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Fuel Cell Project
Quarterly Report, Summer 1997

by

Karen Fleckner
Kevin Houger
Roger Marshall

For Advising Professors:

Eric Stuve
Per Reinhall
Brian Flinn
Reiner Decher
Richard Christie

Excellent Report!

University of Washington
Seattle Washington

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Glossary of Terms

IOP – Initial Operating Procedure

MSDS – Material Safety Data Sheet

SOP – Standard Operating Procedure

TBOH – Tetrabutylammonium Hydroxide

Introduction

This is a continuation of the Fuel Cell Project. The original idea was to build a scaled down locomotive that would be powered by hydrogen/oxygen fuel cells. The Fuel Cell Powered Locomotive project was started in June 1996, as the project progressed, the goals have expanded to include continuous research of fuel cell technology. To reflect these new long-term goals we have renamed the overall project the Fuel Cell Project, and still use the Fuel Cell Powered Locomotive project to distinguish the short term (two year) goals.

Background

During the past three quarters (Autumn 1996-Spring 1997) the fuel cell stack group has been working on the development of a new concept in stack design.[1] It is assumed that the reader has a familiarity with the basic operation of fuel cells, more information can be found in the Fuel Cell Stack Team Final Report, Spring 1997. The first prototype was tested on May 7, 1997 and again May 21, 1997. These experiments did not produce the power expected but they did provide information needed for improvements to the prototype and test stand.

Scope

This report will discuss the goals the team conducted this summer based on the recommendations presented in the Fuel Cell Stack Team Final Report, Spring 1997. These goals were:

Perform research for resources, references, and MSDS's to expedite design and building of the fuel cell.

- Finish the new test stand.
- Develop a wiring harness for the prototype fuel cell.
- Improve the manufacturing process of the membranes.

This report will present the findings the team has made to achieve these goals and will present other information to improve future groups' efforts for the project. In the pursuit of the goals it became necessary to include new procedures to improve the safe handling of gases and chemicals during experimentation. Also included are standard methods for organizing information, writing documents, labeling experiments (see Appendix A). good

Overview

Following the Table of Contents prior to this Introduction is the List of Tables, List of Figures and a Glossary of Terms. Following the Introduction are the following five major sections: Wiring Harness, Test Stand, Membranes, Safety, and Membrane Conditioning Experiment. Each major section will contain a discussion and a conclusion. The rest of the report includes in the following order, Recommendations, References, Acknowledgements, and Appendices.

Wiring Harness

Electrical Connections

A new electrical harness was made from recycled material and is designed to facilitate the quick measurement of the voltage and current of the fuel cell during a test. The new apparatus utilizes banana clips for quick connect/disconnect between series, parallel, and individual circuit tests. See figure 1 below. The fuel cell attach points (electrodes) were redesigned using stainless steel bolts and nuts.

A - Terminal Connector, (open eyelet style, soldered on) → crimp-on would be better (can handle higher currents)

B - 18 gauge stranded copper wire

C - Junction Box

D - Banana Clip receptacles

E - Banana Clip "Jumpers"

