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electrolysis
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nuclear

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Characterization Testing and Analysis of Single Cell SO_2 Depolarized Electrolyzer

Author: J. L. Steimke
Author: T. J. Steeper

REPORT DATE: SEPTEMBER 15, 2006

Westinghouse Savannah River Company
Savannah River Site
Aiken, SC 29808

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SAVANNAH RIVER NATIONAL LABORATORY

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LIST OF ACRONYMS

DAS	data acquisition system
HyS	Hybrid Sulfur Process
MEA	membrane electrode assembly
NHI	Nuclear Hydrogen Initiative
PEM	proton exchange membrane
PES	Proton Energy Systems
S-I	Sulfur Iodine Process
SDE	SO_2 depolarized electrolyzer
SRNL	Savannah River National Laboratory
USC	University of South Carolina

1.0 EXECUTIVE SUMMARY

This document reports work performed at the Savannah River National Laboratory (SRNL) that further develops the use of a proton exchange membrane or PEM-type electrochemical cell to produce hydrogen via SO_2-depolarized water electrolysis. This work was begun at SRNL in 2005. This research is valuable in achieving the ultimate goal of an economical hydrogen production process based on the Hybrid Sulfur (HyS) Cycle.

The HyS Process is a hybrid thermochemical cycle that may be used in conjunction with advanced nuclear reactors or centralized solar receivers to produce hydrogen by water-splitting. Like all other sulfur-based cycles, HyS utilizes the high temperature thermal decomposition of sulfuric acid to produce oxygen. The unique aspect of HyS is the generation of hydrogen in a water electrolyzer that is operated under conditions where dissolved sulfur dioxide depolarizes the anodic reaction, resulting in substantial voltage reduction. Sulfur dioxide is oxidized at the anode, producing sulfuric acid that is sent to the acid decomposition portion of the cycle. The focus of this work was to conduct single cell electrolyzer tests in order to prove the concept of SO_2-depolarization and to determine how the results can be used to evaluate the performance of key components of the HyS Process.

A test facility for conducting SO_2-depolarized electrolyzer (SDE) testing was designed, constructed and commissioned. The maximum cell current is 50 amperes, which is equivalent to a hydrogen production rate of approximately 20 liters per hour. Feed to the anode of the electrolyzer is sulfuric acid solutions containing dissolved sulfur dioxide. The partial pressure of sulfur dioxide may be varied in the range of 1 to 6 atm (15 to 90 psia). Temperatures may be controlled in the range from ambient to 80ºC. Hydrogen generated at the cathode of the cell is collected for the purpose of flow measurement and composition analysis. The test facility proved to be easy to operate, versatile, and reliable.

A versatile electrolyzer cell was designed and built with wetted parts of carbon and Teflon. The cell was tested with six different membrane electrode assemblies (MEA). Testing in 2006 was performed on each MEA at pressures ranging from ambient to 4 atm and temperatures ranging from ambient to 72ºC. SDE operation was evidenced by the appropriate rate of hydrogen production at the cathode and sulfuric acid production at the anode (witnessed by the absence of oxygen generation) and with cell voltages substantially less than the theoretical reversible voltage for simple water electrolysis (1.23 V). Cell performance exceeded that achieved in the two-compartment cells built by Westinghouse Electric Corporation during the original development of the HyS Process (1977 - 1983). Test results were analyzed to determine performance trends, improvement needs, and long-term SDE potential.

All six MEA permitted the transport of some sulfur dioxide from the anode to the cathode, where it reacts with hydrogen gas to form elemental sulfur. However, there was no evidence that the sulfur poisoned the electrocatalyst and it was found that the sulfur was easily washed out of the cathode side of the cells. The minimization of sulfur dioxide crossover is a major concern in determining the capability of PEM cells to operate under SDE conditions. Future work will seek to identify cell modifications, such as improved membranes, to prevent or minimize sulfur dioxide crossover. The current test results are encouraging, however, in that they point to the possibility of operating with a limited amount of sulfur production, provided that operating procedures are developed to mitigate its effects on long-term cell performance.

The primary results of testing six MEA follow.

1. Cell voltages were less than measured for the two cells tested in FY2005 [Steimke and Steeper, 2005]. Can you quantify the difference?
2. Increasing anolyte pressure generally decreased cell voltage, which is attributed to a higher concentration of sulfur dioxide reactant is available.
3. Increasing electrolyzer cell temperature generally decreased cell voltage, which is attributed to increased reaction rates and also to decreased viscosity of anolyte, allowing easier movement of reactants and product.
4. Cell voltage generally increased with increasing acid concentration, at least partially because this increases anolyte viscosity.
5. Electrolyzer cell pressure drops were generally lower than last year and mass transfer was improved.
6. Decreasing the anolyte flowrate below about 0.2 L/min increased the cell voltage. Increasing the flowrate above 0.4 L/min did not significantly decrease cell voltage. By contrast cell potentials in the 2005 graphite electrolyzer cell were still decreasing as the anolyte flowrate was increased to 1.5 L/min. It is concluded that anolyte flowrate can affect mass transfer coefficients. Flowrate also affects single pass conversion of sulfur dioxide in the cell, so there is a slight decrease in average sulfur dioxide concentration in the cell, by less than 1%. It is unlikely that the change in average concentration is the cause of the change in cell potential.
7. Wet chemistry analyses of sulfur dioxide exhibited a large scatter. Some unidentified component in the anolyte may be interfering with the wet chemistry titration.
8. Determination of sulfur dioxide concentration by monitoring pressure in the Anolyte Absorber as a function of injection rate gave results that agreed with those estimated using existing vapor-liquid equilibrium data.
9. Barring mechanical damage to the MEA as the result of pressure imbalances, there was no degradation in cell performance during approximately forty hours of testing with an MEA.
10. Mechanical damage to the cell has a distinctive signature, voltage increases significantly over a twenty minute time frame. Presently, the voltage becomes stable in less than a minute.

Each section starts on a new page

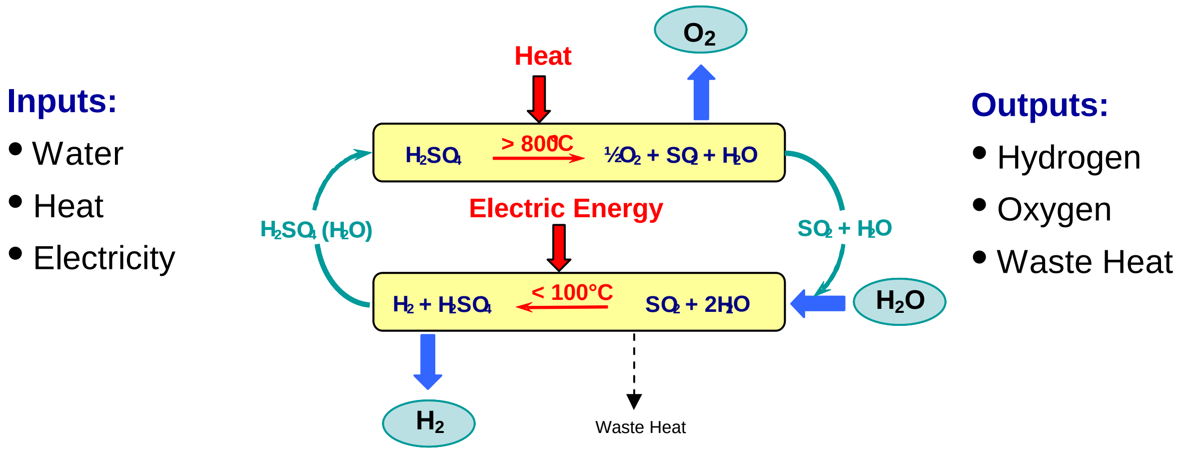
2.0 INTRODUCTION

As President Bush acknowledged in his January, 2003 State of the Union address, hydrogen has the potential to play a major role in America's future energy system. The U.S. Department of Energy recognizes that the development of this abundant element as an "energy carrier" will help address national concerns about energy supply, security, and environmental protection [DOE Hydrogen Posture Plan, February 2004].

The DOE Office of Nuclear Energy, Science, and Technology has created the Nuclear Hydrogen Initiative (NHI) program with the objective of advancing nuclear energy to meet future energy needs. The NHI has been established to develop the production technologies that can be most effectively coupled to next generation nuclear reactors for hydrogen production. Thermochemical water-splitting cycles, which use thermal energy to produce hydrogen through the dissociation of water molecules, are leading technologies that are being studied within the NHI program. Thermochemical cycles are of interest for nuclear hydrogen production because they have the potential for high efficiencies and have favorable scaling characteristics.

Research programs in the United States, Japan, and France have emphasized the sulfur-based thermochemical cycles as high priority candidates for research and development. The NHI has identified the Sulfur-Iodine (S-I) Cycle and the HyS Cycle as first priority baseline cycles. These cycles have potential for high efficiency, and they have been demonstrated at a laboratory scale to confirm performance characteristics. Both cycles share a common high-temperature reaction step – the catalytic thermal decomposition of sulfuric acid.

HyS is conceptually the simplest of the thermochemical processes and involves only sulfur chemistry. In the HyS Process hydrogen gas (H_2) is produced at the cathode of the electrochemical cell (or electrolyzer). Sulfur dioxide (SO_2) is oxidized at the anode to form sulfuric acid (H_2SO_4) and protons (H^+) as illustrated below. A separate high temperature reaction decomposes the sulfuric acid to water and sulfur dioxide which are recycled to the electrolyzers, and oxygen which is separated out as a secondary product. The electrolyzer includes a membrane that will allow hydrogen ions to pass through but block the flow of hydrogen gas. The membrane is also intended to prevent other chemical species from migrating between electrodes and undergoing undesired reactions that could poison the cathode or reduce overall process efficiency.



In conventional water electrolysis, water is oxidized at the anode to produce protons and oxygen. The minimum possible cell voltage (reversible voltage) for conventional water electrolysis is 1.23 volts at 25 •C. However, commercial electrolyzers typically require higher voltages ranging from 1.8 V to 2.6 V [Kirk-Othmer, 1991]. The oxidation of SO_2 instead of water in the HyS electrolyzer occurs at a much lower potential. For example, the reversible voltage for SO_2 oxidation at 25•C in 50 wt % sulfuric acid is 0.29 V [Westinghouse, 1980]. Since power consumption by the electrolyzers is equal to voltage times current, and current is about the same for the two types of electrolysis, a large reduction in voltage results in a large reduction in electrical power cost.

The research documented in this report had three goals,

1. To build a versatile facility for future testing of innovative electrolyzer designs,
2. To demonstrate hydrogen production with a sulfur dioxide depolarized anode,
3. To begin addressing the technical issues associated with HyS electrolysis.

3.0 DISCUSSION

3.1 BACKGROUND

3.1.1 Previous Work

During the period 1975-1982, researchers at Westinghouse Electric Corporation (Farbman, 1976, Parker, 1982, Westinghouse, 1982 and Lu, 1980, 1981, 1982, 1983) tested electrochemical cells using sulfur dioxide depolarized anodes for producing hydrogen. The half-cell and overall cell reactions are:

Anode reaction $$SO_2(aq) + 2H_2O(aq) \leftrightarrow H_2SO_4(aq) + 2H^+(aq) + 2e^- \qquad [1]$$

Cathode reaction $$2H^+(aq) + 2e^- \rightarrow H_2(g) \qquad [2]$$

Net reaction $$SO_2(aq) + 2H_2O(aq) \leftrightarrow H_2SO_4(aq) + H_2(g) \qquad [3]$$

Figure 1 shows the parallel plate cell and the reaction chemistry that occurs at each electrode. A porous rubber membrane was used that allowed hydraulic communication between the two parallel flow channels. A slight positive pressure difference from the catholyte to the anolyte channels was imposed to minimize SO_2 crossover to the cathode while still allowing diffusion of hydronium ions (protons covalently bound to water molecules) to the cathode.

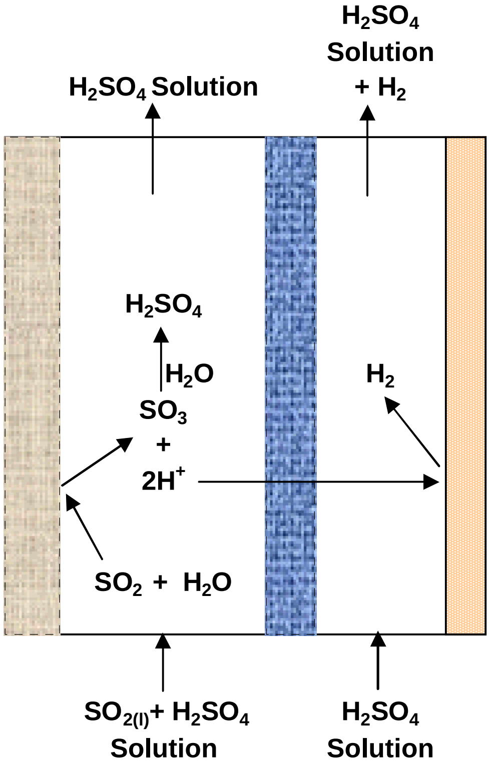


Figure 1 **SO_2-Depolarized Electrolyzer for Hydrogen Production**

In the Westinghouse tests, separate liquid streams fed the electrolyzer and are referred to as the catholyte and the anolyte. The catholyte was a solution of sulfuric acid and water and the anolyte was a solution of sulfuric acid, water, and dissolved sulfur dioxide (SO_2). Sulfur dioxide was oxidized at the anode to produce sulfuric acid and protons. Thus, the outlet anolyte stream had a higher concentration of sulfuric acid than the inlet anolyte stream. The protons produced at the anode transport as hydronium ions across the cation-exchange membrane into the catholyte and are reduced at the cathode to produce hydrogen gas.

Laboratory scale tests by the Westinghouse Electric Corporation measured SO_2 depolarized cell voltages ranging from 0.4 volts to 1.4 volts, depending on current density, electrode materials, and separator type. Thus, the overall power requirement of the HyS electrolyzer, which employs anodic depolarization with SO_2 is much lower than for an electrolyzer employing conventional water electrolysis. Typical results are plotted in Figure 2. Lu improved his cells and measured generally decreasing voltages during his research. Figure 2 also shows Lu’s (1983) prediction for operation at 100°C, 20 atm and 30 wt% sulfuric acid.

Testing by the Westinghouse Electric Company indicated that the anode overpotential decreased with increased temperature, indicating that higher electrical efficiency might occur at higher operating temperature. However, there was little or no improvement in the limiting current with increased temperature at atmospheric pressure [Lu, 1983]. The lack of improvement in the limiting current arises primarily from the reduced solubility of SO_2 at the higher temperatures. To overcome the effects of reduced SO_2 solubility at higher temperature, Lu recommended operating the electrolyzer at elevated pressure. At elevated pressure (e.g., 20 atm) the solubility of SO_2 will be sufficient to allow operation at high current density and low anode overpotential to achieve increased electrical efficiencies. The low anode overpotential was previously demonstrated in laboratory tests in which increasing the pressure from 1 to 20 atm reduced the anode overpotential by about 0.17 V [Lu, 1983].

Subbaiah et al. (2000) used sulfurous acid (sulfur dioxide dissolved in water) as an anode depolarizer in copper electrowinning. Electrowinning refines copper by electroplating. In the test cell the electrodes were separated by a microporous polyethylene membrane. At the anode sulfur dioxide is oxidized to sulfuric acid and at the cathode copper (II) ions are reduced to copper metal. With graphite electrodes, the addition of 40 g/L of sulfurous acid to the anolyte reduced the cell voltage by 1.0 volt, for a current density of 20 mA/cm^2. The sulfuric acid product would be used in the copper refining process.

Weidner (2005) tested an alternate concept for hydrogen production using a sulfur dioxide depolarized anode. His cell used the membrane electrode assembly (MEA) concept, where the electrodes were carbon with platinum catalyst. He introduced sulfur dioxide gas at the anode and water as the catholyte. His results are also plotted in Figure 2. His cell potentials are approximately the same as Lu’s best results. Water diffused across the Nafion® membrane from the cathode to the anode where it reacted with sulfur dioxide to form a sulfuric acid solution, which dripped out of the cell. Hydrogen was formed at the cathode and bubbled into the water there. After a week of testing, the cell was disassembled and the cathode passages were found to be full of sulfur. Apparently, some of the sulfur dioxide crossed through the membrane where it was reduced by the hydrogen gas to elemental sulfur.

Steimke and Steeper [2005] tested two electrolyzer cells with sulfur dioxide depolarized anodes. Both cells incorporated Nafion® Proton Exchange Membranes (PEM). One cell was a commercial electrolyzer and the second cell was a research electrolyzer built from graphite. The present work is a continuation of the 2005 work.

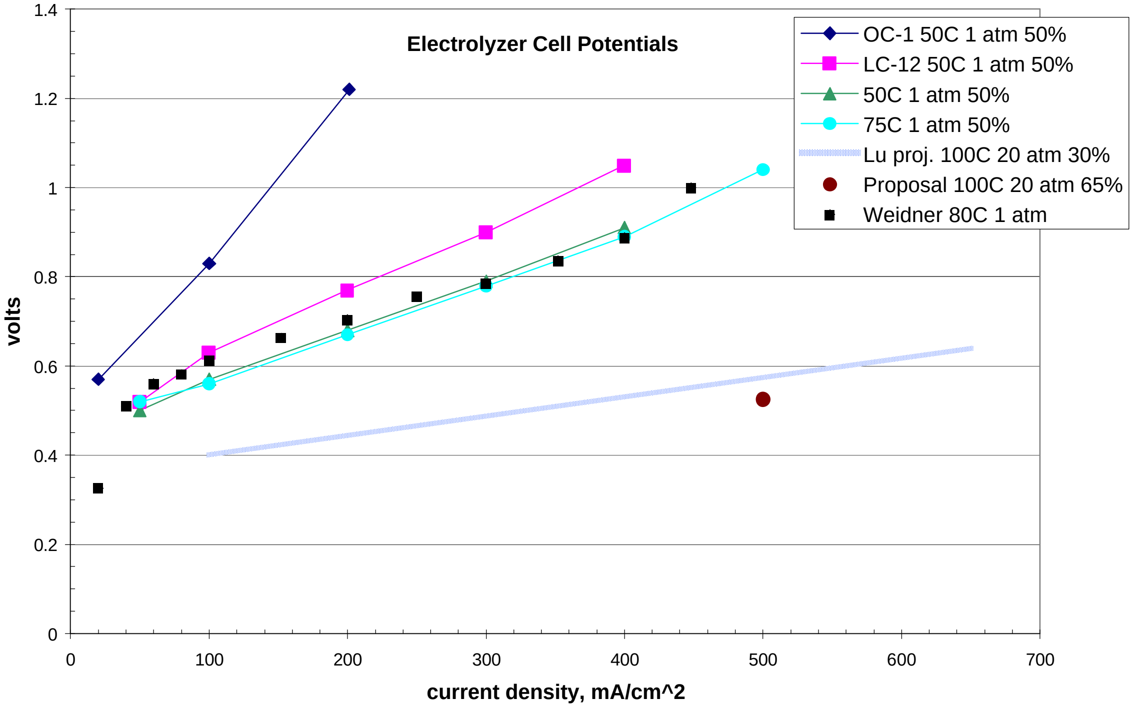


Figure 2 Cell Potentials Measured in Previous Work (what are the materials of these cells?) Also show your 2005 results on this plot.

3.1.2 Conduct of Engineering at SRNL

SRNL follows a formal procedure for planning and conducting all experimental work performed at the laboratory. A Task Technical and Quality Assurance Plan (Appendix 1) was written for the work documented in this report. Then all steps of Manual L1, Procedure 7.02, “Administration of Conduct of Research and Development Integrated Safety Management Hazards Assessment” were followed and documented. A formal Job Hazard Analysis was performed by committee chaired by John Steimke of SRNL. A peer reviewed Work Instruction (Appendix 2) was prepared and followed for this work. The Pressure Protection Committee analyzed those issues, made calculations and specified requirements.

