EXPLORING OPERATING CONDITIONS AND NAFION MEMBRANES FOR THE DIRECT METHANOL FUEL CELL (DMFC)

A Major Qualifying Report

Submitted to the faculty of
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December 23, 2008

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Table of Contents

TABLE OF FIGURES

LIST OF TABLES

ABSTRACT

Direct methanol fuel cells (DMFCs) are highly effective alternative sources of portable power and have the potential for battery replacement for personal electronics and laptops. Conditions for improving the performance were investigated for DMFCs. Membrane thickness, molar concentration of methanol feed and temperature were the experimental variables of interest. Of the four different Nafion membrane thicknesses tested, ranging between 3.5 and 10 mil, 5 mil performed best. 5M methanol feed and 80 °C proved best for Nafion 117, Nafion 1110 and Nafion 1035 membranes and 7M at 70 °C in the Nafion 115 membrane. The results provided indications for improving the design and operation of DMFCs.

1. INTRODUCTION

Fuel cells have gotten a lot of attention lately, because they are efficient, don't produce gaseous pollutants such as CO and NO_x, and are relatively simple to build and operate, as there are no moving parts involved. However, many issues remain to be resolved to make the fuel cell less expensive, more efficient and more durable. This study investigates some of the design and operating parameters in making direct methanol fuel cells (DMFCs) more effective.

1.1 The Fuel Cell

The fuel cell is a source of electrical energy in the form of an electrochemical cell that converts chemical energy into electrical energy. More common electrochemical cells are batteries. Though the two have much in common, batteries are considered energy storage devices rather than energy producers.

1.1.1 The Battery and Fuel Cell Explained

A battery consists of two half-cells. Each half-cell is made up of an electrode surrounded by a conductive electrolyte in which either oxidation or reduction occurs. Oxidation takes place at the anode and reduction at the cathode. These redox reactions cause electric charge transports through the electrolyte and complementary electron flow or current that performs work on the external load. The ability to push a current from the electrode is called the electromotive force. When the two electrodes are connected, they form an electrochemical cell and a potential difference develops. If the potential, or "terminal voltage," is neither charged nor discharged, it is named "open-circuit voltage," and should have the same value as the electromotive force of the battery. Due to internal kinetic and transport resistances, a charging battery exceeds the open-circuit voltage, and one that is discharging falls below it at finite currents. The voltage and performance depends on the compounds used for the chemical reactions. In Fig. 1, an example of a Zinc-Carbon battery invented by Georges LeClanche is shown. The housing is made of zinc, which functions as the battery's anode. The cathode mix is commonly a slightly moistened mix of manganese dioxide powder, special carbon black, and an electrolyte. The rod running through the middle is a carbon electrode and top and bottom are metal covers. The battery can produce up to 1.7V.

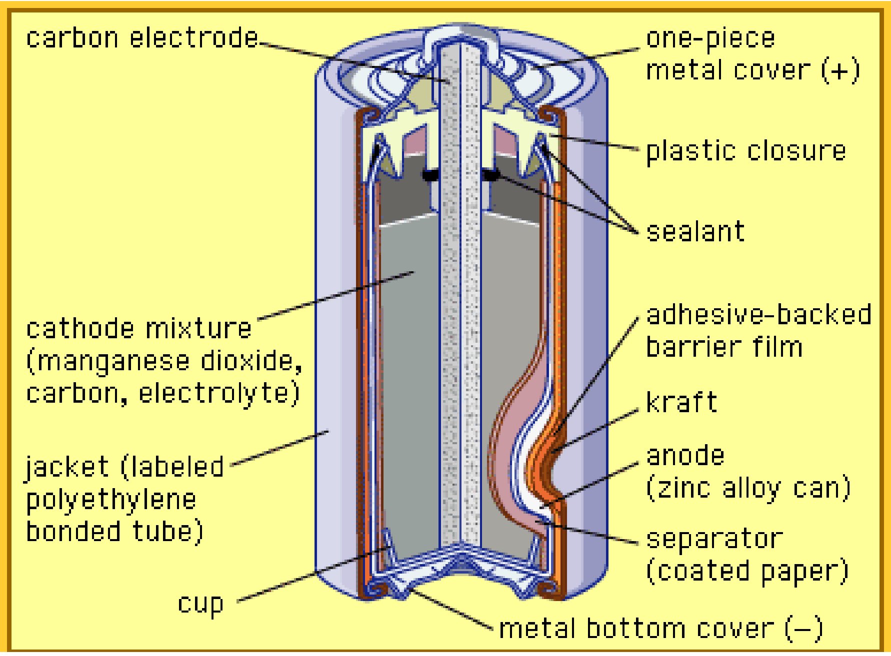


Figure 1. Schematic of a Zinc-Carbon battery. (Encyclopedia Britannica, Inc., 2005).

Some batteries are rechargeable, i.e. they use reversible chemical reactions to extend the life of the device. An electrochemical reaction reverses by applying a reverse current. However, generally, rechargeable cells are more toxic than disposable ordinary batteries.

Fuel cells are like batteries in many respects, except that the fuel and the oxidant may be continuously supplied to the fuel cell to produce power.

The first fuel cells came about in 1838 using hydrogen and oxygen (Hoogers, 2003). The fuel cell is a type of battery that does not store the chemical energy. It consumes the reactant. Therefore, it generates power as long as fuel is fed into the cell. It generates power at a high efficiency with minimal environmental effect, because there is no high temperature combustion. Furthermore, a fuel cell‘s electrodes are catalytic and remain relatively stable.

There are several types of fuel cells based on the electrolyte used. For example, there are polymer electrolyte fuel cells (PEFC), alkaline fuel cells, phosphoric acid fuel cells, molten carbonate fuel cells and solid oxide fuel cells (Hoogers et al., 2003). The electrolyte determines at what temperature the cell can operate and thus the thermomechanical and physiochemical properties of the fuel and the other components used. The type of fuel cell that is explored here is a PEFC-type fuel cell. The two most developed PEFCs are the ones using either hydrogen or methanol as the fuel and oxygen as the oxidant (Izenson and Hill, 2004). They are easy to make and maintain, and operate at low temperatures (Jung et al., 2007). Methanol has advantages over the use of hydrogen, because it is easier and safer to store and has a higher energy density. Furthermore, it is cheap and readily available. On the other hand, the oxidation of hydrogen is about one order of magnitude faster than the methanol oxidation.

Shell and Esso invented the direct methanol fuel cell (DMFC) around 1963 (Hoogers et al., 2003). A methanol fuel cell is called "direct" because it does not need reforming into hydrogen before being fed to the cell. Theoretically, the DMFC has an open-circuit voltage of 1.21 V (Jung et al., 2007). This is limited by several factors discussed below. DMFCs have potential for use in small portable devices like chargers and generators, and micro-applications in radios, laptops and cellular phones. In addition, there is a potential for vehicular applications (Aricò et al., 2001, Tasa et al., 2006).

1.1.2 Components of the Direct Methanol Fuel Cell

Generally, the DMFC consists of two metal or graphite bipolar plates, two electrodes, and a proton exchange membrane (see Fig. 2). The electrode consists of woven web of carbon cloth or paper with catalyst ink applied to it. The electrodes and the membrane together form the Membrane Electrode Assembly (MEA). The bipolar plates are placed on the outside of the cell through which the reductant (methanol) and the oxidant (oxygen) flow. Channels in a serpentine pattern are etched or machined into the bipolar plate for that purpose. An aqueous solution of methanol on the anode side and oxygen on the cathode side diffuse through the channels in each plate into the Gas Diffusion Layer (GDL) and then to the catalyst at the electrode. The catalyst facilitates the electrochemical reaction separating the electrons from the protons. The protons flow through the Proton Exchange Membrane (PEM) from the anode to the cathode. Electrons can't pass through the membrane, because it is electron insulating. Instead, the electrons flow through an external circuit supplying the power to an external load or device, and then arrive at the cathode where they meet up with the protons arriving via the electrolyte and oxygen from air at the electrocatalyst to form water.

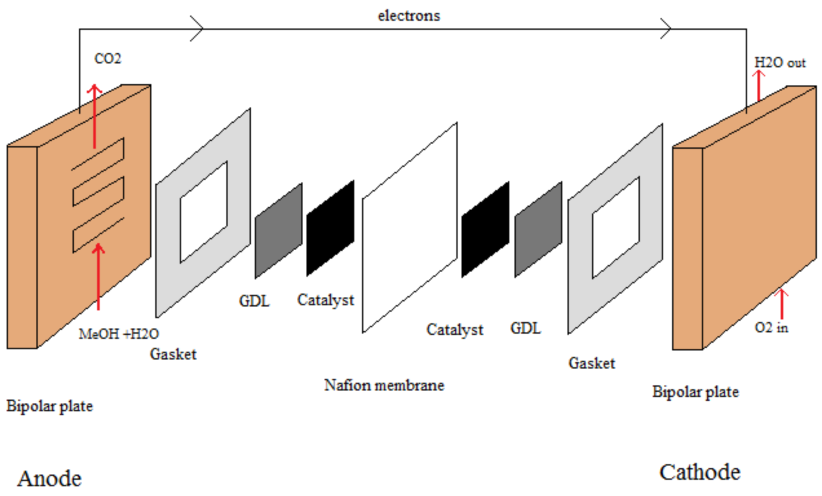


Figure 2. Components of a direct methanol fuel cell.

1.1.3 The Electrochemical Reactions

Several reactions take place in the cell. On the anode side, liquid methanol dissolved in water is fed through the bipolar plates and diffuses though the GDL to the catalyst where the oxidation of the methanol takes place. Methanol and water react to form electrons, protons, carbon dioxide, and other intermediates. The electrons flow up through the GDL, which contains carbon for that purpose, to the external circuit from anode to cathode. In addition, the GDL on the anode side functions to transport out the carbon dioxide that forms, when the methanol reacts, back to the bipolar plate. The oxidation of methanol is a slow process. So far, platinum and platinum alloys such as platinum/ruthenium have proven to be the best catalyst for DMFCs (Aricò et al., 2001).

There are several intermediates formed during the oxidation, but the exact reaction pathways are unknown (García et al., 2004). Presumably, some of the steps include dehydrogenation, chemisorption, and surface reactions between carbon monoxide and hydroxide. The first step involves formation of carbon monoxide, a stable intermediate that is absorbed by the catalyst, preventing further methanol access.

$$CH_3OH \rightarrow CO + 4H^+ + 4e^-$$

Therefore, ruthenium, tin, or gold is added to activate the water molecules to yield hydroxide radicals:

$$H_2O \rightarrow OH\bullet + H^+ + e^+.$$

This happens at relatively large anode overpotentials causing efficiency losses. The hydroxide radical that formed, oxidizes the carbon monoxide to form gaseous carbon dioxide:

$$CO + OH\bullet \rightarrow CO_2 + H^+ + e^+.$$

By bubbling out the carbon dioxide across the GDL, the methanol has access to the catalyst surface. The overall oxidation half reaction thus is:

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

The protons travel from the anode to the cathode through the membrane. The membrane must therefore be a good proton conductor. Commonly, a Nafion membrane is used (Aricò et al., 2001). It is a sulfonated tetrafluorethylene (Teflon) copolymer manufactured by DuPont. Perfluorovinyl ether groups are terminated with sulfonate groups ($-SO_3H^+$) on a Teflon backbone. Protons dissociate and form conductive hydronium ions in the pores of the membrane that are responsible for charge conduction largely by Grotthus mechanism, while electrons are stopped from flowing through it (Heitner-Wirguin, 1998). The combination of a Teflon backbone with the sulfonate groups makes the Nafion membrane electrochemically stable. When Nafion membranes are used, the cell can operate at a temperature up to 90 ºC and atmospheric pressure, as the membrane softens above 100 ºC as it approaches its glass-transition temperature (Lobato et al., 2006).

The main disadvantages of Nafion membranes is that the ionic channels or pores also allow methanol to readily cross over along with water reaching at the cathode with oxygen to form CO_2 and H_2O chemically, i.e. without producing electrons. In fact, Nafion needs water to become a good proton conductor. However, too much water uptake results in less ion conductivity. An aqueous methanol solution is fed at the inlet and the chemical reactions in the fuel cell produce water as well. Both to avoid methanol cross over and to reduce CO poisoning of the anode catalyst, a very dilute methanol feed (around 1 mol% or 3 weight % methanol) is employed.

At the cathode the protons that traveled through the membrane react with the oxygen and the electrons to form water. The reduction half reactions that take place at the cathode are:

$$3/2O_2 + 6H^+ + 6e^- \rightarrow 3H_2O$$

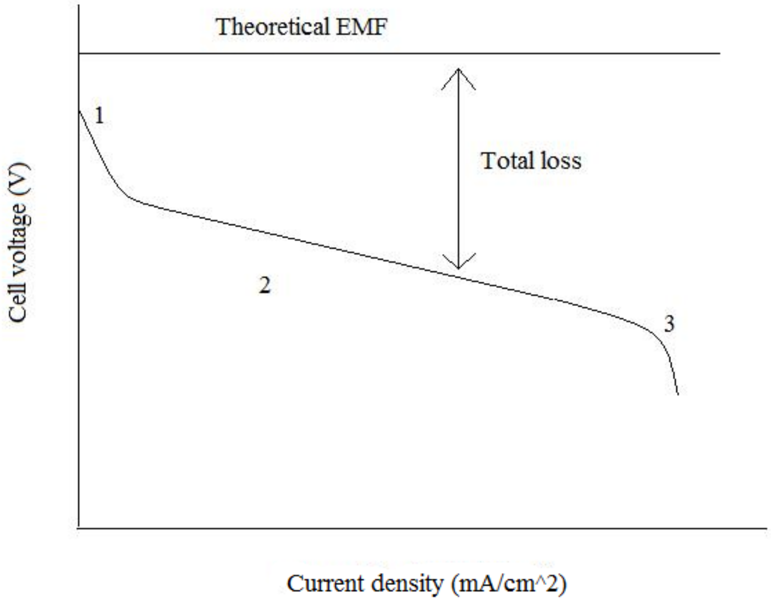
The reaction is slow, but not as slow as the methanol reduction, causing a significant further drop in voltage and efficiency (Schultz, 2001). The net reaction is:

$$CH_3OH + 3/2O_2 \rightarrow CO_2 + 2H_2O$$

The cathode overpotential, or losses, are exacerbated by the methanol permeating through the membrane.

1.1.4 Limitations on DMFC Performance

The performance of a DMFC is measured in cell voltage at a certain current or power density. The performance depends on the operating conditions and the cell components. The thermodynamically determined voltage of a DMFC is 1.21V, based on operating conditions (Jung et al., 2007). During operation, however, the cell loses energy (and efficiency) due to 1) inefficient cathode kinetics, 2) methanol cross-over, 3) carbon monoxide poisoning of the anode, 4) slow proton conductivity, 5) insufficient flow of reactants and 6) slow removal of byproducts such as CO_2 (Jung et al., 2007, Lu et al., 2004, Schultz et al., 2001). The different types of losses appear at different current densities (see Fig. 3). At low current densities the cell suffers reaction rate loss. This is the activation polarization region. At higher current densities, energy (efficiency) loss is due to slow proton conductivity. This is the ohmic polarization region. Finally, the concentration polarization region at high current densities is caused by mass transfer inefficiencies, i.e. by slow feeding of reactants and or slow removal of byproducts. Methanol cross-over decreases with an increase of current density, because methanol is utilized more at the anode (Heinzel et al., 1999).



1 = Region of activation polarization (reaction rate loss)

2 = Region of ohmic polarization (resistance loss)

3 = Region of concentration polarization (gas transport loss)

Figure 3. Ideal versus actual fuel cell potential as a function of current density.

1.2 Goals of This Study

1. To increase the performance of the direct methanol fuel cell, several different conditions and membranes were explored. The thickness of the membrane affects the methanol and proton mass transfer; too thin a membrane allows methanol to cross-over more easily, too thick a membrane and the proton conductivity is impaired as well. To find the ideal Nafion membrane thickness, four different membranes were tested.

2. Methanol concentrations of 1M in water are most commonly used in DMFC applications. However, the more concentrated the methanol feed, the smaller the

feed tank needs to be. Therefore, molar concentrations of 1M, 3M, 5M, 7M and 10M were tested on each of the four membranes to find the optimum feed concentration.

3. In addition, the kinetics of the methanol reaction at the anode should increase with increasing temperature. All the membranes were tested at 7M at 70 and 80°C.

4. Furthermore, the use of home-made catalyst ink was compared to commercially prepared electrodes. The ink was sprayed directly onto the membrane.

5. Finally, the commercially available electrodes were treated with a small amount of Nafion to see if it would increase power density.

2. LITERATURE REVIEW

Much research has been done to overcome the challenges of the DMFC, because it has such great potential in portable and vehicular applications. This chapter discusses the four primary types of performance losses, i.e. 1) retarded methanol oxidation due to formation of intermediates, 2) methanol cross-over, 3) carbon dioxide control, and 4) water management.

