

Multi-cell Fuel Cell Stack Team
University of Washington
Seattle, WA 98105

June 6, 1997

Professor Eric Stuve
Department of Chemical Engineering
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Seattle, WA 98105

Dear Professor Stuve:

The fuel cell stack team has completed the first year of research and development on the multi-cell fuel cell design. It has been both an exciting and challenging endeavor.

Please find the attached final report for spring quarter 1997. This report represents a cooperative effort by the undersigned.

We would like to thank you personally as well as Professor Per Reinhall and Professor Norman McCormick, both of the Mechanical Engineering Department at the University of Washington.

Thank you.

Sincerely,
The Fuel Cell Stack Group

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Matt Clemens - ME 495
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Handwritten signatures of the Fuel Cell Stack Group members, including Jesse Cherian, Matt Clemens, Kevin Houger, Roger Marshall, Janel Martinsen, and Yao Huang.

Fuel Cell Stack Group Spring Quarter 1997



University of Washington
College of Engineering
6/6/97

Roger Marshall, Yao Huang, Janel Martinsen,
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A. Introduction - Fuel Cell Concepts

The University of Washington is design and building a fuel cell powered locomotive. The team working on the project is broken into two groups, locomotive design and fuel cell design. The fuel cell design group is further broken into a multi-cell stack team and a single cell team.

Background

Fuel cells were a technology founded by Sir William Robert Grove, in 1839. Since then, the technology use has spread into, space exploration, power generation, and transportation. In the coming century, fuel cell technology could well become the “zero-emission” fuel source that society needs.

Fuel cells are simple devices. Batteries only have a finite life defined by the chemicals that are housed inside. Fuel cells on the other hand can theoretically operate forever as long as fuels, and oxides are supplied. Different fuels are used in fuel cells. The University of Washington design used hydrogen gas as the fuel and oxygen as the oxide. Figure 1 shows a schematic of a fuel cell.

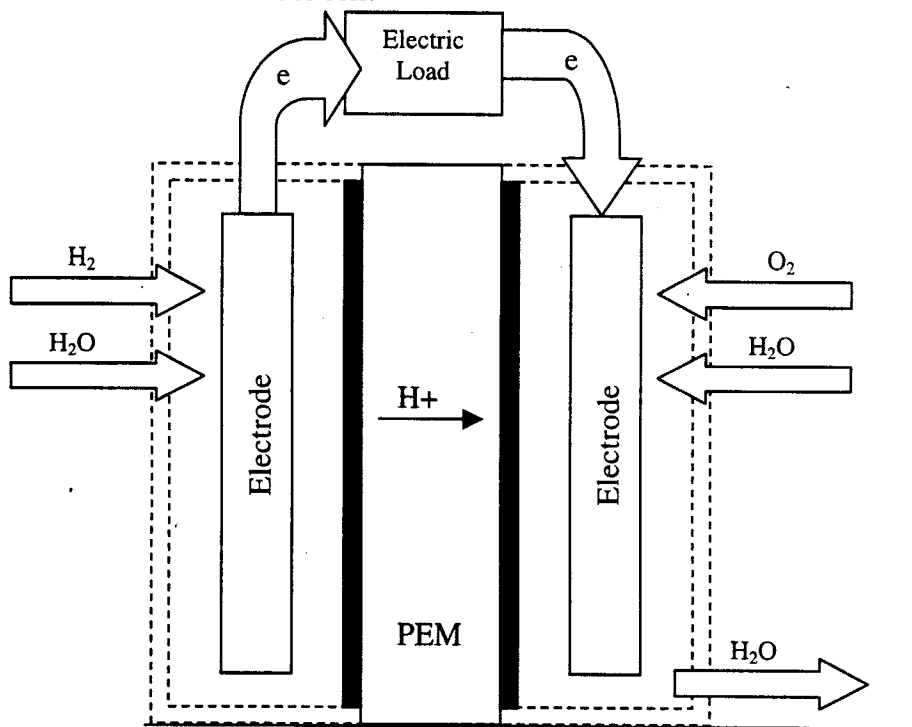


Figure 1: Cross-section of a hydrogen fuel

The fuel cell is a simple device in terms of components. Figure 1 shows the major components of any fuel cell. The fuel cell has a housing, two electrodes, a proton exchange membrane (PEM), and a catalyst coating on the PEM. Two compartments are

separated by the PEM. Hydrogen gas is pumped into the fuel side of the cell. At the catalyst coating the electron is separated for the hydrogen atom. The electron travels to the electric load where work is extracted. The hydrogen ion travels through the PEM to the oxygen side. In the oxygen side, the electron and hydrogen ion are recombined with the oxygen atoms to form water.

The University of Washington's fuel cell design uses Nafion PEM, and a carbon-platinum ink coating. Nafion is a perfluorinate (a fluorinated long chain polymer with sulfuric acid attached). The catalyst coating is a carbon-platinum ink that acts as an electrode.

Purpose

The purpose of this report is two-fold. The document is to be used as a resource for the future students, and faculty working on the fuel cell locomotive in the future. Also, the report is to let interested individuals know the major findings by the spring 1997 fuel cell team, and recommendations that are made based on the teams findings.

Scope

The scope of this report will encompass the findings of the multi cell fuel cell team, and any recommendations from the team findings over the term. This report will thoroughly explain what the team has done all term long, to include test done and the data obtained from each test.

Overview

The following section will discuss the findings, ideas, and recommendation for the fuel cell stack team of spring 1997. The report will then have a conclusions section followed by any pertinent recommendations the team has. References and Appendices will finish off the report.

B. - Original Design

The University of Washington is currently designing a fuel cell powered locomotive to be used during the Engineering Fair held in spring 1997. The over all team is broken into two groups the locomotive group and the fuel cell group. The fuel cell group further broken into two groups, a multi cell stack team and a single cell team.

The objective of this report is to explain the findings of the spring 1997 multi cell stack team, and any recommendation based on findings from the term. The purpose of this report is to explain to students continuing on the project and to explain to interested people where the fuel cell is as of the end of spring 1997.

The school has been working on the fuel cell locomotive for one year. As of the end of winter 1997, the multi cell stack team had created a prototype design that was built spring 1997.

Fundamental Components of a Fuel Cell

The fundamental components of the University of Washington's fuel cell are the membrane, the carbon-platinum ink coating, the gases, and the Teflon coated carbon filter paper. The membrane separates the fuel cell into a fuel side and an oxide side. The membrane is biphasic, meaning that the membrane is hydrophilic in the middle and hydrophobic on the surface. A rigorous membrane initialization step is performed before the carbon platinum ink can be painted on the membrane's surface. The initialization procedure will be presented later in the report.

The carbon-platinum ink acts as the catalyst and electrode. The platinum separates the hydrogen electron from the hydrogen atom. An analysis of the actual amount of platinum present in the coating will be presented later in this report. The coating also acts as the electrode. The electrons travel up the coating out the electrical connection, through the electric load, then into the oxygen side.

As stated above, hydrogen and oxygen are used as the fuel and oxidizing gases respectively. Safety problems exist with the use of hydrogen. Hydrogen is an extremely flammable. Because of the high flammability of hydrogen, safety became a major concern for the fuel cell team. A discussion of safety issues is presented later in this discussion.