3.1.3 Analysis

An important component of commercial development of the HyS Process is optimization of an electrolyzer design that features low cell fabrication cost and operates at high current density, low cell voltage and low energy consumption for pumping anolyte. Low cell cost and operation at high current density are important to limit the capital cost of the plant. Minimizing the cell voltage reduces the operating cost and increases the overall thermal efficiency of the plant. Reducing pump energy also reduces operating cost. Thermal efficiency is defined as the total lower heating value of the hydrogen generated divided by the total heat input, part of which goes to generate the electric power required to operate the electrolyzers. Achieving low cell cost and operation at high current density and low cell potential will involve trade-offs. For example, increased use of catalysts may reduce the cell voltage, but increases cell cost. Also, increasing current density increases cell voltage, all else held constant. Increasing anolyte flowrate increases pumping cost but decreases cell voltage.

The previous work by Westinghouse utilized two-compartment electrolytic cells with various cell dividers, such as diaphragms and membranes. An objective of the SRNL work was to utilize a cell based on current Proton Exchange Membrane (PEM) technology. PEM cells offer the capability for high current densities, high efficiencies and low capital costs. Considerable advancement has been made in PEM technology due to the interest in PEM fuel cells for automotive applications.

It is important to minimize the cell voltage, so it is helpful to separate the total cell voltage into five components as shown in Equation 4. Note that this test allowed the measurement of only the total cell voltage. Future electrolyzer tests will be designed with more measurements of electrical potential to separately measure the different components of voltage.

Cell voltage $$E = E_{rev} + \bullet_{a} + \bullet_{c} + \bullet_{ohm} + \bullet_{hw} \qquad [4]$$

E_{rev} , reversible cell potential, is a weak function of temperature and a stronger function of acid concentration. It increases with increasing acid concentration. It is directly proportional to the free energy change for the reaction and is therefore independent of catalyst and current density.

$\bullet_{a}$, anode overpotential, is a function of effective surface area of catalyst, catalyst type, current density, SO_2 concentration and acid concentration. It increases with increasing current density and decreases with increasing SO_2 concentration. SO_2 concentration is limited by the saturation concentration, which depends on temperature and pressure.

$\bullet_{c}$, cathode overpotential, is smaller than anode overpotential and is a function of catalyst surface area and type. It increases with increasing current density.

$\bullet_{ohm}$, ohmic loss, is due to the resistance across the fluids and is proportional to current density. It can be reduced by placing anode and cathode close together.

$\bullet_{hw}$, hardware loss, is proportional to current density. It can be reduced by careful hardware design and material selection.

3.2 HARDWARE AND PROCEDURE

3.2.1 Overview of Test Facility

A test facility capable of testing sulfur dioxide depolarized electrolyzers at pressures up to six atm and temperatures up to 80ºC was designed and constructed. The facility is capable of operating with electrolyzer currents up to 50 amperes or a current density of 1000 mA/cm^2 for a cell area of 50 cm^2. A current of 50 amperes is sufficient to generate approximately 20 liters per hour of hydrogen.

The test facility proved to be versatile and easy to use. One cell was easily replaced with another. The data acquisition system computer controlled anolyte flowrate, even with changing hydraulic resistance. Computer interlocks were easily added. It was relatively easy to change liquids, flush both sides of the cell and isolate part of the piping. The accurate measurement of hydrogen generated helped to explain other observations and to quantify the amount of hydrogen that reacted with sulfur dioxide. Sulfur could be flushed with water from the cathode side of the cell and collected. The DAS has additional voltage inputs available for use with future cells with provisions to measure individual components of the overall cell voltage. For the current work only the total cell potential was measured.

3.2.2 Apparatus

3.2.2.1 Design of Electrolyzer Cell

The electrolyzer cell is of the Membrane Electrode Assembly (MEA) type where the membrane is a Proton Exchange Membrane (PEM). The MEA is a "sandwich" consisting of an anode where sulfur dioxide and water in the anolyte are oxidized to produce hydrogen ions and sulfuric acid, an electrically insulating membrane that allows the hydrogen ions and water to pass through, and a cathode where the hydrogen ions are reduced to hydrogen gas. The remainder of the electrolyzer serves to deliver the anolyte to the anode and remove the sulfuric acid reaction product, remove the moist hydrogen gas and any contaminates or by-products from the cathode, provide the current paths to the electrode, allow temperature control and contain the internal pressure.

The electrolyzer was designed to operate at up to 90 psig (7 atm) and 80^{o}C to meet the testing requirements for 2006. The ability to handle even higher pressures and temperatures to support testing in the future would be an advantage if it did not increase the cost or fabrication schedule excessively. The electrolyzer was required to handle an anolyte consisting of 30-70 wt% sulfuric acid saturated with sulfur dioxide gas at relatively high flow rates and a low pressure drop while providing high mass transfer at the MEA. It was required to permit flushing any solid sulfur forming on the cathode side. Finally, the electrolyzer had to be easy to disassemble and reassemble with a new MEA to minimize downtime.

The final design including minor revisions incorporated during testing is shown in Figures 3 through 8. To understand the electrolyzer, it is first necessary to study the makeup of the MEA. This assembly consists of the individual parts shown in the box labeled item 7 in Figure 4 and shown further in Figure 5. The MEA for the SRNL electrolyzer is a "sandwich" made up of a layer of porous carbon, a thin film of catalyst, a membrane, another film of catalyst, and another layer of porous carbon. The porous carbon layers may be either a cloth woven of threads spun from carbon fibers, or a fairly stiff paper made of randomly oriented carbon fibers pressed together. The porous carbon layers may, or may not, have a Teflon coating applied to the surface facing the membrane. The membrane is a material that ideally allows free passage of hydrogen ions but prevents transport of all other materials, either gasses or liquids. The thin catalyst film is formed by spraying an "ink" made of platinum-on-carbon-powder, liquid binder, and solvent onto the surface of the membrane. The catalyst films, and sometimes the porous carbon layers, are hot pressed together so they bond intimately. Typical thicknesses of these materials are: carbon paper 0.007", carbon cloth 0.012", catalyst film 0.001", and membrane 0.005".

Figure 4 provides an exploded sectional view of the electrolyzer. Anolyte is pumped into the lower port on the anode side, flows through the electrically insulating Anode Flow Connector (item 8), and enters the lower flow distributing slot of the Graphite Seal Block (item 4, Figure 6). Flow is distributed uniformly through the slots in the Bottom Flow Distributor (item 15, Figure 7) that match up with slots in the graphite MEA Support/Flowfield Insert (item 6, Figure 8). Since the porous carbon is compressed between the MEA Support/Flowfield Insert and the membrane of the MEA, the grooves on the face of the insert form dead ended flow channels, with half of them connected to the inlet and the other half connected to the outlet. Once the anolyte flows into the inlet channels, it must flow edgewise through the thin porous carbon to one of the adjacent outlet channels. As the anolyte flows through the porous carbon, some of it is forced into contact with the catalyst layer where electrochemical reactions take place. The remaining anolyte with the reaction products leaves the outlet flow channels of the MEA Support/Flowfield Insert by passing through the top slots and into the Top Flow Distributor (item 14, Figure 7), and then through another Anode Flow Connector to the outlet port.

Hydrogen ions formed during the electrochemical reactions at the anode catalyst layer pass through the membrane to the cathode catalyst layer. There they are converted by the addition of an electron into neutral hydrogen atoms. Pairs of atoms combine into diatomic hydrogen gas molecules, flow through the porous carbon to the flow channels of the cathode side MEA Support/Flowfield Insert, and leave the electrolyzer through the Cathode Flow Connectors (item 10). During normal operation the hydrogen is discharged from the cathode through both ports.

Although the membrane ideally prevents passage of everything except hydrogen ions, the membranes currently available do let an appreciable amount of water and a little sulfur dioxide pass through. Any water passed through the membrane would probably be beneficial to the overall plant process. However, the sulfur dioxide that goes through reacts with the hydrogen gas at the cathode to form elemental sulfur. At best this reaction is a nuisance that uses up some of the hydrogen product and deposits material that will have to be flushed out periodically. If the sulfur poisons the catalyst, or causes permanent plugging of the porous carbon, it could destroy the electrolyzer. For research purposes external valves have been provided in the electrolyzer test facility to route water into the top port and out the bottom port to flush out any elemental sulfur that may be present. During this mode of operation, the cathode side will operate similarly to the anode side.

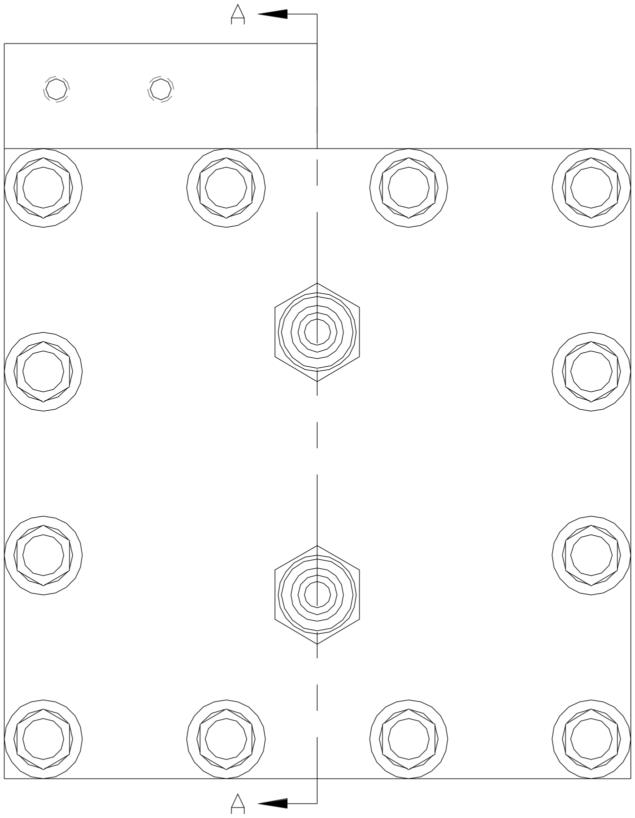
Note that the grooves in the face of the MEA Support/Flowfield Insert are not placed symmetrically. That way the anode side and cathode side inserts are identical, but when they are installed facing each other (with the MEA between), the grooves do not line up directly across from each other. If there should be a differential pressure between the anode and cathode side, the MEA will be better supported. Flow leaving the grooves in one insert doesn’t directly impinge on the MEA where it is unsupported by the groove in the insert on the other side.

The membrane of the MEA is sealed to the Graphite Seal Block (item 4) by a flat gasket (item 13) on both sides. Both the Anode Flow Connector (item 8) and the Cathode Flow Connector (item 10) are sealed with viton o-rings (item 16) to the Graphite Seal Blocks. O-rings were used to minimize stress on the brittle graphite during frequent assembly and disassembly. The Anode Flow Connector is made of PTFE (Teflon) so it is an electrical insulator. It also has an o-ring (item 21) that seals to a 3/8” PFA tube (similar to Teflon). The PFA tube can handle the highly corrosive anolyte, but does not have sufficient strength at the maximum temperature to handle the maximum pressure by itself. External to the electrolyzer the PFA is encased inside ½” S/S tubing that has sufficient strength, but cannot handle the corrosive anolyte. The S/S tube connects to the swagelok caps (nuts and ferrules not shown) welded to the Anode Side Pressure Plate (item 1). The Cathode Flow Connector is 316 S/S so it needs a separate Cathode Flow Connector Insulator (item 9) to provide electrical insulation. The 316 S/S can handle the hydrogen gas containing the mildly corrosive sulfur dioxide contaminant. Standard 316 S/S tubing unions (not shown) are used to make the external tubing connections.

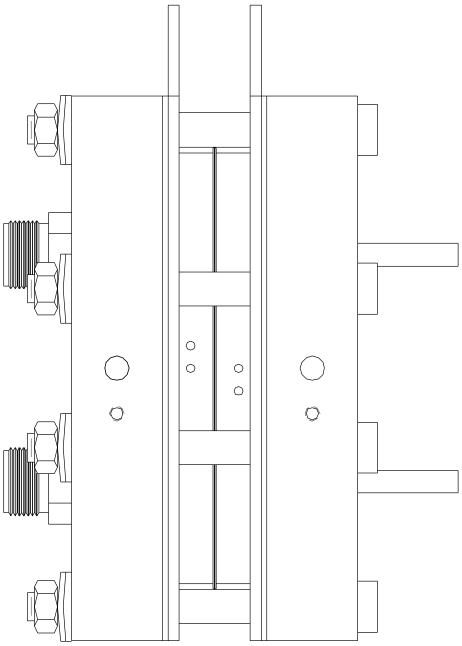
Thick S/S Pressure Plates (items 1 and 20) hold everything together and flat while resisting the pressure inside the electrolyzer. Twelve sets of Shoulder Screws (item 17), Belleville Spring Washers (item 18), Flat Washers (item 5), and Nuts (item 19) provide sufficient holding force while providing a little give to handle thermal expansion. Copper Terminal Plates (item 3) make the necessary good electrical connection to the Graphite Seal Blocks, while Insulators (item 2) prevent the Terminals Plates from shorting out to the Pressure Plates. Four sets of screws (item 12) and insulators (item 11) on each side hold many of the parts together and aligned during assembly and disassembly of the electrolyzer to install a new MEA for testing. PVC Alignment Pins (item 22) help to hold the gaskets, porous carbon, and MEA in proper alignment during assembly.

The metal Flow Distributors (items 14 and 15) were originally provided to provide a good flow path while helping to resist the pressure inside the electrolyzer, especially if a valving error should cause a large differential pressure across the electrolyzer. Although these parts were made of highly corrosion resistant Hasteloy B-2 alloy, they still corroded quickly (about 500 mils/yr) in the anolyte. After testing MEA #2 these parts were removed.

Ports were provided in each of the thick S/S Pressure Plates for installation of cartridge heaters. Ports were provided in the Graphite Seal Blocks for installation of thermocouples used for data collection, feedback to the heater control, and input to an independent high temperature shutdown for the heaters.

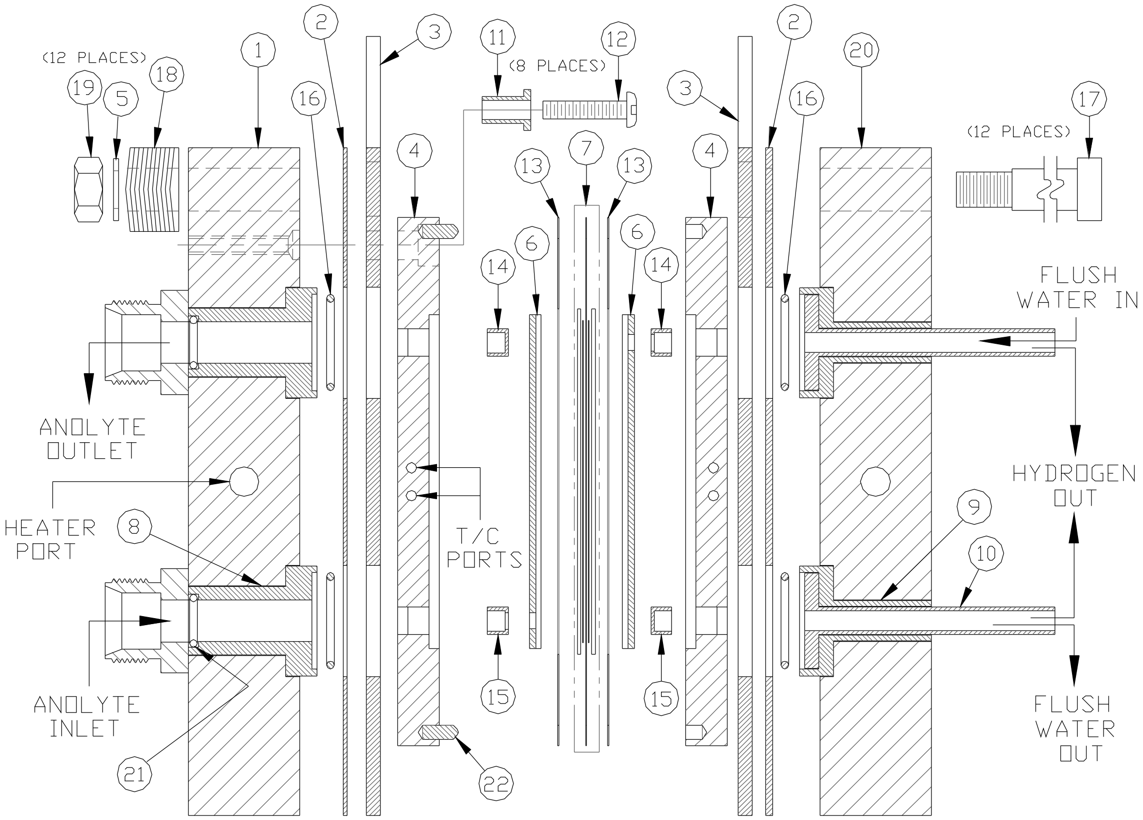


Left Side



Front

Figure 3 SRNL High Pressure Electrolyzer



Item	Description	Supplier Info	Material	Rq'd
1	Anode Side Pressure Plate	SRNL per Sketch	304 S/S	1
2	Insulator	SRNL per Sketch	Fiberglass	2
3	Terminal Plate	SRNL per Sketch	Copper	2
4	Graphite Seal Block	SRNL per Sketch	Graphite	2
5	3/18" Flat Washer, drilled to 3/8" id	Commercial	304 S/S	12
6	MEA Support/Flowfield Insert	SRNL per Sketch	Graphite	2
7	MEA	Fab By Hector		1
8	Anode Flow Connector	SRNL per Sketch	Teflon	2
9	Cathode Flow Connector Insulator	SRNL per Sketch	Teflon	2
10	Cathode Flow Connector	SRNL per Sketch	316 S/S	2
11	Screw Insulator	SRNL per Sketch	Teflon	8
12	Screw, #8-32 UNC, 3/4" long, Pan Head	Commercial	304 S/S	8
13	Gasket	Fab By Hector		2
14	Top Flow Distributor	SRNL per Sketch	Hasteloy B2	2
15	Bottom Flow Distributor	SRNL per Sketch	Hasteloy B2	2
16	O-Ring, Size 018, 0.879" od x 0.739" id x 0.070" thk	McMaster-Carr 9464K72	Viton	4
17	Shoulder Screw, 3/8" od x 3.5" long, 5/16"-18 UNC	McMaster-Carr 90298A638	18-8 S/S	12
18	Belleville Disk Spring, 3/4" od x 3/8" ID x 0.040" thick x 0.059" high, 237 lbs @ 0.010" deflection, 415 lbs flattened	McMaster-Carr 9713K71	302 S/S	120
19	Nut, 5/16"-18 UNC	Commercial	304 S/S	12
20	Cathode Side Pressure Plate	SRNL per Sketch	304 S/S	1
21	O-Ring, Size 012, 0.504" od x 0.364" id x 0.070" thk	McMaster-Carr 9464K17	Viton	2
22	Alignment Pin,).120" OD x .31" lg. with rounded ends	Commercial	CPVC	2

