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# Principles of High Performance MEA Fabrication

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**Principles of High Performance  
Membrane Electrode Assembly Fabrication**

A Major Qualifying Project Report:

submitted to the Faculty

of the

WORCESTER POLYTECHNIC INSTITUTE

in partial fulfillment of the requirements for the

Degree of Bachelor of Science

By

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Date: April 27<sup>th</sup>, 2007

Approved:

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<b>Table of Symbols.....</b>	<b>3</b>
<b>Abstract .....</b>	<b>11</b>
<b>Chapter I. Introduction .....</b>	<b>13</b>
Introduction to a Proton Exchange Membrane .....	13
Proton Exchange Membrane Fuel Cell Components .....	15
Applications and Advantages of Fuel Cells.....	18
MEA Fabrication Literature Review .....	20
Carbon Blacks .....	21
Catalysts .....	21
Membranes.....	22
Gas Diffusion Layers.....	23
Electrode ink formulation.....	24
Hot-pressing/assembly of MEA .....	26
Porosity and wettability if the electrode structure .....	27
Literature Review .....	28
Project Goals and Objectives.....	38
<b>Chapter II. MEA Theory.....</b>	<b>40</b>
PEMFC Model.....	40
Fuel Cell Single Stack Model .....	53
Membrane Sorption .....	59
<b>Chapter III. Experimental Methodology .....</b>	<b>62</b>
Factors that affect performance .....	62
Decal Method .....	65
Preparation of catalyst ink.....	65
Application of Catalyst ink on Teflon .....	66
Drying procedure.....	66
Hot-press conditions.....	67
Post-treatment .....	69
Fuel cell test station.....	69
Direct Spray Method .....	70
MEA Pre-Treatment.....	70
Catalyst Ink Preparation .....	71
Application of Catalyst Ink on MEA.....	72
Drying Procedure .....	73
MEA Post Treatment.....	73
Hot Press Conditions.....	73
Fuel Cell Test Station Conditions.....	74
<b>Chapter IV. Results .....</b>	<b>75</b>
Decal Method .....	75
Spray Method .....	83
<b>Chapter V. Conclusions and Future Works .....</b>	<b>107</b>
Decal Method .....	107
Spray Method .....	108
<b>Chapter VI. Recommendations.....</b>	<b>111</b>
Decal Method .....	111
Spray Method .....	113
<b>Chapter VII. References &amp; Appendices.....</b>	<b>116</b>
Bibliography .....	116
Appendix I-Detailed Methodology for Spray Method.....	119
Table of Solvents .....	120
Appendix II-Experimental Data.....	121
Decal Method .....	121
Spray Method .....	124

## Table of Symbols

$a_i$	activity of species $i$
$a_w$	activity, or relative humidity RH, of water $=p_w/p_w^0$
$a_\alpha$	mean pore radius of porous layer $\alpha$ (nm)
$A$	geometric area of PEM in fuel cell
$A_\rho$	pre-exponential factor of reaction $\rho$
$A_i^{z_i}$	species $i$ with charge $z_i$
$B_{0\alpha}$	d'Arcy permeability of layer $\alpha$ ( $\text{cm}^2$ )
$c$	total concentration of mixture $= \sum_i c_i$ ( $\text{mol}/\text{cm}^3$ )
$c_{\text{HA},0}$	concentration of membrane acid groups $= 1/\lambda \bar{V}_2$ ( $\text{mol}/\text{cm}^3$ pore solution)
$C_{iS}$	concentration of species $i$ in region S
$c_{iT}$	concentration of species $i$ in region T
$c_{i\alpha}$	concentration of species $i$ in layer $\alpha$ ( $\text{mol}/\text{cm}^3$ )
$C$	BET constant
$d_M$	catalyst metal microcrystallite diameter (nm)
$D_{ij}$	mutual diffusion coefficient for species $i$ and $j$ ( $\text{cm}^2/\text{s}$ )
$D_{iL}$	liquid-phase diffusion coefficient of species $i$ ( $\text{cm}^2/\text{s}$ )
$D_{iG}^e$	effective gas-phase diffusion coefficient of species $i$ in the gas-diffusion backing ( $\text{cm}^2/\text{s}$ )
$D_{ij}^e$	effective mutual diffusion coefficient of species $i$ and $j=K_1 D_{ij}$ ( $\text{cm}^2/\text{s}$ )
$D_{ij}^{e0}$	pressure independent effective binary diffusion coefficient of species $i$ and $j=pD_{ij}^e$ ( $\text{bar cm}^2/\text{s}$ )
$D_{iK}^e$	effective Knudsen diffusion coefficient of species $i$ ( $\text{cm}^2/\text{s}$ )
$D_{iM}^e$	effective diffusion coefficient for interaction of species $i$ and matrix M $=K_0 D_{iM}$ ( $\text{cm}^2/\text{s}$ )

$D_{i\alpha}^e$	effective diffusion coefficient of species $i$ in layer $\alpha$ ( $\text{cm}^2/\text{s}$ )
$E_{A,\Phi_0}$	effective activation energy of $i_{A,0}$ or $\bar{k}_{A,\Phi_0}^*$
$E_\mu$	activation energy for viscosity ( $\text{kJ/mol}$ )
$F$	Faraday's constant, 96,487 C/eq
$F_T$	volumetric flow rate in anode
HA	acid group (e.g., $-\text{SO}_3\text{H}$ ) in membrane
$\Delta H^0$	enthalpy change for proton solvation ( $\text{kJ/mol}$ )
$i$	fuel cell current density ( $\text{A/cm}^2$ of geometric electrode area)
$i_A$	anodic current density ( $\text{A/cm}^2$ of geometric electrode area)
$i_0$	exchange current density ( $\text{A/cm}^2$ of geometric electrode area)
$i_{A,L}$	anodic limiting current density ( $\text{A/cm}^2$ of geometric electrode area)
$i_{A,0}$	anodic exchange current density ( $\text{A/cm}^2$ of geometric electrode area)
$i_C$	cathodic current density ( $\text{A/cm}^2$ of geometric electrode area)
$i_{C,L}$	cathodic limiting current density ( $\text{A/cm}^2$ of geometric electrode area)
$i_{C,0}$	cathodic exchange current density ( $\text{A/cm}^2$ of geometric electrode area)
$i^*$	current density ( $\text{A/cm}^2$ of metal catalyst surface)
$i_0^*$	exchange current density ( $\text{A/cm}^2$ of metal catalyst surface)
$i_{A,0}^*$	anodic exchange current density ( $\text{A/cm}^2$ of metal catalyst surface)
$i_{C,0}^*$	cathodic exchange current density ( $\text{A/cm}^2$ of metal catalyst surface)
$k_B$	Boltzmann constant
$k_A^*$	effective rate constant of overall anode reaction
$\bar{k}_{A,\Phi_0}^*$	rate constant of anode reaction at equilibrium electrode potential $\Phi_0$
$k_C^*$	effective rate constant of overall cathode reaction

$\bar{k}_{C,\phi_0}^*$	rate constant of anode reaction at equilibrium electrode potential $\Phi_0$
$\bar{k}_\rho^*$	rate constant of forward elementary reaction $\rho$ ( $s^{-1}$ )
$\bar{k}_\rho^*$	rate constant of reverse elementary reaction $\rho$ ( $s^{-1}$ )
$\bar{k}_{\rho,\phi_0}^*$	rate constant of forward elementary reaction $\rho$ at equilibrium electrode potential $\Phi_0$ ( $s^{-1}$ )
$K_{A,C}$	equilibrium constant for proton solvation in terms of concentrations
$K_\rho$	equilibrium constant of reaction $\rho$
$K_{\rho,\phi_0}$	equilibrium constant of reaction $\rho$ at equilibrium electrode potential $\Phi_0$
$K_{0\alpha}$	dusty-gas constant of layer $\alpha$ for effective Knudsen diffusion coefficient (cm)
$K_{1\alpha}$	dusty-gas constant of layer $\alpha$ for effective binary diffusion coefficient
$L_\alpha$	thickness of layer $\alpha$
$m_I$	ionomer loading in catalyst layer (g metal/cm <sup>2</sup> geometric electrode area)
$m_M$	catalyst loading (g metal/cm <sup>2</sup> geometric electrode area)
$n$	total number of species
$n_w$	total number of water layers sorbed on the pore surface
$n_\rho$	number of electrons participating in reaction $\rho$
$N_i$	flux of species $i$ (mol/cm <sup>2</sup> geometric electrode area)
$p$	total pressure (bar)
$p_i$	partial pressure of species $i$ (bar)
$p_S$	total pressure in cathode chamber (bar)
$p_T$	total pressure in anode chamber (bar)
$p_w^0$	vapor pressure of water (bar)

$P$	power density ( $\text{W}/\text{cm}^2$ geometric electrode area)
$P_{i\alpha}$	permeability of layer $\alpha$ for species $i=D_{i\alpha}\kappa_{i\alpha}/L_{\alpha}$ ( $\text{cm}/\text{s}$ )
$q$	Bruggeman or critical exponent=1.5
$q_I$	ionomer loading in catalyst layer ( $\text{cm}^3$ ionomer/ $\text{cm}^3$ void volume)
$q_{\alpha}$	liquid loading of layer $\alpha$ ( $\text{cm}^3$ liquid/ $\text{cm}^3$ void volume)
$r$	net rate of reversible reaction $\rho = \vec{r}_{\rho} - \overleftarrow{r}_{\rho}$ ( $\text{mol}/\text{cm}^3$ catalyst particles s)
$\vec{r}_{i_0}$	rate of forward reaction under open circuit conditions ( $\text{mol}/\text{cm}^3$ catalyst particles s)
$r_A^*$	net rate of anodic reaction ( $\text{mol}/\text{cm}^2$ metal catalyst area s)
$r_C^*$	net rate of cathodic reaction ( $\text{mol}/\text{cm}^2$ metal catalyst area s)
$r^*$	net rate of reversible reaction $\rho = \vec{r}_{\rho}^* - \overleftarrow{r}_{\rho}^*$ ( $\text{mol}/\text{cm}^2$ metal catalyst area s)
$r_{\rho 0}$	reaction rate at open circuit
$R$	universal gas constant, 8.3143 J/mol K
$R_I$	interfacial resistance ( $\Omega \text{ cm}^2$ )
$s$	surface coordination number
$S$	catalyst site
$S_M$	specific surface area of metal crystallites ( $\text{cm}^2/\text{g}$ metal)
$S_S$	specific surface area of carbon support particles ( $\text{cm}^2/\text{g}$ carbon)
$T$	temperature (K)
$V$	fuel cell potential $=\phi_{M,C}-\phi_{M,A}$ (V)
$V_0$	open circuit potential $=\Phi_{0,C}-\Phi_{0,A}$ (V)
$\overline{V}_i$	partial molar volume of species $i$ ( $\text{cm}^3/\text{mol}$ )

$W$	$W \equiv 1 + \frac{B_0 c R T}{\mu} \sum_{h=1}^n \frac{x_h}{D_{hM}^e}$
$z$	coordinate
$z_i$	charge number of species $i$
$\alpha$	degree of acid group dissociation
$\bar{\alpha}_A$	effective transfer coefficient of overall anode reaction = $\frac{1}{2}$
$\bar{\alpha}_C$	effective transfer coefficient of overall cathode reaction = 1
$\beta_p$	symmetry factor of elementary reaction $\rho = \frac{1}{2}$
$\gamma_M$	roughness factor ( $\text{cm}^2 \text{ Pt}/\text{cm}^2$ geometric electrode area)
$\gamma^\ddagger$	activity coefficient of transition-state complex
$\delta$	ratio of mutual to matrix effective diffusion coefficients, $D_{H^+ w}^e/D_{H^+ M}^e$
$\varepsilon$	volume fraction of water in hydrated membrane, or wet porosity
$\varepsilon_0$	percolation threshold volume fraction of water in hydrated membrane
$\varepsilon_\alpha$	porosity for porous layer $\alpha$
$\eta$	overpotential = $\Phi - \Phi_0$ (V)
$\eta_A$	anodic overpotential (V)
$\eta_C$	cathodic overpotential (V)
$\theta_i$	fraction of surface sites occupied by species $i$
$\kappa$	transmission coefficient
$\kappa_{i\alpha}$	partition coefficient of species $i$ in layer $\alpha = (c_{i\alpha}/c_{iG})_{\text{eq}}$
$\lambda$	water loading, number of water molecules per $-\text{SO}_3\text{H}$ group



$\lambda_m$	water loading at monolayer coverage, number of water molecules per $-\text{SO}_3\text{H}$ group
$\lambda_i^0$	equivalent conductance for ionic species $i$ at infinite dilution ( $\text{S cm}^2/\text{equiv.}$ )
$\mu$	fluid mixture viscosity ( $\text{g/cm s}$ )
$\mu_i$	chemical potential of species $i$ ( $\text{J/mol}$ )
$\mu_i^e$	electrochemical potential of species $i$ ( $\text{J/mol}$ )
$\nu_{\rho i}$	stoichiometric coefficient of species $i$ in reaction $\rho$
$\nu_{\rho e}^-$	stoichiometric coefficient of electrons in reaction $\rho$
$\rho_I$	ionomer density ( $\text{g/cm}^3$ )
$\sigma$	effective conductivity of PEM (layer B) ( $\text{S/cm}$ )
$\tau_\alpha$	tortuosity factor for porous layer $\alpha$
$\varphi$	inner potential (V)
$\phi_I$	fraction of accessible catalyst surface participating in electrocatalysis
$\phi_M$	fraction of metal crystallite surface that is accessible
$\Phi$	electrode potential (V)
$\Phi_0$	equilibrium electrode potential (V)
$\Phi_0^0$	standard equilibrium electrode potential for unit activities (V)
$\omega_M$	metal catalyst mass fraction ( $\text{g metal/g catalyst particles}$ )
A	layer A (anode electrocatalyst)
B	layer B (PEM)
C	layer C (cathode electrocatalyst)
d	diluent gas
D	layer D (anode gas-diffusion backing)

E	layer E (cathode gas-diffusion backing)
G	gas phase
H <sup>+</sup>	H <sub>3</sub> O <sup>+</sup>
<i>i</i>	species <i>i</i>
I	ionomer
M	membrane
M	metal, membrane matrix
S	layer S (cathode chamber)
<i>T</i>	at constant temperature <i>T</i>
T	layer T (anode chamber)
w	water
0	open circuit conditions, dry membrane, reference, percolation threshold
298	at reference temperature, 298 K
$\alpha$	generic layer
$\rho$	reaction $\rho$
$\Phi_0$	at equilibrium electrode potential
*	per cm <sup>2</sup> metal area
$\lambda_i^C$	strongly interacts with acid sites (dimensionless)
$\lambda_{i,m}$	monolayer coverage of absorbed molecules (dimensionless)
K <sub>1</sub>	first ionization constant of sulfuric acid (dimensionless)
$\nu$	number of chemical equilibrium steps of the reaction
$\nu$	Poisson's ratio
$\lambda_i$	solvent molecules per acid site

$r$	ratio of partial molar volumes of the polymer membrane
$\chi$	fitted (dimensionless)
$G$	shear modulus of the polymer
$S$	specific pore surface area ( $\text{m}^2/\text{cm}^3$ )
$\sigma$	surface tension of solvent ( $\text{mN/m}$ )
$\theta$	contact angle of saturated solvent vapor in Nafion

## Abstract

A well-designed fuel cell that gives good performance, while being durable and relatively inexpensive, involves the careful consideration of several aspects. In this project, the focus is on the MEA, or the membrane electrode assembly, and the improvements that can be made to the design and fabrication of the MEA. A theoretical model proposed by Thampan et al<sup>[14]</sup>, of MEA performance was considered in order to develop an understanding of the key aspects affecting it. Further, a literature review was done to gain an experimental understanding of the various factors involved in the fabrication and performance of the MEA. With this background, as well as from experimental observations, the process for fabricating high performance MEAs was considered and an effort made to fabricate MEA with superior performance.

One aspect that was closely examined was the catalyst ink preparation and the application technique. Of the available procedures for catalyst application to membrane, the decal method, the spray method and the painting method were examined. The direct application of the catalyst to the membrane rather than to the gas-diffusion electrode was found to yield the best performance both in the literature as well as in our experimental practice. The procedure involved the replication of MEA fabrication procedures from the literature reported to give good performance, followed by a critical evaluation of the parameters said to affect the performance. The parameters that affect catalyst application and MEA performance range from the Nafion content, type of organic solvent, hot press and baking temperature, the sequence of pre- and post-treatment, as well as the addition of other ingredients. By varying each factor individually, a correlation between that factor and the performance of the MEA was established.

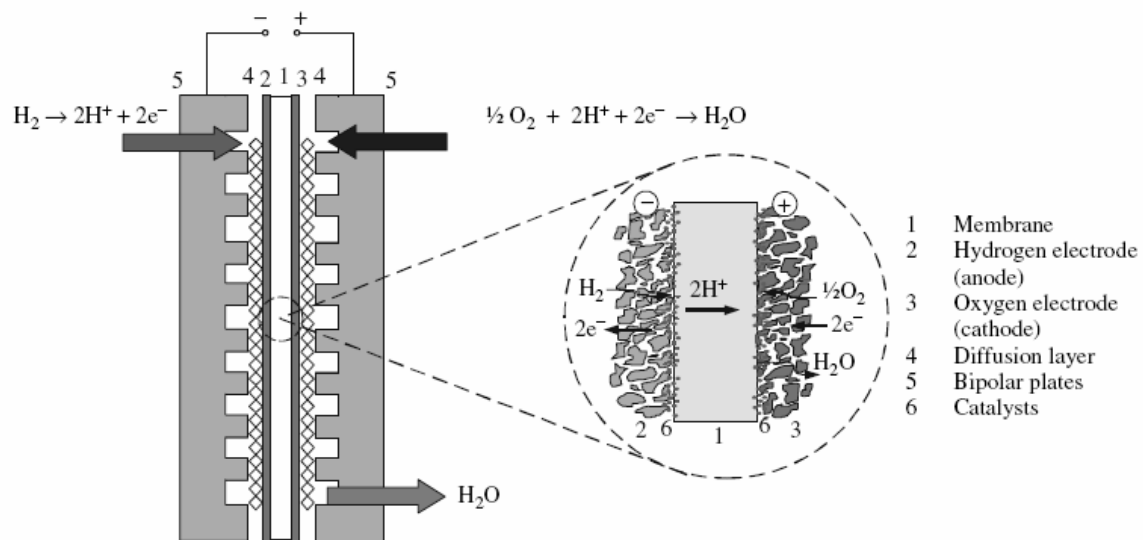
The understanding that was developed, based on theoretical and experimental investigation of the various aspects, was used to propose fabrication methodologies for high performance MEAs, along with an explanation of why the proposed procedure results in MEAs that provides high performance.

From experimentation, the spray method gave better results when compared to the decal or painting method. The spray method involved the direct application of the catalyst ink onto the membrane and resulted in a more even catalyst layer. The direct spray application method gave better performance despite using only 15mg Pt/C catalyst compared to painting and decal that used twelve times as much catalyst. The advantages of the spray method were that it limited the effect of other factors that might influence the performance. This method involved a catalyst ink of Nafion, PTFE, 20%Pt/C and a solvent which are mixed and later applied to the membrane. The decal method involved the application of the catalyst ink to the Teflon, which was problematic, and then the transfer of the catalyst layer onto the membrane. This method involved the incorporation of a roughening agent such as Fluoroglide which lowered performance by forming a diffusion barrier. Sand paper was then used as a replacement. However this adds another unknown that may affect performance. Additionally, in order to transfer the catalyst the membrane had to be hot pressed, which lowers performance. The spray method directly onto the membrane ensures good contact between the catalyst and the membrane and thus provided better performance. Methanol was found to be the best solvent for ink preparation as it had the best combination of swelling and volatility, allowing for the formation of good MEA.

# Chapter I. Introduction

## *Introduction to a Proton Exchange Membrane*

In the 1960's the first Proton Exchange Membrane (PEM) Fuel cell technology was developed by General Electric. It was used as part of a research program for the Navy and Army having the benefit of allowing them to have compact and portable power generation. The downside was that the cost was very high; a trait that remains in the PEM fuel cells today. Essentially a PEM Fuel Cell, is an electrochemical device that directly converts the chemical energy of a fuel, such as hydrogen and oxygen, into electrical energy following the reactions in Figure 1.1<sup>[1]</sup>



**Figure 1.1 Proton Exchange Membrane Fuel Cell <sup>[1]</sup>**

This electrochemical energy conversion is achieved through two reactions that occur at the anode and cathode of the fuel cell. The anode is the negative side of the fuel cell and is the left half of the PEM fuel cell in Figure 1.1. On the anode side, the hydrogen fuel enters and is dispersed over the catalyst layer where electrons are liberated from the

hydrogen and conducted through an external circuit. The catalyst layer is usually composed of platinum nanoparticles which can also contain additional alloying elements. Simultaneously the protons diffuse through the membrane to the cathode. The cathode is the positive side of the fuel cell where oxygen enters and combines with the diffused protons as well as the electrons conducted from the external circuit onto the catalyst to form water and heat. In the anode chamber are also etched pathways in the bipolar plates to direct the hydrogen over the catalyst area. There is an identical pathway etched onto the cathode side as well. The processes on the anode and cathode side work together to perform electrical work and produce DC current. In essence a fuel cell is very similar to a battery, in that, through the combination of chemicals within the system, electrical energy is produced. However, while a battery will run out of power due to depletion of chemicals, a fuel cell is constantly being re-supplied the chemicals necessary to continue the reactions for extracting electrical energy. The fuel may be supplied in the form of a gas, such as hydrogen and methane, or in liquid form, e.g.; methanol. Fuel cells come in several types, but one of the most promising is the PEM fuel cell, with a 50-60% efficiency, up to 250kw power generation and low operating temperature, 50-100°C<sup>[2]</sup> It is compact and lightweight, which makes it an ideal candidate for small portable applications as well as stationary application in buildings and even in transportation in cars and buses.

## ***Proton Exchange Membrane Fuel Cell Components***

The PEM fuel cell, consists of several parts that work together to perform the necessary electrochemistry.

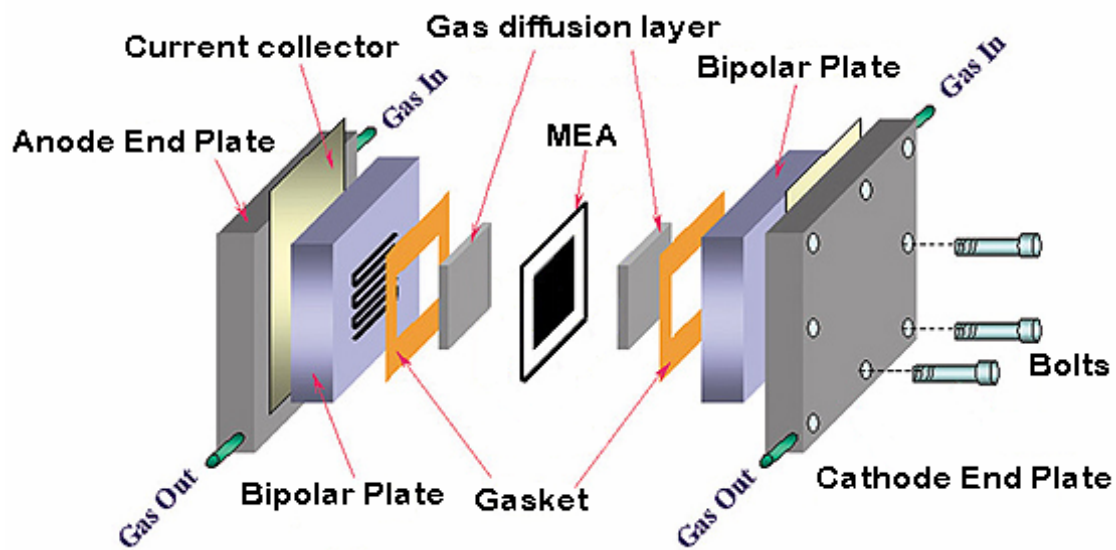
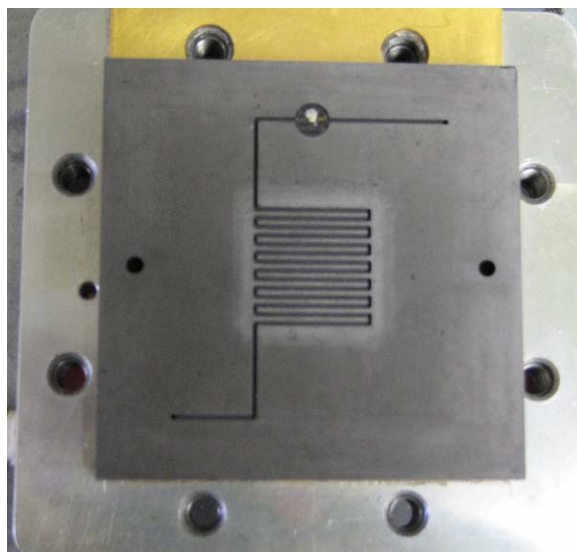


Figure 1.2 PEMFC Components<sup>[3]</sup>

Figure 1.2 displays the setup of the apparatus that is involved in a single cell PEM fuel cell. Working from the outside inward one encounters the bipolar plates. They are made of graphite and have channels etched in them that direct the gas flow evenly across the catalyst layer.





**Picture 1.1 Serpentine Flow channels**

The plates must be chemically stable, impermeable to gases and electrically conductive. The design of these plates is integral to the efficiency of the PEMFC as the design regulates the amount of fuel in contact with the catalyst as well as the humidification supplied and the distribution of current across the cell. The typical PEMFC required sensitive humidification control. Too little humidification results in high membrane resistance to proton conduction. Conversely too much humidification results in flooding.

The next component is the gasket which has its purpose to secure a seal between the plates and the membrane. This is required to separate the gasses entering the fuel cell. Typically a silicone rubber is used as the material of choice for a gasket due to their elasticity and heat resistance. However the environment the gaskets endure within the PEMFC is acidic and as a result the gaskets are degraded overtime and must be changed periodically to avoid decrease in PEMFC performance.

Another component designed to regulate fuel flow is the gas diffusion layer, GDL, which is composed of porous carbon paper or carbon cloth. This can be treated with PTFE to maintain the hydrophobicity necessary for water vapor to reach the

membrane and allow the water produced at the cathode to leave the cell. Mass transport limitations of oxygen to permeate the GDL directly affect the limiting current density of the cathode reaction, and therefore the overall performance.

The electrode is the catalyst layer which consists of platinum, which is a rare metal, and as a result is expensive. To avoid waste of the precious metals, nano-sized particles of platinum are dispersed on carbon based Vulcan XC support. This catalyst is then made into a slurry that can be applied to the gas diffusion layer or directly to the membrane. The composition of this layer is constantly being augmented to allow this layer to tolerate a range of operating conditions and optimize performance.

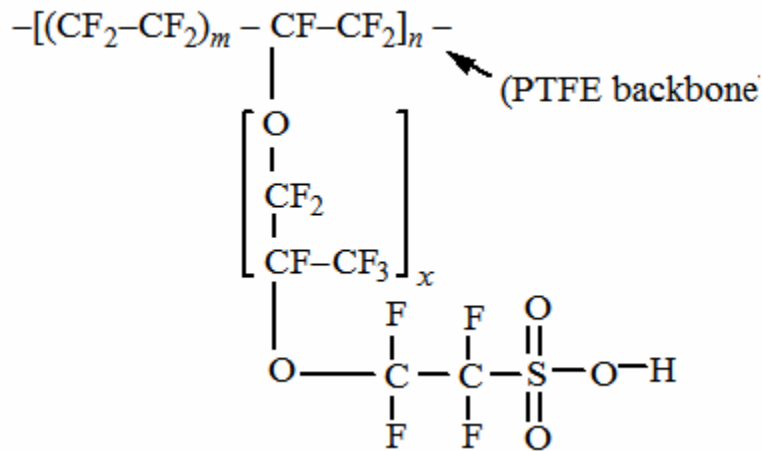


Figure 1.3 Nafion Structure<sup>[15]</sup>

The final component is the solid polymer electrolyte, which is a Nafion from DuPont, membrane that conducts protons from anode to cathode and keeps the reactant gases from mixing directly. It needs to be stable, mechanically strong, possess high proton conductivity and low gas permeability. Nafion is a perfluorosulfonic acid with a similar structure to PTFE as seen in Figure 1.3, which gives it a good balance between being hydrophobic and proton conducting.

## ***Applications and Advantages of Fuel Cells***



**Picture 1.2 Toyota Prius. Hybrid automobile. <sup>[4]</sup>**

Since fuel cells are able to convert chemical energy directly into electricity, they can be used for many devices of everyday usage. The most obvious application of fuel cells is in the automotive industry. Cars such as Honda, Toyota and Lexus are just some of the brand names that use fuel cells in some of their prototype models. The fuel cells produce electricity to drive electric motors and provide “maximum torque at low rpm.” By further capturing the energy used to stop the vehicle or driving down an incline, these cars can take that lost energy and also convert it into electricity for the motor. The advantage of this application is that fuel cells are efficient, hydrogen may or may not be derived from fossil fuels and pollution is far less. Though many believe that it takes a long time to refuel a hydrogen tank, it takes the same amount of time as pumping gas.<sup>[5]</sup> However, adequate storage of hydrogen on board is still an issue.

Fuel cells can also be used to supply electricity in our homes, work places and any other building. Not only are fuel cells in buildings efficient, but reliable as well. An example of how fuel cells are used for power is the building located at 4 Times Square in New York City. The building uses fuel cells to “power its base load.” The cells have the capability of powering the lights outside of the building and other certain components. Banks as well have used fuel cells for their reliability, especially when powering the

credit card transaction unit. Fuel cells are able to power the unit even during power outages. This helps banks and companies tremendously by saving them money.<sup>[5]</sup>



**Picture 1.3 Tower in New York City which uses fuel cells as a supplemental energy supply.** <sup>[5]</sup>

Fuel cells can be used even in the electronics we depend on daily basis such as cell phones, laptops and MP3 players. Any electronic that is transportable that uses batteries can run on “micro fuel cells.” The “micro fuel cells” are able to power a laptop almost three times longer than using a battery. This is true because fuel cells provide higher “energy density” than batteries. Another advantage of using micro fuel cells is that it can be refueled completely (not using a recharge or adapter) while the appliance is still on. <sup>[5]</sup>

Fuel cells have already been introduced into our society by being incorporated into some of the devices and appliances we use daily. Though fuel cells can and are being used in automobile prototypes, powering buildings and to power our electronics, as time progresses, fuel cells might become our primary source of electrical energy. This would decrease the amount of pollutants we emit from using fossil fuels and decrease our dependence on the depleting fossil fuels. <sup>[5]</sup>

## ***MEA Fabrication Literature Review***

In order to produce a high performing MEA that is durable and to gain a thorough understanding of how MEAs work, identification and understanding of the important variables which structure the MEA is needed. There are seven key elements of the fabrication process of MEAs that affect its performance. They are: the carbon blacks, the catalysts, the membranes, the gas diffusion layer, the electrode ink formulation, hot-pressing/assembly of MEA and finally the porosity and wettability of the electrode structure. These variables will be described as to their purpose within the MEA, as well as the impact each has on the MEA performance.

To gain the necessary competence, a rigorous literature review was done to acquire an understanding of current techniques and how they could be replicated and improved in the laboratory. Inspection of methods of MEA preparation is an integral part of developing a basis for a methodology. Using conclusions from research one can build a sound basis for experimental examination.

Before results are presented from researchers, it is important to understand that there are many different methodologies for fabrication of good MEAs. Therefore, each must be examined to evaluate the factors that yield better performance, rather than choosing the method that gives the best results. This section will be organized according to the different principles of the fabrication of MEAs that affect the performance and methods used in fabricating MEAs.

## Carbon Blacks

As a catalyst support, carbon blacks are used within the MEA assembly to provide a support for the diffusion of platinum. Within the MEA, carbon blacks provide low thermal expansion, thermal conductivity, a permeable and porous surface area medium for the carrying of gases such as O<sub>2</sub>, H<sub>2</sub>, and air, as well as water and electrical conductivity.

In order to choose the most suitable carbon support, the chemical, electrochemical, and physical properties of the carbon black must be studied. Carbon is unstable thermodynamically, to oxidation at operating voltages greater than 0.4V (kinetics are slow at moderate voltages and temperatures in PEMFCs).<sup>[6]</sup> The mechanism of electrochemical oxidation of carbon entails hydrolysis of the oxide, the lattice oxidation of carbon, and a disproportionation reaction that yields CO<sub>2</sub> and carbon surface oxides.<sup>[6]</sup> In conclusion, determining a certain carbon black for an MEA depends greatly on the lifetime needed in the stack and the specific operating conditions of the performance.

