Investigation of Membrane Electrode Assembly Design and Fabrication Parameters

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Abstract

Several aspects must be considered when attempting to design a fuel cell that will perform well and show durability without being expensive. This project focused on the membrane, gas-diffusion, and catalyst layers of the MEA, or the membrane electrode assembly, and improvements that could be made to both the process and parameters of its design and fabrication. By first understanding the main aspects of MEA performance and fabrication, several factors were decided upon to investigate further from among the wide range of possible experimental variables. In order to rationalize this, a theoretical model proposed by Thampan et al [7], of MEA performance was considered. A literature review was also preformed to guide the experimental phase of the project and to gain knowledge of current research being done on the relevant topics. Through the research of current practices coupled with the experimentation and observations in the lab, we narrowed down the list of design and fabrication parameters that could lead to the superior performance of the MEA, which were then experimentally investigated.

By changing the structure of the membrane layer, we investigated other forms of Nafion for catalyst deposition followed by performance evaluation, which were then compared to the performance of the commercially available electrodes. The Nafion® layer was transformed from its current common proton form to Sodium, Lithium, Cesium, and Potassium forms respectively, in order to investigate membrane swelling during catalyst ink spraying. It was found that they all affect the rate of solvent uptake differently. Potentially, this means that the membrane will absorb less solvent leading to less swelling and possibly making the catalyst layer more uniform if alternate forms if Nafion were utilized during MEA fabrication. (J, Memb Sci. 254 (1-2), 31-38).

Another parameter to be investigated was the amount of PTFE within the catalyst ink. This is used to make the catalyst layer hydrophobic. Varying the amount of PTFE between the anode and cathode sides and comparing their subsequent performance led to conclusions regarding the influence of the PTFE on the layer's anode side. Also, it was decided to look at the catalyst loading to see if the anode does not need as much to produce a satisfactory performance. Finally, a different gas-diffusion layer was investigated in an effort to improve performance.

Through experimentation it was established shown that the E-TEK GDL provides the best performance with the proton form of Nafion®, exceeding that of the commercially available MEA. When not using the E-TEK GDL, the cesium and potassium forms provided the highest performance, but not surpassing the commercial MEA. PTFE did not hinder performance when left off of the anode side, however it did lead to flooding becoming a more common occurrence. It is hoped that this work will form the basis of subsequent research to optimize MEA fabrication for superior performance.

Chapter 1. Introduction

The Proton Exchange Membrane (PEM) Fuel Cell

The fuel cell is a technology that has survived over 100 years. The Proton Exchange Membrane or PEM Fuel Cell has existed for nearly half of that lifetime. General Electric began developing the PEM Fuel Cell technology in the 1960’s as it had a wide appeal due to its on site power generation which was also portable. The research was novel and new, but had several limitations. A major one being the high cost due to expensive materials. Regardless of this, the research continued and the industry is making strides to produce efficient fuel cells with reasonable costs that are expected to decline further. This is where the industry still lies today.

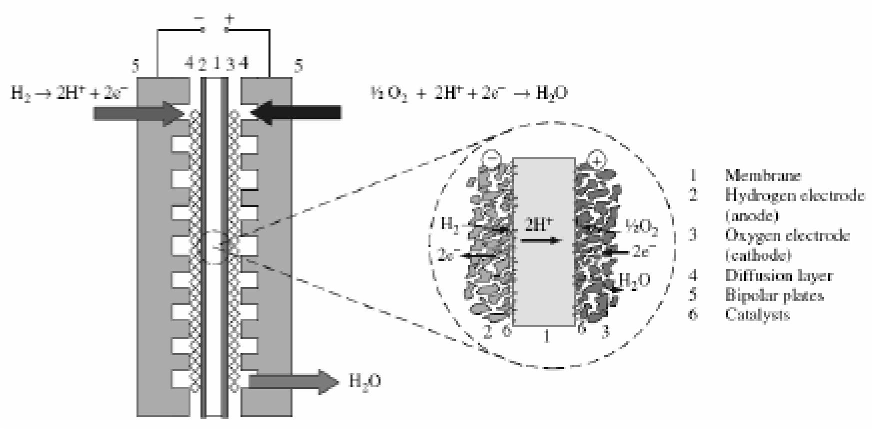

Figure 1.1 PEM Fuel Cell [1]

Figure 1.1 is a PEM Fuel Cell[1] which yields electrical energy from a series of chemical reactions as detailed in the figure. The left side of Figure 1.1 represents the negative side or the anode side of the cell. Hydrogen enters the system here and is spread throughout the catalyst layer. Through anode reactions, the electrons are freed and then conducted through a circuit constructed externally to the system shown. Protons produced at the anode diffuse through the membrane to the cathode layer. The cathode side, which is the right side of Figure 1.1, is the positive side of the fuel cell. This is where the oxygen is introduced and forms water exothermically by meeting with the protons and electrons produced at the anode.

Channels are etched into identical bipolar graphite plates for both the anode and cathode sides. These channels are used to direct the hydrogen across the catalyst layer. The combination of the positive and negative sides working together ultimately produces a DC current, and thus the electrical energy. This process is continuously re-chargeable by the introduction of more fuel, which can be either in a gaseous or liquid form e.g. hydrogen or methanol. Fuels such as methane may be used in higher temperature fuel cells, e.g., solid-oxide fuel cells (SOFC).

As per commercial standards, the PEM Fuel Cell is reasonable for possible power in the transportation industry and has countless applications for military use, small power grids, and household energy supply. It has an efficiency capability of 60% with up to 250kM power generation, while maintaining a reasonably low operating temperature range of 50-100°C.[2] It is small and portable which is what makes it one of the most promising fuel cell types currently being researched.

Proton Exchange Membrane (PEM) Fuel Cell Elements

This electrochemical device is made of several parts that contribute to its unique energy producing capabilities.

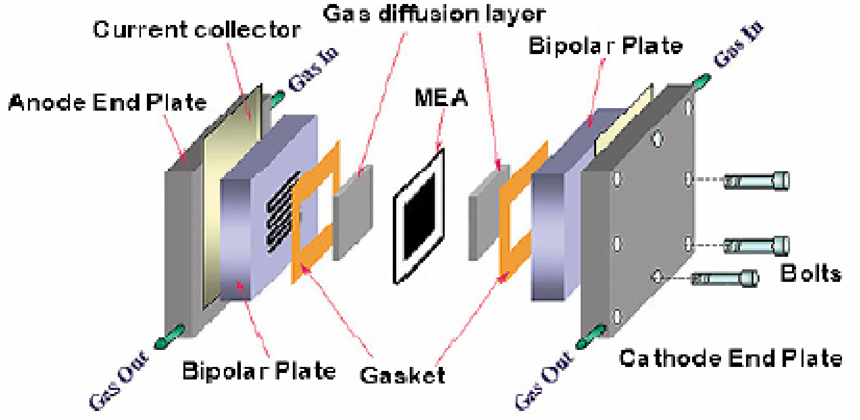

Figure 1.2 PEM Fuel Cell Components [3]

A PEM Fuel Cell is dissected in Figure 1.2 showing all the parts that make up this single cell. The bipolar plates (Figure 1.3), as mentioned previously, have channels etched into them in order to provide a path for the gas to flow over the catalyst layer. These plates which are identical are made of graphite. The purpose of this part is to control the amount of gas that makes its way to the catalyst layer making the plates an integral part in the construction of a cell.

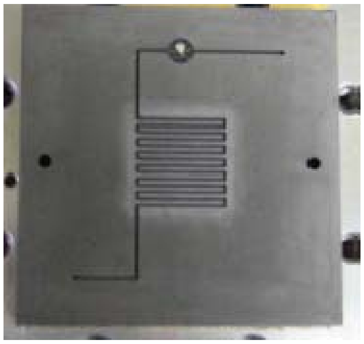

Figure 1.3 Plate Channels

The gasket acts as a sealing layer between the membrane and the plates restricting the flow to the channels and obscuring leaks. Heat resistance is a vital aspect to consider when choosing a material and therefore silicone is used. This material will not withstand the acidity of the reaction so a periodic equipment check and perhaps replacement is needed. The Gas Diffusion Layer, or the GDL, is in direct contact with the membrane layer. It is comprised of a carbon cloth which is put through a treatment process with Polytetrafluoroethylene (PTFE) in order to allow for water vapor to meet with the membrane by maintaining the hydrophobic nature of the cloth. The platinum layer represents the electrode. A slurry is made using the platinum particles and is directly applied to the membrane or the GDL.

The Nafion® layer which is a solid polymer electrolyte made by DuPont allows the conduction of protons from the anode to the cathode. It has a similar backbone structure to the PTFE, which is why it behaves hydrophobically but also is conductive to protons, due to the presence of side chains culminating in sulfonic acid sites.

MEA Fabrication

The performance of an MEA can only be optimized after an understanding of the structure of the MEA is obtained. When categorized, there are seven main elements which contribute to this structure. These are carbon blacks, catalysts, membranes, the gas diffusion layer, the electrode ink formula, the act of hot pressing/assembly, and the porosity and wettability of the electrode. Each of these aspects will be described individually and then their influence on the MEA will be described.

In addition to research done on these key structural elements, a literature review was completed to acquire an understanding of current advancements within the field and their impact on the performance of the MEA. Changes to the methodology of the fabrication of the MEA were the focus of the literature review as to determine the components that would lead to an equal if not higher performance compared to the commercially available MEA. With a good understanding of fabrication, key elements, and possible areas for further investigation, an experimental plan can be developed.

Carbon Blacks

Carbon blacks are utilized to provide a support for the platinum nano particles. They provide thermal conductivity and a surface medium for the passing of gases such as O_2, and H_2, air, and water. It also provides electrical conductivity for the electrons.

The aspects of carbon blacks that are looked at in order to find optimal carbon support are those of the chemical, electrochemical, and physical. Carbon is susceptible to oxidation at operating voltages of 0.4V (kinetics are slow at moderate voltages). [4] Electrochemical oxidation of carbon involves a mechanism that requires hydrolysis of the oxide and a reaction that yields CO_2 and carbon surface oxides. [4] The determining factors in deciding on a carbon black for MEA assembly are the operating conditions of the cell and desired stability.