The Concept of a Stack

Many important physical attributes will be discussed in this report concerning the fuel cell, input gases, and electrical connections. Humidity was one of the main areas of concentration for the fuel cell team. A small target humidity range exist for the inlet gases. If the humidity is too high the fuel cell will flood with water, therefore stopping the reaction. If the humidity is too low the propagation of the hydrogen ion to the oxygen side will not take place. The winter 1997 in Appendix A report has the calculations for the amount of water needed for proper operation. A discussion of the humidification system designed spring 1997 is presented in this report.

Another important physical attribute is the temperature of the inlet gases, the fuel cell, and the humidification water. The operating temperature for the fuel cell is 80(C. The reaction produces heat which must be removed to maintain the fuel cell at the specified operating temperature. The calculations for heat generation, and operating temperature can be found in the winter 1997 report in Appendix A. Temperature also will define the amount of humidity of the inlet gases. The humidified gases must be less than 80(C or the cell will be flooded as the water condenses out of the gas.

Another attribute is how the fuel cell is connected either in series or parallel. Figure 2 shows the outside of a fuel cell with the electrical connections connected in series.

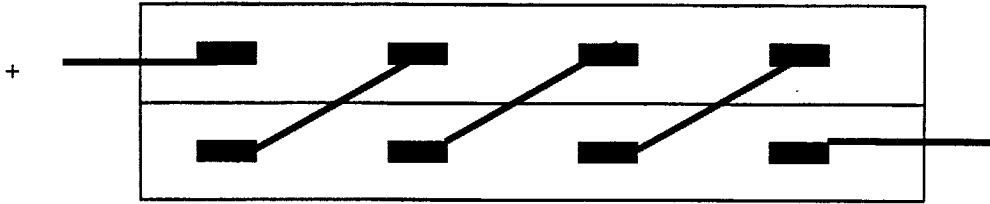


Figure 2: Fuel cell stack connected in series

The advantage of connecting the fuel cell in series is the voltage is increased. The locomotive needs approximately 350 volts. The University of Washington design will connect the cells in series to obtain the 350 volts needed.

By connecting the fuel cell in parallel a higher current can be obtained. Figure 3 shows the drawing of a fuel cell connected in parallel.

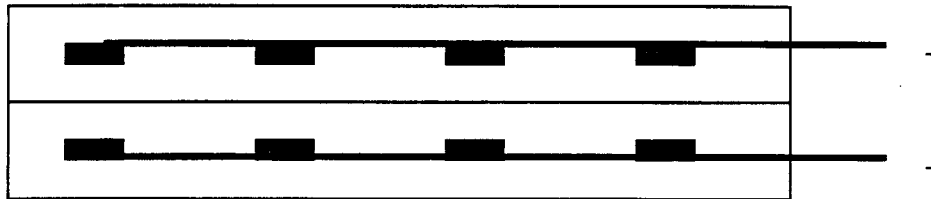


Figure 3: Fuel cell stack connected in parallel

Even though we do not plan to use this configuration, some of our testing was done with the cell connected in parallel.

C. Original Prototype Design

Winter quarter the stack group designed a multi-celled stack. The stack would have four cells separated by five millimeters. This means that when the cells are wired in series the complete stack could potentially produce 2.8-3.2 volts DC (open circuit.) Manufacture of the first prototype began winter quarter with the following items completed Spring quarter:

- Adhesives tested.
- Completion of tabs.
- Mesh.
- Clamps.
- O-rings.
- Membrane.
- Assembly.
- Fittings tested.

Weldon-16 and Araldite 2042 was tested using the adhesive test devised winter quarter^x. The construction of the test plate for the adhesive also tests the adhesives machinability. Weldon-16 and Araldite 2042 have adequate machinability. The adhesive was tested in a bath of water at 85 °C and subjected to increasing pressure to 80 psi. Both the Weldon-16 and the Araldite 2042 held satisfactory. The Weldon-16 caused spider-web cracking along the surfaces of the Lexan and was rejected for use in the prototype. Until a better adhesive is found Araldite 2042 will be used to the prototype.

Each stainless steel tab was custom fitted to the plates by the use of various machining techniques: filing and grinding. Strips of Lexan were cut to fit the grooves above the tabs. The tabs and Lexan strips were glued into place with Araldite 2042 and the adhesive was allowed to cure. After the Araldite 2042 cured the excess Lexan and adhesive was removed by milling.

Stainless steel screens were selected for the meshes and were coated by method 5 developed winter quarter (see Appendix A).

The clamp was made from the following plane (**Figure 4**). Each side of the clamp was made from 0.25 thick aluminum plate. Eight (0.25 x 2-inch NC Allen socket-head) bolts and nuts hold the clamp together. Two holes were cut out of each side of the clamp for viewing the prototype while in operation.

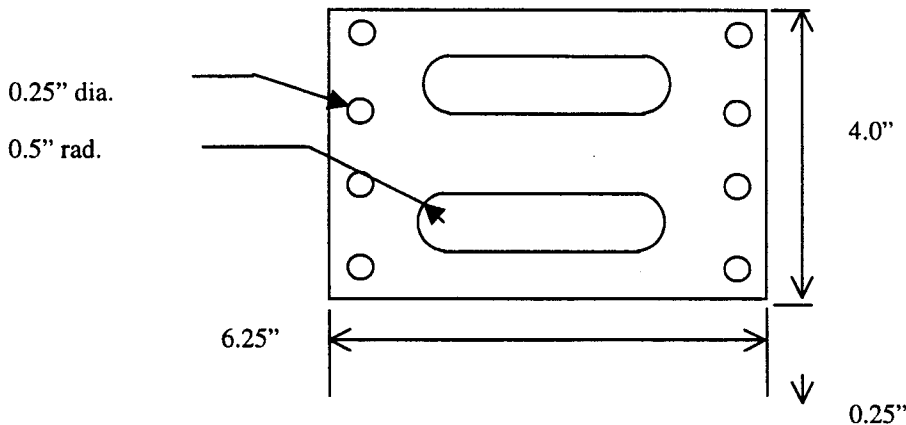


Figure 4: Fuel cell clamp

The O-rings were made from silicone O-ring cord. The cord was laid into the O-ring groove cut from the Lexan plate to find the length and cut. The ends of the O-ring cord were attached with clear RTV silicone adhesive.

The supply holes in the plates were tapped for a 1/16 NPT thread. A 1/16 NPT to 1/4 Swagelok fitting was screwed into the plate.

Assembly of the prototype required several hands. In both plates heavy screens were laid into each recessed area followed by a finer mesh screen and last by carbon paper. The membrane was stretched by hand across the carbon paper and held tight to the plates. With two people holding the edges of the membrane to the edges of the plate, the plate was turned over onto the opposite plate being careful not allow the screens and carbon paper to move out of place. When assure that all the parts are in place the clamp was put on the prototype and the bolts tighten in the following order: 2,7,6,3,1,8,5,4 (see Figure 5.)

