NON-PLATINUM GROUP METAL OXYGEN REDUCTION CATALYSTS AND THEIR MECHANISM IN BOTH ACID AND ALKALINE MEDIA: THE EFFECT OF THE CATALYST PRECURSOR AND THE IONOMER ON OXYGEN REDUCTION

Michael Robson

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NON-PLATINUM GROUP METAL OXYGEN REDUCTION CATALYSTS AND THEIR MECHANISM IN BOTH ACID AND ALKALINE MEDIA: THE EFFECT OF THE CATALYST PRECURSOR AND THE IONOMER ON OXYGEN REDUCTION

by

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DISSERTATION

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DEDICATION

This work is dedicated to my two daughters, Abigail Love and Summer Elizabeth, as well as any future children that my wife, Lacie, and me may have. They are the source of such joy and love in my life, and it is for them that I labor cheerfully.
ACKNOWLEDGMENTS

I first and foremost recognize God and Jesus, as they are the source of all of the blessings in my life, and by which their grace has been given unto me, I am in a position to pursue such an endeavor.

The support network that has enabled me to further my professional goals must be recognized. My beautiful wife, Lacie, has kept my life balanced and grounded; not allowing me to lose focus of all that truly matters in this world. My precious girls motivate me to achieve the things that will secure our future, yet they draw me home with so much love and affection. My mother and father, W. Mike and Penni, never waivered in teaching me about the work ethic, perseverance, and values that have made me the man that I am today. My in laws, Mike and Judy Ledford, have been two of my greatest cheerleaders through this process, and they have never failed to step up to cover for my dereliction of fatherly duties when school required my full time and attention. To my brother, Marc, with whom my love of competition has been fostered over the course of many years, but always in the spirit of brotherhood and friendship.

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frequent fount of advice and knowledge. Our paths will cross many more times, both personally and professionally.

Heather Armstrong is worthy of her own paragraph in which to be acknowledged. She has been a tireless advocate and promoter throughout this process. I often say that befriending her is the smartest thing that I have done in the past several years, as she has not only made my life much easier around school, but has also been the source of much entertainment and good conversation, and has enriched my life greatly. Thank you, Heather, for being such a wonderful friend.

And last, I would like to express my thanks to all of my lab mates, professors, and all others who have not been named directly here. Your contributions will not soon be forgotten.
Non-platinum catalysts are an attractive strategy for lowering the cost of fuel cells, but much more development is needed in order to replace platinum, especially at the cathode where oxygen is reduced. Research groups worldwide have donated material for a study in which precursor structure to catalyst activity correlations are made. The donated samples have been divided into three classes based on their precursor; macrocyclic chelates, small molecule, and polymeric precursors. The precursor is one activity-dictating factor among many, but it is one of the most influential. It was found that macrocyclic chelates on average produced the most active catalysts, having the highest limiting, diffusion-limited, kinetic, and exchange current densities, as well as the
lowest overpotentials and \( \text{H}_2\text{O}_2 \) production. This suggests that the M-N\(_4\) atomic structure of the precursor remains largely static throughout heat treatment, as the M-N\(_x\) motif is the accepted active site conformation. The other classes were somewhat less active, but the breadth of precursor materials that range in structure and functionality, as well as low associated costs, make them attractive precursor materials.

Careful precursor selection based on this analysis was applied to a new generation of catalyst derived from iron salt and 4-aminoantipyrine. An extensive investigation of the reduction of oxygen on the material performed in both acid and alkaline media, and it was found that reduction follows a two-step pathway. While the peroxide reducing step is also very fast, the first step is so rapid that, even at low active site density, the material is almost as active as platinum if all diffusion limitations are removed.

In addition to bottom-up catalyst design, the catalyst:ionomer complex, by which catalyst is incorporated into the membrane electrode assembly, also affects reductive kinetics. A series of novel anionically conductive ionomers have been evaluated using a well-described cyanamide derived catalyst, and the ionomeric influence on activity was mechanistically evaluated. It was found that the water-uptake percentage of the ionomer and the ion exchange capacity has a major role in catalyzing the reaction. The ionomer content of the complex must balance ionic and electrical charge transfer, as well as manage a certain degree of hydration at the active site.

In order for a catalyst to perform optimally in an operational fuel cell, design considerations must be addressed at the precursor, support, synthesis, morphological, and ionomer-complexing levels. If any level of design is neglected, catalytic performance will be sacrificed.
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<tr>
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<th>Description</th>
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<tbody>
<tr>
<td>$\alpha$</td>
<td>Electron Transfer Coefficient</td>
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<td>$\eta$</td>
<td>Overpotential/Ion Exchange Capacity</td>
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<tr>
<td>$\chi$</td>
<td>Peroxide Yield</td>
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<tr>
<td>$\omega$</td>
<td>Rotation Rate</td>
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<td>$\nu$</td>
<td>Kinematic Viscosity of the Electrolyte</td>
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<td>PEMFC</td>
<td>Proton Exchange Membrane Fuel Cell</td>
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<tr>
<td>RHE</td>
<td>Reversible Hydrogen Electrode</td>
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<td>RPM</td>
<td>Revolutions Per Minute</td>
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<td>RDE</td>
<td>Rotating Disk Electrode</td>
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<td>RRDE</td>
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<td>RE</td>
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<td>SEM</td>
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<td>WE</td>
<td>Working Electrode</td>
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<td>XPS</td>
<td>X-ray Photoelectron Spectroscopy</td>
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1. Introduction and Background

1.1. The Future Of Energy

Today, more than ever before, concerns about energy are ruminating throughout the global economy, and almost no human being on the planet is immune from it. While the sources of concern are diverse, it does illustrate how important the issue is to civilization and our dependence upon it. The various sources of this trepidation extend from cleanliness, abundance, sustainability, and reliability; and the frame of reference for most people for this dependence is oil. Oil has been the primary energy source for the industrialized world for over a century, and many parties across the globe are heavily invested in it, and those who control it have a certain degree of leverage over others whom are dependent upon it, yet cannot produce their own.

Such a global economic model inserts a high degree of volatility into the price of the commodity, and conflict between nations, elections, terrorist acts, extreme weather events, accidents, etc. have all been known to spike prices. And while there is much debate as to how much oil is recoverable, it is almost universally agreed that there is a finite amount. This combination of supply chain instabilities can cause costs to skyrocket, as was seen in 2007 (Fig. 1).

Furthermore, the incomplete combustion of alkanes produces toxic chemicals, such as carbon monoxide, and impurities in the fuel can be released into the atmosphere in the process. This is not only unsightly, but heavy pollution has been definitively linked to a host of health related maladies. The anxieties that the oil based economy has caused over time has spurred many to find another option.
As the call for alternatives to hydrocarbon based power sources continues to grow louder the world over, more groups and institutions are dedicating research towards the commercialization of various forms of renewable energy sources. Most consumers in developed nations have a high degree of economic exposure to hydrocarbons in the form of fuel for automobiles, and therefore the demand for alternatives is the strongest in that market space. The success of hybrid technology and the reintroduction of electric vehicles is a testament to this demand. However, the power demand of larger vehicles renders the battery an insufficient energy storage medium. While batteries are a viable energy storage strategy for small commuter vehicles, they would not be able to meet the needs of extended range vehicles, trucks, vans, and large commercial vehicles such as 18-wheelers and garbage trucks. Currently, the fuel cell is the only realistic zero emissions alternative to the internal combustion engine.

1.2. Oxygen Reduction At High And Low PH
Hydrogen has the highest power density per unit mass of any fuel source [1], and it is therefore a very attractive source for motive purposes. Of all the different types of hydrogen fuel cells, there are two primary types that are being considered for mobile or portable applications: polymer electrolyte membrane fuel cells (PEMFCs) and Alkaline Fuel Cells (AFCs), along with its counterpart the liquid electrolyte free alkaline membrane fuel cell (AMFC). The primary reason for their consideration for such purposes is that they have sufficient power output at low temperatures (<200 °C), whereas others like solid oxide fuel cells (SOFCs) require very high temperatures (>600 °C). This low temperature range allows for portability of the unit because an external heating source is not necessary.

The primary difference between the PEMFC system and the AFC is the mechanism by which the oxygen is reduced to water, due to the ions that are available. At low pH, the electrolyte has an abundance of H\(^{+}\) available to drive the reaction to completion, and can be compartmentalized into 2 half reactions (Eqs. 1.1 and 1.2), yielding the overall reaction (Eq. 1.3) [2-4].

\[
\begin{align*}
2H_2 & \rightarrow 4H^+ + 4e^- \quad (1.1) \\
O_2 + 4H^+ + 4e^- & \rightarrow 2H_2O \quad (1.2) \\
2H_2 + O_2 & \rightarrow 2H_2O \quad (1.3)
\end{align*}
\]

By contrast, the alkaline mechanism (Fig. 2) relies on the preponderance of hydroxide ions in the solution to be oxidized (Eq. 1.4), freeing electrons to reduce oxygen to hydroxide at the cathode (Eq. 1.5), thereby yielding the same overall reaction (Eq. 1.6) as the acidic mechanism (Eq. 1.3) [5].

\[
2H_2 + 4OH^- \rightarrow 4H_2O + 4e^- \quad (1.4)
\]
Due to the charge of the ions in the electrolyte, the directionality of the conduction of ions across the membrane is opposite between the two. In acid, the hydrogen molecule is oxidized at the anode to protons, which need to be conducted through the membrane to the cathode. In alkaline media, hydroxides are formed at the cathode, which are then reformed to water by the anode when the hydrogen molecule is oxidized (Fig. 2). Therefore, in acid the ions are conducted from the anode to the cathode, and in alkali they are conducted from the cathode to the anode.

AFCs offer more favorable thermodynamic conditions for the oxygen reduction reaction (ORR) [6], which brings the cathodic activity to better parity with the anodic activity. Also, the transport of the hydroxyl ions and the electro-osmotic drag that results prevents crossover of reactants, while the consumption of water at the cathode promotes water management. Furthermore, the enhanced stability of metal at high pH is also beneficial.

A 1968 report on the state of fuel cell research and applications by Ernest Yeager described a litany of hindrances that were preventing AFCs from

\[
\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^- \\
2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}
\]
finding applications outside of the space program, and were perceived as being insurmountable with the then-current technology [7]. This report was the impetus for a shift in research in fuel cell technology from alkaline media to acid media, where acid media dominated fuel cell research for several decades.

As detailed in the report, PEMFCs have several other advantages over AFCs. They have higher power density from greater current production, low sensitivity to orientation because of the polymer electrolyte, and quick start up times [8]. However, as mentioned prior, they are more corrosive, are sensitive to impurity, and require more expensive catalysts. As in alkaline media, the reaction kinetics of the redox couple in PEMFCs is limited by the activity of the cathode, where the reduction of the oxygen by free electrons can occur in a multistep pathway [4]. This pathway is also susceptible to incomplete reduction, whereby a peroxide byproduct can desorb.

1.3. The Problem With Platinum

Platinum is the catalyst of choice for fuel for cells, especially in PEMFCs, for several reasons. It’s noble status as a metal makes it resistant to corrosion, although not immune, and is conductive. As an anodic catalyst [9], it readily oxidizes molecular hydrogen. On the cathode, it rapidly reduces oxygen [10] with a strong binding affinity for the reactant [11], but not too strong of an affinity for the product. While it is not the only material that is capable of reducing oxygen, it is the most effective, and therefore is the yardstick by which all other materials are measured. Of course, it is not without shortcomings.

The cost of platinum contributes about 37% to the cost of the fuel cell [12], and comprises the highest cost contribution to the overall price. Platinum, as a commodity is expensive, in part due to its precious metal status, and in part due to the geopolitical...
environment that has only a few nations producing it in any appreciable quantity. Much like oil, it too experiences large price fluctuations making it difficult for industry to project costs (Fig. 3). And, like other precious metals, there is a finite supply of platinum, and only a few select locations from which to mine it [13]. This is a concern, especially if fuel cell vehicles (FCV) are to ever be mass-produced. Most estimates project ample availability of platinum for such purposes [14], but any long-term cost projections are nearly impossible to make.

For fuel cells to be adopted by the average consumer in any capacity - be it automotive, combined heat and power, or personal electronics – the cost of the cell must be reduced. On the subject of platinum, there are two basic strategies to address this problem. The first involves maximizing the performance of the fuel cell per unit mass of platinum, known as ultra-low loading [15-18]. This involves techniques such as alloying and maximizing the exposure of the platinum. The second strategy foregoes platinum altogether by employing non-precious metals. Coordinated transition metal precursors

![Figure 3](image_url)

**Figure 3.** Historical 10 year chart (8/2002 to 8/2012) for the price of platinum/g in $USD, data courtesy of Monex.com.
have been explored in order to overcome this shortfall, and the inherent reduction of activity has precipitated much research and engineering to overcome this [19]. Heretofore, the bulk of the activity in non-PGM catalysis has centered on the cathode due to the greater technical challenge that is to be overcome [20, 21], while relatively few groups have studied the anode [22]. The anodic reaction is very facile, and it requires somewhere between 25 and 66% of the platinum that the cathode requires for fuel cell operation, and thus there is less need for anode research.

1.4. Non-Platinum Cathode Catalysts

The non-PGM strategy has gained much traction in recent years as the state-of-the-art has advanced to a point that non-PGM catalyst performance is competitive with that of platinum. Although it is unrealistic to expect that a non-platinum catalyst will perform better than a platinum catalyst, it is apparent that they can be made to perform almost as well, but for a fraction of the cost, and any loss in performance can be compensated for by increased loading of the electrocatalytic material.

As the non-platinum catalyst research has progressed, three distinct categories of electrocatalysts have emerged, classified on the basis of their precursor material. They are materials based on transition metal chalcogenides (primarily ruthenium selenide) [23-31], heteroatomic polymeric precursors [32-34], and small molecule derived M-N-C frameworks [19-71][35-84]. Among the small molecule class, one can further segregate coordinated metal macrocyclic compounds [34-48] from metal salt and nitrogen/carbon precursor molecules [33-71] as the sole source for formation of M-N-C networks (M=metal, N=nitrogen, and C=carbon).
The remainder of this discussion will focus only on non-PGM research that employs a metallic transition metal (primarily iron, cobalt, or copper), and this group will be subdivided as follows: small molecule precursor, macrocyclically coordinated metal precursor, and polymeric precursor derived materials.

1.5. The State Of Non-PGM Catalysts

Characterization studies have suggested that pyridinic and graphitic nitrogen are the most active catalytic sites for oxygen reduction. A significant contributing factor to this is the fact that pyridinic nitrogen possesses a lone pair of electrons, while simultaneously contributing an electron to the conjugated bond, which facilitates the adsorption of oxygen and prevents \( \text{H}_2\text{O}_2 \) desorption.

The most prevalent ORR active site hypothesis and the mechanism of reaction on non-PGM catalysts states that the Me-N\(_4\) carbon support integrated center (Fig. 4) is the catalytically active surface feature, and the metallic ion center within the chelate plays a critical role in the reaction [85-89]. The later part of the hypothesis is subject to some debate, as it is suggested that the transition metal only serves stabilize nitrogen as it is incorporated into the graphitic support [90, 91]. Regardless of the role that the metal has, it would appear that nitrogen-based carbon defects help facilitate \( \text{O}_2 \) adsorption and reduction, without the irreversible formation of oxygen functionalities at the catalyst surface [92].

Many assumptions about ORR on non-PGM materials are extensions of those made using an ideal platinum electrode, commonly a Pt (111) surface [93-95]. The mechanism of the reaction on non-PGM catalysts is likely to be much more complex, but the net effect is the same as on platinum, and it is therefore an adequate starting point to build an
understanding. Unlike a planar Pt electrode, however, there are many considerations that affect the activity of a non-PGM catalyst; such as the transport of analyte through the material, the sorption of reactants, intermediates, and products, active site formation, and active site density, among others.

1.6. Challenges Facing Non-PGM Catalysts

At both low and high pH and regardless of the catalyst, the cathodic reaction is the rate-limiting step in the redox couple, as the oxidation of hydrogen is a very rapid process while the reduction of oxygen is much slower. Several strategies have been employed to improve the performance of cathode catalysts, most of which are designed to create more active sites per unit of mass of catalyst [96].

Increasing the relative pore volume of catalysts serves to maximize the surface area of the material, and by which an active site can be formed within [79]. A porous surface controls the diffusion of reactants and products, and immobilizes the reactants at the active sites and prevent any intermediate species from desorbing, allowing for reaction control via mass transport [97]. A common approach to this is to synthesize the catalyst on high surface area carbon blacks. More sophisticated techniques have been developed that use very high surface area, mesoporous silica to template carbon and metal containing species before pyrolyzation [98], which allows for greater control over the
morphology of the catalyst. The silica is then etched away, leaving an open framed network of carbon and active sites that has a very high catalytic surface area.

Nitrogen, and specifically pyridinic nitrogen has been shown to be a vital component of the active site, even more so than the transition metal (Fig. 5) [88]. Some even theorize that a transition metal is not even required to catalyze the reduction of oxygen, but this statement remains to be proven [64]. Therefore, by optimizing the amount of surface nitrogen, the reaction kinetics can be maximized. Nitrogen containing precursor molecules and nitrogen doping by degradation of ureic compounds has been shown to improve the nitrogen content catalysts [99].

The conductivity of the cathode material also helps to increase the efficiency of the reaction. Improving conductivity reduces ohmic losses and serves to maintain a ready supply of free electrons available for reducing the oxygen when it is adsorbed on to the active site. Graphitic carbon is the material of choice in most catalysts, not only because they are conductive, but also very stable. In the case of carbon black, it is the support on which the catalyst is synthesized, but other approaches use carbon precursors such as sucrose graphitize the carbon through pyrolysis [100]. The carbonaceous powder that results forms small particles, and to a lesser but still significant extent, the size of this particle is correlated to the activity, with small particles being more active than larger particles [101].

Due to the performance deficit that non-PGM catalysts have to the platinum catalysts that they are intended to replace, every factor that influences the kinetics of the non-PGM catalyst must be considered in the design process in order to bridge this gap. Fortunately, they do not need to be as active as platinum in order make an impact as a power source.
Improving the activity to a point where non-PGM catalysts are competitive with platinum in terms of performance and durability would make fuel cells a viable energy alternative to the ICE, hybrid technology, and batteries.