Catalysts

The most common choice of cathode catalyst is carbon supported platinum. Several ways of catalyst preparation are utilized within industry such as impregnation and colloidal adsorption. A Pt/C with weight percent greater than 50% and a 2.5-4 nm particle size has been developed. Platinum with 50 wt % has made it possible fabricate electrodes that are very thin and therefore provide high power densities with low mass transfer resistance.[4] Research has also concluded that rather than solely using Pt, a Pt/Ru alloy has been proven more of a carbon monoxide tolerant catalyst in anodes.

The ultimate result of the choice of Pt wt % and carbon support is the cell performance as well as the cell decay rate and electrode layer thickness.

Membrane

The commercially available membranes that seem to perform the best are currently Nafion® 112, Nafion® 115, and Nafion® 117. Often, these membranes have an H^+ form. They are pre or post treated in 0.5M hydrogen peroxide, then boiled in deionized water, 0.5M sulfuric acid and the boiled again in deionized water, before use.

Nafion membranes determine such factors as tensile strength, operating temperature, water uptake, and water permeability among others. It also has several characteristics such as density and conductivity which allow structural calculations to be made. [4]

The conductivity depends on the equivalent weight, the pre treatment, and the casting method while being a function of relative humidity. As the temperature of the heat treatment increases the conductivity decreases because the water uptake of membrane is lowered. A temperature range from 45-80°C shows an increase in conductivity because a sustainable humidification is observed more at these temperatures than at higher ones, although, the fabrication of an MEA utilizes a hot-pressing procedure at temperatures above 100°C. The permeability of oxygen and hydrogen in the membrane also depends on temperature, humidity, and partial pressure. It was found to decrease within the cation structure of the membrane [4].

Gas Diffusion Layer

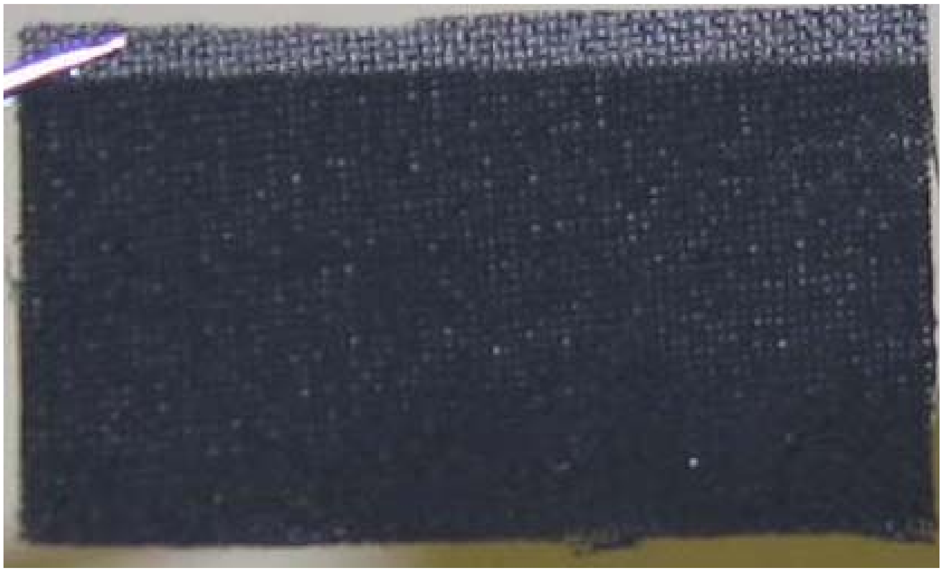

Figure 1.4 Catalyzed Gas Diffusion Layer

The gas diffusion layer or GDL (Figure 1.4) is used to as an energy conductor, to carry and deliver gases, and to manage water. It is made of a woven carbon fiber. This woven cloth is then given hydrophobic and hydrophilic characteristics which determine its role in water management.

Electrode Ink Formulation

At first, PEMFC electrodes were made from PTFE bonded electrodes. [4] Because of high temperature and pressure, a high Pt loading was needed. When solubilized membranes were made, electrodes were able to be painted with the ionomer that lowered the Pt loading [4] by providing ease of transport of protons. The PTFE in the structure leads to the prevention of flooding in the pores and allows for better hydrophobicity, or the gas phase diffusion of the reactants. [4]

Catalyst ink containing Pt/C, glycol, and ionomer while using the decal method lend to high performance in the MEA as proven by Wilson et al. [5] The MEA's utilizing this ink also showed low mass transfer and low catalyst loading. Wilson's method was improved by giving the catalyst layer a heat treatment by using a Na^+ form of the membrane after an increased temperature casting process and also a melt-processable solubilized ionomer in the TBA^+ form which allows for a strong electrode structure. [5]

Uchida et al [6] researched solvent choices in the catalyst slurry fabrication. The investigation focused on solvents with different dielectric constants. A colloid was developed after the addition of a PFSI solution with a dielectric constant within the range of 3-10. Pt was added and a clear supernatant resulted from the PFSI dispersing and being absorbed upon the surface. "Cross-linkages" between the PFSI's were formed through sonication. A paste which could be applied directly onto the gas diffusion layer was the result. [6]

Hot Pressing and MEA assembly

Figure 1.5 Hot Press

Hot pressing (Figure 1.5) allows for better adhesion and implants a portion of the electrode into the membrane. It is used in all methods of MEA fabrication. Nafion® has a glass transition temperature of approximately 100-150°C, which governs the temperature used for the hot press and assembly. If a higher temperature is used, it increases the strength and reduces the solubility of the ionomer. Where as lower temperatures cause a lack of pliability of the Nafion thus not forming a good contact between the ionomer and the catalyst resulting in poor utilization. [4] Because of these limitations, the step of hot pressing involves about 1-5 minutes at a temperature of 120-160°C and a pressure of 5000-15000 kPa.

If peeling or cracking occurs after hot pressing as a result of swelling in the H^+ form of the membrane, another technique is utilized. This method entails the surface of the membrane be hydrolyzed to the ionic form. Then the catalyst slurry is applied onto the membrane. This expands the membrane to improve electric contact with the cell. [4]

Porosity and Wettability of the Electrode

High porosity of GDL decreases gas diffusion losses. A conventional range is about 30-60%. [4] Porosity, with wettability factors of hydrophylicity and hydrophobicity can be controlled through the ionomer and carbon ratio as well as through the carbon selection and method used to fabricate the MEA. [4]

Zawodzinski et al [4] determined that the ionomer surface shows a large range of contact values with water. The angle of contact “relaxes slowly from one value to the other over tens of minutes as the ionic groups reorient to the changing environment and has implications for cell performance with time.” [4] Pore wettability relates to high activity through ionomer contact. The relationship helps to optimize the electrode and the gas diffusion layer of a cell. [4]

Literature Review

In research done by Jalani et al, [10] several properties of Nafion® were explained and examined. The protonic form is most commonly used in PEM fuel cells. This membrane is vital to the performance of the fuel cell because of the intricate balance it has reached with a combination of good water uptake, ion exchange capacity, proton conductivity, low gas permeability, and great electrochemical stability. Proton conductivity directly relates to the water content of the membrane. The water content is determined by the water sorbed in the Nafion as a function of the relative humidity. It is this property that gives good performance of the fuel cell. In terms of structure, Nafion consists of PTFE which makes it hydrophobic with side chains with sulfonic acid groups building off of that base. It is this structural makeup which enhances the conductivity through bulk diffusion by pushing the water away from the PTFE base.

Solvent uptake in Nafion is affected by temperature, ion-exchange capacity, pretreatment of the membrane, cationic forms of the membrane, and the physical state of absorbing water. Hydration, swelling, and drying of the membrane have been studied often and it has been found that the adsorption from the liquid phase is quicker and more extensive than that of the vapor phase. It has also been discovered that pretreatments which are done concurrently with the membrane synthesis and purifications cause micro structural changes leading to another affect on the membrane behavior during solvent sorption. In this paper, swelling was highlighted as being effected by equivalent weight, temperature, and the cationic forms of H^+, Li^+, Na^+, K^+, and Cs^+ on several sorbates.

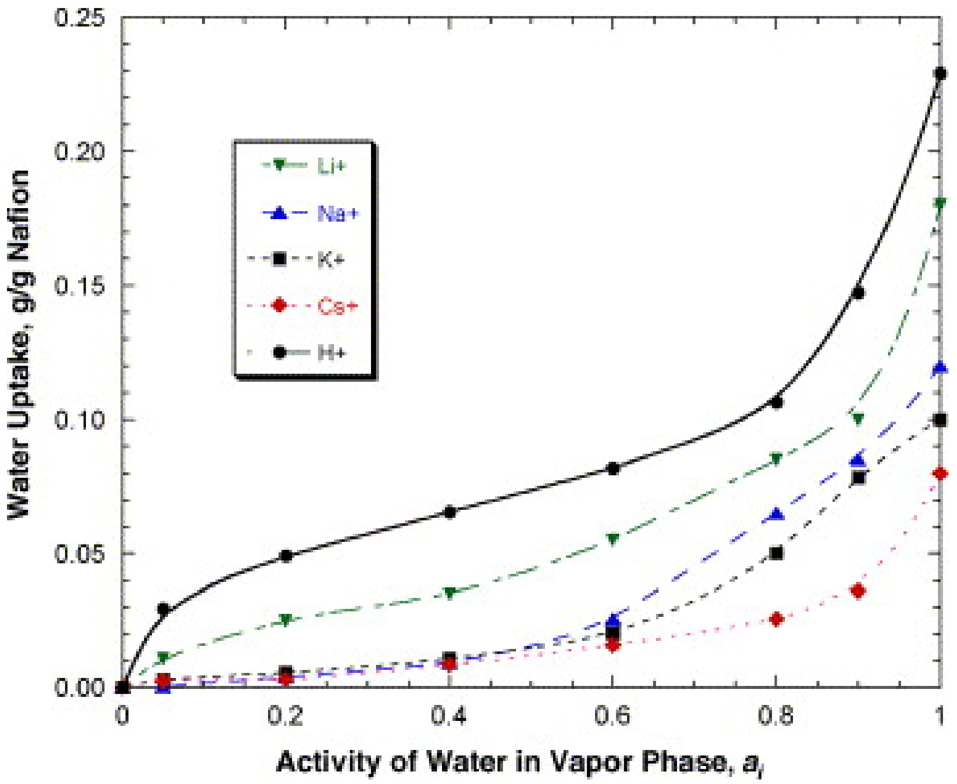

Figure 1.6 Effect of various cationic forms on water uptake vs. activity of water vapor for Nafion membrane at 30˚ C

