be maximized, and thus minimizing the solution flocculation. However, this technique would not be appropriate for the desired purpose, for it is most effective at extreme pH values.

Steric stabilization, on the other hand, works on a very different concept. Polymers of various molecular weight are used to build up a physical barrier around the particles, forming a "micelle-like" structure around the particles. These act to separate the particles, thus not allowing them to come in contact with one another. The problem with this technique is that the polymer chains generally attach to the oxide of the particles in the solution. Platinum does not form an oxide in normal conditions, and therefore this technique would not be suitable either.

If one can not prevent agglomerates from forming, the next best solution would be to break up the clumps that have formed. In the current process, the solution is sonicated for one hour to accomplish this task. However, there is literature that suggests that other methods can be more effective at breaking up agglomerates than sonication. One such method is ball milling. In this method, the solution is poured in to a hollow, round cylinder along with hard, wear resistant grinding media (such as alumina or zirconia balls). The cylinder is then placed in a roller for a certain amount of time [5]. The impact of the grinding media crashing against one another is very effective at dispersing the solution. This is one area that is very promising, and should be investigated further next quarter if it is determined that the amount of platinum on the membrane is indeed a performance limiting factor.

Status of Single Cell Group Goals

The group goals and timetable introduced during the proposal is given as Table 5 on the following page. As seen in the table, the primary goal of the group during the quarter was to

produce a MEA in order to achieve a current density of 25 $mA \cdot cm^{-2}$ at a potential of 0.6 V. Due to the damage sustained by the airbrush, the group was unable to produce a

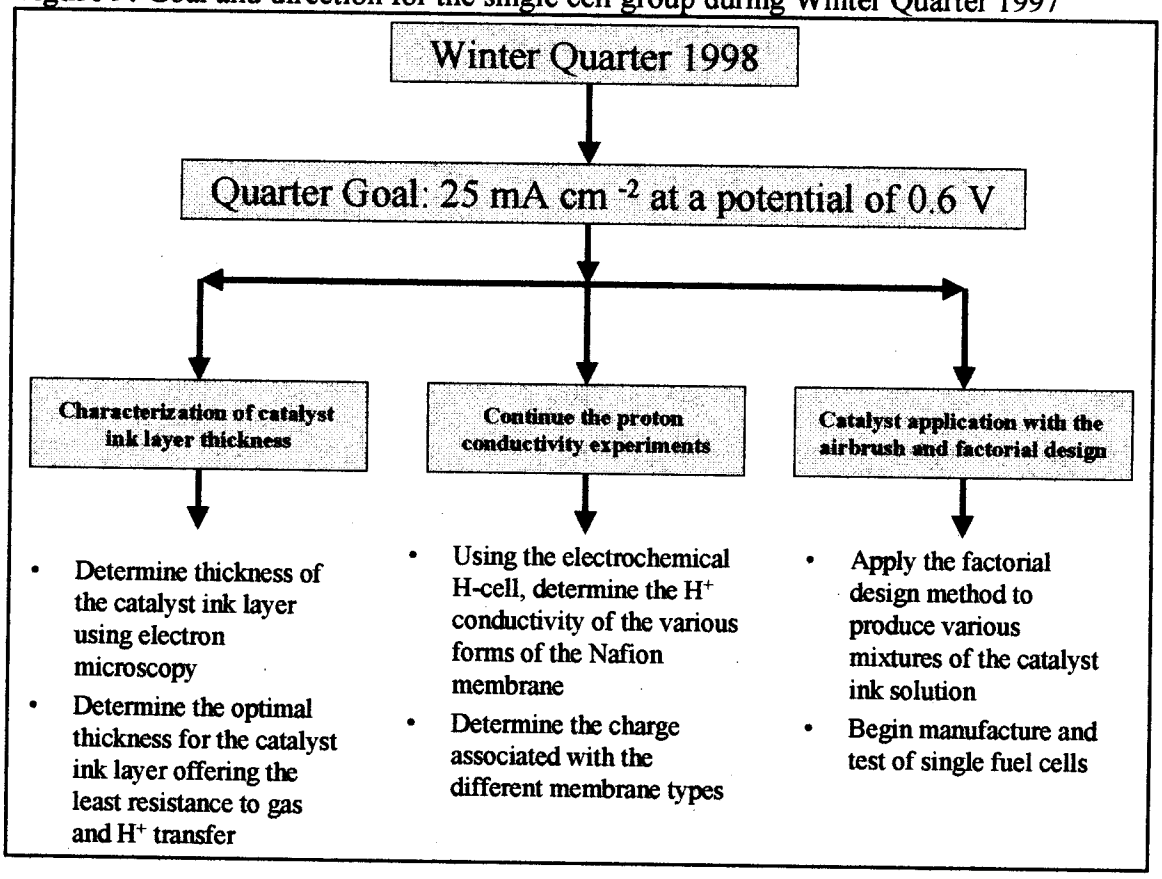
Table 5: Preliminary goals and timetable introduced in the preliminary proposal

