Single Cell Group
Department of Chemical Engineering
University of Washington
Seattle, WA 98195
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E. M. Stuve
Department of Chemical Engineering
University of Washington
Box 351750
Seattle, WA 98195-1750

Dr. E. M. Stuve:

Attached is a copy of the progress report for the single cell group. The progress report includes information on what has been accomplished since the presentation of the proposal, what is currently being pursued, and a revised time table that includes information on what will be investigated in the future. A summary of problems encountered during the past seven weeks is also included in this report.

Sincerely,

Single Cell Group:

Johnny Ferara

Timothy King

Michael Nguyen

Seana Seraji

Single Cell Group

Progress Report

November 14, 1997

Johnny Ferara
Timothy King
Michael Nguyen
Seana Seraji

Summary:

As of week seven, fall quarter, several tasks have been completed, while other goals still remain to be achieved. Some of the goals have been accomplished ahead of schedule. The electrochemical H-Cell will be completed by November 15, 1997; two weeks earlier than planned. However, other tasks have somewhat fallen behind. Due to complications with the airbrush, the fabrication of membranes has been delayed. The electrical resistance tests were completed. This verified that the aluminum flow field plates will not prevent the fuel cell from producing the desired power output of 25 mA cm^{-2} at 0.6 V.

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Problem List

One of the first tasks was to analyze the various parameters of the experiment and determine what affect if any they may have on the overall performance of the cell. One of the group's first accomplishments was that a "problem list" was generated. The process that the membranes undergo was analyzed and all of the possible variables were listed. These variables were then given a rating according to the probability that altering that variable would affect the outcome performance of the cell. The table below lists these variables with their ranking and current test status.

Variable	Potential Problem?
Membrane Clean • Change H_2O_2 boil time.	**Not likely**
Conversion to Sodium Form • Alter NaCl boil time	**Questionable**
Binder Application • Alter amount of Nafion in liquid solvent	**Not likely**
Catalyst Application • Airbrush application • Paint Brush application	**Yes** *(Testing In progress)*
Solvent Formation • Alter concentrations of the various components in the catalyst solution • Vary platinum content	**Yes** *(Testing In progress)*
Hot Pressing • Change time, temperature and pressure of the hot pressing step.	**Yes** *(Testing In progress)*
Conversion to Hydrogen Form • Adjust sulfuric acid boil time	**Yes** *(Testing In progress)*
Hydration • Alter the hydration time of the membrane	**Questionable**
Gas Layer Diffusion • Remove carbon backing • Coat carbon backing	**Questionable**
Graphite coating • Change composition of Electro-dag solution	**Not likely**

Gas Feed • Alter humidity of incoming gasses • Change gas flow rates	**Not likely**
Test Cell Assembly • Allow the cell to operate for longer periods of time •	**Questionable**
Electrical Contacts • Improve connections and contacts from aluminum blocks	**Yes**
Test Protocol • Institute a standard method for testing the fuel cell to improve reproducibility	**Yes**

Progress for Membrane Characterization

Electrochemical H-Cell:

As mentioned in the previous report [1], there needs to be a means of measuring the proton conductivity of the Nafion membrane, with and without Pt catalyst. This test will assist in quantifying the conductivity of the membrane after extended boiling in various solutions of sodium chloride and deionized water. It will also characterize our catalyst application techniques.

The proton conductivity test will be performed using an electrochemical H-cell (Fig. A.1). Each half of the H cell consists of a 600-mL Pyrex beaker connected with a glass joint (4.1 cm I.D.) on the side wall. Each joint has a groove for an O-ring. The joints and Teflon O-rings were purchased through Ace Glass Inc. Initially, there was concern about a leaking problem if the two halves were put together. However, a leak test has been performed by inserting a non-processed membrane between the two glass joints that were clamped together with a stainless steel clamp. The joints were then oriented vertically and filled with water. No leaking was observed. The joints were

inverted and filled with water again. Again, there was no leaking. This gave a green light for the construction of the cell with no modification of the purchased materials.

The purchasing process of the materials was time consuming since it was done the first time. Difficulty in getting approval and getting a hold of the right person was not anticipated. With more experience, this difficulty will be avoided in the future. Despite the time spent, the time to receive the materials was still less than what it would have taken the glass shop. The phone ordered materials (joints and O-rings) have been received and given to Mr. Bob Morley, the glass blower in the Physics building. It is expected that the construction of the apparatus will be finished this Friday, November 14. Next week will be spent putting together a test cell (with Pt electrodes) and to devise a data collection procedure. A theory of the conductivity test was presented in [3].