1.7. The Ionomer

In the 1960’s, scientists at DuPont developed a perfluorinated, carbon backbone polymer with sulfate groups attached to the end of the dangling side chains (Fig. 6), which came to be known as Nafion®. This polymer was quickly adopted as the polymer of choice for the membrane in PEMFCs because it is durable, corrosion resistant (like its chemical cousin Teflon®), and is conductive to cations, such as H⁺, while being impermeable to water. Thus far, only modifications to Nafion® have resulted in a better membrane than what is supplied by DuPont [102-104], and novel ionomers have yet to overtake the top spot for membranes in PEMFCs.

Nafion®, as a cation conductor, has a sixty-year history of development and refinement, and is the de facto industry standard AFCs. The pendulum side chains of the
The ionomer have negatively charged sulfate ends that readily conduct protons along its length and across the membrane. In alkaline systems, it is the negatively charged hydroxyl groups that must be shuttled, which sulfates are not equipped to do.

The bulk of anionically conductive ionomer research has centered on the membrane. Several strategies have been employed, such as cross-linking functionalized polystyrene, but this suffers from instability at high pH [105]. Other approaches to this challenge have altered membranous poly(sulfone)s [106], poly(vinyl alcohol)s [107], and poly(ether-imide)s [108], where the anionically conductive functionalization was performed in a postpolymerization reaction. The drawback here is that this involves toxic solutions and long reaction times. Other approaches involve bromomethylation of the polymer before the functionality is substituted for an anionically conductive quaternary amine group [109, 110]. Poly(sulfone)s and poly(phenylene)s, which are thermally and chemically stable, can have their mechanical properties enhanced by blending with other polymers[111]. Furthermore, when cast into membranes, these mechanically fortified polymers can be made thin enough as to minimize resistance in the cell.

Poly(sulfone)s and poly(phenylene)s are promising candidates for an AFC specific membrane ionomer standard because they are stable at high pH and anionically conductive, but also suitable as a catalyst binder [112]. The binder provides structural
support for the catalyst layer and assists in establishing the tri-phase boundary where catalyst surface, electrolyte, and analyte all converge [113]. Additionally, it is advantageous for the binder to have symmetry with the membrane, which mitigates problems such as corrosion currents and material expansion [114], and alleviates problems related to pH gradients [115]. Having this symmetry simplifies the fuel cell system by reducing the overall number of different materials used. For these reasons, evaluation of the ionomer as a binder is a critical aspect for researching its efficacy in an operational system.

Solvated Nafion® is the standard ionomeric binder for any low temperature fuel cell system that utilizes either platinum and/or non-PGM catalysts. There exists an optimal weight ratio of Nafion® to catalyst where ionic and electrical connections are balanced between the electrode and the membrane [113], resulting in an ohmic region that covers the smallest potential range, a small overpotential, and where the mass transport region is least affected. Deviation from the optimum creates inefficiencies in all three of these regions, and it is therefore imperative to evaluate a catalyst in terms of limiting current ($i_{lim}$), half-wave potential ($E_{0.5}$), peroxide yield, and efficiency in order to find this optimal ratio. This ratio is unique to each catalyst, and an optimization must be carried out for each new catalyst.

The same rigor must be applied when using a new ionomer as a binder, as the local conditions around the active site will be different than with Nafion®. Ideally, a novel membrane will be paired with its constituent ionomer as a binder for the catalyst on the membrane, so there is a continuity of material across the membrane electrode assembly
Thus, for optimal MEA performance, the catalyst ink should be evaluated at a minimum of three catalyst-to-ionomer mass ratios.

1.8. Approaches To Improved Catalyst Design

At the core of catalyst design, as mentioned previously, is the need to maximize the available surface area, while attaining the ideal pore size distribution and pore connectivity. A common approach to achieving this is to start with a material that already has the desired features and to carbonize it, such as starting with a mesoporous silica support structure [116]. The method for creating this type silica allows for the control of the porosity and surface area. This silica, which can be designed to have surface areas greater than 1000 m$^2$·g$^{-1}$, has been employed as a template for non-PGM catalysts (Fig. 7). Since the support must be conductive, and silica is not, a conductive framework is formed through the graphitization of an impregnated carbon rich material, such as sucrose. The silica template can then be etched, leaving only the conductive framework, which has the inverse structure of the silica template.

Controlled and homogeneous impregnation of the carbon source and the active site precursors can be difficult because the precursors must be made to penetrate the pores of the silica without clogging them before they can be filled. Most of the chemicals used to synthesize the catalysts are only soluble in aqueous solution [117], a solvent that has a high surface tension. This surface tension prevents the solvent from wetting the entire surface of the substrate, and thus not allowing for transport of the pre-pyrolyzed material into the pores of the silica. To overcome this, a fluid with low surface tension that is miscible with water is added to the solution, typically acetone or acetonitrile [118]. This allows the solution to penetrate and wet the pores. For optimal penetration of the pores,
we have determined that the solution must be added to the silica slowly, with time to allow the silica to dry between additions, lest much of the material will be lost to the walls of the vessel.

The next level of design is the active site. There are two basic ways to build an active site, either by using a molecule that already has the desired configuration and hoping that it retains that form through the pyrolyzation process, or by using precursors that will form an active site through additional processing.

The former approach typically involves using macrocyclic chelates as a precursor. The transition metal component of the catalyst is a required component, at least for stabilizing the active site in the synthesis process. Macrocyclic chelates have a transition metal in place, coordinated by oxygen and/or nitrogen atoms that are incorporated into chemical groups in the molecule. These precursors adsorb to the substrate and are pyrolyzed, thus incorporating the molecule into the greater structure of the catalyst, with the transition metal coordinating and stabilizing the atomic configuration of the catalyst, preventing them from sintering. One such macrocycle that has demonstrated good activity when used as a precursor is tris(2,2’-bipyridine) Co(II)hexafluoro-phosphate (CoTMPP) [37, 119].

Figure 7. A mesoporous hierarchically structured silica particle.
The later of the two approaches provides for more design and engineering opportunities, as there are far more potential component compounds than chelates or macrocycles, and they have a range of chemical structures and functionalities. Poly(pyrrole)s were identified early on as a catalytically active material [120]. It, and other nitrogen containing polymerizing materials, creates surfaces that are capable of catalyzing several reactions. The polymerization occurs at high temperatures, which dovetails nicely with the pyrolyzation step in the synthesis process. A transition metal once again stabilizes the forming active site. Cobalt poly(pyrrole) is one such example of an ORR catalyst designed by this method.

Alternatively, metal salts and low molecular weight nitrogen-containing compounds can be combined, where the metals and precursors will adsorb to the support. The transition metal ionically coordinates the precursors around it, with the nitrogen components of the precursors aligning to the metal. This atomic arrangement mimics that active site, and promotes proper atomic placement when the material is pyrolyzed, which establishes the active site.

1.9. **Catalyst-Ionomer Interaction**

Understanding how a particular catalyst interacts with an ionomer begins with the catalyst itself. The most ubiquitous tool for dissecting the kinetic activity of an electrocatalytic material is the rotating ring disk electrode (RRDE) After a catalyst has been optimized for performance (as determined by RRDE), the polarization curves that result, along with the ring current, can be manipulated to extract information about what the catalyst does, how it does it, and how fast. This will be addressed in detail later.
This work will evaluate an array of catalysts that are derived from the three precursor categories mentioned in section I.5. The mechanism by which they facilitate the ORR will be evaluated extensively, and a structure to property assessment will be made based on this kinetic data.

In order to advance the state of the cathode catalyst in particular, an extensive investigation of a catalyst that is the basis for a new generation of non-PGM catalyst designed by the Atanassov lab group will be discussed in detail. This material leverages many lessons learned from previous generations of catalysts that were investigated for this body of work. The catalyst has been optimized, and what is reported is a highly active catalyst synthesized from a 4-aminoantipyrine and iron nitrate precursor solution [121]. This composition was selected because the oxidation of the aromatic amine by the oxidizing agent, iron nitrate, results in a stable condensate in which the reaction has been carefully studied and understood [122]. It has been shown that the active site for the catalysis of the ORR is a surface feature composed of carbon and nitrogen that is coordinated or stabilized by a metal species. It is believed that the condensate’s structure, which has the general atomic configuration of an idealized active site, is largely maintained throughout the heat treatment. Heat treatment is the critical step in active site formation [43], where time, temperature, and to some extent temperature ramp rate are all factors, however, the exact nature of these active sites is still the subject of debate, and by extension, so is the mechanism of reduction.

Several groups have investigated the mechanism of oxygen reduction on a variety of catalysts [123-125], and have been able to calculate the number of electrons transferred in each catalytic event from the ratio of ring current \( i_r \) to disk current in a RRDE
experiment [126]. This method gives an indication to the number of electrons that are exchanged, and thereby the effective efficiency of the electrocatalyst, but useful information about the mechanism cannot be extrapolated because it assumes a single site mechanism. Our experience using macrocyclic compounds as precursors for ORR catalysts has shown that a dual site mechanism is in fact at play [34], at least in some systems.

In this work, we engage in a deep mechanistic study of the active site of non-PGM catalysts made from iron and 4-aminoantipyrine (Fe/AAPyr). It has been previously investigated to determine the optimal metal(s) composition and ratio of metal to precursor [121, 127, 128], as well as for the ratio of monometallic iron to 4-aminoantipyrine in the pre-pyrolysis slurry was optimized for ORR performance [121]. The activity of the material is investigated over a range of loadings in both acid and alkaline media, and the kinetic parameters of the reduction are determined.

Armed with an extensive understanding of the mechanism of an electrocatalytic electrode, the kinetics can be further improved by optimizing the ionic conductivity and water uptake of the ionomer that is used in both the membrane and the catalyst. Nafion® is a better cation conductor than it is an anion conductor, and is therefore more suitable for PEMFCs than it is for AFCs [129, 130].

Several groups around the world have been researching new generations of ionomers, and the Hibbs group out of Sandia National Laboratories (SNL) has synthesized two classes of anionically conductive ionomers that are stable in alkaline media (Fig. 8), and that are stable in high pH conditions [109, 131]. The two classes of ionomer are trimethylammoniated poly(sulfone) (ATMPS) and trimethylammoniated poly(phenylene)
(ATMPP). These ionomers, along with others such as the Tokuyama ionomer, may further improve the efficiencies of non-PGM catalysts.

These new ionomers will be evaluated in conjunction with a catalyst derived from iron and cyanamide (Fe/Cyan), which has been well characterized [72, 132]. The material evaluated here, deviated from the previously reported catalyst only in its morphology, as it was deposited onto a hierarchically structured silica (HSS) support, which is removed after pyrolysis.

Figure 8. Monomer structure of the poly(sulfone)-derived ionomer (top) and the poly(phenylene)-derived ionomers (bottom), where $R = \text{CH}_3$ or $\text{N}^+{\text{CH}_3}_3\text{Br}^-$. 
2. Objectives

Fuel cells, be they PEMFC or AFC, are complex systems. Although devoid of moving parts, the electrochemical processes that occur therein are just as intricate and involved as any combustion engine, and therefore designing a fuel cell is an involved process that requires contributions from many parties.

Some of the issues involved, although not all of them, include fuel storage (especially involving hydrogen), gaseous or fuel transport, cell design, stack design, water management, membrane processing, catalyst application, heat dissipation, gas diffusion, electrical system design, integration, and so on. Outside of that, as has been dwelt upon already in this text, is the issue of catalyst and ionomer design, and how they interact. This interaction will ultimately be considered when the ink is applied to the membrane, assembled in a cell, which is then put in a stack, and integrated into a system that is expected to produce a constant and reliable supply of electricity for a predictable period of time.

In short, the catalyst and ionomer are at the heart of such a device. Its position of prominence amongst all the other vital organs of the fuel cell is cause for a deep level of understanding so that it can be engineered intelligently as to provide the most benefit for the cost. The goals of this project seek to expand this body of knowledge with the overarching goal of pushing fuel cell technology out into the market place. The high minded ideal is to diversify our energy stock while making it cleaner, more sustainable, abundant, and stable. But the path to this, as it pertains to this contribution, are more incremental.

2.1. Enhance Understanding Of ORR On Non-PGM Materials
A lesser, but notable goal of this research is to demonstrate that the process by which non-PGM materials catalyze the reduction of oxygen most likely follows the 2x2 pathway, and are not capable of directly reducing oxygen to either water (in acid media), or hydroxyl (in alkaline media). The basis for this analysis is ORR studies conducted on Pt surfaces, but the mechanistic pathways that follow should still be valid.

Non-PGM materials are highly engineered microparticles that are designed and built from the atomic level up to achieve a desired result. Although there exists a myriad of candidate fuels for fuel cells, this work will focus on the reduction of oxygen within the context of a traditional hydrogen fuel cell.

The pathways by which molecular oxygen can be reduced is complex on its own, but the currents produced, how they are affected by the diffusion of reactants, how the products are formed and released, and the extent to which the reduction occurs are all important parameters of the reaction that must be considered when engineering a better non-PGM catalyst.

Much of this work will involve the analysis of the polarization curve(s) resulting from the ORR on a catalyst under certain conditions, as measured by the rotating disk electrode, where the voltage is swept while the current is measured. The amount of current produced is affected by the catalyst:ionomer (C:I) ratio, electrode loading of the catalyst, temperature, and rotational speed of the electrode, and the impact that such variability has on how a catalyst facilitates the ORR will be analyzed. The curve(s) will be normalized and corrected, and then various values will be extrapolated from the data. The data can then be fitted to a simplified equation that allows for the investigation of how the C:I ratio promotes or inhibits kinetics, and how loading and diffusion change the
observed current density. The primary analyses will involve Koutecky-Levich theory and Tafel equation calculations. A flux analysis of the involved species will also be performed in some cases, as well as peroxide experiments to determine how well the material reduces the intermediate to full O₂ reduction. All of this information will be used to enhance our understanding of the nature of the catalyst in order to design future generations of catalysts for more activity, less byproducts, and better durability.

2.2. Correlation Between Structure And Properties

The first major goal of this dissertation is to provide definitive evidence for the impact that the structure of the precursor has on kinetics of the catalyst. The hypothesis of this part of the work states that the precursor molecule has a very large role in dictating how the active site will be formed. While there are other influential factors that dictate this process, the precursor is the most influential.

As fuel cell catalyst research has advanced, it became apparent that some precursor materials produce better catalysts than others when all else is equal. With a nearly unlimited selection of candidate precursors, a catalyst designer can draw upon one of two strategies to make a better catalyst than the one before: blind luck or intelligent precursor selection.

While it is easy to make a black powder that can reduce oxygen, it is a much more difficult task to make one that does it well and for a prolonged period of time with minimal performance loss. It is therefore in the best interest of the catalyst designer to know what features of a precursor give rise to a better value for a given performance metric.
This objective is rather involved, as the precursors often times react with one another, dissolve poorly in some solvents, adsorb poorly to the template surface, or aggregate before the pyrolyzation step. The pyrolyzation process, which decomposes the precursors and alters their chemical state, changes the precursors even more, so that what is left is typically nothing like the starting material. However, understanding what the atomic structures will do throughout this process by examining the post-pyrolyzed material provides insight as to what precursors ought to be examined and which ones ought not be examined. Even the pyrolyzation process is to be examined, as time, temperature, atmosphere, and subsequent pyrolyzations have all been shown to impact the activity. Also to be considered are post-pyrolyzation treatments, such as acid leaching, also change the nature of the material.

Characterization of a material at several levels provides such insight. Particle size, porosity, surface area, metal content, atomic species and their binding states all give clues as to what transformations the material made during the course of synthesis. Even computational methods, such as density functional theory (DFT) are useful for determining composition. Such information is necessary to determine what the active site looks like, where it resides, and how it acts.

In tandem with the electrochemical and mechanistic analysis, the data collected from such techniques will be used to correlate the catalyst activity to various physical characteristics of the material. Determining which precursors beget which structures that beget a desired level of performance is a powerful tool in the thoughtful and intelligent engineering of a next generation material.

2.3. Novel Design Methods
The next major objective of this dissertation is to make the case that non-PGM catalysts can perhaps be as, or more active as an ORR catalyst than platinum. The hypothesis put forth in the body of this work suggests that some non-PGM catalysts have active sites that are much more active than a platinum surface, but that the density of the active sites is relatively low. By employing a host of methods and techniques, it may be possible to overcome certain structural limitations that are imposed on current generations of non-PGM cathodic materials.

The need for stability and electrical conductivity in an ORR catalyst for fuel cells made carbon black the host of choice for catalyst deposition. This graphitic carbon is cheap, abundant, and comes in a variety of particle sizes, surface areas, and morphologies, but most importantly of all, it is stable under cell operating conditions. Furthermore, the graphitic carbon is conjugated, whereby the p-orbitals overlap one another between neighboring carbon atoms, which are in plane all other carbons in the sheet. This allows the electrons to delocalizes, and conduct throughout the material [133]. It is also known to reduce oxygen, but also release a good amount of H$_2$O$_2$ as it does so, and some carbon blacks do this than others. It is therefore a natural choice as a support for deposited catalysts.

However, one metric by which a catalyst can be measured is by the current produced per unit mass, which is useful when comparing the activity to that of platinum. Using a carbon support is disadvantageous in this regard, because adding material results in an increased mass. If the goal is to cover the carbon support in a material that is more catalytically active than the support is, the contribution to activity from the support is lost, but mass is increased, which lowers the mass activity of the catalyst.
To circumvent this problem, as was touched upon earlier, a method to create a self-supported framework of carbonaceous material is pursued here. This method, the SSM as it has become known, in general involves depositing precursor material onto a non-graphitic material that has a negative of a surface feature that is desired, i.e. if a pore is desired, then the template should have lumps on the surface. After the material has been set, which involves pyrolysis for this work, the substrate can be etched away. The result is a “lost wax” replica of the support, much like the method that sculptors use to sculpt clay.

This method forgoes the carbon support altogether, instead creating a carbonaceous matrix from the atomic level up. Without the carbon black core, there is only one layer of material in the active sites can be created, as opposed to two (catalytic layer and the support). The theoretical density limit of the active sites is therefore 100% of the total mass, as opposed to the density being limited by the mass of the support.

The goal of this design method is to create such a carbonaceous network that is densely populated with active sites, but also to create one that is porous yet open. Specifically, it is a mesoporous structure that is sought after (pore sizes in the range of 10-100 nm, although this is a subjective range as some accounts say 2-50 nm), as they have demonstrated more activity than nanopores or micropores with similarly constituted material [134]. Additionally, an open framed structure allows for the diffusion of reactants into the material, while simultaneously providing channels for the products to move out.