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 to achieve a current density of 25 $mA \cdot cm^{-2}$ at a potential of 0.6 V.
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 construction of the H-cell.
9. (11/24-11/26)	Continue construction 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 and Final Presentation

single fuel cell in order to test the current density. However, the aluminum FFPs resistance test was completed successfully, and the design and the manufacture of the electrochemical H-Cell were completed on the eighth week. The conductivity of various forms of the Nafion® membrane (e.g., the Na^+ and H^+ form as well as the catalyzed form) was determined using the electrochemical H-cell on the final two weeks. The application of catalyst was hindered this

quarter because of equipment problems. Figure 9 below illustrates the future goals for the next quarter.

Figure 9: Goal and direction for the single cell group during Winter Quarter 1997



Conclusions

This quarter the main goals were to receive a current density of 25 mA cm^{-2} from a Nafion® 117 membrane operating in a small scale fuel cell block, and to characterize the membrane electrode assembly which is used in this fuel cell block. Unfortunately, the primary goal was not met. In order to achieve this goal, it was necessary to produce a membrane electrode assembly. A membrane electrode assembly was not produced because the airbrush used to apply the catalyst layer malfunctioned due to a fracture in the tip of the airbrush. The other main goal was to characterize the membrane electrode assembly. A factorial design was set up in order characterize several variables involved in producing a membrane electrode assembly. However, the factorial design could not be implemented because this design depended on the ability to make a membrane electrode assembly. The primary objective was not met, but other tests were done in the meantime.

One test involved looking at the small scale fuel cell block. The goal of this test was to determine whether this block had an overall resistance that would hinder the harnessing of current from a working membrane. It was determined that the resistance of the block was not the limiting factor in receiving low current densities. Another goal was to determine the conductivity of the membranes. Three different membranes were used in this test: an unprocessed membrane, a membrane converted to the sodium form, and a fully processed membrane with a catalyst layer. This test showed overall that the conductivity of the sodium form membrane was about the same as the non-sodium form. The conversion from the sodium membrane into the pure membrane is desired, but it should not affect the conductivity of the membrane greatly. These tests also showed that the resistance of the fully processed membrane decreased as more current applied to the membrane. However, no concrete conclusion can be

made from the results because further trials were not conducted for the catalyst layered membrane.

Recommendations

This section highlights what the single cell group recommends for next quarter in light of all the successes and shortcomings this quarter. In order to achieve a current density of 25 mA cm^{-2} the single cell group will have to first be able to apply the catalyst to the processed membranes. The group is currently waiting for the return of the repaired airbrush. If this does not occur in a timely matter, then the sputter coating technique will be investigated into applying the catalyst directly to the surface of the membrane. This however will not solve the problem of applying the catalyst solution to the membrane to controlled thickness, because the sputtering technique will only apply pure platinum. Another recommendation by the single cell group is to continue tests using the H-cell apparatus to verify the results so far and to further test fully processed membranes with catalyst layers.

Acknowledgements

1. The single cell group would like to acknowledge Bob Morley for helping us construct the electrochemical H-cell.

2. We would also like to thank Jerry Hestbeck for his help in ordering necessary materials.

3. And last but not least, we would like to thank Professor Stuve for all his guidance and support throughout the project.

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Appendix A: Raw Data from Aluminum FFPs Resistance Test

Table A.1 below lists the voltage reading when the multimeter was connected in series with the positive power outlet of the power supply during the first trial of the resistance test.

Table A.1: Voltage readings for trial 1 when the multimeter is connected to the positive power outlet.

	Voltage reading (V)
Clip #1	0.014
Al FFP #1	0.039
Lead	0.045
Al FFP #2	0.051
Clip #2	0.133

Table A.2 below lists the voltage reading when the multimeter was connected in series with the negative power outlet of the power supply during the first trial of the resistance test.

