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Savannah River National Laboratory
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Prepared for the U.S. Department of Energy Under
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SRNL™

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LIST OF ACRONYMS

atm	atmospheres
DAS	data acquisition system
HyS	Hybrid Sulfur Cycle
MEA	membrane electrode assembly
NHI	Nuclear Hydrogen Initiative
PEM	proton exchange membrane
SDE	SO_2 depolarized electrolyzer
SEM	Scanning Electron Microscopy
SRNL	Savannah River National Laboratory
USC	University of South Carolina

1.0 EXECUTIVE SUMMARY

This document reports the development and testing of a method that eliminates the formation of a sulfur layer previously observed in membrane electrode assemblies (MEA) used in the Hybrid Sulfur Cycle electrolyzer. Testing was performed during the first quarter of FY 2009 at the Savannah River National Laboratory (SRNL) using an electrolyzer cell and test facility designed and built at SRNL. The results of this testing are very important because the sulfur layer increased cell voltage and eventually destroyed the MEA that is the heart of the cell. The sulfur elimination method was tested with eight MEAs. Some tests failed because of hardware and software problems. The most successful tests were conducted with the last two, MEA 36 and MEA 37. MEA 36 was tested 212 hours with stable cell voltage and no formation of sulfur as determined by scanning electron microscopy. This test was completed on June 3, 2009 and satisfied DOE Milestone M1NSR07TC030134 which had a required completion date of June 30. The test of MEA 36 was discontinuous because the system computer crashed midway through. MEA 37 was also tested for 212 hours, but continuously. Cell voltage was stable and no sulfur formed. This test was completed on June 12, 2009 and satisfied DOE Milestone M3NSR07TC030140.0 for September 15.

The HyS Cycle 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. The HyS Cycle utilizes the high temperature (>800ºC) thermal decomposition of sulfuric acid to produce oxygen and regenerate sulfur dioxide. 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. Low cell voltage is essential for both high thermodynamic efficiency and low hydrogen cost. Sulfur dioxide is oxidized at the anode, producing sulfuric acid that is sent to the high temperature acid decomposition portion of the cycle. Sulfur dioxide from the decomposer is cycled back to electrolyzers.

The electrolyzer cell uses the MEA concept. Anode and cathode are formed by spraying platinum containing catalyst, usually platinized carbon, on both sides of a Proton Exchange Membrane (PEM), usually Nafion®. The maximum electrolyzer cell active area was 54.8 cm^2. Feed to the anode of the electrolyzer was a sulfuric acid solution containing sulfur dioxide. The partial pressure of sulfur dioxide could be varied in the range of 1 to 6 atm (15 to 90 psia) yielding sulfur dioxide concentrations up to 2 molar depending on temperature, although concentrations in the range from 0.3 molar to 0.5 molar were more typical. Temperatures could be controlled in the range from ambient to 80ºC. Hydrogen generated at the cathode of the cell was collected for the purpose of flow measurement and compositional analysis. The test facility proved to be easy to operate, versatile, and reliable.

After testing MEA 31 the facility was automated. Prior to that, 24 hour operation required the presence of at least one person at all times. After automation the facility was unmanned at night and weekends and the data acquisition system (DAS) computer performed the following actions.

1. Controlled anolyte pressure by controlling the rate of addition of sulfur dioxide to the Anolyte Tank. Sulfur dioxide was consumed in the anode reaction and also left the tank when excess anolyte was removed.
2. Controlled anolyte density (wt% acid) by controlling the rate of addition of water to the Anolyte Tank. Water was consumed in the anode reaction and left the tank when excess anolyte was removed. Because sulfuric acid was generated in the anode reaction, water was required to maintain the desired concentration in the anolyte.
3. Drained excess anolyte to control the anolyte volume.

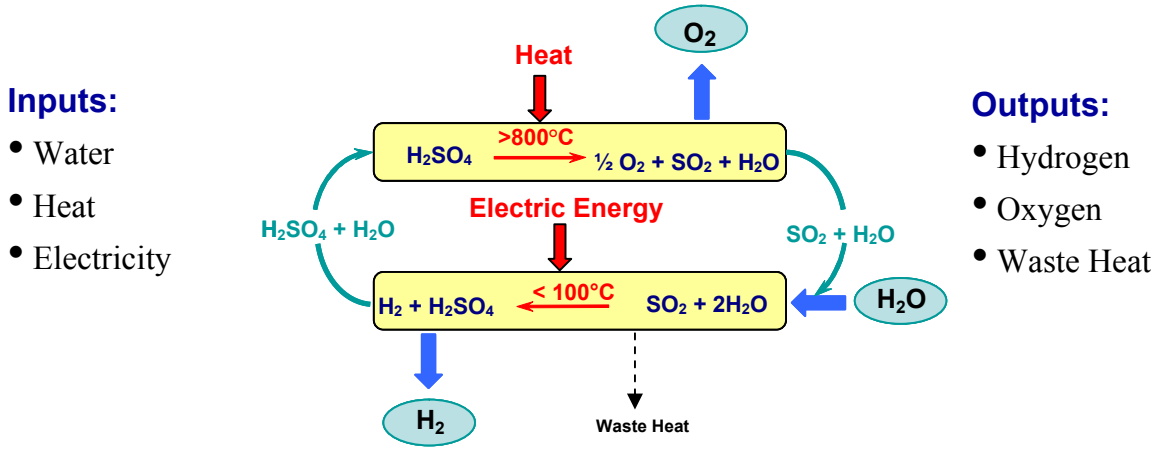
4. Refilled the sulfur dioxide syringe pump with liquid sulfur dioxide when it emptied.
5. Refilled the water syringe pump when it emptied.
6. Controlled power to the Anolyte Pump to control anolyte flowrate. Power to the pump was not allowed to fall below a specified minimum so that anolyte flowrate would not fall to zero.
7. Stopped flow of sulfur dioxide to the Anolyte Tank if anolyte temperature fell below a specified minimum.
8. Detected and ignored occasional false density meter readings so that these readings would not disrupt the algorithm for controlling density.
9. Alarmed if voltage, pressure or temperature was outside limits. Also alarmed if the hood flow failed or there was a spill in the hood. Alarm signals were displayed in a continuously manned Control Room on the SRNL campus. Also the image of the DAS control panel was displayed at the homes of two of the authors of this report.

This report describes observations and tests that led to a method for controlling the concentration of sulfur dioxide in the anolyte that prevented formation of a sulfur layer between the membrane and cathode of the MEA. The method was tested on eight MEAs and the following observations were made.

1. The tests increased in duration from 50 hours to 210 hours.
2. Some of the tests failed because of hardware and software problems unrelated to the method to prevent sulfur formation.
3. During the most successful final two tests there was little or no increase in cell voltage, as would be expected if sulfur had been formed.
4. Analysis of MEA 30, MEA 31, MEA 36 and MEA 37 after the conclusion of the test revealed no accumulation of sulfur.
5. The method resulted in the generation of much less hydrogen sulfide at the cathode than previously, so process efficiency is slightly higher because less product hydrogen is lost to the parasitic reaction that forms hydrogen sulfide. During some runs a gas chromatograph was used to analyze the product hydrogen. A typical hydrogen sulfide concentration was 500 ppm or 0.05 mole %. Therefore, 0.15% of product hydrogen was consumed by the parasitic reaction that forms hydrogen sulfide. In a commercial plant the hydrogen sulfide would be separated from the hydrogen and oxidized to sulfur dioxide for reuse.
6. The production rate of hydrogen was measured and agreed with theoretical to within measurement uncertainty.
7. The change of operating conditions described in this report will make it easier to clean the product hydrogen in a large scale process because there is less impurity in it.
8. Operating conditions were chosen that were very likely to eliminate formation of sulfur. However, the conditions have not yet been optimized for low cell voltage. Voltage could be reduced by increasing anolyte flowrate (decreasing sulfur dioxide conversion) or slightly increasing sulfur dioxide concentration.
9. Other than a slightly higher cell voltage there is only one known disadvantage to the new operating conditions. After implementing the method the hydrogen product stream became corrosive to Type 316 stainless steel, whereas it had not been before. Apparently the altered composition of the product stream de-passivated stainless steel. Affected stainless steel components were replaced with PFA or Teflon components.

2.0 INTRODUCTION

HyS is conceptually the simplest of the thermochemical cycles and involves only sulfur chemistry. In the HyS Cycle 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.



The electrolyzer half-cell and net cell reactions are:

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

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

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

In conventional water electrolysis, water is oxidized at the anode to produce protons and oxygen. The standard cell potential 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 sulfur dioxide instead of water in the HyS electrolyzer occurs at a much lower potential. For example, the standard cell potential for sulfur dioxide 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 proportional to hydrogen production, a large reduction in voltage results in a large reduction in electrical power cost per unit of hydrogen generated.

3.0 DISCUSSION

3.1 BACKGROUND

3.1.1 Previous Work

Previous reports by Steimke and Steeper have summarized work done on sulfur dioxide depolarized electrolyzers from SRNL as well as other places. This section of this report will summarize only more recent work by Steimke, Steeper and Herman.

Steimke and Steeper [2005, 2006] tested a graphite based electrolyzer cell designed and built at SRNL with six MEA. The cell was durable and cell voltages were similar to the lowest cell voltages measured by other researchers. Steimke and Steeper [2007] performed a 100 hour long Longevity Test in the SRNL cell. Hydrogen production efficiency was high but cell voltage slowly increased during the test. This was later determined to be the result of the formation of a sulfur layer. Steimke and Steeper [2008] continued the work on the SRNL electrolyzer. Steimke and Herman [2008] tested a three cell stack. The present work is a continuation of the 2006-2008 work with a single cell and with modifications to the cell, associated equipment and operating technique.

3.2 TEST FACILITY

3.2.1 Overview of Test Facility

A test facility capable of testing sulfur dioxide depolarized electrolyzers at pressures up to 6 atm and temperatures up to 80ºC was designed and constructed. The facility is capable of operating with electrolyzer currents up to 120 amperes. A current of 120 amperes is sufficient to generate approximately 50 liters per hour of hydrogen. The test facility proved to be versatile and easy to use. The MEA and flowfields inside the electrolyzer cell were easily replaced. The data acquisition system (DAS) 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.

3.2.2 Electrolyzer Cell

Figure 1 shows a schematic of the electrolyzer cell. The heart of the electrolyzer is a membrane electrode assembly (MEA) consisting a Proton Exchange Membrane and an anode and cathode sprayed on the two sides of it. Anolyte containing the reactants water and sulfur dioxide is pumped past the anode where the chemical reaction of equation 1 occurs. Sulfuric acid generated in the reaction can not cross the membrane. Hydrated hydrogen ions cross the membrane from the anode to the cathode where the chemical reaction of equation 2 occurs and hydrogen gas is generated. Hydrogen gas can not cross the membrane. Water is introduced to the cathode. Depending on conditions there can be a net flux of water in either direction resulting from three mechanisms. Electro-osmotic drag of hydrogen ions transports water from anode to cathode. The concentration gradient of water tends to transport water in the opposite direction. A pressure difference across the membrane drives a water flux. Sulfur dioxide can diffuse across the membrane from anode to cathode where it can be reduced by hydrogen to elemental sulfur or hydrogen sulfide. Sulfur dioxide can also be transported by water flux.

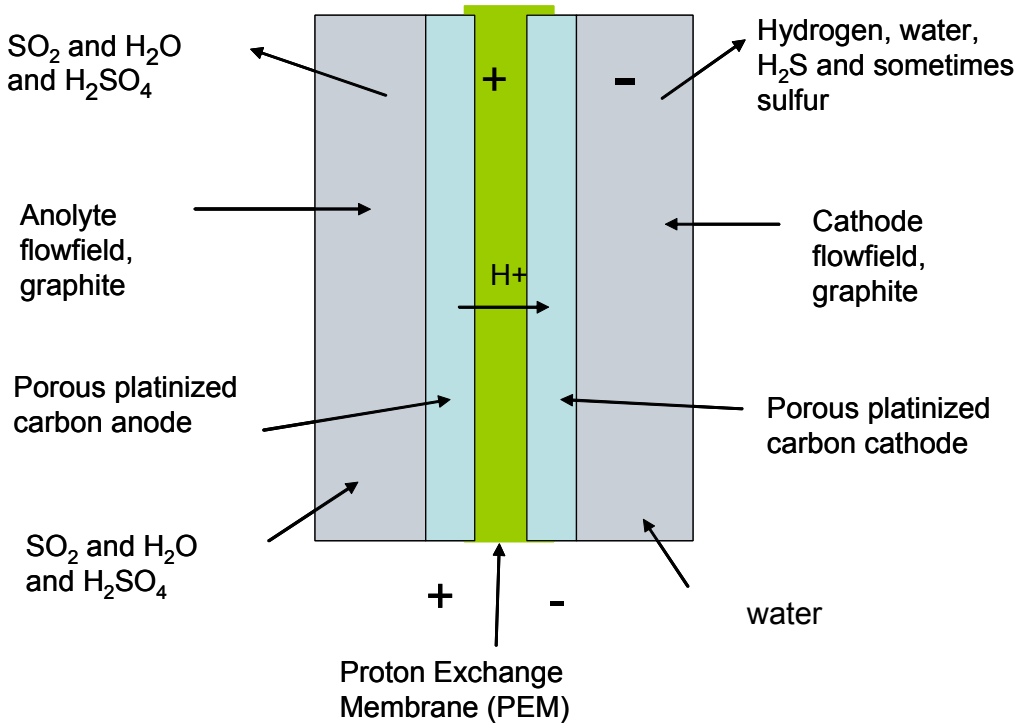


Figure 1 Schematic of Electrolyzer Cell

3.2.3 Preparation of Membrane Electrode Assemblies

Membrane electrode assemblies (MEAs) for the Hybrid Sulfur Process are currently prepared using Nafion® 115 membranes from DuPont with platinized carbon (TKK, 45.9 wt% PT) as the electrode materials. Spray deposition technique is used to prepare the electrodes. The "ink" used for spray deposition has a final dry weight target of 75 wt% catalyst and 25 wt% Nafion® ionomer using a ethanol and water solvent mixture. Following spray deposition, the MEA is heat pressed at 140°C at 5000 psi. Anode and cathode target loadings typically range from 0.8 mg to 1.8-0.9 mg Pt /cm^2. Characteristics of 37 MEAs are summarized in Table 1.

3.2.4 Hybrid Sulfur Electrolyzer Test Facility

Figure 2 is a schematic of the equipment in the facility, which was located in a chemical hood. Air flow was maintained in the hood to sweep away any gas leaks. The two anode reactants, sulfur dioxide and deionized water, were pumped into the Anolyte Tank and Absorber using ISCO 500 D syringe pumps. To facilitate refilling the sulfur dioxide pump with liquid, the inverted 15 lb. supply cylinder was heated to 50°C to increase the internal pressure. Had this not been done, a mixture of liquid and vapor would have flowed to the syringe pump. A thermocouple measured the cylinder temperature. In the event of a heater malfunction that created a high temperature the DAS cut power to the heater. A backpressure regulator downstream of the sulfur dioxide pump prevented flashing inside the pump. Vaporization of liquid sulfur dioxide occurred in the back-pressure regulator, which was always covered with water droplets. Sulfur dioxide vapor was absorbed in anolyte in a packed bed filled with glass Raschig Rings. Four laser level detectors were attached to the Anolyte Tank at different elevations. If no liquid was present the laser beam missed its paired detector. The presence

of liquid diffracted the beam into its detector. The four elevations were low alarm, low operate, high operate and high alarm.