## Catalysts

Carbon supported platinum is the common choice as a cathode catalyst. Different procedures are implemented in preparing catalysts such as colloidal adsorption, impregnation and ion-exchange techniques. Over years of research, Pt/C with weight percent greater than 50% and with a small particle size (2.5-4 nm) have been produced.<sup>[6]</sup> Platinum with 50 wt % has made it possible to fabricate extremely thin electrodes that offer low ionic and mass-transfer resistance, and provide high power densities. It has been apparent that as opposed to just Pt, Pt/Ru has proved to be a better carbon monoxide tolerant catalyst in PEMFC anodes.<sup>[6]</sup> Choosing a certain Pt wt % and carbon support

affects the catalyst utilization, cell performance, the recrystallization rate of the Pt and cell decay characteristics and electrode layer thickness.

## **Membranes**

The best membranes found in today's market include Nafion 112, and 117. There are also other membranes such as Nafion 115. These membranes are usually in the H<sup>+</sup> form and are usual pre or post-treated in the sequence of 0.5 M hydrogen peroxide, then boiled in deionized water, then 0.5 M sulfuric acid, and finally boiled deionized water.

Nafion membranes possess properties such as density, hydrogen and oxygen permabilities, and specific conductivity that make it possible to calculate electrode structures.<sup>[6]</sup> Also, other important characteristics that can be determined from the membranes are tensile strength, percent elongation at break, creep, operating temperature on mechanical properties, ion-exchange capacity, water uptake and water permeability just to name a few.

Using two or four-electrode techniques for the conductivity of Nafion immersed in water or under humidified gases, the conductivity of Nafion can be characterized. The conductivity of Nafion is a function of relative humidity, yet also depends on the equivalent weight, pretreatment of the membrane and the casting method. As the heat treatment temperatures increases, the conductivity of the membrane decreases, due to a lowering of water uptake by the membrane. This is an important result given that membranes are hot-pressed in the fabrication process of MEAs at temperatures above 100°C. <sup>[6]</sup> At temperatures ranging from 45-80°C, it has been apparent that the

conductivity increases because humidification is more sustainable at these temperatures as opposed to higher temperatures.

Oxygen and hydrogen permeability in Nafion membranes is also noteworthy property. The permeability of  $O_2$  and  $H_2$  into the membrane depends on factors of operation such as humidity, temperature, partial pressure, membrane water content, and lower ion-exchange capacity and was found to decrease with the cation form of the membrane.<sup>[6]</sup> In order to select an appropriate membrane, pressure, lifetime and temperature of the fuel cell stack must be estimated.

### **Gas Diffusion Layers**



**Picture 1.4 Catalyzed GDL**

A gas diffusion layer's primary purpose is to manage water, distribute gases, collect current, conduct energy and provide mechanical support. The ways in which GDLs are comprised are of carbon fibers that are woven into a cloth. This cloth is then treated to have hydrophobic and hydrophilic characteristics which will work with a fuel cell and facilitate in water management.



## Electrode ink formulation

There are many techniques implemented when formulating electrode inks. Originally, electrodes for the PEMFC were constructed from PTFE bonded electrodes.<sup>[6]</sup> These electrodes were formulated for the PAFC, and through high temperature and bonding pressure, required high Pt loadings and were partially penetrated. After solubilized membranes were engineered<sup>[6]</sup>, electrodes painted with ionomer were produced. The painted electrodes aided in lowering the platinum loading. The presence of PTFE in the structure helps facilitate the prevention of pore flooding and enhances gas phase diffusion of reactants, also known as hydrophobicity.

Research done by Wilson et al.,<sup>[10]</sup> proved that ink comprised of Pt/C, glycol and ionomer using the decal method technique resulted in high performance MEAs that displayed low mass-transfer and electrode ionic resistance while providing very low catalyst loading. Wilson's procedure was improved by heat treating the catalyst layer, using an increased temperature casting process with Na<sup>+</sup> form of the membrane and using a melt-processable solubilized ionomer in the TBA<sup>+</sup> form to produce strong electrode structures.<sup>[10]</sup>

Further, research done by Uchida et al.<sup>[16]</sup> in which the choice of solvents used to fabricate the catalyst slurry was investigated. Uchida investigated solvents with different dielectric constants. The study consisted ethers ( $\epsilon \sim 3-8$ ), esters ( $\epsilon \sim 3-8$ ), hydrocarbons ( $\epsilon \sim 2.25$ ), alcohols ( $\epsilon \sim 17-33$ ), acetones and ketones ( $\epsilon \sim 9-20$ ), amines ( $\epsilon \sim 5-7$ ), acids ( $\epsilon \sim 1-6$ ) and glycerols ( $\epsilon \sim 5-43$ ). A colloid was formed as a result of the addition of a PFSI

solution whose dielectric constant was between 3 and 10. Platinum was added to the colloid, and a clear supernatant was formed as a result of the dispersed PFSI adsorbed onto the surface. Sonication was applied to form “cross-linkages between the PFSIs. The result was a paste which could be used to apply onto a GDL.<sup>[16]</sup>

Electrodes can be formed from two separately formed factors. The first factor contains a metal catalyst impregnated with ionomer. The second factor contains carbon combined with hydrophobic polymer (two components with fixed ratios are combined and crushed together with a solvent.

There are many different methodologies implemented in electrode ink formulation. All components and parameters are important in the formulation, however, one in particular is of interest, and that is the ionomer to carbon ratio ( $I/C$ ). The best amount and distribution of the ionomer in the catalyst layer is “a balance between the requirement for minimum electrode resistance, maximum contact of ionomer with Pt particles and maximum access of the reactant gas to the catalyst through the gas pores.” This ratio is normally adjusted for each method and formulation.

## Hot-pressing/assembly of MEA



Picture 1.5 Hot-press machine

Hot-pressing and assembly of the fabrication of MEAs is implemented with all methods. The glass transition temperature of Nafion, which is approximately 150°C governs the temperature used for the hot-pressing and assembly. Lower temperatures used for hot-pressing cause Nafion to not flow thus form good ionic contact with the catalyst (results in poor utilization). Use of high temperatures increases strength and reduces ionomer solubility. Higher temperatures of more than 150°C also results in a partial delamination of electrode from membrane, some water loss retention properties of Nafion and acid catalyzed degradation of the ionomer. [6] Therefore, the time span, temperature and pressure implemented while hot-pressing are 1-5 minutes, 120-160°C

and 5000-15000 kPa. Hot-pressing promotes adhesion and implants a portion of the electrode into the softened membrane.

Another hot-pressing method exists wherein the peeling and cracking occurs of the electrode after hot-pressing due to swelling of the H<sup>+</sup> form of the membrane. In this method, the surfaces of the membrane are hydrolyzed to the ionic form in which the slurry mixture adheres to the membrane. After this procedure is completed, the membrane is hydrolyzed after all the catalyst slurry is applied onto the membrane. This method facilitates in expanding the membrane along the thickness to improve electrical contact within the fuel cell.<sup>[6]</sup>

### **Porosity and wettability of the electrode structure**

An important factor in determining a “good” fuel cell is its porosity. High porosity is required to decrease gas phase diffusion losses (exceedingly high porosities increase electrode resistance). A conventional range of porosities in PEMFCs is approximately 30-60%.<sup>[6]</sup> Porosity, hydrophilicity and hydrophobicity in combination with each other can be controlled by the choice of ionomer/carbon ration, choice of carbon and fabrication methodology.

Researcher Zawodzinski et al.<sup>[6]</sup> have shown in their studies that the ionomer surface demonstrates a large range of contact values with water. The contact angle “relaxes slowly from one value to the other over tens of minutes as the ionic groups re-orient to the changing environment and has implications for cell performance with time.” High activity through contact with ionomer is related with the wettability of the pore structure for the optimization of the electrode and GDL of a fuel cell.<sup>[6]</sup>

## Literature Review

In research performed by Y.-G. Yoon et al.<sup>[7]</sup> implementing the spray method to the catalyzed gas diffusion layer, the primary objective was to produce numerous secondary pores using different types of catalytic layer which would improve gas transport through the catalytic layer. Researchers used three kinds of catalytic layers to produce the secondary pores: Type 1 (droplet size from fine to coarse mode when spraying on carbon cloth); Type 2 (droplet size from fine to coarse mode when spraying on polyimide film); and Type 3 (droplet size to normal mode when spraying on polyimide film). The preliminary treatment used was to take the carbon cloth backing and coat it with the slurry containing carbon black power and PTFE emulsion. The drying times and temperature was 80°C for two hours. The hot-press pressure, time and temperature implemented were 77 atm, 210 seconds and 135°C. The components of Type 1 were the electrocatalyst, Nafion and water. The components of Type 2 were the same as Type 1 with the addition of TBAOH. The components of Type 3 were the same as Type 2 with the addition of ethylene glycol. All three types were post treated (0.5 M hot sulfuric acid for 60 minutes and then rinsed with deionized water). The temperature used to operate a single cell under pure H<sub>2</sub>, O<sub>2</sub> and air was 80°C, while the humidification temperature was 95°C. The results of this research proved that addition of a thermoplastic agent such as TBAOH and ethylene glycol improve the cell voltage as opposed to MEAs made without a thermoplastic agent and ethylene glycol. Also, it is apparent from the literature that ethylene glycol lowers the level of O<sub>2</sub> gain in the fuel cell.<sup>[7]</sup>

Similar finding as to the benefits of TBAOH were found in a paper by Robert D. Mitchell.<sup>[17]</sup> The MEA was fabricated from perfluorosulfonic acid ionomer of 800

equivalent weight. It was cut into 100 cm by 11cm sheets and converted into the Na<sup>+</sup> form by a bath of NaOH. The electrode ink was made by mixing 1.08g of a 5.79 weight percent solution, in a 50:50 volume percent ethanol/water solution. 0.1875g of 20 weight percent Pt/C, 0.114g of TBAOH, and 0.6g of propylene carbonate was then added to the ink. This was then mixed overnight and an additional 1.2g of propylene carbonate was added to the mixture. The ink was applied using the decal method to the Teflon blanks, which were dried and then transferred onto the membrane. Shown below is the result of this experiment labeled as Example 1 in Figure 1.4.

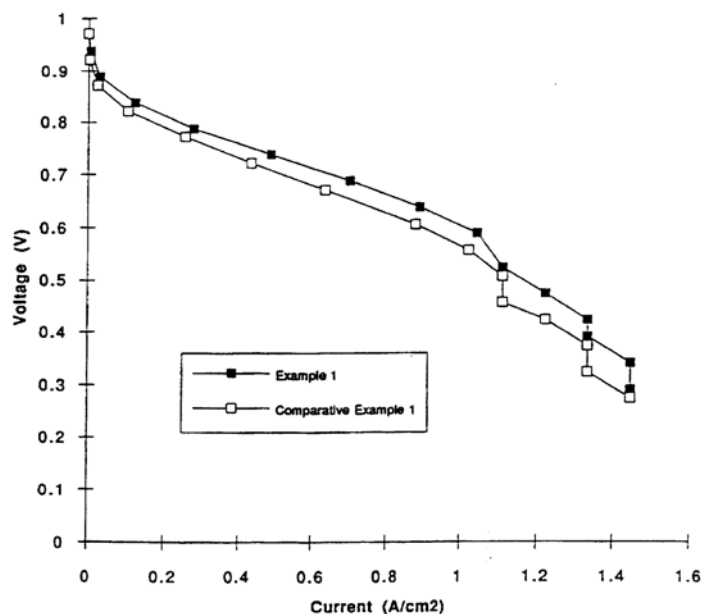


Figure 1.4 Example 1: MEA with TBAOH<sup>[17]</sup>

Another MEA<sup>[17]</sup> was made using the same measurement as in Example 1 except without TBAOH. The results can be seen in Figure 1.5 below on the plot labeled Example 2.

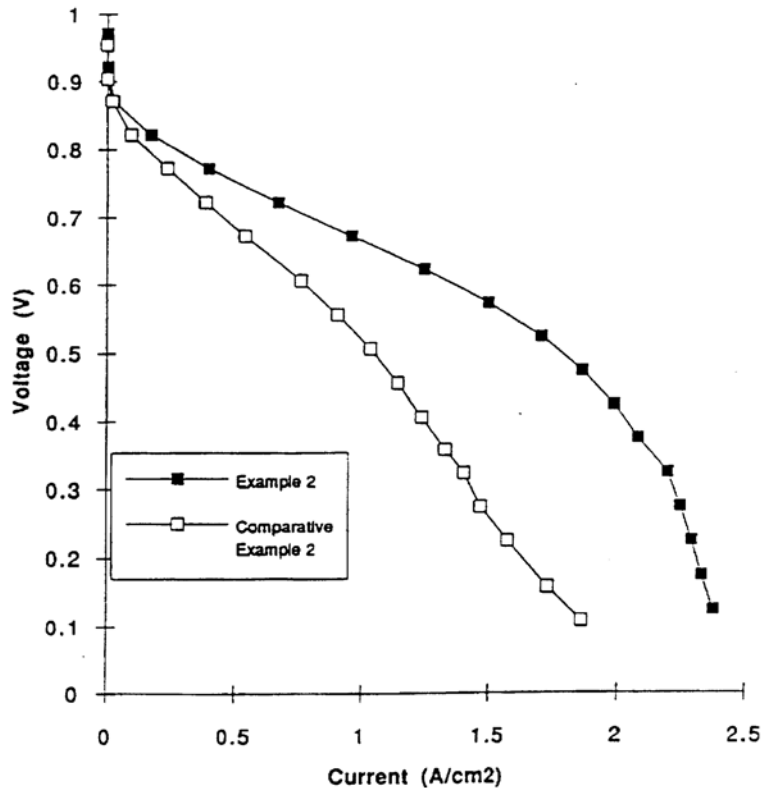
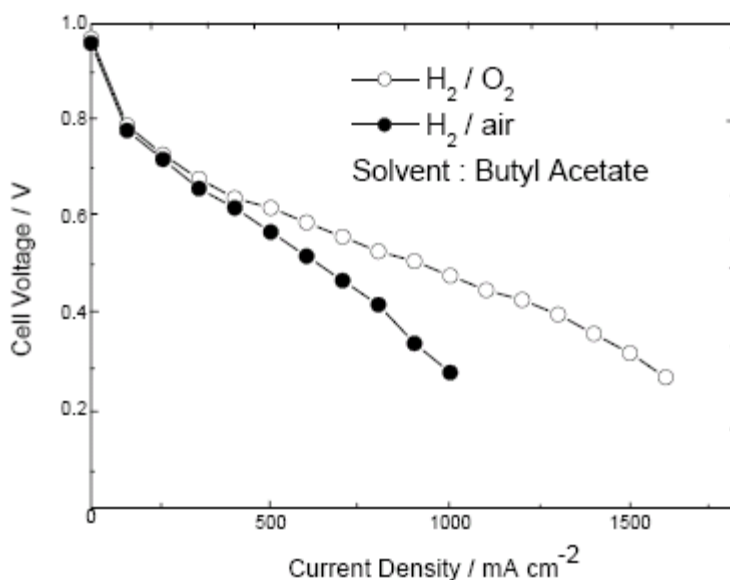


Figure 1.5 Example 2: Without TBAOH<sup>[17]</sup>

These results are impressive but are in conflict with the findings of others with TBAOH, thus questioning the purpose of TBAOH addition to catalyst ink. The cell operation conditions were a current density based feed flow of O<sub>2</sub> and H<sub>2</sub> at 30 and 400 psig for the anode and cathode respectively. The cell was operated at 80°C and 100 °C for the anode humidifier and 85 °C for the cathode humidifier.

Yang et al,<sup>[8]</sup> also incorporated TBAOH into the MEA preparation. The membrane was converted to the Na<sup>+</sup> form by boiling it in NaOH. The catalyst was 20 wt% Pt/C which was made into slurry, to which 5 wt% Nafion was added along with other organic solvents. The protonated form of Nafion within the slurry was converted to the TBA<sup>+</sup> form by addition 1 M TBAOH dissolved in methanol. This gave it the thermoplastic property and 50% excess was also added to minimize the thermal

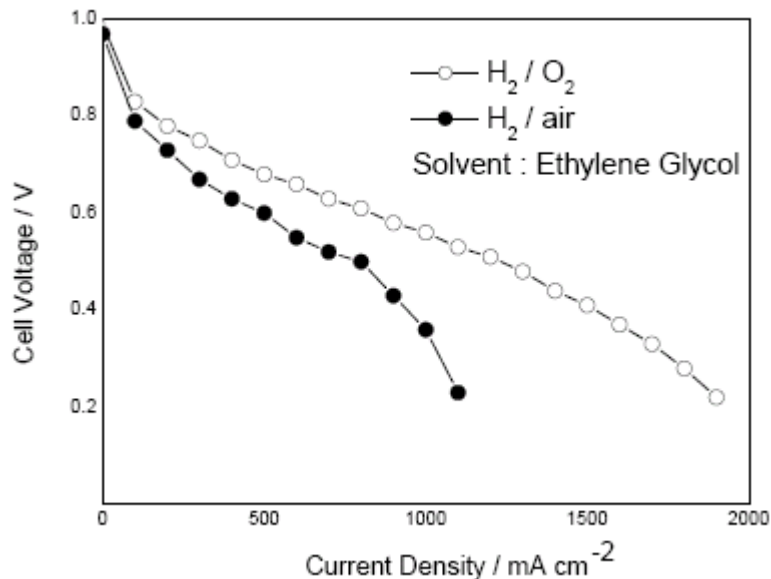
degradation of the ionomer. The TBAOH was added after the catalyst and Nafion were allowed to mix to avoid the coagulation that occurs with direct mixing. The authors did an analysis of dielectric constants and how the different forms of the solution behaved compared to predictions. The catalyst mixtures were applied using the painting method. For the solvent butyl acetate with a dielectric constant of 5.01 the performance was obtained are shown below in Figure 1.6.



**Figure 1.6 Butyl acetate**

At low dielectric constants a colloidal form of solution is said to form that would apply more homogeneously. To compare this, another slurry was made in the solution form using Ethylene Glycol, with a dielectric constant of 38.66. However the results deviated from what was suggested as seen in Figure 1.7.





**Figure 1.7 Ethylene Glycol**

As seen above ethylene glycol gave better performance than the butyl acetate despite being in the solution form. The preparation techniques were the same for each except that there was an addition of glycol to the butyl acetate slurry to increase paintability. The cell was operated at 80°C and fed with H<sub>2</sub> and O<sub>2</sub> with humidifier at 95°C. While this neither disproves nor affirmed the result of the addition of TBAOH, it did refute the idea that only low dielectric constant solvents, or colloidal solutions would result in good performance.<sup>[8]</sup>

In another experiment, where researchers S.-J. Shin et al.<sup>[9]</sup> followed the spray method to catalyze the gas diffusion layer, the primary objective of the research was to determine if solution inks based on isopropyl alcohol (IPA) or colloidal inks made with normal butyl-acetate (NBA) perform better. The preliminary treatment used for the solvent NBA was ultrasonic treatment, after which ink was sprayed onto carbon paper, already coated with carbon layer. Also, Nafion 115 membrane was pretreated earlier.

The preliminary treatment used for the solvent IPA was that the ink was fully suspended in IPA solvent, after which the ink was sprayed onto carbon paper, already coated with carbon layer. There was no drying temperature and time specified, however the hot-press pressure, time and temperature were 200 atm, 140°C and 1.5 minutes. The components of the catalyst slurry were Pt/C (40 wt % Pt), Nafion solution, and the solvent. The temperature used to operate a single cell under pure H<sub>2</sub>, O<sub>2</sub> and air was 80°C. The results of this research proved that the colloidal method performed better than the solution method. The current density at voltage 0.6 V was 700 mA/cm<sup>2</sup> for IPA and 800 mA/cm<sup>2</sup> for NBA.<sup>[9]</sup>

Wilson et al.<sup>[10]</sup> followed the catalyzed gas diffusion layer methodology using both the decal method and direct application method, where thermoplastic ionomers were used to assist low platinum loading electrodes for the fuel cells. The objective of the experiment was to use a thermoplastic agent of the solubilized ionomer in the membrane catalyzed process to obtain high performances with low platinum loading. The drying temperature implemented for the direct application methodology was 150°C. The hot-press pressure, time and temperature for the decal method were 30 atm, 5 minutes and 200-210°C. For the direct application method, the pressure used was 31 atm, while the hot-press time and temperature remained the same as for the decal method. The components used for the decal method were 20 wt % Pt, 5 wt % Nafion, 1M TBAOH (25-50% excess) in methanol, glycerol, Nafion 117, 105, DOW and Membrane "C." The components used for the direct application method were 20 wt % Pt, 5 wt % Nafion, 1M TBAOH (25-50% excess) in methanol and glycerol. The post treatment technique used for both methods was boiling the membrane in 0.5 M hot sulfuric acid (60 minutes) and

then rinsing with deionized H<sub>2</sub>O. The fuel cell station was operated at 80°C with H<sub>2</sub> with a pressure of 3 atm for H<sub>2</sub> and 5 atm for air. The humidification temperatures were 105°C and 90°C for the anode and cathode. It was found in the experiment that the addition of TBAOH in the slurry improves long-term performance and allows for smaller temperature requirements. The best performance was using the Dow membrane. At 0.60 V, the current density was greater than 1.5 A / cm<sup>2</sup>.<sup>[10]</sup>

The fuel cell station was operated at a cross sectional area of 9 cm<sup>2</sup>. 1.0 M methanol was supplied to anode chamber at rate of 1.0 ml/min while the O<sub>2</sub> pressure was 2 atm for both methods.. The best results were obtained with the multi layer electrode thin film, with 20% PTFE, with pore forming additive (NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub> and an operating temperature of 90°C. ).<sup>[10]</sup> Results can be seen below:

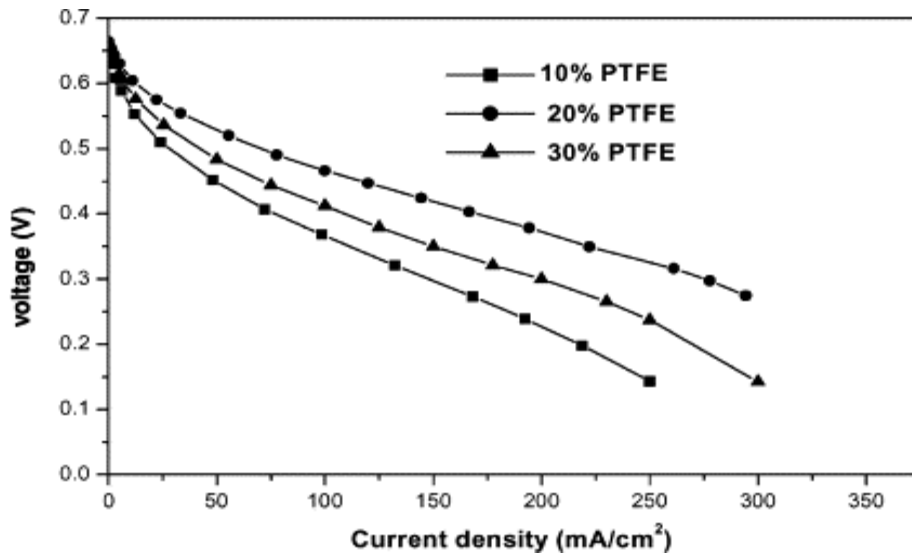


Figure1.8 Effect of PTFE in anode thin layer.<sup>[10]</sup>

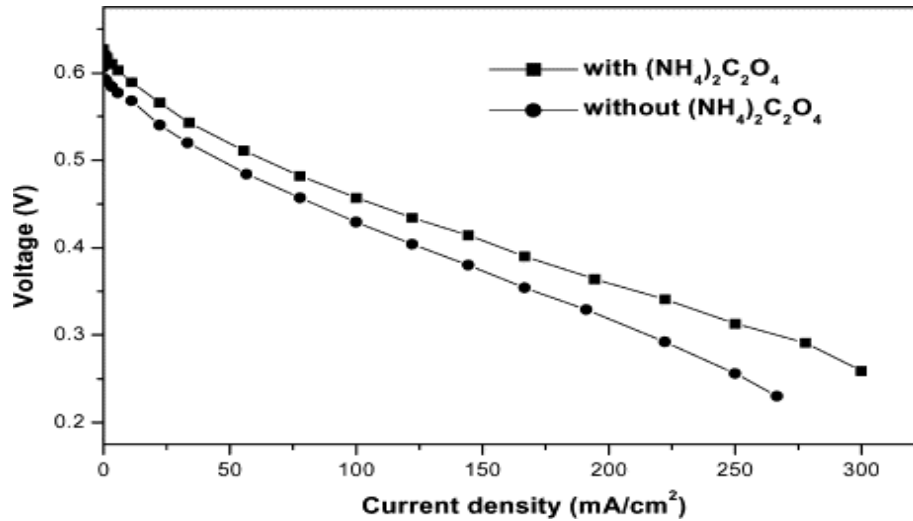


Figure 1.9 Effect of pore forming additive on anode film.<sup>[10]</sup>

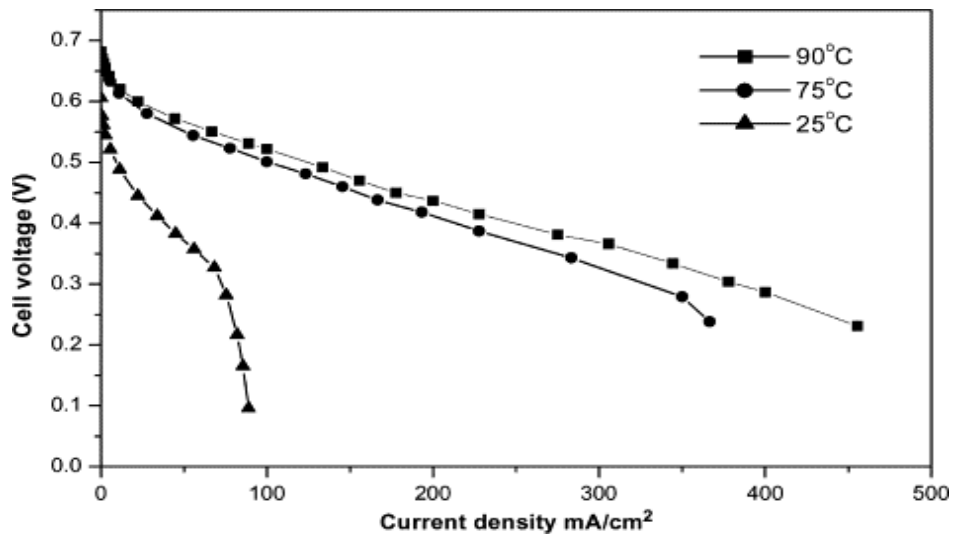


Figure 1.10 Current-voltage curves of the cell with the thin film at various temperatures.<sup>[10]</sup>

In another experiment, researchers Song et al. <sup>[11]</sup> implemented the catalyzed membrane method using the decal method. The goal of the experiment was to determine the effect of the performance of direct methanol fuel cells based on the decal procedure and the conventional method (direct application onto the membrane). The preliminary treatment was as follows: the Nafion 115 membrane was boiled in 3-5% H<sub>2</sub>O<sub>2</sub>, deionized water, 0.5 mol H<sub>2</sub>SO<sub>4</sub>, and deionized water (each 1 hour). The membrane was

then treated in boiling 0.5 mol NaOH, and deionized water two times for one hour each. The membrane was pre-heated at 160°C-200°C for one minute. The hot-press pressure, time and temperature used was 100 kg cm<sup>2</sup>, one minute and 160-200°C. The main components used for the experiment were Pt-Ru, 5% Nafion solution (water pre-wetted) and ethanol. The fuel cell station operating conditions were not specified. Results show that the decal method run with O<sub>2</sub> at 2 atm shows the best cell voltage as opposed to the decal run with air, and the conventional methods run with air, and O<sub>2</sub>. Results are shown in the following figures.<sup>[11]</sup>

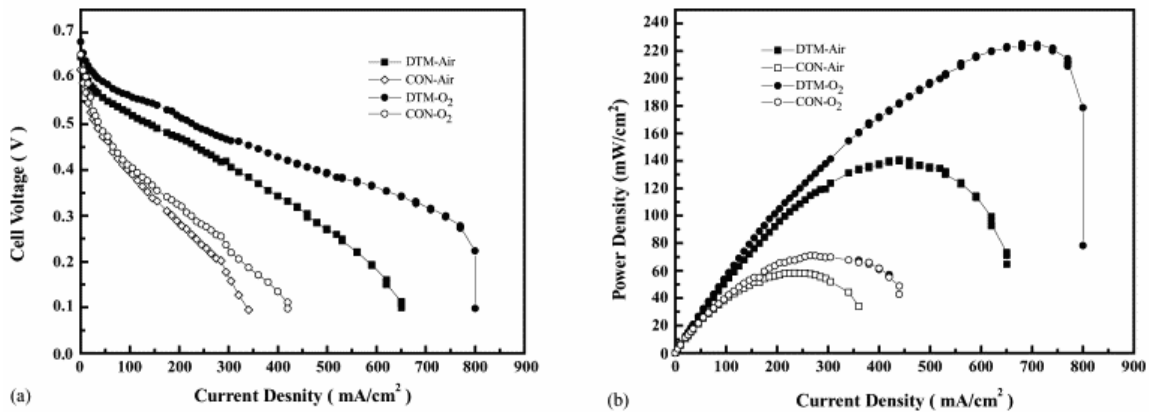


Figure 1.11 Single DMFC cell performance comparison.<sup>[11]</sup>

Another comparative study was done by Chun et al.<sup>[12]</sup> to determine if the conventional (catalyzed membrane) method or thin-film method (both direct coating and transfer printing) produced the best performance. The preliminary treatment for the conventional method was as follows: boiled membrane (Nafion 117) in 3 wt % H<sub>2</sub>O<sub>2</sub> (60 minutes), followed by deionized water (60 minutes), followed by a rinsing in fresh sample of deionized water (60 minutes), then rinsing in 0.5 M H<sub>2</sub>SO<sub>4</sub> (60 minutes) and finally boiling the membrane in two different samples of deionized water (60 minutes). The preliminary treatment for the thin-film method was as follows: boiling membrane

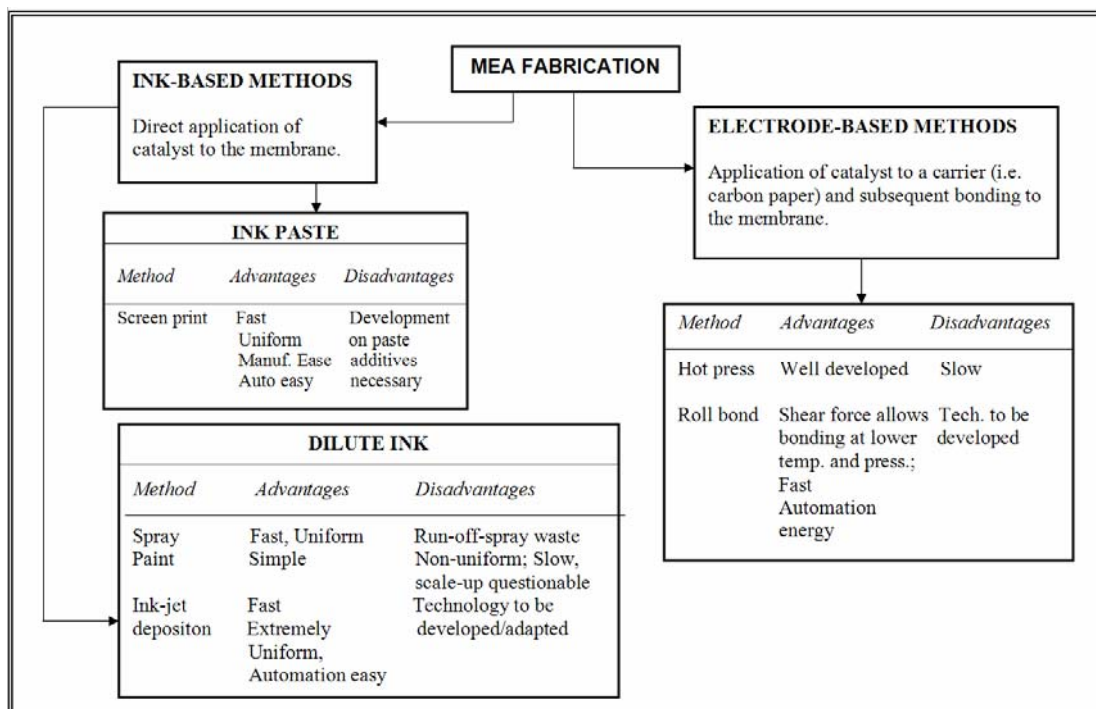
(Nafion 115) in 3 wt %  $\text{H}_2\text{O}_2$  (60 minutes), followed by a rinsing in deionized water (60 minutes) and finally rinsing in a of deionized water (60 minutes). The preliminary methodology for the direct coating method was the same as for the thin-film method with the only difference that for direct coating, the membrane was also pre-treated in 20 wt % NaOH, followed by a rinsing in deionized water (60 minutes), then dried in vacuum oven at  $80^\circ\text{C}$ . The drying temperature and time for the conventional method was 1 day air dry, followed by  $225^\circ\text{C}$  for 30 minutes . The membrane was dried at  $80^\circ\text{C}$  for 60 minutes after the membrane was coated in Nafion. The drying temperature and time for the thin-film direct coating method was  $140^\circ\text{C}$  for 60 minutes on a vacuum table, while for the transfer printing method, the values were  $135^\circ\text{C}$  for 120 minutes in a vacuum oven. The hot-press pressure, time and temperature for the conventional method were 193 atm, 3 minutes and  $145^\circ\text{C}$ . The hot-press pressure, time and temperature for both the thin-film direct coating method and transfer printing method were 77 atm, 1.5 minutes and  $195^\circ\text{C}$ . The components for the conventional method were 20 wt % Pt-C, PTFE emulsion, a bridge-builder, a peptization agent and 5 wt % Nafion solution. The components for the thin-film method for both methods were 5 wt % Nafion, 20 or 40 wt % Pt-C, glycerol and TBAOH in methanol. The post-treatment for all three methods was a rinsing in 0.5 M  $\text{H}_2\text{SO}_4$  (60 min) followed by a rinsing in deionized water. The fuel cell station was operated at a temperature of  $60\text{-}90^\circ\text{C}$  under  $\text{H}_2/\text{O}_2$ . The humidification temperature was 90 and  $80^\circ\text{C}$  for  $\text{H}_2$  and  $\text{O}_2$ . Results show that the thin-film method for direct coating gave the highest performance having a current density of approximately  $400 \text{ mA}/\text{cm}^2$  at  $0.6 \text{ V}$ .<sup>[12]</sup>

## ***Project Goals and Objectives***

The goal of this project is to identify the factors that influence MEA performance. This knowledge will then be utilized to develop a procedure for the fabrication of higher performance MEA. A comparison will then be made of the MEA to commercially available MEA. The objectives that we fulfilled to achieve our goal within the project were the following:

- Compare different MEA preparation Techniques to determine which produces better MEA.
- Systematically investigate the degree to which a parameter (such as thickness, sorption, conductivity, dielectric constants just to name a few) affects MEA performance.
- Design a procedure for the production of high performance MEAs.

