The Effect of Temperature on the Performance of Direct Methanol Fuel Cells

A Major Qualifying Report

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Worcester, MA 01609
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By:

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Samantha Do

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Kaitlyn Spetka

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Matthew Suarez

Approved by:

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Professor Ravindra Datta

Abstract

This project investigates the effect of temperature on the performance of a Direct Methanol Fuel Cell (DMFC) using two different types of commercially available membrane electrode assemblies (MEAs): Nafion®117-based and Celtec®-P 1000 PBI-based. With various methanol feed concentrations, the Nafion®-based MEA operated between 20 and 80°C with liquid feed, while the PBI-based MEA operated between 160 and 180°C with vapor feed. Results showed that the DMFC performance increased with temperature. However, at higher temperatures, methanol crossover became more prevalent at higher feed concentrations and thus reduced performance. The PBI-based MEA provided good performance despite having a lower catalyst loading and operating with higher feed concentrations.

Executive Summary

Fuel use and energy consumption is of concern to many people. The most common fuels used for transportation and heat are based on finite hydrocarbon resources, and must be used as efficiently as possible. Currently, there is a significant difference between the potential amount of energy that can be utilized from a fuel source and the actual amount of energy that is used. This is because fuel must be processed before it can be used. Furthermore, this fuel may be converted into more useful forms, such as electricity. Many current popular technologies that require the use of hydrocarbons also require energy-intensive processing that reduces the overall efficiency of the energy use.

One energy conversion technology that is gaining popularity is the fuel cell. Fuel cells can be fed with fuels that require less energy to process and are source independent, fossil or renewable. Typical fuel cells are fed hydrogen at the anode and oxygen or air at the cathode. Hydrogen-oxygen fuel cells typically provide high efficiencies and very good performance. However, since hydrogen is expensive and difficult to store, there are other types of fuel that can be used in a fuel cell. One type of fuel that shows particular promise is methanol, an inexpensive fuel that has a high energy density and is easy to store and transport. However, a lot of obstacles must be overcome to improve performance, reduce costs, and improve durability before Direct Methanol Fuel Cells (DMFCs) become feasible for general consumer use. Major problems with DMFCs include catalyst poisoning and methanol crossover. The use of ruthenium at the anode and higher platinum loadings at the cathode help prevent catalyst poisoning. However, this results in higher capital costs for the cell. Further, researchers are attempting to produce membrane materials that are more resistant to methanol crossover, which reduces fuel utilization as well as fuel cell performance and efficiency. The most conventional membrane used in a DMFC, Nafion®, is still one that is highly susceptible to crossover.

In order to contribute to the understanding of the effect of temperature on the performance of DMFCs, we tested two different types of commercially-available Membrane Electrode Assemblies (MEAs) with methanol as the feed. The first type of MEA was based on a Nafion® 117 membrane and had catalysts and loadings designed for use in a DMFC. This MEA type was tested at various temperatures between 20 and 80°C and with methanol concentrations between 1 and 4M. The second type of commercial MEA was based on a polybenzimidzole (PBI) membrane and had catalysts that were designed for use with reformate or hydrogen, not methanol. This PBI-based MEA type was tested at various temperatures between 160 and 180°C and with methanol concentrations between 3 and 10M.

It was observed that the DMFC performance increased with temperature. The best performance obtained from the Nafion® 117-based MEA was at 70°C with 2.5M methanol feed and pressurized oxygen fed to the cathode to overcome the rising vapor pressure of water. The best performance obtained from the Nafion®117-based MEA without using pressurized oxygen feed to the cathode was at 60°C and with 2.5M methanol feed. Experiments showed that the best performance obtained from the PBI-based MEA was at 180°C with a 5M methanol feed concentration. The good performance for the PBI-based MEA shows the effectiveness of operating at higher temperatures when using lower catalyst loadings, demonstrating the possibility of developing DMFCs with lower costs. However, research needs to be performed to develop optimum membrane thicknesses and catalyst compositions and loadings suitable for vapor-phase DMFCs.

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Chapter 1: Introduction

The world consumes an annual average of 100 quintillion Joules (J) of raw energy, yet can only produce an average of 70 quintillion Joules of usable energy (EIA, 2012). Most of the world's energy is derived from fossil fuels such as coal, petroleum, and natural gas. While fossil fuels are naturally occurring substances, their sources are finite and over time, the prices for fossil fuels will continually increase as the supply will decrease. Further, they are causing greenhouse gas accumulation in the atmosphere with dire potential consequences. As a result, new methods to generate energy using renewable fuels are being researched and developed. Currently, renewable energy accounts for 10 percent of the world's energy production and can be provided by solar, wind, biomass, and hydroelectric technologies. Over the last few years, the use of fuel cell technology has gained much interest as a provider of renewable energy for its ability to efficiently produce electricity from the energy of a chemical reaction between a fuel and an oxidant (Spivey et. al, 2011). While typical internal combustion engines have an average energy efficiency of about 20 percent, most fuel cells have an average efficiency of around 60 percent (US Department of Energy, 2011). In addition to its capability of utilizing alternative fuels, it produces little to almost no emissions and has significantly less environmental effects than other fossil fuel-based technologies.

The concept of fuel cells is not new. Experiments demonstrating electrochemistry date as early as the 17th century with Alessandro Volta producing electrical current from a pile of various metals and electrolytes (Vielstich et. al, 2004a). The first fuel cell is considered to be Sir William Grove's gas voltaic battery developed in 1839, which was able to create electricity from the conversion of hydrogen and oxygen gas (Smithsonian Institution, 2004). While the physical aspects have changed over the last two centuries, all fuel cells follow the same basic chemical mechanism: at the anode catalyst, fuel (i.e., hydrogen, alcohols) is oxidized to produce electrons and hydrogen ions, or protons. The electrons are fed to an external circuit to be used as direct current electricity while the protons travel through a Proton Exchange Membrane (PEM) to the cathode catalyst. At the cathode, the protons meet the electrons and react with an incoming oxidant to produce a water product. Small amounts of carbon dioxide can also be produced if an alcohol, such as methanol or ethanol, is used as fuel.

Due to their similar chemical mechanisms, fuel cells are often compared to batteries. However, batteries store a finite amount of energy while fuel cells can continuously generate energy provided that they are being fed with fuel. Many fuel cells use hydrogen fuel, which can be fed directly to the cell from a gas tank or be produced within the fuel cell power plant from the reforming of methane, the principal component of natural gas (Union Gas Ltd., 2012). Alternative fuels such as alcohols are being researched to avoid the need to use hydrogen, which can be difficult to transport and involves complex plants if it is produced directly from methane. Direct Methanol Fuel Cells (DMFCs) are a promising alternative to hydrogen fuel cells as there are many advantages to using liquid methanol solutions in place of hydrogen. Methanol is significantly cheaper than hydrogen, pricing at 1.34USD per gallon whereas the cost of hydrogen can exceed 15USD per equivalent gallon (Methanex, 2012; FSEC, 2007; EIA, 2012). Methanol fuel is easier to manufacture and transport since it remains in a liquid state and does not require special storage (i.e., highly compressed gas tanks). Additionally, methanol does not need to be reformed into hydrogen and can be fed directly into the cell (Olah et. al, 2006). Currently, direct methanol fuel cells are mostly used for portable and micro power applications, such as chargers for mobile phones and laptops (Fuel Cell Markets, 2012). However, they have also been used in forklift and automobile applications. Once limited by low efficiencies, DMFCs have seen improved power density with the progression in catalyst and membrane technology for DMFCs.

Though DMFCs are presently used in commercial applications, there are a number of issues that prevent them from operating to its theoretical potential. Slow kinetics is experienced at the anode catalyst as a result of the slow rate of the oxidation reaction of methanol and water. DMFCs have a theoretical voltage of about 1.09 Volts (V). Unfortunately, due to slow kinetics, its actual voltage can decrease to about 0.9V (Olah et. al, 2006). Methanol is converted to a number of intermediates before it becomes carbon dioxide. Some of these intermediates, especially carbon monoxide, are able to cling onto the anode catalyst and block the surface, preventing any more reactions from occurring. Studies have shown that bimetal catalysts, such as Platinum-Ruthenium (PtRu), help convert carbon monoxide into carbon dioxide, and reduce the catalyst poisoning and potential losses. However, this problem is not completely avoidable as catalysts, like ruthenium, can leach from the anode and eventually lose activity with time.

In addition to slow kinetics, methanol crossover is another concern because it lowers the cell's current efficiency and negatively impacts the cathode catalyst. Crossover occurs when methanol passes through the membrane and reacts at the cathode instead of at the anode. The rate of crossover increases with increasing methanol concentrations, so many DMFCs operate with very low concentrations of methanol fuel.

To better understand the performance of a DMFC, an MQP group from 2011 conducted tests using a Nafion®-based DMFC (Cox et. al, 2011). Nafion® is a sulfonated fluoropolymer membrane that is commonly used as the polymer membrane in DMFCs. They found that an increase in operating temperature (from 20°C to 90°C) as well as methanol concentration in the feed (from 1M to 3M) increased the overall performance of the cell. However, the Nafion® 117-based Membrane Electrode Assembly (MEA) became unstable at temperatures exceeding 100°C. To exceed this temperature limit, they used a polybenzimidazole (PBI)-based MEA from BASF in place of Nafion®. PBI is a synthetic fiber that has a higher melting point and is more thermally and chemically stable than Nafion®. A DMFC with a PBI-based MEA can operate at temperatures up to 200°C. Unfortunately, the research team did not get conclusive data with use of a PBI membrane due to a number of problems during their experiments, most of which involved the fuel cell set-up and feeding fuel.

In order to improve the performance of a DMFC, we investigated the effect of temperature on the cell performance. Increasing the operating temperature increases the rate kinetics of both the anode and cathode, as stated by the Butler-Volmer equation (personal communication, Ravindra Datta, 2011):

$$\mathrm{k} = \exp\left(\frac{-\mathrm{E_A}}{\mathrm{R} \cdot \mathrm{T}}\right) \cdot \exp\left(\frac{\upsilon \cdot \mathrm{F} \cdot \Phi}{\mathrm{R} \cdot \mathrm{T}}\right)$$

As a result, DMFC performance should theoretically increase. While rate kinetics are dependent on a number of different factors (such as concentrations or flow rates), increasing the temperature can improve the rate by increasing the rate constant, k. Additionally, varying the temperature does not affect (and therefore does not sacrifice) the potential, Φ, which can be influenced by a change in the overall rate. In order to test this hypothesis, the project was separated into two parts. The first part of experiments involved running the DMFC with a Nafion® 117-based MEA produced by ECOtality, Inc. The cell operated at different temperatures and methanol feed concentrations, ranging from 20 to 80°C and 1 to 4M, respectively. At temperatures of 70°C and higher, the oxygen was pressurized to counter the rising vapor pressure of water that is experienced as temperature increases. For the second part of the project, the DMFC was operated using Celtec®-P 1000, a PBI-based MEA produced by BASF. In these experiments, only the temperature and fuel concentration parameters were varied, from 160 to 180°C and 3 to 10M, respectively. Performance curves for every operating parameter were measured by drawing a set current from the DMFC using a load box and recording the corresponding voltage. By collecting the voltage data at various operating conditions, we were able to determine the effect of temperature on cell performance as well as the optimum operating conditions studied for a DMFC using a Nafion®-based or a PBI-based MEA.

In the following background chapter, the history and the individual components of a direct methanol fuel cell are highlighted along with reviews of a DMFC's typical performance using a Nafion®-based or PBI-based MEA. The subsequent chapters note the methods we used to collect the performance data and the analysis of the performance curves at the various operating conditions. From these results, we were able to provide recommendations for further DMFC studies and for future MQP groups.

Chapter 2: Background

This section outlines a number of aspects related to fuel cells and Direct Methanol Fuel Cells (DMFCs), including its history, the components of a DMFC, and the typical performances of a DMFC. A background review is necessary to understand the operation and the obstacles that are presented when operating a DMFC.

2.1 History

A fuel cell is a device that converts chemical energy of a fuel into direct current electricity, which is then used to do work. The first fuel cell is considered to be developed by Sir William Grove who dubbed his invention a “gas battery” (Alternative Energy, 2011). Grove's cell utilized sulfuric acid, platinum electrodes, and combined hydrogen and oxygen gas to generate a potential (Vielstich et. al, 2004a, p. 158). The mechanism of his "gas battery" is still the model for most modern-day fuel cells. Grove’s gas battery consisted of two sealed containers, platinum electrodes and a container of sulfuric acid (Smithsonian Institution, 2004). One of the sealed containers was filled with oxygen and liquid water, the other was filled with hydrogen and liquid water. Platinum electrodes were inserted into the sealed containers such that half of the electrode was in the container and half stuck out. The gases were obtained from electrolysis of water, which decomposed water into hydrogen and oxygen gas into the sealed containers. The containers were then immersed in the container with sulfuric acid and a constant current would then flow through the electrodes, from the hydrogen to the oxygen (Carhart, Primary batteries, 107). As the current flowed, the water levels in each of the containers rose over time. While Grove’s invention is considered to be a fuel cell, it is actually a battery and stores energy from electrolysis of water for later usage; modern fuel cells produce energy.

The first modern hydrogen fuel cell was developed by Thomas Francis Bacon in early 1933 (Andujar & F. Segura, 2009). His fuel cells were used in British submarines in World War II and in the Apollo spacecraft. Over time, the uses of fuel cells have spread to cover both stationary and moving purposes. The most well-known fuel cell is the hydrogen fuel cell, which uses a hydrogen feed and an oxygen or air feed to produce electrical energy. The byproducts of the system are water and waste heat, i.e., the part of the heat of combustion of this fuel that is not converted into electricity. Many other types of fuels can be used, such as alcohols or natural gases, as fuel cell system can reform hydrogen directly from the fuel. Fuel cells have become more prevalent in recent years since they are more efficient and less detrimental to the environment than internal combustion or other heat engines and do not have to rely solely on finite sources such as crude oil, which is much more scarce now than when it was first developed as a fuel source over a century ago (Andujar & Segura, 2009).

Fuel cells are considered a good and more efficient alternative to batteries and the internal combustion or heat engine. Unlike batteries, fuel cells produce energy instead of storing it. Batteries are characterized by a finite lifetime and can only run until their stored energy is completely used up. Fuel cells can operate continuously as long as there is a fuel feed to the cell. In comparison to internal combustion or heat engines which average at about 20 percent efficiency, fuel cells operate at an average efficiency of 60 percent (US Department of Energy, 2011). Internal combustion engines emit greenhouse gases such as carbon dioxide (CO_2), carbon monoxide (CO), and nitrogen oxide (NO_x), whereas fuel cells produce water as the main byproduct, in addition to carbon dioxide if an alcohol feed is used (Liberman, 2008, p. 335).

Fuel cells have been developed to power buildings and different modes of transportation, such as buses. For example, UTC Power has been supplying the U.S. with buses that run on fuel cells since they developed their first fuel cell powered bus for Georgetown University in 1998 (UTC Power, 2012).

Fuel cells can be operated anywhere and are used in areas that do not have access to the electric grid. UTC Power has sold stationary fuel cell stacks to companies, such as Coca-Cola Refreshments, Price Chopper, and the New York Port Authority, that use the stacks in addition to the electric grid or as backup power. Overall, fuel cells cut down on pollution rates of greenhouse gas production due to their higher efficiencies. They also produce less pollutants and noise than combustion engines. These differences are useful in highly-populated areas such as cities.

2.2 Overview

Most active (e.g., directly fed) direct methanol fuel cells follow a standard plate-frame design integrated with a Membrane Electrode Assembly (MEA). The MEA usually consists of the Proton Exchange Membrane (PEM) with an anode electrode and a cathode electrode on either side. The electrode usually consists of a carbon fiber-type Gas Diffusion Layer (GDL) with a thin layer of catalyst on the side of its surface that is in contact with the PEM. Figure 1 shows a general schematic. A detailed description of the cell assemblies used in the project can be seen in section 3.1.

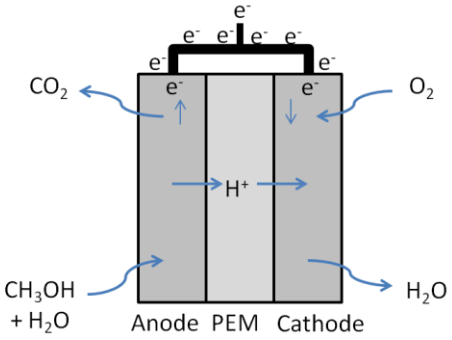

Figure 1: A Schematic of a direct methanol fuel cell (DMFC)

The electrode and overall reactions in a DMFC are:

Anode: $CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$

Cathode: $1.5O_2 + 6H^+ + 6e^- \rightarrow 3H_2O$

Overall: $CH_3OH + 1.5O_2 \rightarrow 2H_2O + CO_2$

Diluted methanol fuel is fed to the anode side of the cell. Once in contact with the anode catalyst, methanol and water react to produce hydrogen ions (i.e., protons), electrons, and carbon dioxide. The carbon dioxide leaves mostly at the anode side through the waste stream as off-gas and the electrons are fed from the anode to an external circuit to provide direct current electricity. The protons travel through the PEM and meet the oxygen or air feed at the cathode catalyst. At the cathode, the electrons that were directed through the electric device return with less energy and react with the protons and oxygen to form water.

This section highlights the components of a DMFC, including the feed fuel, the anode, the PEM, and the cathode. Past and current research regarding each component is emphasized to note the progress of improving the DMFC. While methanol has advantages over hydrogen, including its availability and ease of transportation, some limitations prevent methanol from producing its theoretical output. This section also underscores the obstacles that are encountered at each component.

2.2.1 Methanol as Fuel

Methanol is a colorless, water-soluble liquid that is the simplest of all alcohols (Olah et. al, 2006). Methanol was first isolated in the mid-17th century through the distillation of boxwood. Up until the 1920s, distillation of wood was the primary source of methanol, which is why methanol is also referred to as wood alcohol. In 1923, BASF chemists in Germany were credited with developing the first synthetic methanol derived from a gaseous mixture containing carbon monoxide and hydrogen (i.e., syn-gas) (Tijim et.al, 2001). Methanol was initially processed at high pressures of 250-350 bar and temperatures of 320-450°C. Over the years, operating temperatures and pressures have considerably decreased to about 40-50 bar and 230-250°C, respectively (Olah et. al, 2006). Additionally, the low pressure process more efficiently operates and maximizes the production of methanol. Methanol is commonly used as a feedstock to produce other various chemicals, such as formaldehyde. As of 2005, about four percent of methanol produced is used as fuel.

Methanol is a viable alternative to coals and fossil fuels, as it is more convenient to use and has a relatively higher energy density in comparison to hydrogen fuel (Olah, 2005). Unlike hydrogen fuel, methanol fuel does not require the use of fuel reforming to produce the hydrogen. The fuel fed to a direct methanol fuel cell is generally a solution of water and methanol. Methanol requires the presence of water as a reactant in order to form carbon dioxide, protons, and electrons. Ideally, the methanol fuel fed to the cell reacts at the anode catalyst. In actuality, the fuel can also directly leave the cell through the waste stream or get carried across the membrane to the cathode. Some membranes, such as Nafion, need hydration from water in the fuel to carry the protons from the anode to the cathode. Methanol, being highly soluble and loosely bound with water, gets pulled across the membrane as well. This phenomenon is known as methanol crossover and is discussed in section 2.2.4.

The DMFC fuel feed usually has relatively low concentrations of methanol to avoid self-poisoning of the anode as well as excessive crossover; this can be as much as 10M or as low as 0.5M (Vielstich, 2004b, p. 644). The performance of the fuel cell varies with methanol concentration. For example, Jung et. al (1995) found that for a liquid-fed DMFC, the 3M methanol solution generally had a better performance than the 1M solution at an operating temperature of 50°C. The increased number of methanol molecules increased the number of electrons produced at the anode. As a result, their DMFC was able to reach higher current densities and voltages. Methanol concentrations greater than 4M are usually reserved for vapor-fed DMFCs which more commonly operate at temperatures exceeding 100°C (e.g., the boiling point of water). Vapor-fed DMFCs experience relatively less methanol crossover and can therefore have more concentrated fuel (Xu et. al, 2010). Unfortunately, the use of vapor feed (and consequently more concentrated fuel) is not ideal for DMFCs for portable applications due to the high operating temperature.

2.2.2 Anode

In many DMFCs, the anode electrode consists of a carbon fiber gas diffusion layer with a thin layer of catalyst coated on one side. The catalyst coated side of the electrode is imbued in Nafion® and is in contact with the PEM so that the protons can immediately move through the membrane to the cathode. While the individual compositions can vary among different research groups, a combination of Platinum (Pt) and Ruthenium (Ru) is commonly used as the anode catalyst. Platinum and ruthenium have the capability of oxidizing and removing the reaction intermediates that form during methanol oxidation; platinum oxidizes alcohols and ruthenium dehydrogenates alcohols (Kang et. al, 2011, p. 1). The formation of carbon dioxide from methanol is a stepwise reaction network that consists of series and parallel steps. The reaction diagram is shown in Figure 2.