2.1. Slow Methanol Oxidation

The methanol oxidation at the anode is a slow process. The catalysts most often used in DMFCs are a mixture of platinum and ruthenium at the anode and pure platinum at the cathode (Arbizzani et al, 2008). The catalyst may be supported on carbon to enhance the performance, because it increases catalyst dispersion (Derbyshire et al., 1986). The catalyst can be sprayed onto the membrane directly or onto the gas diffusion layer. Better results have been had with applying the catalyst directly on the membrane. (Gleason et al., 2008). The GDL is made out of carbon for better conductivity and catalyst loading (Bang et al., 2007). Unfortunately, this conflicts with the need for high mass transport of methanol and oxygen, which is slowed down by the dense packing of carbon particles.

During the oxidation, carbon monoxide and other intermediates, e.g. formaldehyde and formic acid, are produced and adsorbed onto the platinum reducing the surface sites of the catalyst available for methanol oxidation. This significantly reduces the methanol consumption efficiency and power density of the fuel cell. To remove the carbon monoxide, the most stable of the intermediates, ruthenium, gold or tin is added to the catalyst. The metals form hydroxyl radicals from water, which at somewhat lower overpotentials than pt alone, oxidize the carbon monoxide. Another method is to increase the temperature of the fuel cell, limited by the membrane by 100 °C or less, to enhance catalyst activity (Casalegno et al., 2007, Wang et al., 2006). Typically, a Nafion membrane is operated between 50 and 90 °C (YanYang, 2004). At or above 100 °C the water in the membrane is hard to maintain and proton conductivity decreases dramatically. At even higher temperatures, the polymer chain can start to rearrange leading to structural changes in the membrane. This results in membrane softening and less stability, performance and lifetime of the membrane.

Bang et al. (2007) prepared porous carbon materials by using ultrasonic spray pyrolysis that would disperse platinum particles well and also conduct electrons at a high rate. They mixed regular Vulcan XC-72 with PC-I carbon. The latter improved the overall mass transport of methanol at the anode while the first provided good electron transport. Adding PC-II to E-TEK commercial platinum for the cathode proved to enhance performance as well.

A little Nafion-water solution may be added to the catalyst solution to aid the protons' movement. The nature and density of the "three-face interface" where electrode, catalyst and electrode meet determines the performance of the cell. The better the contact, the better the performance. Instead of carbon, conducting polymers may alternatively be used to support the catalyst (Arbizzani et al., 2008). For example, poly(3,4-ethylenedioxythiophene)-polystyrene-4-sulfonate (pEDOT-pSS) is a stable electronic-ionic mixed conductor that facilitates fast electronic transport and appears to work well in DMFCs.

The search for improving the kinetics of the methanol oxidation is ongoing and better catalysts are being developed (Bang et al., 2007). Furthermore, research is being done on preparation methods of catalysts, either through impregnation or colloidal methods (Aricò et al., 2001).

2.2. Methanol Cross-Over

The proton exchange membrane separating the anode from the cathode promotes the transport of the protons. Unfortunately, perfluorinated membranes like Nafion also allow methanol to cross over. Once the methanol has reached the platinum at the cathode, it will oxidize and produce intermediates and electrons. As a result, an additional electrode overpotential occurs at the cathode and the potential drop between electrodes is reduced causing a decrease in power density of the fuel cell.

The hydration of the Nafion membrane promotes the formation of ionic channels through which protons and methanol travel (Fig. 4). Fortunately, the rate at which protons and methanol cross over differs. In Nafion membranes protons flow via three different means: surface diffusion, Grotthuss diffusion, and vehicular diffusion (Choi et al, 2005). The type of diffusion depends on the water content of Nafion. At the aqueous pore surface of the Nafion molecules there is less water content and protons hop between water molecules and sulfonate groups. It is a slow means of diffusion. Vehicular and Grotthuss diffusion are faster and occur at the center of the pore. A proton can use a water molecule as a vehicle forming H_3O^+, which carries the proton along as the hydronium ion diffuses in response to the concentration gradient (Kreuer, 1996). This is vehicular or *en masse* migration. Grotthuss diffusion involves protons being transferred within the hydrogen bonds from one water molecule to another. The reorganization of the proton environment form a continuous path for proton transport. Grotthus diffusion is an order of magnitude faster than vehicular diffusion.

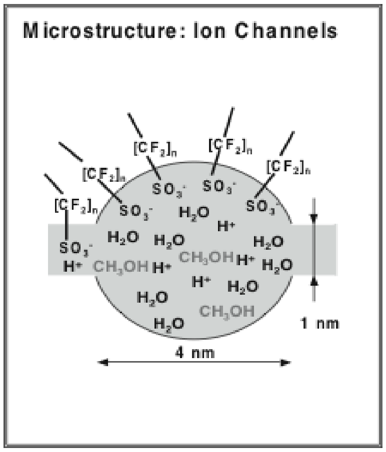


Figure 4. Ion channel (water-filled micropore) in Nafion (Schultz, 2001).

Methanol on the other hand, only diffuses through vehicular diffusion. It is thus important to limit vehicular diffusion while promoting surface and Grotthuss diffusion within the membrane. One way to accomplish this is to decrease the water uptake in the membrane. However, a decrease in hydration will also affect the other two means of transport, lowering the performance of the fuel cell. Another method to slow down methanol cross-over is to make the membrane thicker, because this decreases the concentration gradient (Jung et al., 2005). However, at higher current densities the membrane resistance starts to play a bigger role than transport phenomena. Finally, methanol diffusion may be slowed by incorporating inorganic particles within the aqueous channels, which serve as impediments (Gleason et al., 2008). Sulfated silica particles, for example, are acidic in nature and block methanol cross over more effectively than Nafion membranes. Nonetheless, reduced proton diffusion and reduced methanol diffusion appear to go hand-in-hand.

The methanol concentration at the anode may be lowered to decrease the concentration gradient (Ren et al., 2000). The disadvantage of a more dilute fuel is the decrease in the amount of oxidation at the anode and the need for a bigger size fuel tank. Alternatively, the acidity of the membrane may be lowered (Hensley et al., 2007). This results in less water uptake and thus a decrease in *en masse* diffusion. The Nafion membrane's acidity can be reduced by using a higher equivalent weight or substituting carboxylic acid groups for sulfonic acid groups. Also, cross-over is decreased at lower temperatures (Jung et al., 1998). Lu et al. (2004), experimented with backing layers with low methanol permeability and found that this allowed use of thinner membranes. Finally, the membrane may be treated with dopants and fillers like zirconia and silica to block the methanol molecules. But clearly, whenever methanol cross-over is limited, proton transport is limited and the performance of the cell is affected. Table 1 summarizes the effects of varying the operating conditions on methanol cross-over and performance of the fuel cell.

Table 1. Effect of increasing operating parameters on methanol cross-over and cell performance.

Nafion membranes			
		Cell performance	
MeOH cross-over		Low current density	High current density
Membrane hydration	Positive	Positive	Positive
Membrane thickness	Negative	Positive	Negative
Methanol concentration	Positive	Negative	Positive
Membrane acidity	Positive	Positive	Positive
Cell temperature	Positive	Positive	Positive
Dopants and fillers	Negative	Negative	Negative

One of the latest Nafion membranes is Nafion 211, which is the thinnest Nafion membrane on the market at 25.4 μm. Jung et al. (2007), compared it to Nafion 112 (50.8 μm) and 117 (178 μm) to see whether it would perform better. The thinner the membrane, the easier the protons are transported from anode to cathode. However, there was also increased methanol cross-over.

In addition, they tested DuPont's Nx-424, a 30 μm Nafion membrane treated with polytetrafluoroethylene (PTFE) fibers, which is primarily used for chloro-alkali production. The membrane has the property of direction and thus is unusable when the protons travel in the reverse direction. The hydrophobic properties of PTFE decrease the permeability of water with methanol through the membrane. The effect of PTFE on the performance of a cell had not been explored before.

The tests showed that the weight percent of methanol in the liquid flowing out of the cathode decreased with thickness of the membrane (see Fig. 5). The Nx-424 had the least amount of methanol cross-over, but it also had the lowest cell performance (Fig. 6). The tests proved that at lower current density the performance of the cell improved with membrane thickness and reduces at higher current densities. Interestingly, even though the thinnest membrane had the highest methanol cross-over, it also performed better than the others.

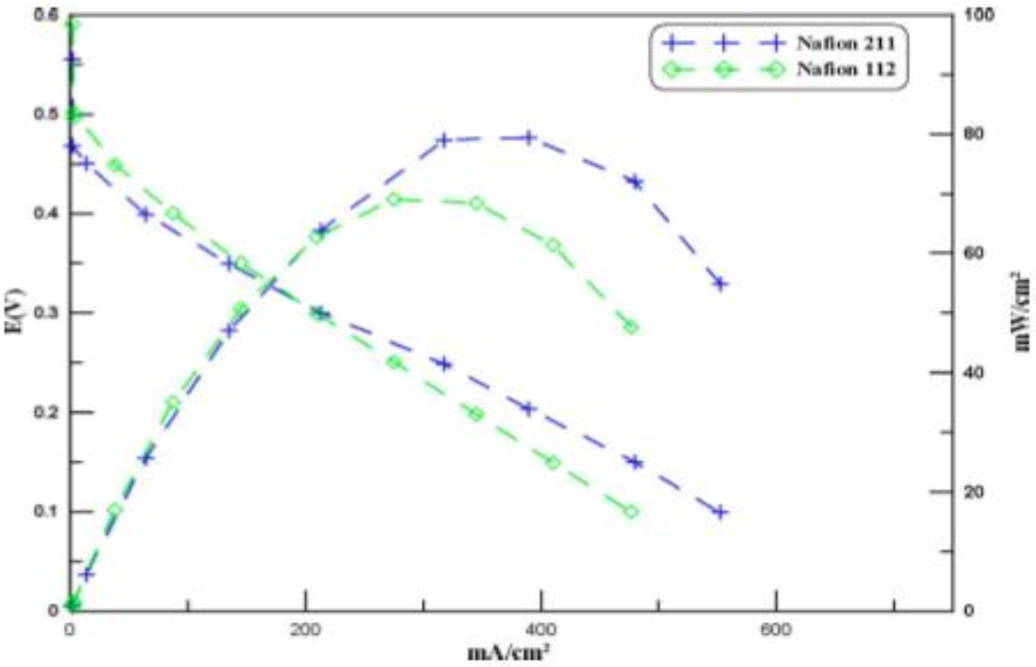


Figure 5. Performance of Nafion 211 compared to Nafion 112 at 2M methanol 5 cc/min and 70°C, oxygen at 150 cc/min (Jung et al., 2007).

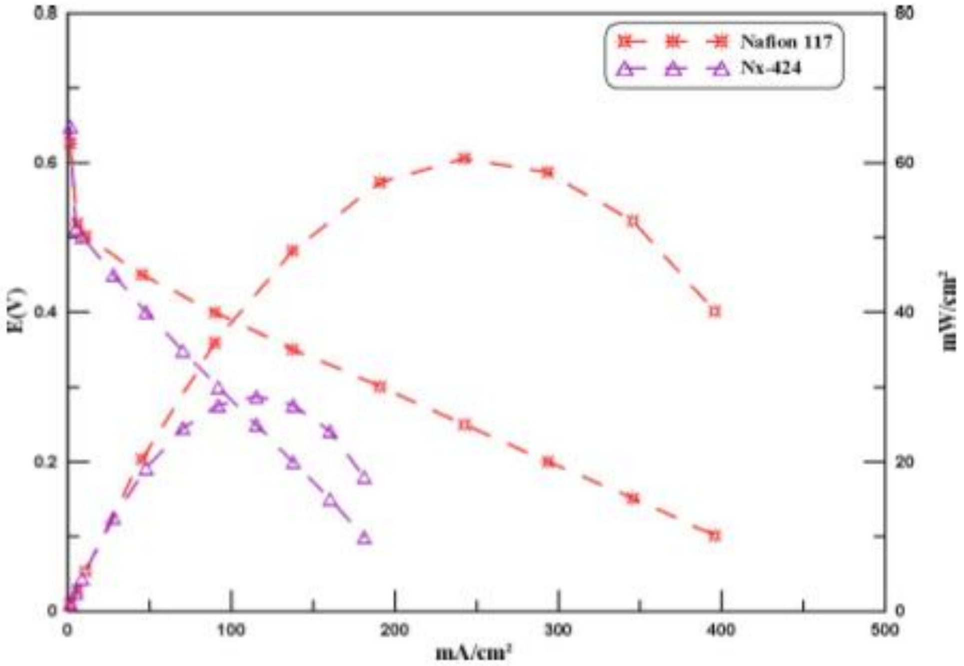


Figure 6. Performance of Nafion 117 compared to Nx-424 at 2 M methanol 5 cc/min and 70 °C, oxygen at 150 cc/min (Jung et al., 2007).

Another modification of a Nafion membrane was explored by Lin et al (2005). A PTFE membrane was treated with a Nafion solution and compared to Nafion 117 and 112 membranes. The reason for exploring this option was that the composite membrane was cheaper, mechanically stronger in swollen or non-swollen state, and it had good thermo-stability. In addition, the membrane measured only 20 μm, which should improve proton conductivity significantly.

The porous PTFE membrane was impregnated with 5 wt.% of 1100 EW Nafion dissolved in a 2-propanol/water mixture. Lin et al. used different methanol concentrations and determined that over-all the methanol diffusion and electro-osmosis cross-over was the lowest in the composite membranes. When increasing the thickness of the Nafion 117 membrane to decrease the methanol permeability, it performed worse than the composite membrane due to the high proton resistance. Therefore, the PTFE membrane combined with the Nafion solution is a better alternative to the Nafion membranes, because methanol cross-over is limited and proton conductivity is maintained resulting in better cell performance.

2.3. Carbon Dioxide Management

Gaseous carbon dioxide is created during methanol oxidation. The gas bubbles form on the surface of the GDL hindering the effective mass transfer area (Lu et al., 2004). Once the bubbles reach a certain size, they are released from the surface and blend with the methanol solution in the channels forming a two-phase liquid. At a certain concentration of carbon dioxide bubbles, they will coalesce and form slugs. The slugs then obstruct the methanol diffusion process. When methanol diffusion is slowed down, the oxidizing process slows down and the current density is decreased. To prevent the bubbles or remove them when formed, the pressure and flow rate of the aqueous methanol feed can be increased. Lu et al. (2004), observed that the release of the carbon dioxide bubbles may be managed by choosing the right GDL. They found that the regularly distributed pores on carbon cloth produce smaller bubbles that release more easily than when carbon paper is used. Alternatively, a selective pervaporation membrane may be placed in the MEA (Schultz et al., 2001). The membrane may be arranged as hollow fibers with a stripping gas at lower pressure on the outside. The methanol feed flows through these fibers. The higher pressure of the methanol feed is the driving force behind the transfer of carbon dioxide through the membrane into the stripping gas. The difficulty lies in improving selectivity towards carbon dioxide.

2.4. Water Management

Another issue with DMFCs is the flooding of the cathode with water, so that oxygen diffusion to the catalyst surface is reduced. In order to limit the methanol cross-over, dilute solutions of methanol are used as reactant. The water fed to the cell at the anode is transported to the cathode via diffusion and electro-osmotic drag. In addition, water is a product at the cathode. For every mol of methanol, one mol of water reacts and approximately 3 moles of water are produced at the cathode. Factors effecting water management are the humidity of the air at the inlet, volumetric flow rates, current density, temperature, and the water transport properties of the membrane (Lu et al., 2004).

One way to combat flooding at the cathode is to increase the flow rate of air. However, the cathode effluent then requires condensing in an external cooler to replenish the anode. This consumes extra power and makes the entire system bulkier. Lu et al. (2005), designed an MEA using a Nafion 112 membrane and a hydrophobic compact microporous layer (TFE, DuPont) on the GDL to create hydraulic pressure at the cathode. This caused a water back-flow through the membrane, resulting in less water cross-over through the membrane. Consequently, a higher concentration of methanol could be used.

3. EXPERIMENTAL PROCEDURES

Several different procedures were used depending on the type of membrane and whether a commercial electrode was used or not. Except for the commercial MEA, all membranes were treated before testing. Catalyst ink was made in the lab and applied to the membrane in case no commercial electrode was used.

3.1 The Types of Membrane and Electrodes

First, a commercial MEA was tested and its performance was used as a base case. Four different membranes were then tested and compared.

3.1.1 Commercial MEA from BASF Fuel Cell, Inc.

A commercial MEA was purchased from E-Tek, Inc., now a subsidiary of BASF Fuel Cell, Inc. The ES12D-W-5L MEA is a 5 layer assembly with the GDL on woven web. The assembly is constructed with Selectra® high performance catalysts using advanced ELAT® carbon cloth flow fields for the cathode and anode. The exact composition of the catalyst is a trade secret. The GDL on the anode side, however, detaches after a day’s use and the MEA also warps significantly after use, but it performs well nonetheless. The ion exchange membrane is a polymer electrolyte ionomer and the MEA is recommended for use up to 80°C and suitable for low pressure operation.

