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Abstract of Dissertation

Today’s high and growing energy demands are unsustainable given the cost and depleting nature of fossil fuel sources, and has long been accepted as a major factor in climate change. Due to these factors, alternative clean and renewable energy sources have long been an interest in both academic and industrial research. Electrochemical energy conversion has become one of the leading fields, encompassing both battery and fuel cell technology. Despite being less prevalent in today’s society, and still more in the commercially primitive stages, fuel cells demonstrate several benefits over battery technology. Firstly, they can operate consistently, assuming a constant fuel supply, without the need of being shut down and recharged. Additionally, certain systems have potential for residual heat to be collected and used, with these systems being referred to as combined heat and power (CHP) devices.

Currently, Pt-based materials are the state-of-the-art catalysts for the hydrogen oxidation reaction (HOR) and oxygen reduction reaction (ORR) in acid fuel cells, and are responsible for a large portion of the cell stack cost in commercial systems. However, due to the sluggish kinetics and higher overpotentials associated with ORR compared to HOR, a higher Pt catalyst loading is traditionally required. Pt-based materials are inherently more susceptible to poisons, reducing their power output over the lifetime of the system. Therefore, the cathode of the fuel cell has been traditionally studied for Pt alternatives, whether that be through the reduction of Pt loading or through substitution of Pt with platinum group metal (PGM)-free materials. PGM-free catalysts traditionally have been synthesized through the mixture of a metal and nitrogen precursors in the presence of a carbon support material, followed by heat treatments to form metal-nitrogen coordinated materials on a carbon support.
This dissertation will focus on two major aspects related to PGM-free materials in proton exchange membrane fuel cells. Chapter 1 will give the necessary background into fuel cell technology, and the numerous systems that are currently studied for various applications, as well as providing the electrochemical background for the methodologies used to study these materials. Chapter 2 will demonstrate a combined experimental and theoretical approach to gaining increased understanding of mass transport effects within a PGM-free catalyst layer in the PEMFC environment. Experiments using low concentration oxygen cathode fuels combined with a previously-developed model allow for mass transport resistances to be calculated based on limiting current scenarios. Chapters 3 and 4 will introduce several PGM-free materials developed through different techniques, including a Sacrificial Support Method (SSM) and the formation of Metal-Organic-Framework (MOF) structures, for their use in high-temperature PEMFCs (HT-PEMFCs), which have potential in stationary power generation applications. In addition to rotating ring disk electrode (RRDE) studies to evaluate the ORR pathway associated with these catalysts, these materials will demonstrate immunity to phosphate poisoning at low temperatures. Additionally, they will be evaluated for performance and durability in the HT-PEMFC environment. Chapter 5 will evaluate a potential alternative to a pure PGM-free cathode, where PGM-free materials are combined with low loadings of Pt catalysts in an effort to match the performance of high loading Pt membrane electrode assemblies (MEAs). These systems would allow for at least a 70% reduction in the total platinum content within the MEA, increasing the commercial viability of these systems. Chapter 6 will summarize the findings in Chapters 2-5 while also discussing the ongoing and future efforts of this work.
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<td>Contact angle</td>
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<td>κ</td>
<td>Catalyst layer ionic conductivity</td>
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<td>φ</td>
<td>Phase shift</td>
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<td>A</td>
<td>Electrode active area</td>
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<td>A</td>
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<td>α</td>
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<td>AEMFC</td>
<td>Anion exchange membrane fuel cell</td>
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<tr>
<td>B&lt;sub&gt;L&lt;/sub&gt;</td>
<td>Levich constant</td>
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<td>b</td>
<td>Tafel slope</td>
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<td>C</td>
<td>Local dry reactant concentration</td>
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<td>C</td>
<td>Double layer capacitance</td>
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<td>C&lt;sub&gt;0&lt;/sub&gt;</td>
<td>Oxygen concentration in electrolyte</td>
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<td>CHP</td>
<td>Combined heat and power</td>
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<td>C&lt;sub&gt;O*&lt;/sub&gt;</td>
<td>Concentration of oxidized species</td>
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<tr>
<td>C&lt;sub&gt;R*&lt;/sub&gt;</td>
<td>Concentration of reduced species</td>
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<td>CV</td>
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<td>D&lt;sub&gt;KA&lt;/sub&gt;</td>
<td>Knudsen diffusion coefficient</td>
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<td>D&lt;sub&gt;0&lt;/sub&gt;</td>
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<td>DX6</td>
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<td>Amplitude of potential signal</td>
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<td>E&lt;sup&gt;0'&lt;/sup&gt;</td>
<td>Formal cell potential</td>
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<td>E&lt;sub&gt;anode&lt;/sub&gt;</td>
<td>Anode half-reaction cell potential</td>
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<tr>
<td>E&lt;sub&gt;rev&lt;/sub&gt;</td>
<td>Reversible potential</td>
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<tr>
<td>ECSA</td>
<td>Electrochemical surface area</td>
</tr>
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<td>EIS</td>
<td>Electrochemical impedance spectroscopy</td>
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<tr>
<td>F</td>
<td>Faraday’s constant</td>
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<tr>
<td>f</td>
<td>Ratio of inert gas to reactant gas</td>
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<td>F&lt;sub&gt;d&lt;/sub&gt;</td>
<td>Inert cathode diluent flux</td>
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<tr>
<td>f&lt;sub&gt;HO&lt;/sub&gt;</td>
<td>Catalyst layer hydrophobic fraction</td>
</tr>
<tr>
<td>F&lt;sub&gt;O&lt;/sub&gt;</td>
<td>Change in oxygen molar flow rate</td>
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<tr>
<td>f&lt;sub&gt;r&lt;/sub&gt;</td>
<td>Reactant fraction</td>
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<td>F&lt;sub&gt;T&lt;/sub&gt;</td>
<td>Total molar flow rate</td>
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<td>Fe-N-C</td>
<td>Iron-nitrogen-carbon</td>
</tr>
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<td>ΔG°</td>
<td>Gibbs free energy</td>
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<td>GDE</td>
<td>Gas diffusion electrode</td>
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<tr>
<td>GDL</td>
<td>Gas diffusion layer</td>
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<td>HFR</td>
<td>High frequency resistance</td>
</tr>
<tr>
<td>HOR</td>
<td>Hydrogen oxidation reaction</td>
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<tr>
<td>HT-PEMFC</td>
<td>High-temperature proton exchange membrane fuel cell</td>
</tr>
<tr>
<td>I&lt;sub&gt;0&lt;/sub&gt;</td>
<td>Amplitude of current signal</td>
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Current density
Experimental limiting current
Flow rate dependent current density
Limiting current
Kinetic current
Mass transport current
Catalyst layer exchange current density
Local flux of oxygen
Mass transport coefficient
Gas-phase mass transport coefficient
Local mass transfer coefficient
Non-gas-phase mass transport coefficient
Channel length
Metal-nitrogen-carbon
Molar mass of diluent
Membrane electrode assembly
Mercury intrusion porosimetry
Metal-organic-framework
Molecular weight of diluent
Number of electrons for given electrochemical reaction
Overpotential
Open circuit potential
Oxygen reduction reaction
Pressure
Dry inlet reactant partial pressure
Ohmic resistance
Mass transport resistance
Ideal gas constant
Catalyst layer resistance
Charge transfer resistance
Membrane resistance
Shunt resistor
Mass transport resistance
Gas-phase resistance
Non-gas-phase resistance
Volume-specific reaction rate
Pore radius
Reversible hydrogen electrode
Rotating ring disk electrode
SHE  Standard hydrogen electrode
SSM  Sacrificial support method
T   Temperature
v   Kinematic Viscosity
ν   Volume flow rate
V_m  Molar volume
V_{O_2}  Oxygen flow rate
W   Effective channel width
ω   Radial frequency
ω   Rotation rate
XRD  X-Ray Diffraction
x_o  Mole fraction of oxygen
x_w  Vapor-phase mole fraction of water
y   Dimensionless path length through flow field
y   Mercury surface tension
Z   Impedance
Z'   Real component of impedance
-Z''  Imaginary component of impedance
z   position along the flow channel
Chapter 1

Fuel Cell Technology and PGM-Free Catalyst Development

1.1 Introduction to Renewable Energies

The current world-wide consumption of fossil fuels is unsustainable for a few reasons. Firstly, fossil fuels are a finite resource, and a costly one at that to extract and refine. Given that it is a dwindling resource, it is vital that alternative energy sources are developed. Secondly, the emissions from the use of fossil fuels (including but not limited to carbon dioxide) have been identified as one of the leading causes of climate change. Even if it were possible to use fossil fuels in a cleaner manner, reducing the emissions into the atmosphere, the issue stands that it is a finite resource that is decreasing in availability while our nation’s population and subsequent energy needs continue to rise. It is these factors that have largely led to research worldwide in an effort to generate cleaner and more renewable energies that could handle the planet’s growing energy needs. This research has led to increased studies of electrochemical energy conversion devices including batteries and fuel cells. Fuel cells have several advantages over battery technology, including significantly higher theoretical power densities and not needing to be shut down to recharge. It is for these reasons that they are a valuable potential clean alternative to fossil fuel technology.

1.2 Fuel Cell Technology

1.2.1 Background

The fuel cell environment will be the primary focus of the work in this dissertation, as it will be evaluated through numerous methods in an effort to gain further understanding regarding its potential commercial use as a necessary alternative to fossil fuel technology. Fuel cells rely
on the basis of converting chemical energy of a fuel to electrical and mechanical energy. In theory, the only requirement for a fuel cell system to continue operating without interruption is a constant fuel supply.

Numerous types of fuel cells have been studied for various applications. Far and away the most commonly studied is the low temperature proton exchange membrane fuel cell (PEMFC), most often operating in the 60-80 °C temperature range. Also at that temperature (although traditionally not operating over roughly 60 °C), is the alkaline equivalent to PEMFCs, the anion exchange membrane fuel cell (AEMFC). PEMFCs in particular have been studied as potential energy conversion devices for mobile applications including automotive. As the operating temperature is increased, more fuel cell systems have been and are studied, including high-temperature PEMFCs (HT-PEMFCs), also referred to commonly as phosphoric acid fuel cells (PAFCs), operating in the 150-220 °C temperature range. These units have potential for stationary power applications, including in-home power generation amongst other combined heat and power (CHP) applications. At slightly higher temperatures, systems such as solid acid fuel cell (SAFC) have been evaluated for mobile energy conversion by the military (operating at approximately 250 °C). And finally, at even higher temperatures (600-1000 °C), molten carbonate fuel cells (MCFC) and solid oxide fuel cell (SOFC) have been studied for stationary power applications. The work in this dissertation will be focused on PEMFC and HT-PEMFC technologies.

1.2.2 Proton Exchange Membrane Fuel Cells (PEMFCs)

Figure 1.1 shows the general schematic of a fuel cell. The anode and cathode electrodes are separated by a proton conducting membrane (traditionally based on Nafion® technologies for PEMFC systems), acting as the electrolyte for the system. Nafion-based systems rely on proper
and specific humidification within the cell. Subsequently, they are often operated at 100% relative humidity, achieved through humidification of the anode and cathode gas feeds prior to entering the cell. Hydrogen is passed over the anode, where the hydrogen oxidation reaction (HOR) will occur (equation 1.1), during which the hydrogen gas is split into a pair of protons and electrons. The electrons will pass through an external circuit, allowing for conversion to mechanical energy while protons pass through the membrane. At the cathode, protons and electrons will recombine in the presence of oxygen (or oxygen content of an air feed) to complete the reduction of oxygen (ORR, equation 1.2) to water. Therefore, contrary to fossil fuel technologies, where carbon monoxide and other byproducts, and generated, the sole products of a fuel cell are electricity and water. Both potentials for equations 1.1 and 1.2 are listed vs. the standard hydrogen electrode (SHE), where the oxidation and evolution of hydrogen are defined as being at 0.00V.
Figure 1.1 - Schematic of a proton exchange membrane fuel cell. Courtesy: Department of Energy, EERE

Anode: \[ H_2(g) \leftrightarrow 2H^+ + 2e^- \quad E^o = 0.00 \text{ V vs. SHE} \] (eq. 1.1)

Cathode: \[ \frac{1}{2}O_2(g) + 2H^+ + 2e^- \leftrightarrow H_2O(l) \quad E^o = 1.23 \text{ V vs. SHE} \] (eq. 1.2)

Through combination of the two half reactions shown above, the full cell potential of the cell can be determined, using equation 1.3, and yielding equation 1.4.

\[ E_{\text{cell}} = E_{\text{Cathode}} - E_{\text{Anode}} \] (eq. 1.3)

Overall: \[ H_2(g) + \frac{1}{2}O_2(g) \leftrightarrow H_2O(l) \quad E_{\text{cell}} = 1.23 \text{ V} \] (eq. 1.4)

These fuel cells operate under acidic conditions due to the presence of protons within the system (while AEMFC rely upon the transport of hydroxide ions across the membrane).
membrane material (Nafion®) has two purposes. First, as mentioned, it is a proton conductor and allows for proton transport from anode to cathode. Secondly, it acts as a physical separator of the two electrodes, preventing contact and subsequent short circuits. Nafion® has been the state-of-the-art PEMFC membrane since the 1960s when the perfluorosulfonic acid (PFSA) material was first developed. Figure 1.2 shows the chemical structure of the Nafion membrane, utilizing a tetrafluoroethylene (Teflon) backbone and perfluorovinyl ether groups with sulfonate groups at the terminus of the chain. It is these sulfonate groups that facilitate proton transport between acid sites. As mentioned earlier, these systems have become the research standard for automotive applications.

![Figure 1.2 - Structure of Nafion polymer, where x and y are quantities of the polymer sequence](image)

### 1.2.3 High Temperature PEMFCs

The premise of the HT-PEMFC (or PAFC) environment utilizes the same basic principles in terms of reactions as the lower temperature systems. However, there are some key differences, including an alternative to the Nafion® membrane (due to its instability at the higher operating temperatures). Early development of HT-PEMFC utilized a silicon carbide separator between the two electrodes, while utilizing phosphoric acid within the catalyst layer as a proton
conductor\textsuperscript{1}. However, newer generations of materials have switched away from the silicon carbide separator to alternative membrane materials. The commercial standard is the polybenzimidazole (PBI) membrane, which is prepared through a sol-gel process and imbibed with phosphoric acid\textsuperscript{2, 3}. It contains very low content of solids (roughly 5%), although newer modified versions are being investigated with a higher solids content\textsuperscript{4, 5}. During preparation of the membrane electrode assembly (MEA), this acid is squeezed out of the membrane and into the catalyst layer. It is through this process that the electrode gains its proton conductivity. Due to the higher operating temperature (150-220 °C), concentrated acid is required (85-100 %) for this process. One of the unique benefits given the higher operating temperature is the possibility of using the water produced and expelled from the system for heat generation. It is because of this combined heat and power (CHP) that these devices can operate at just over 80 % CHP efficiency, higher than any other style of fuel cell.

Despite these benefits, there are several drawbacks to the HT-PEMFC systems, including lower ionic conductivity and lower oxygen permeability than the lower temperature Nafion® systems. Additionally, the Pt catalyst required for both reactions can be poisoned from phosphate anions present in the electrolyte. This poisoning will increase the overpotentials of the chemical reactions, and therefore reduce the power density generated at any given potential. Another drawback is that these systems traditionally utilize higher Pt catalyst loadings than low temperature systems (roughly an order of magnitude higher). While these systems demonstrate a higher CHP efficiency, they tend to operate at a lower overall power density than lower temperature systems.

A typical fuel cell polarization curve can be seen in Figure 1.3 below. A typical curve is composed of 3 regions: the activation region (low current density), the ohmic region (linear
portion), and a mass transport region (high current density). The voltage losses in the activation region are associated with the energy to force the electrochemical reaction. The kinetics of the oxygen reduction reaction (catalyst dependent) control the magnitude of those losses. The ohmic losses are due to the transfer of ions, and the mass transport losses are due to poor oxygen and product transport to and from the active site.

![Fuel Cell Polarization Curve](image)

**Figure 1.3 - Typical fuel cell polarization curve**

In the absence of a mass transport region, modeling of polarization curves can be done by fitting the data to the following equation\(^6\):

\[
E = E_{rev} - b \log(i) - R \cdot i
\]  

(eq. 1.5)

\(E\) and \(i\) are experimental values of potential and current density, respectively. \(E_{rev}\) is the reversible potential of the cell (adjusted thermodynamic cell potential given changes to
temperature and partial pressure of hydrogen and oxygen). \( b \) is the Tafel slope, and \( R \) is the ohmic resistance. In the absence of electrochemical impedance spectroscopy, fitted polarization data can be used to elucidate the ohmic resistance for iR compensation. This model however is not usable in the event of a clear mass transport region. For that, equation 1.6 is used, adding a term to account for the mass transport region\(^7\).

\[
E = E_{rev} - b \cdot \log(i) - R \cdot i + B \cdot \ln\left(1 - \frac{i}{i_L}\right) \quad (eq. \ 1.6)
\]

In this case, \( i_L \) is the limiting current density, and \( B \) is an empirical parameter. This equation can be utilized for getting an estimate of the limiting current density. While these are suitable ways for calculating the ohmic resistance of the cell, electrochemical impedance spectroscopy (EIS) is one of the common experimental methods used, along with a current interrupt method.

### 1.2.4 Electrochemical Impedance Spectroscopy (EIS)

In electrochemical impedance spectroscopy, a potential is applied to the system in a sinusoidal wave. As a result, a sinusoidal current is observed in response. This current wave, however, is shifted out of phase from the applied potential wave. The potential applied to the system can be shown through the equation below:

\[
E_t = E_0 \sin(\omega t) \quad (eq. \ 1.7)
\]

where \( E_t \) is the potential at time \( t \), \( E_0 \) is the amplitude of the signal, and \( \omega \) is the radial frequency, calculated as a function of the frequency in Hertz via \( \omega = 2\pi f \). Subsequently, the current response can be shown through a similar equation, shifted in phase (\( \phi \)) and represented as:

\[
I_t = I_0 \sin(\omega t + \phi) \quad (eq. \ 1.8)
\]

The impedance can be calculated through:
\[
Z = \frac{E_l}{I_c} = Z_0 \frac{\sin(\omega t)}{\sin(\omega t + \phi)}
\]  
(eq. 1.9)

allowing the impedance to be expressed in terms of its magnitude \((Z_0)\) and phase shift \((\phi)\). Through a conversion using Euler's relationship, the impedance can be re-written as:

\[
Z(\omega) = \frac{E}{I} = Z_0 \exp(j \phi) = Z_0(\cos(\phi) + jsin(\phi))
\]  
(eq. 1.10)

This allows the impedance to be listed as a complex equation, comprised of a real and imaginary portion. When for a series of frequencies, the negative of the imaginary is plotted as a function of the real component, a Nyquist Plot is generated. The high frequency resistance is the first point at which the imaginary portion of the impedance is equal to 0. At that point, the intercept (real component) can be used as a value for the ohmic resistance, and iR-corrections can be carried out for Tafel analysis.