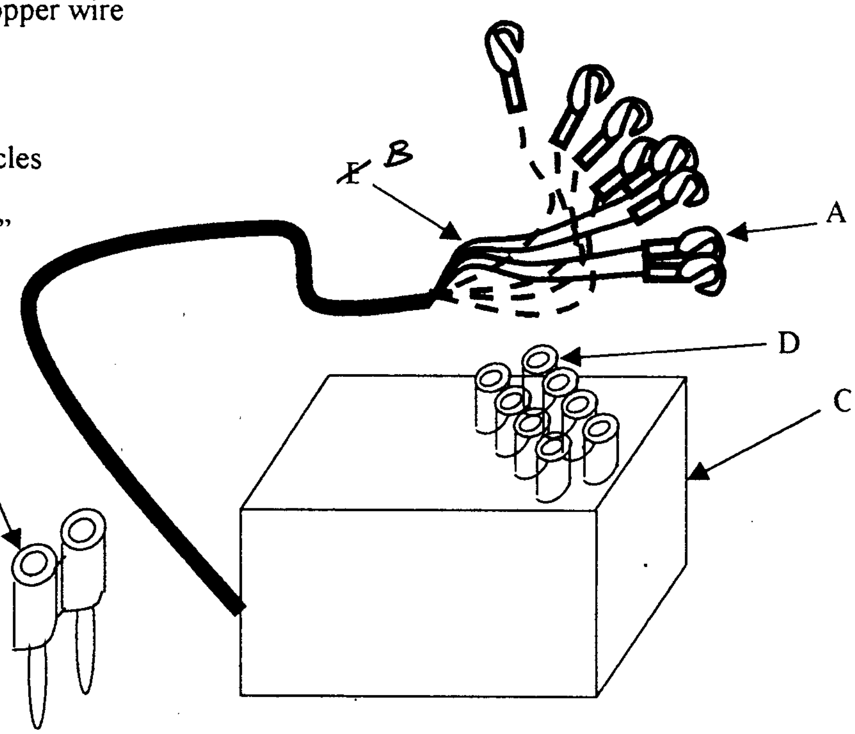


Figure 1

Test Stand

By the end of the Spring quarter the basic Test Stand had been constructed. It consisted of a rectangular base of steel channels welded and two channel uprights welded to top of the rear channel. Using more channels, two upright legs were bolted to the front of the stand and a shelf was created to hold a water bath for the prototype (page 23-24 ref. 1.) Hydration bottles were filled with boiling chips and attached to the rails of the shelf. The water bath was made of Plexiglas.

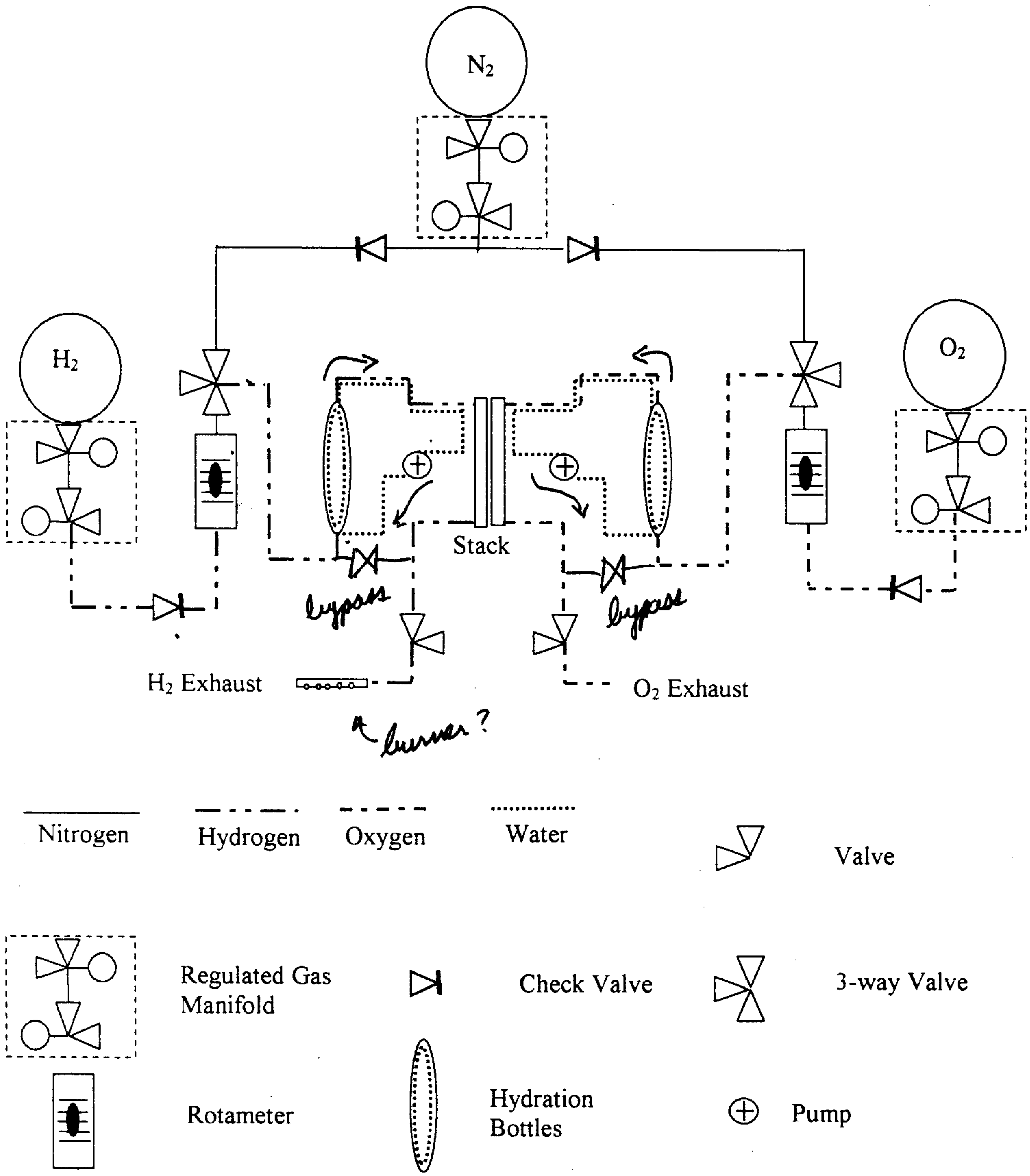
dang. modifier

To complete the test stand the following need to be assembled: design and construction of the hydration system, plumbing of the purge and feed lines, and the exhaust system. Also needed were methods to gather significant information while conducting experiments. Figure 2 shows the test stand as currently assembled for the Membrane Conditioning: Experiment 1.