3.1.2 Nafion Membranes from ElectroChem, Inc.

Four types of Nafion membranes were bought from ElectroChem, Inc., a subsidiary of DuPont, Inc. They are transparent non-reinforced films based on Nafion PFSA polymer, a perfluorosulfonic acid/PTFE copolymer in acid form. The membranes vary in thickness:

- Nafion membrane N1035, (1000EW, 3.5 mil thick)
- The EC-NM-115 N115 membrane (1100 EW, 5 mil thick)
- Nafion membrane N117 (1100 EW, 7 mil thick)
- Nafion membrane N1110, (1100EW, 10 mil thick)

Squares of 5 cm^2 were cut with scissors and treated in deionized water, hydrogen peroxide and sulfuric acid. All membranes were used with ElectroChem electrodes already containing catalyst. In addition, the 115 and 117 membranes were also used with a home-made catalyst ink and commercially available GDLs from E-Tek, Inc.

3.1.3 The Electrodes

The electrodes were obtained from ElectroChem, Inc. For the anode, an EC-Electrode-C1 was used. It is an EC-40-60-PtRu-C electrode with a catalytic layer consisting of 40 wt% Pt and 20 wt% Ru/C and a loading of 4 mg Pt Ru/cm^2. The backing is made of carbon cloth with a Nafion coating. The cathode electrode is an EC-Electrode-C2. The EC-40-40 Pt-C has a catalyst applied to it with 40 wt% Pt/C. It has the same loading and backing layer as the anode electrode. Squares of 0.875 $inch^2$ were cut and placed on either side of the membrane (see Fig. 7). The entire assembly was carefully aligned before being hot pressed. A careful notation was made on the membrane with permanent marker to identify cathode and anode side.

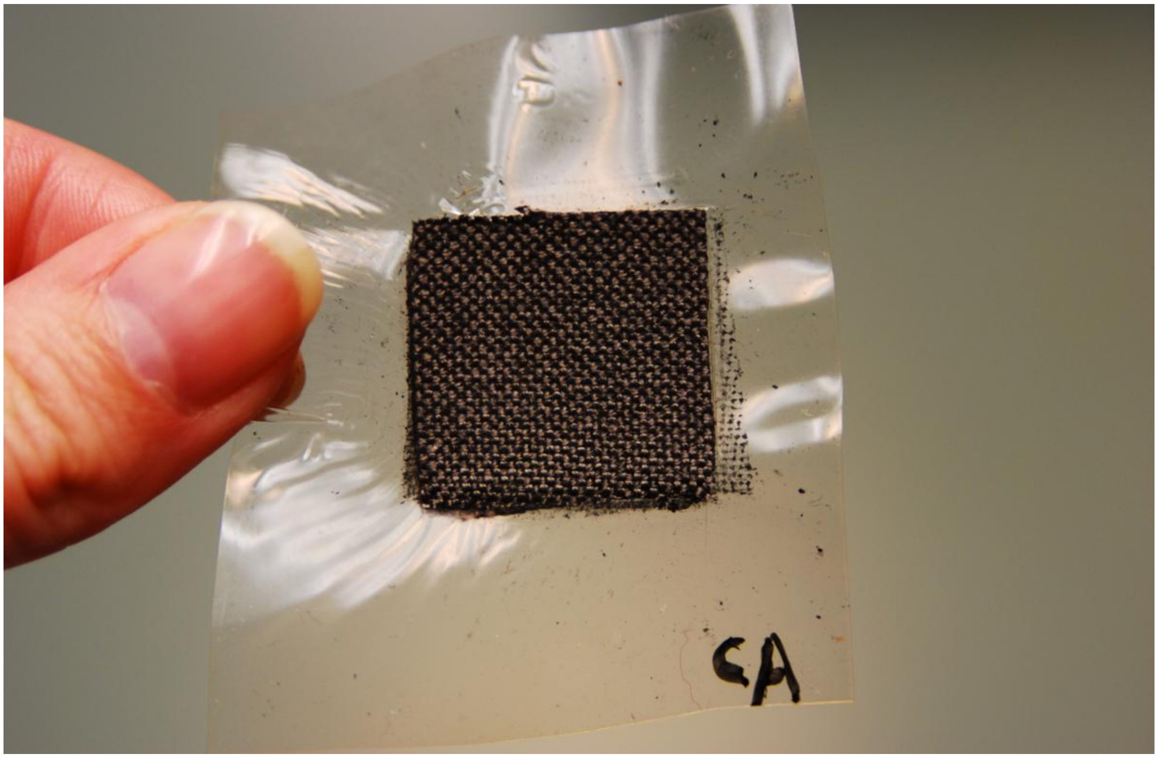


Figure 7. Front view of the cathode side of a MEA with a Nafion membrane and a carbon cloth electrode.

3.2 Membrane Treatment

The Nafion membranes that were used with the commercial electrodes followed the same procedure. They were soaked at a low boil in several different solutions to clean and protonate (see Table 2). Too high a boil could damage the membrane surface.

Table 2. Treatment of Nafion membranes.

Time	**Process**
1 hour	Deionized water
1 ½ hour	3 wt % Hydrogen peroxide
1 hour	Deionized water
1 ½ hour	0.5M Sulfuric acid
1 hour	Deionized water

The hydrogen peroxide is used to oxidize any organic impurities and the sulfuric acid protonates the sulfonic acid sites in the Nafion facilitating the proton transport. After the last boil, the membrane was flattened and dried between Kim wipes and metal plates in the Carver hot press for 10 minutes without heat or pressure. This prepared the membrane for electrode application (see below).

The Nafion membranes to which the home-made catalyst ink was applied followed a different procedure. They were first pre-treated in the deionized water, followed by the hydrogen peroxide and another deionized water boil. Then, the catalyst ink was applied and the membrane was subsequently dried in the oven at 70 °C. Post treatment with sulfuric acid and deionized water followed (see appendix X). The sulfuric acid, however, expanded the catalyst site and thus leaving a less concentrated active area.

3.3 Catalyst Preparation and Deposition

The catalyst used for the experiments with the Nafion 115 and 117 membranes was prepared in the lab. To mix the solution properly, two different methods were used; the sonicator in the fuel cell lab or the Microfluidizer at Microfluidics, Inc.

3.3.1 The Catalyst Ink

The catalysts contained 4 ingredients (see Table 3). A platinum/ruthenium on carbon mix was used for the anode and platinum on Vulcan for the cathode. A few drops of deionized water were added to wet the catalyst powder to prevent combustion when the methanol was added. Before the methanol, 10 wt% Nafion was added as well to increase protonic conduction. The mixture formed a black liquid with small solid particles (see Fig. 8 and 9).

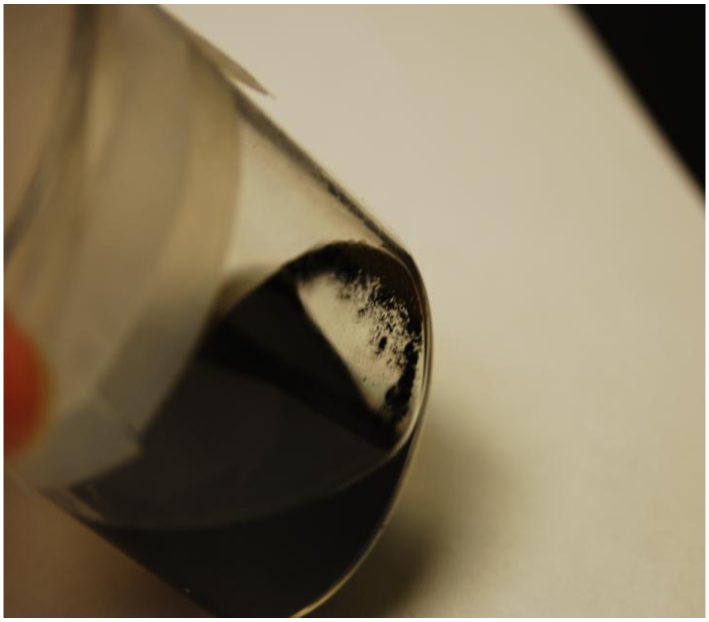


Figure 8. Solid particles form at the bottom of the catalyst ink and need to be dispersed.

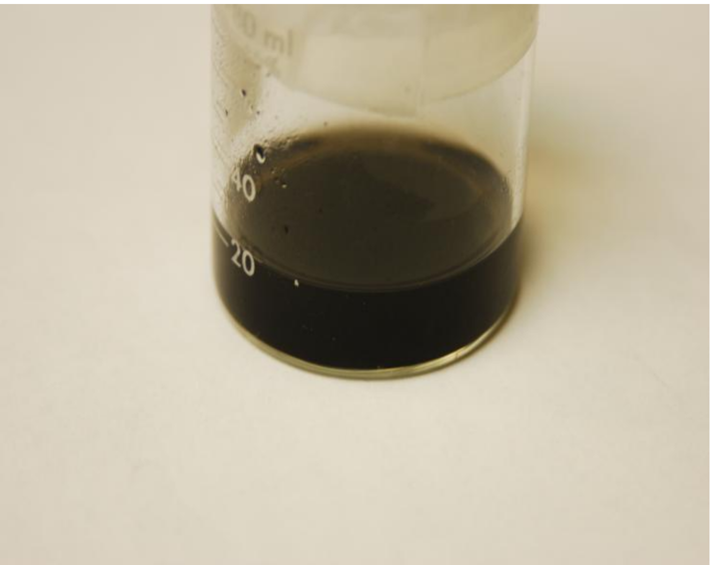


Figure 9. Catalyst ink before it is treated in the sonicator.

Table 3. Catalyst ink composition.

Anode catalyst ink	**Cathode catalyst ink**
24 mg platinum/ruthenium on optimized carbon	24 mg of platinum on Vulcan for the cathode
1-3 drops DI water	1-3 drops DI water
35 mg of 10 wt% Nafion	35 mg of 10 wt% Nafion
5 ml methanol	5 ml methanol

It was then either put in a sonicator for three hours or passed through the Microfluidizer at Microfluidics, Inc. When sprayed on the membrane, it appeared relatively opaque. This resulted in a catalyst loading of approximately 4 mg/cm^2 on an active area of 5 cm^2. About 4 mg were lost in pouring the catalyst ink into the container for the spray gun and in ensuring the gun functioned properly with the right flow rate and spray thickness. A high catalyst loading ensures a sufficient oxidation rate, but too much catalyst ink would incur mass transfer limitations.

3.3.2 The Sonicator

A sonicator uses sound waves to agitate particles in a solution. The platinum/ruthenium particles in the catalyst mixture did not mix easily with the Nafion and methanol, but 3 hours in the sonicator dispersed the compounds well. The sonicator in the fuel cell lab is a Fisher Scientific® Solid State/Ultrasonic FS-14 model (see Fig. 10). In addition a Branson 2210 model was used with similar results. The water heated up during the process and was replaced with cool water every 30-45 minutes.

Figure 10. The Fisher Scientific Solid State/Ultrasonic FS-14 sonicator.

3.3.3 The M-110S Microfluidizer® Materials Processor

Microfluidics, Inc. has invented a high shear processor named the Microfluidizer. It is used for emulsions, dispersions, liposomes, cell disruption and liquid-liquid or liquid-solid processing applications. This machine contains an air-powered intensifier pump which applies pressure at a constant rate to a product stream. The sample for the M-110S can be as small as 14 ml and as large as 25 ml. The sample flows through microchannels and is divided into two streams within a chamber. The high pressure ensures that when the two product streams meet at very high velocities, the particle size reduces through shear stresses. Flow rates as high as 600 ml/min can be reached by utilizing pressures of up to 23,000 psi with standard lab air.

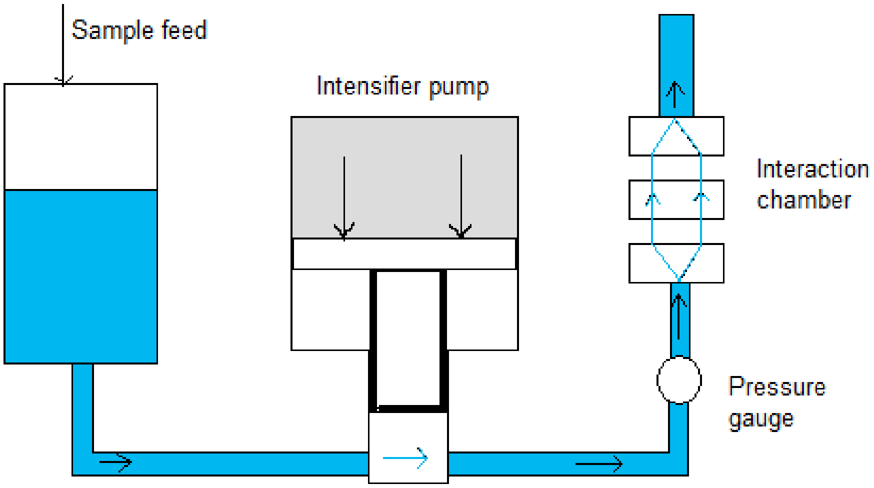


Figure 11. Schematic of a standard Microfluidizer Processor.

3.3.4 Spraying of the Catalyst Ink

The spray gun used for depositing the catalytic ink directly onto the 115 membrane was a Badger Professional 150 (see Fig. 12). The gun was cleaned before use with ethanol and cleaning solution.

Figure 12. The Badger Professional 150 air brush gun with which the catalyst ink was applied onto the membranes.

The membrane was dried with Kim wipes and pressed in the Carver hot press without heat and zero pressure for approximately 10 minutes to ensure a relatively flat and dry membrane before spraying. If the membrane is not flat, the catalyst cannot be sprayed evenly onto the membrane and may pool in some areas. Each layer is applied as evenly as possible and with a low flow rate. Too much catalyst ink deposited at one time my wet the membrane and causes swelling. The membrane is hot pressed at the end of the treatment procedure and if it was not entirely flat, the catalyst might crack causing methanol to cross over more easily during testing.

3.4 Assembling the MEA

Once the membranes had been treated, the GDLs or electrodes were hot pressed onto them. For the experiments where the catalyst ink was sprayed directly onto the membrane, GDL microporous layer on woven web Etek LT1400W ELAT were used. The GDL and the electrode had a smooth and a rough side. The smoother side with carbon particles deposited on the carbon cloth faces the catalyst or membrane (see Fig. 13). The GDL or electrode was carefully aligned onto the active area of the membrane.

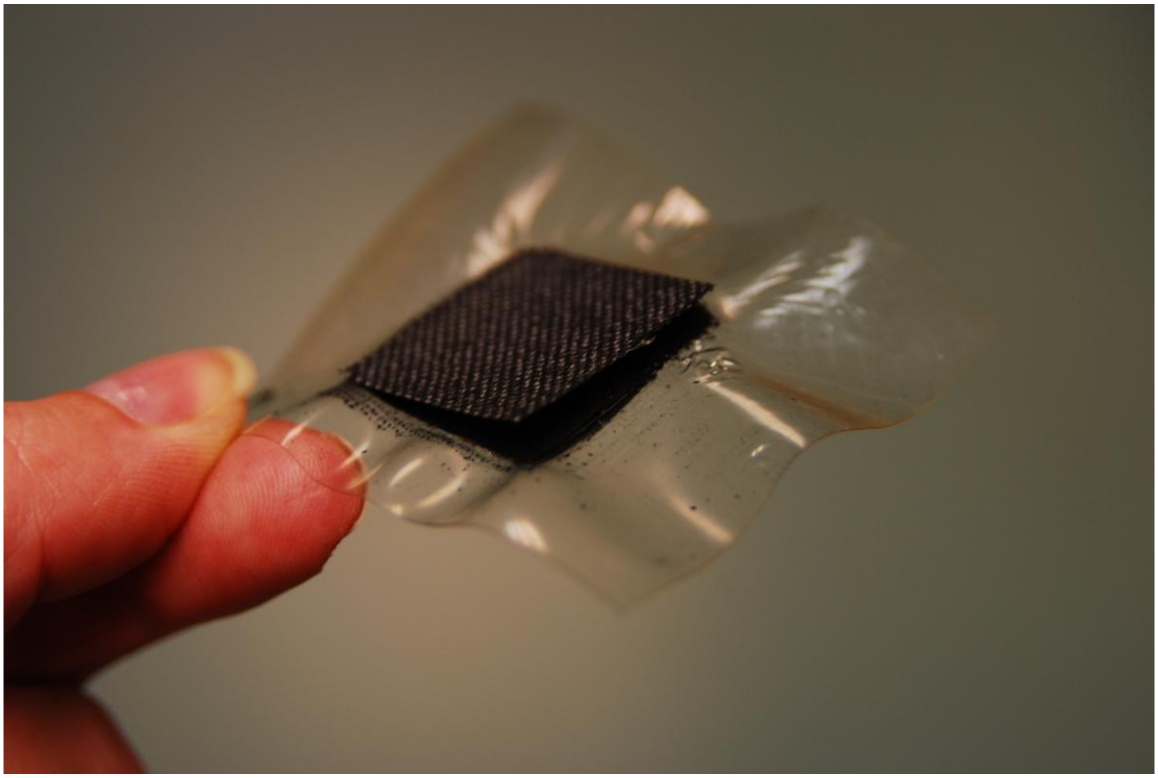


Figure 13. A used Nafion membrane with slightly detached ElectroChem electrodes pressed on either side of the membrane.