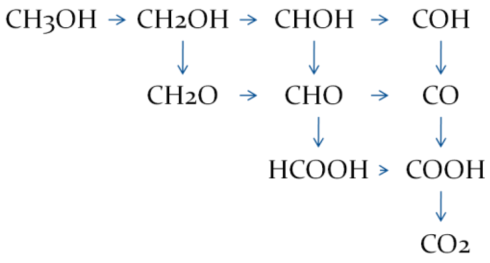

Figure 2: Stepwise mechanism for the oxidation of methanol (adapted from Vielstich et.al, 2001, & Modestov et. al, 2009)

The series and parallel steps produce protons, but parallel steps also involve the formation of a carbon-oxygen double bond. Five hydrocarbon intermediates are produced before carbon dioxide is formed. As noted by Modestov et. al (2009), the presence of intermediates such as formic acid, formaldehyde, and methyl formate have been previously detected by Differential Electrochemical mass spectroscopy and online mass spectroscopy. Due to the formation of stable intermediates that cover the catalyst surface, methanol oxidation proceeds much more slowly than hydrogen oxidation, resulting in slower kinetics at the anode. Therefore, DMFCs have an actual power output that is lower than ideal. A feed of 1M methanol theoretically should generate a thermodynamic cell voltage of 1.2V for both the anode and cathode. However, the actual voltage produced is only around 0.9V or less (Vielstich, 2004, p. 305).

The use of a platinum-ruthenium bimetallic catalyst caters to the two different types of reactions seen in Figure 2 and helps improve the performance of the DMFC. Unfortunately, the degradation of the anode catalyst "is mainly ascribed to the ruthenium dissolution from [PtRu]" (Kang et. al, 2011, p. 1). Ruthenium is susceptible to leaching from the catalyst and crossing from the anode side to the cathode side (Liu & Zhang, 2009, p. 249). The ruthenium deposits on the cathode, resulting in reduced cell performance and inhibition of the Oxygen Reduction Reaction (ORR). Ru crossover can reduce the fuel cell's performance by reducing its maximum current to between 40 and 200 mA lower than ideal (Liang et.al, 2008, p. 166). A decrease in ruthenium at the anode increases the accumulation of intermediates on the surface of the anode catalyst. The intermediate that is of most concern is carbon monoxide. Modestov et. al (2009) noted that a greater amount of carbon monoxide was able to be oxidized with the addition of ruthenium, in comparison to using just a platinum catalyst. Unfortunately, without ruthenium, the incoming methanol and water molecules are unable to react significantly once the anode catalyst is blocked.

A few researchers have studied different components that could be added to the catalyst to stabilize ruthenium and prevent dissolution. Liang et. al (2008) found that the incorporation of gold by deposition on the PtRu catalyst significantly decreased the dissolution of ruthenium by increasing ruthenium's oxidation potential. They also noted that gold assists in the oxidation of carbon monoxide at low temperatures by directing the carbon monoxide directly to the oxygen groups on Ru sites. Other researchers have tried adjusting the application of the ruthenium catalyst. Nandanwar et. al (2011) added in their platinum catalyst ruthenium nanoparticles that were dispersed in a mixture of ethylene chloride and poly(N-vinyl-2-pyrrolidone) (PVP), a water-soluble polymer. PVP contains nitrogen and oxygen atoms that develop dipolar bonds with the Ru nanoparticles. As a result, this stabilizes the ruthenium and prevents the nanoparticles from agglomerating and being unevenly distributed across the electrode. Nandanwar et. al found that an increased molar ratio of PVP to Ru nanoparticles better stabilized Ru while managing its particle size and reducing the ions.

While platinum-ruthenium catalysts are most frequently used, many different catalysts are being studied to further improve anode performance. The performance of the PtRu catalyst can change depending on the ratio of platinum to ruthenium on the anode (i.e., 1:4 Pt-Ru, 2:3 Pt-Ru, etc.). However, there are a limited number of useful combinations of platinum and ruthenium that can be made. Many researchers have studied the effect of adding different composites to PtRu catalysts, such as molybdenum or lead. While there is no one catalyst that is better than another, some platinum-ruthenium composites have shown improvement over traditional PtRu catalysts. For example, Chen et. al (2010) analyzed the performance of a platinum-ruthenium-molybdenum catalyst and found that the DMFC showed better performance (i.e., greater voltages and higher current densities) at increased temperatures compared to using PtRu alone. Researchers at Symex, Inc. studied platinum-ruthenium-lead catalysts which showed enhanced current, in comparison to the traditional PtRu catalysts (Vielstich, 2004b, p. 341).

In addition to different anode catalyst composites, the supports on which the catalyst is coated and catalyst application procedures have also undergone improvements, including changes in the material (i.e., carbon nanotubes) and use of different binders (i.e., Nafion). Kang et. al (2011) compared the performance of a DMFC with a commercial carbon fiber-supported and with a carbon nanotube-supported PtRu catalyst. Lower concentrations of PtRu catalyst (i.e., 40 percent) on the carbon nanotube electrode were "more efficient in the methanol electro-oxidation than the commercial catalyst by a factor of 1.5 at 0.4 V" (p. 9). However, high concentrations of the nanotube-supported catalyst (i.e., 70 percent) showed comparable performance to the fiber-supported catalyst. Many studies regarding the anode are still being researched to optimize its performance without having significant additional costs. Consequently, the use of platinum-ruthenium supported on carbon is still the most popular catalyst combination.

2.2.3 Membrane

This section highlights the two different types of membranes used in the MQP project: Nafion® and PBI. The properties of the membranes are discussed as well as their behavior in fuel cell operation.

2.2.3.1 Nafion®

Dr. Walther Grot, a researcher at DuPont, first developed Nafion® in the mid-1960's by modifying Teflon, one of their existing polymer products (Perma Pure LLC., 2011). Nafion® is physically stable between 25 and 125°C, making it ideal for use in low temperature fuel cells (Vielstich et. al, 2004c, p. 647). Nafion® polymer has strong ionic properties which allow it to be used as membranes in fuel cells. Before Nafion® was produced, the membranes used in fuel cells were unstable and had short lifetimes. In a two year testing period conducted by DuPont, Nafion® 120 produced 60 thousand hours of stable operation in a multi-cell stack at temperatures between 43 and 82°C (2004c). Other membrane polymers are incapable of producing such stable performance.

Nafion® is the most widely used electrolyte for DMFCs. The structure for the Nafion® polymer is shown in Figure 3.

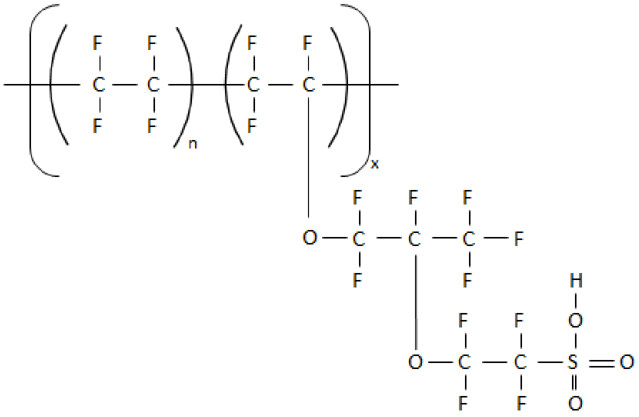

Figure 3: Structure of Nafion® Polymer
(Adapted from Hoogers, 2003, p. 412; O'Hayre et. al, 2009, p. 131)

Sulfonic acid electrolyte groups are attached to a polytetrafluoroethylene (PTFE) backbone with perfluorovinyl ether side chains (Vielstich et. al, 2004d, p. 862). In the presence of water, these dissociate to form the hydronium ions responsible for conduction of protons via Grotthuss and vehicle mechanisms. Nafion's short polymer chains prevent leaching of the sulfonic acid group from the membrane when liquid fuel, such as methanol, is used at relatively low temperatures. The polymer chains are also the reason why Nafion® is so stable; the PTFE backbone does not react in the reducing and oxidizing environments present in a fuel cell (p. 861).

The ability of a membrane to absorb water and acid is important since both are necessary for proton conduction across the membrane. Nafion® 117 absorbs 35 to 40 weight percent of water content after soaking in water at 100°C for one hour. After this treatment, the permeability of the membrane to hydrogen molecules is $4.5\text{x}10^{-5}$(cm^3 cm m^{-2} s kPa), its permeability to oxygen is $2.5\text{x}10^{-5}$(cm^3 cm m^{-2} s kPa), and its resistance to proton conduction is $0.21\Omega\text{cm}^2$ (Vielstich et. al, 2004c, p. 648). This means that protons travel through the membrane easily while hydrogen and oxygen, frequently gas feed fuels, do not. This is critical for proper functioning of a fuel cell because the anode feed (such as hydrogen) should remain at the anode and the cathode feed (such as oxygen or air) should remain at the cathode to perform necessary reactions while protons move through the membrane to keep the reactions going.

In order to enable proton conduction across a Nafion® membrane, it must be “activated” using sulfuric acid to protonate the side chains (personal communication, Matthew Perrone, 2011). Water filled pores within the Nafion® polymer chains are about one nanometer in size and are lined with the sulfonic acid groups and sulfuric acid molecules (O'Hayre et. al, 2009, p.131-132). These pores are occupied by protons in the form of hydronium ions. Individual hydronium ions do not remain in individual pores for long because the hydrophobic PTFE backbone causes the hydronium ions to travel from pore to pore. This moves the protons through the membrane to the cathode. Moreover, Nafion® membranes must be kept well hydrated in fuel cells to encourage proton transport. If the Nafion® membrane becomes dehydrated, protons cannot be conducted because hydronium ions will not be formed via the dissociation of the acid sites.

Nafion® membranes also suffer from lower proton conductivity at temperatures above 100°C because the water in the membrane vaporizes and escapes the pores more easily, which dehydrates the membrane. The membrane itself begins to degrade at temperatures higher than 125°C. Once this temperature is reached, the sulfonic acid group breaks down into SO_x gases and exits to the atmosphere (personal communication, Ravindra Datta, 2011). In addition to temperature constraints of the membrane material, Nafion® membranes should be stored in their shipping package, out of direct sunlight, at temperatures between 10 and 30°C, and relative humidities of 30 to 70 percent. The relative humidity of the surroundings should be at least 30 percent to prevent the membrane from drying out. The relative humidity should not exceed 70 percent because the resulting excess water in the membrane could cause permanent deformations of the membrane structure.

2.2.3.2 PBI

Polybenzimidazole (PBI) doped with Phosphoric Acid (PA) is currently of interest in fuel cell technology as it is capable of being used at higher temperatures than Nafion®. The PBI membrane is known to have excellent thermal, oxidative and hydrolytic stability (Gubler et al., 2007, p. 982). The PBI-PA membrane was developed by Wainright et al., Li et al., and BASF Fuel Cells GmbH (which acquired PEMEAS GmbH) (p. 982). The structure of PBI is shown in Figure 4.

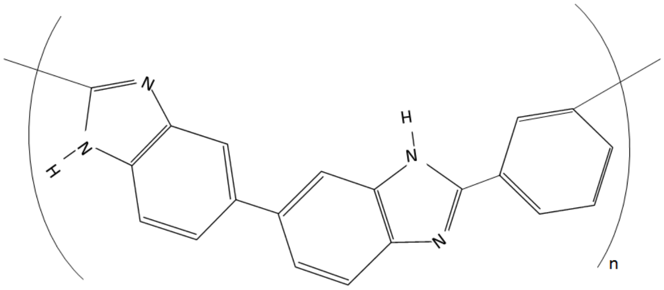

Figure 4: Structure of PBI polymer (adapted from Pabby et al. p.811)

PBI can be treated in several ways to promote proton conduction, the most common being by doping it with phosphoric acid. BASF Fuel Cells currently offers this brand of membrane under their trade name Celtec®-P. However, only two units of phosphoric acid can bind to each repeating unit of PBI and this causes most of the doped acid to become "free acid". This free acid exists between the chains and is therefore susceptible to being leached out of the membrane by liquid water, so the PBI-based fuel cell must be operated at temperatures above 100°C to prevent liquid water from leaching the electrolyte.

These membranes are meant to be used at a range of 100 to 200°C (Modestov et al., 2009). One benefit of running at temperatures in this range is that the Pt catalyst is more resistant to CO poisoning than at lower temperatures so that impure hydrogen can be used as a feed. Proton conduction in phosphoric acid doped PBI occurs through the Grotthus mechanism, which is also known as the “proton hopping” mechanism (Cukierman, 2006). Protons “hop” across the PBI membrane by breaking and forming covalent bonds with water molecules to get from the cathode side to the anode side. Other types of acids, such as hydrochloric or nitric acid, can be used to dope the membrane as well and will show similar properties with association to the proton conduction (Roziere & Jones, 2003). Acid dopings can reach up to 5 mol phosphoric acid per repeating unit of PBI, resulting in higher proton conductivity than that of lower acid doping levels. PBI can also be used as a polymer blend with other types of membranes, such as Nafion®, in order to incorporate the desirable aspects of both membranes into a singular unit.

PBI-based MEAS are currently best suited for stationary power applications due to the amount of time it takes to initialize the cell (Li et al., 2008). Volkswagen considered using a PBI-based PEMFC as an auxiliary power unit to help charge the batteries in their hybrid cars so as to extend the driving range. These cells could use either reformed hydrogen or vapor methanol fuel.

Another type of membrane, Celtec®-V, was produced by BASF until 2008 (personal communication, Emery Dicastro, 2012). This membrane was designed for lower operating temperatures and liquid methanol solutions for a DMFC. Celtec®-V was doped with polyvinylphosphonic acid rather than phosphoric acid. Polyvinylphosphonic acid is useful because PBI secures it inside itself with covalent bonding, cross-linking and interpenetration (Gubler et al., 2007). The polyvinylphosphonic acid electrolyte is more resistant to being leached out by the liquid feed and is therefore capable of operating at temperatures similar to that of Nafion®. However, Celtec®-V was discontinued because the performance was not much better than a Nafion®-based DMFC operating at similar conditions (personal communication, Emery Dicastro, 2012).

2.2.4 Crossover

A common problem in direct methanol fuel cells is methanol crossover. Once methanol has crossed through the membrane to the cathode, both methanol oxidation and oxygen reduction reactions occur at the cathode and prevent the production of useful electrical energy. The permeability of methanol through a membrane is primarily dependent on protonic drag of methanol through the membrane, concentration of methanol in the feed, and operating conditions (Ahmed & Dincer, 2011).

As discussed in Section 2.2.3.1, liquid water is necessary for the conduction of protons through a Nafion® membrane in a fuel cell. Methanol crossover is prevalent in Nafion® membranes because liquid methanol behaves similarly to liquid water (Hoogers, 2003, p. 4-16). This allows methanol to easily cross through Nafion® membranes. Methanol molecules loosely bond to water molecules and are then pulled along when water passes through the membrane during proton transport in addition to transport by ordinary diffusion.

The thickness of a Nafion® membrane in a DMFC has a significant effect on methanol crossover. Typically, an increase in the membrane thickness results in a decrease in crossover (Ahmed & Dincer, 2011, p. 1222). A film that is 5 or 7 mils thick is more commonly used than thinner options. Cho et al. (2009) studied the effect of methanol crossover on the cathode catalyst using a 2 mil thick Nafion® membrane. They used this membrane thickness to ensure that sufficient crossover occurred during their experiments. They knew that there would be enough crossover for their study since thin membranes have less resistance to the natural tendency to reduce the concentration gradient across the cell.

The concentration gradient in the fuel cell is dependent on the feed concentration. Pure oxygen or air is fed to the cathode side and a methanol-water mixture is fed to the anode, producing a concentration gradient across the cell. When first entering the cell at the anode, methanol concentration is relatively high. As methanol travels through the membrane to the cathode or is reacted at the anode, the concentration decreases. A higher concentration of methanol in the feed results in a greater driving force for methanol crossover (Ahmed & Dincer, 2011). Also, as methanol concentration is increased, the permeability of Nafion® to methanol increases. As mentioned in Section 2.2.1, there is an optimum feed concentration range which will provide the fuel cell with relatively high power output and low amount of crossover.

The operating condition that has the greatest effect on methanol crossover is operating temperature. As the temperature increases, the membrane becomes more susceptible to methanol crossover. According to Ahmed and Dincer (2011), this trend is common of all the membrane types they included in their research.

To reduce methanol crossover in direct methanol fuel cells, other membrane films, such as PBI, have been developed and are being tested. While PBI membranes are not completely resistant to methanol crossover, they do not rely on water molecules for proton conduction. Since proton conduction through a PBI membrane does not require the assistance of water molecules, the polymer structure can be such that water and methanol cannot pass through easily. This significantly reduces but does not completely eliminate methanol crossover. More studies must be done to completely evaluate crossover in proton exchange membranes.

2.2.5 Cathode

The overall Oxygen Reduction Reaction (ORR) at the cathode is:

$$\frac{1}{2}\mathrm{O_2} + 2\mathrm{H^+} + 2\mathrm{e^-} \rightarrow \mathrm{H_2O}$$

On the cathode side of the membrane, the protons and electrons are brought into contact with oxygen in the presence of a catalyst, such as platinum. The catalyst is necessary to enhance the activity of the ORR, which is a sluggish reaction and involves a complex mechanism (personal communication, Ravindra

Datta, 2012). As a result, the catalyst loading at the cathode needs to be higher than the loading at the anode. The high catalyst loading requirement for platinum in the cathode (of both hydrogen and methanol fuel cells) is a barrier to large scale production due to the high cost of platinum. Research is being done to optimize the size and distribution of platinum particles in cathodes to reduce costs. Some studies have shown that the optimum particle size is 2 or 3 nm (O'Hayre et. al, 2009, p. 300). Smaller particles showed reduced performance of the catalyst layer.

In an effort to improve the performance of the cathode, platinum alloys and activated carbon supports have been investigated. Cho et al. (2008) studied various methanol concentrations using different catalyst loadings at the cathode. They concluded that at low methanol concentrations it was appropriate to use platinum black on the cathode, whereas at higher methanol concentrations it was more appropriate to use a platinum catalyst supported by carbon. In 2010, Wang et al. performed a study of the effect of various carbon supports on the performance of platinum catalyst at the cathode. They concluded that the use of Vulcan XC-72R caused a slight decrease in performance. This was due to the low surface area of the support reducing the utilization of the catalyst. The other two carbon supports tested, Ketjen Black EC 300J and Black Pearls 2000, resulted in an improvement in performance. This was because both supports had a high surface area and so increased the utilization of the catalyst.

Cathode catalysts are also subject to degradation. Liu et al. (2009) reported that the degradation of the cathode catalyst was a result of several factors: platinum dissolution, the non-ideal contact between the electrode and the membrane, and crossover of methanol and ruthenium from the anode. The MEAs Liu et al. (2009) tested were not subjected to a hot press in order to investigate the effect of mass transfer through the interface. Therefore, the contact between the electrodes and the membrane was not optimal. One result of their study was the conclusion that at high cathode potentials in an oxygen rich environment, platinum catalyst particles dissolve and deposit elsewhere in the layer, reducing the useful area of platinum catalyst (p. 6180).

One way to reduce or prevent this migration of platinum catalyst at the cathode is to alloy it with another metal. Yu et al. (2005) reported that adding cobalt to the cathode catalyst layer significantly reduces the performance loss due to platinum migration at the cathode. Other studies reported that platinum catalyst was more stable when mixed with another metal. In one of these studies, Colón-Mercado and Popov (2006) conclude that, while using an alloy at the cathode increases stability of the catalyst, dissolution and redistribution of the other metal may result in additional causes for MEA deterioration over long periods of time.

As mentioned in section 2.2.4, methanol crossover is a frequent problem in DMFCs. If the fuel cell were an ideal system, the formation of water would be the only reaction at the cathode. However, when methanol fuel passes through the membrane, it undergoes Methanol Oxidation Reaction (MOR) on the cathode side. In addition, there is an ORR at the cathode, so that the overall reaction is:

$$\mathrm{CH_3OH} + \frac{3}{2}\mathrm{O_2} \rightarrow \mathrm{CO_2} + 2\mathrm{H_2O}$$

While this reaction produces the same products as the fuel cell as a whole, the energy released is as heat and not electricity.

2.2.6 Typical Performance

There are several parameters that have influence over the performance of a DMFC, namely the operating temperature, the flow rate of methanol to the anode, the methanol feed concentration, and the pressure of oxygen (or air) on the cathode side.

Performance of a Nafion®-based DMFC can be influenced by the operating temperature of the cell. Jung et. al (2005) found that with 1M methanol feed, increasing the cell temperature from 50°C to 80°C also increased the maximum current density that the cell was able to achieve. In addition to temperature, they found that the performance of the cell also varied with the methanol feed concentration. In Jung et. al's research, higher concentrations demonstrated better performance at lower temperatures since the effect of crossover increased with temperature. For example, at an operating temperature of 50^{o}C a 3M methanol concentration showed the best performance, while at 80°C, a 1M methanol feed showed the best performance.

Another parameter that has a direct effect on the performance of a Nafion®-based DMFC is the flow rate at the anode. In a recent study, the current densities of a Nafion® 117 membrane-based MEA (operating at 70^{o}C and using a feed concentration of 1M MeOH) increased as the flow rate went from 0.5 mL/min to 5.0 mL/min; flow rates higher than 7.0 mL/min showed no noticeable increase in performance (Ge & Liu, 2004). Increasing the flow rate of oxygen at the cathode also caused the performance of the cell to increase. However, the increased performance also capped at an oxygen flow rate of 1600 sccm. An oxygen flow rate of 1600 sccm was able to achieve a maximum current density of 0.48 A/cm^2, while an oxygen flow rate of 2000 sccm had a maximum current density of 0.5 A/cm^2.

