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Theory of Proton Exchange  
Membranes Fuel Cells and the Testing of  
Performance Characteristics of Polymer  
Electrolyte Membranes

By

Tizoc Cruz-Gonzalez

Submitted to the Department of Mechanical  
Engineering in Partial Fulfillment of the Requirements  
for the Degree of

Bachelor of Science

at the

Massachusetts Institute of Technology

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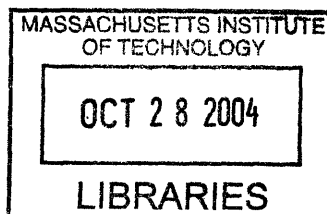
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Abstract

Proton exchange membrane (PEM) fuel cells hold great promise as source of power. A hydrogen and oxygen PEM fuel is a simple fuel cell that can be theoretically characterized. The performance of a PEM fuel cell can be characterized if the contents of the two gas lines are known, the back pressure is controlled, the operating temperature of the fuel cell is known and the ohmic resistances of the cell are known. The voltage output will vary with the current density that the cell is loaded with.

To completely characterize the fuel cell performance it is required that a fuel cell testing station or equivalent controllers be used to direct the operating conditions. The main aspects that the testing station will control is the temperature of the fuel cell, the relative humidity of the gas lines, the back pressure in the fuel cell, and the load the fuel cell will experience. With the information in this paper it is possible describe the performance characteristics of PEM fuel cell.

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## Introduction

In modern industrialized society we need a significant amount of energy for many purposes in our every day life. Whether we use the refrigerator, TV, computer, whether we drive by car or by subway or whether we only enjoy light and heat, the driving force is always energy. The sources of 90 % of our energy requirement come from fossil fuels: coal, petroleum and natural gas[1]. These fuels are not renewable, and once burnt they are gone forever. In this context there are two problems that are paramount. One problem is the limited number of years that fossil fuels will be available, and the other is the pollution caused by burning fossil fuels. A solution to these problems is the use of hydrogen as an energy transport medium. Wind, solar and hydro power can produce hydrogen fuel that is 100% pollution-free and 100% renewable. Hydrogen can be made from water, and when burned, turns back into water.

There are two methods to using hydrogen as a fuel: one is to use it as a thermal source of energy and the other is to use it as an electrochemical source of energy. The use of hydrogen to produce thermal energy is useful because it can be easily integrated into the existing energy conversion systems: Internal combustion engines, turbines, and gas fired energy plants. The long term advantage of hydrogen as an energy source is that it can be used as an electrochemical energy source in fuel cells. As an electrochemical energy source, hydrogen has a higher efficiency than the maximum Carnot efficiency that governs thermal energy conversion systems. The development of fuels cell technology is important to the future of the hydrogen economy.

There are five main different types of fuel cells that use hydrogen as an energy source and are technologically feasible: Alkaline Fuel Cell (AFC), Proton Exchange Membrane Fuel Cell (PEMFC), Phosphoric Acid Fuel Cell (PAFC), Molten Carbonate Fuel cell (MCFC), and Solid Oxide Fuel Cell (SOFC). The PEM fuel cell holds many promises for the future because of the small size, ease of handling, lightness, and very high efficiency and also because as a reaction gas it requires only atmospheric oxygen instead of pure oxygen. The power output of a PEM fuel cell can be controlled very dynamically. Therefore, it is suitable for mobile applications and decentralized power

plants that require different power outputs over short periods of time.

There are many important factors that influence the performance characteristics of PEM fuel cells. Some of the important factors are temperature of the fuel cell, pressure of the gas streams, mass flow rate of the gas streams, the humidity of the gas streams and the hydration of the proton exchange membrane. The hydration of the proton exchange membrane is important because the membrane loses ion conductivity as it dries out, which can contribute significantly to lower fuel cell performance. The following sections can give a fundamental understanding of PEM fuel cells and their performance testing.

## **Basic Model**

The process that produces electricity in a fuel cell is rather simple. Inside the fuel cell there is a catalyzer area and two gas circuits that the gaseous oxygen and hydrogen flow into, which traverse the catalyzer area. While in contact with the catalyzer the hydrogen molecules ( $H_2$ ) are split into two  $H^+$  protons. At the same time each hydrogen atom sends out one electron along an external electric circuit. The protons move through the electrolyte (Proton exchange membrane) to the cathode area. The electrons move from the anode to the cathode and cause an electric current. This electric current can supply an electric capacitor with electric charge. Next, two electrons recombine with one Oxygen molecule at the cathode. The now-generated oxygen ions have a negative load. They move to the positively loaded hydrogen protons that have traversed the electrolyte. Then finally the oxygen ions give their electrons to the two hydrogen protons and oxidize into water, thus completing the PEM fuel cell process, Figure 1.