1.3 Oxygen Reduction Reaction

1.3.1 Background

While the potential power output of a fuel cell is determined primarily by the kinetics of the two necessary reactions (HOR and ORR), there are factors such as mass transport limitations that are dependent on other factors including fabrication of the MEA. There are a few key differences between the HOR and ORR reactions. As is shown in Figure 1.1, this is a two-electrode systems (anode, cathode), where the anode acts as both a counter and reference electrode in order to mimic a three electrode system. This is possible is because the HOR reaction is reversible and fast. Because of this, if the anode utilizes a state-of-the-art Pt catalyst, it can be considered as both a counter and reference electrode. The ORR reaction at the cathode (working electrode) does not demonstrate those same reaction characteristics. Compared to HOR, the kinetics are significantly slower, and demonstrate significantly higher overpotentials\(^8\).
While the HOR reaction is a single electron transfer, the ORR reaction requires 4 electrons to convert one diatomic oxygen molecule to a pair of water molecules. Additionally, there are numerous pathways by which ORR can proceed. In acidic media (like both of these fuel cell systems), there are two predominant pathways. The first is a direct 4-electron process (equation 1.11), while the second is a 3-step process through a peroxide intermediate (equations 1.12-1.14).

Direct 4-electron: \[ O_2(g) + 4H^+ + 4e^- \rightarrow 2H_2O(l) \quad E_0 = 1.229V \] (eq. 1.11)

Peroxide (step 1): \[ O_2(g) + 2H^+ + 2e^- \rightarrow H_2O_2(l) \quad E_0 = 0.67V \] (eq. 1.12)

Peroxide (step 2): \[ H_2O_2(l) + 2H^+ + 2e^- \rightarrow 2H_2O(l) \quad E_0 = 1.77V \] (eq. 1.13)

Peroxide (step 3): \[ 2H_2O_2(l) \rightarrow 2H_2O(l) + O_2(g) \] (eq. 1.14)

In this case, a 4-electron reduction is desired, in order to avoid the peroxide intermediate which can poison certain surfaces. A Koutecký-Levich analysis, as will be done in Chapters 3 and 4, can be used to determine which mechanism for oxygen reduction is preferred for a given catalyst.

1.3.2 Electrochemistry

All chemical reactions that revolve around the transfer of electrons from one species to another can be categorized as redox (oxidation-reduction) reactions. Electrons are gained during a reduction process, and electrons are lost during an oxidation process. The potentials of the half reactions shown in equations 1.1 and 1.2 can be calculated, as can any half reaction potential, through the Nernst equation:

\[ E = E^{\circ} + \frac{RT}{nF} \ln \left( \frac{C_0}{C_R} \right) \] (eq. 1.15)
where $E^0$ is the formal potential, $R$ is the gas constant, $T$ is the temperature, $n$ is the number of moles of electrons in the reaction, $F$ is Faraday’s constant, and the ratio of $C_{O^*}$ to $C_{R^*}$ represents the bulk concentration of the oxidized and reduced species.

The potential of the cell is the difference between the cathode and anode half reaction potentials. Additionally, using the cell potential, the Gibbs free energy of the reaction can also be calculated

$$\Delta G^0 = -nFE^0_{cell} \quad \text{(eq. 1.16)}$$

While the thermodynamically calculated cell potentials are good approximations, there will be differences between those values and experimentally calculated values. The difference between those is values (the additional potential required to drive the reaction) is referred to as the overpotential of the reaction ($\eta$).

Kinetics of a reaction can be modeled in the absence of mass transport effects through the Butler-Volmer equation (1.17):

$$i = i_0 \left[ \exp(-\alpha \eta f) - \exp((1 - \alpha) \eta f) \right] \quad \text{(eq. 1.17)}$$

The current density is represented by $i$, $i_0$ is the exchange current density, $\alpha$ is the charge transfer coefficient, $\eta$ is the overpotential, and $f = F/RT$ where $F$ is Faraday’s constant, $R$ is the gas constant, and $T$ is the temperature. In the event of large overpotentials, the second term in the equation above can be discounted, the equation can be rearranged, and the overpotential can be calculated through the following Tafel equation:

$$\eta = \left( \frac{RT}{\alpha F} \right) \ln(i_0) - \left( \frac{RT}{\alpha F} \right) \ln(i) \quad \text{(eq. 1.18)}$$

This equation can allow for the calculation of parameters including the Tafel slope, equal to (-2.3RT/αF). Pt systems have very well defined Tafel slopes, allowing PGM-free materials to be evaluated in reference to Pt systems through these methodologies.
1.3.3 Rotating Ring Disk Electrode (RRDE)

Figure 1.4 shows a general schematic of the RRDE setup, which allows for information to be gained regarding the kinetics of a particular electrochemical reaction, such as ORR. Two working electrodes are used: a glassy carbon on which the catalyst of note is deposited, and a gold ring that surrounds it (separated by a Teflon ring). When the electrode is rotated, convection will cause oxygen dissolved into the electrolyte to flow towards the catalyst surface. This allows for evaluation of a catalyst in an environment that is mass transport limited. Additionally, the rotation causes the products formed at the catalyst surface to be expelled past the ring, and, if desired, detected through a separate redox reaction. This is key in the case of ORR, where if the reduction occurs through the peroxide pathway, peroxide can be detected at the gold ring by simultaneously applying a fixed potential (suitable for oxidation of peroxide) to the ring while sweeping a potential over the working electrode.

![Rotating Ring Disk Electrode (RRDE) Schematic](image)

Measured current density ($i$) in an RRDE profile can be broken down into a series combination of current densities, kinetic ($i_k$) and limiting ($i_{lim}$), via the equation below:
\[
\frac{1}{i} = \frac{1}{i_{\text{lim}}} + \frac{1}{i_k}
\]  
(eq. 1.19)

The kinetic current can be calculated using a rearrangement of that equation, as is shown below:

\[
i_k = \frac{(i_{\text{lim}} \cdot i)}{(i_{\text{lim}} - i)}
\]  
(eq. 1.20)

where the limiting current density, \(i_{\text{lim}}\), can be calculated using the equation below:

\[
i_{\text{lim}} = 0.62nFD_0^{2/3}v^{-1/6}C_0\omega^{1/2}
\]  
(eq. 1.21)

Here, \(n\) is the number of moles of electrons in the electrochemical reaction, \(F\) is Faraday’s constant, \(D\) is the diffusion coefficient of oxygen in the electrolyte, \(v\) is the kinematic viscosity, \(C_0\) is the concentration of oxygen within the electrolyte, and \(\omega\) is the rotation rate in radian per second. The diffusion coefficient, kinematic viscosity, and concentration are literature values dependent on the species (oxygen), electrolyte (0.1M HClO₄), and temperature (room temperature) of the experimental setup.

1.3.4 PGM-Free Catalyst Development

As stated earlier in this section, the kinetics of the half-cell reactions will dictate the current output of the cell, which is why catalysts are used to increase the kinetics of the relevant reactions. Platinum is considered the state-of-the-art catalyst for both HOR and ORR in acidic media. However, due to the cost and scarcity of Platinum, developing cheaper alternatives has long been a focus of increased research. Until alternatives are found, it will be extremely difficult for fuel cells to become mass commercialized either for transportation applications or for stationary power generation.
The development of PGM-free materials has been a long process starting back in the 1960s when Jasinski et al. demonstrated that a metal-N<sub>4</sub> coordinated molecule could reduce oxygen species<sup>9</sup>. Given that these materials demonstrate similar coordination to the heme coordination in the human body, it is unsurprising that they are ORR active. Over the following 1-2 decades it was determined that pyrolysis of these materials can create an increasingly active catalyst<sup>10</sup>. To date, there is still no consensus on exactly what comprises the active site for ORR within these materials. Some evidence suggests that it is the metal-nitrogen coordination that is the active site, while others contend that the metal is simply necessary to catalyze the formation of the active sites embedded within the carbon matrix. Despite this discrepancy, countless work has been done in the field of metal-based PGM-free materials<sup>11-16</sup> as well as non-metal-based PGM-free materials<sup>17</sup>.

1.4 Scope of Dissertation

The premise of this dissertation is to gain further understanding of PGM-free materials and their implementation into different fuel cell systems (PEMFCs & HT-PEMFCs). Chapter 2 focuses on techniques to elucidate mass transport characteristics through a combined experimental and theoretical approach for a pair of PGM-free materials. Chapter 3 focuses on the implementation of two PGM-free materials of the same class (Metal-Organic- Framework, MOF) into a new application, HT-PEMFC, while also evaluating their immunity to phosphate anion poisoning. Chapter 4 demonstrates the application of a different class of material (Sacrificial Support Method, SSM) into the HT-PEMFC environment, while also evaluating the durability of the catalyst. Finally, Chapter 5 will discuss an alternative to a pure PGM-free cathode, where low loadings of Pt are combined with a PGM-free catalyst base in an effort to demonstrate similar performance to a state-of-the-art, high Pt loading MEA.
1.5 Chapter 1 References


Chapter 2

A Combined Experimental and Theoretical Approach to a Further Understanding of Mass Transport Characteristics of PGM-Free Materials in Proton Exchange Membrane Fuel Cells

2.1 Introduction

Due to the high and volatile cost of Pt for proton exchange membrane fuel cell (PEMFC) applications, much work has been done in recent years to investigate potential catalyst alternatives for the oxygen reduction reaction (ORR) at the cathode. Traditionally, this reaction has required a higher Pt loading than the anode due to inherently sluggish kinetics when compared to the hydrogen oxidation reaction (HOR) at the anode. This work has revolved around two distinct approaches: the reduction of the required Pt loading\textsuperscript{1-4}, or the use of a Pt-group metal (PGM)-free catalyst\textsuperscript{5-20}. Over the past several decades, there have been major breakthroughs in the field of PGM-free catalyst development, yielding materials to date that have showed comparable performance to Pt-based systems. While there are many potential synthetic pathways and transition metals that have been evaluated for this function, one of the most commonly evaluated families of materials relies upon metal-nitrogen-carbon (M-N-C) interactions, specifically iron (Fe-N-C). For the purpose of this work, the two materials in question were developed through distinct synthetic approaches. The first approach is that of a silica-based Sacrificial Support Method (SSM) material, where a ferrous iron salt and a nitrogen-containing charge-transfer salt are pyrolized in the presence of a silica template. The silica template is then etched from the system, leaving behind only the porous Fe-N-C structure\textsuperscript{21-23}. The second approach is through the formation of a Metal-Organic-Framework (MOF) structure. The particular material in question for this work is unique in that, while being highly active
towards ORR, it also lacks any direct coordination of iron to nitrogen, instead containing iron-carbon and iron-iron interactions\textsuperscript{24}. Both of these materials have previously demonstrated very high activity for ORR in both acid electrolyte rotating ring disk electrode (RRDE) studies as well as in PEMFCs.

As mentioned, much work has already been done on the development of materials for ORR in PEMFC environment. Additionally, substantial effort has been placed in understanding both the mechanism of ORR in acid and alkaline environments\textsuperscript{25} as well as the potential degradation mechanisms of these materials during operation. However, one aspect that remains largely unstudied is the mechanism of mass transport through these materials when used in the form of a catalysts layer in PEMFCs. Some fundamental work has been previously done, including by Baker \textit{et al.}, who studied the effect of oxygen partial pressure on mass transport, and were subsequently able to identify the pressure-dependent and pressure-independent components of the mass transfer coefficient\textsuperscript{26-28}. For low-loading Pt electrodes, similar approaches have been done to understand barrier thicknesses of Nafion and subsequently effects on transport\textsuperscript{29}. Recently, Reshetenko \textit{et al.}, amongst others, investigated Pt-based systems, and reported an experimental approach in which numerous insert carrier gases were used as oxygen diluents in the cathode feed\textsuperscript{30-32}. As demonstrated in their work, this variation of the carrier gas will have a substantial impact on the oxygen diffusivity through the carrier gas. This alteration as a function of diluent will allow for experimental calculations of the gas-phase and non-gas-phase transport resistance. While these experiments are extremely useful and largely provided a premise and starting point for the work demonstrated here, only Pt-based systems have been evaluated to date\textsuperscript{30}. In this work, efforts were made to expand upon those studies, and use similar techniques for studying mass transport through PGM-free catalyst layers.
At the low potentials or high current densities associated with limiting current scenarios, the limiting current can be represented as:

$$i_l = nFkc$$  \hspace{1cm} (eq. 2.1)

where $i_l$ is the limiting current, $n$ represents the number of electrons in the reaction (4 for ORR), $F$ is Faraday’s constant, $k$ is the mass transport coefficient, and $c$ is the local dry reactant concentration in the flow field channel. From that, the mass transport resistance can be determined through the following relationship:

$$k = \frac{1}{R}$$  \hspace{1cm} (eq. 2.2)

However, at the limiting current density and when using a low concentration oxygen source, the concentration of the reactant is not constant over the course of the flow field. Therefore, a modified calculation has to be done as function of $y$, the dimensionless point in the flow field. This limiting current can be demonstrated as:

$$i_l(y) = \frac{nFkp_r f_r}{RT} \cdot e^{-\frac{nFkp_r y}{RTef}}$$  \hspace{1cm} (eq. 2.3)

where $p_r$ represents the dry inlet reactant partial pressure (calculated by subtracting the vapor pressure at the operating temperature from the sum of atmospheric and gauge pressure), $f_r$ is the reactant fraction, $R$ is the ideal gas constant, $T$ is the temperature, $i_e$ is the flow rate dependent current density, and $f$ is the ratio of inert gas to reactant gas. The flow rate dependent current density can also be calculated via the equation:

$$i_e = \frac{nFVO_2}{AV_m}$$  \hspace{1cm} (eq. 2.4)
where $V_{O_2}$ represents the oxygen flow rate (mL/s), $A$ is the active area of the electrode (cm$^2$), and $V_m$ is the molar volume (22414 mL/mol)

The average limiting current density can be calculated as well, in order to account for the change as a function of the dimensionless pass length, $y$, and can be shown as:

$$i_{ave} = i_e \left(1 - e^{-\frac{nFkr}{RT}}\right)$$  \hspace{1cm} (eq. 2.5)

Following rearrangement, it can be displayed as:

$$\ln \left(1 - \frac{i_{ave}}{i_e}\right) = -\frac{nFkr}{RT} \cdot \frac{1}{i_e}$$  \hspace{1cm} (eq. 2.6)

Such a rearrangement allows for a linear plot to be generated where the slope contains the sole dependency on the mass transport coefficient. The product $i_ef$ can be correlated to the flow rate of the reactant and the limiting current $i_{ave}$ can be experimentally determined. This linear plot should contain a negative slope and pass through the origin. While it is expected that the mass transport coefficient, $k$, that can be determined from the slope, is heavily dependent on the diffusivity of oxygen within the carrier gas, it is also depend on numerous other factors, including Knudsen diffusion, transport through the ionomer, and the presence of the vapor-phase and liquid water within the catalyst layer. The Knudsen diffusion coefficient is dependent on the molar mass of the diluent ($M_A$) as well as the pore diameter ($d$), and is calculated through:

$$D_{KA} = \frac{d}{3} \left(\frac{8RT}{\pi M_A}\right)^{1/2}$$  \hspace{1cm} (eq. 2.7)

This experimental work was paired with theoretical work by Prof. Scott Calabrese Barton at Michigan State University. A one-dimensional isothermal model had previously been designed for the purpose of steady-state characterization of PGM-free materials in PEMFCs$^{33}$.  

38
Previously, the model incorporated multiphase transport through the significantly thicker catalyst layer than is present with Pt-based materials. As mentioned, the gas concentration cannot be considered to be constant over the course of the serpentine flow fields, and therefore the model was adapted into a pseudo two-dimensional system, where the oxygen concentration varies as a function of the flow field path.

2.2 Experimental

2.2.1 Catalyst Synthesis

Synthesis of the catalyst derived through the Sacrificial Support Method (SSM, referred to as NPC-2000) was carried out by Pajarito Powder (Albuquerque, NM) using a proprietary method based on a scaled-up version of a previously-published method at the University of New Mexico\textsuperscript{22}. Gas diffusion electrodes (GDEs) were prepared and manufactured onsite at Pajarito Powder prior to being provided to Northeastern University for final membrane electrode assembly (MEA) preparation and testing.

The second catalyst evaluated in this work is of the MOF variety (referred to as MOF SR). Following a previously-published protocol\textsuperscript{24}, 2-methylimidazole was dissolved into room temperature methanol. In a separate flask, 1,10-phenanthroline monohydrate and zinc(II) nitrate \textit{x}-hydrate were also dissolved into room temperature water. Following the completion of the two dissolutions, the aqueous was poured into the methanol solution. Iron(II) acetate was added, and the solution was allowed to stir for an additional 24 hours. The solution was then passed through a series of centrifuges and methanol washes. The final solid was dried in a vacuum oven, prior to a pair of pyrolysis steps. First, the sample was heat treated at 1050 °C in argon (1hr dwell time) before being heat treated again at 1050 °C in ammonia (18min dwell time).
2.2.2 Electrode and MEA Fabrication

Following catalyst synthesis, inks were prepared for electrode fabrication at NEU. Inks were composed of 55mg catalyst, 900mg of a 5% Nafion® (Dupont, USA) dispersion, 8.5mL of IPA, and 1.5mL of H₂O (Millipore). Inks were homogenized for 1hr at 17000rpm (IKA T25) while suspended in an ice bath. Spray guns (IWATA HP-BCS) were used to spray the catalyst ink onto commercial Sigracet 25BC gas diffusion layers (GDL) (Ion Power). Cathode catalyst loading was 2mg/cm². For all MEA anodes (both PGM-free and Pt reference), commercial Pt GDEs were used (Johnson Matthey ELE0162, 0.4mgPt/cm²). For the Pt reference MEA, a similar procedure was used to manufacture a cathode with loading of 0.36mgPt/cm². Commercial 46% Pt/C (Tanaka Kikinzoki International KK, Japan) was used for the Pt reference cathode. Nafion contact layers were added to all anodes and cathodes (0.5mg/cm²). Electrodes were trimmed to 4.62cm² (2.1cm x 2.2cm). MEAs were prepared with Nafion 211 membrane through a single hot-pressing procedure at 130 °C (5 minutes, 400psi).

2.2.3 Mercury Intrusion Porosimetry (MIP)

Mercury intrusion porosimetry (MIP) studies were done on both PGM-free samples at MSU. In order to simulate the catalyst layer setup, identical inks were prepared as were for cathode preparation. Ink samples were sprayed onto a heated borosilicate glass panel, and then the resulting material was scraped off the glass and send for analysis. Samples were analyzed using a Micromeritics AutoPore IV 9500. A Penetrometer of 3mL total volume and 1.1mL stem volume was loaded with 0.1g of sample material. Mercury intrusion volume was obtained for pressures of 0.1 to 30000psia. The pore radius, \( r_p \), was obtained from the pressure, \( p \), using the Washburn equation\textsuperscript{34}: 

\[ r_p = \frac{2 \sigma \cos \theta}{p} \]
$$r_p = \frac{2ycos\theta}{p} \quad \text{(eq. 2.8)}$$

with a contact angle $\theta = 130^\circ$ and mercury surface tension $y = 485 \text{ dyn/cm}$.