Then, the assembly was placed between Teflon layers and metal plates. Once the Carver hot press (see Fig. 14) was heated to 135°C the MEA was pressed at 2 metric tonnes for 2 minutes. This procedure ensures that the MEA sticks well together even when activated and used for a period of time. If the GDL or electrode shifts, the active areas are no longer aligned and performance is lost. In addition, the connection between the different layers must be such that protons can transfer easily.

Figure 14. The Carver hot press.

3.5 Testing the Fuel Cell

The MEA was placed between two gaskets onto the bipolar plate of the cell (see Fig. 15).

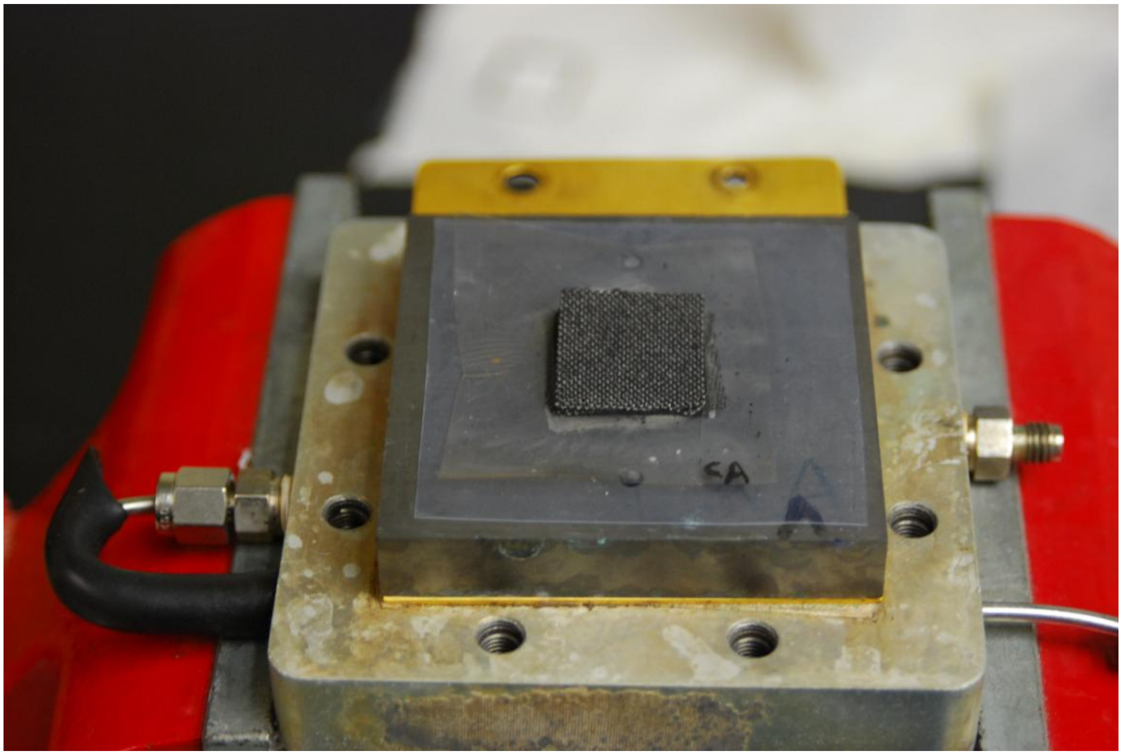


Figure 15. Anode bipolar plate with Teflon gasket and MEA aligned.

The second plate was carefully placed on top and bolted shut (see Fig. 16). First, 60 in-lb torque was carefully applied so as not to shift the MEA in the process. Then, the bolts were tightened even further at 65 in-lb.

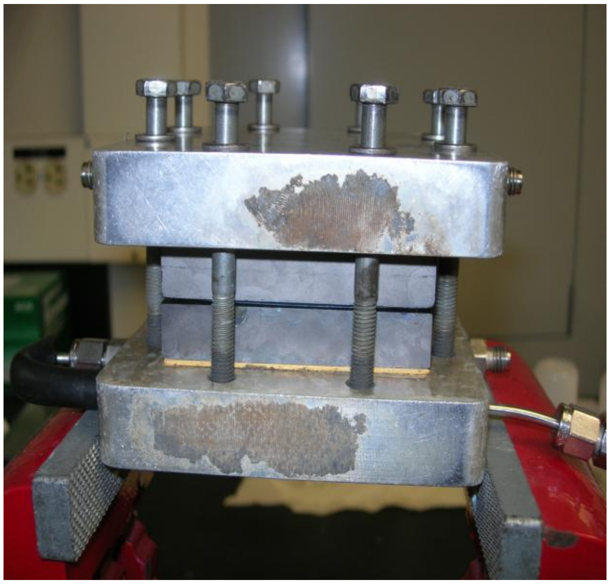


Figure 16. The fuel cell assembly.

Next, the cell was hooked up to the fuel cell testing station. As shown in Fig. 17, the pump containing the methanol feed was filled with the appropriate molar concentration and attached to the cell assembly. After the power of the testing station was turned on, the oxygen tank was opened and a flow of 70 mL/min was established to the cell. The temperature of the cell was set to 70 or 80°C and the humidifier for the oxygen to around 35°C. The aqueous methanol feed was run at 1.00 mL/min. After approximately 5-10 minutes the open circuit potential was noted and a load of 0.3V was applied to activate the MEA. The process was run for 4-6 hours to reach steady state. Then, different voltages between 0.6 and 0.1V were applied and the current was noted after each run reached steady state at the new voltage.

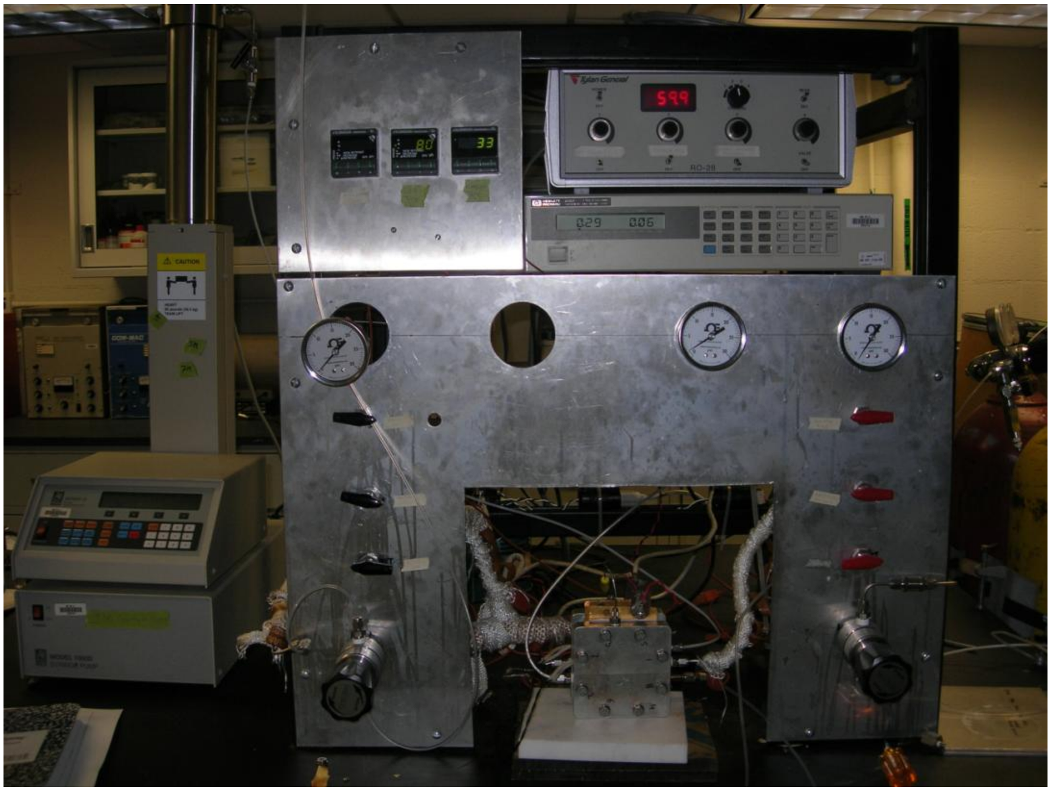


Figure 17. The fuel cell testing station with methanol fuel pump on the left.

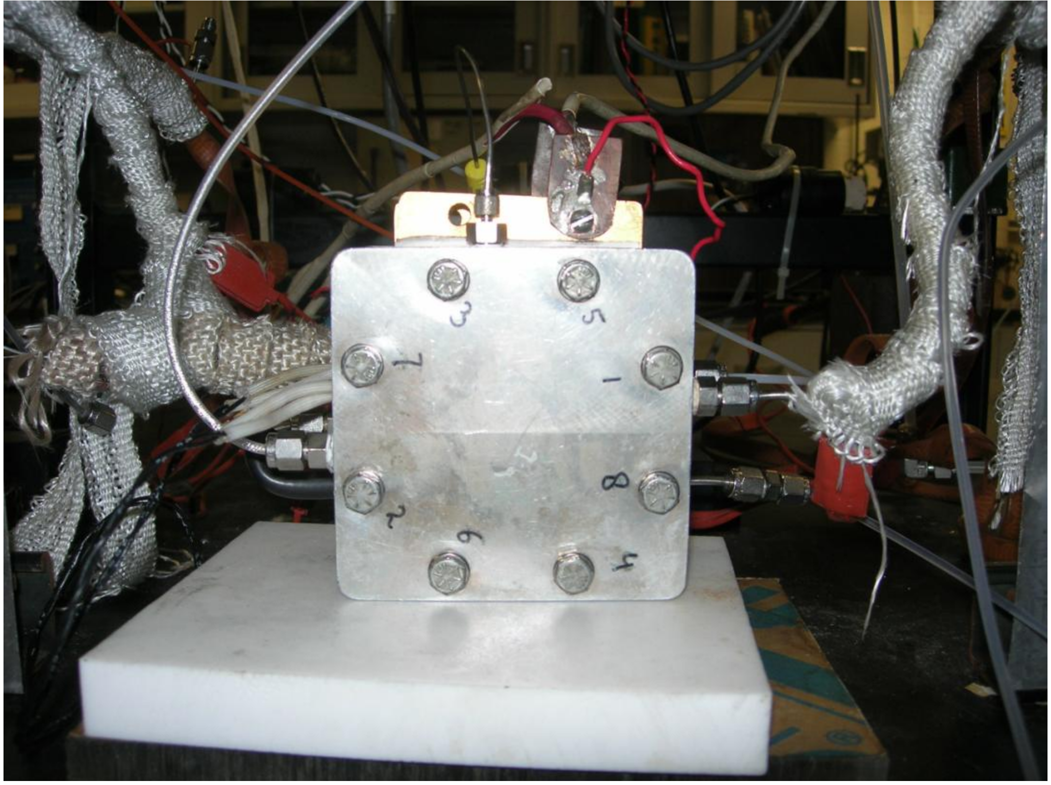


Figure 18. The fuel cell assembly hooked up to the testing station.

4. RESULTS AND DISCUSSION

Five different methods were tried and compared to the performance of a commercially available MEA from E-Tek, Inc. First, catalyst ink was prepared in the fuel cell lab and applied to two different membranes. The mixing of the ink to obtain better dispersion of the particles was done either in a sonicator or the Microfluidics' Microfluidizer. Then, membranes with different thicknesses were compared using commercially available electrodes from ElectroChem, Inc. These membranes were tested with varying molar feed concentration of methanol and at different operating temperatures. Finally, the commercially available electrode from ElectroChem was treated with a small amount of 10% Nafion solution to see its effects.

4.1 Testing the Commercial E-Tek Nafion 115 MEA

The E-Tek MEA served as a base case to which other membranes were compared. The MEA was tested with different methanol concentrations and at different temperatures with the optimum concentration. The GDL was not pressed tightly to the membrane and when the cell was opened up after it was tested with four different methanol concentrations (approximately 24 hours of operation), the GDL on the anode side fell off. The remaining MEA was very warped and crinkled. But, when put back together and aligned carefully, it still had an open circuit potential of approximately 0.77V. This could mean that it is not necessary to hot press the electrodes to the membrane. In fact, hot pressing may damage the catalyst layer, allowing methanol to cross over more easily.

On the other hand, the MEA was clearly not as robust as when the electrodes are firmly attached to the membrane.

Varying the methanol concentrations at an operating cell temperature of 70 °C and humidifier temperature of 40 °C performed well as can be seen in Fig. 19. Initially, by increasing the methanol concentration from 3M to 5M, the performance was better. Perhaps it performed better because there was more methanol to react with the catalyst. However, when 7M and 10M concentrations were used, the performance declined. This might be explained by the increase in methanol increasing methanol cross-over. The concentration gradient of methanol increases with a higher concentration of methanol in water, driving the methanol across the membrane. At voltage above 0.4 results are all very similar. The difference is noticeable at lower voltages and higher current densities between 0.3 and 0.4V. The current density of the 5M concentration feed was higher than that of the others, especially when a smaller voltage was applied to the cell. The MEA was damaged too much to test with 1M methanol feed.

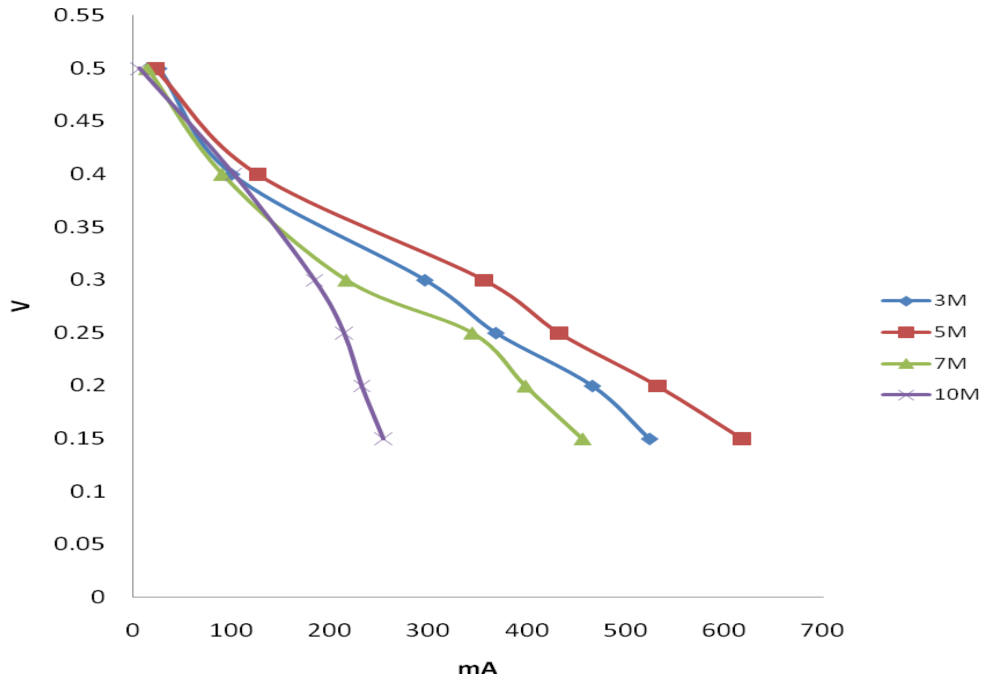


Figure 19. Performance of a commercial E-Tek MEA at four different methanol molar concentrations and a cell temperature of 70 °C.

4.2 Nafion 117 Membranes with Home-Made Catalyst Inks

Numerous attempts were made to create an MEA on a 117 membrane with the home-made catalyst ink in the sonicator. Only one MEA came out well, but still did not perform great. For inexplicable reasons, the other inks once applied with the airbrush came out light as compared to the one membrane (see Fig. 20). Furthermore, the anode ink was much lighter than the cathode ink. Lightness indicated that catalyst was not adequately transferred to the membrane.