<u>Hydration Systems</u>

The first issue to resolve was the construction of the hydration system. During discussions with Professor Eric Stuve it was decided to use jacketed annular supply lines for the hydrogen and oxygen. The outside annulus would have hot water entering at the stack flowing to the hydration bottles. The interior annulus would have the humidified hydrogen or oxygen entering at the hydration bottle and flow to the stack. The jacketed annular supply line would act as a counter-flow heat exchanger. The goal is to have humidified gases entering the stack at 80°C so the water would be kept as a vapor by continuous increased heating.

could also describe this as a refluxing gas feed line



N_2
H_2
O_2
Stack
bypass
bypass
H_2 Exhaust
O_2 Exhaust
burner?
Nitrogen
Hydrogen
Oxygen
Water
Valve
Regulated Gas Manifold
Check Valve
3-way Valve
Rotameter
Hydration Bottles
Pump

Figure 2

To achieve "rainforest conditions", a special fitting (see Figure 3) was made from a 3/8 NPT-1/4 Swagelok fitting connecting the annular line to the hydration bottle. Twelve holes inject water along the interior wall of the hydration bottle; an O-ring prevents water from flowing down the inside annulus where it may be drawn into the humidified gas. The heated water enters the annular line by a Swagelok tee fitting with the smaller gas line running through the tee. A thermocouple was install through the wall of the tee to measure the entrance temperature of the water.

The water entering the outside annulus is heated by wrapping heat tape around the outside of a copper tube prior to the tee connection on the jacket annular line. The hydration system was tested with de-ionized water being pumped by a peristaltic pump to see if a temperature of 80°C could be achieved. Initially, the water temperature stabilized at ~60°C. It was necessary to insulate the hydration bottle, the lines to and from the bottle, and the jacketed annular line. After applying insulation the temperature reached about ~75°C. Slowing the flow-rate, the water temperature reached 82°C.

Hydrogen Exhaust

The team agreed that future experiments using the test stand would be conducted inside of a fume hood to reduce the risk of igniting the hydrogen. A special tube was made to reduce the risk of a flame from entering the system from the exhaust. Previous research has revealed that the quenching distance (the largest diameter hole before a flame front may pass through) is 0.06 cm (Appendix A)[2]. A thirteen-inch long ¼ inch copper tube was sealed on across one end and a Swagelok fitting attached to the other. Twenty 0.0160 inch (0.041cm) holes were drilled into the tube one half-inch from the sealed end (Figure 4.)

