Performance Characteristics of PBI-based High Temperature Direct Methanol Fuel Cells

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By

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Abstract

This thesis investigates the effect of temperature, methanol concentration, and oxidant type on the performance of a Direct Methanol Fuel Cell (DMFC) using two versions of a commercially available polybenzimidazole (PBI)-based membrane electrode assembly (MEA): the Celtec®-P 1000 MEA of original thickness and double thickness. The PBI-based MEA's were tested under the vapor-phase methanol concentrations of 1M, 2M, 3M, 5M, 7.5M, and 10M, temperatures of 160-180°C, and oxidants of oxygen and air. It was found that performance increased with temperature and that oxygen outperformed air as methanol concentrations increased. The double thickness PBI-based MEA, was more resistant to methanol crossover and performed better with increasing methanol concentrations. Thus, these commercial MEAs may be suitable for developing higher temperature DMFCs

Acknowledgements

There a great many individuals that I would like to acknowledge for their support and contribution to this project and the fuel cell laboratory.

First, I would like to thank Jack Farraro, Felicia Vidito, and Paula Moravek for their quick responses and assistance in receiving project materials and other necessary preparations.

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Next, I would like to thank the undergraduates who persevered and made a significant impact to the direction of research that the laboratory has today. Thanks go out to Ray Gasper for completing never-ending hours of fuel cell testing and for making the experience an enjoyable one.

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Chapter 1: Introduction

1.1   Statement of Purpose

Fuel cells are not an energy source themselves, but an energy converter. They convert

the chemical energy of a fuel into electricity via reaction with an oxidant. The majority of fuel

cells today operate with air and high purity hydrogen due to the high energy density of

hydrogen and the low amount of impurities that could potentially poison fuel cell membranes

(Bagotsky 2009). Operational temperature ranges go from room temperature to approximately

200°C and from 600-1000°C. An overview of fuel cell types with corresponding operating

temperatures, fuels, oxidants, and ionic species can be seen in Figure 1.1.
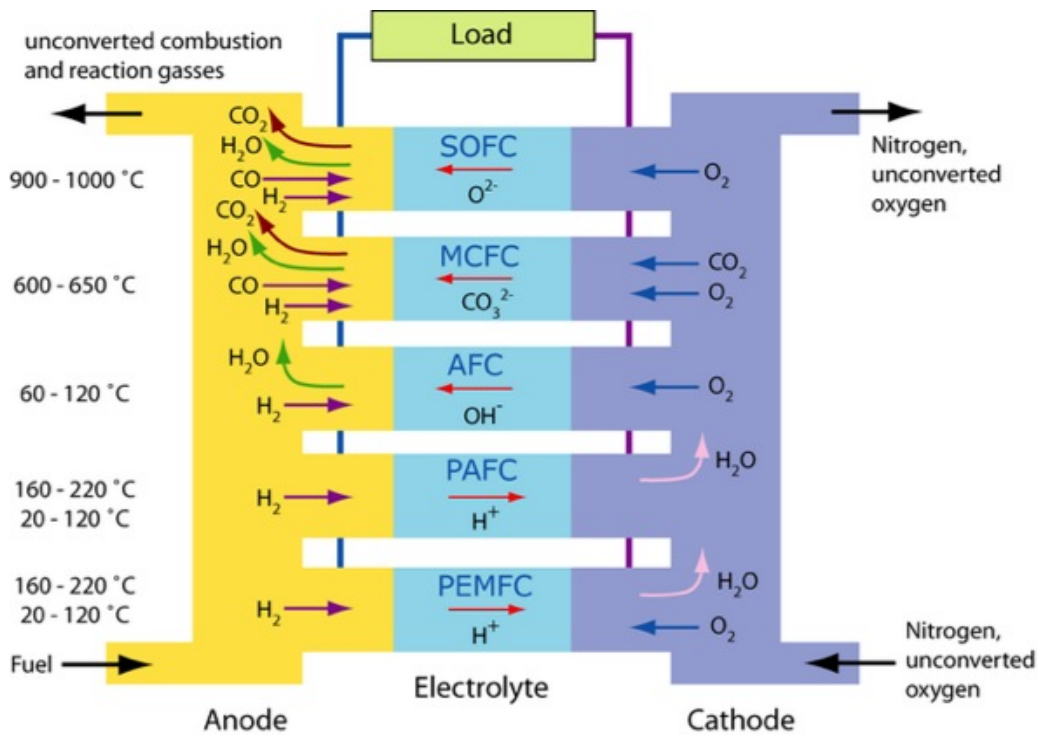
Figure 1.1: Fuel cell schematic

As shown in Figure 1.1, a fuel consists of: 1) an anode where the fuel (e.g., H_2) reacts on a catalyst to product electrons and ions; 2) an electrolyte that allows ion transport, but not electrons which are then forced to proceed via the external circuit where work is extracted from then, and 3) a cathode where the depleted electrons and ions react with the oxidant on a catalyst.

In a proton-exchange membrane (PEM) fuel cell (FC), the electrolyte is a polymer electrolyte such as Nafion® that allows proton transport and uses a Pt catalyst at the anode and cathode. The use of water in Nafion for proton transport restricts its operating temperature to less than 90°C, making the Pt catalyst susceptible to poisons such as CO. The phosphoric acid fuel cell (PAFC) uses phosphoric acid imbibed in a SiC matrix for proton transport thus raising the temperature of operation from 160-200°C.

On the other hand, an alkaline fuel cell (AFC) uses an aqueous alkali solution for the transport of hydroxyl ions, but is also limited to less than 120°C. For still higher temperatures, the molten carbonate fuel cell (MCFC) utilizes a molten salt of carbonates (lithium and potassium carbonates) at 650°C for the transport of carbonate ions as charge carriers. The solid-oxide fuel cell (SOFC), on the other hand, operates at 800-1000°C, where a ceramic electrolyte (yttria-stabilized zirconia) allows transport of oxygen anions as charge carriers. These higher temperature fuel cells can tolerate high levels of CO in hydrogen fuel and can even use natural gas directly. It is noteworthy (Figure 1.1) that there are no fuel cells in the temperature range of 200-600°C because of a lack of practical electrolytes.

The fuel cells that operate on the low end of the scale require lower heat effects, but suffer from poor kinetics and possible CO poisoning. However, high temperature fuel cells have very favorable kinetics in that reactions readily go from reactants to products, reducing the cell potential losses or overpotential (Bagotsky 2009). Figure 1.2 shows the temperatures in which existing fuel cells operate as well as how fuel is supplied, and the over-potentials present.
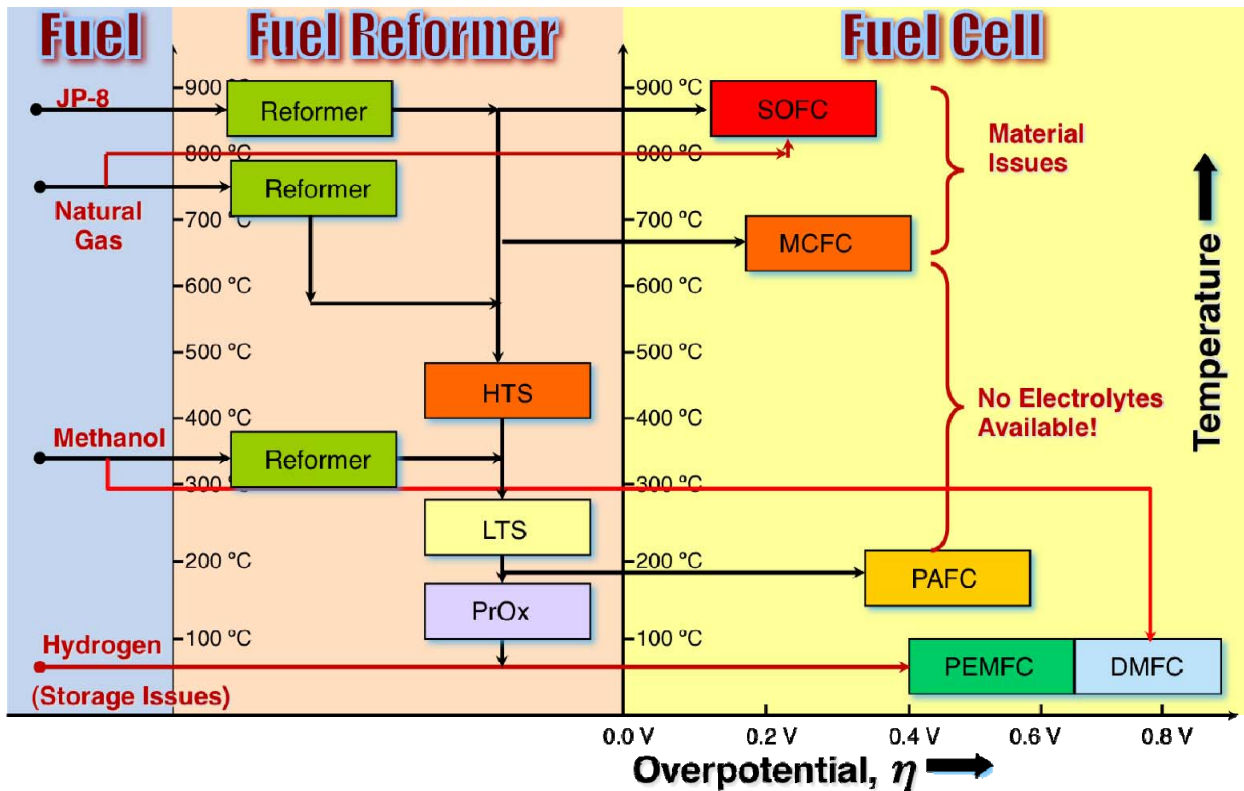
Figure 1.2: Fuel cell over-potentials

Figure 1.2 demonstrates that a variety of fuels including hydrogen, methanol, natural gas, and JP-8 (or gasoline) may be used in fuel cells. Beginning with low temperature fuel cells, the polymer electrolyte fuel cell (PEMFC) requires water to be present in its membrane to ferry protons from the anode to cathode. Nafion®, for example is the mainstream membrane in use for PEMFC, and must be operated below 90°C to retain water (Lobato et al. 2007). It also uses

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hydrogen for fuel although others may be reformed as well. One issue with hydrogen includes the presence of carbon monoxide, in low purity cases, which poisons the catalyst (Aliberti et al. 2001). Additionally, PEMFC's suffer from high overpotentials because of the low operating temperatures. The Direct Methanol Fuel Cell or (DMFC) makes direct use of a methanol fuel and operate at the low temperatures. It also makes use of a PEM, but has different electrode reactions. One of the major hurdles in using methanol as a fuel is that in high concentrations and thin membranes it may pass through the anode layer and proceed to the cathode and degrade it by reacting with oxygen. As the temperatures increase the overpotentials become lower and lower. With the phosphoric acid fuel cell or (PAFC), phosphoric acid electrolyte is used and the operating temperature is between 160 and 180°C. Since, carbon monoxide is not a threat at this temperature, reformed hydrogen may be used. There are no practical fuel cells in the range of temperatures between 200 and 600°C due to an absence of practical electrolytes available. The high temperature fuel cells include molton carbonate fuel cells (MCFC) and solid oxide fuel cells (SOFC) which operate between 650 and 1000°C. Due to the high temperature, simpler reformers may be used and significantly lower the overpotentials that are involved. However, these high temperatures present many material challenges. An additional benefit, however, is that high temperature allows for use of the excess heat in combined heat and power (CHP) applications.

The downside to high temperature fuel cells lies in maintaining the high temperatures which is quite costly, along with material issues. Herein lies the goal of this study, to develop a direct methanol fuel cell (DMFC) that operates in the temperature range of 160°C to 180°C to

take advantage of more favorable kinetics, but to lower the cost of operation and the amount of catalyst needed at the anode and cathode.

1.2   Limiting Factors

There are several reasons why intermediate temperature fuel cells have not succeeded thus far. One concern is the viability of polymer gaskets for sealing. Most polymer gaskets can operate up to 200°C with some reaching as high as 375°C. This temperature range allows for some flexibility for operation, but higher than this temperature range requires other materials such as ceramics. Another concern is adequate insulation for the fuel cell. At the solid oxide temperature of approximately 1000°C, cells are well insulated with the use of ceramics and thus work to minimize heat loss. On the lower end of the temperature scale between 25°C-200°C, cells are typically less insulated and thus have greater heat loss. Generally, optimal performance for this temperature range is achieved, but heat losses could be minimized using thermally insulated housings. Such heat losses are also experienced in the intermediate temperature range.

Durability of membranes is necessary to making fuel cells a viable part of the energy infrastructure. At the intermediate temperature range, life cycles for fuel cells are typically short. This is caused by deactivation of catalyst, loss of electrolyte, clogging of gas channels and more. Therefore, designing a membrane electrode assembly (MEA) capable of being easily replaced or repaired is vital.

Electrolyte retention is also a great challenge amongst intermediate temperature fuel cells. For example, aqueous acids are great proton carriers, but tend to evaporate above 150°C,

ir are washed out at lower temperatures. So, binding them to a support is difficult. Molten salts and alkali are more viable replacements, but tend to act as rigidizers to membranes thus making membranes less pliable and more susceptible to mechanical stresses.

1.3   Work Accomplished

Keeping the limitations and benefits that low and high temperatures provide in mind, it was decided to investigate materials that take advantage of both. By previously working with Nafion®, the functionting of a direct methanol fuel cell was explored. Thereafter, PBI was investigated as a proton exchange membrane fuel cell that showed significant methanol tolerance and operated from 120-180°C (BASF). By using methanol vapor as a fuel, and a PBI membrane electrode assembly, better kinetics are observed and an alternate fuel to high purity hydrogen utilized directly. This thesis shows that commercially available BASF PBI-based MEAs can be successfully used for DMFC.

Chapter 2: Background

2.1   Fuel Cell Components

Fuel cells exist in all shapes and sizes and have varying kinds of operational components. However, there are several key components which are common to all fuel cells. As with all living organism, fuel cells require a fuel source that is consumed to produce energy, in this case electrical. To facilitate this phenomenon, oppositely charged electrodes are placed on either side of the membrane, the negatively charged anode on the fuel side and the positively charged cathode on the oxidant side. In order for the fuel and oxidant to react and generate a cascade of ions, electrons, and products; an electrolyte is utilized. Additionally, separators placed between the electrodes aid in the prevention of possible electrical and fuel shortages. Also, the placement of product streams on either side of the cell allow for product removal. A basic outline of a fuel cell is represented in Figure 2.1 (Bagotsky, 2009):
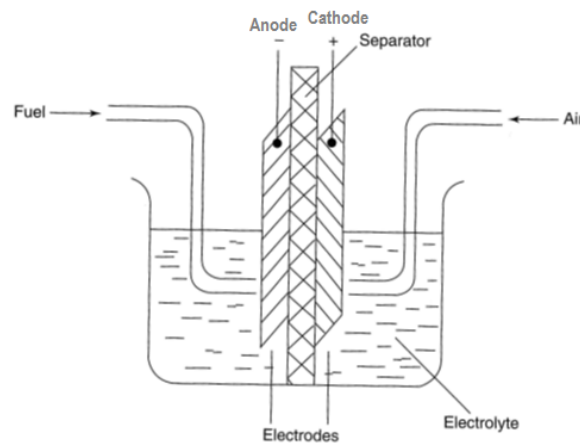
Figure 2.1: Basic fuel cell (Bagotsky, 2009)

2.2 Fuel Cell Mechanism

For the case of pure hydrogen fed as fuel and oxygen as the oxidant, there are two separate reactions occurring at the anode and cathode. On the anode side the following reaction occurs:

$$H_2 \rightarrow 4H^+ + 4e^-$$

While the protons merely diffuse across the electrolyte toward the cathode, the electrons release the energy within their excited state via the anode and then travel across the external circuit cathode. The reaction that occurs on the cathode side is as follows:

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$
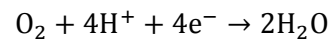
Once water is formed, it exits via tubes on either side of the fuel cell and then disposed of.