Figure 4: Exploded Cross Section of SRNL High Pressure Single Cell Electrolyzer

Figure 5: Front View Membrane Electrode Assembly with Porous Carbon

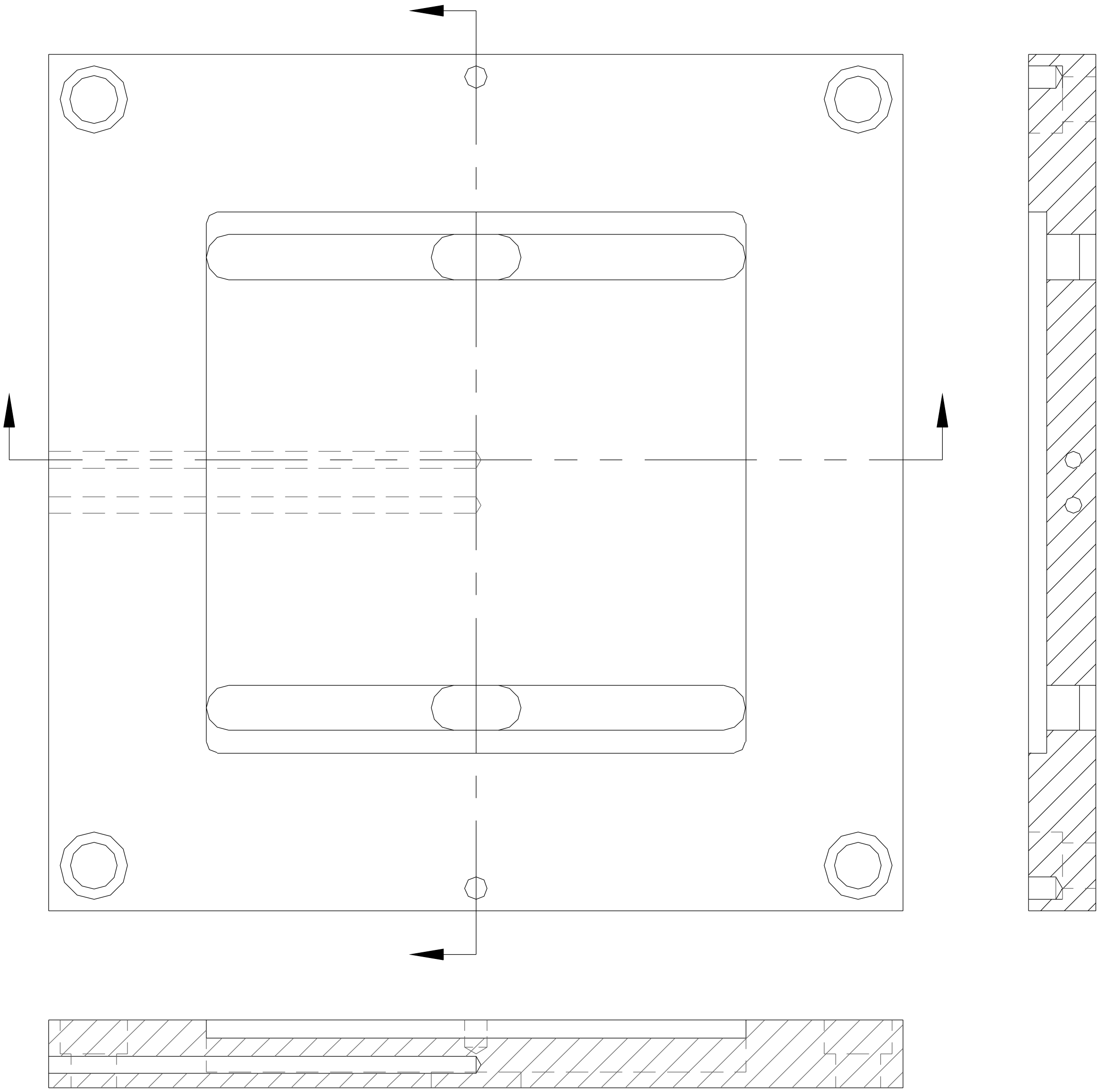


Figure 6: Graphite Seal Block

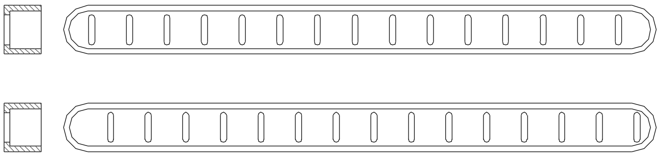


Figure 7: Top and Bottom Flow Distributors

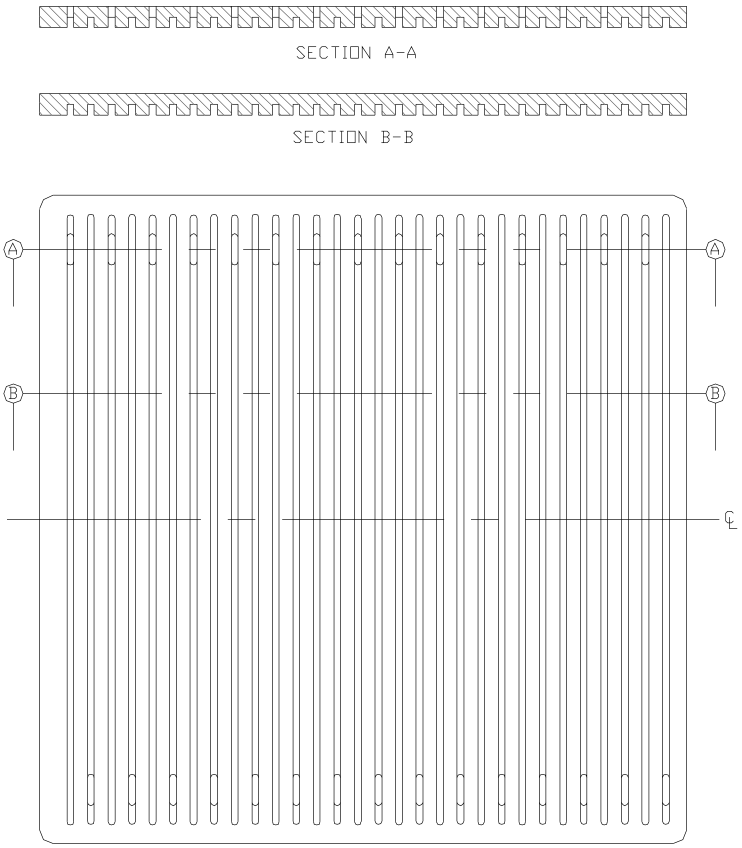


Figure 8: MEA Support/Flowfield Insert

3.2.2.2 Membrane Electrode Assemblies

An electrolyzer cell was tested with six different membrane electrode assemblies (MEA) in sulfur dioxide depolarized operation. The electrolyzer has an active area of about 48 cm^2. The first four MEA tested in the electrolyzer cell used Nafion® 115 or Nafion® 117 membranes which are 5 mils thick and 7 mils thick, respectively. Nafion® membranes are designed to pass water and hydrogen ions, but not gases. Unfortunately, Nafion® membranes also pass dissolved sulfur dioxide to some extent. The last two membranes were made of polybenzimidizole (PBI). The selection of PBI resulted from a study by Colon-Mercado, et al. [2006] which determined that it has good ionic conductivity and lower diffusion of sulfur dioxide than Nafion®. The characteristics of the six MEA are summarized in Table 1.

MEA #1 included commercial woven carbon cloth with Teflon gas diffusion layers (E-Tek LT-1400-W) and a Nafion 115 membrane. The catalyst used for all membranes was platinized carbon powder, 45 wt% Pt and 20 µm diameter. An ink was prepared by mixing one gram of platinized carbon catalyst with 4 grams of water, 20 grams of methanol and 6.7 grams of Nafion solution. The Nafion solution contains 5 wt% Nafion, 5 wt% methanol, 22 wt% isopropanol and the balance water. Therefore, after drying, the catalyst layer was 25 wt% Nafion and 75 wt% platinized carbon. The catalyst containing ink was sprayed on the shiny Teflon coated side of each gas diffusion layer with a loading of 0.65 mg/cm^2 for both the anode and cathode. A sandwich of two gas diffusion layers with the catalyst facing the Nafion membrane was hot pressed at 230 psi pressure and 140ºC temperature for three minutes. MEA #1 was installed with a 6 mil glass reinforced Teflon gasket on each side.

MEA #2 was made from Nafion 117 membrane. The same ink formulation as for MEA #1 was sprayed on both sides of the membrane and hot pressed at 230 psi pressure and 140ºC temperature for three minutes. The platinum loadings were 1.13 mg/cm^2 and 1.14 mg/cm^2 for the anode and cathode, respectively. On either side of the MEA was 7 mil thick Teflon free carbon paper (EC-TP1-060) purchased from Electrochem, Inc. (www.fuelcell.com). Teflon gaskets, 6 mils thick, were used to give an expected 1 mil of compression. However, the platinized carbon layers added a unexpected 4 mils of thickness and Nafion swelling added another mil of thickness. The resulting excessive compression cracked the carbon paper at each groove of the anode and cathode flow distributors. The pressure drop for flow of water was high and increased with time. The cell was rebuilt with the 7 mil thick carbon paper on the anode side of the second MEA and 12 mil thick Teflon free carbon cloth (EC-CC1-060) purchased from Electrochem, Inc. on the cathode side. MEA #2 was used with two 10 mil glass reinforced Teflon gaskets.

MEA #3 was installed with 7 mil carbon paper on the anode side, 12 mil carbon cloth on the cathode side, and 10 mil gaskets as used during the rebuild of MEA #2. For MEA #3 the anode and cathode loadings were 1.44 mg Pt/cm^2 and 1.32 mg Pt/cm^2, respectively. A thin platinum wire was installed to touch the membrane adjacent to but not quite touching the anode catalyst layer. The intention was to measure the voltage at the anode catalyst/membrane interface relative to the cathode bus connection, but the reading matched the overall cell voltage. It was thought that the disturbance in the gasket seal at the wire allowed the highly conductive anolyte to contact the wire, essentially shorting it to the anode bus. The use of the platinum wire was not attempted again. Upon disassembly, it was noticed that slight slippage of the gasket and carbon paper had occurred during assembly leaving a very small portion of the grooves in the MEA Support/Flowfield Insert uncovered by the porous carbon paper.

MEA #4 was installed almost identically to MEA #3. For MEA #4 the anode and cathode loadings were 0.88 mg Pt/cm^2 and 0.99 mg Pt/cm^2, respectively. The square opening in the Teflon gaskets was made 0.10” larger in both directions and the carbon paper and carbon cloth were enlarged 0.08”. This change was made to ensure all of the grooved area of the MEA Support/Flowfield Inserts was covered by the porous carbon, and to eliminate any possibility of overlap of the gasket and porous carbon. PVC alignment pins were introduced to better ensure everything stayed aligned during assembly.

MEA #5 was different from the first four. It used a Celtec-L membrane which is PBI doped with phosphoric acid and is 2 mils thick. It used the same catalyst ink formulation as the other membranes. The platinum loadings for both the anode and cathode were 1.0 mg/cm^2. The membrane was so thin that electrical shorting occurred.

MEA #6 used two Celtec-L membranes to give twice as much thickness as MEA #5 , avoiding the electrical shorting problem. An attempt was made to bond the two membranes together, but this was not successful. Two membranes were installed in the cell with the catalyst layers facing outward.

Table 1 Summary of MEA Characteristics (move this table to fit on one page)

MEA #	Membrane	Membrane thickness, mils	Anode flow field	Cathode flow field	Anode Pt loading, mg/cm2	Cathode Pt loading, mg/cm2	Active area, cm2
1	Nafion	5	E-Tek	E-Tek	0.65	0.65	49.0
2	Nafion	7	Carbon	Carbon	1.13	1.14	51.3

			paper, 7 mil	cloth, 12 mils			
3	Nafion	7	Carbon paper, 7 mil	Carbon cloth, 12 mils	1.44	1.32	48.1
4	Nafion	7	Carbon paper, 7 mil	Carbon cloth, 12 mils	0.88	0.99	49.7
5	Celtec-L	2	Carbon paper, 7 mil	Carbon cloth, 12 mils	1.0	1.0	46.3
6	Celtec-L 2 layers	4	Carbon paper, 7 mil	Carbon cloth, 12 mils	1.47	2.16	49.9

A photograph of the electrolyzer cell is shown in Figure 9. The protruding copper tabs are the electrode electrical connections. Most of the electrolyzer components are made from graphite., although the outermost plates were made from 1” thick stainless steel for strength. The inside of the electrolyzer has passages for the flow of anolyte and catholyte.

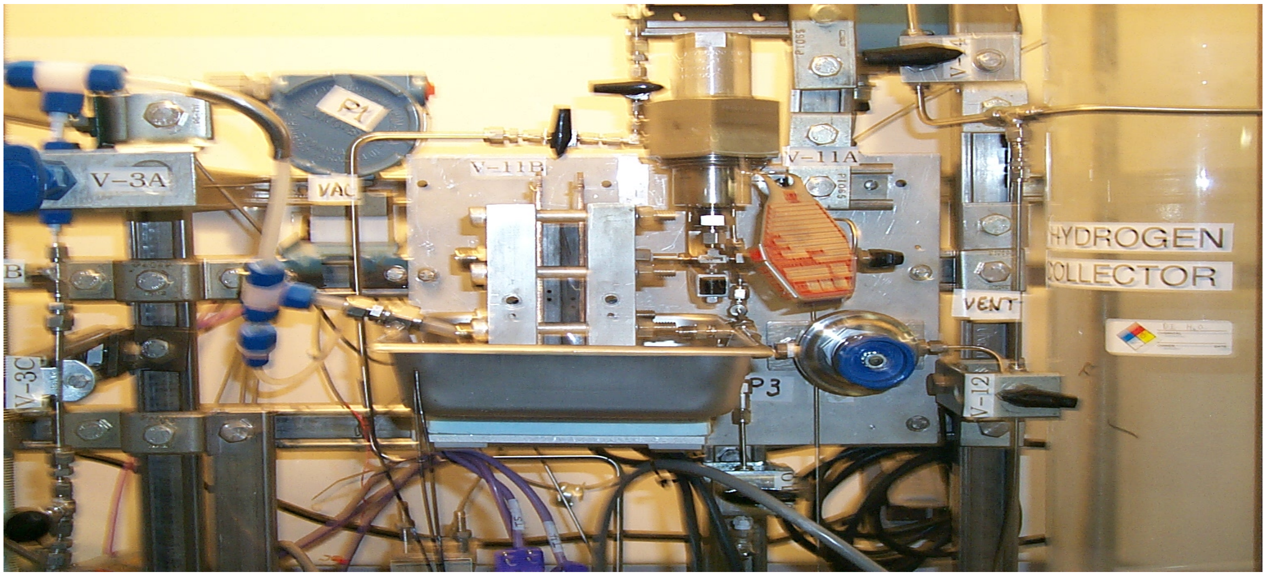


Figure 9 Photograph of Electrolyzer Cell

The facility was located in a large chemical hood as shown in Figure 10. Air flow was maintained whenever hydrogen or sulfur dioxide was present in the hood. The hood was effective, as evidenced by the absence of sulfur dioxide odor outside the hood enclosure. In Figure 10, the 100 lb. cylinder of sulfur dioxide is located on the left and is positioned upside down to deliver liquid sulfur dioxide to the piston pump. To the right of the SO_2 cylinder was the SO_2 Absorber. The SDE cell is located in the upper middle of the picture. Below the cell is the Anolyte flowmeter and below that is the Anolyte Pump. Further to the right is the Hydrogen Collector.

Figure 11 is a schematic of the equipment in the facility which shows the locations of the valves and instruments. There are two backpressure regulators that control process conditions. The first one controls the pressure in the Sulfur Dioxide Absorber. The second controls the hydrogen pressure at the cathode of the electrolyzer.

Figure 10 Photograph of Electrolyzer Test Facility

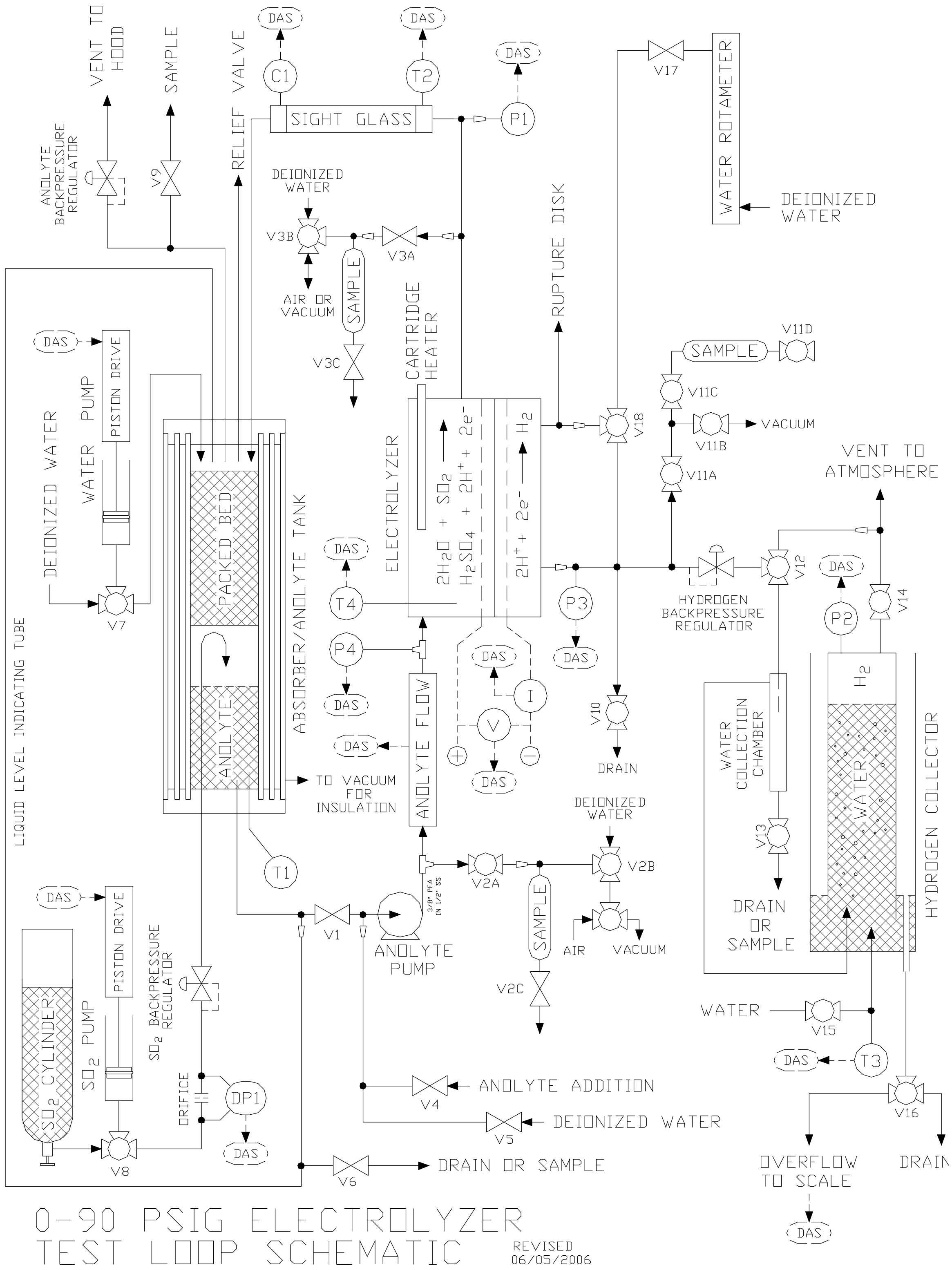


Figure 11 **Schematic of Electrolyzer Test Facility**

The facility includes an Absorber where sulfur dioxide gas is absorbed into solutions of sulfuric acid and water to form anolyte. The Absorber contains 96 cm of 8 mm by 8 mm by 1 mm wall glass Raschig Rings in a column having an inside diameter of 13.4 cm (5.275"). Below the packed bed is a reservoir for about a liter of anolyte. The Absorber operates in countercurrent operation, anolyte flows into the top and sulfur dioxide gas flows upward. Excess sulfur dioxide gas is used to initially saturate the anolyte and also to purge air from the Absorber. Excess gas is vented. Anolyte is pumped out the bottom of the Absorber, through a flowmeter, through the anolyte side of the electrolyzer and back into the top of the Absorber.

