Paper 126c
Generation of Hydrogen Using Electrolyzer with Sulfur Dioxide Depolarized Anode

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SUMMARY

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. Hydrogen is generated at the cathode. 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). 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].
2. Increasing anolyte pressure generally decreased cell voltage, which is attributed to a higher concentration of sulfur dioxide reactant that 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, probably because of decreased mass transfer coefficients.
7. Barring mechanical damage to an MEA, there was no degradation in cell performance during approximately forty hours of testing with an MEA.

Overview of Test Facility

A test facility capable of testing sulfur dioxide depolarized electrolyzers at pressures up to six atm and temperatures up to 80°C 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.

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°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.

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.

Table 1   Summary of MEA Characteristics

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 paper, 7 mil	Carbon cloth, 12 mils	1.13	1.14	51.3
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

Figure 1 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.
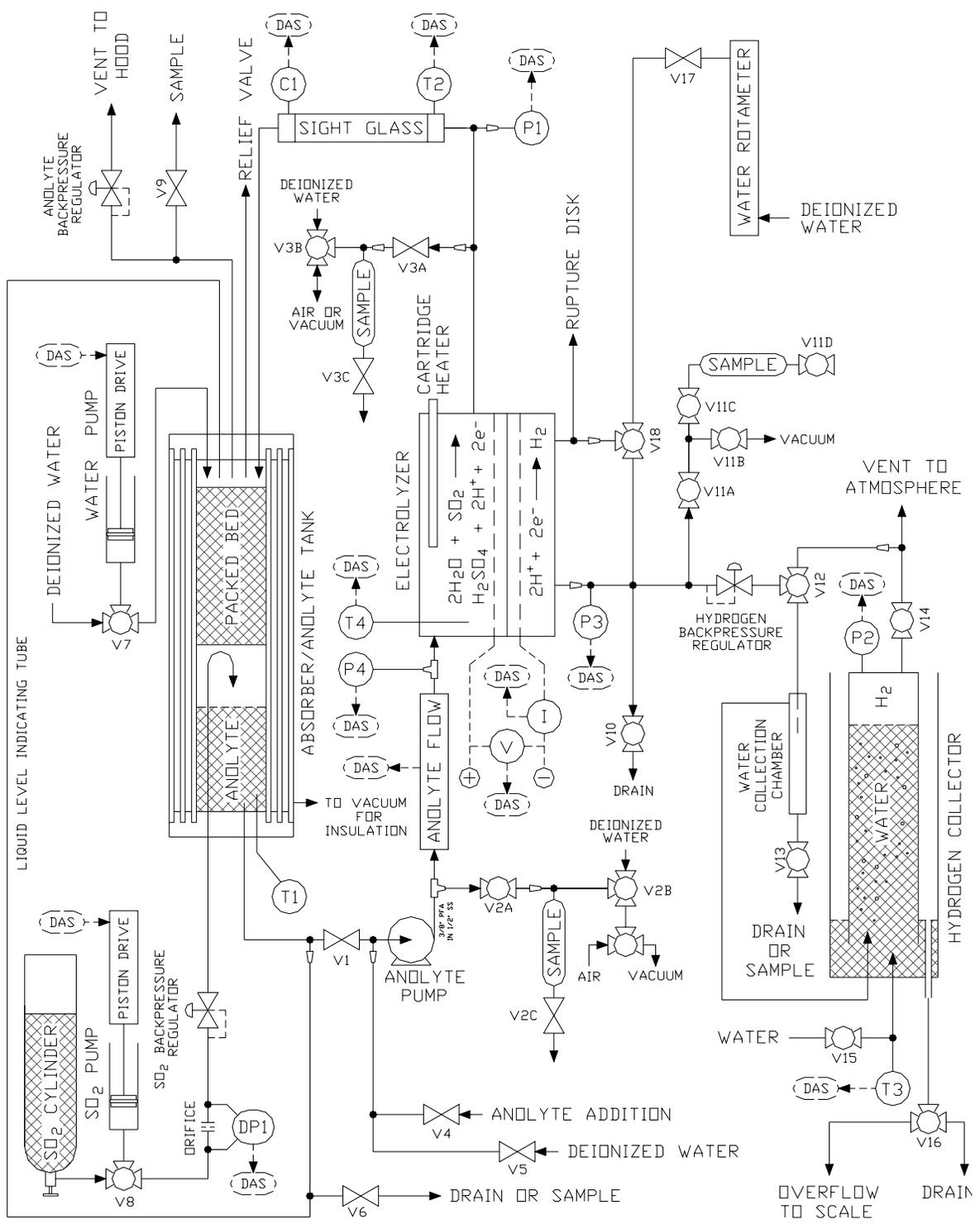
0-90 PSIG ELECTROLYZER
TEST LOOP SCHEMATIC

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Figure 1   Schematic of Electrolyzer Test Facility

The facility includes an Absorber filled with Raschig Rings where sulfur dioxide gas is absorbed into solutions of sulfuric acid and water to form 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. Liquid sulfur dioxide was pumped into the Absorber using a piston pump.

The cathode side of the electrolyzer being tested is connected to the hydrogen handling side of the facility. 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 the Hydrogen Collector which operates by 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.

Abbreviated Procedure

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 loaded to the flow loop.