2.3   Direct Methanol Fuel Cell

The direct methanol fuel cell (DMFC) is an up and coming fuel cell technology that has the advantage of using an inexpensive and commonly available liquid fuel source, rather than a gaseous fuel like hydrogen which has storage and transport challenges. Methanol allows for simpler storage and transport in a wide range of consumer and transportation applications. Conventional DMFC's operate on the lower temperature range of room temperature to 80°C, and are based on Nafion®. Unfortunately, Nafion® acts as a poor separator and has extensive methanol permeation issues (Chen et al. 2009). The resulting methanol crossover not only reduces efficiency, it also affects performance by reducing cell voltage by increasing potential

losses at the cathode due to depolarization (Lobato et al. 2008). A visual representation of a DMFC is shown in Figure 2.2:
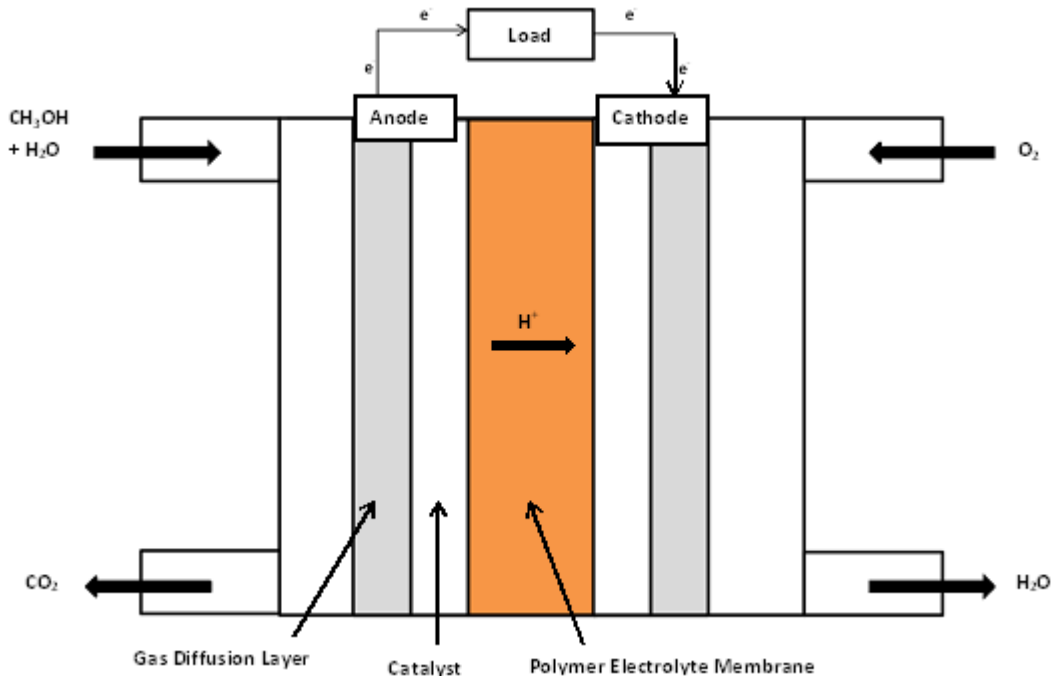
Figure 2.2: DMFC schematic

Beginning with the anode side, a solution of methanol and water is fed to the anode. The two then decompose into carbon dioxide and six protons and electrons at the catalyst layer. Carbon dioxide exits the fuel cell while electrons proceed to the electrical circuit and protons are ferried through the polymer electrolyte membrane (PEM). When the electrons release their energy they then proceed to the cathode. At the cathode catalyst site oxygen binds and combines with the depleted electrons and protons from the PEM to form water. Water then exits the fuel cell.

2.3.1 DMFC Reactions

As with typical proton exchange membrane (PEM) fuel cells, DMFC's utilize proton transfer across an electrolyte membrane. The following reactions occur at the anode side:

$$CH_3OH + H_2O \xrightarrow[\leftrightarrow]{Pt/C} CO_2 + 6H^+ + 6e^-$$
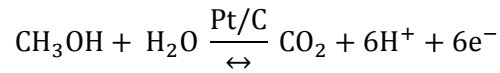
Methanol enters the anode side and binds with the catalyst site, breaking down into carbon dioxide, protons, and electrons. The carbon dioxide is vented whereas the protons are ferried through the membrane and the electrons proceed to the electrical circuit. The anode reaction proceeds through the intermediate carbon monoxide, which poisons the anode catalyst and dramatically reduces performance.

On the cathode side, a reaction occurs to consume the depleted electrons and protons with the addition of oxygen, forming water. The cathode side reaction can be seen as follows:

$$1.5O_2 + 6H^+ + 6e^- \xrightarrow[\leftrightarrow]{Pt/C} 3H_2O$$
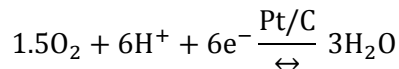
The two electrode reactions can be combined into an overall displayed below:

$$OR: CH_3OH + 1.5O_2 \xrightarrow[\leftrightarrow]{Pt/C} 2H_2O + CO_2$$
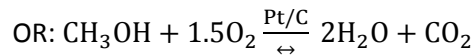
2.4 DMFC Components

2.4.1 Nafion®

Nafion® remains one of the best membranes in use for today's polymer electrolyte fuel cell. It makes use of chains of perflourovinyl ether linked to tetrafluoroethylene (Teflon®) that

provide it with resistance to degradation, and terminated with sulfonic acid groups, which dissociate in the presence of water to provide protons for conduction from anode to cathode. A representation of Nafion® can be seen below in Figure 2.3 (Seung et al. 2004):
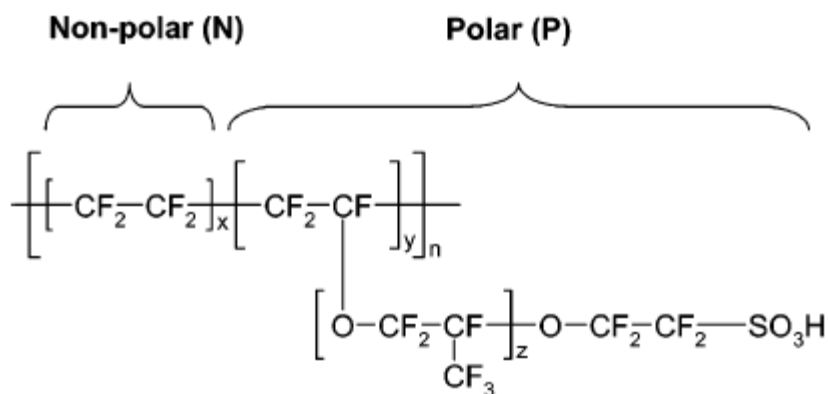
Figure 2.3: Nafion® Structure (Seung et al. 2004).

Upon dissociation in the presence of water, the sulfonic acid groups allow for proton conduction across the membrane. Additionally, it has been found that operating with a humidified feed aids in water retention which also aids in proton conduction. Due to the necessary presence of liquid water, the limiting temperatures of operation remain 20°C-80°C. Nafion® is also present in different forms and thus has varying designations. Nafion® 117, for instance is a widely used for of the membrane. The "11" refers to the equivalent weight of 1100 g and the "7" refers to its thickness of .007 inches. Other Nafion® membranes include Nafion® 115 and Nafion® 112.

2.4.2 DMFC Anode and Cathode Catalysts

Since the majority of DMFC's operate at low temperatures catalysts are necessary to improve the kinetics of the fuel cell. Platinum (Pt) is currently the best catalyst, but by itself is

not selective as to which species it binds. For this reason gas feeds with impurities such as carbon monoxide are able to bind with Pt and are difficult to unbind from the surface, effectively poisoning the catalyst site. Thus high purity fuels must be used in conjunction with Pt to encourage high performance.

For the purpose of running a DMFC, it has been shown that using Pt alloys encourages methanol oxidation and improves performance. One of the most common alloys for fuel cell purposes is platinum alloyed with ruthenium (Pt-Ru). The amount of Pt-Ru in mg/cm^2 also directly impacts the performance of the DMFC . For Nafion® it was shown by Nakagawa & Xiu, that an increase in Pt-Ru amount of anode catalyst improved performance to a point. They found that with Nafion® 112 at 353 K, 3.75 mg/cm^2 offered the best performance of 0.073 W/cm^2 (2003). Commercial DMFC MEAs typically have a loading of Pt at the anode of 2.5 mg/cm^2 and at the cathode of 2.0 mg/cm^2.

2.4.3 Polybenzimidazole

Polybenzimidazole (PBI) is a well-known polymer that is highly resistant to changes in temperature and durable. In order to raise the DMFC temperature, this study utilizes a PBI membrane incorporating phosphoric acid that is responsible for proton conduction. Due to its chains of aromatic compounds and interspersed imidazole groups, PBI has the ability to isolate multiple electrolytes. However, amphoteric acids maintain high proton conductivity and are preferred as they can act as a proton donor or recipient (Li et al. 2004). In fuel cell applications, PBI works as a good support for phosphoric acid by aiding in its retention. The polymer may be viewed below:
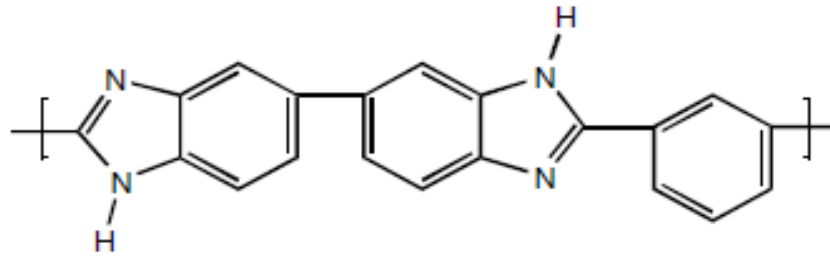
The research group of Seonghan and Benicewicz (2009), looked into variations of PBI. It was found that the derivative (poly(2,20-(dihydroxy-1,4-phenylene)5,50-bibenzimidazole) or (2OH-PBI) had the best conductivity. Additionally, the fuel used for these sets of experiments was high purity hydrogen and oxygen with the performance being .69 V at 0.2 A/cm^2 at 180°C. Also, using a Pt-Ru alloy allowed for the best performance with the highest conductivity being.43 S/cm with an acid doping level of 28.3 phosphoric acid/ repeating unit .

The conventional PBI-phosphoric acid (PA) membrane is made by soaking a PBI film in phosphoric acid. In an alternate commercial (BASF Fuel Cell, Inc.) version of the synthesis of the PBI-PA fuel cell membrane, the phosphoric acid is incorporated even before the polymerization step (Schmidt and Baurmeister, 2008). Thus, the polymerization of the monomers, tetra-amino biphenyl and an aromatic di-carboxylic acid, is done at elevated temperatures in polyphosphoric acid (phosphoric acid with concentrations above 100%), to produce a sol from which the membrane is cast and subsequently hydrolyzed. Thereupon, it undergoes a sol–gel transition resulting in the final membrane, which can have up to 70 phosphoric acid molecules per PBI unit. The commercial MEAs produced from these membranes include roughly 1 mg/cm^2 Pt supported on Vulcan XC 72 at the anode, and a similar amount of Pt-alloy at the cathode,

which is more resistant to phosphate ion adsorption at the cathode. The MEAs function well at 160-180 ºC for reformed hydrogen containing up to 3% CO, and have shown good durability in micro-CHP applications. The durability is attributed to the inherent resistance of PBI to peroxide degradation. Of course, any condensation of water produced, due, e.g., to any temperature incursions, must be completely avoided, as this would lead to leaching of the phosphoric acid from the membrane.

2.5 Previous Work with PBI-based DMFCs

The use of phosphoric-acid (PA) doped PBI in DMFCs operating at high temperatures has so far received little attention, although it was originally investigated by Savinell and coworkers (Wainright et al., 1995; Wang et al., 1996) when PBI-PA was first developed. However, besides their pioneering work, there is little subsequent work on PBI-PA based DMFC reported in the open literature, although some researchers have tried to raise the DMFC temperature via Nafion nanocomposites, including Nafion-PBI blends (Ainla and Brandell, 2007; Hu et al., 2008). An important exception is the recent work of Lobato et al. (2008), who demonstrated the use of PBI-PA membranes in a DMFC with a vapor feed. Lobato et al. (2008) were able to reduce the catalyst loading down to 1 mg/cm^2 Pt-Ru/C at the anode and Pt black at the cathode. More recently, Mamlouk et al. (2011) used a PBI-PA membrane with 2 M methanol vapor and oxygen, and 1.7 mg/cm^2 60 wt% Pt-Ru/C anode, and 0.5 mg/cm^2 Pt/C cathode. They observed lackluster performance, however, with a peak performance of 10-16 mW/cm^2.

Chapter 3: Methodology

3.1   PBI Membrane Based Celtec® MEA

The MEA that was used for this study is a Celtec®-P1000 MEA provided by BASF Fuel Cell. It is a well-developed MEA that performs well at intermediate temperatures (160-180°C) using hydrogen/ oxygen or hydrogen/ air. The MEA is composed of a 45 cm^2 active area with an electrode on either side. The electrodes are believed to be carbon cloth with a catalyst loading of 1.8 mg/cm^2 in total. This includes 1.0 mg/cm^2 Pt at the anode and 0.8 mg/cm^2 Pt alloy at the cathode. The MEA can be seen in Figure 3:
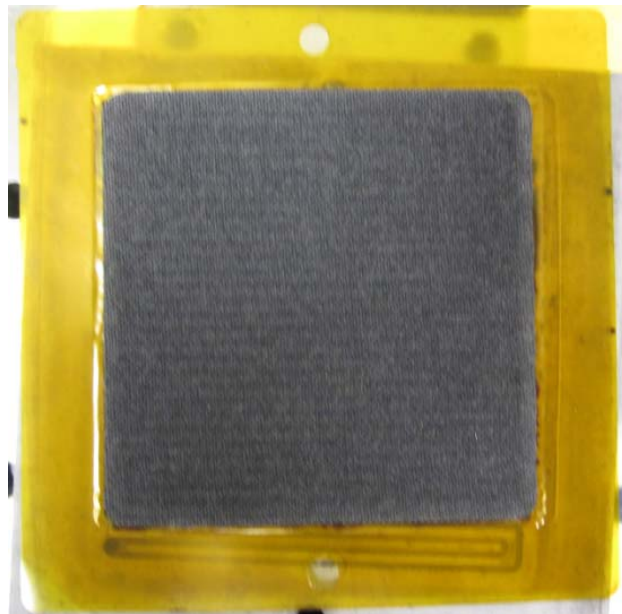
Figure 3: Celtec® P-1000 MEA from BASF

3.2   PBI Fuel Cell

In selecting a fuel cell for testing the PBI MEA, BASF's high temperature fuel cell was chosen. In order to minimize the chance of failure with using a fuel cell from one company and a membrane from another, it was decided to order both from BASF. In this case, the main variables would be methanol concentration and temperature. The layout of the fuel cell may be viewed in the following figure from BASF:

Figure 3.1: BASF High Temperature Fuel Cell

The fuel cell layout provided by BASF (Figure 3.1) is described from left to right. The flexible heater is on the outermost part of the fuel cell frame at integrates with a thermocouple in the fuel cell station to adjust the inner fuel cell temperature from 50°C to 180°C as needed for the current testing regimen. Next, sits a segment of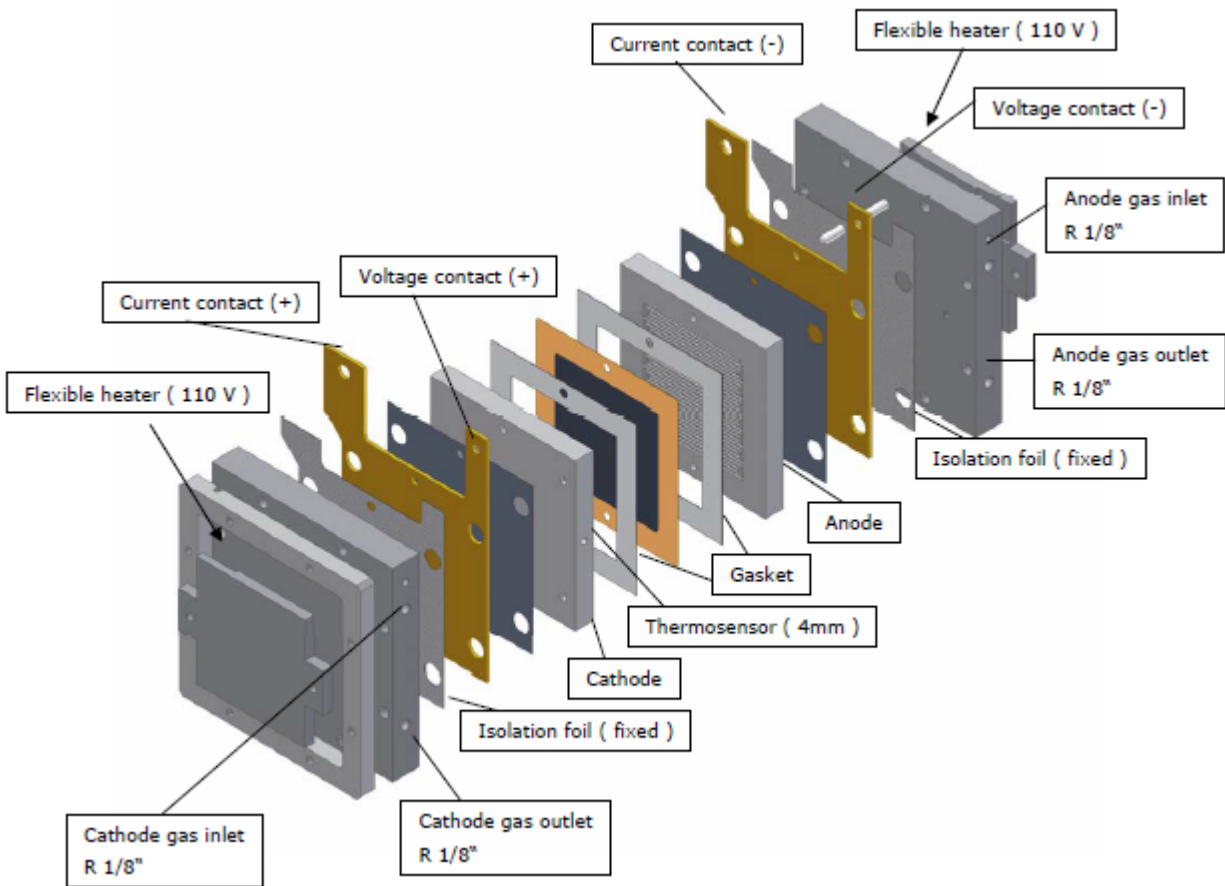 metal plate that contains holes for the inlet and outlet flows to and from the cathode. In order to separate the heater and the cathode plate electrically, a thin piece of isolation foil is placed between the metal plate and the cathode side voltage/ current contact plate. Following the contact plate is another piece of isolation foil that in this case conducts electrons from the graphite plate to the contact plate. The graphite plate contains a series of serpentine channels that allow for efficient gas diffusion to and from the membrane as well as applying even pressure as to avoid membrane tearing. Directly in the center of the device is the MEA or heart of the fuel cell.

3.3　PBI Fuel Cell Test Station
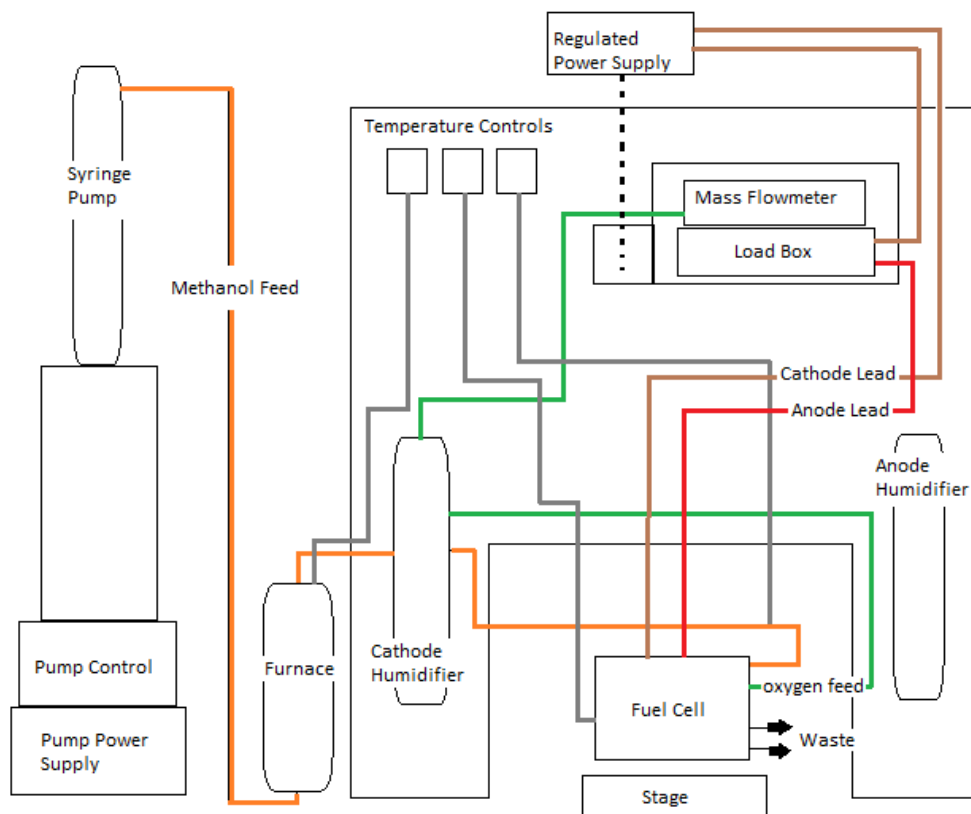
Figure 3.2: Fuel Cell Test Station

In Figure 3.2, the schematic of the Fuel Cell Test Station is shown. The station has several major pieces of equipment that participate in the proper regulation of the fuel cell apparatus. The syringe pump (ISCO, Model 1000D), is connected to the pump control (ISCO, Series D Pump Controller) which allow for a constant flow of methanol to the cell. The temperature controllers (Omega CN9000A) regulate the temperature of the furnace for vaporizing feed; methanol feed pipe wrapped in heating tape, and fuel cell. To the right of the temperature controllers is the regulated power supply (Lambda Electronics, Inc., LFS-46-5) which allows for proper power allocation from the fuel cell to the load box (Hewlett Packard 6060B). Above the load box is the Mass Flowmeter (Tylan General, RO-28), that may

be used for low flowrates of oxygen, hydrogen, or nitrogen. This piece of equipment is not regularly used however, since the alternative bypass streams may achieve higher flow rates. There are also two humidifiers on either side of the fuel cell for Nafion® systems, but were not used for the PBI DMFC test.

Below in Figure 3.3 is an image of the high temperature BASF fuel cell apparatus. All inlet and outlet streams are on the right of the cell. The anode feed in this case is the insulated methanol feed pipe which may be switched out for a gas feed that supplies hydrogen or nitrogen instead. In addition the cathode feed supplies oxygen, air, or nitrogen. Below both feeds, are the corresponding outlets where carbon dioxide is release on the anode side and water on the cathode side. The cathode lead and anode lead are on alternating connector plates as to allow for proper voltage and current regulation throughout the cell. On the left of the cell is the thermocouple which interfaces with the temperature controller to regulate the fuel cell. The front and back faces are where the heating plate administer temperature changes based on the thermocouple's readings.
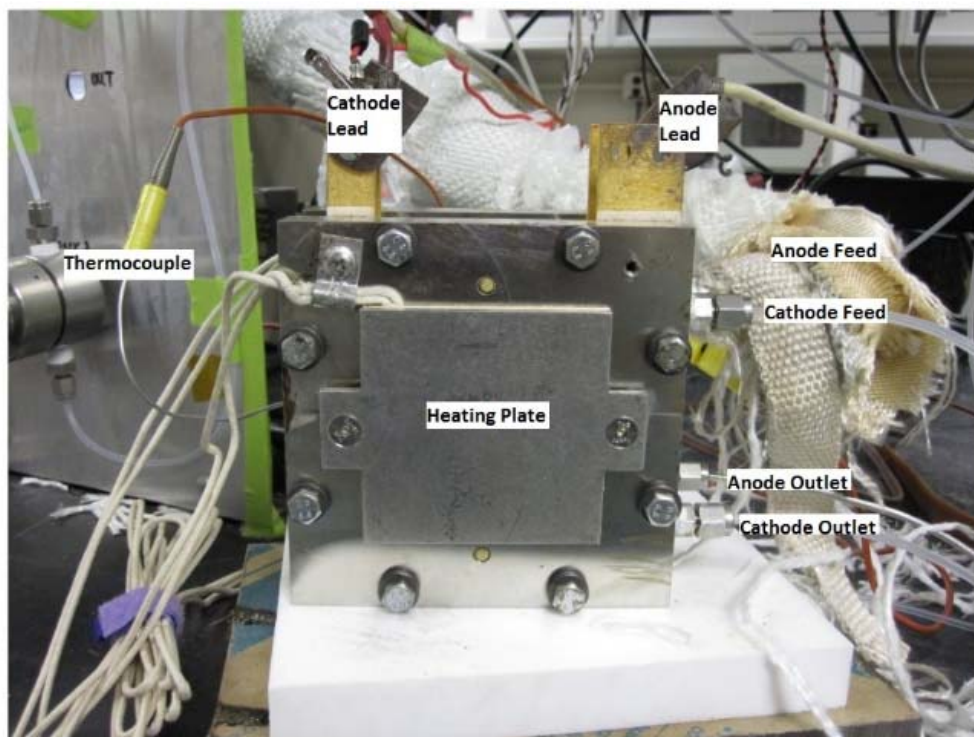
Figure 3.3: PBI fuel cell

3.4   PBI Test Regimen

The MEA that were available for testing were two Celctec P-1000 membranes supplied from BASF and one Celtec® P-1000 at double thickness. These MEA are designed hydrogen/oxygen or hydrogen/ air, but were shown to have significant methanol tolerance by studies performed by BASF. Based on this and previous tests with Celtec® P-1000, it was decided to gather more insight as to their performance with specific methanol concentration as well as varying temperature. The temperatures under consideration are 160, 170, and 180°C as well as the methanol solution concentrations of 1-3M, 5M, 7.5M, 10M with oxidants being oxygen or air. Prior to this study, data was collected for 3M, 5M, and 10M to give an initial understanding of methanol behavior (Do et al. 2012), but additional insight was needed.

For any membrane electrode assembly, it is best to undergo an activation step. This step allows the membrane to become accustomed to the types of fuel that will be used over time and adapts electrochemically to achieve the best performance. The suggested activation by BASF, was a 50 hour test cycle at 160°C under hydrogen and air feeds with a 10A load. Initial testing with methanol showed that performance would improve after 15 hours under 3M methanol conditions with load cycling at 160°C. Additionally, so as to facilitate activation oxygen was used to replace air.

Chapter 4: Results and Discussion

The MEA's used were all Celtec®-P1000 provided by BASF. There are three MEA's with four separate classifications. The classifications are as follows. PBI 1.0 denotes a used Celtec®-P1000 of the original thickness, PBI 1x is the same MEA as PBI 1.0, but re-impregnated with electrolyte, PBI 1.0v is simply a virgin version of PBI 1.0, and the final MEA is the PBI 2x which contains a membrane that is twice as thick as PBI 1.0 and PBI 1.0v. The following sections are broken up into the effects of temperature, methanol concentration, and oxidant type on fuel cell performance for each MEA.

4.1   PBI 1.0 Performance

4.1.1 PBI 1.0 Temperature Effects

With an increase in temperature it was predicted that the performance of PBI 1.0 will improve due to improved kinetics. The following figure demonstrates the improved performance of PBI 1.0 with temperature for a 2.0 M methanol feed:
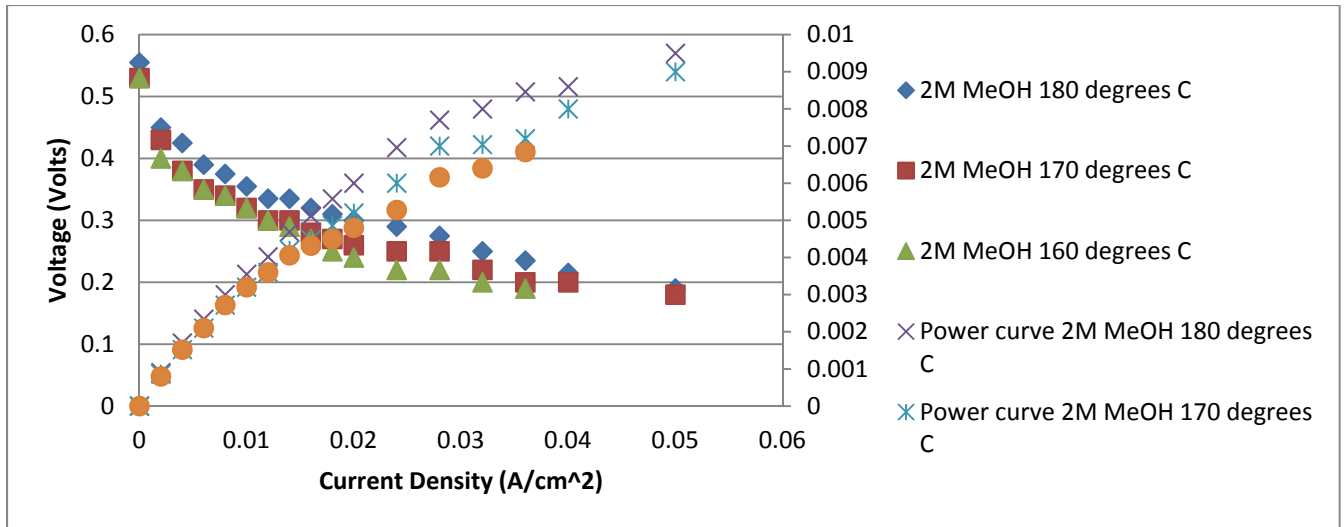
Figure 4.1: PBI 1.0 performance with 2M MeOH using air

However, several negative effects were demonstrated by particular MEA over time. From a measure of change in mass of the membrane overtime, attributed to phosphoric acid loss perhaps because of liquid droplets due to incomplete vaporization of feed, the performance began to dwindle. Whether it was from degrading of the cathode side catalyst layer, loss of electrolyte, or mechanical failure, the MEA began to lose its ability to maintain a good performance. At this stage since many changes were being made to the fuel cell station as well as the activation and test regimen, it was decided to attempt to add additional electrolyte (phosphoric acid) to the membrane. The electrolyte was added by alternating the sides of the MEA in a 85% phosphoric acid bath, thus taking advantage of capillary action. Excess phosphoric acid was dabbed away and reinserted into the fuel cell housing. With this addition of electrolyte, the membrane became designated as PBI 1x.