Membrane Fabrication Progress

Processing Steps Completed:

To create a working fuel cell membrane, a portion of Nafion must first undergo an involved process that consists of numerous steps, ranging from cleaning to applying catalyst and hot pressing. Thus far in the quarter, several of these steps have been completed successfully. Throughout the processing, the weight of the membranes are measured, and observations are made in order to allow the experiments to be as quantitative as possible. For example, if the initial weight of the membrane is known, then the degree of saturation can be calculated.

The first step was to cut a section of Nafion to fit the flow field plates. A round aluminum tube with a sharpened edge was used in a cookie cutter fashion, to cut a circle

out of the sheet of Nafion. When cutting the membrane care was taken to minimize hand contact with the Nafion, and the size was made to account for the swelling of the membrane in water. The Nafion was then baked for approximately ten minutes at 45 °C in order to drive off any moisture from the Nafion. The "bone-dry" weights of the membranes were then measured.

The cut Nafion membrane was then cleaned. This was accomplished by boiling the Nafion membrane in hydrogen peroxide solution for one hour [2]. The membrane weights after this step were again recorded.

Next, the Nafion membrane was boiled in a one-molar sodium chloride solution for one hour. The purpose of this was to convert the Nafion to the sodium form, thus enhancing its processing characteristics.

The next step was to mask off the center area for catalyst application. This was done by clamping the membrane between two Teflon blocks with 4.5 cm diameter openings in the center. This was held together at the bottom by a clamp stand, and at the top with C-clamps on each corner. Please see Fig. A.2 for a schematic of this set up. This entire apparatus (except for the holes in the Teflon) was then covered with plastic wrap to ensure that only the Nafion membrane was coated with the catalyst solution. The membrane was ready to be coated when the problems with the airbrush were encountered. This halted the progress, because the catalyst could not be applied to the membrane with out the airbrush operating correctly.

In total there have been six membranes processed up to this point. Two were inherited from the previous group, however no weight measurements are available for these. The others were processed this quarter. One membrane was not converted to the

sodium form. This step was omitted for this membrane so that proton conductivity measurements can be made for both hydrogen and sodium forms of the Nafion. This will assist in the determination of the degree of sodium conversion in the membranes.

Preliminary calculations have been made for the percent hydration of two of the membranes. The percent hydration of a membrane was 30.55 %, and 32 % for another. These results are within the range reported for degree of saturation of Nafion [3]. The percent hydration was calculated from Equation (1) given below:

$$\%\,\text{hydration} = \frac{(\text{Wet Weight} - \text{Bonedry Weight})}{(\text{Wet Weight})} \times 100\% \qquad \textit{Equation (1)}$$

Proposed Membrane Preparation Procedure:

It was hypothesized that the catalyst solution is one experimental variable that can affect the current density of the fuel cell. This catalyst solution itself has three variables, which can be adjusted: the concentrations of the isopropanol, glycerol, and Nafion solution.

The hot pressing of the catalyst layer on the membrane is another alterable parameter that may have an impact on the overall current density of the system. This heating of the membrane will affect the catalyst layer, and consequently the composition of the catalyst. As a result, the hot pressing will interact with the catalyst solution, thus forming a new, compound variable.

To uncouple the relationships between the above-mentioned variables, design of experiment (DOE), or specifically factorial design will be implemented. There are three variables in the catalyst solution, which are assumed to be used in either high (+) or low (-) concentrations. This gives (2^3) or 8 possible combinations. These combinations can be conveniently depicted in a DOE cube as shown in Fig.3 below.

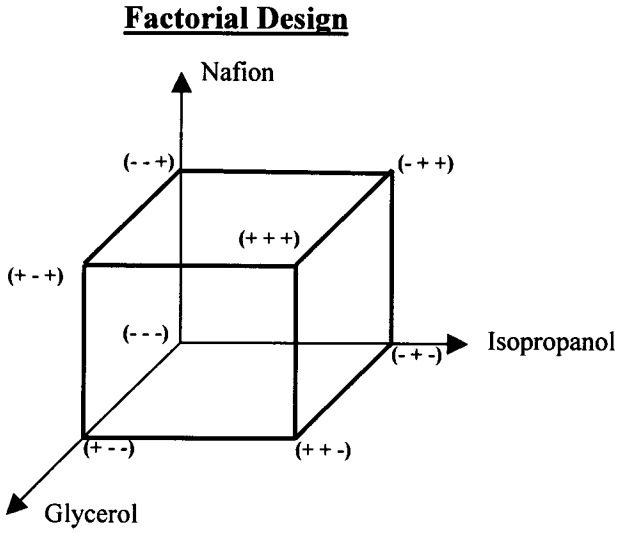

Figure 3. DOE cube

Since Nafion is quite expensive, and the processing is very time intensive, each membrane will be sectioned into quarters. Each quadrant of the membrane will have different concentrations of the catalyst solution, and thus all eight combinations can be tested using only two membranes. Fig. 4 on the following page illustrates the patterning scheme of the membranes.