Sulfur dioxide is supplied in a 100 lb. cylinder and the flowrate is measured using an accurate piston pump, Teledyne ISCO Model 500D. The cylinder has a capacity of 504 mL and can pump flowrates up to 200 mL/min at pressures up to 3750 psig. The piston pump measures the pressure in the cylinder and has a high pressure shutdown feature which is set at 500 psig. The design calls for delivering sulfur dioxide to the Absorber in the liquid phase. To assure this the sulfur dioxide cylinder is inverted so that liquid is drawn off the bottom and a backpressure regulator is placed downstream of the piston pump. This backpressure regulator is set above the vapor pressure of sulfur dioxide at room temperature, 34 psig. An orifice flowmeter is installed between the piston pump and the SO_2 Backpressure Regulator (BPR). The intention is to provide an independent means to shut down the piston pump if a malfunction made the piston run too fast. Hovever, this feature proved troublesome and was not used. Note, no credit is taken for this feature in safety analyses or Pressure Protection analyses for the test facility.

The system design intended to control the pressure inside the SO_2 Absorber using another Backpressure Regulator. In this design, excess sulfur dioxide gas would be pumped to the Absorber with the excess escaping through Absorber Backpressure Regulator. The ability to increase the Absorber pressure is important because it increases the concentration of dissolved sulfur dioxide. However, this backpressure regulator did not function well due to accumulation of condensed water vapor. Pressure was easily controlled by the rate of SO_2 addition to the Absorber, sometimes accompanied with a small bleed from valve V9, so the use of this backpressure regulator was discontinued.

A clear cylinder was placed around the Absorber forming a jacket through which hot water could be passed to achieve temperatures greater than ambient. The hot water jacket was not used for the testing reported here. Outside the jacket was another annulus for which a vacuum of about 5 torr was pulled to provide an insulating layer to reduce heat losses.

The chemical reaction consumes water, so a second piston pump was provided to supply makeup water. Although it is theoretically possible to continuously add just enough water to maintain the anolyte acid concentration constant, in practice it is difficult to do. Water is consumed in the reaction at the anode and is transported through the membrane to the cathode. In addition, since sulfuric acid is made at the anode, additional water has to be added to keep the acid concentration from increasing. Since the concentration of one liter of anolyte does not change appreciably even with several hours of operation of this electrolyzer, water was not added during a run. For future long term operation for endurance testing where the consumption rate should be well characterized, continuous water addition remains a desirable option.

All tubing, valves, connectors, and seals in the anolyte flow loop are made from fluorocarbon polymer (PTFE, PFA, or FKM). Upstream of the electrolyzer cell, where pressures are higher, stainless steel tubing is placed over the fluorocarbon tubing to provide more strength. Where there was no stainless steel covering, the translucent tubing is used to determine if lines were full of liquid or are passing a two-phase mixture.

Liquid sampling stations are provided both upstream and downstream of the electrolyzer cell so that anolyte samples may be collected. The sample volume may be connected to the anolyte loop, vacuum, compressed air or water.

The cathode side of the electrolyzer being tested is connected to the hydrogen handling side of the facility. For safety, a rupture disk rated at 168 psig burst pressure is connected to the hydrogen outlet of the electrolyzer. A Backpressure Regulator is provided to demonstrate the ability of the electrolyzer to generate hydrogen at elevated pressures. This is an important capability because this would reduce the cost of compressing the product hydrogen in a production plant. Downstream of the Backpressure Regulator is a three way valve that can direct product hydrogen either directly outside the building or to the Hydrogen Collector. Just upstream of the Hydrogen Collector is a Water Collection Chamber with a purge valve to allow capture and sampling of any condensate that might appear.

The method for measuring hydrogen generation with the Hydrogen Collector is water displacement from an inverted cylinder positioned with its base in a shallow pool of water. This method is simple yet allows accurate measurement of low flow rates. Water temperature, hydrogen gage pressure in the inverted cylinder, and atmospheric pressure are measured to allow for volume correction. The inner cylinder of the Hydrogen Collection Cylinder is made from glass because the ASME B31.3 - 2002, Process Piping Code prohibits the use of thermoplastics with flammable gasses. An outer cylinder made from acrylic protects the glass cylinder and facilitates filling the inner cylinder with water between runs. To prepare for hydrogen collection the inner cylinder vent valve V3 is opened, both cylinders are filled with water, the vent valve is closed, and the drain valve V15 opened to remove water from the outer cylinder. This procedure leaves the inner cylinder filled with a sufficient vacuum at the top of the inner chamber to hold up the water column.

The power supply was a Model 710 from The Electrosynthesis Company, Inc. of Lancaster NY. It was usually operated in constant current mode rather than in constant voltage mode. The maximum current and maximum voltage are 50 amperes and 20 volts, respectively. It has an analog signal output for current ranging from 0 to 5 volts, corresponding to 0 to 20 amperes. In addition, a calibrated shunt (instrument # 3-2937) was connected to the output of the power supply to allow for independent measurement of current. Voltage taps independently connected to the cell terminals were connected to the DAS.

The instruments used in the test; thermocouples, pressure gages, flowmeters and a scale are listed in Table 1. The instrument signals were connected to the data acquisition system, a Dell computer with special acquisition boards and Labview software. Typical raw data from the DAS are shown in Appendix 3. Observations and some data are recorded in a laboratory notebook.

Table 2 Instrument List for Hydrogen Electrolyzer Test Facility (move to fit this table on one page)

You may want to list uncertainty values in this table.

instrument	number	lower range	upper range	units	location
P1	TR-03761	0	100	psig	cell anolyte outlet pressure
P2	TR-03531	-3	1	psig	Hydrogen Collector pressure

P3	TR-20263	0	100	psig	cell hydrogen outlet pressure
P4	TR-03540	0	120	psig	cell anolyte inlet pressure
T1	TR-03763	0	100	°C	Anolyte tank temperature
T2	TR-03764	0	100	°C	cell anolyte outlet temperature
T3	TR-02812	0	100	°C	hydrogen collector temperature
T4	TR-02808	0	100	°C	anode temperature
T5	TR-03805	0	100	°C	cathode temperature
T6	TR-03806	0	100	°C	cathode temperature
T7	TR-03807	0	100	°C	
High temp. shutdown	TR-03812	0	100	°C	cell temperature
Heater controller	TR-03813	0	100	°C	cell temperature
Anolyte flow	TR-03562	0	2	L/min	anolyte flow
rotameter	Brooks s/n 41568	0	0.54	L/min	air flow
rotameter	Brooks s/n 0104010251452/001	0			water flow
scale	TR-30074	0	100	lb	weight of water displaced from H_2 collector
voltage		0	20	volts	total voltage across cell
current		0	50	amps	reads as 0 - 5 volts
current	3-2937	0	50	amps	shunt

3.2.3 Test Matrix

The Test Matrix included electrical currents ranging from 1 ampere to 50 amperes. However, currents resulting in cell voltages greater than 1.2 volts were not tested, one reason for this was to avoid possible generation of oxygen which could damage the carbon based cell. Anolyte flowrates up to 1.5 liters per minute were tested. Figure 12 illustrates the possible ranges of pressure and temperature. The numbers of the plot are estimated sulfur dioxide concentrations in grams per 100 grams of solution.

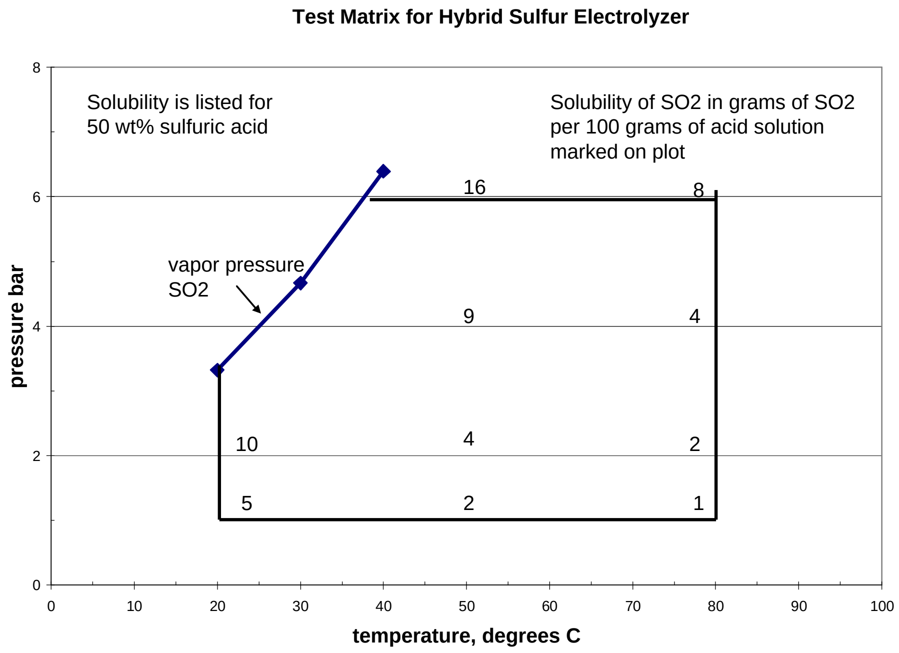


Figure 12 Graphical Test Matrix

3.2.4 Shakedown

A shakedown process was conducted with air and water. All systems and operations were exercised. The anolyte loop was run over the full range of flowrates, pressures and temperatures. Pressures above ambient were created by injecting air. Liquid sampling was tested. Also, air was injected at the cell cathode and the operation of the Hydrogen Backpressure Regulator and Hydrogen Collector were tested.

3.2.5 Abbreviated Procedure

The following is a summary of the Work Instruction (Appendix 2) prepared for this work. Any previous contents of the facility were drained. Hood ventilation was used whenever the Absorber contained sulfur dioxide or if hydrogen was being generated or stored in the Hydrogen Collector. After the cell containing an MEA was installed in the loop, water was briefly circulated to check for liquid leaks, then the water was drained. A liter of the desired acid solution was mixed in a bottle using Fisher Certified sulfuric acid with an assay of 95.8%. During testing, the anolyte was drained and replaced as much as daily. A tube was attached to valve V4 and inserted into the bottle of acid solution. Valve V1 was closed and the pump was used to draw the acid into the Absorber. Valve V1 was opened and V4 was closed and the acid solution was circulated through the cell and absorber at a flowrate of 0.6 L/min.

The sulfur dioxide piston pump was charged with sulfur dioxide from a 100 lb. gas cylinder. This transfer worked best if a heat gun was used to warm the cylinder for five minutes previous to the transfer. This heating increased the cylinder pressure by about 3 psi. Otherwise most of the volume in the cylinder was occupied by vapor. The piston pump was deadheaded until a fast pressure increase was observed to eliminate any vapor. Then, liquid sulfur dioxide was pumped into the Absorber at an initial rate of 5 mL/min to allow the anolyte to saturate with the Absorber vented to atmosphere through V9. The liquid sulfur dioxide instantly flashed to vapor. After about 20 minutes the sulfur dioxide flow was reduced to 0.2 mL/min which exceeded the rate of consumption by the electrolyzer.

Current was passed through the cell after the anolyte was saturated. Typically one current was maintained for at least five minutes and also until the cell voltage did not change over a two minute period. To increase the Absorber pressure, V9 was closed and the sulfur dioxide flowrate was increased to 5 ml/min. The loop included a back-pressure regulator on the Absorber but it did not work well. After the desired pressure had been achieved, the flowrate of liquid sulfur dioxide was reduced to 0.2 mL/min and V9 was opened slightly to maintain pressure.

To achieve higher temperature operation, a 400 watt heater was imbedded in the thick stainless steel anode backing plate. Briefly, two heaters were used in the cell, one each on the anode and cathode sides. The intention was to heat the cell faster, but because of operation difficulties, the cathode heater was removed. The only heater was placed in the anode plate rather than the cathode plate because the anode has continuous liquid flow. Temperature control was achieved using thermocouples. One was inserted in the anode non-porous plate and two were placed in the cathode non-porous plate. The anode thermocouple was recorded on the DAS. One cathode thermocouple controlled the heater using an Omega CSC32 Benchtop controller. The other controlled the high temperature shutdown circuit, which was set at 80ºC and which protected the Teflon tubing from over heating. Note that for the testing reported here, the only source of heat to the facility was the one heater. Anolyte flow heated the Absorber and Anolyte reservoir.

3.2.6 Measurement of Hydrogen Production Rate

The SRNL Facility measured hydrogen flowrates by displacement of water from a cylinder to allow identification of any discrepancy from the theoretical rate. There were actually three possible measurements of hydrogen flowrate. The first method is a manual method, whereas the second and third methods use the DAS. Hydrogen volumes and flowrates listed in this report are adjusted to one atmosphere and 20°C. For those conditions, a mole of hydrogen or two grams occupies 24.45 liters. The first method was to use the ruler on the side of the Hydrogen Collector to measure the height of the gas-water interface, which was multiplied for cross sectional area to give raw volume, which was then adjusted using measured pressure and temperature. The first method was used only briefly because it was labor intensive. The second method uses the pressure transducer at the top of the cylinder, which was calibrated in inches of water, to indicate the height of water. Initially, the Hydrogen Collector has a sub-atmospheric pressure, about -55 inches of water. As water is displaced by hydrogen the water level drops, and the pressure approaches atmospheric pressure. The volume was adjusted for temperature and absolute pressure. The third method was to weigh the water displaced from the column. The density of water was used to compute the volume of hydrogen. This volume was also adjusted for temperature and absolute pressure.

3.2.7 Liquid Sampling Technique and Wet Chemistry

The anolyte is saturated with SO_2 gas at the system pressure. It is not possible to simply open up a sample valve and collect a meaningful anolyte sample because the SO_2 gas will boil out of the solution as soon as the pressure is reduced. The sample has to be discharged slowly into a solution that will ensure the SO_2 remains dissolved. An accurately known volume of sample must be obtained so the dilution factors can be determined.

Liquid sampling positions were located both upstream of the electrolyzer cell (valves V2A, V2B, V2C) and downstream (valves V3A, V3B, V3C). The following describes sample collection for V2, but the process for V3 is the same. A supply of 0.1 M sodium hydroxide solution is prepared in a labeled bottle. To prepare to collect a sample, valve V2B was turned to the vacuum pump. Between the vacuum pump and V2B there is a vacuum gage and a clear bottle to protect the vacuum pump from liquid. The vacuum is connected to the sampler until the reading on the vacuum gage no longer changes, typically 6 torr. Valve V2B is then closed.

Valve V2A is briefly opened to draw in the anolyte sample, about 2.5 mL. A beaker is tared on a scale, approximately 100 mL of 0.165 M sodium hydroxide is poured in it, the beaker is weighed, the weight is recorded and the scale is re-tared. The valves are set to connect the sample chamber to air pressure and the beaker is placed under V2C so that the tube attached to V2C is under the liquid surface. V2C is slowly opened allowing the contents of the sampler to be mixed into the beaker and then V2C is closed. A solution of 0.165 M sodium hydroxide is used instead of water because it rapidly converts the sulfur dioxide to bisulfite, which is non-volatile and greatly decreases the rate of sulfur dioxide loss. The beaker is re-weighed and the scale is re-tared. Some anolyte remains in the sampler, so valve V2B is turned to water, then the beaker is placed under V2C and V2C is slowly opened to allow about 20 mL of rinse water to flow into the beaker and then V2C is closed. The beaker is re-weighed and the scale is re-tared. The result of sampling is a dilute, stabilized sample.

To prepare the sample chamber for re-use, valves are set to connect the sample chamber to air, another beaker is placed under V2C and V2C is briefly opened to blow liquid out of the sample space. Then the sample chamber is valved to the vacuum to evaporate water and remove air from the sample space.

Wet chemistry using the Bunsen Reaction was used to analyze the concentration of sulfur dioxide in the sample.

$$SO_2 + I_2 + 2H_2O = H_2SO_4 + 2HI$$

The diluted anolyte sample is poured into a 30 mL buret. A beaker is prepared with 75 mL of deionized water, 1 mL of 0.1 N iodine solution and 1 mL of starch indicator. The iodine turns the water brown and the indicator turns it blue. The beaker is placed on a magnetic stirrer and diluted anolyte is titrated into it until the blue solution turns colorless.

3.3 TEST RESULTS

3.3.1 Summary of Testing

After Shakedown testing, MEA #1 was installed in the cell on June 27, 2006 and the cell was installed in the test facility. Pressure drops were relatively high. Testing covered currents from 1 to 15 amperes and pressures of 1 atm and 2 atm. The temperature was 23ºC. The acid concentration of the anolyte was 20 wt%. Cell voltages increased over the three days of testing ending on June 29. The layers of the MEA, namely the two diffusion layers and the Nafion membrane, were observed to have delaminated. The sulfur dioxide back-pressure regulator (BPR) was observed to be corroded inside. The anolyte BPR had black viscous fluid inside.

On July 11, MEA #2 was installed with carbon paper on each side of it. Water was initially circulated in the loop. Pressure drops were high and increasing. The loop was disassembled and it was observed that the carbon paper was pressed into most of the flow distributor grooves at both the anode and cathode. The carbon paper was cracked into thin strips by the pressure against the groove edges. When removed from the cell the MEA bowed up 1.2 cm in the middle. The next morning the MEA had dried and was once again flat. This indicated that there was appreciable swelling of the MEA in the anolyte which would increase the compression on the carbon paper. The decision was made to change to thicker gaskets (10 mil thick), with 7 mil carbon paper on the anode side and 12 mil (uncompressed) carbon cloth on the cathode side. The carbon cloth is much more resilient than the paper and was expected to help maintain an adequate but acceptable compression on the anode side carbon paper. There was a concern that disassembly and reassembly of the electrolyzer with different carbon layers might remove some of the catalyst layer, so that the amount of catalyst would not be known definitely. It was decided to make a new MEA to avoid this uncertainty, but to reinstall MEA #2 and run it while the new MEA was being made. The rebuilt MEA #2 was tested for currents from 1 to 20 amperes, and pressures of one and two atm, ending on July 18. Pressure drops were much lower and steady. Upon disassembly, the MEA and porous carbon layers were observed to be in good condition.

On July 19 MEA #3 was installed. This MEA was tested at temperatures up to 80ºC and pressures up to 4 atm. Initially, the wet chemistry analysis did not work, because there was no clear loss of blue color. Early on July 24, the anolyte was drained, the loop was rinsed and the anolyte was replaced. Thereafter, the wet chemistry seemed to work properly. As the cell was being heated to 80ºC it began to leak sulfur dioxide gas and it was difficult to maintain pressure. After the cell cooled, the gas leak disappeared. Early on July 26 the nuts on the bolts that hold the cell together were removed individually. A stack of eight Belleville spring washers was added to each, four pairs of washers facing each other. The nuts were tightened nearly to the point of flattening the washers. Testing resumed and no gas leaks were observed, although for the remaining testing of MEA #3, the cell temperature did not exceed 35ºC.

On July 31 MEA #4 was installed. This time, ten Belleville washers were installed on each bolt, all pointing the same direction, which generates more force but less deflection capability than when they are paired. Shoulder bolts were used so the deflection would be controlled to identical amounts. When the nuts were tightened down to the shoulder, the washers were nearly flattened resulting in about 4000 lbs force on each bolt. No gas leaks were observed during testing.

On the morning of August 1 it was observed that the sulfur dioxide piston pump was not completely filling with liquid sulfur dioxide from the supply cylinder. Apparently the cylinder was slightly cooler than the pump so the SO_2 vaporized as it was drawn into the pump cylinder. This was confirmed by operating the pump slowly with the discharge valve closed until the pressure suddenly increased dramatically. Deadheading the piston pump compressed 250 mL of liquid and vapor down to 102 mL of liquid. If the pump is filled partially with vapor the vapor must be compressed to liquid before SO_2 is actually pumped to the absorber. Prior to this discovery, it was thought that it took a considerable amount of SO_2 to reach saturation, at which point the amount of SO_2 needed to maintain saturation dropped sharply. In fact, most of the “considerable amount of SO_2” was simply vapor being compressed to liquid. It took considerably longer to reach steady state operation before this problem was understood but had no other detrimental effect on the data collected. Once the vapor was compressed the pump supplied liquid SO_2 at a known rate. After August 1st, two precautions were employed when refilling the piston pump. First the supply cylinder was heated using a heat gun for five minutes before the transfer which increased the cylinder pressure by about 5 psi. Second, the piston pump was always deadheaded after filling and periodically during testing to eliminate vapor void.