### 2.2.4 PEMFC Testing

Cell housings (5cm$^2$) with serpentine flow fields from Fuel Cell Technologies were used for this work. While the reference work from Reshetenko *et al.* used a segmented cell, single point voltage and current density measurements were taken in this case instead due to equipment limitations. Testing was done with the cell temperature held at 80 °C and the water vessels held at 85 °C in order to ensure 100% relative humidity throughout the cell during testing. 7psig of backpressure was applied throughout testing (21psi total pressure). Flow rates were set to specific ratios in order to facilitate water transport as demonstrated in previous work$^{30}$. All cathode gases were 4% oxygen, with a diluent of argon, nitrogen, or helium. All testing was done on home-built test stations running in conjunction with a Metrohn Autolab (PGSTAT302N) and 20A current booster (PGSTAT30). Polarization curves and electrochemical impedance spectroscopy (EIS) spectra were taken potentiostatically using NOVA software. EIS spectra were collected using data points collected at 50 different frequencies on a logarithmic scale from 20kHz to 100mHz at a series of six potentials between roughly 800mV and 400mV (slight differences sample to sample based on open circuit potential). Spectra were taken with each set of flow rates that was used in polarization curves for proper comparison.

### 2.2.5 Model Development

As mentioned earlier, the model used in this work was a modified version of a previously-devised one-dimensional model. In this case, the major modification was accounting for changes in composition of the cathode gas as it travels through the flow fields. Given the low
oxygen concentration (4%), as the gas is consumed it results in significant drops in oxygen concentration. The modified model can be referred to as a pseudo two-dimensional model following this adaptation. A second modification was the inclusion of a particle-scale mass transfer term, $k_{MT}$, which was used to consider local mass transfer effects.

A first order mole balance was used to demonstrate the change in oxygen molar flow rate, $F_O$, as a function of position along the flow channel, $z$:

$$\frac{dF_O}{dz} = j_O W ; \quad F_O|_{z=0} = \frac{x_O P v}{RT}$$

(eq. 2.9)

where $j_O$ represents the local flux of oxygen in the flow field due to reactions within the electrode, and $W$ is the effective channel width, including both channels and lands. $A$ is the flow field area, while $L$ is the channel length, calculated through $W = A/L$. The local flux is calculated using the above-mentioned previously-described one-dimensional electrode/GDL model. The initial value of $F_O$ is calculated using the pressure, $P$, the volume flow rate, $v$, the mole fraction of oxygen, $x_O$, and the temperature, $T$, while $R$ represents the ideal gas constant.

In addition to the oxygen, the flow within the channel comprises several other species, including water vapor, diluent gas (helium, argon, nitrogen), and liquid water. While the local flux clearly changes as a function of path length through the flow fields, the same cannot be said of the inert cathode diluent flux, $F_d$, and therefore it is considered constant such that $dF_d/dz = 0$. This is due to the high concentration of the diluent (96%, and increasing throughout the flow field path). It is also assumed throughout the channel that the flow is saturated to a consistent level, and therefore, for constant temperature and pressure, the vapor-phase mole fraction of water, $x_w$, remained constant. For this model, that is held true using the following equation:
\[
\frac{dF_w}{dz} = \frac{x_w}{1-x_w} \left( \frac{dF_O}{dz} + \frac{dF_d}{dz} \right)
\]  
(eq. 2.10)

For any component \( i \) addressed thus far (vapor-phase water, oxygen, inert diluent), the mole fraction at any given point throughout the flow field, \( x_i \), can be calculated. This calculation is done via the following equation:

\[
x_i = \frac{F_i}{F_T} \quad (eq. 2.11)
\]

where \( F_T \) is the total molar flow rate, and \( F_T = \Sigma F_i \). The final remaining component of the flow through the flow fields as previously listed is the liquid water. Due to low molar volume of liquid water (0.019 L/mol) compared to vapor-phase water (29 L/mol), this contribution was ignored.

As mentioned earlier, the second modification to the existent model was done through introduction of a local mass transfer coefficient, \( k_{MT} \). By linking this value to the ORR reaction, a volume-specific reaction rate, \( r_{ORR} \) (mol cm\(^{-3}\) s\(^{-1}\)) can be calculated as:

\[
r_{ORR} = \frac{k_{ORR}x_O}{1+k_{ORR}/k_{MT}} \quad (eq. 2.12)
\]

\( k_{ORR} \) represents a volumetric rate constant that is defined by local conditions within the catalyst layer such as potential. \( x_O \) represents the local oxygen mole fraction. Additional factors that were used as adjustable parameters while fitting the experimental polarization and EIS spectra included the catalyst layer exchange current density \( (i_0, \text{ A cm}^{-3}) \), catalyst layer ionic conductivity \( (\kappa, \text{ mS cm}^{-1}) \), and the catalyst layer hydrophobic fraction \( (f_{HO}) \).
2.3 Results & Discussion

2.3.1 Mercury Intrusion Porosimetry

Figure 2.1 below demonstrates the results of the MIP testing, while Table 2.1 shows the calculated pore modes for each of the two catalysts, reproduced with permission. While both materials demonstrated significant mode volume in the 100-300nm range, only the NPC-2000 material demonstrated significant contribution of smaller pores (<10nm). These distributions were included within the pseudo two-dimensional model.

![Figure 2.1](image.png)

*Figure 2.1 - Pore size distributions by mercury intrusion porosimetry (MIP) for catalyst layers prepared from NPC-2000 and MOF SR catalyst. Markers indicate experimental data points, while dashed lines are used to indicate how the two materials were deconvoluted into two (MOF SR) and three (NPC-2000) log-normal distributions of mean radius r₀.*

<table>
<thead>
<tr>
<th>Table 2.1. Pore Size Results for Fig. 2.1</th>
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<tbody>
<tr>
<td><strong>NPC-2000</strong></td>
</tr>
<tr>
<td>r₀ / nm</td>
</tr>
<tr>
<td>4.1</td>
</tr>
<tr>
<td>98</td>
</tr>
<tr>
<td>121</td>
</tr>
</tbody>
</table>
2.3.2 Mass Transport (HelOx) Testing

Fuel cell performance was measured via polarization curves using 4% oxygen diluted with helium, argon, or nitrogen carrier gases at 80 °C and various pairs of anode & cathode flow rates. Prior to the evaluation of the two PGM-free materials (NPC-2000 & MOF SR), a Pt reference cell was tested for comparison with previously-published results and to be used as a standard for better direct comparison with PGM-free materials. In the case of the Pt cell, higher flow rates were used than for the PGM-free materials in order to get a wider range of O₂ utilization. Figure 2.2 demonstrates the polarization curves of the Pt-based reference cell at various flow rates, while Figure 2.3 shows the analysis described earlier in equation 2.6, where the linear correlation between the experimental limiting current and the flow rate of the cathode gas is apparent. As is evident in the polarization curves, the helium performance exceeded both the nitrogen and argon, while the latter two showed virtually identical performance. This was expected as the Knudsen diffusion coefficients of oxygen in argon and nitrogen are very similar, while oxygen diffuses significantly easier through helium due to its low molecular weight and smaller atomic size. In Figure 2.3 there is good linearity demonstrated between the logarithmic function and the inverse of the stoichiometric current density, especially at the higher flow rates (lower 1/iₑ values). Lower values of the logarithmic expression demonstrate exponentially higher utilization of oxygen within the catalyst layer. It was demonstrated by Reshetenko et al. that at low flow rates (and subsequently, extremely high utilization of oxygen), the data can deviate from the demonstrated linear trend. With only the lowest of the flow rates evaluated here does that become at all apparent. Additionally, a fitted line is applied to the data in Figure 2.3. The slope of the line can be represented by \(-\frac{nFk_p}{RT}\) from equation 2.6. In accordance with equation 2.6, the intercept is defined as the origin as utilization of oxygen should trend towards 0.
as the flow rate becomes infinitely high. From this slope, the mass transport coefficient, and subsequently the mass transport resistance (via equation 2.2) can be calculated.

Figure 2.2 - Pt Polarization Curves as a function of flow rate. Testing was done at 80 °C, 100% RH. Cathode catalyst loading is 0.36mg/Pt/cm².
The two PGM-free materials were evaluated through a similar testing protocol. With the PGM-free materials, in order for the fuel cell to show a true limiting current region at low potentials, the flow rates had to be decreased significantly, as is apparent in Figure 2.4. This is based off a combination of differences between the inherent activity as well as the active site densities of these materials compared to Pt-based catalysts. While individually, the two materials demonstrated the same trend as Pt in terms of performance changes based on the diluent, it was apparent that there were slight differences between the overall performances of the two materials. The NPC-2000 material demonstrated slightly higher current densities independent of flow rate, as would be expected given that prior publications of those materials showed that the NPC-2000 was slightly more active than the MOF SR. The NPC-2000 also
demonstrated slightly more variation as a function of flow rate, which could be heavily influenced by the different pore size distributions that were evident in MIP results shown earlier.

In general, Figure 2.5 demonstrates that the PGM-free materials follow the same linear trends that the reference Pt as well as Reshetenko et al. showed previously. Again, at very low flow rates, they are some deviations for the linear trends. For that reason, the lowest flow rates
are excluded from the fitting results in order to more accurately represent the linear region of the figure. Results of the fitting and calculations of the diffusion coefficient as well as mass transport coefficient are shown in Table 2.2.

Figure 2.5 - Logarithmic function of limiting current in relation to inverse of stoichiometric current density for both PGM-free materials and all three diluents.
### Table 2.2. Calculated Mass Transfer Coefficients

<table>
<thead>
<tr>
<th>Diluent</th>
<th>$MW_{d}$ g mol$^{-1}$</th>
<th>$D_0_{2}$ cm$^2$ s$^{-1}$ @ 60 °C</th>
<th>$D_0_{2}$ cm$^2$ s$^{-1}$ @ 80 °C</th>
<th>$k$ / m s$^{-1}$ × 10$^3$</th>
<th>MOF SR</th>
<th>NPC-2000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Helium</td>
<td>4.0</td>
<td>0.891$^{30,36}$</td>
<td>0.982</td>
<td>2.9 ± 0.05</td>
<td>3.1 ± 0.09</td>
<td></td>
</tr>
<tr>
<td>Argon</td>
<td>39.9</td>
<td>0.236$^{30}$</td>
<td>0.261</td>
<td>2.4 ± 0.11</td>
<td>2.6 ± 0.06</td>
<td></td>
</tr>
<tr>
<td>Dinitrogen</td>
<td>28.0</td>
<td>0.247$^{30}$</td>
<td>0.274</td>
<td>2.4 ± 0.07</td>
<td>2.5 ± 0.03</td>
<td></td>
</tr>
</tbody>
</table>

As is evident from Figure 2.5 and calculated in the rightmost two columns of Table 2.2, the nitrogen- and argon-diluted samples showed very similar mass transport coefficients, while the mass transport coefficient was substantially higher for helium. The higher mass transport coefficient will correlate to a lower mass transport resistance via equation 2.2. This is well in line with the diffusion calculations shown in Table 2.2, and it would be expected that oxygen could transport more easily through a helium diluent rather than argon or nitrogen. Again, while it is noted that there are some slight deviations from the linearity at low flow rates, it can be clearly seen in Table 2.2 that there are very low error estimates for the mass transport coefficient.

In order to further break down the mass transport coefficient, it should be noted that the mass transport coefficient through the cathode should be considered as a series combination of the gas-phase resistance, $R_g$, and the non-gas-phase resistance, $R_0$:

$$ R_{MT} = \frac{L}{kA} = R_g + R_0 = \frac{L}{k_g A} + \frac{L}{k_0 A} \quad \text{(eq. 2.13)} $$

Subsequently, the mass transport resistance, $k$, will also consist of a series combination of gas-phase and non-gas-phase resistances:

$$ \frac{1}{k} = \frac{1}{k_0} + \frac{1}{k_g} \quad \text{(eq. 2.14)} $$
where \( k_g \) is linearly dependent on the diffusivity of oxygen through the diluent gas of choice. As was first documented by Reshetenko et al., we note that the second term in equation 2.14 should be linearly proportional to the molecular weight of the diluent gas, \( MW_d \). Figure 2.6 demonstrates this, as the data from Table 2.2 is plotted as a functional of \( MW_d \). If the line is extrapolated to \( MW_d = 0 \), this gives a good estimate of \( 1/k_0 \). This is a logical assumption, as when \( MW_d = 0 \), theoretically there is no diluent, and subsequently no gas-phase resistance due to Knudsen diffusion, etc. Table 2.3 provides the intercept and slope values, and subsequently the \( k_0 \) value for both PGM-free materials, the Pt reference, and the literature Pt values from Reshetenko et al.

![Graph showing the inverse of mass transport coefficient as a function of molecular weight. Extrapolation of the line to a molecular weight of 0 provides an estimate of 1/k0, the non-gas-phase mass transport resistance.](image-url)
As shown in Table 2.2, both PGM-free materials showed very similar values of the mass transport coefficient, \( k \). Additionally, the show very comparable slope and intercept, corresponding to the gas-phase and non-gas-phase coefficients. When comparing the sample to Pt (and the reference Pt data from Reshstenko et al.), while the slopes are not significantly different, it is noted that there is a much higher intercept. The intercept in this work corresponds to \( 1/k_0 \), which (when \( 1/k_g = 0 \)) is equal to the mass transport resistance. Therefore, the two PGM-free materials demonstrate significantly higher mass transport resistances within the catalyst layer than the Pt system. This is explainable experimentally largely due to the fact that the catalyst layers of the PGM-free materials are significantly thicker than those of Pt. Given a similar packing of the catalyst material during preparation (which is a good assumption given the spray technique used), there is just over twice the total catalyst material in the PGM-free cathodes than the Pt cathode. Subsequently, the mass transport resistance being roughly twice as high in the PGM-free materials is understandable when operating under the assumption that the mass transport coefficient and resistance are considered to be dependent on the thickness of the catalyst layer.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Slope m(^{-1}) s(^{-1}) g(^{-1}) mol</th>
<th>Intercept m(^{-1}) s</th>
<th>( k_0 ) m s(^{-1} \times 10^3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>MOF SR</td>
<td>2.38 ± 0.64</td>
<td>332 ± 18</td>
<td>3.2 ± 0.16</td>
</tr>
<tr>
<td>NPC-2000</td>
<td>2.3 ± 0.32</td>
<td>314 ± 9.0</td>
<td>3.2 ± 0.091</td>
</tr>
<tr>
<td>Pt</td>
<td>2.3 ± 0.93</td>
<td>156 ± 26</td>
<td>6.4 ± 1.1</td>
</tr>
<tr>
<td>Pt(^{30})</td>
<td>1.0 ± 0.084</td>
<td>78 ± 7.7</td>
<td>12.8 ± 1.3</td>
</tr>
</tbody>
</table>
2.3.3 Model Results

Fitting of the experimental data was done using the pseudo 2-D model described earlier. The pore size distributions that were determined through mercury intrusion porosimetry, as well as the EIS spectra, were used as inputs. Experimental polarization curves using helium and argon were fit to the model using nonlinear fits. Nitrogen was excluded due to its similarity to argon. Four fitting parameters were used in the nonlinear fit: ionic conductivity, exchange current density, hydrophobic porosity, and the catalyst layer mass transfer coefficient. These parameters would allow for further distinguishing of the two catalysts. Fits were simultaneously run on all polarization curves, allowing for parameters to be determined that would best fit at least 4 to 5 of the polarization curves. Figure 2.7 demonstrates the results of these fittings for the argon and helium polarization curves, and the fitted parameters are calculated and shown in Table 2.4.
As can be seen in Figure 2.7, the model results show good correlation to the experimental polarization curves, especially at higher potentials. As the potential decreases, there are some slight deviations from the model. However, it is interesting to note that at higher flow rates, the model will underestimate the theoretical limiting current compared to the experimental, while the opposite is true as low flow rates. Therefore, the experimental limiting current shows a higher dependency on the flow rate than the model predicted. This can be explained through a pair of experimental artifacts: the isothermal nature of the model as well as slight pressure changes at
lower flow rates. Experimentally, increased current densities associated with higher flow rates will raise the local temperature in the electrode, which will have an effect on the transport and reaction properties within the catalyst layer. This is not accounted for within this model. Despite this minor deficiency, the mass transfer coefficient determined from the model, $k_{MT}$, shows very good association with the experimentally determined values for both PGM-free materials, as shown in Figure 2.8. The slope is representative of the gas-phase mass transport coefficient, and was in very good accordance with the experimental values, while only slight deviations were apparent with the intercept (non-gas-phase mass transport coefficient).

![Figure 2.8 - Model and Experimental Results fitted with respect to molecular weight of diluent gas](image)

**2.4 Conclusions**

Two PGM-free catalysts (NPC-2000 & MOF SR), of different synthetic methodologies (Sacrificial Support Method & Metal-Organic-Framework) were analyzed in an effort to gain a
further understanding of transport properties within the catalyst layer. In this case, polarization curves were taken at low flow rates using a low concentration oxygen feed, diluted with various inert carrier gases (helium, argon, nitrogen). This allowed for the cell to achieve a region of limiting current at low potentials. Experimental results indicated that the two PGM-free materials displayed similar transport characteristics, in particular mass transport coefficients and subsequently, mass transport resistances. A Pt cell that was evaluated for a more accurate comparison than the literature data demonstrated mass transport resistances of roughly one half of the PGM-free materials, which is in line with the thickness differences as well between the two. Several trends were apparent in both PGM and PGM-free systems, including that the helium polarization curves demonstrated higher limiting currents than the argon or nitrogen polarization curves at equal flow rates. This is due to the higher diffusion coefficient of oxygen through a helium diluent than through a nitrogen or argon diluent. This trend is reinforced in the calculations that demonstrated a higher mass transport resistance in the argon and nitrogen system than in the helium-diluted system.

In addition to the experimental work and calculations, a pseudo two-dimensional model was developed based off a previously-developed one-dimensional model. This was done through the introduction of a few modifications, including a depleting oxygen concentration as it progresses through the flow fields and a local mass transfer term. Mercury intrusion porosimetry data, experimental polarization curves, and experimental EIS spectra were used as inputs for the various materials that were evaluated, and the data was fit to the model using nonlinear algorithms, allowing for the calculation of several parameters, including catalyst layer conductivity, exchange current density, hydrophobic fraction, and mass transfer coefficient. This demonstrated the first use of these experiments combined with a theoretical model approach on
PGM-free materials in the PEM environment to further understand transport properties. Developing a further understanding of these transport properties is vital if the PGM-free materials are going to demonstrate commercial viability as a suitable replacement for the state-of-the-art Pt-based systems.