Factorial Design with Hot Pressing

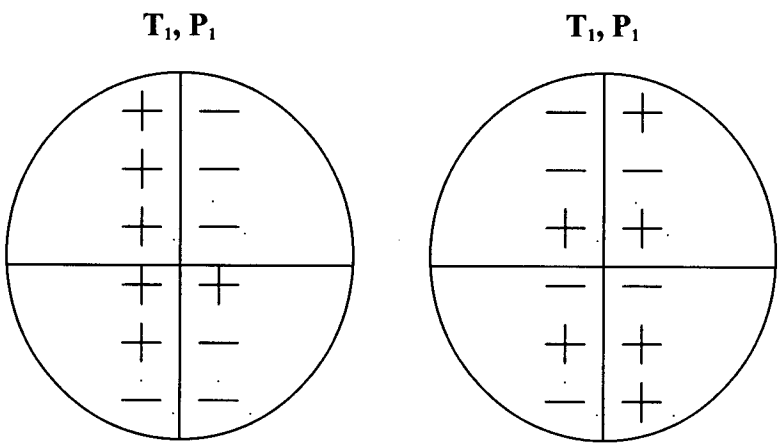

Figure 4: Catalyst Application Scheme for Each Quadrant of the Membrane

The results from this experimental design will show the relationship between the concentrations of the chemical constituents of the catalyst. However, this setup alone would neglect the effects of the hot pressing. To account for this, two groups of the previously designed membranes will be made. Both groups will then be pressed at different settings. From this series of experiments the relationships between hot pressing and the concentrations of the components of the catalyst should become apparent.

Electrical Resistance Test Result for the FFPs

An electrical resistance test was performed on the aluminum flow field plates (FFPs). This test was to determine if the poor performance of the single fuel cell is a result of the design of the current FFPs. The aluminum FFPs were assembled with the carbon backings and a lead (Pb) sheet simulating the membrane electrode assembly (MEA). Lead was chosen due to its conductive properties and its malleability. The lead sheet was sanded prior to the resistance test in order to remove the oxide coating. The electrical resistance was determined by measuring the voltages at various points on the

assembled FFPs with a multimeter as shown in Figures A.3 and A.4. These figures also include a graphical representation of the setup of the experiment. As shown in either Figure A.3 or A.4, when the multimeter is connected in series, it was used to determine the voltage of the:

❶ Clip #1
❷ Aluminum FFP #1
❸ Lead sheet
❹ Aluminum FFP #2
❺ Clip #2

The resistance can be determined from the voltage readings at these various locations. The resistance can be determined using a modified form of Ohm's Law as shown below as Equation (2):

$$R = \frac{(V_2 - V_1)}{I} \qquad \textit{Equation (2)}$$

where R is the resistance, I is the current, and V_1 and V_2 are the voltages at point 1 and point 2, respectively. Using a constant current of 1 ampere, the resistance can be determined using Equation (2) above. Figure 5 below shows the resistance model during

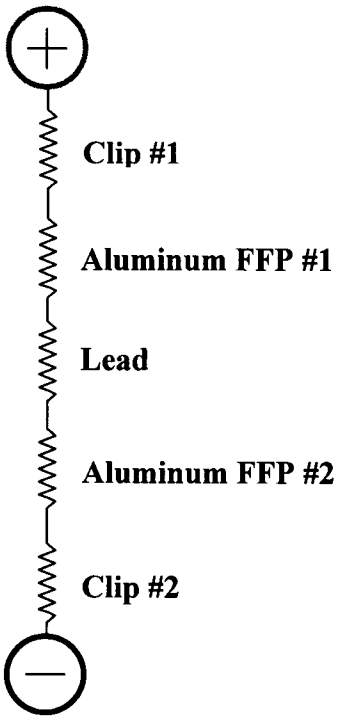

Figure 5: The resistance model during the resistance test on the assembled aluminum FFPs.

the resistance test. The results from the resistance test when the multimeter is connected in series to the positive outlet of the power supply as shown in Figure A.3 for each trial are listed in Table 1 displayed below.

Table 1: Resistance test results when the multimeter is connected in series to the positive outlet of the power supply.