2.4. Blending Ionomers With Non-PGM Catalysts Onto An MEA
The true test of a catalyst’s performance is how it works when implemented into an MEA. It is therefore useful to know how the mechanism of reduction is affected by the ionomer that is used to bind the catalyst and keep it in contact with the membrane. This work will serve to further define the role that the functionalities of an ionomer have on ORR. The objective for the last part of this dissertation will define the role that the ionomer has in the reduction of oxygen in alkaline media, and how improvements can be made on future generations of ionomers.

In regards to Nafion®, there has been a large body of research established on its roll in the reduction of oxygen, especially in acid [63, 135-137]. This is not true for the prior mentioned set of novel ionomers that were synthesized with alkaline conditions and anionic conductivity in mind.

While the bulk of this task requires a simple optimization experiment in finding the best ratio of catalyst to ionomer, a more involved process of analyzing the diffusion-limited current will be conducted, as well as an exploration of the effects that temperature has on reaction kinetics.

In order to understand how the ionomer effects the performance of the catalyst, it the activity will be subjected to a similar analysis as was done in analyzing the myriad of catalysts that were derived from the 3 classes of precursors. However, the focus of this line of research will be on linking the properties of the ionomers (ion exchange capacity, water uptake, and ionic conductivity) to the observable, quantifiable activity of the catalyst.
Drawing on this information, recommendations will be made on how to advance the state of the alkaline specific ionomer for AFCs, defining the important aspects of such an ionomer.

2.5. Summary of Objectives

- Correlate catalyst precursor structure to catalyst activity
- Identify the dominant mechanism to oxygen reduction by materials of each precursor class of catalysts
- Assess the effectiveness of each precursor class at promoting activity
- Perform a rigorous mechanistic study at high and low pH on a next generation of cathode catalyst
- Evaluate the oxygen and peroxide reducing activity of this catalyst, as well as peroxide yield and electron transfer efficiency
- Identify which properties of anionically conductive ionomers help better facilitate the ORR
- Compare the ionomeric performance of the novel ionomers to Nafion®
- Make recommendations on how new generations of anionically conductive ionomers can be improved
3. Methods and Materials

3.1. Chemicals

All reagents were purchased from commercial vendors and used without any further purification. The catalysts referred to as Fe/Cyan, Fe/AAPyr, and Fe/PEI were synthesized in the laboratory at the University of New Mexico. All others presented in this work were synthesized via their respective routes as described in the supplemental material to the article, “Cross-Laboratory Experimental Study of Non-Noble-Metal Electrocatalysts for the Oxygen Reduction Reaction” [96].

3.1.1. Catalyst synthesis materials

The hydrochloric acid (37%, ACS grade, diluted to 0.01 N), sulfuric acid (95% ACS grade, diluted to 2.0 M), and sucrose (ACS grade) were purchased from EMD Chemicals, gmbh. Acetone (production grade) was purchased from VWR International. Cyanamide (>98% pure) was purchased from Alfa Aesar. Iron(II) sulfate heptahydrate (>99%, ACS grade), 2-Propanol (>99.99%), Ethanol (99.7%) was purchased from Koptec. The 4-aminoantipyrine and Fe(NO$_3$)$_3$·9H$_2$O were purchased from Sigma-Aldrich, and the acetone (0.1 µm filtered) from Ultra Pure Solutions, Inc. Poly(etheleneimine) (the molecular weights (MW) used were: 2,000; 25,000; 600,000; 1,000,000; (Sigma-Aldrich was the source of the PEI and it was used as obtained).

3.1.2. Support materials

For the HSS, tetraethylorthosilicate (TEOS, Purum >98%), hexadecane (99%), and cetyltrimethylammonium bromide (CTAB, >99%) was purchased from Sigma-Aldrich. Polyether-polysiloxane/dimethicone copolyol surfactant (ABIL EM 90) was purchased from Evonik, gmbh.
The sacrificial support used in the non-HSS SSM supported catalysts, unless otherwise stated, was Cab-O-Sil™ EH-5 fumed silica (surface area: ~400 m²·g⁻¹), obtained from Cabot.

3.1.3. Synthesis of trimethyl aminated poly(benzylmethyl sulfone) (ATMPS)

The poly(sulfone) based class of ionomer was synthesized in accordance to the methods of Yan and Hickner [131]. Two samples of ATMPS were made (PS-A and PS-B), which vary in degree of functionality, ion exchange capacity, water uptake percentage, and ion conductivity, and those values are listed in Table 7.

3.1.4. Synthesis of trimethyl aminated poly(phenylene) (ATMPP)

The poly(sulfone) based class of ionomer was synthesized in accordance to the methods of Hibbs, Fujimoto, and Cornelius [109]. As with the ATMPS polymers, two samples were made (PP-D and PP-E) and their corresponding values for the same functional parameters are listed in Table 7.

3.1.5. Electrolyte and ink

Potassium hydroxide (ACS grade), sulfuric acid (95% ACS grade), and perchloric acid (ACS grade) were purchased from EMD Chemicals, gmbh. Nafion® (1100EW, 5%) is a product of DuPont, and was acquired from Solution Technology, Inc. The 2-Propanol (>99.99%) was purchased from Koptec.

3.2. Catalyst Synthesis

3.2.1. Synthesis of HSS

The monodispersed mesoporous silica particles were fabricated using the method of Carroll et al [116, 138], yielding a material with a surface area determined by BET surface area analysis to be on the order of 818.2622 m²·g. The aqueous phase of the
precursor solution was prepared by dissolving CTAB (1.82 g) in diH₂O (20 g), stirring rapidly at 40 °C until the solution cleared. The solution was then cooled to room temperature and TEOS (5.2 g) and 1 N HCl (0.57) was added and stirred for 30 min. The pH was then adjusted to 2.0. Preparation of the oil phase began by first dissolving ABIL EM90 in hexadecane at 3% by weight. The two phases were then blended together and shaken vigorously before being transferred to a 1000 mL round-bottom flask where it was heated to 80 °C for 3 hrs and at 70 mTorr. The solution was centrifuged to separate the phases, and the oil phase was decanted off. The aqueous phase was placed in a Rotovap for 40 min, and then calcined in air at 500 °C for 5 hrs.

3.2.2. Iron and cyanamide derived catalyst

The non-PGM catalyst for oxygen reduction in this experiment was first reported by Chung et al [72, 132], but the material used here was deposited onto the mesoporous silica, and the SSM resulted in a self supported iron-cyanamide derived carbonaceous material (FeCyan/C). Deposition of the precursor material was performed via the dry-impregnation method of Pylypelenko et al [98], which was used to deposit platinum particles onto similar a silica material.

Sucrose, cyanamide, and FeSO₄·7H₂O (3:2:2 by mass) were dissolved in acetone (~5 mL/g of precursor) and 2 M sulfuric acid (~2.5 mL·g⁻¹ of precursor). The solution was sonicated at 3 W for 2 min, followed by the drop-wise addition 2M H₂SO₄ is added drop wise until any remaining solids were dissolved. The solution was added in ~30 aliquots onto the silica, folded in, stirred with a glass rod, and allowed to dry before the next deposition. The material was dried for 1 hr at 150 °C after half the solution was added before proceeding to deposit the rest. After the final deposition, the material was allowed
to dehydrate overnight in a vented oven at 150 °C. The vessel was then scraped, and the material was ground to a fine powder with mortar and pestle.

The material was pyrolyzed in a tube furnace under an ultra-high purity N\textsubscript{2} atmosphere. The temperature was ramped up to 200 °C at 3 °C·min\textsuperscript{-1} for 60 min before the temperature was increased to 850 °C at 10 °C·min\textsuperscript{-1} for 4 hrs. The material was subsequently allowed to cool back to room temperature before it was reground to a fine powder using the mortar and pestle. To remove the silica template and to leach away excess metal, the material was placed in a Corning 50 mL centrifuge tube and etched for 24 hrs in HF buffer solution. It was then centrifuged, decanted, and rinsed a minimum of 4 times before being allowed to dry at 55 °C overnight. The powder was then ground up one last time using the mortar and pestle.

3.2.3. Iron and 4-Aminoantipyrine derived catalyst

The Fe/AAPyr catalyst was prepared by wet impregnation of iron and aminoantipyrine precursors onto the surface of fumed silica in a ratio of 1:8 iron (from FeNO\textsubscript{3}·9H\textsubscript{2}O) to 4-aminoantipyrine by mass. First, a calculated amount of silica was dispersed in water in an ultrasonic bath. Then, an equal mass aminoantipyrine was dissolved in a minimal amount of acetone was added to the silica, followed by ultrasonication for 20 minutes. Finally, an aqueous solution of iron nitrate was added to the SiO\textsubscript{2}-AAPyr solution and ultrasonicated for 8 hours (the total metal loading on silica was calculated to be ~15wt.%). After ultrasonication, the viscous solution of silica and Fe/AAPyr was dried overnight at 85 °C. The resulting solid was ground to a fine powder in an agate mortar, and then subjected heat treatment (HT). The general conditions of HT were UHP N\textsubscript{2} (flow rate 100 cc·min\textsuperscript{-1}), 10 °C·min\textsuperscript{-1} temperature ramp rate, and a 3 hour
heat duration at 800 °C. After pyrolyzation, the powder was etched with HF buffer solution overnight to remove the silica.

3.2.4. Iron and poly(etheleneimine)

Fe-PEI catalysts were prepared via wet impregnation of iron and poly(etheleneimine) precursors onto the surface of fumed silica. First, a calculated amount of silica was dispersed in water using the sonobath. Then, a solution of poly(etheleneimine) in water was added to silica, and sonicated for 20 minutes. Then, an aqueous solution of iron nitrate was added to the SiO$_2$-PEI solution (the total metal loading on silica was calculated to be ~15wt.%), and then sonicated for 8 hours in the sonobath. After sonication, a viscous solution of silica and Fe-PEI was dried overnight at T=85 °C. The solid was ground to a fine powder in an agate mortar, and then subjected to the heat treatment (HT). The general conditions of HT were: UHP N2 atmosphere flowing at a rate of 100 cc·min$^{-1}$, HT temperatures of 700, 800, and 900 °C, HT temperature ramp rates of 10, 20, and 30 °C min$^{-1}$, and HT durations of 1, 2 and 3 hours. Initially, the iron to PEI ratio selected was 1:1 (by mass), and the catalyst was denoted as Fe-PEI. In the experiments involving the variation of Fe:PEI ratios, catalysts with Fe-PEI, Fe-2PEI, Fe-3PEI and Fe-4PEI were synthesized (again, the ratios were by mass).

3.3. Preparation Of The Working Electrodes

Working electrodes were prepared by first mixing 5 mg of the Fe/AAPyr electrocatalyst with 850 µL of isopropyl alcohol and 150 µL of Nafion® (0.5% wt., DuPont). The mixture was sonicated before being pipetted onto a glassy carbon disk with a sectional area of 0.2472 cm$^2$.  

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For the ionomeric studies, each experimental ionomer solution was diluted to 1% by weight (when necessary). The solution was added to a stock solution to an 80%-20% mixture of diH2O to isopropyl alcohol (4:1) so that the final concentration of ionomer in 4:1 equated to a mass ratio of ionomer to catalyst of 0.30. The appropriate amount of this ionomer solution in 4:1 was added to a known mass of catalyst. The ink was then sonicated for 2 min at 3W with a probe tip sonicator just before use for better dissolution of the particles.

### 3.4. Electrochemical Measurements

#### 3.4.1. Rotating disk electrode

Capacitance measurements were performed using the Pine Instrument Company electrochemical analysis system and a Pine Instruments RRDE. The rotational speed, although immaterial to the measurement, was 1600 RPM at a scan rate of 10 mV·s⁻¹, and the ring current was ignored. The electrolyte - 0.1 M HClO₄, 0.5 M H₂SO₄, or 1 M KOH - was purged with N₂, and in some instances Ar, for at least 10 min before use. When necessary, the cell was heated using a Thermo temperature regulator. The reference electrode was Ag/AgCl in all acid studies and Hg/HgO in all alkaline studies. The counter electrode used in all experiments was either an encapsulated Pt wire or graphite rod.

#### 3.4.2. Rotating ring disk electrode

Electrochemical analysis for synthesized catalysts was performed using the Pine Instrument Company electrochemical analysis system and a Pine Instruments rotating ring disk electrode. The rotational speeds reported commonly were 100, 400, 900, and 1600 RPM, with a scan rate of 10 mV·s⁻¹, with the ring potential held at 1100 mV. The
electrolyte was 0.5 M H$_2$SO$_4$ for studies in acid media, and 1 M KOH for alkaline studies, both saturated in O$_2$ at room temperature. A platinum wire counter electrode, a Ag/AgCl reference electrode for acidic media, and a Hg/HgO reference electrode for alkaline media were used. The electrode commonly loadings used in this study were 40, 50, 80, 100, 200, 400, 600, and 800 µg·cm$^{-2}$.

3.5. Characterization

3.5.1. Scanning electron microscopy

Scanning electron microscopy (SEM) was performed on a Hitachi S-800 instrument.

3.5.2. Transmission electron microscopy

Transmission electron microscopy (TEM) imaging was carried out on a JEOL 2010 instrument on a copper grid.

3.5.3. X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) spectra were acquired on a Kratos Axis Ultra X-ray photoelectron spectrometer using a Al Kα source monochromatic operating at 150 W with no charge compensation. The base pressure was about 2x10$^{-10}$ torr, and operating pressure was around 2x10$^{-9}$ torr. Survey and high-resolution spectra were acquired at pass energies of 80 eV and 20 eV, respectively. Acquisition time for survey spectra was 2 min, for C1s and O1s spectra - 5 min, for N 1s and Fe 2p –30 min. Data analysis and quantification were performed using CasaXPS software. A linear background subtraction was used for quantification of C1s, O1s and N1s spectra, while a Shirley background was applied to Fe 2p spectra. Sensitivity factors provided by the manufacturer were utilized. A 70% Gaussian/30% Lorentzian line shape was utilized in the curve-fit of N 1s.
3.5.4. Brunauer, Emmett, and Teller surface area analysis

Brunauer, Emmett, and Teller (BET) surface area analysis was performed on a Gemini BET Surface Area Analyzer, using at least 10 mg of sample that was heated at 120 °C for >4 hours in N₂ atmosphere.
4. Results and Discussion

4.1. Non-Platinum Group Metal Catalysts (Cross Lab II Sample Set)

4.1.1. Macrocyclic metal chelate precursor derived catalyst

Macrocyclic precursors are, in theory, an ideal precursor to a non-PGM catalyst because the active site constituent atoms begin in the appropriate conformation, where the metal is coordinated by at least two nitrogen species. Commonly, these precursors are iron or cobalt coordinated N₄ chelates (Me-N₄ chelates).

4.1.1.1. Synthesis

The general approach to synthesizing a catalyst of this class is to combine the Me-Nₓ chelate with extra metal and any other supporting materials. Pyrolysis is performed in an unreactive vessel and placed in a quartz glass tube, and heated under constant flow of a reductive or inert gas (N₂, Ar) or a reactive gas (NH₃) in a furnace. The heat treatment consists often times of a low temperature (<400 °C) dwell to drive off solvent or partially decompose the precursors, and at least one step at high temperature (~800 °C) for an extended period of time, typically >45 min. After cooling under inert gas, the catalyst is then leached in acid, followed by a wash in diH₂O, and then dried. The product obtained is often subjected to a 2nd, and even 3rd heat treatment, followed by a 2nd and/or 3rd acid leach and washing. The product will then be ground to a fine powder.

4.1.1.2. Characterization

The materials examined in this work that are of this class of non-PGM catalyst are UK63 and UK65 (Helmholtz-Zentrum, Berlin), CHb200900 (Osaka Municipal Technical Research Institute, Osaka) and CoTMPP-700 (University of New Mexico, NM). The catalyst macrocyclic Me-N₄ chelates are FeCITMPP for UK63, CoTMPP for both UK65
and CoTMPP-700, and hemoglobin for CHb200-900. The SEM images suggest that the precursor might influence the particle size of the resulting powder. CHb200-900 (Fig. 8A), CoTMPP-700 (Fig. 9B), UK63 (Fig. 9C), and UK65 (Fig. 9D) vary in particle size and morphology. The two that employ the CoTMPP precursor (Figs. 9B and 9D) both have a fairly dispersed morphology with thin, broad platelet like structures that span a wide range of widths. The CHb200-900 is almost uniformly small particle size in nature, ~200 nm, and unaggregated, while the UK63 is almost uniformly aggregated with larger particle sizes.

TEM imaging was performed on the materials, in which are depicted CHb200-900 (Fig. 10A), CoTMPP-700 (Fig. 10B), UK63 (Fig. 10C), and UK65 (Fig. 10D). The images show some of the same features that were seen in the SEM, but in addition the metal particles are visible amid the graphitic superstructure of the particles.

The surface areas of the materials as calculated using the BET method tended to be in the vicinity of about 800 m²·g⁻¹, and more specifically were reported to be 715, 766, 869, and 818 m²·g⁻¹ in respect to alphabetical order of the sample names (Table 1).

4.1.1.3. Electrochemical analysis

The effects of electrode loading on the various aspects of ORR was investigated using a range of loadings, from the very low (40 µg·cm⁻²) to the very high (800 µg·cm⁻²)
acid, RRDE technique. As loading increases, so does the limiting current and half-wave potential, while the amount of peroxide that desorbs and does not get completely reduced to water decreases. Changes in the rate of diffusion also impact the amount of current produced, which is unequivocally demonstrated at a high loading of 400 µg·cm⁻² (Fig. 11), as the diffusion-limited current increases and more peroxide evolves from the catalyst surface.