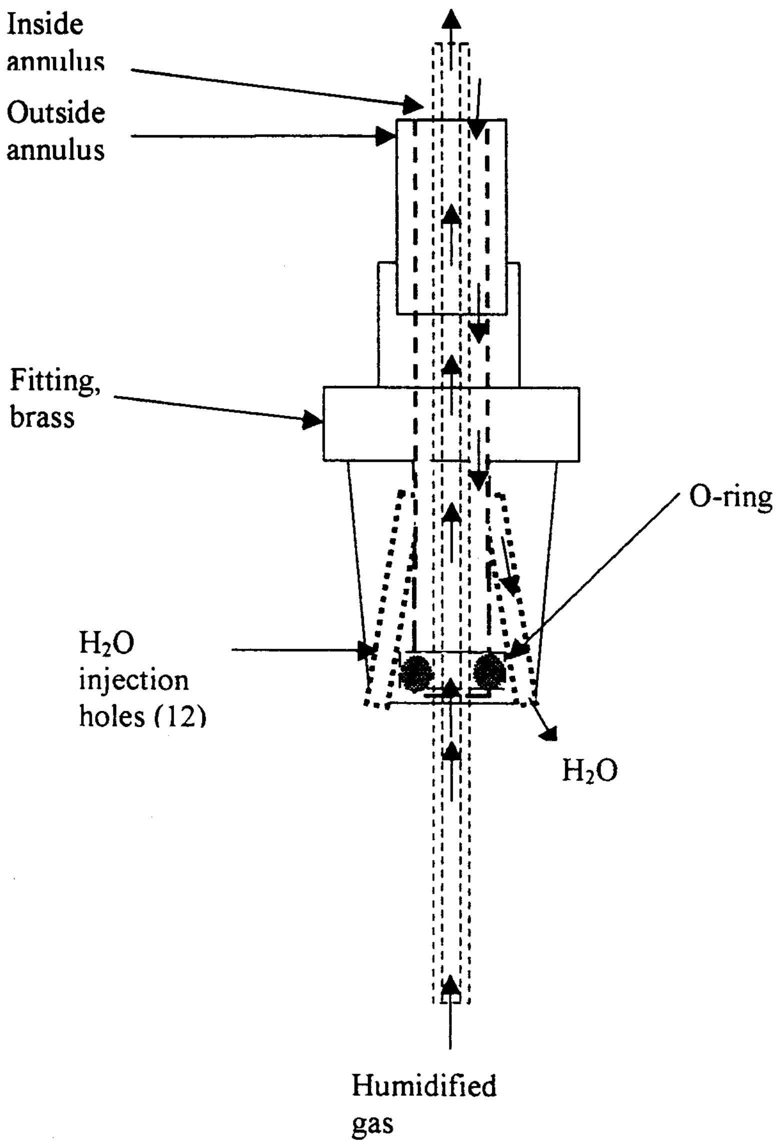


Figure 3

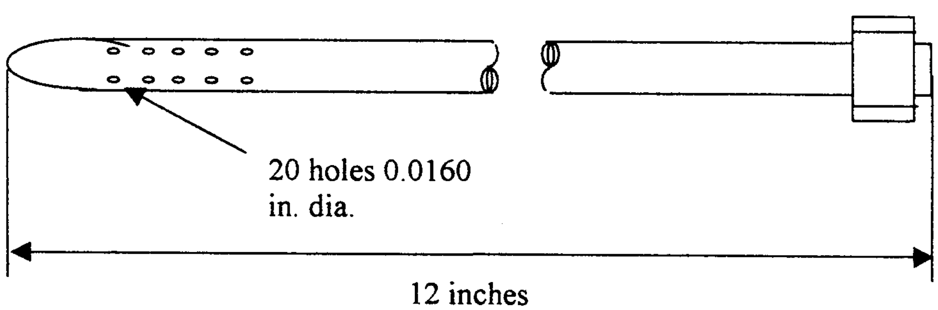


Figure 4

Assembly and Leak Testing

The test stand was assembled without the stack, the jacketed lines, or heating sections and placed in the fume hood in Roberts room 202. The yellow rotameter calibrated by the fuel cell stack group (page 24, Appendix B, Ref. 1) was used to measure the flow of H_2. A rotameter calibrated in Standard Cubic Feet per Hour (SCFH) was used to measure the flow of O_2. Using a piece of acetate to act as a temporary membrane, the system was completely assembled including using a peristaltic pump for the hydration system. Quarter-inch polyvinyl tubing was used with the pump. To monitor each exhaust line a pressure gauge and a thermocouple was installed. A Test Stand Leak Testing Procedure (IOP FCP-970705, Appendix A) was written for testing the stand prior to an experiment.

The stand then was tested using only the nitrogen. The water was pumped though the hydration systems and then the heating elements were activated with the Vari-AC (adjusted to maximum volts). The nitrogen valve was opened until 10-15 psi was measured at the exhaust pressure gauges. When the exhaust valves were opened water began to be pushed through the exhaust. This caused a problem with water getting into the gas lines. The stainless steel screens (used to prevent small boiling chips from being carried into the gas lines) inserted into the top of each of the hydration bottles. The screens are cone-shaped and acted as cups to hold the water, therefore allowing the gas to push water into the inside annulus of the jacket line. When the screens were removed the system worked as expected.

Conclusions

The jacketed lines worked well in the final leak test and continued to work well during the following experiments. No water could be seen moving through the stack. Some water was condensing in the exhaust line but most was in vapor-state.

The hydration system should be redesigned. During the experiment the water never reached the 80°C needed for optimum efficiency, even after insulating the polyvinyl tubing, jacketed line, and hydration bottles. Another drawback was the need to stop the pumps and turn off the gas while added more de-ionized water.

The exhaust thermocouples may be influenced by the heated water bath, since they are positioned about six inches away from the last cell in the stack.

Check valves should have been place between the rotameters and the hydration tank. This would prevent water from draining out of the hydration tanks and accumulating in the rotameters (causing inaccurate readings).