There are many methods for fabrication of MEAs. As seen in Table 1.1, there are ink-based methods as well as electrode-based methods, listing sub-methods along with their advantages and disadvantages. There are two sub-methods of the ink-based methods: ink paste and dilute ink. In our experiments, both ink-based and electrode-based methods were implemented. In particular, both the spray and painting method were used from the ink-based methods in our laboratory investigations. As seen below there are many different possibilities of the fabrication of MEAs.



**Table 1.1 MEA fabrication methods.**<sup>[13]</sup>

In the course of our investigation, we found that the painting method is difficult to reproduce and is a very tedious process. Also, the thin layers applied to the Teflon blanks were difficult to apply evenly throughout the surface. Due to repetitions of the application of the catalyst slurry onto the Teflon surface and baking, the dried catalyst flaked off of the blanks and hence could not be tested. As for the electrode-based methods in which the catalyst slurry was sprayed onto the carbon paper, there was an uneven catalyst layer, some of the catalyst was being wasted and not all was present at the three-phase interface. The best reproducible results were obtained using the spray method. This method proved not only to be accurate, but fast as well. Though there was literature found where the paint method was used and gave high performance, in general most of the literature found implemented the spray method, which overall gave the best performance.<sup>[11]</sup>



## Chapter II. MEA Theory

The contents in this section provide a detailed derivation of the equations used to describe the PEM fuel cell model originally proposed by Thampan et al.<sup>[1]</sup> The equations themselves and model were taken from a previous paper discussing the PEMFC as a membrane reactor. Understanding the theory behind PEM fuel cell model will enable us to understand what factors affect MEA performance and will assist us in predicting the performance of our MEAs based on those factors.<sup>[1]</sup>

Within this section, a detailed drawing of the PEMFC is presented as well as the in depth derivation of equations that make up the fuel cell model. This information is provided to supply a theoretical understanding of the MEA. Using the theory, the model is then used to show a single cell performance and predict the effect of certain physical parameters on PEM fuel cell performance. This understanding should provide insights into the dominant processes and resistances and how the performance might be improved.

### ***PEMFC Model***

A model of the PEMFC that was used within our research can be shown below in Figure 2.1.

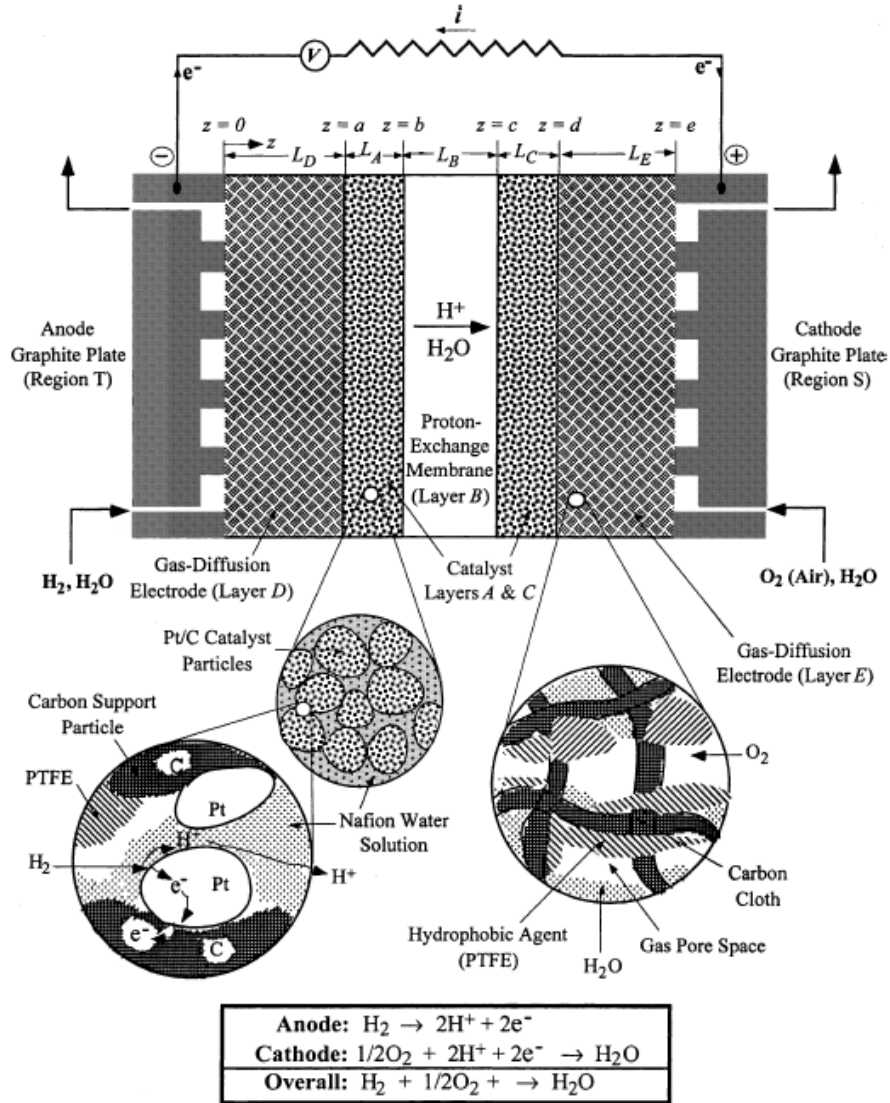


Figure 2. 1 A schematic representation of the PEMFC cross-section consisting of gas-diffusion backing (layers D and E), catalyst layers (layers A and C), and the PEM (layer B).<sup>[1]</sup>

### Constitutive Relations

The mass balance for species  $i$  ( $i = 1, 2, \dots, n$ )

$$\nabla \cdot N_i = \sum_{\rho=1}^q i_{\rho} r_{\rho} \tag{2-1}$$

can be solved in the different layers of the fuel cell.

In order to do this, flux is needed in each different layer along with the kinetics at the cathode and anode reactions. The current density is obtained from

$$i = F \sum_{i=1}^n z_i N_i \quad (2-2)$$

once the fluxes are determined.

### *Dusty Fluid Model*

The dusty-fluid model (DFM) is the flux model for  $N_i$  in a porous layer  $\alpha$ . By summing all of the species, the Stefan-Maxwell terms cancel out. After eliminating the convective driving force on its right hand side, the DFM can be written as

$$-c_i / RT \nabla_T \mu_i^e = \sum_{\substack{j=1 \\ j \neq i}}^n 1 / c D_{ij}^e (c_j N_i - c_i N_j) + N_i / D_{iM}^e - c_i B_o RT / \mu D_{iM}^e W \sum_{j=1}^n N_j D_{jm}^e \quad (2-3)$$

( $i=1, 2, \dots, n$ )

This other form of the DFM includes the driving force on the left-hand side, and all the fluxes on the right hand side. It is important to note here that if the ratio of fluxes ( $N_j / N_i$ ) are known through the stoichiometry, the Fickian form for flux may be attained

$$N_i = -\frac{1}{RT} D_i^e c_i \nabla_T \mu_i^e \quad (i=1, 2, \dots, n) \quad (2-4)$$

where the effective diffusivity is given by

$$\frac{1}{D_i^e} = \sum_{\substack{j=1 \\ j \neq i}}^n \frac{1}{c D_{ij}^e} (c_j - c_i \frac{N_j}{N_i}) + \frac{1}{D_{iM}^e} - \frac{c_i B_o RT}{\mu D_{iM}^e W} \sum_{j=1}^n \frac{1}{D_{jm}^e} \frac{N_j}{N_i} \quad (i=1, 2, \dots, n) \quad (2-5)$$

### **Transport of gases in gas-diffusion backing (layers D and E)**

The effective diffusivity in a partially liquid-filled porous layer  $\alpha$  is given by the equation

$$D_{i\alpha}^e = (1 - q_w)^q D_{iG}^e + q_w^q \kappa_{iL} K_1 D_{iL} \approx (1 - q_w)^q D_{iG}^e \quad (2-6)$$

where  $D_{iL}$  is the liquid-phase diffusivity and  $D_{iG}^e$  is the gas-phase diffusivity for the *dry* porous layer. Equation (2-6) accounts for transport of the or through the gas pore space as well as any through the liquid. It is assumed that low solubility is not important with the flux contribution of the aqueous phase and hence right hand side can be approximated (small partition coefficient,  $\kappa_{iL}$ ). The gas phase diffusivity is written in terms of partial pressures, not concentrations

$$\frac{1}{D_{iG}^e} = \frac{1}{D_{iK}^e} + \sum_{\substack{j=1 \\ j \neq i}}^n \frac{1}{D_{ij}^{e0}} (p_j - p_i \frac{N_j}{N_i}) - \frac{p_i B_0}{\mu W D_{iK}^e} \sum_{j=1}^n \frac{N_j}{N_i} \frac{1}{D_{jK}^e} \quad (2-7)$$

( $i=1, 2, \dots, n$ )

Secondly, it is assumed that the gas phase within the pores is saturated with vapor, which is another way of saying that the partial pressure of water is equal to its vapor pressure. Basically, there is no partial pressure gradient of water vapor in GDB under isothermal conditions. Also, it is an assumption that water transport occurs only in the liquid phase. Further, it is assumed that the fluxes of the diluent species,  $N_d$ , are equal to zero. Using Equation (2-7) which simplifies the DFM, the effective diffusivity for  $i$ , ( $H_2$  in the case of anode, or  $O_2$  in the case of cathode) is

$$\frac{1}{D_{iG}^e} = \frac{p_w}{D_{iG}^{e0}} + \frac{p_d}{D_{id}^{e0}} + \frac{1}{D_{iK}^e} \left\{ \frac{1 + (B_0 / \mu)((p_w / D_{wK}^e) + (p_d / D_{dK}^e))}{1 + (B_0 / \mu)((p_i / D_{iK}^e) + (p_w / D_{wK}^e) + (p_d / D_{dK}^e))} \right\} \quad (2-8)$$

### Transport of protons in PEM (layer B)

It is apparent that for the binary case of proton transport in a PEM with water as the solvent (species  $w$ ), hydronium ion ( $H_3O^+$ ), denoted as species  $H^+$ , as the charge carrier and a spatially uniform sulfonic acid groups within PEM together with electroneutrality

and assuming equimolar counter-diffusion, due to the similarity among water and the hydronium ion, the effective diffusivity equations become

$$\frac{1}{D_{H^+}^e} \approx \frac{1}{D_{H^+w}^e} + \frac{1}{D_{H^+M}^e} \quad (2-9)$$

Further, with  $\sigma = (F^2 / RT)D_{H^+}^e c_{H^+}$ , and  $c_{H^+} = c_{HA,0}\alpha$ , and in terms of the equivalent

conductance,  $\lambda_{H^+}^0 \equiv F^2 \left|_{z_{H^+}} \right| D_{H^+w}^e / RT$ , the conductivity of the PEM becomes

$$\sigma = (\varepsilon_B - \varepsilon_{B0})^q \left( \frac{\lambda_{H^+,298}^0}{1 + \delta} \right) \exp \left\{ \frac{E_\mu}{R} \left( \frac{1}{T} - \frac{1}{298} \right) \right\} c_{HA,0} \alpha \quad (2-10)$$

where the ratio  $\delta \equiv D_{H^+w}^e / D_{H^+M}^e$ , and the degree of dissociation in terms of the equilibrium constant  $K_{A,C}$  is

$$\alpha = \frac{(\lambda + 1) - \sqrt{(\lambda + 1)^2 - 4\lambda(1 - 1/K_{A,C})}}{2(1 - 1/K_{A,C})} \quad (2-11)$$

where

$$K_{A,C} = K_{A,C,298} \exp \left( \frac{-\Delta H^0}{R} \left( \frac{1}{T} - \frac{1}{298} \right) \right) \quad (2-12)$$

Both the number of water molecules sorbed per acid group and the number of volume fraction are related where

$$\varepsilon_B = \frac{\lambda}{(\bar{V}_M / \bar{V}_w) + \lambda} \quad (2-13)$$

where  $\bar{V}_M \approx EW / \rho_0 = 537 \text{ cm}^3 / \text{mol}$ , and  $\bar{V}_w = 18 \text{ cm}^3 / \text{mol}$ . The water molecules sorbed can be written in terms of relative humidity,  $a_w$

$$\frac{\lambda}{\lambda_m} = \frac{[C a_w / (1 - a_w)] \left[ 1 - (n_w + 1) a_w^{n_w} + n_w a_w^{n_w + 1} \right]}{1 + (C - 1) a_w - C a_w^{n_w + 1}} \quad (2-14)$$

### Electrocatalysis: general considerations

In this section, it is important to consider how rates are influenced by potential. Consider the electrode surface reaction  $\rho$

$$\sum_{\substack{i=1 \\ i \neq e^-}}^n \nu_{\rho i} A_i^{z_i} + \nu_{\rho e^-} e^- = 0 \quad (2-15)$$

among  $n$  species,  $A_i^{z_i}$ , carrying a charge  $z_i$ , where  $\nu_{\rho e^-}$  is the stoichiometric coefficient of the electron in reaction  $\rho$ . It is true that  $\nu_{\rho e^-} = +n_\rho$  for an anodic reaction while  $\nu_{\rho e^-} = -n_\rho$  for a cathodic reaction, where  $n_\rho$  is the number of electrons involved in the reaction  $\rho$ . As a result, overall charge balance in the electrode reaction is

$$\sum_{\substack{i=1 \\ i \neq e^-}}^n \nu_{\rho i} z_i = \nu_{\rho e^-} \quad (2-17)$$

The net rate of reaction per unit supported metal catalyst surface area,  $r_\rho^*$  from the thermodynamic formulation of the transition-state theory (TTST) for an *elementary* electrode reaction  $\rho$  is

$$r_\rho^* = \vec{r}_\rho^* - \overleftarrow{r}_\rho^* = \vec{k}_\rho^* \prod_{i=1}^r a_i^{-\nu_{\rho i}} - \overleftarrow{k}_\rho^* \prod_{i=r+1}^r a_i^{-\nu_{\rho i}} \quad (2-17)$$

where the first  $r$  of the total of  $n$  species are assumed to be the reactants while the remaining are products. The potential dependence of the rate constant

$$\vec{k}_\rho^* = \vec{k}_{\rho, \phi_0} \exp\left\{\frac{\beta_\rho \nu_{\rho e^-} - F\eta}{RT}\right\}, \overleftarrow{k}_\rho^* = \overleftarrow{k}_{\rho, \phi_0} \exp\left\{\frac{(\beta_\rho - 1)\nu_{\rho e^-} F\eta}{RT}\right\}, \quad (2-18)$$

where  $\vec{k}_{\rho, \phi_0}$  is the rate constant at the equilibrium electrode potential  $\Phi_0$ ,

$$\vec{k}_\rho^* \equiv A_\rho \exp\left(\frac{E_{\rho, \phi_0}}{RT}\right) \quad (2-19)$$

and similarly for  $\overleftarrow{k}_{\rho, \phi_0}$ . Under open-circuit conditions for the equations (2-17) and (2-18) can be written as

$$\overrightarrow{r}_{\rho 0} = \overrightarrow{k}_{\rho, \phi_0}^* \prod_{i=1}^r a_i^{-\nu_i} = \overleftarrow{r}_{\rho 0} = \overleftarrow{k}_{\rho, \phi_0}^* \prod_{i=r+1}^n a_i^{\nu_i} \quad (2-20)$$

which means that forward and reverse reactions rates are equal and a dynamic equilibrium is established. Using the kinetic equations and equations (2-18), equation (2-17) can be written in the Butler-Volmer (pseudo-irreversible) form

$$r_{\rho}^* = k_{\rho}^* \prod_{i=1}^r a_i^{-\nu_i} \quad (2-21)$$

where the rate constant is written as

$$k_{\rho}^* = \overleftarrow{k}_{\rho, \phi_0}^* \left\{ \exp\left(\frac{\beta_{\rho} \nu_{\rho e^-} F \eta}{RT}\right) - \exp\left(\frac{(\beta_{\rho} - 1) \nu_{\rho e^-} F \eta}{RT}\right) \right\} \quad (2-22)$$

For the common value  $\beta_{\rho} = \frac{1}{2}$ , this may be written in the more convenient alternate

form

$$k_{\rho}^* = \overleftarrow{k}_{\rho, \phi_0}^* \left\{ 2 \sinh\left(\frac{\nu_{\rho e^-} F \eta}{2RT}\right) \right\} \quad (2-23)$$

The corresponding current density of  $i^*$  is found from

$$i^* = F \nu_{\rho e^-} r_{\rho}^*, \quad i_0^* = F \nu_{\rho e^-} r_{\rho 0}^* \quad (2-24)$$

for open and closed circuit cases. The current density  $i$  in terms of A/cm<sup>2</sup> of geometric

(MEA) area is  $i = \gamma_M i^*$  and  $i_0 = \gamma_M i_0^*$ . The equation used to show the ratio of electrochemically active metal catalyst surface area to the geometric MEA area (aka roughness factor) is

$$\gamma_M = \phi_I m_M \left( \frac{6\phi_M}{\rho_M d_M} \right) \quad (2-25)$$

Using Equation (2-25), the current density is related to exchange-current density and over-potential by

$$\frac{i^*}{i_0^*} = \frac{i}{i_0} = \left\{ 2 \sinh \left( \frac{v_{pe} - F\eta}{2RT} \right) \right\} \quad (2-26)$$

For large overpotential  $\eta$ , this reduces to the familiar Tafel equation

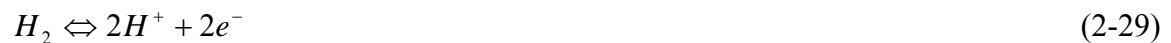
$$\frac{i}{i_0} \approx \exp \left( \frac{v_{pe} - F\eta}{2RT} \right) \quad (2-27)$$

whereas a linear approximation is used for a small overpotential  $\eta$ , written as

$$\frac{i}{i_0} \approx \frac{v_{pe} - F\eta}{RT} \quad (2-28)$$

### Hydrogen oxidation reaction

The catalytic hydrogen electrode reaction (HOR)





The rate expression for the hydrogen electrode reaction is

$$r_A^* = \overrightarrow{k}_A^* c_{H_2} \exp\left(\frac{\overrightarrow{\alpha}_A F \eta_A}{RT}\right) - \overleftarrow{k}_A^* c_{H^+}^2 \exp\left(\frac{-\overleftarrow{\alpha}_A F \eta_A}{RT}\right) \quad (2-30)$$

The HOR can be simplified using  $\overrightarrow{\alpha}_A = \overleftarrow{\alpha}_A = \frac{1}{2}$ , and be written in the pseudo-irreversible form

$$r_A^* = k_A^* c_{H_2} \quad (2-31)$$

with

$$k_A^* = \overrightarrow{k}_{A,\phi_0}^* \left\{ 2 \sinh\left(\frac{\overrightarrow{\alpha}_A F \eta_A}{RT}\right) \right\} \quad (2-32)$$

### Oxygen reduction reaction

The kinetics of the catalytic oxygen reduction reaction (ORR)



The rate expression for the oxygen reduction reaction is

$$r_C^* = k_C^* c_{O_2} c_{H^+} \quad (2-34)$$

with

$$k_C^* = \overrightarrow{k}_{C,\phi_0}^* \left\{ 2 \sinh\left(\frac{-\overrightarrow{\alpha}_C F \eta_C}{RT}\right) \right\} \quad (2-35)$$

### MEA analysis

In order to derive MEA performance in terms of the different layers, the following steady-state one-dimensional conservation equations are considered:

#### Anode Chamber (Region T)

$$F_T(c_{iT,0} - c_{iT}) = N_{iz}(0) \cdot A \quad (2-36)$$

### GDB (Layers D and E)

$$\frac{dN_{iz}}{dz} = 0, \quad N_{iz} = -D_{i\alpha}^e \frac{dc_i}{dz} \quad (2-37)$$

### PEM (Layer B)

$$\frac{di}{dz} = 0, \quad i = -\sigma \frac{d\phi}{dz} \quad (2-38)$$

### Catalyst (Layers A and C)

$$\frac{dN_{iz}}{dz} = v_{\rho i} r_{\rho}, \quad N_{iz} = -\frac{1}{RT} D_{i\alpha}^e \left( \frac{dc_i}{dz} + z_i c_i F \frac{d\phi}{dz} \right) \quad (2-39)$$

### Cathode Chamber (Region S)

$$F_s(c_{iS,0} - c_{iS}) = N_{iz}(e) \cdot A \quad (2-40)$$

Many assumptions were made for equations (2-36) through (2-40). The assumptions are as follows: the anode and cathode chamber equations represent a single fuel cell, not the entire stack, pure oxygen and hydrogen were used, and the GDBs' diffusivity were need constant with respect to its position. By integrating Fickian flux equation for constant flux, constant effective diffusivity is

$$N_{i\alpha} = P_{i\alpha} \left\{ c_{iG} - \frac{c_{i\alpha}(L_{\alpha})}{\kappa_{i\alpha}} \right\} \quad (2-41)$$

In this equation, the permeability of species  $i$  is  $P_{i\alpha} \equiv \kappa_{i\alpha} D_{i\alpha} / L_{\alpha}$ , where  $\kappa_{i\alpha} \equiv (c_{i\alpha} / c_{iG})_{eq}$  is the partition coefficient for phase  $\alpha$ .

For the PEM with constant conductivity, the solution is

$$i = \frac{\sigma}{L_B} \{ \phi_{S,B}(b) - \phi_{S,B}(c) \} \quad (2-42)$$

In order to obtain a simple analytical solution, we will assume the catalyst layers are thin enough that (i) there is no potential drop and further, (ii) there are no diffusional limitations within these layers. The rate of the anodic reaction within the catalyst layer under these assumptions can be written as  $r_A^* = k_A^* c_{H_2,A}(a)$  from Equation (2-31). Making the assumption that the concentration of hydrogen throughout the catalyst layer is equal to its value at  $z=a$  and using these equations:  $i_A^* = Fv_{Ae^-} r_A^*$  and  $i_A = \gamma_M i_A^*$  gives the anode current density which can be written as

$$i_A = \gamma_{MA} F v_{Ae^-} k_A^* c_{H_2,A}(a) \quad (2-43)$$

where the rate constant for the anode layer is given by Equation (2-32) while  $\gamma_{MA}$  is given by Equation (2-25). Similarly, the anode exchange-current density is

$$i_{A,0} = \gamma_{MA} F v_{Ae^-} \overrightarrow{k_{A,\phi_0}^*} \kappa_{H_2,A} c_{H_2,T} \quad (2-44)$$

under equilibrium conditions.

The hydrogen flux at  $z=a$  for a PEM that is impervious to it is obtained from material balance

$$N_{H_2}(a) = \gamma_{MA} (-v_{AH_2}) k_A^* c_{H_2,A}(a) \quad (2-45)$$

The flux of hydrogen in the gas-diffusion backing of anode (Layer D) is obtained by Equation (2-41)

$$N_{H_2}(0) = N_{H_2}(a) = P_{H_2,D} \left\{ c_{H_2,T} - \frac{c_{H_2,A}(a)}{\kappa_{H_2,A}} \right\} \quad (2-46)$$

An expression for the anodic current density can be obtained by equating Equations (2-25) and (2-46), solving for  $c_{H_2,A}(a)$ , and then using it in

$$i_A = \frac{\gamma_{MA} v_{Ae^-} F k_{A,\phi_0}^* \kappa_{H_2,A} c_{H_2,T}}{1 + (\gamma_{MA} (-v_{AH_2})) k_A^* \kappa_{H_2,A} / P_{H_2,D}} \quad (2-47)$$

Equation (2-47) is simplified to

$$i_{A,L} = \left( \frac{v_{Ae^-}}{v_{AH_2}} \right) F P_{H_2,D} c_{H_2,T} \quad (2-48)$$

Using Equations (2-22) and (2-48) in (2-47) with some rearranging the equation is written

$$\frac{k_A^*}{k_{A,\phi_0}^*} = \left\{ \frac{i_A / i_{A,0}}{1 - i_A / i_{A,L}} \right\} \quad (2-49)$$

Now, using Equation (42) in (62) we can solve for the anodic overpotential

$$\eta_A = \frac{RT}{\alpha_A F} \sinh^{-1} \left[ \frac{1}{2} \left\{ \frac{i_C / i_{C,0}}{1 - i_A / i_{A,L}} \right\} \right] \quad (2-50)$$

A similar derivation on the cathode (Layer C) yields an expression for the cathodic overpotential

$$-\eta_C = \frac{RT}{\alpha_C F} \sinh^{-1} \left[ \frac{1}{2} \left\{ \frac{i_C / i_{C,0}}{1 - i_C / i_{C,L}} \right\} \right] \quad (2-51)$$

where the cathodic limiting current is

$$i_{C,L} \equiv \left( \frac{v_{Ce^-}}{-v_{C,O_2}} \right) F P_{O_2,E} c_{O_2,S} \quad (2-52)$$

### Overall fuel cell performance

To find a relationship between voltage and current, the above results are combined to give

$$V = V_0 - \frac{RT}{\alpha_A F} \sinh^{-1} \left\{ \frac{1}{2} \left( \frac{i/i_{A,0}}{1-i/i_{A,L}} \right) \right\} - \frac{RT}{\alpha_C F} \sinh^{-1} \left\{ \frac{1}{2} \left( \frac{i/i_{C,0}}{1-i/i_{C,L}} \right) \right\} - i \left( \frac{L_B}{\sigma_B} \right) - i(R_l)$$

(2-53)

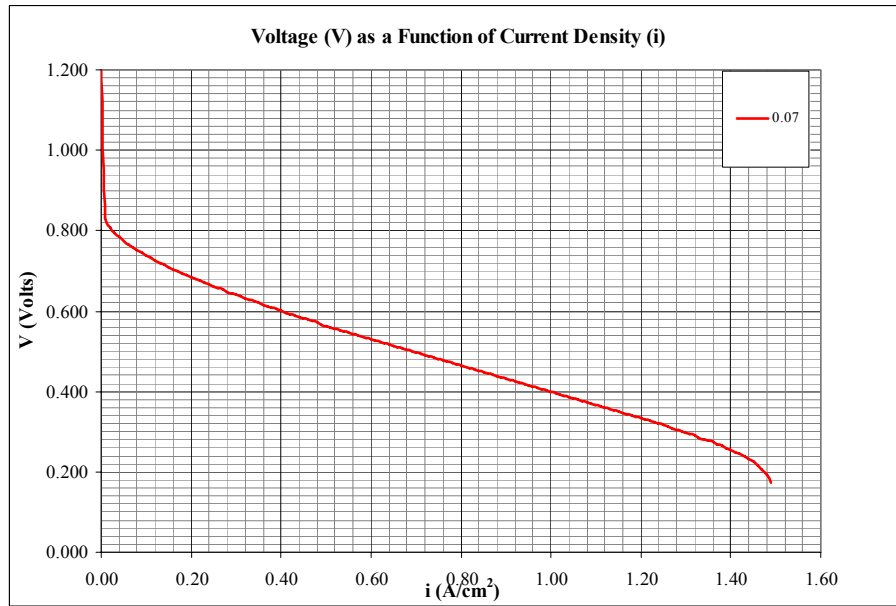
## Fuel Cell Single Stack Model

The PEMFC single stack model from the previous section can be used to investigate operating characteristics for a PEMFC and the effect of various operating and design parameters. These operating curves make it possible to choose conditions that maximize power density, efficiency and current density of the cell. The operating characteristics for the PEMFC are very important for creating a high performing MEA because they can aid in the evaluation of the extent to which a factor may be important in overall performance.

$V_o$	1.23 volts	$\vec{\alpha}_c$	1
R	8.314 J/mol*K	$i_{C,0}^*$	$1*10^{-11} \text{ cm}^2 \text{ Pt}$
T	353 K	$i_{C,0}$	$1.5*10^{-9} \text{ A/cm}^2$
$\vec{\alpha}_A$	0.5	$i_{C,L}$	$1.5 \text{ A/cm}^2$
F	96485 C/eq	$L_B$	0.0125 cm
$i_{A,0}^*$	$1*10^{-3}$	$\sigma_B$	0.07 S/cm
$i_{A,0}$	$0.15 \text{ A/cm}^2$	$R_l$	0
$i_{A,L}$	$4 \text{ A/cm}^2$	$\gamma_M$	$150 \text{ cm}^2/\text{cm}^2$

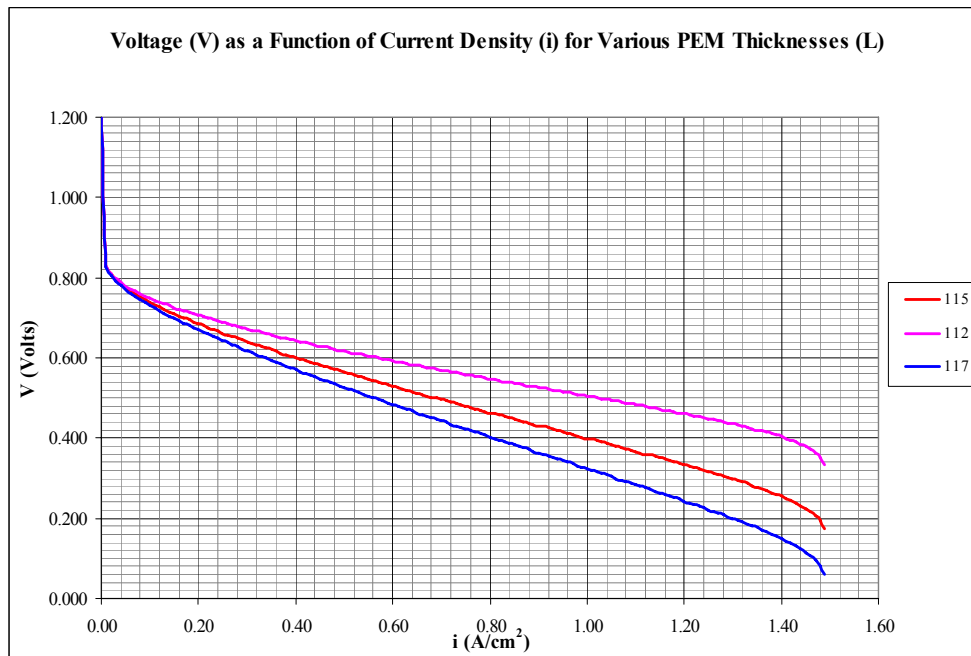
**Table 2. 1 Fuel cell model parameters.**

Using the parameters listed in Table 2.1 the MEA performance can be performed. The parameters in Table 2.1 were modeled in Figure 2.2.