Increasing the partial pressure of oxygen at the cathode also shows a direct relationship with the performance of a Nafion®-based MEA. Scott et. al (1998) conducted a Nafion®-based DMFC test at 80^{o}C with 1M methanol feed and cathode feed pressures of 0 barg (e.g. atmospheric pressure), 1 barg and 2 barg. With increased oxygen feed pressure, the cell was able to achieve higher voltages and current densities. The researchers theorized that the increased partial pressure of the oxygen reduced the methanol crossover in the cell, thereby increasing the performance with increasing pressure.

For a PBI-based MEA using atmospheric oxygen at the cathode and a water to methanol mole ratio of 2:1, Wang et. al. (1995) experimented with a variation in temperature from 150 to 200°C. The cell performance increased with temperature, demonstrating an increase of open circuit voltage (OCV) from 0.67V to 0.71V at 150°C and 200°C, respectively. Lobato et. al (2008) also worked with a PBI-based DMFC and studied its performance at operating temperatures between 125°C and 200°C and with a methanol to water feed ratio of 0.5:1 and a pure oxygen feed. These tests also showed a positive correlation between increasing the temperature of the cell and the performance of the cell. This trend is the similar to that of Nafion®-based MEAs, where increasing operating temperature also increased overall cell performance.

A similar trend was found when the methanol to water mole ratio was decreased (e.g. decreasing the methanol feed concentration). In the tests conducted by Wang et al. (1995), as the methanol to water ratio decreased from 1:1 to 0.25:1, the performance consequently increased due to lower cell resistance from lower crossover rates and better anode performance. Justo et al. (2008) also ran similar tests, but at 175°C and with a pure oxygen feed and at varying methanol to water mole ratios. The ratios used were 0.25:1, 0.5:1, 1:1 and 2:1 for these tests. The data showed an increase in performance from as the methanol concentration increased (from 0.25:1 to 0.5:1). However, increasing the concentration of the feed caused the cell performance to decrease. The initial increase in methanol feed concentration increases the cell performance up to a certain concentration, at which point methanol crossover becomes more prevalent and causes the cell performance to decrease.

PBI-based MEA performance is also dependent on the oxygen partial pressure in the cathode feed. Lobato et al. (2008) compared the effects of using air at the cathode instead of pure oxygen as well as the effect of oxygen feed pressure on the DMFC performance. Their fuel cell operated at 175°C with a methanol to water ratio of 0.5:1 and with varying air and oxygen feed pressures. In comparison to using air, the use of a pure oxygen feed resulted in higher current densities at each voltage due to the higher concentration of oxygen molecules being provided to the cathode. Nafion®-based DMFCs show similar trends (in terms of oxygen feed pressure) where increasing the pressure of the cathode feed increases the performance of the cell.

Chapter 3: Methodology

For this study, commercially available Membrane Electrode Assemblies (MEAs) were tested under various conditions using methanol feed. The first tests were conducted using MEAs based on Nafion® 117 membranes. After these tests were completed, MEAs with polybenzimidazole (PBI) – phosphoric acid (PA) membranes were tested. All data was collected by defining the load (current) applied to the cell and recording the corresponding voltage. At least three data sets were collected for each temperature/concentration pair and averaged to produce one curve on a graph.

3.1 Apparatus

The Nafion® 117-based MEAs and PBI-based MEAs needed to be tested in different assemblies due to different active area sizes. As an example, an exploded view of the Nafion®-based DMFC assembly is shown in Figure 5. A detailed explanation of how to put together a fuel cell assembly can be found in Appendix C.

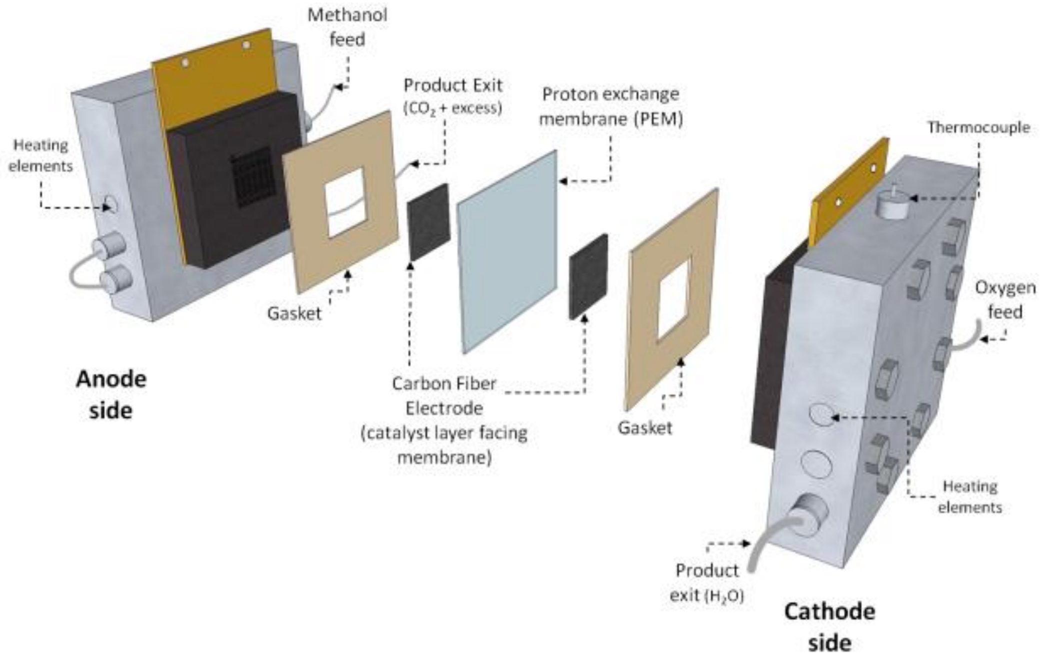

Figure 5: Fuel Cell Assembly Design

End plates are located at either end of the fuel assembly. Both plates are attached to current collectors, which are attached to graphite blocks. The current collectors have holes at the top which facilitate the attachment of leads, attaching the fuel cell to the load box. The anode side aluminum plate has a methanol inlet feed and a waste stream for the CO_2 and excess feed. The methanol feed flows to the cell from an external syringe pump and the waste stream empties into a collection beaker. The cathode side aluminum plate has an inlet for the oxygen feed and an outlet for the water product and excess oxygen. As shown in Figure 5, a thermocouple connection is located at the top of the cathode plate and both plates have an opening on one side in which a heating element is inserted. The heating elements are used to heat the fuel cell to a desired temperature while the thermocouple provides feedback to the temperature controller to ensure the cell does not overheat excessively.

The graphite blocks each have a serpentine flow channel. The flow channels allow the methanol and oxygen feed to distribute evenly in their respective carbon fiber electrodes. Gaskets lie on top of the graphite blocks. The outside edges of these gaskets are the same size as the graphite block, and there are squares cut from the center that are an appropriate size in relation to the carbon fiber electrodes. For the Nafion® 117-based MEAs the inner square was the same size as the electrodes, while the PBI-based MEAs required a small gap on each side of the electrode to prevent negative effects of over compression. The use of gaskets evenly distributes pressure across the MEA. The MEA consists of two carbon fiber electrodes and the Proton Exchange Membrane (PEM). The PEM is usually hot-pressed to the electrodes prior to use in the cell. The electrodes are about the same size as or slightly larger than the flow channels and the PEM is the same size as the graphite blocks. The gaskets should fit around the electrodes and cover the exposed PEM completely to ensure there will be even pressure applied to the membrane and to prevent fuel from crossing through the membrane before it comes into contact with the anode electrode. The fuel cell is secured with eight lag bolts (only heads shown in Figure 5) from the cathode side to the anode side. The bolts do not come in contact with any part of the assembly except the end plates and are secured at the anode side plate.

The fuel cell assembly used to test the Nafion® 117-based MEAs can be seen in Figure 6.

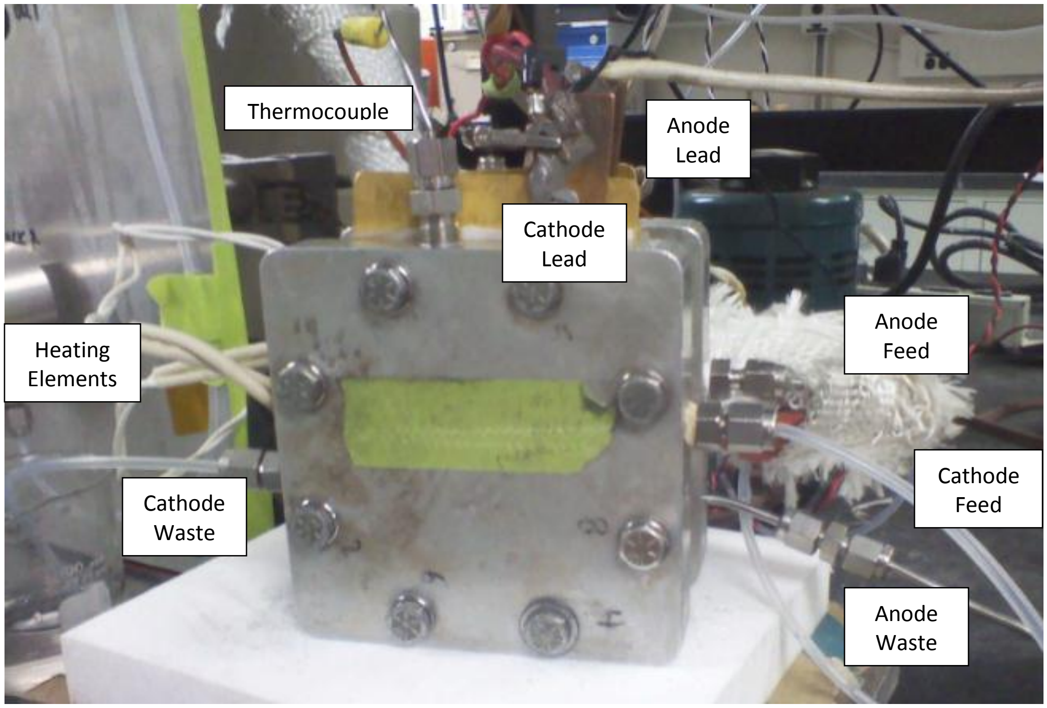

Figure 6: Fuel cell assembly used to text 5 cm^2 Nafion® 117 based MEAs

For this assembly, the cathode feed (usually oxygen) stream connects to the cell on the right (with the cathode side facing you) and the waste stream connects on the left side of the cathode side end plate. The anode feed and waste streams both connect to the cell on the right side of the anode side end plate. One heating element is inserted in each end plate on the left side, and a thermocouple is inserted on the top of the cathode side end plate. The red (positive) lead is attached to the cathode side current collector and the black (negative) lead is attached to the anode side current collector. This assembly is designed for use with MEAs that have an active area of 5 cm^2.

The fuel cell assembly used to test the PBI-based MEAs can be seen in Figure 7.

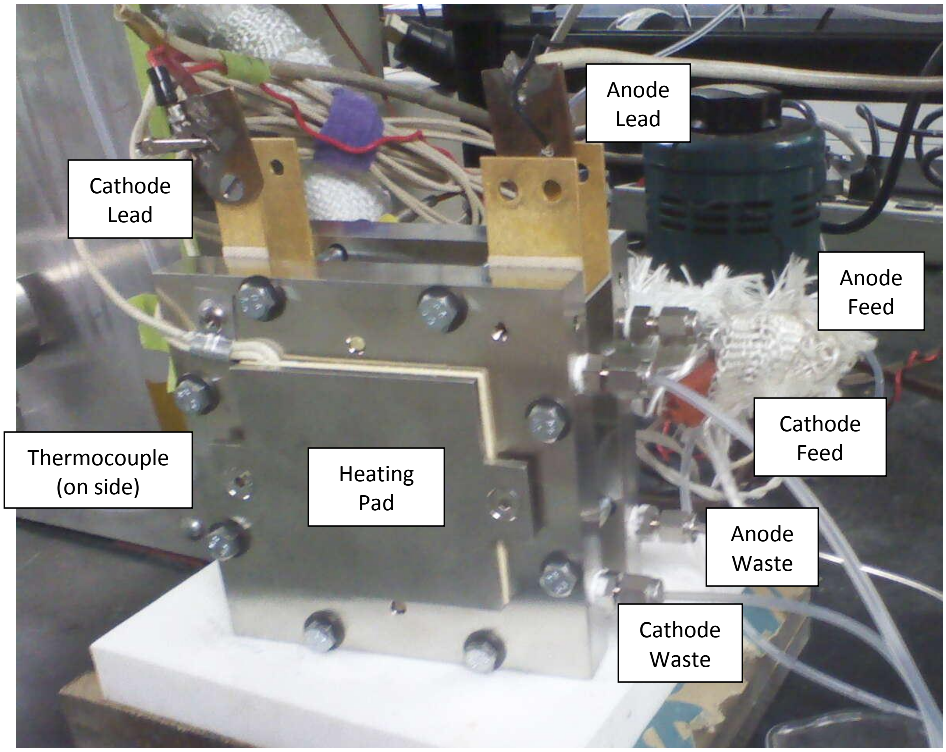

Figure 7: Fuel cell assembly used to test 50 cm^2 PBI based MEAs

For this assembly, all feed and waste streams connect on the right (with the cathode side facing you). The feed lines connect at the top and the waste streams connect at the bottom. There is a heating pad attached to the outside of each end plate, and a thermocouple is inserted in the side of either graphite block. The red (positive) lead is attached to the cathode side current collector and the black (negative) lead is attached to the anode side current collector. This assembly is designed for use with MEAs that have an active area of 50 cm^2.

The same test station was used regardless of the DMFC assembly attached. The test station can be seen as a schematic in Figure 8 and a photograph in Figure 9.

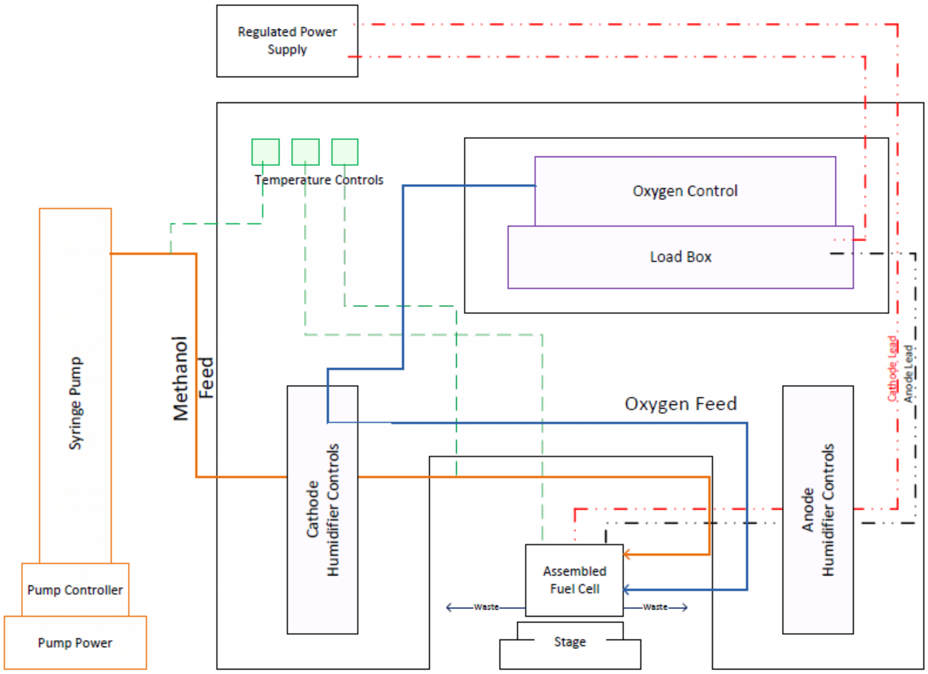

Figure 8: Fuel cell test station schematic

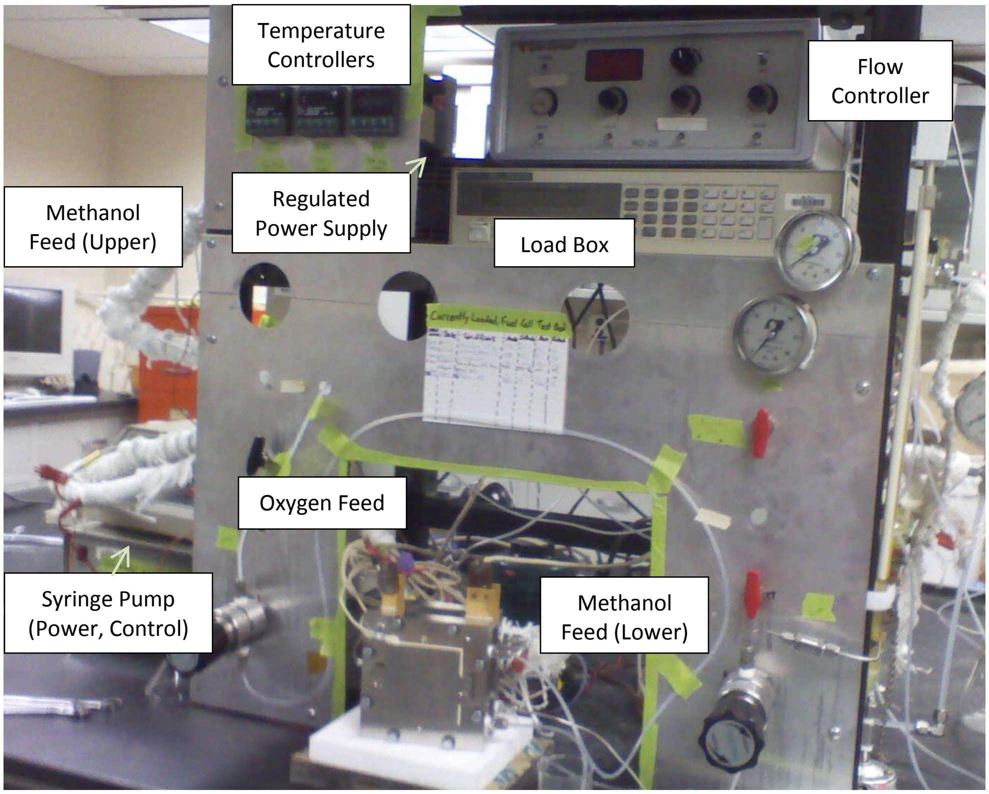

Figure 9: Fuel cell test station photograph, PBI assembly attached

The major equipment in the test station consisted of a syringe pump (ISCO, Model 1000D), the syringe pump controller (ISCO, Series D Pump Controller), a flow controller (Tylan General, RO-28), a load box (Hewlett Packard 6060B), a regulated power supply (Lambda Electronics, Inc., LFS-46-5), and temperature controllers (Omega CN9000A). The syringe pump is used to feed methanol to the cell and is controlled using the pump controller. It can hold about 1L of methanol. When in use, the syringe pump forces methanol through the feed line and into the cell. The temperature at the upper section of the methanol feed line is controlled using the leftmost temperature controller and the temperature of the lower section of that line is controlled using the rightmost temperature controller. The middle temperature controller regulates the temperature of the fuel cell assembly.

The flow controller can be used to regulate the flow of oxygen (valve 1), hydrogen (valve 2), or nitrogen (valves 1 and 2). The flow through the flow controller was frequently measured to be essentially atmospheric. When a gas feed needed to be pressurized or the flow rate exceeded the maximum of the controller, it was sent through a bypass instead.

The load box was used in conjunction with the regulated power supply to collect data. The anode lead is connected directly to the load box. The cathode lead is connected directly to the regulated power supply, which in turn is connected to the load box. It is possible to pull small current densities from the cell if the regulated power supply is off, but there is a point at which the load box cannot pull more current without the regulated power supply active. Data was collected galvanostatically, setting the current and recording the corresponding voltage. The first data set was taken after 30 minutes at Open Circuit Voltage (OCV). Subsequent data sets were collected after the cell was subjected to a low current for 55 minutes followed by 5 minutes at OCV. The small current was applied because it is not good practice to leave a fuel cell at OCV for long periods of time, and the short OCV period was introduced so that we would be sure that performance was not dependent on the small current applied between tests. Detailed instructions for use of the test station and equipment can be found in Appendix D.

3.2 Nafion® 117-Based MEAs

The Nafion® 117-based MEAs used in this series of experiments were obtained through ECOtality's Fuel Cell Store's website (fuelcellstore.com). For each MEA, the electrodes were 2.3 cm long by 2.3 cm wide, with an active area of 5 cm^2, and the membrane was 5.5 cm long by 5.5 cm wide. The anode electrode had a catalyst loading of 4.0 mg/cm Pt-Ru (platinum-ruthenium) and the cathode electrode had a catalyst loading of 2.0 mg/cm Pt. The bolts that secured the assembly were tightened to a torque of 65 lb_f-in. Detailed instructions for putting together the assembly can be found in Appendix C. A picture of one of these MEA types is shown in Figure 10.

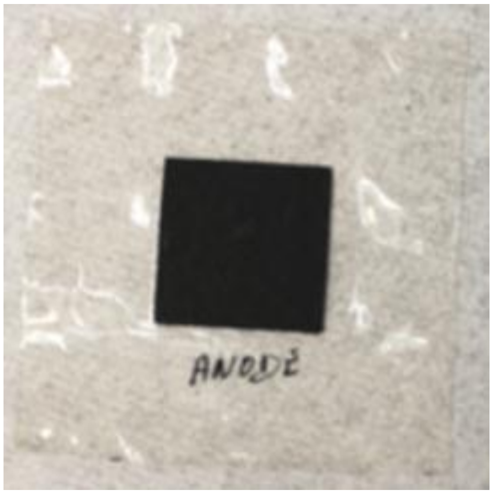

Figure 10: Nafion®-117-based MEA before first test, anode side up

3.2.1 Activation

Prior to testing, the MEAs were activated to provide more stable performance. The cell was assembled (see Appendix C) and heated to 60°C. A 0.5M methanol feed at 1.5 mL/min was fed to the anode while oxygen through the flow controller was fed to the cathode. The cell was allowed to sit at

OCV for half an hour. After this initial half hour, the voltage of the cell was set using the load box. The designated voltage was decreased in increments of 0.05V every fifteen minutes until the voltage reached 0.1V. Once at this point, the cell was subjected to a constant current (to maintain the set voltage) for four hours. At the end of this four hour period, the cell was returned to OCV and kept there for another half an hour.

