 5 cm² serpentine flow fields. Humidification of the MEA was performed for 60 minutes by flowing N₂ (100% RH) at a cell temperature of 80 °C. The operating temperature of the fuel cell was 80 °C and the cell was activated with H₂/O₂ (inlet temperatures 85 °C, 100% RH, 22 psi back pressure). Load cycling followed a protocol from Nissan Technical Center North America (NTCNA) designed to simulate accelerated drive cycle conditions based on transitions between open circuit voltage and idling in automobile operation. Durability was tested at 80 °C with N₂ flowing on the cathode while stepping potential from 0.6 to 1.0 V vs RHE with 3s hold at each potential step. ORR durability cycling followed a protocol from Department of Energy’s Durability Working Group (DOE-DWG) designed to evaluate the electrocatalyst durability mechanistically. Durability was tested at 80 °C with O₂ flowing on the cathode while cycling potential from 0.2 to 1.1 V vs RHE at 50 mV/s, each cycle lasting approximately 43 s.

5.2.3 Rotating Ring Disk Electrode (RRDE) Measurements

Perchloric acid electrolyte (0.1 M) was prepared using double-distilled 70% perchloric acid (GFS Chemicals). Electrochemical measurements were carried out on glassy carbon (GC) disk (5.61 mm diameter, Pine Instruments) that was polished with 0.05-micron alumina paste (Buehler, Lake Bluff, IL) and then sonicated in distilled water and Isopropyl alcohol. The gold
ring electrode was held at 1.3 V vs RHE to detect stable peroxide intermediate. Catalysts inks were prepared by dispersing the catalyst in a volume of 1:1 Millipore water:isopropyl alcohol with 10 vol% of 5 wt% Nafion® as a binder. The ink solution was then sonicated approximately 60 minutes to get a uniform suspension. A small volume of the catalyst ink was deposited on the GC substrate to obtain a non-PGM loading of approximately 600 µg/cm². All electrochemical measurements were carried out at room temperature (RT, 20-25 °C) in a standard electrochemical cell (Chemglass) with a 0.1 M perchloric acid (HClO₄) electrolyte using a rotating disk electrode (RDE) setup from Pine Instrument Company connected to an Autolab bipotentiostat (PGSTAT302N). Cyclic voltammetry (CV) was run on non-PGM catalysts in 0.1 M HClO₄ bubbled with argon. ORR was investigated by the RDE technique after bubbling oxygen in the electrolyte solution followed with rotations at 100, 400, 900, 1600 and 2500 rpm. Scans were recorded at 20 mV/s and all potentials are referenced to a RHE scale made from the same solution as the electrolyte. ORR durability cycling followed a similar protocol from the DOE-WG fuel cell evaluation designed to evaluate the electrocatalyst durability mechanistically. Durability was tested at RT in O₂ saturated 0.1 M HClO₄ electrolyte while cycling potential from 0.2 to 1.1 V vs RHE at 50 mV/s and 900 rpm for 6,200 cycles. ORR performance measurements were collected at RT in O₂ saturated 0.1 M HClO₄ electrolyte while cycling potential 0.05 to 1.2 V vs RHE at 20 mV/s and 1600 rpm after certain number of ORR durability cycles. Hydrogen peroxide cycling protocol was designed to address any issues related to (a) unstable exposed Fe and (b) stability of the carbon nitride structure, both being very sensitive to the presence of relatively high concentration of peroxide. The catalyst durability was tested at RT in argon saturated 0.5 M H₂SO₄ electrolyte, with and without 70 mM H₂O₂, while cycling potential 0.05 to 1.2 V vs RHE at 20 mV/s and 900 rpm for 50 cycles. ORR performance measurements were
collected at RT in O\textsubscript{2} saturated 0.1 M HClO\textsubscript{4} electrolyte while cycling potential 0.05 to 1.2 V \textit{vs} RHE at 20 mV/s and 1600 rpm after certain number of hydrogen peroxide cycles. Start-Stop cycling was designed as a fast aggressive protocol to simulate the fuel cell stack conditions related to fuel starvation, in which insufficient current from the anode due to lack of hydrogen causes the cell potential to increase until oxidation of carbon occurs. The catalyst durability was tested at RT in argon saturated 0.1 M HClO\textsubscript{4} electrolyte while cycling potential 1.0 to 1.5 V \textit{vs} RHE at 100 mV/s and 1600 rpm for 6,700 cycles. ORR performance measurements were collected at RT in in O\textsubscript{2} saturated 0.1 M HClO\textsubscript{4} electrolyte while cycling potential 0.05 to 1.2 V \textit{vs} RHE at 20 mV/s and 1600 rpm after certain number of start-stop cycles.