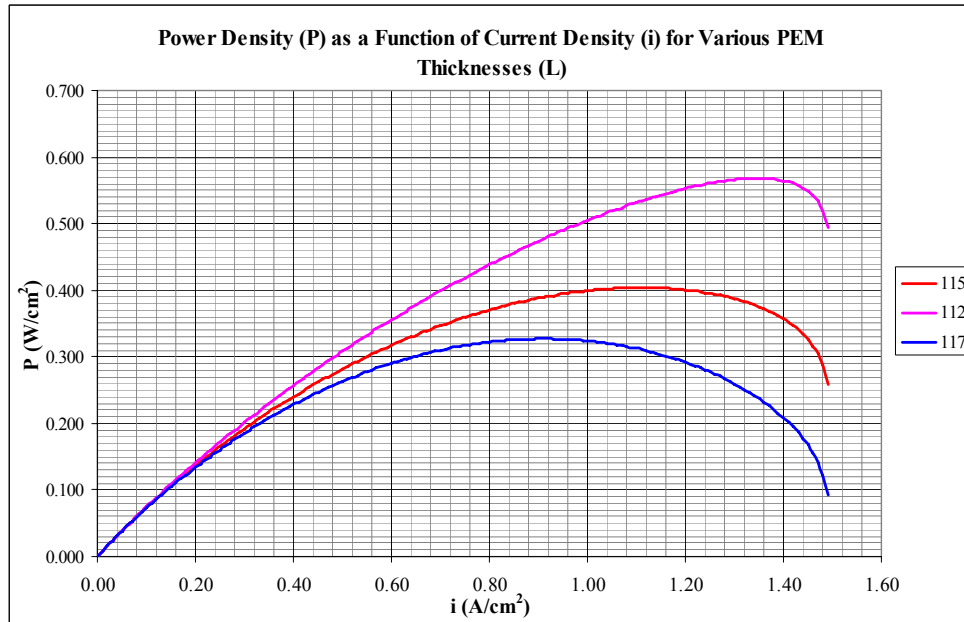
**Figure 2.2 Voltage versus current density**

Using this initial model several of the parameters can be easily varied to develop a model comparison of the role each factor plays in MEA performance. For example if we take the membrane thickness a variable, we can model the effect it has on MEA performance, which is shown in Figure 2.3.



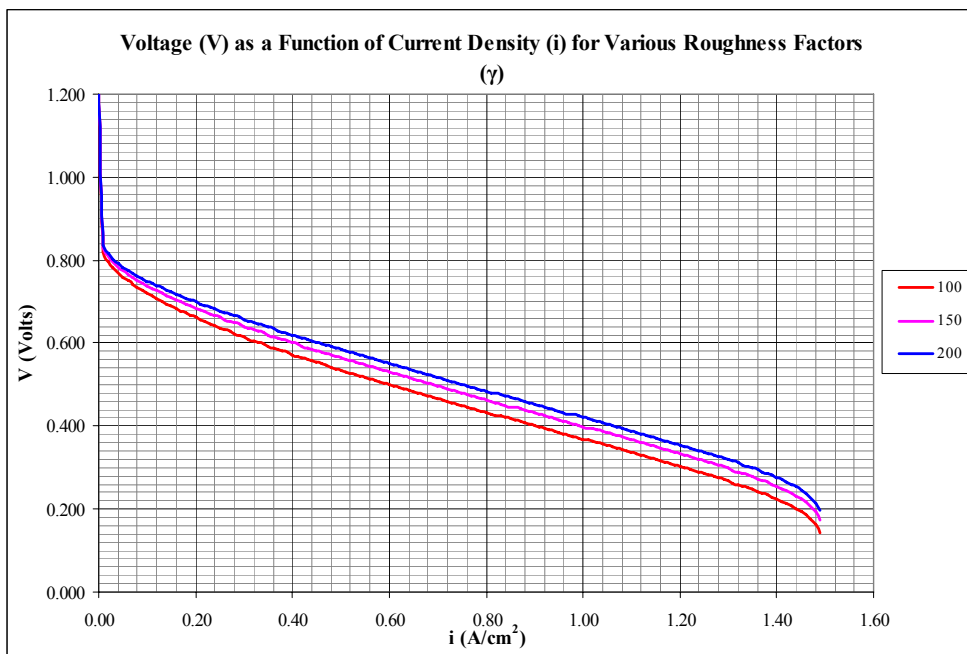
**Figure 2.3 Membrane Thickness Comparison**

Similarly, using the relationship between power and voltage, the power density can be predicted as shown in Figure 2.4.



**Figure 2.4 Power Density vs. Current Density - Thickness Comparison**

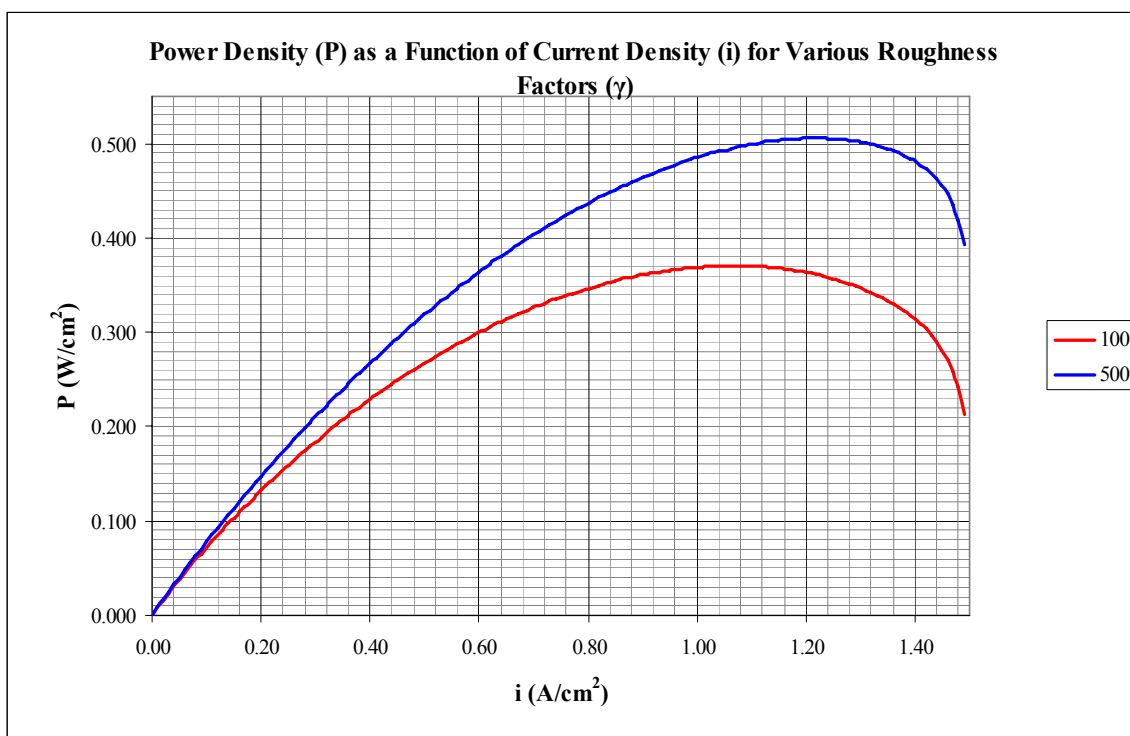
Another parameter that can be investigated is the roughness factor  $\gamma$ , which changes with Nafion content and amount of catalyst in the mixture being applied to the membrane. The result of varying this is shown in Figure 2.5.



**Figure 2.5 Roughness Factor Comparison**



While it does play a role in the overall performance of PEM fuel cells, only significant changes to the roughness factor affect the overall performance of the PEM fuel cell sign. The effect of roughness factor on power density can be seen in Figure 2.6.



**Figure 2.6 Power: Roughness Factor Comparison**

For a roughness factor of  $100 \text{ cm}^2/\text{cm}^2$  at  $1 \text{ A}/\text{cm}^2$  you get about  $0.4 \text{ W}/\text{cm}^2$ . To increase to  $0.5 \text{ W}/\text{cm}^2$  (at the same current) the roughness factor has to be almost five times as much. While this may be possible, the stability of the membrane may become an issue. Thus, it may not be wise to change the catalyst slurry solely to improve the roughness factor, but instead find a way to roughen the membrane before application of the catalyst ink.

In PEM fuel cells humidification is one of the key aspects in determining how much the fuel cell costs as well as how well the MEA will perform. This is due to the fact that at lower humidities the membrane becomes too dry and its resistance increases, thus lowering its relative humidity conductivity. Conversely, at too high humidity the membrane gets flooded with water and this inhibits the reactions in the fuel cell. As a result, the humidification for PEM fuel cells must maintain a balance in order to maintain good conductivity. In Figure 2.7, one can see the effect of conductivity,  $\sigma$ , on the overall performance.

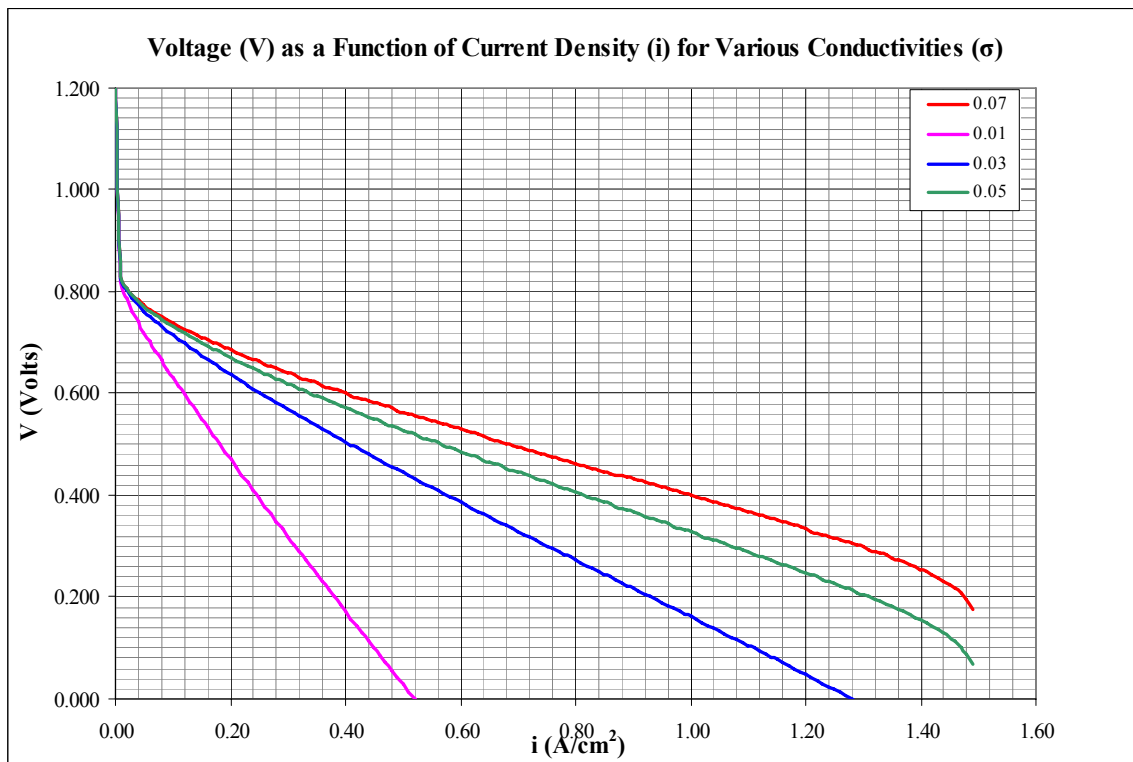
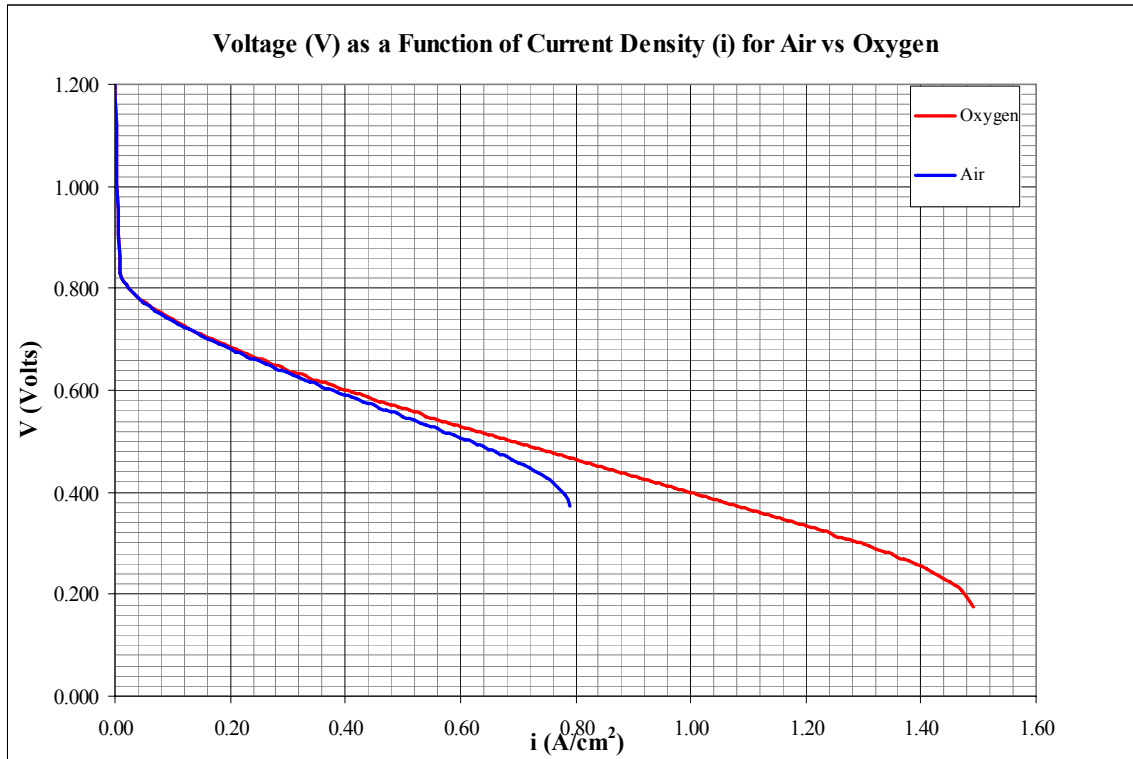


Figure 2.7 Conductivity Comparison

Finally, the operating conditions of the PEM fuel cell may be examined to determine the effect they have on the overall performance for example using air as cathode feed instead of  $O_2$ . This would result in a cathode limiting current density,  $i_{C,L}$ , of  $0.8A/cm^2$  A comparison of  $O_2$  to Air can be seen in Figure 2.8 below.



**Figure 2.8 Cathode Limiting Current density comparison: Air vs. Oxygen**

## Membrane Sorption

A sorption theory was modeled by Choi et al.<sup>[2]</sup> to determine the amount of swelling that occurs within the membrane. Swelling occurs when the Nafion membrane absorbs the organic solvent used into it. This is a very important factor seeing as more the swelling a membrane endures, the more deformed it becomes and performance is hindered. For the projects purpose, we are only interested in swelling of the vapor phase.<sup>[2]</sup>

The two equations that govern absorption are

$$\lambda_i^C = \lambda_{i,m} \left( \frac{K_1 a_i}{1 - a_i} \right) \left\{ \frac{1 - (\nu + 1)(a_i)^\nu + \nu(a_i)^{\nu+1}}{1 + (K_1 - 1)a_i - K_1(a_i)^{\nu+1}} \right\} \quad (2-54)$$

in which  $\lambda_i^C$ , is the type of equation where the solvent molecules strongly interact with the acid sites.  $\lambda_{i,m}$  is the monolayer coverage of absorbed molecules,  $K_1$  is the first ionization constant of sulfuric acid,  $\nu$  is the number of chemical equilibrium steps of the reaction,  $\nu$  is Poisson's ratio (0.5 in this case) and  $a_i$  is the activity of the organic solvent in the vapor phase.

In order to determine the solvent uptake of a membrane based on the activity, the following equation must be implemented

$$\ln \left( \frac{\lambda_i - \lambda_i^C}{\lambda_i + r} \right) + \left( 1 - \frac{1}{r} \right) \left( \frac{\lambda_i^C + r}{\lambda_i + r} \right) + \chi \left( \frac{\lambda_i^C + r}{\lambda_i + r} \right)^2 - \ln a_i = - \frac{\bar{V}}{RT} \left\{ \left[ \frac{2}{3} G \left[ \left( \frac{r}{\lambda_i + r} \right)^{1/3} - \left( \frac{r}{\lambda_i + r} \right)^{7/3} \right] - S \sigma \cos \theta \left( 1 + \frac{r}{\lambda_i} \right) \right] \right\} \quad (2-55)$$

in which  $\bar{V}_i$  is the partial molar volume of the solvent,  $R$  is the gas constant,  $T$  is temperature,  $S$  is specific pore surface area,  $\sigma$  is the surface tension of solvent,  $\theta$  is the

contact angle of saturated solvent vapor in Nafion and  $\lambda_i$  is the solvent uptake. Table 2.2 shows the parameter values for water (organic solvent) in an experiment.

$\bar{V}_M$	537 cm <sup>3</sup> /mol
$\bar{V}_i$	18 cm <sup>3</sup> /mol
S	210 m <sup>2</sup> /cm <sup>3</sup>
K <sub>1</sub>	1000
v	5
$\lambda_{i,m}$	1.8
$\sigma$	72.1 mN
$\theta$	98
$\chi$	Fitted

**Table 2. 2 Sulfuric acid parameters.**

In general, the main parameters that change from solvent to solvent are  $\bar{V}_i$ ,  $\sigma$  and  $\chi$ . In order to compare the way solvent uptake changes as solvents change, three other solvents were selected and plotted against each other. Water, as well as methanol are graphed together in Figure 2.9 as a way to compare the differences of sorption of different solvents. [2]

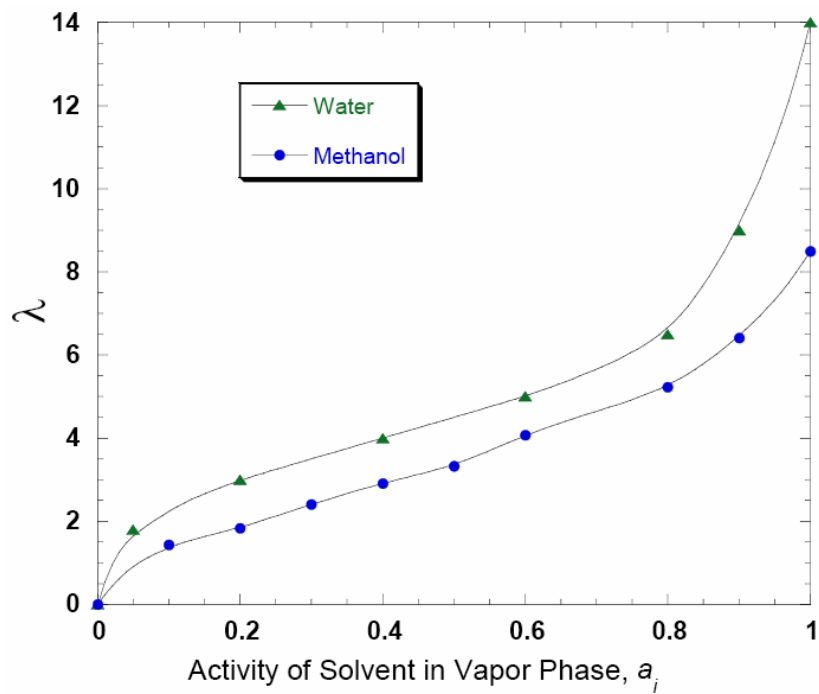


Figure 2.9 Estimated sorption of solvents in Nafion membrane.<sup>[5]</sup>

As it is apparent, as the activity in the vapor phase increases, the sorption increases. The sorption of methanol into the membrane is predicted here to be less than the sorption of water. Less sorption decreases swelling and deformation and MEA performance increases. It is important to notice that as  $\bar{V}_i$  increased within each solvent, the surface tension of that particular solvent decreased. This results in more solvent uptake at the same activity, as opposed to solvents with a lower partial molar volume and higher surface tension.<sup>[2]</sup>

## Chapter III. Experimental Methodology

### *Factors that affect performance*

In order to identify the factors that affect MEA performance, a method of varying only one parameter at a time was adopted. The catalyst layer is an integral part in the performance of the MEA. For example, the application of the catalyst layer to a rough surface as opposed to a smooth surface would increase the roughness factor of the MEA and thus increase overall performance. Another aspect of the catalyst layer is the medium to which it is applied. The catalyst mixture can be applied to the gas diffusion layer, to Teflon blanks or directly to the membrane. Each of these have advantages and disadvantages that must be weighed in order to determine which method should be used. The catalyst layer must be uniform, even and uninhibited in order to give optimal performance. Gas diffusion layer application may not be even if standard carbon cloth without a carbon baking is used. Decal method of application may result in uneven catalyst transference as well as accumulation of contaminants on the catalyst surface. Direct application of the catalyst ink will give even distribution of the catalyst loading, but may yield a poor catalyst layer if the solvent is absorbed into the membrane. This is because the membrane swells as the solvent is absorbed and as the solvent evaporates the membrane shrinks resulting in an uneven catalyst layer.

In order to limit the effect on the catalyst layer another important factor is the solvent itself. The solvent determines how well the catalyst ink adheres to the membrane, how even the catalyst layer can be applied, as well as how homogeneously the catalyst ink is mixed. The solvent must be such that it does not interact with the membrane at all, but

instead serves as a means to apply the catalyst. Solvent boiling point plays a critical role, as higher the boiling point, the longer the solvents takes to vaporize and more solvent is left on the membrane to contribute to an adverse reaction. In contrast the lower the boiling point of the solvent, less is the amount of solvent and catalyst mixture to adhere onto the membrane. The appropriate range of boiling points must be examined. Finally the catalyst ink's ability to form a homogeneous mixture is determined by the solvent as it is present in the greatest volume. The catalyst ink is typically composed of Pt/C, 10% PTFE and 10%Nafion, both of which are in water. Thus the solvents ability to mix with water would directly impact the ability of the catalyst ink to mix thoroughly.

From the literature it was found that the solvent also affects the form of the catalyst solution as shown by Uchida et al<sup>[1]</sup>. The dielectric constant is a critical factor that decides the form of the solution. From the research it is said that solvents with dielectric constants from 3-10 form a colloidal solution. Those with higher dielectric constants form a solution and those with lower dielectric constants result in precipitate.<sup>[3]</sup> It is said that Nafion ionomers in the colloidal form are absorbed more homogeneously on the Pt/C than in the solution form. This would then aid in the development of a uniform three phase interface, which must be optimized to increase performance.

The final factor that affects MEA fabrication and performance is the membrane itself. The membrane can be treated before, after, or in-between catalyst application. These treatments in a low boil often allow the membrane to expand. If the membrane is already catalyzed this expansion may result in more porous catalyst layer. Also the form of the membrane also plays a role. The conversion into protonated form by boiling in 0.5M sulfuric acid contributes to the performance by ensuring the catalyst layer is also in



the protonated form. The conversion to the sodium form by boiling in NaOH limits the absorption of the solvent into the membrane. Combinations of the form of the membrane are vital to ensure desired results.

The composition of the catalyst ink also influences an MEA. The addition of more of one component than the others may yield better results and must be optimized through testing. An example of this would be PTFE, which may not be necessarily added at same amount for anode and cathode since the removal of water is more crucial at the cathode than at the anode. Another would be the catalyst loading. The amount necessary for the anode may be lower than that for the cathode. Further variation of the catalyst ink components is another aspect that determines the performance of an MEA.

## ***Decal Method***

This section describes a detailed procedure of how the MEA using the decal method via airbrush was fabricated. The detailed procedure includes: the preparation of the catalyst ink procedure, the application of the slurry onto the Teflon blanks procedure, the baking temperature and time conditions, the hot-press conditions, post-treatment and the fuel cell station conditions.

### **Preparation of catalyst ink**



**Picture 3.1** Sonication of catalyst ink

In order to prepare the catalyst ink used for the MEA fabrication via decal method, the catalyst ink preparation methodology was adopted from Wilson et al<sup>[2]</sup>. The procedure follows the exact ratios:

1. 1: 5: 20 (Pt/C, deionized water, organic solvent)
2. 1: 3 (ratio of Nafion 10% solution to Pt/C)

Also, in some of the later experiments, the ratio to determine the amount of PTFE needed in the catalyst ink was (3/7) Pt/C. The slurry in the beaker was covered with parafilm and sonicated for three hours. It is important to note that the amounts listed above were used for one Teflon blank. Two Teflon blanks were needed in order to hot-press catalyst onto both the sides of the membrane. Before the slurry was applied to the blanks, the untreated Nafion 115 membrane was weighed to determine the loading amount after the transfer.

### **Application of Catalyst ink on Teflon**

Once the slurry in the beaker was sonicated for three hours, it was removed from the sonicator and sprayed onto a Teflon blank with an airbrush (The surfaces of the blanks were roughened using silica paper). The blanks were evenly coated and dried with a blow-dryer in between each layer for 10-30 seconds.

### **Drying procedure**

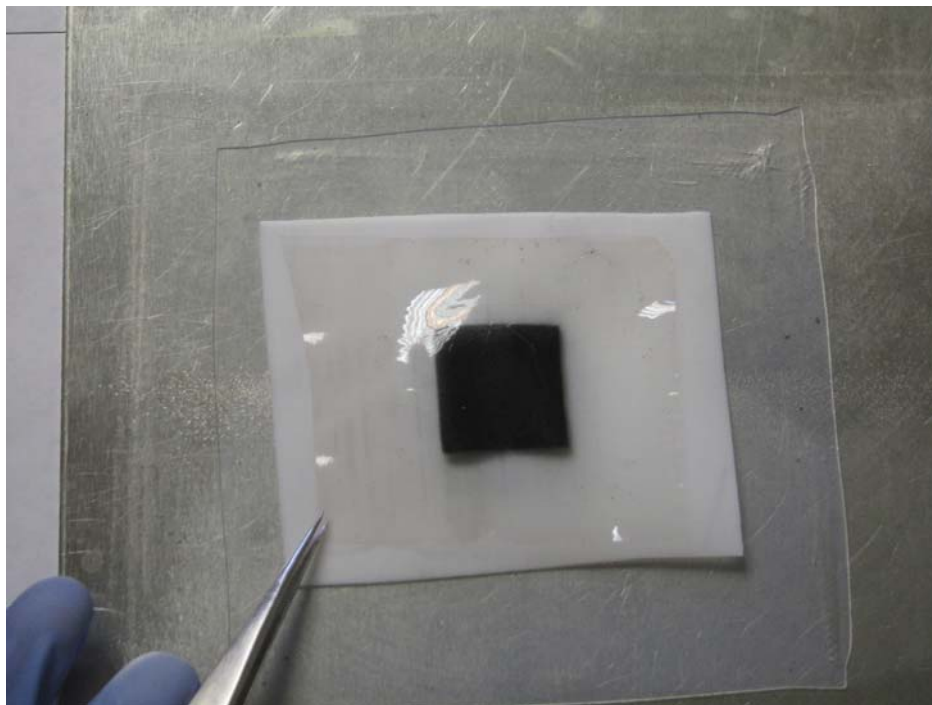
After the catalyst ink was evenly applied to the Teflon blanks, the blanks were placed into a drying oven at a temperature of 195°C for an hour and a half. Once dried, the blanks were removed from the oven using clean tweezers and placed under a tissue paper on a counter surface to cool.



Picture 3.2 Hot-press

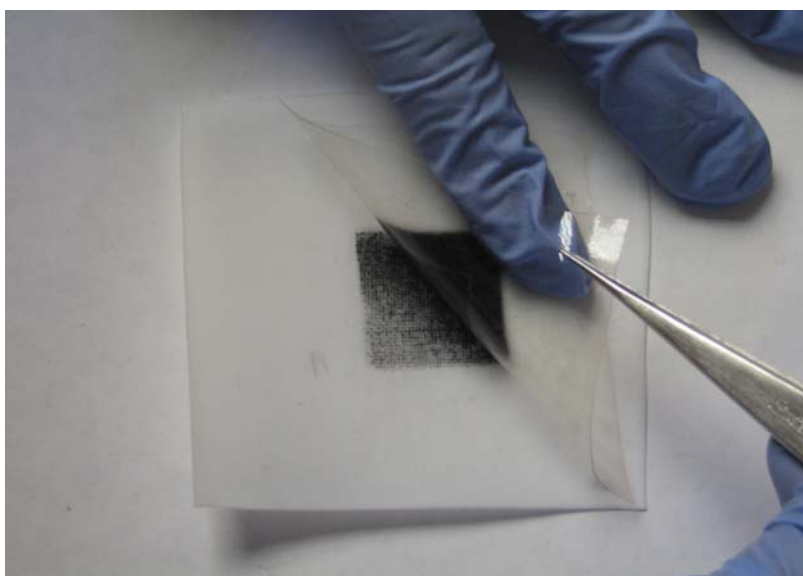
### Hot-press conditions

Once the blanks were cooled, the Nafion membrane was sandwiched between the two blanks containing the dried catalyst (as can be seen in Picture 3.2). Once the sandwich was formed, it was placed between two metal plates.



**Picture 3.3** Placing non treated membrane in between two catalyzed Teflon blanks.

After the membrane and the blanks were placed between the metal plates, it was hot-pressed under a pressure of 5 MPa and 275°F for two minutes.



**Picture 3.4** Once hot-pressed, catalyzed membrane is separated from Teflon blanks.

The MEA thus prepared was then placed onto a counter surface to cool. After the metal plates were cooled, the catalyzed membrane was separated from the Teflon blanks as seen in Picture 3.4, and then the membrane was ready for treatment.

### **Post-treatment**

After the membrane cooled, it was carefully peeled from the blanks and then weighed on a scale to measure the loading amount. Then, the membrane was treated in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution for 1.5 hours. The membrane was then treated in DI water for 1 hour. The membrane was lightly dried before it was placed inside of the fuel cell.

### **Fuel cell test station**

Before the membrane was placed into the cell, two equal pieces with the dimensions 2.236 cm x 2.236 cm of carbon cloth were cut. Firstly, one piece of the carbon cloth was placed inside the cell, then the membrane and finally the second piece of carbon cloth, making sure the assembly was aligned within the cell. Finally the cell was assembled. The MEA was tested under fuel cell test station conditions of both 70°C and 30°C using H<sub>2</sub> / O<sub>2</sub> and H<sub>2</sub> / Air and under 100 % relative humidity.

## ***Direct Spray Method***



**Picture 3.5 Applying catalyst slurry directly to the membrane with airbrush.**

This section contains the detailed experimental procedure, preparation and laboratory conditions involved in the spray method. The spray method involves application of the catalyst ink directing onto a membrane using a spray gun. The components that will be described are MEA pre-treatment, catalyst ink preparation, application of catalyst ink on MEA, drying procedure, MEA post treatment, hot press conditions and fuel cell test station conditions.

### **MEA Pre-Treatment**

First a piece of 2.5 in<sup>2</sup> Nafion 115 membrane is cut and then placed into a 600 mL beaker containing 250 mL of deionized water. It is then set to a low boil for one hour. A 35% H<sub>2</sub>O<sub>2</sub> is reduced to a 3% H<sub>2</sub>O<sub>2</sub> by dilution with deionized water in eleven parts deionized to one part hydrogen peroxide. To make enough for 250 mL, 21 mL of 35wt%

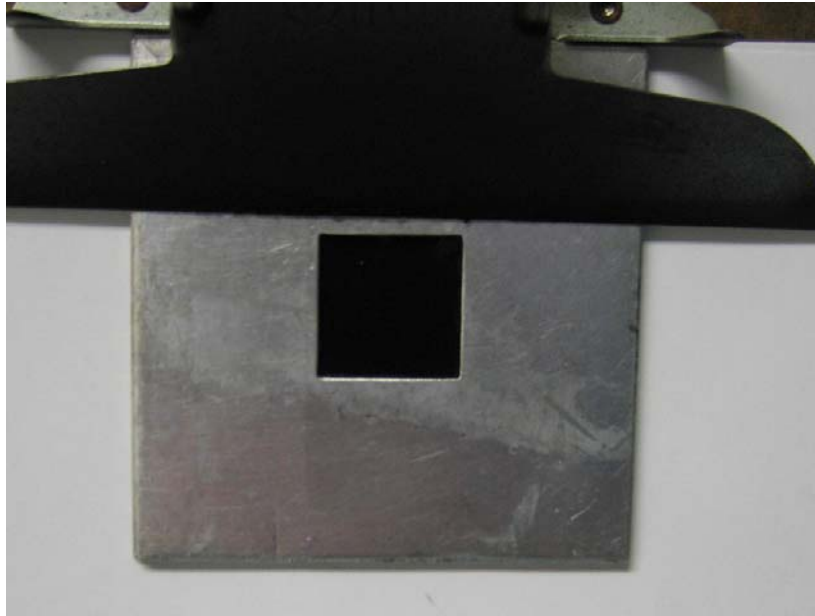
H<sub>2</sub>O<sub>2</sub> is added to 229 mL of deionized water. The membrane is then transferred from deionized water to the prepared 3% H<sub>2</sub>O<sub>2</sub> solution where it is set to a low boil for one and a half hour. Next the membrane is again immersed in 250 mL of H<sub>2</sub>O for one hour. Finally the membrane is placed between sheets of tissue paper and dried in press at 0.2 metric tons for 5 minutes.