3.2.2 Testing

The Nafion® based MEAs used for this study were subjected to methanol concentrations of 1, 2.5, and 4M methanol feed and temperatures of 20, 40, 60, 70, and 80°C. The methanol feed rate for all tests was 1.5 mL/min. The tests were organized by using a given methanol concentration with increasing operating temperature until every temperature was studied for that concentration. Upon the completion of the first set of tests, 1M methanol feed at each of the temperatures, it was noticed that the performance at 70 and 80°C was worse than that at 60°C. It was determined that this was probably due to a relatively low partial pressure of oxygen at the cathode by virtue of increasing vapor pressure of water. This resulted in an investigation of the effect of oxygen pressure at the cathode at 70°C with 1M feed to the anode. An optimum pressure was determined for these conditions and consequently used for tests at 70 and 80°C for each concentration. The tests at 20, 40, and 60°C for 2.5 and 4M feeds were conducted using oxygen fed through the flow controller at essentially atmospheric pressure and about 47.7 mL/min.

3.3 PBI-Based MEAs

The PBI based MEAs used in this series of experiments were commercially available Celtec®-P 1000 MEAs, intended for use with hydrogen or reformate. They were obtained from BASF (basf.com). For each MEA, the electrodes were 7.2 cm long by 7.2 cm wide, with an active area of 50 cm^2, and the membrane was about 100 cm long by 100 cm wide. According to representatives from BASF, the overall catalyst loading for a Celtec®-P 1000 MEA is 1.8 mg Pt/cm^2, but the individual anode and cathode loadings are proprietary. However, in an article published in the Journal of Power Sources, Schmidt and Baurmeister (2008) reported: “The cathode contains a Vulcan XC 72 supported Pt-alloy with 0.75 mg Pt/cm^2. The anode contains a Vulcan XC 72 supported Pt catalyst with 1 mg Pt/cm^2.” The bolts that secured the assembly were tightened to a torque of 62 lb$_f$-in. Detailed instructions for putting together the assembly can be found in Appendix C. A picture of one of the PBI-based MEA types is shown in Figure 11.

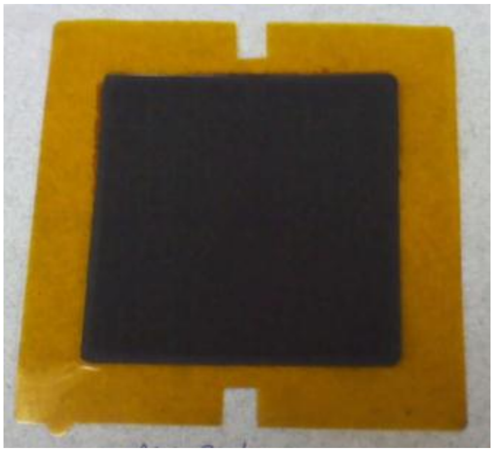

Figure 11: PBI based MEA before first test, anode side up

3.3.1 Activation

The Celtec®-P 1000 MEAs used in this study were activated using a modified version of the [confidential] instructions provided by BASF. For unknown reasons, the given stoichiometric values and flow rates would not allow the required current density to be applied. It was decided that applying the designated current density was more important than having the same flow rates, so the flow rates of hydrogen and oxygen were increased until the required current density could be supported. The first MEA used was activated for the entire lower limit of the activation time frame supplied. During this time, the performance only changed for the first fifth of the activation time. This MEA was, however, unintentionally subjected to liquid methanol, which promptly leached out the PA electrolyte. Thus, another MEA was activated under the same conditions as the first, but the activation time was shortened to half of the activation time of the first one because the same trend in performance change was noted.

3.3.2 Testing

The PBI based MEAs in this study were initially going to be subjected to methanol concentrations of 1, 3, 5, and 10M and temperatures of 160, 170, and 180°C. The methanol feed was vaporized before being introduced to the cell. The methanol feed line initially was not capable of vaporizing the feed, so modifications were made. The length of the methanol feed line was increased and another section of heating tape was introduced to heat the new tubing. It was possible to vaporize the feed by setting the two different sections of heating tape on the feed line to different temperatures. The upper section of heating tape (closer to the pump) was heated to 20 degrees above than the lower section (closer to the cell), which was set to the same temperature as the cell. For example, when running the cell at 160°C, the upper section of heating tape was set to 180°C and the lower section to 160°C.

Unfortunately, when a test using 1M methanol was attempted, the voltages corresponding to set currents fluctuated wildly. It was determined that 1M methanol did not contain enough methanol molecules at flow rates the test station was capable of providing to steadily support specified loads. This concentration was subsequently removed from the test schedule in the interest of not starving the cell. The remaining tests were conducted as planned, using the same methanol concentration with increasing operating temperature until every temperature was studied for a given concentration. The methanol flow rate for these tests was 1.0 mL/min. Due to time constraints, an optimum cathode oxygen pressure was not investigated. Oxygen was fed to the cathode through the flow controller at about 47.7 mL/min, the same flow as the Nafion® tests between 20 and 60°C.

Chapter 4: Results and Discussion

In this chapter, results for the Nafion®117-based Membrane Electrode Assembly (MEA) and the PBI-based MEA are analyzed. The performance for each type of Direct Methanol Fuel Cell (DMFC) is shown as polarization curves for voltage and power density. The voltage polarization curves represent the actual voltage the cell produces at a given current density. The power density polarization curves show the optimum current density at which the cell delivers the best performance.

4.1 Nafion® 117-Based MEA

DMFC testing began with the Nafion®-based MEA. Over the course of experimenting, we encountered a number of problems that needed to be addressed, namely adjusting the oxygen feed pressure. The following section highlights the initial tests using the Nafion®-based MEA, the pressure study conducted for 70°C operation with 1M methanol feed to determine a suitable oxygen feed pressure, and the final results which include the performances with pressurized oxygen feed for the higher temperatures.

4.1.1 Initial Tests with 1M

The first set of experiments at various temperatures with 1M methanol feed using a Nafion® 117-based MEA was completed using an oxygen feed through the flow controller at atmospheric pressure. The resulting voltage and power density polarization plots are shown in Figure 12.

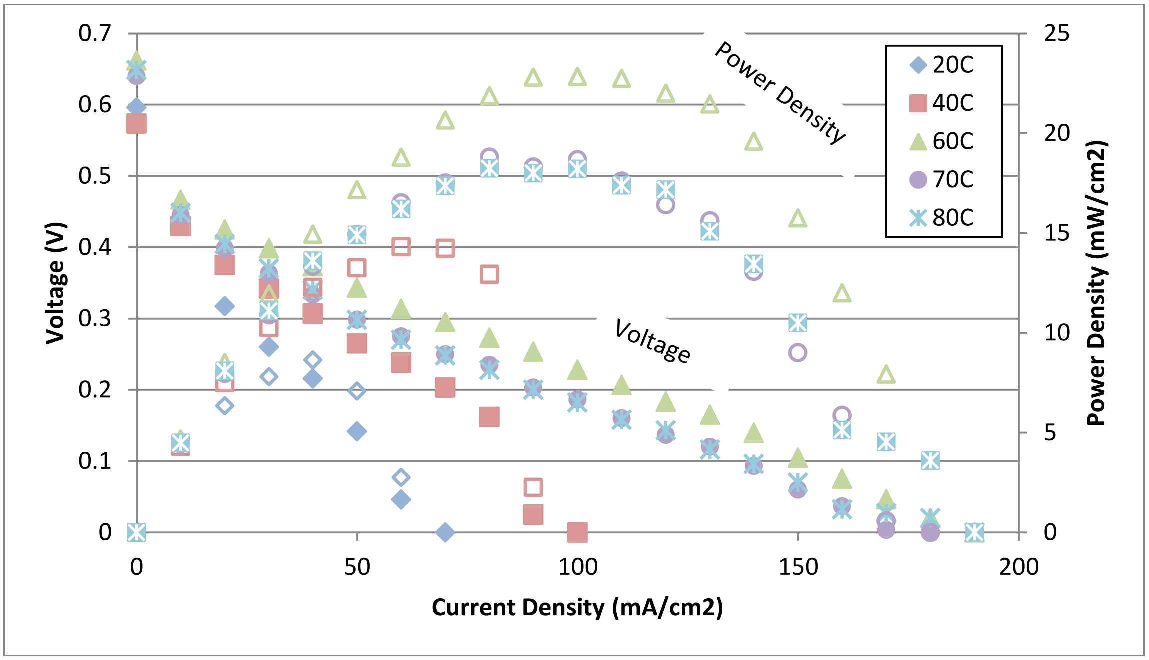

Figure 12: Variation of temperature for Nafion® 117-based MEA with 1M methanol feed and atmospheric oxygen feed (initial results)

From 20 to 60°C, the performance of the DMFC increased with temperature. This was expected because increasing the operating temperature improves the kinetics of the oxidation of methanol at the anode and that of the oxygen reduction reaction at the cathode. However, at 70°C and 80°C, the DMFC showed a decrease in performance. Moreover, 70°C and 80°C have approximately the same trend. This decrease was possibly caused by a low partial pressure of oxygen at the cathode as the vapor pressure of water increases with temperature. The following section is a study on how pressure thus affected the performance of the Nafion® 117-based MEA with 1M methanol feed and at an operating temperature of 70°C.

4.1.2 Pressure Study with 1M Feed at 70°C

It was reasoned that with an increase in operating temperature, the DMFC usually experiences decreased oxygen partial pressure at the cathode as well as increased oxygen crossover (Broka & Ekdunge, 1996). As a result, the cathode potential of the cell decreases, reducing the overall cell performance. As seen from the initial experiments with the Nafion® 117-based MEA highlighted in section 4.1.1, the fuel cell experienced a significant decrease in performance above 60°C. The operation at 60°C was determined to not need an increase in oxygen pressure at the cathode as the fuel cell yielded a lower performance with 5.5psig of pressure than with standard pressure; the maximum current density was reduced by about 120 mA/cm^2. As a result, changes to the cathode oxygen pressure were only applied at operations at 70 and 80°C.

The effect of cathode pressure on DMFC performance was studied using 1M methanol feed at an operating temperature of 70°C. Since the oxygen flowing from the mass flow controller enters the cell at standard pressure, the oxygen pressures tested ranged from 2.5 to 10psig. The voltage polarization curves at every pressure tested are shown in Figure 13.

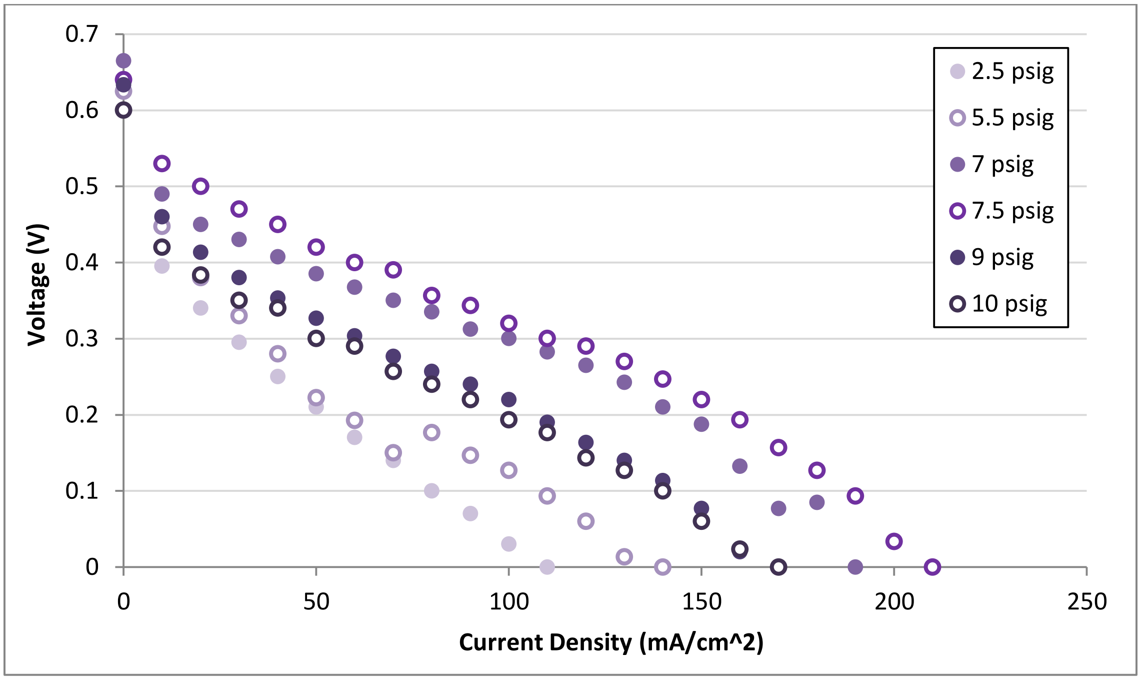

Figure 13: Variation of oxygen feed pressures for Nafion® 117-based MEA with 1M methanol feed at 70°C

As seen in Figure 13, it was found that the performance increased with increasing pressure to a certain extent. The best performance was achieved with a cathode pressure of 7.5psig. Higher oxygen pressures, such as 9 and 10psig, showed decreased performance and had a voltage polarization curve similar to the DMFC with oxygen flowing in at standard pressure. The reasons for this trend are not entirely clear. Due to the altered water content and the hydration level of the membrane, we suspected that the effect of pressure includes a balance of the increase of the oxygen partial pressure and the permeation through the gas diffusion layer. Based on these results, a cathode pressure of 7.5psig was used for Nafion® tests at 70 and 80°C. We recognize that a similar study of cathode pressures should have been performed for operation at 80°C and at other methanol feed concentrations. However, due to time constraints, an oxygen pressure of 7.5psig was assumed to be ideal for both 70 and 80°C at all methanol concentrations for the Nafion® tests.

4.1.3 Final Results

With the establishment of a cathode oxygen pressure at temperatures above 60°C, we were able to complete the series of Nafion® 117-based MEA tests. All of the data collected for operation temperatures between 20 and 60°C were with oxygen flowing into the fuel cell at standard pressure; the data for 70 and 80°C were with a cathode oxygen pressure of 7.5psig. This section discusses the results of the experiments as they vary by operating temperature and by methanol feed concentration.

4.1.3.1 Effect of Temperature on Performance

The performance curves generated using 1 and 2.5M methanol feed at various temperatures are shown in Figure 14 and Figure 15, respectively.

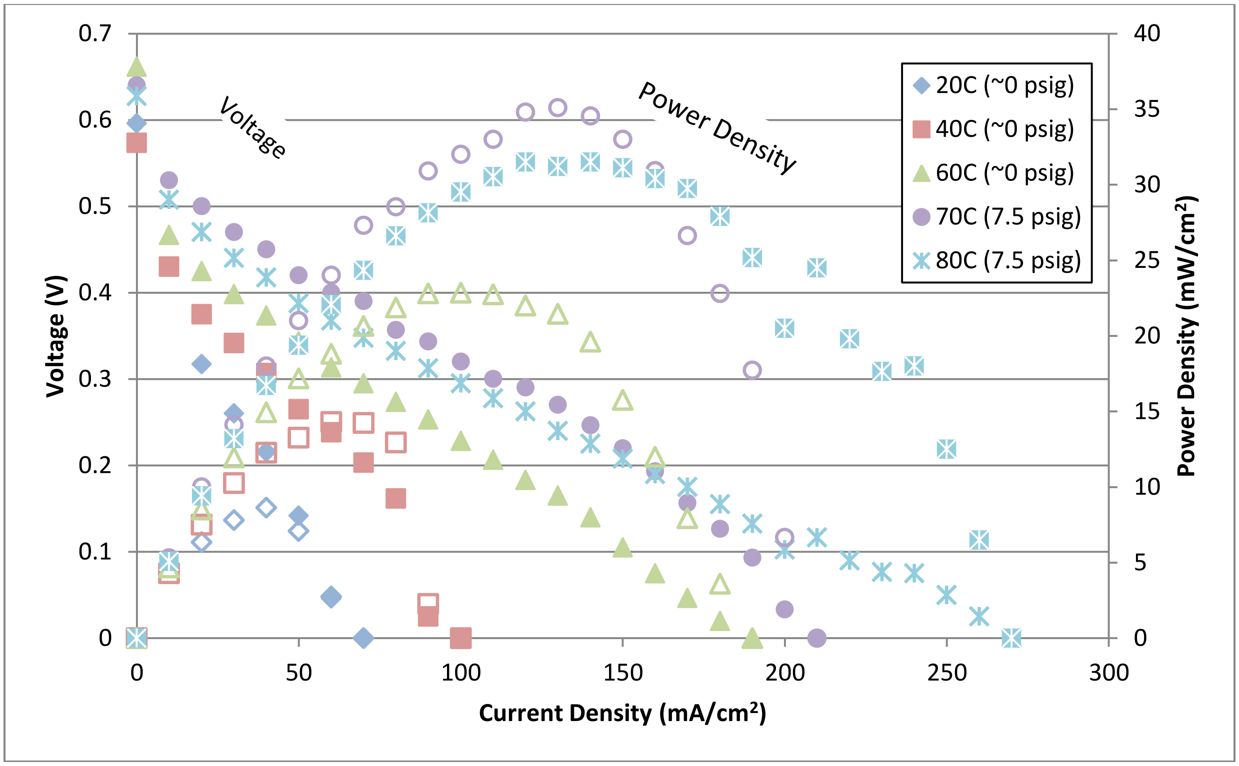

Figure 14: Variation of temperature for Nafion® 117-based MEA with 1M methanol feed; 20-60°C uses atmospheric oxygen feed, 70 and 80°C uses 7.5psig of oxygen feed

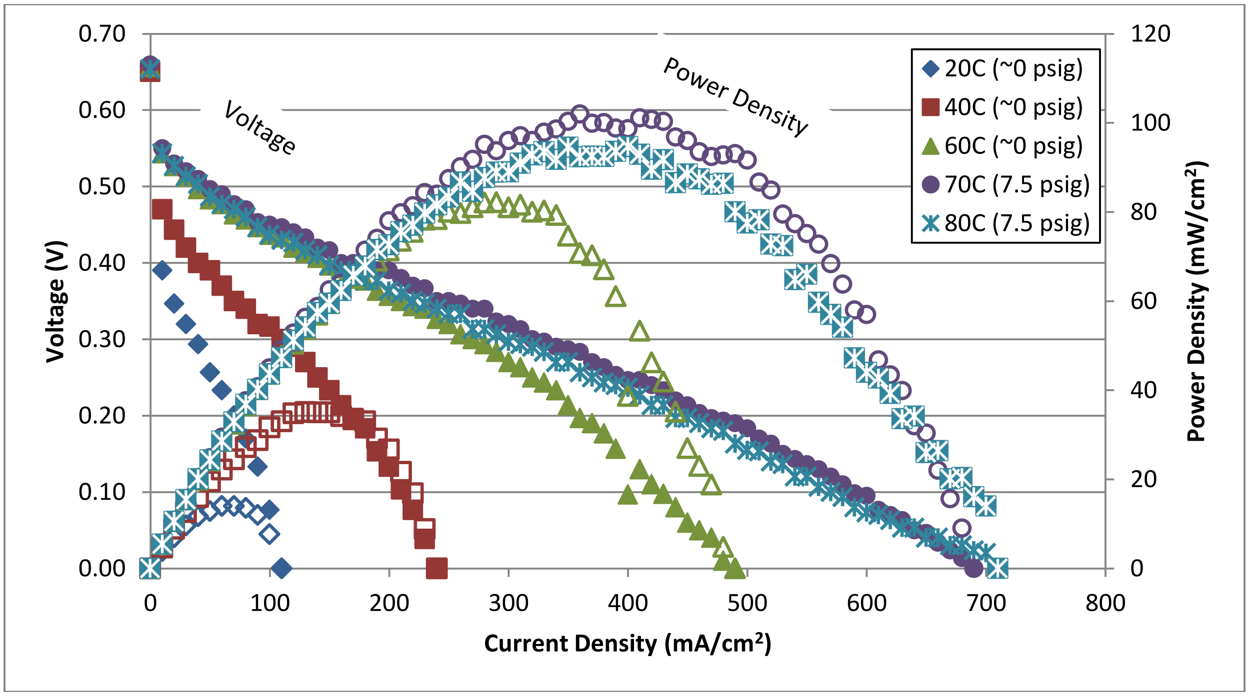

Figure 15: Variation of temperature for Nafion® 117-based MEA with 2.5M methanol feed; 20-60°C uses atmospheric oxygen feed, 70 and 80°C uses 7.5psig of oxygen feed

With the adjustments made in cathode pressure for 70°C and 80°C, the overall trend of these performance curves for 1M and for 2.5M is close to our anticipated results since the anode potential and the proton conductivity of the membrane both increase with temperature. The DMFC showed an increase in maximum current densities from 1M feed to 2.5M feed, although the voltage at lower current densities was lower at higher concentrations. A higher concentration of methanol in the feed allows for more methanol molecules to undergo oxidation and therefore produce a higher current density at lower voltages.