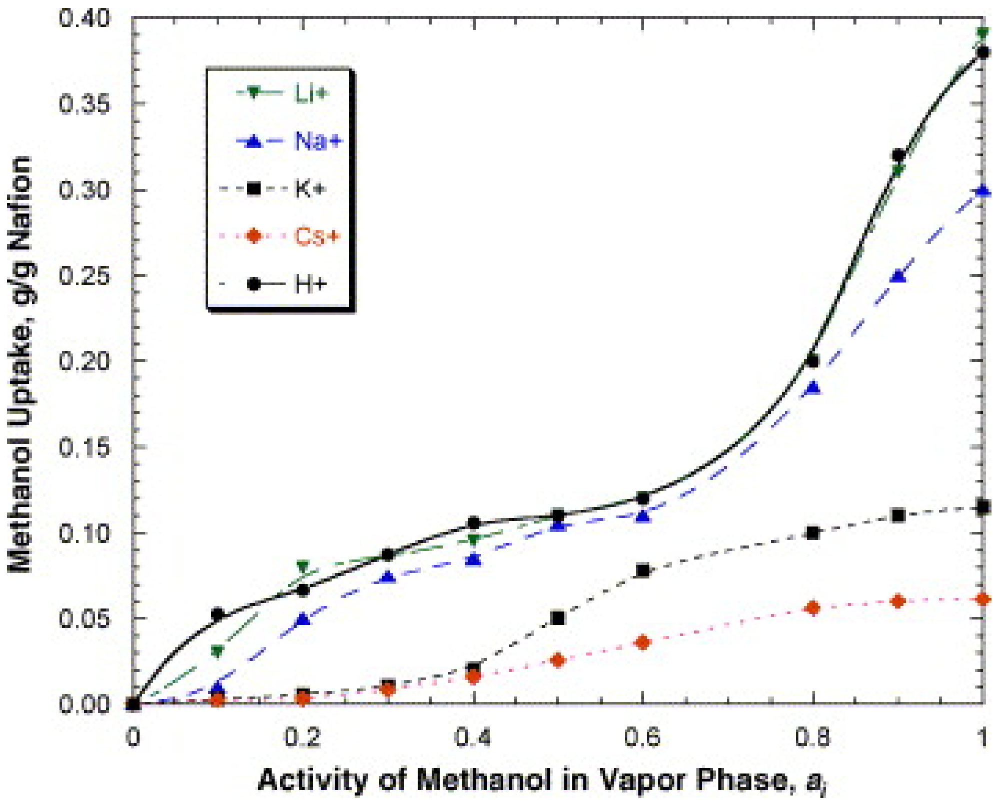

Figure 1.7 Effect of various cationic forms on methanol uptake vs. activity of methanol vapor for Nafion membrane at 30˚ C

The results of the research showed in figures 1.6 and 1.7 that for water sorption, H^+>Li^+>Na^+>K^+ >Cs^+ in order of decreasing water sorption isotherm. The trend is mimicked to a degree in methanol with the only variance being that both H^+ and Li^+ show comparable sorption. Based on these trends it can be concluded that the sorbed amount of water decreases due to the reduction of ionic hydration capacity from H^+ to Cs^+, decrease in the charge density, and decrease in swelling from H^+ to Cs^+ stemming from an increase in Young's modulus. This causes a close to equal number of solvent molecules to reach equilibrium at higher solvent activities. [10]

Jalani et al [12] also investigated the adsorption from liquid phase versus the vapor phase is shown. It was found that Nafion adsorbs 22 water molecules per acid site from liquid water but only 14 from saturated vapor. As the authors of this paper explain, this is known as Schroeder's Paradox. There is a significant research activity to investigate water/methanol and other solvent sorption isotherms for Nafion and other membranes alike. The conventional way of performing these experiments has proven to be slow while providing data with low accuracy. With these techniques the data is influenced by flow patterns, bypassing, and incomplete contact of the gas and sample. This paper[12] highlights a new technique known as the tapered element oscillating microbalance (TEOM) as seen in figure 1.8 accurately measures water/methanol sorption isotherms in relatively little time.

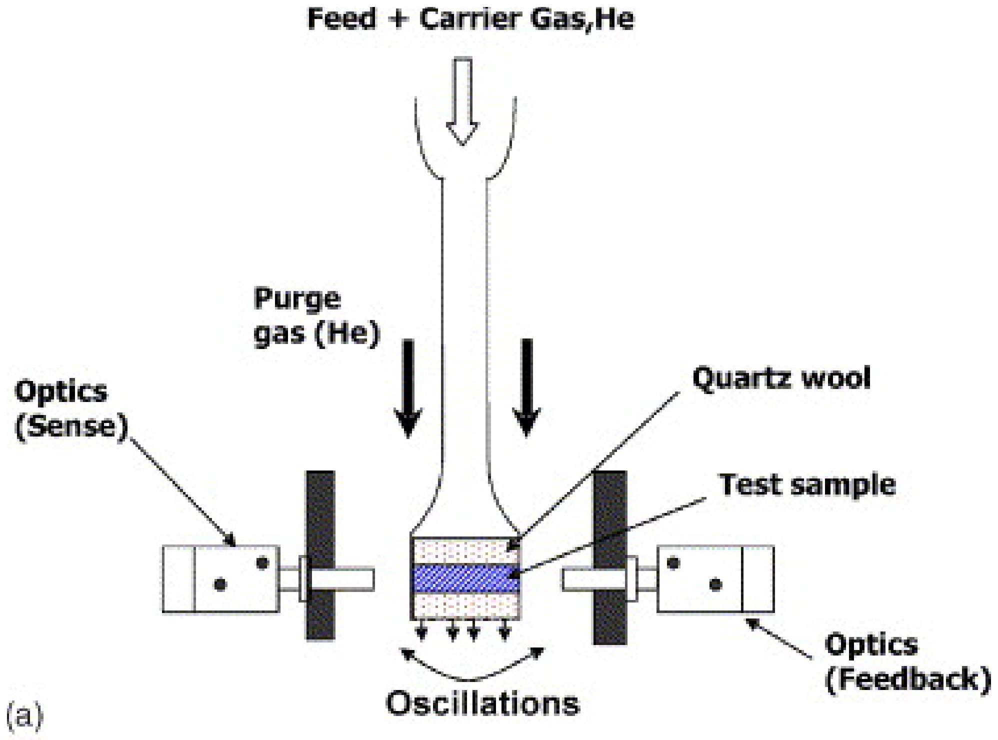

Figure 2.8 Simplified flow diagram of the TEOM test bed and optics. The flow of inlet gas is shown by large arrows.

In figure 1.9, the sorption curve is provided as measured with TEOM. This data is in agreement with published data from other experiments showing the validity and accuracy of the TEOM testing technique.

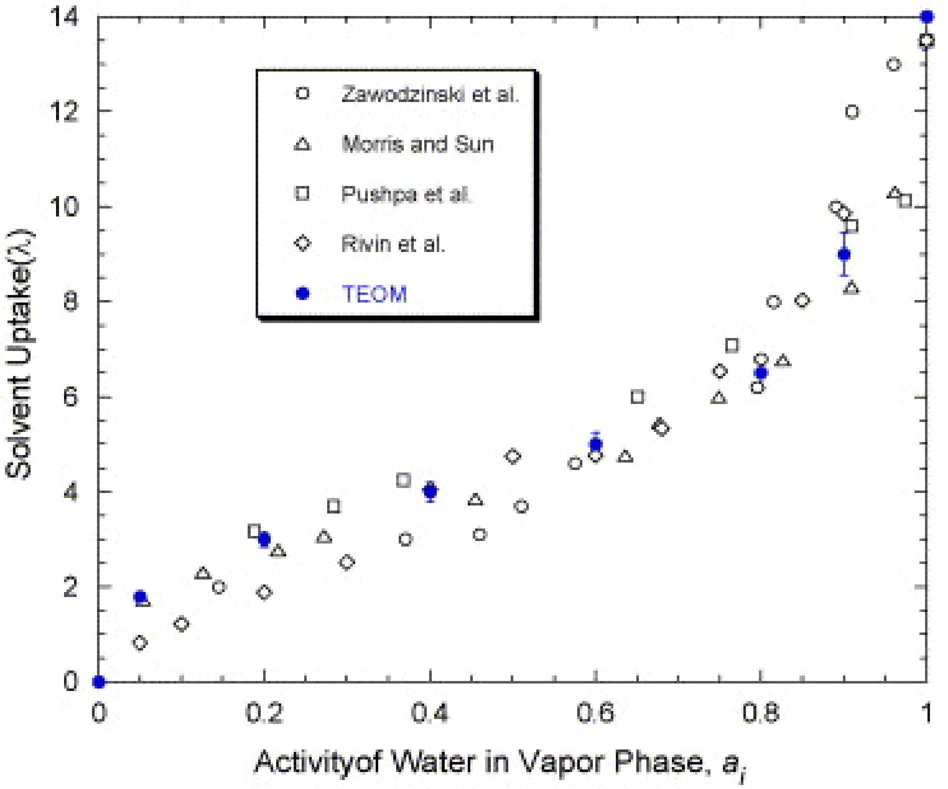

Figure 1.9 Water uptake vs. activity of water vapor for 1100 EW Nafion membrane at 30˚ C

The isotherm of the methanol follows the same trend as that of the water. From the results, a mass uptake of 0.106g for methanol at 0.4 activity is about the same as three methanol molecules per acid site compared to five molecules for water sorption.

Pretreatment of the membrane also affects water sorption. The hot pressing pretreatment is an important step during MEA preparation. However, this pretreatment method actually exhibited the lowest sorption which would result in lower performance. The highest sorption was seen in the membrane being heated at 110°C. [12]

In research performed by Choi et al, [13] it was highlighted again that the proton exchange membrane is central for proton conduction in PEM fuel cells. Studies were performed in order to understand that mechanism itself as well as to aid in further design applications. As seen in other research, Nafion is the favored membrane as it has excellent proton conductivity when soaked in water. Proton transport depends on the structure and physiochemical nature of the polymer in relation to its saturated state. This paper discussed a conductivity model that gives a detailed picture of proton transfer within the Nafion membrane.