Testing of MEA #4 was conducted at cell temperatures up to 70°C and anolyte pressures up to 4 atm. MEA #4 was tested longer than any other MEA with the consequence that the acid strength in the anolyte increased significantly, increasing the cell voltage. On the morning of August 8 the anolyte was drained and fresh anolyte was added, then the final day of testing with MEA #4 was performed.

MEA #5 was installed in the cell on August 11. Testing was performed for one day only at 1 atm and 23ºC. Cell voltages were surprisingly low, but then it was observed that hydrogen production rates were also very low. It was concluded that there was an electrical short through the MEA so much of the current was not going toward hydrogen production. A probable cause was that hot pressing the MEA forced some catalyst particles on opposite sides of the membrane into contact.

MEA #6 was installed in the cell on August 21 and tested only that day. At ambient conditions the cell voltages were less than for the Nafion® based membranes.

More detailed results on testing the MEA are described in the following sections. Appendix 4 presents tabular results. For that table the temperature was measured at the cell. The pressure was measured at the top of the Absorber tank. Because the partial pressure of water vapor and sulfuric acid are both relatively low, the total pressure listed is close to the partial pressure of sulfur dioxide. The electric charge listed is the cumulative charge in coulombs during testing. Weight percent acid was calculated based on electrical charge passed since fresh anolyte was installed in the loop.

3.3.2 Results for MEA #1

Pressure drops for water flow were measured for the anode side of the electrolyzer, as shown in Figure 13. The cathode side is hydraulically identical. Pressure drops were undesirably large. Figure 14 plots cell potentials. The data sets were plotted in chronological order and there was a steady increase in cell potential with time. Because of the high pressure drops and deteriorating voltages, MEA #1 was replaced with MEA #2.

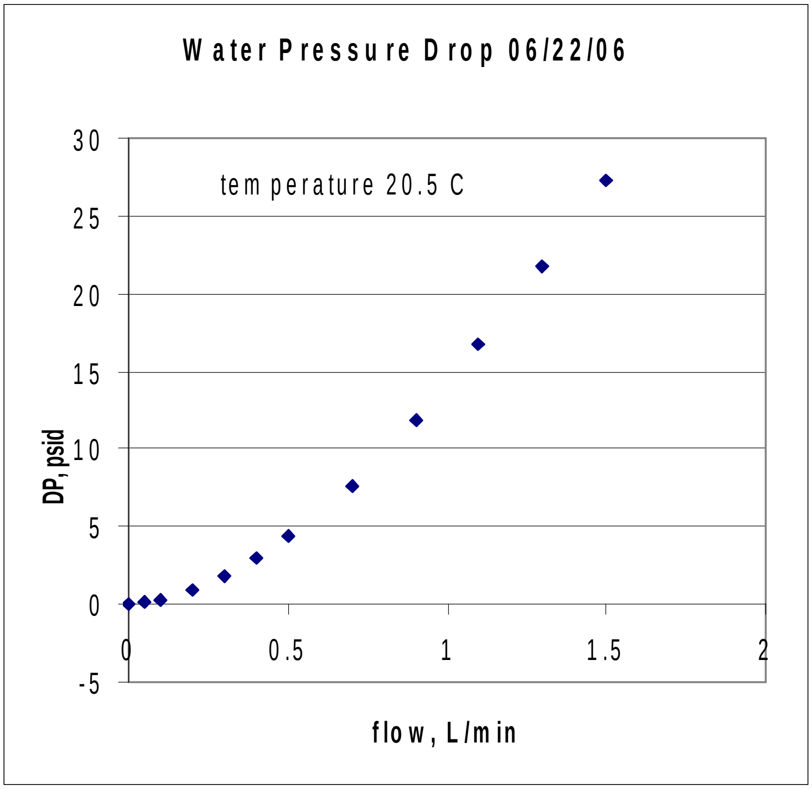


Figure 13 Pressure Drop for Anolyte Side of MEA #1

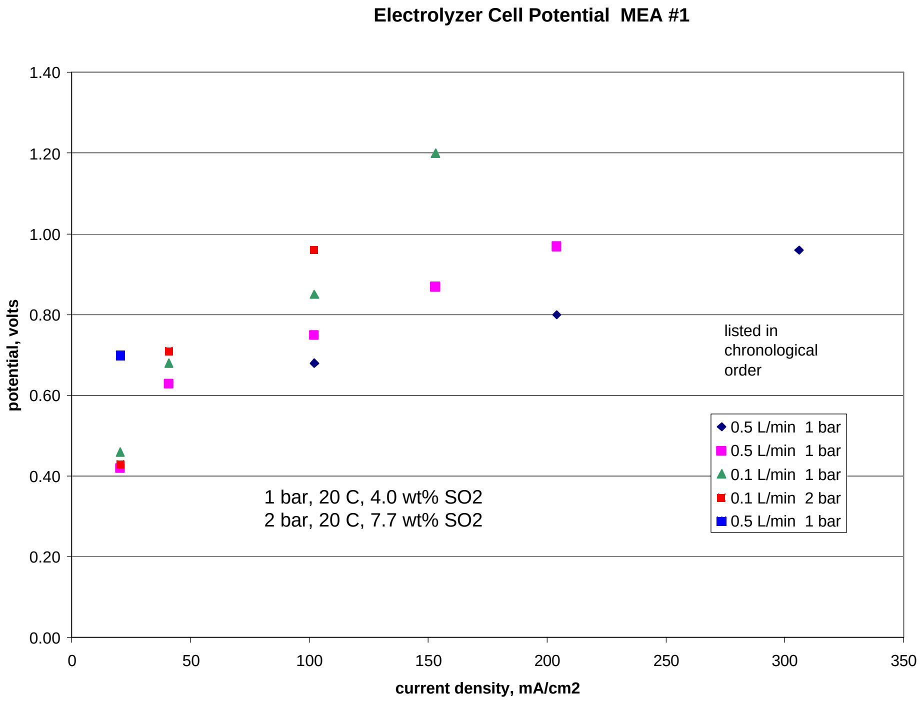


Figure 14 Cell Voltages for MEA #1 (enlarge the axis captions to enhance readability)

3.3.3 Results for MEA #2

After MEA #2 was initially installed, flow measurements showed high and increasing pressure drops. The cell was disassembled and rebuilt as described in "Summary of Testing". Figure 15 shows that the pressure drop for water was about one-sixth as much as for MEA #1. The acid solution has about twice the pressure drop as water as a result of its higher density and viscosity. Figure 16 plots the cell voltages for MEA #2. All testing for this MEA were at ambient temperature and pressures of 1 atm and 2 atm. Initial cell voltage were relatively low, but increased during the period of testing. At the time it was concluded that exposure to corrosive conditions or poisons was degrading the catalyst performance. Later it was observed degraded performance corresponded to unbalanced pressures across the membrane. For two atm operation there was a pressure difference of 1 atm across the membrane. In addition, at the start of the second 1 atm data set there was an unbalanced pressure with the higher pressure being on the cathode side. It was later concluded that the unbalanced pressures mechanically stressed the catalyst layer. Also, prior to the first unbalanced pressure, step changes in cell current were accompanied by changes in voltage that reached steady state in about a minute. After exposing the cell to unbalanced pressures it could require tens of minutes to reach steady state.

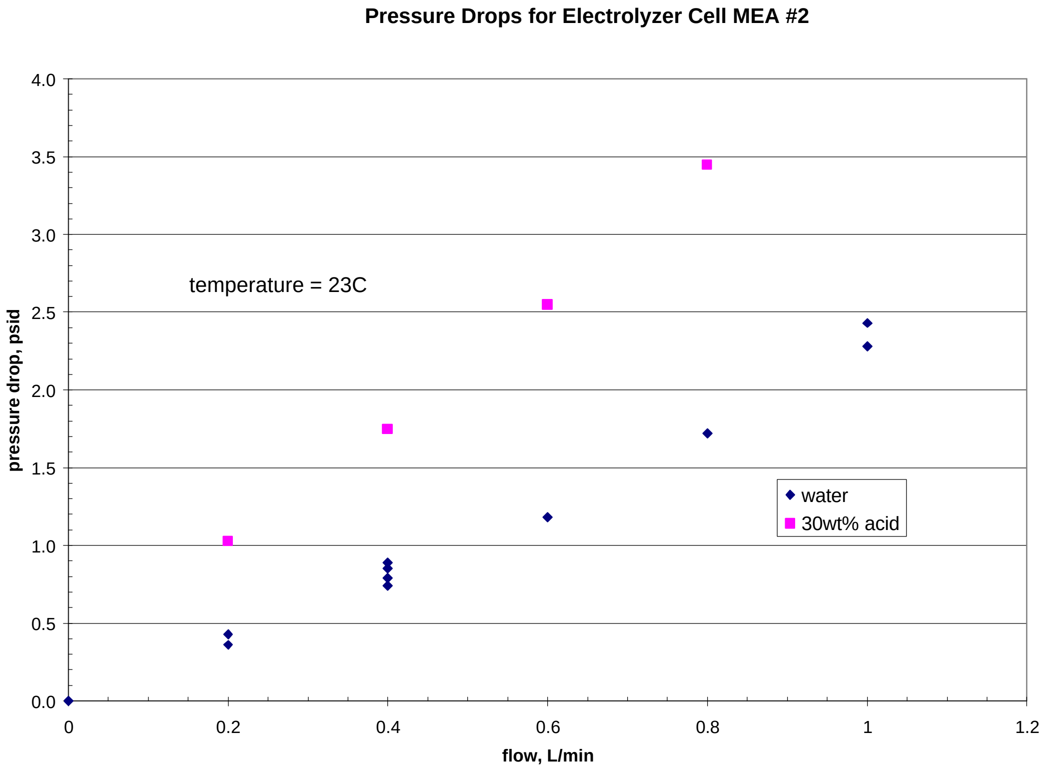


Figure 15 Pressure Drop for MEA #2

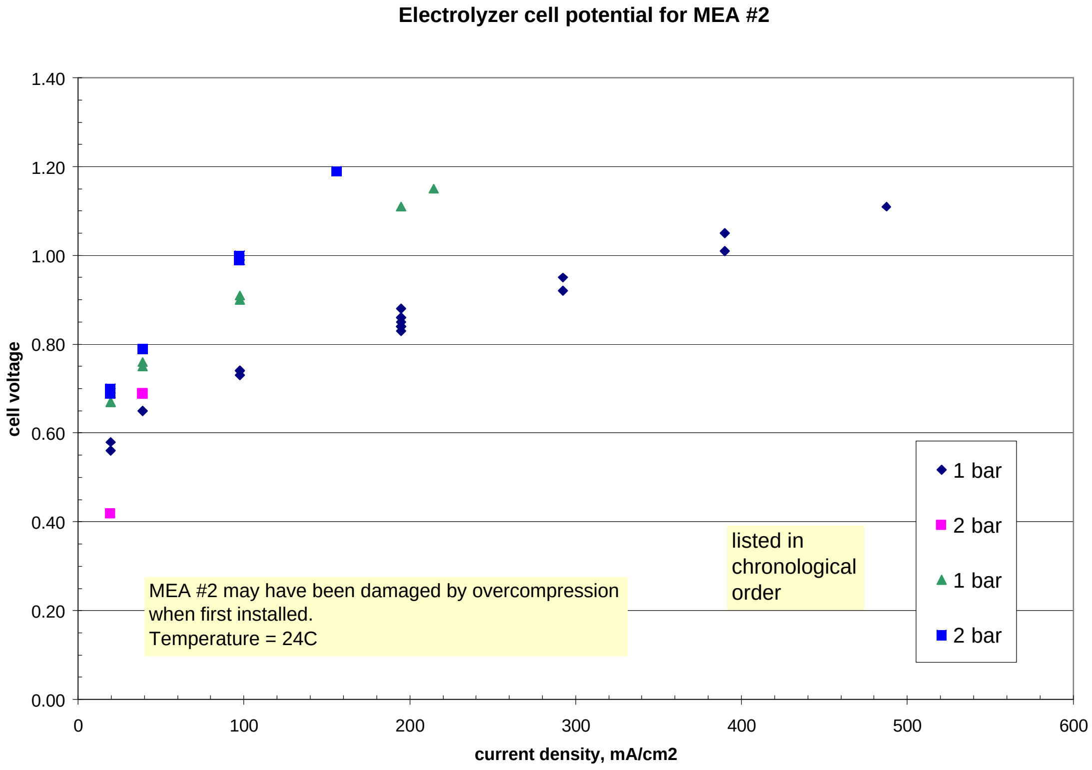


Figure 16 Cell Voltages for MEA #2

3.3.4 Results for MEA #3

Starting with MEA #3, an effort was made to balance pressure across the membrane to prevent mechanical damage to the catalyst layers. As a result MEA #3 and MEA #4 exhibited no degradation in performance during testing. Some cell voltages measured for MEA #3 are plotted in Figure 17. Increasing from 1 atm to 2 atm pressure decreased the cell voltage, but a further increase in pressure did not decrease cell voltage.

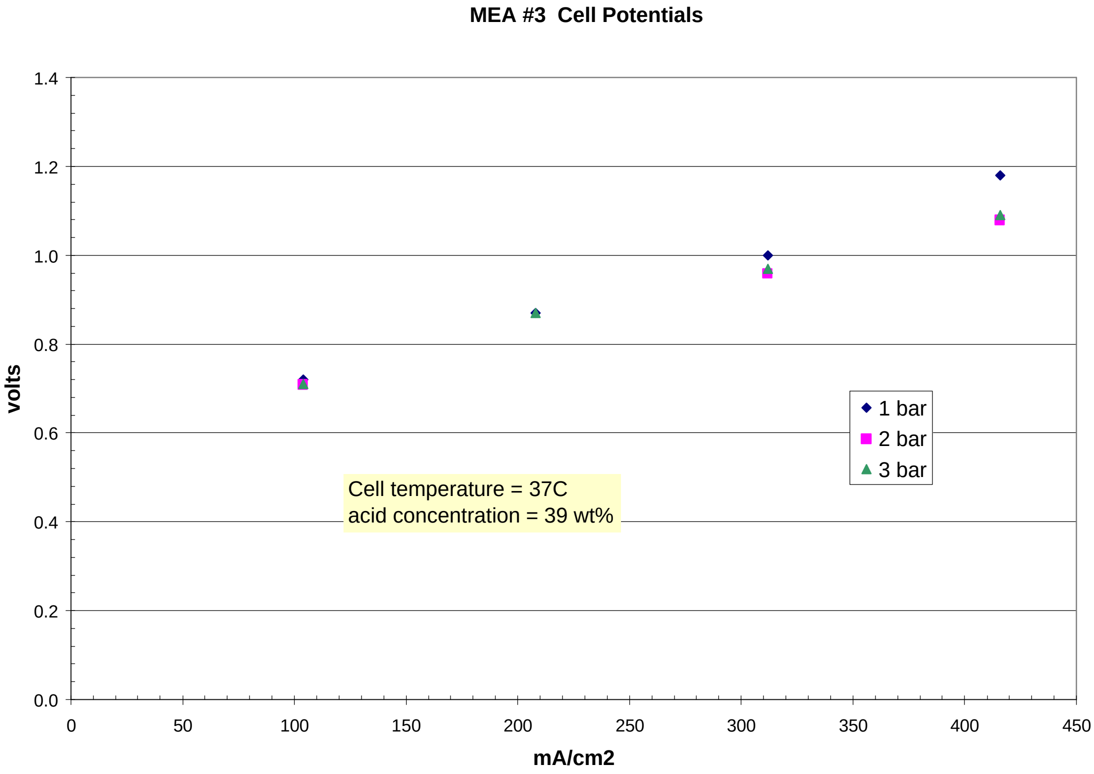


Figure 17 MEA #3 Cell Potentials for 37ºC and 39 wt% Acid

3.3.5 Results for MEA #4

MEA #4 was the most carefully treated Nafion® based MEA. Attention was paid to avoiding pressure drops across the membrane, the cell was left full of anolyte at the end of every day of testing and Belleville spring washers were used in the cell assembly to accommodate thermal expansion. As the result of these measures, MEA #4 showed no degradation during testing. Figure 18 compares cell potentials for the first and last day of testing MEA #4 for ambient conditions. Cell potentials for the last day of testing are actually slightly less, as the result of a slightly higher temperature and a slightly lower acid concentration. Figure 19 plots cell potentials for combinations of temperature and Anolyte Absorber pressure. Increasing pressure from 1 atm to 2 atm at 25ºC decreased cell potential by 30 mV. However, changing from 3 atm to 4 atm at 70ºC made no significant change in cell potential. Modest increases in temperature had a significant effect on cell potential. Increasing temperature from 25ºC to 50ºC at 2 atm decreased potential by about 120 mV. Increasing temperature from 50ºC to 70ºC at 3 atm decreased cell potential by about 60 mV.