At higher current densities for both concentrations, performance loss is dominated by mass transport limitations. Since proton conductivity increases with temperature, it is unsurprising that the DMFC can achieve higher current densities at 80°C than 70°C. However, in general, the DMFC operating at 70°C outperformed the operation at 80°C. There are a few possible reasons for this. One probable reason is that Nafion® experiences a greater susceptibility to methanol crossover at higher temperatures. An increase in methanol crossover from the anode to the cathode results in poorer performance as methanol has the opportunity to oxidize at the cathode catalyst. Additionally, a decrease in performance may be a direct result of the oxygen feed pressure that was adequate for 70°C and not for 80°C.

The performance of Nafion® 117-based MEA with 4M methanol feed was found to be significantly different from that of 1 and 2.5M feed. The voltage and power density polarization curves for operation with 4M methanol feed are shown in Figure 16.

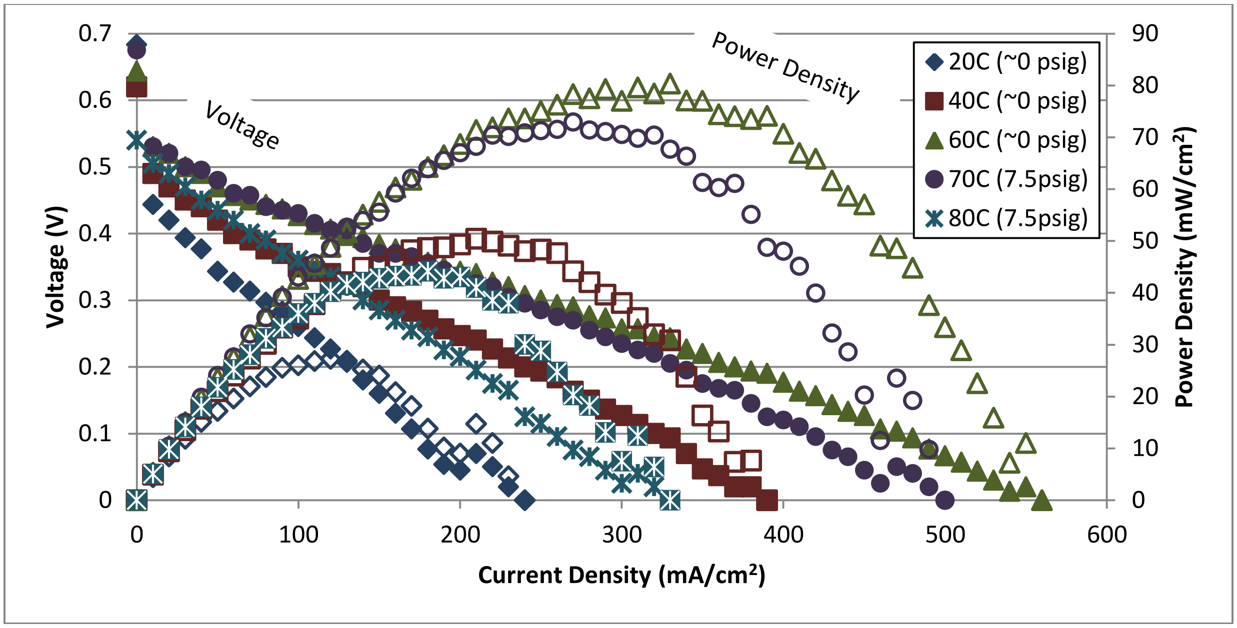

Figure 16: Variation of temperature for Nafion® 117-based MEA with 4M methanol feed; 20-60°C uses atmospheric oxygen feed, 70 and 80°C uses 7.5psig of oxygen feed

The overall trend of the performance curves generated between 20 and 60°C is similar to trends seen for 1 and 2.5M, although it achieves higher current densities. The significant decrease in performance from 60 to 70°C and from 70 to 80°C was unexpected. Part of this performance decrease can be attributed to lowered oxygen partial pressure. A higher oxygen feed pressure may have given improved results for the Nafion® 117-based MEA with 4M methanol feed. Unfortunately, this could not be investigated further due to time constraints. In this vein, however, increased methanol crossover at higher temperatures seemed to have contributed dominantly to the reduced performance. Nafion® membranes are more susceptible to methanol crossover at higher temperatures and higher concentrations of methanol produce larger gradients across the MEA. Since the performance curves of 70 and 80°C are notably different, it is likely that methanol crossover contributed more to the reduced performance in the 4M methanol tests than the effect of reduced oxygen partial pressure.

4.1.3.2 Effect of Methanol Feed Concentration on Performance

In addition to studying the effect of temperature on DMFC performance, it is important to also analyze the effect of methanol concentration at a given temperature. The performance curves for various methanol concentrations at 20 and 40°C are shown in Figure 17 and Figure 18, respectively.

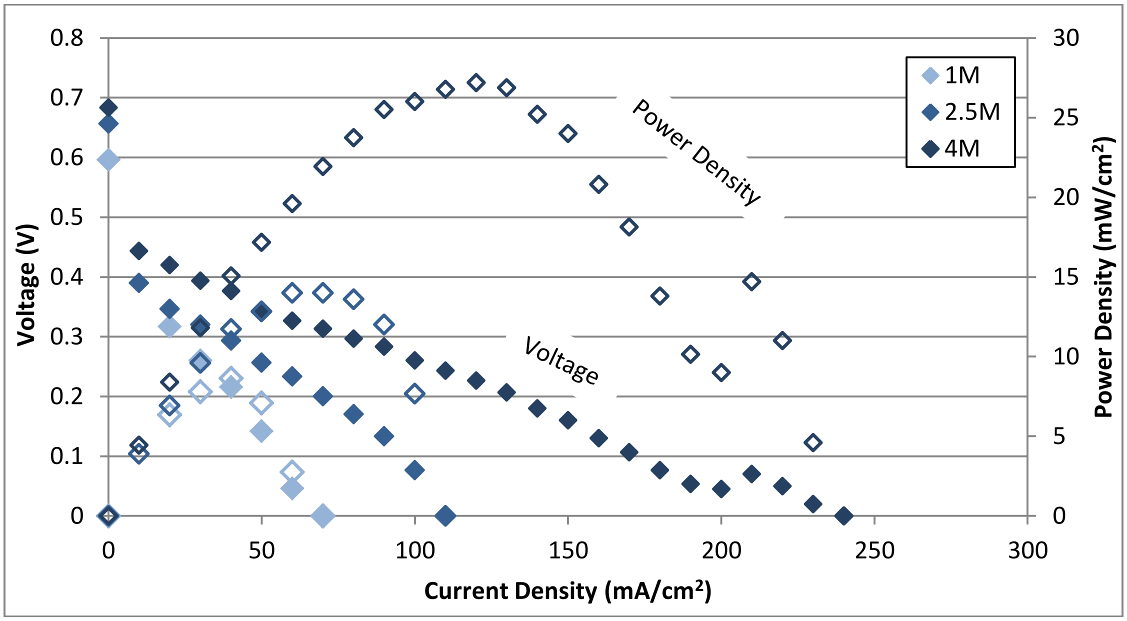

Figure 17: Variation of concentration for Nafion® 117-based MEA at 20°C and with atmospheric oxygen feed

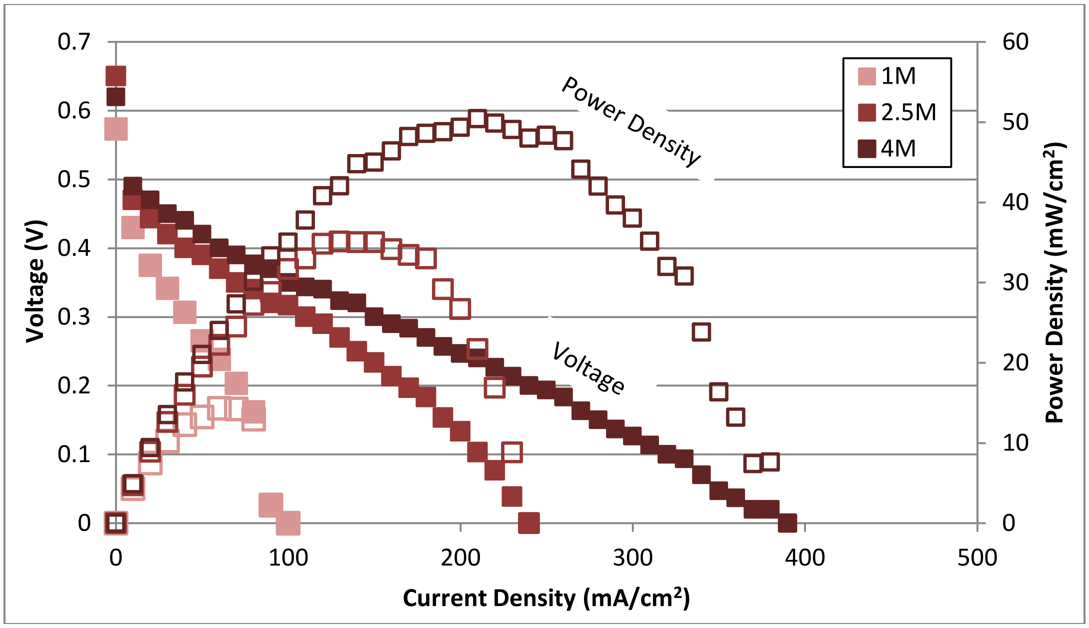

Figure 18: Variation of concentration for Nafion® 117-based MEA at 40°C and with atmospheric oxygen feed

The DMFC operating at 40°C showed consistently better performance than that at 20°C for a given methanol concentration. However, the 4M feed at 20°C was able to support relatively high current densities, with its maximum current density being similar to the fuel cell operating at 40°C with 2.5M feed. The effect of methanol crossover does not appear to have a significantly detrimental effect on performance at 20 or 40°C at the concentrations studied here.

While the DMFC operating with 4M methanol feed at 60°C was able to achieve higher current densities, its power output was lower than anticipated based on the concentration trends observed at 20 and 40°C. Figure 19 shows the variation of concentration for the Nafion® 117-based MEA at 60°C.

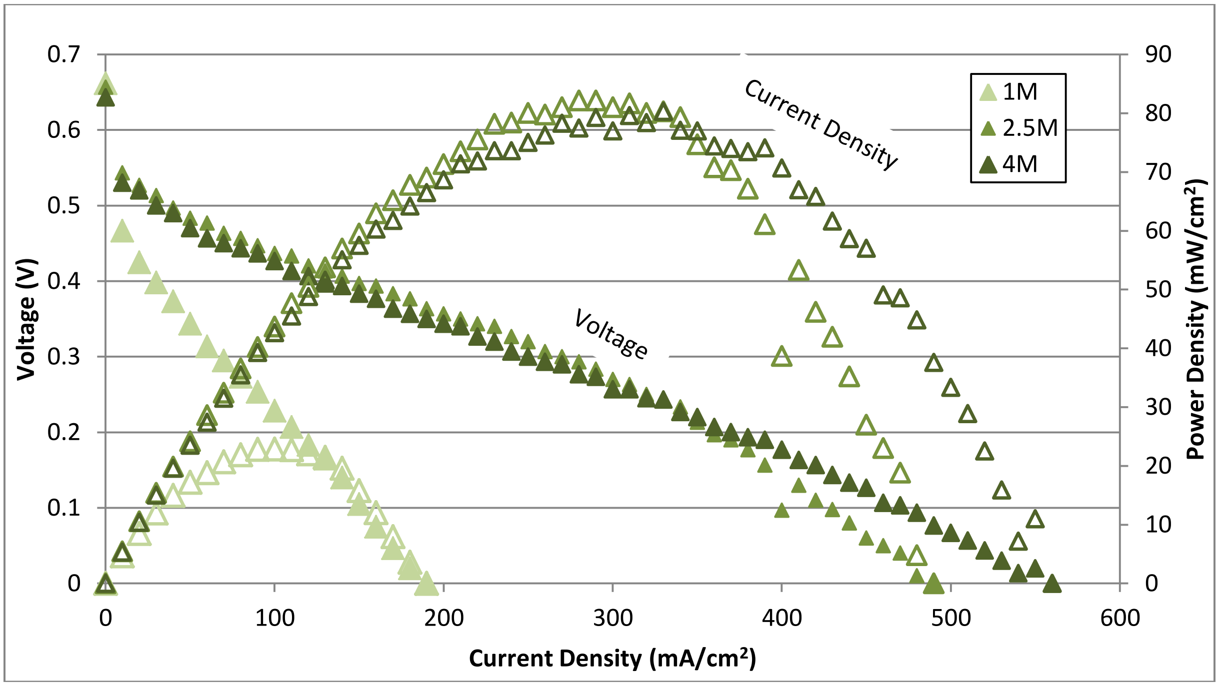

Figure 19: Variation of concentration for Nafion® 117-based MEA at 60°C and with atmospheric oxygen feed

The performance of the cell at 60°C was consistently better than the performance of the cell at both 20 and 40°C for the same methanol feed concentrations. Although the DMFC was able to reach higher current densities, the similar voltage values (corresponding to current densities up to 350mA/cm^2) for 2.5 and 4M suggest that the effect of increasing methanol feed concentration has leveled off due to self-poisoning of the anode and increasing crossover. This effect on performance appears to nearly negate the expected performance increase resulting from greater amounts of fuel availability.

At temperatures above 60°C, operating with 4M methanol feed consistently showed a lower performance than that of 2.5M methanol feed. Voltage and power density polarization curves at 70 and 80°C are shown in Figure 20 and Figure 21, respectively. Note that at these two temperatures, the oxygen feed was pressurized to 7.5psig.

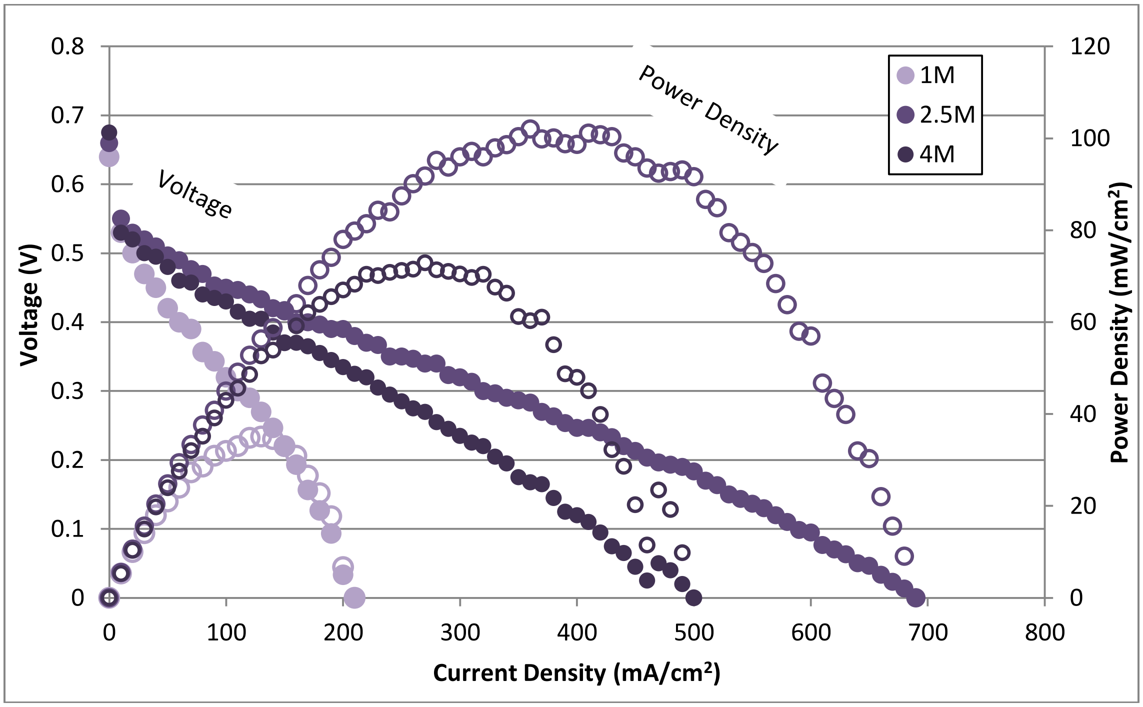

Figure 20: Variation of concentration for Nafion® 117-based MEA at 70°C and with 7.5psig pressurized oxygen feed

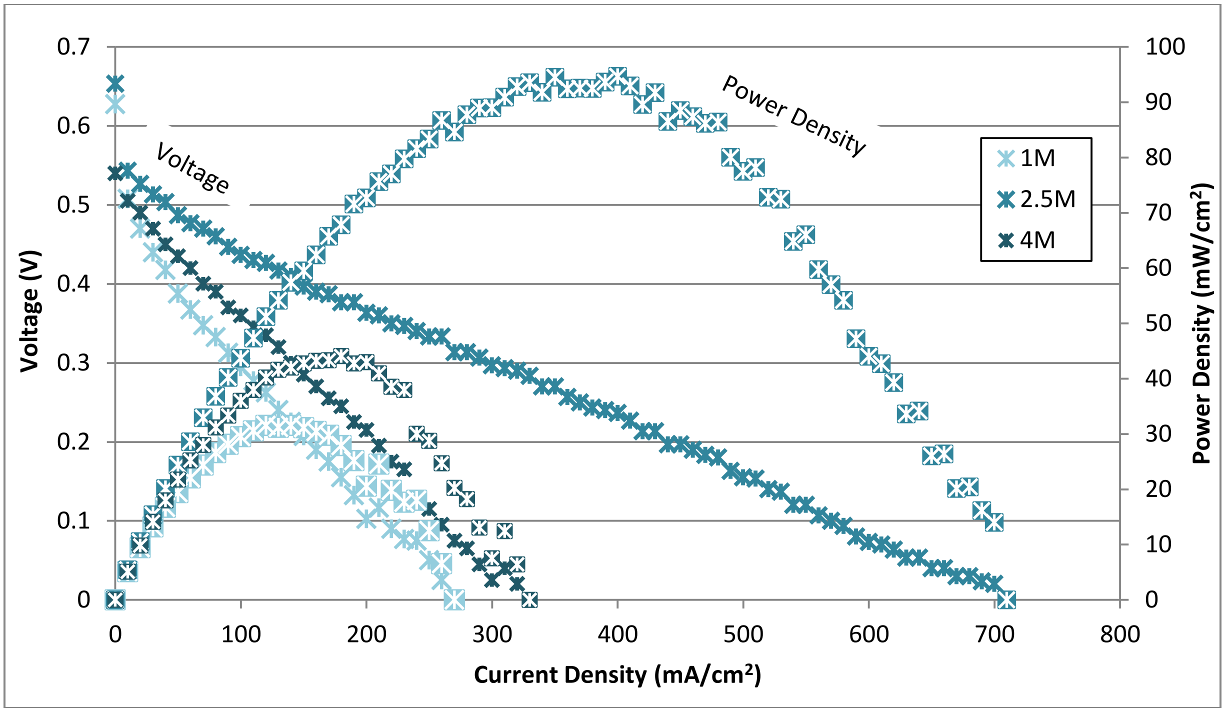

Figure 21: Variation of concentration for Nafion® 117-based MEA at 80°C and with 7.5psig pressurized oxygen feed

The performance of the cell at 70°C was similar to the performance observed at 80°C at 1 and 2.5M methanol feeds. Though, there is a notable difference between the performances when operating with 4M methanol feed. The lowered performance with 4M feed can be attributed to the increased methanol crossover which, as previously explained, reduces cell potential. At 80°C, the polarization curve for 4M is almost approximately equal to the performance for 1M.

4.1.4 Overall Best Performance

Regardless of problems experienced during testing, a peak performance was achieved with 2.5M methanol at 70°C. As shown in Figure 15, the DMFC produced increasing power density trends from 20 to 70°C, hinting at the possibility that the MEA experienced some sort of limitation at 80°C which caused the performance to decline (reasons for this are mentioned in section 4.1.3.1). The fuel cell was able to demonstrate a maximum power density of 107 mW/cm^2 (around a current density of 440 mA/cm^2) using 2.5M methanol feed, pressurized oxygen feed, and an operating temperature of

70°C. The maximum power density without using pressurized oxygen feed was 81 mW/cm^2 (also with 2.5M methanol feed) but at an operating temperature of 60°C.

4.2 PBI-Based MEAs

The DMFC performance using PBI-based Membrane Electrode Assemblies (MEAs) was fairly low. This can be explained by a variety of circumstances. Care was taken during the course of the experiments to minimize exposure of the PBI membrane to liquid methanol feed. However, some electrolyte may have leached during testing. We are confident that if there was any leaching of the electrolyte, the amount lost should not have a significant effect on the overall performance.

4.2.1 Effect of Temperature on Performance

The experiments using PBI-based MEAs were all completed using an oxygen feed through the flow controller at atmospheric pressure. The resulting performance curves generated with 3M methanol feed at various temperatures are shown in Figure 22.