Anolyte was pumped to the cell using a gear pump. The gears were ceramic and the casing was Carpenter Alloy 20. Flow was measured using a magnetic flowmeter, with zirconium electrodes. Anolyte flowing out of the cell passed through an Anton Paar tantalum density meter and back to the Anolyte Tank. The DAS opened a motorized valve downstream of the pump when the anolyte level reached high operate and closed the valve when anolyte drained down to low operate. Anolyte Tank pressure forced excess anolyte to flow to a waste drum located outside the building.

A low flow of deionized water, 10 mL/min, was provided to the cathode of the cell to help maintain membrane hydration. Hydrogen and water exiting the cathode flowed to the hydrogen-water separator. Hydrogen flowed through a backpressure regulator, a Sierra Instruments mass flowmeter, past a gas chromatograph sample point and out the building. The backpressure regulator was set to maintain the cathode pressure 15 psi higher than the anode pressure. An infrared liquid level sensor controlled the solenoid valve at the bottom of the separator. Water flowed to the previously mentioned waste drum.

3.2.5 Gas Chromatograph

The composition of the hydrogen generated by the electrolyzer was monitored during testing of MEA 34 through MEA 37 using an Agilent 3000 Micro Gas Chromatograph (GC). Gas samples were usually taken hourly. The GC was configured with a MolSieve 5A PLOT with PLOT U backflush module for Channel A and a PLOT U module for Channel B. Channel A was used to quantify oxygen and nitrogen. Channel B was used to quantify carbon dioxide and hydrogen sulfide. Water was also detected with channel B, but it was not quantified due to the poor quality of the peak and lack of a standard. Sulfur dioxide would be detected on Channel B, but none was identified in these experiments. During testing of MEA 34, argon was used as the GC carrier gas. At the start of testing MEA 35 the carrier gas was changed to helium at the suggestion of the vendor. Helium carrier gas increases carbon dioxide and hydrogen sulfide sensitivity by over a factor of ten.

Commercial gas standards were not available for these experiments. Instead, air was used as the calibration gas. Per discussion with the GC vendor, hydrogen sulfide has a similar response to carbon dioxide. Therefore, the calibration factor for hydrogen sulfide (mole%/area) was set to that of carbon dioxide in air. Results for testing MEA 34 could not readily be compared to later MEAs because of the difference in carrier gases.

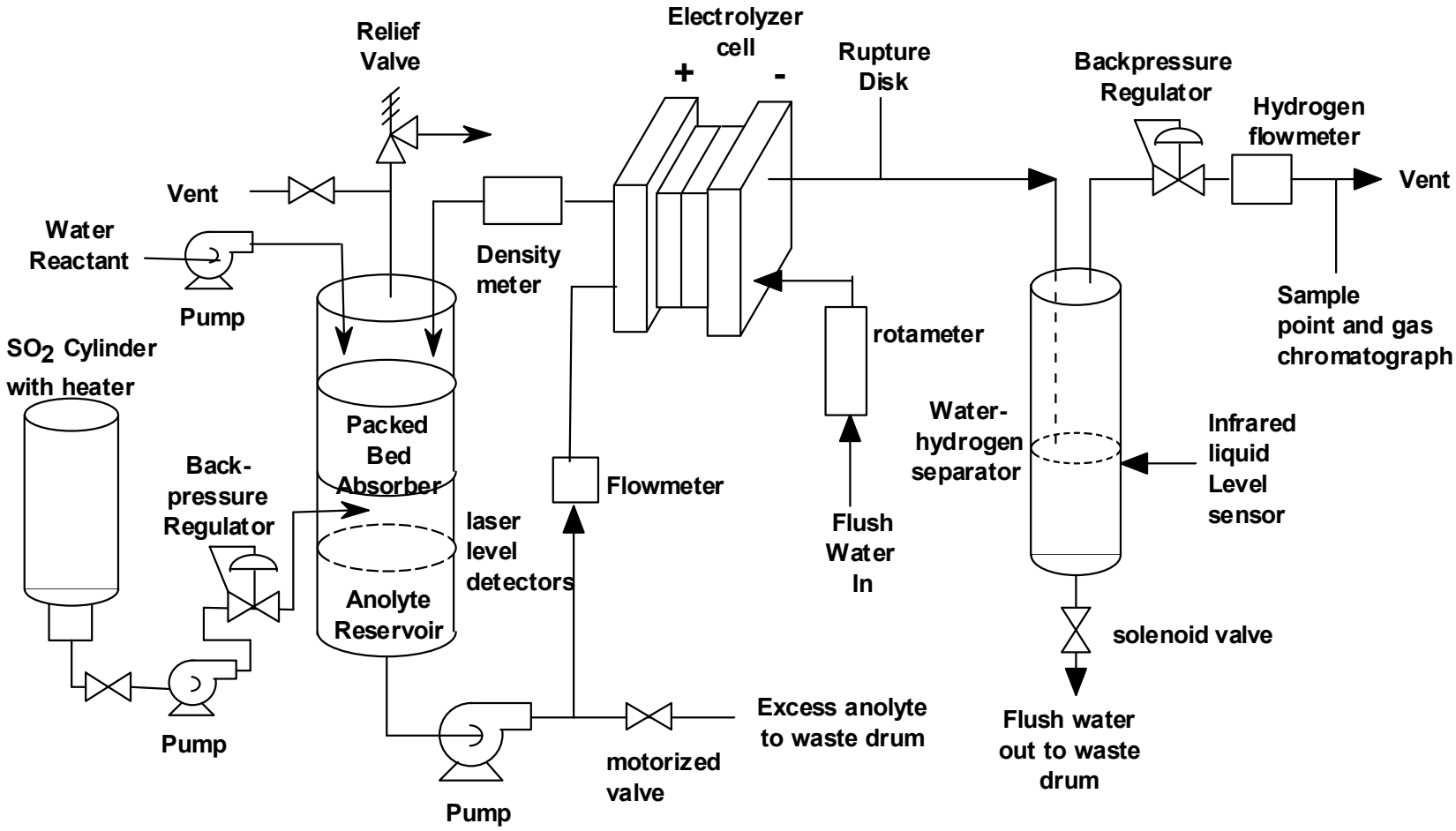


Figure 2 Schematic of Hybrid Sulfur Electrolyzer Test Facility

3.3 TEST RESULTS

3.3.1 Observations of Cell Voltage Increase and Sulfur Formation

Over the past two years of testing of MEAs at SRNL, see list in Table 1, it was observed that cell voltage generally increased over the period of testing for an MEA, which was usually intermittent over a period of as long as two months. At the time it was not known whether this was the result of degraded membranes or poisoned catalyst or some other cause. This observation was complicated by the fact that cell voltage is influenced by current density, cell temperature, anolyte pressure (which affects concentration of sulfur dioxide in the anolyte), anolyte flowrate, membrane type and thickness and concentration of sulfuric acid in the anolyte. The Longevity Test, MEA 12, provided valuable information about the process of cell voltage increase because it was run for 100 continuous hours at nearly constant conditions.

MEA 12 was tested briefly on Friday, May 4, 2007 at ambient conditions and cell voltages were among the lowest for ambient conditions that had been measured up to that time. Over the weekend the cell was stored with the anode immersed in anolyte saturated in sulfur dioxide and the cathode was exposed to hydrogen gas. The Longevity Test began on Monday morning May 7. The cell voltage for ambient conditions at that time was about 90 mV higher than on May 4. On Monday May 7 operation was initially at 20°C and 1 atm. Temperature and pressure were then increased to 80°C and 4 atm and held there for 100 continuous hours. Anode and cathode pressures were equal. Anolyte flowrate was 80 mL/min and anolyte concentration was nominally 30 wt%. Catholyte flush water flowrate was 2 ml/min. Figure 3 shows a subsequent gradual increase in voltage of an additional 60 mV over the one hundred continuous hours of operation. Also, Figure 4 shows a generally increasing pressure drop for flow of anolyte through the cell which would result from a thickening MEA.

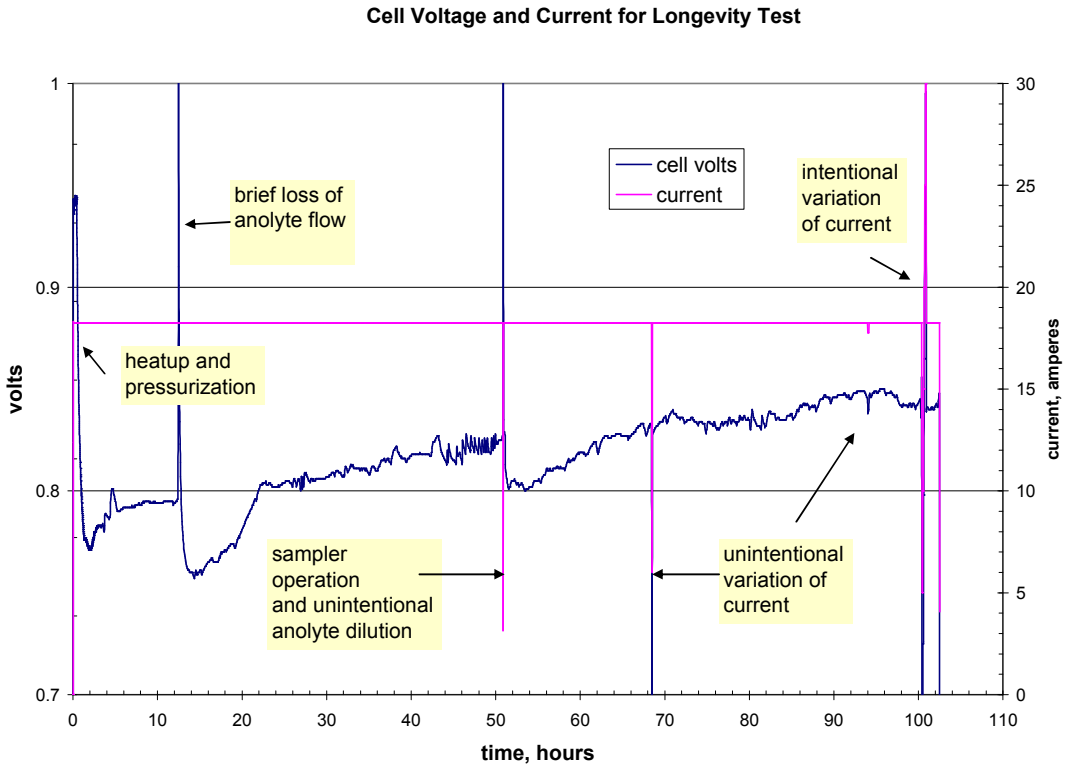


Figure 3 Cell Voltage During 100 Hour Longevity Test

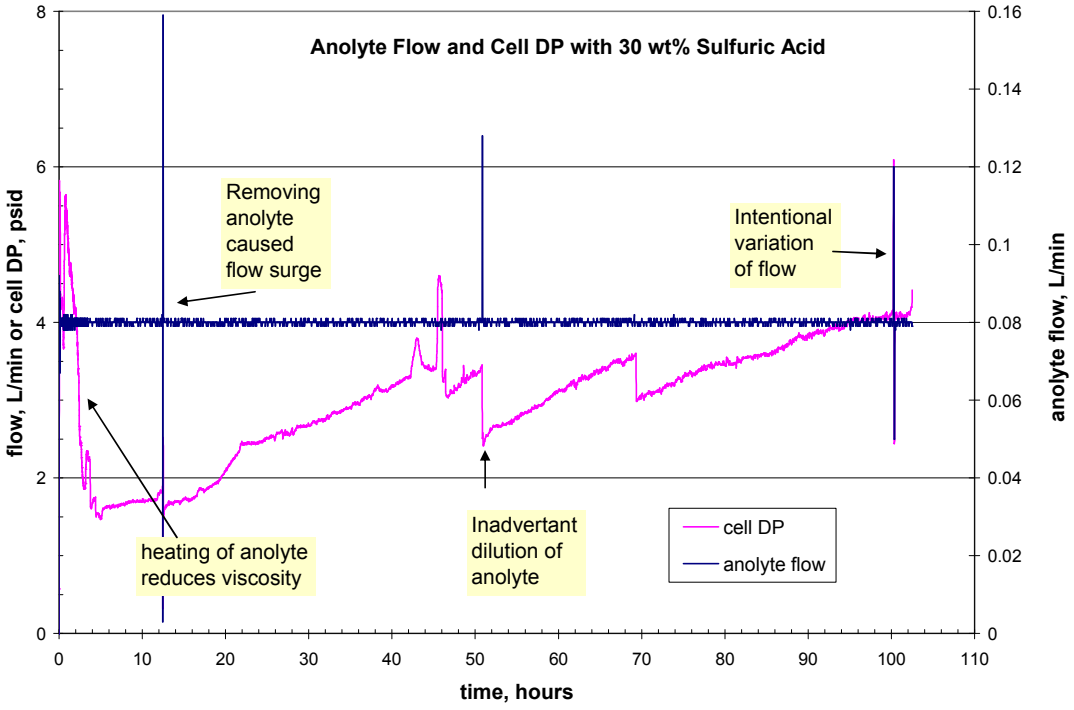


Figure 4 Pressure Drop for Longevity Test

An additional observation was made during the Longevity Test. During initial ambient condition startup on May 7 colloidal sulfur was observed in the Sulfur Collector, but no additional sulfur was observed after a couple of hours into the run. At the end of the test MEA 12 was cleaned, removed and mounted for Scanning Electron Microscopy (SEM). Figure 5 shows the formation of a sulfur layer between the cathode and membrane as thick as the membrane. It was concluded that the sulfur layer added ohmic resistance to the MEA which increased cell voltage and also pressed the MEA into anode flow passages which increased pressure drop.

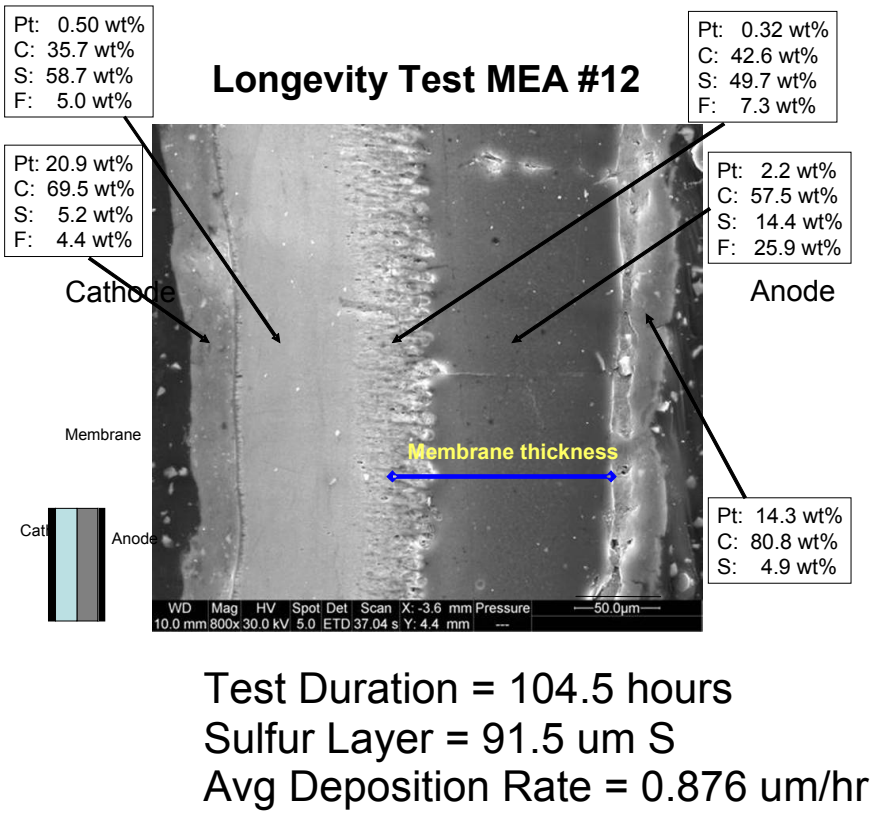


Figure 5 Scanning Electron Micrograph of MEA 12

Sulfur layer thickness was measured directly by SEM for ten MEAs and indirectly for six other MEAs by using a micrometer to measure total MEA thickness and then subtracting the membrane anode and cathode thickness. Figure 6 plots sulfur layer thickness for MEAs run in the usual way versus the integral of sulfur dioxide partial pressure (atm) with time. The latest MEA in the plot is MEA 29. The concept was that both time and concentration of sulfur dioxide contribute to sulfur production. In fact the integral of pressure with time correlates fairly well with sulfur layer thickness up to 50 atm-hr, although some MEA exhibited less than expected sulfur formation. Also, there was no additional increase in thickness for values of the integral larger than 50 atm-hr. A four mil thick sulfur layer may interfere with transport of sulfur dioxide which is necessary to form additional sulfur.