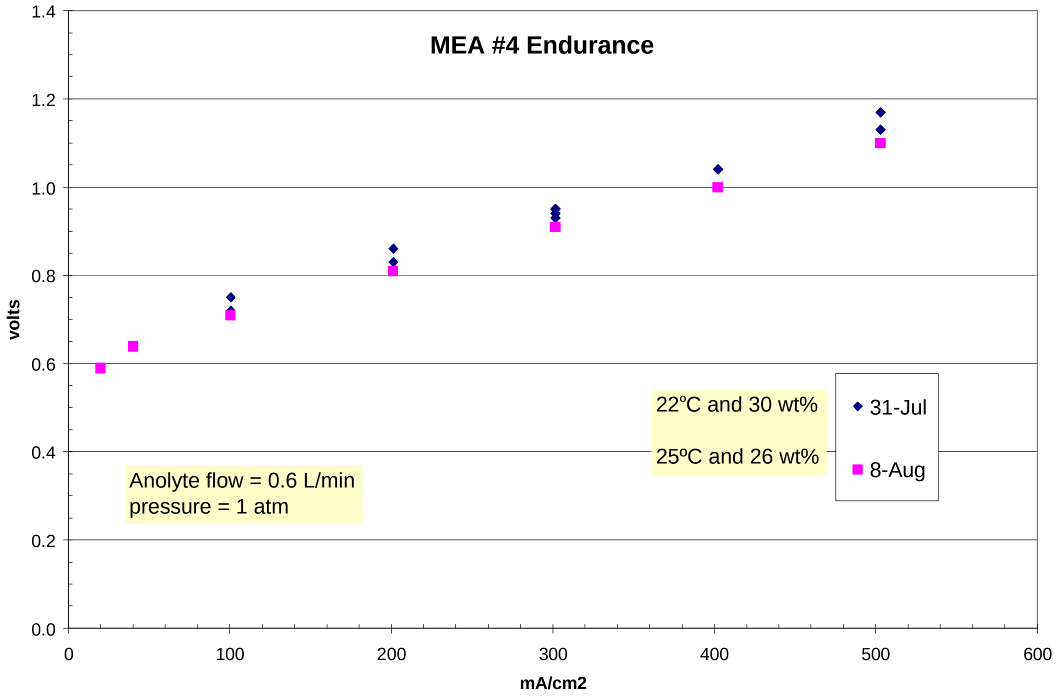


Figure 18 Comparison of MEA #4 Cell Potentials for First and Last Days of Testing

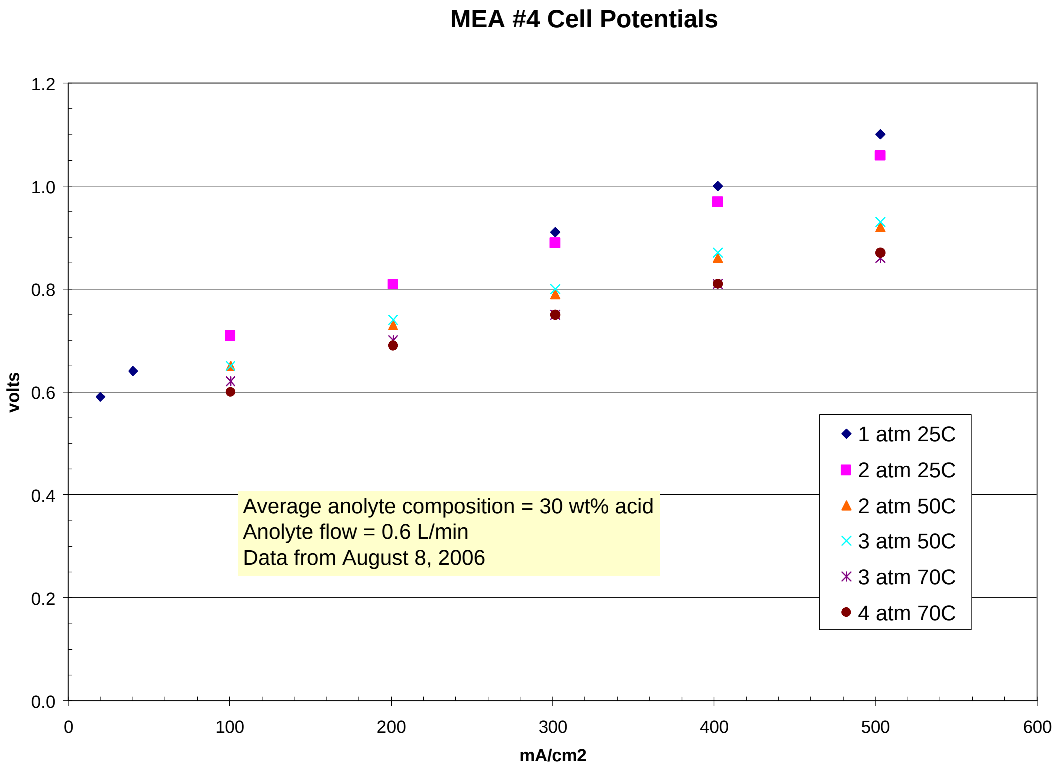


Figure 19 Cell Potentials for Last Day of Testing MEA #4

3.3.6 Results for MEA #5

MEA #5 was observed to have unexpectedly low voltages, but also very low rates of hydrogen production. We conclude that the low hydrogen production resulted from an electrical short through the MEA. We speculate that hot pressing this thin 2 mil membrane caused catalyst particles on opposite sides of the membrane to short electrically. An effort was made to correct the data by assuming that the effective current density was equal to current required to generate the measured amount of hydrogen, divided by cell area. The results are shown in Figure 20, in which the corrected results for MEA #5 are compared to MEA #4. While the data correction introduces scatter, the results were comparable. MEA #5 was removed from service after limited testing.

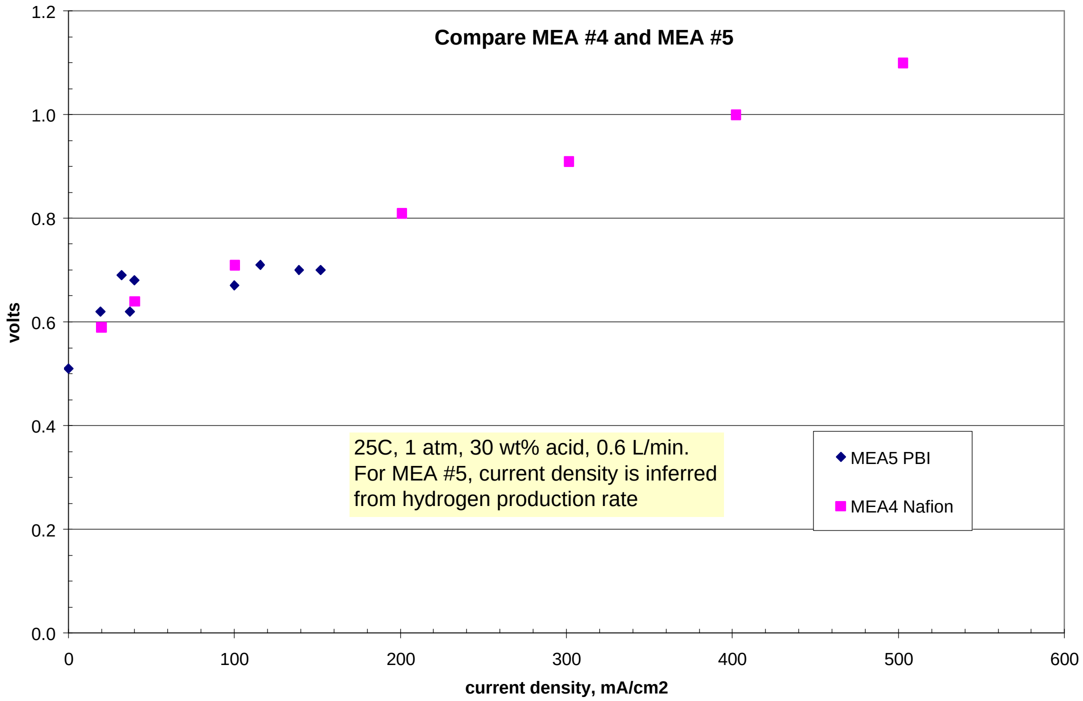


Figure 20 Comparison of Cell Potentials for MEA #5 and MEA #4

3.3.7 Results for MEA #6

MEA #6 was constructed by coating catalyst on one side of two separate 2 mil PBI membranes. The two catalyst coated membranes were then installed in the cell with the catalyst layers facing outward. Cell potentials for ambient conditions are plotted in Figure 21 and were as much as 100 mv less than for MEA #4. This was expected because Colon-Mercado, et al. [2006] measured 20% higher ionic conductance for Celtec-L PBI than for Nafion® 117. Figure 22 plots hydrogen production rate for the two membranes. The PBI membrane gave a lower measured hydrogen rate, implying that more sulfur dioxide crossed the membrane and reacted with product hydrogen. This was counter to expectation, because the measured diffusion coefficient for Celtec-L is one-seventh as much as for Nafion. The explanation may be that the hydrogen ions are dragged electrically across the membrane. They carry water molecules with them, which carry sulfur dioxide molecules with them. These effects were not captured in the measurement of diffusivity.

Testing of MEA#6 was extended to 2 atm pressure. No steady conditions were obtained. For a current of 15 amperes, the cell voltage continuously increased at a rate of 10 mV per minute. An insulating layer may have been forming between the two membranes. Upon disassembly, nothing out of the ordinary was observed.

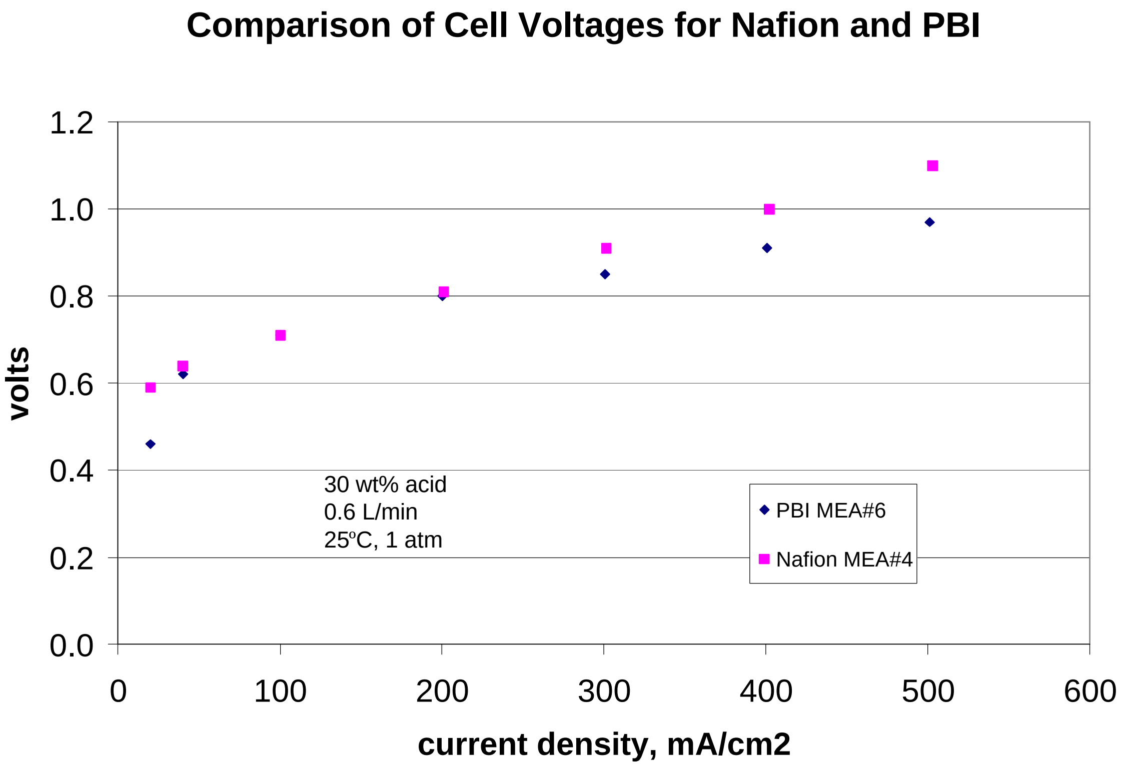


Figure 21 Comparison of Cell Potentials for MEA #6 and MEA #4

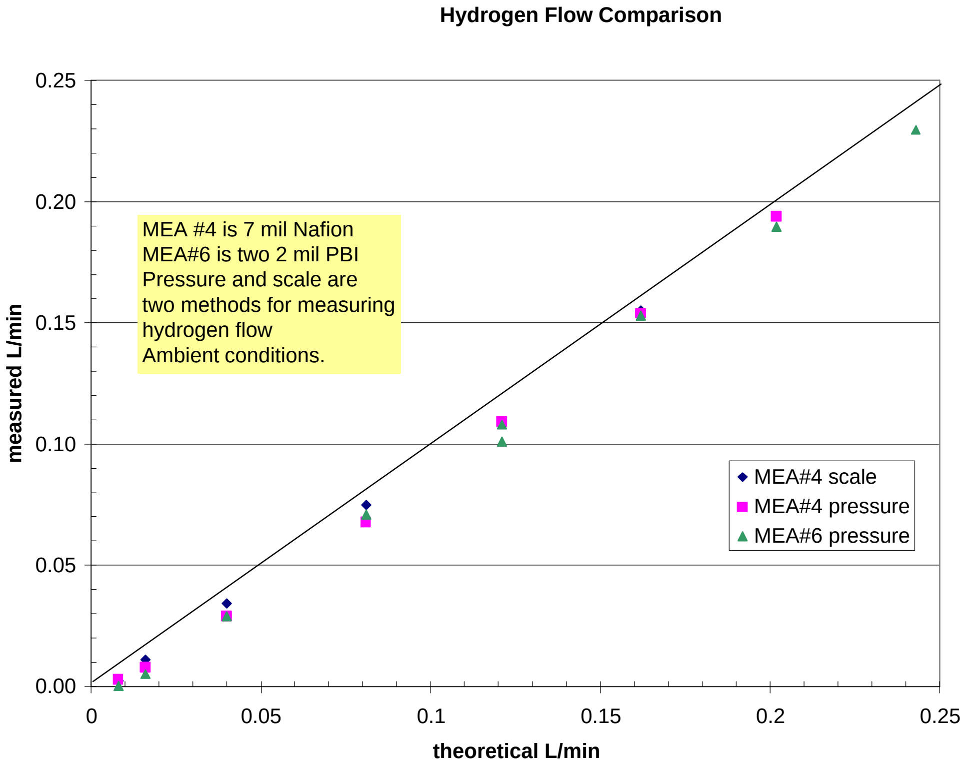


Figure 22 Hydrogen Flow Comparison for Nafion and PBI

3.3.8 Effect of Acid Concentration on Cell Potential

Figure 23 shows the effect of acid concentration on cell potential for MEA #4 and ambient temperature. Cell potentials were the least for acid concentrations of 26 wt% and the most for 45 wt%. The difference was about 100 mv.

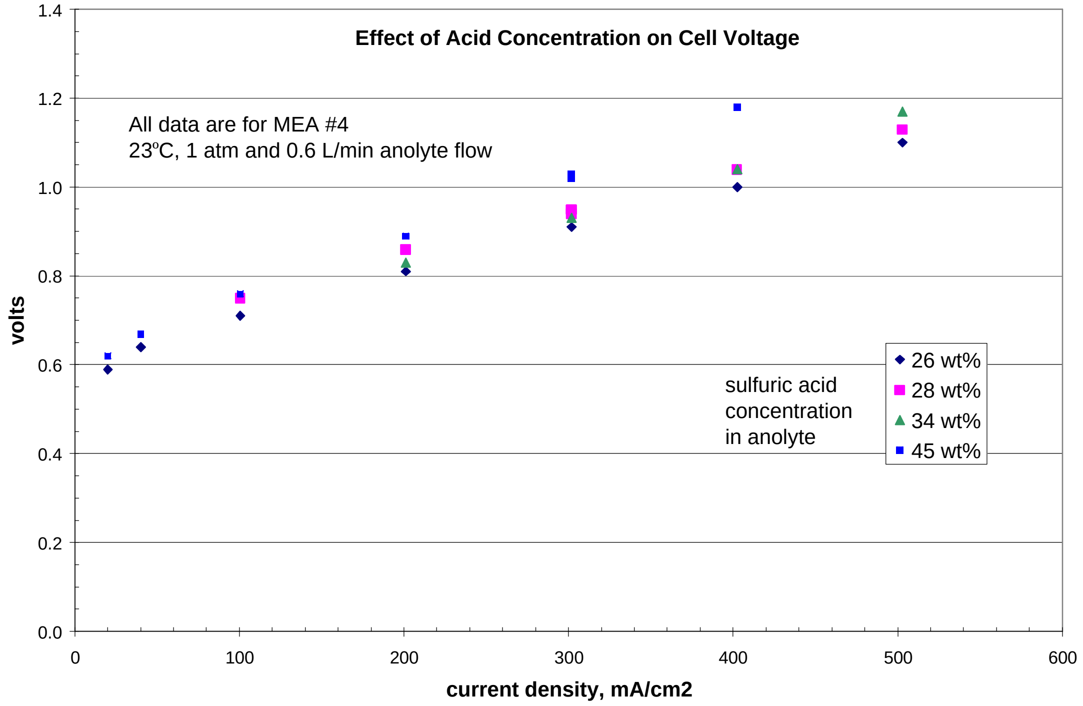


Figure 23 Effect of Acid Concentration on Cell Potential

3.3.9 Effect of Anolyte Flowrate on Cell Potential

For most of the testing, the anolyte flowrate was kept high, typically 0.6 L/min, to assure that the cell was not mass transfer limited and that the concentration of sulfur dioxide reactant was uniformly high throughout the cell. This gave the minimum voltage in the cell for a particular MEA, cell temperature and partial pressure of sulfur dioxide. On five occasions, a range of anolyte flowrates was used to test the effect of flowrate, all else being held constant. The results are plotted in Figure 24. Decreasing the flowrate below 0.2 L/min always increased the cell voltage, but the size of the increase varied. For two cases, the cell voltage increased by less than 0.1 volt. But for one case the voltage increased by more than 0.28 volt. For the case just mentioned, the increase in cell voltage was probably not the result of depletion of sulfur dioxide reactant because single pass conversion was small, for the lowest flowrate it was 8%. Conversely, the exit concentration of sulfur dioxide was 92% of the inlet concentration. This indicates the potential for improving the cell design to increase mass transfer at relatively low flowrates.

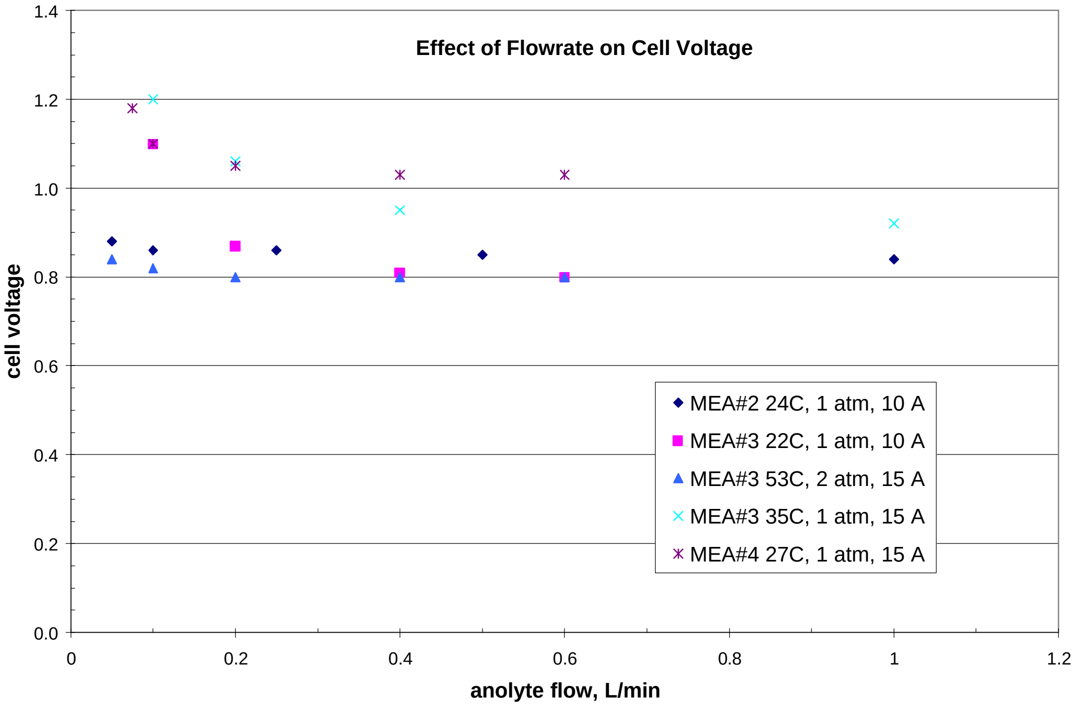


Figure 24 Effect of Anolyte Flowrate on Cell Voltage

3.3.10 Effect of Pressure on Net Hydrogen Production Rate

Figure 25 plots data for hydrogen production rate for MEA #4 for ambient temperature pressures of one and two atmospheres. Hydrogen rate using the two measurement methods is compared with the theoretical production rate. Net hydrogen production was less at the higher pressure. This is consistent with more sulfur dioxide crossing the membrane at the higher pressure and thus, higher SO_2 concentration in the anolyte. Sulfur dioxide crossing the membrane reacts with and consumed product hydrogen.