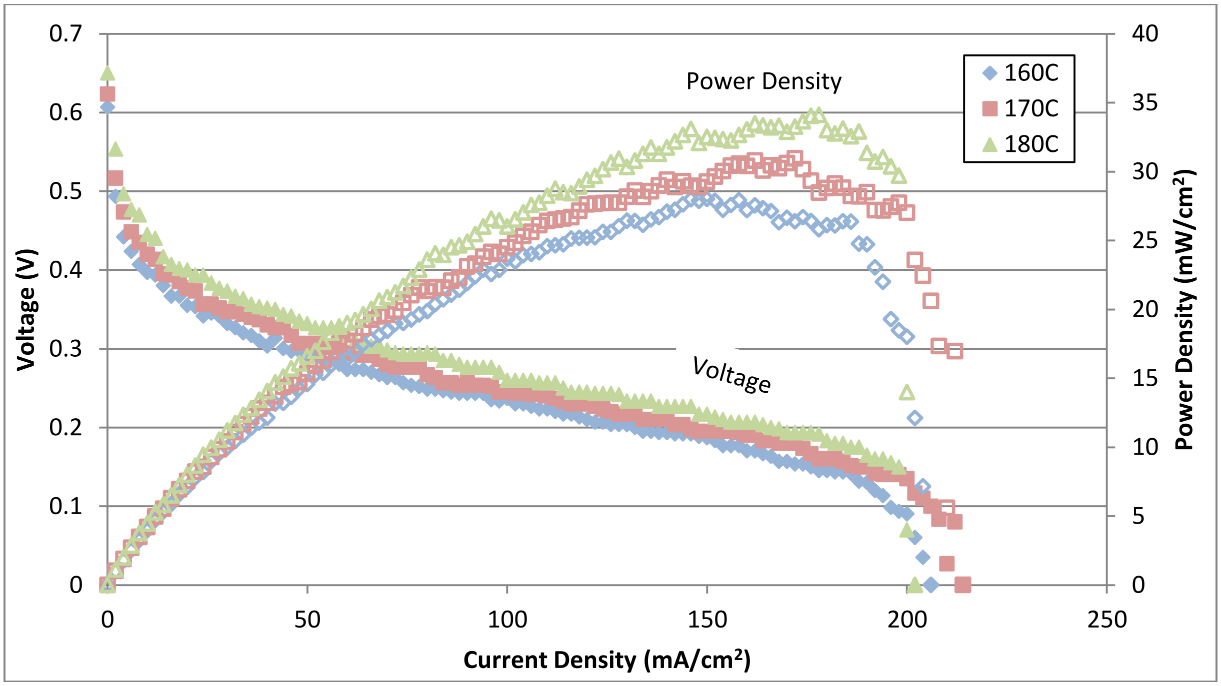

Figure 22: Performance of PBI MEA at various temperatures with 3M methanol feed and atmospheric oxygen feed

Since the PBI tests were conducted within a relatively narrow temperature range, it was expected that the performance curves generated with each methanol feed concentration would be in close range of each other. As such, the close proximity of performance curves in Figure 22 was expected. During data collection it was noted that the voltage corresponding to the defined current would oscillate. This could possibly be due to the low methanol flow rate being used. It is clear that the performance of the PBI-based MEAs is substantially poorer than that of Nafion-based MEAs. The poor performance of the PBI-based MEAs can be attributed to anode catalyst poisoning due to the absence of ruthenium (Ru) at the anode or the low catalyst loadings at both the anode and the cathode.

It was expected that the PBI-based MEAs would suffer some performance loss due to the absence of ruthenium at the anode. However, it was not expected that the current densities would be as low as they proved to be. According to BASF, Celtec®-P 1000 MEAs have some resistance to carbon monoxide poisoning at the anode, but it is possible that having more than trace amounts of methanol in the anode feed overpowered this resistance. This would result in significant catalyst poisoning which reduces the number of catalyst sites that can be used in the oxidation of methanol. Additionally, the PBI-based MEA has a much lower catalyst loading, which further reduces the number of active catalyst sites. A final possibility is the increased resistance to mass transfer due to the feed being in vapor form.

Due to time constraints, we were unable to explore the effect of oxygen feed pressure at the cathode. Since a thorough study could not be performed, it was decided that all performance curves would be collected using oxygen through the flow controller at essentially atmospheric pressure. We believe that performance could be increased with appropriately pressurized cathode feed.

Although PBI is more resistant to methanol crossover than Nafion®, PBI is still subject to its effects. This means that some performance loss can likely be attributed to crossover. The extent of this effect, however, is difficult to quantify due to the performance losses caused by anode catalyst poisoning, low catalyst loading and low cathode feed pressure, in addition to vapor feed.

The performance curves generated with 5M methanol feed at various temperatures are shown in Figure 23.

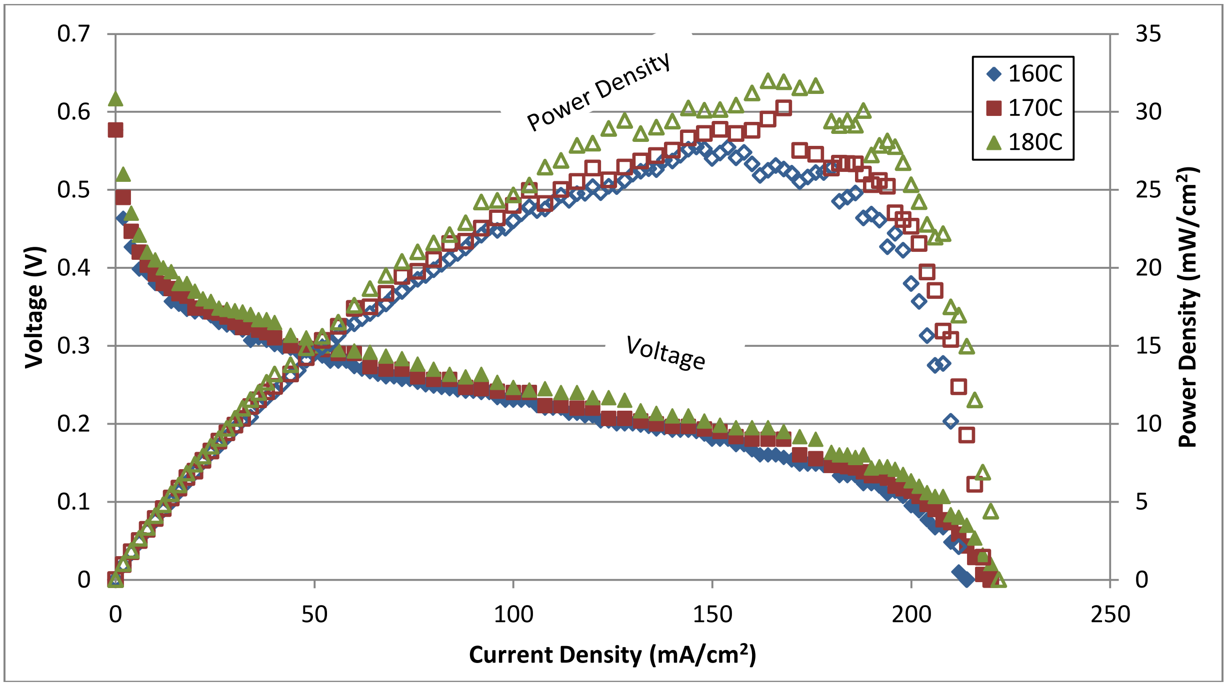

Figure 23: Performance of PBI MEA at various temperatures with 5M methanol feed and atmospheric oxygen feed

The close proximity of performance curves was expected for the same reason as the performance recorded with 3M methanol feed. It was noted during data collection that the voltage corresponding to the defined current was more stable with 5M methanol feed than with 3M methanol. The poor performance of the PBI-based MEAs can again be attributed to the following main factors: anode catalyst poisoning, low catalyst loading, low partial pressure of oxygen at the cathode, and methanol crossover. Each of these influences has the same effect as discussed above for the case of the 3M methanol feed.

The performance curves generated with 10M methanol feed at various temperatures are shown in Figure 24.

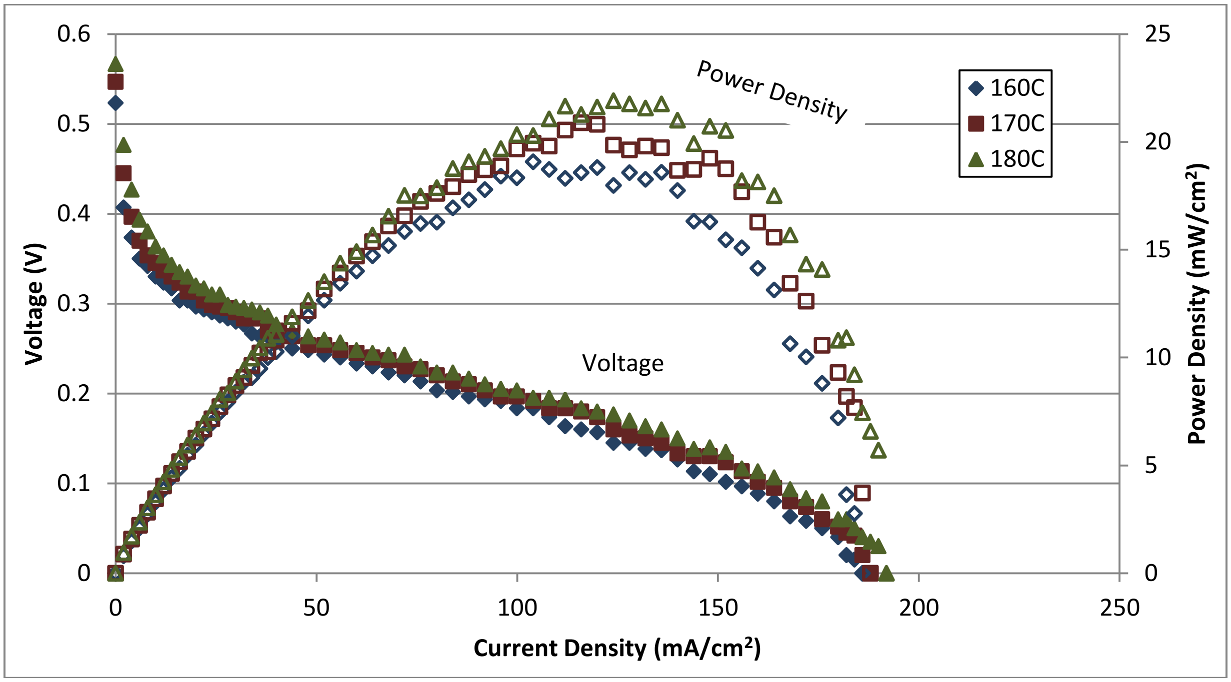

Figure 24: Performance of PBI MEA at various temperatures with 10M methanol feed and atmospheric oxygen feed

The close proximity of performance curves was, again, expected. It was noted during data collection that the voltage corresponding to the defined current had again increased in stability with the increase in methanol feed concentration. The poor performance of the PBI-based MEAs can be attributed to the same main factors as before and for the same reasons.

4.2.2 Effect of Methanol Concentration on Performance

In addition to studying trends in performance through various temperatures at one methanol feed concentration, it is important to study the effect of methanol concentration on performance at each temperature studied. Performance curves for various methanol concentrations studied at 160°C are shown in Figure 25.

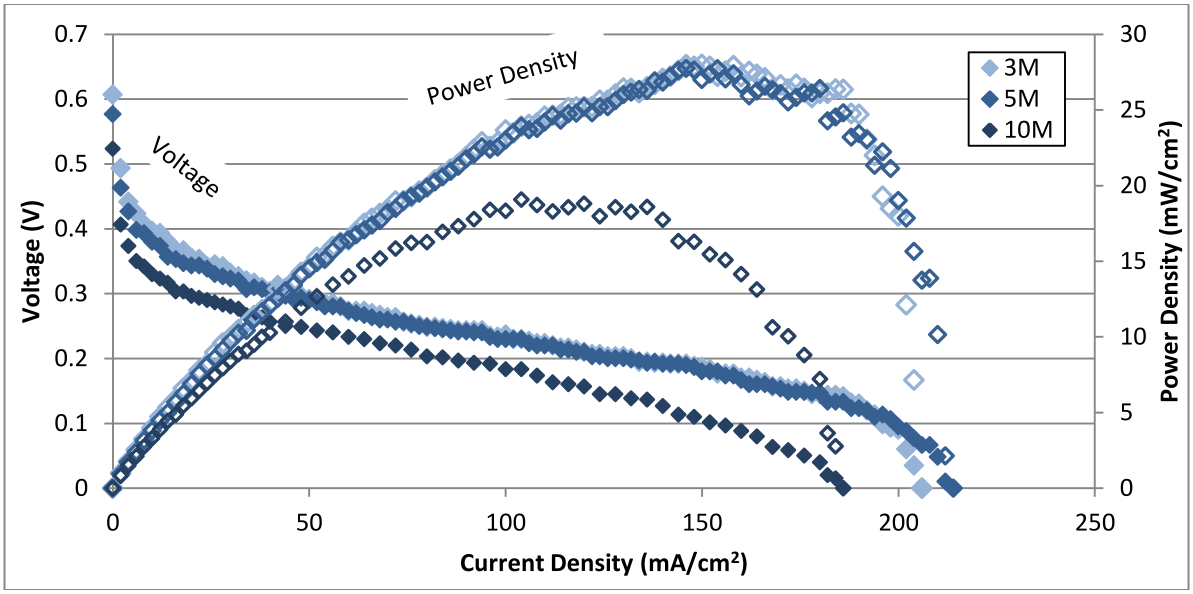

Figure 25: Performance of PBI MEA at 160°C with various methanol feed concentrations and atmospheric oxygen feed

The performance observed at 160°C for 3 and 5M methanol feed concentrations was very similar. For low- and mid- range current densities, the voltage at any given current density for 5M methanol feed is slightly lower than the corresponding voltage at the same current density for 3M methanol feed. This trend is broken at high current densities in the mass transport region of the performance curves, where the cell can support slightly higher current densities with 5M methanol feed than with 3M feed. This, combined with the phenomenon mentioned earlier in which stability of voltage was gained with increased concentration, indicates that 5M methanol feed is more advantageous to use at 160°C than 3M methanol feed. When the feed was increased from 5 to 10M methanol, the performance decreased significantly. This could be due to increased crossover and anode catalyst poisoning in the MEA as a result of the high methanol content of the feed.

The next set of performance curves, using various methanol concentrations studied at 170°C, are shown in Figure 26.

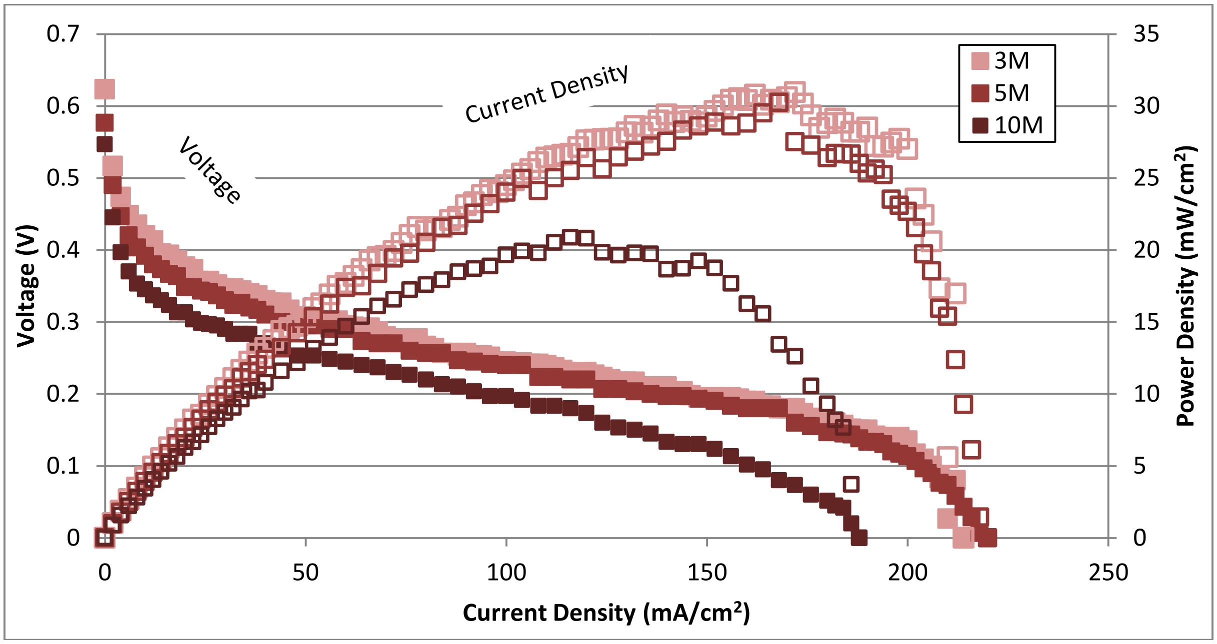

Figure 26: Performance of PBI MEA at 170°C with various methanol feed concentrations and atmospheric oxygen feed

The performance observed at 170°C for 3 and 5M methanol feed concentrations was also very similar. For low- and mid- range current densities, the voltage at any given current density for 5M methanol feed is slightly lower than the corresponding voltage at the same current density for 3M methanol feed. This trend is again broken at high current densities in the mass transport region of the performance curves, where the cell can support slightly higher current densities with 5M methanol feed than with 3M feed. This, combined with the phenomenon mentioned earlier in which stability of voltage was gained with increased concentration, indicates that 5M methanol feed is also more advantageous to use at 170°C than 3M methanol feed. When the feed was increased from 5 to 10M methanol, the performance again decreased significantly. This, too, was probably due to increased crossover and anode catalyst poisoning in the MEA.

The final set of performance curves for various methanol concentrations at 180°C are shown in Figure 27.

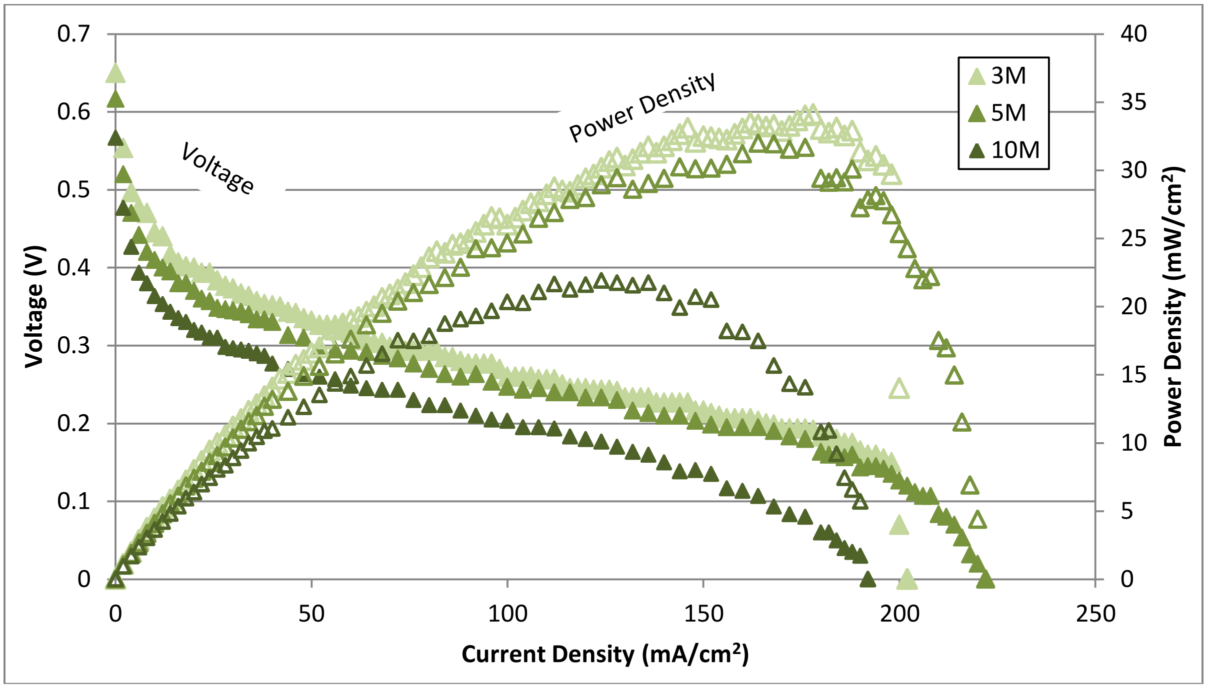

Figure 27: Performance of PBI MEA at 180°C with various methanol feed concentrations and atmospheric oxygen feed

As with 160°C and 170°C, the performance observed at 180°C for 3M and 5M methanol feed concentrations was very similar. The trends of the curves are the same for 180°C as they were for both 160 and 170°C, for the same reasons.

4.2.3 Best Performance

While DMFC operation with the Celtec®-P 1000 MEA at 180°C and 3M feed gave the highest power density (34 mW/cm^2 at a current density of 178 mA/cm^2), the unstable feed supply to the anode makes 3M an unsuitable concentration for the feed. Since use of a 5M feed provides a more stable operation, we consider the best performance to be at an operating temperature of 180°C with 5M methanol feed. At these conditions, the DMFC was able to produce a power density of 32 mW/cm^2 at a current density of 100 mA/cm^2. The amount of power the cell was able to produce with the PBI-based

MEA is three times lower than the maximum power density achieved with the Nafion®117-based MEA (i.e., 81 mW/cm^2), although this feed concentration is twice that used in the Nafion®117-based MEA. However, the PBI-based MEA had three times lower catalyst loadings as well as vapor phase operation (to avoid H_3PO_4 acid leaching). As studied in section 4.1.2 for Nafion®117, an increase in oxygen feed pressure greatly improved the performance of the cell at higher temperatures (i.e., 70°C and 80°C). The same results may occur if the oxygen feed is pressurized for PBI operation.