### **Catalyst Ink Preparation**

The catalyst ink is made to be applied over a 5 cm<sup>2</sup> area, with a desired loading of 0.4 mg/cm<sup>2</sup>. However to account for any losses in the preparation and application of the catalyst ink is made to apply a loading of 0.6 mg/cm<sup>2</sup> area. First a clean 100 mL Beaker is obtained and zeroed on the scale. 15 mg of 20wt% platinum on carbon is weighed, then 64 mg of 10 % PTFE is added. Next 35 mg of 10% Nafion solution is added. To this mixture is then added 5.5 mL of solvent. The solvent is typically an organic solvent such as an alcohol, ketone or ether. This catalyst slurry is then sealed with parafilm and placed in a sonicator for three hours. The sonicator gradually warms the water which the beaker is placed in, so for lower boiling point solvents, the water temperature should be monitored and changed as necessary to avoid overheating. For significantly low boiling point solvents that are more volatile, shorter sonication times are necessary. (See Appendix I for steps and calculations)



## Application of Catalyst Ink on MEA



**Picture 3.6 Final catalyzed membrane.**

After the membrane is pretreated and the catalyst ink sonication is complete the membrane is aligned in metal plates that only expose the desired 5 cm<sup>2</sup> of the membrane to be sprayed on each side. The catalyst slurry is then applied directly onto the pretreated membrane by spraying for about 10 seconds and then dried for 20 seconds with a hair dryer. This is repeated until all of the ink has been applied. Care is taken to observe enough distance between the spray gun and the membrane to limit the amount of solvent applied to the membrane. The membrane may swell if sprayed to close or for too long a time. A second amount of catalyst must be prepared for the other side. The metal plates are then turned over and sprayed with the second batch of catalyst ink.

## **Drying Procedure**

The solvent is used mainly as a medium to mix the ingredients of the catalyst layer. In order to remove the solvent and limit the possibility that it would interfere with the catalyst layer, the assembly is placed into an oven at a few degrees Celsius above the boiling point of the solvent. The catalyzed membrane is dried for one and a half hour.

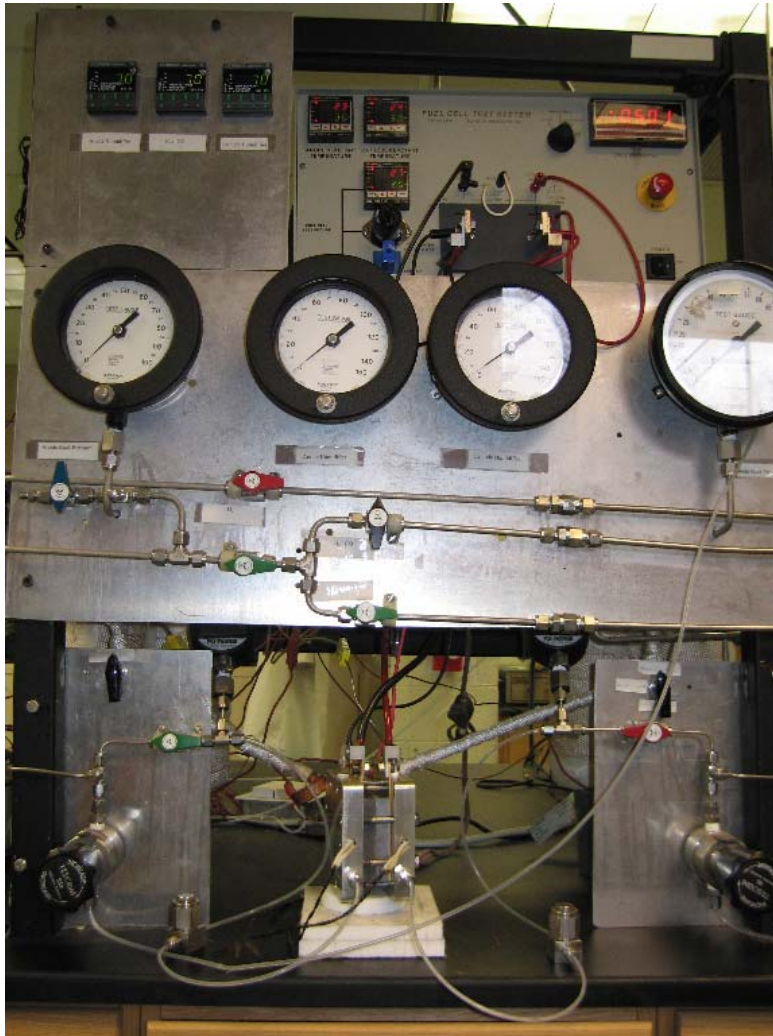
## **MEA Post Treatment**

After being dried in the oven the catalyzed MEA is placed in 250 mL 0.5M sulfuric acid and set to a low boil for an hour and a half. Then the catalyzed MEA is immersed in deionized water and set to a low boil for one hour. The MEA is then dried again in the press at 0.2 metric tons.

## **Hot Press Conditions**

Two equal pieces of carbon cloth of 5 cm<sup>2</sup> area are cut and assembled onto either side of the catalyst area on the MEA. This is then placed between two sheets of Teflon and then between two metal plates. This is assembled onto itself in layers with the catalyzed MEA on the middle the two carbon cloths on either side, then the two Teflon sheets the two metal plates. This assembly is placed into the hot press machine. It is set to 2 MPa and the thermostat is set to 275 °C. Upon each plate reaching 275 °C the setup is timed for two minutes. Once the two minutes are complete the thermostat is turned off and the pressure is released. The Metal plates are removed and set to cool.

## Fuel Cell Test Station Conditions



**Picture 3.7 Fuel cell station.**

Once cooled the prepared MEA is assembled into a single fuel cell. The humidifier and the thermostat is turned on and when the temperature reached above 100°C for the heating line and 30°C for the thermostat the fuel cell, the load box was turned on. The program was initiated and the fuel of H<sub>2</sub> and O<sub>2</sub> was started with 100 % humidification. Once consistent performance is shown at 30°C, the Station is set to 70°C. Once this temperature is reached it is conditioned at 70°C, then tested and again tested at 30°C. The membrane is again tested at 70°C and 30°C for air instead of O<sub>2</sub> at the cathode side.

## Chapter IV. Results

### *Decal Method*

Before results are presented for the decal method, it is important to mention that firstly, the painting decal method was used in the beginning of the laboratory work. catalyst slurry was made using glycerol as the solvent, while the other ingredients and weights remained the same as mentioned in the experimental methodology.



**Picture 4.1 Cracking of catalyst layer in painting decal method.**

Unlike Wilson's et al work, the painting method however proved to be unsuccessful. Painting thin layers of slurry onto a Teflon blanks and baking in between each layer caused cracking of the catalyst layer (as shown in Picture 5.1), which then caused the layer to peel off from the blanks. As a result, a new approach was taken, the spraying decal method.<sup>[1]</sup>

Using the spraying decal method proved to be quite easy with easy reproducibility (Again, another notable comment worth mentioning is the fact that the numbers

corresponding to each MEA do not go in a simple 1 to 10 fashion due to many cases where the MEAs were unable to be tested).

The data for MEA 002 under a fuel cell station temperature of 70°C and tested under hydrogen and oxygen is presented below. A dry lubricant spray Fluoroglide was used to assist in the removal of the catalyst ink from the Teflon blanks to the membrane during hot-pressing. Also, ethylene glycol was used as the solvent due its high boiling point, which is desirable for the decal method. Ethylene glycol is desirable for the decal method because it has a high boiling point which can withstand the high baking temperatures of the oven and has a high viscosity which makes it easier for the catalyst slurry to adhere to the Teflon blank when painted or sprayed.

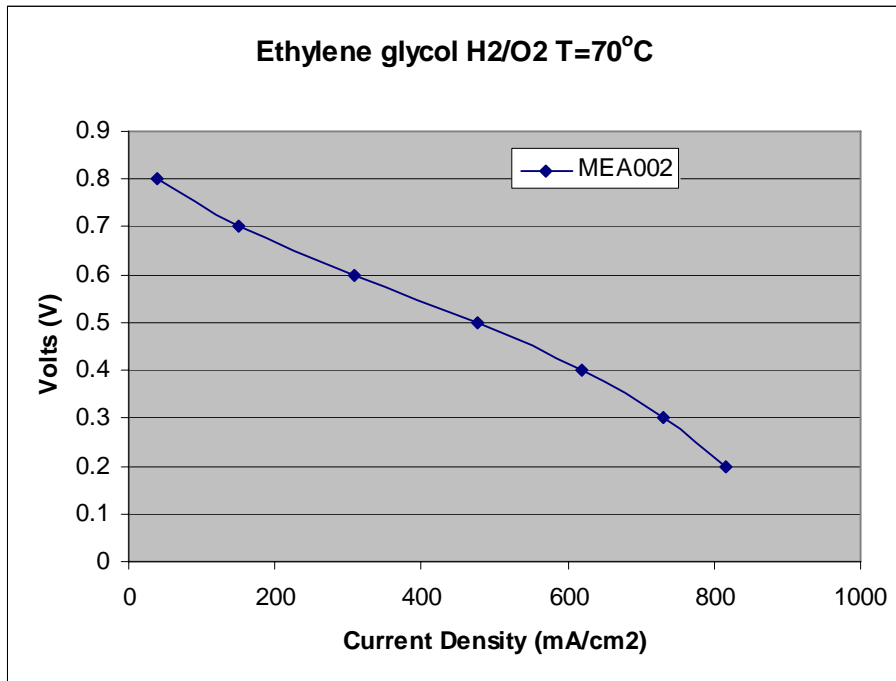
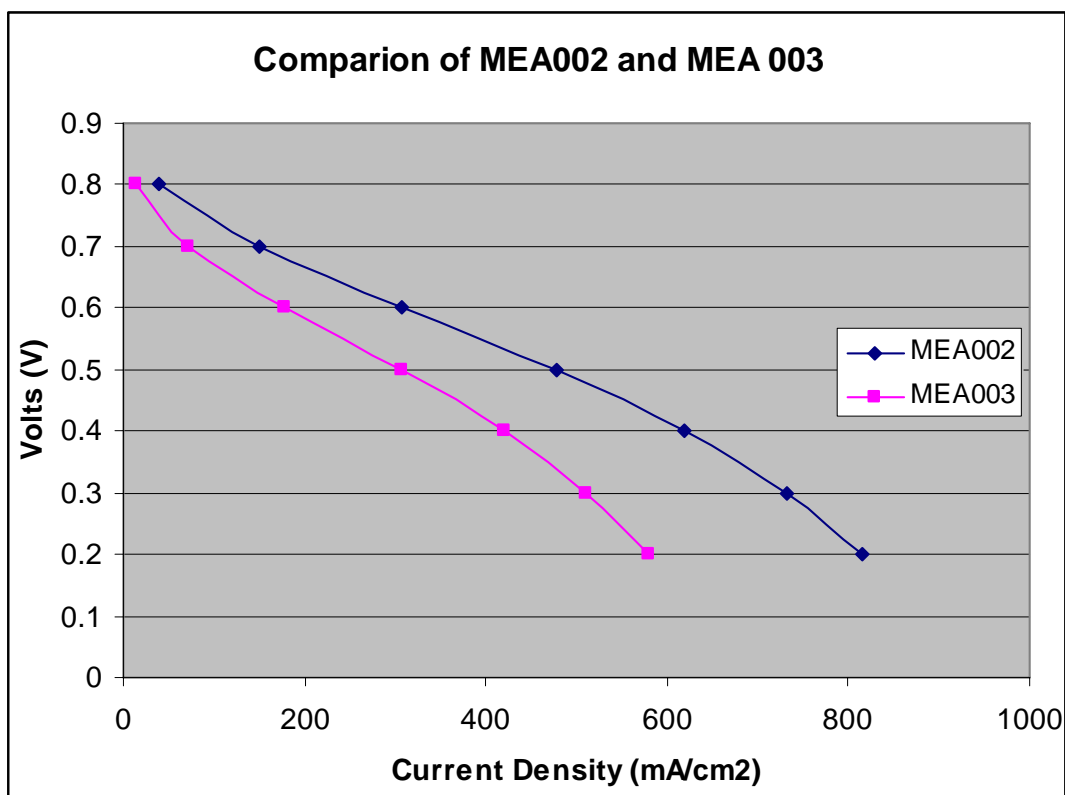


Figure 4.1 MEA 002: Results using ethylene glycol using Fluoroglide to prevent catalyst layer sticking.

As seen in Figure 4.1, although the performance was lower than the literature by more than half, it was a good starting point for further research.<sup>[2]</sup> Further research was needed because it was thought that the anti-stick agent used (Fluoroglide) had some type of

negative effect on the performance of the membrane. As a conclusion from these results, Fluoroglide (dry lubricant spray) affects the performance of MEA. By inhibiting the three-phase interaction by “blocking” the gases from permeating into the catalyst layer which in turn prohibits the reaction on the catalyst layer.

After MEA 002, MEA 003 was prepared. While preparing MEA 003, the Teflon blanks surfaces’ were roughened using silica sand paper. Ethylene glycol was also used as the solvent, with the other parameters were the same as in MEA 002.



**Figure 4. 2 MEA002 and MEA003: In MEA003, silica paper was used to roughen surface. In MEA002, Fluoroglide was used to roughen surface.**

As seen above in Figure 4.2, the current density obtained using silica paper to roughen the Teflon surface was lower than that obtained with Fluoroglide, as in MEA 002. The problem however was that a pressure of five metric tons was used accidentally for five

minutes to dry the membrane after the post-treatment instead of 0.2 metric tons that was used in MEA 002. The current density may have been lower because of excessive pressure application that causes permanent deformation of the membrane and could increase the ionic resistivity.

Initially 5 metric tons of pressure was used for drying the membrane instead of the recommended 0.2 metric tons. Another MEA was made as the same method implemented in MEA 003. The only variable that was changed in MEA 004, was the drying pressure, to 0.2 metric tons. As can be seen in Figure 4.3, the results are drastic. Changing the drying pressure of the MEA causes a noticeable change in the MEA.

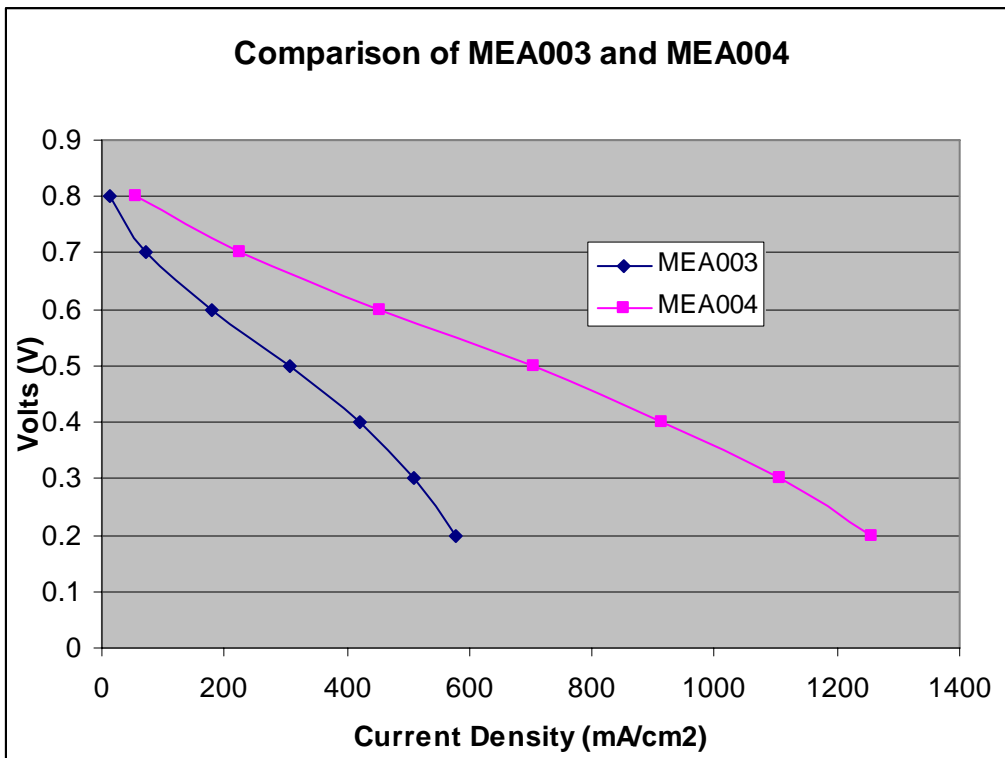
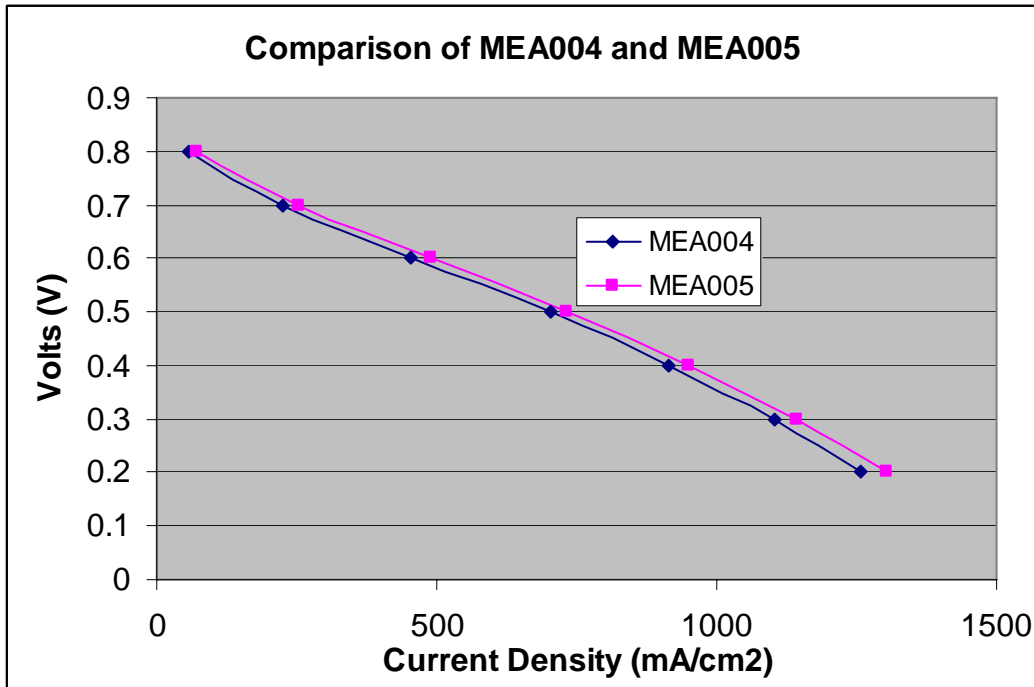


Figure 4.3 Comparison of how drying pressure changes performances in MEA003 and MEA004.



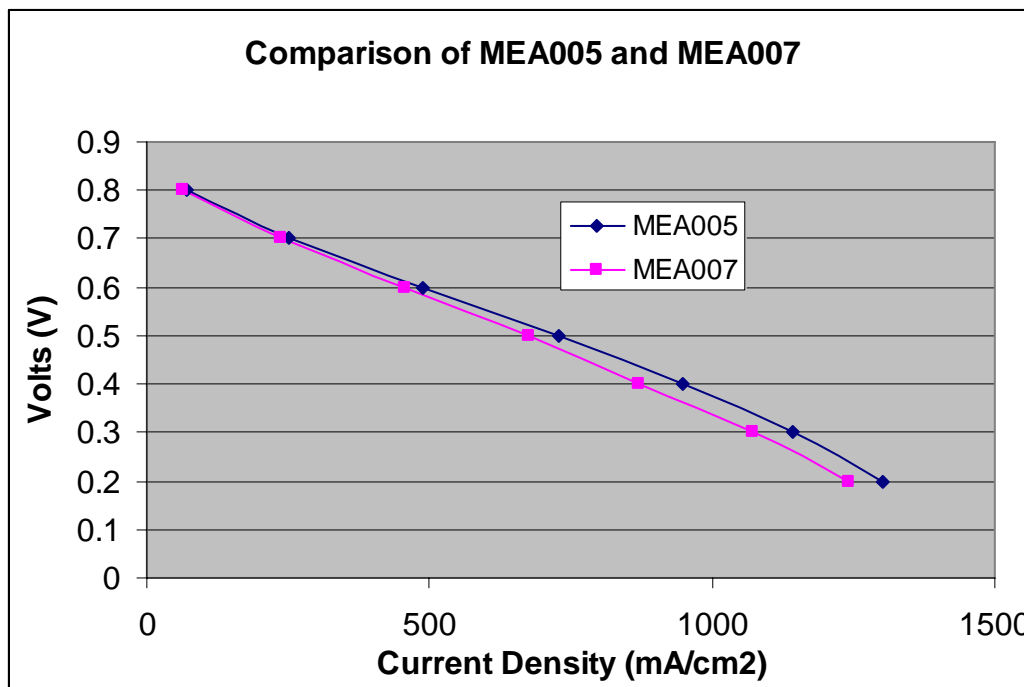
**Figure 4.4 MEA004 and MEA005: Comparative results using ethylene glycol using sand paper to roughen Teflon blank surface as well as using 0.2 metric tons to dry membrane in both MEAs.**

Another experiment was attempted to verify the performance obtained in MEA 004. As can be seen above, the performance of MEA 005 was very similar to the performance of MEA 004, which is expected seeing as the same methodological approach was followed. There is a slight difference in performance however, approximately around a current density 750 mA/cm<sup>2</sup>. This however is to be expected seeing as it is very difficult to control each aspect in the fabrication process of MEAs perfectly. Nonetheless, MEA 005 is another confirmation which proves that increased pressure during the drying process of fabricating an MEA adversely affects the performance greatly.

From this point on, another experiment was attempted to determine the impact of adding PTFE to the catalyst slurry. The reason for adding PTFE (amount specified in Decal Methodology) into the catalyst layer slurry was because it was researched from



literature<sup>[2]</sup> that adding PTFE increases hydrophobicity of the catalyst layer which aids in the removal of water formed at the cathode of the cell. Inadvertently, PTFE could cause MEAs to perform better than MEAs without it. Based on the results shown in Figure 4.5 below however, the addition of PTFE decreased the performance slightly. The decreased performance can be seen at a current density of approximately 500 mA/cm<sup>2</sup>. The possible reason for the lower performance is because too much PTFE was used inhibiting the three-phase interface.



**Figure 4.5 Comparison of MEA005 and MEA007. Both methods were similar, however MEA007 included PTFE, whereas MEA005 did not.**

After decreasing the amount of catalyst used in the slurry, MEA 008 was made to compare the results with the previous membranes made with ethylene glycol and roughening the surface with silica paper. MEA 008 was made without PTFE and hence is compared with MEA 005, which was also made without the addition of PTFE. As it can be seen in Figure 4.6 below, performance was much lower compared to MEA 005.

This is due to the lower amounts of the components within the slurry which caused lower performance. Since less catalyst was used, it is obvious that the MEA performance would decrease.

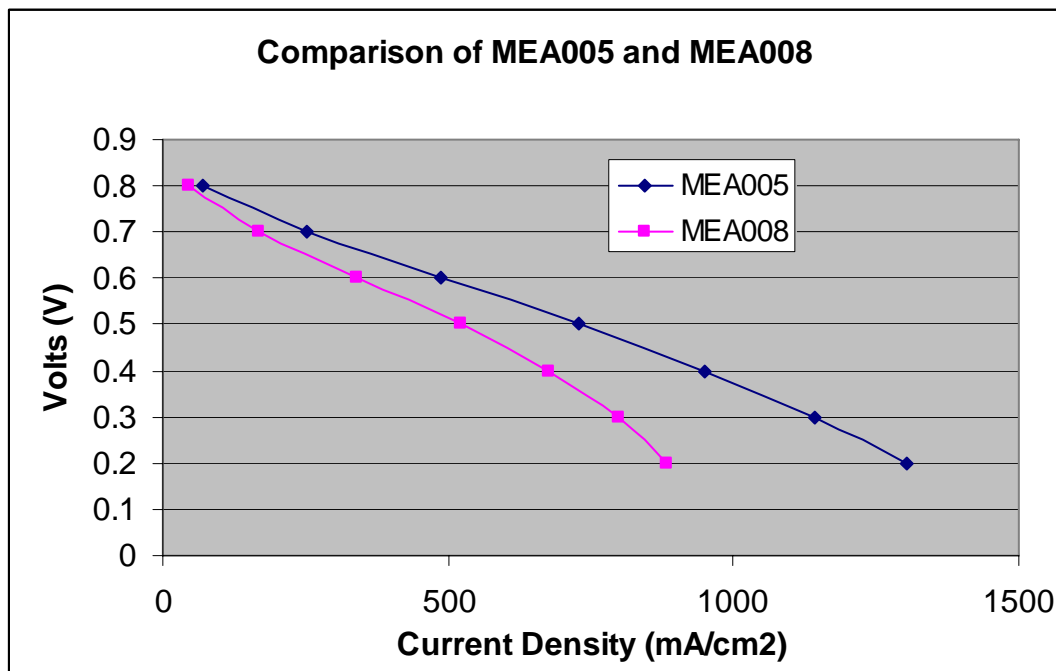


Figure 4.6 Comparison of MEA005 and MEA 008: Methodology was the same in both cases, only that the ratios were recalibrated in MEA008.

Another MEA was made using the same altered ratios as in MEA 008, however PTFE was added to the catalyst slurry. MEA 008 and MEA 010 are compared below in figure 4.7 to determine how the addition of PTFE affects the performance of the MEA once again. As in the comparative results of MEA 005 and MEA 007, the addition of PTFE decreases the performance of the MEA. The reasoning is the same as mentioned above with MEA 005 and MEA 007.

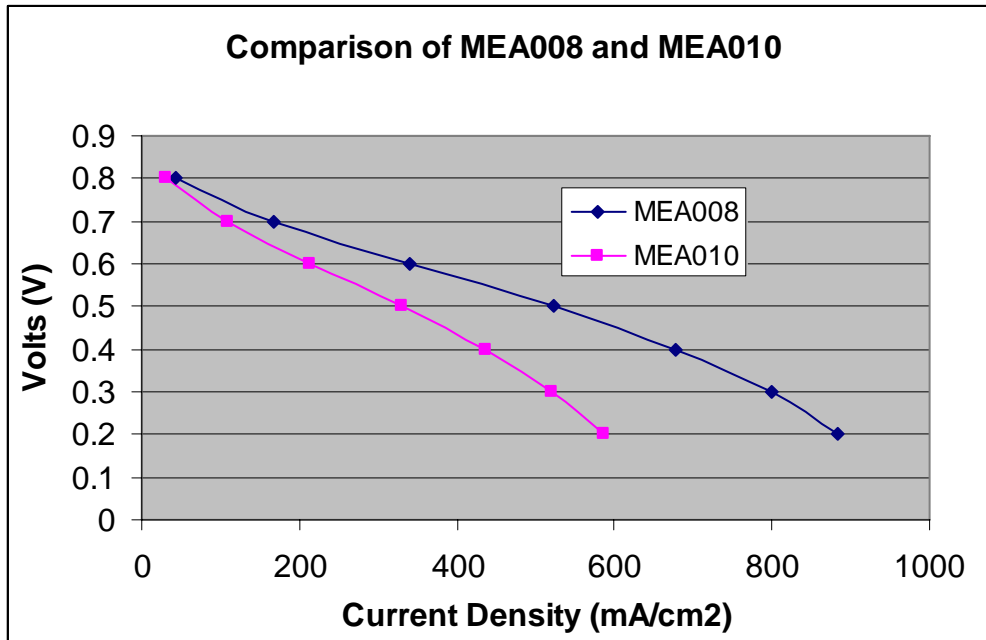


Figure 4.7 Comparison of MEA008 and MEA010: Methodology was the same in both MEAs, however the ratios on MEA010 were recalibrated (both MEAs contained PTFE).

## ***Spray Method***

Initially a MEA for the spray method was made through the application of the catalyst ink directly onto the gas diffusion layer. The application can be seen in the Picture 4.2 below.



**Picture 4.2 Catalyzed GDL: Catalyst applied directly to carbon cloth.**

In the picture the darker black area denotes the area to which the catalyst was applied. While the gas diffusion layer is a type of woven mesh, it is still rather porous. Thus, when the catalyst ink is applied to the carbon cloth, less amount of the ink is lost. This experiment used ethanol as a solvent. The result of this can be seen in Figure 4.8

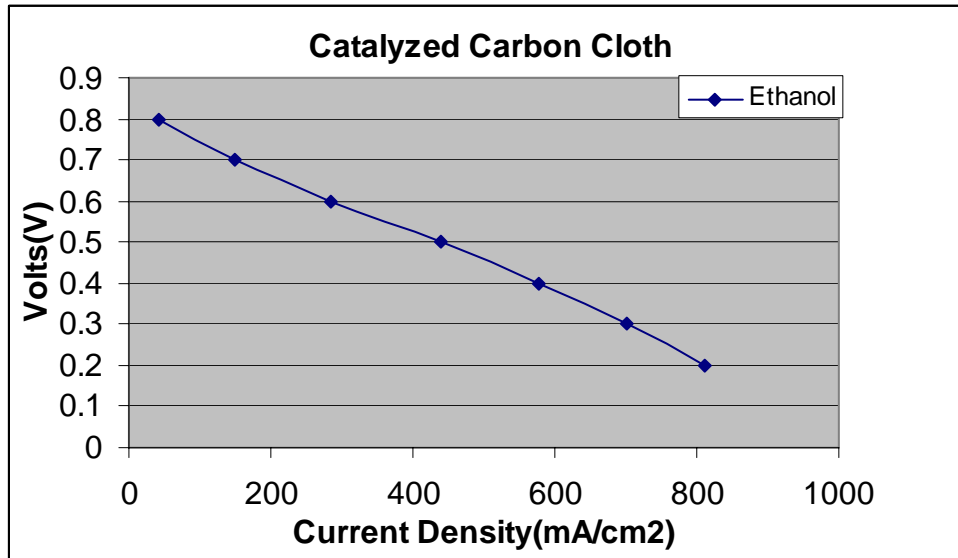
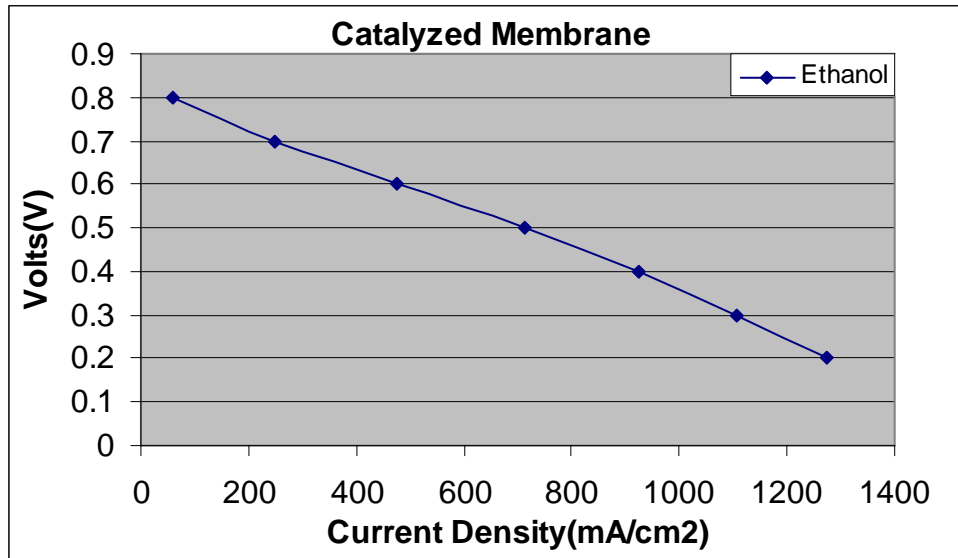


Figure 4.8 Ethanol catalyzed carbon cloth

The results and any following are from testing at 70°C with H<sub>2</sub> and O<sub>2</sub> as fuel for the anode and cathode respectively. The preparation of this type of MEA involved the complete pretreatment of the membrane through baths of DI water, 3% H<sub>2</sub>O<sub>2</sub>, DI water, 0.5M H<sub>2</sub>SO<sub>4</sub> then DI water once more. This experiment established a base line for the performance of the spray method under the laboratory conditions available.