2.5 Chapter 2 References


Chapter 3

Evaluation of Metal-Organic-Framework Catalysts for Oxygen Reduction in High-Temperature Proton Exchange Membrane Fuel Cells

3.1 Introduction

It is more apparent than ever that today’s society is in need of clean energy replacements for the diminishing fossil fuel supply. This has led to significant increases in both academic and industrial research into potential clean energy alternatives. One potential clean energy alternative includes hydrogen fuel cells. Traditionally, these systems have been studied in the low temperature environment, utilizing Nafion® technologies, often for automotive applications. The work presented in Chapter 2 was a demonstration of fuel cells of this type. However, there are also possibilities of commercialization for other applications, such as stationary power generation, including in-home power generation. For these applications, higher-temperature systems (HT-PEMFCs) have traditionally been studied, operating in the 150-220 °C range. There are some key material differences between these systems and the lower temperature PEM systems, including that higher temperature systems do not utilize a Nafion binder or membrane, as the polymer would not be stable in the operational temperature range. These systems have several inherent benefits and deficiencies when compared to lower temperature fuel cell systems. One of the benefits associated with these systems include a higher combined heat and power (CHP) efficiency than lower temperature systems, as they are able to surpass 80% total CHP efficiency (Source: EEA/ICF). Additionally, they typically demonstrate higher immunity to the effects of poisoning at the higher temperature. Above 160 °C, these systems typically have a carbon monoxide tolerance of roughly 2%, as well as sulfide tolerance of close to 100ppm. Both of those metrics far outperform the traditional low-temperature PEM systems\textsuperscript{1-3}. Unfortunately,
there are also some serious drawbacks. The primary drawback is the higher loading of the state-of-the-art Pt catalysts that are used for both the HOR and ORR reactions. Often, these higher temperature systems will utilize at least 1mgPt/cm², roughly an order of magnitude higher than the current state-of-the-art for lower temperature systems⁴-⁶. Additionally, from a power standpoint, these systems do traditionally have lower maximum power outputs than lower temperature systems. This is largely due to the fact that there are two fundamental aspects in which the high temperature systems are deficient compared to Nafion® systems: oxygen permeability and conductivity. Because of the operating temperature, dry gas feeds are used, and the conductivity of un-humidified air is roughly 6 times lower than that of air saturated at 60 °C, the lower temperature threshold of standard PEM operation. Additionally, conductivity of PBI membranes are at least 5 times lower than Nafion® at ~105 °C, the upper threshold of Nafion® stability and the lower threshold of PBI stability⁷. While the conductivity and oxygen permeability are significant issues, the high Pt loading that is required is the more pressing one, as these systems can fluctuate in and out of commercial viability simply due to the market cost of the Pt catalyst. It is this factor that this work attempts to address, as Platinum-group metal (PGM)-free catalysts were evaluated as potential alternatives to Pt catalysts. While much work has been done to further understand the mechanisms of the oxygen reduction reaction (ORR) in acid and alkaline as well as in PGM-free catalyst development⁸⁻²⁸, this work helps expand that work into the previously uninvestigated higher temperature environment.

Two PGM-free materials, both of the Metal-Organic-Framework (MOF) methodology were evaluated as potential ORR catalysts in HT-PEM environment. One of those materials (referred to as MOF SR) was developed through a solution reaction synthetic procedure previously published²⁹. The second catalyst was developed through a reactive ball-milling
procedure (referred to as MOF SSR), also through a previously-published methodology\textsuperscript{30}. The two materials are inherently different in their catalyst structure. The MOF SR material is unique in that it does not contain any evidence of direct Fe-N\textsubscript{x} coordination. Rather, it contains evidence of iron carbide and metallic Fe interactions. On the other hand, the MOF SSR material contains almost exclusively Fe-N\textsubscript{4} coordination. This has been previously demonstrated through XAS and Mossbauer spectroscopy studies. Additionally, the MOF SSR catalyst contains far more amorphous carbon in its support than the MOF SR catalyst, which demonstrates a highly graphitic carbon support, demonstrated through Raman spectroscopy.

Given the inherent differences in structure of these two materials, both materials were evaluated using the RRDE technique to identify the likely ORR pathway through Koutecký-Levich analysis. Additionally, RRDE was used as a methodology to ensure that the two materials would both be immune to phosphate anion poisoning at room temperature. Given the previously mentioned susceptibility of Pt catalysts to phosphate anion poisoning at lower temperatures, this resistance is key in developing PGM-free materials. Once it was determined that the two materials were not at risk of phosphate poisoning, they were evaluated in the HT-PEMFC environment for their respective performance, using 5cm\textsuperscript{2} single cell membrane electrode assemblies (MEAs). Tafel analysis of the catalysts was done using the high frequency resistance from electrochemical impedance spectroscopy. This Tafel analysis on oxygen data allowed for the determination of the iR-free potential, a more representative evaluation of the catalytic activity within a fuel cell. Both materials, when evaluated in the HT-PEMFC environment, showed promise as potential alternatives to the state-of-the-art Pt catalysts typically utilized in this system.
3.2 Experimental

3.2.1 Catalyst Synthesis

The MOF SR catalyst was synthesized in accordance with previously published methodologies\textsuperscript{29}. 2-methylimidazole was dissolved into methanol at room temperature. Simultaneously, 1,10-phenanthroline monohydrate and zinc(II) nitrate x-hydrate were dissolved into room temperature water. Following the combination of the two solutions, iron(II) acetate was added, and the solution was stirred for an additional 24hrs. Following a series of centrifuging steps and methanol washes, the final solid was dried in a vacuum oven. The final step of the synthesis comprised a pair of pyrolysis treatments. The first was in argon at 1050 °C (1hr dwell time), while the second was conducted in ammonia (18min dwell time), also at 1050 °C.

The MOF SSR catalyst was synthesized at Pajarito Powder (Albuquerque, NM) using modified and optimized methodologies based off of prior established techniques\textsuperscript{30}. Prior to catalyst preparation, zinc oxide was heat treated at 400 °C. The zinc oxide, as well as 2-methylimidazole & ammonia sulfate, were ball-milled for one hour in the presence of a small quantity of methanol. This first step will result in the formation of ZIF-8 MOF structure. 1,10-phenanthroline and iron (II) acetate were added following this step, and the mixture was ball-milled for an additional two hours. This is done to coat the exterior of the ZIF-8 structure with the iron-phenanthroline complex. As with the MOF SR material, the catalyst underwent a pair of pyrolysis steps: argon for 1hr (1050 °C) and then ammonia for 18min (1050 °C). Finally, the catalyst went through an acid leaching process for at least 12hrs using 0.1M hydrochloric acid (HCl) in order to remove the metallic iron.
3.2.2 Rotating Ring Disk Electrode (RRDE) Studies

All RRDE testing was done using a Pine Instrument Company setup connected to a Metrohm Autolab Bipotentiostat (PGSTAT302N), using the included Nova software. 0.1M perchloric acid electrolyte was prepared by dilution of double-distilled 70% perchloric acid (GFS Chemicals). All studies were done using a glassy carbon electrode (active area of 0.247cm$^2$) following polishing with 0.05 micron alumina paste (Buehler, Lake Bluff, IL). Platinum mesh was used as a counter electrode, while a reversible hydrogen electrode (RHE) was used as a reference electrode. The RHE was prepared by filling the chamber with electrolyte (0.1M HClO4), then applying a potential of 20V for roughly 15 minutes, until the Pt mesh inside the chamber was roughly half-immersed in electrolyte, with the remainder of the chamber full of the generated hydrogen. Catalyst RRDE inks were composed of 3.1mg catalyst, 465μL of isopropyl alcohol, 150.2μL of Millipore water, and 6.2μL of Nafion® dispersion (5 wt%, DuPont, USA). Following preparation, the ink was sonicated for 60 minutes to ensure a well-dispersed ink. 30μL of catalyst ink was drop-casted (6μL aliquots, 10 minutes apart to allow for drying) to achieve 600μg/cm$^2$ catalyst loading. Electrodes were submerged in 25mL of electrolyte and subjected to an oxygen purge for 30 minutes before conditioning began. Conditioning was carried out by cycling over a potential range of 1.05V to 0.05V at 20mV/s, at least 10 complete cycles, until scan-to-scan performance had stabilized. ORR curves were taken using cathodic scans from 1.05V to 0.05V at 20mV/s in oxygen-purged electrolyte (0.1M HClO4). Oxygen would remain flowing as a blanket over the electrolyte surface to ensure maximum dissolution of the oxygen while not disturbing the electrolyte surface. Testing was done at 400, 625, 900, and 1600rpm. 0rpm argon-purged scans for baseline correction were also taken under the same conditions following 30 minute purge. For phosphate poisoning studies, electrolyte was doped
with appropriate quantities of 1mM H₃PO₄ to achieve 1mM and 10mM phosphate concentration within the electrolyte (250μL and 2.25mL, respectively). The electrolyte was doped with concentrated (85%) phosphoric acid to achieve 100mM phosphate concentration (148μL). In addition to preliminary testing (0mM phosphate), ORR performance was evaluated at 1mM, 10mM, and 100mM phosphate concentrations. 1600rpm data was used for the purpose of phosphate poisoning evaluation.

Koutecký-Levich analysis was carried out at a series of potentials. Equation 1 below is the general form of the Koutecký-Levich equation:

\[
\frac{1}{i_m} = \frac{1}{i_K} + \frac{1}{i_{MT}}
\]  

(eq. 3.1)

where \( i_m \) is the measured current, \( i_K \) is the kinetic current, and \( i_{MT} \) is the mass transport current. In RRDE experiments, when the catalyst is evaluated at a series of rotation rates, the Koutecký-Levich equation can be written as:

\[
\frac{1}{i_m} = \frac{1}{i_K} + \frac{1}{B_L \omega^{0.5}}
\]  

(eq. 3.2)

where \( B_L \) is the Levich constant and \( \omega \) is the angular rotation rate of the electrode. In that case, the Koutecký-Levich plot will yield a straight line with a slope of \( 1/B_L \) and a y-intercept of \( 1/i_K \), when plotted as a function of the inverse square root of the rotation rate. From this calculation of \( B_L \), it is possible through the following equation to determine the number of electrons in the electrochemical reaction in question.

\[
B_L = 0.62nFC_0(D_0)^{2/3}v^{-1/6}
\]  

(eq. 3.3)

where \( n \) is the number of electrons, \( F \) is Faraday’s constant, \( C_0 \) is concentration of oxygen in the electrolyte, \( D_0 \) is the diffusion coefficient of oxygen in the electrolyte, and \( v \) is the kinematic
viscosity. The diffusion coefficient, concentration of oxygen in electrolyte, and kinematic viscosity are literature values based on the species (oxygen) and electrolyte (0.1M HClO₄) in question. From this, the value of $n$ can be determined, in order to match the kinetics of ORR to either a 4- or 2-electron pathway. Reference lines corresponding to 2- and 4-electron pathways were added to Koutecký-Levich plots for easier comparison.

### 3.2.3 Electrode & MEA Fabrication

Commercial gas diffusion layers (LT1400, NuVant Systems Inc., USA) were used for cathode fabrication. Cathode inks were prepared using modified versions of proprietary methodologies from Advent Technologies. In general, it is a primarily aqueous ink (low IPA content for both better ink dispersion as well as easier coating onto a hydrophobic gas diffusion layer) where a particular catalyst to polytetrafluoroethylene (PTFE) ratio (optimized in this case to be 3:2) is maintained. Additionally, a few other proprietary additives and surfactants are added, primarily for ink stabilization. Once inks were prepared, application to the GDL was done through a draw-down coating method (Elcometer 4340 Automatic Film Applicator). Thin catalyst coats were applied and then dried using a handheld dryer. After several coats, the electrode was removed and weighed to determine catalyst loading. Final catalyst coating for the MOF SR was 1.95mg/cm², while the final catalyst coating for the MOF SSR was 1.5mg/cm². Electrodes were trimmed using a die cutter to 2.5cm by 2.5cm. Traditionally, electrodes made through these techniques will be sintered following coating, which will have several effects. First, it will allow for removal of the additives that were included into the catalyst layer. Additionally, sintering to the crystalline melting point of PTFE is typical as a method of increasing the hydrophobicity of the catalyst layer. However, in these cases, due to stability concerns of the PGM-free materials under the sintering conditions, sintering processes were
excluded. Commercial Pt electrodes were used as a simultaneous counter (anode) and reference electrode for all cells (Advent Technologies A1100W, 1.0mgPt/cm²). Polybenzimidazole (PBI) membranes were used for all tests as well. Electrodes were hot-pressed to a polymer-coated Kapton subgasket (Advent Technologies). The Kapton subgasket will bind with the PTFE within the catalyst layer. Additionally, this will help create a proper seal around the exterior of the electrode to prevent leaks during pressurized operation. Given the soft PBI membrane, this subgasket also prevents the edges of the electrodes from cutting into the membrane, potentially creating short circuits. The active area of the electrode is determined by the area not sealed to the subgasket, which in this case is 4.62cm² (2.1cm by 2.2cm). Following subgasket presses, the final MEA is prepared by hot-pressing the two electrodes (and their bound subgaskets) to the PBI membrane. Stainless steel shims were used to control the final compression of the MEA. This is vital in the preparation, as the PBI membrane is commercially prepared through a sol-gel process and is imbibed with phosphoric acid. The time, temperature, and pressure of the hot-press procedure will determine the quantity of acid that is squeezed out of the membrane and into the catalyst layer. This phosphoric acid is what provides the proton conductivity within the catalyst layer (similar in purpose to Nafion® in low temperature fuel cell systems). Too little acid and the electrode layer will have poor proton conductivity, while too much acid can flood the cathode layer, resulting in poor gas and mass transport characteristics. Following hot-press, the MEA was dried in an oven (air, 160 °C, 30min), in order to remove any residual moisture from the MEA.

3.2.4 HT-PEMFC Testing

Cell testing was done in standard 5cm² cell housings from Fuel Cell Technologies, with a serpentine flow field. Home-built test stations were used to control gas flow, temperature,
humidity, and backpressure of the system. An HP 6050A DC load supply and LabView programs were used to control the current for polarization curves, while a Metrohm Autolab (PGSTAT302N) and 20A current booster (PGSTAT30) with Nova software were used to collect electrochemical impedance spectroscopy (EIS) spectra potentiostatically at each set of conditions (applied backpressure, cathode gas) where polarizations were collected.

Cells were heated under nitrogen flow from room temperature to 100 °C. At that point, the anode and cathode gases were switched to hydrogen and oxygen, respectively, and the cell was heated to the operating temperature of 200 °C. Once the cell temperature had stabilized at 200 °C, the backpressure was increased to 0.5bar applied backpressure and a conditioning program was carried out in order to establish a baseline performance. The cell was stepped down in potential from a high potential near the open circuit potential of the cell down to roughly 300mV (50mV increments, roughly 2 minutes per step), then back up to the open circuit potential. This process was repeated until the cell would establish a steady current at each potential. Once the conditioning was complete, polarization curves were taken at incrementally increased backpressures (0.5bar to 2.5bar gauge, 1.5bar to 3.5bar total). Following oxygen testing, air was purged through the system for 30 minutes while the cell was maintained at 3.5bar total pressure. Similar testing was done in air as the backpressure was decreased. Following polarization curves, oxygen was purged back through the system, and EIS spectra were taken potentiostatically in oxygen and air at the same backpressures as polarization curves. High frequency resistance values from the EIS spectra were used to correct for iR-losses in the oxygen polarization data in order to complete the Tafel analysis.
3.3 Results & Discussion

3.3.1 Rotating Ring Disk Electrode (RRDE) Studies

3.3.1.1 MOF SR

Studies were done to evaluate the ORR performance of the MOF SR catalyst, as well as to evaluate the phosphate immunity of the catalyst. Figure 3.1 shows the initial performance of the catalyst in 0.1M HClO₄ in the absence of H₃PO₄ doping in the electrolyte. As is the case in RRDE evaluation, the limiting current increased as a function of the rotation rate. The data shown in Figure 3.1 is well in accord with data previously published following the initial development of this catalyst.

![Figure 3.1 - Performance of MOF SR catalyst in 0.1M HClO₄, with no doping of H₃PO₄, evaluated at a series of rotation rates](image-url)
To evaluate the catalyst simply beyond the performance, but to instead glean additional information regarding the ORR pathway, Koutecký-Levich analysis was carried out. For this, calculations described earlier were used (equations 3.1-3.3), and the measured current was evaluated as a function of the rotation rate. The results of this analysis are shown in Figure 3.2. The analysis shown below was done on the sample without presence of H$_3$PO$_4$ in the electrolyte.

![Koutecký-Levich analysis for MOF SR catalyst in 0.1M HClO$_4$, with no H$_3$PO$_4$ doping, calculated at multiple potentials, along with reference lines for 2- and 4-electron pathways.](image)

Given that the slopes of MOF SR lines (regardless of potential) were very similar to that of the 4-electron pathway, it would be expected that the calculated $n$ value should be roughly 4. When calculated using equation 3.3, the value of $n$ was 3.9, indicating that the catalyst will almost exclusively reduce oxygen through a 4-electron pathway. If extrapolated to the axis, this
line would yield a non-zero intercept, indicating the presence of a kinetic current ($i_k$, equation 3.1). Kinetic current can be correlated to the catalytic activity of the catalyst. Since the inverse of the intercept represents the kinetic current, intercept values closer to the origin correlate to higher kinetic currents and catalytic activity.

Figure 3.3 shows the cyclic voltammograms for the MOF SR catalyst, and the subsequent small changes in the catalyst as a function of the phosphate poisoning. These slight changes are insignificant compared to the effect of phosphate on Pt systems$^1$. The changes in the ORR region can be emphasized by looking at the ORR curves at 1600rpm, where the argon baseline has been subtracted from the oxygen curves, and the cathodic scan is isolated. This is shown in Figure 3.4.
Figure 3.3 - Cyclic Voltammetry (CV) curves for MOF SR in argon and oxygen-purged 0.1M HClO₄, with oxygen data included for the various H₃PO₄ doping levels.
Figure 3.4 - ORR curves at a series of H₃PO₄ concentrations in 0.1M HClO₄ at 1600rpm, demonstrating high immunity to phosphate poisoning.

From this, any shift in the ORR performance due to phosphate poisoning can be clearly identified. In this case the shift is rather minute, only consisting of roughly 15mV at the half wave potential ($E_{1/2}$, the potential at which the current density is equal to half of the limiting current density). This indicates that the phosphate anion is unable to bind onto the catalyst surface, or more explicitly, and ORR active site of the catalyst. This lack of a shift can also be seen in the Tafel analysis (Figure 3.5), where the high frequency resistance from electrochemical impedance spectroscopy is used to complete the iR correction. Again, the shift seen from the addition of 100mM H₃PO₄ is only roughly 15mV.
3.3.1.2 MOF SSR

Similar studies were carried out for the MOF SSR catalyst as were previously shown for the MOF SR catalyst. Figure 3.6 shows the initial performance of the catalyst at various rotation rates.