Chapter 5: Conclusions & Recommendations

In this MQP research project, we analyzed a Direct Methanol Fuel Cell (DMFC) operating with different Membrane Electrode Assemblies (MEAs), methanol feed concentrations, operating temperatures, and oxygen feed pressures in order to determine the effect of temperature on the DMFC performance. As stated by the Butler-Volmer equation, an increase in temperature should improve the cell performance by increasing the rate kinetics at both the anode and cathode without sacrificing the potential of the cell. The experiments were divided into two parts and were characterized by the type of MEA used for DMFC operation: Nafion® 117-based MEAs and Celtec® P-1000 PBI-based MEAs. These two MEA types require very different operating conditions (i.e., temperature) and, therefore, helped the team analyze DMFC operations over a wide range of parameters.

The DMFC operating with a Nafion® 117 MEA was able to reach a maximum power density of 107 mW/cm^2 at a current density of 440mA/cm^2 with 2.5M methanol feed, pressurized oxygen feed, and an operating temperature of 70°C. With atmospheric oxygen feed, a maximum power density of 81 mW/cm^2 (at a current density of 310 mA/cm^2) occurred at a temperature of 60°C with 2.5M methanol feed. In general, the performance of the cell increased with temperature, supporting the idea that the temperature improves the rate kinetics of the fuel cell. While the cell performance also increased with methanol concentration, there was a point at which the effect of methanol crossover outweighed the effect of concentration. Additionally, the oxygen feed at temperatures exceeding 60°C needed to be pressurized as the partial pressure of oxygen decreased with increasing temperature due to the rising vapor pressure of water. We assumed an oxygen feed pressure of 7.5psig based on a study for 1M methanol feed at 70°C. However, due time constraints, the best oxygen feed pressures for other concentrations and temperatures could not be determined.

Many obstacles were encountered in testing the Celtec®-P 1000 PBI membranes. At lower methanol feed concentrations, the DMFC was relatively unstable. Such fluctuations may be ascribed to periodic accumulation and subsequent cleaning of carbon monoxide on the catalyst surface. However, the oscillation lessened at methanol feed concentrations of 5M and above, but the effect of methanol crossover and self-poisoning of the anode hindered the cell performance; all of the tests with 10M methanol feed had consistently lower performance than that of both 3 and 5M methanol feed. Additionally, a pressure study was not conducted for PBI tests and the oxygen feed always entered the cell at standard pressure. Aside from the problems encountered, an increase in operating temperature was shown to have an improvement on the cell performance, also supporting our hypothesis. The PBI-based MEA showed a maximum power density of 32 mW/cm^2 at current densities around 100 mA/cm^2 with operation at 180°C using 5M methanol feed. This low amount of power is likely caused by the lack of ruthenium in the anode catalyst for the PBI-based MEA. Ruthenium is necessary to ensure hydrocarbon intermediates oxidize to produce carbon dioxide.

While we were able to establish the trend with operating temperature as well as present the optimal parameters of those covered in our investigation for Nafion® 117-based MEA and Celtec®-P 1000 PBI-based MEA operation, there are a number of recommendations for further work. Firstly, we experimentally found an ideal pressure for the oxygen feed based at one set of conditions and then applied that pressure to a number of tests at other operating conditions. Since the partial pressure of oxygen varies with temperature, we recommend that pressure studies be performed for every temperature and concentration. For example, the Nafion® 117-based MEA operating at 80°C for 2.5M showed similar polarization curves to that of 2.5M at 70°C. We attributed the loss in performance to both crossover and lower oxygen partial pressure, so an increased oxygen pressure should increase the current and power densities of the cell at higher temperatures.

Another consideration is the flow rates in Celtec®-P 1000 PBI-based MEA. For the PBI-based tests, we experimented with different flow rates and adjusted the fuel cell test station setup to ensure that the feed entering the cell would be completely vaporized, since any liquid in the feed would leach the phosphoric acid electrolyte from the PBI membrane. At lower concentrations of methanol feed, we experienced very unstable voltage readings which may have been caused by a low flow rate. With our current set-up, we were unable to completely vaporize a methanol feed rate of more than about 1mL/min, which might not have provided enough fuel to the anode. We recommend that testing the feed flow rates (especially for the methanol feed) be conducted with the Celtec®-P 1000 PBI-based DMFC.

In addition to testing various feed flow rates, we recommend increasing the methanol feed concentration in smaller increments. The PBI-based DMFC operated with three different methanol concentrations, but there was a large gap between 5 and 10M. The change in performance between using 5M methanol feed to 10M showed a significant decrease in performance. However, we were unable to investigate the trends for the methanol concentrations within that range (i.e., 7.5M methanol feed could have better or worse performance than 5M methanol) due to time constraints. Data should at least be collected for a 7.5M methanol feed at different temperatures to establish a more accurate trend of varying concentrations with temperature.

One key consideration to take into account is the significant difference in catalyst loadings between the two membranes. The Nafion® 117-based MEA had a platinum-ruthenium (PtRu) alloy on the anode while the PBI-based MEA had only Pt on the anode side. Since the PBI-based MEA lacks ruthenium, its anode was more susceptible to catalyst poisoning during operation. We recommend that the PBI-based MEAs contain similar, if not the same, catalyst loading as the Nafion® 117-based MEA to be able to properly compare the two different types of membranes.

Our final recommendation is that an investigation be done regarding the thickness of the PBI membrane used in a DMFC. Since the thickness of a Nafion® membrane has a significant impact on the prevalence of crossover in the cell, it can be inferred that the thickness of a PBI membrane would have a similar impact. Since we suspect that methanol crossover may have contributed to the PBI-based MEA's poor performance, there is a possibility that increasing the thickness of the membrane will reduce methanol crossover and therefore improve the cell performance.

References

Ahmed, M. & Dincer, I. (2011). A review on methanol crossover in direct methanol fuel cells: challenges and achievements. *International Journal of Energy Research, 35*, 1213-1228.

Alternative Energy. (2011). *History of Fuel Cells.* Retrieved on October 21, 2011 from http://www.altenergy.org/renewables/fuel_cells_history.html

Andujar, J. & Segura, F. (2009). Fuel cells: History and updating, A walk along two centuries. *Renewable and Sustainable Energy Reviews, 13*, 2309-2322.

Broka K. & Ekdunge, P. (1996). Oxygen and hydrogen permeation properties and water uptake of Nafion® 117 membrane and recast film for PEM fuel cell. *Journal of Applied Electrochemistry, 27 (2),* 117-123.

Cho, Y., Park, H., Cho, Y., Park, I., & Sung, Y. (2008). The improved methanol tolerance using Pt/C in cathode of direct methanol fuel cell. *Electrochemica acts, 53*, 5909.

Colon-Mercado, H., & Popov, B. (2006). Stability of platinum-based alloy cathode catalysts in PEM fuel cells*. Journal of Power Sources*, 155, 253-263.

Cox, P., Fulton, M., & LaBarre, C. (2011 April 28). The Study of the Effect of Temperature on Direct Methanol Fuel Cells. Worcester Polytechnic Institute. Retrieved on September 6, 2011 from http://www.wpi.edu/Pubs/E-project/Available/E-project-042811-151527/

Cukierman, S. (2006). Et. tu. Grotthuss! and other unfinished stories. *Biochem Biophys Acta*, 876-885.

FSEC: Florida Solar Energy Center. (2007). Hydrogen Basics - Production. Retrieved on February 15, 2012 from http://www.fsec.ucf.edu/en/consumer/hydrogen/basics/production.htm

Fuel Cell Markets. (2012). DMFC - Direct Methanol Fuel Cells Portal Page. Retrieved on February 15, 2012 from http://www.fuelcellmarkets.com/fuel_cell_markets/direct_methanol_fuel_cells_dmfc/4,1,1,2504.html

Ge J. & Liu H. (2004). Experimental Studies of a Direct Methanol Fuel Cell. *Journal of Power Sources*, 56-69.

Gubler, L., Kramer, D., Belack, J., Ünsal, O., Schmidt, T., & Scherera, G. (2007). Celtec-V: A Polybenzimidazole-Based Membrane for the Direct Methanol Fuel Cell. *Journal of the Electrochemical Society*, 981-987.

Hoogers, G. (2003). *Fuel cell technology handbook.* CRC Press: Boca Raton, FL.

Jung, G.., Su A., Tu C., & Weng, F. (2005). Effect of Operating Parameters on the DMFC Performance. *Journal of Fuel Cell Science and Technology*, 81-85.

Kang, S., Lim, S., Peck, D., Kim, S., Jung, D., Hong, S., Jung, H., & Shul, Y. (2011). Stability and durability of PtRu catalysts supported on carbon nanofibers for direct methanol fuel cells*. International Journal of Hydrogen Energy*, *30*, 9.

Liang, Z., Zhao, T., & Xu, J. (2008). Stabilization of the platinum-ruthenium electrocatalyst against the dissolution of ruthenium with the incorporation of gold. *Journal of Power Sources, 185*, 166-170.

Liberman, M. (2008). *Introduction to Physics and Chemistry of Combustion*. Springer-Verlag. Berlin: Germany.

Liu, H. & Zhang, J. (2009). *Electrocatalysis of Direct Methanol Fuel Cells: from Fundamentals to Applications*. Wiley-VCH. Darmstadt: Germany.

Liu, P. Yin, G., & Caia, D. (2009). Investigation on cathode degradation of direct methanol fuel cell. *Electrochemica Acta, 54,* 6178-6183.

Lobato, J., Canizares, P., Rodrigo, M., Linares, J., & Lopez-Vizcaino, R. (2008). Performance of a vapor-fed polybenzimidazole (PBI)-based direct methanol fuel cell. *Energy & Fuels, 22 (5),* 3335-3345.

Methanex. (2012). Methanol Price. Retrieved on February 15, 2012 from http://www.methanex.com/products/methanolprice.html

Modestov, A., Tarasevich, M., Filimonov, V., & Zagudaeva, N. (2009). Degradation of high temperature MEA with PBI-H3PO4 membrane in a life test*. Electrochimica Acta,* 7121-7127.

Nandanwar, S., Chakraborty, M., Mukhopadhyay, S., & Shenoy, K. (2011). Stability of ruthenium nanoparticles synthesized by solvothermal method. *Crystal Research and Technology, 46 (4),* 393-399.

O'Hayre, R, Cha, S., Collella, W., & Prinz, F. (2009). *Fuel cell fundamentals*. John Wiley & Sons: Hoboken, NJ.

Olah, G. (2005). Beyond Oil and Gas: The Methanol Economy (Essay). *Angewandte Chemie International Edition, 44,* 2636-2639.

Olah, G., Goeppert, A., & S. Prakash. (2006). *Beyond Oil and Gas: The Methanol Economy*. Wiley-VCH Verlag GmbH. Weinheim: Germany.

Pabby, A. (2008). *Handbook of Membrane Separations: Chemical, Pharmaceutical, Food, and Biotechnological Applications.* CRC Press: Boca Raton, FL.

Perma Pure LLC. (2011). History. Perma Pure LLC. Retrieved on October 23, 2011 from http://www.permapure.com/company/history/

Roziere, J. & Jones, D. (2003). Non-Fluorinated Polymer Materials for Proton Exchange Membrane Fuel Cells. *Annual Review of Materials Research, 33,* 503-555.

Schmidt, T. & Baurmeister, J. (2007). Properties of high-temperature PEFC Celtec®-P1000 MEAs in start/stop operation mode*. Journal of Power Sources, 176*, 428-434.

Scott, K., Taama, W., & Cruickshank, J. (1998). Performance of a direct methanol fuel cell. *Journal of Applied Electrochemistry, 28 (3)*, 289-297.

Smithsonian Institution. (2004). Fuel Cell Origins. Retrieved on February 15, 2012 from http://americanhistory.si.edu/fuelcells/origins/orig1.htm

Spivey, J., Shekhawat, D., & Berry, D. (2011). *Fuel Cells: Technologies for Fuel Processing*. Elsevier. Oxford: United Kingdom.

Tijim, P., Waller, F., & Brown, D. (2001). Methanol technology developments for the new millennium. *Applied Catalysis A: General, 221*, 275-282.

Union Gas Ltd. (2012). Chemical Composition of Natural Gas. Union Gas: A Spectra Energy Company. Retrieved on February 15, 2012 from http://www.uniongas.com/aboutus/aboutng/composition.asp

US Department of Energy. (2011). Fuel Cells. US Department of Energy: Energy Efficiency & Renewable Energy. Retrieved on April 13, 2012 from http://www1.eere.energy.gov/hydrogenandfuelcells/fuelcells/fc_types.html

UTC Power. (2012). UTC Power. Retrieved on November 1, 2011 from http://utcpower.com/

EIA: U.S. Energy Information Administration. (2012). Monthly Energy Review. Retrieved on January 27, 2012 from http://www.eia.gov/totalenergy/data/monthly/#summary

Vielstich, W., Lamm, A., & Gasteiger, H. (2004a). *Handbook of Fuel Cells Volume 1: Fundamentals and Survey of Systems.* John Wiley & Sons Ltd. Hoboken: New Jersey.

Vielstich, W., Lamm, A., & Gasteiger, H. (2004b). *Handbook of Fuel Cells Volume 2: Electrocatalysis.* John Wiley & Sons Ltd. Hoboken: New Jersey.

Vielstich, W., Lamm, A., & Gasteiger, H. (2004c). *Handbook of Fuel Cells Volume 3: Technology and Applications.* John Wiley & Sons Ltd. Hoboken: New Jersey.

Vielstich, W., Lamm, A., & Gasteiger, H. (2004d). *Handbook of Fuel Cells Volume 4: Technology and Applications.* John Wiley & Sons Ltd. Hoboken: New Jersey.

Xu, C., Faghri, A.,& Li, X. (2010). Development of a high performance passive vapor-fed DMFC fed with neat methanol. *Journal of the Electrochemical society, 157 (8)*, 1109-1117.

Wang, G., Sun, G., Wang, Q., Wang, H., & Xin, Q. (2011). Effect of carbon black additive in Pt black cathode catalyst layer on direct methanol fuel cell performance. *International Journal of Hydrogen Energy, 35*, 11245-11253.

Wang, J., Wainright, J., Savinell, R., & Litt, M. (1995). A direct methanol fuel cell using acid-doped polybenzimidazole as polymer electrolyte. *Journal of Applied Electrochemistry, 26,* 751-756.

Yu, P., Pemberton, M., & Plasse, P. (2005). PtCo/C cathode cathode catalyst for improved durability in PEMFCs. *Journal of Power Sources, 144*, 11-20.

Zhu, S., Wang, S., Gao, Y., Jiang, L., Sun, H., & Sun, G. (2010). Effect of $RuO_2 \cdot xH_2O$ in anode on the performance of direct methanol fuel cells. *International Journal of Hydrogen Energy, 35 (20)*, 11254-11260.

Appendix A: Acronym List

A	Amperes (Amps)
cm	Centimeter
CO	Carbon monoxide
CO_2	Carbon dioxide
DMFC	Direct methanol fuel cell
GDL	Gas Diffusion Layer
M	Molarity
MEA	Membrane electrode assembly
MeOH	Methanol
mL	Milliliter
MOR	Methanol Oxidation Reaction
NO_x	Nitrogen oxide
OCV	Open Circuit Voltage
ORR	Oxygen Reduction Reaction
PA	Phosphoric Acid
PBI	Polybenzimidazole
PEM	Proton exchange membrane
PTFE	PolyTetraFluoroEthylene (Teflon®)
sccm	Standard cubic centimeter per minute
V	Voltage
W	Watts

Appendix B: Glossary

Ampere (A)	Measure of current being drawn from the cell
Anode	Where methanol and water react to produce protons, electrons, and carbon dioxide
Cathode	Where the protons, electrons, and oxygen react to form water product
Crossover	Occurs when methanol loosely bonds to water and is pulled along across the membrane when water passes to the cathode side; crossover may result in decreased cell performance
Electric Potential	Work done by the movement of electrons; measured in volts (V)
Electrode	Material that holds the catalyst that facilitates the chemical reaction at the anode and cathode; usually carbon fiber
Hygroscopic	Ability of absorbing water, especially under some humidity and temperature conditions
Leaching (of Electrolyte)	The process by which phosphoric acid is removed from a PBI membrane due to contact with liquid water.
Membrane electrode assembly (MEA)	Consists of the membrane hot-pressed between the anode and cathode electrodes, with the catalyst layer in contact with the membrane
Mil	One-thousandths of an inch; indicates thickness of film
Molarity	Concentration of a solution; moles of solute (methanol, in this project) per liter of solution (deionized water)
Pinhole	Refers to small holes in the membrane film that allow the products and reactants to flow freely through the membrane
Proton	A hydrogen ion; forms at the anode and crosses the membrane to react at the cathode
Proton exchange membrane	The polymer membrane in which the protons cross from the anode to the cathode
Reformate	Hydrogen that has been produced from another type of fuel and that may still contain trace amounts of that fuel.
Voltage (V)	Measure of the electric potential of the cell

Appendix C: Instructions for Assembly

When running a fuel cell, the first thing done is assembling the fuel cell using a Membrane Electrode Assembly (MEA). The MEAs used in these experiments were commercially prepared. Prior to placement in the assembly, photographs were taken of the anode and cathode sides of the MEA and the mass of the MEA was recorded. The characteristics of the MEA being tested, such as mass and appearance, were recorded in a lab notebook. The anode side end plate (see Figure 5) was clamped in place, parallel to the ground with the serpentine channels in the graphite block facing up. Once secured, a gasket was placed on the block. The square cutout in the center of the gasket was aligned with the serpentine flow channels in the graphite plate. The MEA was placed on top of the gasket with the anode side facing the anode side aluminum plate. For the Nafion® MEAs, the electrode were the same size as the square cutout in the center of the gasket. For the PBI MEAs, there was a gap of 1mm between the carbon cloth on the cathode and the gasket on each side to help prevent over-compression. A second gasket, cut with the same dimensions as the first, was placed on top of the MEA around the cathode electrode. Once aligned, the cathode side end plate was placed on top with the collector plates aligned with the current collector plates on the anode side. Precaution was taken to ensure the gaskets and MEA did not shift and become misaligned with the serpentine channels while cathode side end plate was being positioned. To fully secure the assembly, eight lag bolts are tightened in a star pattern to prevent uneven pressure distribution. The bolts were tightened to a torque of 65 lb_f-in for Nafion® and 62 lb_f-in for PBI.

Once the cell was assembled, it was connected to the fuel cell test station. The fuel cell was placed on a heat resistant platform with the cathode side of the assembly facing the user. The fuel cell was connected to the load box by attaching the red lead to the cathode side collector plate and the black lead to the anode side collector plate using small screws. The feed and waste lines (four in total) were then attached and tightened in their respective places. The waste lines were directed into separate beakers to collect liquid waste and give visual evidence of gaseous waste or product (in the form of bubbles). For the Nafion® assembly, the heating elements and thermocouple were inserted into the end plates. For the PBI assembly, the attached electric plug for the heating plates had to be plugged into the control relay and the thermocouple inserted into the anode side graphite block.

Prior to testing, the fuel cell was heated to the desired operating temperature. After the temperature was reached, the oxygen feed was sent through the oxygen flow controller, set to 60.1 (about 47.7 mL/min). A methanol flow rate, 1.5 mL/min for Nafion® and 1.0 mL/min for PBI, was specified using the syringe pump flow controller and the methanol feed started. Once there was visual evidence of methanol in the methanol waste line, the load box was turned on. The fuel cell was allowed to equilibrate for half an hour, during which the Open Circuit Voltage (OCV) was monitored to ensure that there were no immediate problems with the cell, such as blockages. After this half hour at OCV, performance data were collected galvanostatically. In between collecting sets of data, the cell was subjected to a low current for 55 minutes. This was followed by 5 minutes at OCV, after which the next data set was collected.

At the end of each test, the load box was turned off. The methanol feed was then stopped, followed by the oxygen feed. Then the oxygen flow control, syringe pump control, and syringe pump power supply were turned off. The cell is allowed to reach room temperature and all feed and waste lines are detached from the cell. Then the leads were detached, the thermocouple was removed, and heating elements removed or unplugged depending on the assembly. The methanol waste was stored in an appropriate waste container and the collection beaker replaced for use in the next experiment. The assembly was again clamped into place with the anode side end plate down. The MEA was removed from the assembly, weighed, and inspected for damage. Pictures were taken of the anode and cathode sides of the MEA for comparison to the pictures taken before the experiment. The MEA was placed in a sealed bag and stored in a drawer away from direct sunlight. Any changes in mass or appearance of the MEA were noted and analyzed with the data.