Table A.2: Voltage readings for trial 1 when the multimeter is connected to the negative power outlet.

	Voltage reading (V)
Clip #1	0.014
Al FFP #1	0.094
Lead	0.100
Al FFP #2	0.105
Clip #2	0.126

Table A.3 below lists the voltage reading when the multimeter was connected in series with the positive power outlet of the power supply during the second trial of the resistance test.

Table A.3: Voltage readings for trial 2 when the multimeter is connected to the positive power outlet.

	Voltage reading (V)
Clip #1	0.014
Al FFP #1	0.038
Lead	0.043
Al FFP #2	0.049
Clip #2	0.070

Table A.4 below lists the voltage reading when the multimeter was connected in series with the negative power outlet of the power supply during the second trial of the resistance test.

Table A.4: Voltage readings for trial 2 when the multimeter is connected to the negative power outlet.

	Voltage reading (V)
Clip #1	0.014
Al FFP #1	0.106
Lead	0.111
Al FFP #2	0.116
Clip #2	0.151

Table A.5 below lists the voltage reading when the multimeter was connected in series with the negative power outlet of the power supply during the third trial of the resistance test.

Table A.5: Voltage readings for trial 3 when the multimeter is connected to the negative power outlet.

	Voltage reading (V)
Clip #1	0.623
Al FFP #1	0.56
Lead	0.53
Al FFP #2	0.537

Appendix B: Raw and Calculated Data for Electrochemical H-Cell Tests

Table B.1: Data from the electrochemical H-cell test using no membrane

	20-Nov	26-Nov	
	No-Membrane (mV)		AvG. Resistance(miliOhm)
Current (mA)	Run 1	Run 2	Average
0.4	1.210	0.200	1.205
0.6	1.320	0.320	1.318
0.8	1.374	0.372	1.373
1.0	1.427	0.403	1.415
2.0	2.042	1.970	2.006
3.0	2.209	2.001	2.105
4.0	2.305	2.075	2.190
5.0	2.479	2.046	2.263
6.0	2.567	2.150	2.358
7.0	2.701	2.168	2.435
8.0	2.910	2.112	2.511
9.0	3.034	2.133	2.584
10.0	2.812	2.150	2.481
20.0	4.057	4.773	4.415
30.0	5.385	5.885	5.635
40.0	6.550	7.130	6.840
50.0	7.825	8.225	8.025
60.0	8.905	9.550	9.225
70.0	10.600	10.250	10.425
80.0	11.180	12.050	11.615
90.0	12.360	13.250	12.805
100.0	13.500	14.540	14.020

Table B.2: Data from the H-cell tests using the sodium form of the membrane

	20-Nov	25-Nov	
	Sodium Form (V)		AvG. Resistance(miliOhm)
Current (mA)	Run 1	Run 2	Average
0.4	1.880	1.736	1.256
0.6	1.772	1.835	0.793
0.8	1.826	1.877	0.599
1.0	1.882	1.925	0.469
2.0	2.031	2.013	0.009
3.0	2.250	2.156	0.037
4.0	2.348	2.328	0.038
5.0	2.552	2.443	0.051
6.0	2.682	2.550	0.045
7.0	2.756	2.768	0.047
8.0	2.896	2.900	0.048
9.0	3.015	3.034	0.049
10.0	2.736	3.121	0.047
20.0	3.580	4.000	-0.019
30.0	5.700	5.360	-0.003
40.0	6.310	6.380	-0.010
50.0	7.000	7.050	-0.006
60.0	8.700	8.140	-0.004
70.0	9.930	10.250	-0.005
80.0	11.110	11.320	-0.004
90.0	12.300	12.700	-0.003
100.0	13.450	14.000	-0.003

Appendix C: Schematics of the Entire System and the Single Fuel Cell Test Stand

Note: Several valves are not needed if we test our MEAs using dead-end hydrogen.