4.2   PBI 1x Performance

4.2.1   PBI 1x: Temperature Effects

With the addition of phosphoric acid the immediate outlook was promising. The

performance of the membrane began to improve immediately. This membrane also

demonstrated improved performance with increasing temperature as is shown in Figure 4.2
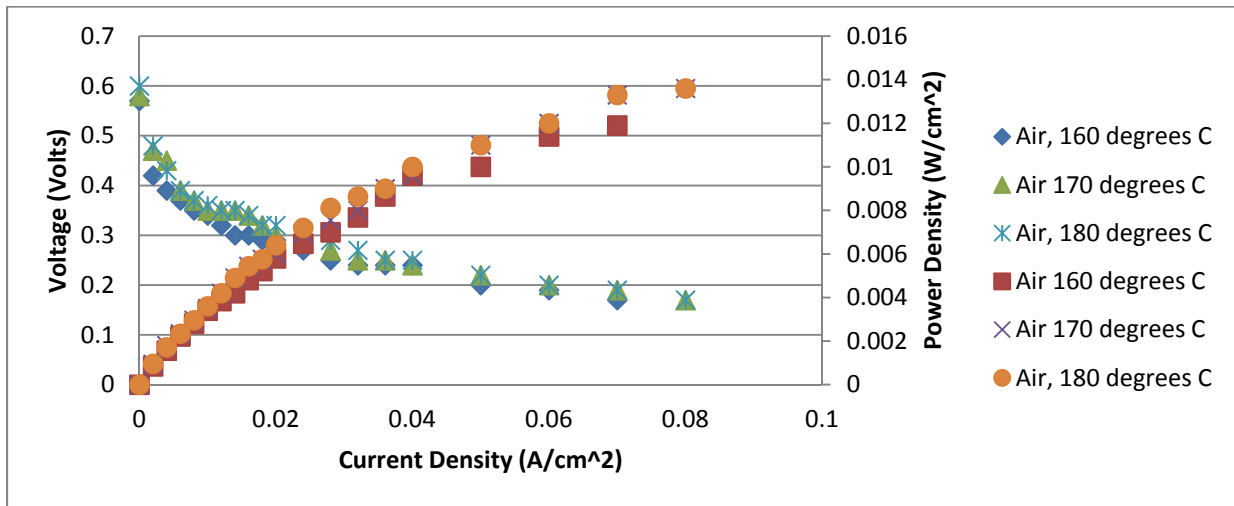
below:

Figure 4.2: PBI 1x performance with 2M MeOH using air

4.2.2   PBI 1x: Effect of methanol Concentration on Performance

As the concentration of methanol increases, more oxygen is required to complete the

overall reaction for the DMFC. Thus, using oxygen versus air becomes more viable because the

overall flow rate is lower and less stress is placed on the assembly. Additionally, when gauging

the performance of the cell it is possible to see if the MEA is even capable of performing at

higher methanol concentrations. The performance of MEA PBI 1x may be seen in the Figure 4.3:
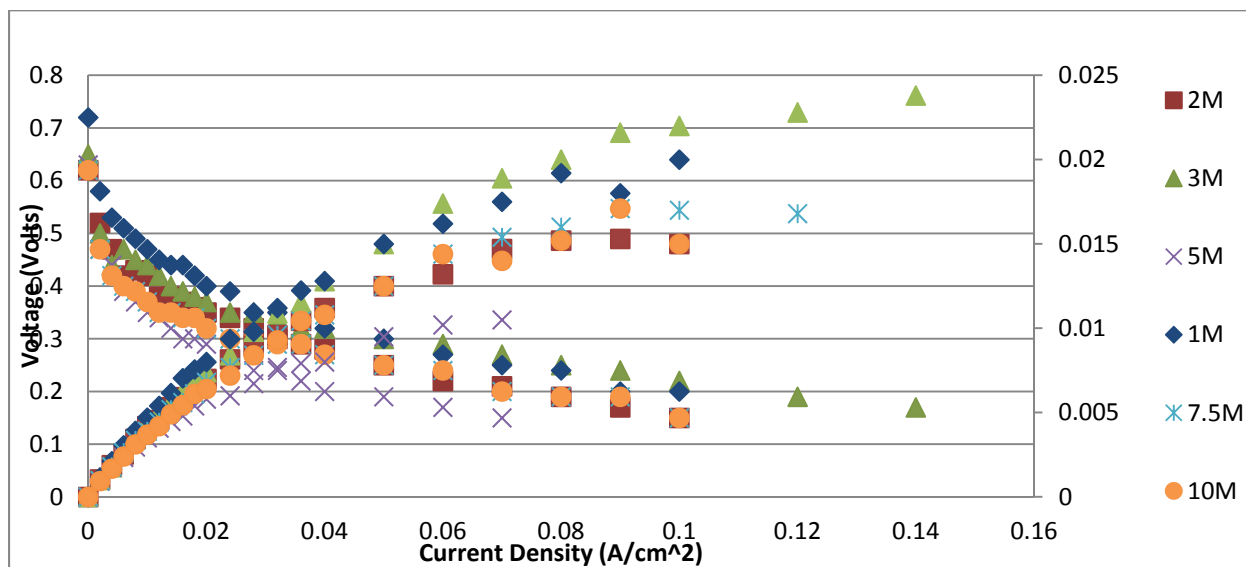
Figure 4.3: PBI 1x performance with MeOH using oxygen at 180°C

At this stage in testing of PBI 1.0 and PBI 1x the performance was promising, but not entirely convincing as to the best performance for this type of membrane. As seen with other research groups, the performance of methanol concentration increases to a point and then begins to falter. For this membrane, the performance increased from 1M to 3M with 2M acting as a slight outlier from the expected trend. It is believed that the poor 2M performance can be attributed to the instability of the re-impregnated membrane. More specifically, voltage fluctuations were present and averages of voltage values were recorded for various loadings. Moreover 5M, 7.5M, and 10M began to lose performance significantly, although 5M performance was expected to perform better than 7.5M and 10M.

With the irregular performance after the re-impregnation step to create PBI 1x, it was concluded that another testing of the Celtec®P1000 virgin MEA, denoted as PBI 1.0v would be

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necessary to better understand the effects of increasing temperature concentration. This is

described later.

4.2.3 PBI 1x: Effect of oxygen vs. air on Performance

There are several advantages and disadvantages to using air as an alternative to oxygen.

One of the most advantageous reasons for using air is that it is readily available and cheaper

than using high purity oxygen. However, the percentage of air that is oxygen is approximately

21% which is one of its major limitations. For the purpose of a methanol fuel cell, oxygen allows

for the cathode reactions to go to completion. As the concentration of methanol increases in

the feed, the flow rate of oxygen to the cell must also increase. Inevitably, at high

concentrations of methanol, high flow rates of air must be used and not only make the diffusion

of oxygen difficult but put added stress on the membrane. The limitation of air may be seen in
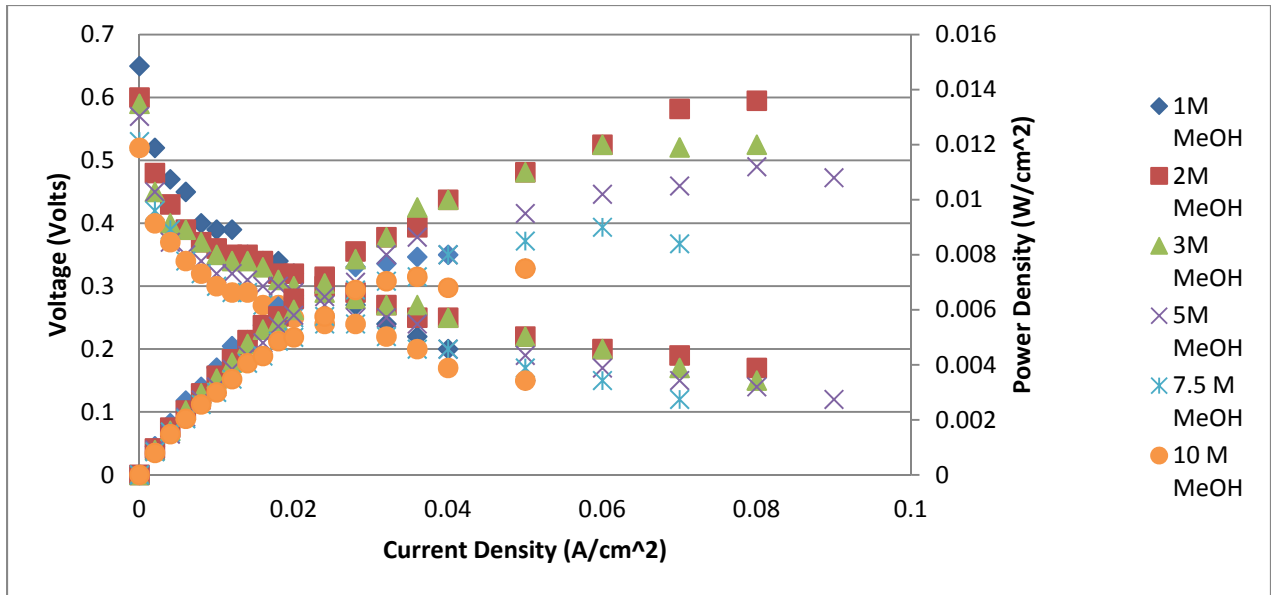
Figure 4.4:

Figure 4.4: PBI 1x: performance with MeOH using air @ 180°C

Figure 9 shows that for PBI 1x, the maximum power density is achieved for 2M methanol with a value of approximately 1.38x10^-2 W/cm^2 at a current density of 8.00x10^-2 A/cm^2. Additionally, it may be noted that 7.5M faltered at 7.00x10^-2 A/cm^2 and 10M at 5.00x10^-2 A/cm^2. In contrast, oxygen's best performance was approximately 2.40x10^-2 W/cm^2 at 1.4x10^-2 A/cm^2. Moreover, 10M achieved a maximum power density of approximately 1.70x10^-12 W/cm^2 at 8.00x10^-2 A/cm^2, which is greater than the best performance with air. This graph shows that at higher concentrations of methanol, performance is strongly limited because of oxygen limitations in air.

4.3   PBI 1.0v Performance

4.3.1.1   PBI1.0v: Temperature Effects

PBI 1.0v provided a chance to test a specially designed activation regimen as well as minimize possible losses in performance. By adding 15 hours of load cycling at 160°C with 3M methanol and using oxygen, the membrane became stabilized and was more consistent with providing good performance. Figure 4.5 below depicts performance with increasing temperature with oxygen fed at the cathode.
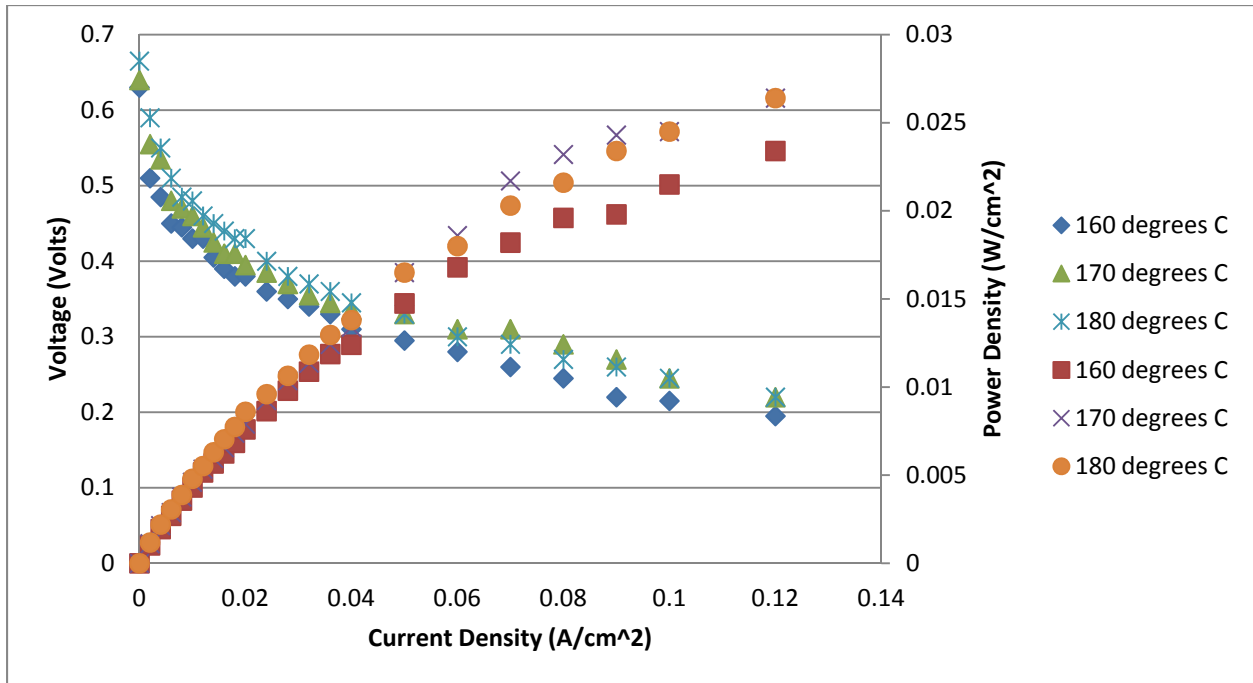

Figure 4.5: PBI 1.0v performance with 1M MeOH using oxygen

The performance with increasing temperature does also increase, but with several outliers. At some points 170°C performs better than 180°C, but overall they performed similarly. The most consistent trend is that 160°C is simply not high enough for high power densities.

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4.3.2 PBI 1.0v: Effect of Methanol Concentration on Performance

With the minimization of performance losses, more convincing trends were conveyed by the data collected. By maintaining the integrity of the membrane throughout the testing process, higher performance was realized for higher concentrations than previously encountered. The effect of methanol concentration can be seen below:
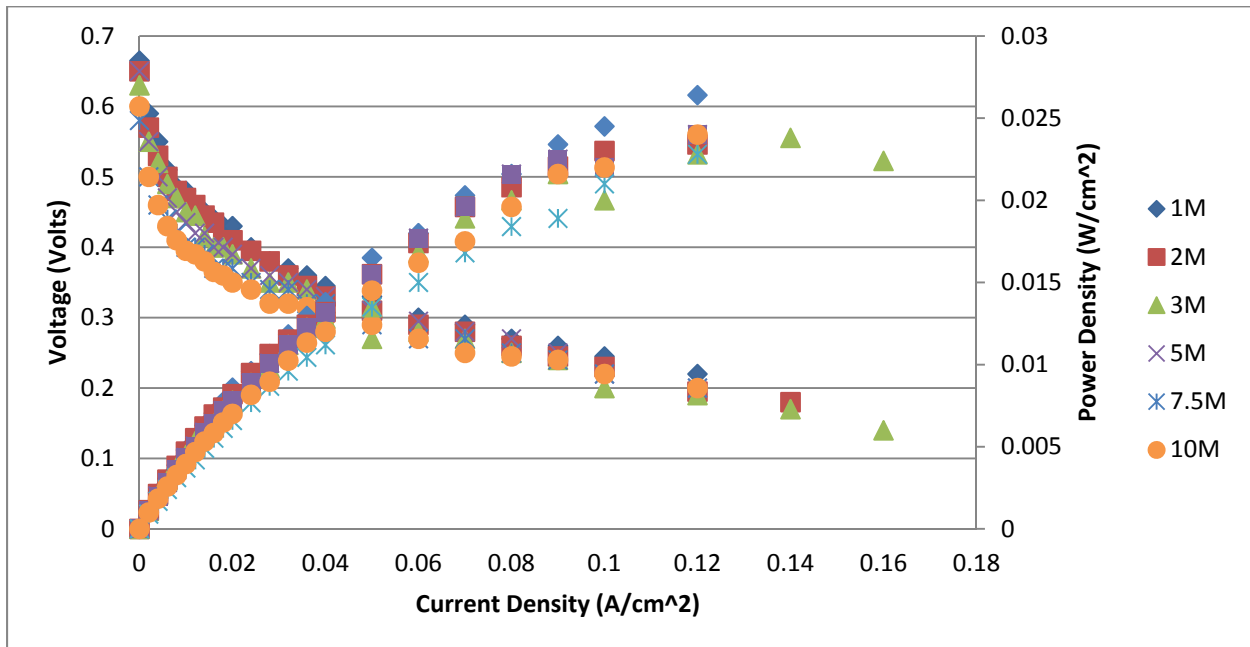
Figure 4.6: PBI 1.0v performance with MeOH using oxygen @ 180°C

The performance that was achieved for PBI 1.0v is very promising. By maintaining the stability of the membrane, much higher performance was generated. As before it was shown that 1M generally performs well, but it can be shown that it suffers from mass transfer limitations for higher current densities. With increasing concentration, higher current densities are possible. What was very surprising was that 10M was capable at performing well at high current densities and did not falter over time due to increased methanol crossover.