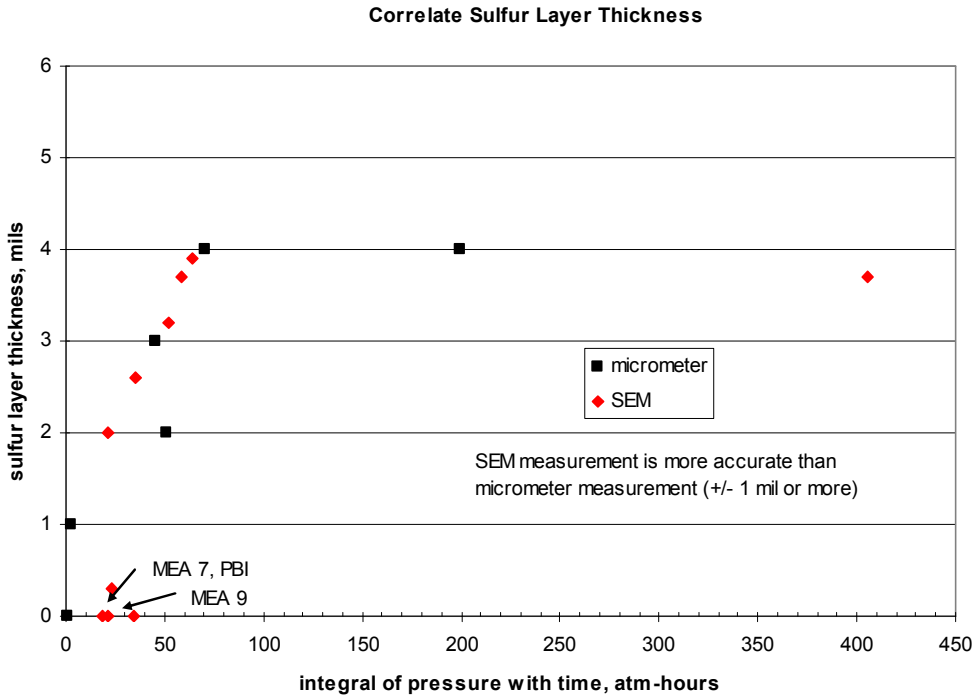


Figure 6 Correlation of Sulfur Layer Thickness

3.3.2 Observations of Colloidal Sulfur and Hydrogen Sulfide

Sometimes the cell current was abruptly stopped after the cell had been operating. Then after a couple of minutes a cloud of colloidal sulfur appeared in the Sulfur Collector (SC). A couple of minutes after resuming the current the contents of the SC started to clear.

An important observation during the testing of all MEAs was the sometimes strong odor of hydrogen sulfide emitted by the water flowing out of the SC. This was initially a surprise because some sulfur dioxide was expected to cross the membrane from the anode to the cathode. There was no noticeable odor of sulfur dioxide at the SC. Having the cathode pressure greater than the anode pressure decreased the appearance of colloidal sulfur in the SC and the odor of hydrogen sulfide in the effluent from the SC.

3.3.3 Observations on Cell Voltage

Figure 7 shows typical cell voltages as a function of current density for initial testing. The voltage at very low current density is the reversible voltage, approximately 200 mV. The kinetic over-potential term adds about 400 mV at 150 mA/cm^2 current density. At currents densities greater than 150 mA/cm^2 there is a linear region resulting from ohmic-overpotential and above some higher current density, not shown in Figure 8, the curve turns up because of mass transfer over-potential. This last term is the result of mass transfer limitations, either the supply of reactants to the active catalyst sites is limiting or diffusion of sulfuric acid product away from catalyst sites is limiting. In fact for the Hybrid Sulfur Cycle electrolyzer any mass transfer limitation was always the result of an inadequate supply of sulfur dioxide. The blue line and the red line on Figure 3 show the linear regions for ambient temperature and 80°C, respectively. Note that increasing the temperature decreases both the

slope and intercept of the line tracing the linear region. Typical intercepts for ambient operation and 80°C operation are 0.62 volt and 0.58 volt, respectively.

Cell voltages generally increase over the course of testing an MEA. Figure 8 illustrates this trend for some ambient temperature operation. Note that all three data sets have the same intercept, 0.62 volt. This behavior is consistent with an increasing internal electrical resistance of the MEA, which would be expected with an increasing layer of sulfur.

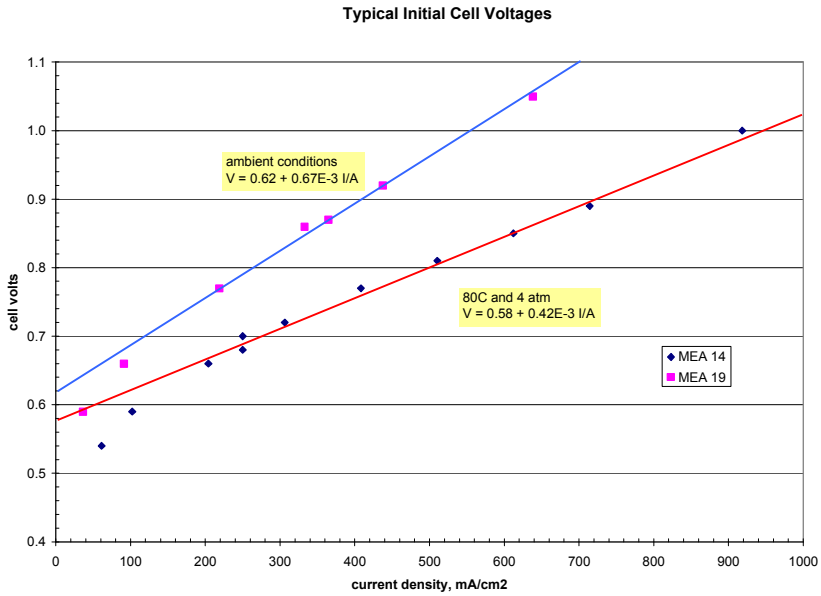


Figure 7 Typical Initial Electrolyzer Cell Voltages

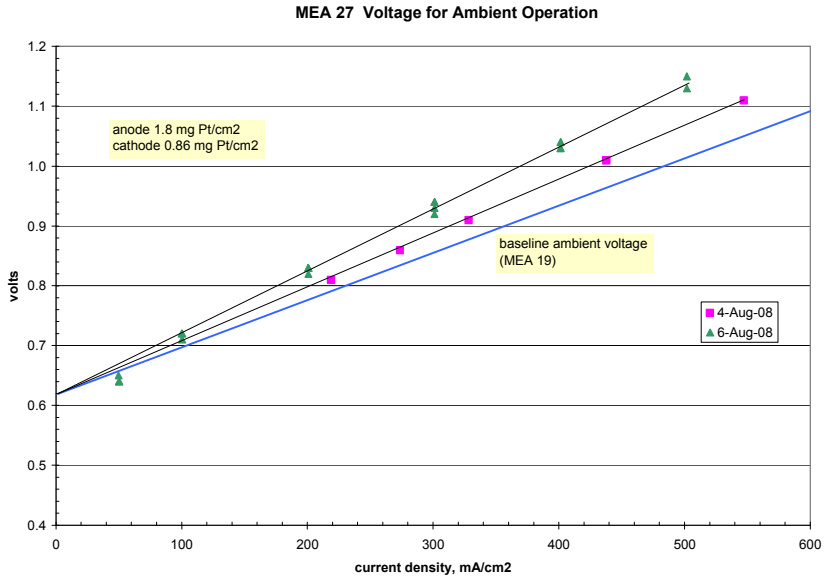


Figure 8 Increasing MEA Ohmic Resistance with Time

Inspection of cell polarization data like Figures 7 and 8 showed an important simplification. For current densities greater than 150 mA/cm^2 and less than the current density for which mass transfer became important, which could be 1000 mA/cm^2 or greater, the plot could be approximated by an intercept and a slope. For most MEAs tested, the intercept was about 0.58 volt for 80°C and 0.62 volt for ambient temperature. The slope, which has units of ohm-cm^2, measured for initial testing of an MEA depended on membrane type and thickness and on catalyst loading. As testing progressed the slope increased, but the intercept, either 0.58 volt or 0.62 volt depending on temperature, usually remained the same because a sulfur layer of increasing thickness was adding an electrical resistance to the cell.

3.3.4 Effect of Sulfur Dioxide Concentration in Anolyte

Figure 9 plots cell voltage for MEA 8 for four anolyte pressures; 1, 2, 3 and 4 atm. The corresponding sulfur dioxide concentrations at 80°C and 30 wt% H_2SO_4 in the anolyte are 0.14, 0.37, 0.61 and 0.85 molar. The cell voltage for the highest concentration can be represented by a line with intercept 0.61 volt and slope 0.49 Ω-cm^2 and no data points indicate a mass transfer limitation. When the pressure was reduced to 3 atm the voltage was unaffected except for current densities above 800 mA/cm^2 where there was a mass transfer limitation. When the pressure was reduced to 2 atm the voltage was unaffected except for current densities above 500 mA/cm^2 and when the pressure was reduced to 1 atm the voltage was unaffected except for current densities above 250 mA/cm^2. The interpretation is that a certain concentration of sulfur dioxide is necessary as reactant for the anode reaction to proceed at a particular rate and the necessary concentration depends on current. Increasing the current increases the reaction rate and the necessary concentration of sulfur dioxide. If less concentration is provided than the necessary concentration the cell voltage increased because a reactant is limited. If more concentration is provided, there is no effect on cell voltage.

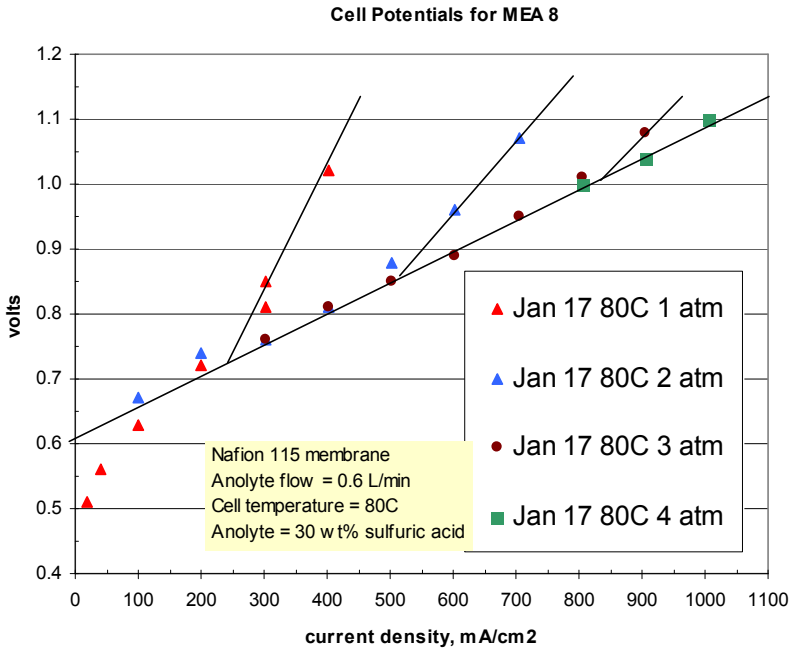


Figure 9 Effect of Sulfur Dioxide Concentration on Cell Voltage

3.3.5 Hypothesis for Formation of Sulfur Layer

Sulfur dioxide in the anolyte crosses the membrane to the cathode under the action of two forces. First, concentration gradient always drives sulfur dioxide from the anode to the cathode. Second, sulfur dioxide dissolves in water and is transported by the flux of water through the membrane which can be in either direction. Water flux has three components, electro-osmotic drag always drives water from the anode to cathode. Activity (concentration) gradient of water always drives water from cathode to anode. Recall that the anolyte is typically 30 wt% sulfuric acid and 70 wt% water while pure water is supplied to the cathode. Pressure gradient across the membrane can drive water in either direction. The electrically driven anode reaction reduces the sulfur dioxide concentration at the anode.

The first location where sulfur dioxide can contact hydrogen gas in the presence of catalyst is the interface between membrane and cathode. Two chemical reactions, listed below, are necessary to form elemental sulfur. The first reaction, which is energetically preferred, forms hydrogen sulfide and the second reaction forms elemental sulfur.

$$SO_2 + 3H_2 = H_2S + 2H_2O \qquad \Delta H_0 = -70.5 \text{ kcal/mole S} \qquad (3)$$

$$2H_2S + SO_2 = 3S + 2H_2O \qquad \Delta H_0 = -18.7 \text{ kcal/mole S} \qquad (4)$$

A hypothesis was formed that limiting the concentration of sulfur dioxide at the interface between the membrane and cathode would result in all sulfur dioxide arriving at the interface being consumed in the first and preferred reaction, leaving no sulfur dioxide to participate in the second reaction. There are at least four ways to reduce the concentration of sulfur dioxide at the interface.

1. Reduce the sulfur dioxide concentration in the anolyte.
2. Increase current density to consume more sulfur dioxide at the anode. This decreases the concentration at the anode and membrane interface.
3. Increase the net water flux from cathode to the anode.
4. Decrease the permeability of the membrane to sulfur dioxide.

There are possible disadvantages to all four methods.

1. If sulfur dioxide concentration is reduced enough cell voltage will increase, see Figure 10.
2. Increasing current density generates more hydrogen production from a given cell but increases cell voltage.
3. A sufficiently high water flux from cathode to anode might interfere with hydrogen ion diffusion through the membrane and this increase cell voltage.
4. A membrane that was less permeable to sulfur dioxide might also be less permeable to hydrogen ions.

3.3.6 Mapping Cell Operation

Inspection of Figure 9 for MEA 8 suggests that higher concentrations of sulfur dioxide in the anolyte allow higher current densities before the cell becomes mass transfer limited. Therefore, the three current densities at the branch points in Figure 9 were plotted against the corresponding sulfur dioxide molarities in Figure 10. Also, five similar data points from testing MEA 29 were plotted. It should be noted that MEA 8 was tested with a previous design of the anolyte flowfield that was developed for higher anolyte flowrates. While there is significant scatter in the data, they suggest proportionality between sulfur dioxide concentration and mass transfer limited current density. A line was plotted on the graph that passed through the origin and between the data points. The anode reaction was mass transfer limited for points below the line. The further below the line, the higher the

cell voltage, but the less likely formation of sulfur is. For points above the line the anode reaction is not mass transfer limited. Moving further above the line does not change the cell voltage but it was hypothesized that sulfur formation is more likely and faster. Figure 11 plots where other MEAs were operated on the Operating Map. Note that the weekend period during MEA 12 testing when it was stored in sulfur dioxide saturated anolyte was the MEA 12 data point furthest from the dividing line on Figure 11 and also the period when the greatest increase in voltage occurred.