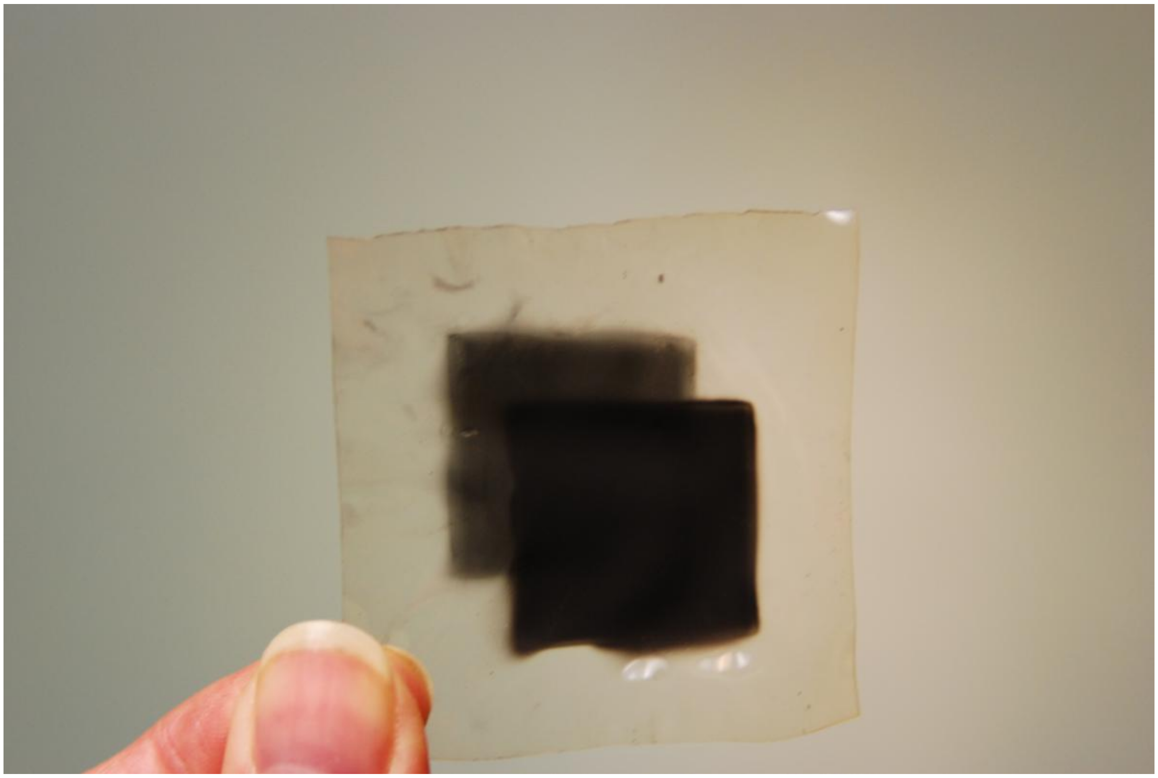


Figure 20. Nafion membrane with anode and cathode ink applied. The anode ink is lighter than the cathode ink application.

Different efforts were made to find out what the cause was of the light application. The scale had been fluctuating at times while the ingredients for the ink were measured. Therefore, the scale was leveled anew and left on all the time, so it was warmed up when used. The scale remained unreliable at times, however, drifting down or up once an ink component was added to the scale. A new airbrush was purchased as well, because the tip of the needle was damaged and the gun could not be controlled to produce a thin enough ink stream. The new airbrush allowed for more precision in the flow of the ink.

The first attempt at improving the ink was to add 6 mg more platinum or platinum/ruthenium to the mix. The methanol was increased to 5.5 mL. The reason for increasing the amount was to prevent ink from evaporating too much during the process.

Though this seemed to help a little, the catalyst layer was still too thin when sprayed onto a membrane. Then, the use of the sonicator was varied as well to check any issues with it. The anode ink had always been prepared first and put on the left side in the sonicator. The ink never caked onto the beaker, even after three hours in the sonicator, while the cathode ink did. Therefore, the cathode ink was prepared first and put on the left side in the sonicator. However, both cathode and anode ink came out badly. Then, the water was refreshed more often to prevent it from warming up and evaporating the catalyst. This did not help either. Finally, the inks were prepared one at a time with the thought that perhaps the ink would heat up too much with two beakers in the sonicator, or that position within the sonicator mattered. The results remained the same, though the cathode ink remained better than the anode ink.

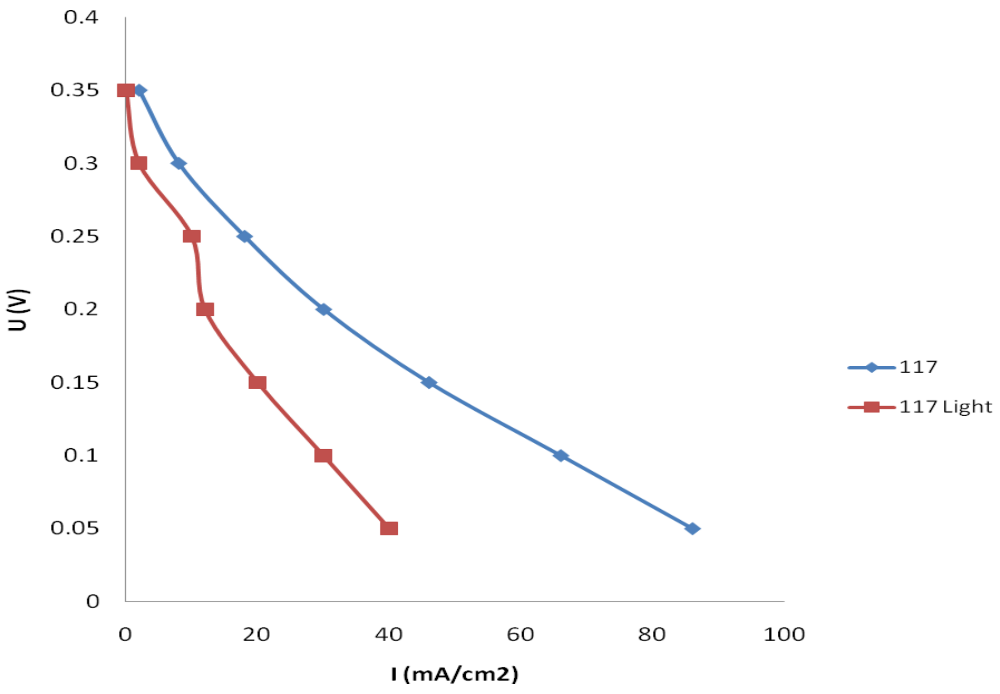


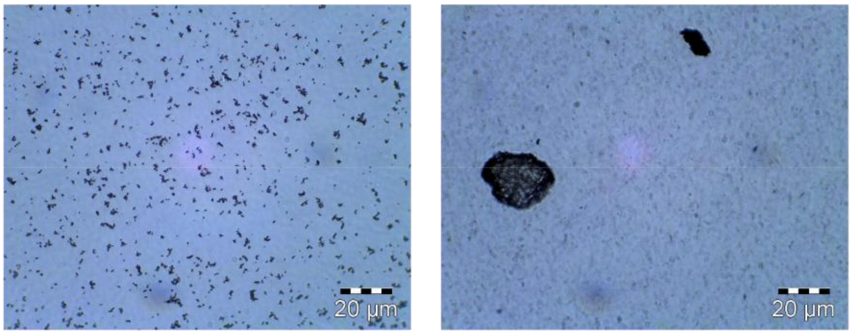
Figure 21. Difference in performance between opaque and less opaque catalyst ink application on a Nafion 117 membrane at 70°C.

Unfortunately, this problem remains unsolved. The difference between a membrane with a less opaque catalyst ink to one with a completely opaque ink is shown in Fig. 21. Clearly, when the catalyst ink looks less opaque, there truly is less catalyst on the membrane and there is not enough for the methanol to react with.

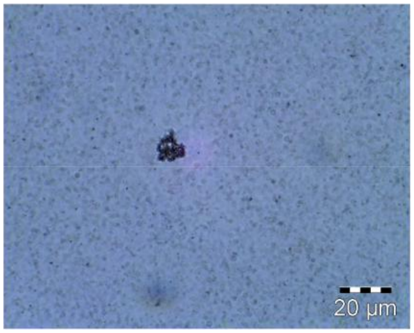
4.3 Testing Nafion 115 Membranes with Catalyst Prepared with the Microfluidizer® and the Fisher Scientific® Sonicator

Because the ink application procedure had worked in the past, a 115 membrane was treated with the same procedure. Unfortunately, the results were similar to the 117 membranes. The catalyst ink came out very light once sprayed onto the membrane. The same procedure had worked in the past (see appendix I), and so it seemed most likely that there was something wrong with the equipment. Therefore, a different sonicator, the Branson 2210, was used. However, this made no difference either. It was time to try a different way of dispersing the particles in the ink.

The Microfluidizer at Microfluidics, Inc. is a different way of dispersing the components as discussed in the last chapter. The catalyst ink was prepared at the fuel cell lab at WPI and brought over to the Microfluidics facility in Newton. A batch of about 20 mL was stirred slowly for about a minute before pouring it into the machine. The sample made 15 passes through the processor using the Y configured interaction chamber. It was then analyzed under an optical microscope and particle analyzer. The particle size in the anode ink was reduced to approximately 150 nm and the cathode ink particles reduced to about 197 nm. Images of the ink before and after processing show that the particle size reduced greatly and a more homogenous solution resulted.



Unprocessed **1 pass**



2 passes

Figure 22. Images of cathode catalyst ink after various stages of processing in the M-110S Microfluidizer at 20,000 psi with the F12Y interaction chamber.

The first Nafion 115 membrane was sprayed with 10.3 ml of catalyst and the second was sprayed the next day with 8.4 ml. A thick black coat was the result once sprayed on the membrane. But, when the membranes were tested, methanol leaked from the cell damaging the second membrane. The bipolar plates and connecting tubes were cleaned out and the first membrane was tested again. However, the performance was low (see Fig. 23).

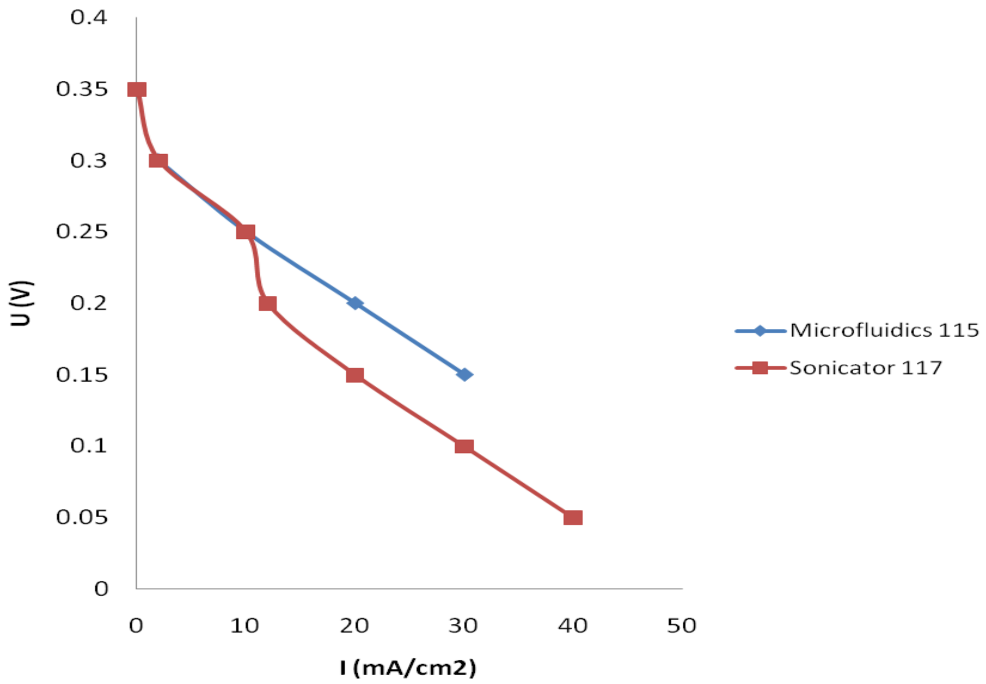


Figure 23. Comparison at 70 □ C between a Nafion 117 membrane with catalyst ink prepared in a sonicator with a Nafion 115 membrane with ink prepared in the Microfluidizer.

The Microfluidizer ink performed better, but a heavier catalyst loading was applied. Therefore, it cannot be said that the Microfluidizer *worked* better than the sonicator. There was more catalyst for the methanol to react with. It is more likely that there was something wrong with the catalyst ink preparation or compounds. Since all the equipment had been either replaced or tested to make sure it was not the cause of the light ink, and the exact same procedure was used as when it was working, the cause must be one of the ingredients. Though none of them were old enough to expire, impurities may have mixed in with one or more components, affecting the quality.

4.4 Comparing Different Methanol Concentrations

Five different aqueous solutions of methanol were prepared and tested with the four membranes and the commercial ElectroChem electrodes. The Nafion 115 membrane tested very well. First, 3M, 5M and 7M methanol concentrations were tried. Two weeks later, 1M and 10M solutions were tested.

The Nafion115 membrane performed well at 5M and 7M methanol concentrations. There was very little difference between the two concentrations, but 7M was slightly better. 1M, 3M and 10M performed considerably worse.

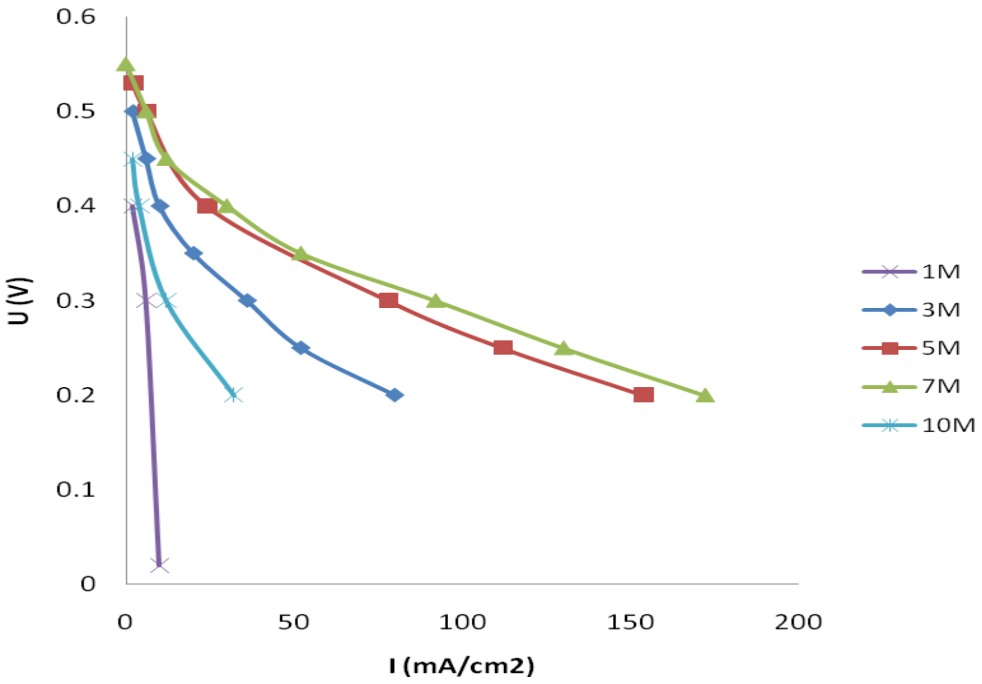


Figure 24. Results of testing a Nafion 115 membrane with ElectroChem electrodes at different methanol feed concentrations and 70 °C.

This lead to the thought that perhaps the time that had passed since the first day of testing the membrane and use had damaged the membrane. Therefore, another membrane (Nafion 1035) was tested at the same molar concentration as two weeks before, and it actually performed better (see Appendix III). Thus, the passing of time between testings and use should not effect the results. For the particular Nafion 115 membrane, it is possible that the membrane was damaged or not properly aligned.

The Nafion 117 membrane was tested and 7M concentration of aqeous methanol feed performed worse than with the Nafion 115 membrane. In fact, 3M and 5M were the better concentrations with 5M performing much better at lower voltages (see Fig. 25).