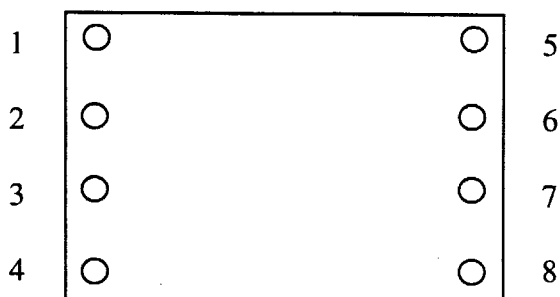


Figure 5: Bolt numbering for clamp

The prototype was installed into the test stand in Benson room 215. Using nitrogen the prototype and all of the fittings were tested to 20 psi. The prototype held the pressure. Some of the fittings had small gas leaks, which could be stopped by tightening the fitting. One fitting had to be replaced.

D. Experiments

The first task for this quarter was to build the prototype that was designed winter quarter of 1997. Next, an experiment was designed and performed. Finally, the experiment was carried out and analyzed.

Building the Prototype

The initial prototype was designed during winter 1997 (for further details, please refer to the report from winter 1997, "Fuel Cell Locomotive; Fuel Cell 'Stack'").

Lexan, a polycarbonate material was chosen as the shell of the stack for its resistance to heat, electricity and corrosion. Lexan also provides the added feature of transparency, allowing the operation of the stack to be observed. The shell was hand-milled and an auto-cad drawing of the shell prepared to allow for CNC production of future prototypes.

Tabs had to be designed and manufactured to connect the electrode to the exterior of the cell. Their sole function is to carry the current from an electrode out to a terminal. Stainless steel was chosen for durability and easy machining. The tabs were bent and filed to fit, then glued into place using an adhesive called Araladite.

A way to seal the stack, isolating each gas compartment was needed. A groove was milled around the perimeter of the membrane. A 1/8th inch, silicon O-ring was glued into the groove with RTV silicon.

The stack was in need of a clamping system. Aluminum plates were designed and milled to cover the exterior of the cell. The width of the plates exceeds that of the Lexan plates, allowing for an area to insert bolts and nuts to hold the aluminum plates together, holding the stack together.

Once the exterior of the prototype was manufactured, a membrane needed to be prepared. Because of the intricate pattern of electrodes on the membrane, a template is needed. The template will assist in the painting of the electrodes in the proper place.

A template was designed and manufactured. Two Teflon plates with the pattern of the electrodes cut away were made. The membrane is placed between them. To keep the assemble stationary, two more plates were fabricated out of aluminum with the same cut away. The Teflon plates are placed inside the aluminum plates, and c-clamps are fastened around the assembly.

Before the electrodes can be painted on the Nafion membrane, it must be pre-treated. This pre-treatment is a very time consuming and involved process. First, the membrane must be cut to size then boiled in hydrogen peroxide for one hour to remove the oil and dirt. Next, the membrane is boiled in sodium chloride for one hour to attach sodium to the Nafion surface. Now the membrane is ready for electrode application. Catalyst ink is prepared by placing carbon powder and platinum in a solution with isopropanol and glycol. The viscosity is determined by the amount of each ingredient. The desired consistency is that of house paint. The ingredients must be sonicated for several hours to insure proper mixing.

Once the ink is prepared, the membrane is placed in the template. A thin layer of catalyst ink is painted on and allowed to dry. Consecutive layers are painted on each side until complete coverage results. It is often helpful to hold the template assembly up to the coverage is adequate.

The membrane must be allowed to thoroughly dry before it is removed from the template. Once the membrane has been removed from the template it is allowed to dry again, this time, the entire surface must be dry, not just the electrode.

The completely dry membrane is place between two Teflon sheets and placed in a hot press. After five minutes of pressing the membrane at 4500 psi and 150° C, the membrane is removed from the press.

The membrane is boiled in one molar sulfuric acid for two hours to replace the sodium on the surface of the Nafion with sulfanate groups. Finally, the membrane is boiled for two hours in de-ionized water and it is ready for use.

Experiment 1a

The following is the formal report of the first experiment performed with the prototype on May 7, 1997

PURPOSE

The purpose of this experiment is to test the power output produced by each individual pad in the single membrane multi-pad (SMMP) fuel cell prototype.

APPARATUS

The apparatus used in this experiment is pictured in chart 1. The SMMP fuel cell is connected to the oxygen tank on the cathode side and the hydrogen tank is connected to the anode side. The pressure of the tanks will be regulated. The reactant gases are saturated with water in the hydration unit before entering the fuel cell. The temperatures after the hydration unit will be to monitor the fuel cell. Hygrometers will be used to measure the humidity of the reactant gases right before it enters into the fuel cell. The hydrogen gas stream will be “dead ended” in the anode side, where as the cathode stream will be purged. The purge, which is consisted of excess oxygen and water, will be collected in a bucket. The temperature and the flow rate of the purge will be determined to approximate the fuel cell stack temperature and the water produced in the electrochemical reaction through a mass balance. A voltmeter will be connected to the electrical taps of the fuel cell to determine the power output.

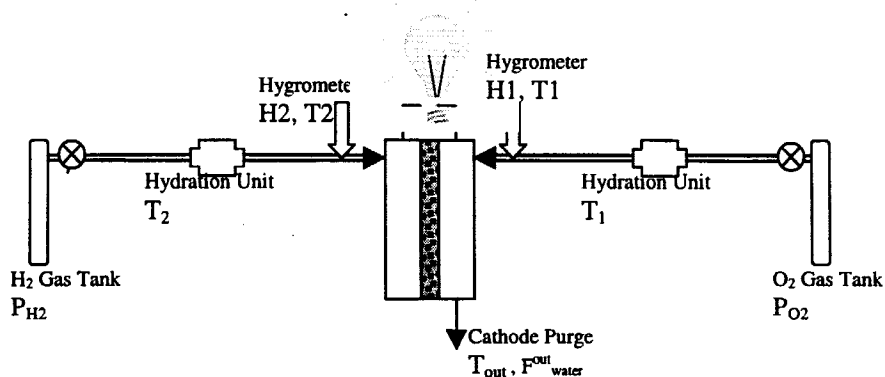


Figure 6 : Prototype in experiment 1a

PROCEDURE

Start up

1. Review the safety protocol for hydrogen usage.
2. Check for leaks using nitrogen gas.
3. Heat up fuel cell stack around 80-70°C by running hot water through the cathode stream.
4. Purge the anode stream with nitrogen to remove any oxygen.
5. Purge the anode stream with hydrogen to remove the nitrogen.
6. Close the anode purge to “dead end” the hydrogen stream.
7. Start the apparatus using the initial start up conditions.
 - ♦ $P_{O_2} = 1.5$ atm.
 - ♦ $P_{H_2} = 1$ atm.
 - ♦ T_1 and $T_2 = 85^\circ C$.
8. Measure the voltage between the each individual tab using the voltmeter.
9. Measure the temperatures and the humidity of the reactant gases.
10. Measure the temperature and the flow rate of the cathode purge.