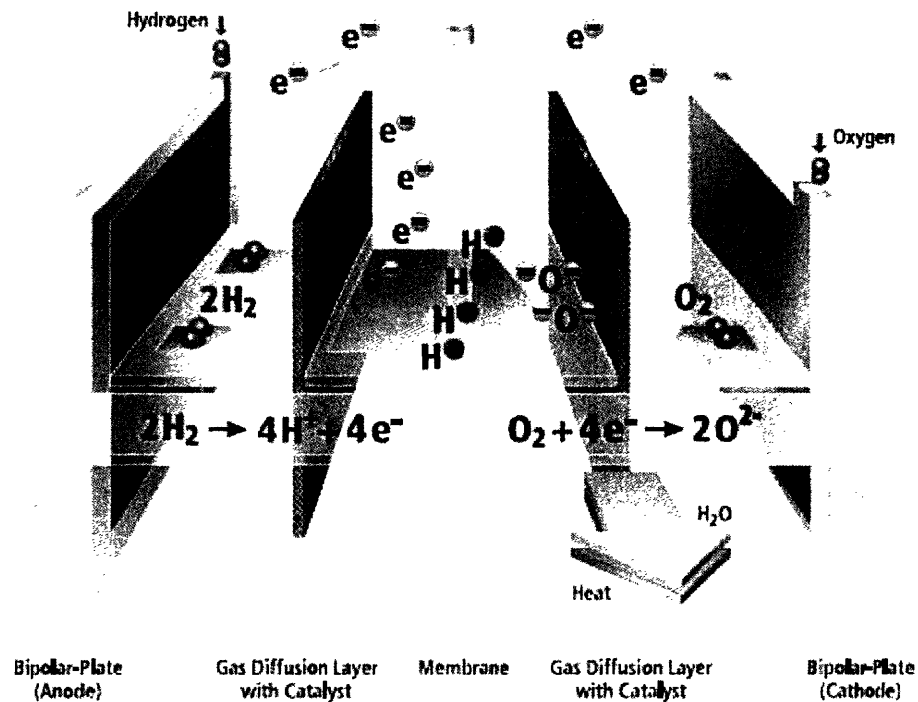


Figure 1. Schematic of a how a fuel cell works. [2]

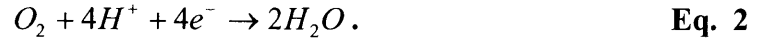
### Open Circuit Voltage [3]

The maximum energy potential in a fuel is dependent on the anodic half cell voltage potential and the cathodic half cell voltage potential. The anodic reaction is the oxidation process by which hydrogen is converted into hydrogen protons and two electrons:



The half cell voltage potential for this anodic reaction,  $\epsilon_{anode}^0$ , at 25°C is 0.0V. This means that at the right temperature and with a catalyst no energy is required to split the hydrogen molecule. The cathodic half cell reaction is the reduction process by which oxygen reacts with 4 hydrogen protons and 4 electrons to form water:





The half cell voltage potential for this cathodic reaction,  $\varepsilon_{cathode}^o$ , at  $25^\circ C$  is  $1.229V$ . In other words, when the water molecule is formed, this much energy was released. The half cell voltage potentials are dependent on temperature and the voltage will increase as the reaction temperature of the fuel cell is increased. Combining the two half cell reactions, it is possible to develop the overall reaction that takes place in a Hydrogen and Oxygen PEM fuel cell,



The total cell potential is a combination of the negative of the anodic half cell potential in addition the cathodic half cell voltage potential:

$$\varepsilon_r^o = -\varepsilon_{anode}^o + \varepsilon_{cathode}^o, \quad \text{Eq. 4}$$

where  $\varepsilon_r^o$  is the reference voltage potential at a reference temperature.

At equilibrium the Nernst equation governs the reaction voltage potential of a PEM fuel cell.

$$\varepsilon_r = \varepsilon_r^o - \frac{RT}{n_e F} \ln \Pi a_i^{v_i}, \quad \text{Eq. 5}$$

where  $\varepsilon_r$  is the maximum open circuit voltage that the fuel cell can produce,  $\varepsilon_r^o$  is the total cell potential at the reference temperature,  $R$  is the universal gas constant,  $T$  is the cell temperature,  $n_e$  is the number of electrons involved in the formation of one species in the cathodic reaction,  $F$  is Faraday's constant,  $a_i$  is the activity coefficient which will be described later in greater detail, and  $v_i$  are the stoichiometric coefficients involved in the total fuel cell reaction. For a hydrogen and oxygen fuel it is possible to simplify Equation 5 by replacing the activity coefficient of the gases with the partial pressures of the gas lines,

$$\varepsilon_r = \varepsilon_r^o - \frac{RT}{n_e F} \ln \frac{a_{H_2O_l}}{p_{H_2}^1 p_{O_2}^{\frac{1}{2}}}. \quad \text{Eq. 6}$$

The equation can be further simplified because the activity of liquid water is one and the electron involved in an anodic reaction is two. The final result is that the open cell voltage is dependent on the pressures of the gas, and the temperature of the cell:

$$\varepsilon_r = \varepsilon_r^o + \frac{RT}{2F} \ln p_{H_2}^1 p_{O_2}^{\frac{1}{2}}. \quad \text{Eq. 7}$$

### **Overpotential [4]**

During operation a fuel cell is not an ideal system and the electrochemical processes occur at finite rates that do not correspond to the equilibrium or open circuit voltage. In Electrochemistry the deviation of the equilibrium voltage potential and the experimental voltage is called the overpotential,  $\eta$ . The overpotential for a specific oxidation reduction reaction is defined as the absolute difference between the experimentally measured voltage and the voltage predicted at equilibrium by the Nernst equation,

$$\eta = \left| \varepsilon_{\text{experimental}} - \varepsilon_r \right|. \quad \text{Eq. 8}$$

The total overpotential can be subdivided into three sections: activation overpotential, Mass transfer overpotential, and ohmic overpotential. The activation overpotential is caused by chemical processes that are not ideal. The Mass transfer overpotential exists because there are finite limits to mass transfer that will affect the speed at which the reaction can take place. The ohmic overpotential is caused by the electrical impedances that occur in the circuit and by the ion resistance of the electrolyte.

Combining the three overpotentials it is possible to define the fuel cell voltage in terms of the current density and other factors:

$$\varepsilon_{\text{experimental}} = \varepsilon_r - \eta_a - \eta_c - \eta_{\Omega}. \quad \text{Eq. 9}$$

### **Activation Overpotential [5]**

The activation overpotential,  $\eta_a$ , characterizes the limiting reaction rates of the anodic and cathodic reaction, which usually take place within the electrical double layer. The electrical double layer is defined as the region near the electrode surface where there is a separation of charges and a layer of solution with different composition from the bulk solution. The electro-chemical reactions described, Equations 1 and 2, are simplifications of the actual reactions that take place. Two of the non-simplified reactions steps are disassociation and adsorption. All the reaction steps have unique over potentials but they are very hard to separate and characterize individually, so an overall overpotential is used to define the activation barrier for rate limiting reaction. The current is related to the activation over potential with the Butler-Volmer equation:

$$i = i_o \left( \exp \left[ \frac{-\alpha F \eta_a}{RT} \right] - \exp \left[ \frac{(1-\alpha) F \eta_a}{RT} \right] \right), \quad \text{Eq. 10}$$

where  $i_o$  is the exchange current density and  $\alpha$  is the transfer coefficient. The current exchange density is defined as

$$i_o = F A k^\circ [O]^* \quad \text{Eq. 11}$$

where  $k^\circ$  is the standard reaction constant and  $[O]^*$  is the bulk concentration of the oxidized and reduced species.