While the application of the catalyst ink onto the carbon cloth maintains good contact with the membrane, the porosity of the GDL, results in an uneven and porous catalyst layer. The direct application of the catalyst ink onto the membrane was then examined in an attempt to remedy the flaws of the carbon cloth application. Again the solvent used was ethanol and results of the direct application onto a completely pretreated membrane can be seen in Figure 4.9.



**Figure 4.9 Catalyzed Membrane**

The direct application of the solvent did create a more uniform catalyst layer, but also created more stress on the membrane. When the solvent comes into contact with the membrane it is absorbed and the membrane expands, and as it is dried, in between the application of the catalyst ink, the membrane contracts back to an almost flat surface. Several layers of catalyst ink are sprayed before completion of the catalyst layer, so the membrane undergoes a significant amount of expansion and contraction. Nevertheless the direct application of the catalyst ink to the membrane yielded better results than the application to the GDL. This can be seen in Figure 4.10.

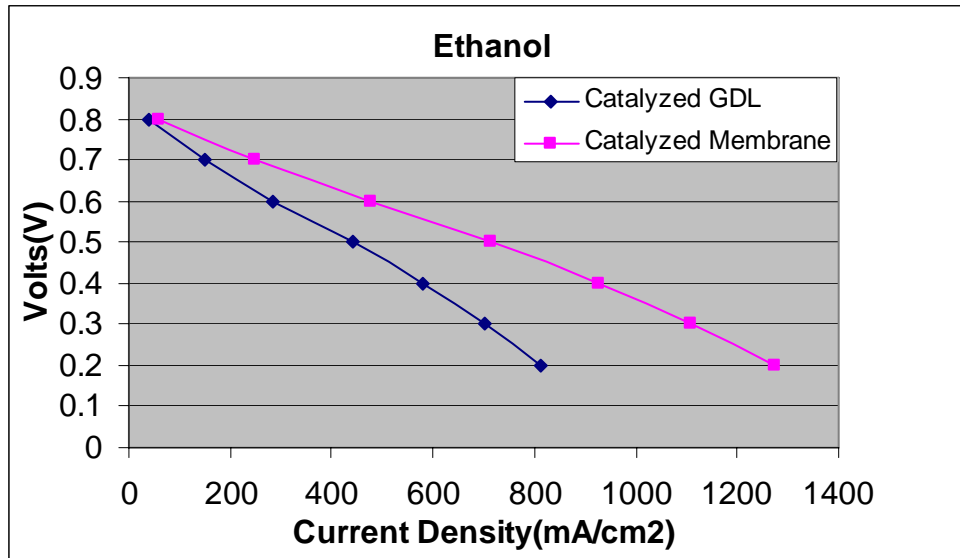


Figure 4.10 Comparison: Application on Catalyzed GDL vs. Membrane

These results were promising but a replica of this was made to ensure the accuracy of the results. The performance of which, was almost identical with the initial MEA. There was negligible difference at lower current densities. The comparison of the replica to the first MEA can be seen in Figure 4.11.

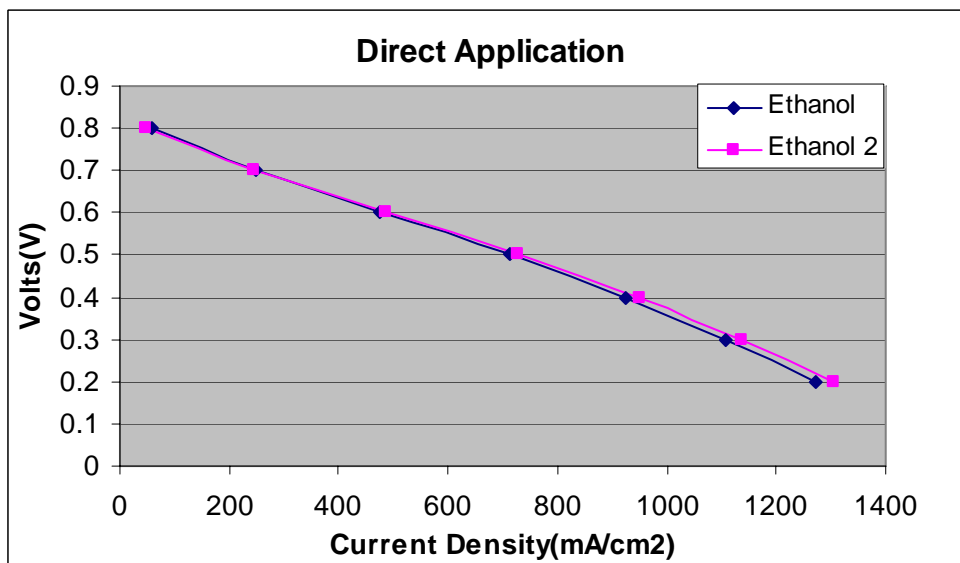


Figure 4.11 Direct Application Replication Comparison

Having confirmed the performance of the direct application method for the preparation of an MEA, the treatment process was then examined to determine the effect it has on the MEA performance. This was the purpose of the design of the next experiment.

Instead of using a completely treated membrane, the catalyst ink was applied to an untreated membrane which was later subjected to the complete treatment of DI water, 3% $H_2O_2$ , DI water, 0.5 M  $H_2SO_4$  then DI water once more. It was observed that when the catalyzed MEA was placed into the 3% Hydrogen Peroxide, there was a rapid bubbling that occurred over the catalyst layer. This was due to the fact that the platinum in the catalyst layer was oxidizing the  $H_2O_2$ . The occurrence of reaction of the catalyst layer was not favorable but the results of the experiment were better than expected. The performance of the complete treatment of the catalyzed membrane can be seen in Figure 4.12.

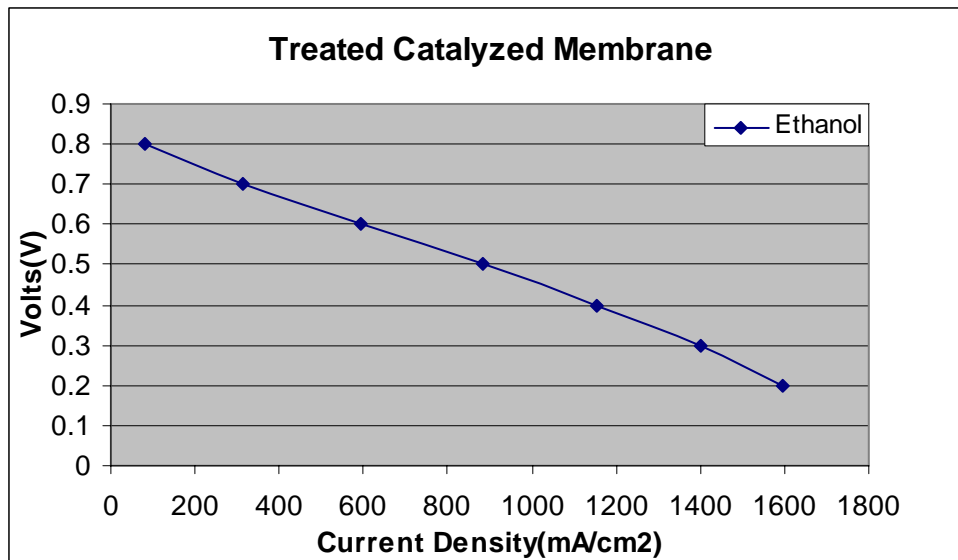


Figure 4.12 Catalyzed membrane then treated membrane

The result of this experiment was uncertain due to the fact that the catalyst layer sprayed was less than the desired amount. A lower catalyst loading may result in better results.



This MEA was again made to confirm the performance. The result of this can be seen in Figure 4.13 labeled as Ethanol 2.

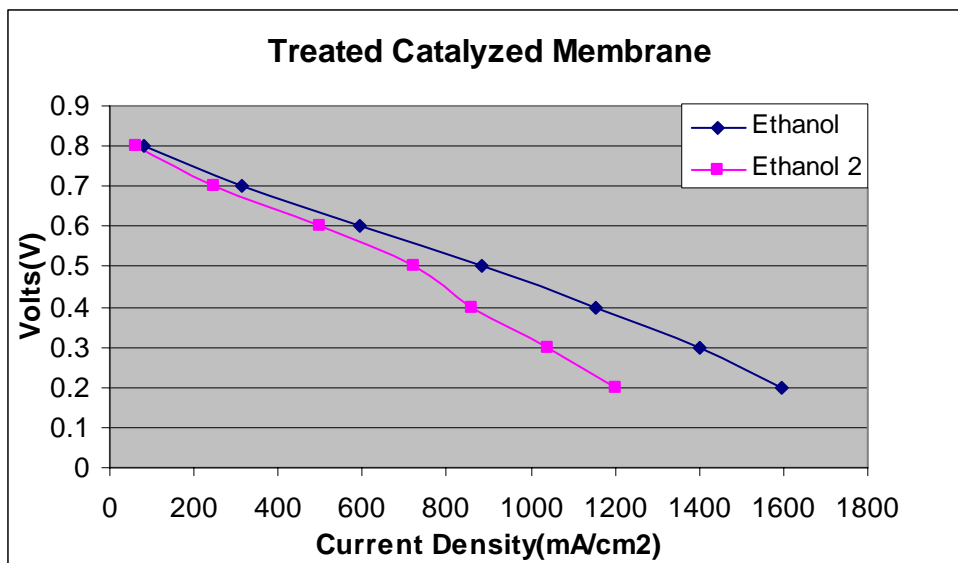
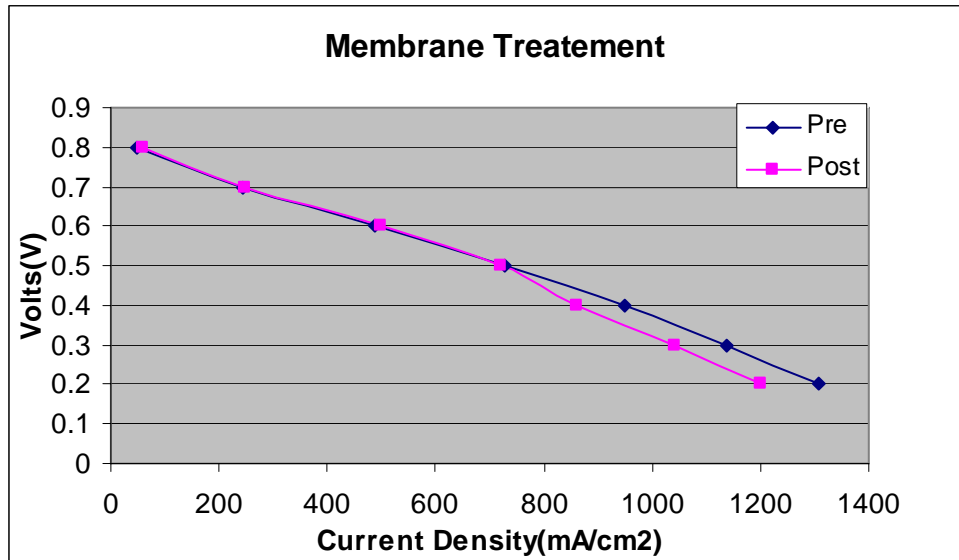


Figure 4.13 Replication of Treated Catalyzed Membrane

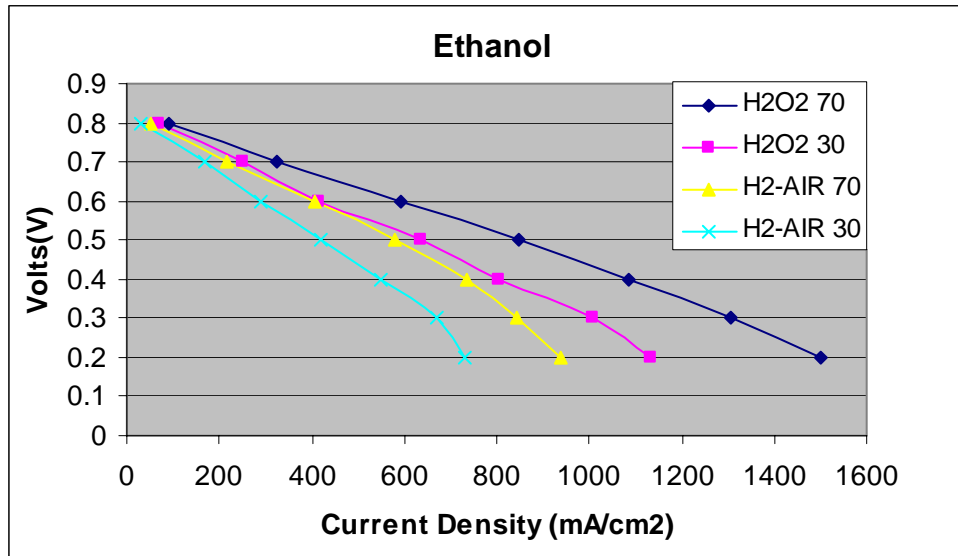
The performance of the replica was to be expected. The Hydrogen peroxide forms hydroxyl radicals that can attack the Nafion chain.<sup>[5]</sup> Thus the post treatment of the catalyzed membrane gives lower performance as opposed to the pretreatment of the catalyzed membrane. The post treatment method was replicated again and gave almost exactly the same result. The initial post treatment could not be replicated and may have been a due to undesired catalyst loading. A comparison of the pretreatment to the post treatment of the membrane can be seen in Figure 4.14



**Figure 4.14 Comparison: Pretreatment of Membrane vs. Post Treatment of Catalyzed Membrane**

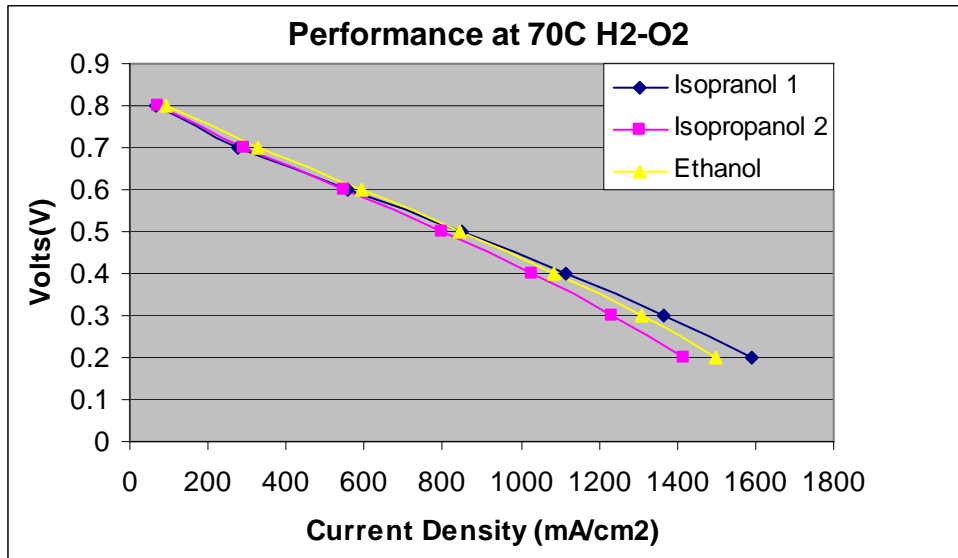
This difference between the use of a completely pretreated membrane, as opposed to the complete treatment of a catalyzed membrane, indicates that the treatment process does affect overall performance. In order to achieve better performance a pre and post treatment was developed and is what was used for all MEA preparation from this point onward. This involved treated the MEA with DI water, 3% $H_2O_2$ , DI water, then applying the catalyst layer to avoid the membrane degradation that may occur with  $H_2O_2$  in presence of Pt. Once the membrane is catalyzed it is then dried in the oven through baking, and then treated with 0.5 M  $H_2SO_4$  then DI water once more. The detailed procedure is listed in the experimental methodology for the spray method.

An MEA was prepared following the procedure listed in the spray method description using ethanol as a solvent. The oven temperature used for Ethanol was 80°C. From this, a performance curve was obtained with runs at 70°C and 30°C for hydrogen and oxygen and hydrogen and air and shown in figure 4.15.



**Figure 4.15 Ethanol Performance**

The lower temperature runs always gave lower performance and similarly the air runs gave even lower performance. This remained true for all other solvents, therefore only the performance at 70°C was compared. With this as a base, the procedure was repeated using other organic solvents. A paper (by Yang et al)<sup>[3]</sup> found that solvents with a dielectric constant between 10 and 3 form a colloid solution, which is best to facilitate the three phase interface necessary for optimum performance. Ethanol has a dielectric constant of 24.3, so solvents with lower dielectric constants were examined. A table was made of the properties that were found to be important to MEA performance and from it isopropanol was selected. It has similar properties to ethanol and a slightly lower dielectric constant of 20.1. The oven temperature used was 80°C. The MEA was made following the spray method procedure in Section III, experimental methodology. A replica MEA of the isopropanol was also made. The results of this can be seen in Figure 4.16



**Figure 4.16 Comparison: Isopropanol vs. Ethanol**

While it is evident that the performance of isopropanol is quite similar to that of ethanol it was observed that isopropanol was less absorbed into the membrane than ethanol. Upon closer inspection of the membrane, the swelling due to absorption of the solvent into the membrane was found to yield MEAs that give lower performance. To reduce the swelling, it was considered that the use of more volatile solvents could be useful. Amyl acetate and ethyl acetate were chosen for their low dielectric constants of 5 and 6 respectively, so they would produce a solution of catalyst ink in the colloidal form. However, they proved too volatile and low adsorbing so that the catalyst layer would not adhere to the membrane leading to flaking off of the catalyst layer after baking. It was also observed that while spraying these solvents seemed to instantaneously vaporize. This was unexpected due to the affect that amyl acetate has a boiling point of 149°C but a vapor pressure of 0.65kPa<sup>[2]</sup> and ethyl acetate had a boiling point of 77°C and a vapor pressure of 12.49kPa. Ethanol has 78°C and vapor pressure of 5.95kPa similar to that of ethyl acetate. It could be that the significantly low vapor pressure of amyl acetate

increases its volatility despite the high boiling point. Thus, the vapor pressure of the solvent may also be a critical factor in determining whether it an acceptable solvent to use.

Despite the failure of the acetates, in order to achieve better MEA performance the membrane swelling has to be reduced. Water was found to have low gravimetric swelling, so a mixture of water and ethanol was tested. From this assumption, the addition of water to ethanol in a 50-50 dilution was utilized. However the experimental results showed that the 50-50 water ethanol solution was more absorbed than ethanol alone leading to lower MEA performance. Figure 4.17 does reflects this, with the performance yielding slightly lower results.

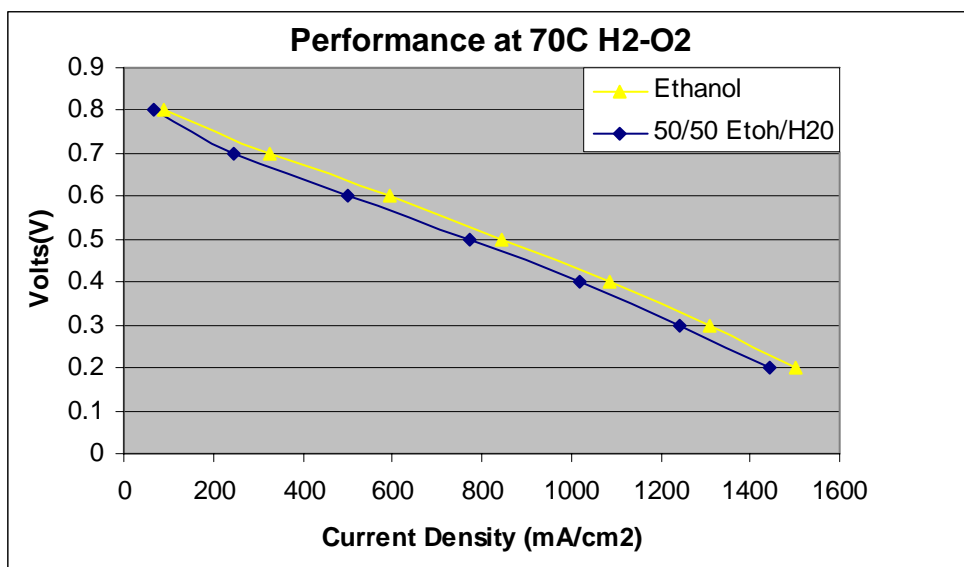
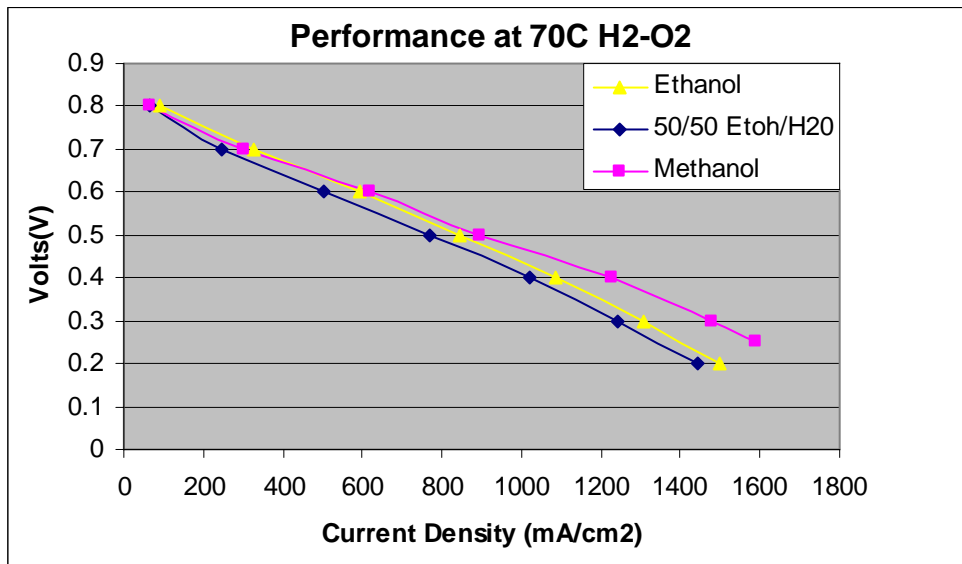


Figure 4.17 Comparison: Ethanol vs. 50%EtoH & H2O

Ethanol consistently gave higher performance than the other solvents tested so far, but it was more absorbed into the membrane than was desired. To limit absorption into the membrane the table of solvent properties [See Appendix] was examined for solvents with similar properties to ethanol. The alcohols were seen to have good solvent properties that

yield desirable results so another alcohol, methanol, was chosen. With a slightly higher dielectric constant of 32.6 and a higher volatility than ethanol, methanol might prove to perform slightly better. This may be true since a paper [By Yang et al<sup>[3]</sup>] that was based on the assumption that the colloidal solution is said to absorb more homogenously, but the solution with higher dielectric constant solvents appear to give better performance than those of lower dielectric constants.<sup>[4]</sup> The methanol MEA was prepared following the experimental methodology procedure with the oven temperature at 60°C. The performance of this MEA can be seen in Figure 4.18



**Figure 4.18 Comparison: Methanol vs. Ethanol**

From initial experimental results, methanol did indeed give better results at higher current densities than ethanol.

Returning to solutions that have lower dielectric constants, which are said to form a colloidal solution, ethyl acetate was again examined. Since it was too volatile water was added to it to aid in the adherence to the membrane. Instead of a 50% dilution with water, it would be one third of the ethyl acetate solution. This was then a total solvent of

5.5 mL composed of 3.5 mL ethyl acetate and 2 mL water. Water has a high dielectric constant of 88 and added to the low dielectric constant of ethyl acetate of 6. It should thereby yield a solution with a high dielectric constant somewhere in a range similar to that of methanol.

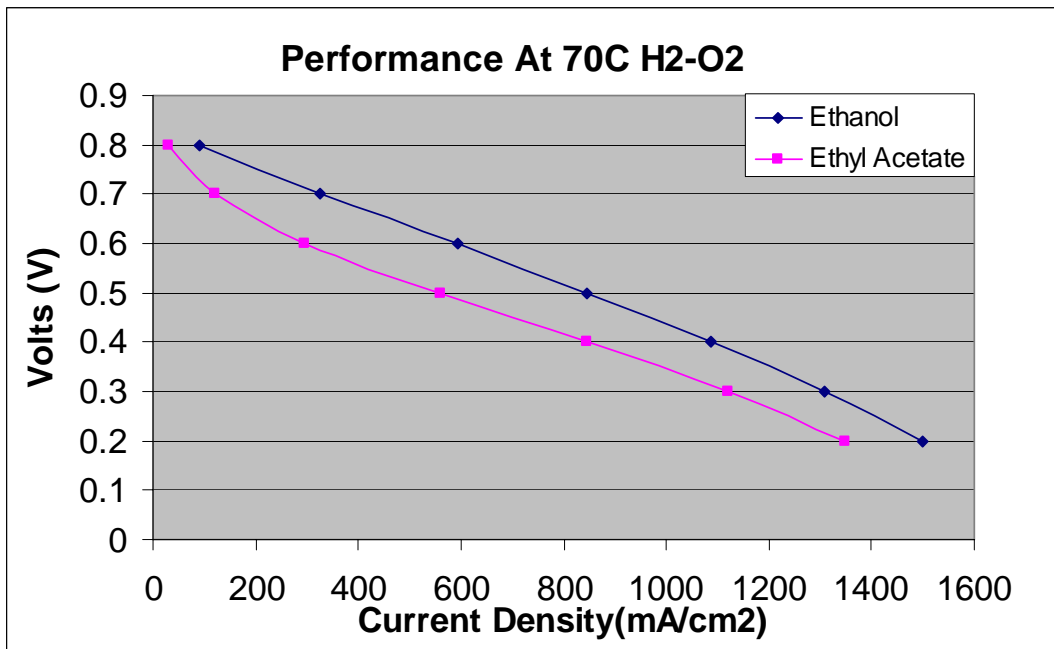


Figure 4.19 Comparison: Ethyl Acetate vs. Ethanol

From experimental observations the membrane did have significant swelling. With ethyl acetate dissolving only 8% in water at room temperature, it may be wise to reduce the amount of water added.

Another MEA was made with ethyl acetate and 1ml of water to make the total solvent mixture being 5.5ml. This MEA is the yellow curve shown in Figure 4.20

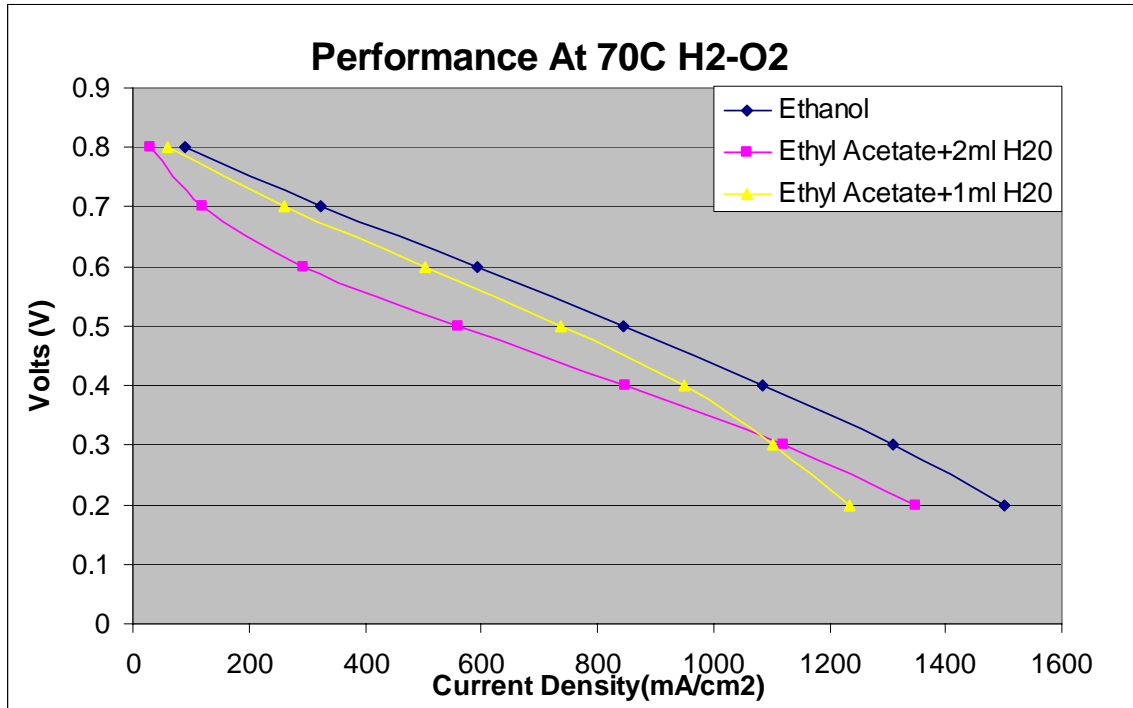


Figure 4.20 Comparison: Ethyl acetate+ H<sub>2</sub>O amounts

It is clear that the amount of water added has an effect on the performance of the MEA. While water has low gravimetric swelling it has a high boiling point and this results in the solvent mixture staying on the membrane surface rather than vaporizing. This results in some swelling and may be the cause of the lower performance of the ethyl acetate and water combination.

As a comparison an MEA was made with methanol and water to examine the effect that an addition of 1ml of water had on the performance. This data is displayed below in Figure 4.21



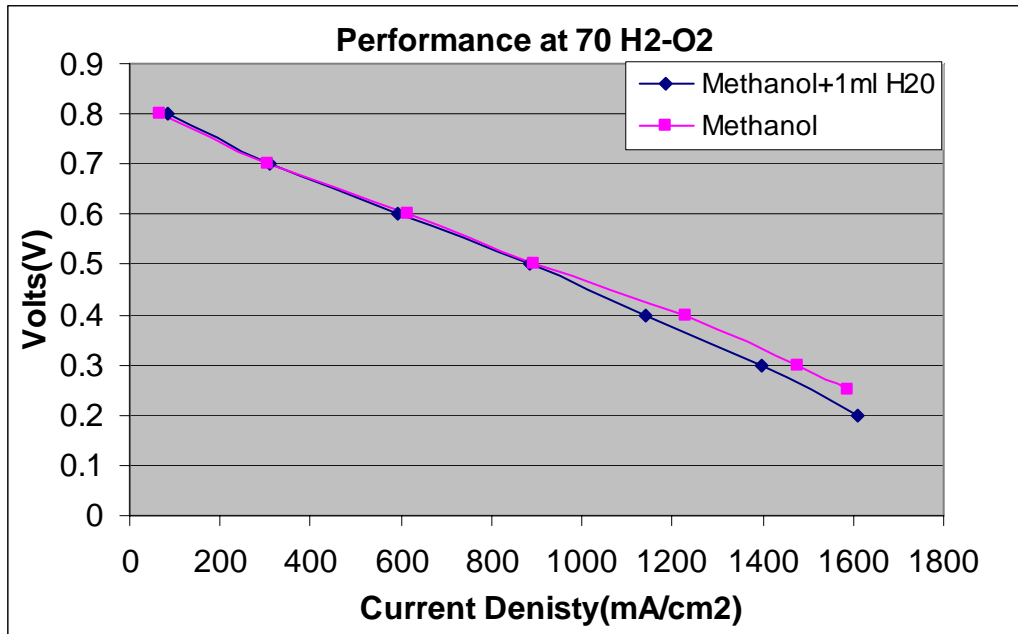
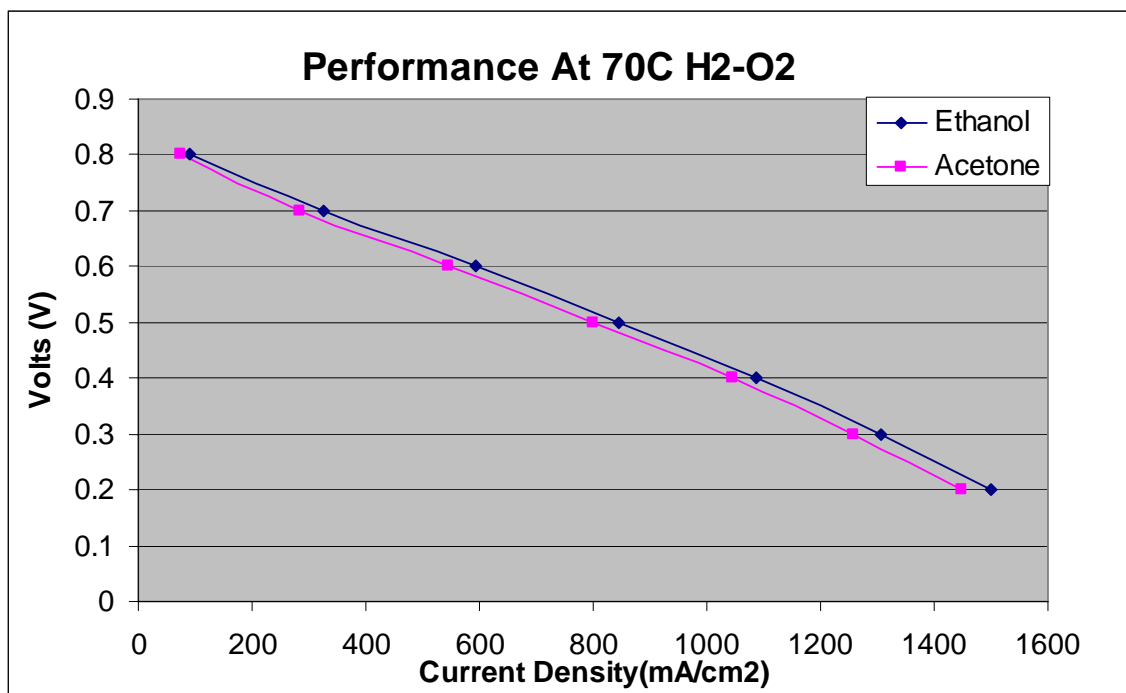


Figure 4.21 Comparison: Methanol vs. Methanol+H<sub>2</sub>O

The data shows a slight relationship between the water addition and the performance of the MEA but nothing significant. The difference in the performance of these two membranes is inconclusive, as reproductions of one type of MEA with the exact same techniques have shown as much disparity in the data as the methanol compared to the methanol and water.