The electrocatalyzed reduction of oxygen macrocyclic Me-Nₓ chelate precursor derived materials was quantitatively analyzed using the Koutecky-Levich theory at both 40 and 400 µg·cm⁻² loadings, current-potential curves were obtained at five different rotational speeds: 100, 400, 900, 1600, and 2500 RPM (Fig. 11). The disk current (iₐ) can be used to find the kinetic current through the relationship [139]:

\[
\frac{1}{i_d} = \frac{1}{i_k} + \frac{1}{0.62nFCD_O^2D_O^{-1/2}v^{-1/6}ω^{1/2}A}
\]  

(4.1)

where \(i_k\) is the electrode potential dependent kinetic current density of the ORR, \(n\) is the

<table>
<thead>
<tr>
<th>Class</th>
<th>Sample</th>
<th>BET S.A. (m²·g⁻¹)</th>
<th>(E_{0.5}) (mV)</th>
<th>(i_{\text{lim}}) (mA·cm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Macrocycle</td>
<td>CHb200-900</td>
<td>715</td>
<td>0.427</td>
<td>-1.489</td>
</tr>
<tr>
<td></td>
<td>CoTMPP-700</td>
<td>766</td>
<td>0.585</td>
<td>-3.370</td>
</tr>
<tr>
<td></td>
<td>UK63</td>
<td>869</td>
<td>0.607</td>
<td>-3.289</td>
</tr>
<tr>
<td></td>
<td>UK65</td>
<td>818</td>
<td>0.547</td>
<td>-3.954</td>
</tr>
<tr>
<td>Small Molecule</td>
<td>FC280</td>
<td>710</td>
<td>0.517</td>
<td>-0.917</td>
</tr>
<tr>
<td></td>
<td>GAdFeCu</td>
<td>543</td>
<td>0.433</td>
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<td>M786</td>
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<td>-3.062</td>
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<td></td>
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<td>-1.122</td>
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<td></td>
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<td>0.630</td>
<td>-0.968</td>
</tr>
<tr>
<td></td>
<td>Fe/PEI</td>
<td>&gt;1000</td>
<td>~0.600</td>
<td>~5.500</td>
</tr>
</tbody>
</table>
average number of electrons transferred per catalytic event (the theoretical maximum is 4), $F$ is the Faraday’s constant (96,487 C·mol$^{-1}$), $C_{O_2}$ is the concentration of molecular oxygen in the electrolyte (1.117 E$^{-6}$ mol·mL$^{-1}$), $D_{O_2}$ is the $O_2$ diffusion coefficient in aqueous media (1.9 E$^{-5}$ cm$^2$·s$^{-1}$), and $\nu$ is the kinetic viscosity of the electrolyte (0.01000 cm$^2$·s$^{-1}$), $\omega$ is the angular momentum in rads·s$^{-1}$, and $A$ is the sectional area of the electrode.

By plotting $|i_d|^{-1}$ against $\omega^{-1/2}$, Eq. 4.1 allows us to extrapolate the $i_k$ and $n$ in a system where all of the other values are known. Using data reported at 0.20 V, the Koutecky-Levich plot for all loadings at both low and high pH (Fig. 12) shows how the...
number of electrons transferred per turn at each loading compares to the theoretical 2 and 4 electron pathways, as determined by similarity to the slope of the line compared to either of the theoretical lines. The line for each sample is clearly parallel to, or even steeper than the theoretical 2 electron line. Table 2 lists the values for the kinetic data as calculated by the Levich equation (Eq. 4.1) for low loadings, and the general consensus for the macrocyclic Me-N\textsubscript{x} chelate class is that electron transfer is low averaging 1.4 electrons, and the diffusion-limited current, \( i_k \), averages 3.045 mA·cm\textsuperscript{-2} with a standard deviation of 0.851. At high loadings there is a shift to a higher \( i_k \) of 5.672 mA·cm\textsuperscript{-2} (\( \sigma_x = 0.417 \)) and an average electron transfer coefficient of 3.1. The calculated values for each sample are tabulated in Table 3.

The Tafel method was used to analyze the ORR as catalyzed by this class of material, and the kinetic parameters of the reaction were obtained. For each electrode loading in
the low current regime of the Tafel plot (not shown, but is apparent from the kinetic region of the plots in Fig. 11), there was strong agreement for the \( i_d \) independent of rotational rate down to a potential of about 0.7 V. The strong concurrence here suggests that at this high potential, the electrochemical current density is purely kinetic. The kinetic current density can be described using the expression [140]:

\[
E = E^0 + \frac{2.303RT}{an_αF} \log(i^0) - \frac{2.303RT}{an_αF} \log(i_d)
\] (4.2)

where \( α \) is the symmetry coefficient for electron transfer in the rate-determining step (RDS), \( n_α \) is the number of electrons transferred in the RDS, and is presumed to be 1, \( E \) is the electrode potential as applied, \( E^0 \) is the thermodynamic electrode potential of the ORR (1.23 V vs RHE), \( R \) is the universal gas constant (8.314 J·mol\(^{-1} \)·K\(^{-1} \)), \( T \) is the temperature in terms of K (298 K), and \( F \) is the Faraday constant (96,487 C·mol\(^{-1} \)). The plot of \( E \) as a function of \( \log(i_d) \) (Fig. 13) gives information about the kinetic parameters of the ORR that can be derived from the line equation for specific regions of the plot. The Tafel slope (=\( 2.303RTα^{-1}n_α^{-1}F^{-1} \)) and the intercept (=\( E^0 + (2.303RTα^{-1}n_α^{-1}F^{-1})\log(i_d) \)) allow for the values of \( α \) and \( i^0 \), Figure 12. Koutecky-Levich plots of ORR on A.) CHb200-900, B.) CoTMPP-700, C.) UK63, and D.) UK65 at low (□) and high (○) loadings.
which is the exchange current density, to be calculated when all other values are known. The corresponding values for $i^0$ for both loadings are listed in Tables 2 and 3, for low and high loading, respectively. Also listed is the kinetic rate constant ($k_e$) for the RDS, which is defined by the relationship between $i^0$ and $k_e$ as [141]

$$i^0 = nFk_eC_{O_2}$$

(4.3)

where the $n$ is the Koutecky-Levich determined number of transferred electrons in the rate determining step of the reaction. The values for $i_k$, $\eta$, $i^0$, and $k_e$ are consistent among all interclass samples for both loadings ($\sigma_2$ for all samples, $\sigma_1$ for all but CHb200-900). For the low loading, these values are 3.045 mA·cm$^{-2}$, 1.4 electrons, 1.706 x10$^{-6}$ mA·cm$^{-2}$, and 1.078 x10$^{-5}$ cm·s$^{-1}$, respectively. There is a statistical non-outlier (within 2$\sigma$ of the mean) that is very different from the others in the set in the low loading for CHb200-900, and when this sample is ignored, these averages become 3.470 mA·cm$^{-2}$, 1.4 electrons, 1.193 x10$^{-6}$ mA·cm$^{-2}$, and 1.193 x10$^{-6}$ cm·s$^{-1}$, respectively ($\sigma_k = 0.083, 0.3, 1.208 x10^{-6}, 5.990 x10^{-6}$, respectively again). For the high loading, the averages, respecting the convention of order here, are 5.672 mA·cm$^{-2}$, 3.1 electrons,
6.523 \times 10^{-6} \text{ mA}\cdot\text{cm}^2$, and $3.598 \times 10^{-6} \text{ cm}\cdot\text{s}^{-1}$, and with $\alpha_x$ of 0.417, 1.1, 1.234 $\times 10^{-5}$, $7.009 \times 10^{-5}$.

The fact that this class of catalyst in general will transfer 3.1 electrons out of 4 per catalytic event is indicative the 2x2 pathway, or perhaps a combination of active sites that follow either the 4 electron pathway or the 2x2 pathway, is being used to reduce oxygen. The inefficiency of the materials likely stems from desorption of the peroxide during before being fully reduced. Even if a material fully reduces oxygen to water, the pathway used could still be a 2x2 route to reduction if the material can effectively reduce peroxide. However, at full efficiency, if a material cannot reduce peroxide appreciably, then the direct 4 electron pathway is the only path available. If there is incomplete reduction of oxygen on a material, this same experiment will also reveal the pathway used. If peroxide is evolving, measuring the amount of peroxide reduction can provide insight into the

<table>
<thead>
<tr>
<th>Class</th>
<th>Sample</th>
<th>$R^2$ Fit</th>
<th>$I$</th>
<th>$i_h$ (mA\cdot\text{cm}^{-2})$</th>
<th>$i_k$ (mA\cdot\text{cm}^{-2})$</th>
<th>$k_e$ (cm\cdot\text{s}^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Macrocyclie</td>
<td>CHb200-900</td>
<td>0.996</td>
<td>1.3</td>
<td>1.773</td>
<td>$3.244 \times 10^{-6}$</td>
<td>$2.236 \times 10^{-5}$</td>
</tr>
<tr>
<td></td>
<td>CoTMPP-700</td>
<td>0.975</td>
<td>1.2</td>
<td>3.546</td>
<td>$3.151 \times 10^{-7}$</td>
<td>$2.414 \times 10^{-6}$</td>
</tr>
<tr>
<td></td>
<td>UK63</td>
<td>0.932</td>
<td>1.3</td>
<td>3.481</td>
<td>$6.926 \times 10^{-7}$</td>
<td>$4.618 \times 10^{-6}$</td>
</tr>
<tr>
<td></td>
<td>UK65</td>
<td>0.955</td>
<td>1.7</td>
<td>3.382</td>
<td>$2.570 \times 10^{-6}$</td>
<td>$1.371 \times 10^{-6}$</td>
</tr>
<tr>
<td>Small Molecule</td>
<td>FC280</td>
<td>0.902</td>
<td>0.9</td>
<td>2.035</td>
<td>$2.013 \times 10^{-8}$</td>
<td>$1.966 \times 10^{-7}$</td>
</tr>
<tr>
<td></td>
<td>GAdFeCu</td>
<td>0.884</td>
<td>0.9</td>
<td>1.512</td>
<td>$1.161 \times 10^{-7}$</td>
<td>$1.118 \times 10^{-6}$</td>
</tr>
<tr>
<td></td>
<td>LANL-Fe-CM-C</td>
<td>0.778</td>
<td>1.4</td>
<td>1.500</td>
<td>$1.212 \times 10^{-7}$</td>
<td>$7.437 \times 10^{-7}$</td>
</tr>
<tr>
<td></td>
<td>M786</td>
<td>0.967</td>
<td>1.2</td>
<td>2.479</td>
<td>$1.614 \times 10^{-8}$</td>
<td>$1.229 \times 10^{-7}$</td>
</tr>
<tr>
<td></td>
<td>MSUcat800</td>
<td>0.958</td>
<td>1.1</td>
<td>3.218</td>
<td>$7.925 \times 10^{-10}$</td>
<td>$6.167 \times 10^{-6}$</td>
</tr>
<tr>
<td>Polymer</td>
<td>DAL900A</td>
<td>0.957</td>
<td>1.3</td>
<td>1.354</td>
<td>$9.955 \times 10^{-8}$</td>
<td>$6.780 \times 10^{-7}$</td>
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<tr>
<td></td>
<td>DAL900C</td>
<td>0.977</td>
<td>0.9</td>
<td>2.960</td>
<td>$3.785 \times 10^{-7}$</td>
<td>$3.541 \times 10^{-6}$</td>
</tr>
<tr>
<td></td>
<td>Fe/PEI</td>
<td>NA</td>
<td>~3.1</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
</tbody>
</table>
dominant route by measuring the efficacy of the material at reducing peroxide, and finding its contribution to the observable current.

Reduction H₂O₂ on non-PGM materials is affected by the diffusion rate of reactant in anaerobic solution, although some materials are very poor at reducing it, and the change in current between rotational speeds in small. To measure this, the 0.5 M H₂SO₄ electrolyte was purged with N₂ and a small amount of peroxide was added so that the final concentration of peroxide was 1.3 mM, which corresponds to the concentration of molecular oxygen in a saturated solution.

Even at the highest diffusion rate, the only material of this class that had an appreciable reduction current in dilute, anaerobic peroxide was UK65. The reduction current, corrected for capacitance, for the samples at 0.005 V was -0.161, -0.320, -0.221, and -0.870 mA cm⁻² for CHb200-900, CoTMPP-700, UK63, and UK65, respectively.

The ability of a material to reduce H₂O₂ may partially be dependent on the precursor,

| Table 3. | Electron transfer coefficient (# of e⁻), kinetic current density \( i_k \) (mA cm⁻²), exchange current density \( i_0 \) (mA cm⁻²), and electron transfer rate constant \( k_e \) (cm s⁻¹), along with the R² fit for the Koutecky-Levich plot for each sample at 400 \( \mu \)g cm⁻², segregated according to precursor class. |
|----------|-------------------------------------------------|------------------|-----------------|-----------------|-----------------|
| Class    | Sample  | R² Fit | \( \eta \) | \( i_k \) (mA cm⁻²) | \( i_0 \) (mA cm⁻²) | \( k_e \) (cm s⁻¹) |
| Macrocycle | CHb200-900 | 0.976 | 1.6 | 5.219 | 2.503 x 10⁻⁶ | 2.411 x 10⁴ |
|          | CoTMPP-700 | 0.900 | 3.7 | 5.420 | 4.224 x 10⁻⁷ | 1.013 x 10⁻⁶ |
|          | UK63      | 0.882 | 4.0 | 5.971 | 7.914 x 10⁻⁸ | 1.742 x 10⁻⁷ |
|          | UK65      | 0.927 | 3.1 | 6.077 | 5.610 x 10⁻⁷ | 1.612 x 10⁻⁶ |
| Small Molecule | FC280   | 0.950 | 1.7 | 5.988 | 7.917 x 10⁻⁷ | 4.020 x 10⁻⁶ |
|          | GAdFeCu   | 0.968 | 2.0 | 5.363 | 1.322 x 10⁻⁷ | 5.976 x 10⁻⁷ |
|          | LANL-Fe-CM-C | 0.912 | 3.1 | 5.542 | 6.834 x 10⁻⁸ | 1.968 x 10⁻⁷ |
|          | M786      | 0.951 | 2.2 | 5.782 | 2.539 x 10⁻⁷ | 1.038 x 10⁻⁶ |
|          | MSUcat800 | 0.968 | 1.7 | 5.559 | 2.180 x 10⁻⁷ | 1.161 x 10⁻⁷ |
| Polymer  | DAL900A   | 0.858 | 5.0 | 5.542 | 5.792 x 10⁻⁸ | 1.021 x 10⁻⁷ |
|          | DAL900C   | 0.925 | 2.9 | 5.833 | 2.137 x 10⁻⁷ | 6.864 x 10⁻⁷ |
|          | Fe/PEI    | NA    | ~3.9 | NA    | NA              | NA              |
and partially on the preparation of the catalyst. CoTMPP-700 and UK65 are the two that have the most reduction current with a H₂O₂ analyte, and they both use CoTMPP as the precursor molecule, but UK63 has nearly 2.5-fold the current that of CoTMPP-700 at this potential.

The case for the preparation is made in the fact that UK63 demonstrated significant reduction of peroxide at the highest rotational speed, performing nearly twice as well as CoTMPP-700 at 2500 RPM. The reported current densities at this speed are -0.217, -0.367, -0.637, and -1.259 mA·cm⁻² in the same order. UK63 and UK65 both were made using the same procedure, but UK63 used an iron precursor and UK65 used a cobalt precursor. The sudden improvement in reduction at high rotational speeds in UK63 suggests that the material is unfavorable to the diffusion of peroxide through the material or it is very hydrophilic and water must be kinetically forced to desorb from the surface.

4.1.2. Small molecule precursor derived catalyst

Small molecule precursors have all of the atomic constituents that are required to comprise a catalyst, and have more versatility than the metal chelates, as there are a multitude of compounds, with vastly different properties, that can be employed. The functional groups of these atoms have properties that can be exploited to influence morphology, active site composition, carbon or metal content, etc. Furthermore, they are far less expensive than most metal chelates. For these reasons, the small molecule class of catalyst is an attractive approach to catalyst design.

4.1.2.1. Synthesis

This synthesis method involved with this route typically begins with a metal salt as the sole source of metal, while a N-containing molecule proves the N content for the
product. These can be supplemented with a carbon source to increase the carbon content if necessary. They are often deposited onto porous carbon blacks, and the small molecules are employed to penetrate the pores where the active site is to be formed. Pyrolysis is performed in an unreactive vessel and placed in a quartz glass tube, and heated under constant flow of a reductive or inert gas (N$_2$, Ar) or a reactive gas (NH$_3$) in a furnace. The heat treatment consists often times of a low temperature (<150 °C) dwell to drive off solvent or partially decompose the precursors, and at least one step at high temperature (~800 °C) for an extended period of time, typically >45 min. After cooling under inert gas, the catalyst is then leached in acid, followed by a wash in diH$_2$O, and then dried. The product obtained is often subjected to a 2nd, and even 3rd heat treatment, followed by a 2nd and/or 3rd acid leach and washing. The product will then be ground to a fine powder.

4.1.2.2. Characterization

The materials examined in this work that are of this class of non-PGM catalyst are GAdFeCu (Osaka Municipal Technical Research Institute, Osaka), FC280 and M786 (Institut National de la Recherche Scientifique, Quebec), LANL Fe/CM/C (Los Alamos National Laboratory, Los Alamos), MSUcat800 (Michigan State University, East Lansing. The catalyst macrocyclic Me-N$_4$ chelates are FeCITMPP for UK63, CoTMPP for both UK65 and CoTMPP-700, and hemoglobin for CHb200-900. The SEM images depict mostly monodispersed, amorphous small particles. FC280 (Fig. 14A), LANL/Fe/CM/C (Fig. 14C), and M786 (Fig. 14D), have a similar spherical particle morphology as well as size (100-1000 nm), while GAdFeCu (Fig. 14B) has a large, sheet-like structure.
TEM images, where FC280 (Fig. 15Aa and 15Ab), GAdFeCu (Fig. 15Ba and 15Bb), and M786 (Fig. 15Ca and 15Cb) are represented, and show that the material is composed of a graphitized carbon matrix with small metal agglomerates, from 10 to 40 nm in diameter.

Generalizing the BET surface areas of the small molecule derived catalysts is not instructive, as they range from 543 m$^2$·cm$^{-2}$ on the low end (GAdFeCu) to 1088 m$^2$·g$^{-1}$ on the high (M786), an improvement of over 200%. Rounding out the series are LANL/Fe/CM/C, FC280, and MSUcat800 at 604, 710, and 762 m$^2$·g$^{-1}$ (Table 1), respectively.

4.1.2.3. Electrochemical analysis

Again, the effects of electrode loading on the ORR was investigated across a range of loadings, from 40 µg·cm$^{-2}$ to 800 µg·cm$^{-2}$, using the RRDE. Predictably, as the loading is increased, the $i_{\text{lim}}$ and $E_{0.5}$ improve, and more H$_2$O$_2$ evolves. The effects of diffusion on 400 µg·cm$^{-2}$ of the representative materials are visible in Figs. 16 and 17 as the diffusion current increases and more peroxide evolves from the catalyst surface.

The Koutecky-Levich method of analysis was employed again, for both 40 and 400 µg·cm$^{-2}$ loadings, and $i_d$ as a function of $E$ was plotted for the five diffusion
rates (Figs. 16 and 17). Equation 4.1 then yields information about the kinetics of the reaction.