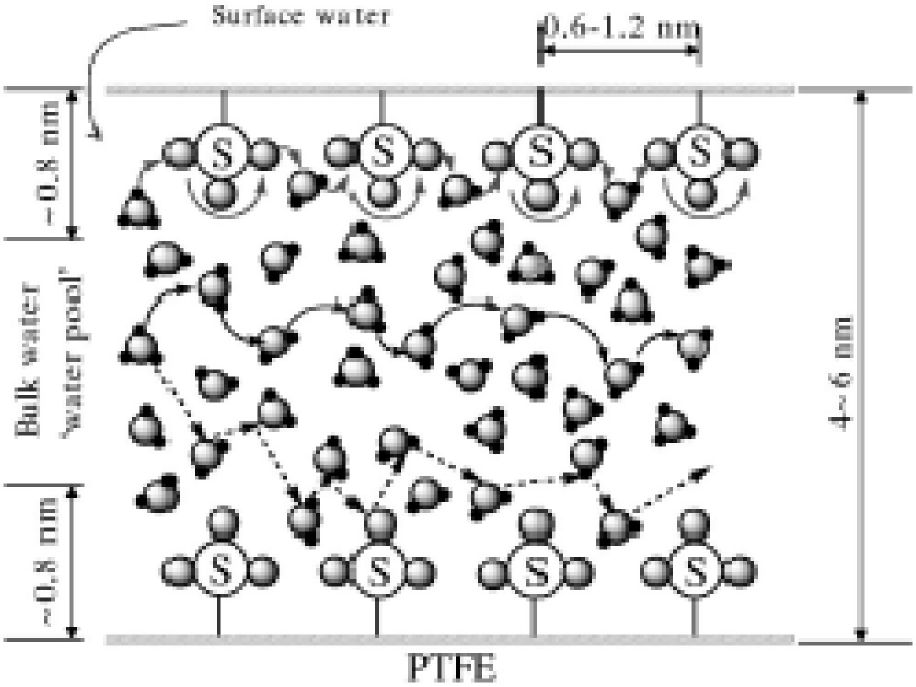

Figure 1.10 Simplified picture of structure and proton transfer in Nafion in hydrates state

Proton conductivity results from the nanostructure and water content of the Nafion membrane (Figure 1.10). If at low water contents, acid sites are not completely dissociated leading to low bonding odds of hydrogen is low which limits the water molecule interaction. Though at higher water contents, water in Nafion behaves like bulk water showing two separate water environments within the membrane. Seen in the research of this paper, it was determined that the transport of protons in Nafion was carried out through a surface diffusion mechanism under low water activity and bulk diffusion under high water activity conditions [13].

Project Goals

The goal of this project is to investigate several factors in MEA fabrictaion that influence MEA performance. With this, changes to the existing procedure could potentially be made to raise the efficiency of the MEA. The factors that were investigated in this project are as follows:

- Eliminating PTFE on the anode side of the cell.
- Investigating changes to the Nafion structure and catalyst loading.
- Investigating the effects of a new GDL

Chapter II. Methodology

Factors affecting MEA performance

In order to fully investigate the effect of each changing parameter, only one was varied per experiment. The catalyst layer plays an extremely important role in the performance of the MEA. The catalyst mixture or ink can be applied to the gas diffusion layer (GDL), to the membrane itself, or to Teflon blanks. The catalyst layer must be uniform and even in order to perform at its optimal potential. The GDL application, may not be even if the carbon cloth is used without first baking it. The roughness factor of the MEA is increased when the catalyst layer is applied to a rough surface as opposed to a smooth surface, and by increasing this factor the overall performance will be better. The direct spray method of applying the catalyst ink to the MEA was used in all experiments in this study. It provides an even distribution for the catalyst loading, but could result in a poor catalyst layer if the membrane absorbs the solvent excessively. This happens because the membrane swells as the solvent in the catalyst ink is absorbed and as the solvent evaporates the membrane shrinks resulting in an uneven catalyst layer.

The solvent affects application of the catalyst layer. It is in fact, the deciding factor as to how well the catalyst ink adheres to the membrane and the even application of the catalyst layer. The solvent and membrane must be balanced so that it does not interact excessively with the membrane as it is serving mainly as the vechile to apply the catalyst. An important property of the solvent is the boiling point. The higher it is, the longer the solvent will need to vaporize and there will be more of an opportunity for a negative interaction between the solvent and membrane. The lower the boiling point is, the more rapidly it will evaporate upon spraying. It is too quick, catalyst will not adhere will to the membrane.

Another factor which affects the MEA is the membrane itself. The membrane treatments which take place in at a low temprature allow the membrane to expand. The form of the membrane is central as well. Boiling it in 0.5M sulfuric acid converts the membrane into a protonated form and ensures that the catalyst layer is also in the protonated form. Other forms can be created by boiling in other solutions. For instance, converting to a sodium form is done by boiling the membrane in NaOH. This limits the absorption of the solvent into the membrane.

Experimenting with different ratios of components within the catalyst ink will also affect the performance of an MEA. Changing the amount of PTFE added to both sides, varying the amounts between the two sides, or not adding it to one side completely will perhaps yield better results. Removal of water is more crucial at the cathode than at the anode so a lower amount or no PTFE at anode may produce similar results. Varying other components of the ink would also potentially affect the performance of an MEA as well.

Procedure

The procedure for fabricating the membrane electrode assembly (MEA) can be broken down into three main sub-divisions. First, the membrane undergoes a *pre-treatment*. During this first step, the catalyst ink is prepared in anticipation for the second step, which is the *application of the catalyst ink*. Finally, after the ink is dried, the membrane is put through a *post-treatment* before MEA can be tested in a fuel cell test stand.

Membrane Pre-treatment

The first step in membrane preparation is to cut a piece of the Nafion® 115 sheet with an area of approximately 20 cm^2. This allows for enough space on the membrane to apply the catalyst ink and the gas diffusion layer (GDL) and still be able to handle the MEA.

Once the Nafion® is cut out, it is boiled in deionized water (250-350 ml) for one hour. After the DI water, the membrane is boiled in a 3% hydrogen peroxide aqueous solution (250 ml) for one hour to remove any metallic or organic impurities. Following the H_2O_2 treatment, the Nafion® is again boiled in DI water for another hour.

During the original procedure, after the membrane is boiled for the second time in DI water, it is placed between Teflon® sheets and Kim® Wipes, then two metallic plates and in the hot press with 0.2 metric tons of pressure at room temperature for about 10 minutes. This is to ensure that the membrane is flat.

However, when the ionic form of Nafion® is altered, an additional two steps are added between the second DI water boil and the hot press. The first step is to boil the membrane in a 1 M aqueous solution of the desired form at low tempratire for 12 hours. Boiling the membrane in DI water a third time follows this extra step.

After the membrane is pressed, it is ready for the application of the Catalyst Ink, which would have been prepared in parallel during the membrane pre-treatment.

Catalyst Ink Preparation & Application

Figure 2.1 Sonication Bath

Two batches of ink are required, one for each side of the membrane. Each batch is made to cover 5 cm^2, with the desired catalyst loading of 0.4 mg/cm^2. Expecting slight losses of catalyst in the preparation and application of the ink, enough ink is actually made for a loading of 0.7 mg/cm^2.

The ingredients used in each batch consist of: Nafion®, 10% (0.7 mg/cm^2), PTFE, 10% (3:7 ratio with the catalyst powder), catalyst powder, 20% (Pt/C), and organic solvent (i.e. methanol, ethanol). In a clean beaker, zeroed on a scale, 15 mg of 20% Pt/C, 35 mg of 10% Nafion®, 64.3 mg of 10% PTFE, and 5.5 ml of Methanol are added together. The mixture is stirred manually until all of the catalyst powder is visibly mixed into the solution.

Stirring the mixture manually is not enough though, and the catalyst powder requires further mixing. At this point, the beaker is covered with Parafilm® and placed in an ultrasonic bath (Figure 2.1). The solution sonicates for 3 hours, and is added to the air gun for the application (Figure 2.2).

Figure 2.2 Application of the Catalyst Ink

After the membrane is pressed for 10 minutes, it is placed between two stainless steel stencils with 5-cm^2 squares cut out in the middle. The stencils are held in place on a clipboard. The ink, being loaded onto the air gun, is sprayed as evenly as possible across each face of the membrane (one batch of ink for each side). To minimize swelling of the membrane, a hair dryer is used to dry remaining solvent from the membrane in between sprays, leaving only the catalyst and PTFE adhering to the membrane.

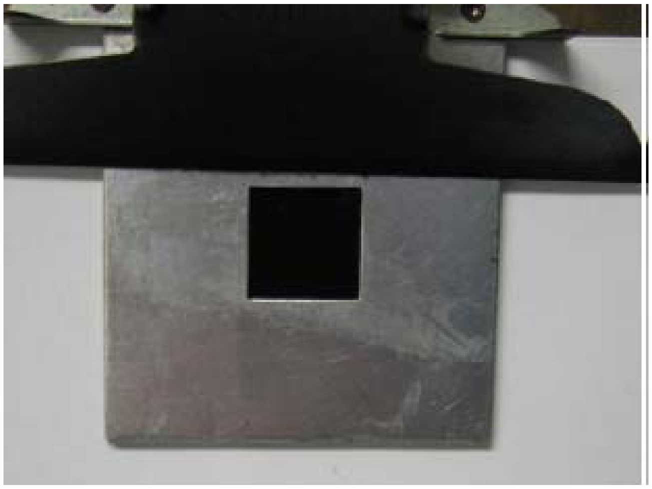

Figure 2.3 Application of the Ink is ready to begin on the second side of the membrane

Once the catalyst ink has been applied to both sides of the membrane (Figure 2.3), it is dried in an oven at 70˚ C for 1.5 hours.

Post-treatment

The post-treatment is very important to the quality and function of the MEA in the fuel cell. Out of the oven, the catalyzed membrane is boiled in 200-250 ml of 0.5 M sulfuric acid for 1.5 hours to convert the membrane into proton form. The membrane is then boiled with deionized water for an hour to remove excess sulfuric acid.

Figure 2.4 GDL is applied to the membrane in the hot press

Again, the membrane is pressed for 10 minutes at room temperature with negligible pressure.

Once the catalyzed membrane has cooled off from the DI water boil, the GDL is placed on each side, lined up with the catalyzed portion, and hot pressed between two Teflon® sheets and metallic plates with a pressure of 2 metric tons (figure 2.4). The hot press heats to a temperature of 275° Fahrenheit, and after this point, the membrane is left in the press for an additional 2 minutes before removal.

After the MEA cools, it can be placed into the fuel cell assembly between the graphite plates, and then the cell is wired into the test station, and the break-in can begin (Figure 2.5).