4.3.3   PBI 1.0v: Effect of oxygen vs. air on Performance

Regardless of the poor overall performance of PBI 1x, the effects of oxygen vs. air are equally as prevalent in PBI 1.0v. The performance was significantly increased and is depicted in the following figure:
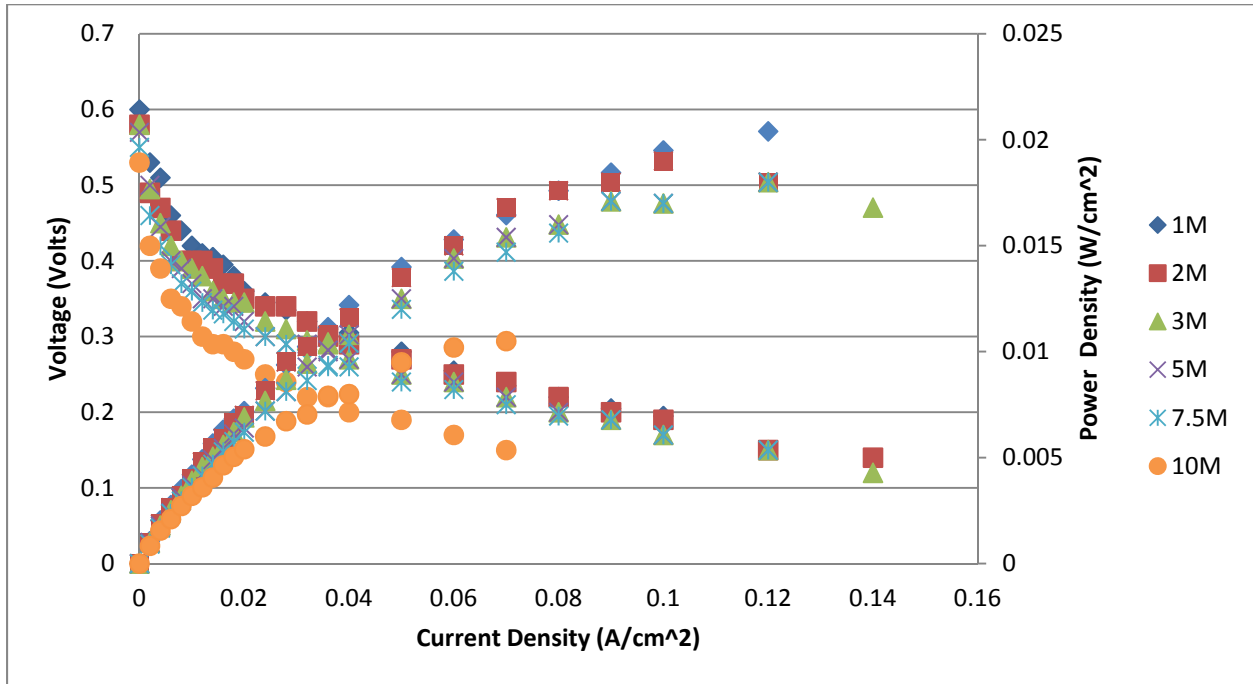

Figure 4.7: PBI 1.0v performance with MeOH using air @ 180°C

PBI 1.0v achieved a noteworthy improvement in performance showing a maximum power density for 1M of approximately 2.10x10^-2 W/cm^2 at a current density of 1.20x10^-1 A/cm^2. The corresponding maximum for oxygen was 2.70x10^-2 W/cm^2 at 2.00x10^-1 A/cm^2. Additionally, higher concentrations performed better than previously observed with air, but still faltered at 10M.

4.4   PBI 2.0 Performance

Due to the promising results with Celtec®-P1000, BASF supplied us with a double thickness membrane based MEA, which was designated PBI 2x. The concept behind testing this MEA was that due to its increased thickness it would be more tolerant to higher concentrations of methanol and would inhibit methanol crossover.

4.4.1   PBI 2.0: Temperature Effects

The PBI 2x membrane demonstrated its increased stability and improved performance with increases in temperature. It was more promising as well as consistent over time. The following depiction of the membrane's performance with temperature may be viewed in Figure 4.8:
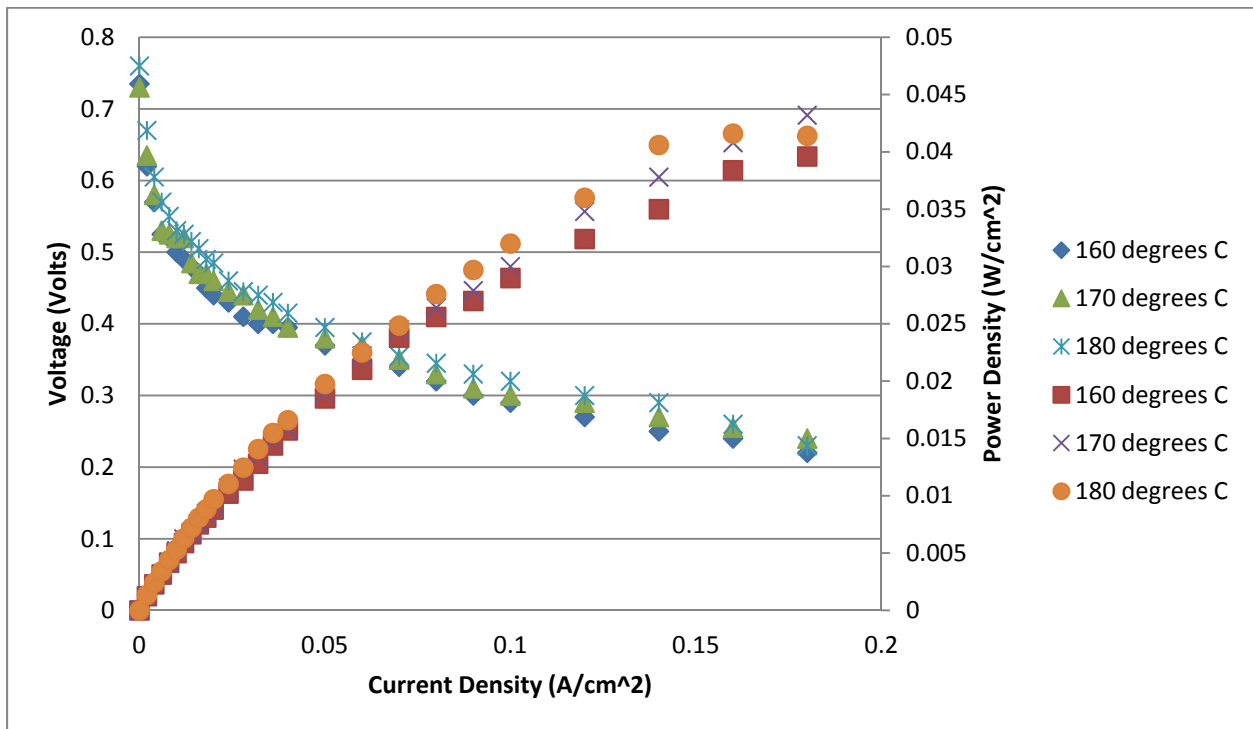

Figure 4.8: PBI 2.0 performance with 1M MeOH using oxygen

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As was shown previously, performance increases with temperature. Except for one outlier for the 170°C plot, PBI 2.0 performs the best at 180°C. It may also be noted that the graphs for PBI 2.0 are smoother and less erratic over time than with previous membranes.

4.4.2 PBI 2.0: Effects of methanol concentration on Performance

Increasing the thickness of the membrane was able to accomplish several feats simultaneously. The overall goal is to reduce crossover and improve performance, but to what extent was unknown. With Nafion®, thicker membranes have proven to more strongly inhibit methanol crossover and thus preserve the performance. With PBI, the hypothesis is that the increased thickness will support higher performance and minimize electrode degradation due to methanol crossover. The performance of the PBI 2.0 membrane over various concentrations can be observed in Figure 4.9 below:
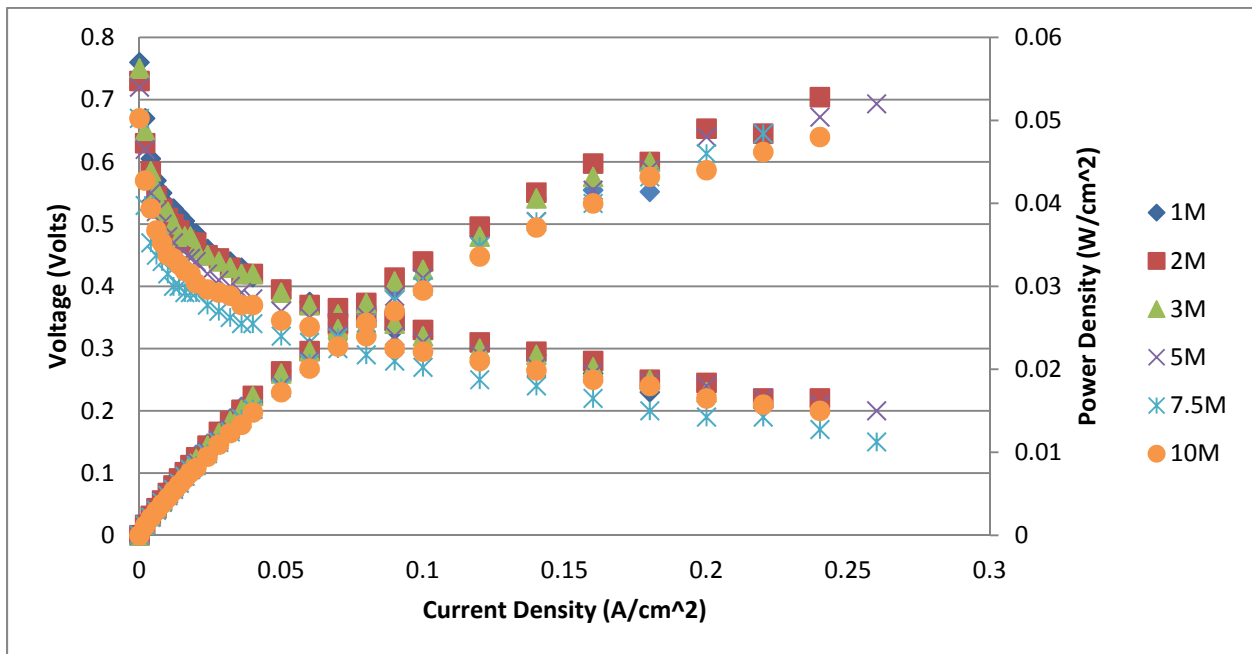

Figure 4.9: PBI 2.0 performance with MeOH using oxygen @ 180°C

With PBI 1.0v, it was shown that the membrane could support up to 10M effectively which was not possible with PBI 1x. So, it was expected that PBI 2.0 would also be able to support 10M. In addition, the MEA proved to perform stronger with 5M than with 10M, with a maximum power density of approximately .055 W/cm^2 for 5M at 180°C. Conversely, PBI 1.0v showed a maximum of .027 W/cm^2 both for 7.5M and 10M at 180°C. This shows that by doubling the thickness of the membrane, the power density was also effectively doubled. Another general fact that was notable was that from in-house testing of PBI and Nafion® membranes, high concentrations of methanol performed poorly, which is not a non-limiting factor.

4.4.3 PBI 2.0: Effect of Oxygen vs. Air on Performance

The use of air with PBI 2x resulted in similar results as PBI 1x and PBI 1.5x, but managed to outperform both membranes for their oxygen runs. The results with increasing concentration were also rather surprising as the MEA remained stable with the diffusion limitations of air. The effects are showcased in the following figure:
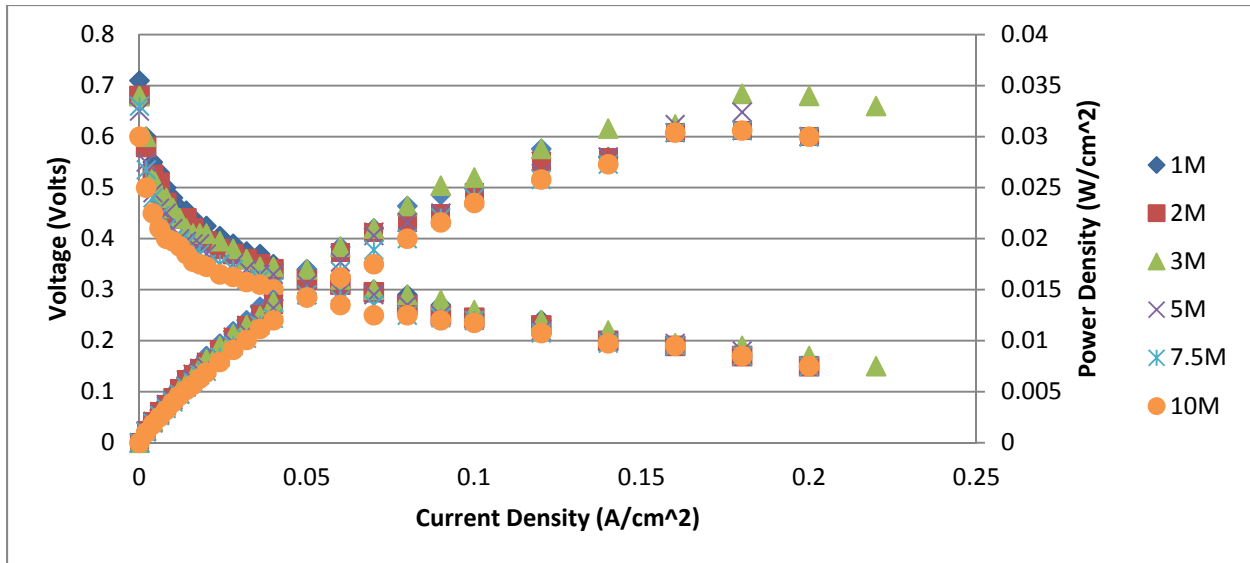
The maximum performance was achieved at approximately 3.4x10^-2 W/cm^2 at approximately 1.8x10^-1 A/cm^2. The corresponding maximum for oxygen was 5.7x10^-2 W/cm^2 for 3.3x10^-1 A/cm^2. One of the most prominent observations from this figure is that 10M followed similar trends as lower concentrations with air for increasing current densities.

Chapter 5: Conclusions & Recommendations

Fuel cells in today's society remain the most efficient means for producing power. However, they inherently possess several limitations that inhibit them from becoming a mainstay of the world's energy economy. By limiting the amount of precious metals used, and varying the types of fuel and oxidant, the fuel cell is becoming a more attractive alternative to the traditional combustion engine and batteries. Polybenzimidazole is a fuel cell membrane that shows promise in achieving this goal. It was shown in this work that the commercial PBI-based Celtec®-P1000 MEA, even though designed for reformed hydrogen, performed well with vapor feed as a DMFC. It was shown further in this report that by doubling the thickness of the membrane, the power density was increased by 2.70×10^{-2} W/cm^2 to 5.50×10^{-2} W/cm^2 with methanol. Additionally, it was proven that PBI performs optimally at 180°C with oxygen vs. air. However, air may be used, but with a significant loss in performance. Moreover the membrane exhibited greater stability and did not lose performance over the course of the test cycle. By adding Pt-Ru at the anode side of the MEA, methanol oxidation may occur at a faster rate as shown in traditional DMFC's and may increase the fuel cell performance even further. It is also recommended that the fuel cell test station employ a more suitable form of insulation for the methanol feed pipe as to lower the furnace temperature. PBI presents a stepping stone for fuel cells because of its proven benefit from higher temperature operation and lower platinum content. With additional life cycle testing, PBI fuel cells have the potential to contribute significantly to the competiveness and viability of a fuel cell energy economy.