The plot of $|i_d|^{-1}$ versus $\omega^{1/2}$ for both low and high loadings (Figs. 18 and 19) from a reporting potential of 0.20 V, compares catalysts to the theoretical 2 and 4 electron pathways. Again, even more so than what was seen with the macrocyclic chelate precursor set, the line for each sample is steeper than the theoretical 2 electron line. A tabulation of the values are in Table 2 for the low loading Levich analysis. The average for the small molecule precursor derived catalysts at this loading is 1.1 electrons, and an $i_k$ average of 2.149 mA·cm$^{-2}$ ($\sigma_x = 0.723$). The 400 $\mu$g·cm$^{-2}$ loading is vastly improved, where the $i_k$ is increased to an average 5.647 mA·cm$^{-2}$ ($\sigma_x = 0.242$), which is at parity with the macrocyclic chelates, and an average electron transfer number

![SEM images of small molecule derived catalysts. A) FC280, B) GAdFeCu, and C) M786. Not shown is LANL Fe/CM/C and MSUcat800.](image)
improves to 2.1. The individual calculations for each sample are compiled in Table 3 for the high loading.

The catalysis of ORR was again analyzed using the Tafel equation (Eq. 4.2). As catalyzed by this class of material, the kinetic parameters of the reaction were obtained for the low current regime of the Tafel plot. The diffusion independent regime of the polarization curve went to a slightly lower potential, down to \( \sim 0.65 \, \text{V} \) (Figs 20 and 21).

For this class of samples, there was good agreement between the samples as to their kinetic parameters, and how they reduce oxygen. For the low loading, the average \( i^0 \) was found to be \( 5.488 \times 10^{-8} \, \text{mA} \cdot \text{cm}^{-2} \), and the average \( k_c \) was \( 4.374 \times 10^{-7} \, \text{cm} \cdot \text{s}^{-1} \). For the high loadings, the averages were \( 2.536 \, \text{mA} \cdot \text{cm}^{-2} \) and \( 1.194 \times 10^{-6} \, \text{cm} \cdot \text{s}^{-1} \) respectively.

Reduction \( \text{H}_2\text{O}_2 \) on the small molecule precursor class of materials had no consistent trend across the sample set, with some

![Figure 16. RRDE currents for ORR on 400 \( \mu\text{g} \cdot \text{cm}^{-2} \) of A.) FC280, B.) GAdFeCu, C.) LANL Fe/CM/C, and D.) M786 at (\( \circ \)) 100, (\( \circ \)) 400, (\( \circ \)) 900, (\( \circ \)) 1600, and (\( \circ \)) 2500 RPM.](image)
being nearly incapable of the task (FC280), and others clearly showing the ability to reduce the specie (GAdFeCu).

For this set, the reduction currents reported at 0.005 V at 1600 RPM was -0.172, -0.355, -0.350, -0.231, and -0.181 mA·cm⁻² for FC280, GAdFeCu, LANL/Fe/CM/C, M786, and MSUcat800, respectively. The only sample to show consistent diffusion dependent reduction was LANL/Fe/CM/C, which had a predictable increase in current as the rotational speed was increased. The other samples did not follow this trend, with only modest increases in current at higher speeds. The MSUcat800 sample statistically did show an improvement, but the baseline could be considered noise, and the reduction current at 1600 RPM was very low (-0.181 mA·cm⁻²). However, at 2500 RPM the reduction current suddenly materialized, producing -0.894 mA·cm⁻², the highest of all the samples of this class.

![Figure 18. RRDE curves for MSUcat800 under the same conditions as in Fig. 16.](image)

![Figure 17. Koutecky-Levich plots of ORR on A.) CHb200-900, B.) CoTMPP-700, C.) UK63, and D.) UK65 at low (□) and high (○) loadings.](image)
Again, as was the case with the macrocyclic chelates series, this could be explained by the precursor selection and/or the synthesis approach. Clearly, some catalysts possess the ability to reduce peroxide at any diffusion rate, while others are devoid of this capability, and yet others will do so at high diffusion rates. The active site moiety no doubt dictates the reductive performance of peroxide, but the structure and the hydrophilicity of the support is likely controlling the flux of reactants and products, which drives the reaction rate.

4.1.3. Polymer precursor derived catalyst

Nitrogen containing polymers, that are often electrically conductive, are typically employed as a catalyst precursor. They have the ability to coordinate a metal ion to make a proto-active site prior to heat treatment. Polymers are of interest as a precursor because of the versatility of polymers, and their ability to have their properties tuned. Molecular weight, crystallinity, and functionality are all parameters that are easily tuned, and which will affect the morphology of the

![Figure 20.](image1.png)

**Figure 20.** Koutecky-Levich plot of ORR on MSUcat800 under the same conditions as Fig. 18.

![Figure 19.](image2.png)

**Figure 19.** Tafel plots of the ORR in the kinetic region of A.) FC280, B.) GaFeCu, C.) LANL Fe/CM/C, and D.) M786 at low (□) and high (○) loadings.
product. They are commonly inexpensive, and therefore an attractive approach to catalyst synthesis.

4.1.3.1. Synthesis

This synthesis method involved with this route typically begins with a metal salt as the sole source of metal, while N-containing monomers provide the product’s N content. They can be deposited onto carbon blacks, or easily templated onto a sacrificial support before they are decomposed. Pyrolysis follows the usual protocols, being heated under constant flow of a reductive or inert gas (N₂, Ar) or a reactive gas (NH₃) in a furnace. The heat treatment at high temperature (~800 °C) is performed for an extended period of time, typically >45 min. An acid leach often follows pyrolysis, which is followed by a wash in diH₂O before drying. The product can then subjected to a 2nd, and even 3rd heat treatment, followed by a 2nd and/or 3rd acid leach and washing.

4.1.3.2. Characterization

The two primary materials examined from this class are DAL900A and DAL900C (Dalhousie University, Dalhousie), and to a lesser extent Fe/PEI (University of New Mexico, Albuquerque). The SEM images reveal small, uniform particles that are about 20 nm in diameter for both DAL900A (Fig. 22A) and DAL900C (Fig. 22B), and a highly porous material with a uniform pore size of 30 to 70 nm for Fe/PEI (Fig. 22C).

TEM images of DAL900A (Fig. 23Aa and 23Ab) and DAL900C (Fig. 23Ba and XBBb) are nearly indistinguishable, as DAL900C begins life as DAL900A, but receives a second metal deposition and pyrolysis treatment. The images show that both materials are heterogeneous and graphitic, with small metal aggregates interspersed throughout.
BET surface areas measurements for the polymer derived catalysts are all very high, which, especially in conjunction with high porosity, is beneficial. They are all in the vicinity, and often in excess of 1000 m$^2$·g$^{-1}$ (Table 1).

4.1.3.3. Electrochemical analysis

The conventional range of loadings - 40 μg·cm$^{-2}$ to 800 μg·cm$^{-2}$ – was investigated for DAL900A and DAL900C, but Fe/PEI was not included in this set, and will be largely disregarded for this portion of the discussion. As we have seen before, $i_{lim}$, $E_{0.5}$, and H$_2$O$_2$ evolution increase with loading. The 400 μg·cm$^{-2}$ loadings of this catalyst (Fig. 24) set clearly demonstrate the dependence of diffusion on $i_t$ and $i_d$.

Koutecky-Levich analysis of the 40 and 400 μg·cm$^{-2}$ loadings was performed, and $i_d$ as a function of $E$ was plotted for the five diffusion rates (Fig. 25), and the following kinetic data was obtained.

![Figure 22. SEM images of A.) DAL900A, B.) DAL900C, and C.) Fe/PEI.](image)
At kinetic dependence on loading is observable in the plot by comparing the low and high loadings at a reporting potential of 0.20 V. The low loadings for both catalysts tack closest to the theoretical 2 electron transfer, suggesting inefficient reduction of the intermediate specie. The average electrons transferred for this set at low loading was 1.1, but from the values listed in Table 2, the positive contribution came from DAL900C, which showed better diffusion-limited current characteristics than DAL900C across the board. The picture changes for high loadings, where the average transfer of electrons begins to near full transfer at 3.9.

**Figure 23.** TEM images of A.) DAL900A and B.) DAL900C.

**Figure 24.** RRDE currents for ORR on 400 µg·cm⁻² of A.) DAL900A and B.) DAL900C at (−) 100, (−) 400, (−) 900, (−) 1600, and (−) 2500 RPM.
However, an examination of the related values in Table 3, and of the Koutecky Levich plots, show that there is a disparity in the calculated electron transfer number. The $R^2$ value for DAL900A is lower than normal, and therefore this may not be an adequate analysis for this catalyst at this particular loading, and therefore the values for DAL900C should receive more consideration. For this set, the average number of electrons transferred per turn is likely closer to 3.0, but the average $i_k$ value remains valid at 5.867 mA·cm$^{-2}$.

Tafel analysis of the ORR as catalyzed by polymerically derived materials show good agreement between the kinetic parameters of the reaction in the low current regime (Fig. 26). In this region of the reduction curve, diffusion begins to control kinetics at around 0.7 V.

Between the two samples of this set, there was good agreement between the samples at both loadings in regard to the exchange current density and the rate constant. For the low loading, the average $i^0$ was found to be 2.390 x10$^{-7}$ mA·cm$^{-2}$, and the average $k_e$ was 2.210 x10$^{-6}$ cm·s$^{-1}$. For the high loadings, the averages were 1.358 mA·cm$^{-2}$ and 3.942 x10$^{-7}$ cm·s$^{-1}$ for the respective values. The values in the low current regime are relatively low, which confirms what is seen on the polarization curves in that the change in the
amount current requires a larger change of potential than in other materials. This is also true for Fe/PEI, as the kinetic region of the curve spans about 0.25 V (Fig. 27).

An examination of H₂O₂ reduction on the polymer precursor set shows very little affinity for catalyzing the reaction. Reporting again 0.005 V and 1600 RPM, DAL900A produced a $i_{\text{H}_2\text{O}_2}$ of -0.172 mA·cm⁻², which is almost negligible, and DAL900C actually had a positive value due to the capacitance correction. As has been observed on several samples prior to this set, a reduction current begins to emerge at higher diffusion rates, but it remains very low, reaching -0.378 and -0.036 mA·cm⁻², respectively.

As neither of the representative samples of the polymeric precursor class have been shown to produce peroxide, it is difficult to draw conclusions about this aspect of the class. Furthermore, there is very little variation between the two polymers in either

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**Figure 26.** Tafel plots of the ORR in the kinetic region of A.) DAL900A and B.) DAL900C at low (□) and high (○) loadings.

**Figure 27.** ORR on Fe/PEI in acid. Depicted in this curve are 3 variants of the material that differ only in duration of the heat treatment, which were 1, 2, and 3 hrs as indicated by the inset legend.
composition or processing. The iron supplementation of DAL900C may be said to hinder peroxide reduction, but because the baseline on which that statement is made is so poor (reduction of peroxide on DAL900A), this is a subjective conclusion.

It has been suggested that the active site of the catalyst is a pyridinic nitrogenous site with a proximal metal atom, and that the number of N atoms at this site dictates the activity, with M-N$_2$C$_2$ sites are more active than M-N$_4$ sites [84, 142, 143] (Fig. 28). The macrocyclic chelate class of materials begins with atomic arrangement, and it is the goal to retain the motif through the synthesis process as much as possible. The other two classes attempt to recreate that conformation via a reaction or exploiting intermolecular forces.

A head to head comparison of the categories may provide some insight into how effective each approach is at retaining that atomic motif, at least relative to one another. For purposes of the discussion, the emphasis on the results from the low loading will be weighted more heavily, as low catalyst loadings allow for the true nature of the catalyst to be expressed, as there is no obfuscation of chemical processes due to transport of reactants, products, and byproducts within the catalyst layer. With this in mind, the category that produced the best results was the macrocyclic chelate derived catalyst group.

As calculated using the Levich equation (Eq. 4.1), the number of electrons transferred per turn of the active site was 1.4, versus 1.1 as per the other two groups. Referring to Table 4, the average $i_k$ was higher than the other groups, indicating that the active site that is formed in this process is more active. It is unlikely that more active sites are formed using this method, but that could also present itself in the form of higher activity.
The average value for $i^0$ was also highest with the macrocyclic chelate set by an order of magnitude. The extremely small value of the exchange current density diminishes the importance of this, but it is an important value to know because it is a measure of how quickly a material can generate more amperage.

The high loadings serve to reinforce this assessment, but the polymer derived class showed by far the most improvement at this loading, although the DAL900A contribution may have been over estimated due to a poor linear fit of the Koutecky Levich data. If the

![Figure 28](image)

Figure 28. Pyridinic nitrogen coordinated iron in graphitic carbon, (A) FeN$_4$, (B) cis-coordinated FeN$_2$, and (C) trans-coordinated FeN$_2$ active sites, where Fe can be substituted with another transition metal (Co, Cu, Mn, etc.).

Table 4. Average electron transfer coefficient $\bar{\alpha}$ (# of e$^-$), average kinetic current density $\bar{i}_k$ (mA·cm$^{-2}$), standard deviation of $\tilde{i}_k$, average exchange current density $\tilde{i}^0$ (mA·cm$^{-2}$), and average electron transfer rate constant $k_e$ (cm·s$^{-1}$) at both loadings for each class of catalyst.

<table>
<thead>
<tr>
<th>Class</th>
<th>Loading</th>
<th>$\bar{\alpha}$</th>
<th>$\bar{i}_k$ (mA·cm$^{-2}$)</th>
<th>$\sigma_{\tilde{i}_k}$</th>
<th>$\tilde{i}^0$ (mA·cm$^{-2}$)</th>
<th>$k_e$ (cm·s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Macrocycle</td>
<td>40 μg·cm$^{-2}$</td>
<td>1.4</td>
<td>3.245</td>
<td>0.851</td>
<td>$1.706 \times 10^6$</td>
<td>$1.078 \times 10^4$</td>
</tr>
<tr>
<td></td>
<td>400 μg·cm$^{-2}$</td>
<td>3.1</td>
<td>5.672</td>
<td>0.417</td>
<td>$6.523 \times 10^6$</td>
<td>$3.598 \times 10^4$</td>
</tr>
<tr>
<td>Small Molecule</td>
<td>40 μg·cm$^{-2}$</td>
<td>1.1</td>
<td>2.149</td>
<td>0.723</td>
<td>$5.488 \times 10^6$</td>
<td>$4.374 \times 10^7$</td>
</tr>
<tr>
<td></td>
<td>400 μg·cm$^{-2}$</td>
<td>2.1</td>
<td>5.647</td>
<td>0.242</td>
<td>$2.536 \times 10^7$</td>
<td>$1.194 \times 10^7$</td>
</tr>
<tr>
<td>Polymer</td>
<td>40 μg·cm$^{-2}$</td>
<td>1.1</td>
<td>2.160</td>
<td>1.140</td>
<td>$2.309 \times 10^7$</td>
<td>$2.110 \times 10^6$</td>
</tr>
<tr>
<td></td>
<td>400 μg·cm$^{-2}$</td>
<td>3.9</td>
<td>5.687</td>
<td>0.206</td>
<td>$1.358 \times 10^7$</td>
<td>$3.942 \times 10^7$</td>
</tr>
</tbody>
</table>
data for DAL900C is considered in lieu of the average, that it is in line with the other two categories, performing slightly worse overall than the macrocyclic chelate catalysts, but better than the small molecule precursor catalysts.

As with most complex engineering challenges, there are tradeoffs that must be considered when selecting the precursor for a non-PGM catalyst. While the macrocyclic chelates group performed the best overall, the performance advantage was not so great on a cost basis to justify selecting one for use in a commercially available device. For example, 5,10,15,20-tetrakis(pentafluorophenyl)-21H,23H-porphyrin iron(III) chloride (FeTMPP·Cl) is available from Sigma-Aldrich for $121.00 for 100 mg, where as the same amount of money could buy enough material to make several grams of a catalyst made from poly(aniline). Furthermore, the material set described here is not the state-of-the-art, and the polymeric and small molecule precursor catalyst groups have been greatly improved.

Next, a small molecule precursor derived catalyst will be intensively investigated that is more emblematic of the potential that non-PGM catalysts have to power the devices that we rely upon. It is far less expensive to produce than a macrocyclic chelate precursor catalyst, where the raw materials to make over 100 g cost about $180.

4.2. Iron and 4-Aminoantipyrine Derived Catalyst

A material derived from the condensation of iron and 4-aminoantipyrine [121] has been produced in the Atanassov lab that is has moved the current state of non-PGM catalysis closer to US Department of Energy defined performance goals in terms of activity, peroxide yield, and durability. The following section is an investigation into the effect of electrode loading on activity, and simultaneously provides a detailed
examination of the mechanism by which oxygen is reduced, and includes a study the fate of the peroxide intermediate, if it is formed at all.

4.2.1. Catalyst characterization

Morphological analysis of the Fe/AAPyr catalyst shows that the materials possesses a well-developed pore structure, with pore sizes of ~50-70 nm (Fig. 29), with highly dispersed, small (~20 nm) iron clusters (Fig. 30). The pore diameters correspond to the diameter of the SiO$_2$ particles, which is indicative of their formation as a direct result of the SSM. Leaching of these SiO$_2$ particles results in the creation of pores within the framework of a self-supported catalyst, and the phenomenon can be explained due to the fact at the selected heat treatment temperature (800 °C), the silica does not react with the carbon, which is forming as the aminoantipyrine decomposes. The result is a material with a very high surface area, which was found to be ~1000 m$^2$.g$^{-1}$.

The combination of high surface area and mesoporosity are morphological attributes that promote improved activity in

Figure 29. SEM of a Fe-AAPyr SSM derived catalyst synthesized at 800 °C for 3 hrs, at a ramp rate of 10 °C/min. The cavities left by the vacated silica are clearly visible.
catalysts, and the aforementioned characteristics are a direct result of the SSM. By contrast to conventional synthesis methods, the SSM foregoes decorating carbon supports with active material, but instead uses a temporary scaffolding upon which to create a self-supported material that results in higher surface areas. The catalytic material that forms during thermal decomposition of the Fe/AAPyr composite is comprised of a substantial amount graphitic, conductive carbon that has been derived from the aminoantipyrine. Ultimately, the formed catalytic material is self-supported once the sacrificial support is removed, and it possesses densely populated active sites.