Membranes

Introduction

The purpose of this investigation was to establish standard operating procedures for making a Proton Exchange Membrane (PEM). A new method of applying the catalyst ink to the Nafion membrane by airbrushing was used. An outlined procedure for the membrane production will be presented after which a discussion of the results and recommendations will be given. A major concern over safety issues such as proper storage of hazardous chemicals and reviewing copies of material safety data sheets (MSDS's) in the laboratory safety manual in Benson Hall, room 215 needs careful reviewing before membrane production occurs. — UNCLEAR

Methods and Materials: for membrane production

An attempt to duplicate the methods for the fabrication of the membrane documented by Larry Bailey and Edward Goldmann was made. The procedure was slightly modified and titled Procedure for Nafion Membrane Preparation and Ink Application (Appendix A, IOP FCP-970809). The modifications reflect the use of an airbrush for the application of the catalyst ink onto the membrane.

Results and Discussion Need more detail in this section

The membranes made by using this process seemed to be successful. Results based on power produced from the actual test, the membrane gave us confirmation the membranes were an apparent success. GRAM

The airbrushing of the catalyst ink produced a more consistent, even, and precise application to the membrane. It was the goal of the group to use an airbrush in hopes of producing a membrane more efficiently than by using a paintbrush. Certainly the quality of the coverage of ink on each pad was more uniform with less variations of ink density (unavoidable with a paintbrush). An added bonus was that less ink was needed for each membrane when using the airbrush. The group was generally pleased with the results. good

A few problems arose during the membrane fabrication process. First, much time was spent on locating all of the necessary MSDS's. This was done in order to avoid mishaps. One problem encountered had to do with inaccurate assumptions made about substituting a higher weight, by percent, platinum catalyst for the usual 10% catalyst. This resulted in a highly exothermic reaction. — need more detail here

use of higher pt catalyst

which one?

Also alarming is the storage of a certain hazardous solution which suggest different conditions then the one that it is currently being stored under (see Safety). Another problem arose. — huh? A molar ratio of Nafion solution to TBOH was required and not exactly known.

molec. wt. 1100

— why not check orig. literature ? (Gottesfeld)

The company who manufactures Nafion solution, Electrosysthesis, was called and a message was left but no contact was made. A 25%-50% excess of TBOH is desired but one needed to know how many sulfonate groups in Nafion solution was present so a proper calculation of excess could have been made. Phone calls to Janel Martinesen and Larry Bailey were made but either they could not be reached or they did not recall if it ~~were~~ was 1:1 ratio or a 1:3 ratio. So a decision was made to use a 1:1 ratio and the excess of TBOH was based upon that assumption (see sample calculation Appendix C). — check Gottesfeld

Finally, the two membranes were used Nafion 112 and Nafion 117. Until modifications in the clamping of the membranes to the test stand apparatus are made, Nafion 112 is too delicate to use for purposes of this experiment. The Nafion 112 tore and allowed for leaking of gases in the test stand. This process still has a few spots of uncertainties, which need to be cleared up before other subsequent members the join the project and begin to manufacture membranes. However, the modifications to the membrane process and the addition of the safety material data sheets will help reduce waste of materials and potential future accidents.

Conclusions

1. Applying the catalyst ink to the membranes with an airbrush is certainly an improvement with regards to precision and consistency.

2. Mixture calculations, MSDS's, Laboratory Safety Lab Manual, and general procedures should be read and understood before membrane production is started.

3. Adequate documentation should be kept of all procedure modifications in the preparation of the catalyst ink solution and changes to the application to ensure safe and consistent results.

What about the accident with the 20 wt% catalyst?

Safety

Safety became more significant this quarter. In an effort to prevent future accidents the team developed and improved Standard Operating Procedures (SOP's) and collected the relevant Material Safety and Data Sheets (MSDS's).

Lab Safety Manuals

Upon reviewing the Safety Manual for the Schwartz Lab it was discovered that MSDS were missing as well as some of the relevant SOP's that are required to be present at all times. Several weeks were spent finding the MSDS for the chemicals used in the preparation of catalyst ink as well as developing operating procedures, which may be standardized in time.

Good!

A lab manual has been developed for the Test Stand and is to remain with the test stand at all times. It includes information about general lab safety (including emergency phone numbers), leak testing, starting and shutting down experiments, use of compressed gas, and emergency shutdown procedures. Also included are the MSDS's for compressed nitrogen, hydrogen, and oxygen gases.

Handling of Chemicals

The MSDS's for all chemicals are of vital importance. A good example of why they are needed before any handling of chemicals can illustrated as follows. During the preparation of the catalyst ink, a volatile and highly exothermic reaction occurred unexpectedly. Previous methods for ink preparation called for one part 10% by weight of platinum in carbon powder mixture to be combined with three parts Nafion solution. Upon inspection of materials prior to ink fabrication, it was noted that there was a limited amount of 10% by weight platinum in carbon powder. 20% by weight platinum in carbon powder was selected because of availability. After consultation with members of last year's fuel cell team, the conclusion that half of the 20% by weight platinum carbon could be used. This was not the case. The components were mixed and then the isopropanol was added drop-wise. A small flame ensued followed by what appeared to be a glowing mound of carbon, platinum, and Nafion solution initialized by the isopropanol. MSDS's were immediately referred to and copious amounts of water were added to dilute and put out flame and heat.