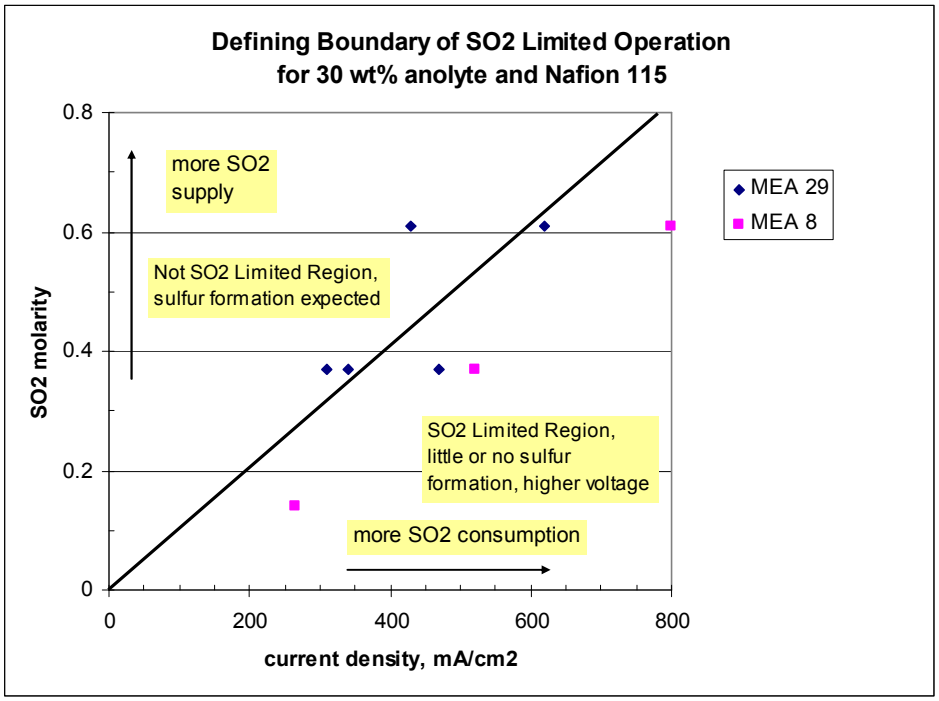


Figure 10 Boundary for SO2 Limited Operation

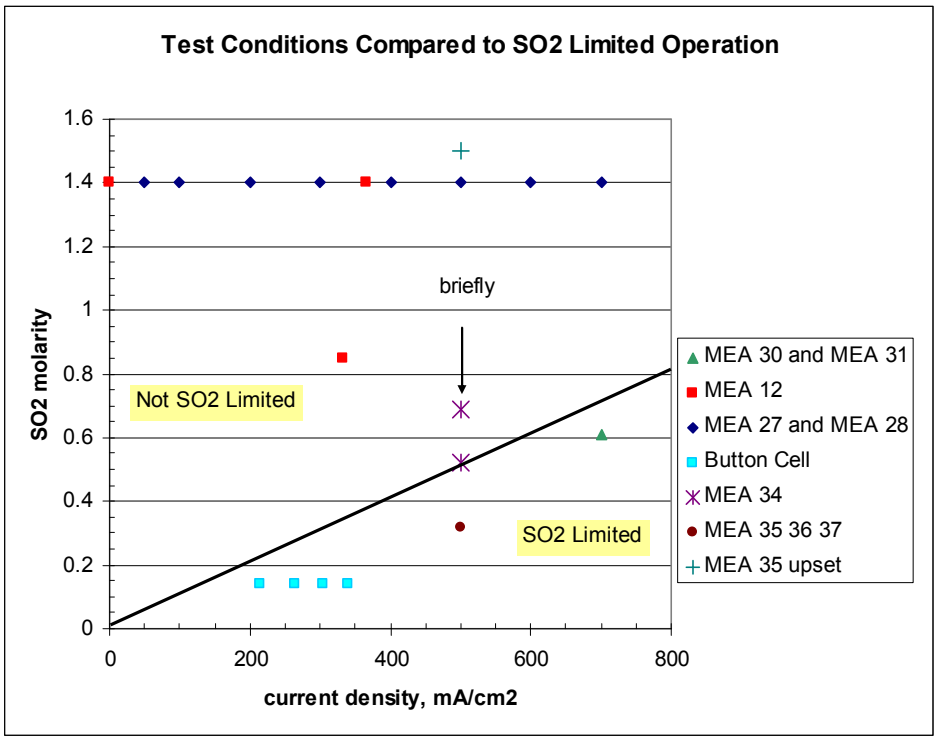


Figure 11 Map of Test Conditions

3.3.7 New Operating Procedure

The new operational concept is to operate at all times just below the dividing line on Figure 10 and Figure 11 so that cell voltage is, at most, slightly increased and sulfur formation is greatly reduced or eliminated. It is important to stay below the line not only during steady state operation but also during startup and shutdown. At startup this is accomplished by loading fresh anolyte with no sulfur dioxide. The power supply is used to impress 0.9 volt across the cell and anolyte and cell are heated to the desired temperature. The voltage 0.9 volt is insufficient to accomplish conventional water electrolysis, for which the reversible cell voltage is 1.22 volts, and only traces of sulfur dioxide are present so cell current is small. Then sulfur dioxide is slowly added. This increases anolyte pressure, concentration of sulfur dioxide and current density. Use Figures 12, 13 and 14 to convert anolyte temperature and pressure to sulfur dioxide concentration. Verify that the transition conditions remain below the line. When the target current is reached change the power supply to current control and thereafter voltage will decrease. If an increase in sulfur dioxide concentration does not decrease cell voltage, then decrease concentration until the first indication of increase in cell voltage.

Shutdown of the facility is accomplished with the following steps. While current and operating temperature are maintained, the feed of sulfur dioxide is stopped which slowly decreases anolyte pressure. Venting sulfur dioxide vapor to accelerate the pressure decrease causes the anolyte pump to vapor lock. The pressure reduction decreases the concentration of sulfur dioxide and causes cell voltage to increase. When the cell voltage increases to 0.9 volt the power supply automatically switches to voltage control at which time current decreases. When anolyte pressure decreases to atmospheric, the power supply and the anolyte pump are simultaneously de-energized while allowing the cathode flush to continue. Then valve V1 at the outlet of the Anolyte Tank is closed and the

anode of the cell is flushed with deionized water. The anode and cathode sides of the cell are stored in water.

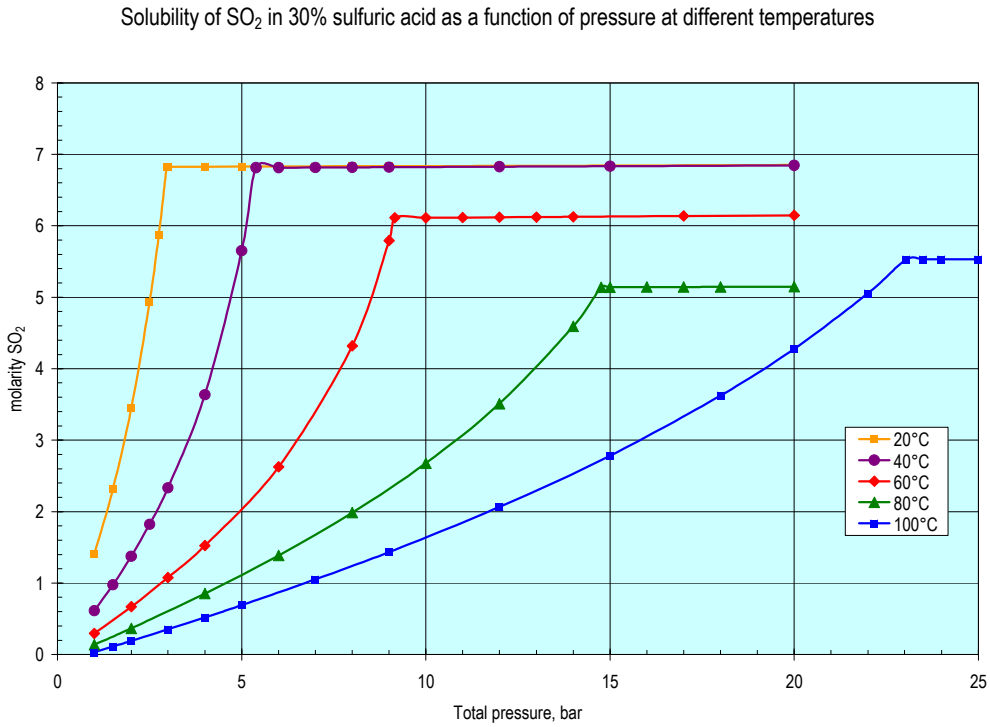


Figure 12 SO2 Molarity in 30 wt% Sulfuric Acid

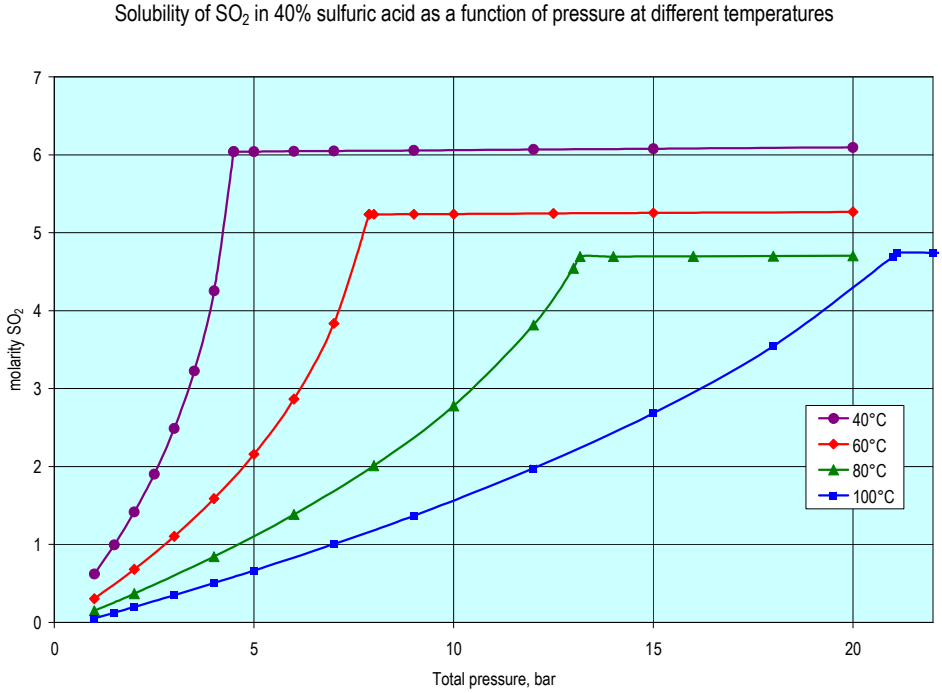


Figure 13 SO2 Molarity in 40 wt% Sulfuric Acid

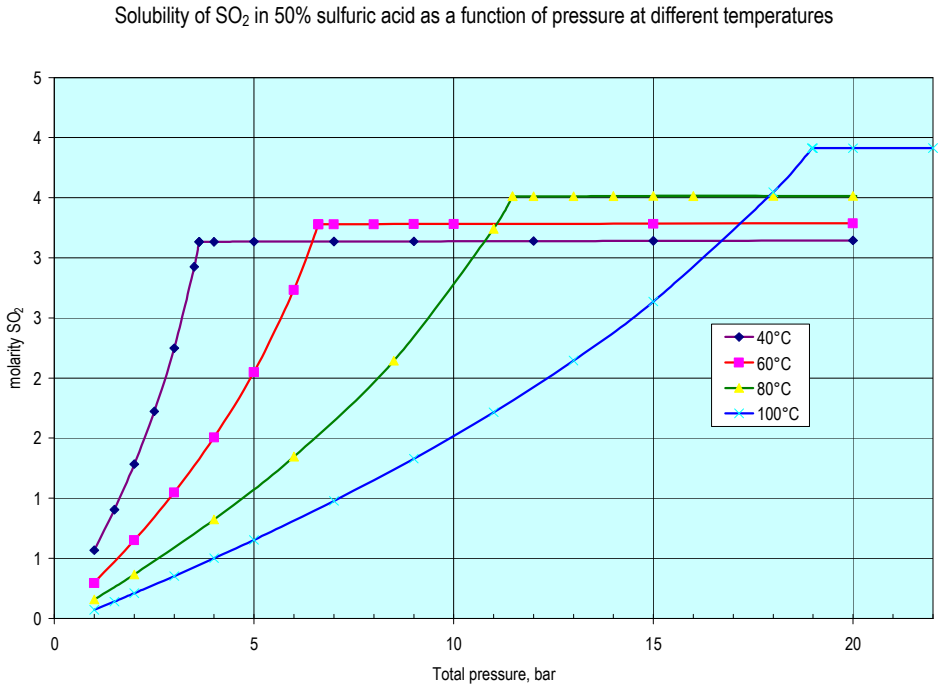


Figure 14 SO2 Molarity in 50 wt% Sulfuric Acid

3.3.8 Normalization of Cell Voltage

To allow better comparison of data collected over a range of conditions, a method was developed to normalize cell voltage with respect to current density and temperature. Normalization of cell voltage was accomplished by dividing the slope of the linear part of the voltage response by the slope of a standard MEA. Based on an earlier report by Steimke and Steeper [2008] the standard response for ambient conditions was defined as that for MEA 19.

$V = 0.62 + 0.67$ ohm-cm^2 I/A
Where I and A have units of amperes and cm^2, respectively.

The standard response for 80°C was defined as that for MEA 14.
$V = 0.58 + 0.42$ ohm-cm^2 I/A

Note that both the intercept and slope decrease when the temperature increases from ambient to 80°C. Inplementation of normalization for ambient and 80°C used the following two equations.

$V_{norm} = (V_{meas} - 0.62)/ (0.67\ I/A)$ for ambient operation (5)

$V_{norm} = (V_{meas} - 0.58)/ (0.42\ I/A)$ for 80°C operation (6)

The normalization process can be thought of as comparing the ohmic loss of an MEA to the baseline ohmic loss. When the normalized voltage is 1.2 the ohmic loss is 20% higher than baseline.

Equation 5 and equation 6 were used to normalize cell voltage from the Longevity Run as shown in Figure 15. Normalized cell voltage was initially about 1.0 implying good performance. After the weekend it increased to 1.4, so that ohmic resistance had increased by 40%. At the end of the run ohmic resistance was 90% higher than originally.

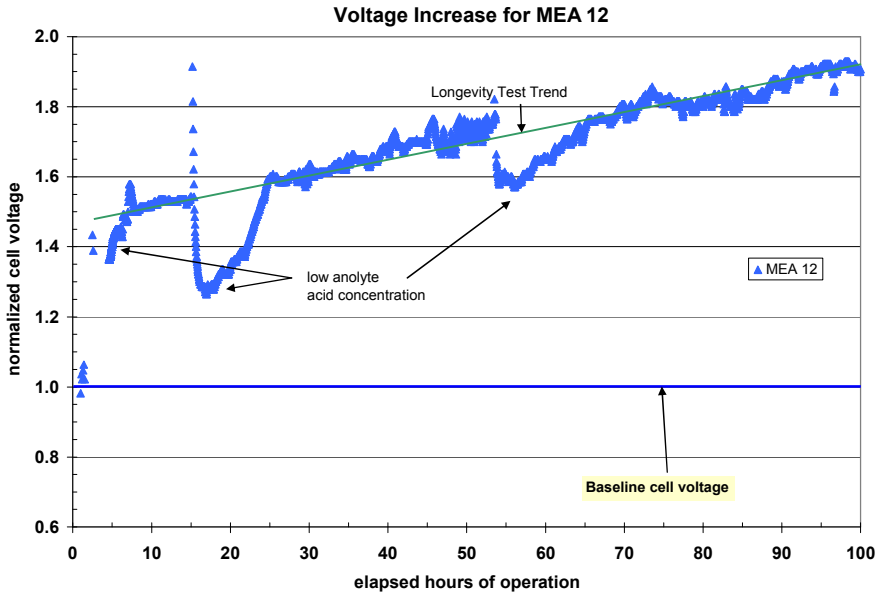


Figure 15 Normalized Voltage for MEA 12

3.3.9 Testing Summary for MEA 27 through MEA 37

Details will follow on testing and results for MEAs 27 through 37 which were tested during the period October 2008 to June 2009. Table 2 contains a summary of test conditions. MEA 27 and MEA 28 were tested before the new operating technique was conceived. MEA 27 formed a thin sulfur layer, while MEA 28 did not. It is not known why there was a difference. The new technique was conceived part way through testing of MEA 29 which did not form a sulfur layer. MEAs 30 and 31 were intentionally tested with the new technique and neither formed a sulfur layer. Those two MEAs exhibited little or no increase in cell voltage. The facility was automated after testing MEA 31. Various hardware and software problems were resolved during testing of MEA 32 through MEA 35. The most successful tests were with MEAs 36 and 37.