It was considered that lower the boiling point of the solvent chosen, lower is the amount of solvent available to be absorbed into the membrane. This leads to better the overall performance of the MEA, and thus acetone was chosen as solvent. With a boiling point of 56°C acetone would be an ideal case for solvents with low boiling points. The results of this experiment are shown below in Figure 4.22



**Figure 4.22 Comparison: Ethanol vs. Acetone**

Acetone gave lower performance than ethanol despite the fact that it has a lower boiling point and several of the properties, as seen in the property table (See appendix), are very similar. A comparison can be made with acetone to other components with similar properties. Acetone had similar dielectric constants as ethanol and methanol however it had about half the polarity as well as a dipole moment of 2.9 with water having a dipole moment on 1.97 and ethanol and methanol having a dipole moment of 1.7. This could have been the cause of its lower performance.

Solvents that were said to give good performance with other application techniques such as the decal method were also tried; however these solvents had significantly higher boiling points. For example ethylene glycol was tried but with its high boiling point of 198°C, most of it stayed on the membrane when sprayed and was absorbed, to the point where the membrane deformed such that it could not return to its

original form. An example of the deformation that occurs to the membrane with ethylene glycol as the solvent can be seen in the Picture 4.3 below.



**Picture 4.3 Swollen/deformed membrane.**

This experiment suggests that lower boiling point solvents may be better for the direct spray method. From the property table, the solvents that possess low boiling points were the ethers. Another desirable characteristic is that ethers have low dielectric constants as well. An analysis of these solvents may give insight as to how these two properties affect MEA fabrication.

Before the examination of more solvents, the performance of a commercial MEA was examined to determine how the results compare. The commercial catalyst used was the E-tek electrode along with E-tek carbon cloth as opposed to the Electrochem carbon cloth used in previous experiments. The catalyst layer came mounted on the carbon cloth. The assembly of the E-tek MEA involved the spraying of the catalyst layer with a solution of ethanol with 35mg of 10 % Nafion. It was then dried in the oven at 80°C. Of

the solvents tried, methanol and ethanol were the most promising and were compared to the performance of E-tek as see in Figure 4.23

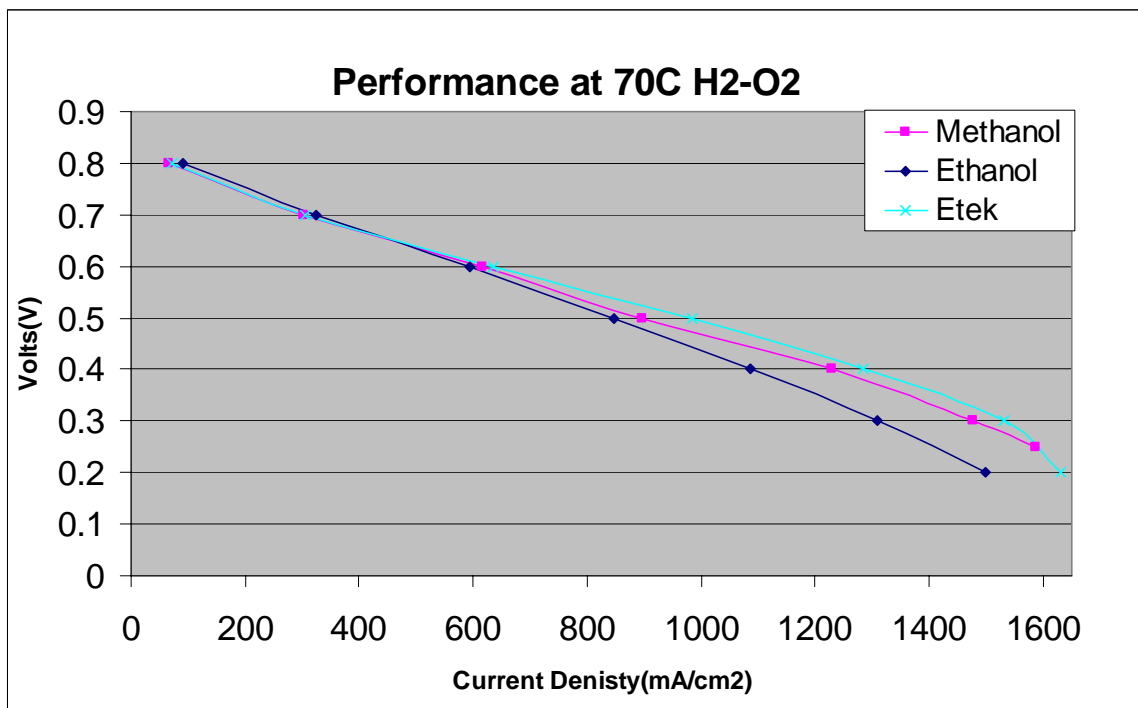


Figure 4.23 Comparison: Commercial E-tek electrode vs. Methanol and Ethanol

The E-tek electrode gave slightly better performance than that of the methanol, but nothing that was significant suggesting that augmentation to the preparation of the methanol MEA could yield performance superior to that of the commercial E-tek electrode.

To understand the manipulation necessary to improve the methanol MEA performance, some of the preparations conditions were examined. The first of which was the carbon cloth. The Electrochem carbon cloth was originally used to make the methanol MEA, but to accurately compare them it would be necessary to keep as many aspects similar as possible. As such the methanol MEA was again made using the E-tek carbon cloth. Since all MEA will be compared to the commercial MEA, all MEA made from this

point on also used E-tek Carbon cloth. The difference E-tek carbon cloth made as opposed to the Electrochem carbon cloth can be seen in Figure 4.24

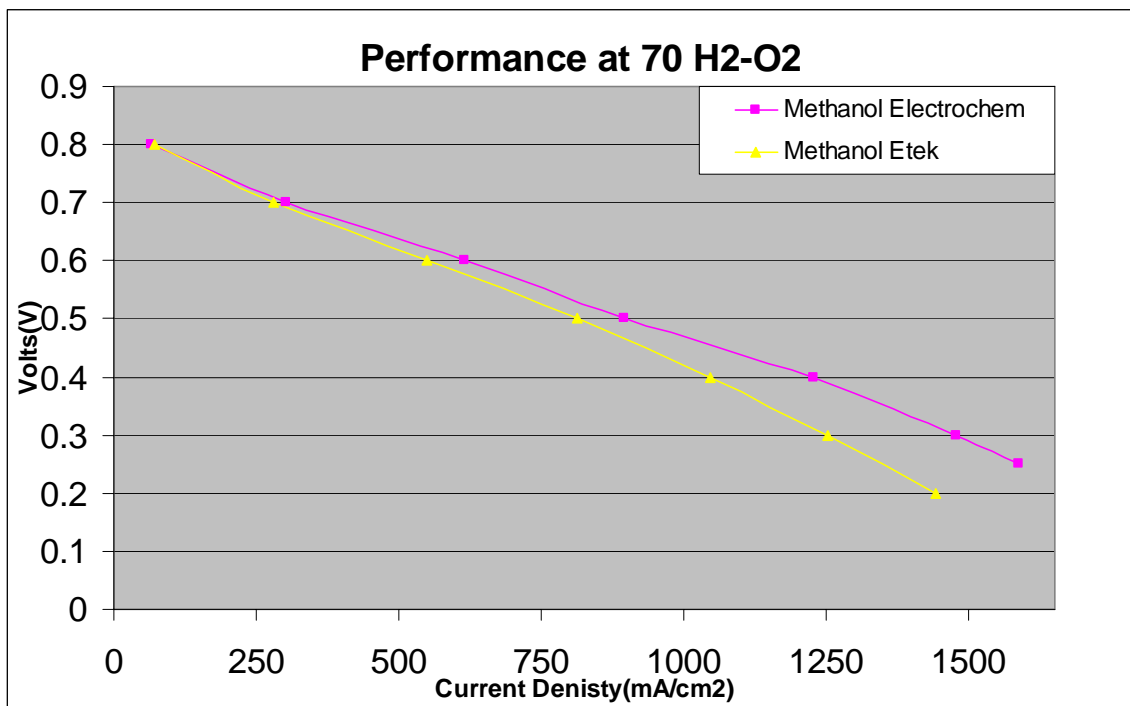


Figure 4.24 Comparison: E-tek vs. Electrochem Carbon Cloth

From this experiment it is evident that the type of carbon cloth clearly affects performance and that E-tek carbon cloth lowers performance, especially at higher current densities. Another factor examined was the complete pretreatment of the membrane before the application of the catalyst ink. As seen before with ethanol, this procedure gave lower performance and should be mirrored by methanol. The other condition examined was the affect PTFE has on the performance. PTFE is added to aid in the removal of water from the system by making the catalyst layer hydrophobic to prevent water from blocking the gasses from the catalyst layer. While this is a necessary feature, water is not formed on the anode side so the addition of PTFE to the anode side may actual hinder the performance. To examine this, a MEA was made using methanol as the

solvent, without PTFE on anode side. This was then placed on the anode side of the fuel cell. The results of these two factors can be seen on Figure 4.25

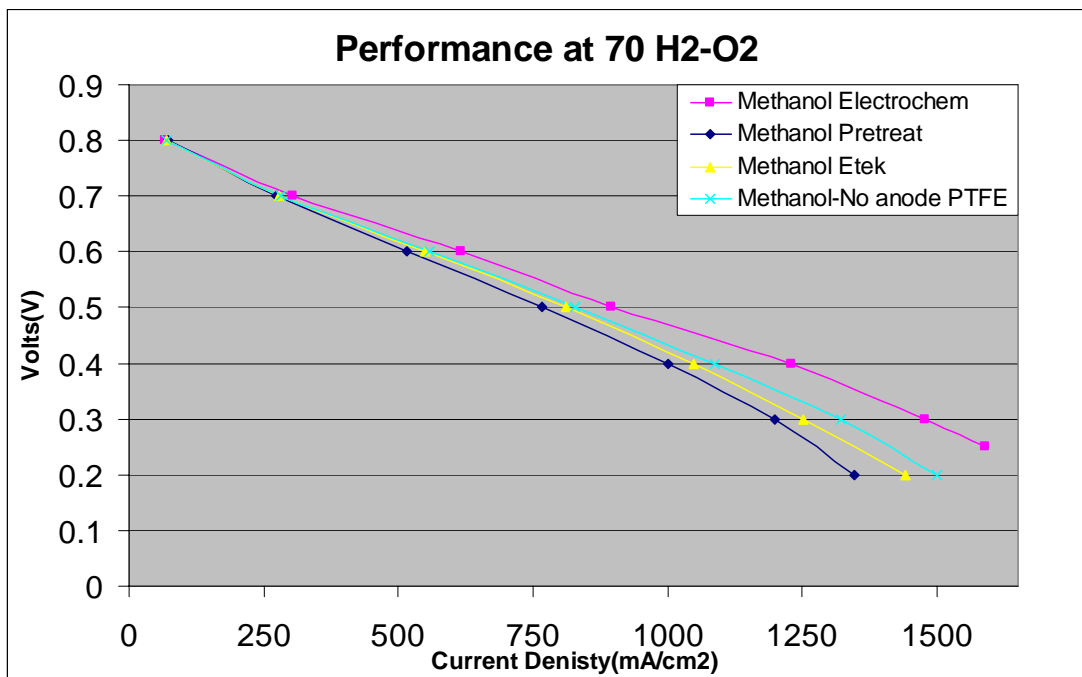


Figure 4.25 Comparison: Complete pretreatment of membrane, no anode PTFE

As shown in previous experiments the complete pretreatment method shows lower performance even with the E-tek carbon cloth. On the other hand the removal of PTFE from the anode side did slightly improve the performance of a MEA again using E-tek carbon cloth.

In the literature <sup>[4]</sup>, it was stated that treating the membrane so that it is in the sodium form would reduce swelling. This then should lead to better overall performance. The procedure followed in the preparation of this MEA involved the pretreatment method listed in the experimental methodology, followed by two addition steps. These were that after the pretreatment of DI water, 3% H<sub>2</sub>O<sub>2</sub>, DI water the membrane was then set to a low boil in 0.5M NaOH, and then again boiled in DI water. The normal procedure was then

followed for the rest of the fabrication of this MEA. The solvent chosen to test this was again methanol and the results of this experiment can be seen in Figure 4.26

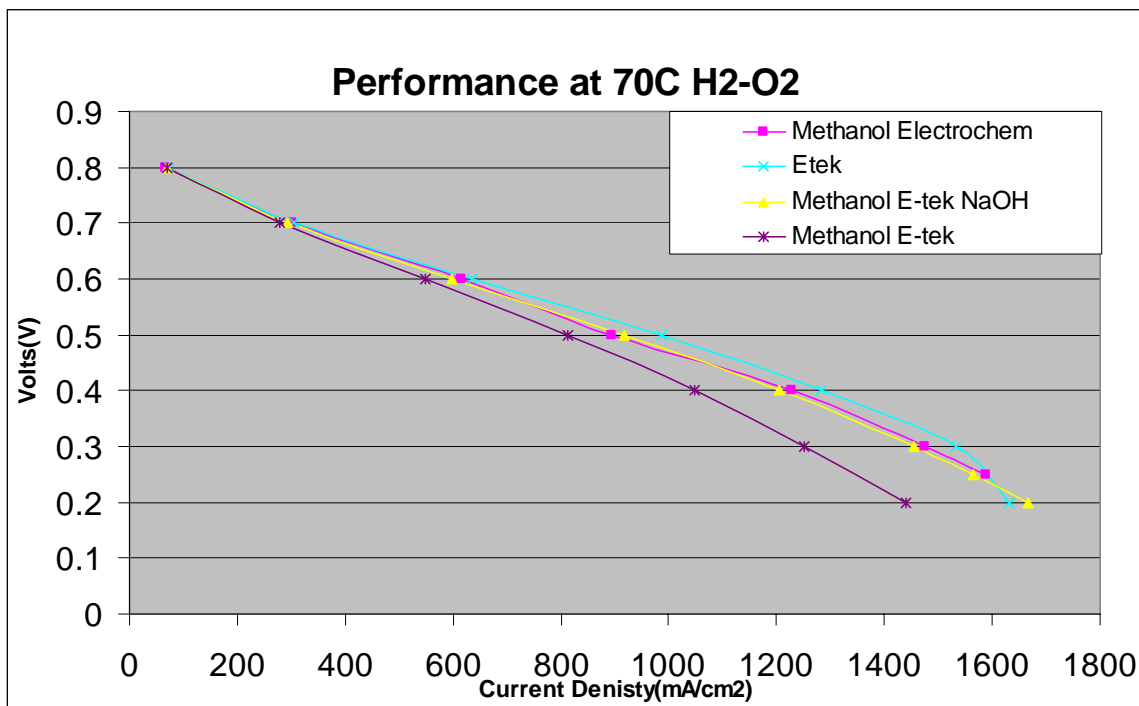
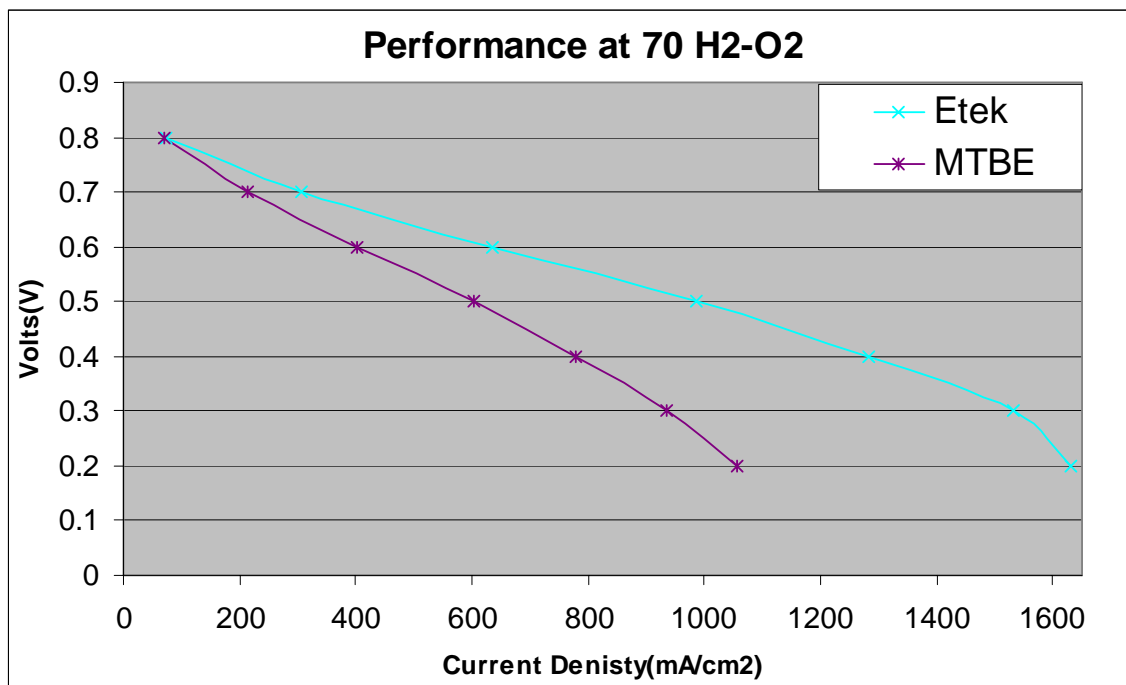


Figure 4.26 Comparison: Sodium form of membrane vs. Regular treatment

The results of this experiment indicate that the sodium form of the membrane does improve the performance significantly. Also, no swelling of the membrane was observed as the catalyst layer was applied. The conversion of the MEA to the sodium form improved the performance of the MEA made with E-tek carbon cloth, to that comparable to the MEA made with the Electrochem carbon cloth. It is possible that the Electrochem carbon cloth methanol MEA can be advanced to surpass the E-tek MEA, if it is converted to the sodium form as well before the catalyst ink application.

The colloidal form of the catalyst solution is said to form for solvents in the dielectric constant range of 3-10. In order to examine the effect of the colloidal form solvents in that range were selected. The first of which was MTBE, Methyl Tert Butyl

Ether, with a dielectric constant of 4.5. Though the solvent applied to the membrane with little swelling after being dried in the oven at 60°C, and then set to a low boil in 0.5M sulfuric acid, the catalyst layer began to come off from the membrane. In order to gain data from this solvent the membrane was completely pretreated and then the catalyst layer was applied. The result of this can be seen in Figure 4.27



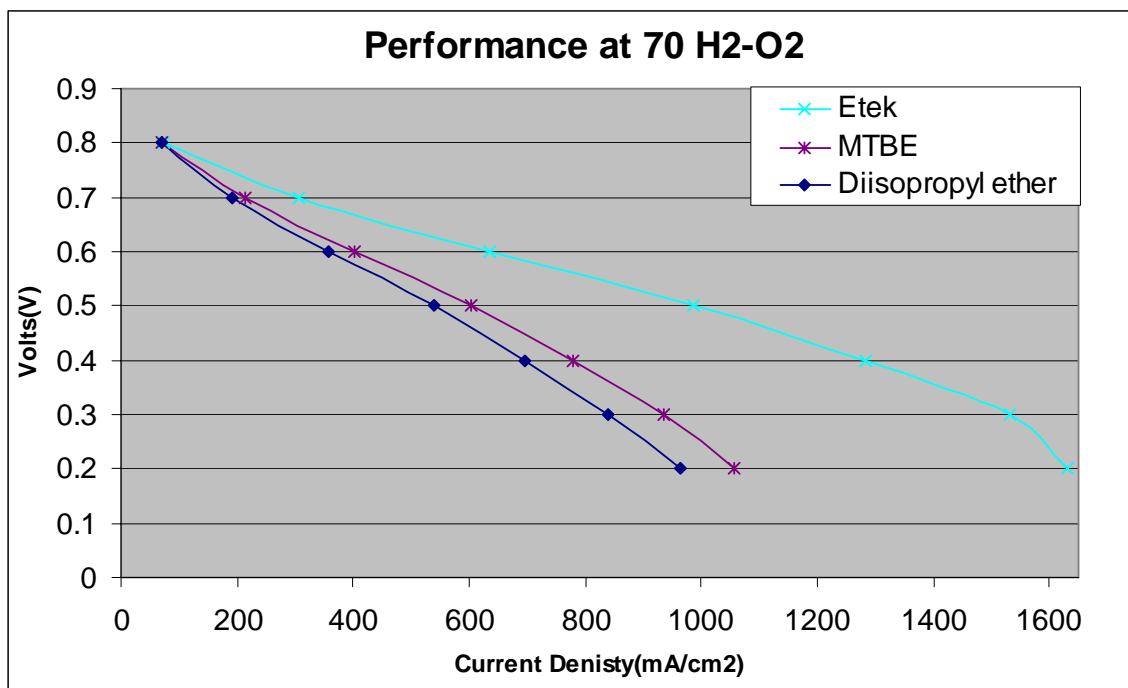
**Figure 4.27 Comparison: MTBE vs. Commercial catalyst**

Though the pretreatment method did allow for the testing of this MEA, it is known that this gives lower performance. Even if the membrane could be made following the established procedure or pre and post treatment the improvement would still be dwarfed as compared to the performance of the commercial E-tek MEA. The fact that the MTBE did not remain adhered to the membrane, suggest that MTBE may not be a good solvent under given conditions.

Continuing an examination of low dielectric constant solvents, a less volatile ether, diisopropyl ether, was chosen. It has a boiling point of 68°C compared to the



MTBE boiling point of 55°C, along with a lower dielectric constant of 3.9. The isopropyl ether MEA was made following the standard procedure and dried in the oven at 70°C. Figure 4.28 shows the result of this experiment.



**Figure 4.28 Comparison: Diisopropyl ether vs. MTBE**

As shown above, the performance of isopropyl ether was lower, suggesting that lower dielectric constant solvents may not be better. Testing solvents that form the colloidal solution with higher dielectric constants may yield better results.

Tetrahydrofuran, THF, was selected possessing similar characteristics to diisopropyl ether, with a 66°C boiling point and 7.6 dielectric constant versus diisopropyl ether that has a 68°C boiling point and 3.9 dielectric constant. THF also possesses similar characteristics to methanol which was a boiling point of 64°C and a dipole moment of 1.7 compared to THF which has a dipole moment of 1.75. The performance of the solvent may indicate the effect of form of the catalyst ink slurry. Methanol with a dielectric constant of 32.6 forms a solution, while THF with a dielectric constant of 7.6 should form

a colloidal solution. Using THF as a solvent very little swelling of the membrane was noted, similar to that of methanol. The oven temperature used for drying was 70°C. The result of this experiment is shown in Figure 4.29

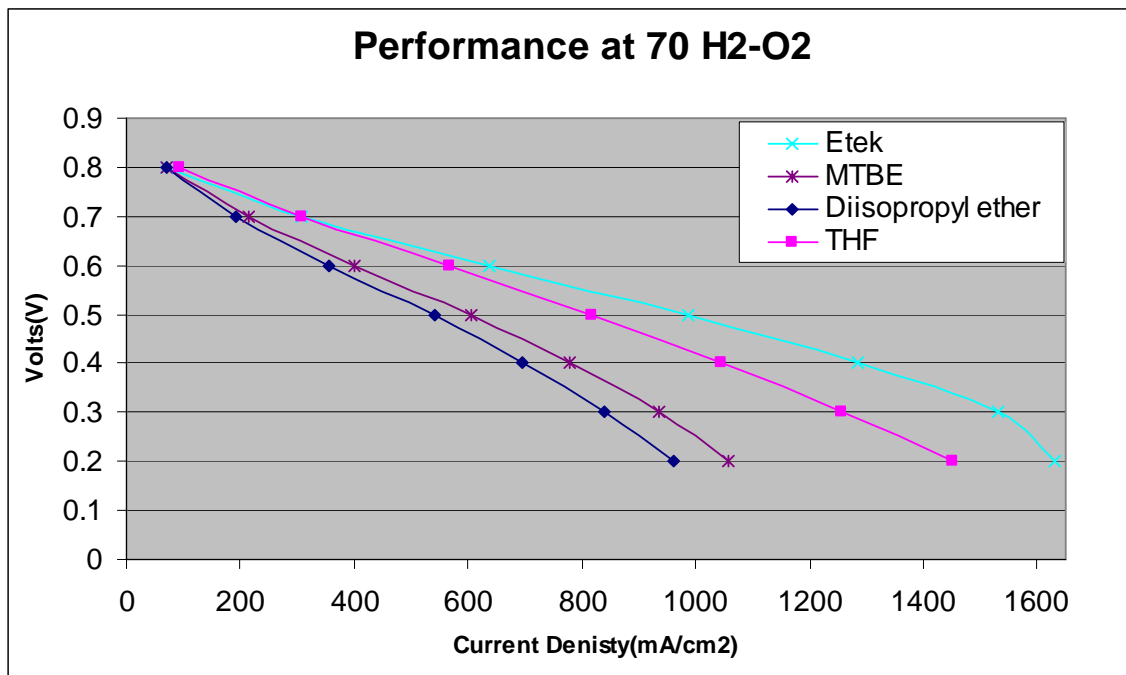


Figure 4.29 Comparison: Tetrahydrofuran vs. MTBE and Diisopropyl ether

From the graph it is clear that THF performed significantly better than other ethers. This could be due the similar properties of methanol or the higher dielectric constant. To continue on this path more solvents were chosen to examine the relationship between dielectric constants and performance.

The next solvent examined was Methyl Ethyl Ketone, or MEK. This solvent has very similar properties to acetone and would be expected to give similar results. The Dielectric constant is 18.5; slightly lower than that that of acetone which has a dielectric constant of 20.6. The difference between the dielectric constants of these two solvents is almost the same as that of MTBE and THF, which also have similar properties. If the

dielectric constant really did make the difference in the performance of MTBE vs. THF, this should be reflected in MEK vs. acetone. This MEA was made following the procedure, using E-tek carbon cloth and was dried in the oven at 82°C. The results of this can be seen in Figure 4.30

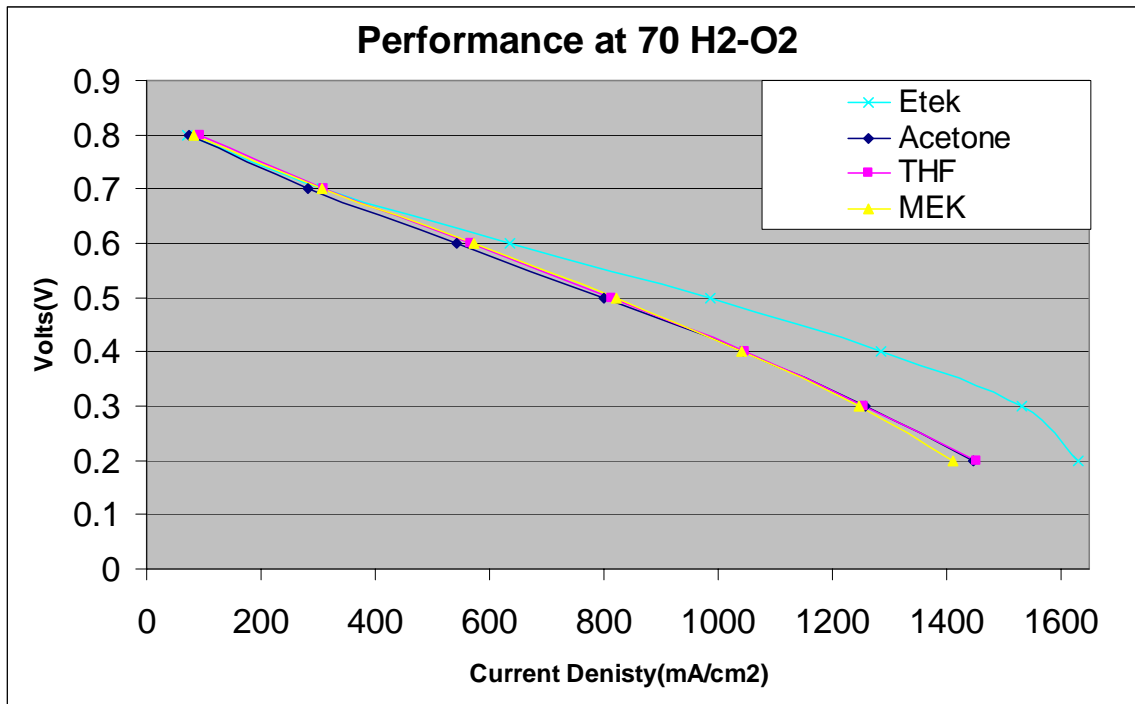


Figure 4.30 Comparison: MEK vs. Acetone and THF

Despite the difference in dielectric constants, MEK, THF and acetone were almost identical in performance. This then suggests that dielectric constant may not be as great a factor as previously thought.

This concludes the experimental results. The appendix provides the data points obtained from the entire laboratory experimental as well as any conditions applied in the MEA fabrication process that deviate from the experimental methodology.

## **Chapter V. Conclusions and Future Works**

This section is meant to provide a summary of our results as well as the conclusions that were based on those results for both the decal method and spray method. Our recommendations will follow at the end of our conclusions.

### ***Decal Method***

After reviewing the results, it appears that there are many solid conclusions that can be made. Firstly, it is important to roughen the Teflon surface blanks with silica paper as opposed to Fluoroglide (dry lubricant spray). Fluoroglide inhibited the three-phase interaction by “blocking” the reaction within the catalyst layer, while silica paper just roughens the surface.

Drying pressure is extremely crucial in the performance of MEAs. As seen in our results, the higher the pressure applied onto the membrane results in deformation of the membrane and increases ionic resistivity (lowering conductivity). These combined, will cause the performance of the MEA to decrease.

The addition of the hydrophobic agent PTFE also impacts MEA performance. It was shown in the results that the addition of too much PTFE can block the three-phase interface which decreases cell performance.

Finally, the amount of catalyst affects MEA performance drastically as well. The less catalyst used, in particular, the less platinum used, the lower the performance of the MEA.

Though there were some advancement in the methodology which showed some improvement in performance, in general, performance via decal method was quite

disappointing. There is however literature that describes how and why the decal method might actually not be the best method to use and how it hinders MEA performance. In a paper presented by researchers Xie et al<sup>[1]</sup>, a Nafion ionomer skin forms on top of the catalyst layer. This skin makes the catalyst layer less active by blocked gases from accessing the catalytic sites. Also, at higher current densities, the skin worsens flooding within the fuel cell.<sup>[1]</sup>

### ***Spray Method***

For the direct spray method, from experimental observations it is clear that there is a direct relationship between membrane swelling and performance. Thus, several experiments were performed to try to reduce swelling. It was found that solvents with low boiling points, typically in the range 50°C-80°C, were suitable due to the fact that they would evaporate quickly at room temperature limiting the time that the membrane is in contact with the solvent. Solvents of lower boiling points were too volatile resulting in poor adhesion. Conversely, solvents with higher boiling points were too viscous and remained on the membrane being slowly absorbed, causing distortion to the membrane.

