

Proton Exchange Membrane Fuel Cells

Adam Kamor

Faculty Advisor: Prof. Paul Kohl

Mentors: Drs. Li and Bartling

In 1839 William R. Groves created what most consider the first Fuel Cell, calling it a gaseous voltaic battery. It consisted of two tubes inverted in a solution of sulfuric acid. One tube, the cathode contained oxygen or air and was reduced via a platinum electrode. The anode contained hydrogen and was oxidized by a platinum electrode. The protons from the oxidation of hydrogen reacted with the oxygen ions to produce water and a potential. Today, that same principle is being carried out in the form of a modern fuel cell. However, in order to make this technology commercially feasible many things had to be changed. For example, instead of inverted tubes, flow field plates are used, which transport the fuel (Hydrogen) in a serpentine fashion to maximize its contact with a platinum sputtered electrode. Also, sulfuric acid is no longer used as a reaction medium. Nafion, a perchlorinated sulfonic acid polymer is used. The anode and cathode, both sputtered with catalyst are separated by a thin nafion membrane which because of its molecular structure selectively transports protons across its membrane. The hydrogen fuel is first oxidized into two protons which are then transported across the membrane to the cathode side where oxygen has been reduced to oxygen ions. The oxygen ions and the protons react to produce water. This hydrogen fuel cell still has obstacles to overcome before it can become commercially feasible. For instance, transportation of hydrogen gas is dangerous and there is no existing infrastructure to dispense hydrogen fuel to automobiles. Also, to

produce hydrogen gas requires the electrolysis of water, which requires energy. To cheaply produce fuel cell grade hydrogen gas would require the use of nuclear power plants. Luckily liquid fuels are available, for example, Methanol and ethylene glycol. Little change would be required to change gas stations to methanol or ethylene glycol dispensing stations. Also, it is much safer for a car to carry methanol or ethylene glycol. The workings of a Direct Methanol Fuel Cell or DMFC and a DEGFC are very similar to that of a hydrogen fuel cell. The only difference is the catalysts used for the electro-oxidation and the products. Instead of two platinum electrodes the anode of the DMFC is Platinum and Ruthenium in a 1:1 ratio. Ruthenium is added not to help in the oxidation of methanol, but rather to prevent carbon monoxide poisoning of the platinum catalyst. Some CO is produced in the oxidation and CO is adsorbed onto platinum greatly reducing the surface area of the catalyst. Ruthenium is a catalyst in the oxidation of carbon monoxide to carbon dioxide which is completely harmless to the platinum catalyst. For a DEGFC it is best to use a nickel sputtered anode, however a Pt-Ru anode and Pt cathode will work as well. The products of a DMFC are carbon dioxide and water, while that of a DEGFC is carbonate ions and oxalate ions, assuming the ethylene glycol is in a basic solution.

The Nafion membrane, sandwiched between two carbon cloth electrodes, the anode and cathode, is called the MEA, or the membrane electrode assembly. It is considered the heart of the fuel cell. A majority of my eight week stay at Georgia Tech has been devoted to developing a simple method to create MEAs for use in a DMFC or DEGFC. In order to create an MEA, first the cathode, normally a carbon cloth material is sputtered with platinum to obtain a catalyst loading of anywhere between one and three milligrams per centimeter squared. Then

a catalyst ink solution must be made by mixing a Pt-Ru powder with Di(ethylene glycol) and Nafion Solution. Then they are put in a sonic bath to break up colloidal suspension. The solution is then heated to evaporate off enough alcohol until the desired viscosity is reached. Then the ink is painted onto the anode carbon clothe until the desired loading is reached, normally between two and three milligrams. The best loading is six milligrams, however, that becomes too expensive. Anything after six milligrams has no effect because even though there is more catalyst there is a reduction in the porosity of the carbon clothe. After the electrodes have been fabricated you must condition your nafion membrane. First, put it into a 1 Molar solution of Nitric Acid to remove any impurities in the membrane, after cleaning in Deionized water, the Membrane must be rehydrated in a 1 Molar Solution of Sulfuric Acid, which replenishes the amount of protons in the membrane. After the membrane has been conditioned a combination of heat and pressure is used to bond the two electrodes to the nafion membrane. Normally a pressure of 1250 pounds per square inch and a temperature of 130 degrees Celsius will do the trick.