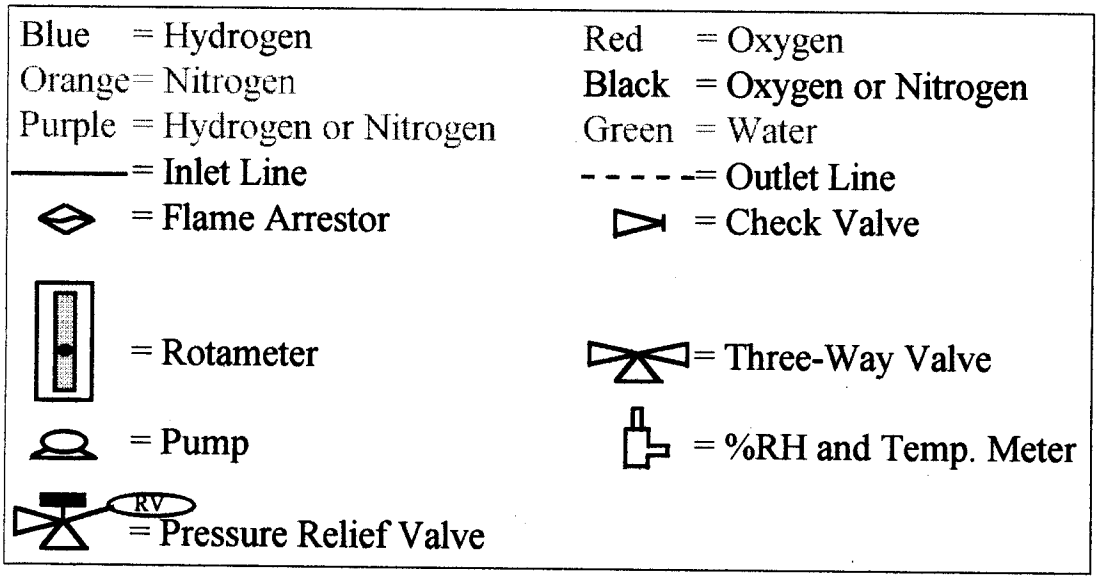

Figure C.1: Legend for both Figures C.2 and C.3

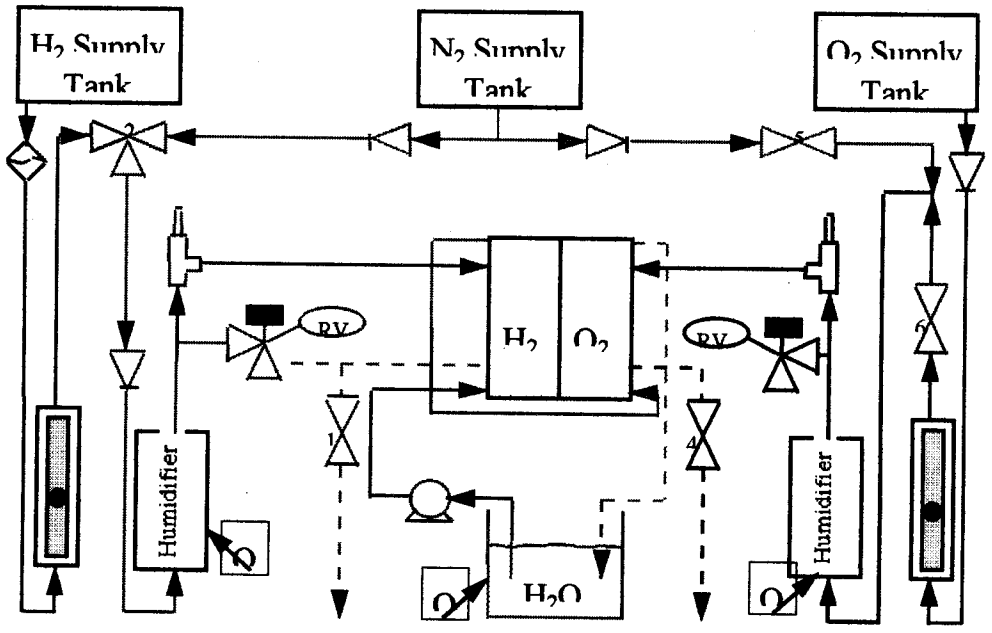

Figure C.2: Flow diagram of single fuel cell test stand

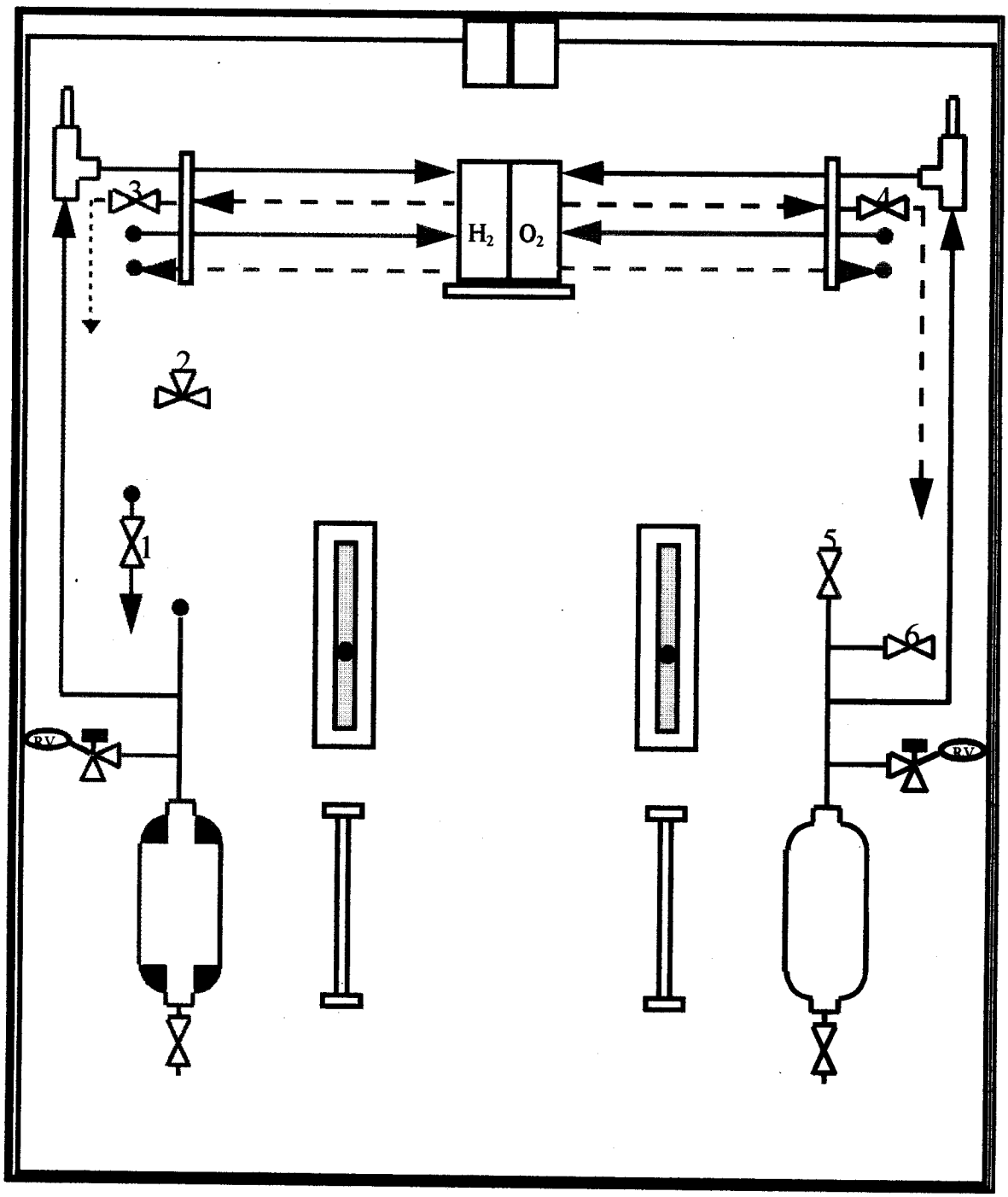

Figure C.3: Front of the single fuel cell test stand

Valve 1 = hydrogen purge; **Valve 2** = three-way hydrogen/nitrogen selection valve;

Valve 3 = hydrogen flow control valve; **Valve 4** = oxygen flow control valve;

Valve 5 = nitrogen feed for oxygen side; **Valve 6** = oxygen feed

Appendix D: Standard Operating Procedure for Test Cell and Stand (With Dead-Ended Hydrogen Operation)

0. Emergency Shutdown Method

0.1 For a runaway cell, immediately turn off main hydrogen and oxygen cylinder valves,

making sure you cannot be burned from this action. If this is not possible, turn off gases with small valves on front of apparatus.

0.2 Flush both sides of gas delivery system with nitrogen gas.

0.3 Disconnect electrical power supply to band heaters and water supply system.

NOTE: Under no circumstance are hydrogen and oxygen gases allowed to contact one another while at elevated temperatures or in the presence of the platinum catalyst.

1. Test Cell Assembly

1.1 Flow field plates (FFPs) should be coated with ElectroDag and be in good condition. If either has been dropped or severely scratched, it should be checked to ensure that it can still function properly and then repaired.