5.2.4 \textit{X}-ray Absorption Spectroscopy (XAS) Measurements

The \textit{in situ} XAS studies at the Fe K-edge (7112 eV) were performed at X3B beamline of National Synchrotron Light Source (NSLS, Brookhaven National Laboratory, NY). The electrode inks for the EXAFS electrodes were composed of 1:1 (wt%) 18.2 M\textOmega purity deionized water (Millipore) and 2-propanol (HPLC-grade, Aldrich), a 5 wt% Nafion solution (Aldrich), and the catalyst powder. The composition was chosen to give a final electrode with a dry Nafion loading of 5 wt%. The ink was hand-painted onto a Zoltek\textsuperscript{©} carbon cloth and dried for 15 minutes in a 65°C vacuum oven between coats. The final iron geometric loadings were chosen to give 0.05 edge heights at the Fe K-edge. A specially designed spectro-electrochemical cell\textsuperscript{23} was flooded with N\textsubscript{2} or O\textsubscript{2}-saturated 0.1 M HClO\textsubscript{4} electrolyte during operation. Full range Fe K-edge spectra were taken at various static potentials along the anodic sweep of the CV. Data were collected in fluorescence mode with a 32-element Ge solid state detector and a Fe foil positioned between I\textsubscript{2} and I\textsubscript{3} as a reference. The voltage cycling limits were 0.05 to 1.20 V \textit{vs} RHE. Data collection was performed at the chosen potentials held during anodic sweeps. Before each
measurement, the cell was held for 5 minutes to reach a pseudo-steady state. The electrode was fully cycled following each potential hold in order to clean the electrocatalyst surfaces after each potential hold.

Scans were calibrated, aligned and normalized with background removed using the IFEFFIT suite. The data was processed and fitted using the Athena and Artemis programs. The \( \chi(R) \) transforms were modeled using scattering paths calculated by the FEFF6 code. Data analysis for Delta-Mu (\( \Delta \mu \)) studies at the Fe K-edge involved specific normalization procedures detailed elsewhere. Difference spectra were obtained using the equation

\[
\Delta \mu = \mu(V, \text{Ar or O}_2) - \mu(0.3 \text{ V, Ar}) \tag{5.1}
\]

where \( \mu(V, \text{Ar or O}_2) \) is the XANES of the catalyst at various potentials in Ar or O\(_2\)-saturated electrolyte, and \( \mu(0.1 \text{ V, Ar}) \) is the reference XANES signal at 0.1 V in Ar-saturated electrolyte at which potential no evidence for electrochemical adsorbates (H*, O(H)*) were found on these Fe-based catalysts.

5.3 Results and Discussions

5.3.1 Proton Electrolyte Membrane (PEM) Fuel Cell Durability Cycling

Two distinct durability protocols were carried out on a single PEM fuel cell to estimate the lifetime of a fuel cell operating with a FePhen@MOF-ArNH\(_3\) cathode. The nitrogen cycling protocol employs an inert oxidant gas on the cathode and simulates fuel cell stack conditions using a potential step excitation (3 s hold at 0.6 and 1.0 V vs RHE). The oxygen cycling protocol employs a reactive oxidant gas on the cathode while simulating drive cycles by using a cyclic potential sweep excitation (50 mV/s from 0.2 to 1.1 V vs RHE).
Polarization curves were collected under the U.S. Department of Energy (DOE) suggested testing conditions of 80 °C, 100% relative humidity, 1 bar partial pressure of \( \text{H}_2/\text{O}_2 \) (1.5 bar total pressure) and/or 0.4 bar partial pressure of \( \text{O}_2 \) in \( \text{H}_2/\text{air} \) (2.5 bar total pressure). A constant ionomer/carbon ratio of 60% and cathode catalyst loading of \(~2\) mg/cm\(^2\) was maintained for both durability tests. \( \text{H}_2/\text{O}_2 \) polarization plots were measured initially and periodically throughout the durability tests (Fig. 5.1) to evaluate the effect of cycling on cell performance.