Shut down

11. Close the reactant gas valves.
12. Purge the anode stream in a vented area to remove the hydrogen.

RESULTS

Table 1: Voltage under 10Ω Load in Series

Cell #	Voltage
1	0.286
2	0.245
3	0.290
4	0.325
Sum of 1-4	1.146
Total in Series	0.326

Table 2: Voltage in open circuit in series

Cell #	Voltage
1	0.937
2	0.936
3	0.944
4	0.928
Sum of 1-4	3.745
Total in Series	3.016

Table 3: Current across cell in series

Between Cells #	Amps
1-2	0.03
2-3	0.01
3-4	0.01

Table 4: Voltage in parallel

With No Load	0.933 V
With 5Ω Load	0.50 V
With 10Ω Load	0.680 V

Table 5: Voltage in series

Cell #	Voltage Under 10Ω Load	Voltage with No Load
1	-0.034	0.764
2	-0.195	0.624
3	0.110	0.720
4	0.522	0.840
Sum of 1-4	0.403	2.948
Total System	0.409	2.943

Table 6: Voltage of each cell if not connected

Cell #	Voltage Under 10Ω Load	Voltage with No Load
1	0.342	0.937
2	0.275	0.939
3	0.410	0.936
4	0.623	0.932

Table 7: Voltage of system connected in parallel

	Voltage Under 10W Load	Voltage with No Load
Entire System	0.720	0.934

DISCUSSION AND CONCLUSIONS

All of the data was collected at a constant fuel gas pressure. The hydrogen tank was set at a pressure of 8.5 psia. The oxygen tank was set at 12 psia.

The most interesting result from Experiment 1a is seen the table E1a.5. In this table we observe a negative voltage across cells one and two. This is not expected. All of the cells should have a positive voltage. These voltages should sum across the stack. There are several explanations for this strange result. The first place to look is at the membrane. By repeating the experiment with the membrane turned 180° it is possible to determine if the

membrane is causing this problem. The other strong possibility is the pressure gradient through the stack. A reverse reaction may be occurring due to a strong pressure drop.

The next point of interest provided by the data is that of current leakage. The goal of this form of stack is to increase the voltage, without using additional seals. One of the primary initiatives of running the prototype was to determine if the cells would exhibit current across the membrane. To test the efficiency of the stack, the summation of all of the cells in series is compared to the summation of each cell when connected in series. This data is found in Table E1a.5. The difference in voltage is 0.06 V. It can safely be assumed that no current leakage is occurring.

Not much information has been obtained from this data, a further experiment should include more data gathering. The voltage as a function of load needs to be further analyzed and the cell needs to run for a longer period of time. When purge screws on the hydrogen compartment were loosened and hydrogen allowed to flow out of them, the voltage of the cell increased. This leads to the conclusion that the hydrogen needs to be flowing past the cell, not dead-ended.

RECOMMENDATIONS

This experiment needed to be repeated with the membrane turned 180°. The pressure of the fuel gases should be changed to attempt to eliminate the negative voltage. At least two different pressure settings should be used to determine if this is a deciding factor in efficiency and performance.

A longer experiment should be performed, gathering more data. Recirculation of the hydrogen gas should be implemented to improve fuel cell efficiency.

Experiment 1b

The procedures of this experiment are exactly the same as those for Experiment 1a with the exception of the positioning of the membrane. The purpose and apparatus are the same as well.

The membrane was rotated 180° to determine if the negative potential was caused by a defective cell. Voltage readings were taken at different resistance during a longer time span to determine if the cell is able to reach steady state and perform better.

The experiment did prove the new concept was workable. When connected in series, the total voltage was about equal to the sum of the individual cells. The overall cell potential was about 3.016V while the sum of the cells 3.745V at open circuit, Experiment 1a. At a 10 ohm load, for example, the overall cell potential was 0.257V compared to the sum of 0.272V.

Negative potentials were still observed on cells 1 & 2, which were closest to the oxygen gas inlet. The 180° rotation of the Nafion membrane showed that the negative potential

was not the results of a defective membrane but maybe due to the reactant gas distribution.

With poor control of the operating parameters of the cell, the results showed that the system was not at steady state. The temperature of the cell cooled overtime, the humidify rate of the gases unknown, and the flow rate of the gases were unknown.

Several intangibles occurred. The fuel cell stack was originally heated with tap water, which contained impurities. The stack was submerged in distilled water, which corroded the clamping system and exposed the cell to rust.

The cells were flooded due to water condensation in the gas lines that transferred into the stack. In addition, the hydrogen stream was dead-ended causing accumulation. However, when the hydrogen was purged, an increased in the voltage was observed.

This lead to the recommendation of constructing a new test stand to incorporate the problems encountered in the experiment. A gas recirculating system, flow meters to control the amount of gas and a more compact test stand are features that are incorporated in the next test stand.

E. New Design Concepts

With the completion of experiments 1a and 1b, the stack project was ready to go to another level. A more complex test apparatus could allow for greatly stability and control when running the fuel cell. The areas explored were safety, humidification, learning more about the membrane and electrode, temperature control, and ease of manufacturing.

Safety

The issue of safety has been a priority through the entire project. Before any experiment is run, a leak test is performed with nitrogen to determine if there is a chance of hydrogen escaping uncontrolled. This is not enough.

Oxygen can remain in a fuel line or in the hydrogen side of the cell prior to running the cell. To avoid the potential danger of mixing hydrogen and oxygen, the hydrogen side of the cell is flushed with water. This will remove any oxygen and humidify and heat the stack. The oxygen side is flushed with nitrogen to remove any air or potential hydrogen.

Because blowing hydrogen over the catalyst is believed to increase cell efficiency, a method to safely do this must be found. Recirculation is the safest way to insure hydrogen gas does not escape. A closed system with a recirculation pump is necessary.

The final way to insure a safe run of the fuel cell stack, even for long periods of time is to place it in a hood. If a leak should develop, all of the hydrogen gas will vent to the atmosphere, allowing immediate dilution. To do this, the entire experimental apparatus must fit into a hood.

Humidification

As previously stated, the humidification level of the incoming gases is crucial to high performance in the fuel cell. If the gases are too moist, flooding will occur, slowing the reaction. If there is not enough moisture, the membrane will dehydrate and fail to perform with any level of efficiency. The necessary moisture was calculated during the winter, 1997 quarter (Please refer to "Fuel Cell Locomotive; Fuel Cell 'Stack'" for details).

The temperature at which the gases are exposed to water dictates the humidity level. This temperature must be controlled. By placing heating tape around the humidification tanks and plugging them into variable AC controllers, the temperature can be controlled. When the gases leave the humidification tanks, the temperature must either remain constant or increase to prevent condensation. This issue will be addressed shortly.

There are a variety of ways to increase the contact between a gas stream and the water it is to absorb. The test stand built in previous years for the department of Chemical Engineering had a humidification system that consisted of two water tanks. The gas is carried to the bottom of the tanks and blown out through an aspirator. It travels up through the tank absorbing moisture as it goes.

The stack group implemented a change to this system. By filling the water tanks with a packing material, a packed tower is created. The goal of this packing material is to increase the turbulence in the tank. By creating a more tortuous path, the gas interaction with water improves, increasing the potential for the water to be absorbed.