For large activation overpotentials,  $|\eta_a| \geq 50 \text{ mV}$ , and if the overpotential is negative, then the activation overpotential can be defined by the empirical Tafel formula:

$$\eta_a = a - b \log i, \quad \text{Eq. 12a}$$

where

$$a = \frac{2.3RT}{\alpha F} \log i_o \quad \text{Eq. 12b}$$

and

$$b = \frac{2.3RT}{\alpha F} . \quad \text{Eq. 12c}$$

The Tafel formula also assumes that there are no mass transport limitations, which is accurate for low current densities.

### ***Mass Transfer Overpotential*** [6]

The mass transfer overpotential or concentration overpotential, denoted by  $\eta_c$ , is a result of different concentration of the oxidized and reduced species. If there is a concentration overpotential than the concentration of the reactants and the products near the surface of the electrode differ from the bulk concentrations. Unlike activation overpotential it is possible to avoid having any significant mass transfer overpotential. With the proper design of the flow channels for the gases, the mass transfer is performed by convection, rather than through concentration gradients, which causes the concentration in the reaction area to remain equal to the bulk concentrations.

The second manner that mass transport can affect the fuel cell performance is if the fuel cell becomes flooded. A fuel cell becomes flooded when too much liquid water collects in the cathodic reaction area. This can be avoided through good design of the flow channels of the gases, regulating the humidity of the gas streams, and by controlling the mass flow rate of the gas streams. Both the pressure and temperature of the fuel cell can influence when the fuel cell will flood, but they should be optimized for open circuit voltage and activation over potential.

### ***Ohmic Overpotential*** [7]

Ohmic overpotential, denoted as  $\eta_\Omega$ , can be broken down into five main categories: the lead resistance of the anode and cathode wires, the resistance of the

anode current collector, the resistance of the cathode current collector and the ionic resistance of the electrolyte. The only resistance that is difficult to measure and is variable is the ionic resistance of the electrolyte because the resistance is dependent on the hydration of the membrane, which is a function of the pressures of the gas streams, the humidity of the streams, the mass flow rate of the streams and the temperature of the fuel cell.

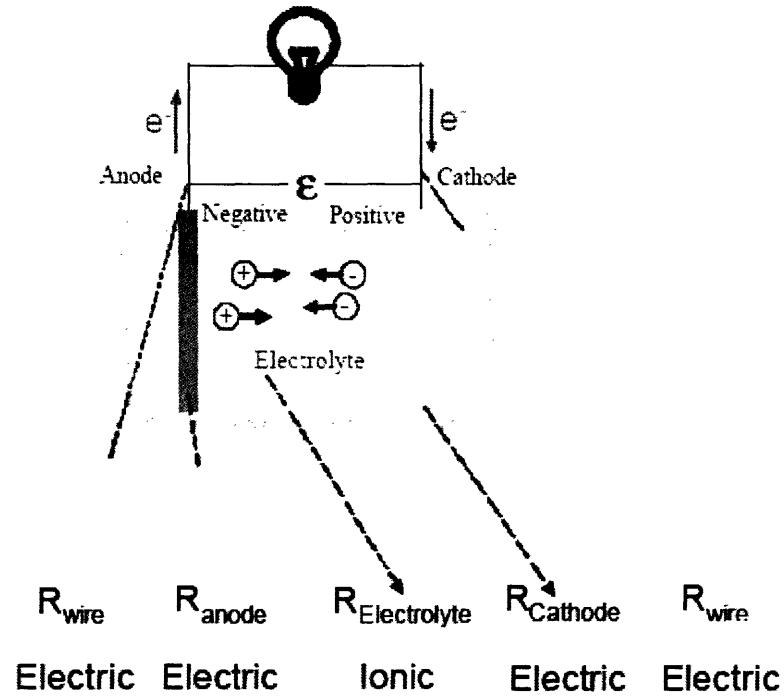


Figure 2. These five resistances contribute significantly to the ohmic overpotential. [8]

The ohmic overpotential is dominated by the Electrolyte ionic conductivity resistance. Therefore it is possible to define the ohmic resistance in the proton exchange membrane as

$$\eta_{\Omega} = iR_m + iR_e = i\left(\frac{l}{kA}\right) + iR_e, \quad \text{Eq. 13}$$

where the ionic conductivity of the electrolyte is  $k$ , the thickness of the electrolyte is  $l$ , the area of the electrolyte is  $A$ , and the other resistances are lumped together in the electronic resistance term,  $R_e$ . The ionic conductivity constant is dependent on the hydration of the electrolyte.

There are two processes that control the hydration of the membrane: electro-osmotic drag and diffusion. Electro-osmotic drag transports water molecules from the anode to the cathode by protons traveling across the membrane. The rate of water transport due to electro-osmotic drag is thus proportional to current density. The number of water molecules dragged per hydrogen proton is relatively independent of membrane hydration in the range at which the membrane is sufficiently conductive. The current theory states that as a hydrogen ion moves across the electrolyte it drags a water molecule along with it. This theory dramatically simplifies the process of electro-osmotic and should only be used as an approximation. [9]

Electro-osmotic drag, the production of water on the cathode, and the uptake and evaporation of water give rise to water gradients inside the membrane. These gradients cause diffusion, which acts in the opposite direction to the electro-osmotic drag and is referred to as back-diffusion. [10]

### ***Efficiencies*** [11]

When referring to fuel cells there are three efficiencies that are important: the electrochemistry efficiency, utilization efficiency and the fuel utilization efficiency. The electrochemistry efficiency is the maximum work that can be performed over the total energy change. The utilization efficiency is the work out over the ideal work out. The fuel utilization efficiency is the work out over the total energy that was available to perform that work. Using these efficiencies it is possible to quantify the performance of fuel cells.