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Appendix A: Fuel Cell Assembly

Proper assembly of the fuel cell is crucial to obtaining optimal performance. It is important to make note of the MEA's mass and take pictures of the current state of the MEA is it may change during testing. A key factor with any MEA is proper labeling of the anode side and cathode side of the electrodes as improper assembly may reduce performance. With the anode side of the fuel cell housing clamped in place with its serpentine channels up, place the MEA, with gaskets on either side, on top of the anode side serpentine channels. When this is accomplished proceed to gently place the cathode side fuel cell housing on top of the MEA. Next place the two dowels through the alignment holes in the center of the housing. Additionally, place all eight through bolts in each corresponding slot with two washers on the cathode side and one nut underneath on the anode side. At this time hand-tighten all the through bolts and prepare to tighten with a torque wrench. As over-compression is a constant concern with FC assembly, the recommended torque for PBI is 62 lb_f*in. It is also important to tighten the bolts in a crisscross pattern as to evenly displace the down force on the MEA.

Now that the fuel cell is assembled it can attached to the fuel cell station. The fuel shell should be placed with the cathode side facing away from the station and all inlets and outlets facing towards the right on top of the heat resistant stage. First connect the long waste line to the anode side outlet and the short waste line to the cathode side outlet. Each end of the outlet lines are placed in beakers filled with D.I. water as to visibly show waste flow. The next step is to screw in the oxygen/air feed line to the cathode side inlet and the hydrogen feed line to anode side inlet. The thermocouple may be placed in the graphite plate and the male heater plug may be inserted into the female temperature controller plug. The last step for assembly is attaching the load box leads to the fuel cell. The red lead is

to be connected to the cathode side connector plate whereas the black lead is connected to the anode side collector plate.

The activation procedure for PBI was adapted by BASF to ensure proper performance for the fuel cell. The fuel cell was heated to 160°C under a nitrogen atmosphere. Once it reached 160°C, hydrogen and oxygen were fed to the cell via bypass. Optimal feed rates were monitored via the best performance from the load box. When the best open circuit voltage (OCV) was achieved a load of 10 A/cm^2 was placed on the fuel cell for 50 hours. After 50 hours, switch fuel and oxidant to nitrogen and either lower the fuel cell temperature to 50°C or prepare for testing under current conditions. Note, that it is important to turn off the load box when nitrogen is flowing through the fuel cell.

It was found that a second activation of 15 hours for use of methanol was necessary to achieve the best performance with the current setup. The syringe pump was filled with 1000mL of 3M methanol while the furnace was set to 300°C and the methanol feed line to 200°C. These temperatures are necessary as the two corresponding heaters are separated by a 2.5 ft. stainless steel pipe wrapped in insulating cloth. The methanol feed line is first connected to a 3 ft. tube connected to a beaker that is used to confirm vaporization of methanol. When temperatures are achieved, the flowrate from the syringe pump is set to 1 mL/min and vaporized. Upon vaporization, switch off nitrogen flow and run oxygen to the cathode side while attaching the methanol feed pipe to the cell. With all feed lines running, switch on the load box and begin activation. Once activation is completed, switch back to nitrogen and begin to vaporize the methanol concentration of interest for testing purposes.

Appendix B: Fuel Cell Test Station
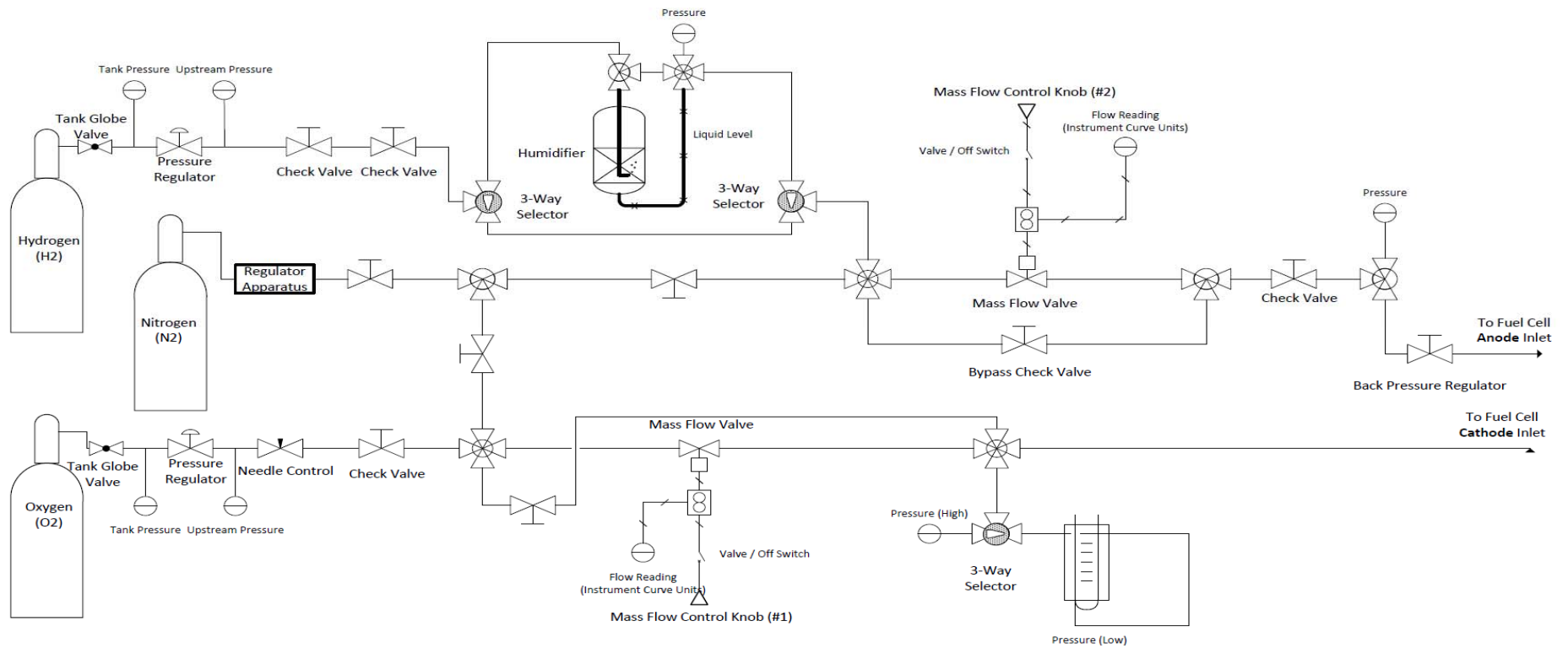
Process Flow Diagram

Figure B1: Fuel Cell Spreadsheet (Personal communication, Perrone 2012)

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Bypass

<u>Hydrogen Feed Start</u>

1. Begin by opening the globe valve to the hydrogen tank.

2. Change pressure regulator to a stream pressure of choice.

3. Open the first and second check valves closest to the hydrogen tank.

4. If using the bypass, open the bypass check valve.

5. Open the last check valve.

<u>Hydrogen Feed Stop</u>

1. Close the hydrogen tank globe valve.

2. Change the pressure regulator to no pressure.

3. Proceed to close first and second check valves from the hydrogen tank.

4. Adjust the first and second three way valves to neutral position

5. Close the bypass check valve

6. Close the last check valve

7. Turn the back pressure regulator off

<u>Oxygen Feed Start</u>

1. Open the oxygen tank globe valve

2. Change pressure regulator to stream pressure of choice

3. Open the needle valve.

4. Open the check valve.

5. Open the bypass check valve.

6. Adjust pressure and flowrate with the back pressure regulator.

Oxygen Feed Stop

1. Close the oxygen tank globe valve.

2. Change the pressure regulator to no pressure.

3. Shut off the needle valve.

4. Shut off the check valve.

5. Close the bypass check valve.

6. Shut off the back pressure regulator.

Nitrogen Anode Feed Start

1. Open the nitrogen tank globe valve.

2. Change the pressure regulator to the stream pressure of choice.

3. Open the needle valve.

4. Open the check valve.

5. Following the line that junctions with the hydrogen line, open the check valve with the green handle leading to the hydrogen lines.

6. Open the bypass check valve.

7. Using the back pressure regulator, change the pressure and flowrate as needed. Note, that only a low flow rate of nitrogen is necessary to keep the streams clear.

Nitrogen Anode Feed Stop

1. Close the nitrogen tank globe valve.

2. Change the pressure regulator to no pressure.

3. Close the needle valve.

4. Close the check valve.

5. Following the line that junctions with the hydrogen line, close the check valve with the green handle leading to the hydrogen lines.

6. Close the bypass check valve.

7. Close the last check valve.

Nitrogen Cathode Feed Start

1. Open the nitrogen tank globe valve.

2. Change the pressure regulator to the pressure of choice.

3. Open the needle valve.

4. Open the check valve.

5. Following the line that junctions with the oxygen pathway, open the check valve with the black handle that leads to the oxygen lines.

6. Open the bypass check valve.

7. Use the backpressure regulator to change the pressure and flow rate.

Nitrogen Cathode Feed Stop

1. Close the nitrogen tank globe valve.

2. Change the pressure regulator to no pressure.

3. Close the needle valve.

4. Close the check valve.

5. Following the line that junctions with the oxygen pathway, close the check valve with the red handle.

6. Close the bypass check valve.

Syringe Pump Instructions
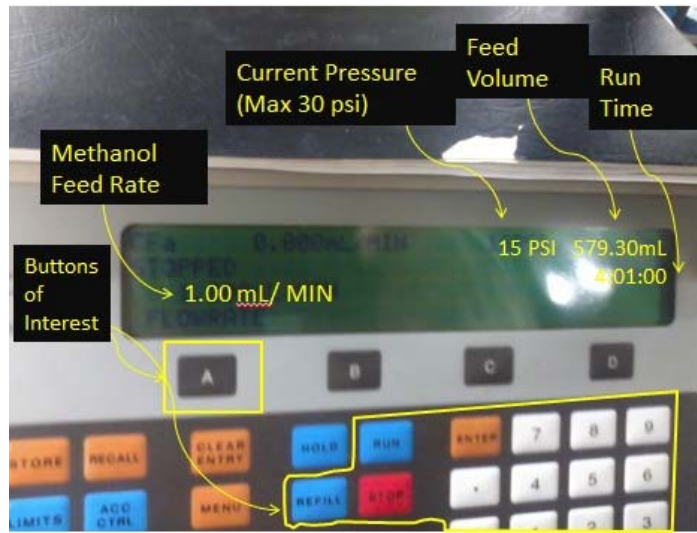
- When pump is inactive, filled with D.I. Water

- In order to empty tank:

  - Press "A"

    - Enter flow rate via number keys

      - Note: Max flow is 1000 mL

  - Press "Enter"

  - Press "Run" to empty tank contents into D.I. Water container via feed line

- In order to fill tank:

    - Prepare 500 mL of "X" Molar methanol

    - Place Syringe Pump Feed Line in methanol solution

    - Press "Refill"

- To operate Syringe Pump for methanol feed:

    - Press "A"

        - Enter "1.00" mL/min

    - Press "Enter"

    - Press "Run"

Thermo-controller Instructions

Figure B3: Thermocontroller

- In order to set temperature:

  o Hold "star" button

  o Hold either "down arrow" or "up arrow"

  o Release arrow button once desired temperature is achieved

- Three Temperature Controllers

  o Central controls fuel cell temperature

  o Left controls furnace temperature

  o Right controls methanol feed line temperature

Load Box Instructions
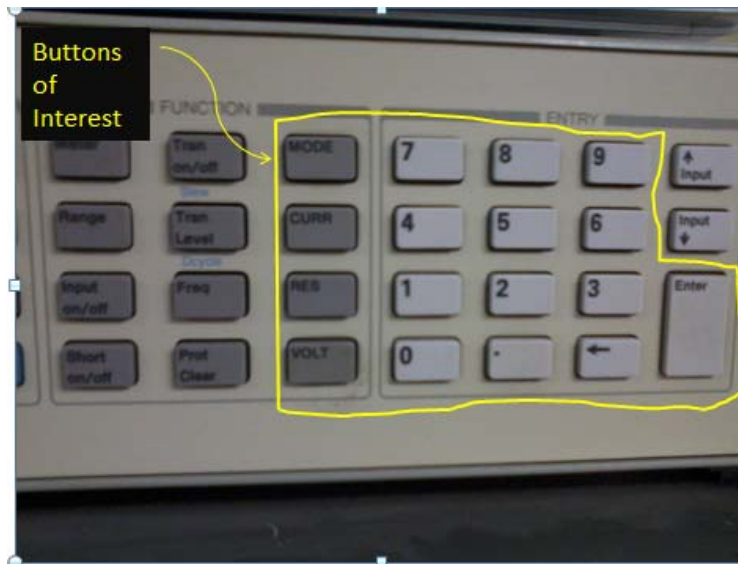
Figure B4: Load Box Control Panel

- In order to determine Open Circuit Voltage (OCV):

  – Press "Mode"

  – Press "Current"

  – Press "0.00"

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- Press "Enter"

- In order to vary current and determine voltage change:

  - Press "Mode"

  - Press "Current"

  - Press "0.1"

    - Note: this is in Amps

    - Press "Enter"