The material used as packing material must be resistant to corrosion and reaction. It must be small enough to increase turbulence as much as possible, but large enough that it is not sucked out of the tank. Economics also restrain the material used. The material chosen was boiling chips. They meet all of the specifications. This change should help improve the hydration of the fuel gases.

The Membrane and Electrode

Three aspects of the membranes and electrode were examined. The membrane was characterized, the platinum content examined and wet weights of the membrane taken.

OVERVIEW

The uses of the surface analysis technique, X-Ray Photoelectron Spectroscopy (XPS) in the analytical world are wide and diverse. While this technique is specific to the very top *surface* of the materials being analyzed, the applications include materials analysis and chemical characterization, failure analysis of mechanical components, new alloy development, polymer studies, biological suitability of implants interfaces, or even the historical study of Roman Bronzes. There are many other applications, too numerous to list. Our attempt is to show how the use of XPS

can characterize the surface differences between the different states of proton exchange membrane (PEM) and various process steps, which may change the surface characteristics of the PEM. This characterization is done in support of the hydrogen fuel cell project at the University of Washington.

INTRODUCTION

A better understanding of the data acquired by means of *X-Ray Photoelectron Spectroscopy (XPS)* is possible after a few terms are defined.

The term *surface* means different things to different engineers. For our purposes, the *surface* is usually defined as the top 5 - 50 Å of the sample surface (see Figure 1.) A 1cm² sample area has approximately 10¹⁵ atoms in its analysis regime. This understanding of what region is being analyzed is fundamental to interpreting the data. For example, bulk analysis of Monel, might reveal 70% Ni, and 30% Cu within the substrate of the material, when analyzed by an electron microprobe (EDX, or Energy Dispersive X-Ray Spectroscopy). In contrast, the XPS of the surface of the same sample might show 45% C, 15% O, 28% Ni, and 12% Cu. Carbon adsorbed to the *surface*, known as adventitious carbon, along with oxides and or hydroxides species may occupy the top 200 angstroms of the surface of the sample.

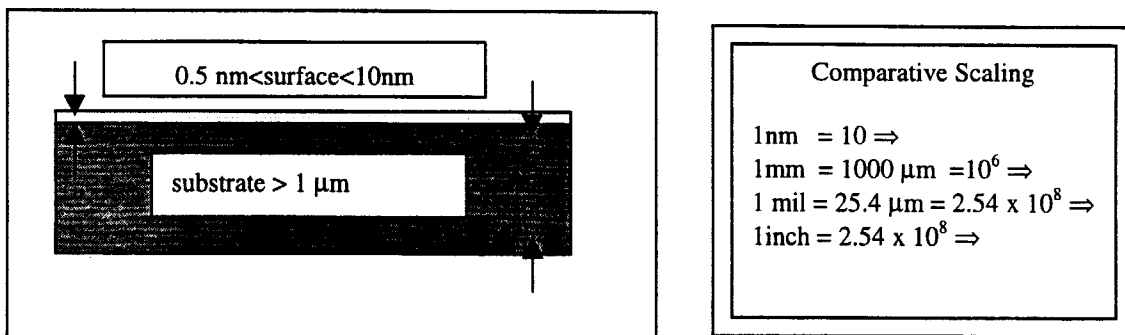


Figure 7: Defining the surface

Auger Electron Spectroscopy (AES) is a closely related surface analysis technique. The following background information for XPS and AES gives insight into these techniques. *Auger Electron Spectroscopy (AES)* is a *surface* sensitive technique for solid materials. Elemental composition can be determined for the region defined as the *surface*, to within 1% atomic concentration. The data or spectra are actually a x-y plot of the number of Auger electrons detected as a function of electron kinetic energy. The name, Auger comes from Pierre Auger, a French physicist. He was the first to describe the emission process (1925) which came to be known as the Auger process. AES can be thought of a three-step process. First, a high-energy particle, usually an electron beam between 3kV and 10kV is impinged upon the sample surface. This causes the ionization of core level electrons, usually K-shell electrons for light elements, and higher core levels of the heavier elements. As a hole is created in the core shell, an electron from a higher shell falls into its place. The second step in AES is completed as the energy of the higher shell

electron makes the transition to a lower shell. The energy liberated as kinetic energy is known as the Auger electron emission. The third and final step of AES is the detection of the emission. There is another possibility for this transition from a higher shell to a lower shell, as x-ray fluorescence, or the emission of a photoelectron. This emission phenomenon is the basis of *X-Ray Photoelectron Spectroscopy (XPS)*, which is discussed later.

Another term fundamental to understanding the detection of the Auger electrons is the Inelastic Mean Free Path (IMFP). The IMFP is the distance an electron can travel through a solid before it is scattered. The probability of an electron escaping out of the solid without scattering has been shown to be a function of its depth within the solid. In most instances, 95% of the electrons detected come from within the distance of 3 IMFPs. This is what makes the Auger technique *surface* sensitive. While atoms below the 3 IMFP region or approximately the defined *surface* may become excited by the incident beam, those electrons emitted are scattered, either going in another direction, or losing energy, prior to leaving the surface. The signal from this dissipated radiation becomes the background noise against which the emitted Auger electrons are detected.

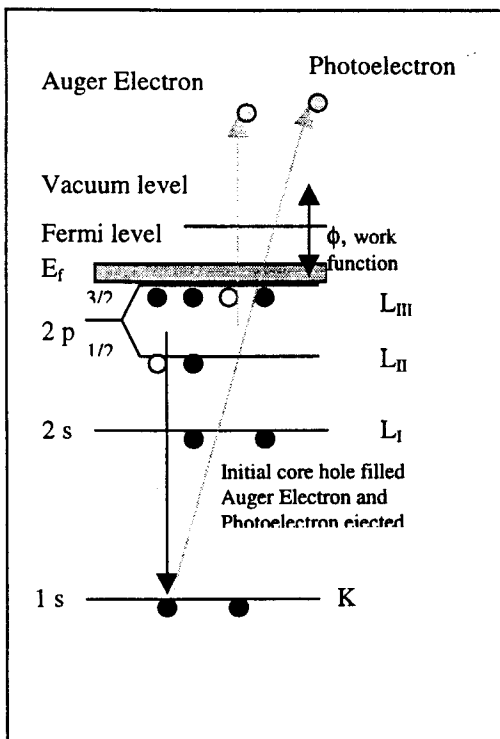
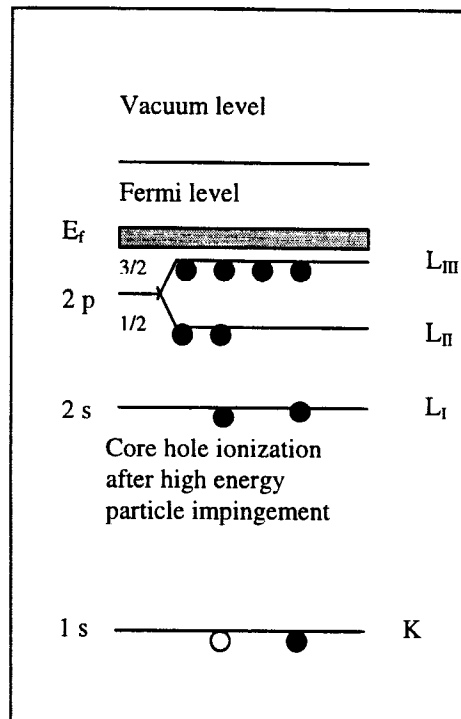
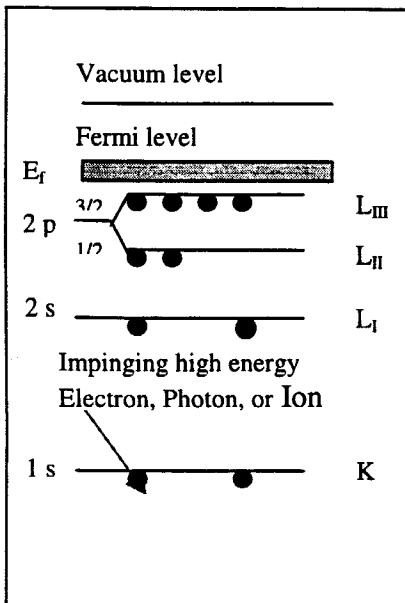
This describes the kinetic energy for an Auger electron emitted from L shells, as the core hole from the K shell is filled. Figure 1 gives a graphical representation of the incident high energy beam, irradiating, or impinging upon the sample surface, and the resulting Auger electron and photoelectron emissions. As the last model, or final state shows, the relaxed atom has emitted an Auger electron, leaving behind two core holes, in the L_I and the L_{II} shell. In this state, the atom is doubly ionized.