**Figure 5.1: Fuel Cell Durability Cycling.** (a) \( \text{H}_2/\text{O}_2 \) fuel cell polarization curves for FePhen@MOF-ArNH\(_3\) cathode (loading of 2 mg/cm\(^2\)) using Nafion (NRE 211) membrane measured intermittently 0 to 10 k load cycles (using 3 second hold and pulses between 0.6 to 1.0 V under nitrogen flow). (b) \( \text{H}_2/\text{O}_2 \) fuel cell polarization curves for similar MEA from (a) measured intermittently 0 to 5k accelerated stress cycles (50 mV/s potential cycling between 0.2 to 1.0 V under oxygen flow).
As shown in Figure 5.2 a, the H\textsubscript{2}/O\textsubscript{2} cell performance with a FePhen@MOF-ArNH\textsubscript{3} cathode was remarkably stable during the nitrogen durability cycling. The cell maintained an OCV of 0.95 V \textit{vs} RHE throughout 10,000 load cycles and the high-frequency resistance (HFR), a measure of the resistance of all the MEA components, remained at 5 mΩ/cm\textsuperscript{2} after the durability cycling. After 10,000 cycles there were no changes to the shape of the polarization curve indicating that FePhen@MOF-ArNH\textsubscript{3} seems to be electronically stable in the potential range scanned (0.6 to 1.0 V \textit{vs} RHE). At a cell voltage of 0.8 V, where ORR is mostly under kinetic control, the current density dropped by 39% indicating either degradation of ORR active sites or reduced electrochemical surface area. At a cell voltage of 0.6 V, where ORR is controlled by kinetics and mass transport, the current density only dropped by 14% indicating that mass transport properties of the electrode were not negatively affected. The H\textsubscript{2}/Air polarization curves were more telling of the mass transport properties of a cathode catalyst due to the lower concentration of oxygen (~20% \textit{vs} 100%). As can be seen in Figure 5.2 b, there is a
hysteresis at approximately 0.3 V at which point the current density of the cycled MEA actually increases above the current density obtained with the fresh MEA. This indicates that the mass transport properties are actually enhanced after the nitrogen durability cycling of FePhen@MOF-ArNH₃.

The FePhen@MOF-ArNH₃ cathode based MEA was much less stable with the oxygen cycling durability test (Fig. 5.3). The open circuit voltage (OCV) dropped by 11% after just 1,000 cycles (0.89 vs 0.73 V vs RHE) and there was a 26% increase in the HFR (6 mΩ/cm² to 8 mΩ/cm²). At 0.8 V the current density decayed by 98% indicating significant destruction of the ORR active site under these conditions. At 0.6 V the current density experienced an 84% drop and at 0.2 V the reduction in current density was only 47%. Although the oxygen durability
cycling was far more destructive to the FePhen@MOF-ArNH\textsubscript{3} cathode based MEA, it still appears that the degradation mechanism is most catastrophic in the low current density region. Cycling with oxygen flowing to the cathode enables ORR, which results in the formation of water in the cathode catalyst layer. The presence of water could cause flooding issues that would inhibit oxygen from reaching the active site\textsuperscript{28}. Another possibility is the presence of water while cycling the cell could induce oxidation of the carbon support causing a decrease in the conductivity of the catalyst layer\textsuperscript{29}. If the carbon is being electrochemically oxidized, the hydrophobicity/hydrophilicity of the carbon would change and increased hydrophillicity would decrease the gas permeability\textsuperscript{30}. However, there are different types of carbon present in the catalyst layer (graphite, CNTs, etc.) as well as the gas diffusion layer (GDL). Since the fuel cell is made up of several components (electrocatalysts, membranes, GDLs, and bipolar plates) it is difficult to determine the degradation mechanism and which component is affected.

5.3.2 Rotating Ring Disk Electrode (RRDE) Durability Cycling

In an effort to isolate the degradation mechanisms that are happening to the electrocatalyst alone, three different durability tests were performed using the RRDE technique. First, the ORR durability cycling protocol used previously in PEMFC was also carried out in 0.1 M HClO\textsubscript{4} for 6,200 cycles. Next, cycling of larger potential window (0.05 to 1.2 V vs RHE) was carried out in the presence of hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}, product of 2e\textsuperscript{-} ORR mechanism) to explore the possibility of catalyst degradation from H\textsubscript{2}O\textsubscript{2} attack of active sites. Finally, high voltage cycling (1.0 to 1.5 V vs RHE) was conducted to explore electrocatalyst degradation from the electrochemical oxidation of the carbon (carbon corrosion). Fuel starvation on the anode due to fuel cell start/stop conditions can cause the cell potential to increase and consume the carbon in place of the absent fuel.
The ORR mechanism on FePhen@MOF was investigated in detail in Chapter 3. Briefly, Fe/Fe₃C nanoparticles are encapsulated in a nitrogen-doped (N-doped) carbon structure and ORR activity is attributed to the N-doped carbon surface. The presence of Fe in the synthesis
is critical for catalyzing the graphitization of the carbon precursors, but could enhance the electronic properties of the carbon to enable easier adsorption of O\textsubscript{2} and promote the full 4e\textsuperscript{−} reduction to water in acidic media. The RRDE profile of FePhen@MOF-ArNH\textsubscript{3} before and after ORR durability cycling in 0.1 M HClO\textsubscript{4} is shown in Figure 5.4. The potential was cycled from 0.2 to 1.1 V \textit{vs} RHE with a scan rate of 50 mV/s in oxygen saturated 0.1 M HClO\textsubscript{4} with an electrode rotation of 900 rpm. The performance RDE profiles were measured in O\textsubscript{2} saturated 0.1 M HClO\textsubscript{4} using a scan rate of 20 mV/s and an electrode rotation rate of 1600 rpm, before and after 6,200 durability cycles. Following the ORR durability cycling of FePhen@MOF-ArNH\textsubscript{3} the overpotential for ORR increased by 30 mV and the half-wave potential (E\textsubscript{½}) shifted cathodically by 60 mV (0.69 V \textit{vs} 0.75 V). Additionally, there is a slight reduction in the magnitude of the diffusion limiting current (i\textsubscript{lim}) which is defined by the Levich equation:

\[
i_{\text{lim}}=0.62nF^{2/3}D^{1/6}v^{-1/6}C_{o}
\]

where \(n\) is the number of moles of electrons transferred, \(F\) is the Faraday constant, \(D\) is the diffusion coefficient of O\textsubscript{2} in 0.1 M HClO\textsubscript{4}, \(v\) is the kinematic viscosity and \(C_{o}\) is the concentration of O\textsubscript{2} in the electrolyte. The electrolyte used in the RRDE experiment remained constant, which implies the number of electrons transferred is the only variable from eqn (5.2) that could be affected by the ORR durability cycling. A second working electrode (ring electrode held at 1.3 V \textit{vs} RHE) was used to detect the peroxide intermediate produced from the 2e\textsuperscript{−} reduction mechanism of oxygen. As can be seen in Figure 5.4, the onset of the peroxide oxidation peak detected at the ring electrode coincides with the onset of ORR at the disk electrode for the fresh electrocatalyst. At very high overpotentials (\(E < 0.5\) V) FePhen@MOF-ArNH\textsubscript{3} becomes more efficient for ORR and the peroxide detected at the ring decreases. After ORR durability cycling the oxidation of peroxide still commences with the onset of ORR, but the
peroxide detected continues to increase at high overpotentials (~0.4 V). It has been shown in basic media that an increase in peroxide production at this potential is due to the 2e⁻ reduction of oxygen by the hydroquinone/quinone functionalities on the carbon support\textsuperscript{31-33}. The CV of FePhen@MOF-ArNH\textsubscript{3} (Fig. 5.4 inset) after ORR durability cycling shows an increase in the peak current at ~0.55 V from the hydroquinone/quinone redox couple formed on the surface of the carbon\textsuperscript{34}. The CV is only able to quantify the surface oxides that are electrochemically active, but these results suggest that the carbon is electrochemically oxidized during the ORR durability cycling protocol and the new surface oxide groups either destroy some of the original active sites or inhibit oxygen from reaching the active site. ORR on the original active site proceeds predominantly through a 4e⁻ reduction pathway, but the increase of surface oxides on the carbon results in an increase of the peroxide produced. The increase in peroxide produced by ORR durability cycled FePhen@MOF-ArNH\textsubscript{3} could be due to the contribution of 2e⁻ reduction of oxygen by the quinone functionalities.
Next, the stability of the active sites of FePhen@MOF-ArNH$_3$ in the presence of a high concentration of H$_2$O$_2$ was investigated. The RRDE profile of FePhen@MOF-ArNH$_3$ in 0.1 M
HClO$_4$ before and after H$_2$O$_2$ durability cycling is shown in Figure 5.5. To test the catalyst durability the potential was cycled from 0.05 to 1.2 V vs RHE with a scan rate of 20 mV/s in argon saturated 0.5 M H$_2$SO$_4$ with 70 mM H$_2$O$_2$ and an electrode rotation of 900 rpm. The performance RDE profiles were measured in O$_2$ saturated 0.1 M HClO$_4$ using a scan rate of 20 mV/s and an electrode rotation rate of 1600 rpm, before and after 50 durability cycles. Following the H$_2$O$_2$ durability cycling of FePhen@MOF-ArNH$_3$ the overpotential for ORR increased by 30 mV and the E½ shifted cathodically by 40 mV (0.7 V vs 0.74 V). Despite the decay in the ORR activity the magnitude of the diffusion limiting current was unaffected by the H$_2$O$_2$ durability cycling, which implies that the original active site is not degraded. The peroxide oxidation ring current of the H$_2$O$_2$ durability cycled catalyst still coincides with the onset of ORR at the disk, but has a slightly higher magnitude. Additionally, the H$_2$O$_2$ durability cycled FePhenMOF-ArNH$_3$ still exhibits efficient 4e$^-$ reduction of oxygen at higher overpotentials. The CV of the H$_2$O$_2$ durability cycled catalyst does display a very slight increase in the redox peak from the hydroquinone/quinone redox couple, indicating the introduction of some surface oxides. It is known that H$_2$O$_2$ will decompose in acidic media to form peroxide radicals (•OH and •OOH) that lead to corrosion of carbon$^{35}$. Based on these results it appears that active site of FePhen@MOF-ArNH$_3$ is stable in the presence of H$_2$O$_2$, but it is likely that some of the carbon will be oxidized by the peroxide radicals to form oxygen functionalities on the surface.
Finally, high voltage (start/stop) cycling was conducted to further explore the effects of carbon corrosion on FePhen@MOF-ArNH$_3$. The RRDE profile of FePhen@MOF-ArNH$_3$ before and after start-stop durability cycling in 0.1 M HClO$_4$ is shown in Figure 5.6. To test the
durability of the carbon in FePhen@MOF-ArNH₃, the potential was cycled from 1.0 to 1.5 V vs RHE with a scan rate of 100 mV/s in argon saturated 0.1 M HClO₄ with an electrode rotation rate of 1600 rpm. The performance RDE profiles were measured in O₂ saturated 0.1 M HClO₄ using a scan rate of 20 mV/s and an electrode rotation rate of 1600 rpm, before and after 6,700 durability cycles. Following the start-stop durability cycling of FePhen@MOF-ArNH₃, the overpotential for ORR increased by 150 mV and the E½ shifted cathodically by 270 mV (0.48 V vs 0.75 V) indicating significant degradation of the active sites. The reduction of available active sites is further supported by the lack of a well-defined diffusion limiting current as well as a slight reduction in magnitude following the start-stop durability cycling. The onset of the peroxide oxidation peak detected at the ring electrode coincides with the onset of ORR at the disk electrode for both the fresh and cycled catalyst. However, the ring current of the cycled catalyst continually increases as the overpotential is increased, indicating that start-stop cycling makes FePhen@MOF-ArNH₃ less efficient for the 4e⁻ reduction of oxygen. The CV of the start-stop cycled catalyst (Fig. 5.6, inset) shows dramatic changes from the cycling protocol. There is a decrease in the double layer charging above 1 V after the durability cycling, indicating that the surface area has been reduced. The peak from the hydroquinone/quinone redox has increased significantly indicating introduction of considerable amounts of surface oxides to the carbon surface. Based on these results it appears the start-stop cycling causes electrochemical oxidation of the carbon surface introducing surface oxides and some removal of carbon from the conversion of surface oxides to CO₂ according to the following mechanism in acidic media:

\[ \text{Cs} \rightarrow \text{Cs}^+ + e^- \quad \quad (5.3) \]

\[ \text{Cs}^+ + \frac{1}{2}\text{H}_2\text{O} \rightarrow \text{CsO} + \text{H}^+ \quad \quad (5.4) \]
Each of the three RRDE durability cycling procedures introduced surface oxides onto FePhen@MOF-ArNH₃ and as the amount of surface oxides increased the reduction of E½ also increased (Fig. 5.7). These results indicate that the introduction of surface oxides is the main degradation mechanism of FePhen@MOF-ArNH₃, either due to the blocking/destroying of the active site or changes to the surface hydrophobicity.

4.3.3 Identification of Effect of Durability Cycling on Iron
One of the major concerns of using Fe-based non-PGMs as cathode catalysts in electrochemical energy conversion devices is the stability of the iron during operation. The presence Fe-ions and their potential to catalyze any Fenton type process resulting in peroxide free radical formation would contribute to degradation of multiple device components that are essential for long-term durability. As discussed in Chapter 3, the presence of iron in the synthesis of FePhen@MOF-ArNH₃ is imperative to form the most active ORR electrocatalyst, even
though the iron is not directly involved in the ORR mechanism. FePhen@MOF-ArNH₃ is unusual in that there are no detectable Fe-Nₓ moieties present in the preliminary catalyst, but it is important to investigate what the effect the durability cycling will have on the Fe that is encased in the graphitic carbon network. X-ray absorption spectroscopy (XAS) is an element specific technique that allows us to probe changes in the structural and electronic properties of Fe under simulated operating conditions of a fuel cell using a specially designed spectro-electrochemical cell²³. The three distinct durability protocols that were performed using RRDE (Fig. 5.7 a) were also carried out on XAS electrodes. Spectra were collected of fresh and cycled electrodes as a function of potential in 0.1 M HClO₄ electrolyte saturated with either oxygen or nitrogen. An in situ X-ray absorption near-edge spectrum (XANES) is an extremely powerful tool for capturing the key feature of ORR on a Fe-Nₓ active site. As the potential applied to the XAS electrode is increased from 0.1 up to 0.9 V, the Fe K−edge shifts toward a higher energy due to the Fe²⁺/Fe³⁺ redox transition of the Fe-Nₓ species. The XANES edge shift arises exclusively from the Fe-Nₓ species, since the valence state of the metallic iron encapsulated in the carbon matrix does not change with applied potential. The XANES of the durability cycled electrodes are shown in Figure 5.7 b, and it can be seen that FePhen@MOF-ArNH₃ remains free of Fe-Nₓ moieties after the ORR and H₂O₂ cycling. However, the XANES of the start-stop cycled electrode has the signature edge shift indicating some the metallic Fe has been dissolved and is now present as Fe-ions that experience the Fe²⁺/Fe³⁺ redox transition. Based on these results, we conclude that some of the Fe/FeₓC nanoparticles that are covered by fewer graphitic sheets are exposed to the acidic environment during the carbon corrosion treatment and hence are dissolved. One of the original active site theories proposed by Yeager³¹,³⁶,³⁷, the formation of M-Nₓ sites resulted from the dissolution of exposed metal/metal oxides in acidic electrolyte and their eventual adsorption on
nitrogen sites coordinated to the carbon. The start-stop cycling could allow some of the dissolved Fe-ions to either adsorb on nitrogen sites that are doped into the carbon matrix to form the Fe-Nₓ active site, similar to the active site formation previously proposed by Yeager. In another theory proposed by Goellner et al, the carbon embedded Fe particles that are exposed from high voltage cycling produce Fe³⁺ ions that precipitate to form Fe³⁺ hydroxides (Fe(OH)₃).