The electrochemical efficiency, which is the maximum work over the change in energy, is also known as the first law efficiency. The maximum work that can be performed is by an isothermal process with no entropy generation, which is the Gibbs free energy change of the reaction. The change in energy is equal to the change in enthalpy from the products to the reactants. Thus the electrochemical efficiency can be defined as

$$\eta_{chem,max} = \frac{W_{max}}{Q_{in}} = \left| \frac{\Delta G_r}{\Delta H_r} \right|, \quad \text{Eq. 14}$$

where the Gibbs free energy change per mole of reactants of the reaction is  $\Delta G_r$  and the Enthalpy change per mole of reactants of the reaction is  $\Delta H_r$ . The advantage of getting energy from electrochemistry is that the maximum efficiency is not limited by the Carnot efficiency.

The utilization efficiency, which is work out over the maximum work, is also known as the second law efficiency. The work out is the practical work produced by the system. Therefore the utilization efficiency is

$$\eta_{second\ law} = \eta_{II} = \frac{W_{out}}{W_{max}} = \frac{W_{out}}{\Delta B}, \quad \text{Eq. 15}$$

where the change in the exergy from an initial state to a final state is  $\Delta B$ . The second law efficiency is useful because it provides measure of the operating condition compared to an ideal system and can provide insight into improving a system.

The fuel utilization efficiency is a ratio of work out to the energy supplied to the system. This efficiency is highly dependent on the design and operated of the system. The mathematical definition of the efficiency is

$$\eta_{fuel\ efficiency} = \frac{W_{out}}{m_{fuel} \Delta h_{fuel}}, \quad \text{Eq. 16}$$

where the mass of the fuel is  $m_{fuel}$  and the enthalpy of fuel combustion is  $\Delta h_{fuel}$ . Changing the mass flow rate of the fuel gases can dramatically change this efficiency.

## Theoretical Modeling

An area of interest is the hydration effects on fuel cell performance that can be directly related to the relative humidity of the gas streams. As described in Equation 9, the experimental circuit voltage is dependent on the open circuit voltage, Equation 7, the activation overpotential which is approximated using the Tafel formula, Equation 12, and the ohmic overpotential, Equation 13. The mass transfer overpotential is ignored as being negligible in the range of the operating conditions that fuel cell is used. Therefore it possible to combine the former equation and derive the experimentally expected output voltage:

$$\varepsilon_{\text{experimental}} = \varepsilon_r - (a_a - b_a \log i) - (a_c - b_c \log i) - R_m i - R_e i, \quad \text{Eq. 17}$$

where  $\varepsilon_r$  is the open-circuit voltage,  $a_a$  and  $b_a$  are the Tafel constants for the anode reaction,  $a_c$  and  $b_c$  are the Tafel constants for the cathode reaction,  $i$  is current density,  $R_m$  is membrane resistance, and  $R_e$  are electronic resistances. Since only parameter of interest for this analysis is the resistance of the proton exchange membrane,  $R_m$ , it is possible to lump all the other factors that contribute to the experimental output voltage into a single factor which is a function of current:

$$\varepsilon_{\text{experimental}} = \varepsilon(i) - R_m i = \varepsilon(i) - i \left( \frac{l}{kA} \right), \quad \text{Eq. 18}$$

where

$$\varepsilon(i) = \varepsilon_r - (a_a - b_a \log i) - (a_c - b_c \log i) - R_e i.$$

This transformation can be used because all the parameters that influence the output voltage except the relative humidity and the current density are fixed. These parameters are the operating temperature of the fuel cell, the back pressure of both gas lines, the mass flow rate of the gas lines, and stoichiometric relation of the gas lines. The relative humidity will have a small effect on the partial pressures of the gas lines, but it is assumed to be negligible compared to the back pressure of the gas lines. Experiments could then be performed to determine experimentally the relationship between the relative humidity of the gas lines and the ionic conductivity of the membrane. The ionic conductivity would be a function of the relative humidity:



$$k = f(\text{relative humidity}). \quad \text{Eq. 19}$$

Previous studies have shown that this relationship can best be described by a third order polynomial, but no scientific theoretical justification has been proposed [12].

The next step in the experimental modeling is to create an empirical relationship between conductivity and the temperature and humidity of the fuel cell. Using the equation derived to relate conductivity to the humidity of the fuel cell, experimental results based on changing the temperature could be used to develop an experimental equation relating humidity and temperature to membrane resistance. The conductivity of the fuel cell correlates to the temperature in the form of the following equation,

$$k = A \exp\left(-\frac{E_a}{RT}\right) [1], \quad \text{Eq. 20}$$

where  $A$  is the frequency factor,  $E_a$  is activation energy for ionic conduction,  $R$  is the universal gas constant, and  $T$  is the operating temperature of the fuel cell. Using Equation 4 and the experimental data, an experimental model can be developed that relates the conductivity of the membrane to the relative humidity and the temperature:

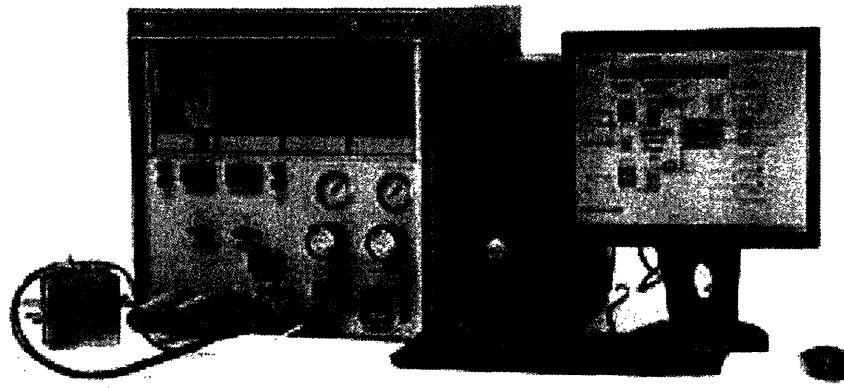
$$k = f(\text{relative humidity}, T). \quad \text{Eq. 21}$$