The equation for the kinetic energy of the emitted Auger electron can be stated as follows:

$$\text{Auger Kinetic Energy (K.E.)} \quad \text{---} \quad E_{KLL} = E_K - E_{L_I} - E_{L_{II}}^* \quad (1)$$

E_{KLL} is the kinetic energy of the emitted Auger electron, which is the difference of the binding energies: E_K , the binding energy of the core electron in the K shell, E_{L_I} , the released energy as the core hole in K is filled from L_I, and the $E_{L_{II}}^*$, the binding energy released as the electron in the L_{II} shell to fill the core hole left behind in L_I. As was noted earlier, it should be recalled that as the core level K shell electron is ionized, the loss of energy might be emitted as a photon, rather than as an Auger electron. The photon's energy is the sum of its kinetic and binding energies. Einstein's photoelectron relation leads to the following:

$$\text{Photoelectron Binding Energy (B.E.)} \quad \text{---} \quad \text{K.E.} = h\nu - \text{B.E.} \quad (2)$$



Auger Kinetic Energy

$$E_{KLL} = E_K - E_{L_I} - E_{L_{II}}^*$$

Einstein's Relation for Photon Energy

$$h\nu = E_{(K.E. + B.E.)}$$

Where h = Planck's Constant = 6.62×10^{-34} J s

ν = Frequency (Hz) of the radiation

X-Ray Photoelectron Binding Energy

$$K.E. = h\nu - B.E. - \phi$$

Where ϕ = the work function of the spectrometer

Figure 8: Graphical explanation of XPS

X-Ray Photoelectron Spectroscopy (XPS) is also known as Electron Spectroscopy for Chemical Analysis (ESCA). This is a *surface* sensitive technique for solid materials, similar to AES. Again, the IMFP is very short for the escaping photoelectrons, so the *surface* sensitivity of the emissions corresponds to the first few molecular layers. XPS spectra are typically reported as a plot of the actual number of photoelectrons detected versus the binding energy of the photoelectrons. In this case, the emission of the photoelectrons is accomplished by irradiating the sample surface with x-rays. Again, other high-energy particles can produce the photoelectron emission, as discussed earlier. Commonly, monochromatic, soft x-rays are used, usually $MgK\alpha$ (1253.6 eV), or $AlK\alpha$ (1486.6 eV). As the photoelectron impinges on the atom, the emission of a photoelectron from the core holes created occurs as discussed earlier, and shown in Figure 1. Since the emission process is actually elastic, with losses from the material and the spectrometer among other things, the work function ϕ is introduced to balance the energy equation. The work function term is usually fixed for the instrument. This work function can actually be calculated:

$$\phi = E_F - E_V \quad (3)$$

where E_F = the Fermi level, or the assumed zero binding energy level
and E_V = the Vacuum level, or the true zero energy level

For both AES and XPS, elemental composition can be determined for the region defined as the *surface*, to within 1% atomic concentration. Elements present in the material will emit more photoelectrons or Auger electrons than the background emission, appearing as peaks against the background. The atomic concentration of those elements can be determined, based upon the peak heights or areas under the peaks. XPS spectral shifts in the precise binding energy of individual peaks can indicate the specific chemical state of the element. In some cases, chemical state information can be determined to a limited extent, based upon the peak shapes of specific Auger transitions as well.

Instrumentation methodology will not be covered in this paper. The physics of that is well established, and can be accessed in the literature.

EXPERIMENT

Specimen handling of samples designated for XPS is crucial. Having seen earlier how thin a *surface* is actually examined, it becomes easy to understand that even fingerprints left behind from naked hands touching the sample *surface* are considered gross contamination of the sample. In the case of the duct, the process engineer who submitted the duct handled it while wearing special powder free vinyl gloves. These gloves are especially designed for use with equipment requiring ultra-high vacuum, and consequently, extreme cleanliness.

Specimens were obtained from the Single Fuel Cell Group, Chemical Engineering, University of Washington. Care was taken to avoid contamination from handling. An additional data point was collected prior to XPS analysis. Specimens 5.0 in² of old and new membranes were weighed as is, and after the hydration and cleaning process (2 hours in boiling H₂O₂).

XPS analysis was conducted on the old Nafion and the new Nafion. Wide scan spectra were obtained, to provide qualitative and quantitative analysis of the elements present in the *surface* area. High resolution spectra, focusing in on C (1s) peak were also obtained, in order to determine if possible, what shifts in binding energy had occurred from the normal position consistent with Nafion. A wide scan spectra followed the high-resolution test, to determine if the x-ray beam had damaged the specimen during analysis. In addition, analysis was done 30 days later on the new membrane to see if exposure to ambient air produced any changes in the surface chemistry of the membrane. Next, analysis on the cleaned and hydrated membranes was done, followed by analysis on the membrane after the electrode film had been added (inked).