Fourier Transform (FT) extended X-ray absorption fine structure spectra (EXAFS) of the fresh and durability cycled electrodes collected at 0.3 V in nitrogen saturated electrolyte are shown in Figure 5.7c. Electrodes held at 0.3 V vs RHE are considered to be free of adsorbates, and therefore represent a catalyst structure with a clean surface. The Fe K-edge of fresh FePhen@MOF-ArNH₃ is characterized by a peak at ~2.2 Å, which was previously fit with a Fe-Fe scattering path with a bond length that corresponds well with bulk iron and/or iron carbide (2.51 Å vs. 2.49/2.48 Å, respectively). The small shoulder off the main peak was fit with a Fe-C/N scattering path with a bond length of ~1.96 Å. As mentioned previously, XAS is effective tool for probing the structural and electronic properties of Fe, but has an inherent limitation in that it is unable to distinguish between low Z elements (C, N and O). Therefore, we are unable to conclusively say whether the shoulder contribution comes from C, N or O. The FT EXAFS of the fresh and durability cycled electrodes shown in Figure 5.7c show very little changes and reveal that the majority of the iron present in FePhen@MOF-ArNH₃ remains metallic through the durability cycling.
After H$_2$O$_2$ cycling, there is a slight increase in the main peak (2.2 Å), and this increase is more intense after H$_2$O$_2$ cycling. The fitting results (Table 5.1) of the H$_2$O$_2$ cycled FT EXAFS shows that the Fe-Fe scattering path coordination number (CN) increased from 7 to 8.7. These results indicate that the smaller Fe/Fe$_x$C NPs are selectively removed when high concentrations of peroxide are present during operation. The start-stop durability cycling produces very few differences in the FT EXAFS, but we know from the XANES that some of the metallic Fe has been dissolved into Fe-ions. However, the FT EXAFS of the start-stop cycled electrode indicate that most of the Fe is still present in the metallic form. Based on these results it appears that the iron present in FePhen@MOF-ArNH$_3$ is stable under normal driving conditions, but becomes vulnerable to dissolution during the high voltage transients experienced during start up and shutdown.

Most interestingly, the start-stop cycled catalyst is so heavily oxidized that after cycling the onset of the ORR curve shifts so far cathodically that is now coincides with the hydroquinone/quinone redox couple (Fig 5.7 a). This could indicate the surface has become so heavily oxidized that the

<table>
<thead>
<tr>
<th></th>
<th>Fresh</th>
<th>H$_2$O$_2$ Cycled</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe-N/C</td>
<td>Fe-Fe</td>
</tr>
<tr>
<td>CN</td>
<td>-</td>
<td>7.0 ±0.05</td>
</tr>
<tr>
<td>R (Å)</td>
<td>-</td>
<td>2.50 ±0.01</td>
</tr>
<tr>
<td>$\sigma^2 \times 10^{-3}$</td>
<td>-</td>
<td>8 ±1</td>
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</tbody>
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Table 5.1: In Situ EXAFS Fit Results After Hydrogen Peroxide Cycling. EXAFS fit results for FePhen@MOF-ArNH$_3$ before and after hydrogen peroxide cycling. Experiments performed at the Fe K-edge (7112 eV) as a function of potential in N$_2$ saturated 0.1M HClO$_4$ electrolyte. Coordination number (CN) and phase-corrected bond length (R) in angstrom are shown.
original carbon active site has been destroyed and ORR is now proceeding on the oxidized carbon surface.