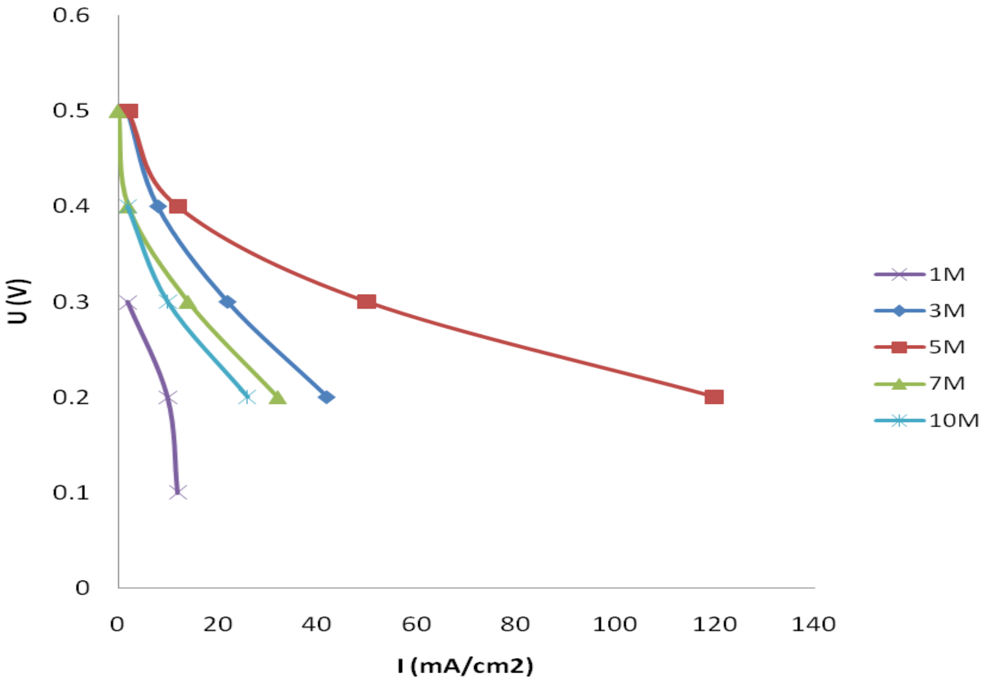


Figure 25. Results of testing a Nafion 117 membrane with ElectroChem electrodes at different methanol feed concentrations and at 70 °C.

The Nafion 1110 membrane was tested next and 5M outperformed all other concentrations (see Fig. 26).

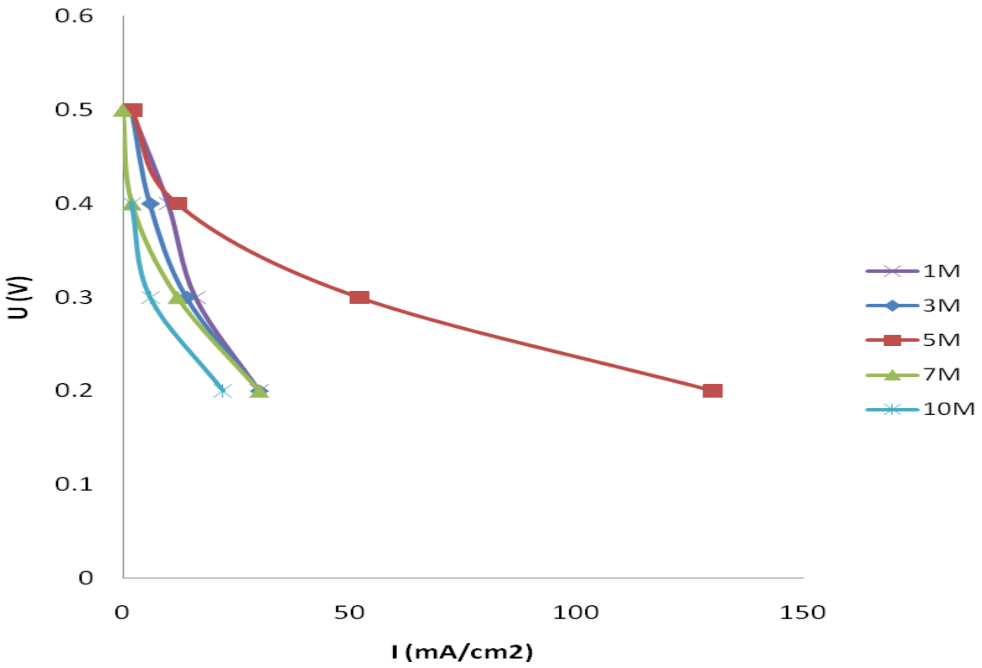


Figure 26. Results of testing a Nafion 1110 membrane with ElectroChem electrodes at different methanol feed concentrations and at 70 °C.

Finally, the Nafion 1035 membrane was tested. As Fig. 27 shows, 1M and 5M were the best feed concentrations. 1M was better at high voltages and 5M at lower voltages.

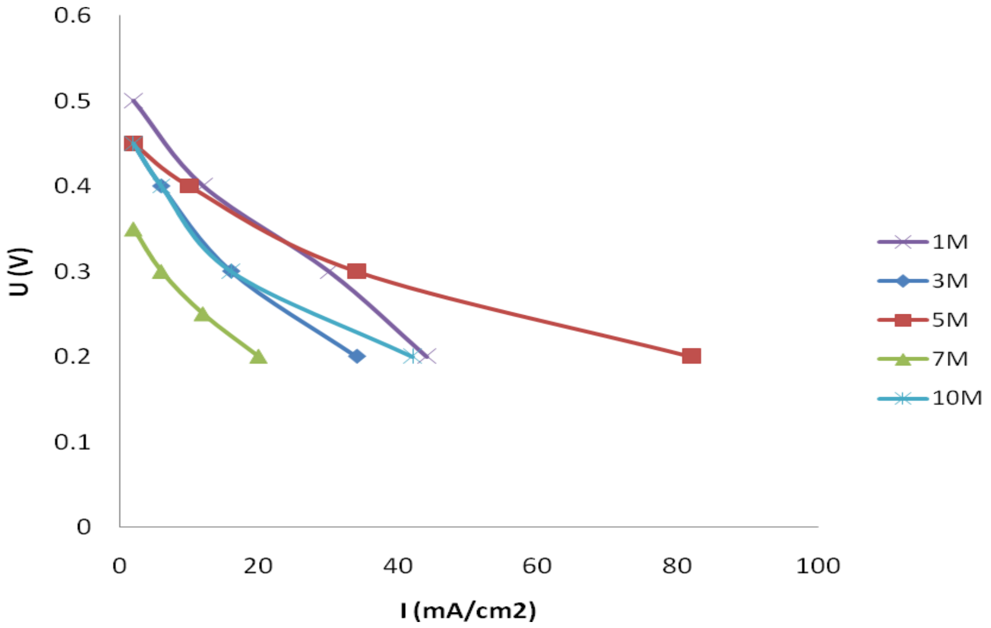


Figure 27. Results of testing a Nafion 1035 membrane with ElectroChem electrodes at different methanol feed concentrations and at 70 °C.

It is clear from the experiments that there is not one concentration that is best for all membranes. However, 5M methanol feed concentration seemed to work well for all. None of the membranes came close to the performance of E-Tek's commercial MEA though. The results might have been more conclusive if each test was run three different times with three different MEAs. However, the margin of error cannot be too large, as the only difference between each set of three membranes would be in the pretreatment of the membrane and the alignment of the MEA.

4.5 Comparing Different Operating Temperatures

Increasing the operating temperature of the fuel cell should improve the kinetics of the oxidation at the anode and the mass transfer of the reactants. The usual procedure in the lab was to set the temperature to 70°C and so every membrane was first tested at that temperature. The commercial E-Tek MEA performed best with a 5M methanol feed and thus, the MEA was tested at two higher temperatures with that same concentration. The results are below in Fig X.

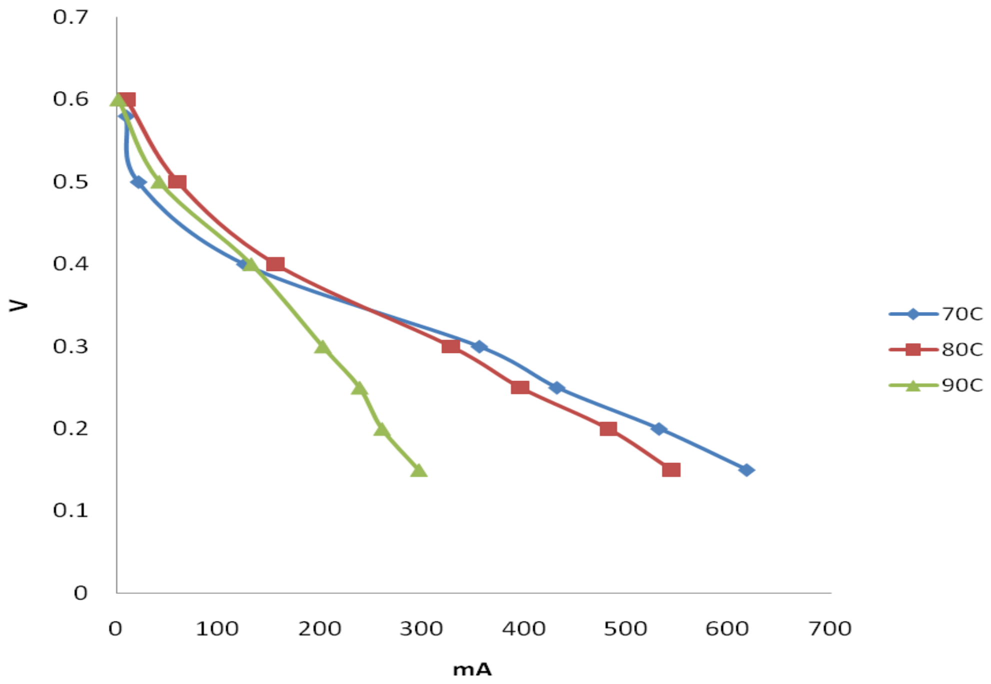


Figure 28. Results of commercial E-Tek MEA at different temperatures with a 5M methanol feed.

At lower current densities the MEA performed best at 80 °C and at higher densities 70 °C was the better temperature. Because the region between 0.3 and 0.6V is of most interest, 80 °C is the optimal operating temperature. At 90 °C the performance decreased sharply at higher current densities. This might be explained by the fact that methanol crosses over more easily with the increased temperature poisoning the cathode. The cross-over is encouraged because the fluorinated chain in the polymer membrane is softened, resulting in increased methanol permeation and water transfer.

The other four membranes were tested at two different temperatures. Based on the experiment with the commercial MEA, 70 °C and 80 °C were chosen. As shown in Fig. 29, the Nafion 115 membrane did not show a clear difference in performance between the two temperatures.

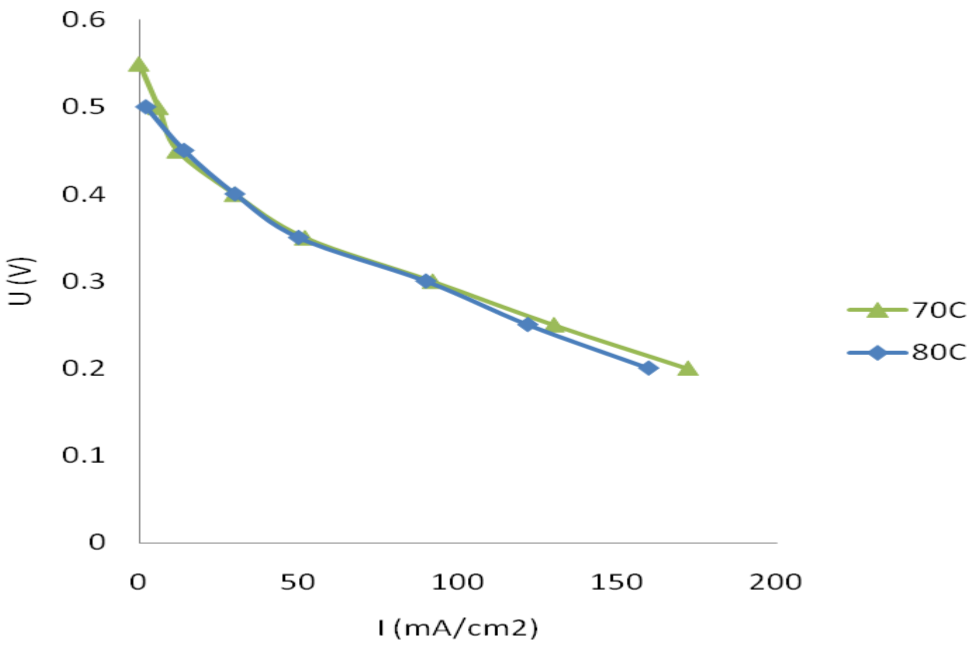


Figure 29. Results of testing a Nafion 115 membrane with 7M feed at different temperatures.

There was a difference noticable in temperatures with the other three membranes; 80 °C was better, just as it was for the commercial MEA (see Figs. 30-32).

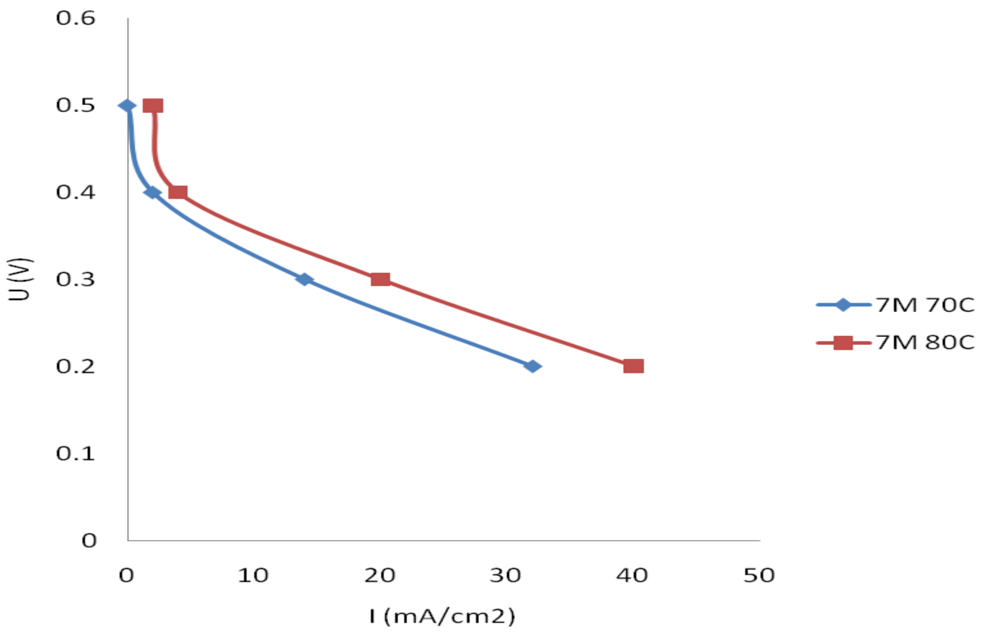


Figure 30. Results of testing a Nafion 117 membrane with 7M feed at different temperatures.

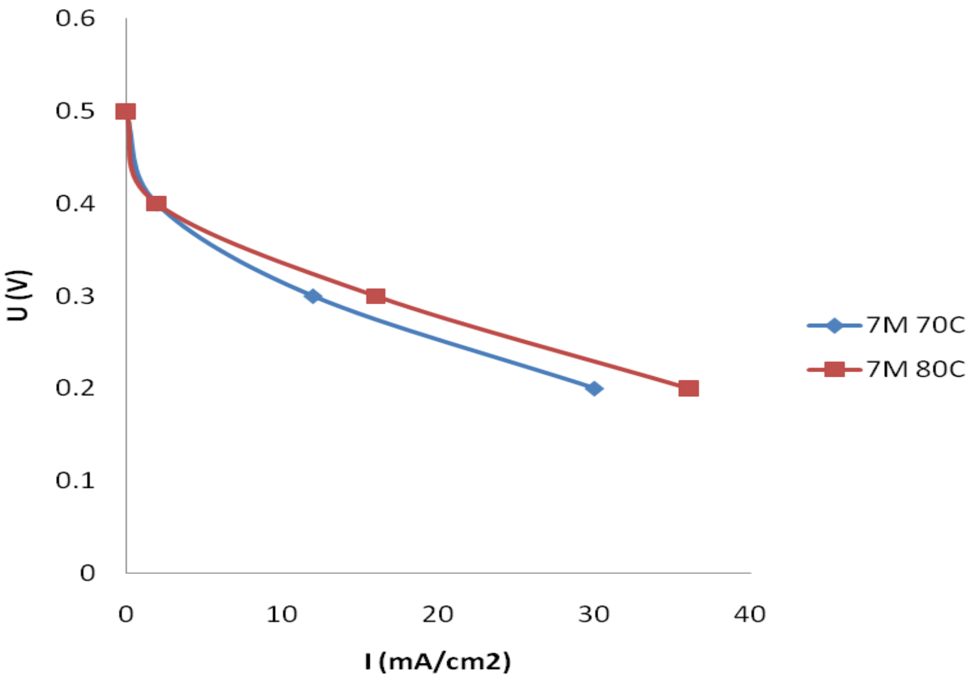


Figure 31. Results of testing a Nafion 1110 membrane with 7M feed at different temperatures.