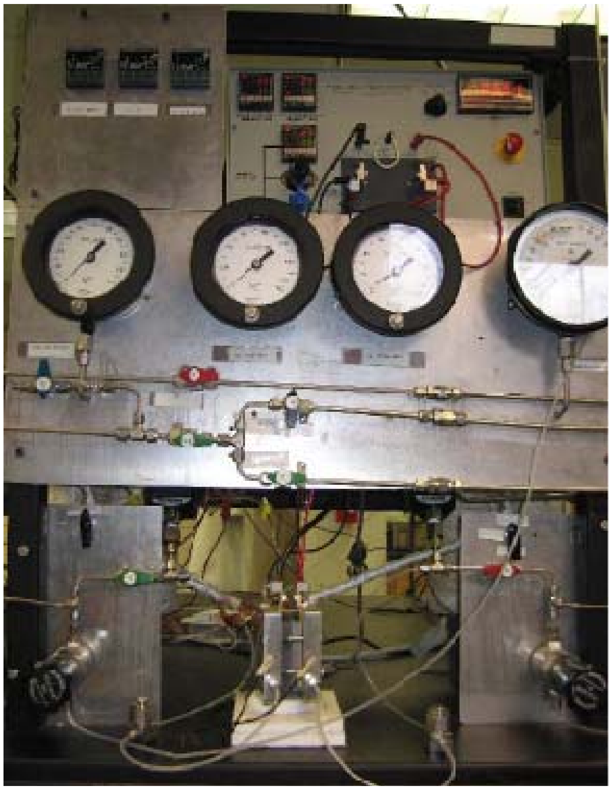

Figure 2.5 Fuel Cell Test Station

In the station, the humidifier and thermostat are turned on, and once the heating line reaches 100˚ C and the thermostat and fuel cell reach 30˚ C, the load box is turned on. The computer program begins and the gas added to the fuel cell. After performance levels off at 30˚ C, the station is set to 70˚ C. The MEA is conditioned at this temperature for 16-20 hours, and then it can be tested for performance.

Chapter III. Results

All experiments had the same goal, which was to improve the quality of the fuel cell by improving the basic MEA fabrication procedure and more importantly fabricating a MEA that would perform better than the MEAs that are already commercially available. Before the hypotheses could be tested and proven, a benchmark needed to be established in order to have a baseline to compare future experiments. The months of practicing the basic procedure ensured both competence and consistency in the basic and altered procedures. The basic procedure was completed until a set of results were found to be reproducible consistently as seen in Figure 3.1. There is assumed to be some degree of human and mechanical error throughout all of these results.

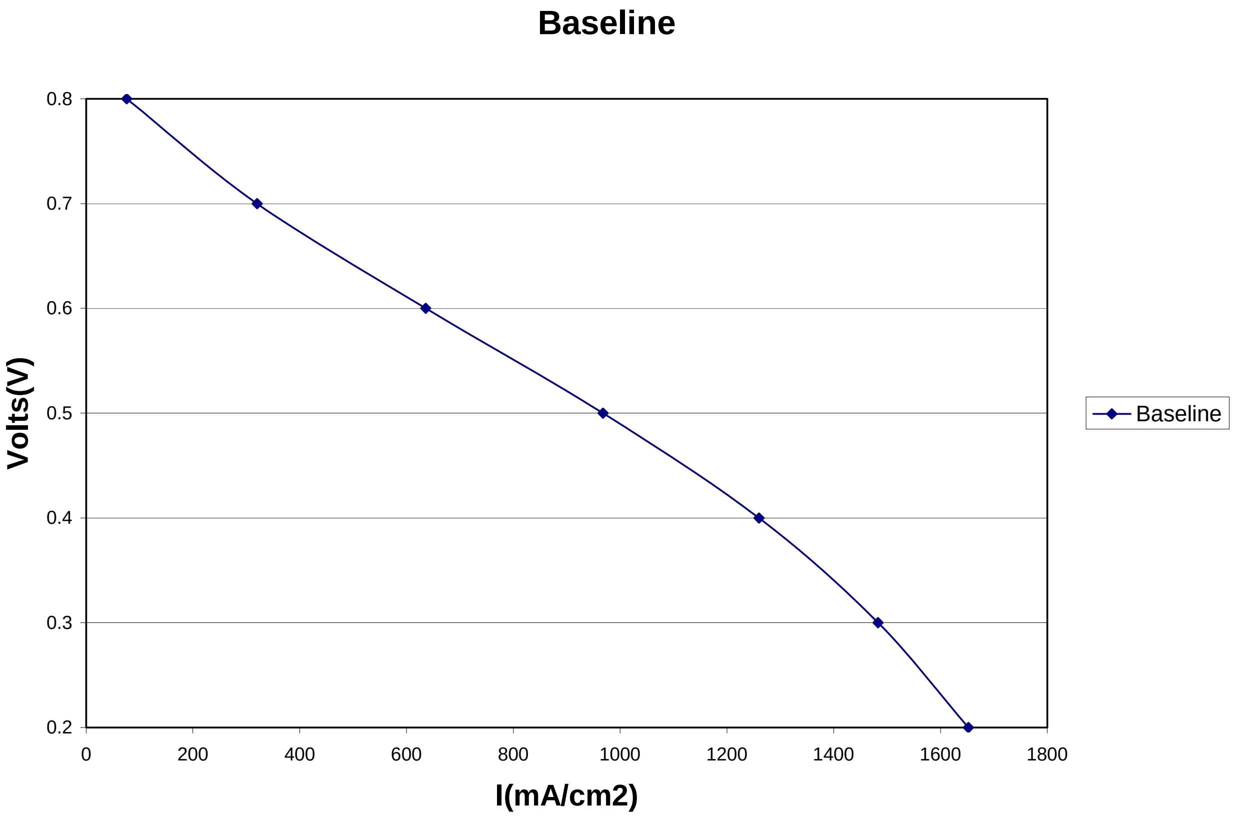

Figure 3.1 Performance of the benchmark MEA at 70°C and 1atm

Changing the Form of Nafion®

Based on the Jalani et al. paper[10] different forms of Nafion® were tested to determine the effects on performance. Thus, potassium, cesium, lithium, and sodium forms were used for MEA fabrictaion in addition to the preexisting proton form of Nafion and were also compared to the commercially available MEA. The cesium and potassium forms were expected to yield the best results based on the best swelling (Figures 1.6 and 1.7).

Altering the form of Nafion requires a small variance of the basic procedure. In reference to the procedure in chapter 2, at the end of the membrane pre-treatment, two additional steps are added: the Nafion is boiled in a 1 M aqueous solution of the desired form at low heat for 12 hours and then the membrane is boiled in deionized water for an hour before being pressed. Thereupon, the catalyst ink was sprayed on and MEA was fabricated as described in chapter 2.

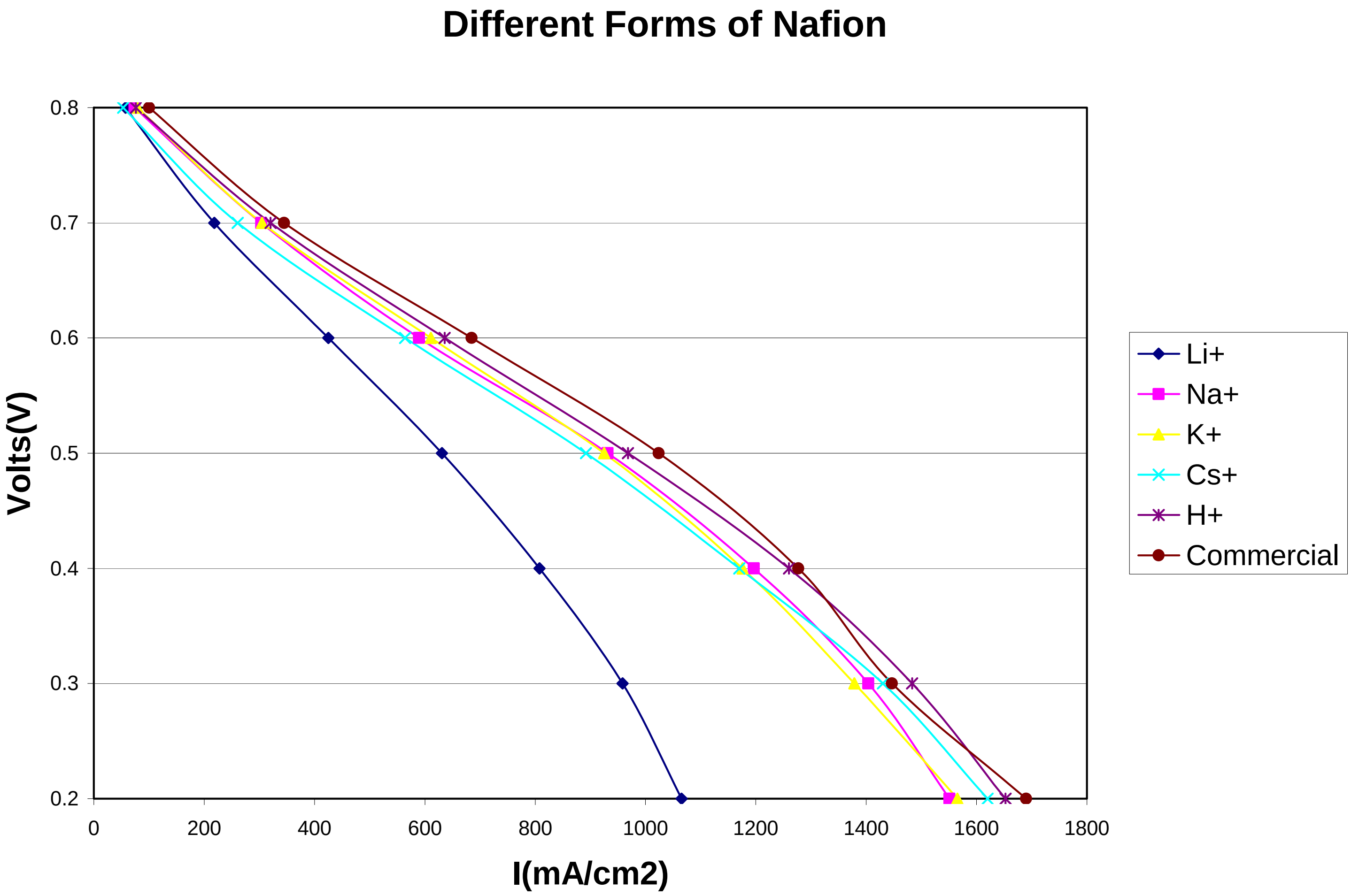

Figure 3.2 Results of MEAs with altered forms of Nafion® compared with the commercial MEA at 70°C and 1atm

As shown in Figure 3.2, potassium and cesium based MEAs gave the highest performance per surface area. The Sodium and Lithium forms gave similar results to the proton form. When the form is changed, the membranes appeared to get stiffer. Also, after the ink is applied and placed in the oven, the applied area expands during the soaking of the post treatment as the membrane is converted into proton form. None of these results exceeded the performance of the commercially available MEA. The inferiority of these results to the commercial standard is most likely because of well-developed fabrications procedures by the supplier, and beacsue of expansion of the MEA area beyone the 5cm^2 active area.