1.2 O-rings are installed in each half, each should be retained in the gland even

1.3 A piece of Teflon coated carbon paper is placed in the recess in one of the halves, which has been suspended with the flow field facing up (the corner of a box works well for this).

1.4 A prepared membrane is then placed over the carbon paper, centering the electrode as well as possible on the flow area.

1.5 An identical piece of carbon paper is placed on top of the membrane, again centering as well as possible.

1.6 The second half of the cell is then brought down on this sandwich of parts. As it is brought down, it is imperative that the carbon paper finds its way into and remains in the recesses above the flow fields. IF IT IS SUSPECTED THAT THE CARBON PAPER IS NOT SEATED PROPERLY, DO NOT CONTINUE!!! PROCEEDING WITH THIS MISASSEMBLY WILL RESULT IN MEMBRANE DAMAGE AND A VERY EXPLOSIVE MIXTURE OF HYDROGEN AND OXYGEN

1.7 After it has been made certain that the carbon papers are seated and the Nafion® is making contact all around with the O-rings, bolt up can now be done. Using the nylon bolts, insert them all finger tight, then use the deep socket wrench only to tighten then in a circular pattern. Tighten to about 4 foot-pounds each (not very tight). Never use a wrench other than a box type or socket, as the nylon could be easily damaged.

1.8 After bolt up, unit is placed on the shelf of the test stand and all connections are made.

1.8.1 Attach feed gas tubes (these must connect to one of the center ports on the test cell.

1.8.2 Attach purge gas tubes to the other center ports.

1.8.3 Attach water feed and discharge lines to the outer ports on the test cell.

1.8.4 Connect resistive load to the cell.

1.8.5 Connect voltmeter to the cell.

2. Start Up of the System

2.1 Leak testing must first be performed.

2.1.1 With all valves closed, open main nitrogen cylinder valve 1/4 turn. Regulator pressure should not exceed 45 psi.

2.1.2 SLOWLY crack the valves feeding into the water bottles, one side of the cell at a time. This will charge the system through the cell. After charging, leave this valve open 1-2 turns.

2.1.3 Crack each exit valve for about 5 seconds to bleed air and charge entire system with feed gas. Then close these valves securely.

2.1.4 Close main cylinder valves tightly. A leak, if any, is now evidenced by a falling pressure reading on the high pressure gauge. If this pressure is falling faster than 100 psi/min., a substantial leak is present, and should be located/corrected. Detect and fix the leak before continuing.

2.2 Disconnect gas supply to the test cell

2.2.1 Release gas pressure to both sides of the cell using the purge valves

2.2.2 Disconnect the gas supply lines to the cell

2.3 Start heating

2.3.1 Start water bath for heating of the cell, and turn on bottle heater VariACs to a setting of '60 V'. It may take up to 1/2 hour for substantial temperature rise.

2.3.2 Flow nitrogen gas through the system to heat the gas delivery lines (nitrogen will be vented to atmosphere at the cell gas supply lines).

2.4 When gas delivery lines reach the desired temperature and the nitrogen gas venting from the lines appears humid (collect it on a piece of paper), cell testing can begin.

3. Testing

3.1 Reconnect the gas supply lines to the test cell and disconnect the exit lines from the cell.

3.2 Start heating/cooling water flow to the cell.

3.3 Allow the test cell to come up to the desired temperature while nitrogen gas flow continues.

NOTE: The membrane must remain humidified. Do not heat the cell to a higher temperature than that of the humidified feed gas!

3.4 Reconnect the exit gas lines to the cell.

3.6 Be sure that valve 3 is at least partially open and start the hydrogen re-circulation pump.

3.7 Open the main valves on the hydrogen and oxygen supply tanks.

3.7.1 Adjust the pressure regulators to the desired pressure (less than 45 psig!)

3.7.2 BE SURE that the pressure on the nitrogen regulator is higher than that on the hydrogen or oxygen regulators. This ensures that there is no cross-flow of these gases through the nitrogen supply system.

3.7.3 Perform a second leak test as described previously in 2.1

3.8 Purge the nitrogen from both sides of the system using the two vent valves.

3.9 The cell should now be operational

3.10 Select different loads (resistance) to measure the voltage. Voltages are measured, and the resultant voltage versus current graph produced.

3.11 NOTE: Make sure water level and temperature in humidifier tanks is high enough to maintain good operation. This is one of the major problems with long term operation of the cell.