The final step of the experimental modeling would be to determine whether the correlation is accurate with a variable membrane thickness. The data would probably reveal that the correlation does not match and that as the thickness of the membrane is increased, the resistance increases more than is expected. The theoretical reason for the change is that the extra thickness affects the back diffusion process of hydrating the membrane. The ability of the membrane to diffuse water through the membrane does not decrease linearly with thickness, but in a more pronounced manner. In this case, an experimental equation should be developed that would relate the ionic conductivity of the proton exchange membrane to the relative humidity of the gas lines, the operating temperature of the fuel cell, and the thickness of the proton exchange membrane:

$$k = f(\text{relative humidity}, T, \text{Thickness}). \quad \text{Eq. 22}$$

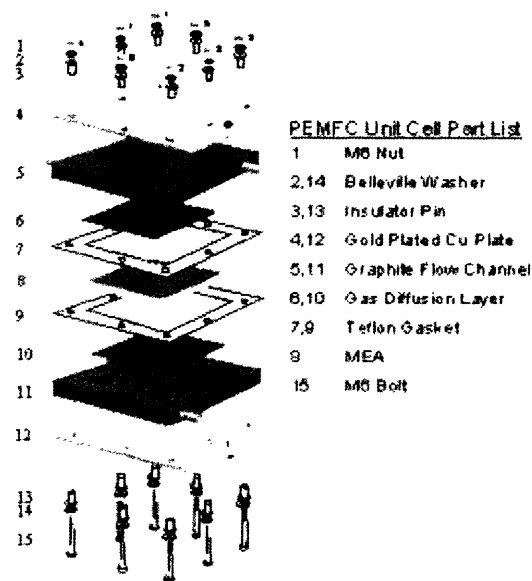
## Fuel Cell and Testing Station

This section will describe the experimental setup for a PEM fuel cell and the corresponding requirements for a fuel cells testing station. When attempting to verify the theoretical derived performance characteristics it is necessary to have the correct type of fuel cell and a testing station that will be able to control all the inputs that influence the performance of the fuel. The design used in this experiment is a simple hydrogen and oxygen PEM fuel cell, Figure 3



**Figure 3. Fuel cell technologies PEM fuel cell and fuel cell testing station. [13]**

A typical PEM fuel cell will contain electric heating plates, current collectors/bipolar plates, gaskets and a membrane electrode assembly (MEA). These components are then stacked together to form a basic PEM fuel cell, Figure 3.



**Figure 4. Assembly diagram of a simple hydrogen and oxygen fuel cell. [14]**

The electrical heating plates are required for a PEM fuel cell for temperature regulation and are also used as the leads for connecting the fuel cell to an external circuit. The performance of a fuel cell is strongly dependent on the temperature, therefore it is very important to be able to accurately control the temperature. The type of electric heater most commonly used is an electric resistance heater controlled by the temperature measured within the fuel cell. Figure 3 contains a picture of a typical heater for a single PEM fuel cell.

The bipolar plates in a PEM fuel cell serve three main purposes: they are used as structural support, as current collectors and as guides for the flow fields for the reactant gases. A common material used for the bipolar plate is graphite. Graphite provides strong structural support for the whole assembly, but an issue of concern is the brittleness of the material. As a current collector a graphite bipolar plate is an acceptable material because it provides low electrical resistance. The graphite material is partly ideal because it will not react with fuel flows. It is also a good material because it is possible to machine very precise fluid flow patterns into the surface. For many materials durability is a significant issue because the fuel gases are corrosive, but graphite is very good

material to make the Bipolar plate out of because its only limitation is that it is a brittle material and otherwise it has great characteristics. In the literature many studies have been done to calculate the performance characteristics of different flow patterns and one of the simplest and most effective is the serpentine path with cross flow.

A typical membrane electrode assembly consists of five layers: two gas diffusion layers, an anode catalyst layer, a cathode catalyst layer, and proton exchange membrane, Figure 4. The two gas diffusion layers serve the same general purpose. The anode diffusion layer transports the hydrogen and water, if the gas stream is humidified, from the gas stream to the anode catalyst layer where the hydrogen goes through the oxidation process and forms two hydrogen ions and two electrons. The gas diffusion layer on the cathode side transports oxygen to the catalyst layer where it reacts with four hydrogen ions and four electrons to form two water molecules. The cathode diffusion layer also transports the newly formed water away from the catalyst layer into the main stream or from the stream to the proton exchange membrane. The proton exchange membrane transports the hydrogen ions from the anode to the cathode side. The proton exchange membrane most often used is Nafion® a polymer electrolyte membrane that is owned by Dupont Corporation.