Application of Polytetrafluoroethylene (PTFE)

PTFE is added to the catalyst ink to keep water from building up around the membrane. Most of the water is formed on the cathode side of the MEA, therefore the need for PTFE on both the anode and cathode sides was questioned. The idea is that because little to no water is formed on the anode side of the membrane, PTFE does not need to be applied. In order to investigate this, the basic procedure was edited to not include PTFE in the preparation of the anode catalyst ink.

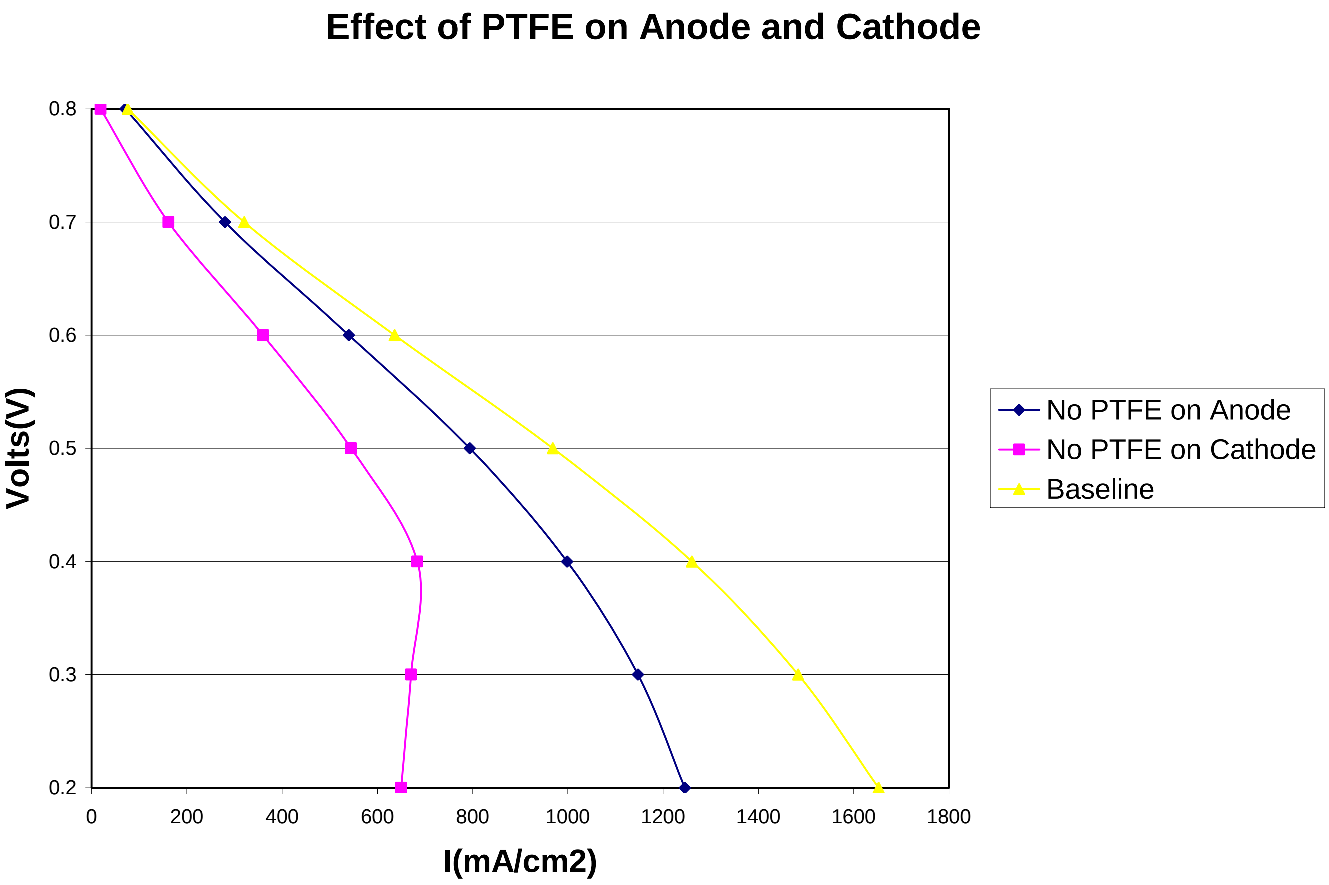

Figure 3.3 Results of the effect of PTFE on the Anode and Cathode sides of the MEA

When the PTFE was omitted from the anode side, the results were similar to those MEA's where PTFE was included. However, flooding occurred more frequently than had prior to the PTFE being removed from the ink. The membranes with no PTFE on the cathode side achieved poor results, as can be seen in Figure 3.3.

Using a New GDL

A new carbon gas diffusion layer was investigated in the hopes of further improving the performance of the MEA. The new GDL is from the E-TEK Division of PEMEAS Fuel Cell Technologies. It is their low temperature ELAT GDL microporous layer on a woven web product that was investigated for performance enhancement versus the previously used GDL, ECC-CC1-060T from the Columbian Chemical Company. The E-TEK GDL was expected to improve the membrane performance, mimicking the same performance trends seen in the previous experiments of different Nafion® forms. With this in mind, cesium and potassium were again expected to give the highest performance while remaining under the performance curve of the commercially available MEA. The same procedure was used, with the only difference being the new E-TEK GDL instead of the Columbian Chemical Company's GDL. Further, since swelling was a concern, a new template with a smaller window was constructed in anticipation of the area of the membrane that would swell upon post treatment (Figure 3.4).

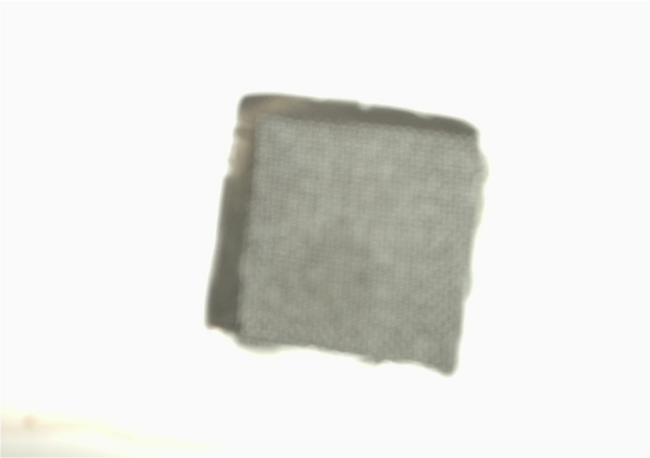

Figure 3.4 Swelling of catalyzed membrane

The new template window was approximately 1mm smaller on all sides, which took into account the amount of swelling normally seen. As the initial area sprayed onto the membrane was smaller, the desired area of 5 cm^2 area was achieved during post treatment (Figure 3.5).

Figure 3.5 Swelling of catalyzed membrane with new template, a perfect fit

The results were somewhat surprising, but very promising.

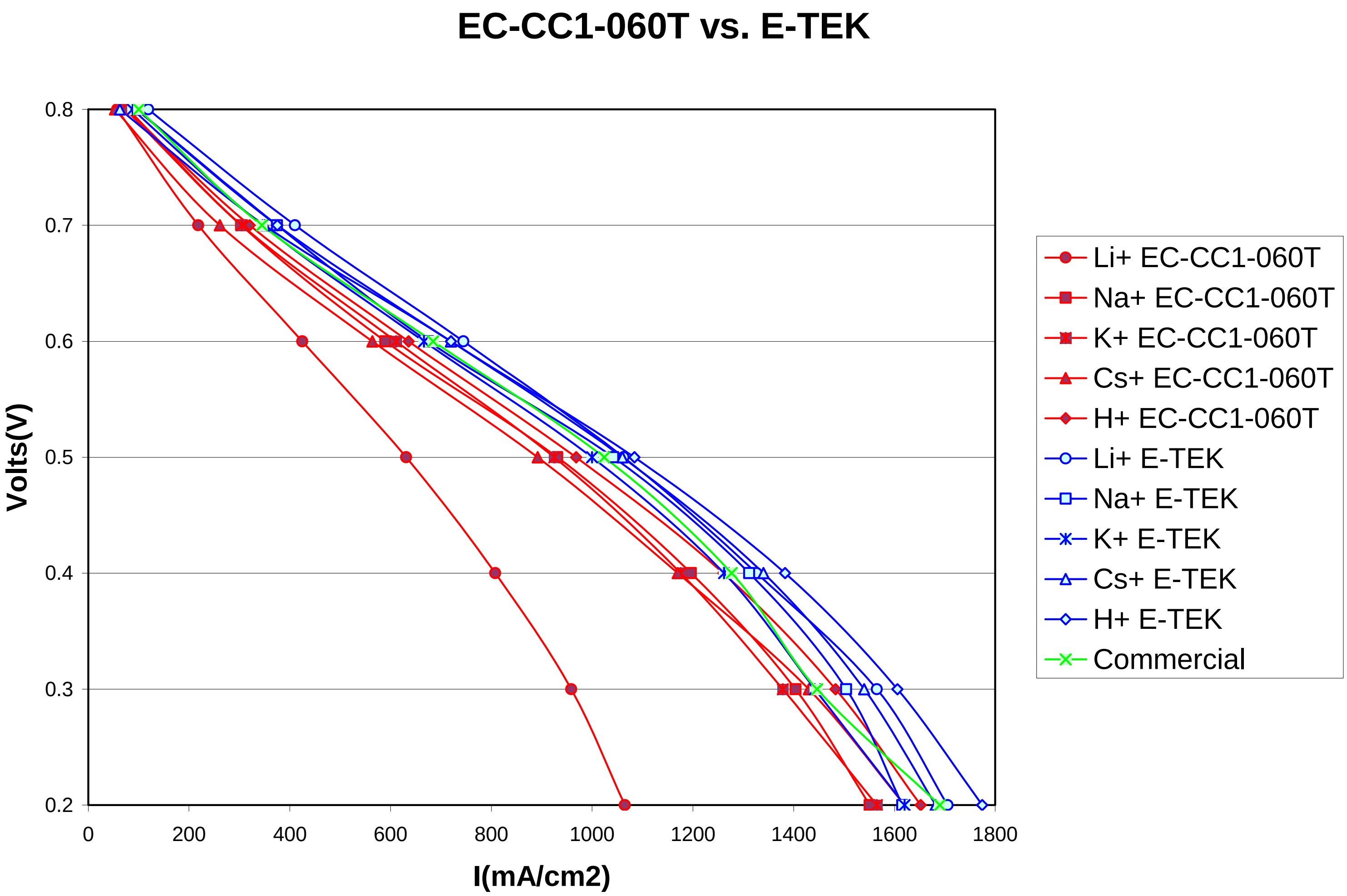

Figure 3.6 Comparison of different forms of Nafion® with both old and new GDLs

The E-TEK GDL affected all forms by yielding a higher performance (Figure 3.6) than what was seen with the EC-CC1-060T GDL from Columbian Chemical Company. The expected result of cesium and potassium performing highest was not seen, however.