3.3.10 MEA 27

MEA 27 was tested from July 31 to August 7, 2008. Anolyte flowrate was 80 mL/min and anolyte concentration was nominally 30 wt%. Catholyte flush water flowrate was 15 ml/min. MEA 27 was operated on four days and a total of 23 hours at 30°C and 1.2 atm at current densities up to 650 mA/cm^2. Anode and cathode pressures were equal. Figure 21 shows a sulfur layer 9 µm (0.35 mil) thick for MEA 27.

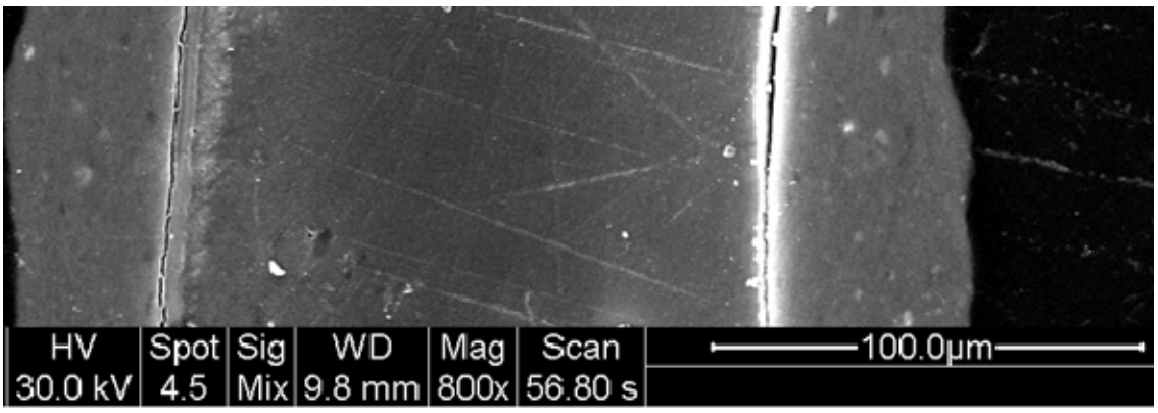


Figure 16 SEM of MEA #27

3.3.11 MEA 28

MEA 28 was tested from August 20 to August 28, 2008. Anolyte flowrate was 80 mL/min and anolyte concentration was nominally 30 wt%. Catholyte flush water flowrate was 15 ml/min. MEA 28 was operated on five days and a total of 34 hours at 30°C and 1.2 atm at current densities up to 1000 mA/cm^2. Anode and cathode pressures were equal. MEA 28 was damaged when the anolyte pump stopped pumping and cell voltage increased to 1.7 volts, enough to generate oxygen that oxidized some of the graphite in the MEA. SEM shows no sulfur formation.

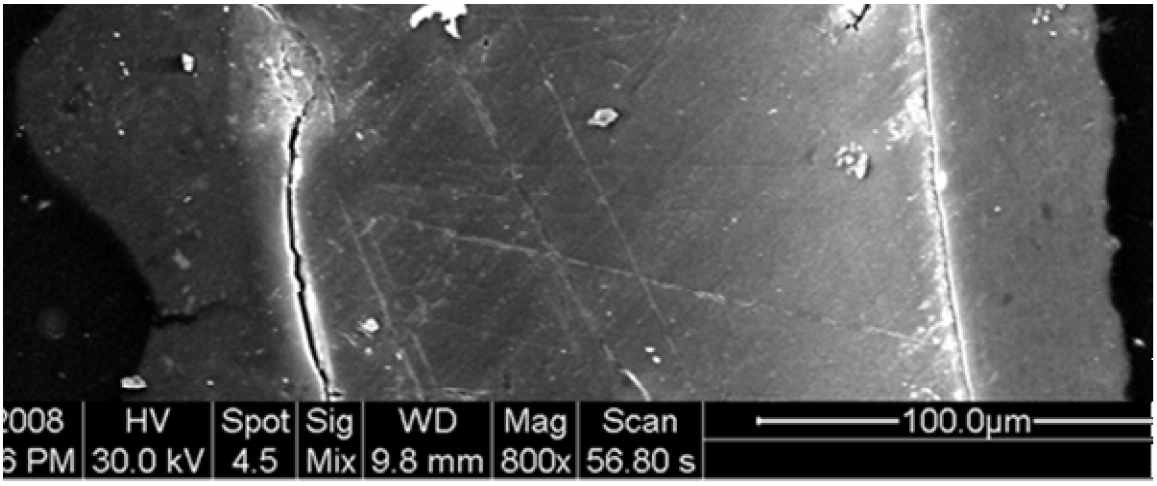


Figure 17 SEM of MEA #28

3.3.12 MEA 29

MEA 29 was tested from October 8 to October 21, 2008. Anolyte flowrate was 80 mL/min and anolyte concentration was nominally 30 wt%. Catholyte flush water flowrate was 15 mL/min. On the first two days of testing MEA 29 was operated a total of 12 hours at 30°C and 1.2 atm at current densities up to 650 mA/cm^2 similar to the operation of MEA 27 and MEA 28. Cathode pressures was controlled to be about 5 psi greater than anode pressure. Then MEA 29 was operated for three days and a total of 21 hours at 80°C and pressures ranging from 2 to 5 atm at current densities up to 1000

mA/cm^2. Some of the test conditions for those three days of testing were intentionally in the mass transfer limited regime. Cell voltages were measured at the start of each day of testing for ambient conditions, see Figure 18. Ambient voltages were about the same on the first and second days of testing and slightly higher on the morning of the third day. Later on the third day the cell was run part of the time in the mass transfer limited regime. The morning of the fourth day the lowest ambient voltages for all MEA 29 testing were measured. This suggested a benefit for operation in the mass transfer limited regime. Testing of MEA 29 was discontinued when the anode was inadvertently pressurized to 80 psig which damaged the MEA and carbon paper.

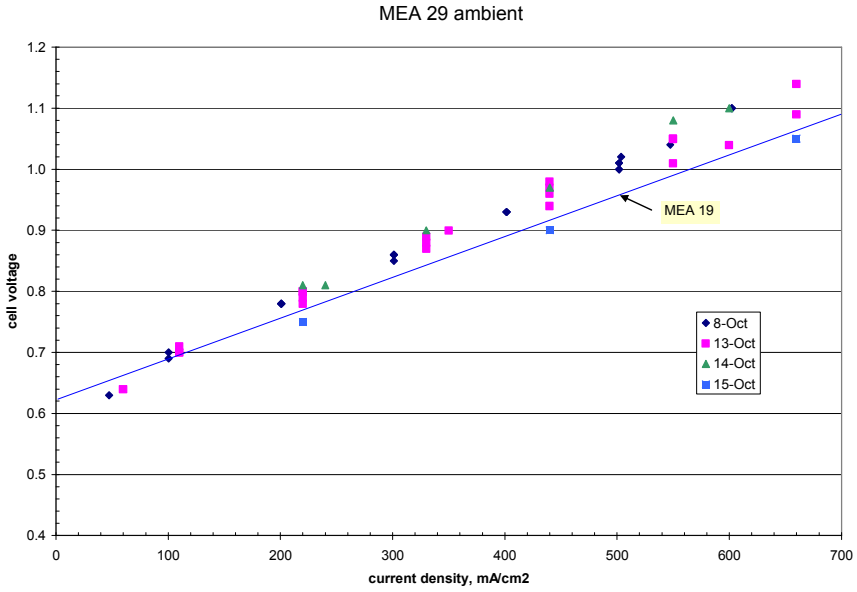


Figure 18 MEA 29 Performance for Ambient Conditions

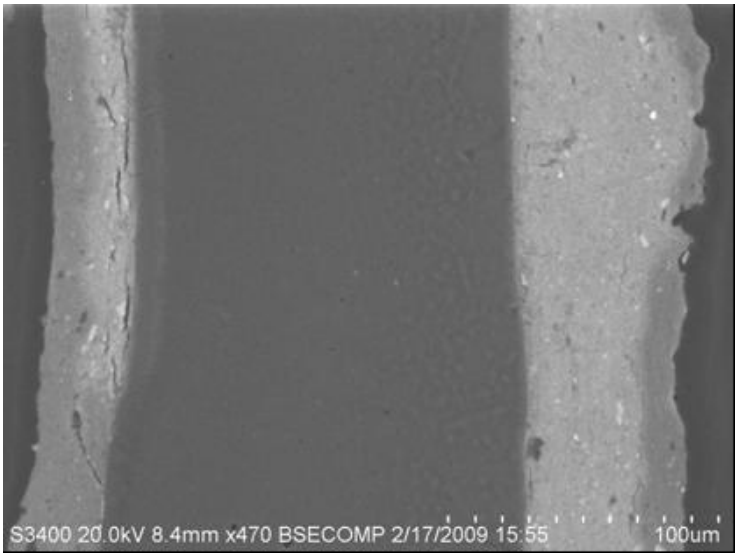


Figure 19 SEM of MEA 29

3.3.13 MEA 30

MEA 30 was tested discontinuously from October 29 to December 8, 2008 on seven days of testing and was the first MEA to be tested with the on-line anolyte density meter in the facility. Anolyte flowrate was 80 mL/min and anolyte concentration was nominally 30 wt%. Temperature was 80°C. Catholyte flush water flowrate was 15 mL/min. Anode pressure was 30 psig and cathode pressure was controlled 5 to 15 psi greater than anode pressure. Each day of testing started with the power supply in voltage control mode at 1.0 volt. The cell and anolyte were heated to 80°C and then sulfur dioxide was added to increase anolyte pressure to 3 atm (30 psig). The power supply was switched to current control mode and 700 mA/cm^2. At the end of the work day sulfur dioxide was vented. When the pressure was near ambient the power supply and anolyte flow were discontinued. Both the anode and cathode sides of the cell were stored in deionized water.

Cell voltages are plotted in Figure 20. Voltages are not plotted for periods of startup or shutdown. Variations in voltage reflect imperfect control of cell temperature, anolyte pressure and anolyte acid strength. There seems to be a small upward trend in voltage, but the amount of voltage increase during testing was less than for any previous MEA. Normalized voltage for MEA 30 is plotted in Figure 21 and compared with some previous MEAs. No data points are plotted for the startup period or shutdown period each day. Voltage varied because of variations in anolyte acid concentration and sulfur dioxide concentration in the anolyte. Normalized voltage was initially less than 1.0, which is desirable, and increased to about 1.0. The amount of voltage increase during testing was less than for any previous MEA. But there was concern that the numerous startups and shutdowns might have caused the voltage increase.

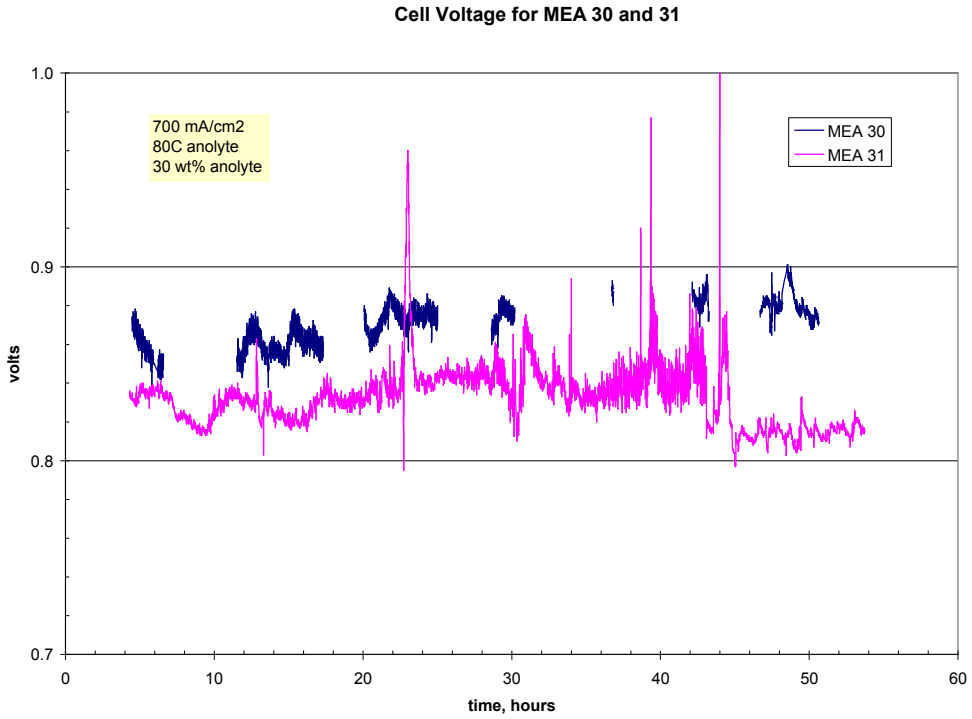


Figure 20 Cell voltages for MEA 30 and 31

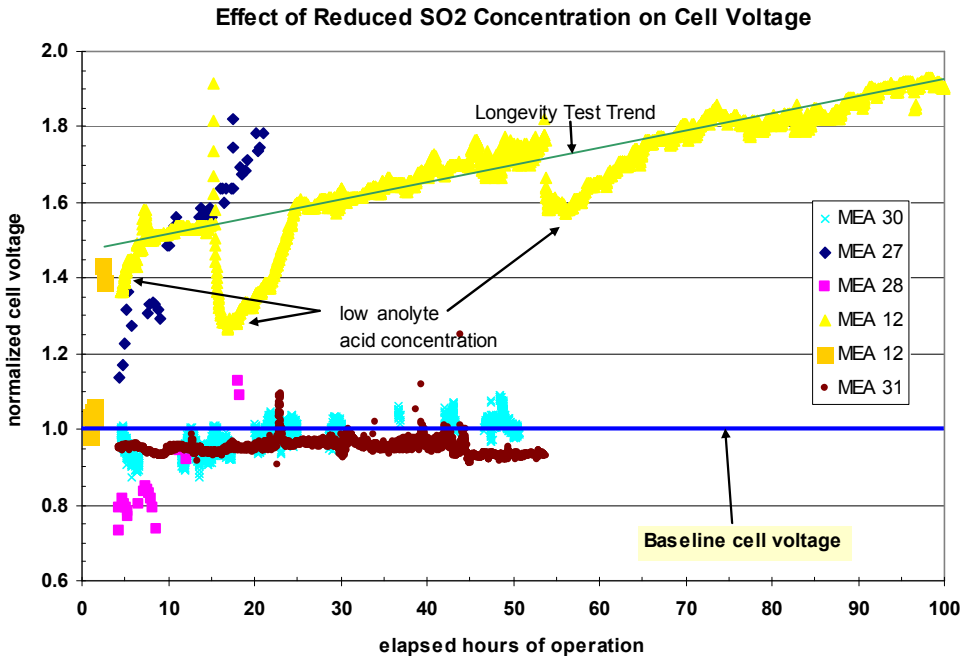


Figure 21 Normalized Cell Voltages

A sample was taken from the center of MEA 30 SEM analysis. The image in Figure 22 shows no presence of a sulfur rich layer.