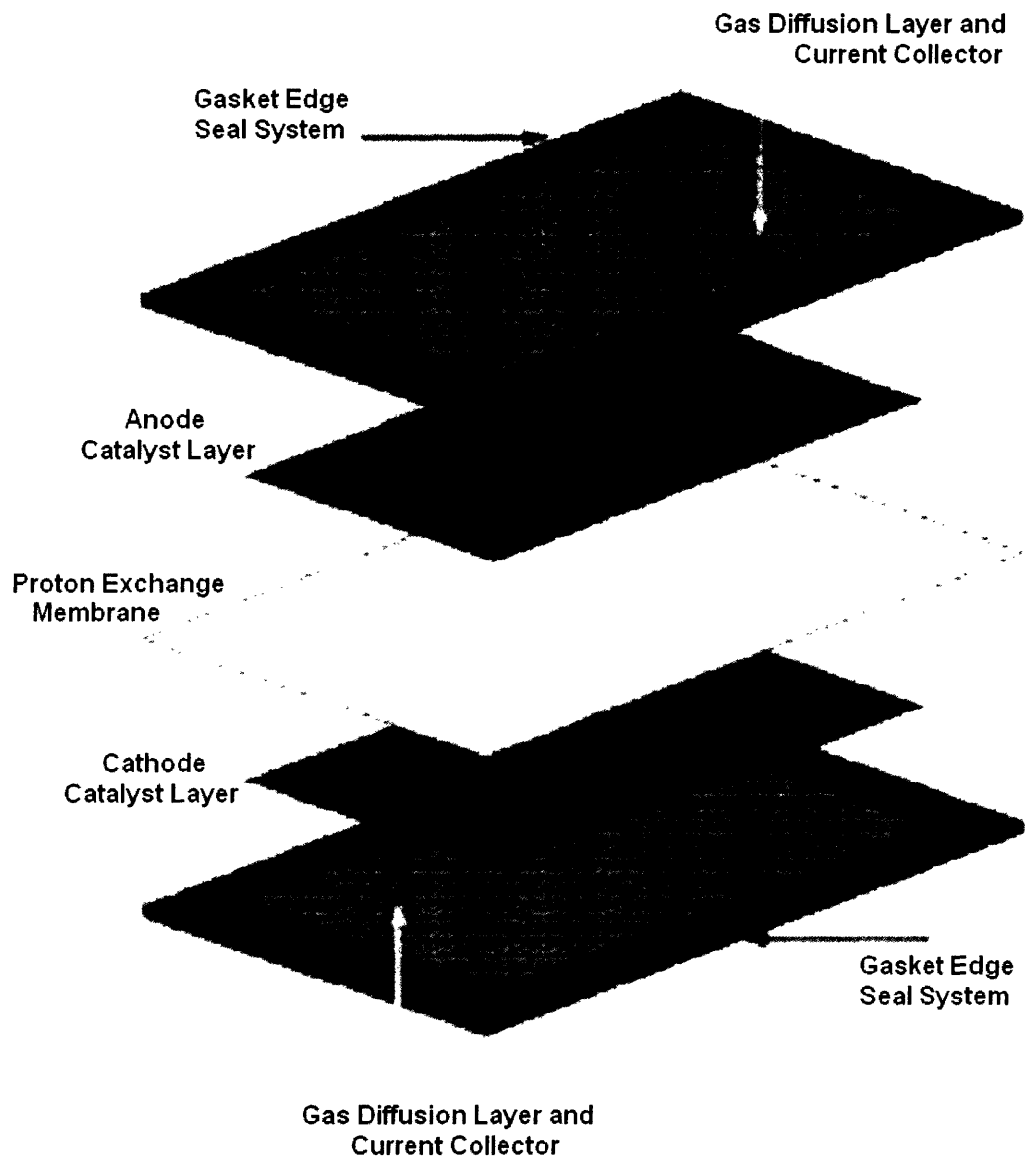


Figure 5. MEA. [15]

To get the best performance out of Nafion®, it is necessary for it to be put through a rigorous series of pretreatments before placement in the fuel cell. The first step is to boil the membrane in 3%  $H_2O_2$  aqueous solution for one hour; the purpose of  $H_2O_2$  is to oxidize any small-molecule contaminants that might block ion conducting channels. Then the membrane should be rinsed in deionized water repeatedly. The

membrane should then be boiled in a 0.5 molar  $H_2SO_4$  solution for one hour. This step is designed to change all acidic sites, in the membrane, to proton form. The final step is to rinse the membrane in deionized water repeatedly again; this final step rinses away the excess acid. If the polymer electrolyte membrane is not going to be used immediately it should be stored under deionized water until it is needed. It is also possible to make a membrane electrode assembly but for quality control it is better to purchase a standard MEA. [16]

The other major requirement for doing any research into fuel cells is a fuel cell testing station. A fuel cell testing station is a requirement because of the multiple parameters that influence the performance of a fuel cell. The only way to get accurate results is to be able to completely control all the major parameters. The important parameters are the temperature of the fuel cell, the type of fuel gases, the relative humidity of the gas line, the current drawn from the fuel cell, the pressure of the gas lines, and last of all the flow rates of the gas lines.

The most important requirement is the temperature control of the fuel cell. The open circuit voltage is strongly related to the operating temperature of the fuel cell. The temperature of the fuel cell should be measured as closely to the cathode area as possible because the cathodic reaction is exothermic so this area will have the highest temperature.

The next important step is to be able to control the humidity of the fuel cell lines. The humidification is important because the hydration of the polymer electrolyte membrane strongly affects the performance of the fuel cell. The lines from the humidifier should be heated so that the water cannot condense inside the transport line. Short transport lines will also aid in the prevention of condensation of the water vapor.

Controlling the back pressure is important because the back pressure is the same as the pressure of the gas flows inside the fuel cell and the pressure inside the fuel cell directly influences the cell performance. In most PEM fuel cells there is a limit on how high the back pressure can be placed. The reason is that at very high pressure the gases will be able to escape from the gaskets that seal the anodic and cathodic reactions areas.

The mass flow rates of the gases are important for two main reasons; one is to help avoid mass transfer limitations and the other is to help with the calculations of the fuel cell efficiencies. The mass transfer limitation can be lessened by proper mass flow rates because the flows through the anode and cathode reaction areas can possibly produce good convection of the reacting molecules. The efficiency calculations are based on the amount of fuel supplied and fuel utilized. The easiest way to evaluate the fuel supplied is to control the mass transfer rates of the two gas streams. Since the humidity is being controlled, it will be possible to calculate the amount of fuel supplied.

A moisture trap for the hydrogen and oxygen is important if the cell efficiencies are going to be calculated. A moisture trap should be able to remove all the vapor water in the gas lines and separate it into a container. The container can then be weighed to determine the amount of water in the gas lines. Using the known relative humidity of the gas lines it will then be possible to calculate the amount of water formed by the fuel cell. The water formed information will allow for the calculation of the overall cell utilization efficiency.