Appendix C: Additional Performance Curves

PBI 1x
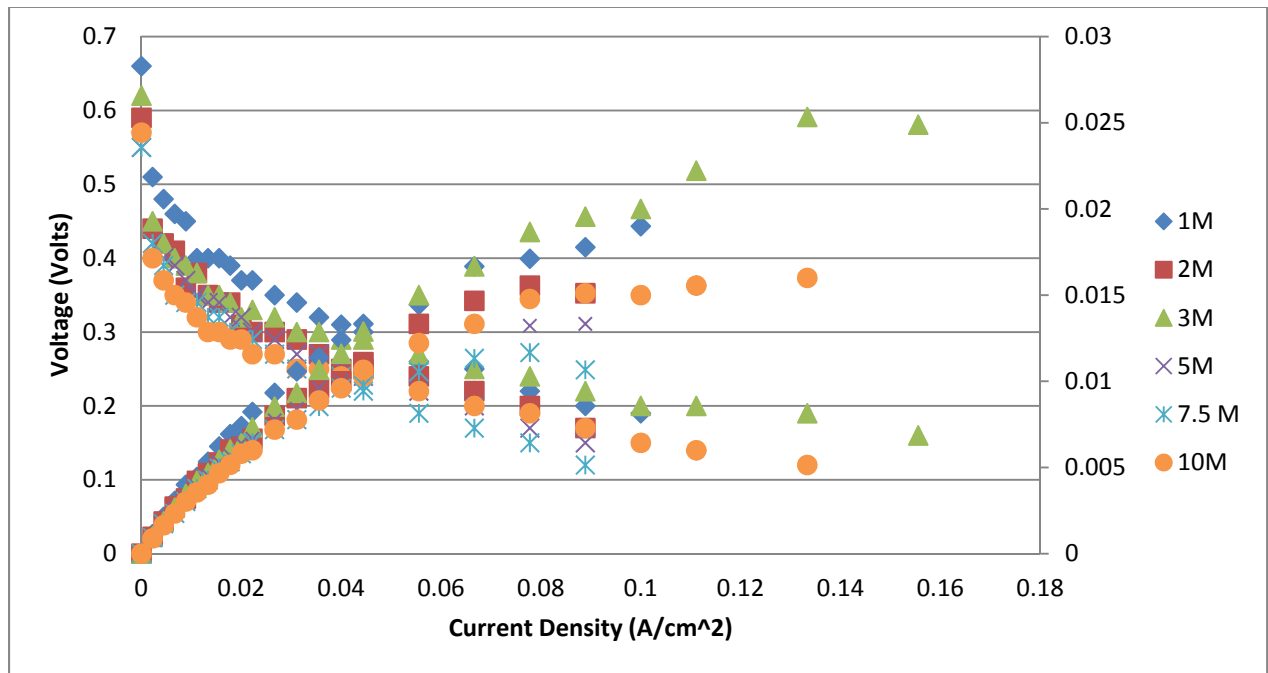
Figure C1: PBI 1x performance with MeOH using oxygen @ 160 degrees C
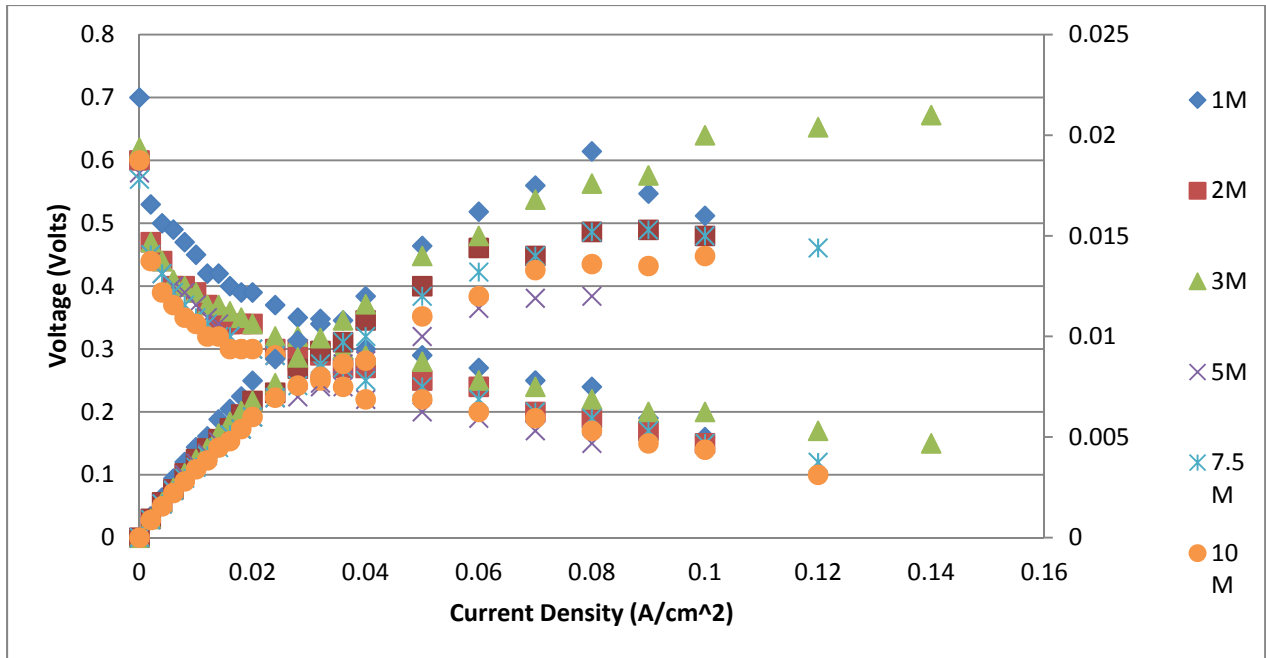
Figure C2: PBI 1x performance with MeOH using oxygen @ 170 degrees C
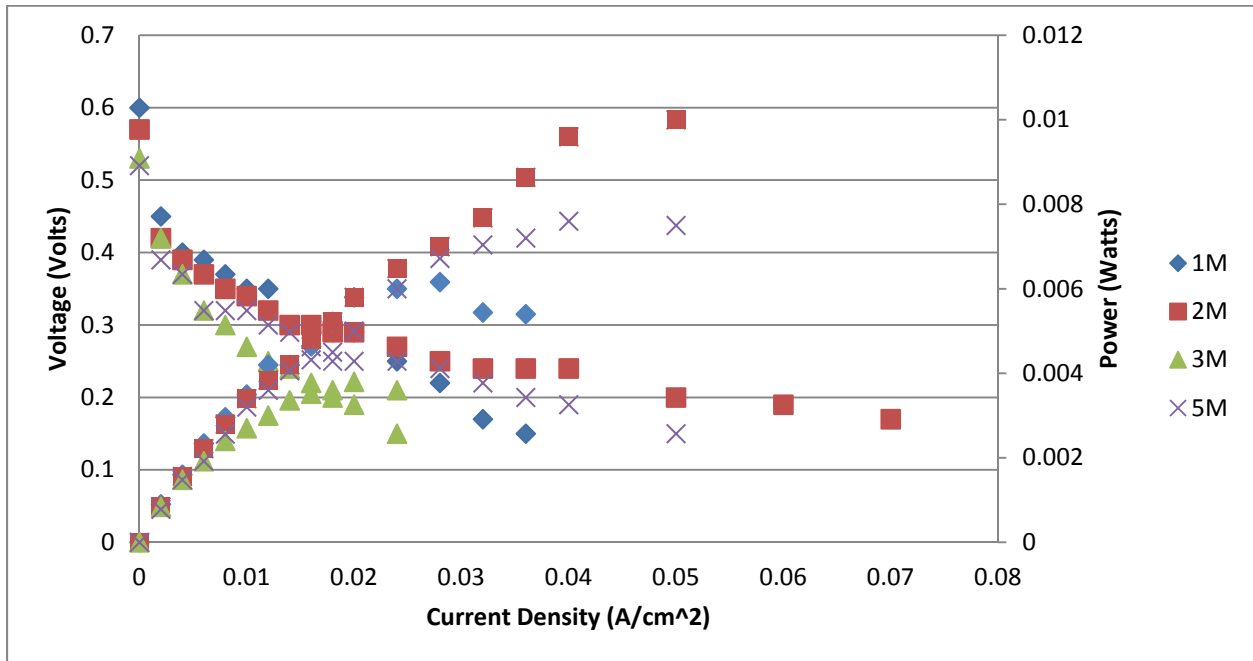
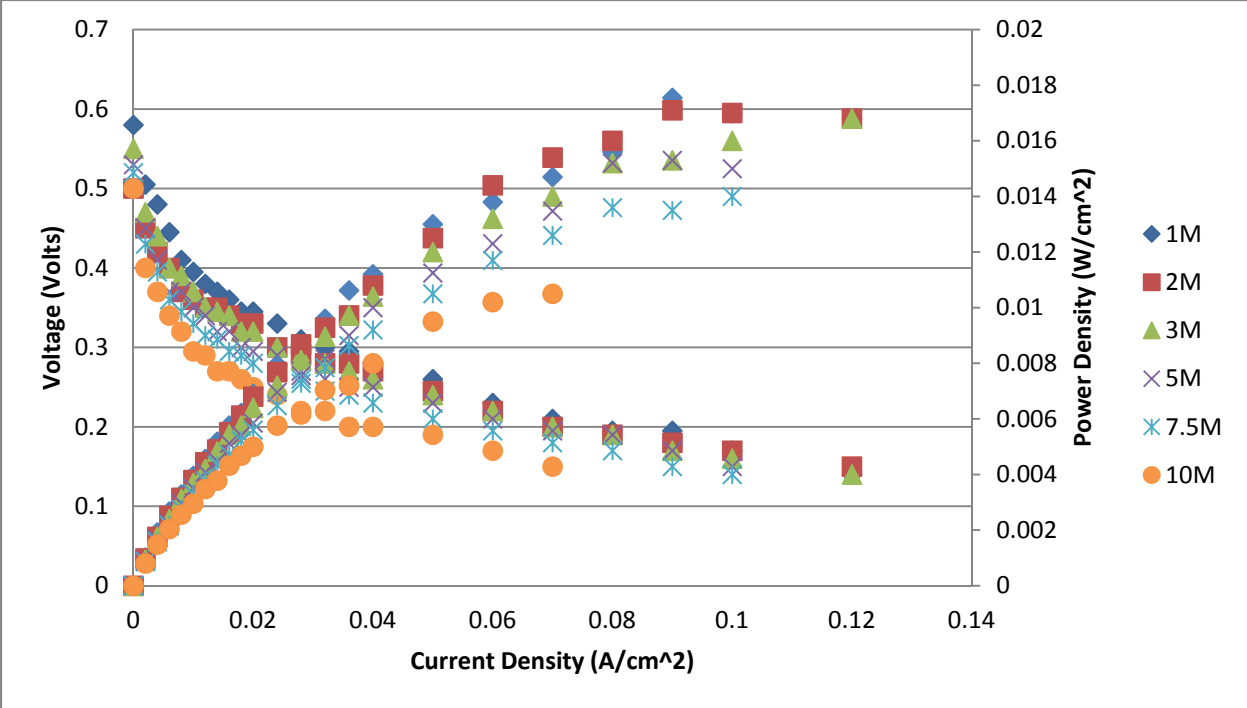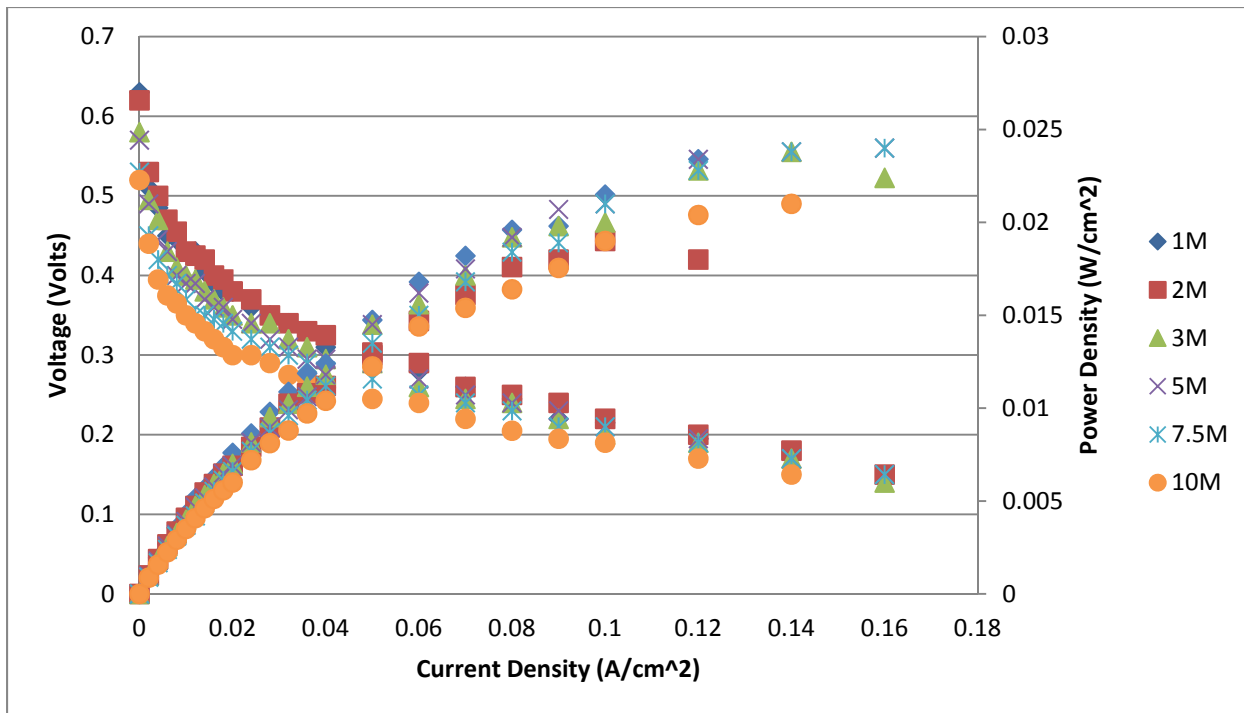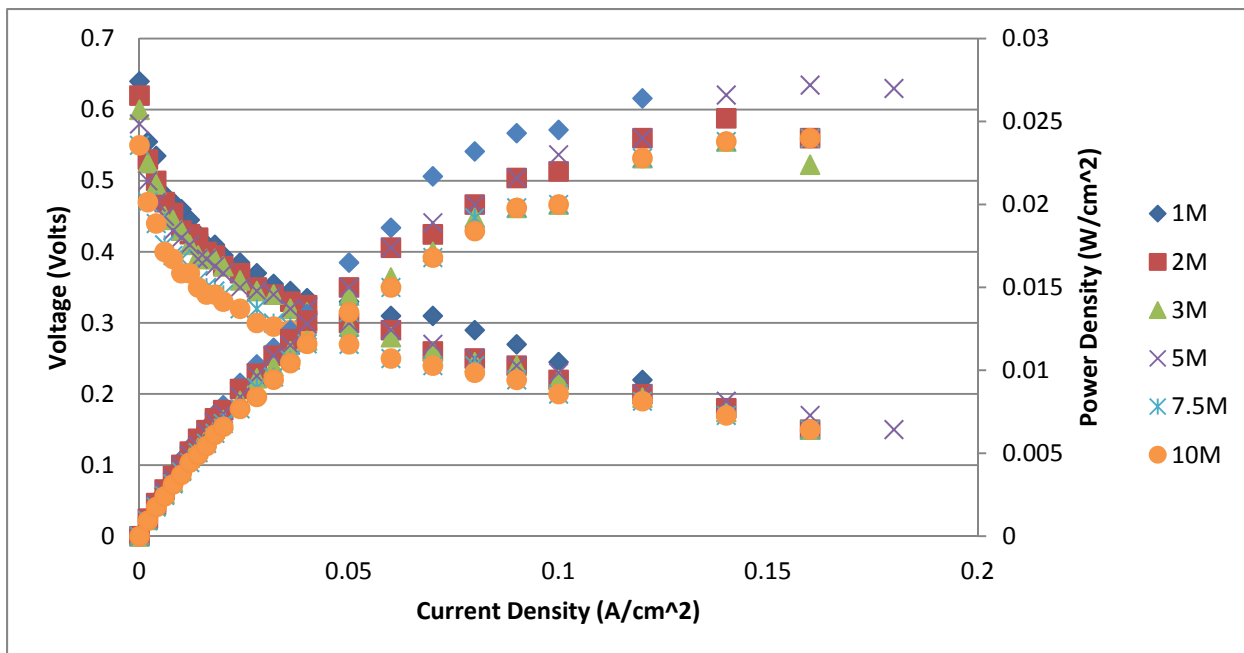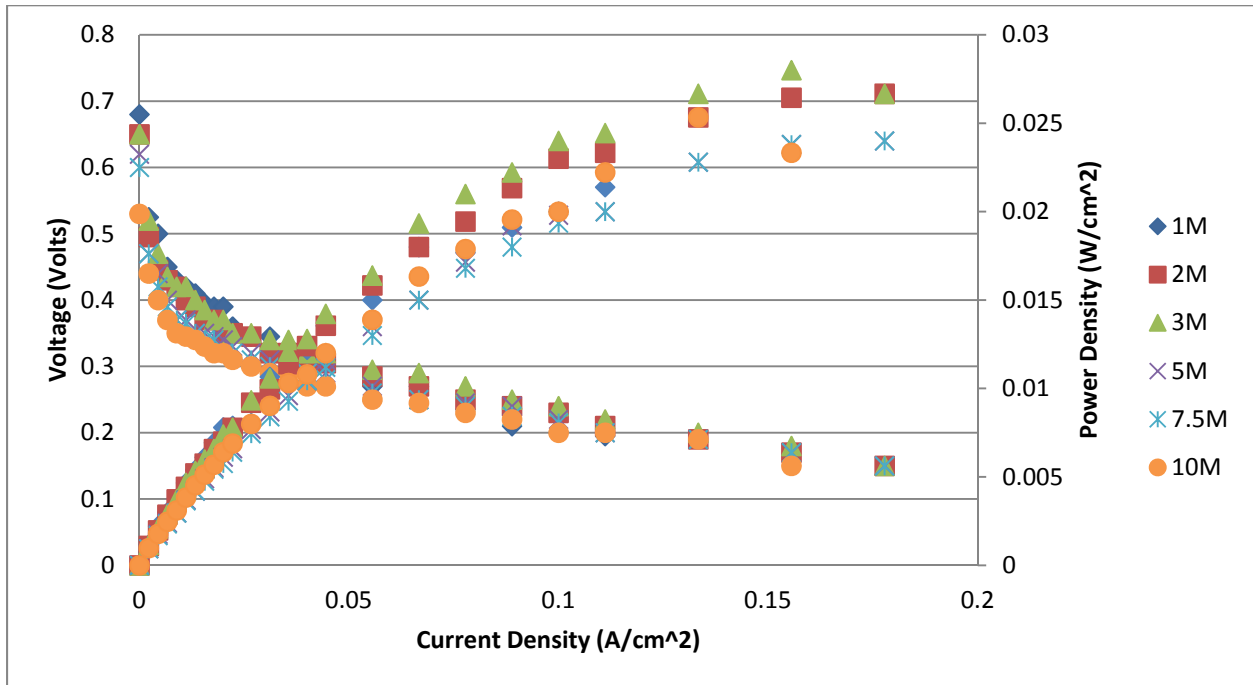Figure C3: PBI 1x performance with MeOH using air @ 160 degrees C
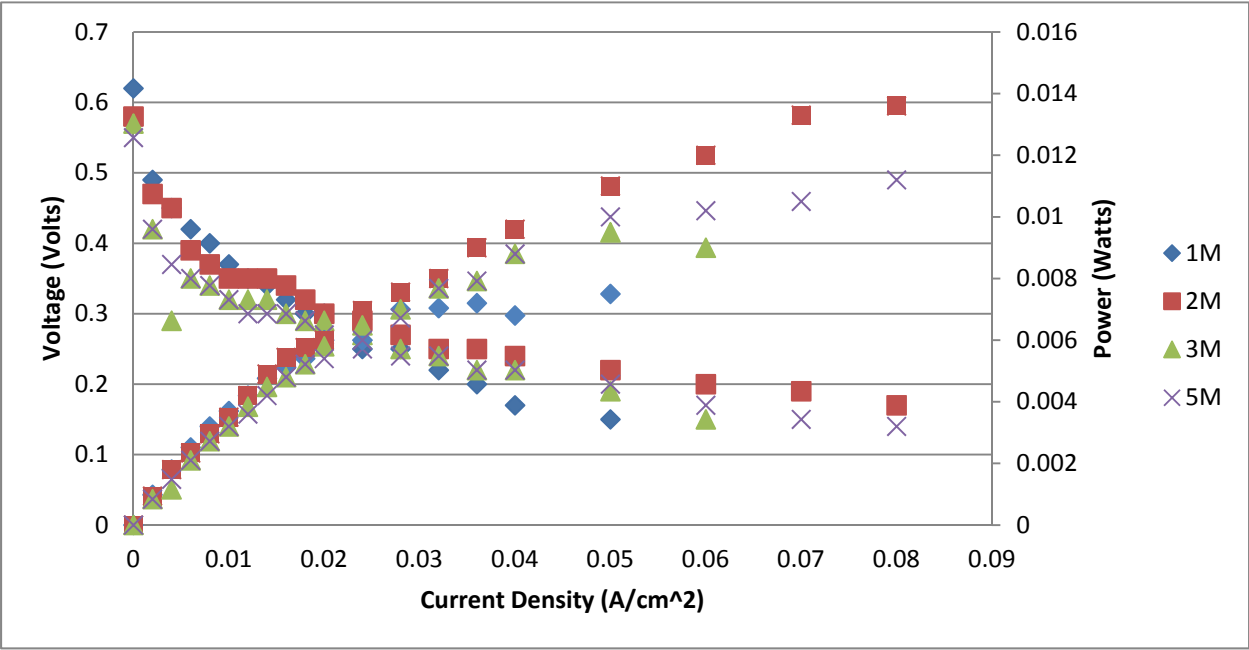
Figure C4: PBI 1x performance with MeOH using air @ 170 degrees C