However, not until recently was a successful MEA created, this MEA has a nickel anode and a platinum cathode. Unfortunately it can only be used for a DEGFC because nickel will not oxidize methanol. Once an MEA is created successfully there are several tests that can be done to the fuel cell to determine the fuel cell's parameters. Some examples are the open circuit voltage, or OCV of the fuel cell. The theoretical voltage of a DMFC is 1.2 volts while that of a DEGFC is around 1 volt. Other parameters are the power density of the fuel cell, which is in the units of milliwatts per square centimeter. Also, it is important to attach different loadings to the fuel cell and record the voltage across the load compared to the time. This is done

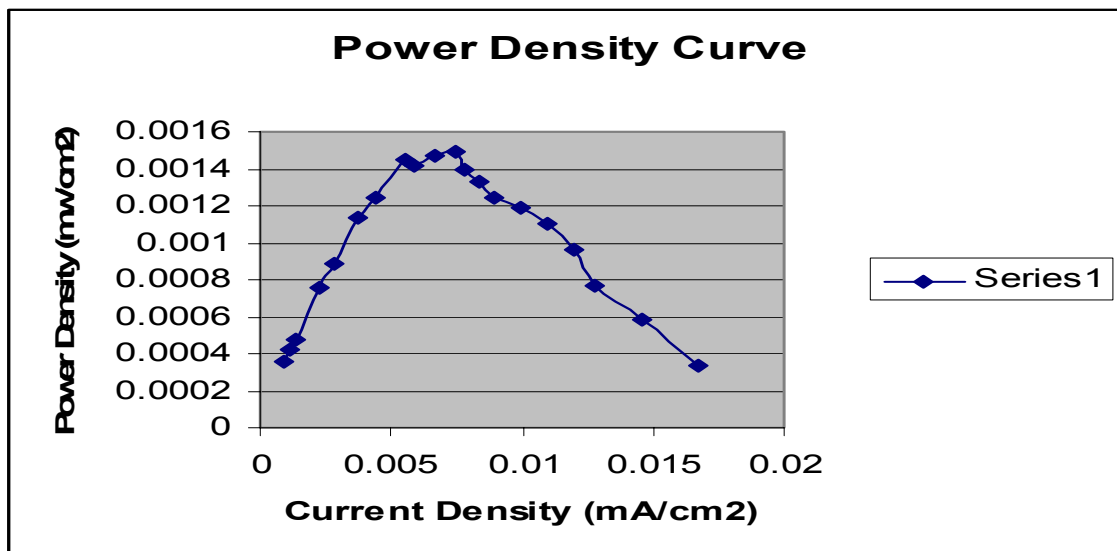
by simply attaching a resistor across the electrodes and measuring its potential drop. The power is calculated by measuring the voltage drop across the resistor with one multimeter and the current through the resistor with a different multimeter. Another important parameter to be measured and recorded is the internal source resistance of the fuel cell. This can be measured by forcing a current through the MEA by use of a Potentiostat/Galvanostat and then with an oscilloscope to measure the voltage drop across the MEA when the current is abruptly interrupted. The resistance is then calculated by ohms law. This is known as the current interrupt method.

From this data of voltage versus time for a DMFC you can notice that the higher the load resistance the more voltage is dropped across the load, relative to the OCV. This is because the load resistor is competing with the internal source resistance which can be symbolized by a single resistor. By using ohms law you can see that the higher the resistance of the load the more voltage is dropped across it.