Figure 3.5 - Tafel analysis with iR-free potential calculated from high frequency resistance of electrochemical impedance spectroscopy shown for various concentrations of $H_3PO_4$. 
The ORR performance of this catalyst is also well in line with the previously published work by Li et al. during its development\textsuperscript{30}. There are a few differences that should be noted between the two materials in question beyond what has been previously stated regarding structural differences, and this becomes apparent in Figure 3.7, where the Koutecký-Levich analysis is carried out at a series of potentials. Like with the MOF SR material, the Koutecký-Levich analysis was done in the absence of phosphate ions. The solid and dotted lines represent the 2- and 4-electron pathways for ORR.
One of the apparent differences is that there is a significantly larger gap between the 4-electron pathway standard and the experimental values (although the slope appears relatively well in line with the standard). This is again indicative of a kinetic current, and in this case a significantly higher intercept than with the MOF SR material. Through Butler-Volmer relations, the kinetic current can be correlated to the catalytic activity of the material. The kinetic current is represented by the inverse of the intercept. Subsequently, it can be stated that the MOF SSR catalyst contains a lower kinetic current than the MOF SR catalyst already evaluated.

Figure 3.8 shows the cyclic voltammograms with no rotation for the argon-purged (0mM H₃PO₄) as well as the oxygen-purged (all H₃PO₄ concentrations). Slight shifts in the CV can be
seen as the concentration of phosphoric acid is increased, primarily in the region of ORR (cathodic scan, from roughly 1.0V to 0.5V). However, like with the MOF SR catalyst, when compared to previously published work that contains similar analysis for Pt catalysts, these shifts are rather insignificant. With a Pt catalyst, not only would the shift in the ORR region be more pronounced, but there would also be significant changes in the region associated with hydride formation (anodic scan, from roughly 0V to 0.3V). On a Pt catalyst, these changes in the hydride formation can be correlated to changes in the electrochemical surface area (ECSA).

Again, the region associated with ORR is isolated and examined by the introduction of a rotated electrode, at 400, 625, 900, and 1600rpm in this case. This can be seen in Figure 3.9, where the cathodic scan at 1600rpm is shown. Here, the shift at the half wave potential ($E_{1/2}$) is
only roughly 10mV. This is also clearly demonstrated in Figure 3.10, the Tafel analysis for the MOF SSR catalyst. Table 3.1 shows the change in limiting current \((i_L)\) and half wave potential \((E_{1/2})\) for both PGM-free materials and previously-published Pt/C results, demonstrating the high immunity of these two PGM-free materials to phosphate poisoning (100mM H₃PO₄).

![Figure 3.9 - ORR curves at various H₃PO₄ concentrations in 0.1M HClO₄ at 1600rpm to demonstrate phosphate immunity.](image-url)
Table 3.1. Effect of Phosphate Poisoning on PGM and PGM-Free Materials

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Shift in $E_{1/2}$</th>
<th>loss in $i_L$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MOF SR</td>
<td>14mV</td>
<td>3.8%</td>
</tr>
<tr>
<td>MOF SSR</td>
<td>12mV</td>
<td>6.8%</td>
</tr>
<tr>
<td>Pt/C (MOF Phosphate Ref.)</td>
<td>120mV</td>
<td>10%</td>
</tr>
</tbody>
</table>

3.3.2 HT-PEMFC Testing

Following the demonstration of phosphate immunity shown above, both materials were evaluated for use in the HT-PEMFC environment. Figure 3.11 below shows the performance of the MOF SR catalyst, both in oxygen and in air, while Figure 3.12 shows the performance of the MOF SSR catalyst. While these materials are inherently different in terms of atomic coordination and hypothesized active sites, they showed very similar performance when put into
fuel cells. The MOF SR performance was slightly higher than that of the MOF SSR. One potential reason for the difference in performance is the difference in catalyst loading of the two systems. Up until a certain point, increased catalyst loading will yield increased performance due to the increase in actives sites. However, at a certain point, the catalyst layer becomes thick enough that active sites embedded in the middle of the catalyst layer become inaccessible, and additional catalyst material will not yield additional performance gains. To avoid that scenario, catalyst loadings in these cells was kept below 2mg/cm$^2$. However, from 1.5 to 1.95mg/cm$^2$, there likely would still be slight performance increases. A second reasoning goes back to the Koutecký-Levich analysis. The MOF SR demonstrated a smaller y-intercept, and subsequently a higher kinetic current, which can be related to the kinetic activity of the catalyst.

Both materials showed incremental increases in performance as the applied backpressure was increased, as is typical in fuel cells. While traditional PBI systems are run at 160 °C, these cells were run at 200 °C. Figure 3.13 shows the temperature-dependent performance of the MOF SSR catalyst, with testing done at 160 °C, 180 °C, and 200 °C. As would be anticipated, the performance increased as the temperature was increased, as the increased temperature will benefit the kinetics of the typically sluggish oxygen reduction reaction. Realistically, in single cell tests such as these, 200 °C is likely the highest operating temperature where the catalyst could be evaluated, as the PBI membrane will start to become unstable by approximately 210 °C. Therefore, any local hotspots that develop during heating and conditioning of the cell could potentially begin to degrade the membrane. Were a weak point to develop due to a local hotspot, the cell would likely develop a short circuit. It was partially for this reason that long term durability beyond a few hundred hours would not be achievable under these testing conditions. However, the purpose of this work was to develop materials that showed promise for high initial
performance rather than specifically for longer term durability. Therefore, the cell was operated at a higher temperature to improve the kinetics of the reactions. Additionally, were this to be commercialized, larger MEAs than the 5cm² cells would have to be used, and they would also be operated in a stack format, rather than single cell. Operating under these conditions would likely cause a higher frequency of more severe hotspots to develop, and the cell would subsequently have to be operated at a lower temperature.

One feature of the polarization curves in both air and oxygen for both PGM-free catalysts is the lack of a clear mass transport region. While the air data is displayed on a logarithmic scale, if it were to be displayed on a linear scan, there would be no deviation from the linear region at low potentials. In part, for both oxygen and air, this could be a feature of the testing not going to very low potentials. However, Pt-based systems will start developing a mass transport region (where the potential drops faster than during the kinetic region) due to the cell not being able to accommodate higher electron transfer despite a reduction in the potential. This is generally due to products formed at the ORR active site not vacating fast enough to allow a higher turnover frequency of the active site. These PGM-free materials have lower active site densities than Pt systems (by roughly 3 orders of magnitude), so it is surprising that they did not display similar mass transport regions. One mitigating factor in this work was the use of higher than usual flow rates. Commercial systems generally operate on a stoichiometric flow rate, where the flow rate is adjusted based on the current density being drawn by the system. However, in this work, due to equipment limitations, a constant flow was implemented. This meant that at most potentials, a higher flow rate was used than would typically be used in commercial systems. This excess of oxygen or air is likely the major reason why these samples did not display clear mass transport regions. Despite this, were the potential of the cell brought
down to even lower levels (less than 200mV for example), it would likely introduce a more visible mass transport region as the constant flow rate would be less than what is called for when using a stoichiometric flow rate.
Figure 3.11 - (a) Oxygen polarization curves with Tafel analysis (insert) and (b) air polarization curves for MOF SR catalyst at 200 °C. Catalyst loading is 1.95mg/cm², PBI membrane.
Figure 3.12 - (a) Oxygen polarization curves with Tafel analysis (insert) and (b) air polarization curves for the MOF SSR catalyst at 200 °C. Catalyst loading is 1.5mg/cm², PBI membrane
3.4 Conclusions

A pair of PGM-free materials, both of the MOF variety, were synthesized and explored for potential use in HT-PEMFC. One catalyst was prepared through a solution reaction approach (MOF SR) while the other was prepared through a reactive ball-milling, or solid state reaction (MOF SSR). While these materials were prepared using essentially the same precursors, they have been previously shown to develop inherently different atomic coordination around the iron. The MOF SR material is different from the majority of iron-based PGM-free materials in that is does not contain any evidence of direct Fe-N₅ coordination. Instead it contains evidence of iron carbide and metallic iron coordination. On the other hand, the MOF SSR catalyst does display evidence of primarily Fe-N₄ coordination. Despite the significant differences in the catalyst
structure, both materials showed high immunity to phosphate poisoning, especially when compared to Pt materials (both carbon-supported Pt as well as Pt single crystals). Following the assurance that both materials would be immune to phosphate poisoning in room temperature RRDE experiments, both materials were evaluated through single cell testing in the HT-PEMFC environment. Testing was primarily conducted at 200 °C to increase reaction kinetics and subsequently the single cell performance, despite the potential long-term durability concerns of the MEA. In the case of the MOF SSR catalyst, the performance was also evaluated as a function of the operating temperature, further supporting this claim of increased performance at higher operating temperatures. The MOF SR performed slightly better than the MOF SSR catalyst, and these differences can potentially be attributed to differences in the catalyst loading of the electrodes, as well as a higher kinetic current demonstrated in RRDE. While the raw performance of the PGM-free materials still lags behind the single cell performance of PGM materials (shown later in Figure 4.7), especially at the high loading associated with commercial HT-PEMFC operation, this represents some of the highest PGM-free performance reported to date in the HT-PEMFC environment. Despite this deficiency, this work represents a viable alternative to Pt-based catalysts in a fuel cell environment that has lagged behind low temperature systems in PGM-free catalyst development. Chapter 4 will further study a different PGM-free material developed through a very different methodology, while focusing more heavily on catalyst durability in the HT-PEMFC environment.

3.5 Chapter 3 References


Chapter 4

A High-Performing and Stable PGM-Free Catalyst for Use in High-Temperature Proton Exchange Membrane Fuel Cells

4.1 Introduction

As mentioned in the introduction of Chapter 3, much work has been done to investigate the use of platinum group metal (PGM)-free materials for the oxygen reduction reaction (ORR), both in rotating ring disk electrode (RRDE) and in proton exchange membrane fuel cells (PEMFCs)\(^1-20\). These materials, however, are typically engineered and evaluated for their performance in fuel cells whose operating temperature rarely exceeds 80 °C, as they are heavily dependent on humidity within the cell. The lower operating temperature of these cells can contribute to increased risk of poisoning\(^21-23\). Higher temperature fuel cell systems (HT-PEMFCs), operating in the range of 150-220 °C, are typically more immune to such poisons. However, with this operating temperature in mind, there are material differences between membrane electrode assemblies (MEAs) fabricated for the higher temperature environment. Rather than using the traditional Nafion-based membranes, one common material that is used is a polybenzimidazole (PBI) membrane. This membrane has a low solids content (<10wt%), is produced through a sol-gel method, and is imbibed with phosphoric acid during said process.

There are some inherent benefits and drawbacks to operating fuel cells at higher temperature. For example, as mentioned earlier, they benefit from being far less at risk of poisoning, as well as operating at a higher combined heat and power (CHP) efficiency than lower temperature systems, making them potentially ideal systems for stationary power generation, and in particular, micro-CHP devices. However, two of the major drawbacks to these systems are the lower oxygen permeability and conductivity that they provide. But the largest drawback of these
systems is the fact that the state of the art system requires a platinum total loading (anode plus cathode) of roughly 1.8mgPt/cm², meaning that these systems require roughly an order of magnitude more Pt than a lower temperature system. This alone makes these systems difficult to justify as large-scale commercial products, especially given the volatility of the market price of Pt. Recently, however, PGM-free materials have begun to be investigated for use in these systems (as seen in Chapter 3), as it would result in a massive reduction in cost by eliminating almost 50% of the associated platinum cost.

Recently, one of the methods by which these PGM-free materials have been developed is through the use of a silica-based Sacrificial Support Method (SSM)¹⁶. The premise is that the necessary catalytic precursors are coated onto a silica support which can be tailored to induce particular final catalyst porosity. Following pyrolysis, the silica support is removed by etching with hydrofluoric acid, leaving behind the desired porous catalysis structure. These materials have been proven to show high performance in proton exchange membrane fuel cells¹⁴-¹⁶. This material (hereon referred to as PMF-2010) was first evaluated in the RRDE environment for ORR activity, and shown to demonstrate immunity towards phosphate poisoning.

Subsequently, it was evaluated for performance in a HT-PEMFC fuel cell. Additionally, it was evaluated for durability through a pair of protocols. One protocol called for a 3hr hold at open circuit potential (OCP) (H₂/air, 2.5bar total pressure) in order to facilitate corrosion of the carbon-based support. A second involved a 48hr hold at 650mV (H₂/air, 2.5bar total pressure) in order to simulate prolonged use. Finally, MEAs were scaled from 5cm² to 45cm² to simulate a more commercial like environment, as typically they would be utilized in a stack formation of MEAs of at least 45cm². To date, this represents the highest performing PGM-free material for use in HT-PEMFC environment.
Additionally, in an effort to further understand the resistances within the MEA, as this is a novel use of a PGM-free material, Electrochemical Impedance Spectroscopy (EIS) was used with the aid of an equivalent circuit. This allowed for characterization of a membrane resistance, active layer resistance, charge transfer resistance, and double layer capacitance. As the preparation of these materials into electrodes is a new, custom design, this is key for understanding if performance deficiencies are due to electrode fabrication or inherent catalyst activity.

4.2 Experimental

4.2.1 Catalyst Synthesis & Characterization

The PMF-2010 catalyst evaluated here was synthesized at Pajarito Powder (Albuquerque, NM) using a modified version of the Sacrificial Support Method (SSM) published by Serov et al. at the University of New Mexico\textsuperscript{14-16}. Powder samples were provided to NEU for gas diffusion electrode (GDE) & membrane electrode assembly (MEA) fabrication. As the material is proprietary, characterization was carried out at Pajarito Powder and provided to NEU.

4.2.2 Rotating Ring Disk Electrode (RRDE) Studies

The catalyst was evaluated for ORR activity and phosphate immunity using the RRDE techniques using the same techniques as were described thoroughly in Chapter 3. Catalyst ink was composed of 3.1mg catalyst, 150.2µL of H2O (Millipore), 465µL of IPA, and 6.2µL of Nafion (5wt% dispersion, DuPont, USA). The ink was sonicated for 60 minutes. Spin-coating was done by depositing 4 aliquots of 7.5µL onto a Pine Instrument glass carbon electrode (0.247cm\(^2\) area, gold ring). Electrode was spun at 500rpm until dry between depositions. Final catalyst loading was 600µg/cm\(^2\). All experiments were conducted in 0.1M HClO\(_4\) electrolyte, using a reversible hydrogen electrode (RHE) reference electrode and a Pt mesh counter
electrode. The electrolyte was purged with oxygen for 30 minutes prior to testing. Conditioning was done by scanning the electrode through a potential window (0.05V to 1.05V) at least 10 times, until the results scan-to-scan were consistent. Then ORR activity was evaluated at a series of rotation rates (400, 625, 900, 1600rpm) while the oxygen was provided as a blanket to keep the electrolyte saturated but not disturb the electrolyte surface. Argon-purged CVs were taken as well at 0rpm to provide the baseline to be subtracted from the oxygen scans. For phosphate studies, the electrolyte was doped with the corresponding amounts of either 0.1M H₃PO₄ (250µL and 2.25mL to achieve 1mM and 10mM phosphate) or concentrated H₃PO₄ (85%, GFS Chemicals, 148µL to achieve 100mM phosphate), and the ORR activity was re-evaluated through an identical process. Koutecký-Levich analysis was carried out as well on this catalyst. The in-depth description of that analysis technique can be found in Chapter 3, experimental section 3.2.2. This was done to evaluate whether the PMF-2010 material promoted ORR through either the 2-electron peroxide or 4-electron direct pathway.

4.2.3 Electrode & MEA Fabrication

For all cells, Pt GDEs with a loading of 1.0mgPt/cm² (A1100W, Advent Technologies, GR) were used as anodes. PBI membranes were also provided by Advent Technologies. Cathodes used a commercial gas diffusion layer (GDL) from NuVant Systems Inc. (LT1400, FuelCellStore). Inks were prepared using a modified version of proprietary Advent Technologies methodologies. While other additives, primarily for ink stabilization, were used, the catalyst to PTFE ratio within the catalyst layer was maintained at 3:2. Inks were coated onto the electrode using a draw-down procedure (Elcometer 4340 Automatic Film Applicator). Electrodes were weighed after every few coatings to determine catalyst loading, and catalyst loading was maintained at 2mg/cm². MEAs were prepared using a series of hot-presses. First,
electrodes were hot-pressed to a polymer-coated Kapton subgasket. Following those two presses, the pair of electrodes was hot-pressed to the PBI membrane. MEAs were dried in the oven at 160 °C for 30 minutes following pressing. Reference MEAs were fabricated using the A1100W Pt GDE as cathode.

### 4.2.4 HT-PEMFC Testing

Cell testing was done in Fuel Cell Technologies hardware (both 5cm² and 50cm² housings) on home-built fuel cell test stations. The cells were operated at 200 °C, with a dry gas feed. Cells were heated from room temperature to 100 °C in the presence of nitrogen on both anode and cathode, before being heated to 200 °C under hydrogen and oxygen gas feeds on the anode and cathode, respectively. A break-in protocol was carried out, consisting of slowly stepping from near OCP to 0.3V (50mV increments, 2-3 minutes per step), until the performance had stabilized. Break-in and polarization curves were taken with custom LabView programs running in conjunction with a HP 6050A DC Load Supply. Polarization curves were taken galvanostatically with both oxygen and air cathode gas feeds (with a 30 minute purging time used when switching between the two) as a function of backpressure, from 0.5bar gauge pressure to 2.5bar gauge pressure (0.5bar increments). Tafel analysis of oxygen data to compensate for iR losses was done using the high frequency resistance (HFR) from Electrochemical Impedance Spectroscopy (EIS, described later). Two durability protocols were applied to the system. In order to study carbon corrosion of the material, the cell was held at OCP for 3hrs (H₂/air flow, 2.5bar total pressure). Secondly, the cell was held at 650mV for 48hrs (post break-in, H₂/air flow, 2.5bar total pressure). For comparison of performance before and after durability protocols, performance under air flow at 2.5bar total pressure was used.
4.2.5 Electrochemical Impedance Spectroscopy (EIS) & Equivalent Circuit Analysis

EIS testing was done using a Metrohm Autolab (PGSTAT302N) paired with a 20A current booster (PGSTAT30) in conjunction with associated Nova software. Spectra were comprised of 50 data points at different frequencies taken over a range from 20kHz to 100mHz in logarithmic increments, with an amplitude of 10mV for all tests. The high frequency resistance was the first point at which the spectra crossed over the x-axis (where the imaginary portion of the resistance is 0). Spectra were taken potentiostatically at 6 potentials from 400mV up to just below OCP (roughly 100mV increments). Equivalent circuit analysis was done using the Scribner ZView software. The equivalent circuit used was identical to those previously used in literature for HT-PEMFC analysis\textsuperscript{24}. A DX6 distributed element was used in series with an inductance loop (to account for natural inductance of the equipment wiring) and another resistor. Figure 4.1 below is a schematic of the distributed element equivalent circuit model that was used. As shown in the figure, four resistances are calculated through the fitting. However, $R_t$ is a shunt resistor that goes to 0 as the system is repeated. The model used here involved 50 repeating units, and therefore $R_t$ was assumed to be 0. The other three resistances calculated were $R_m$ (membrane resistance), $R_{el}$ (active layer resistance), and $R_{ct}$ (charge transfer resistance). Additionally, C, the double layer capacitance was determined through the fit.
Figure 4.1 - Equivalent circuit used in ZView as well as two visualizations of the DX6 distributed element. For each pair of vertically stacked resistors, the top represents the charge transfer resistance while the bottom one represents electrode (active layer) resistance.