4. Shut Down of the system

4.1 Turn off hydrogen main cylinder valve, allow system hydrogen pressure to come to atmospheric pressure.

4.2 Turn off oxygen main cylinder valve, allow system to come to atmospheric.

4.3 Turn off heating units, water bath and bottle heaters.

4.4 Purge both sides of the system with nitrogen

4.5 Turn off the voltmeter.

4.6 Allow unit to cool sufficiently before handling

4.7 Disassemble the cell and inspect components as desired.

5. Storage of the Test Cell

5.1 Unit should be stored disassembled with membrane faces secure from any form of damage

5.2 Over time, the ElectroDag coating may need to be replaced. This should be done with all components removed from the blocks, save the plugs in the water jacket. Follow the procedure appearing in previous works.

5.3 Membranes should be stored under deionized water in labeled containers. If it is necessary to store more than one in the same container, then they should all be

discernible in some way. A suggested method is to cut very small notches into the periphery of the membrane, the part falling outside the sealing area.

5.4 Dry membranes should not be placed into the test cell. When put into use, the membrane will swell. Only fully saturated membranes should be installed.

6. Other Notes

6.1 Carbon papers are cut using cookie cutter and nylon block in the press. Only run the press to 1500 psi, this is sufficient to cut through the paper. In the future, a new cutter will be made from a more suitable material (steel) once the correct size is known.

6.2 Nafion® discs are cut from DRY stock with cutter an nylon block in press. This time around 2000 psi should be used. Don't worry if they appear small, upon saturation with water it will grow to the appropriate size.

6.3 It is unknown at this point the actual longevity of this cell. The ElectroDag coating is supposed to render the areas treated quite inert to this type of environment, but it unknown whether or not sufficient coating is being achieved.

Appendix E: Fuel Cell Membrane Fabrication Procedure

This procedure is a newly revised version of last year [1]. Initially, the procedure was basically a reproduction of the procedure outlined in [2]. Preliminary results from last year using this procedure were very encouraging. However, reproduction of these results was problematic.

Preparation:

Nafion® Membrane

Materials:

- Nafion® 117 membrane (MW = 1100, 0.175 mil thickness)
- 3% aqueous peroxide solution
- 1 M sodium chloride solution

Procedure:

- Cut membrane with the Aluminum cutter.
- Boil in a 3% by weight aqueous peroxide solution for 1 hour
    - performed to clean the membrane and saturate it with water
- Boil in approximately 1 M aqueous sodium chloride solution for 1 hour
    - performed to ensure complete conversion to the sodium form

Catalyst Ink

Materials:

- Nafion® solution from Aldrich, 5% solubilized Nafion® by weight
- Platinum catalyst

- 10 % platinum by weight on carbon black Vulcan XC 72-R, the Electrosynthesis Company

- Tetrabutyl ammonium Hydroxide solution (TBOH), 1 M from Aldrich

- Glycerol, from Aldrich

- Isopropanol

Procedure:

- Combine Nafion® solution and platinum catalyst material (1:3 Nafion® to platinum ratio by mass) in a small flask

- Add isopropanol and glycerol until the "desired" consistency is achieved

-**Sonicate a minimum of 2 hours**. This helps ensure the catalyst is distributed evenly in the Nafion® solution

- Add a 25 to 50% excess of the TBOH solution to create an alkaline mixture to minimize heat degradation of the membrane.

- TBOH must react with each sulfonate group in the Nafion® solution. Knowing the amount of Nafion® present, its molecular weight (1100), and the molecular weight of TBOH, the correct amount can be calculated.

- Sonicate a minimum of 2 hours

Membrane Assembly:

Materials:

- Small oven

- Airbrush

- Catalyst ink assembled above

- Copper gaskets from 2.75" Conflat flange

- Small screw-type hose clamps

- Lab press with heated platens

- Previously prepared Nafion® Membrane

- Two Teflon (6in x 6in) sheets.

Procedure:

- Preheat small oven and press platens to 150 ^{o}C

- Clamp Nafion® membrane between gaskets, centering it carefully

- At this point, there are two options, both of which have been utilized successfully

1. Apply the catalyst ink onto the membrane surface using the airbrush.

2. Place two to three drops of Nafion® solution on one side the membrane, followed by a paintbrush application of the catalyst ink.

NOTE: The addition of Nafion® solution prior to the catalyst application aids adhesion of the ink.