The pyrolyzed and etched sample contains ~3.5% of N, 7% of O, 0.10% of Fe and 89% of C detected. N is the most important element, whose chemical state has been reported to be directly related to catalytic activity [144]. Figure 31 shows high resolution N 1s spectra with an indication as where major N species, such as imine or nitrile at 398 eV, pyridinic N at 398.8 eV, N bonded to Fe at 399.8, pyrrolic N at 400.6 eV, quaternary N at 402.1 eV and graphitic N at 403.6 eV, are

---

**Figure 30.** TEM image of a Fe/AAPyr catalyst depicting small (10-20 nm wide) aggregates of iron (A). The higher magnification image (B) is of one such aggregate that is both highly dispersed and encapsulated by several layers of graphitic material.
detected. This represents a typical distribution of N species with dominating contribution of pyridinic, pyrrolic as well as nitrogen associated with metal in pyrolyzed non-PGM electrocatalysts [145].

4.2.2. Effect of loading on ORR catalytic activity

The effects of electrode loading on the various aspects of ORR was investigating using a range of loadings, from the very low (50 µg·cm⁻²) to the very high (600 µg·cm⁻²) in both acid (Fig. 32 A) and alkaline (Fig. 32 B) media using the RRDE technique. Predictably, as loading increases, so does the limiting current and half-wave potential, while the amount of peroxide that desorbs and does not get completely reduced to water decreases.

However, there are diminishing returns on performance as the loading is increased. This phenomenon is clearly seen in Fig. 32, but a plot of the peroxide yield (Fig. 33), which has been identified by the U.S. Department of Energy as an important performance parameter for non-PGM catalysts, incontrovertibly demonstrates that too high of a loading is both wasteful and detrimental in acid media for this material. The plot is calculated using the relationship between the disk current and the ring current [77] as:

\[
\eta = \left| \frac{4i_d}{i_d - i_r} \right|
\]  

(4.4)

where \( \eta \) is the number of electrons transferred out of the theoretical limit of 4, \( i_d \) is the disk current, and \( i_r \) is the ring current. The peroxide yield [146] is found using \( \eta \) by
\[ Y = \frac{4-\eta}{2} \times 100 \] (4.5)

and the yield is calculated for each potential where data is collected.

It is known that higher loadings result in thicker catalyst films in which analyte transport issues begin to affect the performance. The thicker loadings inhibit the availability of the catalyst material to interact with the reactant because the tortuosity of the path to active sites deep within the catalyst layer increases exponentially [147]. This same model also explains why peroxide detection at the ring experiences no appreciable increase as loading is increased. The incompletely reduced byproduct may desorb from the surface, but it is trapped within the matrix of the catalyst layer. The peroxide will then resorb, where it

![Figure 32. Polarization curve of the ORR on Fe-AAPyr catalyst at (—) 50 \( \mu \text{g} \cdot \text{cm}^{-2} \), (—) 100 \( \mu \text{g} \cdot \text{cm}^{-2} \), (—) 200 \( \mu \text{g} \cdot \text{cm}^{-2} \), (—) 400 \( \mu \text{g} \cdot \text{cm}^{-2} \), (—) 600 \( \mu \text{g} \cdot \text{cm}^{-2} \) in O\(_2\) saturated electrolyte at 1600 RPM in A.) 0.5 M H\(_2\)SO\(_4\) and B.) 1 M KOH.](image)
is completely reduced to water.

4.2.3. Electrochemical analysis

The electrocatalyzed reduction of oxygen using Fe/AAPyr material was quantitatively analyzed using the Koutecky-Levich theory. For the 200 µg·cm⁻² loading, current-potential curves were obtained at four different rotational speeds: 100, 400, 900, and 1600 RPM (Fig. 34) in both acid and alkaline media. The disk current (i_disk) can be used to find the kinetic current through the relationship described in Eq. 4.1 [139], where i_k is the electrode potential dependent kinetic current density of the ORR, n is the average number of electrons transferred per catalytic event (the theoretical maximum is 4), F is the Faraday’s constant (96,487 C·mol⁻¹), C_O₂ is the concentration of molecular oxygen in the electrolyte (1.117 E⁻⁶ mol·mL⁻¹), D_O₂ is the O₂ diffusion coefficient in aqueous media (1.9 E⁻⁵ cm²·s⁻¹), and v is the kinetic viscosity of the electrolyte (0.01000...
cm²·s⁻¹ for acid, and 0.01073 cm²·s⁻¹ for alkaline), ω is the angular momentum in rads·s⁻¹, and A is the sectional area of the electrode.

By plotting |i_d|⁻¹ against ω⁻¹/², Eq. 4.3 allows us to extrapolate the i_k and n in a system where all of the other values are known. Using data reported at 0.425 V, the Koutecky-Levich plot for all loadings at both low and high pH (Fig. 35) shows how the number of electrons transferred per turn at each loading compares to the theoretical 2 and 4 electron pathways. From the figure, it can be clearly seen that the slope is generally parallel to the 4 electron pathway under diffusion controlled conditions, however, as the loading increases, the slope moves closer to, and eventually becomes slightly more shallow than the slope of the 4 electron line.

Figure 34. Polarization curve of the ORR on a 200 mg cm⁻² loading of Fe-AAPyr catalyst at (—) 100 RPM, (—) 400 RPM, (—) 900 RPM, (—) 1600 RPM in O₂ saturated electrolyte A.) 0.5 M H₂SO₄ and B.) 1 M KOH.
When the loading exceeds 200 µg·cm\(^{-2}\) in acid and 400 µg·cm\(^{-2}\) in alkaline, the Levich equation begins to break down because it assumes an infinite, planar disk model. Conversely, at the lowest loading, the surface of the disk is unlikely to be completely covered with catalyst.

For this reason, we shall disregard the lowest and the higher loadings, and focus on 100 µg·cm\(^{-2}\) and 200 µg·cm\(^{-2}\) for discussion of the mechanism. Table 5 lists the calculated values for \(n\) at all loadings, and the values for \(n\) at in the appropriate loading range is found to be 3.7 to 4.6 in acid, and 3.0 to 3.4 in alkaline. Outside of the 100 to 200 µg·cm\(^{-2}\) loading range, the calculated number of electrons exchanged breaks down, but within that window the data shows that the 2x2 electron pathway is employed by the Fe/AAPyr electrocatalyst. This is readily apparent in alkaline media, as the roughly ~3.0 electrons transferred appears to correspond to this assumption. But in acid, the >3.7 electrons seems to strongly suggest a 4 electron pathway. The number of electrons transferred as calculated by Koutecky-Levich analysis is close to, but

![Koutecky-Levich plot of the ORR on Fe/AAPyr catalyst at (---) 50 µg·cm\(^{-2}\), (---) 100 µg·cm\(^{-2}\), (---) 200 µg·cm\(^{-2}\), (---) 400 µg·cm\(^{-2}\), (---) 600 µg·cm\(^{-2}\) in O\(_2\) saturated electrolyte in A.) 0.5 M H\(_2\)SO\(_4\) and B.) 1 M KOH. Also shown are the theoretical lines for 2 (---) and 4 (---) electron transfer.](image)
slightly less than the values calculated by Eq. 4.1, which are 3.8 and 3.9 for the 100 and 200 μg·cm⁻² loadings in acid, and 3.6 for the same loadings in base (Fig. 36).

Referring again to Table 5, the values for $i_k$ generally show an upward trend with respect to increased loading for ORR in both media, but the calculated values are much higher than the current that was observed on the working electrode. The high kinetic current emphatically demonstrates that the catalyst’s reaction kinetics are diffusion-limited, as $i_d < i_k$. It should be noted that the value for the 400 μg·cm⁻² loading in acid is negative because the line of the Koutecky-Levich plot for that loading ($R^2$ fit of 0.998824) intercepted the y-axis (i.e. no diffusion) at -179 [A⁻¹].

Further interpretation of the data that indicates that oxygen is reduced via the 2x2 pathway. The accepted pathways in acid and base have a two-step mechanism to reduction (Fig. 37) [3], and when oxygen is reduced on the Fe/AAPyr catalyst one step is faster than the other. The rate-limiting step for this reaction is likely to be $k_3$ as has been
peroxide would desorb before it can be completely reduced, yet the observed peroxide yield is low. This suggests that \( k_3 \) is also quite rapid. It is easy to conclude that the catalyst electrocatalyzes oxygen via the direct 4 electron pathway due to the two methods described earlier and its low peroxide yield, but it does produce a small, albeit measureable peroxide current.

The extent to which Fe/AAPyr reduces \( \text{H}_2\text{O}_2 \) is affected to an extent by the diffusion rate of reactant in anaerobic solution at pH 1 (Fig. 38 A) and pH 14 (Fig. 38 B). Applying the form of the Levich equation (Eq. 4.1), where \( C_{\text{H}_2\text{O}_2} \) is the concentration of molecular peroxide in the electrolyte (1.3 E\(^{-6}\) mol\( \cdot \)mL\(^{-1}\)), \( D_{\text{H}_2\text{O}_2} \) is the \( \text{H}_2\text{O}_2 \) diffusion coefficient in aqueous media (1.3 E\(^{5}\) cm\(^2\)\( \cdot \)s\(^{-1}\)), and all other parameters are the same as in Eq. 4.4, we get predicted diffusion-limited currents of 0.600, 1.200, 1.800, and 2.400 mA\( \cdot \)cm\(^{-2}\) at rotational speeds of 100, 400, 900, and 1600 RPM, respectively. However, the observed currents with a 400 \( \mu \)g\( \cdot \)cm\(^{-2}\) at 0.05 V are 0.307, 0.534, 0.709, 0.847, and 0.960 mA\( \cdot \)cm\(^{-2}\) in 0.5 M \( \text{H}_2\text{SO}_4 \), and 0.364, 0.638, 0.851, and 1.021 mA\( \cdot \)cm\(^{-2}\) in 1 M KOH, respectively once again. While the expected 400% increase in the diffusion-limited

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**Table 5.** ORR overall electron transfer (\( n \)), kinetic current density \( i_k \) (mA\( \cdot \)cm\(^{-2}\)), electron transfer coefficient (\( \alpha \)), exchange current density \( \beta \) (mA\( \cdot \)cm\(^{-2}\)), and electron transfer rate constant \( k_e \) for the rate determining step (cm\( \cdot \)s\(^{-1}\)) in both acid and alkaline media at 25 °C, and all loadings.

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Loading</th>
<th>( n )</th>
<th>( i_k ) (mA( \cdot )cm(^{-2}))</th>
<th>( \alpha )</th>
<th>( \beta ) (mA( \cdot )cm(^{-2}))</th>
<th>( k_e ) (cm( \cdot )s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5 M ( \text{H}_2\text{SO}_4 )</td>
<td>50</td>
<td>2.9</td>
<td>8.381</td>
<td>0.51</td>
<td>3.559( \times )10(^{-5})</td>
<td>1.029( \times )10(^{-4})</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>3.7</td>
<td>11.712</td>
<td>0.61</td>
<td>1.072( \times )10(^{-5})</td>
<td>2.462( \times )10(^{-5})</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>4.6</td>
<td>12.630</td>
<td>0.61</td>
<td>2.071( \times )10(^{-5})</td>
<td>4.672( \times )10(^{-5})</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>2.8</td>
<td>-22.636</td>
<td>0.58</td>
<td>6.593( \times )10(^{-5})</td>
<td>1.165( \times )10(^{-4})</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>6.5</td>
<td>11.876</td>
<td>0.58</td>
<td>1.006( \times )10(^{-4})</td>
<td>1.910( \times )10(^{-4})</td>
</tr>
<tr>
<td>1.0 M KOH</td>
<td>50</td>
<td>2.8</td>
<td>8.015</td>
<td>1.18</td>
<td>1.527( \times )10(^{-7})</td>
<td>4.732( \times )10(^{-7})</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>3.0</td>
<td>8.660</td>
<td>1.00</td>
<td>3.002( \times )10(^{-6})</td>
<td>1.071( \times )10(^{-5})</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>3.4</td>
<td>9.743</td>
<td>0.93</td>
<td>1.204( \times )10(^{-5})</td>
<td>3.789( \times )10(^{-5})</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>4.8</td>
<td>9.498</td>
<td>0.87</td>
<td>4.083( \times )10(^{-5})</td>
<td>9.863( \times )10(^{-5})</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>4.8</td>
<td>10.457</td>
<td>0.94</td>
<td>2.260( \times )10(^{-5})</td>
<td>4.646( \times )10(^{-5})</td>
</tr>
</tbody>
</table>
current from 100 RPM to 1600 RPM does not materialize, a more modest, yet significant 2.8-fold increase is seen in both media. This would suggest that the reduction of peroxide is caught somewhere between diffusion and kinetic control, as the catalyst is capable of reducing much of the available flux of H$_2$O$_2$. With this in mind, it can it is likely that Fe/AAPyr materials effectively mimic the 4 electron pathway through the mostly complete reduction of a peroxide intermediate.

### 4.2.4. Tafel analysis for the ORR using a Fe/AAPyr catalyst

The Tafel method was used to analyze the ORR as catalyzed by Fe/AAPyr, and the kinetic parameters of the reaction were obtained. For each electrode loading in the low current regime of the Tafel plot (not shown), there was strong agreement for the $i_d$ independent of rotational rate, down to 0.75 V in acid, and 0.90 V in alkaline. The values
in this region all fell within two standard deviations (most within one) of the mean at all rotational speeds. The strong concurrence here suggests that at this high potential, the electrochemical current density is purely kinetic. The kinetic current density can be described using the expression (Eq. 4.2) [140], where \( \alpha \) is the symmetry coefficient for electron transfer in the rate-determining step (RDS), \( n_\alpha \) is the number of electrons transferred in the RDS, and is presumed to be 1, \( E \) is the electrode potential as applied, \( E^0 \) is the thermodynamic electrode potential of the ORR (1.23 V vs RHE), \( R \) is the universal gas constant (8.314 J·mol\(^{-1}\)·K\(^{-1}\)), \( T \) is the temperature in terms of K (298 K), and \( F \) is the Faraday constant (96,487 C·mol\(^{-1}\)). The plot of \( E \) as a function of \( \log(i_d) \) (Fig. 39) gives information about the kinetic parameters of the ORR that can be derived from the line equation for specific regions of the plot. The Tafel slope \((=2.303RT\cdot\alpha^{-1}n_{\alpha}^{-1}F^{-1})\) and the

Figure 38. Effect of diffusion rate on \( \text{H}_2\text{O}_2 \) reduction. 1.3 mM \( \text{H}_2\text{O}_2 \) in A.) 0.5 M \( \text{H}_2\text{SO}_4 \) and B.) 1 M \( \text{KOH} \), (—) 100 RPM, (—) 400 RPM, (—) 900 RPM, (—) 1600 RPM, 400 mg·cm\(^{-2}\) working electrode loading.
intercept \(=E^0+(2.303RT\cdot\alpha^{-1}n^{-1}_a F^{-1})\log(i_d))\) allow for the values of \(\alpha\) and \(i^0\), which is the exchange current density, to be calculated when all other values are known. The corresponding values for \(i^0\) for each loading in both media are listed in Table 5, along with the kinetic rate constant \((k_c)\) for the RDS, while Table 6 lists the suitability of the fit of the line in the region of interest, as well as the slope and y intercept, for the Tafel plots from which this information was obtained. The relationship between \(i^0\) and \(k_c\) is defined in Eq. 4.3 [141], where the \(n\) is the Koutecky-Levich determined number of transferred electrons.

It is interesting to note that both \(i^0\) and \(k_c\) are fairly consistent regardless of loading or electrolyte in the loading range of 100 \(\mu g\cdot cm^{-2}\) to 400 \(\mu g\cdot cm^{-2}\). An examination of these values, which are high in relation to other non-Platinum catalysts, suggests that the reaction occurs rapidly on this material at both high and low pH.

Furthermore, reduction is favored when the ORR is catalyzed with Fe/AAPyr materials, especially in alkaline media, which is known to be thermodynamically favorable for the reaction. The symmetry coefficients for the reaction (Table 5) at all loadings in acid fall within the accepted range of 0.25 to 0.75 for a reversible reaction, but trending more towards favoring reduction at 0.61 within the mechanistically useful loading range of 100

<table>
<thead>
<tr>
<th>Media</th>
<th>Loading (mg·cm⁻²)</th>
<th>R² Fit</th>
<th>Slope (mV·dec⁻¹)</th>
<th>Y_int (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid</td>
<td>50</td>
<td>0.995</td>
<td>116.3</td>
<td>0.713</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0.997</td>
<td>97.6</td>
<td>0.745</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>0.991</td>
<td>96.4</td>
<td>0.779</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>0.985</td>
<td>101.6</td>
<td>0.805</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>0.973</td>
<td>102.4</td>
<td>0.821</td>
</tr>
<tr>
<td>Alkaline</td>
<td>50</td>
<td>0.965</td>
<td>49.9</td>
<td>0.890</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0.990</td>
<td>59.3</td>
<td>0.902</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>0.985</td>
<td>63.5</td>
<td>0.918</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>0.985</td>
<td>68.2</td>
<td>0.930</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>0.979</td>
<td>62.8</td>
<td>0.938</td>
</tr>
</tbody>
</table>
to 200 $\mu$g·cm$^{-2}$. In alkaline media, the observed symmetry coefficients are firmly ensconced in the range that irreversibly favors reduction, near 1.0 in the useful loading range.

The Tafel slopes for Fe/AAPyr in both acid and base (Table 6) within the interrogated loading range, ~100 and 60 mV/dec respectively, reflect how quickly the current density changes at low overpotentials. In the kinetic region, a change of only 100 mV in potential in acid is sufficient to increase or decrease the current by an order of magnitude, while in an alkaline electrolyte only a 60 mV change is sufficient to achieve the same result. This shows the thermodynamic favorability of oxygen reduction in alkaline systems over that of acid systems, and more specifically $k_2$ is enhanced. This is further evidenced by the increase in the peroxide yield in alkaline media over acid (Fig. 33), where the observable ring current is still low, but much higher than in acid. While the Tafel slope considers the totality of the reaction, it is clear that when all parameters of the ORR are investigated

Figure 39. Tafel plots of the oxygen reduction reaction of Fe-AAPyr catalyst at 900 RPM and 50 $\mu$g·cm$^{-2}$ (□), 100 $\mu$g·cm$^{-2}$ (♦), 200 $\mu$g·cm$^{-2}$ (△), 400 $\mu$g·cm$^{-2}$ (○), and 600 $\mu$g·cm$^{-2}$ (×) in O$_2$ saturated A.) 0.5 M H$_2$SO$_4$ ad B.) 1 M KOH. The insets depict the interrogated region of the reported Tafel slopes, intercepts, and $R^2$ values.
that a two step process is involved where oxygen is rapidly reduced to peroxide, and then further reduced to water in a slower step.