Appendix D: Test Station Use

Syringe Pump

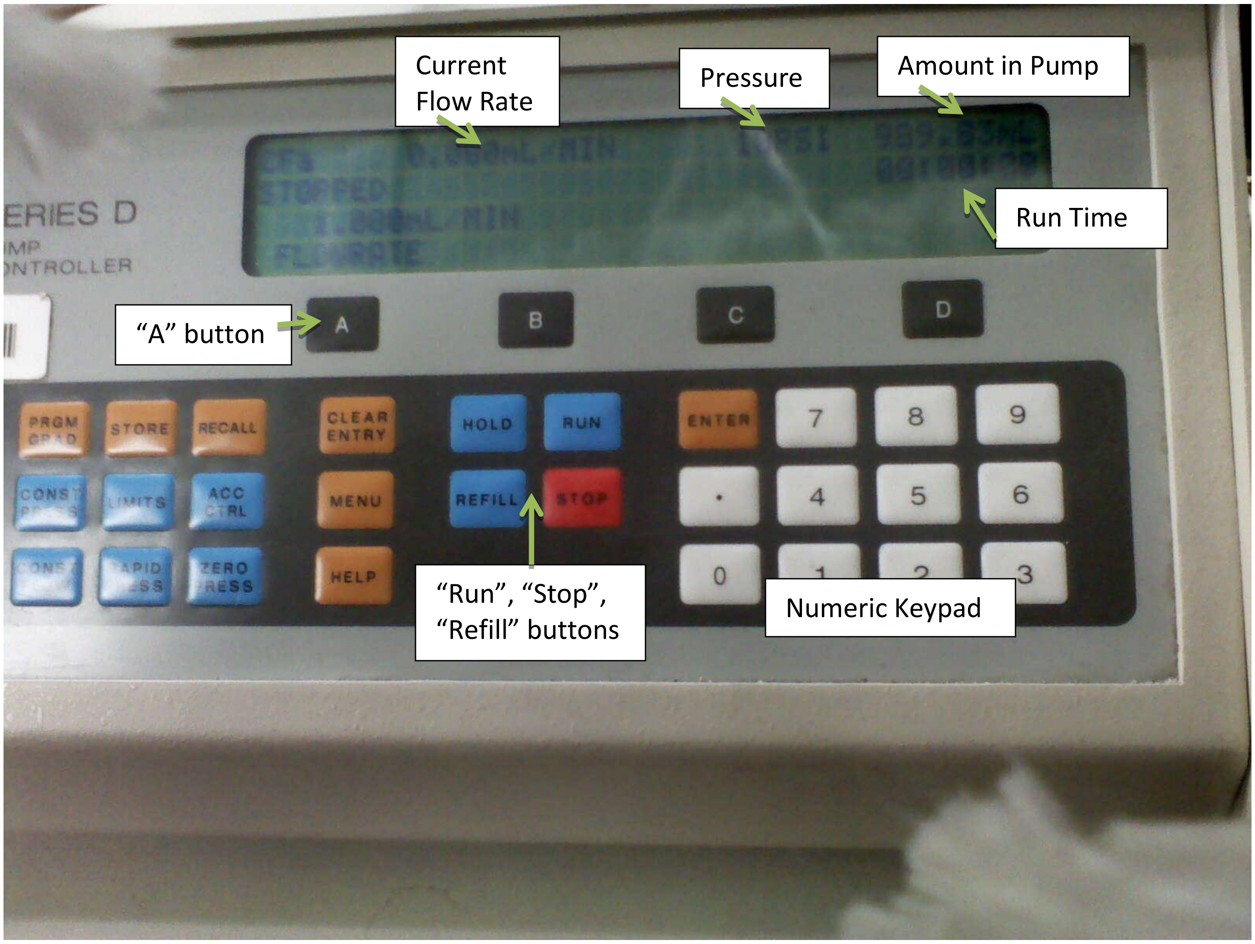

Figure 28: Syringe pump control

Filling

1. If the pump is not on, turn on the power for the pump and then the power for the controller.
2. Detach the fitting connecting the plastic tubing to the insulated metal tubing.
3. Place end of plastic tubing in container and submerge with methanol/DI water.
4. Push "A" button (below display).
5. Enter flow rate (###.#) using numeric keypad.

6. Press “Enter”.
7. Press “Refill”.
8. Wait for pump to take in as much liquid as it can.
   a) Be careful when using less than 1L of liquid to fill pump because pump will take in air when there is no more water or methanol.
9. Run the pump (repeat steps 4-6 and then press “Run”) until some liquid returns to the storage container in order to produce suction head, and then reattach the plastic line.

Running/Emptying

1. If the pump is not on, turn on the power for the pump and then the power for the controller.
2. If the pump is being emptied, detach the fitting that connects the plastic tubing to the insulated metal tubing and place it in the storage container. If the pump will be sending methanol to the cell, open the methanol feed valve.
3. Push “A” button (below display).
4. Enter flow rate (###.#) using numeric keypad.
5. Press “Enter”.
6. Press “Run”.

Warnings/Hints

- Always double check that the pump is running at the specified flow rate. The pump is finicky and will sometimes revert to an old flow rate, which can be unpleasant.
- Refilling the pump at too high a flow rate can cause too much air to be taken in. 150-200 mL/min is usually fine and does not take excessively long to refill.
- After filling pump, it is a good idea to run at a relatively high flow rate (ex: 15 mL/min) to remove air bubbles.

- The pressure in the pump should not exceed 30 psi. The normal operating pressure appears to be around 18 psi.
- When emptying the pump, higher flow rates result in higher pressure. Exceeding flow rates of about 150 mL/min can make the pressure too high.
- Rinse the pump out between methanol concentrations (ex: when going from 10M to 3M methanol, remove the 10M methanol, fill the pump with DI water, remove the water, and then fill the pump with the 3M methanol) to prevent cross contamination.
- If you are not going to be using the pump for more than a week, remove any methanol from the tank and fill it with water.

Flow Controller

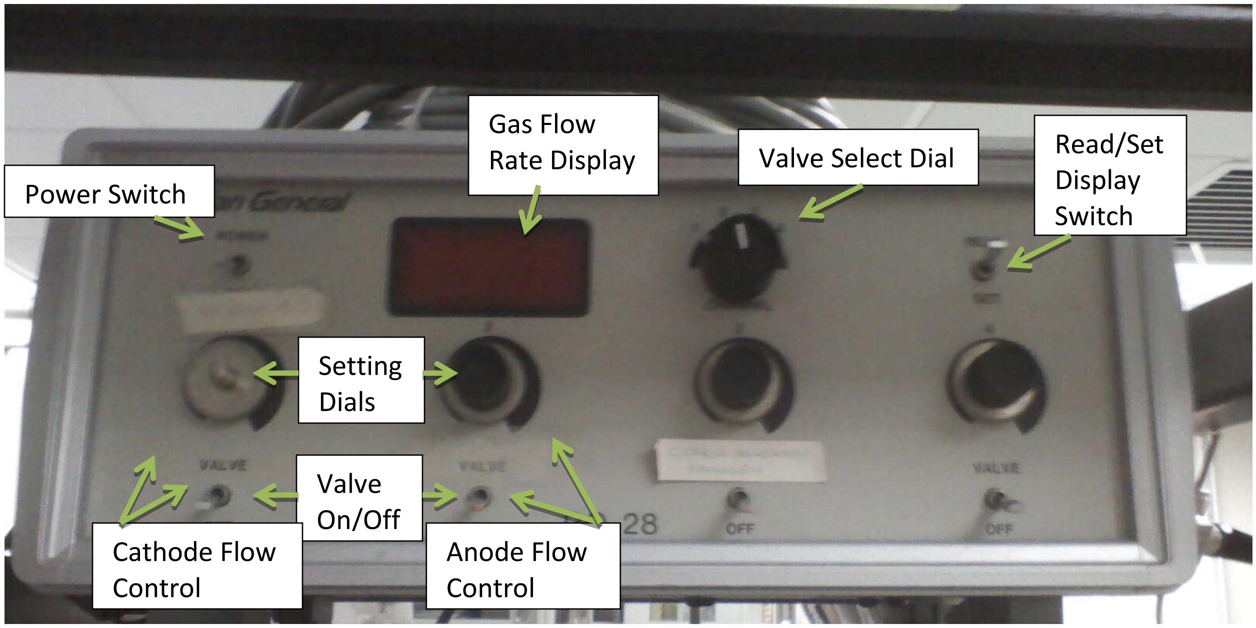

Figure 29: Gas Flow Controller

Start/Stop

1. When using the flow controller, turn on the power and then open the desired valve (valve 1 for the cathode, valve 2 for the anode).
2. When the flow controller is no longer needed, close the active valves before turning off the power.

Setting Flow Rates

1. Turn the valve select dial to the number of the valve being used (valve 1 for cathode, valve 2 for anode)
2. Turn the setting dial for the desired valve until the necessary flow rate is reached. There is a calibration curve taped to the top left corner of the test station.

Temperature Controllers

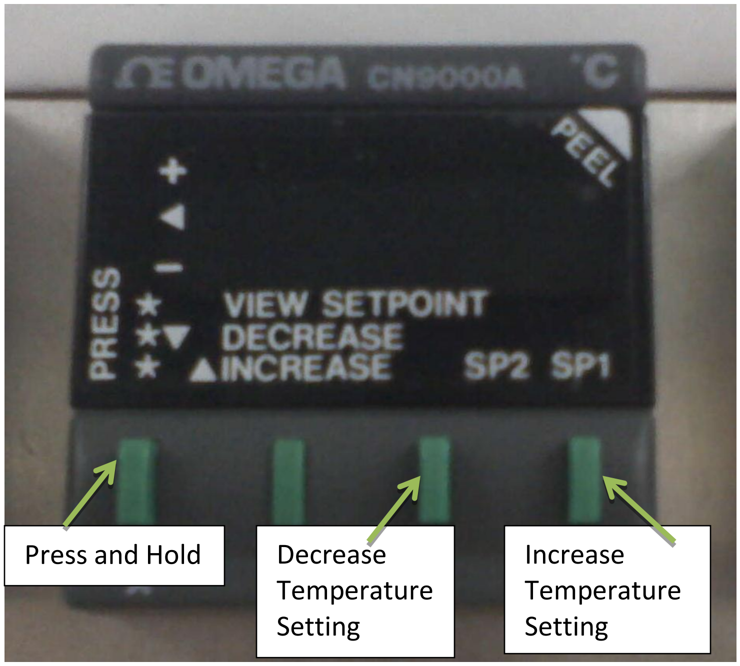

Figure 30: Temperature Controller

- There are three temperature controllers on the test station. The leftmost one controls the upper section of the methanol feed. The middle one (pictured) controls the temperature of the assembly. The rightmost one controls the lower section of the methanol feed.
- These controllers control heating only, cooling must be done through conduction and convection.
- Temperature controls are only on when power strip in back is also on.

Load Box

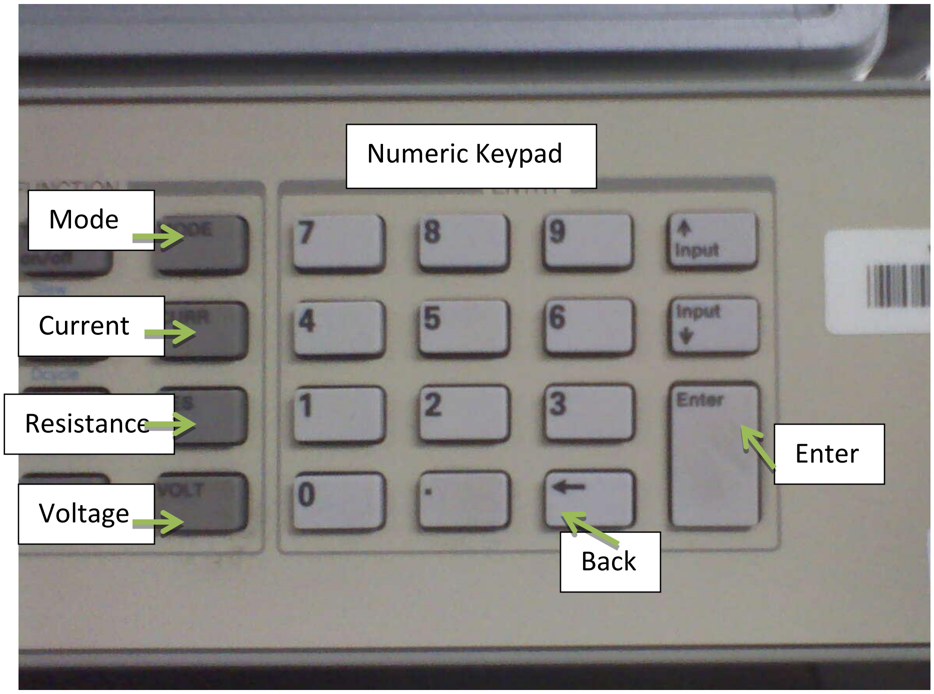

Figure 31: Load Box Controls

1. Turn on load box.
2. To specify the current (and record corresponding voltage), press “Curr”; to specify the voltage (and record the corresponding current), press “Volt”
3. Enter desired value using numeric keypad.
4. Press “Enter”.
5. For subsequent settings, press “Curr” or “Volt” and then repeat steps 3 and 4.

Feed Instructions

In order to switch from any set of conditions to any other set of conditions, stop the current feed and then start the next feed.

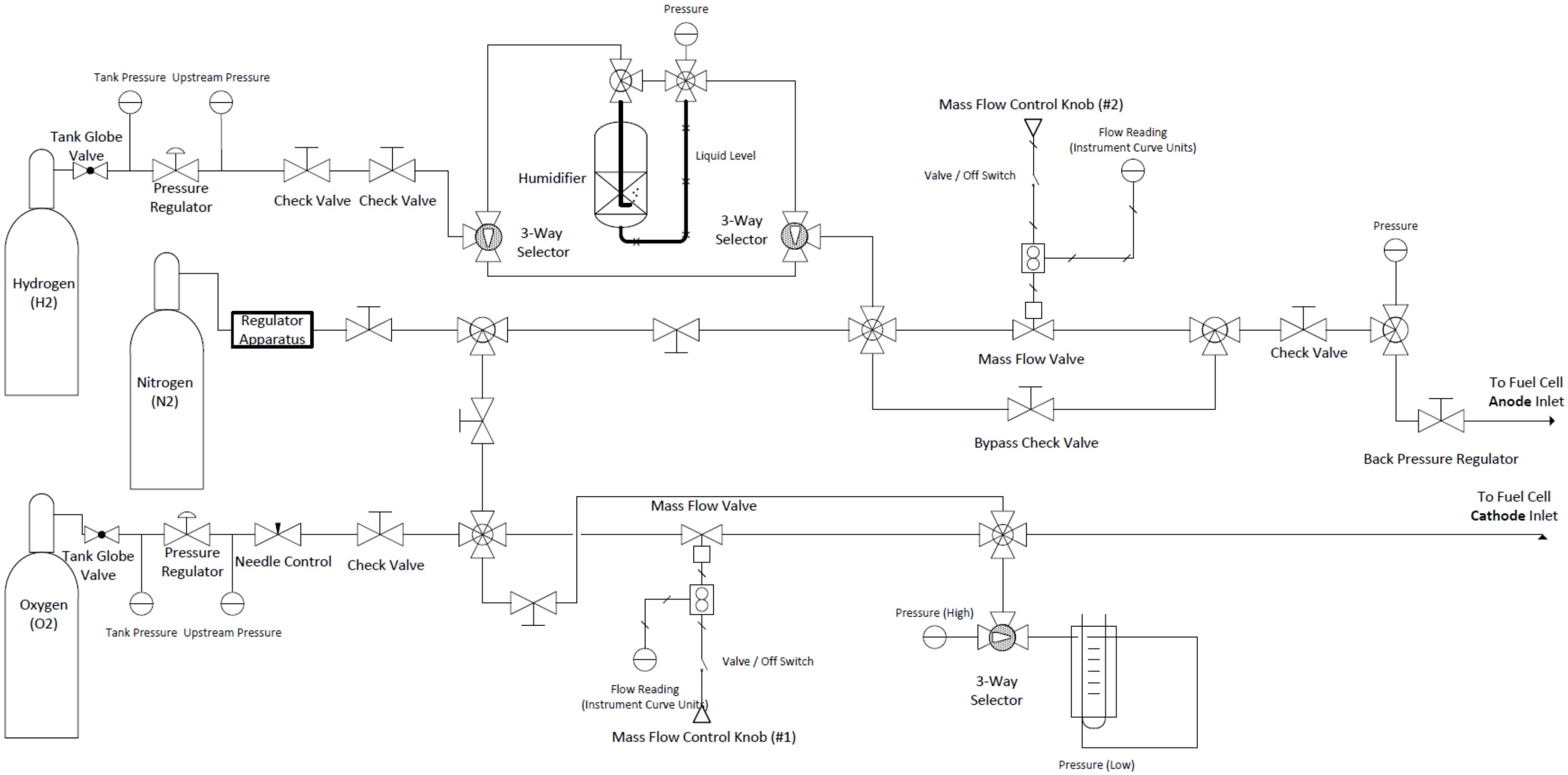

Figure 32: Test station upstream process flow diagram (personal communication, Matthew Perrone, 2012)

Hydrogen to the Anode

Starting Feed

1. Open the globe valve on the hydrogen tank.
2. Adjust pressure regulator to desired stream pressure.
3. Open the first and second check valves, following the line leading from the hydrogen tank.
4. If humidifying the hydrogen stream, turn the first and second three way valves so that the arrows on both handles point toward the humidifier. If not humidifying the hydrogen stream, turn the first and second three way valves so that the arrows on both sides point toward the bypass (away from the humidifier).
5. If using the flow controller, follow the instructions above for the use of the flow controller. If not using the flow controller, open the bypass check valve. **Do not use the flow controller with a humidified hydrogen stream.** The flow controller does not like water.
6. Open the remaining check valve.
7. If using the flow controller, open the back pressure regulator completely. If not using the flow controller, use the back pressure regulator to adjust the pressure and flow rate of the stream as desired.

Stopping Feed

1. Close the globe valve on the hydrogen tank.
2. Adjust pressure regulator to low/no pressure.
3. Close the first and second check valves, following the line leading from the hydrogen tank.
4. Return the first and second three way valves to neutral.
5. If using the flow controller, close valve 2 and then turn off power. If not using the flow controller, close the bypass check valve.

6. Close the remaining check valve.
7. Close the back pressure regulator.

Oxygen to the Cathode

Starting Feed

1. Open the globe valve on the oxygen tank.
2. Adjust pressure regulator to desired stream pressure.
3. Open the needle valve.
4. Open the check valve.
5. If using the flow controller, follow the instructions above for the use of the flow controller. If not using the flow controller, open the bypass check valve.
6. If using the flow controller, open the back pressure regulator completely. If not using the flow controller, use the back pressure regulator to adjust the pressure and flow rate of the stream as desired.

Stopping Feed

1. Close the globe valve on the oxygen tank.
2. Adjust pressure regulator to low/no pressure.
3. Close the needle valve.
4. Close the check valve.
5. If using the flow controller, close valve 1 and turn off the flow controller. If not using the flow controller, close the bypass check valve.
6. Close the back pressure regulator completely.

Nitrogen to the Anode

Starting Feed

1. Open the globe valve on the nitrogen tank.
2. Adjust pressure regulator to desired stream pressure.
3. Open the needle valve.
4. Open the check valve.
5. Follow the lines to the check valve that intersects with the hydrogen pathway. Open the check valve that leads to the hydrogen lines. This check valve has a green handle.
6. If using the flow controller, follow the instructions above for the use of the flow controller. If not using the flow controller, open the bypass check valve.
7. Open the remaining check valve.
8. If using the flow controller, open the back pressure regulator completely. If not using the flow controller, use the back pressure regulator to adjust the pressure and flow rate of the stream as desired. If leaving the cell running with nitrogen overnight, a flow controller setting of about 10 is sufficient.

Stopping Feed

1. Close the globe valve on the nitrogen tank.
2. Adjust pressure regulator to little/no pressure.
3. Close the needle valve.
4. Close the check valve.
5. Follow the lines to the check valve that intersects with the hydrogen pathway. Close the check valve that leads to the hydrogen lines. This check valve has a green handle.

6. If using the flow controller, close valve 2 and turn off the flow controller. If not using the flow controller, close the bypass check valve.
7. Close the remaining check valve.
8. Close the back pressure regulator completely.

Nitrogen to the Cathode

Starting Feed

1. Open the globe valve on the nitrogen tank.
2. Adjust pressure regulator to desired stream pressure.
3. Open the needle valve.
4. Open the check valve.
5. Follow the lines to the check valve that intersects with the oxygen pathway. Open the check valve that leads to the oxygen lines. This check valve has a black handle.
6. If using the flow controller, follow the instructions above for the use of the flow controller. If not using the flow controller, open the bypass check valve.
7. If using the flow controller, open the back pressure regulator completely. If not using the flow controller, use the back pressure regulator to adjust the pressure and flow rate of the stream as desired. If leaving the cell running with nitrogen overnight, a flow controller setting of about 10 is sufficient.

Stopping Feed

1. Close the globe valve on the nitrogen tank.
2. Adjust pressure regulator to little/no pressure.
3. Close the needle valve.

4. Close the check valve.
5. Follow the lines to the check valve that intersects with the oxygen pathway. Close the check valve that leads to the oxygen lines. This check valve has a red handle.
6. <u>If using the flow controller</u>, close valve 1 and turn off the flow controller. <u>If not using the flow controller</u>, close the bypass check valve.
7. Close the back pressure regulator completely.

Methanol to the Anode (Nafion®)

<u>Starting Feed</u>

1. Check that there is enough methanol in pump.
2. Follow directions for filling the pump if necessary.
3. Adjust temperature for bottom section of feed line.
4. Open methanol feed check valve.
5. Follow directions for running methanol feed from pump.

<u>Stopping Feed</u>

1. Stop syringe pump.
2. Return temperature setting to room temp or below.
3. Close methanol feed check valve.

Methanol to the Anode (PBI)

*Heat up PBI assembly under nitrogen and then switch over to methanol.

Starting Feed

1. Check that there is enough methanol in pump.
2. Follow directions for filling the pump if necessary.
3. Adjust temperature for top section of feed line.
4. Adjust temperature for bottom section of feed line.
5. Open methanol feed check valve.
6. Follow directions for running methanol feed from pump.
7. Run methanol feed into container or hood until vaporized.
8. Switch from nitrogen feed to methanol feed.

Stopping Feed

1. Stop syringe pump.
2. Return temperature settings to room temp or below.
3. Close methanol feed check valve.
4. Allow PBI assembly to cool down under nitrogen to prevent water condensation.