5.4 Conclusions

In this chapter we investigated the durability and degradation of FePhen@MOF-ArNH₃ in a PEM fuel cell environment using single-cell cycling, RRDE cycling and in situ XAS investigations. The device components of a PEMFC are exposed to strongly acidic and oxidizing conditions at elevated temperatures, which necessitate the use of a first class electrocatalyst. Extensive research into the use of transition metal based electrocatalysts in place of the state-of-the-art platinum based electrocatalysts has produced highly active materials, but little is known about their degradation mechanisms. FePhen@MOF-ArNH₃ was very stable during the nitrogen fuel cell durability cycling, but suffered significant performance decline during the oxygen fuel cell cycling. Three RRDE durability cycling protocols revealed that increased surface oxides due to electrochemical oxidation of the carbon resulted in a decrease of the ORR activity. In situ XAS revealed that the Fe is stable during normal fuel cell operating conditions, but aggressive carbon corrosion can expose the Fe/Fe₃C particles leading to dissolution. Based on all of these results it appears the main degradation mechanism is the electrochemical oxidation of the carbon, which produces surface oxides that change the conductivity and hydrophobicity of FePhen@MOF-ArNH₃.

3.5 Acknowledgements

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5.5 Chapter 5 References


Chapter 6

Summary, Future Directions and Conclusions

6.1 Introduction

Concerns of climate change and depleting fossil fuel resources have encouraged researchers to develop the proton exchange membrane fuel cell (PEMFC) as a replacement for the internal combustion engine in automotive transportation. Replacement of the traditional platinum-based cathode electrocatalyst would significantly lower the cost of the system and allow possible commercialization of the technology. Extensive research into the use of transition metal based electrocatalysts in place of the state-of-the-art platinum based electrocatalysts has produced highly active non-platinum group metal (non-PGM) catalysts. However, the exact nature of the active site is still debated and little is known about its degradation mechanisms. A better understanding of these materials is needed to take the critical next step in replacing platinum as the cathode electrocatalyst in the PEMFC. The aim of the work in this dissertation was to develop and characterize two different non-PGMs in an effort to identify the source of ORR activity.

6.2 Summary

6.2.1 Chapter Two Summary

Chapter two detailed the synthesis of a Co-based non-PGM electrocatalyst (Co$_2$(bpbp)/F-K$_{600}$) by subjecting a tetranuclear cobalt cation to a high temperature heat treatment in inert atmosphere. The synthesized Co based catalyst heat treated above 600 °C were the most active for ORR and were found to be comprised of Co-N and Co NP moieties. Co$_2$(bpbp)/F-K$_{600}$-800
was used for investigation into the ORR mechanism and was found to be an effective catalyst for the 2e⁻ reduction of oxygen in acidic electrolyte. It was believed that the stability of the peroxide intermediate on the catalyst surface was enhanced in alkaline media and the Co NPs could then act as a second active site that allowed a series of two 2e⁻ reductions, resulting in an overall 4e⁻ reduction of oxygen to water. However, in acidic media the Co NP moieties were capable of acting as a second active site, but the instability of the peroxide intermediate on the catalyst surface had to be overcome. It was found that high loadings of catalyst would allow further reduction of some of the peroxide before it was released into the electrolyte.

The Hbpbp ligand is capable of binding different types and metals. Some preliminary tests with iron showed enhanced activity, but we were unable to confirm the structure of the tetranuclear cation. Future work investigating the effect of binding iron and cobalt could elucidate the role each of these metals play in the synthesis and final ORR mechanism.

6.2.2 Chapter Three Summary

In chapter three we introduced a Fe-based non-PGM ORR electrocatalysts, FePhen@MOF-ArNH₃, which utilizes a MOF-support that acts as a host for the Fe-based sites. Orderly dispersion of the Fe-chelates was achieved with the encapsulation. The FePhen@MOF-ArNH₃ electrocatalyst exhibited high activity for ORR in acidic media and outperformed the benchmark Pt/C catalyst in alkaline media. Membrane electrode assemblies were manufactured with a FePhen@MOF-ArNH₃ cathode and exhibited exceptional PEM fuel cell performance and demonstrated excellent mass-transport properties and stability that has not been witnessed by previous non-PGM cathodes. Characterization techniques revealed the Fe is present as Fe/Fe₃C nanoparticles that are sub-surface to a nitrogen-doped (N-doped) carbon overlayer, however they
seem to play an important role in the electrocatalysis by imparting a synergistic effect on the N-doped carbon that allows stabilization of the peroxide intermediate and enables the full $4e^-$ reduction of oxygen to water. The work in this chapter is the first definitive proof of a non-PGM electrocatalysts with high ORR activity that lacks direct Fe-N$_x$ coordination when studied using \textit{in situ} synchrotron XAS at the Fe K-edge under simulated conditions of operating PEM cell. All previous reports in the literature have been obtained under \textit{ex situ} conditions that cannot account for catalyst structure changes at the catalyst-electrolyte interface with an applied potential. The lack of evidence suggesting the presence of Fe-N$_x$ moieties under \textit{in situ} conditions allows us to conclusively attribute the majority of the ORR activity to the N-doped carbon structure. Based on our results we believe the Fe first acts as a catalyst for the graphitization of N-doped carbon during the heat treatment in which some iron is integrated into the carbon and enhances the electrocatalytic properties enabling the $4e^-$ reduction of oxygen.