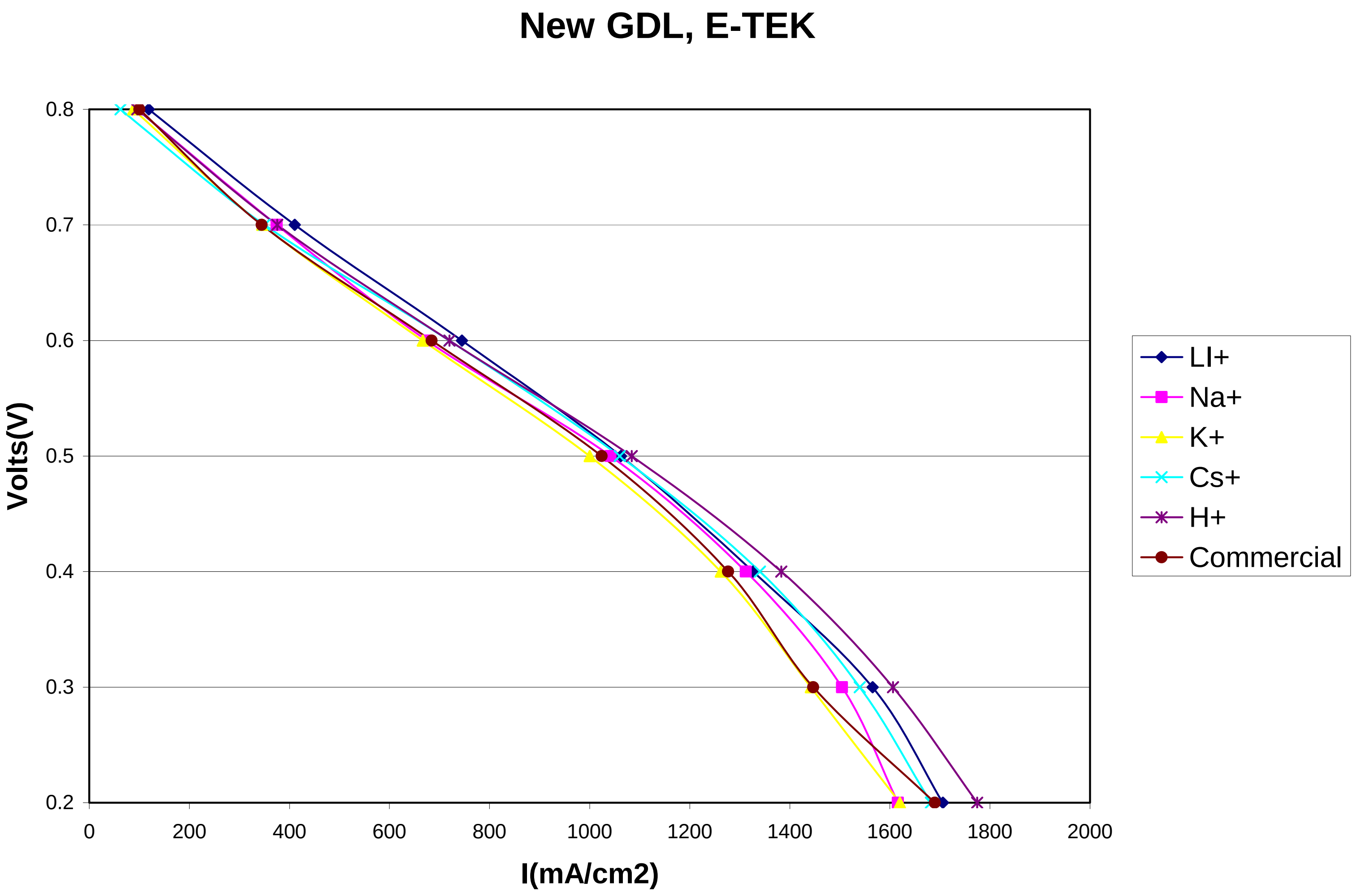

Figure 3.7 Results of the varying forms of Nafion with E-TEK

The hydrogen form with the E-TEK GDL not only performed the highest of the examined Nafion® forms, it also performed higher that the commercially available MEA (Figures 3.7 and 3.8).

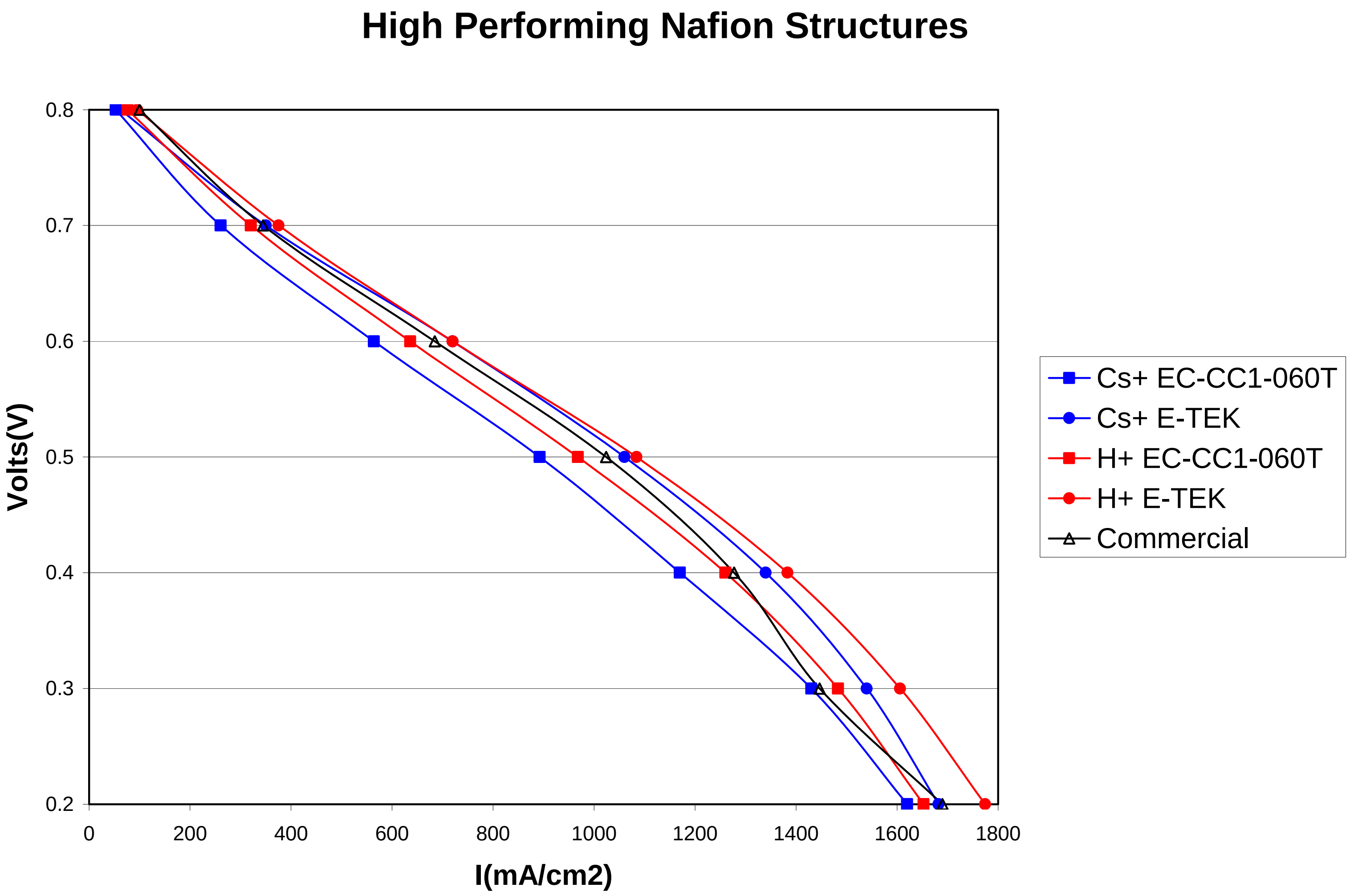

Figure 3.8 Comparison of high performances in EC-CC1-060T vs. E-TEK vs. commercial MEA

The Figure 3.8 compares performance of MEAs providing the best performances. It is clear that by following alternate fabrictaion procedures, higher performance can be attained as compared to the commercial MEA.

Chapter IV. Conclusions & Recommendations

This section is to serve as a summary of our results and the conclusions that were made based on our experiments. Recommendations for future work will follow in each section.

Different Forms of Nafion

According to research done by Jalani et al, cesium and potassium forms of Nafion were expected to provide the better performance because of overswelling during ink application. This conclusion was largely supported by the results of the experiments performed. With the Columbian Company GDL, cesium was most definitely the highest performer, but still fell short when compared to the commercially available MEA. The inability to exceed the commercial MEA performance is most likely because of the human error that is inherent within the procedure and potential problems or inaccuracies from trial to trial in the fuel cell test station. The commercial MEA is also made using a combination of several optimized parameters whereas the experiments performed throughout this project investigated only one parameter at a time.