4.3. Catalyst And Ionomer Interaction

The catalyst is often the central focus of the fuel cell, as it has been to this point in this body of research, but it is important to recognize the fact that its properties, both physical and catalytic, are greatly enhanced through the presence of an ionomer. Therefore the ionomer must always be considered when designing a system. The lack of research over several decades in the alkaline environment has created a need for an alkaline specific ionomer that is an analogue to Nafion® at high pH, and several ionomers have been made for this purpose. In this section, the effect of these novel ionomers on the ORR will be investigated using the aforementioned techniques, and the impact that they have on the activity will be used as the basis for future research.

In order to mitigate any deviation from the infinite disk model that Koutecky-Levich theory hinges upon, a low catalyst loading of 40 μg·cm⁻² was used. Polarization curves for the ORR on each ionomer-FeCyan/C complex (Fig. 40) at low loading show how the activity is influenced by the ionomer in the absence of the distortional, albeit positive, effects observed high loading.

High catalyst loadings serve to lower the overpotential, drive the onset potential higher, generate more current, and depress peroxide desorption. However, to investigate the kinetics of a catalyst as honestly as possible, a low loading should be used. This discussion is limited to a model that assumes monolayer catalyst coverage of the electrode surface, whereby no correction or fitting to the Levich equation is necessary. At
high catalyst loadings, the film creates channels in which the reactants, products, and byproducts must travel as they diffuse across the electrode surface.

4.3.1. Effect of ionomer properties on oxygen reduction

The electrocatalyzed reduction of oxygen FeCyan/C complexed with each ionomer was quantitatively analyzed using the Koutecky-Levich theory. For each catalyst-ionomer complex, current-potential curves were obtained at five different rotational speeds: 100, 400, 900, 1600, and 2500 RPM (Fig. 41). The value of \( i_k \) can be extrapolated from \( i_d \) through the relationship described in Eq. 4.1.

Plotting \( |i_d|^{-1} \) against \( \omega^{-1/2} \) reveals the diffusion rate dependent linear relationship (R^2 >0.90) from which Eq. 4.1 yields \( i_k \) and \( n \) in a system where all other values are known.

The Koutecky-Levich plots for each ionomer-FeCyan/C (Fig. 42) illustrate how the number of electrons transferred per turn is affected by the ionomer. From the figure, it can be clearly seen that the slope is generally parallel to the theoretical 2 electron pathway under diffusion controlled conditions.

To reiterate, Nafion® is the standard ionomer employed in AFC research, and therefore our examination of the kinetics of oxygen reduction at high pH on FeCyan/C catalyst will be pegged to the catalytic material that uses Nafion® as the binding ionomer. Under these conditions, the calculated \( i_k \) is 1.782 mA·cm\(^{-2}\) and the number of electrons transferred per catalytic event is 0.74. Clearly, this catalyst reduces oxygen via a peroxide intermediate (Fig. 37B), which is prone to
desorption. To further investigate how well the catalyst:ionomer complex reduces oxygen and peroxide, it is instructive to first plot $n$, which is the electrode potential-dependent ratio of fully reduced oxygen to the total amount of partially and fully reduced oxygen, normalized to the number of electrons transferred in full reduction, against potential (Fig. 43), which is done using the Eq. 4.4. Having calculated the value of $n$ at any given potential, the peroxide yield can be found through the Eq. 4.5, and the peroxide yield can be plotted again as a function of potential (Fig. 44). The graph of the peroxide yield shows that the Nafion® complexed FeCyan/C has a yield in excess of 60%.

The Tafel method was also used to analyze catalysis the ORR on Nafion® complexed FeCyan/C, kinetics of the onset of the reaction was obtained. This analysis focuses on the low current regime of the Tafel plot, where $i_d$ observed is independent of the rate of diffusion. At this high potential, the electrochemical current density is purely kinetic, and is described by the expression of Eq. 4.2. The plot of $E$ as a function of $\log(i_d)$ (Fig. 45) across 50 mV of the low current regime yields a linear regime whereby the line equation
for this region can be found. The Tafel slope \(=2.303RT\cdot\alpha^{-1}n_{\alpha}^{-1}F^{-1}\) and the intercept \((=E^0+(2.303RT\cdot\alpha^{-1}n_{\alpha}^{-1}F^{-1})\log(i_0))\) gives us \(i^0\) when all other values are known. By extension, \(k_e\) can be found when \(i^0\) is known. The relationship between \(k_e\) and \(i^0\) is found through Eq. 4.3.

For the Nafion® sample, the \(i^0\) was found to be \(4.308 \times 10^{-6}\) mA·cm\(^{-2}\) under the aforementioned conditions, and this value of \(i^0\) yields a \(k_e\) of \(1.460 \times 10^{-5}\) cm·s\(^{-1}\) for this catalyst. This catalyst, in conjunction with Nafion®, is an active catalyst by which changes in activity due to the ionomer can be measured, and the benchmark values for the kinetic parameters of FeCyan/C by which the ionomers will be measured are provided (Table 7).

The effect of the poly(sulfone)s varies between the two samples. PS-A suppressed \(i_k\), as well as inhibiting the transfer of electrons, where the \(i_k\) decreased by 25.1% and the
number of electrons transferred by 35.5% in relation to Nafion®. Conversely, PS-B moderately improved the reaction kinetics on FeCyan/C by 8.3% and 3.2% respectively. A similar trend is observed with potential-dependent \( n \) values (Fig. 43), where the PS-A sample yields \( \sim 2.25 \) electrons and the PS-B sample yields \( \sim 3.0 \) electrons versus the Nafion® sample’s \( \sim 2.4 \) electrons. In keeping with this trend, PS-A had a peroxide yield of \( \sim 20\% \) points higher than Nafion®, while PS-B is \( \sim 10\% \) points lower.

A Tafel analysis of the same low current region of the poly(sulfone) complexed FeCyan/C reveals something interesting about the onset of the reaction. Contrary to what was observed about the ORR reaction kinetics when only mass transport issues are a factor, the PS-A sample displayed a higher \( i_0 \) than the Nafion® sample (2.084 x 10-4 mA·cm-2 vs 4.308 x 10-6 mA·cm-2), and therefore a higher \( k_e \) (1.119 x 10-3 cm·s-1 vs 1.460 x 10-5 cm·s-1). It is worth noting, however, that the low current region was shifted \( \sim 20 \) mV lower than the Nafion® sample. Meanwhile, the PS-B sample had no appreciable change from the reported values of the benchmark Nafion® sample.

There is a clear-cut difference between the ORR reaction kinetics on this non-PGM catalyst when the ink is prepared with PS-A and when it is prepared with PS-B. The
values for IEC, swelling, and σ for all ionomers are listed in Table 7. Limiting the discussion at this point to PS-A and PS-B, lower values for IEC, σ, and swelling of the ionomer yielded much improved catalyst performance, but at best on par with that of the Nafion® benchmark.

The poly(phenylene) class of ionomers also demonstrated some differences between the interclass samples. In terms of Koutecky-Levich analysis, the PP-D sample performed markedly better than the PP-E sample under standard conditions for this experiment. When compared to the benchmark sample, the PP-D sample showed a stronger \( i_k \), and improved electron transfer as determined by Eq. 4.1. This ionomer improved the ORR kinetics of the FeCyan/C catalyst; increasing \( i_k \) by 29.0% and \( \eta \) by 183.3% (up from 0.74 in the Nafion® sample to 2.10). The potential-dependent \( \eta \) values (Fig. 43) for both PP-D and PP-E, as calculated by Eq. 4.2, was determined to be \( \sim 2.50 \) electrons for both samples versus the Nafion® sample’s \( \sim 2.4 \) electrons. Although the poly(phenylene)s showed modest improvement in the average number of electrons transferred, they did yield more peroxide than the Nafion® and poly(sulfone) samples (Fig. 44).

Analysis of the low current region immediately after the onset of the ORR on poly(phenylene):FeCyan/C exposes how the ionomer affects the \( i^0 \). The results show that

\[ \text{Figure 45. Tafel plot of ORR on Fe/Cyan/C with } (\rightarrow) \text{ Nafion®}, (\rightarrow) \text{ PS-A}, (\rightarrow) \text{ PS-B}, (\rightarrow) \text{ PP-D, and (---) PP-E at 40 \mu g cm}^{-2} \text{ at 1600 RPM.} \]
in this phase of the reaction, the PP-D: FeCyan/C had a lower $i^0$, $k_e$, and a steeper Tafel slope than the PP-E:FeCyan/C. Comparing these values to Nafion®:FeCyan/C, PP-D resulted in an $i^0$ that was nearly one order of magnitude lower, while PP-E increased it by the same degree and more.

The net effect of ionomeric properties between PP-D and PP-E are less dramatic than what was observed in with the poly(sulfone) class. This is somewhat reflected in the IEC, swelling, and $\sigma$ values (Table 7), as they are much closer, especially with respect to swelling, than those of PS-A and PS-B. For the poly(phenylene)s, PP-D, which has higher values in all 3 categories, demonstrated better performance than PP-E.

A head-to-head comparison of the best performing ionomer of each class, PS-B and PP-D, has the PS-B:FeCyan/C sample performing better by almost every metric discussed in this study. In the low current regime, this difference was the most dramatic, where the $i^0$ is $\sim$1298% better with PS-B than with PP-D. However, the absolute value of the $i^0$ is only a pittance in relation to the overall current, as it is measured in microamps, and therefore this improvement is not a significant advancement toward the goal of improving power in the AFC. More encouraging is the $\sim$60 mV positive shift in the onset potential that was seen with PS-B:FeCyan/C. The improved average electron transfer number and lower overall peroxide yield also fortifies the position of PS-B as the most beneficial non-Nafion® ionomer in this study.

<table>
<thead>
<tr>
<th>Ionomer</th>
<th>D.F.$^a$</th>
<th>I.E.C. (mequiv g$^{-1}$)</th>
<th>Water Uptake (wt. %)</th>
<th>$\sigma$ (mS·cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS-A</td>
<td>1.26</td>
<td>2.01</td>
<td>224</td>
<td>54</td>
</tr>
<tr>
<td>PS-B</td>
<td>1.12</td>
<td>1.74</td>
<td>87</td>
<td>27</td>
</tr>
<tr>
<td>PP-D</td>
<td>2.28</td>
<td>2.03</td>
<td>76</td>
<td>41</td>
</tr>
<tr>
<td>PP-E</td>
<td>1.80</td>
<td>1.89</td>
<td>60</td>
<td>31</td>
</tr>
</tbody>
</table>

$^a$Degree of functionalization equates to the average number of bromomethyl groups per monomer unit.
A comparison of the two best samples, PS-B has a lower IEC and σ, but swells more than PP-D, and it is difficult to draw definitive conclusions from this. However, if the highest value of $i_k$ (PS-B) is assumed to be the highest $i_k$ achievable for a catalyst, then assuming that the water uptake % is the parameter optimized for to achieve this $i_k$, the percentage by which the % swelling differs from the optimal value corresponds to the percentage by which $i_k$ differs from the hypothetical maxima. The exception to this is PS-A, which swells 257% more than the next highest swelling ionomer (PS-B). This suggests that there is a nonlinear trend in which the water uptake % improves the kinetic parameters up to a point, and thereafter it begins to affect performance.

The hydrophilicity of ionomer has a role in managing the water content at the active site. As the reaction proceeds, it is important to remove the product of the reaction so that the equilibrium will be shifted forward. In the AFC and alkaline membrane fuel cell (AMFC), this entails bringing water to the active site and displacing hydroxyl anions. Too little swelling effectively dehydrates the active site, while too much swelling drives the equilibrium to the left, creating an abundance of reactant in the vicinity.

**Table 8.** ORR on Fe/Cyan/C $R^2$ fit for the Koutecky-Levich plot, electron transfer ($n$), kinetic current density $i_k$ (mA·cm$^{-2}$), Tafel slope (mV·dec$^{-1}$), exchange current density $i_0$ (mA·cm$^{-2}$), and electron transfer rate constant $k_e$ for the rate determining step (cm·s$^{-1}$) in both acid and alkaline media at 25 °C, and all loadings.

<table>
<thead>
<tr>
<th>Ionomer</th>
<th>$R^2$ Fit</th>
<th>$n$</th>
<th>$i_k$ (mA·cm$^{-2}$)</th>
<th>$m_{\text{Tafel}}$ (mV·dec$^{-1}$)</th>
<th>$i_0$ (mA·cm$^{-2}$)</th>
<th>$k_e$ (cm·s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nafion</td>
<td>0.997998</td>
<td>2.1</td>
<td>5.513</td>
<td>65.7</td>
<td>2.477 x10$^{-16}$</td>
<td>2.961 x10$^{-16}$</td>
</tr>
<tr>
<td>PS-A</td>
<td>0.998863</td>
<td>1.4</td>
<td>4.217</td>
<td>61.2</td>
<td>8.729 x10$^{-12}$</td>
<td>1.602 x10$^{-11}$</td>
</tr>
<tr>
<td>PS-B</td>
<td>0.998351</td>
<td>2.2</td>
<td>6.902</td>
<td>56.1</td>
<td>4.604 x10$^{-16}$</td>
<td>4.220 x10$^{-16}$</td>
</tr>
<tr>
<td>PP-D</td>
<td>0.976552</td>
<td>3.0</td>
<td>4.964</td>
<td>110.4</td>
<td>1.158 x10$^{-23}$</td>
<td>9.998 x10$^{-24}$</td>
</tr>
<tr>
<td>PP-E</td>
<td>0.972854</td>
<td>2.5</td>
<td>4.367</td>
<td>57.2</td>
<td>3.702 x10$^{-12}$</td>
<td>6.332 x10$^{-12}$</td>
</tr>
</tbody>
</table>
5. Conclusions

5.1. Classification Of Non-PGM Catalysts (The Cross Lab II Set)

In this work, we have had the unique opportunity to discuss and compare the research and the resulting catalysts from many groups around the world. This research has been used to identify trends in non-PGM catalysts and to evaluate how the synthesis approaches that were used to make these materials impact the catalyst performance. This dissertation has put forth evidence that precursors that closely resemble the active site before heat treatment give rise to more active catalysts.

Three general categories of non-PMG catalysts were defined where the precursors used to form the active site determined the category in which they were placed. The first category included all materials that started with a macrocyclic compound that coordinates a metal ion. These chelates are the sole source of metal and nitrogen in the catalyst, and the desired active site conformation is present in the precursor. The second group of materials begins as a blend of small molecules and salts. The salt is the source of metal in this method, while another molecule proved the nitrogen content. Often, a supplemental molecule will provide additional carbon content to the product. Unlike the macrocyclic chelates, the active site is formed though an interaction between the N-containing species and the metal ion from the salt, whereby they are deposited onto a support and adsorb to the surface in a coordinated manner by which the general arrangement of the active site is made. The third category is in many ways similar to the small molecule precursor group, but involves the use of a N-containing monomer that is polymerized at some point before the heat treatment, in some cases even before being combined with the other components.
(Fe/PEI). The polymer coordinates itself with the metallic ion from a metal salt as it adsorbs to the support or template, where it is decomposed and the active site is formed.

In a head to head comparison of the three classes, and all conditions being equal, the macrocyclic chelate precursor derived catalysts produced on average the most active material for ORR in acid. These catalysts were consistently low peroxide evolvers with a strong current produced on the disk. The diffusion-limited current was highest for these materials and the electron transfer number was the highest, especially at a low loading of 40 mg·cm⁻² where the underlying kinetic processes are unobscured by the effects of loading. It was found that these materials have a preferable reaction profile in the low current regime, where the exchange current densities are higher, thus shortening the potential range over which the current is increased by defined amount. This is an important parameter for a fuel cell, as it needs to respond to changes in the demand for power very quickly. In addition, the peroxide yield was lowest for this category, and they showed some propensity for reducing peroxides. Only the UK65 sample had a clear diffusion dependent peroxide reduction current that approached full reduction of the specie, except at very high diffusion rates.

Polymer precursor catalysts also were shown to perform well in low pH media, and their overall activity was only moderately less than the macrocyclic precursor material set. One advantage they have is their very high surface area, which is beneficial in exposing active sits at the surface to have them available to catalyze the reaction. The $i_k$ was off by about 1.000 mA·cm⁻² from that of the first set, and the Koutecky Levich plot and the Tafel slope were both steeper. However, the peroxide yields were very low for
both samples. The low kinetic currents are compensated for by a stronger diffusion-limited current, which keeps the peroxide yield down.

The last class, small molecule precursors, had the lowest averages in this study. At low loadings, the averages were lower than those of the other two classes, but there were some samples that had $i_k$ or $n$ values that were in line with the macrocyclic chelate class. For example, the MSUcat800 sample had an $i_k = 3.218$ mA·cm$^{-2}$, which is indistinguishable from the 3.245 mA·cm$^{-2}$ average for the macrocyclic chelates class. However, the small molecule precursor samples consistently had low values, while the macrocyclic chelates had consistently high values. This trend is extended to the high electrode loadings, but the disparity between the averages of the class samples is not as dramatic, and each class is has a sample that scored well in accordance to the criteria described.

The small molecule class, although had the least favorable representation here, is not to be discounted. In each of the measured activity parameter categories ($i_k$, $n$, $l^0$, and $k_e$), a polymeric precursors and small molecule precursor sample performed as well as the average macrocyclic precursor derived catalyst. Additionally, there are samples within the set that are better than the best polymeric precursor derived catalyst (DAL900C).

This study has shown that it is easy, in terms of precursor selection, to make a good catalyst using a macrocyclic chelate precursor. The general performance of this category suggests the proto-active site is largely retained through the heat treatment and acid leaches, or that the atoms begin the decomposition process in such a position that they ultimately situate themselves and form the appropriate bonds to make efficient active site.
The fact that these precursors ultimately cost as much, or more than platinum makes them an unrealistic source for a commercially successful non-PGM catalyst. For this reason, the polymeric and small molecule precursor catalysts merit more research. It has been shown that some samples are able to perform up to the metal macrocyclic chelate standard, and it therefore becomes necessary to uncover what precursors, or aspects of precursors, give rise to an active site that is better able to reduce oxygen.

Examining the Cross Laboratory II experiment samples on an individual basis, and ranking them accordingly, it is possible to make some inferences about the how raw materials and the synthesis methods that were used to make them affect the overall reductive ability of the material, or how they influence certain aspects of the complex process that is oxygen reduction. The aforementioned hierarchy of activity is UK65 > UK63 > CHb200-900 > DAL900C > CoTMPP-700 > M786 > FC280 > MSUcat800 > LANL-CM-Fe-C > GAdFeCu > DAL900A, and considers all calculated parameters of activity at both loadings.