Location	Trial 1	Trial 2
	Resistance (Ω)	Resistance (Ω)
Aluminum FFP #1	0.025	0.024
Pb sheet	0.006	0.005
Aluminum FFP #2	0.006	0.006
TOTAL:	0.037	0.035

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The results from the resistance test when the multimeter is connected in series to the negative outlet of the power supply as shown in Figure A.4 for each trial are listed in Table 2 shown below.

Table 2: Resistance test results when the multimeter is connected in series to the negative outlet of the power supply.

Location	Trial 1	Trial 2	Trial 3
	Resistance (Ω)	Resistance (Ω)	Resistance (Ω)
Aluminum FFP #2	0.080	0.092	0.063
Pb sheet	0.006	0.005	0.03
Aluminum FFP #1	0.005	0.005	0.007
TOTAL:	0.091	0.102	0.100

As shown in both Tables 1 and 2 above, the resistance of the aluminum FFPs do not pose any threat to the current quarter goal of obtaining 25.0 mA cm^{-2} at a potential of 0.6 V. With a surface area of approximately 10 cm^2 and a current density of 25.0 mA cm^{-2}, the maximum allowed resistance of the entire aluminum block assembly is 2.4 Ω. As listed in Tables 4 and 5, the resistance of both aluminum FFPs are under the value of the maximum allowed resistance. Therefore, the aluminum block assembly is adequate for the single cell group's current goal.

Three trials were performed when the multimeter was connected in series with the negative power outlet of the power supply since this setup tended to yield a higher resistance as shown in Tables1 and 2 above. It was thought that there was not a good contact between the aluminum FFP and the lead sheet. However, after disassembling the block assembly after the resistance test, it was observed that the texture of the carbon

backing was engraved on both sides of the lead sheet in place of the MEA. This observation indicates that there was good contact between both the aluminum FFPs and the lead sheet. A possible explanation to this occurrence is that it due to slight physical differences between the two aluminum FFPs.

Past and Present Time Tables

Table 3 below includes information about the time line from the proposal given several weeks earlier. A revised goals and times table can be found in Table 4 on the following page.

Table 3: Preliminary goals and times table

Week	Goals
1. (9/29-10/3)	Understanding of the design problem and write preliminary proposal
2. (10/6-10/10)	Research and begin preliminary resistance test
3. (10/13-10/17)	Define goals and write proposal
4. (10/20-10/24)	Continue resistance test, practice catalyst applications, and research electrochemical H-cell
5. (10/27-10/31)	Begin manufacturing MEAs with revised techniques and start coordinating with the Systems Group to modify the test stand to dead end hydrogen flow
6. (11/3-11/7)	Test current density on newly manufactured MEAs. Adjust fabrication techniques accordingly. Continue to research H-cell, and order materials to build H-cell
7. (11/10-11/14)	Make more MEAs with newly adjusted techniques. Write progress report
8. (11/17-11/21)	Investigate methods to quantify sodium concentration. Begin building the H-cell.
9. (11/24-11/26)	Continue building the H-cell.
10. (12/1-12/5)	Continue testing current density on MEAs with newly derived techniques.
11. (12/8-12/10)	Finals Exam Week

Table 4: Revised preliminary goals and times table

Week	Goals
1. (9/29-10/3)	Understanding of the design problem and write preliminary proposal
2. (10/6-10/10)	Research and begin preliminary resistance test
3. (10/13-10/17)	Define goals and write proposal
4. (10/20-10/24)	Continue resistance test, practice catalyst applications with the airbrush, and research electrochemical H-cell
5. (10/27-10/31)	Begin cutting nafion membrane to begin the cleaning process. Continue practicing catalyst application with the airbrush.
6. (11/3-11/7)	Begin mixing the catalyst ink and order chemicals that are in short supply. Order materials for the electrochemical H-cell
7. (11/10-11/14)	Go over testing apparatus and prepare it in order to conduct current density tests. Begin building electrochemical H-cell. Write progress report
8. (11/17-11/21)	Begin the application of catalyst ink on the nafion membrane in order to create MEAs. Investigate methods to quantify sodium concentration. Begin proton conductivity tests on the nafion membrane.
9. (11/24-11/26)	Test current density on newly manufactured MEAs. Adjust fabrication techniques of MEAs accordingly. Continue the proton conductivity test on the nafion membrane.
10. (12/1-12/5)	Continue testing current density on MEAs with newly derived techniques. Begin conducting proton conductivity tests on the MEAs.
11. (12/8-12/10)	Finals Exam Week

Recommendations

As far as recommendations, there are several which apply specifically to the catalyst application and the electrochemical H-cell, while there are others that apply to the overall single cell effort. There are four that pertain specifically to the processing of the membrane electrode assembly. One problem is access to room B-5 in Benson Hall. This room is usually open during regular business hours (i.e., 8:00 a.m. to 5:00 p.m.) and access to this room is only allowed under the presence of a graduate student. Since some procedures take more than 4 hours to complete it would be much more efficient to have access 24 hours a day seven days a week to another lab on campus. This lab would only have to have a single fume hood and sink.