RESULTS

Figure No. Title

(Figures given below can be found in Appendix C)

ME495_1	Nafion, old membrane as is
ME495_2	High Resolution C (1s) spectra of old Nafion, as is
ME495_3	Nafion, old membrane, after high resolution analysis
ME495_4	Nafion, new membrane, as is
ME495_5	Nafion, new membrane, as is, 30 days later
ME495_6	High Resolution C (1s) spectra of new Nafion, as is, 30 days later
ME495_7	New Nafion, cleaned and hydrated
ME495_8	High Resolution C (1s) spectra of New Nafion, cleaned and hydrated
ME495_9	Old Nafion, cleaned, hydrated
ME495_10	High Resolution C (1s) spectra of Old Nafion, cleaned and hydrated
ME495_11	Old Nafion, cleaned, hydrated, and inked
ME495_12	New Nafion, cleaned, hydrated, and inked
ME495_13	High Resolution C (1s) spectra of Nafion: Comparison of New & Old Membrane
ME495_14	Nafion: Comparison of New & Old Membrane, cleaned and hydrated
ME495_15	High Resolution C (1s) spectra of Nafion: Comparison of New & Old Membrane, cleaned and hydrated
ME495_16	Nafion: Comparison of New Membrane, as is and after 30 day
Table 1	Wet and Dry Membrane Weights

ANALYSIS/CONCLUSIONS

Our understanding of the Nafion is enhanced by the examination of the spectra obtained. Although there is much yet to be learned regarding the surface chemistry of the Nafion membrane, the following conclusions can be reached:

1. The surface of the Nafion degrades over time.

This is seen when one looks at the old versus new CF_2 peak. In the case of the old (over twenty years?) membrane, the CF_2 peak had started to degrade, and the presence of a CF_3 peak was found. On a small timed test, the Nafion is seen to become dirty, over a thirty-day period of shelf exposure. The adventitious carbon levels are seen to increase, as well as slight increase in oxygen. The surface has likely adsorbed CO_2 or other carbon contaminates, and masked the perfluorinated chain, as also evidenced by the decrease in the F signal.

2. The membrane has a different surface chemistry after cleaning and hydration.

After the cleaning of both the old and the new membranes, the presence of Sn is detected. The interaction of the Nafion with the Sn is unknown, but presumed to be a catalyst in the manufacturing of the Nafion membrane. This would have to be investigated further. In addition, the CF_3 peak is not seen in the cleaned Nafion.

3. Pt concentration at the Nafion surface exceeds the 10% required for fuel cell reaction.

Once the electrode surface comprised of the platinum-carbon ink had been dried to the Nafion surface, a concern was that there might not be enough platinum present at the surface to cause the reaction of the fuel cell to occur. A 10% threshold value had previously been determined. Although the atomic concentration of the Pt was less than 2%, by mass, the percentage is more than 14%. This exceeds the threshold requirements for the reaction to occur.

Temperature Control

Controlling the temperature within a fuel cell stack is of the utmost importance. The reaction rate increases with an increasing temperature but is limited by the temperature constrictions of Nafion. Above 85°C , the reaction rate drops off. The ideal temperature is set at 80°C (Gottesfeld). The temperature must be controlled either by heating the gases at the humidification tanks, or by some other means. Any tubing between the humidification tanks and the stack is a prime opportunity for heat loss. The tubes therefore must be minimized to reduce heat loss.

Another approach to controlling the temperature within the cell is to place the entire stack in an 80°C water bath. The gas has an opportunity to reach 80°C if extra inlet gas line is run around in the bath prior to entrance of the cell. Condensation is less likely to occur, and there is an increase in flexibility for the humidification temperature.

F. New Design Revisions

A completed design can always be optimized - but may also be limited by various resources such as time, money, and available technology. After examining the Fuel Cell Stack prototype, our team determined that several changes could be made to the overall system that would optimize the manufacturing and assembly process.

Design for Manufacturing

Once our initial design parameters were agreed on for the fuel cell stack, our objective was to concentrate on testing the cell. It was clear from the process of manufacturing the prototype that the initial stack design included several areas that could be optimized. This optimization was important for two reasons. 1.) To make necessary changes that would allow simple and efficient manufacturing of another test stack, and 2.) To incorporate these manufacturing changes into our design for the final fuel cell stack design.

Listed below are several items that were identified as redesign components:

Table 8: Items identified as redesign components

Component	Original Design	Redesign
Fuel Cell Stack Housing	Additional Port Filling	No Filling Required
	Complex Machining Process	CNC programmed
	Transfer Electrodes, wire mesh, carbon coated	Reticulated Vitreous Carbon Foam
	Hand-formed SS contacts	SS machine screw contacts
Seals and Gaskets	Machined Groove for O-ring	Flat Gasket, No machining
Catalyst Application	No mask used	Teflon Masking Template
		Aluminum Template Clamp

Refer to Appendix D for manufacturing drawings.

G. Final Experiment

The final experiment for spring quarter using the new test stand and prototype is scheduled for the week of June 9-13. After evaluating the test made on 5/8/97 several conclusions were made about the prototype and the test stand. The design changes to the prototype have already been discussed earlier in this report. The final experiment will include a heated water bath.

During the test water drops were observed moving into the prototype, especially on the hydrogen side during a purge. This caused flooding on the membrane and indicated that the temperature was too low for the hydrogen gas. If the gas temperatures are too low entering the prototype then the membrane will not operate at the optimum reaction rate. The gases were cooling down for the following reasons: first, the copper lines are too long; second, the lines are not insulated; third, the hydrogen should be recirculated.

Test Stand and Final Experiment

A new stand was developed using the following criteria:

- The lines should be as short as possible and still allow easy assembly of apparatus.
- There should be enough room to add pumps.
- It should be easy to modify.

The new test stand was constructed using Unistrut channels and custom made parts. The base of the stand was made from four channels open to the top; they were welded in a (18 x 13.25 inches) rectangle. Two upright channels (12 inches tall), which open to the front were welded to the rear corners. Various channel styles can be bolted to the base upon which components can be attached. The test stand has an added advantage of being able to fit into a fume-hood.

For the next experiment the prototype will be submerged in bath of 80°C water. Having the prototype submerged in a heated bath will help the prototype maintain steady state. A tank was constructed from Plexiglas joined by Weldon-3. Leaks were sealed with RTV silicone sealant. The tank sits on a shelf in the test stand. Water at the proper temperature will be pumped through the tank.

Four pumps are needed for testing the next prototype. The first pump will heat and recirculate water through the bath. Two pumps are needed to recirculate water through the hydration tanks (the hydrogen and oxygen have separate hydration tanks.) This can be accomplished using two peristaltic connected to one drive. The hydrogen will need to be recirculated with another peristaltic pump. The team has obtained all the necessary pumps and drives with the exception of a brushless motor to drive the hydrogen peristaltic pump (See **Figure 9**).

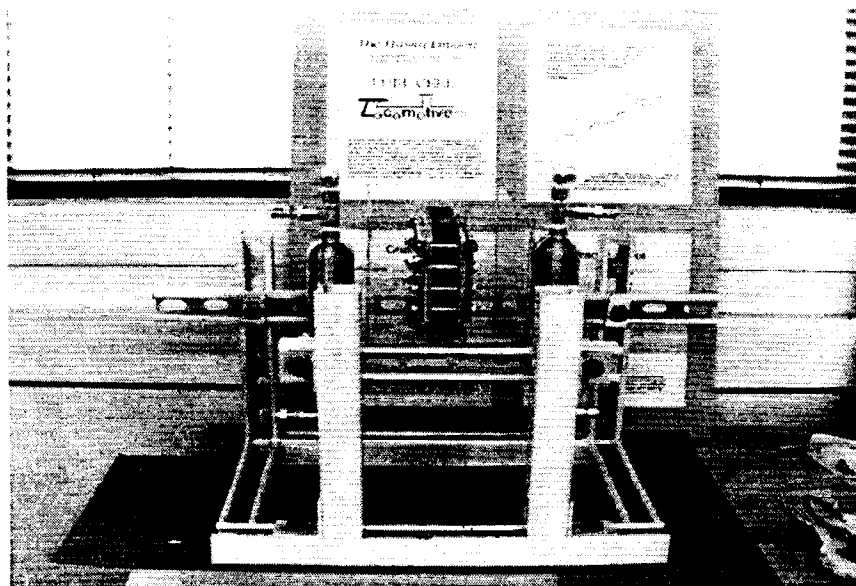


Figure 9: The new test stand

The final experiment will include the tests conducted during experiment 1b and with the additional tests.