Based on these tests, the cesium and potassium forms performed the best so if further work to improve the performance is undertaken they should potentially use these forms.

However, when the E-TEK GDL was used, the results were different. The proton form of Nafion proved not only to be the highest performer of all the forms, it also exceeded the performance of the commercially available MEA. The E-TEK GDL also led to higher performances in the other forms, so it is recommended that this GDL should be adopted as the norm for the GDL in MEA fabrication. With that in mind, cesium, potassium, and hydrogen forms should all be looked at for further optimization. Due to lack of time, the E-TEK experiments should be performed several more times to ensure that the performances were indeed as high as the first run results proved to be before intensive testing is devoted to these three forms with this new GDL.

Application of PTFE

The PTFE was added to both the anode and cathode sides during the tests done throughout this project. However, as one of the tested parameters, the PTFE application on both sides was looked at briefly. As most of the water forms on the cathode side of the MEA there does not theoretically seem to be a need for PTFE to be applied on the anode side. When this test was done the performance was comparable to the original baseline tests, but flooding became a more often occurrence. When PTFE was not added to the cathode side, the MEA showed very poor performance, as expected. With these results in mind, PTFE should always be added to the cathode side of the MEA but further investigation should be made with regards to the anode side. Rather than PTFE being completely deleted from the anode side catalyst ink, different amounts should be looked at and tested in hopes of finding a balance which helps performance but avoids flooding.

Chapter V. References & Appendices

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Detailed Procedure

Membrane Pre-treatment

- Cut piece of Nafion® 115 sheet with area of approximately 20 cm^2.
- Boil Nafion® in deionized water (250-350 ml) for one hour.
- After the DI water, boil membrane in a 3% hydrogen peroxide aqueous solution (250 ml) for one hour.
- Following H_2O_2 treatment, Nafion® is again boiled in DI water for another hour.
- During original procedure, after membrane is boiled for second time in DI water, place between Teflon® sheets and Kim® Wipes, then two metallic plates and in hot press with 0.2 metric tons of pressure at room temperature for about 10 minutes.
- However, when the structure of Nafion® is altered, an additional two steps are added between the second DI water boil and the hot press.
    - The first step is to boil the membrane in a 1 M aqueous solution of desired form at low heat for 12 hours.
    - Boiling membrane in DI water a third time follows this extra step.
- After the membrane is pressed, it is ready for the application of the Catalyst Ink, which would be prepared during membrane pre-treatment.

Catalyst Ink Preparation & Application

Two batches of ink are required, one for each side of the membrane. Each batch is made to cover 5 cm^2, with the desired catalyst loading of 0.4 mg/cm^2. Expecting slight losses of catalyst in the preparation and application of the ink, the ink is actually made with a loading of 0.7 mg/cm^2.

The ingredients used in each batch consist of: Nafion®, 10% (0.7 mg/cm^2), PTFE, 10% (3:7 ratio with the catalyst powder), catalyst powder, 20% (Pt), and organic solvent (i.e. methanol, ethanol).

- In clean beaker, zeroed on a scale, add 15 mg of 20% Pt, 35 mg of 10% Nafion®, 64.3 mg of 10% PTFE, and 5.5 ml of Methanol together. Stir mixture manually until all of catalyst powder is visibly mixed into solution.
- Cover beaker with Parafilm® and place in ultrasonic bath. Solution sonicates for 3 hours, and is added to air gun for application.

After membrane is pressed for 10 minutes, it is placed between two metal stencils with 5-cm^2 squares cut out in the middle. The stencils are held in place on a clipboard. The ink, being loaded onto the air gun, is sprayed as evenly as possible across each face of the membrane (one batch of ink for each side). To minimize swelling of the membrane, a hair dryer is used to dry remaining solvent from the membrane in between sprays, leaving only the catalyst and PTFE.

- Once the catalyst ink has been applied to both sides of membrane, dry in oven at 70˚ C for 1.5 hours.

Post-treatment

- Out of the oven, the catalyzed membrane is boiled in 200-250 ml of 0.5 M sulfuric acid for 1.5 hours.
- Membrane is then boiled with deionized water for an hour.
- Again, membrane is pressed for 10 minutes at room temperature with negligible pressure.

Once the catalyzed membrane has cooled off from the DI water boil, the GDL is placed on each side, lined up with the sprayed portion, and hot pressed between two Teflon® sheets and metallic plates with a pressure of 2 metric tons. The hot press heats to a temperature of 275 degrees Celsius, and after this point, the membrane is left in the press for an additional 2 minutes before removal.

After the MEA cools, it can be placed into the fuel cell, then the cell is wired into the test station, and the break-in can begin.

In the station, the humidifier and thermostat are turned on, and once the heating line reaches 100˚ C and the thermostat and fuel cell reach 30˚ C, the load box is turned on. The computer program begins and the gas added to the fuel cell. After performance levels off at 30˚ C, the station is set to 70˚ C. The MEA is conditioned at this temperature for 16-20 hours, and then it can be tested.

Raw Data

This section is devoted to the raw data for the experimental runs. The runs prior to the data shown here were dedicated to getting reproducible results to be used as a benchmark.

Test 12 Regular form (H+)

V	I(A)	I(mA/cm^2)
0.8	0.27	54
0.7	1.278	255.6
0.6	2.66	532
0.5	4.185	837
0.4	5.7	1140
0.3	6.95	1390
0.2	7.74	1548

Test 13 Regular form (H+)

V	I(A)	I(mA/cm^2)	AVG (I(mA/cm^2))
0.8	0.282	56.4	55.2
0.7	1.327	265.4	260.5
0.6	2.76	552	542
0.5	4.262	852.4	844.7
0.4	5.687	1137.4	1138.7
0.3	6.8	1360	1375
0.2	7.652	1530.4	1539.2

Test 18 No PTFE on Anode

V	I(A)	I(mA/cm^2)
0.8	0.355	71
0.7	1.402	280.4
0.6	2.7	540
0.5	3.971	794.2
0.4	4.991	998.2
0.3	5.736	1147.2
0.2	6.228	1245.6

Test 19 No PTFE on Cathode

V	I(A)	I(mA/cm^2)
0.8	0.097	19.4
0.7	0.807	161.4
0.6	1.8	360
0.5	2.724	544.8
0.4	3.42	684
0.3	3.355	671
0.2	3.25	650

Test 21 Sodium form

V	I(A)	I(mA/cm^2)
0.8	0.285	57
0.7	1.24	248
0.6	2.608	521.6
0.5	4.2	840
0.4	5.5	1100
0.3	6.6	1320
0.2	7.4	1480

Test 23 Sodium form

V	I(A)	I(mA/cm^2)	AVG (I(mA/cm^2))
0.8	0.26	52	54.5
0.7	1.16	232	240
0.6	2.52	504	512.8
0.5	4.1	820	830
0.4	5.4	1080	1090
0.3	6.516	1303.2	1311.6
0.2	7.43	1486	1483

Test 24 Lithium form Test 25 Lithium form Test 26 Lithium form

V	I(A)	I(mA/cm^2)	V	I(A)	I(mA/cm^2)	AVG (I(mA/cm^2))	V	I(A)	I(mA/cm^2)
0.8	0.29	58	0.8	0.267	53.4	58.1	0.8	0.315	63
0.7	1.233	246.6	0.7	1.225	245	248.5	0.7	1.269	253.8
0.6	2.609	521.8	0.6	2.65	530	530.3	0.6	2.695	539
0.5	4.2	840	0.5	4.15	830	842.0	0.5	4.28	856
0.4	5.547	1109.4	0.4	5.485	1097	1110.8	0.4	5.63	1126
0.3	6.7	1340	0.3	6.55	1310	1334.3	0.3	6.764	1352.8
0.2	7.65	1530	0.2	7.45	1490	1516.7	0.2	7.65	1530

Test 27 Potassium form

V	I(A)	I(mA/cm^2)
0.8	0.323	64.6
0.7	1.351	270.2
0.6	2.92	584
0.5	4.31	862
0.4	5.64	1128
0.3	6.74	1348
0.2	7.65	1530

Test 28 Potassium form

V	I(A)	I(mA/cm^2)	AVG (I(mA/cm^2))
0.8	0.356	71.2	67.9
0.7	1.32	264	267.1
0.6	2.776	555.2	569.6
0.5	4.25	850	856.0
0.4	5.45	1090	1109.0
0.3	6.575	1315	1331.5
0.2	7.55	1510	1520.0

Test 28 Cesium form

V	I(A)	I(mA/cm^2)
0.8	0.264	52.8
0.7	1.304	260.8
0.6	2.82	564
0.5	4.46	892
0.4	5.85	1170
0.3	7.15	1430
0.2	8.1	1620

Commercial membrane

V	I(A)	I(mA/cm^2)
0.8	0.501	100.2
0.7	1.724	344.8
0.6	3.423	684.6
0.5	5.12	1024
0.4	6.385	1277
0.3	7.234	1446.8
0.2	8.45	1690

E-TEK

Test 32 Potassium form

V	I(A)	I(mA/cm2)
0.8	0.439	87.8
0.7	1.729	345.8
0.6	3.333	666.6
0.5	5	1000
0.4	6.31	1262
0.3	7.21	1442
0.2	8.1	1620

Test 33 Cesium form

V	I(A)	I(mA/cm2)
0.8	0.313	62.6
0.7	1.75	350
0.6	3.6	720
0.5	5.3	1060
0.4	6.7	1340
0.3	7.7	1540
0.2	8.41	1682

Test 34 Regular Hydrogen form

V	I(A)	I(mA/cm2)
0.8	0.479	95.8
0.7	1.877	375.4
0.6	3.6	720
0.5	5.42	1084
0.4	6.915	1383
0.3	8.03	1606
0.2	8.872	1774.4

Test 35 Lithium form

V	I(A)	I(mA/cm2)
0.8	0.595	119
0.7	2.052	410.4
0.6	3.723	744.6
0.5	5.313	1062.6
0.4	6.633	1326.6
0.3	7.826	1565.2
0.2	8.529	1705.8

Test 36 sodium form

V	I(A)	I(mA/cm2)
0.8	0.481	96.2
0.7	1.874	374.8
0.6	3.374	674.8
0.5	5.21	1042
0.4	6.561	1312.2
0.3	7.522	1504.4
0.2	8.079	1615.8