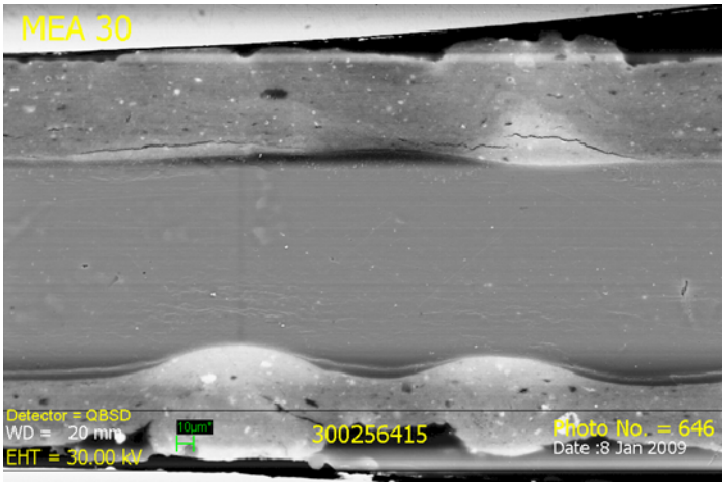


Figure 22 SEM of the center of MEA #30.

3.3.14 MEA 31

MEA 31 was tested from December 17 to December 19, 2008. After two hours of testing the electrolyzer cell developed an internal electrical short. Testing was stopped and the cell was rinsed and removed. The cell was cleaned and internal O-rings were replaced. Testing resumed later that day and continued 24 hours a day for 55 hours. Anolyte flowrate was 80 mL/min, but was increased to 120 mL/min late in the run, and anolyte concentration was nominally 30 wt%. Catholyte flush water flowrate was 15 mL/min. Cathode pressure was controlled 15 psi greater than anode pressure.

MEA 31 cell voltage and normalized voltage are plotted in Figures 20 and 21. Note a small increase in normalized voltage until 44 hours and then a decrease. The reason was accumulation of air in the Anolyte Tank. During testing of MEA 30 and previous MEAs the sulfur dioxide syringe pump was refilled by heating the SO_2 cylinder to increase pressure. For testing of MEA 31 air was added to the SO_2 cylinder to increase pressure. Unfortunately air is somewhat soluble in sulfur dioxide and was introduced to the Anolyte Tank where it interfered with absorption. At 44 hours some of the gas phase in the Anolyte Tank was vented to remove some air. Also anolyte flowrate was increased to compensate for poorer absorption of sulfur dioxide. The run ended with a normalized cell voltage of 0.93, which is excellent. The test of the new technique with MEA 31 was very successful.

A new technique for refilling the sulfur dioxide syringe pump was employed for testing of MEA 31. Rather than heat the sulfur dioxide cylinder to increase its internal pressure, air was added to the cylinder to increase its pressure to 90 psig. However, this caused three operational problems all resulting from the fact that air is soluble to some degree in liquid sulfur dioxide. First, after the syringe pump is refilled the pump is deadheaded to eliminate any vapor. The outlet valve is closed and the pump is operated. Initially, there is little pressure increase. Then there is a rapid pressure increase when all vapor is eliminated and the pump compresses liquid. There was a spongy response to deadheading because of air in the pump. Second, when the sulfur dioxide pump was valved to the Anolyte Tank air under pressure in the syringe pump drove a surge of liquid sulfur dioxide into the tank and increased the pressure by as much as 12 psi. Third, the Anolyte Tank began to accumulate air in the vapor space, which increasingly interfered with the absorption process. To compensate for poorer mass transfer, anolyte flowrate was increased to 120 mL/min.

Figure 23 plots normalized cell voltage for MEA 31 as a function of anolyte pressure. Voltage decreased as pressure increased up to 20 psig and did not change thereafter. Therefore, the test could have been conducted at 25 psig rather than 30 psig. There would have been no voltage penalty and even less hydrogen sulfide would have been formed. Figure 24 plots flowrate and anode pressure drop for MEA 31. Flowrate became more irregular as air accumulated in the anolyte.

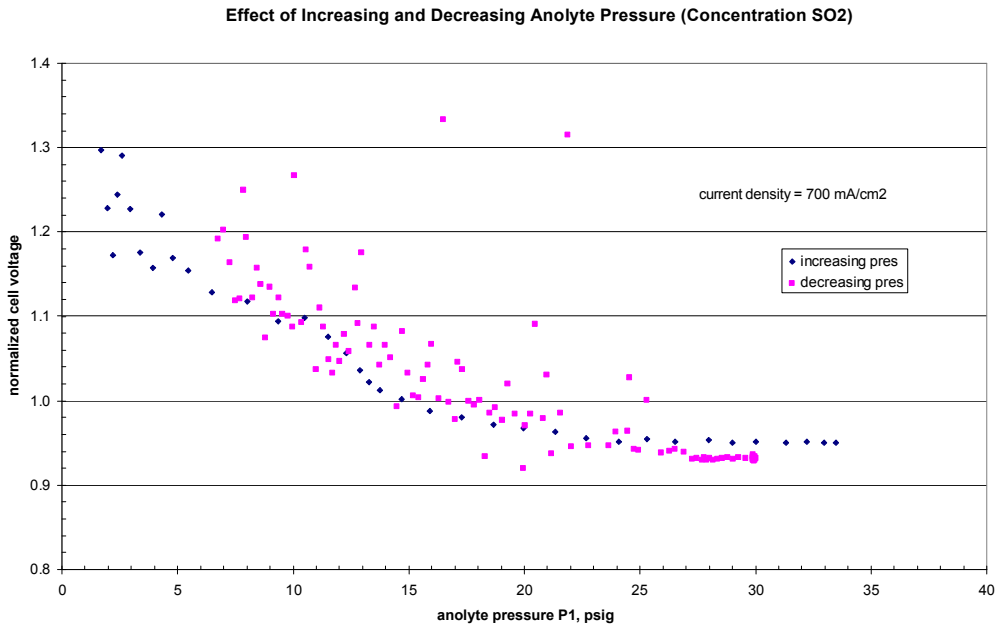


Figure 23 Effect of Sulfur Dioxide Concentration on Cell Voltage

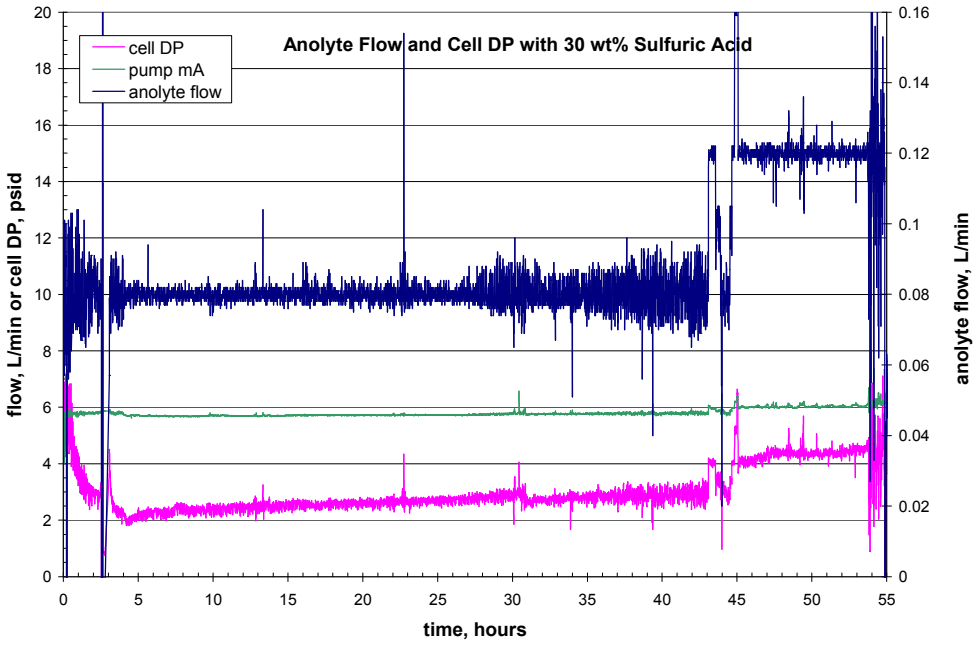


Figure 24 Anolyte Flowrate and Cell Pressure Drop for MEA 31

MEA 31 samples were taken from 3 different locations: close to the inlet, close to the outlet and at the center. See Figures 25 through 27. No image shows the presence of a sulfur rich layer. An extensive

interrogation at the cathode membrane interface for existence of a sulfur layer using EDAX on the location nearest to the anolyte inlet revealed the sulfur content was very small in all locations. These results suggest that sulfur is not accumulating in this MEA near the cathode-membrane interface and no evidence of a precursor stage to a sulfur-rich layer.

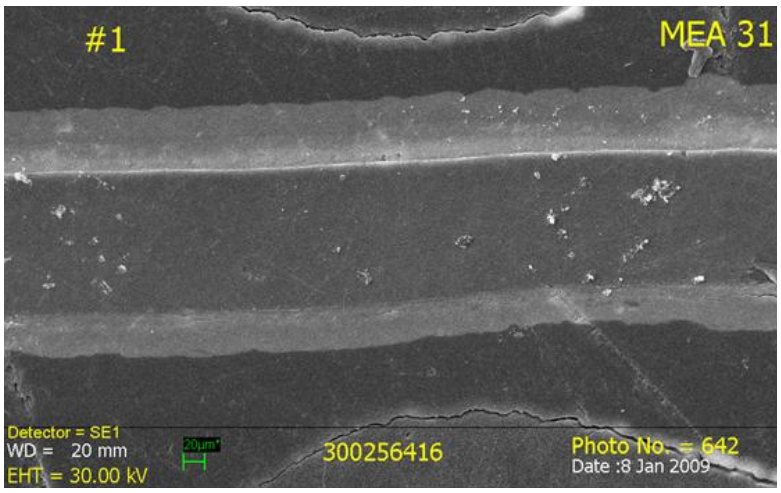


Figure 25 **SEM of the inlet of MEA #31.**

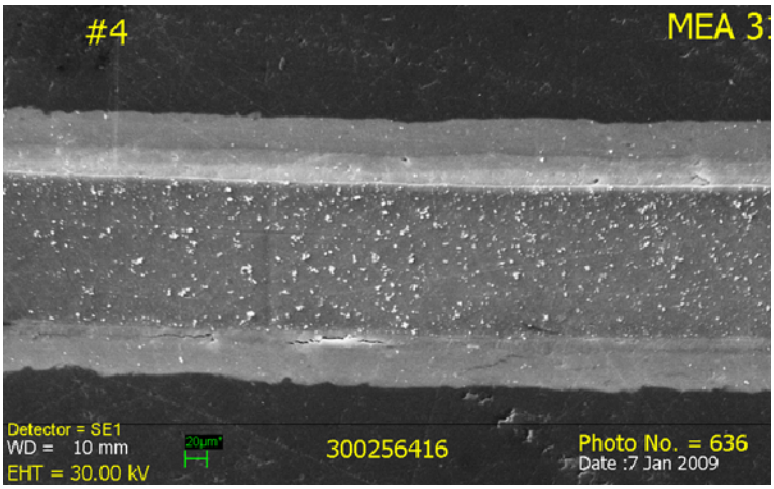


Figure 26 **SEM of the outlet of MEA #31.**

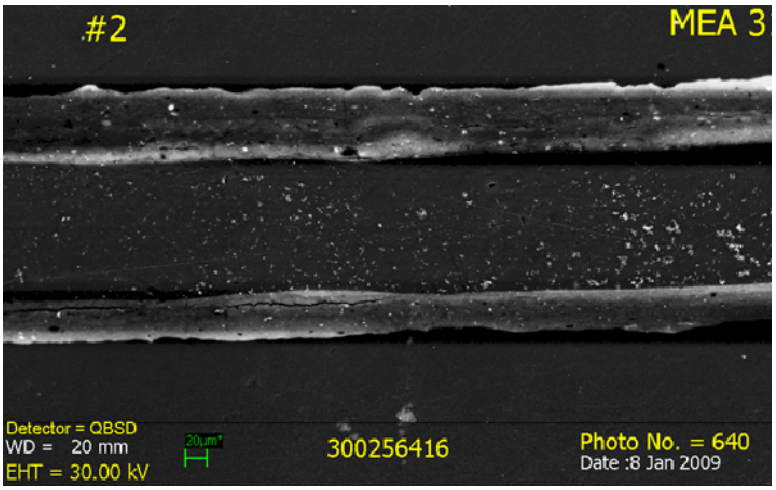


Figure 27 SEM of the center of MEA #31.

3.3.15 MEA 32

Prior to testing MEA 32 the electrolyzer facility was modified to allow automated and unattended operation. Day shift only testing of MEA 32 was performed from April 6 to April 15, 2009. This testing was intended to exercise the changes made to the facility, but not to test the method of preventing sulfur formation.

3.3.16 MEA 33

Testing of MEA 33 commenced on April 16, 2009 with the intention of 24 hour operation. Test conditions were 500 mA/cm^2, 80°C, 24 psig and 30 wt% anolyte. Various measurement and control issues were resolved. For part of the first night digital data were lost. On May 17 there were large pressure fluctuations because the PID controller was inadequately tuned. See Figure 28. The highest pressure was 42 psig rather than the desired 24 psig. The corresponding sulfur dioxide concentrations were 0.81 molar and 0.52 molar, respectively. See Figure 29. The first corrosion problems in the cathode discharge stainless steel piping were observed and a piece was replaced. On April 20 a high cell pressure drop, 50 psid, was observed and later the cell shorted. A short is characterized by hydrogen production much less than theoretical and also relatively low cell voltage. As the result of a number of issues that could compromise the run, testing of MEA 33 was terminated.