The final piece of equipment that is required to accurately measure the performance of a PEM fuel cell is an electric load controller. An electronic load controller allows a source of power such as a fuel cell to be tested with a load that can be changed. The control over the load is important because of the dependency of fuel cells voltage on the current drawn.

## **Experimental Results**

The experimental results should show that the resistance of the proton exchange membrane change significantly with the relative humidity. Data gathered in other research papers have shown an increase of two orders of magnitudes in the conductivity of Nafion polymer membranes with a change in relative humidity from 40% to 100% [17]. The back pressure would be fixed at 200 kPa for all experiments. Table 1 shows the proposed trial runs for determining the relationship between conductivity,

temperature and relative humidity.

**Table 1. The experimental test that should be performed to develop the analytical model of the fuel cell performance.**

Temperature (° C)	Relative Humidity %				
30	20	40	60	80	100
45	20	40	60	80	100
60	20	40	60	80	100
70	20	40	60	80	100
80	20	40	60	80	100

The actual data to be collected would be the fuel cell voltage as the current density is changed, which is known as the polarization curve. The complete polarization curves for each of these curves would be recorded, but for the purposes of developing a model the high current densities, where mass transfer overpotential significantly affects the output voltage, would be ignored.

The trial runs from Table 1 would then be repeated for different membrane thicknesses. The three different membranes are Nafion 112, which has a typical thickness of 51 microns, Nafion 115, which has a typical thickness of 127 microns, and Nafion 117, which has a typical thickness of 183 microns.

One future area for research could be into the specifics of the hydration gradient from the cathode side to the anode side. Research has shown that most of the resistance in the proton exchange membrane occurs near the surface of the anode and that it exists because of a lack of hydration [18]. The gradient in the membrane is such that it is completely hydrated except for near the anode. It may be possible to increase the humidity on the anode side, since flooding should not be an issue and decrease the humidity on the cathode side. By not having the cathode gas line humidified and the anode gas line humidified a diffusion gradient is formed that could aid in the transfer water molecules. Since the current theory states that hydrogen ion conduction through the polymer electrolyte membrane is related to the water transfer from the anode to cathode reaction area, then by creating an artificial water gradient, that causes diffusion, would increase the ionic conductivity of the membrane and therefore improve the overall



cell performance. Using the technique of varying the hydration of the gas lines it may be possible to achieve optimal fuel cell performance. Such results would suggest that diffusion is not strong enough to pass the water back across a thick membrane, and that it is not necessary to humidify the cathode gas flow. The cathode side of the proton exchange membrane should never be in danger of drying out because the cathodic reaction forms water in the reaction area which will keep the local area hydrated.

## **Experimentation**

Upon preliminary operation, the fuel cell testing station in lab did not operate correctly. Due to a software glitch, time constraints and the incorrect operation of the fuel cell, the proposed experiments were unable to be completed. Derivation of the theoretical model depends upon the application of known relations to empirical data. To date, no data has been collected to enable the characterization of the performance of the fuel cell.

The fuel cell testing station used was supplied by Fuel Cell Technologies. The software program used by Fuel Cell Technologies to run the testing station from a computer is called Labview. An error in Labview would not allow a polarization curve to be performed or recorded. With the aid of a Labview technician, the software was reprogrammed to allow the running and recording of the polarization curve. The time constraints of the academic term prevented the proposed experiments from being run. In the future, the complete proposed experimental series of tests can be designed and completed automatically using Labview.

No data was recorded from the fuel cell because when it was first operated the fuel cell was flooded. The possible reasons for the flooding are that the fuel cell was operated at too high a humidity level, too high mass flow rates, or with too low a back pressure. Attempts were made to clear out the fuel cell by changing the relative humidity of the gas lines, operating it without humidity, first in the cathode gas line then in both lines, increasing the flow rate of the cathodic gas line, varying the cell temperature and increasing the back pressure but a working fuel cell was never achieved. There are three

methods that should be performed to clear the flooding of the cathode. First, the back pressure should be raised and quickly lowered to drive the water out. Next, if the cell is still flooded, it should be operated at a high temperature with little or no humidity to evaporate out the extra water. If the fuel cell is still flooded, than it should be disassembled and allowed to dry out. Again due to time constraints, the fuel cell never achieved operating status.

The final goal was to find the optimal operating conditions for the PEM fuel cell described above. If time had allowed, modeling the hydration of the fuel cell would have been attempted. Ultimately, the characterization of the fuel cell performance is the most important objective. Knowledge of the performance characteristics of the cell would help with the future research into completely understanding how the fuel cell works.

The future research being conducted in the MIT Electrochemistry Energy laboratory pertains to proton exchange membrane fuel cell durability. Defining the characteristics of the temperature profile in the membrane is one of the next steps in better understanding the durability of fuel cells. This area of research is important because it impacts the long term maintenance cost of fuel cells. Characterizing the local hydration is necessary if a reliable relationship is to be developed that will relate the ionic conductivity of the proton exchange membrane to the local temperature. It is possible that an elevated local temperature will affect the local conductivity of the membrane which could have consequences in term of the long term durability of the fuel cell membrane.

## Conclusion

The hydrogen economy may not be the complete future of energy transport but it should be a part of the future energy infrastructure. Hydrogen can be synthesized from none polluting renewable energy sources, which makes it a viable medium for the future of mass energy transport. The most efficient use of hydrogen, in terms of energy efficiency, is its use in fuel cells. Fuel cells are not limited by the Carnot efficiency that limits the work out put of heat engines so fuel cells in the future can become extremely energy efficient. The PEM fuel is versatile and holds much promise for the future. Some of the advantages of the PEM fuel cell are that it is small, easy to handle, very light, and it only requires atmospheric oxygen.