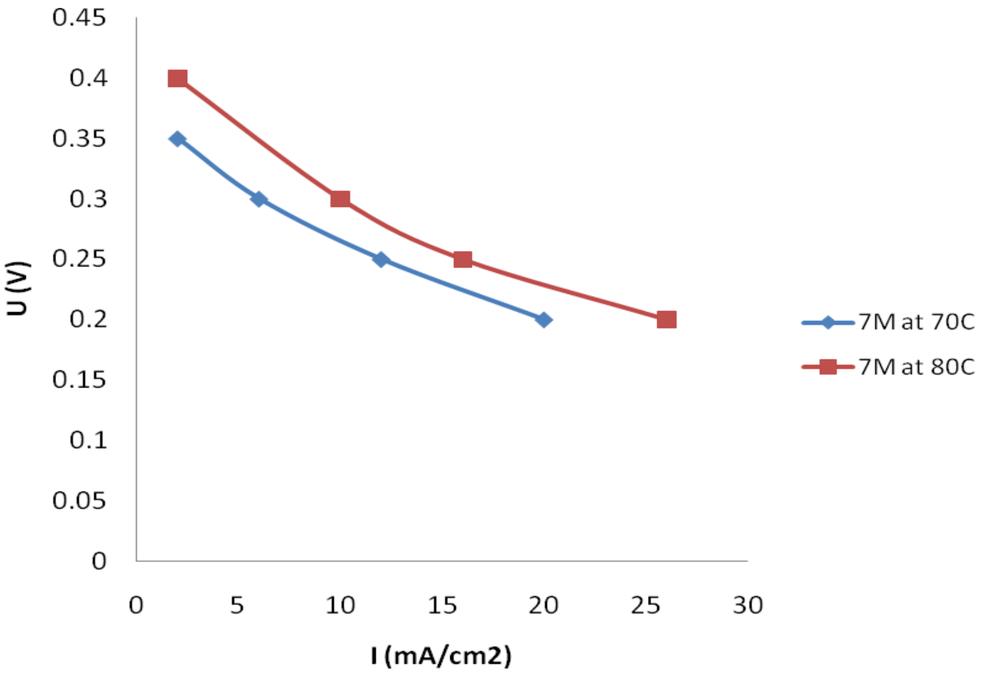


Figure 32. Results of testing a Nafion 1035 membrane with 7M feed at different temperatures.

It would be interesting to see how the cell would perform at 60 °C and 90 °C as well.

4.6 Comparing Different Membrane Thicknesses

The membranes were all tested and the power density was calculated:

$$P = V \times I$$

The best results for each membrane were put in the same graph for comparison (see Fig. 33). The Nafion 115 membrane with 5M at 70 °C reached the highest power density and was thus the best membrane. The Nafion 1035 membrane, which is the thinnest membrane, performed the poorest. Apparently, methanol was able to permeate through the membrane affecting the performance. The thickest membrane, Nafion 1110, performed second best. Thus, the thickness was a good parameter to stop methanol cross over without negsatively affecting the proton transfer.

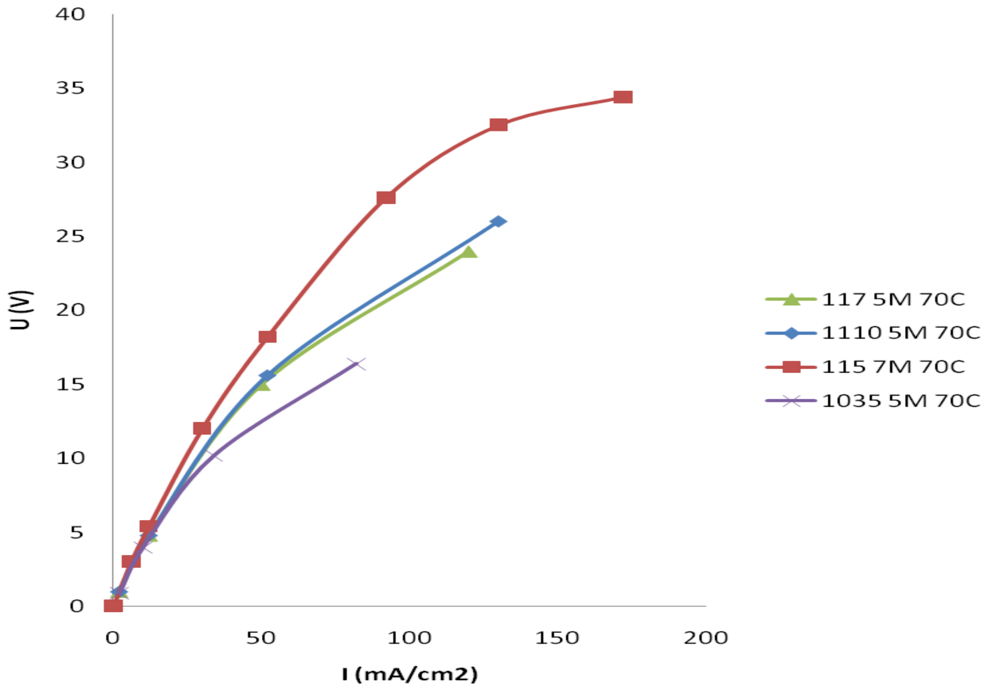


Figure 33. Comparison of power densities between four different thicknesses of Nafion membranes at 70 °C at two different feed concentrations.

The Nafion 115 membrane tested with 5M at 70 °C did not, however, outperform the E-Tek MEA.

4.7 Adding a Thin Layer of 10 wt% Nafion to the Commercial Electrode

The exact composition of the commercial ElectroChem electrode is unknown, and thus a thin layer of 10 wt% Nafion was brushed onto the smooth sides of the anode and cathode electrode. The hope was to improve proton conductivity. However, the membrane performed poorer than electrodes without the added Nafion solution (see Fig. 34).

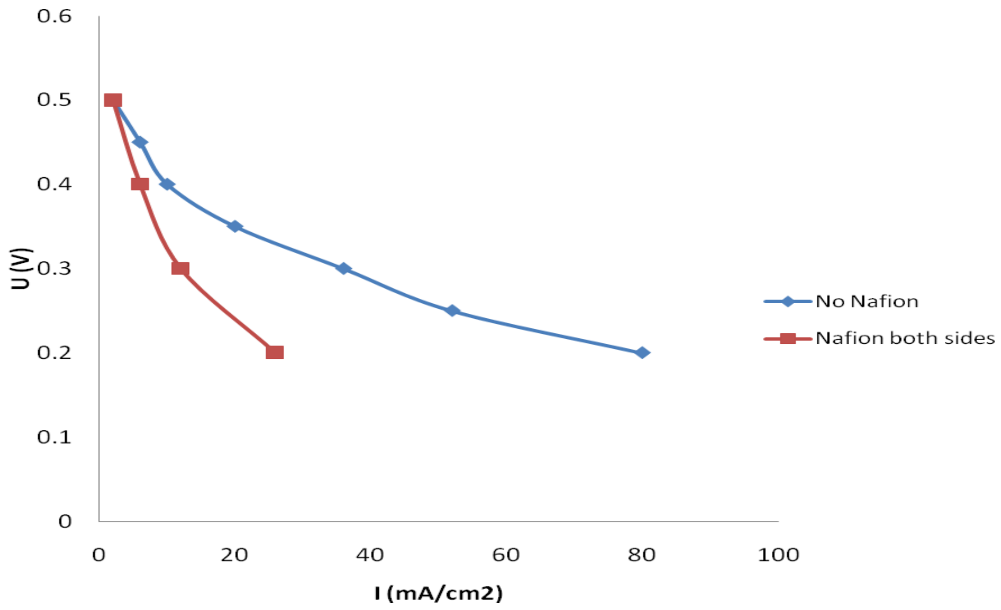


Figure 34. Comparison between 115 membranes with commercial electrodes with and without added 10 wt% Nafion solution.

Most likely, there was too much Nafion solution and it enveloped the catalyst particles (see Fig. 35). The layer inhibits the methanol from quick access to the catalyst site, though methanol will diffuse through the Nafion. The electrons, however, incur greater resistance from it. In addition, the Nafion will create a diffusion barrier for oxygen at the cathode, because Nafion is hydrophilic and will cause water to flow back to the cathode. Both effects result in a lower performance of the cell.

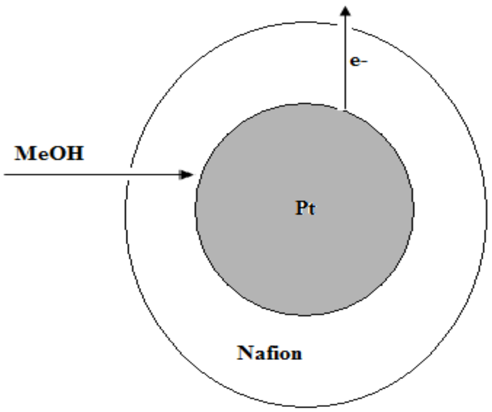


Figure 35. Schematic of the coating of catalyst particle with Nafion.

5. CONCLUSION

The E-Tek MEA performed much better than the home-made MEAs. The optimal operating conditions for the commercial MEA were 5M methanol feed and 80 °C at high voltages and 70 °C at lower voltages. The MEA showed that hotpressing the electrode to the membrane may not be necessary. Both electrodes detached from the membrane, but performance remained good. As long as a good contact is attained between the membrane, catalyst and electrode, the MEA will perform well. In fact, hotpressing may crack the catalyst allowing methanol to cross over more easily.

Home-made catalyst inks did not work, but have worked in the past. Therefore, this issue needs more attention and perhaps the components of the ink can be replaced one by one as the equipment and procedures were checked or replaced and no fault was discovered. The Microfluidizer from Microfluidics, Inc. may work better than the sonicator for dispersing the particles in the catalyst ink, but results are inconclusive as more ink prepeared by the Microfluidizer was applied to the membrane than ink prepared in the sonicator.

5M methanol concentrations performed best for all Nafion membranes except for the Nafion 115 membrane. The latter tested better at 7M. The Nafion 115 membrane also operated better at a different temperature than the other Nafion membranes. 70 °C was the optimal temperature for the Nafion 115 membrane, while the others got better results at 80 °C. The Nafion 115 membrane tested best overall and thus a thickness of 5 mil is recommended. Thicker tested better than thinner membranes, as it prevented methanol cross over without affecting proton transfer too much.

The ElectroChem electrodes did not improve with an additional 10 wt% Nafion layer. The catalyst particles were probably enveloped in the Nafion slowing methanol diffusion to the particles and retarding electron transportation.

6. RECOMMENDATIONS FOR FUTURE WORK

Recommendations for future work:

- Test the membranes at 60 °C and 90 °C to find an optimal operating temperature for each membrane.
- Examine the commercial electrodes to see what the catalyst is made out of and perhaps improve on it.
- Examine the commercial MEA further to understand its components to improve performance of the Nafion membranes used in the experiments for this paper.
- Add Teflon to catalytic ink and spray on commercial electrodes to see if it improves performance of the cell as it is hydrophobic and allowing oxygen to diffuse to the catalyst more easily.
- Experiment with a vapor feed of methanol.
- Conduct same experiments with different (composite) membranes.
- Experiment with highest performing membrane at optimal temperature and methanol concentration, but different periods of time in the hot press, or at different pressures.
- Examine the components of the home-made catalyst ink to see if it can be improved upon.

REFERENCES

Arbizzani, C., Biso, M., Manferrari, E., Mastragostino, M. “Methanol oxidation by pEDOT-pSS/PtRu in DMFC.” *Journal of Power Sources*. 178 (2008): 584-590.

Aricò, A.S., Srinivasan, S. and Antonucci, V. “DMFCs: From Fundamenal Aspects to Technology Development.” *Fuel Cells*, 1(2) (2001): 133-161.

Bang, J.H. et al. “Porous Carbon Supports Prepared by Ultrasonic Spray Pyrolysis for Direct Methanol Fuel Cell Electrodes.” *Journal of Physical Chemistry C*. 111 (2007): 10959-10964.

Casalegno, A., Marchesi, R. and Rinaldi, F. “Systematic Experimental Analysis of a Direct Methanol Fuel Cell.” *Journal of Fuel Cell Science and Technology,* 4 (2007): 418-424.

Choi, P., Jalani, N.H. and Datta, R. “Thermodynamics and Proton Transport in Nafion II. Proton Diffusion Mechanisms and Conductivity.” *Journal of The Electrochemical Society,* 152(3) (2005): E123-E130.

Derbyshire FJ, de Beer VHJ, Abotsi GMK, Scaroni AW, Solar JM, D. J. Skrovanek. “The influence of surface functionality on the activity of carbon- supported catalysts.” *Appl. Catal*. 27 (1986): 117-131.

Fuel Cell Handbook. 7th ed. (2004) retrieved from: http://www.cleanfuelcellenergy.com/FCHandbook7.pdf

García, B.L., Sethuraman, V.A., Weidner, J.W., White, R.E and Dougal, R. “Mathematical Model of a Direct Methanol Fuel Cell.” *Journal of Fuel Cell Science and Technology,* 1 (2004): 43-48.

Gleason, D.A., Jensen, K.G., and Painuly, G. “Proton exchange membranes and membrane electrode assemblies for enhanced direct methanol fuel cell performance.” Major Qualifying Project Report, Worcester Polytechnic Institute, (2008).

Hacquard, A. “Improving and Understanding Direct methanol Fuel Cell (DMFC) Performance.” M.S. Thesis, Worcester Polytechnic Institute (2005).

Heinzel, A and Barragán, V.M. “Review of the state-of-the-art of the methanol crossover in direct methanol fuel cells.” *Journal of Power Sources*. 84(1) (1999): 70-74.

Heitner-Wirguin. C. “Recent advances in perfluorinated ionomer membranes: structure, properties and applications.” *Journal of Membrane Science*. 120 (1996): 1-33.

Hoogers, G. “Fuel Cell Technology Handbook.” CRC Press LLC (2003).

Izenson, M.G., and Hill, R.W. “Water and thermal balance in PEM and Direct Methanol Fuel Cells.” *Journal of Fuel Cell Science and Technology,* 1 (2004): 10-17.

Jung, D.H., Lee, C.H., Kim, C.S., Shin, D.R. “.”*Journal of Power Sources*. 71 (1998): 169-173.

Jung, G.B., Su, A., Tu, C.H. and Weng, F.B. “Effect of Operating Parameters on the DMFC Performance.” *Journal of Fuel Cell Science and Technology,* 2 (2005): 81-85.

Jung, G.B. et al. “Supported Nafion Membrane for Direct Methanol Fuel Cell.” *Journal of Fuel Cell Science and Technology,* 4 (2007): 248-254.

Kreuer, K.D. “Proton conductivity, materials and applications.” *Chem. Mater.* 8 (1996): 610-641.

Lin, H.L. et al. “Nafion/PTFE composite membranes for direct methanol fuel cell applications.” *Journal of Power Sources*. 150 (2005) 11-19.

Lobato, J., M.A. Rodrigo, J.J. Linares and K. Scott. “Effect of the catalytic ink preparation method on the performance of high temperature polymer electrolyte membrane fuel cells.” *Journal of Power Sources*. 157(1) (2006): 284-292.

Lu, G.Q., and Wang, C.Y. “Electrochemical and Flow Characterization of a Direct Methanol Fuel Cell.” *Journal of Power Sources*, 134 (2004): 33-40.

Lu, G.Q., Liu, F.Q., and Wang, C.Y. “Water transport through Nafion 112 membrane in DMFCs.” *Electrochemical Solid-State Letters*. 1 (2005): A1-A4.

Lu, G.Q. and Wang, C.Y. “Development of High Performance Micro DMFCS and a DMFC Stack.” *Journal of Fuel Cell Science and Technology*, 3 (2006): 131-136.

Ren, X. et al. “Recent advances in direct methanol fuel cells at Los Alamos National Laboratory.” *Journal of Power Sources*. 86 (2000): 111-116.

Schultz, T. Zhou, S., Sundmacher, K. “Current status of and recent developments in the Direct methanol fuel cell.” *Chemical Engineering Technology*. 24 (12) (2001): 1223-1233.

Tasa, S., Aapro, T. “Fuel Cells as Energy Sources for Future Mobile Devices.” *Journal of Fuel Cell Science and Technology,* 3 (2006): 492-494.

Wang, M., Guo, H. and Ma, C. “Dynamic Characteristics of a Direct Methanol Fuel Cell.” *Journal of Fuel Cell Science and Technology,* 3 (2006): 202-207.

Yang, C. et al. “A comparison of physical properties and fuel cell performance of Nafion and zirconium phosphate/Nafion composite membranes.” *Journal of Membrane Science,* 237 (2004): 145-161.

Zugic, B. “Investigation of direct methanol fuel cell catalyst synthesis.” Major Qualifying Project Report submitted to Worcester Polytechnic Institute (2006).

ACKNOWLEDGEMENTS

First of all, I would like to thank Professor Datta for giving me the opportunity to work in his fuel cell lab. I am very grateful for his guidance throughout the year and for pushing me to expand my goals. Second, a big thank you to Saurabh Vilekar, who was always there to ask questions to, bounce ideas off of, discuss results with and show me how to do things. You helped me understand the direct methanol fuel cell and stimulated my interest. I would also like to thank Ken and Steve at Microfluidics for their help with preparing our catalysts with the microfluidizer. Jack Ferraro and Doug White for their help in and around the lab, including the bucket of ice! Denise Gleason, Kristoffer Jensen and Garima Painuly for showing me how to run the experiments in the lab. And finally, thanks to my lab partner, Neal Rosenthal. For working many hours side by side in the lab and making it a fun and valuable experience.