4.3 Results & Discussion

4.3.1 Catalyst Characterization

Characterization was done at Pajarito Powder as part of synthesis work in an effort to be able to correlate characterization to fuel cell performance. While this material was originally developed for use in lower temperature systems, it was adapted to the higher temperature environment. Therefore it is vital to be able to understand transport characteristics that are different at the higher temperature. Pore size distribution and Raman spectroscopy were carried out. Figure 4.2 displays the pore size distribution of this material.
This material differs from the MOF-based materials evaluated in Chapter 3 in terms of pore structure and surface area. Both the MOF SR and MOF SSR catalysts evaluated in Chapter 3 demonstrated half pore widths of roughly 20Å, which means that the most abundant pore size in the PMF-2010 material is several times larger than that of either the MOF SR or MOF SSR. Additionally, the surface area of both MOF materials was determined to be roughly 1500m$^2$/g, compared to just 560m$^2$/g for the PMF-2010 material. Further analysis must be done with modifications of the PMF-2010 material in order to correlate pore size distribution and surface area to performance of the various materials. Figure 4.3 below shows the results of Raman spectroscopy. The two major peaks at ~1300cm$^{-1}$ and 1600cm$^{-1}$ correlate to the D and G band of the carbon, indicative of amorphous and graphitic carbon, respectively. In the case of this catalyst, there is a roughly equivalent mix of both amorphous and graphitic carbon present in the
sample. The additional, broad peak at ~2700cm⁻¹, is the 2G band. In single layer graphene, it will be very intense, and it will broaden into multiple peaks and become less pronounced in multi-layer graphene. Therefore this broad peak can likely be attributed to higher order graphite within the catalyst support.

4.3.2 Rotating Ring Disk Electrode (RRDE) Studies

The PMF-2010 catalyst was evaluated for ORR activity and phosphate poisoning immunity through the RRDE technique. Prior to evaluating the phosphate immunity characteristics of the material, the ORR performance was evaluated at a series of rotation rates, and the results of those can been in Figure 4.4 below.
The PMF-2010 catalyst demonstrates higher limiting current and similar onset potential and half-wave potential to the two PGM-free MOF materials evaluated in Chapter 3. Given that there are equal quantities of catalyst in each experimental setup, this would likely indicate a higher active site density in the catalyst. But given that PGM-free materials tend to have very low active densities when compared to Pt, this elevated active site density could be key towards its eventual use in the HT-PEMFC environment. A Koutecký-Levich analysis was carried out similar to those in Chapter 3, and the results at a series of potentials can be seen below in Figure 4.5 for the activity in the absence of phosphate ions.
From these results, substantial information can be gained from the slope and intercept. In the case of Koutecký-Levich analysis, the intercept will correspond to the kinetic current portion of the series combination shown in equation 3.2. In this case, the y-intercept is very close to 0, indicating that the kinetic current of the reaction is extremely high. The kinetic current can be related to the kinetics of the electrochemical reaction, and subsequently the catalyst activity when compared directly to other catalyst kinetic currents. This catalyst demonstrated a higher kinetic current than either of the two MOF materials evaluated in Chapter 3. When the inverse of the slope is calculated, corresponding to $B_L$, equation 3.3 can be used to calculate the number of electrons in the electrochemical reaction. In this case, $n$ is calculated to be 3.54, indicating that 3 out of every 4 diatomic oxygen molecules will proceed through the 4-electron direct
pathway, with the other 1 of 4 proceeding through the 2-electron peroxide pathway. This value is in line with the MOF SSR catalyst, although lower than the MOF SR catalyst.

Prior to the material being evaluated as a Pt alternative in the HT-PEMFC environment, it was imperative to demonstrate that the material is immune to phosphate poisoning at room temperature. Figure 4.6 below shows the ORR activity at 1600rpm of the PMF-2010 catalyst at a series of phosphate concentrations.

Despite the slight loss in limiting current, this material still displays a very high limiting current in the presence of 100mM H₃PO₄. More importantly, there was only a ~5mV shift at the half-wave potential (745mV to 740mV). This material demonstrates even higher immunity to
phosphate poisoning than either of the two MOF materials evaluated in Chapter 3. This was more than sufficient to demonstrate that this material shows potential promise in the HT-PEMFC environment.

### 4.3.3 HT-PEMFC Testing & Durability

Following break-in, performance of the Pt standard cell was evaluated as a function of applied backpressure, and those results are shown in Figure 4.7. Additionally, the PMF-2010 material was evaluated in both oxygen and air as a series of applied backpressures, and the results of that are shown in Figure 4.8. For both materials, there were incremental increases in the performance as the backpressure was increased. This is to be expected, and is typical of fuel cell testing, regardless of operating temperature, as both the kinetics and flux of oxygen are increased at higher pressure. Clearly, while these materials have been demonstrated in low temperature cells to show comparable performance to Pt, there is still a gap between the PGM-free performance and the Pt reference data. For examples, at 200mA/cm² in air at 2.5bar total pressure, the gap between the Pt and PMF-2010 performance was about 100mV. Despite this gap, this performance represents the highest performing PGM-free material in the HT-PEMFC environment to date.
Figure 4.7 - a) Oxygen performance and associated Tafel Plot (insert) and b) Air performance as a function of applied backpressure for a Pt reference cell.
Figure 4.8 - a) Oxygen performance and associated Tafel Plot (insert) and b) Air performance as a function of applied backpressure for the PMF-2010 PGM-free catalyst.
In order to determine whether this material could be tailored to the higher temperature environment in an effort to gain comparable performance to Pt, it has to be diagnosed to determined potential issues causing the lower performance. One method of doing so is to calculate the “oxygen gain”, the difference between the oxygen and air data at a given current density and backpressure. For example, at 500mA/cm² (a high enough current density to put the cell in the linear kinetic region of the polarization curve) and 2.5bar total pressure, the difference between oxygen and air for both the Pt and PGM-free samples was roughly 100mV. If for example, the PGM-free catalyst demonstrated a significantly higher gap, it would indicate that there were higher performance losses when switching from oxygen to air. The typical aspect that would cause such performance losses would be transport-based issues. It would be unsurprising for one of the PGM-free materials to demonstrate worse transport through the catalyst layer than the Pt-based system, given that the catalyst layers are both thicker as well as not properly optimized compared to commercial Pt electrodes.

During earlier stages of this work, a re-design of the catalyst structure was carried out in an effort to optimize performance. This included several steps including the optimization of both the catalyst loading as well as the PTFE content within the catalyst layer, optimization of which commercial cathode GDL and anode GDE to use, the decision to not sinter coated electrodes, and running the cell at a higher temperature. Through all of this work to optimize the activity and morphology of the catalyst layer structure, there were significant performance increases. Despite all of that, the catalyst layer is still significantly thicker than the Pt-based system. In addition to the thicker layer, the commercial Pt materials used to build the Pt GDEs are sieved to very specific metrics so the natural packing of the layer that occurs during fabrication will maximize the transport and utilization of the catalyst. No such studies have been carried out yet
with the PGM-free materials to study packing of electrodes and optimal particle size distributions.

Durability testing was carried out using a pair of protocols. One such protocol was a potentiostatic hold at 650mV (H₂/air, 2.5bar total pressure) was done for 48hrs following the break-in procedure. This was to mimic standard operation of these systems. Typically, a HT-PEMFC system would be heated up, run for a prolonged period of time at constant potential in conjunction with a power storage device, then cooled. This process would be repeated as power is needed. The resulting performance polarization curves can be seen in Figure 4.4. In this case, the performance following the durability protocol was even slightly better than before. There are two key factors to note given that change. First, these performance curves lie within the experimental error given the potential step size of the load supply that was used. Also, Pt MEAs have a very well-defined break-in protocol that was developed by Advent Technologies. Such information does not presently exist for the PGM-free materials. Subsequently, on a cell by cell basis, break-in is carried out manually until it appears that the performance has stabilized, at which point the beginning of life polarization data is be collected. It is possible in this case that the durability protocol may have been started prior to the performance truly meeting its maximum performance, which would give the appearance of a performance increase. However, this performance change was minute, and therefore it can be assumed that the cell was very close to being at maximum performance.
The second durability protocol that was used was designed to study the potential carbon corrosion of the catalyst at high voltages. In low temperature PEM systems, this protocol tends to differ, as a square wave potential is typically applied to the system, and cycling is done between 0.6V and 1.0V. This is done primarily because in the commercial applications for which low temperature systems are designed (automotive being one of the largest), this is a typical operating cycle that is used. The cell is heated and cooled often, and is typically used in drive cycles, rather than being run at constant potential. The fact that the cell goes through potential jumps can also accelerate degradation of carbon materials. In the case of this work, carbon corrosion was studied by holding at the open circuit potential (OCP). This is because, as mentioned in the previous paragraph, the typical operating conditions of these systems do not
necessitate potential jumps, but rather holds at a constant potential. Therefore, there would be significant periods of time where it would be easiest to let the cell sit at OCP. However, in a Pt-based system, this is not possible. The resulting effect of holding a Pt MEA at OCP is shown in Figure 4.5a, while the results of holding the PGM-free material at OCP are shown in Figure 4.5b. Table 4.1 shows the performance losses as a function of potential for both the Pt and PMF-2010 materials.
Figure 4.10 - a) Pt and b) PMF-2010 results before and after 3hr hold at OCP. Polarization curves collected in air at 2.5bar total pressure.
Table 4.1. Current Density Percent Loss for Pt and PMF-2010 Catalysts

<table>
<thead>
<tr>
<th>Potential (mV)</th>
<th>Loss of Current Density (%)</th>
<th>Loss of Current Density (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pt</td>
<td>PMF-2010</td>
</tr>
<tr>
<td>900</td>
<td>0</td>
<td>NA*</td>
</tr>
<tr>
<td>800</td>
<td>8.9</td>
<td>0</td>
</tr>
<tr>
<td>750</td>
<td>15.7</td>
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<tr>
<td>700</td>
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<td>0</td>
</tr>
<tr>
<td>600</td>
<td>22.5</td>
<td>0</td>
</tr>
</tbody>
</table>

*Current was too low for comparison measurements

When the resistance to carbon corrosion for both the Pt and PGM-free materials were evaluated, it clearly demonstrated a well-known issue with Pt-based materials, where they are not stable once the carbon support begins to oxidize and corrode. This is evident in Figure 4.5a, where there was nearly a 20% loss in current density at 650mV as a result of the 3hr hold at OCP. Conversely, the PMF-2010 material showed no change in performance at all following the 3hr OCP test. This indicates one of two things. Either the 3hrs at OCP was not sufficient to begin oxidizing the carbon support, or this material can maintain its activity and withstand corrosion of the carbon support. This is unlikely as the catalyst active sites so heavily rely upon the structural integrity of that support. While future work will certainly include longer holds at OCP to determine at what point there begins to be losses in performance, a test of this scale was certainly sufficient to demonstrate increased stability when compared to Pt-based systems.

In addition to evaluating the durability of these materials, it was imperative to demonstrate that the electrodes could be scaled to larger sizes, which are much more representative of commercial systems. These commercial systems traditionally run on stacks of MEAs, with each MEA measuring more than 100cm². For the purpose of this work (and given test station capabilities), MEAs were fabricated at a size of 45cm². This represents a good intermediate in between the smaller 5cm² electrodes and a more commercial setup. The results of that testing, as well as comparison curves for 5cm² data are shown below in Figure 4.6.
performance curves (black lines, solid & dashed) demonstrate that there were no performance changes between the two electrode sizes. Typically, performance will drop as a function of electrode size. In fact, the oxygen performance increased slightly, although these two performance curves are roughly within experimental and measurement error of the equipment. Slight differences can also be accounted for by slight variations in catalyst loading differences of the MEAs (the 5cm$^2$ was 1.92mg/cm$^2$ and the 45cm$^2$ cell was 2.01mg/cm$^2$). Regardless, this is a key step if systems like these are going to be commercialized while using PGM-free catalyst materials.

**Figure 4.11** - Performance comparison of 5cm$^2$ and 45cm$^2$ MEAs. ~2mg/cm$^2$ PMF-2010 catalyst loading for each cell.
4.3.4 Electrochemical Impedance Spectroscopy (EIS)

Electrochemical Impedance Spectroscopy was used as a technique to evaluate the resistances within the MEA. Using the equivalent circuit shown in Figure 4.1, the Nyquist Plots (shown in Figure 4.7) were fitted, allowing for the extraction of additional information regarding the MEA. The Nyquist Plot deconvolutes the resistance into a complex function, with the real resistance on the x-axis, and the imaginary portion of the resistance on the y-axis. Theoretically, the spectra will appear as a pair of sequential half-circles, starting and finishing at y=0, therefore including 3 crossings of the x-axis. The x-value at the first crossing represents the high frequency resistance, and relates to ohmic losses within the cell. This is the value used for calculating the iR-free potential values associated with a Tafel analysis. The gap between the first and second crossing will represent the activation losses of the anode (in this case assumed to be 0 as a Pt electrode catalyzing the hydrogen oxidation reaction (HOR) is assumed to have negligible losses (which in turn allows it to be used as both a counter and reference electrode in a three-electrode system). The difference in resistance between the second and third crossings of the x-axis represents the activation losses of the cathode. Data at even lower frequencies beyond that can be used to extract information regarding mass transport issues. However, in this case, no information regarding the mass transport effects were extrapolated for two reasons: first, the lowest potential used for the EIS testing was 400mV. When testing in oxygen, and given the flow rates that were used (400sccm H₂, 1000sccm O₂), it would not be expected that there would be any mass transport effects at that high a potential. Tests would have to be conducted at much lower potentials. Secondly, the lowest frequency where data was collected was at 100mHz. Traditionally, testing has to be done at lower frequencies in order to get to the mass transport
region in the spectra. The sinusoidal potential wave has the occasional effect of damaging the MEA, and therefore lower frequency values were not used.

Once the EIS spectra were fitted to the equivalent circuit from Figure 4.1, it was possible to elucidate the membrane resistance, catalyst layer resistance, charge transfer resistance, and double layer capacitance. While the membrane and catalyst layer resistance are self-describing, the charge transfer resistance refers to the resistance against electron transfer between mediums. In this case that refers to the resistance of electron transfer from the electrode to the phosphoric acid electrolyte. Similarly, the double layer capacitance refers to the energy storage capabilities at the interface between the electrode and the phosphoric acid electrolyte. The results of those fits, as a function of potential, are shown in Figure 4.8. As would be expected, there is a general
trend of the resistance increasing as the potential gets higher, and subsequently closer to the open circuit potential. For these cells, a value just over 900mV was typical as an open circuit potential, and therefore no measurements were taken above 875mV to avoid unnecessary strain on the cell at OCP. While the catalyst demonstrated good stability at open circuit, it was desired to avoid influence in EIS analysis from minor changes due to this exposure. Future work would involve studying the changes in the various resistances following the two durability protocols to get a more complete picture of the potential degradation mechanisms, if any losses are in fact observed. The largest potential-dependent resistance belonged to the charge transfer resistance, which increased by roughly 2 orders of magnitude as the potential was shifted from 400mV to 875mV. In general, the trends that were apparent in this testing were well in line with the published literature\textsuperscript{24}, validating this as a potential mechanism for studying changes within the MEA.
Figure 4.13 - Calculated values of the a) membrane resistance, b) catalyst layer resistance, c) charge transfer resistance, and d) double layer capacitance, all acquired through fitting of the EIS spectra to the model equivalent circuit.

4.4 Conclusions

A PGM-free material (PMF-2010) synthesized through a Sacrificial Support Method was first shown to demonstrate good ORR activity and phosphate immunity in RRDE. Then it was evaluated for both performance and durability in the HT-PEMFC environment. The single cell beginning of life performance represents the best catalyst to date in the HT-PEMFC environment, and represents a potential solution for the high cost of these systems due to the Pt catalyst. When evaluated for durability under a pair of protocols (chronopotentiometric hold and open circuit testing), the cell showed virtually no change in performance due to either, which was highly unexpected, given that PGM-free materials have shown struggles with chronopotentiometric durability in the lower temperature environment. One of the major factors
often that contributes to the poor durability at lower temperatures (80 °C typically) is flooding of the catalyst layer with water produced at the cathode. However, given the operating temperature of the PMF-2010 material (200 °C), and the lack of humidification applied to the gas stream (typically 100% RH for low temperature systems), this issue appears mitigated. The stability demonstrated under the open circuit potential hold was the most surprising, as materials that are carbon-based typically do not fare well when exposed to similar tests. In fact, as was demonstrated in this work, Pt materials will see dramatic losses in performance over similar testing, as there was nearly a 20% loss in current density at 650mV for the Pt standard cell, compared to no change for the PGM-free material. Finally, electrochemical impedance spectroscopy was used as a technique to analyze the resistances within the cell. In this case, potentiostatic EIS spectra were fitted to an equivalent circuit, which allowed for the determination of the membrane resistance, catalyst layer resistance, charge transfer resistance, and double layer capacitance. When analyzed as a function of potential, it was clear that the resistances increased as the potential was increased, with the charge transfer resistance being most heavily dependent on the applied potential. This work represents the most promising PGM-free material to date as a potential replacement for Pt on the cathode of HT-PEMFC environment. However, there is still a performance gap between the two materials, indicating that additional catalyst development or electrode development is still necessary. Additionally, the possibility of a mixed Pt and PGM-free cathode in order to maintain a higher performance while introducing a lower total Pt loading will be evaluated as an alternative in Chapter 5.