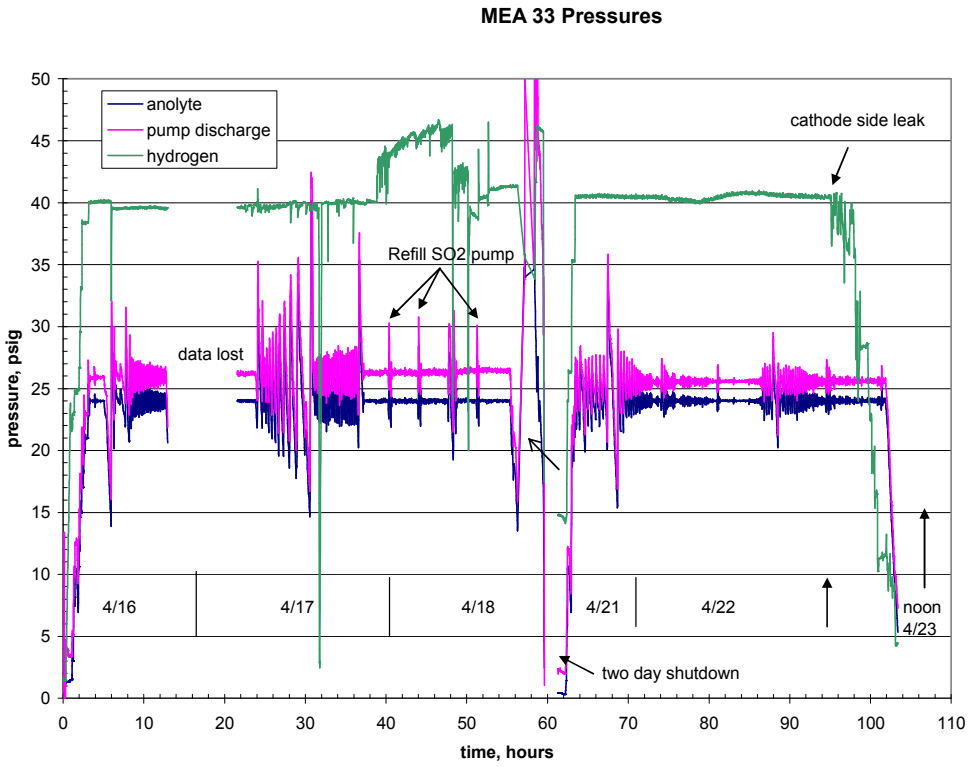


Figure 28 MEA 33 Pressures

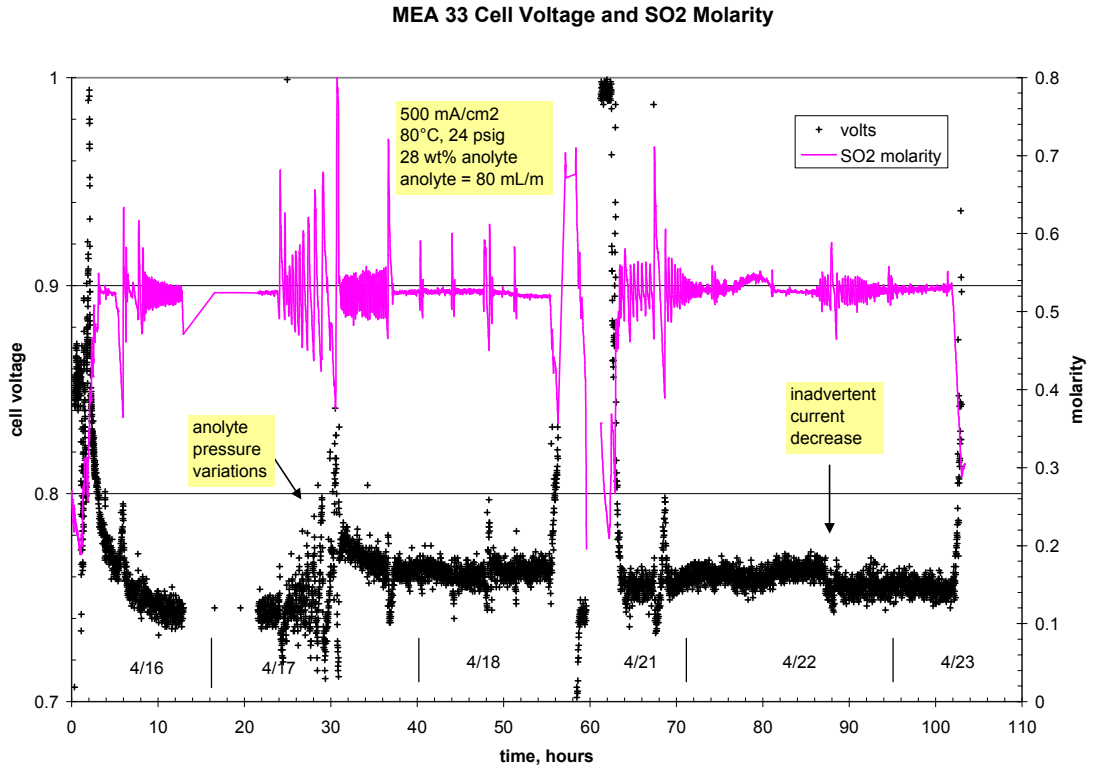


Figure 29 MEA 33 Cell Voltage and SO2 Molarity

3.3.17 MEA 34

The anolyte pump had not been operating well so it was disassembled before testing MEA 34. Carpenter Alloy 20 parts were badly corroded and were replaced. MEA 34 was tested from April 28 to May 17. More corrosion was observed in the stainless steel parts of the Hydrogen-water separator. Testing was stopped from May 1 to May 4 to replace stainless steel components at the discharge of the cell cathode. During the night of May 16-17 there was large pressure oscillations. See Figure 30. On May 17 the water syringe pump tripped offline and it was decided to terminate testing of MEA 34. After disassembling the cell MEA 34 and the carbon paper were observed to have significant damage. During part of MEA 34 testing the anolyte concentration was allowed to increase to measure the effect on cell voltage. Results are plotted in Figure 31. There is a significant effect because Nafion tend to dehydrate. The effect would be less with other membrane materials under consideration.

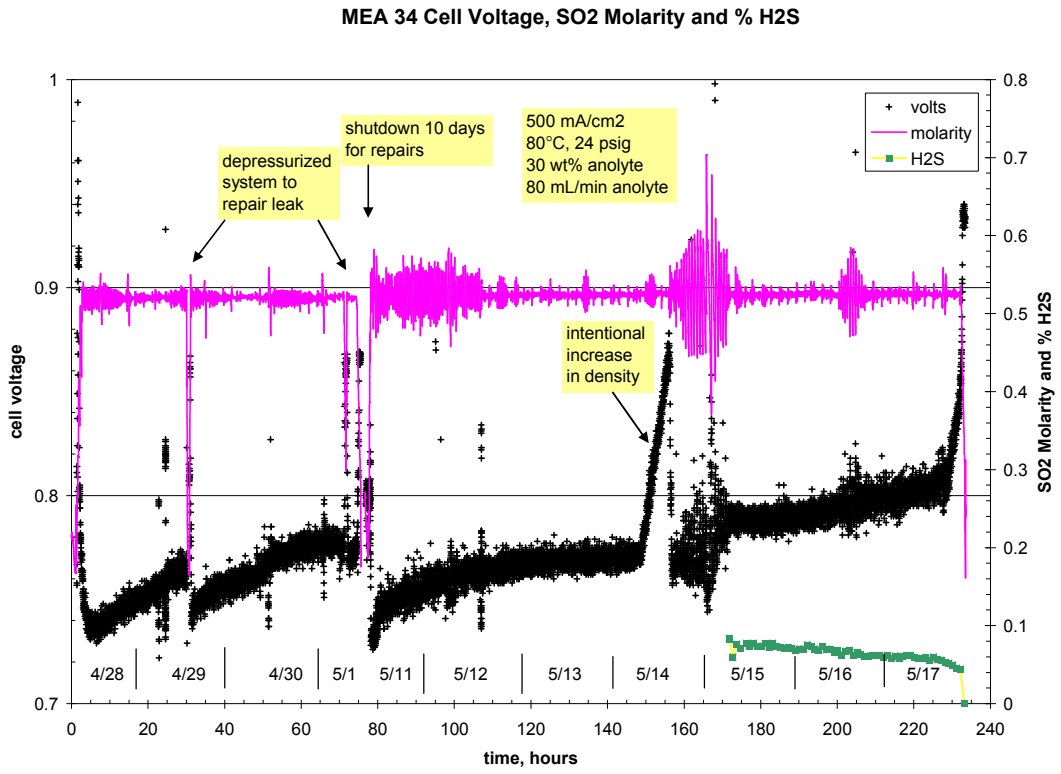


Figure 30 MEA 34 Voltage, SO2 Molarity and % H2S

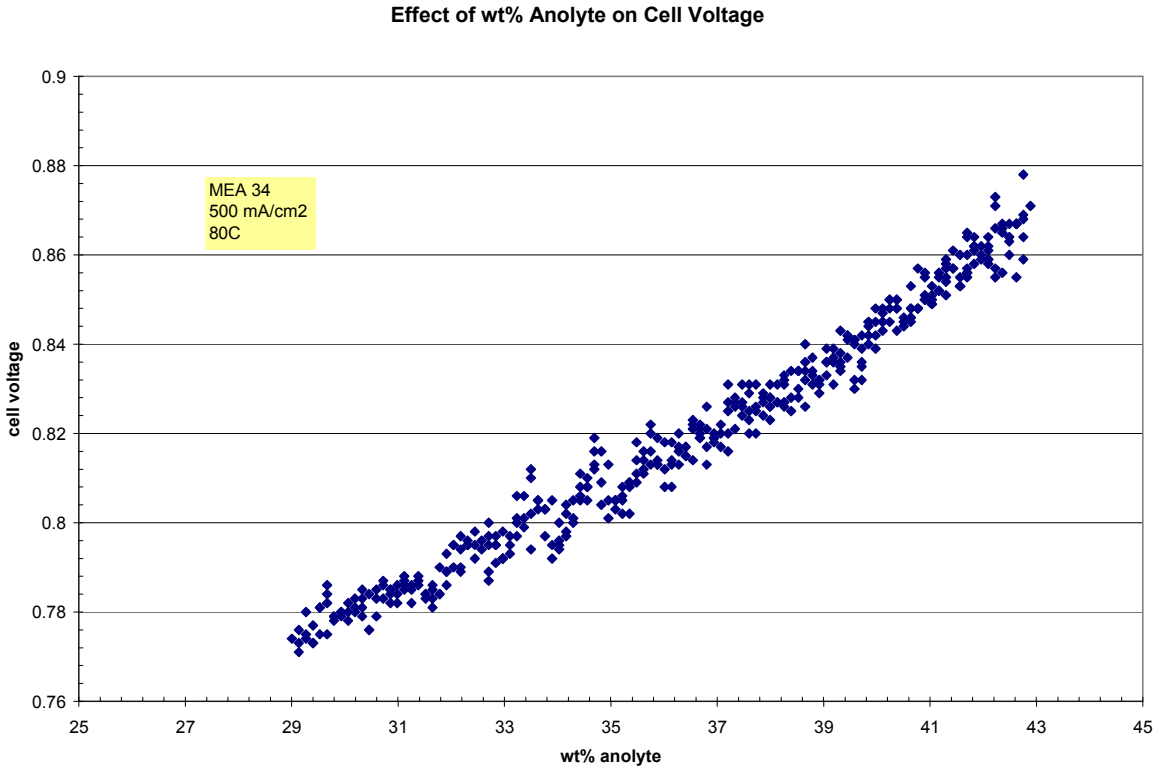


Figure 31 Effect of wt% Anolyte on Cell Voltage

3.3.18 MEA 35

MEA 35 was tested on May 19 and 20. At 14.5 hours and Anolyte Tank bath heater tripped off-line, allowing the anolyte to cool. The computer maintained anolyte pressure as the anolyte cooled, so sulfur dioxide concentration in the anolyte increased from 0.3 molar to 1.5 molar. See Figure 32. Initially the increased sulfur dioxide decreased cell voltage, but formed sulfur inside the MEA. The fact that the bath heater was not working increased the load on the cartridge heaters in the cell and the fuse on the anode heater blew at 16 hours. The fact that the cell cooled increased cell voltage. Hydrogen sulfide in the product hydrogen increased from 0.2% to 2%. After temperatures were restored to normal cell voltage was 70 mV higher than before. The MEA was considered compromised and the run was terminated after 26 hours. The water in the Hydrogen-Water Separator was cloudy, possibly with colloidal sulfur.

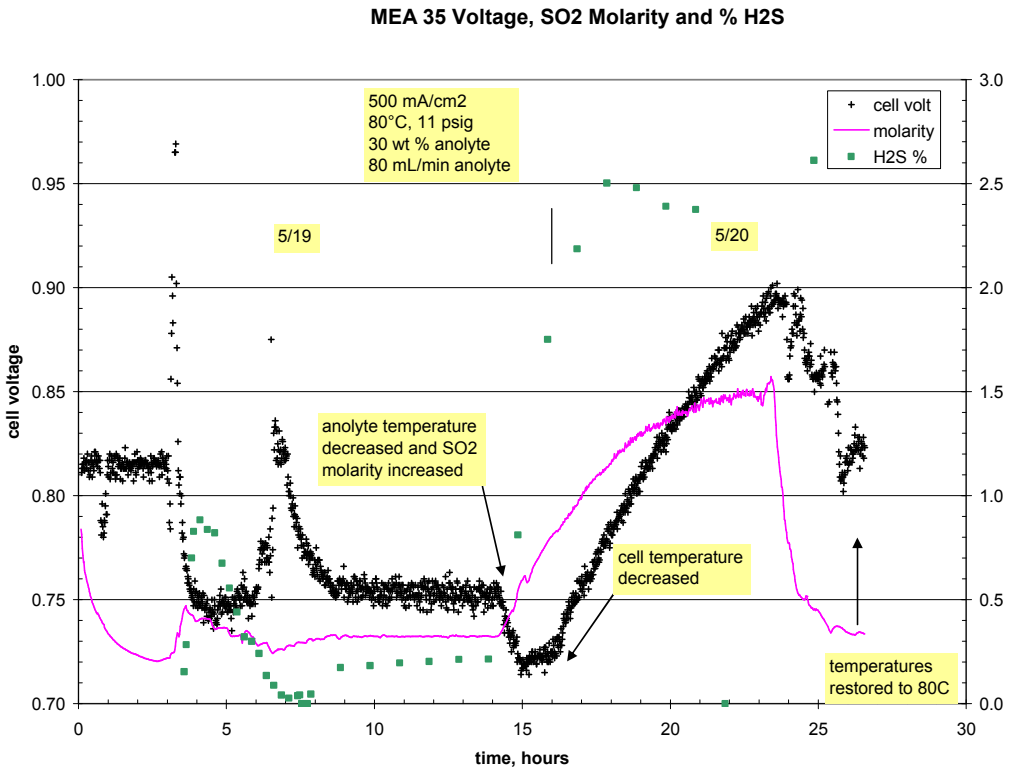


Figure 32 MEA 35 Voltage, SO2 Molarity and % H2S

3.3.19 MEA 36

Before testing MEA 36 a software change was made so that flow of sulfur dioxide would be set to zero if the anolyte temperature fell below a minimum value. This was to avoid the problem of excessive sulfur dioxide concentration encountered during the test of MEA 35. At 12 hours a malfunction caused the anolyte flow to be zero for three minutes. After the computer re-established flow the cell voltage was 40 mV higher.See Figure 33. Also, after the flow cessation the concentration of hydrogen sulfide was less. Apparently the flow cessation caused subtle damage. At 90 hours the computer crashed causing loss of digital data, although some manually acquired data is plotted. The system was shut down blind and three days were required to repair the computer. Immediately after restarting the run cell voltage was less but then increased to the previous steady value. A SEM of MEA 36 exhibited no sulfur layer. See Figure 34.