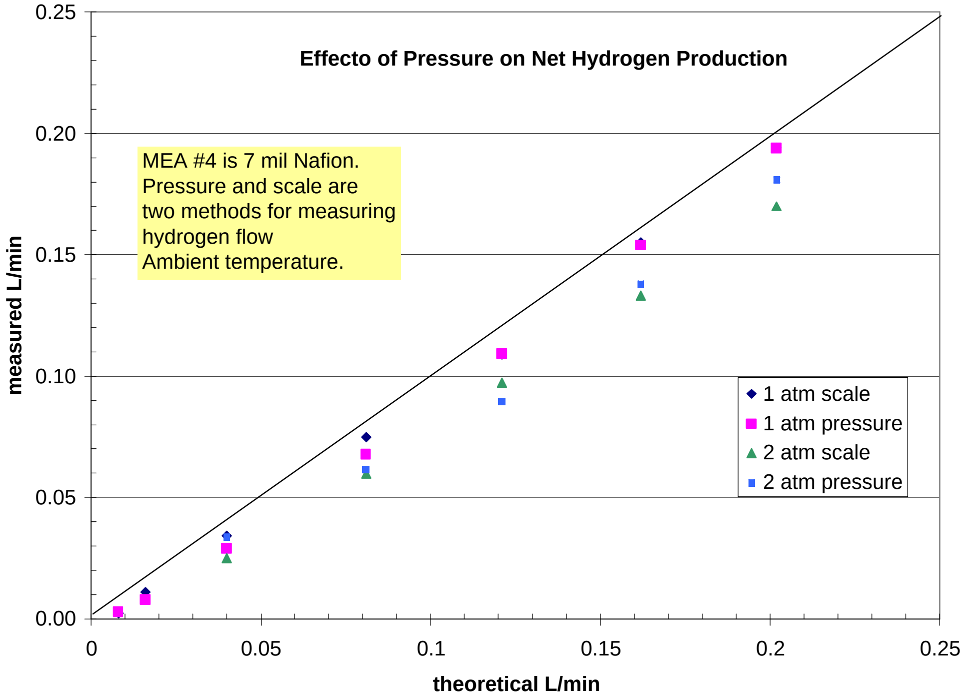


Figure 25 Net Hydrogen Production as Function of Pressure

3.3.11 Results for Sulfur Dioxide Concentration

Samples of anolyte were collected at various times and analyzed for sulfur dioxide using the wet chemistry analysis previously described. Results for 30 wt% acid and 38 wt% acid are plotted in Figure 25 and Figure 26, respectively. Also plotted as connected points are estimates of sulfur dioxide concentration provided by M. Gorensek using literature data. The wet chemistry method measured concentrations that are typically half to two-thirds as large as the Gorensek predictions. The wet chemistry measurements are suspect. One possible explanation for the discrepancy that some of the sulfur dioxide is not dissolved and escapes when the sample is collected. Another explanation is that some chemical species that accumulates in the anolyte, either metallic or sulfur containing, interferes with the analysis. As evidence of this, the sulfur dioxide concentration for the anolyte sample for 30 wt% acid, 2 atm and 45ºC agrees well with the Gorensek prediction and the sample was collected immediately after changing to fresh anolyte.

Sulfur dioxide concentrations were also measured using mass balance. To do this, liquid sulfur dioxide was metered to the Anolyte Absorber while the vent was closed and the rate of pressure increase was monitored. The density of liquid sulfur dioxide is known so the molar rate of addition is known. The moles of sulfur dioxide in the vapor phase was calculated using the Ideal Gas Law using temperature, pressure and volume of the gas space. The balance of the sulfur dioxide was absorbed in the anolyte. Figure 27 shows that pressure increases in proportion to the moles of liquid sulfur dioxide added. This is in agreement with Henry's Law, which is a useful approximation for dissolved gases. For a given temperature, the partial pressure of a solute is equal to the mole fraction of the solute times the Henry's Law Constant. The constant increases with increasing temperature. The partial pressure of sulfur dioxide is slightly less than the total pressure. Table 3 compares the change in sulfur dioxide concentration using mass balance to the Gorensek predictions.

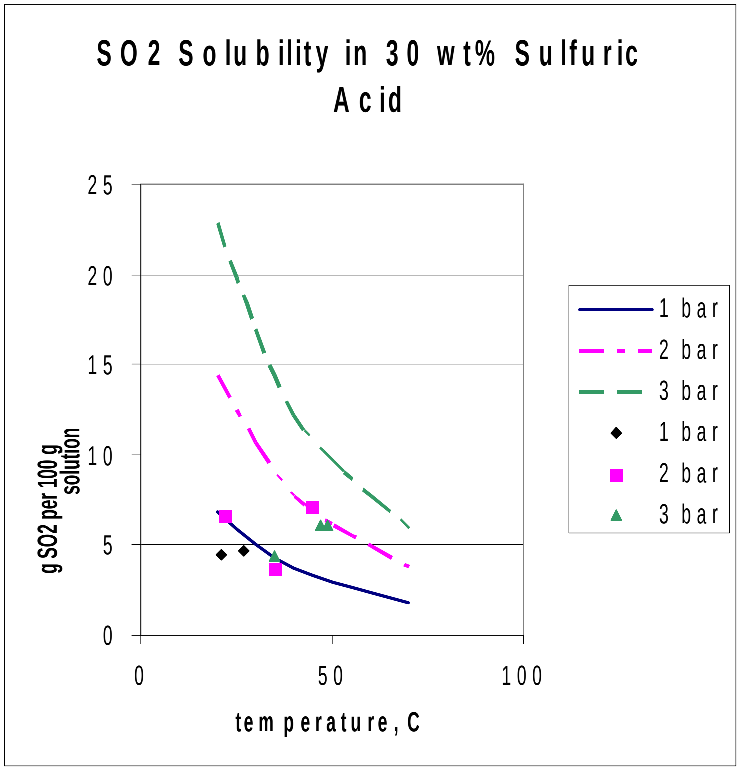


Figure 26 Wet Chemistry Measurement of Sulfur Dioxide, 30 wt% Acid

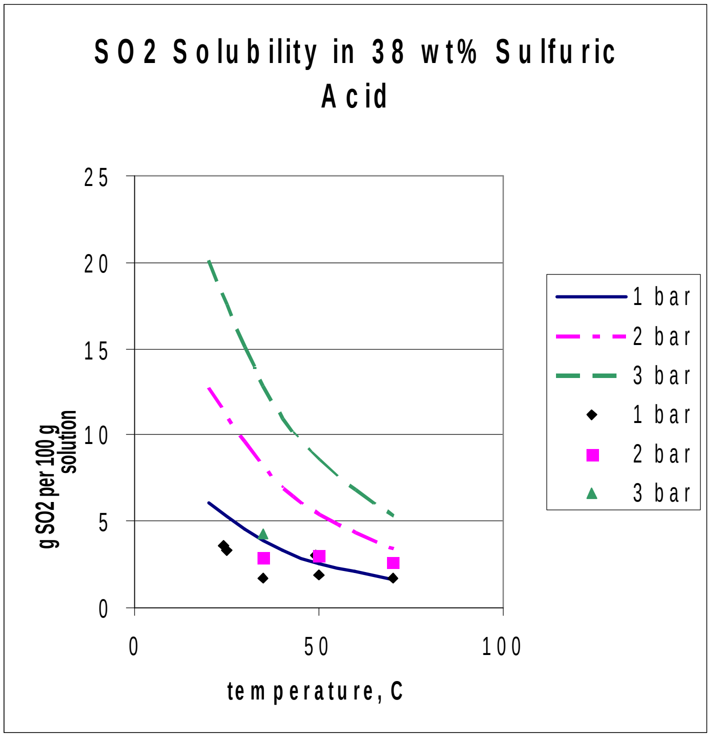


Figure 27 Wet Chemistry Measurement of Sulfur Dioxide, 38 wt% Acid

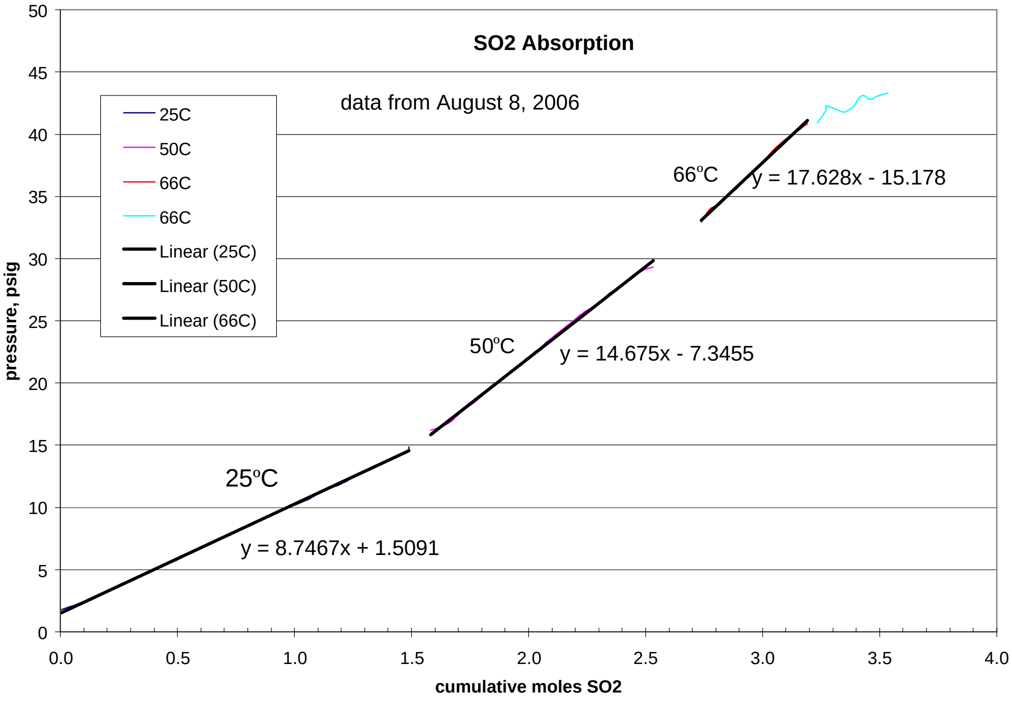


Figure 28 Results of Mass Balance

Table 3 Sulfur Dioxide Concentrations

Temperature, ºC	Initial pressure, atm	Final pressure, atm	Mass balance change in SO_2, g per 100 g anolyte	Gorensek change in SO_2, g per 100 g anolyte
25	1	2	6.7	6.6
50	2	3	3.6	3.5
66	3	4	2.9	2.6

4.0 CONCLUSIONS

The primary conclusions resulting from this work are as follows.

1. The electrolyzer designed, constructed and tested for this study exhibited superior performance to the electrolyzers tested in FY2005.
2. Nafion® based MEA appear to be stable and their performance does not deteriorate when some care is given to avoiding mechanical damage, such as would result from pressure swings across the membrane.
3. The thin 2 mil thick PBI membrane exhibited low efficiency for hydrogen production suggesting that the membrane developed electrical shorts. Using two PBI membranes together solved the electrical short problem and for ambient conditions, the cell voltages were lower. However, the net hydrogen production rates were less, implying more sulfur dioxide crossover. Also, after initial testing the cell voltage increased, implying the formation of an insulating layer between the membranes, either hydrogen, sulfur dioxide gas or elemental sulfur. We recommend testing a thicker PBI membrane.
4. Increasing sulfur dioxide partial pressure generally decreased cell voltage, all else being held constant.
5. Increasing temperature decreased cell voltage, all else being held constant. This was despite a lower solubility of sulfur dioxide in the anolyte. Probable reasons are higher reaction rate at higher temperature and lower viscosity of anolyte which aids mass transfer.
6. Above around 0.4 L/min cell voltage was independent of anolyte flowrate through the cell. Below 0.2 L/min cell voltage increased with decreasing flowrate. The probable reason is mass transfer limitation rather than average concentration of sulfur dioxide in the anolyte. The lowest SO2 concentration tested was 1.8 wt% at 1 atm and 70ºC. At a flow of 0.6 L/min and a current of 20 amperes, only 3% of the sulfur dioxide flowing into the cell reacts.
7. There was no indication of sulfur poisoning of the catalyst, at least for the conditions and periods of time tested.
8. The wet chemistry analysis for sulfur dioxide using the Bunsen Reaction under-predicted the concentration. However, the use of mass balance gave results that were consistent with published literature values.

5.0 FUTURE WORK

Based on the promising results and progress shown in this study we recommend the following activities during FY07 for continued development of the SO2 Depolarized Electrolyzer for hydrogen production.

1. Continue development of MEA with decreased sulfur dioxide crossover and increased ionic conductivity for improved cell performance.
2. Demonstrate operation of a single cell electrolyzer for a minimum of 100 hours.
3. Design, build and test a three cell electrolyzer stack.

6.0 REFERENCES

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7.0 APPENDIX 1 TYPICAL RAW DATA

DATE	TIME	T 1	T 2	T 3	T 4	P 1	P 2	P 3	P 4	anol. flow	SCALE
6/28/2006	13:12:11	21.828	22.307	21.687	22.282	1.735	-1.661	0.166	15.019	0.501	2.772
6/28/2006	13:12:21	21.829	39.114	21.703	22.288	1.735	-1.662	0.17	15.111	0.496	2.772
6/28/2006	13:12:31	21.823	42.864	21.687	22.287	1.733	-1.662	0.16	15.028	0.501	3.242
6/28/2006	13:12:41	21.859	41.722	21.703	22.308	1.733	-1.662	0.13	15.118	0.498	3.278
6/28/2006	13:12:51	21.849	40.373	21.703	22.333	1.724	-1.66	0.12	14.798	0.501	3.295
6/28/2006	13:13:01	21.859	39.589	21.693	22.343	1.729	-1.661	0.114	15.04	0.5	3.314
6/28/2006	13:13:11	21.859	39.927	21.683	22.343	1.728	-1.662	0.105	14.842	0.504	3.393
6/28/2006	13:13:21	21.875	39.693	21.689	22.359	1.728	-1.662	0.099	14.987	0.502	3.55
6/28/2006	13:13:31	21.879	39.207	21.673	22.348	1.728	-1.662	0.107	14.936	0.499	3.686
6/28/2006	13:13:41	21.885	38.079	21.679	22.369	1.726	-1.662	0.093	14.955	0.498	3.741
6/28/2006	13:13:51	21.88	37.986	21.679	22.374	1.724	-1.662	0.014	14.948	0.5	3.79
6/28/2006	13:14:02	21.89	38.236	21.669	22.384	1.722	-1.662	-0.024	15.054	0.5	3.921

DP1	COND	ICELL	E supply	E cell	pmp A flow	pmp A prs	pmp B flow	pmp B prs
2.735	8.341	0	0	0	0	90	1	39.8
2.643	8.341	0.311	0.305	0.307	0	89.8	1	39.6
2.777	8.342	0.963	0.391	0.385	0	89.8	1	39.8
2.67	8.342	1.005	0.398	0.392	0	90.2	1	39.8
2.674	8.342	1.005	0.401	0.394	0	90	1	39.8
2.631	8.342	1.005	0.402	0.396	0	90	1	40
2.662	8.34	1.005	0.404	0.398	0	90	1	39.8
2.67	8.338	1.005	0.405	0.399	0	90.2	1	39.8
2.785	8.339	1.005	0.406	0.401	0	90.2	0	39.8
2.67	8.34	1.005	0.408	0.402	0	90	0	39.8
2.601	8.338	1.005	0.408	0.403	0	90	0	39.8
2.685	8.337	1.005	0.41	0.404	0	90	0	39.8

9.0 APPENDIX 2 DATA SUMMARY FOR 2006

date	time	anolyte flow, L/m	acid Wt%	press. atm	temper-ature, C	current amps	current density mA/cm^2	volts	MEA	kcoul.
27-Jun	14:27	0.5	20.6	1.1	24	10	204	0.80	1	2.2
27-Jun	14:30	0.5	20.6	1.1	24	5	102	0.68	1	4.0
27-Jun	14:40	0.5	20.7	1.1	25	15	306	0.96	1	7.0
28-Jun	13:19	0.5	20.7	1.1	23	1	20	0.42	1	8.8
28-Jun	13:43	0.5	20.8	1.1	23	2	41	0.63	1	10.3
28-Jun	13:47	0.5	20.8	1.1	23	5	102	0.75	1	10.8
28-Jun	13:59	0.5	20.9	1.1	24	10	204	0.97	1	14.4
28-Jun	14:06	0.5	21.0	1.1	24	7.5	153	0.87	1	18.6
28-Jun	14:41	0.1	21.4	1.1	24	1	20	0.46	1	34.3
28-Jun	14:46	0.1	21.4	1.2	24	2	41	0.68	1	34.6
28-Jun	14:55	0.1	21.4	1.2	24	5	102	0.85	1	35.7
28-Jun	15:00	0.1	21.4	1.2	25	7.5	153	1.20	1	37.2
28-Jun	15:21	0.1	21.7	2.1	24	1	20	0.43	1	46.6
28-Jun	15:41	0.1	21.7	2.4	24	2	41	0.71	1	47.8
28-Jun	15:59	0.1	21.7	2.4	25	5	102	0.96	1	50.0
29-Jun	9:40	0.5	21.8	1.1	22	1	20	0.70	1	54.5
14-Jul	10:14	0.5	26.0	1.1	23	1	19	0.56	2	102.1
14-Jul	10:32	0.5	26.0	1.1	23	5	97	0.73	2	103.2
14-Jul	10:35	0.5	26.0	1.1	23	10	195	0.83	2	104.1
14-Jul	10:41	0.5	26.1	1.1	23	15	292	0.92	2	107.7
14-Jul	10:44	0.5	26.2	1.1	24	25	487	1.11	2	110.4
14-Jul	10:47	0.5	26.3	1.1	24	2	39	0.65	2	114.9
14-Jul	10:50	0.5	26.3	1.1	24	5	97	0.74	2	115.2
14-Jul	10:53	0.5	26.4	1.1	24	10	195	0.84	2	116.1
14-Jul	10:56	0.5	26.4	1.1	24	20	390	1.01	2	117.9
14-Jul	11:00	0.1	26.6	1.0	25	20	390	1.05	2	122.7
14-Jul	11:03	0.1	26.7	1.0	24	10	195	0.84	2	126.3
14-Jul	11:06	0.1	26.7	1.0	24	5	97	0.74	2	128.1
14-Jul	11:09	0.1	26.7	1.0	24	2	39	0.65	2	129.0
14-Jul	11:13	0.1	26.8	1.0	24	1	19	0.58	2	129.5
14-Jul	11:21	0.1	26.8	1.0	25	15	292	0.95	2	130.0
14-Jul	12:55	1	27.4	1.1	24	10	195	0.84	2	153.3
14-Jul	13:01	0.5	27.5	1.1	24	10	195	0.85	2	156.9
14-Jul	13:07	0.25	27.6	1.1	25	10	195	0.86	2	160.5
14-Jul	13:11	0.1	27.7	1.0	25	10	195	0.86	2	162.9
14-Jul	13:17	0.05	27.8	1.0	25	10	195	0.88	2	166.5
14-Jul	14:09	0.5	28.7	2.1	26	1	19	0.42	2	197.7
14-Jul	14:47	0.5	28.7	2.0	26	2	39	0.69	2	200.0
17-Jul	12:39	0.5	28.8	1.1	22	1	19	0.67	2	201.8
17-Jul	12:48	0.5	28.8	1.1	23	2	39	0.76	2	202.4
17-Jul	13:13	0.5	28.9	1.1	23	5	97	0.90	2	205.4
17-Jul	13:17	0.5	28.9	1.1	23	10	195	1.11	2	206.6
17-Jul	13:33	0.5	29.2	1.1	24	11	214	1.15	2	216.2