PBI 1.0v
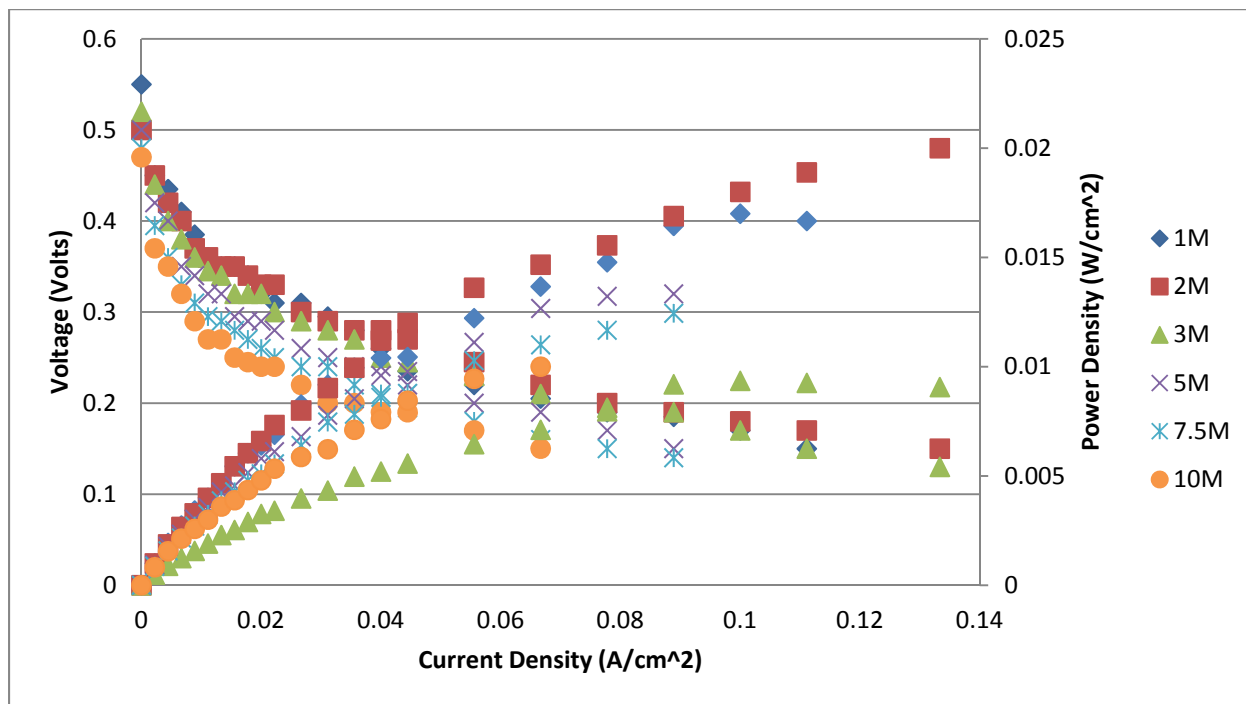
Figure C5: PBI 1.0v performance with MeOH using air @ 160 degrees C

Figure C6: PBI 1.0v performance with MeOH using air @ 170 degrees C

Figure C7: PBI 1.0v performance with MeOH using oxgen @ 160 degrees C

Figure C8: PBI 1.0v performance with MeOH using oxygen @ 170 degrees C

PBI 2.0

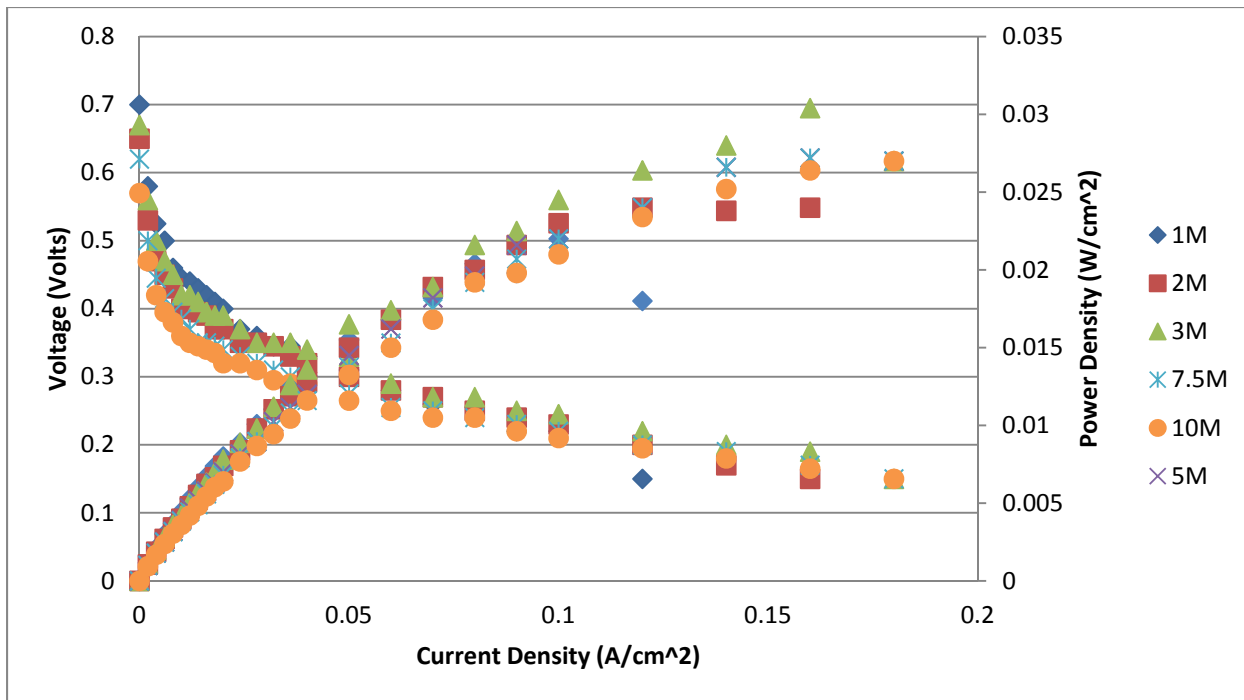**Figure C9: PBI 2.0 performance with MeOH using air @ 160 degrees C**

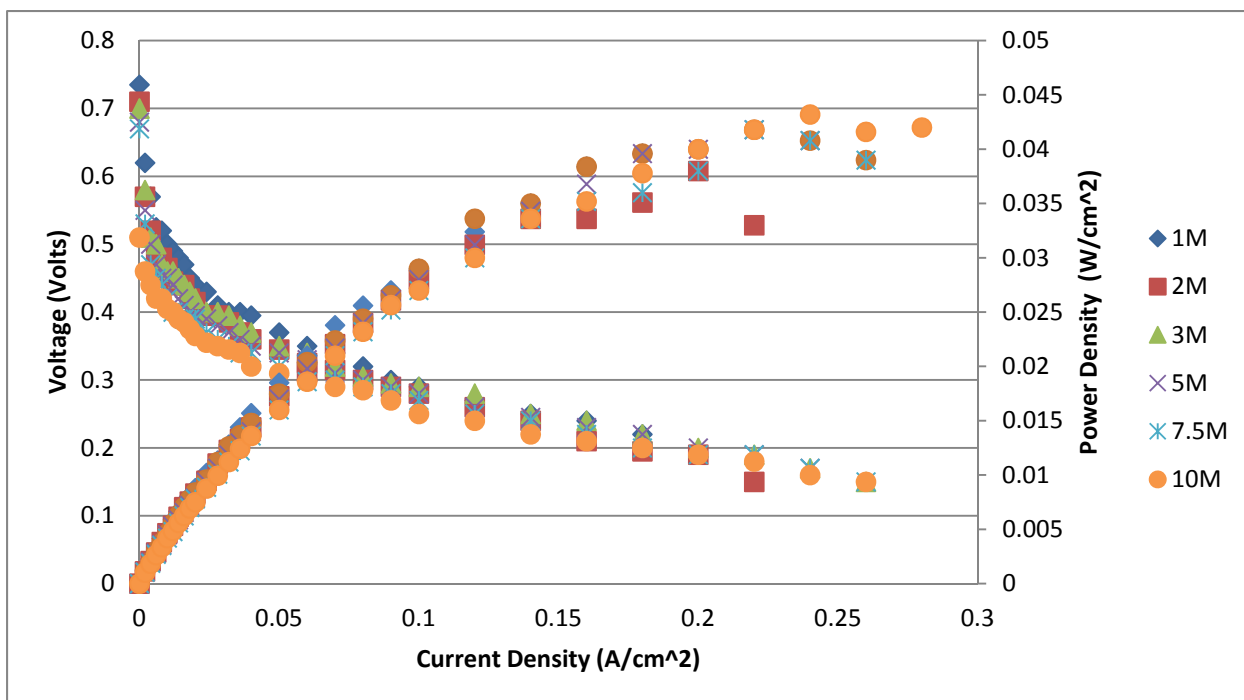Figure C10: PBI 2.0 performance with MeOH using air at 170 degrees C

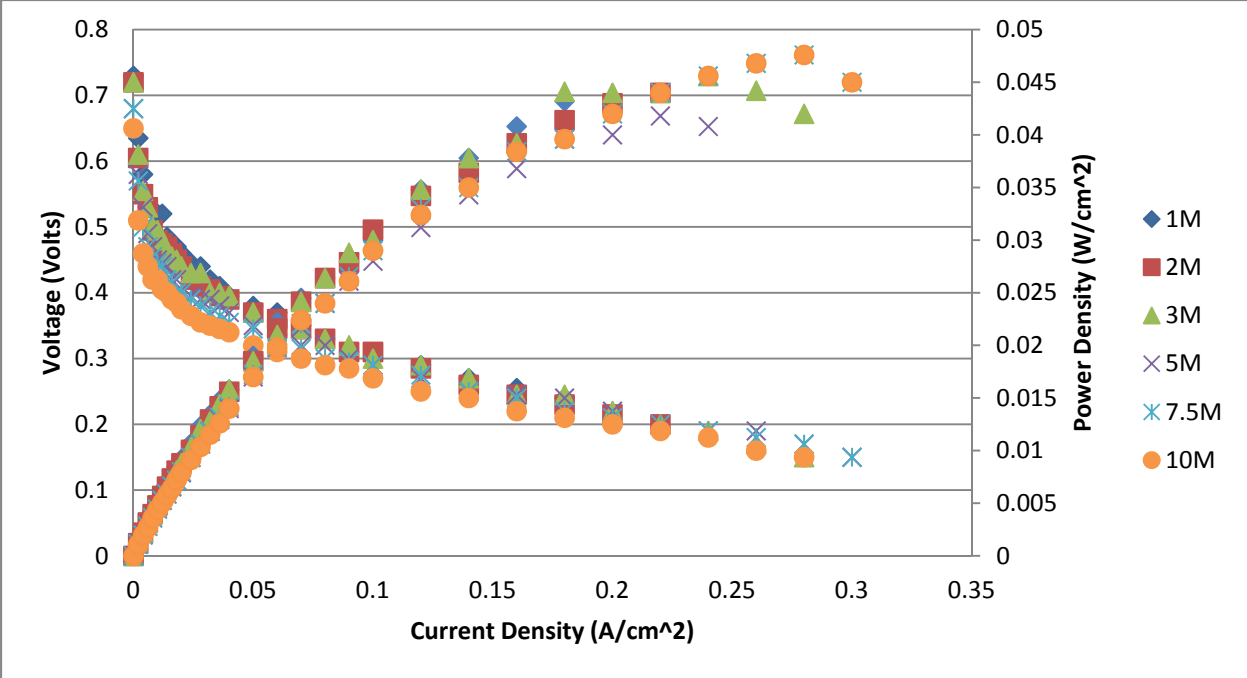Figure C11: PBI 2.0 performance with MeOH using oxygen at 160 degrees C

Figure C12: PBI 2.0 performance with MeOH using oxygen at 170 degrees C