The power output of a fuel cell will vary greatly depending on the design of the fuel cell and the operating conditions of the fuel cell. Although only single cell performances were evaluated it is possible to form fuel cell stakes that can produce large quantities of power. There are four main parts that contribute to the power output of a fuel cell: the open circuit voltage, the activation overpotential, the mass transfer overpotential, and the ohmic overpotential. The two important factors that contribute to the open circuit voltage are the back partial pressures of the two gas lines,  $P_{H_2}$  and  $P_{O_2}$ , and the operating temperature of the fuel cell,  $T$ . The activation overpotential cannot be avoided but it can be minimized by controlling the operation parameters and by operating at the current density that gives the best power performance. If the PEM fuel cell is well designed and operated at the correct range of current density then there should be negligible mass transfer overpotential. The factors that contribute to the ohmic overpotential in a PEM fuel cell are fixed or dominated by the resistance of the polymer electrolyte membrane that conducts the hydrogen protons from the anode reaction area to the cathodic reaction area. The ionic conductivity of the polymer electrolyte membrane is dependent of the hydration of the membrane, which can be partially controlled with the humidity of the gas lines.

To operate a fuel cell at peak operating conditions, all the operating parameters must be controlled. Fuel cell testing station should incorporate everything that is

necessary to operate and evaluate a fuel cell. The minimum requirements for the testing station to control are the temperature of the fuel cell, the type of fuel gases, the relative humidity of the gas line, the current drawn from the fuel cell, the pressure of the gas lines, and the flow rates of the gas lines.

This thesis should give a basic understanding of fuel cells, but this information should only be used as a foundation, and further investigation is necessary to completely understand how the fuel cells work and can be optimized.

## Citations

- [1] - DOE. "United States Country Analysis Brief – Energy".  
[www.eia.doe.gov/emeu/cabs/usa.html](http://www.eia.doe.gov/emeu/cabs/usa.html), 23 October 2003 [30 March 2004].
- [2] - The Energy Technologies Laboratories at Motorola's Research Center for Solid State Technology in Phoenix, Arizona,  
[http://www.celanese.de/gb2002/en/downloadcenter/download/gb2002\\_e\\_seizegrowth\\_1.pdf](http://www.celanese.de/gb2002/en/downloadcenter/download/gb2002_e_seizegrowth_1.pdf)
- [3] - J. W. Tester, and Y. Shao-Horn, "Lecture Note I – Electrochemical Energy Conversion and Storage," Advanced Energy Conversion, March 9, 2004, pp. 1-26.
- [4] - Y. Shao-Horn, "Lecture Note II – Electrochemical Kinetics Part I Electrochemical Energy Conversion and Storage," Advanced Energy Conversion, March 29, 2004, pp. 1-22.
- [5] - Y. Shao-Horn, "Lecture Note II – Electrochemical Kinetics Part I Electrochemical Energy Conversion and Storage," Advanced Energy Conversion, March 29, 2004, pp. 1-22.
- [6] - Y. Shao-Horn, "Lecture Note II – Electrochemical Kinetics Part I Electrochemical Energy Conversion and Storage," Advanced Energy Conversion, March 29, 2004, pp. 1-22.
- [7] - Y. Shao-Horn, "Lecture Note II – Electrochemical Kinetics Part I Electrochemical Energy Conversion and Storage," Advanced Energy Conversion, March 29, 2004, pp. 1-22.
- [8] - Y. Shao-Horn, "Lecture Note II – Electrochemical Kinetics Part I Electrochemical Energy Conversion and Storage," Advanced Energy Conversion, March 29, 2004, pp. 1-22.
- [9] - R. J. Bellows, M. Y. Lin, M. Arif, A. K. Thompson, and D. Jacobson, "Neutron Imaging Technique for In Situ Measurement of Water Transport Gradients within Nafion in Polymer Electrolyte Fuel Cells," The Journal of Electrochemical Society, Vol. 146 1999, pp. 1099-1103.
- [10] - R. J. Bellows, M. Y. Lin, M. Arif, A. K. Thompson, and D. Jacobson, "Neutron Imaging Technique for In Situ Measurement of Water Transport Gradients within

- Nafion in Polymer Electrolyte Fuel Cells,” The Journal of Electrochemical Society, Vol. 146 1999, pp. 1099-1103.
- [11] - J. W. Tester, and Y. Shao-Horn, “Lecture Note I – Electrochemical Energy Conversion and Storage,” Advanced Energy Conversion, March 9, 2004, pp. 1-26.
- [12] - Y. Sone, P. Ekdunge, and D. Simonsson, “Proton Conductivity of Nafion 117 as Measured by a Four-Electrode AC Impedance Method” The Journal of Electrochemical Society, Vol. 143, April 1996, pp 1254-1259.
- [13] - Fuel cell testing station and PEM fuel cell, Fuel Cell Technologies, [http://www.fuelcelltechnologies.com/Products/University\\_Station/college\\_station1.jpg](http://www.fuelcelltechnologies.com/Products/University_Station/college_station1.jpg)
- [14] - NASA's Jet Propulsion Laboratory, <http://www.nasatech.com/Briefs/Aug02/Images/NPO21077.gif>
- [15] - 3M Membrane electrode assembly, [http://www.3m.com/about3m/technologies/fuelcells/images/pdf/pro\\_bull.pdf](http://www.3m.com/about3m/technologies/fuelcells/images/pdf/pro_bull.pdf)
- [16] - J. J. Sumner, S. E. Creager, J. J. Ma, and D. D. DesMarteau, “Proton Conductivity in Nafion® 117 and in a Novel Bis[(perfluoroalkyl)sulfonyl]imide Ionomer Membrane,” The Journal of Electrochemical Society, Vol. 145, Jan 1998, pp 107-110.
- [17] - Y. Sone, P. Ekdunge, and D. Simonsson, “Proton Conductivity of Nafion 117 as Measured by a Four-Electrode AC Impedance Method” The Journal of Electrochemical Society, Vol. 143, April 1996, pp 1254-1259.
- [18] - Buchi, F., and Srinivasan, S., “Operating proton Exchange Membrane Fuel Cells Without External Humidification of the Reactant Gases”, Journal of the Electrochemical Society, Vol. 144, No.8, pp 2767-2772, 1997.