No... you can't do this

Conclusions

Everyone needs to be reminded that safety should be the foremost consideration when working with hazardous chemicals and hydrogen gas. Many of the procedures still contain errors, which should be addressed by the appropriate groups next year.

Experiment: Membrane Conditioning

Discussion

Each experiment was recorded and a copy can be found in Appendix B.

An experiment on August 16, 1997 attempted to condition the membrane. Literature and conversations with experts indicate that the fuel cell improves after it has been in operation for many hours. The procedure and raw data for the experiment can be found in the Appendix B. Membrane Conditioning: Experiment 1, dated 8/16/97. Data ~~was~~ were collected every half-hour and the experiment run for four hours. The experiment was operated with all the cells wired in parallel.

The first of three attempts had to be stopped due to time limitations and wiring problems. The experiment was successful in showing that the prototype in the test stand would work.

The second experiment was completed successfully on 8/16/97. The power output did show significant increase with a peak after three hours. The power decreased slightly for the last two readings. Figure 5 shows how current density and Figure 6 shows how power changed with time while the fuel cell stack was connected in parallel. The graphs were produced using the raw data from *Membrane Conditioning: Experiment 1* conducted on 8/16/97. (See Appendix B.)

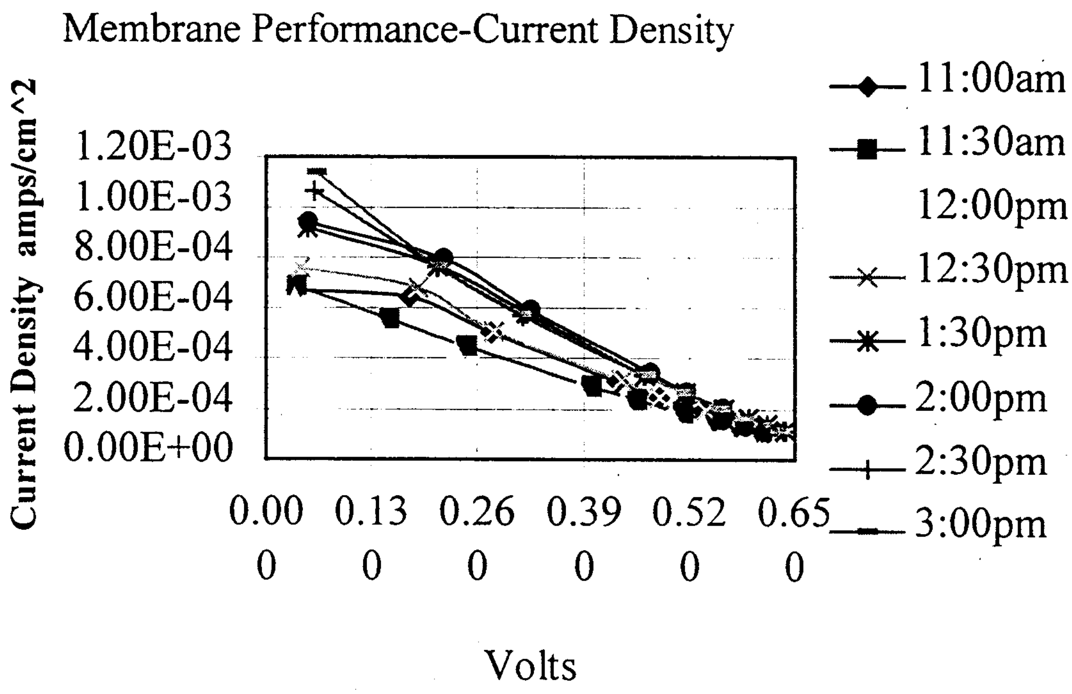


Figure 5

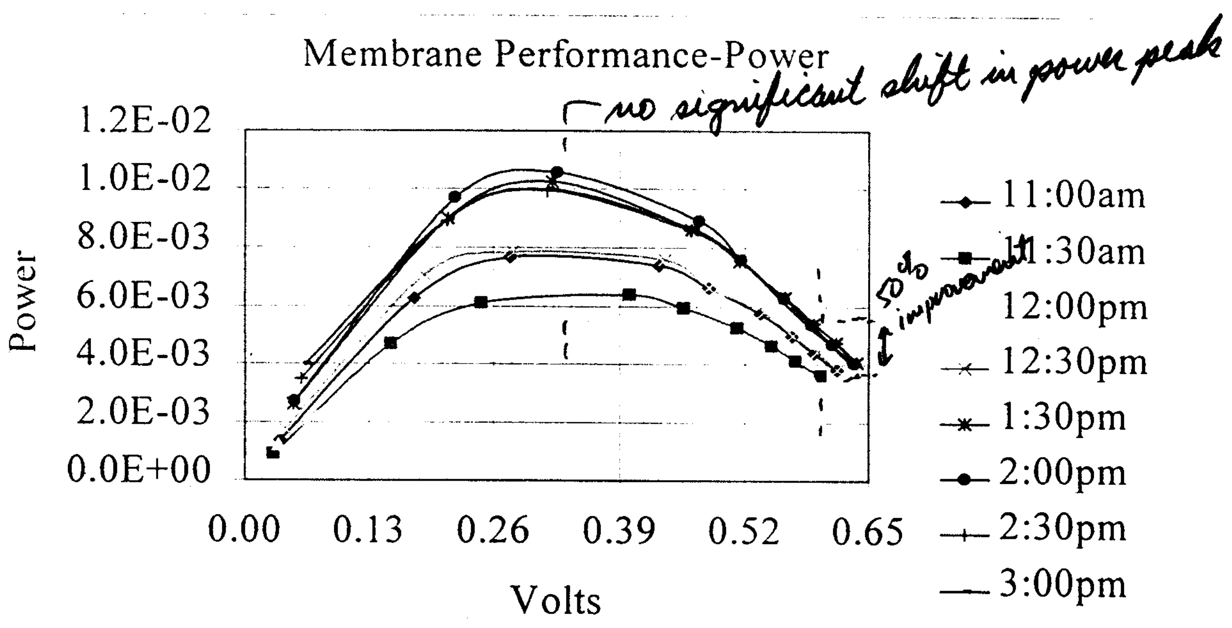


Figure 6

For some reason, extended conditioning causes reduction in mass transfer limitations.

— low voltage performance.

The final experiment could no be completed due to a failure in the Lexan plate during the leak test. (Step 6, Membrane Conditioning: Experiment, date 8/18/97, see Appendix B).

define

These experiments tested the new prototype plates, which were made last quarter[1]. The electrodes in each cell were made from RVC foam and stainless steel screws were used for the electrical path from the foam and the external connection. The extra aluminum plate for the clamp was still insufficient to maintain adequate pressure in the middle of the stack and clamps were added to the top and bottom edges to eliminate gas leakage.

Conclusions

From the experiment on 8/16/97 the new membrane did produce electricity although the results were less than expected. When the power began to decrease on at 11:30 and 12:30 the individual cells were tested (open circuit) with the following results:

Cell 1…~0.815 volts

Cell 2…~0.250 volts

Cell 3…~0.250 volts

Cell 4…~0.815 volts

The electrical connections between the stainless steel screws and carbon foam electrode on cells 2 and 3 were improved by tightening the screws. Each of the cells then began to produce the desired ~0.815 volts.

hmm! that says connections are the problem

Perhaps need to measure cell resistance

At 2:30pm the power decreased slightly, which was not anticipated. Many possible problems may explain the decreased power. The following are only a couple:

- Polyvinyl tubing can produce chorine when hot. The tubing for the hydration systems may have introduced chorine to the stack. We do not know the effect of chlorine has on the catalyst ink or the membrane.
- The volume of oxygen with respect to humidification may have been too high and dried the membrane out reducing its ability to produce electricity.

When trying to complete a third experiment to improve the membrane conditioning the experiment was terminate when a leak test using nitrogen found a leak had developed through the plate. The leak was from several cracks from the interior wall of the exhaust hole through to the exterior surface of the Lexan plate. This may be due to fracture created from the manufacture of the plates or a lubricant use in manufacture may have reacted with the Lexan material. More research should discover the source of the problem.

Recommendations

Wiring Harness

- Plan to locate and use gold plated hardware. - to reduce cell resistance
- Perform conductivity test for circuit efficiency. - Yes

Test Stand

The following elements need to be designed into the test stand:

- A reservoir with a heating cartridge to heat the hydration water. Install a new peristaltic pump with a brushless motor. Locate the pump under the heated water bath to minimize the heat loss due to excessive tube length and to utilize space. The O_2 side of the hydration system can be vented to the atmosphere and the O_2 exhaust directed back into the reservoir. - huh?
- Replace the fiberboard panel with a ¼ inch thick Plexiglas panel. The fiberboard is susceptible to moisture degradation and is harder to clean. Yes Plexiglas is durable and will provide visibility through the test stand. ↑ but it scratches and cracks

Prototype

The failed prototype plate will have to be investigated so a solution can be made in the redesign of a new prototype. The new prototype should also have the following elements:

- The clamp should have the clamping pressure distributed around the cell area. This means all four sides instead of just two sides, as is the current method.