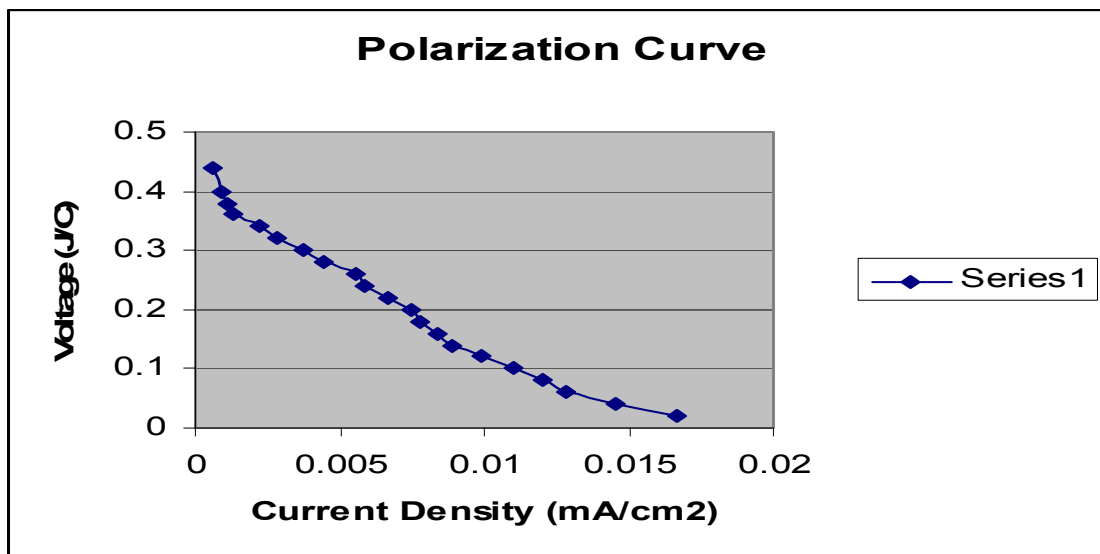
Also, the voltage across a load is constantly dropping. This is because with any current draw electrons must be moving through the resistor. The faster the flow of electrons, the faster the reaction rate. If the reactions are moving at a faster rate more reactant (Methanol) is being used. With my set up, there are no flow field plates and the methanol is kept in close contact with the electrode via a glass container. Since there is no circulation new methanol does not reach the electrode and the reaction rate must drop. Also, at faster reaction rates more carbon dioxide is being used which creates a carbon dioxide blanked at the anode which decreases surface area.

As I stated earlier an MEA for a DEGFC was successfully fabricated on Wednesday August 4. Therefore, I have very little data. However, I was able to calculate the power density of the MEA used in

the DEGFC. The data on this graph was obtained by use of a three electrode cell called a potentiostat. A potentiostat is a device with three electrodes, a working, counter, and reference electrode. You attach the anode and cathode of the fuel cell to the working and reference electrode and with the counter electrode you can change the potential between the working and reference electrodes. This allows you to control the potential between anode and cathode which allows you to control the current flow of the fuel cell. You also have the ability to record the current flow of the fuel cell. Since you know the voltage applied across the fuel cell and the current through the fuel cell, you can calculate the power of the fuel cell. Dividing the power by the area of the electrodes gives you the power density of the fuel cell.



You can notice by looking at the graph of power density versus current density that there is a peak power output given by the fuel cell. This peak power output corresponds to a current density of 0.00744 mA/cm². This gives you a current flow of 0.067 milliAmperes. If the internal source resistance of the fuel cell is known then you can also find the ideal voltage of the fuel cell that will give you ideal power output.



This graph is known as a Polarization Curve, or performance curve. Notice how the current of the Fuel Cell increases as the voltage decreases. This is because Power = voltage * current. Therefore, voltage and current are inversely proportional. The better the fuel cell, the closer to zero the slope of the line. (I.E. A better fuel cell might have a current density of 0.015 mA/cm², as opposed to my 0.011 mA.cm² at a voltage of 0.1 volts)

In conclusion, my research in DMFC and DEGFC gave me lab experience which is priceless and has given me insight into the life of research which I now want to pursue.