The encapsulation synthesis is a novel platform and incorporating different transition metals and nitrogen precursors into the MOF pores would be an interesting experiment.

\textit{6.2.3 Chapter Four Summary}

In chapter four we investigate the effect of phosphate anion poisoning on our Fe-based non-PGM, FePhen@MOF-ArNH$_3$. The effect of poisoning on ORR activity was investigated electrochemically and the interaction of the poison was investigated spectroscopically. The results were compared with a state-of-the-art Pt-based ORR electrocatalyst using RDE and fuel cell polarization testing. It was discovered that FePhen@MOF-ArNH$_3$ had enhanced resistance to phosphate anion poisoning of the ORR active site. Our \textit{ex situ} physicochemical results showed that the Fe/Fe$_x$C/Fe$_x$N particles that make up FePhen@MOF-ArNH$_3$ are surrounded by graphitic
carbon layers doped with nitrogen. The graphitic layers protect the Fe particles from contact with electrolyte and ultimately protect the Fe from adsorption of H$_2$PO$_4^-$. This was also confirmed by our poisoning studies using element specific in situ synchrotron XAS coupled with a surface sensitive subtractive technique. Comparison of experimental data with theoretical models revealed that phosphate anions introduced into the electrolyte do not interact with the Fe in FePhen@MOF-ArNH$_3$. Our results confirmed the Fe present in FePhen@MOF-ArNH$_3$ primarily act as a catalyst for graphitization of the carbon during the synthesis. The ORR active site appears to be the carbon that is modified by N-doping and possibly Fe, participating through a synergistic effect. The presence of phosphate anions in the electrolyte has no detrimental effect on the ORR mechanism on the carbon-based active site.

Only preliminary fuel cell results were reported for the HT-PEMFC with a FePhen@MOF-ArNH$_3$ cathode. MEA optimization could greatly improve the performance of this system. Additionally, durability experiments would need to be conducted to test the lifetime of the system.

6.2.4 Chapter Five Summary

In chapter five we investigated the durability and degradation of FePhen@MOF-ArNH$_3$ in a PEM fuel cell environment using single-cell cycling, RRDE cycling and in situ XAS investigations. The device components of a PEM fuel cell are exposed to strongly acidic and oxidizing conditions at elevated temperatures, which necessitate the use of a first class electrocatalyst. FePhen@MOF-ArNH$_3$ was very stable during the nitrogen fuel cell durability cycling, but suffered significant performance decline during the oxygen fuel cell cycling. Three RRDE durability cycling protocols revealed that increased surface oxides due to electrochemical
oxidation of the carbon resulted in a decrease of the ORR activity. In situ XAS revealed that the Fe is stable during normal fuel cell operating conditions, but aggressive carbon corrosion can expose the Fe/Fe,C particles leading to dissolution. Based on all of these results it appears the main degradation mechanism is the electrochemical oxidation of the carbon, which produces surface oxides that change the conductivity and hydrophobicity of FePhen@MOF-ArNH₃.

There is still significant work that needs to be done in order to understand and fix the degradation mechanisms of FePhen@MOF-ArNH₃. Specifically, running the same fuel cell durability tests in an HT-PEMFC would elucidate the participation of water in the flooding issue due the lack of water in that system.

6.3 Conclusions

The immense theoretical energy density of the H₂/O₂ fuel cell energy conversion technology makes it a feasible alternative to replace the internal combustion engine. Proton exchange membrane (PEM) fuel cells have a demonstrated ability to produce clean and efficient power, but the market integration of this clean-energy alternative is precluded by the requirement of costly platinum (Pt) used to catalyze the oxygen reduction reaction (ORR) on the cathode. The quest for eliminating the use of any noble metals as catalyst for cathode application in a low or medium temperature fuel cell (room temperature to 350 °C) has been the Holy Grail for the electrocatalysis community. We have demonstrated two different types of non-PGM electrocatalyst with very different activities for ORR. The Fe-based catalyst holds significant promise as an effective cathode material in multiple energy conversion technologies. Initial investigations into the durability of these materials are promising, but leave plenty of room for further investigation.