- While the cells are connected in parallel the current through each cell will be measured. This will be repeated for each load.
- The voltage produced by the stack with the four cells connected in series will be monitored over a period of time.

Flow Meter Calibration

The flow meters were calibrated by inverting a graduated cylinder, which was filled with water, in a trough. Figure 9 shows a pictorial of the calibration assembly. A gas line connected to the flow meter was placed into the inverted cylinder. Gas is introduced into the assembly from a gas tank. The calibration was conducted by measuring the time it took to displace a certain volume of water by the gas entering the cylinder. The flow rate at that particular setting was determined by calculating the amount of time it took to displace the volume of water. A calibration chart was done for the gas used at different meter settings. The results of the calibration curves are in Appendix A. The calibration was done for small meter and a large yellow meter. During the calibration, we noticed that the flow rate of hydrogen was about 4 times larger than oxygen.

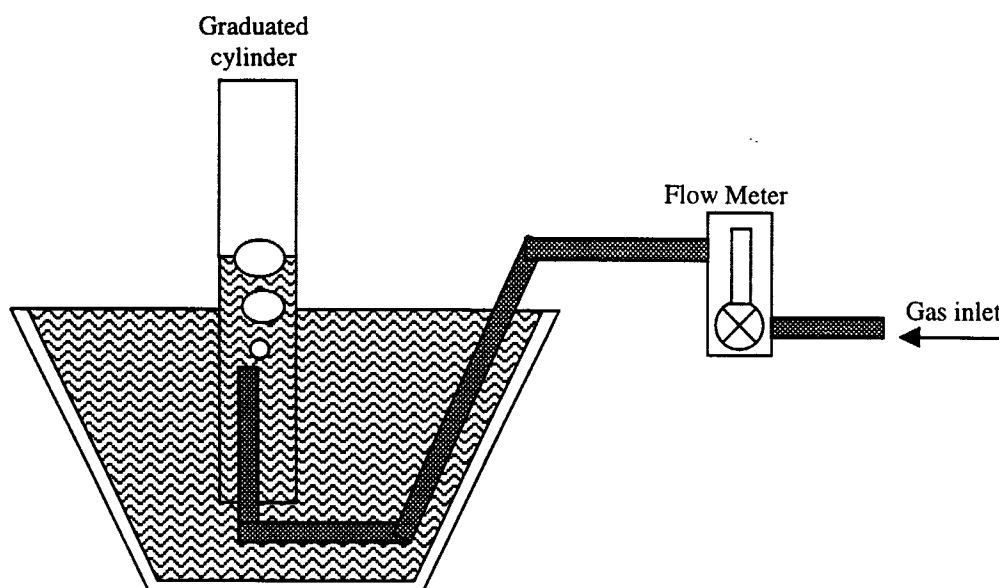


Figure 10: Flow meter calibration schematic

H. Conclusions and Recommendations

Due to the on going nature of this project, it is vital to make clear conclusions of what has been accomplished each quarter as well as to make a clear set of goals for the next quarter. This section of the report contains the conclusions and summary of the 1996-1997 school year of work as well as a section devoted to assisting the next team. Goals, suppliers and required orders of materials are included here.

Overall Conclusions

- Two tests conducted with bridled success
- Final experiment to be conducted next week
- Redesigned the current stack cell with success
- Additional test of prototypes were performed with limited conclusions
- The membrane surface chemistry changes over time
- The membrane has a different surface chemistry after cleaning and hydration
- Platinum concentration at the membrane surface exceeds the 10% required for fuel cell reaction
- Lexan proved to be good material for stack shell

PREVIOUS SUPPLIERS

The majority of the materials required for this project can be obtained locally. Obviously as the project becomes more complex and moves toward the manufacturing stage, the need for materials increases. The following is a list of the primary materials required for this project. A complete list of suppliers and how to contact them is maintained in a green binder in Integrated Learning Factory.

Table 9: Suppliers

Supplier	Material
Commercial Plastics	Lexan and Plexiglass
Seattle Valve and Fitting	Fittings and 3-way Valves
Acheson	Aerodag & Electrodag
Bryan Flinn, PhD (UW Material Science)	Reticulated Vitreous Carbon Foam
Instrumentors	Heating tape, Thermocouples
UW Central Stores	H ₂ , O ₂ and N ₂ gas tanks
UW Chemistry Store	Chemicals, Misc.
UW Physics Store	Tubing, Misc. not at Chemistry Store
Roger Pick (UW Chemical Engineering Department Electronics Shop)	Vari-ACs, flow meters, pumps, motors, regulators, etc.

GOALS

The first goal for the incoming fuel cell stack group should be to carefully review the work performed in previous quarters. The recommended tasks are as follows:

- Repeat the final experiment. Attempt to repeat it. **CAREFULLY** follow procedures.
- Focus on control of humidity and temperature by finding thermocouples from which conditions can be monitored. Stability of operating conditions is the next crucial step.
- Review and interpret data from previous quarters.
- Decide on the best organization for the people involved. If the single cell and stack group divisions don't occur, will there be too many people in one group? If they do, will work be repeated and poor communication result? Is there a better way to divide up the groups?
- Find ways to isolate variables such as temperature, humidity, load, operation time and manufacturing of membranes.
- Improve the template mask for painting carbon catalyst ink on the membrane. If a rough edge is milled into the perimeter of the pad, the ink will not bleed as much.
- The wiring harnesses should be altered. It is too time consuming to hook and unhook each connector and wait for the voltage to level out. Could be improved by using four voltmeters and placing the same load on all four cells.
- Run an experiment for a minimum of eight hours with the cells wired in series time taking measurements of the stack and the individual cells. It is known that the fuel cell efficiency improves with operation
- Improve the packed bed hydration system or develop an injection system for hydration.

- Manufacture a working stack.

TO ORDER

Before any new experiments are designed, it would be beneficial to order the materials required. The first priority is to order new thermocouples. Hygrometers and thermometers should be researched and ordered. It is recommended that a picture of the test stand and the prototype are taken to Instrumentors. They may be able to assist in locating equipment to fit inside the prototype and feed lines.

The fittings, and other materials are already in place. The first step to any experimental design is determine necessary supplies and order them. It is highly recommended that materials be purchased locally if possible. Ordering through the mail can take several weeks.

And to the next fuel cell team, GOOD LUCK!!

I. Acknowledgements

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J. References