4.5 Chapter 4 References


Chapter 5

A Novel Mixed Platinum and PGM-Free Cathode for High-Temperature Proton Exchange Membrane Fuel Cells

5.1 Introduction

As has been discussed in Chapters 3 and 4, there is a great need for potential Pt alternatives for proton exchange membrane fuel cells, both at low and high temperature. It has been additionally shown that proton exchange membrane fuel cells could become commercially viable through a reduction in the Pt loading or the use of a PGM-free catalyst\textsuperscript{1-33}. While the work in Chapters 3 and 4 provides promising evidence that with continued development of catalysts and electrode structure, PGM-free catalysts could represent viable Pt alternatives, they do not yet perform in an HT-PEM single cell to the level of Pt-based catalysts. The work shown here represents a combination of both low Pt loading and PGM-free materials, in a so-called “hybrid” system. Here, a PGM-free material will be combined with low loading Pt catalysts to create a system demonstrating nearly the same performance as a high loading Pt system. In this work, a wider range of catalysts is used than in previous chapters. All six materials are synthesized through modified versions of the two classes of catalysts evaluated previously: Sacrificial Support Method (SSM) and Metal-Organic-Framework (MOF). Further details regarding the nature and synthetic approaches towards these materials will be addressed later. The gas diffusion electrodes (GDEs) and membrane electrode assemblies (MEAs) in this work are fabricated through very different mechanisms than in prior chapters, through a method more similar to the spray technique demonstrated in Chapter 2. Additionally, these materials will use a different membrane material (Advent TPS®) than in Chapters 3 and 4 (phosphoric acid-imbibed polybenzimidazole, or PBI). The TPS® membrane is fabricated through a different
(and proprietary) procedure than the sol-gel method through which PBI membranes are traditionally manufactured. A general schematic of the membrane can be seen in Figure 5.1 below. The TPS® membrane combines an aromatic polyether (green), which provides high thermal and chemical stability, with a pyridine polar group (blue), which is both a proton acceptor and hydrogen bonding site.

![Figure 5.1 - Schematic of Advent Technologies TPS® Membrane. Courtesy of Advent Technologies](image)

Additionally, it is manufactured in a state free of phosphoric acid, while the PBI relies upon phosphoric acid during its manufacturing. This yields a PBI membrane inherently imbibed with phosphoric acid, while the TPS® membrane must be soaked in phosphoric acid prior to use. This leads to some differences in the MEA preparation as well. PBI MEAs rely upon phosphoric acid from the membrane being squeezed into the catalyst layer during preparation, providing the proton conductivity to the catalyst layer. Meanwhile with TPS® MEAs, the phosphoric acid must be independently applied to the catalyst layer to gain such proton conductivity.
5.2 Experimental

5.2.1 Catalyst Synthesis & Characterization

5.2.1.1 NPC-2000 (lots #1027-1, #0609, #0729)

Three of the materials that will be studied in this work are of very similar variety, and will all be referred to as NPC-2000, with the differentiation being the lot numbers. The lot#1027-1 is the standard material, currently synthesized in large commercial batches, while the lot#0609 and lot#0729 were small batch variants on that material. All three NPC-2000 samples were synthesized at Pajarito Powder using modified versions of the Sacrificial Support Method (SSM) developed at the University of New Mexico\textsuperscript{26}. Catalyst samples were then provided to Northeastern University for electrode and MEA preparation. Characterization was carried out at Pajarito Powder on the NPC-2000 lot#1027-1 sample, as it was the baseline material off of which the other two (#0609, #0729) were based. X-ray diffraction (XRD) and Raman spectroscopy were used to analyze the base material. Figures 5.2 and 5.3 below display the results of the XRD and Raman spectroscopy, respectively.
Figure 5.2 - X-Ray Diffraction pattern of NPC-2000 lot #1027-1 material

Figure 5.3 - Raman Spectroscopy pattern of NPC-2000 lot #1027-1 material
The XRD pattern shown in Figure 5.2 is indicative of graphitic carbon sources, with the peaks at roughly 20 25, 43, and 80 being representative of graphitic carbon samples. Peaks indicative of iron carbide and iron oxide are not present in the sample. Both iron oxide and iron carbide would have clear sharp peaks between 35 and 40 in the spectra, yet neither appears in this case. Similarly to the PMF material seen in Chapter 4, this material shows a combination of amorphous and graphitic carbon, as is demonstrated in the Raman spectra via the peaks at 1300cm\(^{-1}\) (D-band) and 1600cm\(^{-1}\) (G-band), respectively. In terms of concentration, the relative intensities of the D and G band peaks demonstrate a roughly equal concentration of the two types of carbon. Again, this sample had a broad peak at roughly 2700cm\(^{-1}\) (2G-band), indicative of higher order graphite, meaning multiple layers of graphite within the catalyst.

The two other NPC-2000 materials (lot#0609 & lot#0729) are made through the same chemistry as the lot#1027-1. However, they display different pore size distributions due to differences in the initial silica support materials. The pore size distribution of that material is heavily based on pores of 10nm and 40nm. However, the lot#0609 is based off of a higher content of small 10nm pores and the lot#0729 material contains a high concentration of large 50nm pores. Therefore, while the chemistry of the materials is the same, these materials should demonstrate different kinetic and transport characteristics based on the pore structures within the catalyst layer. However, given that this work will focus on cathodes combining these materials with low loadings of Pt, it is anticipated that the characteristics of the individual NPC-2000 materials could become less evident in the fuel cell performance. Subsequently, correlation of catalyst characteristics to performance may become less useful.
5.2.1.2 MSG & PGD

Catalyst denoted as MSG-15SG was synthesized by the University of New Mexico (UNM) through procedure recently published\textsuperscript{34}, and then provided to Northeastern University for electrode and MEA preparation. In short, three nitrogen-rich organic precursors were mixed with equal mass ratio (2-Methylimidazole, Streptomycin, and Glucoryl) in water. This mixture was deposited onto an equal weight mixture of two silica supports: OX-50 and an in-house prepared monodispersed silica (50m\textsuperscript{2}/g and 5m\textsuperscript{2}/g surface areas, respectively). Following stirring to ensure uniformity, Fe(NO\textsubscript{3})\textsubscript{3}\cdot9H\textsubscript{2}O was added in a ratio of 1:8 with the previously-mentioned organics. The water was allowed to evaporate at 35 °C and the remaining powder was ground with a mortar and pestle. The first of two heat-treatments (nitrogen environment, 945 °C, 60min) was followed by a 25hr leeching process using 25wt% hydrofluoric acid (HF) in order to remove the silica support. The catalyst was washed using DI water and then dried at 85 °C for roughly 12hrs. The second heat-treatment (ammonia environment, 975 °C, 45min) was then carried out to conclude the synthesis. The PGD-1056 catalyst was synthesized through a similar approach utilizing instead only two nitrogen-rich organic precursors and a carbon source (Phenanthroline, Glucose, and Dimetridazole). Again, this synthesis was carried out by UNM and catalyst powders were provided to Northeastern University.

5.2.1.3 MOF Lot\#104

The MOF Lot\#104 catalyst was synthesized at Pajarito Powder, LLC using modified versions of a previously published procedure developed at Northeastern University. In the original synthetic process, zinc oxide was heat-treat at 400 °C, then ball-milled with 2-methylimidazole and ammonia sulfate in the presence of a small quantity of methanol for 1hr, resulting in the formation of the ZIF-8 MOF structure. 1,10-phenanthroline and iron (II) acetate
were then added, and a second ball-milling step was done for another 2hrs. This step will facilitate the coating of the ZIF-8 structure with the complexed iron and phenanthroline. Two pyrolysis steps were carried out: argon environment for 1hr at 1050 °C followed by ammonia environment for 18min at 1050 °C. As a final step, an acid leeching using 0.1M hydrochloric acid (HCl) for at least 12 hours was done to remove any metallic iron.

5.2.2 Electrode & MEA Fabrication

Gas diffusion electrodes (GDEs) and membrane electrode assemblies (MEAs) for this work were prepared through very different methodologies than previously in Chapters 3 and 4. Additionally, two different hybrid setups were designed: one where the cathode hybrid catalyst layer is a homogenous mix of Pt and PGM-free catalyst, and another where the Pt layer is applied as a top coat to the PGM-free layer. Cathode inks for the homogenous method constituted 45mg PGM-free catalyst, 22.5mg Pt/C (46.6 wt% TKK), 112.5mg PTFE (60%, provided by Advent Technologies), 8.5mL isopropyl alcohol (IPA), and 1.5mL H₂O (Millipore). Anode catalyst ink was composed of 27mg Pt/C, 45mg PTFE, 8.5mL IPA, and 1.5mL H₂O. This was also suitable as the ink recipe for the Pt top coat. All inks were sonicated for 1 hour. E-tek LT1400 gas diffusion layers (GDLs) were used as substrates for both anode and cathode. GDEs were prepared by spraying (IWATA HP-BCS), with target cathode loadings of 2.5mg/cm² of PGM-free material plus the Pt top coat, although there was some slight variation electrode to electrode. In the case of a pure PGM-free cathode, the quantity of Pt/C was substituted with additional PGM-free catalyst such that the ratio of total catalyst to PTFE ratio was maintained at 1:1. Catalyst loading was determined by intermittent weighing of electrodes. Following preparation of both anode and cathode, the electrodes were heat-treated in a muffle furnace (air atmosphere) for 20 minutes at 315 °C (furnace was allowed to preheat before electrodes were
inserted). Electrodes were then sprayed with H₃PO₄ (diluted in IPA) until a 1:1 ratio with catalyst was obtained. Electrodes were trimmed to 4.62cm² (2.1cm by 2.2cm). TPS® membrane (Advent Technologies) was placed in 85% H₃PO₄ (GFS Chemicals) for at least 12 hours at 120 °C. Membrane was weighed to ensure at least 200-250% weight gain from intake of acid. Membranes would expand significantly during this process, so membranes were trimmed to 16cm² (4cm by 4cm) following acid treatment. MEAs were prepared through a multi-step hot-press procedure with temperatures increasing from 60-150 °C and applied load ranging from 5,000-10,000lbs over a roughly 2 hour procedure. The exact steps are confidential and were provided by Advent Technologies. Hot-presses were done in the presence of PTFE gaskets to prevent over-compression (15mil, McMaster-Carr). MEAs were allowed to cool (using fans to increase cooling rate) under mild pressure before use.

5.2.3 HT-PEMFC Testing

All fuel cell testing was done in standard 5cm² hardware (Fuel Cell Technologies) with serpentine flow fields on home-built test stations. HP 6050A DC load supplies (with homemade LabView programs) were used for all polarization curves, while a Metrohm Autolab (PGSTAT302N) and 20A current booster (PGSTAT30) (with Nova software) were used for electrochemical impedance spectroscopy (EIS). High frequency resistance (HFR) from EIS spectra was used in iR corrections for Tafel analysis.

Cells were heated from room temperature to 100 °C with dry nitrogen gas feeds on both anode and cathode. At 100 °C, anode and cathode gas feeds were switched to hydrogen and oxygen, respectively, and the cell was heated to the final operating temperature of 180 °C. Flow rates were set at 300sccm hydrogen & 300sccm oxygen or air. Break-in and conditioning of the cell was done by holding the cell at 200mA/cm² until cell performance had stabilized (typically
Pt cells typically will require at least 12 hours to become fully conditioned. In these cases, due to time and equipment limitations, 2-4hrs (MEA-dependent) was sufficient to achieve very close to maximum performance. It is also possible that MEAs with significant PGM-free contributions will not require the same time for conditioning as Pt MEAs. Polarization curves were taken in both oxygen and air at a series of applied backpressures. Following completion of all polarization curves, EIS spectra were taken at all previously-tested backpressures. Spectra were taken at a series of potentials varying from 900mV to 400mV using 50 frequencies from 20kHz to 100mHz on a logarithmic scale. The amplitude of the sinusoidal wave for all spectra was set at 10mV.

5.3 Results & Discussion

5.3.1 Hybrid Methodologies

Prior to determining whether or not these hybrid systems could be potential replacements for Platinum electrodes, it was imperative to optimize the hybrid system for performance. This was done by evaluating a pair of hybrid electrode structures. The first involved a mixed catalyst layer, where one ink combining both Pt and PGM-free catalysts would form a homogenous catalyst layer. The second technique involved a PGM-free base, with a top coat of Pt/C carbon catalyst. Schematics for these two setups are shown below in Figure 5.4. This comparison was carried out using the NPC-2000 lot#1027-1 catalyst and the results of those tests are visible in Figure 5.5. Tafel analysis was done by correcting the voltage for iR-losses by using the high frequency resistance (HRF) from the electrochemical impedance spectroscopy (EIS).
Figure 5.4 - Schematics of top coat (left) and homogenous (right) hybrid MEA methodologies
Figure 5.5 - a) Oxygen with Tafel and b) air performance comparison of NPC-2000 lot#1027-1 hybrids prepared through both top coat and homogenous methodologies.

When using either a pure oxygen or air cathode feed, it was clear that the methodology using a Pt top coat on the PGM-free catalyst layer outperformed the methodology using a
homogenous catalyst layer in the voltage range at which these systems would be operated (0.5 to 0.7V). However, the improvement is less pronounced when using an air cathode feed. This indicates that the kinetic benefits seen when testing in oxygen are somewhat mitigated in air. This is typically a result of poorer transport characteristics within the catalyst layer. In the case of oxygen flow, because of the high concentration compared to air, transport characteristics are less important than in a diluted air setup. Were these systems to be optimized to run under an air environment (as most commercial systems are), this would indicate that both the homogenous catalyst layer setup as well as the separate Pt and PGM-free catalyst layers would be possible. A second reason why the air data for the homogenous catalyst layer may have underperformed compared to the top coat is an issue of active site density. Pt catalysts have active site densities roughly 3 orders of magnitude higher than these PGM-free materials. And in thick catalyst layers such as these, many active sites imbedded within the electrode become inaccessible, which is why increasing the catalyst loading of PGM-free materials beyond a certain threshold does not further improve the performance. Therefore, in a homogenous layer, a high quantity of the inaccessible active sites will be Pt, and the catalyst layer surface will have a lower overall active site density compared to the top coat methodology. This decrease in surface active site density would have a large influence on the air data since the utilization of oxygen in these systems is already quite low.

Once it was determined the methodology with which to proceed, it was necessary to evaluate numerous PGM-free materials as potential catalysts for this system. In this case, six different catalysts were evaluated. The NPC-2000 lot#1027-1 was used, as were two other NPC-2000 materials (#0609 & #0729), as were two other catalysts from the University of New Mexico (MSG-15SG & PGD-1056), and one MOF material scaled up at Pajarito Powder (MOF
SSR lot#104). The results of this evaluation are shown below in Figure 5.6, and the performance is summarized in Table 5.1. As was the case earlier, Tafel analysis was done using the high frequency resistance (HFR) from electrochemical impedance spectroscopy (EIS).
Figure 5.6 - a) Oxygen with tafel analysis and b) air performance evaluation of 6 PGM-free materials all using Pt top coat hybrid methodology
Table 5.1. Performance Summary of PGM-Free Hybrid MEAs

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Synthetic Method</th>
<th>PGM-Free Loading (mg/cm²)</th>
<th>Pt Loading (mgPt/cm²)</th>
<th>Current Density @ 700mV (O₂, 1.5bar)</th>
<th>Current Density @ 600mV (Air, 2.5bar)</th>
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<td>2.6</td>
<td>0.58</td>
<td>315</td>
<td>401</td>
</tr>
</tbody>
</table>

From the data shown above, many of the PGM-free materials perform in a similar range when tested in this hybrid system. However, there are a few things to note, including that in both oxygen and air testing, the MOF lot#104 was the highest performing catalyst, although that is less pronounced in air testing than in oxygen, where it does significantly outperform the other catalysts. Also, it should be noted that there were some slightly differences cell to cell with regards to the catalyst loading, but there was no clear trend of performance based solely on these minor differences. Therefore, these slight variations in catalyst loading can be discounted.

Additionally, it should be noted that the MSG-15SG catalyst demonstrated significantly higher influences of mass transport effects, as the voltage began to drop significantly at higher current densities when tested in oxygen. This was apparent as well in the air data. This is likely due to one of two things, either an artifact of electrode fabrication or an inherent catalyst property. In terms of electrode fabrication, this could include things such as higher loading, which while adding active sites, can also introduce many inaccessible active sites, at which point
mass transport effects can become more pronounced. Additionally, based on natural hydrophobicity of the catalyst, different concentrations of PTFE within the catalyst layer could be required. If insufficient PTFE were added into the catalyst layer, then there are two issues that could develop over time when testing. First is flooding, where water that is generated at the cathode is not able to leave the catalyst layer fast enough and the number of accessible active sites is essentially reduced over time. However, given the operating temperature of the HT-PEMFCs, this is less of an issue than with lower temperature fuel cells (where the operating temperature is less than the boiling point of water). The second issue that can arise from less than optimal PTFE is too much acid within the catalyst layer. These systems rely on a proper three-phase interface between the catalyst, phosphoric acid, and the oxygen. Over or undersaturation of acid in the catalyst layer will inhibit a proper three-phase interface from forming. And the quantity of acid that seeps into the catalyst layer is heavily dependent on hydrophobicity within the catalyst layer. These represent the potential electrode reasons for higher mass transport losses. As mentioned, the issue could be inherent to the catalyst. Artifacts of the catalyst that can affect transport characteristics include porosity as well as pore size and particle size distribution. Further catalyst morphology characterization is necessary to be able to diagnose whether in this case the transport effects are due to catalyst or electrode properties.

5.3.2 Hybrid vs Platinum Systems

As mentioned earlier, the MOF lot#104 catalyst was the highest performing of all the samples that were tested as part of this screening process. However, unless it can be demonstrated that these hybrid electrodes represent a method of replacing the traditional Platinum loading without significant performance deficiencies, this work would not be relevant. Therefore, two Platinum standards were used as points of comparison. The first sample is a high
level Platinum loading representative of commercial standards that are being investigated for replacement. Therefore, this cell was designed with \(1.59 \text{mgPt/cm}^2\), and was prepared in-house through identical methods as the hybrids. Secondly, a lower level Platinum cell was designed, with loadings equal to the hybrids if the PGM-free catalyst were to be removed. Therefore, this cell had a loading of roughly \(0.55 \text{mgPt/cm}^2\) on both the anode and cathode. Finally, one pure PGM-free standard was used. As noted in the experimental setup, these electrodes were prepared by different methodologies than the PGM-free electrodes evaluated in Chapters 3 and 4. These changes account for the differences in performance of the pure PGM-free catalyst represented in this chapter when compared to the data presented in Chapters 3 and 4 (it should also be noted that this particular MOF sample was not one of the samples evaluated in Chapters 3 and 4). Figure 5.7 below demonstrates the performance the hybrid vs the three reference cells.
Figure 5.7 - a) Oxygen with Tafel analysis and b) air comparison between MOF hybrid and pure PGM-free, high loading Pt, and comparable Pt loading
As is evident, the MOF hybrid performs at nearly the same level as the high loading pure Pt system. Additionally, it far outperforms either a lower loading Pt MEA or pure PGM-free MEA. Clearly, at first glance this indicates a potential route to reducing the total Pt loading in the MEA. In fact, while operating in oxygen, at higher current densities the hybrid system outperforms the high loading Pt cell. While the oxygen performance is roughly equal to that of the high loading Pt MEA, there is still a deficit between the high loading Pt MEA and the MOF hybrid MEA when tested in air. The fact that the gap between the air and oxygen data for the MOF hybrid is greater than that of the Pt MEA is typically an indication of transport properties. It indicates that gas transport in the hybrid is hindered when compared to a Pt system. The potential causes of electrode and catalyst-based transport deficiencies were discussed earlier in this chapter. This could be alleviated in the future through altered manufacturing techniques of the electrodes, more closely replicating the techniques used in Chapters 3 and 4. Despite this deficiency in the air performance, the oxygen performance is incredibly promising. And of note is that these MOF materials have a significantly lower active site density than Pt catalysts (roughly 3 orders of magnitude fewer), which is what traditionally requires higher catalyst loading with PGM-free materials than Pt. However, when evaluated in RRDE, they showed a performance in acid that was comparable to Pt. This indicates that while the active site density is lower, the catalyst is comparably active to Pt. Therefore, it should be possible, if the electrodes are engineered properly, to design a system where a larger contribution of PGM-free materials could alleviate at least some of the required Pt catalyst.