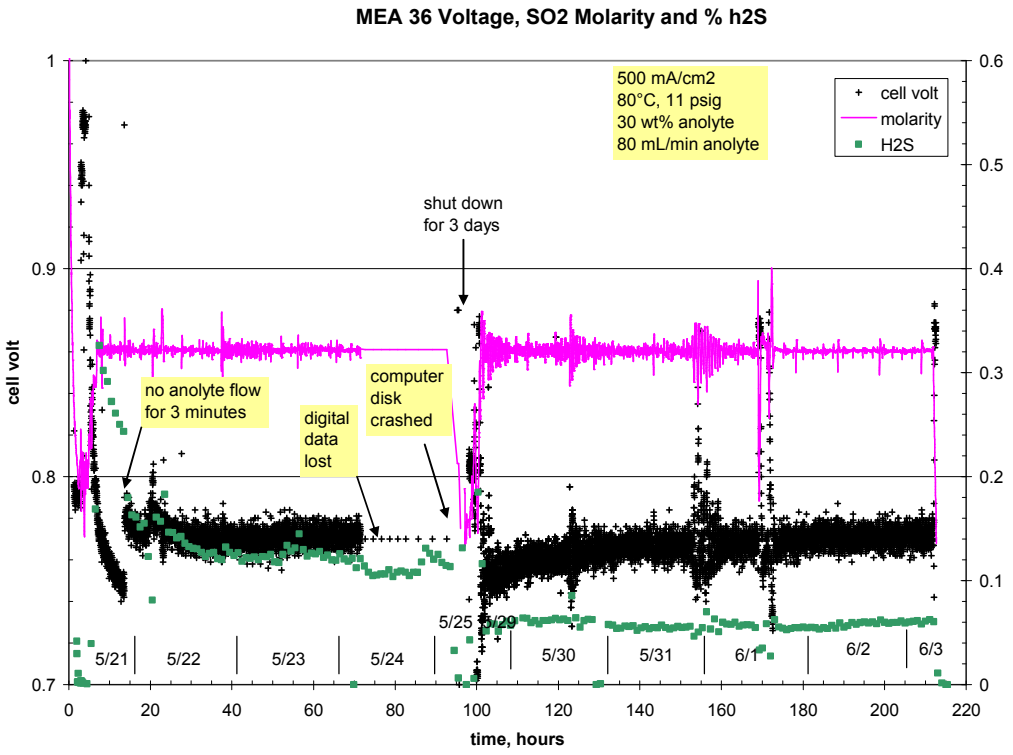


Figure 33 MEA 36 Voltage, SO2 Molarity and % H2S

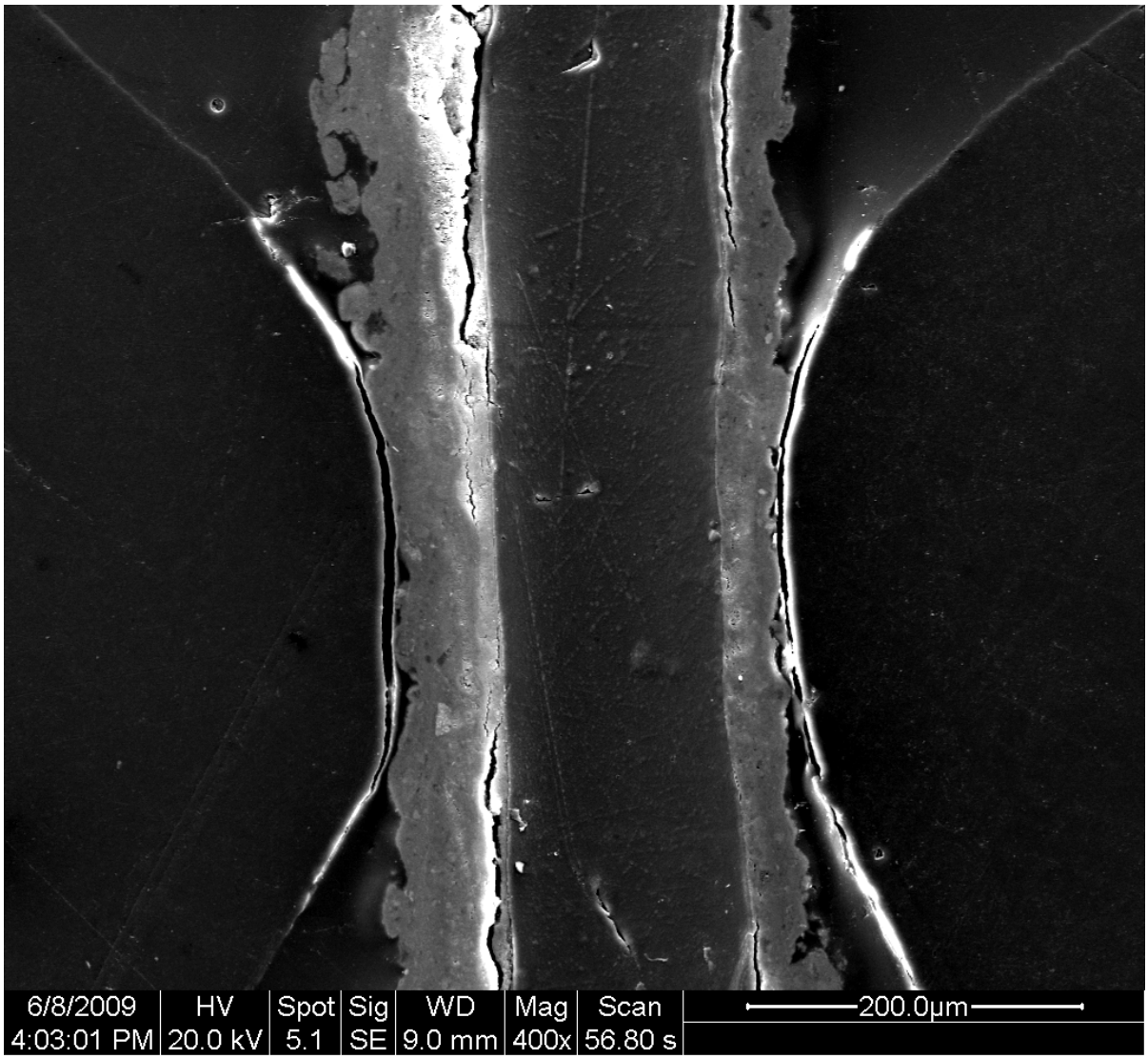


Figure 34 SEM of MEA 36

3.3.20 MEA 37

MEA 37 was tested from June 3 to June 12, 2009. Other than some pressure variations testing was uneventful and cell voltage was steady. See Figure 35. There was a slight downward trend in hydrogen sulfide concentration which may have been an artifact of column aging in the gas chromatograph. At the end of testing MEA 37 appeared to be in pristine condition.

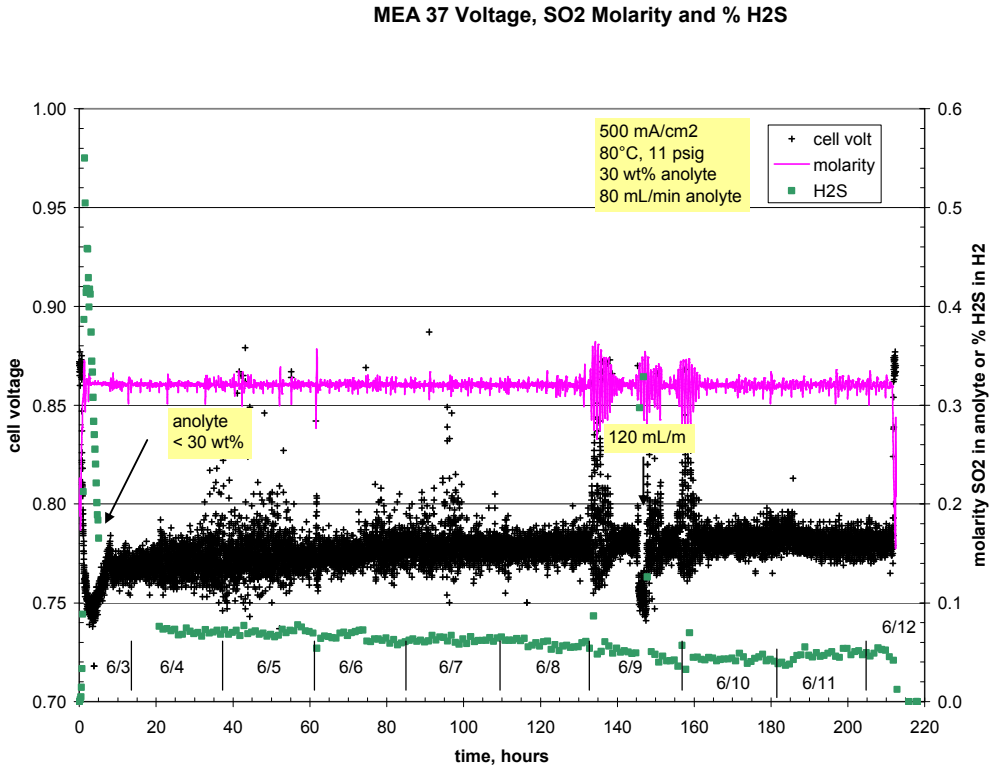


Figure 35 MEA 37 Voltage, SO2 Molarity and % H2S

4.0CONCLUSIONS

The primary observations resulting from this work are as follows.

1. The method for preventing sulfur formation appears to be very successful, at least for test durations as long as 212 hours.
2. In contrast to previous testing there was little or no increase in cell voltage.
3. SEMs of MEAs tested with the new technique revealed no sulfur layers.
4. The method involves only a small cell voltage penalty. The cell voltage does not increase and less product hydrogen is lost in the form of hydrogen sulfide.
5. The method is relatively easy to implement and can be applied to MEAs that employ different membranes and catalysts.
6. System upgrades made to allow unattended operation will make future testing easier.

5.0ACKNOWLEDGEMENTS

Bill Summers served as Program Manager for this work. Vernon Bush and Michael Restivo configured the DAS and wired all instruments. Jerry Corbett installed hardware and assembled the electrolyzer cell. Michael Armstrong performed hydrostatic pressure testing. Douglass Sumpter is the laboratory supervisor. John Pareizs installed the gas chromatograph and analyzer results from it.

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Table 1 Summary of MEA Characteristics in Single Cell Tests

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-115	5	E-Tek	E-Tek	0.65 Pt-C	0.65 Pt-C	49.0
2	Nafion-117	7	Carbon paper, 7 mil	Carbon cloth, 12 mils	1.13 Pt-C	1.14 Pt-C	49.7
3	Nafion-117	7	Carbon paper, 7 mil	Carbon cloth, 12 mils	1.44 Pt-C	1.32 Pt-C	48.1
4	Nafion-117	7	Carbon paper, 7 mil	Carbon cloth, 12 mils	0.88 Pt-C	0.99 Pt-C	49.7
5	Celtec-L	4	Carbon paper, 7 mil	Carbon cloth, 12 mils	1.0 Pt-C	1.0 Pt-C	46.3
6	Celtec-L 2 layers	8	Carbon paper, 7 mil	Carbon cloth, 12 mils	1.47 Pt-C	2.16 Pt-C	49.7
7	Celtec-V	4	Carbon paper, 7 mil	Carbon cloth, 12 mils	0.8 Pt-C	0.8 Pt-C	47
8	Nafion-115	5	Carbon paper, 7 mil	Carbon cloth, 12 mils	0.78 Pt-C	0.61 Pt-C	49.7
9	Nafion-117 Giner	7	Carbon paper, 7 mil	Carbon cloth, 12 mils	4.0 Pt black	4.0 Pt black	49.7
10	Nafion-117 Giner	7	Carbon paper, 7 mil	Carbon cloth, 12 mils	1.0 Pt-C	1.0 Pt-C	49.7
11	Nafion-115	5	Carbon paper, 7 mil	Carbon cloth, 12 mils	1.09 Pt-C	0.72 Pt-C	47.6 and 54.8
12	Nafion-115	5	Carbon paper, 7 mil	Carbon cloth, 12 mils	1.01 Pt-C	1.01 Pt-C	54.8
13	Nafion-115	5	Carbon paper, 7 mil	Carbon cloth, 12 mils	1.02 Pt-C	0.59 Pt-C	54.8
14	Nafion-117 Giner	7	Carbon paper, 7 mil	Carbon cloth, 12 mils	0.8 Pt-C	0.8 Pt-C	49
15	polyphenylene SDAPP 2.2 Hickner	2	Carbon paper, 7 mil	Carbon cloth, 12 mils	1.5 Pt black	1.5 Pt black	46.3

16	polyphenylene SDAPP 2.2 Hickner	2	Carbon paper, 7 mil	Carbon cloth, 12 mils	1.5 Pt-C	1.5 Pt-C	54.8
17	Nafion-212 Lynntech	2	Carbon paper, 7 mil	Carbon cloth, 12 mils	1.5 Pt black	1.5 Pt black	50.
18	Nafion-115	5	Carbon paper, 7 mil	Carbon cloth, 12 mils	0.75 Pt-C	0.75 Pt-C	54.8
19	Nafion-115	5	Carbon paper, 7 mil	Carbon cloth, 12 mils	0.83 Pt-C	0.7 Pt-C	54.8
20	Nafion-115	5	Carbon paper, 7 mil	Carbon cloth, 12 mils	0.782 Pt-C	2.67 Pt black	54.8
21	Nafion-115	5	Carbon paper, 7 mil	Carbon cloth, 12 mils	0.6 Pt-C	2.9 Pt black	54.8
22	Nafion 117 Pt impregn. Giner	7	Carbon paper, 7 mil	Carbon cloth, 12 mils	1.0 Pt black	1.0 Pt black	54.8
23	Nafion 117 Pt impregn. Giner	7	Carbon paper, 7 mil	Carbon cloth, 12 mils	1.0 Pt-C	1.0 Pt black	54.8
24	Nafion 117 Pt impregn. Giner	7	Carbon paper, 7 mil	Carbon cloth, 12 mils	1.0 Pt-C	1.0 Pt black	48.8
25	Nafion 117 Giner	7	Carbon paper, 7 mil	Carbon cloth, 12 mils	4.0 Pt black	4.0 Pt black	54.8
26	Nafion 117 Giner	7	Carbon paper, 7 mil	Carbon cloth, 12 mils	4.0 Pt black	4.0 Pt black	54.8
27	Nafion-115	5	Carbon paper, 7 mil	Carbon cloth, 12 mils	0.86 Pt-C	1.8 Pt-C	54.8
28	Nafion-115	5	Carbon paper, 7 mil	Carbon cloth, 12 mils	1.79 Pt-C	0.87 Pt-C	54.8
29	Nafion-115	5	Carbon paper, 7 mil	Carbon cloth, 12 mils	1.79 Pt-C	0.88 Pt-C	50.
30	Nafion-115	5	Carbon paper, 7 mil	Carbon cloth, 12 mils	0.86 Pt-C	1.80 Pt-C	54.8
31	Nafion-115	5	Carbon paper, 7 mil	Carbon cloth, 12 mils	0.95 Pt-C	1.76 Pt-C	54.8
32	Nafion-115	5	Carbon	Carbon	1.77	0.84	54.8

			paper, 7 mil	cloth, 12 mils	Pt-C	Pt-C	
33	Nafion-115	5	Carbon paper, 7 mil	Carbon cloth, 12 mils	1.92 Pt-C	0.81 Pt-C	54.8
34	Nafion-115	5	Carbon paper, 7 mil	Carbon cloth, 12 mils	0.82 Pt-C	1.87 Pt-C	54.8
35	Nafion-115	5	Carbon paper, 7 mil	Carbon cloth, 12 mils	0.92 Pt-C	1.85 Pt-C	54.8
36	Nafion-115	5	Carbon paper, 7 mil	Carbon cloth, 12 mils	0.85 Pt-C	1.84 Pt-C	54.8
37	Nafion-115	5	Carbon paper, 7 mil	Carbon cloth, 12 mils	1.81 Pt-C	0.87 Pt-C	54.8

Table 2 Summary of Operating Conditions

MEA #	beginning date	ending date	cumulative hours	continuous operation?	current density mA/cm2	anolyte pressure atm	issues
30	10/29/2008	12/8/2008	51	no	700	3.0	none
31	12/17/2008	12/19/2008	53	yes	700	3.0	air dissolved in SO2
32	4/6/2009	4/15/2009	14	no	360	1.7	improved PID control, density and voltage measurement
33	4/16/2009	4/20/2009	103	no	500	2.6	leaks in cathode piping, anolyte pressure swings, short
34	4/28/2009	5/17/2009	233	no	500	2.6	repaired leaks, big pressure swings
35	5/19/2009	5/20/2009	26	yes	500	1.7	bath heater tripped, cartridge heater failed
36	5/21/2009	6/3/2009	212	no	500	1.7	computer crash
37	6/3/2009	6/12/2009	212	yes	500	1.7	none