DATA SUMMARY FOR 2006

date	time	anolyte flow, L/m	acid Wt%	press. atm	temperature, C	current amps	current density mA/cm^2	volts	MEA	kcoul.
17-Jul	13:35	0.5	29.2	1.1	24	10	195	1.11	2	217.5
17-Jul	13:39	0.5	29.3	1.1	24	5	97	0.91	2	219.9
17-Jul	13:44	0.5	29.3	1.1	24	2	39	0.75	2	221.4
17-Jul	13:49	0.5	29.3	1.1	24	1	19	0.67	2	222.0
18-Jul	10:28	0.5	29.3	2.0	23	1	19	0.69	2	222.1
18-Jul	10:32	0.5	29.3	2.0	23	2	39	0.79	2	222.4
18-Jul	10:36	0.5	29.3	2.0	23	5	97	1.00	2	222.9
18-Jul	10:39	0.5	29.4	2.0	23	8	156	1.19	2	223.8
18-Jul	10:44	0.5	29.4	2.0	23	5	97	0.99	2	226.2
18-Jul	10:46	0.5	29.4	2.0	23	2	39	0.79	2	226.8
18-Jul	10:48	0.5	29.5	2.0	23	1	19	0.70	2	227.0
19-Jul	16:06	0.2	25.7	1.1	28	5	104	0.62	3	230.0
19-Jul	16:10	0.2	25.8	1.1	28	10	208	0.75	3	234.0
20-Jul	7:25	0.2	25.8	1.1	22	1	21	0.21	3	234.6
20-Jul	7:32	0.2	25.9	1.1	22	2	42	0.40	3	236.0
20-Jul	7:36	0.2	25.9	1.1	22	5	104	0.68	3	237.6
20-Jul	7:43	0.2	26.0	1.1	22	10	208	0.87	3	240.5
20-Jul	7:51	0.4	26.1	1.1	22	10	208	0.81	3	244.5
20-Jul	7:53	0.6	26.2	1.1	22	10	208	0.80	3	247.0
20-Jul	7:57	0.1	26.3	1.0	23	10	208	1.10	3	249.7
20-Jul	7:59	0.6	26.3	1.1	23	15	312	1.04	3	250.5
20-Jul	8:13	0.6	26.3	1.1	22	5	104	0.67	3	251.0
20-Jul	14:05	0.6	28.6	2.0	52	5	104	0.61	3	331.1
20-Jul	14:15	0.6	28.7	2.0	51	10	208	0.70	3	338.0
20-Jul	14:23	0.6	28.9	2.1	51	15	312	0.76	3	343.4
20-Jul	14:30	0.6	29.1	2.1	51	20	416	0.82	3	351.3
24-Jul	9:23	0.6	25.8	2.1	51	10	208	0.73	3	367.2
24-Jul	9:34	0.6	26.0	2.0	52	15	312	0.79	3	373.8
24-Jul	9:53	0.6	26.5	2.0	51	20	416	0.86	3	390.9
24-Jul	10:02	0.6	26.8	2.1	51	25	520	0.92	3	401.7
24-Jul	10:07	0.6	27.0	2.0	51	5	104	0.63	3	409.2
24-Jul	10:07	0.6	27.0	2.0	51	15	312	0.80	3	409.2
24-Jul	10:11	0.4	27.1	2.0	52	15	312	0.80	3	412.8
24-Jul	10:13	0.2	27.2	2.0	53	15	312	0.80	3	414.6
24-Jul	10:17	0.1	27.3	2.0	53	15	312	0.82	3	418.2
24-Jul	10:19	0.05	27.3	2.0	53	15	312	0.84	3	420.0
24-Jul	10:36	0.6	27.8	3.1	62	15	312	0.79	3	435.3
24-Jul	10:41	0.2	27.9	3.1	52	15	312	0.79	3	439.8
24-Jul	10:51	0.05	28.1	3.1	52	15	312	0.82	3	448.8
24-Jul	10:59	0.6	28.3	3.1	51	25	520	0.92	3	456.0
24-Jul	11:06	0.6	28.6	3.2	52	10	208	0.73	3	466.5
24-Jul	11:10	0.6	28.7	3.3	52	5	104	0.60	3	468.9
24-Jul	12:35	0.6	29.7	3.0	52	10	208	0.73	3	507.0

DATA SUMMARY FOR 2006

date	time	anolyte flow, L/m	acid Wt%	press. atm	temper-ature, C	current amps	current density mA/cm^2	volts	MEA	kcoul.
24-Jul	14:08	0.6	31.2	2.9	73	10	208	0.69	3	562.8
24-Jul	14:16	0.6	31.3	2.9	75	20	416	0.82	3	567.6
24-Jul	14:21	0.6	31.5	2.9	76	25	520	0.88	3	573.6
24-Jul	14:27	0.6	31.7	2.9	76	15	312	0.77	3	582.6
24-Jul	14:33	0.6	31.8	2.9	77	5	104	0.60	3	588.0
25-Jul	10:57	0.6	31.9	1.1	39	15	312	0.95	3	590.0
25-Jul	11:03	0.6	31.9	1.1	39	20	416	1.13	3	592.0
25-Jul	11:10	0.6	31.9	1.1	37	10	208	0.83	3	592.0
25-Jul	11:14	0.6	32.0	1.1	37	5	104	0.70	3	594.4
25-Jul	11:16	0.2	32.0	1.0	38	15	312	1.06	3	595.0
25-Jul	11:20	0.1	32.1	1.1	38	15	312	1.20	3	598.6
25-Jul	11:26	0.4	32.2	1.1	37	15	312	0.95	3	604.0
25-Jul	11:28	1	32.3	1.1	36	15	312	0.92	3	605.8
25-Jul	11:42	0.6	32.6	2.0	37	15	312	0.88	3	618.4
25-Jul	11:57	0.6	32.9	1.9	37	5	104	0.68	3	631.9
25-Jul	12:04	0.6	33.0	2.0	37	10	208	0.79	3	634.0
25-Jul	12:14	0.6	33.1	2.1	37	20	416	0.97	3	640.0
25-Jul	12:27	0.6	33.5	2.0	37	25	520	1.07	3	655.6
25-Jul	12:34	0.2	33.8	2.0	37	15	312	0.91	3	666.1
25-Jul	12:38	0.1	33.9	2.0	37	15	312	0.92	3	669.7
25-Jul	12:53	0.6	34.2	3.2	37	15	312	0.90	3	683.2
25-Jul	13:03	0.6	34.5	3.2	37	20	416	0.97	3	694.0
25-Jul	13:08	0.6	34.8	3.2	37	25	520	1.08	3	706.5
25-Jul	13:13	0.6	34.9	3.2	37	10	208	0.82	3	714.0
25-Jul	13:18	0.6	35.0	3.1	37	5	104	0.68	3	717.0
25-Jul	13:40	0.6	35.3	3.1	51	15	312	0.86	3	728.9
25-Jul	13:48	0.6	35.5	3.0	53	20	416	0.95	3	736.1
25-Jul	13:52	0.6	35.6	2.9	53	25	520	1.03	3	740.9
26-Jul	13:06	0.6	36.9	1.1	23	15	312	1.09	3	800.0
26-Jul	13:13	0.6	37.1	1.1	24	10	208	0.93	3	806.3
26-Jul	13:22	0.6	37.2	1.1	24	5	104	0.76	3	811.7
26-Jul	13:39	0.6	37.3	1.1	38	15	312	1.00	3	816.8
26-Jul	13:44	0.6	37.4	1.1	39	20	416	1.18	3	821.3
26-Jul	13:51	0.6	37.6	1.1	38	10	208	0.87	3	829.7
26-Jul	13:57	0.6	37.7	1.1	37	5	104	0.72	3	833.3
26-Jul	14:33	0.6	37.9	2.0	37	15	312	0.96	3	844.1
26-Jul	14:45	0.6	38.2	2.0	37	20	416	1.08	3	854.9
26-Jul	14:53	0.6	38.4	2.1	37	5	104	0.71	3	864.5
26-Jul	15:09	0.6	38.5	3.0	37	15	312	0.97	3	869.3
26-Jul	15:34	0.6	39.0	3.5	37	20	416	1.09	3	891.8
26-Jul	15:39	0.6	39.1	3.2	37	10	208	0.87	3	897.8
26-Jul	15:42	0.6	39.1	3.2	37	5	104	0.71	3	899.6
26-Jul	15:53	0.6	39.2	4.3	37	15	312	1.00	3	902.9

DATA SUMMARY FOR 2006

date	time	anolyte flow, L/m	acid Wt%	press. atm	temper- ature, C	current amps	current density mA/cm^2	volts	MEA	kcoul.
26-Jul	15:58	0.6	39.3	4.2	37	20	416	1.11	3	907.4
26-Jul	16:06	0.6	39.5	4.1	37	10	208	0.89	3	917.0
26-Jul	16:11	0.6	39.6	4.1	37	5	104	0.71	3	920.0
31-Jul	10:32	0.6	25.7	1.1	24	15	302	0.95	4	929.4
31-Jul	12:11	0.6	28.4	1.1	25	15	302	0.95	4	1024.1
31-Jul	12:29	0.6	28.9	1.1	26	5	101	0.75	4	1040.3
31-Jul	12:34	0.6	28.9	1.1	26	10	201	0.86	4	1041.8
31-Jul	12:39	0.6	29.0	1.1	26	20	402	1.04	4	1044.8
31-Jul	12:44	0.6	29.1	1.1	26	25	503	1.13	4	1050.8
31-Jul	12:50	0.6	29.4	1.1	26	15	302	0.95	4	1059.8
31-Jul	13:34	0.6	30.4	1.1	27	15	302	0.94	4	1099.4
1-Aug	7:09	0.6	33.9	1.1	23	15	302	0.93	4	1236.9
1-Aug	7:15	0.6	34.1	1.1	24	20	402	1.04	4	1242.3
1-Aug	7:25	0.6	34.3	1.1	24	25	503	1.17	4	1254.3
1-Aug	7:30	0.6	34.5	1.1	24	10	201	0.83	4	1261.8
1-Aug	7:35	0.6	34.6	1.1	24	5	101	0.72	4	1263.0
1-Aug	10:35	0.6	34.6	1.1	52	15	302	0.81	4	1264.0
1-Aug	10:41	0.6	34.7	1.1	52	20	402	0.90	4	1269.4
1-Aug	10:46	0.6	34.9	1.1	52	25	503	1.02	4	1275.4
1-Aug	10:51	0.6	35.0	1.1	52	10	201	0.73	4	1282.9
1-Aug	10:56	0.6	35.1	1.1	52	5	101	0.65	4	1285.9
1-Aug	10:58	0.6	35.1	1.1	52	2	40	0.58	4	1286.5
1-Aug	11:00	0.6	35.1	1.1	52	1	20	0.53	4	1286.7
1-Aug	11:13	0.6	35.1	1.1	52	15	302	0.82	4	1287.5
1-Aug	11:44	0.6	35.8	1.1	52	15	302	0.83	4	1315.4
1-Aug	12:28	0.6	35.9	2.0	52	15	302	0.81	4	1320.0
1-Aug	12:35	0.6	36.1	2.0	52	20	402	0.89	4	1326.3
1-Aug	12:40	0.6	36.2	2.0	52	25	503	0.97	4	1332.3
1-Aug	12:52	0.6	36.6	2.0	52	10	201	0.75	4	1350.3
1-Aug	13:01	0.6	36.7	2.0	52	5	101	0.66	4	1355.7
1-Aug	13:54	0.6	37.1	2.0	72	15	302	0.77	4	1371.6
1-Aug	14:02	0.6	37.3	2.1	72	20	402	0.83	4	1378.8
1-Aug	14:13	0.6	37.6	2.1	71	25	503	0.90	4	1392.0
1-Aug	14:20	0.6	37.8	2.0	70	10	201	0.70	4	1402.5
1-Aug	14:25	0.6	37.9	2.1	70	5	101	0.63	4	1405.5
1-Aug	14:33	0.6	37.9	2.1	71	15	302	0.78	4	1407.9
1-Aug	15:02	0.6	38.5	1.1	71	15	302	0.83	4	1434.0
1-Aug	15:08	0.6	38.6	1.1	71	20	402	1.07	4	1439.4
1-Aug	15:09	0.6	38.6	1.1	71	25	503	1.48	4	1440.6
1-Aug	15:18	0.6	38.9	1.1	71	10	201	0.73	4	1454.1
1-Aug	15:23	0.6	39.0	1.1	71	5	101	0.65	4	1457.1
1-Aug	15:26	0.6	39.0	1.1	71	22	443	1.17	4	1458.0
1-Aug	15:28	0.6	38.4	1.1	71	15	302	0.83	4	1430.0

DATA SUMMARY FOR 2006

date	time	anolyte flow, L/m	acid Wt%	press. atm	temper- ature, C	current amps	current density mA/cm^2	volts	MEA	kcoul.
2-Aug	9:09	0.6	38.5	1.1	25	15	302	1.01	4	1434.6
2-Aug	9:19	0.6	38.7	1.1	25	20	402	1.14	4	1443.6
2-Aug	9:24	0.6	38.8	1.1	25	10	201	0.88	4	1449.6
2-Aug	9:29	0.6	38.9	1.1	25	5	101	0.75	4	1452.6
2-Aug	9:34	0.6	38.9	1.1	25	2	40	0.67	4	1454.1
2-Aug	9:47	0.6	39.0	1.1	25	15	302	1.02	4	1455.7
2-Aug	13:34	0.6	43.2	1.1	53	15	302	0.89	4	1660.0
2-Aug	13:42	0.6	43.2	1.1	53	20	402	1.03	4	1663.8
2-Aug	13:47	0.6	43.4	1.1	52	22	443	1.13	4	1669.8
2-Aug	13:58	0.6	43.6	1.1	51	10	201	0.80	4	1684.3
2-Aug	14:03	0.6	43.7	1.1	51	5	101	0.71	4	1687.3
2-Aug	14:08	0.6	43.7	1.1	51	2	40	0.62	4	1688.8
2-Aug	14:13	0.6	43.7	1.1	51	1	20	0.56	4	1689.4
2-Aug	14:36	0.6	43.8	2.1	51	15	302	0.87	4	1690.8
2-Aug	14:43	0.6	43.9	2.0	51	20	402	0.96	4	1697.1
2-Aug	14:48	0.6	44.0	2.0	51	25	503	1.05	4	1703.1
2-Aug	14:55	0.6	44.2	2.0	51	10	201	0.80	4	1713.6
2-Aug	15:00	0.6	44.3	2.0	51	5	101	0.71	4	1716.6
2-Aug	15:14	0.6	44.3	3.1	51	15	302	0.89	4	1720.8
2-Aug	15:20	0.6	44.4	3.0	51	20	402	0.97	4	1726.2
2-Aug	15:25	0.6	44.5	3.0	51	25	503	1.06	4	1732.2
2-Aug	15:29	0.6	44.7	3.0	51	10	201	0.90	4	1738.2
2-Aug	15:32	0.6	44.7	3.0	51	5	101	0.71	4	1740.0
3-Aug	10:18	0.6	44.7	1.1	25	15	302	1.02	4	1741.1
3-Aug	10:27	0.6	44.9	1.1	26	20	402	1.18	4	1749.2
3-Aug	10:33	0.6	45.0	1.1	26	10	201	0.89	4	1756.4
3-Aug	10:38	0.6	45.1	1.1	26	5	101	0.76	4	1759.4
3-Aug	10:43	0.6	45.1	1.1	26	2	40	0.67	4	1760.9
3-Aug	10:46	0.6	45.1	1.1	26	1	20	0.62	4	1761.3
3-Aug	10:50	0.6	45.1	1.1	26	15	302	1.03	4	1761.5
3-Aug	10:54	0.4	45.2	1.1	26	15	302	1.03	4	1765.1
3-Aug	11:00	0.2	45.3	1.1	27	15	302	1.05	4	1770.5
3-Aug	11:05	0.1	45.3	1.1	27	15	302	1.10	4	1775.0
3-Aug	11:10	0.075	45.4	1.1	27	15	302	1.18	4	1779.5
8-Aug	10:25	0.6	25.7	1.1	25	15	302	0.91	4	1781.8
8-Aug	10:31	0.6	25.8	1.1	25	20	402	1.00	4	1787.2
8-Aug	10:39	0.6	26.1	1.1	25	25	503	1.10	4	1796.8
8-Aug	10:45	0.6	26.4	1.1	25	10	201	0.81	4	1805.8
8-Aug	10:51	0.6	26.5	1.1	25	5	101	0.71	4	1809.4
8-Aug	10:56	0.6	26.6	1.1	25	2	40	0.64	4	1815.0
8-Aug	11:00	0.6	26.8	1.1	25	1	20	0.59	4	1820.0
8-Aug	11:16	0.6	27.0	2.0	26	15	302	0.89	4	1828.4
8-Aug	11:23	0.6	27.2	2.0	26	20	402	0.97	4	1836.8

DATA SUMMARY FOR 2006

date	time	anolyte flow, L/m	acid Wt%	press. atm	temper-ature, C	current amps	current density mA/cm^2	volts	MEA	kcoul.
8-Aug	11:28	0.6	27.5	2.0	26	25	503	1.06	4	1844.3
8-Aug	11:33	0.6	27.5	2.0	26	10	201	0.81	4	1847.3
8-Aug	11:38	0.6	27.6	2.0	26	5	101	0.71	4	1848.8
8-Aug	12:19	0.6	29.5	2.1	53	15	302	0.79	4	1917.9
8-Aug	12:31	0.6	29.8	2.1	53	20	402	0.86	4	1928.7
8-Aug	12:36	0.6	29.9	2.0	52	25	503	0.92	4	1934.7
8-Aug	12:42	0.6	30.2	2.0	51	10	201	0.73	4	1943.7
8-Aug	12:47	0.6	30.2	2.0	51	5	101	0.65	4	1946.7
8-Aug	13:01	0.6	30.4	3.0	52	15	302	0.80	4	1950.9
8-Aug	13:06	0.6	30.5	3.1	52	20	402	0.87	4	1955.4
8-Aug	13:11	0.6	30.6	3.1	52	25	503	0.93	4	1961.4
8-Aug	13:16	0.6	30.8	3.2	52	10	201	0.74	4	1968.9
8-Aug	13:19	0.6	30.9	3.2	52	5	101	0.65	4	1970.7
8-Aug	14:18	0.6	31.3	3.1	71	15	302	0.75	4	1988.4
8-Aug	14:23	0.6	31.4	3.1	71	20	402	0.81	4	1992.9
8-Aug	14:30	0.6	31.7	3.1	71	25	503	0.86	4	2001.3
8-Aug	14:35	0.6	31.9	3.1	71	10	201	0.70	4	2008.8
8-Aug	14:40	0.6	31.9	3.1	70	5	101	0.62	4	2011.8
8-Aug	14:51	0.6	32.0	3.9	70	15	302	0.75	4	2015.1
8-Aug	14:57	0.6	32.2	4.0	70	20	402	0.81	4	2020.5
8-Aug	15:01	0.6	32.3	4.1	71	25	503	0.87	4	2025.3
8-Aug	15:06	0.6	32.5	4.3	70	10	201	0.69	4	2032.8
8-Aug	15:08	0.6	32.5	4.2	71	5	101	0.60	4	2034.0
11-Aug	13:21	0.6	25.9	1.1	25	0.90	19	0.62	5	2048.2
11-Aug	13:29	0.6	25.9	1.1	26	6.43	139	0.70	5	2048.6
11-Aug	13:29	0.6	25.9	1.1	26	4.63	100	0.67	5	2048.6
11-Aug	13:41	0.6	26.0	1.1	26	1.49	32	0.69	5	2052.0
11-Aug	13:42	0.6	26.0	1.1	26	1.84	40	0.68	5	2052.1
11-Aug	13:55	0.6	26.0	1.1	26	7.03	152	0.70	5	2053.5
11-Aug	14:00	0.6	26.1	1.1	26	0.00	0	0.51	5	2055.6
11-Aug	14:01	0.6	26.1	1.1	26	1.72	37	0.62	5	2055.6
11-Aug	14:08	0.6	26.1	1.1	26	5.35	116	0.71	5	2056.3
21-Aug	13:12	0.6	29.0	1.0	25	15.00	301	0.85	6	2128.1
21-Aug	13:21	0.6	29.0	1.0	25	20.00	401	0.91	6	2136.2
21-Aug	13:25	0.6	29.0	1.0	25	25.00	501	0.97	6	2141.0
21-Aug	13:48	0.6	29.0	1.0	25	10.00	200	0.80	6	2175.5
21-Aug	13:53	0.6	29.0	1.0	25	5.00	100	0.71	6	2178.5
21-Aug	13:58	0.6	29.0	1.0	25	2.00	40	0.62	6	2180.0
21-Aug	14:03	0.6	29.0	1.0	25	1.00	20	0.46	6	2193.5