Appendix I: Treatment Procedure when Applying Home-Made Catalyst Ink

8:30	1 hour	Cut a 2.0 inch X 2.0 inch sheet of Nafion 117 and boil (setting: 3.5) in 300 mL DI water.
9:00	15 min	Prepare anode side catalyst. Zero small beaker on the scale. Add 24 mg Pt with scalpel (cathode side) Add DI water with dropper. Rinse the sides of the beaker if Pt is stuck to it. 1-2 drops Put beaker back on scale and zero it. Add 35 mg of 10% Nafion with the dropper. Stir in 5 mL methanol with the scalpel. Cover with parafilm and note on there what it is and when it was prepared. Put in sonicater for **3 hours**. Turn knob to “hold” and turn heat on. Make sure the beaker is sealed well and the parafilm stayes above the water. Don’t leave it longer, because ink will evaporate. Keep water cold with ice cubes or refresh every 30-45 min.
9:30	1.5 hours	Low (setting 3) boil in 150 ml 3% H_2O_2
10:40	20 min	Prepare cathode side catalyst. Put in sonicator for 3 hours.
11:00	1 hour	Low boil in 300 mL DI water.
12:00	10 min	Press membrane if not flat without any heat or pressure
12:10	1h30min	Spray anode side.
1:40	1h30min	Spray cathode side.
3:10	1h30 min	Put membrane in watch glass and cover with Kim wipe. Heat in oven upstairs at 70C
4:50	5 min	Remove membrane from oven with gloves.
4:55	1h30min	Low boil in 200 mL of 0.5M H_2SO_4.
6:30	1h	Low boil in 200 mL DI water
7:30	5 min	If not flat, press for 5 min without heat.
7:35	15 min	Turn on hotpress at 275F. Cut small squares out of the carbon cloth. The square is size of metal bar. (The smooth side of the carbon cloth faces the catalyst). Put the smooth side down and place the metal bar on the rough side. With a scalpel cut around bar. Tape SMOOTH white Teflon paper onto the metal book on both sides. Put carbon cloth rough side down. Then the catalyst on the membrane. Then carbon cloth smooth side down. Then white Teflon paper. THE TRICK IS TO ALLIGN EVERYTHING. (2 metric ton for 2 min.)
7:55	10 min	Remove plates from hotpress after 2 min and allow to cool.

8:05		Place hotpressed membrane in fresh zip lock bag and mark with date, type of membrane and treatment.

Appendix II: Preparation of Solutions

1000mL of 3 wt % H_2O_2:
Measure 85.7 mL of 35 wt % H_2O_2
Add 914 mL water

1000 mL of 0.5M H_2SO_4:
Measure 27 mL of 98 wt % $H_2\ SO_4$
Add 973 mL water

100 mL of 0.5M HNO_3:
Measure 2.86 mL of 70 wt % HNO_3
Add 97.1 mL water

Molar concentration of methanol:
1000 mL **3M** methanol → 3 mol x 32.04 = 96.12g
1500 mL **3M** methanol → 144.18 g

1000 mL **5M** methanol → 5 mol x 32.04 = 160.2g
1500 mL **5M** methanol → 240.3 g

1000 mL **7M** methanol → 7 mol x 32.04 = 226.8g
1500 mL **7M** methanol → 340.2 g

1000 mL **10M** methanol → 10 mol x 32.04 = 320.4g
1500 mL **10M** methanol → 480.6 g

Appendix III: Raw Data

TESTING OF THE COMMERCIAL E-TEK MEA

E-Tek MEA	1 mL/min MeOH at **3M**, 70 mL/min O_2, T_{cell} = 70 °C, $T_{humidifier}$ = 35 °C	
U (V)	I (mA/cm^2)	P (mW/cm^2)
0.58	10	5.8
0.5	26	13
0.4	100	40
0.3	296	88.8
0.25	368	92
0.2	466	93.2
0.15	524	78.6

E-Tek MEA	1 mL/min MeOH at **5M**, 70 mL/min O_2, T_{cell} = 70 °C, $T_{humidifier}$ = 35 °C	
U (V)	I (mA/cm^2)	P (mW/cm^2)
0.58	10	5.8
0.5	22	11
0.4	126	50.4
0.3	356	106.8
0.25	432	108
0.2	532	106.4
0.15	618	92.7

E-Tek MEA	1 mL/min MeOH at **7M**, 70 mL/min O_2, T_{cell} = 70 °C, $T_{humidifier}$ = 35 °C	
U (V)	I (mA/cm^2)	P (mW/cm^2)
0.5	14	7
0.4	90	36
0.3	216	64.8
0.25	344	86
0.2	398	79.6
0.15	456	68.4

E-Tek MEA	1 mL/min MeOH at **10M**, 70 mL/min O_2, T_{cell} = 70 °C, $T_{humidifier}$ = 35 °C	
U (V)	I (mA/cm^2)	P (mW/cm^2)
0.5	6	3
0.4	102	40.8
0.3	184	55.2
0.25	214	53.5
0.2	232	46.4
0.15	254	38.1

E-Tek MEA	1 mL/min MeOH at 3M, 70 mL/min O_2, T_{cell} = **80 °C**, $T_{humidifier}$ = 35 °C	
U (V)	I (mA/cm^2)	P (mW/cm^2)
0.6	10	6
0.5	60	30
0.4	156	62.4
0.3	328	98.4
0.25	396	99
0.2	482	96.4
0.15	544	81.6

E-Tek MEA	1 mL/min MeOH at 3M, 70 mL/min O_2, T_{cell} = **90 °C**, $T_{humidifier}$ = 35 °C	
U (V)	I (mA/cm^2)	P (mW/cm^2)
0.6	2	1.2
0.5	42	21
0.4	132	52.8
0.3	202	60.6
0.25	238	59.5
0.2	260	52
0.15	296	44.4

TESTING OF NAFION 117 MEMBRANES WITH HOME MADE CATALYST INK

Nafion 117	Anode: Pt/Ru on optimized carbon, 4 mg/cm^2, cathode: Pt on Vulcan, 4 mg/cm^2, 1 mL/min MeOH at 3M, 70 mL/min O$_2$, T$_{cell}$ = 70 °C, T$_{humidifier}$ = 35 °C	
U (V)	I (mA/cm^2)	P (mW/cm^2)
0.35	2	0.70
0.30	8	2.40
0.25	18	4.5
0.20	30	6
0.15	46	6.9
0.1	66	6.6
0.05	86	4.3

Nafion 117 (**Light**)	Anode: Pt/Ru on optimized carbon, 4 mg/cm^2, cathode: Pt on Vulcan, 4 mg/cm^2, 1 mL/min MeOH at 3M, 70 mL/min O$_2$, T$_{cell}$ = 70 °C, T$_{humidifier}$ = 35 °C	
U (V)	I (mA/cm^2)	P (mW/cm^2)
0.35	0	0
0.30	2	0.6
0.25	10	2.5
0.20	12	2.4
0.15	20	3
0.1	30	.3
0.05	40	2

TESTING OF NAFION 115 MEMBRANES WITH HOME MADE CATALYST INK

Nafion 115 (**Sonicator**)	Anode: Pt/Ru on optimized carbon, 4 mg/cm^2, cathode: Pt on Vulcan, 4 mg/cm^2, 1 mL/min MeOH at 3M, 70 mL/min O_2, T_{cell} = 70 °C, $T_{humidifier}$ = 35 °C	
U (V)	I (mA/cm^2)	P (mW/cm^2)
0.5	26	13
0.4	100	40
0.3	296	88.8
0.25	368	92
0.2	466	93.2
0.15	524	78.6

Nafion 115 (**Microfluidizer**)	Anode: Pt/Ru on optimized carbon, 4 mg/cm^2, cathode: Pt on Vulcan, 4 mg/cm^2, 1 mL/min MeOH at 3M, 70 mL/min O_2, T_{cell} = 70 °C, $T_{humidifier}$ = 35 °C	
U (V)	I (mA/cm^2)	P (mW/cm^2)
0.5	26	13
0.4	100	40
0.3	296	88.8
0.25	368	92
0.2	466	93.2
0.15	524	78.6

TESTING 115 MEMBRANES WITH COMMERCIAL ELECTROCHEM ELECTRODES

Nafion 115	1 mL/min MeOH at **1M**, 70 mL/min O_2, T_{cell} = 70 °C, $T_{humidifier}$ = 35 °C	
U (V)	I (mA/cm^2)	P (mW/cm^2)
0.4	2	0.8
0.3	6	1.8
0.2	10	0.2

Nafion 115	1 mL/min MeOH at **3M**, 70 mL/min O_2, T_{cell} = 70 °C, $T_{humidifier}$ = 35 °C	
U (V)	I (mA/cm^2)	P (mW/cm^2)
0.5	2	1
0.45	6	2.7
0.4	10	4
0.35	20	7
0.3	36	11
0.25	52	13
0.2	80	16

Nafion 115	1 mL/min MeOH at **5M**, 70 mL/min O_2, T_{cell} = 70 °C, $T_{humidifier}$ = 35 °C	
U (V)	I (mA/cm^2)	P (mW/cm^2)
0.53	2	1.06
0.5	6	3
0.4	24	9.6
0.3	78	23.4
0.25	112	28
0.2	154	30.8

Nafion 115	1 mL/min MeOH at **7M**, 70 mL/min O_2, T_{cell} = 70 °C, $T_{humidifier}$ = 35 °C	
U (V)	I (mA/cm^2)	P (mW/cm^2)
0.55	0	0
0.5	6	3
0.45	12	5.4
0.4	30	12
0.35	52	18
0.3	92	28
0.25	130	33
0.2	172	34

Nafion 115	1 mL/min MeOH at **10M** 70 mL/min O_2, T_{cell} = 70 °C, $T_{humidifier}$ = 35 °C	
U (V)	I (mA/cm^2)	P (mW/cm^2)
0.45	2	0.9
0.4	4	1.6
0.3	12	3.6
0.2	32	6.4

Nafion 115	1 mL/min MeOH at 7M, 70 mL/min O_2, T_{cell} = **80 °C**, $T_{humidifier}$ = 35 °C	
U (V)	I (mA/cm^2)	P (mW/cm^2)
0.5	2	1
0.45	14	6.3
0.4	30	12
0.35	50	17.5
0.3	90	27
0.25	122	30.5
0.2	160	32

TESTING 117 MEMBRANES WITH COMMERCIAL ELECTROCHEM ELECTRODES

Nafion 117	1 mL/min MeOH at **1M**, 70 mL/min O_2, T_{cell} = 70 °C, $T_{humidifier}$ = 35 °C	
U (V)	I (mA/cm^2)	P (mW/cm^2)
0.3	2	0.6
0.2	10	2
0.1	12	1.2

Nafion 117	1 mL/min MeOH at **3M**, 70 mL/min O_2, T_{cell} = 70 °C, $T_{humidifier}$ = 35 °C	
U (V)	I (mA/cm^2)	P (mW/cm^2)
0.5	2	1
0.4	8	3.2
0.3	22	6.6
0.2	42	8.4

Nafion 117	1 mL/min MeOH at **5M**, 70 mL/min O_2, T_{cell} = 70 °C, $T_{humidifier}$ = 35 °C	
U (V)	I (mA/cm^2)	P (mW/cm^2)
0.5	2	1
0.4	12	4.8
0.3	50	15
0.2	120	24

Nafion 117	1 mL/min MeOH at **7M**, 70 mL/min O_2, T_{cell} = 70 °C, $T_{humidifier}$ = 35 °C	
U (V)	I (mA/cm^2)	P (mW/cm^2)
0.5	0	0
0.4	2	0.8
0.3	14	4.2
0.2	32	6.4

Nafion 117	1 mL/min MeOH at **10M**, 70 mL/min O_2, T_{cell} = 70 °C, $T_{humidifier}$ = 35 °C	
U (V)	I (mA/cm^2)	P (mW/cm^2)
0.4	2	0.8
0.3	10	3
0.2	26	5.2

Nafion 117	1 mL/min MeOH at 7M, 70 mL/min O_2, T_{cell} = **80 °C**, $T_{humidifier}$ = 35 °C	
U (V)	I (mA/cm^2)	P (mW/cm^2)
0.5	2	1
0.4	4	1.6
0.3	20	6
0.2	40	8

TESTING 1110 MEMBRANES WITH COMMERCIAL ELECTROCHEM ELECTRODES

Nafion 1110	1 mL/min MeOH at **1M**, 70 mL/min O_2, T_{cell} = 70 °C, $T_{humidifier}$ = 35 °C	
U (V)	I (mA/cm^2)	P (mW/cm^2)
0.5	2	1
0.4	10	4
0.3	16	4.8
0.2	30	6

Nafion 1110	1 mL/min MeOH at **3M**, 70 mL/min O_2, T_{cell} = 70 °C, $T_{humidifier}$ = 35 °C	
U (V)	I (mA/cm^2)	P (mW/cm^2)
0.5	2	1
0.4	6	2.4
0.3	14	4.2
0.2	30	6

Nafion 1110	1 mL/min MeOH at **5M**, 70 mL/min O_2, T_{cell} = 70 °C, $T_{humidifier}$ = 35 °C	
U (V)	I (mA/cm^2)	P (mW/cm^2)
0.5	2	1
0.4	12	4.8
0.3	52	15.6
0.2	130	26

Nafion 1110	1 mL/min MeOH at **7M**, 70 mL/min O_2, T_{cell} = 70 °C, $T_{humidifier}$ = 35 °C	
U (V)	I (mA/cm^2)	P (mW/cm^2)
0.5	0	0
0.4	2	0.8
0.3	12	3.6
0.2	30	6

Nafion 1110	1 mL/min MeOH at **10M**, 70 mL/min O_2, T_{cell} = 70 °C, $T_{humidifier}$ = 35 °C	
U (V)	I (mA/cm^2)	P (mW/cm^2)
0.4	2	0.8
0.3	6	1.8
0.2	22	4.4

Nafion 1110	1 mL/min MeOH at 7M, 70 mL/min O_2, T_{cell} = **80 °C**, $T_{humidifier}$ = 35 °C	
U (V)	I (mA/cm^2)	P (mW/cm^2)
0.5	0	0
0.4	2	0.8
0.3	16	4.8
0.2	36	7.2

TESTING 1035 MEMBRANES WITH COMMERCIAL ELECTROCHEM ELECTRODES

Nafion 1035	1 mL/min MeOH at **1M**, 70 mL/min O_2, T_{cell} = 70 °C, $T_{humidifier}$ = 35 °C	
U (V)	I (mA/cm^2)	P (mW/cm^2)
0.5	2	1
0.4	12	4.8
0.3	30	9
0.2	44	8.8

Nafion 1035	1 mL/min MeOH at **3M**, 70 mL/min O_2, T_{cell} = 70 °C, $T_{humidifier}$ = 35 °C	
U (V)	I (mA/cm^2)	P (mW/cm^2)
0.5	2	0.9
0.4	6	2.4
0.3	16	4.8
0.2	34	6.8

Nafion 1035	1 mL/min MeOH at **5M**, 70 mL/min O_2, T_{cell} = 70 °C, $T_{humidifier}$ = 35 °C	
U (V)	I (mA/cm^2)	P (mW/cm^2)
0.5	2	0.9
0.4	10	4
0.3	34	10.2
0.2	82	16.4

Nafion 1035	1 mL/min MeOH at **7M**, 70 mL/min O_2, T_{cell} = 70 °C, $T_{humidifier}$ = 35 °C	
U (V)	I (mA/cm^2)	P (mW/cm^2)
0.35	2	0.7
0.3	6	1.8
0.25	12	3
0.2	20	4

Nafion 1035 (RETEST)	1 mL/min MeOH at **7M**, 70 mL/min O_2, T_{cell} = 70 °C, $T_{humidifier}$ = 35 °C	
U (V)	I (mA/cm^2)	P (mW/cm^2)
0.5	2	0.7
0.4	6	1.8
0.3	12	3
0.2	20	4

Nafion 1035	1 mL/min MeOH at **10M**, 70 mL/min O_2, T_{cell} = 70 °C, $T_{humidifier}$ = 35 °C	
U (V)	I (mA/cm^2)	P (mW/cm^2)
0.5	2	0.9
0.4	6	2.4
0.3	16	4.8
0.2	42	8.4

Nafion 1035	1 mL/min MeOH at 7M, 70 mL/min O_2, T_{cell} = **80 °C**, $T_{humidifier}$ = 35 °C	
U (V)	I (mA/cm^2)	P (mW/cm^2)
0.5	2	0.8
0.4	10	3
0.3	16	4
0.2	26	5.2