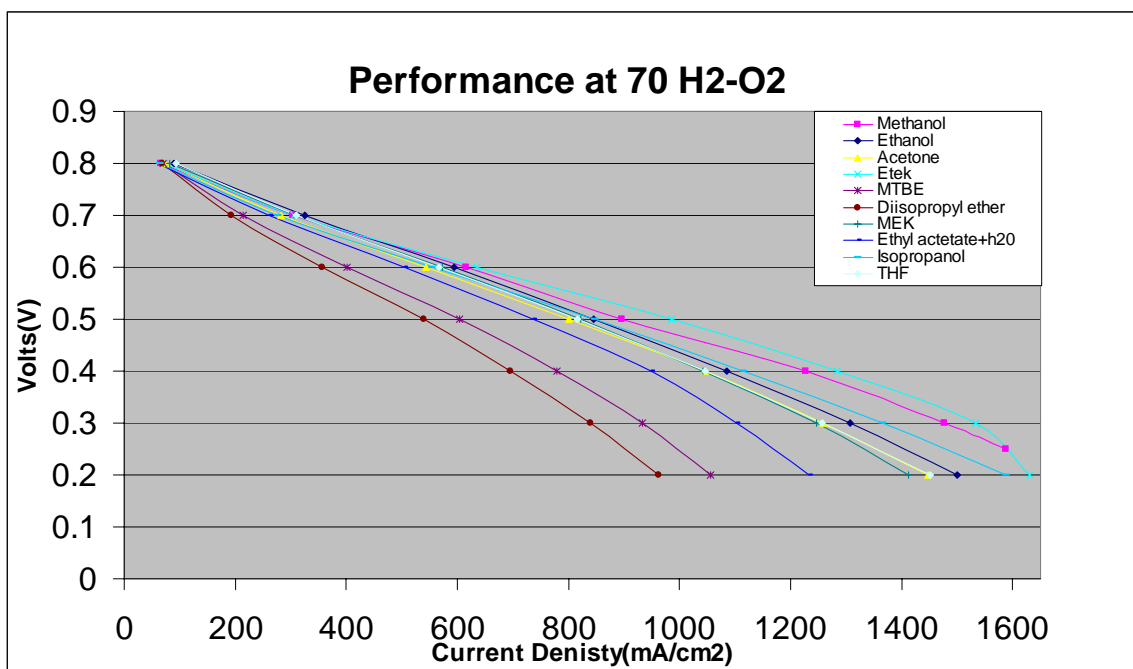
The application method is a critical step in producing high performing MEA, but the medium to which it is adhered is equally important. From experimentation, the application of the catalyst ink onto the carbon cloth was proven to be less effective than the application to the membrane, despite the fact that direct application results in warping of the membrane if the solvent is absorbed. In the case of catalyst application upon carbon cloth, there is zero membrane absorption of solvent yet this method gives lower performance, suggesting that the continuity of the catalyst layer also plays a very important role. Due to the porous nature of carbon cloth for gas diffusion, application of

the catalyst on carbon cloth often results in an inconsistent catalyst layer. The correlation between the consistency of the catalyst layer and performance is reflected in the direct application method. When the catalyst ink was directly applied to the membrane it would swell and then contract upon drying. When examined under SEM the catalyst layer developed cracks due to constant this expansion and contraction, which resulted in MEA that gave lower performance.

Another important factor in MEA fabrication is the treatment of the membrane. As seen in experiments, the treatment of the membrane may improve or hinder overall performance of the MEA. From the research done, it is apparent that one must ensure that the membrane and the Nafion in the catalyst layer are both in the protonated form, which was accomplished through the pre-post treatment developed. Additionally, the incorporation of the sodium form into the pre-post treatment sequence was preferable in direct application as it did limit the sorption of solvent into the membrane and produced MEA with higher performance.

There was little correlation in performance between the dielectric constant of the solvents that yield the colloidal form as opposed to the solution form. However, it was observed that the solvents with dielectric constants 3-10, that are said to form the colloidal form, often did not mix well with the catalyst ink resulting in catalyst slurry in which the particles were suspended in the solvent. This may be why these solvents gave lower performance. The catalyst slurry is composed of 10 wt % PTFE as well as 10wt% Nafion both of which are in water. Since there is so much water added into the catalyst ink, the ability of the solvent to mix well with the catalyst slurry would be dependent on the solvent's solubility in water. An example of this can be seen in the ethyl acetate+

water combinations. Ethyl acetate is only 8% soluble in water at room temperature however during sonication the beakers often get warm, further increasing the solubility. It would then follow that more ethyl acetate would dissolve into a slurry with less water than one with more water. If this is the case then the solution would mix more homogenously and give better performance. This conclusion was reflected in Figure 4.20 of the results section. A look at a comparison of all solvents on one chart, Figure 5.1 below, also shows similar results with the highest performance solvents being those with total solubility in water and decreasing performance as solubility in water decreases.



**Figure 5.1 Solvent Solubility Comparisons**

This explains why THF despite having a low dielectric constant behaved significantly better than its other low dielectric constant siblings. It was the only one with total solubility in water. MEK, though not totally soluble in water, performed slightly lower, suggesting that while total solubility is not the deciding factor, the degree to which a solvent is soluble in water does make a significant difference.

## Chapter VI. Recommendations

### ***Decal Method***

Due to the lack of time, the only parameters investigated concerning the decal method was the addition of PTFE, changing the amount of catalyst used within the slurry in order to determine the affects on MEA performance and drying pressure applied to the catalyzed and treated membrane. There is still much to be investigated via decal method.

The most crucial recommendation is to determine if Xie et al.'s paper is a valid reason as to why the decal method proved to give lower performance then the conventional spray method in this project. There are many different literatures that prove opposite of that literature, and hence more testing needs to be done. If Xie's finding can prove to be correct, then the decal method should not be implemented in the fabrication of MEAs.

Changing the form of the Nafion membrane (i.e. sodium form) which decreases the amount of swelling and deformation of the membrane and increases performance can be investigated.

Changing the solvent with similar properties to ethylene glycol (viscosity, dielectric constant, polarity, boiling point) should also be used within the catalyst slurry to see if similar performance is obtained to that of ethylene glycol. If that is accomplished, it can further be proved that there is a link between MEA performance and the solvents' properties. It is important to note here that solvents with lower viscosities are not ideal for the decal method, seeing as lower viscosity solvents would not adhere to the Teflon blanks.

Finding an optimum temperature time and duration where solvents fully evaporate and in which the membrane is not deformed can be investigated. Decreasing these



parameters can not only shorten the fabrication process, but possibly increase performance by increasing hydration of the membrane. Dehydration of the membrane can promote cracks to form within the membrane, causing the membrane to deform and ultimately lower MEA performance.

Decreasing the amount of PTFE is also something to be investigated. Like mentioned in the conclusions, too much PTFE was used, and possibly decreasing the amount can prove as in the spray method, that the addition of the hydrophobic agent makes very little difference, and could possibly be not used in the MEA fabrication.

The elimination of water within the catalyst slurry should be investigated. Deionized water was used within the catalyst slurry because initially, Nafion 5 wt % was used in the slurry mixture, causing the catalyst powder to spark when applied to the dry powder. Later however, it was decided to use Nafion 10 wt %, which is less acidic than Nafion 5 wt %. Since Nafion 10 wt % is less acidic, it is no longer necessary to wet the catalyst in order to prevent sparking.

These parameters are recommended to be changed as a continuation of this project. Of course there are many factors that can be examined, but these however were of interest to this project and might affect MEA performance the most. An investigation into these recommendations would prove to yield interesting results as well as assist in a better knowledge of the decal method in MEA fabrication.

## ***Spray Method***

Though several solvents were tested, a correlation could not be found between the effects that colloidal form of the catalyst solution to the dielectric constants. Therefore further testing of solvents said to form a colloidal solution, those in the 3-10 dielectric constant range, should be examined. This should be done ensuring that all these solvents have similar properties as well as total solubility in water to avoid limitations from the uneven mixing of the catalyst ink. Another aspect of the solvent to be examined is the effect that the solvent has on membrane degradation. It was observed with the ethers that the membrane began to change color from transparent to pale and even a dull yellow. When these were tested they gave low performance but upon replication gave higher performance suggesting that overtime the solvent may degrade the membrane. While the initial performance of an MEA is desired to be high, it is the maintenance of that performance that is important. Therefore solvent testing should again be evaluated as to how durable a membrane is based on the solvent chosen.

The application to the GDL was found to be lower than the direct application due to the porosity of the resulting GDL catalyst layer. There have been methods developed for applying a carbon backing to the carbon cloth to avoid the waste of catalyst that gets through the GDL. Having a carbon support would provide a more even layer as well as remove the factors of direct application such as membrane swelling, adhesion and side effects from the solvent.

The surface upon which the catalyst is applied also affects the performance, which is expressed by the effect of the roughness factor. From the modeling increasing the roughness factor should increase the performance. To do this the membrane may be

roughened through usage of sand paper or another inert roughening medium. This act would increase the catalyst area without increasing the application area and lead to better performance.

The membrane is dried in the oven to remove the solvent but the drying process subjects the catalyzed membrane to temperature changes that may not be beneficial to the structure of the membrane. Thus variations of the drying temperature may also be examined for the effect it may have on performance. For the direct application method the temperature of the solvents are often not significantly higher than found in the ambient surroundings. Therefore the membrane may also be simply air dried as opposed to oven dried to examine the affect the drying process has on MEA performance. Perhaps the membrane could be simply boiled in DI water to remove the solvent, given that the solvent is soluble in water, as opposed to drying in an oven.

The catalyst in preparation is an integral step in the fabrication process. The sonication of the catalyst ink often results in the heating of both the water for sonication as well as the catalyst ink. This then results in vaporization of the solvent as well as of the other components which later condense. This process has the adverse side effect that when this happens some of the catalyst ink components stick to the side of the beaker and are lost. Being unable to determine which components remain behind and to what extent, results in an unknown amount of catalyst application as well as composition. To avoid this it is recommended that shorter sonication times be used. Instead of a 3 hour sonicator a one and a half hour sonication time may be used to examine the whether or not the sonication time affects performance. The 5.5ml of solvent added to the catalyst slurry accounted for evaporation losses during the sonication process. If shorter sonication times

are tried with desirable results, lower solvents usage may also be attempted. The less solvent used, the less the membrane would deform, thereby limiting the decrease in performance due to solvent sorption.

The composition of the catalyst ink directly impacts the performance of an MEA. Lower catalyst loading may be more efficient for the anode and higher loading for the cathode. As such the composition and ratios of other components may need to be adjusted to account for this and variations of some of the components need to be examined. While initially the addition of Nafion was done on a ratio basis, if less catalyst is added the amount of Nafion needed may be more or less and should be experimentally established. This should also be examined for other components of the catalyst ink as well as the incorporation of other ingredients found to improve performance such as TBAOH.

Finally the membrane undergoes expansion and contraction during the pre-post treatment sequence. It was observed that after the catalyst layer is applied over the  $5\text{cm}^2$  area and the catalyzed membrane undergoes post treatment by low boiling, that the catalyst area is bigger than the area to which it was applied. This suggests that the membrane as well as the catalyst layer has expanded. This may be good in that the catalyst may be rougher due to the expansion or it may exhibit similar results as the absorption of the solvent which resulted in cracked and uneven catalyst layers. The expansion of the catalyzed MEA should be examined by increasing the amount of liquid from 250 to 400ml to avoid high boiling temperatures that occurs during the post treatment as liquid evaporates. Additionally shorter boiling times may be needed.

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## **Appendix I-Detailed Methodology for Spray Method**

Catalyst Preparation for  $0.6\text{mg}/\text{cm}^2$  for a  $10\text{cm}^2$  Area

- 1) Clean 100ml beaker and zero on scale.
- 2) Add 15 mg of 20% Pt/C= $6/0.2=30\text{mg}$  For one side this becomes= $15\text{mg}$
- 3) Add 3:7of PTFE to Pt/C = $3/7*30=12.857\text{mg}$ . Using a 10 % PTFE solution  $12.857*10=128.57\text{mg}$ . For one Side this becomes $128.57/2=64.3\text{mg}$
- 4) Add 10% Nafion solution for  $0.7\text{mg}/\text{cm}^2$  so this becomes 70mg then for one side it is 35mg Nafion
- 5) Add 1-3 drops of DI water, (not necessary)
- 6) Add 5.5 ml of solvent.
- 7) Mix to avoid settling and seal with parafilm.
- 8) Sonicate for 3 hours.

The desired application is  $0.4\text{mg}/\text{cm}^2$ . This procedure makes enough catalyst to apply for  $0.6\text{mg}/\text{cm}^2$  to account for any losses in the preparation and application of the catalyst ink. It is then applied across a  $5\text{cm}^2$  area.

Membrane Preparation

- 1) Cut a piece of  $2.5\text{in}^2$  Nafion 115 membrane.
- 2) Submerge in DI water and set to a low boil. (1hr)
- 3) Submerge in 3%  $\text{H}_2\text{O}_2$  water and set to a low boil. (1.5hr)
- 4) Submerge in DI water and set to a low boil. \*\*\* (1hr)
- 5) Remove membrane and dry in press at  $\sim 0.2$  metric tons pressure (10min)
- 6) Apply catalyst on side one (2hr)
- 7) Apply catalyst on side two (2hr)
- 8) Dry membrane in oven at  $80^\circ\text{C}$  (1.5hr)
- 9) Submerge in 0.5M  $\text{H}_2\text{SO}_4$  and set to a low boil. (1.5hr)
- 10) Submerge in DI water and set to a low boil. (1hr)
- 11) Remove membrane and dry in press at  $\sim 0.2$  metric tons pressure (10min)
- 12) Cut carbon cloth and hot press at  $275^\circ\text{C}$ . (15min)

\*\*\*For sodium form after step 4 boil in 0.5M NaOH for 1.5 hr then in DI water for 1 hr then continue with steps.



## Table of Solvents

<b>Alcohols</b>	Boiling Point [C]	Vapor Pressure @ 21CmmHg	Dipole	Polarity (water 100)	Dielectric Constant (20 C)	Absolute Viscosity (@ 25 C cP)	Solubility (in water 25 C %w/w)
Methanol	64	103	1.7	76.2	32.6	0.6	total
Ethanol	78	45.7	1.7	65.4	22.4	1.08	total
n-Propanol	97	13.4	1.7	61.7	20.1	1.72	total
i-Propanol	82	35.1	1.66	54.6	18.3	2	total
n-Butanol	118	4.8	1.66	60.2	18.2	3	7.3
i-Butanol	108	8.6	1.7	55.2	17.7	3.96	8.7
s-Butanol	99.5	13.2	1.7	50.6	16.56	3.7	19.8
n-Amyl Alcohol	138	3	1.7	56.8	13.9	4	1.7
i-Amyl Alcohol	130	2.4	1.8	56.5	15.2	4.2	2.75
Cyclohexanol	161	1.14	1.8	50	15	52.7	4.3
n-Octanol	194	0.14	1.9	54.3		7.5	0.6
Ethandiol	198	0.12	2.31	79	37.7	20	total
Diethylene Glycol	245	0.019	2.31	71.3	31.7	34	total
1,2-Propanediol	187	0.16			72.2	54	total
<b>Ethers</b>							
Diethyl ether	34.5	462	1.3	11.7	4.3	0.24	6.9
Diisopropyl ether	68	123	1.2			0.33	1.2
Dibutyl ether	142	5.5	1.2	7.1		0.63	0.03
Methyl Tert butyl ether	55	206	1.2	14.8	4.5	0.35	4.3
1,4 Dioxane	101	32	0.4	16.4	2.21	1.3	10
Tetrahydrofuran	66	133	1.75	21	7.6	0.55	total
<b>Ketones</b>							
Acetone	56	194	2.9	35.5	20.6	0.33	total
Methyl Ethyl Ketone	80	75.3	2.8	32.7	18.5	0.41	26
Methyl Isobutyl Ketone	116	16.5	2.81	27	13.1	0.61	8.4
Cyclohexanone	156	3.1	3.1	28	18.2	2.2	2.3
n-methyl-2-pyrrolidone	202	0.3	4.1	36	32.2	1.8	total
Acetophenone	202	0.35	2.9	30.6	17.4	1.74	0.55
Water	100	19	1.87	100	79.7	0.89	

## ***Appendix II-Experimental Data***

This appendix is dedicated to all of the raw data obtained from testing the MEAs in the fuel cell station for both the decal and spray method. Data includes the current density as well as the voltage.

### ***Decal Method***

**MEA 002**-decal method, ethylene glycol using Fluoroglide T=70°C, P=0.2 metric tons for 5 minutes.

V	mA/cm2
0.8	40
0.7	149.2
0.6	308
0.5	477
0.4	620
0.3	731
0.2	816

**MEA 003**-decal method ethylene glycol using sand paper T=70°C, P= 5 metric tons for 2 minutes for drying

V	mA/cm2
0.8	14
0.7	71
0.6	178.8
0.5	306.4
0.4	420
0.3	509.8
0.2	579.2

**MEA 004**-decal method, ethylene glycol using sand paper. T=70°C, P=0.2 metric tons  
for 5 minutes for drying

V	mA/cm <sup>2</sup>
0.8	56
0.7	224.2
0.6	453.4
0.5	703.4
0.4	915
0.3	1105
0.2	1258

**MEA 005**-decal method, ethylene glycol using sand paper, T=70°C, P=0.2 metric tons  
for 5 minutes for drying.

V	mA/cm <sup>2</sup>
0.8	70.6
0.7	252.6
0.6	487.6
0.5	730.4
0.4	949.4
0.3	1144.2
0.2	1302

**MEA 007**-decal method, ethylene glycol using sand paper, T=70°C, P=0.2 metric tons  
for 5 minutes for drying and PTFE (using less catalyst).

V	mA/cm <sup>2</sup>
0.8	64
0.7	237
0.6	454.8
0.5	674.4
0.4	871.6
0.3	1072
0.2	1240

**MEA 008**-decal method, ethylene glycol using sand paper, T=70°C, P=0.2 metric tons  
for 5 minutes for drying and without PTFE (using less catalyst).

V	mA/cm <sup>2</sup>
0.8	44
0.7	168.2
0.6	339.8
0.5	522.4
0.4	677.6
0.3	799.8
0.2	883.4

**MEA 010**-decal method, ethylene glycol with PTFE and sand paper T=70°C, P=0.2  
metric tons for 5 minutes for drying (using less catalyst).

V	mA/cm <sup>2</sup>
0.8	30
0.7	108.8
0.6	214
0.5	330
0.4	435.8
0.3	520.6
0.2	586.6

## Spray Method

Figure 4.8 Catalyzed GDL  
Membrane Pretreatment  
Ethanol Solvent  
Oven at 80 C

<b>H2-O2 FCT 30C</b>			<b>H2-O2 FCT 70C</b>		
V (v)	I(A)	mA/cm2	V (v)	I(A)	mA/cm2
0.8	0.14	28	0.8	0.206	41.2
0.7	0.51	102	0.7	0.74	148
0.6	0.983	196.6	0.6	1.42	284
0.5	1.45	290	0.5	2.2	440
0.4	1.87	374	0.4	2.89	578
0.3	2.23	446	0.3	3.516	703.2
0.2	2.44	488	0.2	4.06	812

Figure 4.9 Catalyzed membrane  
Membrane Pretreatment  
Ethanol Solvent  
Oven at 80 C

<b>H2-O2 FCT 30C</b>			<b>H2-O2 FCT 70C</b>		
V (v)	I(A)	mA/cm2	V (v)	I(A)	mA/cm2
0.8	0.187	37.4	0.8	0.402	80.4
0.7	0.775	155	0.7	1.17	234
0.6	1.46	292	0.6	2.1	420
0.5	2.4	480	0.5	3.27	654
0.4	3.5	700	0.4	4.39	878
0.3	4.2	840	0.3	5.28	1056
0.2	4.8	960	0.2	6.086	1217.2

Figure 4.14  
Complete Post-treatment  
Ethanol Solvent  
Oven at 80C

<b>H2-O2 FCT 70C</b>		
V (v)	I(A)	mA/cm2
0.8	0.3	60
0.7	1.233	246.6
0.6	2.5	500
0.5	3.6	720
0.4	4.3	860
0.3	5.2	1040
0.2	6.01	1202

Complete Pretreatment  
Ethanol Solvent  
Oven at 80C

<b>H2-O2 FCT 70C</b>		
V (v)	I(A)	mA/cm2
0.8	0.24	48
0.7	1.22	244
0.6	2.43	486
0.5	3.64	728
0.4	4.75	950
0.3	5.68	1136
0.2	6.53	1306

Figure 4.15  
 Electrochem carbon cloth  
 Pre-post treatment  
 Ethanol Solvent  
 Oven at 80 C

<b>H2-O2 FCT 70C</b>			<b>H2-O2 FCT 30C</b>		
V (v)	I(A)	mA/cm2	V (v)	I(A)	mA/cm2
0.8	0.45	90	0.8	0.35	70
0.7	1.625	325	0.7	1.25	250
0.6	2.972	594.4	0.6	2.074	414.8
0.5	4.23	846	0.5	3.177	635.4
0.4	5.43	1086	0.4	4.022	804.4
0.3	6.54	1308	0.3	5.04	1008
0.2	7.5	1500	0.2	5.674	1134.8

<b>H2-AIR FCT 70C</b>			<b>H2-AIR FCT 30C</b>		
V (v)	I(A)	mA/cm2	V (v)	I(A)	mA/cm2
0.8	0.25	50	0.8	0.15	30
0.7	1.074	214.8	0.7	0.841	168.2
0.6	2.04	408	0.6	1.45	290
0.5	2.899	579.8	0.5	2.09	418
0.4	3.67	734	0.4	2.75	550
0.3	4.225	845	0.3	3.35	670
0.2	4.686	937.2	0.2	3.658	731.6

Figure 4.16  
 Electrochem carbon cloth  
 Pre-post treatment  
 Isopropanol Solvent  
 Oven at 82 C  
 Isopropanol

<b>H2-O2 FCT 70C</b>			<b>H2-O2 FCT 30C</b>		
V (v)	I(A)	mA/cm2	V (v)	I(A)	mA/cm2
0.8	0.325	65	0.8	0.23	46
0.7	1.382	276.4	0.7	0.958	191.6
0.6	2.776	555.2	0.6	1.948	389.6
0.5	4.234	846.8	0.5	3.008	601.6
0.4	5.574	1114.8	0.4	4.1	820
0.3	6.827	1365.4	0.3	5.16	1032
0.2	7.94	1588	0.2	5.95	1190

<b>H2-AIR FCT 70C</b>			<b>H2-AIR FCT 30C</b>		
V (v)	I(A)	mA/cm2	V (v)	I(A)	mA/cm2
0.8	0.18	36	0.8	0.1	20
0.7	0.837	167.4	0.7	0.6	120
0.6	1.742	348.4	0.6	1.26	252
0.5	2.621	524.2	0.5	1.928	385.6

0.4	3.364	672.8	0.4	2.569	513.8
0.3	3.972	794.4	0.3	3.07	614
0.2	4.432	886.4	0.2	3.58	716

Isopropanol 2

<b>H2-O2 FCT 70C</b>			<b>H2-AIR FCT 70C</b>		
V (v)	I(A)	mA/cm2	V (v)	I(A)	mA/cm2
0.8	0.35	70	0.8	0.15	30
0.7	1.458	291.6	0.7	0.83	166
0.6	2.732	546.4	0.6	1.623	324.6
0.5	3.989	797.8	0.5	2.355	471
0.4	5.14	1028	0.4	2.964	592.8
0.3	6.172	1234.4	0.3	3.483	696.6
0.2	7.089	1417.8	0.2	3.853	770.6

Figure 4.17

Electrochem carbon cloth

50%water 50% Ethanol Solvent

Pre-post treatment

Oven 82C

<b>H2-O2 FCT 70C</b>			<b>H2-O2 FCT 30C</b>		
V (v)	I(A)	mA/cm2	V (v)	I(A)	mA/cm2
0.8	0.325	65	0.8	2.16	432
0.7	1.24	248	0.7	0.868	173.6
0.6	2.503	500.6	0.6	1.732	346.4
0.5	3.857	771.4	0.5	2.687	537.4
0.4	5.101	1020.2	0.4	3.067	613.4
0.3	6.22	1244	0.3	4.462	892.4
0.2	7.219	1443.8	0.2	5.261	1052.2

Figure 4.18

Electrochem carbon cloth

Methanol Solvent

Pre-post treatment

Oven 60C

<b>H2-O2 FCT 70C</b>			<b>H2-O2 FCT 30C</b>		
V (v)	I(A)	mA/cm2	V (v)	I(A)	mA/cm2
0.8	0.33	66	0.8	0.19	38
0.7	1.515	303	0.7	0.893	178.6
0.6	3.08	616	0.6	1.939	387.8
0.5	4.476	895.2	0.5	3.122	624.4
0.4	6.14	1228	0.4	4.272	854.4
0.3	7.381	1476.2	0.3	5.364	1072.8
0.25	7.939	1587.8	0.2	6.244	1248.8

<b>H2-AIR FCT 70C</b>			<b>H2-AIR FCT 30C</b>		
V (v)	I(A)	mA/cm2	V (v)	I(A)	mA/cm2
0.8	0.089	17.8	0.8	0.11	22
0.7	0.772	154.4	0.7	0.588	117.6
0.6	1.76	352	0.6	1.232	246.4
0.5	2.66	532	0.5	1.872	374.4
0.4	3.35	670	0.4	2.476	495.2
0.3	3.85	770	0.3	2.907	581.4
0.2	4.26	852	0.2	3.254	650.8

Figure 4.19  
 Electrochem carbon cloth  
 2ml Water + Ethyl Acetate Solvent  
 Pre-post treatment  
 Oven 60C

<b>H2-O2 FCT 70C</b>			<b>H2-O2 FCT 30C</b>		
V (v)	I(A)	mA/cm2	V (v)	I(A)	mA/cm2
0.8	0.146	29.2	0.8	0.104	20.8
0.7	0.604	120.8	0.7	0.4	80
0.6	1.475	295	0.6	0.836	167.2
0.5	2.806	561.2	0.5	1.429	285.8
0.4	4.234	846.8	0.4	2.203	440.6
0.3	5.601	1120.2	0.3	3.122	624.4
0.2	6.746	1349.2	0.2	4.036	807.2

Figure 4.20  
 Electrochem carbon cloth  
 1ml Water + Ethyl Acetate Solvent  
 Pre-post treatment  
 Oven 60C

<b>H2-O2 FCT 70C</b>		
V (v)	I(A)	mA/cm2
0.8	0.3	60
0.7	1.31	262
0.6	2.52	504
0.5	3.686	737.2
0.4	4.743	948.6
0.3	5.515	1103
0.2	6.165	1233



Figure 4.21  
 Electrochem carbon cloth  
 1ml Water + Methanol Solvent  
 Pre-post treatment  
 Oven 70C

**H2-O2 FCT 70C**

V (v)	I(A)	mA/cm2
0.8	0.42	84
0.7	1.55	310
0.6	2.955	591
0.5	4.418	883.6
0.4	5.696	1139.2
0.3	6.98	1396
0.2	8.055	1611

Figure 4.22  
 Electrochem carbon cloth  
 Acetone Solvent  
 Pre-post treatment  
 Oven 60C

**H2-O2 FCT 70C**

V (v)	I(A)	mA/cm2
0.8	0.37	74
0.7	1.417	283.4
0.6	2.72	544
0.5	4.005	801
0.4	5.227	1045.4
0.3	6.295	1259
0.2	7.235	1447

**H2-O2 FCT 30C**

V (v)	I(A)	mA/cm2
0.8	0.19	38
0.7	0.903	180.6
0.6	1.767	353.4
0.5	2.659	531.8
0.4	3.52	704
0.3	4.333	866.6
0.2	5.052	1010.4

**H2-AIR FCT 70C**

V (v)	I(A)	mA/cm2
0.8	0.18	36
0.7	0.84	168
0.6	1.65	330
0.5	2.42	484
0.4	3.061	612.2
0.3	3.571	714.2
0.2	3.985	797

**H2-AIR FCT 30C**

V (v)	I(A)	mA/cm2
0.8	0.13	26
0.7	0.561	112.2
0.6	1.115	223
0.5	1.646	329.2
0.4	2.138	427.6
0.3	2.535	507
0.2	2.85	570

Figure 4.23 Commercial electrode

E-tek Carbon cloth

0.7mg/cm<sup>2</sup> Nafion

Oven 82C

**H2-O2 FCT 70C**

V (v)	I(A)	mA/cm2
0.8	0.36	72
0.7	1.53	306
0.6	3.18	636
0.5	4.929	985.8
0.4	6.421	1284.2
0.3	7.663	1532.6
0.2	8.153	1630.6

**H2-O2 FCT 30C**

V (v)	I(A)	mA/cm2
0.8	0.27	54
0.7	1.082	216.4
0.6	2.15	430
0.5	3.185	637
0.4	4.105	821
0.3	4.844	968.8
0.2	5.392	1078.4

**H2-AIR FCT 70C**

V (v)	I(A)	mA/cm2
0.8	0.2	40
0.7	0.96	192
0.6	1.906	381.2
0.5	2.646	529.2
0.4	3.206	641.2
0.3	3.686	737.2
0.2	4.13	826

**H2-AIR FCT 30C**

V (v)	I(A)	mA/cm2
0.8	0.16	32
0.7	0.624	124.8
0.6	1.235	247
0.5	1.775	355
0.4	2.188	437.6
0.3	2.54	508
0.2	2.88	576

Figure 4.24

Methanol Solvent

E-tek Carbon cloth

Pre-post treatment

Oven 70C

**H2-O2 FCT 70C**

V (v)	I(A)	mA/cm2
0.8	0.353	70.6
0.7	1.395	279
0.6	2.749	549.8
0.5	4.06	812
0.4	5.234	1046.8
0.3	6.261	1252.2
0.2	7.207	1441.4

Figure 4.25  
 Methanol solvent  
 E-tek Carbon cloth  
 Complete pretreatment  
 Oven 70C

**H2-O2 FCT 70C**

V (v)	I(A)	mA/cm2
0.8	0.365	73
0.7	1.36	272
0.6	2.576	515.2
0.5	3.836	767.2
0.4	5.002	1000.4
0.3	5.993	1198.6
0.2	6.732	1346.4

Figure 4.25  
 Methanol solvent  
 E-tek Carbon cloth  
 No PTFE on anode side  
 Pre-post treatment  
 Oven 70C

**H2-O2 FCT 70C**

V (v)	I(A)	mA/cm2
0.8	0.35	70
0.7	1.412	282.4
0.6	2.79	558
0.5	4.136	827.2
0.4	5.432	1086.4
0.3	6.604	1320.8
0.2	7.496	1499.2

Figure 4.26  
 Methanol solvent  
 E-tek Carbon cloth  
 Pre-post treatment with NaOH  
 Oven 70C

**H2-O2 FCT 70C**

V (v)	I(A)	mA/cm2
0.8	0.352	70.4
0.7	1.46	292
0.6	2.994	598.8
0.5	4.586	917.2
0.4	6.029	1205.8
0.3	7.279	1455.8
0.25	7.825	1565
0.2	8.325	1665

Figure 4.27  
 MTBE solvent  
 E-tek Carbon cloth  
 Complete Pretreatment  
 Oven 60C

**H2-O2 FCT 70C**

V (v)	I(A)	mA/cm2
0.8	0.35	70
0.7	1.07	214
0.6	2.01	402
0.5	3.02	604
0.4	3.9	780
0.3	4.67	934
0.2	5.282	1056.4

Figure 4.28  
 Diisopropyl ether solvent  
 E-tek Carbon cloth  
 Pre-post treatment  
 Oven 70C

**H2-O2 FCT 70C**

V (v)	I(A)	mA/cm2
0.8	0.345	69
0.7	0.96	192
0.6	1.786	357.2
0.5	2.7	540
0.4	3.48	696
0.3	4.2	840
0.2	4.812	962.4

Figure 4.29  
 THF solvent  
 E-tek Carbon cloth  
 Pre-post treatment  
 Oven 70C

**H2-O2 FCT 70C**

V (v)	I(A)	mA/cm2
0.8	0.468	93.6
0.7	1.545	309
0.6	2.835	567
0.5	4.077	815.4
0.4	5.23	1046
0.3	6.283	1256.6
0.2	7.259	1451.8

Figure 4.30  
THF solvent  
E-tek Carbon cloth  
Pre-post treatment  
Oven 82C

**H2-O2 FCT 70C**

V (v)	I(A)	mA/cm2
0.8	0.41	82
0.7	1.538	307.6
0.6	2.862	572.4
0.5	4.112	822.4
0.4	5.209	1041.8
0.3	6.232	1246.4
0.2	7.057	1411.4