Since, the airbrush is temporarily nonfunctioning it will be sent back for repairs to a company called Daniel Smith, Inc. If the repair and shipping time is too long, the group will look into buying pre-compressed spray equipment that is rather cheap and easily obtainable at hardware stores. The problem of the ink gelling up can be easily remedied by capping it correctly with some Teflon tape as an added sealant.

No problems have really occurred yet with the electrochemical H-cell setup, however, the completion and operation of the H-cell will most likely be successful if the group stays in close contact with Professor Stuve.

One recommendation for the entire effort of the single cell group would be setting up short group meetings involving just group members. At these short meetings it would be helpful to let each person talk about what they have done and let the rest of the group give constructive feedback to the questions problems or statements made by each person.

Operational Safety Assessment

Accidents:

Despite careful efforts and adherence to the operating procedures, a problem with the airbrush was encountered. The airbrush is a tool that is commonly used to apply paint however, tests were being conducted to determine the practicality of using this device for catalyst application. During testing, the airbrush ceased to operate correctly. After troubleshooting, the root of this problem was determined, and several plausible causes were found.

Before a prepared membrane was coated with the catalyst, a test area was first sprayed. During this test spray period, the catalyst came out in sporadic bursts for a period of time, and then failed to spray out anything at all. Nothing but air came out of the brush, so the tool was thoroughly cleaned with acetone. The tool was tested again, but catalyst did not come out.

Since the air continued to come out, and the fluid wasn't, the hypothesis was made that the brush had blockage problem from the ink reservoir to the nozzle. The tool was carefully disassembled, and all of the parts were cleaned out from the inside. Several large agglomerates were found.

After reassembling the tool, there was a back flow of air in to the liquid reservoir, thus causing the liquid to bubble out.

Upon close examination of the tool, it was noticed that a small piece of the nozzle assembly was broken. Figure 6 below is a schematic of what is believed to be the problem. It appeared that a portion of the threaded region of the nozzle was left inside the screw area, thus disrupting the tight seal.

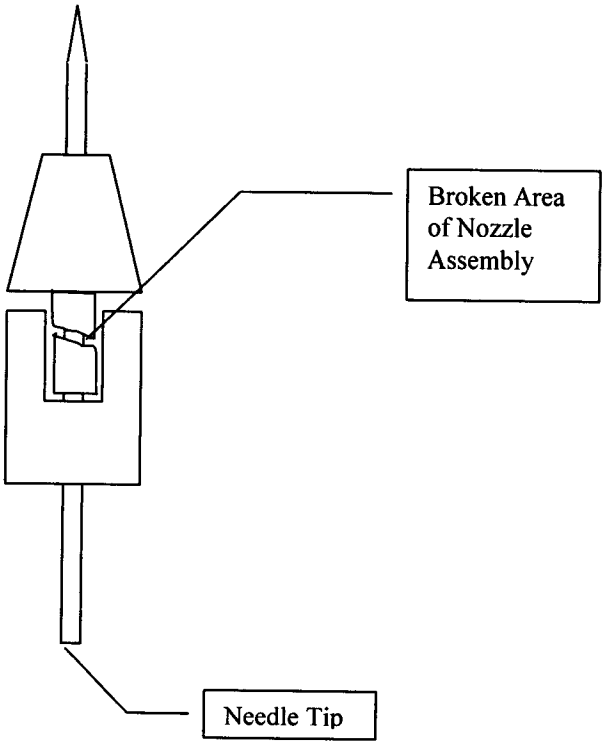

Figure 6: A zoomed diagram of the tip of the damaged airbrush.

This damage may have come from many sources. The sources are as follows:

- The nozzle may have broken during the dismantling of the airbrush.
- It may have broken earlier but was being held together by the assembly. Then when the apparatus was disassembled, it came apart.
- When previous tests were conducted with the airbrush, oxygen was used to propel the catalyst. This resulted in the oxidation of the platinum, which caused the tip of the airbrush to glow. This heating may have weakened the very thin metal in the screw. The heat may have even fused the two pieces together, and when the torque was applied to remove the tip, it broke.