Cobalt was the transition metal for best overall catalyst, UK65. The only other catalyst with a cobalt transition metal was CoTMPP-700, both of which use CoTMPP as the precursor. CoTMPP-700 was the fifth most active overall, suggesting that the synthesis procedure may a significant contribution to the activity. Putting that aside for the moment, the next two best performing catalysts were iron based macrocyclic poly(pyrrole)s. The poly(pyrrole) based DAL900C was 4th best, although some of the data may have skewed it a bit higher. The next two most active catalysts began with iron acetate on a carbon support, flowing gaseous ammonia over the precursors throughout the heat treatment process to introduce nitrogen. The next three were grouped closely on this
basis, and were all small molecule precursor derived. Rounding out the sample set was the poly(pyrrole) and iron based DAL900A performing the most unfavorably of all the materials.

On the basis of precursor structure alone, the general trend that emerges is that precursors that can form the best ring structure around a metal ion will yield more activity. Assuming that the atoms are primarily in the same position prior to pyrolyzation, the macrocyclic precursors have already achieved this. The poly(pyrrole)s have a similar structure to the macrocycles, which are in fact modified poly(pyrrole)s. When ammonia is allowed to react with surface ferric species, iron nitrides are formed with a statistical distribution of the value of x in the FeN$_x$ from 1 to 4, where 4 effectively mimics a macrocyclic chelate in how the iron is encompassed by the nitrogen atoms. With the other small molecules used in this group of catalysts, it is unclear as to how or to what extent this atomic arrangement is achieved, but it is clear that the selected precursors failed to duplicate the active sites, or at least the number of active sites, that the macrocycles were able to produce.

As has been hinted at, the synthesis procedure also impacts the activity of the catalyst. The first commonality that stands out is that the two most active catalysts had a second and third pyrolyzation step. The third and fourth most active materials were subjected to two heat treatments. The seven catalysts that followed were all only pyrolyzed one time. Also, the top four performers were pyrolyzed at either 800 or 900 Cº, while the others were pyrolyzed at either a higher or lower temperature. The atmosphere used may have had an impact, as six out of seven of the most active materials were all pyrolyzed at least once in a reactive atmosphere, the exception was CoTMPP-700 at number five.
Beyond the number of heat treatments, heat treatment temperature, and atmosphere, there appears to be little correlation between activity and pyrolysis time, support, or acid wash. This set of experiments has outlined some factors that should be considered when designing a non-PGM catalyst that should provide a general blueprint before optimizing. This process always begins selecting precursors that will associate with one another in such a way that the general structure of the active site is formed before pyrolysis. The precursor should contain nitrogen that isn’t sterically hindered from associating with a transition metal ion. The nitrogen bonding state that gives rise to the most active material begins with a pyridinic nitrogen, but pyrrolic and nitrile nitrogen species can become activated through pyrolysis by altering their chemical state to that of a pyridinic nitrogen. Furthermore, the precursor must stable enough to not sublime or otherwise not decompose *in situ* though the heat treatment process. Macrocyclic chelates are good precursors for this, but are typically expensive. For this reason, small molecules or polymers are good candidates, and will perform favorably for this purpose. The metal component is commonly iron or cobalt, and both are good candidate transition metals to begin with in the design process. The heat treatment process has been shown to be among the most important steps in the synthesis process, and the parameters under which it is conducted will ultimately affect the performance. This experiment has shown that a two step process produces the best results, and should be conducted between 800 and 900 °C, where the first heat treatment is performed in inert atmosphere, and the second in a reactive oxidative atmosphere to treat the carbonaceous surface, or switch gasses at some point in an extended process.
Many of these lessons have been applied to catalyst development from the time these materials were made and analyzed to the time of this writing (~3 years). The body of knowledge has been built upon, and new generations of materials have been developed. Currently, a new material that has been synthesized from a 4-aminoantipyrine precursor has been made, which forms a complex with iron. This material would fall into the small molecule derived catalyst class of materials, and it has far superior kinetics and activity than even the best macrocyclic chelate derived catalyst, effectively demonstrating the potential of small molecules, and by extension polymers, as a precursor for a highly active non-PGM catalyst.

**5.2. New Generation Non-PGM Catalysts**

We have successfully, and reproducibly synthesized a highly active catalyst that has a potential evolutionary step forward in catalytic activity. This dissertation has demonstrated that it is possible for non-PGM materials to be as active as a Pt catalyst, if only the active site density and any diffusion-limiting properties can be overcome.

Materials derived from iron and aminoantipyrine are very effective at catalyzing the ORR in both acid and alkaline media, and are in-step with the state-of-the-art at the time of this writing. The SSM templated Fe-AAPyr material, which is highly porous, has an effective saturation loading of 400 µg·cm\(^{-2}\), after which there are diminishing returns on performance. At loadings beyond this point, performance gains are negligible and the excess material only serves to complicate mass transport by creating a highly tortuous path for reactants and products in the deep recesses of the catalyst film. The 400 µg·cm\(^{-2}\) loading in acid media achieves a peroxide yield of ~2.5%, which is on par with the DoE performance target for non-PGM catalysts.
In order to conduct a mechanistic investigation into this material, we focus on a slightly lower loading that is sufficient to cover the surface of the disk, yet not create additional transport issues by creating a thick, porous layer through which the analyte must travel. Using the Koutecky-Levich method of analysis on both oxygen reduction and peroxide reduction, it reveals that the preferred pathway is via the peroxide intermediate. In acid, the reduction of the peroxide is so complete that it appears to follow the one step, full reduction of oxygen to water.

Analysis of the ORR using the Tafel method further reveals information about how Fe/AAPyr reduces oxygen. In both acid and alkaline, reduction is favored over oxidation, and irreversibly so in alkali. The analysis of the RDS shows a very strong exchange current density, and therefore a proportionally high kinetic constant. The Tafel slopes of the ORR at both low and high pH are very shallow, but more so for high pH. Such slopes would suggest a rapid k1 step, but when considered in combination with the higher peroxide yield, leads to the conclusion that \( k_2 > k_3 \), and that \( k_1 \) is not the dominant ORR pathway on Fe/AAPyr catalysts.

What has been shown is that the morphology and/or composition of the SSM templated Fe/AAPyr catalyst is highly effective at completely reducing oxygen, but does so in a two-step process. It is so effective in both steps (albeit more so in the first step), that it mimics the direct 4-electron pathway. The Fe/AAPyr material has been shown to be good at reducing peroxide, and warrants further development in this regard. To further improve on non-PGM catalyst performance, and perhaps stability, it will be important to increase the density of the active sites that perform this reduction. The slow step for reduction on this catalyst, the peroxide reducing step, can perhaps be improved and
would theoretically enhance stability by rapidly eliminating the corrosive specie that is present at some point in the reaction. Another strategy that could be pursued is coupling this material with another that is a known peroxide producer so that all species are completely reduced. The information obtained from this study will allow us to use this material to design better non-PGM ORR catalysts.

In order make significant improvements to ORR activity, the role that the ionomer has must be investigated, especially in alkaline media where far less research has been conducted. The catalyst is inextricably linked to the ionomer, be it on the RRDE, on an MEA being tested, or in an operating system. This vital component and how it affects the reduction of oxygen on a catalyst demands to be understood if such a system is to become viable.

5.3. **The Influence Of The Ionomer On Activity**

This work provides evidence for how to produce ionomers that are better suited for oxygen reduction in alkaline media. In this work, we have demonstrated that there are certain functional properties of the ionomer that have an impact on the activity of the catalyst to which the ionomer is bound. This interaction between the catalyst and the ionomer has a measurable influence on the activity of the material.

Electrochemical evaluation of the non-PGM catalyst bound with the featured alkaline ionomer classes over a range of conditions gives insight into how they behave, as well as providing information on how the varying functionalities enhance or inhibit the rate of oxygen reduction. Additionally, an optimization procedure emerges from the data that is instructive for all carbon supported non-PGM catalyst inks using poly(sulfone)s or poly(phenylene)s.
The polymer backbone structure had some influence on facilitating favorable reaction kinetics, where the poly(sulfone)-derived ionomers, PS-A and PS-B, tended to have a slight negative influence on the half-wave potential and the limiting current when compared to those of Nafion® and the poly(phenylene)s. They also exhibited more peroxide desorption and greater limitation in the mass transport regime.

The poly(phenylene)-derived polymers generally performed more favorably, and more in line with the benchmark ionomer, Nafion®. The catalyst showed no significant loss in voltage of the half-wave potential with either PP-D or PP-E. The magnitude of the limiting current was smaller than with Nafion®, but close to it and much greater than what was observed using poly(sulfone)-derived ionomers. Desorption of the peroxide intermediate was higher than the benchmark, and mass transport limitations were also observed, but they are not appreciably worse than Nafion®.

Because of their largely non-polar, aromatic structure, the poly(phenylene)s appear to wet the surface of the carbon-supported catalyst better than the poly(sulfone)s. The poly(phenylene)s solvate O₂ and H₂O in addition to conducting the product away from the active sites in sufficient quantities that the maximum oxygen reduction kinetics for the catalyst is realized.

The WU% may the primary determining factor in ionomeric contribution to an improved rate of reaction, and the swelling of the PS-B and PP-D ionomers is at or near the optimum. A head to head comparison of the four ionomers illustrates a correlation between the WU% and the magnitude of the observed current. PS-A has over 400% higher water swelling than PP-E, resulting in less current density and more peroxide desorption, which equates to very poor efficiency.
The poly(phenylene)-derived ionomers show promise as fruitful line of research in establishing an anion conducting ionomer for alkaline electrolyte fuel cells, where both PP-D and PP-E complexed catalysts performed favorably at the low loading level examined. The PS-B sample, while having the best performance overall at that loading, experienced some instability at higher temperatures that would be common in a functioning fuel cell. Although the Nafion® benchmark outperformed the poly(phenylene)-derived ionomers, there is reason to assume that great improvements can be made to this new class of ionomer. It should also be noted that Nafion® has the benefit of almost 50 years of intensive engineering and research focus, while trimethylaminated poly(phenylene) is a much newer development.

5.4. Contributions To The Art Of Catalyst Design

In this dissertation, several advances have been made on the state of understanding of non-platinum catalysis, and suggestions have been laid forth on how to further improve such materials. We have, for the first time, provided evidence that the full potential of these catalysts has not been approached, and that future iterations of non-PGM catalysts may be every bit as active as platinum.

Understanding how the atomic structure of a N-containing precursor molecule dictates how it forms a complex, or a condensate, with a solvated metal ion is the foundation of non-PGM catalyst design. Selection of a precursor that will ionically interact with the cationic metal specie in the precursor solution to form a complex with the general atomic components will generally result in a more active catalyst. A precursor with low energy nitrogen species and a π–orbital contribution (either graphitic or pyridinic) gave rise to more active catalysts, perhaps because they are already in the low
energy state of nitrogen species in the idealized active site (pyridinic nitrogen). Conversely, precursors with nitrile, primary amine, or to a lesser extent pyrrolic nitrogen produced less active materials.

For a non-PGM catalyst to have activity to have a level of activity that approaches that of a platinum catalyst, a high density of active sites must be created per unit of mass of catalyst. However, for an active site to be active, it must be able distort the electronic structure of the reactant, which requires the reactant to be within a certain proximity to the site. This can only be achieved at the surface of the catalyst, as the reactant and the electrolyte are cannot permeate the solid. The SSM is an effective method for minimizing the amount of non-surface bulk material, as only small deposits of carbonaceous material can form in the spaces between the silica particles in an aggregate. Most of the precursor material will deposit onto the curved surface of the fumed silica and not in the inter-particle space. The fumed silica particles, if selected for properly, will have a diameter that corresponds to the mesoporous diameter that has been shown to be more active than other pore sizes. Pyrolysis graphitizes the precursors into a thin, high surface area carbonaceous shell that encapsulates the silica aggregate.

The graphitization process whereby the carbonaceous material incorporates the nitrogen atoms is an essential part of catalyst synthesis. The process must be performed at a high enough temperature to form graphitic carbon from the nitrogen containing precursors, but not so high as to form crystalline carbon or cause the metal to agglomerate. While there may not be one optimal heat treatment process, the best results would likely come through a sintering processes in an inert atmosphere, followed by a treatment in a reactive atmosphere. After the heat treatment and the subsequent etch to
remove the silica template, the resulting carbon network is an open-framed, porous structure.

In both acid and alkaline media, catalysts made using such guidelines will have favorable transport properties and high activity. Exposure of active sites on the surface of a pore that effectively manages the flux of reactants and products results from this method of synthesis, and the result is a maximized diffusion-limited current, higher kinetic current, lower overpotential, and less peroxide desorption.

In alkaline media, there is even more opportunity for improvement as there is currently no commercially available ionomer standard for high pH. Poly(phenylene) based anion conduction polymers have the potential to improve activity in AFCs and AMFCs by managing the flux of water and hydroxyl groups at or near the surface of the catalyst. It is unclear if they are able to wet the surface of the pores, but their ability to solubilize O$_2$ and swell, along with functional pendulum groups that transport anionic species will enhance the transport of the involved species at the appropriate rate and in the proper direction using future generations of such ionomers.

The data harvested has illuminated several paths forward towards creating more active materials, and some have been used in the creation of the group’s current generation of non-PGM catalyst. Future generations of catalysts will build upon this understanding, providing even more detail as to the best way to create an efficient oxygen reducing catalyst for any electrolytic medium made from non-noble materials.

5.5. Outlook For Future Research

Research on the topic of non-PGM catalysts is far from complete, but the advances in recent years is appreciable. While the 4-aminoantipyrine derived catalyst represents a
significant push forward, along with other catalysts that have been developed by different
groups, there are still improvements that can be made in reducing the amount of peroxide
produced, improving the kinetic current, lowering the overpotential, and decreasing mass
transport losses.

Clearly, new precursor materials should be explored. The overpotential is an
electrode dependent phenomenon, and therefore new catalysts are likely to be made that
can decrease this inefficiency. The intrinsic and extrinsic properties of the active site can
be improved with more suitable raw materials. Assuming a distribution of active site
moieties of the form Fe-N$_x$-C$_y$ (where x and y are both integers from 0 to 4 and x+y=4),
or even Co-N$_x$-C$_y$-O$_z$ (again, x+y+z=4), a material that readily and reproducibly forms a
higher percentage of the most active variety (likely FeN$_2$C$_2$ or FeN$_4$) would have both a
steeper kinetic region and a higher limiting current.

Another branch that this research could take is to develop a better understanding of
how to reduce peroxide on non-PGM materials. We have shown that different Me/AAPyr
catalysts have very different peroxide yields, so one such study might include how the
different metals reduce peroxide on an aminoantipyrine derived catalyst. An active
peroxide reducer could serve a co-catalyst to a highly active peroxide producing catalyst
to effectively lower the peroxide yield, so as to limit corrosion by this specie and to
improve durability of the material. A study of peroxide reduction has not been part of the
standard protocol for catalyst analysis, and it would be a valuable addition to all future
research, as it is an easy indicator of the mechanism by which the material operates (i.e.
no peroxide reduction indicates a direct 4 electron pathway and the presence of a current
suggests the possibility of the 2x2 pathway). Including a peroxide reduction experiment
provides insight as to the diffusion-limited current produced by the catalyst in each step of the pathway.

The support onto which the precursors are templated has been shown to affect the reductive characteristics of the catalyst, typically in the mass transport regime, and therefore some improvements can be made to improve the diffusion of reactant to the active sites simply by selecting for better templates. Some examples of this may include different fumed silica, smectites clays, or hexagonal silica platelets. Additionally, one type of sacrificial support material could be more favorable for reducing peroxide than one that is shown to be better for oxygen reduction.

Many questions still remain involving the heat treatment process in understanding how the process affects the structure of the precursors and their subsequent decomposition. More validation of the assumptions made here about the processes’ repetitions, length, and temperature will be required to diligently test the hypothesis.

Evaluation of new ionomers with varying properties will also be a fruitful line of research. As Sandia National Laboratories develops new ionomers and membranes, understanding how they influence all aspects of oxygen reduction of non-PGM catalysts will provide insight as to how to improve both components for use in alkaline media. As it is not conclusive that the water uptake percentage is the dominant governing factor of activity, an involved experiment investigating this idea could easily produce better results for future generations of ionomer. Using the same methodology as was ascribed in the ionomer experiment here, analyzing the activity of a non-PGM catalyst bound with several iterations of an ionomer that have the same monomeric unit, functional groups, conductivity, IEC, and molecular weight, but differing in swelling would allow for the
design of an catalyst:ionomer complex that would have superior performance characteristics when applied to a high pH MEA.

5.6. Improvements In MEA Performance

Although no MEA data has been presented in this work, it is the culmination of all the lessons learned and applied in fuel cell catalyst research. All aspects of the polarization curve will affect the power produced by the MEA, and even small improvements in RRDE data can yield appreciable results a working system.

Like every other device, Ohms law applies to the MEA. Improving conductivity will reduce overpotentials and narrow the potential range over which the ohmic region of the polarization curve spans. This will serve to decrease the resistive contribution to the power production, thereby yielding more $\text{W} \cdot \text{cm}^{-2}$.

Increasing the amount of current through the cathode is an obvious way to improve the MEA performance, as more current results in more power. However, the improvement in power that results from an increase in current is disproportionate to the increase produced by an improvement in $E_{0.5}$, and for this reason the allure of the AFC has always lingered. Improving both the $i_{\text{lim}}$ and the $E_{0.5}$ are important, but the implications are important to understand, and the impact that both the catalyst and the ionomer have here must be considered.

Any considerations that effect ohmic region of the curve should be considered carefully, as increasing $i_{\text{lim}}$ and the $E_{0.5}$ yield higher power, but the value of $i^0$ will ultimately dictate how quickly the fuel cell can respond to changes in the power demand. If the exchange current density is sluggish, this will prevent the catalyst from being useful in many applications.
As new membranes are developed, it is vital to understand how they contribute to power production of the MEA. Symmetry between the membrane and the binding ionomer can help alleviate some problems involving material incompatibility and help to lower resistance in the catalyst layer, and should thus be considered in addition to ionic conductivity and durability.

In summary, the MEA is a highly complex system with many factors to consider. However, this is the proving ground of the fuel cell and all of the contributions to the power output must be known and understood, and an approach to improve them all must be taken to make the fuel cell a commercially viable concept. Intelligent and deliberate design of the catalyst, ionomer, and the complex they form will all serve to improve the state of the fuel cell and help it to fulfill the promise that it holds.

5.7. Summary Of Conclusions

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• References


[7] E. Yeager, Chemical Engineering Progress, 64 (1968) 92-&.