Not only does the hybrid system outperform both the 0.55mgPt/cm² and pure PGM-free MEAs, its current density at any given potential is actually greater than the sum of the current densities of those two MEAs, indicating some sort of synergistic effect of the hybrid system.
While this was certainly a surprise, there is a plausible explanation. These electrodes were earlier generations of the electrodes used in Chapters 3 and 4, and had previously shown very poor durability when PGM-free materials were evaluated on their own. However, following a redesign of the manufacturing processes that led to the results in Chapters 3 and 4, these PGM-free materials demonstrated very good durability, as shown in Chapter 4. This indicates that performance losses were due to artifacts of electrode manufacturing rather than inherent catalyst instability. Therefore it is possible that over the course of testing the PGM-free catalysts, there may have been drops in performance due to poorer durability, which would not be observable by looking at single polarization curves. This would be a sign that there is a synergistic effect of combining the PGM-free with Pt catalysts, in that it combines the high activity of PGM-free catalysts with the better durability of the Pt systems. If the primary cause of performance losses with pure PGM-free electrodes is attributed to high or low concentration of acid within the electrode, then something related to the Pt catalyst can prevent over- or under-saturation of phosphoric acid. This could be due to pH effects or hydrophobicity of the catalyst layer. There is, however, more work to be done before claims of a true synergistic effect can be validated.

5.3.3 Lower Loading Pt Systems

Following the evidence above that a cathode utilizing both Pt and PGM-free materials could perform at a similar level to a high loading Pt system, it was decided to study what effect a further reduction in the Pt loading would have on the system. For this work, MEAs using the MOF material (highest performing of the previously-studied materials) were designed utilizing only 0.3mgPt/cm². While these systems will certainly not perform to the same level as a high Pt loadings (1.59mgPt/cm²), this would represents more than an 80% reduction in the total Pt required for an MEA. While a reduction from the 0.55mgPt/cm² of the prior hybrid systems to
0.3mgPt/cm² is a huge reduction, it is not expected that significant gains could be made from increasing the amount of PGM-free material beyond the 2.5mg/cm² that was done earlier. Therefore it was not anticipated that this hybrid systems would show the same performance as the ones investigated earlier. The results of these tests can be seen below in Figure 5.8.
Figure 5.8 - a) Oxygen and b) air comparison of lower loading MOF hybrid with pure PGM-free and two lower loading Pt MEAs. TPS® membrane, 180 °C
At first glance, it would appear that the MOF hybrid does not demonstrate the same “synergistic” effect at the lower Pt loadings that it does at 0.55mgPt/cm\(^2\). However, it should be noted in oxygen that this still demonstrates a method of reducing the Pt loading from the 0.55mgPt/cm\(^2\) reference cell without resulting in a loss in performance. As was the case with the 0.55mgPt/cm\(^2\) hybrid, the same could not exactly be said with the air data. In both cases, the performance gap between the hybrid and the higher loading Pt was greater in air than in oxygen, indicating that gas transport is still an issue. Catalyst layer thickness is a driving force for gas transport, and these lower loading hybrids do not use significantly less total catalyst material than the hybrids previously shown. Additionally, given the more primitive nature of these electrodes, it is unsurprising that gas transport is a greater issue in these electrodes. If electrode manufacturing were improved, these hybrid systems would demonstrate incredible promise as alternatives to Pt-only MEAs.

5.4 Conclusions

While in previous Chapters, PGM-free materials have been evaluated as potential alternatives to the Pt catalyst required on the cathode of HT-PEMFCs, this work represents perhaps the best current alternative to the high loading Pt MEAs. While not completely eliminating Pt catalysts at the cathode, it represents a massive reduction in the total Pt content through its combination with a PGM-free catalyst into a so-called “hybrid” cathode. Two methodologies were evaluated: where the PGM-free and Pt catalysts are mixed into a homogenous catalyst layer and where the Pt is applied as a top coat to the PGM-free catalyst layer. In this case, the Pt top coat was determined to perform better than the homogenous layer. The justification for this is that in a thick catalyst layer such as these, active sites can become inaccessible based on porosity characteristics of the electrode. Given the significantly higher
active site density of Pt catalysts compared to PGM-free materials, in a homogenous layer, a higher percentage of total active sites could become inaccessible. When compared to a Pt top coat, the inaccessible active sites would primarily be of the PGM-free catalyst, leaving a higher total active site density in the more accessible portions of the electrode. Once the proper methodology had been determined, a group of six PGM-free materials were evaluated. Five were of the Sacrificial Support Method (SSM), while one was of the Metal-Organic-Framework (MOF) variety. The MOF material, synthesized by Pajarito Powder through a reactive ball-milling process developed at NEU\textsuperscript{19}, outperformed the SSM materials. In single cell testing at 180 °C using an Advent Technologies TPS® membrane, this hybrid system with roughly 1.1mg\textsubscript{Pt}/cm\textsuperscript{2} total loading (0.55mg\textsubscript{Pt}/cm\textsuperscript{2} for both anode and cathode) performed at a very similar level in oxygen to a pure Pt MEA of nearly 3.2mg\textsubscript{Pt}/cm\textsuperscript{2} (1.59mg\textsubscript{Pt}/cm\textsuperscript{2} for both anode and cathode), while far outperforming both a pure PGM-free of 3.3mg/cm\textsuperscript{2} and a Pt MEA of 1.1mg\textsubscript{Pt}/cm\textsuperscript{2} (0.55mg\textsubscript{Pt}/cm\textsuperscript{2} for both anode and cathode). In fact, in oxygen, the current density of the hybrid at any given potential was greater than the sum of the current densities of the lower loading Pt and the pure PGM-free, indicating some sort of synergistic effect, where the high activity of the PGM-free catalyst is combined with the durability of the Pt catalysts.

Additionally, hybrid systems with even lower Pt loading were evaluated. However, these systems definitely did not display the synergistic effect seen previously. This could be due to such a low loading of Pt not demonstrating comparable durability characteristics of the higher loading MEA in such a harsh acidic environment. Despite this, the low loading Pt did significantly outperform a 0.3mg\textsubscript{Pt}/cm\textsuperscript{2} MEA, while showing comparable performance to the 0.55mg\textsubscript{Pt}/cm\textsuperscript{2} MEA. In essence, at lower than 0.5mg\textsubscript{Pt}/cm\textsuperscript{2}, the hybrids demonstrated a
performance equal to the sum of their parts, rather than greater than the sum of their parts due to the potential synergistic effects discussed earlier.

These systems show incredible promise as alternatives to the high Pt loading required in commercial HT-PEMFC systems. Given that these electrodes were also prepared through an earlier generation of manufacturing technology, there are significant improvements that could be demonstrated if they were to be re-evaluated using the current manufacturing techniques used in Chapters 3 and 4.

5.5 Chapter 5 References


Chapter 6

Summary, Future Directions, and Conclusions

6.1 Introduction

Due to the depleting fossil fuel supply not being able to handle the growing energy demands of our society, much work has been done on potential energy alternatives. Hydrogen fuel cells are one of the most promising electrochemical energy conversion alternatives. However, the current state-of-the-art catalyst for both the hydrogen oxidation reaction (HOR) and oxygen reduction reaction (ORR) in acid electrolytes are platinum-based catalyst materials. Unfortunately, due to the high and volatile cost of platinum, these systems are not immediately commercially viable. Therefore, significant work has been done investigating potential platinum group metal (PGM)-free catalyst alternatives for ORR. The focus has largely been on ORR due to the higher Pt loadings required due to the inherently sluggish kinetics associated with ORR. The aim of this work is to gain a further understanding of transport effects through these PGM-free catalyst layers using a combined experimental and theoretical approach. Additionally, PGM-free materials were evaluated in a higher temperature proton exchange membrane fuel cell, which could have potential impacts in stationary power generation. Two designs were evaluated: pure PGM-free cathodes as well as “hybrid” cathodes using a low loading of platinum combined with a PGM-free catalyst layer. These systems were evaluated for both performance and durability under a pair of protocols.
6.2 Summary

6.2.1 Chapter 2 Summary & Future Work

Two PGM-free materials (NPC-2000 from Pajarito Powder and MOF SR from NEU) were evaluated to elucidate further information regarding mass transport characteristics. Experimental work was based off prior work by Reshetenko et al. on Pt MEAs at the Hawaii National Energy Institute (HNEI). Low-concentration (4%) oxygen gases (diluted with inert carrier gases He, Ar, or N₂) were used as cathode gases in order to guarantee a limiting current region at low potentials. Subsequently, the MEAs were evaluated at a series of anode/cathode flow rate combinations, allowing the limiting current to be calculated as a function of the flow rate. When plotting a logarithmic function of the limiting current as a function of the inverse theoretical limiting current, a linear relationship was observed. From the slope of this line, the mass transport coefficient and subsequently the mass transport resistance were calculated. The mass transport resistance can be divided into a gas-phase and non-gas-phase resistance. When the mass transport resistance is plotted as a function of molecular weight and extrapolated to a molecular weight of 0, the non-gas-phase resistance can be isolated (representing true mass transport resistance of oxygen through the catalyst layer). The non-gas-phase mass transport resistances were observed to be significantly (roughly 3x) higher than the Pt reference MEA that was also evaluated, while the gas-phase resistances (represented by slope of the resistance as a function of molecular weight of diluent) of the PGM-free materials were roughly equal to that of Pt.

In addition to the experimental work, modifications were made to a previously-developed model for the cathode catalyst layer at Michigan State University (Prof. Scott Calabrese Barton). These modifications included the addition of a local mass transport factor due to the low oxygen...
concentration. Also, in order to compensate for the non-constant concentration of oxygen through the flow field (as opposed to a higher-concentration oxygen system), a variable to account for the dimensionless path length through the flow field was added. Pore size distributions from mercury porosimetry studies, as well as electrochemical impedance spectroscopy data, were used to differentiate between the two PGM-free catalysts, and fitted results of the polarization curves showed good correlation to the experimental work, with slight deviations being explained by the use of an isothermal model and slight pressure changes based on flow rate. This allowed for the calculation of four variables concerning transport through the catalyst layer: the exchange current density, the ionic conductivity, the hydrophobic fraction, and the local mass transfer coefficient.

In the future, it would be interesting to further enhance the model to be able to compensate for local temperature changes caused by increased current density, which were currently not addressed in the existing isothermal model. Additionally, this technique could prove useful in further studying the HT-PEMFC environment, for which it has not been used to this point. Through the work presented in this dissertation in the HT-PEMFC environment, efficient transport has often been a hindrance in designing the catalyst layer and electrode structure. Therefore, this work could be applied to help design cathodes with optimal gas and mass transport characteristics.

6.2.2 Chapter 3 Summary & Future Work

Two PGM-free materials of the MOF variety were investigated for potential use in the HT-PEMFC environment. One was synthesized through a solution reaction, where the iron-phenanthroline complex is embedded within the MOF structure, and contains no evidence of direct Fe-N₃ coordination. Rather, it contains solely evidence of iron carbide and metallic iron
coordination. The second material was prepared through a solid state reaction (reactive ball-milling), and contains almost exclusively evidence of Fe-N₄ coordination. Despite these two materials having very different coordination, both materials have been previously shown to demonstrate similar activity in both RRDE and PEMFCs. In this work, both materials demonstrated immunity to phosphate poisoning through studies done in the RRDE environment. Additionally, Koutecký-Levich analysis on both samples indicated that both materials will reduce oxygen primarily through a direct 4-electron pathway. The Koutecký-Levich was carried out in un-doped electrolyte (0.1M HClO₄) at several potentials, all of which indicated the same 4-electron pathway. Following RRDE evaluation, both materials were evaluated in the HT-PEMFC environment using 5cm² single cell testing at 200 °C. Testing was done at series of backpressures in both oxygen and air. Tafel analysis was carried out using the high frequency resistance from electrochemical impedance spectroscopy in order to compensate for the iR-losses and gain a better idea for the catalytic activity of the two materials. Additionally, the MOF SSR catalyst was evaluated at a series of temperatures. Performance understandably increased as a function of the temperature, which would be expected given that the increasing temperature will increase the kinetics of the HOR and ORR reactions.

While these materials have demonstrated promise as potential alternatives for the Pt catalyst commercially used in these systems, there is still much that has to be done. Firstly, the only durability studies to date on these MOF materials was done either in RRDE or in PEMFC, where the mechanism of degradation is not very well understood. Additionally, in PEMFC, due to the extra water present from humidified gas, degradation due to flooding is a large issue. This is less so at the higher temperature given that dry gas feeds are used. But to date, a thorough investigation of the durability in the HT-PEMFC environment has not yet been conducted.
6.2.3 Chapter 4 Summary & Future Work

A PGM-free material developed by the University of New Mexico and scaled up in synthesis by Pajarito Powder (Albuquerque, NM) was evaluated for performance and durability in the high-temperature proton exchange membrane fuel cell (HT-PEMFC) environment. Gas diffusion electrodes (GDEs) and membrane electrode assemblies (MEAs) were fabricated at NEU, and single cell MEA testing at NEU was conducted to evaluate performance using both oxygen and air cathode feeds. The single cell performance represents the highest reported performance to date of any PGM-free material in the HT-PEMFC environment. Durability of the material was evaluated through a pair of protocols. First, the cell was subjected to a 48hr potentiostatic hold at 650mV (H₂/air, 2.5bar total pressure) following a break-in procedure. During that protocol, no loss in performance was observed. In fact, a slight performance increase was noted. This is likely due to a less well-defined break-in period when compared to Pt MEAs. The second durability test was used to facilitate corrosion of the carbon support, and was done via a 3hr hold at the open circuit potential. Pt MEAs demonstrated nearly 20% current density losses at 650mV through the same procedure, while the PGM-free material demonstrated no observable losses in current density. Scale-up from 5cm² to a more commercially-representative 45cm² MEAs was done as well, and it was noted that there were no performance changes as a function of this scale-up. Finally, electrochemical impedance spectroscopy was used to further analyze the resistances within the MEA. Using a fit of EIS spectra to an equivalent circuit designed specifically for HT-PEMFCs, it was possible to isolate the membrane resistance, active layer resistance, charge transfer resistance, and double layer capacitance as a function of the applied potential.
While this material represents the highest performing PGM-free material to date in the HT-PEMFC environment, and demonstrates incredible stability, there are still many factors that are in the process of being evaluated. For one, longer term durability is being evaluated, as these systems need to be able to show thousands of hours rather than tens of hours in a commercial setup. While that is beyond the capabilities of the work in this lab, tests in the hundreds of hours are certainly reasonable. Additionally, given the EIS equivalent circuit model that was used to study the resistances, it would be useful to study the resistances of the cell prior to and following the durability protocols. If during a degradation protocol, performance losses were observed, this could potentially act as a mechanism of identifying which aspect of the MEA was the culprit. It could differentiate between issues of membrane stability, catalyst stability (charge transfer resistance), or proton conductivity due to acid content (active layer resistance).

Additionally, modified versions of the PMF-2010 catalyst are currently under evaluation. These materials have been synthesized to have different pore size distributions which could affect gas and mass transport through the catalyst layer. Proper pore size distribution, and proper packing of the catalyst layer (either through modified coating technology or multiple layers of different pore size distributions) will be key towards further improving the performance in an effort to eliminate the need for Pt catalysts on the cathode.

6.2.4 Chapter 5 Summary & Future Work

As a potential alternative to the solely PGM-free cathodes that were evaluated in Chapters 3 and 4, a mixed Pt & PGM-free “hybrid” cathode was evaluated. As this is a novel concept, a proper methodology had to be developed. Therefore, two variants on the hybrid design were tested: one where the Pt and PGM-free catalyst were mixed into a homogenous catalyst layer and one where the Pt catalyst was applied as a top coat to the PGM-free catalyst
layer. It was determined through this evaluation that the Pt top coat slightly out-performed the homogenous catalyst layer. This could be due to the high overall catalyst layer loading and therefore the thick catalyst layer. This thick catalyst layer could inhibit accessibility to some active sites that are embedded deep within the electrode. Given the significantly higher active site density of Pt materials, this inaccessibility could hinder the performance of the homogenous layer more than the Pt top coat method. When the performance of the hybrid was compared to a high loading Pt system, it showed very comparable performance, despite a 70% total reduction in Pt in the MEA. Additionally, it outperformed both a pure PGM-free as well as a comparable low loading Pt cell.

Hybrid systems were also evaluated at even lower Pt loadings (0.3mgPt/cm² instead of 0.5mgPt/cm²). Unfortunately, there was a more significant drop off in performance at such low loadings, and the potential synergistic effect that was present at the higher Pt loadings was not present at the lower loadings. It is likely that given the high Pt loading in traditional systems, the 0.5mgPt/cm² may be the lower threshold to achieve the same performance. This work was done at lower operating temperatures (180 °C) than the work in Chapters 3 and 4 (200 °C), as well as with a different membrane (Advent Technologies TPS® as opposed to PBI). This membrane is a solid membrane that is then soaked in acid rather than a membrane imbibed with acid and formed through a sol-gel process. Because of this, it has higher thermal and compressive stability, which could theoretically allow the system to be run at slightly higher than the 200 °C before membrane stability would become an issue.

This represents the best alternative to a high loading Pt system to date in the HT-PEMFC environment. The electrodes were manufactured using very different technology than those in Chapters 3 and 4, largely because the bulk of this work was done prior to having completed a
redesign of the cathode as a part of investigating pure PGM-free cathodes. Therefore, if these hybrid systems were to be reevaluated now that the manufacturing methodologies have been improved, it is possible that not only would they show comparable performance to high loading Pt systems, but potentially outperform those systems. If that were the case, then they could immediately present a viable alternative to the high loading commercial standard electrodes.

6.3 Conclusions

Fuel cells have incredible promise as a potential alternative to fossil fuel energy technology. However, until the issues regarding the cost of these systems (driven by the cost of Pt catalysts) are resolved through either reduction of Pt without power output losses or the development of PGM-free materials as Pt replacements, they will not become truly viable for large scale commercial use. These Pt cost issues are more pronounced in the HT-PEMFC environment given the higher Pt loading required than in lower temperature fuel cells. This work explored the performance and durability of potential replacements. Both potential resolutions were addressed, as PGM-free materials were evaluated on their own as well as in conjunction with low loadings of Pt catalysts. Additionally, transport characteristics were studied in lower temperature systems, which could yield valuable information for future catalyst development. While this work demonstrates the incredibly high promise of these systems, there is still plenty of work to be done to fully eliminate the Pt requirement in fuel cell technology.