Increase the plate sizes and then drill holes through the plates to hold the clamp and keep the plates aligned.

- Design the feed and exhaust lines to mount rigid to the plates.
- Insert a thermocouple and hygrometer into the exhaust stream of each side of the stack. If done right the pressure could be measure at the same site as the thermocouple.
- The electrical connections between the electrode and external connection need to be redesigned.
- Experiment with different porosity's of the carbon foam electrodes.

Membrane

Find chemical reaction information from manufacturers that would facilitate the understanding of the ink catalyst manufacturing process allowing predictable changes in the catalyst ink preparation process to be made.

Safety

A Safety group needs to be assembled to design safety elements into the test stand and the locomotive. They can also act as a reviewer for all procedures to help improve concise language and logical steps.

General

There are many possibilities to include other departments to accomplish the recommendations of this report.

References

1) Cherian, Jesse; Clemens, Matt; Houger, Kevin; et.al. Fuel Cell Stack Team Final Report, University of Washington Spring –1997.

2) Bailey, Larry; Goldmann, Ed; et.al. Fuel Cell Locomotive-Single Cell Group, University of Washington, June 10, 1997.

Acknowledgments

Dawn Scovell and the rest of the Graduate students from Professors Stuve's Lab for their time, patience and invaluable help while we work in the lab.

Jason a graduate student in a lab on the third floor of Benson, who helped us find the necessary MSDS's for the project.

Professors Eric Stuve, Per Reinhall, and Brian Flinn for there their aid in the development of the test stand and experiment. Especially Eric Stuve who's concern for safety may have prevented a dangerous accident from occurring.

Russ Noe's (Mechanical Engineering Undergraduate Shop) willingness to find time to help and offer excellent suggestions for design solutions.

Appendix A

Documents

Table of Contents

Document	Listed by Index Number
Experiment(s) Start-up/shutdown Procedure	IOP FCP-970704
Test Stand Leak Testing Procedure	IOP FCP-970705
Standard Operating Procedure for Compressed Gas Cylinders	SOP FCP-970709
Chemical Spill/Gas Leak Procedure	IOP FCP-970801
Test Stand Experiment General Safety Protocol	IOP FCP-970802
Membrane Conditioning: Experiment 1	EXP FCP-970803
Stack Experiment: Membrane Conditioning, Record Sheet	FRM FCP-970804
Standards for Labeling Experiments	DOC FCP-970806
Standards for All Documents: Minimum Requirements	DOC FCP-970807
Standards for Quarter and Special Requested Research Reports	DOC FCP-970808
Procedure for Nafion Membrane Preparation and Ink Application	IOP FCP-970809

Experiment(s) Start-up/Shut-down Procedure

state at beginning that leak test should be performed.

Starting up the apparatus.

1. All valves should be closed. 3-way valves turned to "purge."
2. Connect the nitrogen, open N_2 main valve, and adjust regulator to 20 psi.
3. Connect the oxygen and open main valve but regulator should remain closed.
4. Turn on pumps as specified by experiment and operate heating elements at maximum. Wait until the temperature of the water in the hydration tanks and heated bath are near 80°C before continuing with the rest of the set up.

   Install Bypass Valves

5. Connect the hydrogen and open main valve and adjust regulator to 10 psi.
6. Turn H_2, 3-way valve to "feed", adjust rotameter to 50 %, and open hydrogen exhaust valve fully. (This will purge residual air from the supply lines.)

   what about air left in the H_2 lines during connection?

   should do N_2 purge step before H_2 feed step

7. Turn H_2, 3-way valve to "purge" and close H_2 regulator. (Nitrogen will be flowing through the stack to remove remain mixture of air and hydrogen.)
8. Connect the initial electrical load and set regulators as specified for the experiment. (This information is provided by initial values in the experiment procedures.)

   danger of sparking?

9. Check temperatures of the water in the heated bath and hydration tanks and adjust as needed as specified by the initial experimental values.
   - A knob on the control panel controls the water temperature produced by the hot water pump.
   - The temperature produced by the heating tape is controlled with a Variac.
10. Turn O_2, 3-way valve to "feed", partially open O_2 exhaust valve, and adjust O_2 rotameter as desired (if the desired flow isn't reached then try opening the exhaust valve more.)
11. Turn H_2, 3-way valve to "feed", partially open H_2 exhaust valve, and set H_2 rotameter at desired flow (if the desired flow isn't reached then try opening the exhaust valve more.)
12. Conducted experiment as desired.