-Place assembly in front of the small oven and allow it to dry for about 30 sec

-Repeat the above two steps to the other side of the membrane

- Remove membrane from clamp assembly

- Place membrane between Teflon sheets

- Press membrane and Teflon at 150 ^{o}C and 30 atm for five minutes

- Remove the membrane and boil in 0.5 M Sulfuric Acid solution for 2 hours to convert the membrane completely into the proton form.

- Boil in deionized water for 2 hours

- Allow to cool

Appendix F: Standard Operating Procedure for H-Cell Apparatus

0.0 Emergency Shutdown Method

0.1 For any electrical fires or acid spills, immediately unplug the galvanostat and disconnect the wires from the voltmeter.

0.2 In case of a major electrical fire use a fire extinguisher.

0.3 In case of a major acid spill or leak from the middle portion of the H-Cell, neutralize by using a base such as sodium bicarbonate, which is located under the sink.

1.0 H-Cell Apparatus

1.1 H-Cell consists of two 600-ml beakers where each beaker is connected to a tube with a flange on the end. No chips should be present especially in the flange surfaces, and the apparatus should not be used if cracks appear in any portion of the apparatus.

1.2 First, clean the H-Cell using deionized water. Dry off the H-Cell (It does not have to be fully dry).

1.3 Next, hold one half of the H-Cell vertically while placing an o-ring in the flange.

1.4 Place the desired membrane carefully over the flange and o-ring, and wet the membrane by sprinkling some deionized water over the membrane.

1.5 Next, carefully place the other half of the H-Cell over the above configuration.

1.6 Insert the clamp by surrounding the joined H-Cell and twist the clamp finger tight so that the apparatus will not dislodge with minor movements.

1.7 Place the apparatus horizontally over a tray so that any acid spill can be contained.

1.8 Pour in acid solution into one side of the H-Cell until an approximate volume of 465-ml is reached . Remove all air bubbles formed by angling the H-Cell upward.

1.9 Repeat this procedure for the other half of the H-Cell .

1.10 Inspect clamping area for leaks and adjust clamping orientation or tightness if necessary.

1.11 Clean the two electrodes by passing them through a Bunsen burner and then dipping them in deionized water.

1.12 Next place one platinum electrode in each half cell, and suspend it from the cell. Suspend each electrode by threading the wire end through a strip of tape that is taped across the middle of the beaker.

1.13 Position the electrodes in the solution so that the square electrode is submerged with the spot welded platinum portion of wire. Chromium part of the wire should not be submerged in the solution.

1.14 Position the electrode wires toward the center of the H-Cell apparatus.

2.0 Galvanostat/Potentiostat and Voltmeter Setup

2.1 Place galvanostat/Potentiostat near H-Cell set up and turn the control dial to G-stat.

2.2 With the current dial at zero current, connect the two black leads to one of the electrodes, and the red lead to the other electrode. The black leads are the working electrodes and the red lead is the reference electrode. The green electrode is the ground and is not used in this set-up.

2.3 Confirm that the galvanostat is plugged into an AC outlet. Turn polarity switch to positive setting.

2.4 Hook up the black lead to the electrode with the two black galvanostat leads, and hook up the red voltmeter lead to the other electrode.

3.0 Testing of H-Cell

3.1 Turn on the voltmeter and set the reading to units of DC voltage.

3.2 Turn on the galvanostat with current control knob still at zero value.

3.3 Adjust the current in 0.1 miliamp increment or different increment as desired.

3.4 Take voltage reading at every time the current is adjusted.

3.5 Next, wait a minute or more until voltage reading has risen and reached a steady state.

3.6 Repeat this procedure up to 1 miliamp and for the ranges of 1 to 10 miliamps with increments of 1 miliamp. Also repeat this procedure from 10 to 100 miliamps with increments of 10 miliamps.

3.7 Before a new current range is used, change the polarity and cycle until the voltage reaches the same steady state in the opposite direction.

4.0 Shutdown of System

4.1 Return galvanostatto zero current level, turn off voltmeter and turn off potentiostat.

4.2 Disconnect the electrodes and store them away carefully after cleaning them with distilled water.

4.3 Disconnect the leads from the galvanostatand store this unit away.

4.4 Pour out the acid in the H-Cell into two beakers and store acid under the sink.

4.5 Clean the membrane and H-Cell apparatus with deionized water.

4.6 Store the H-Cell in bubble wrap and in a safe place.