The sulfur dioxide piston pump was charged with liquid sulfur dioxide. 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. The liquid sulfur dioxide instantly flashed to vapor. After about 20 minutes the vent was closed and the sulfur dioxide flow was greatly reduced to equal 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, the sulfur dioxide flowrate was increased to 5 ml/min. To achieve higher temperature operation, a 400 watt heater was imbedded in the thick stainless steel anode backing plate.

The Test Facility measured hydrogen flowrates by displacement of water from a cylinder to allow identification of any discrepancy from the theoretical rate.   Hydrogen flowrates plotted in this report were adjusted to one atmosphere and 20°C using measured temperature and pressure.

Summary of Testing and Results

After Shakedown testing, MEA #1 was installed in the cell and the cell was installed in the test facility. Pressure drops were relatively high and cell voltages increased over the three days of testing. The layers of the MEA, namely the two diffusion layers and the Nafion membrane, were observed to have delaminated. Then, MEA #2 was tested. Pressure drops were much

lower and steady but cell voltages increased, possibly because of mechanical damage to the MEA.

MEA #3 and MEA #4 were similar and operated with relatively low pressure drops and relatively low and stable cell voltages. They were tested at temperatures up to 80ºC and pressures up to 4 atm. The most thorough testing was conducted with MEA #4 and it was also the most carefully treated Nafion® based MEA to avoid mechanical damage. Attention was paid to avoiding pressure drops across the membrane.   As the result, MEA #4 showed no degradation during testing. Cell potentials were the same for the first and last day of testing. Figure 2 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.

MEA #4 Cell Potentials

Average anolyte composition = 30 wt% acid
Anolyte flow = 0.6 L/min
Data from August 8, 2006

Legend:
- 1 atm 25C
- 2 atm 25C
- 2 atm 50C
- 3 atm 50C
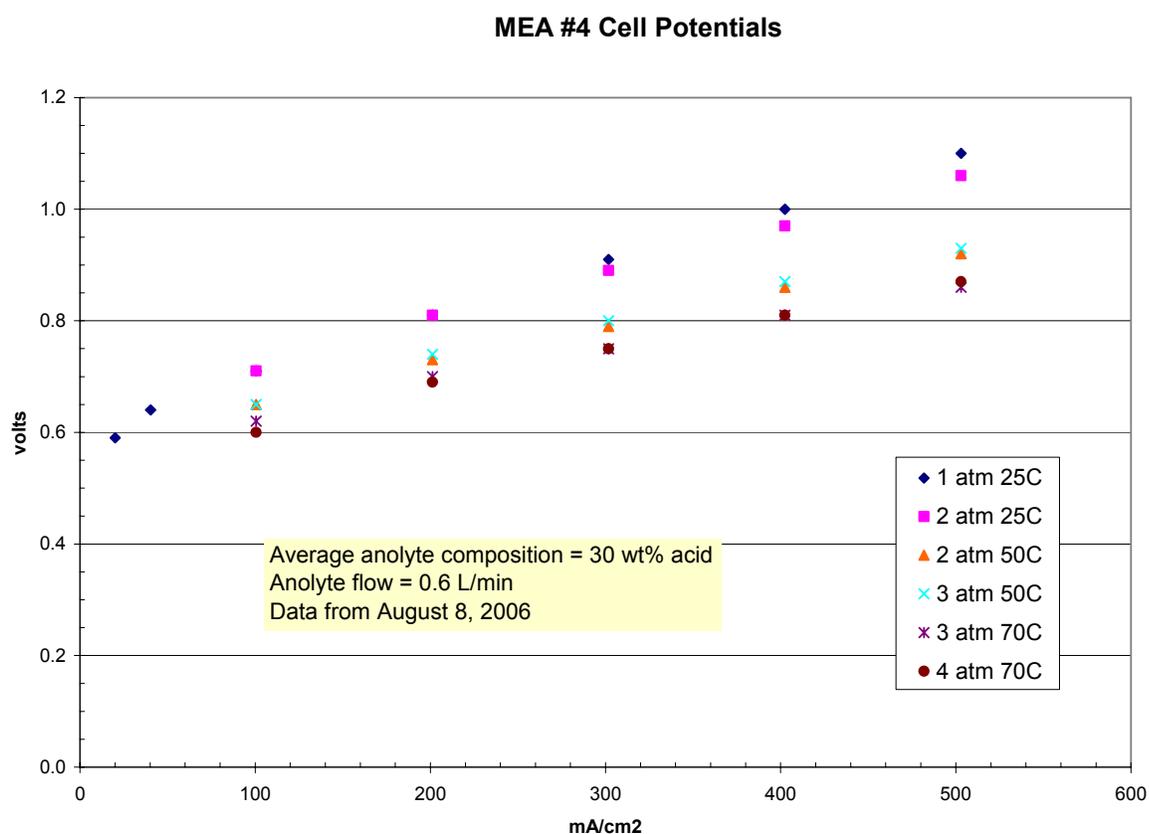- 3 atm 70C
- 4 atm 70C

Figure 2 Electrolyzer Cell Potentials for MEA #4

MEA #5, which used a different type of membrane, namely PBI, displayed surprisingly low cell voltages, 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 thin 2 mil membrane into contact.

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 3 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 4 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. 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 unusual was observed.

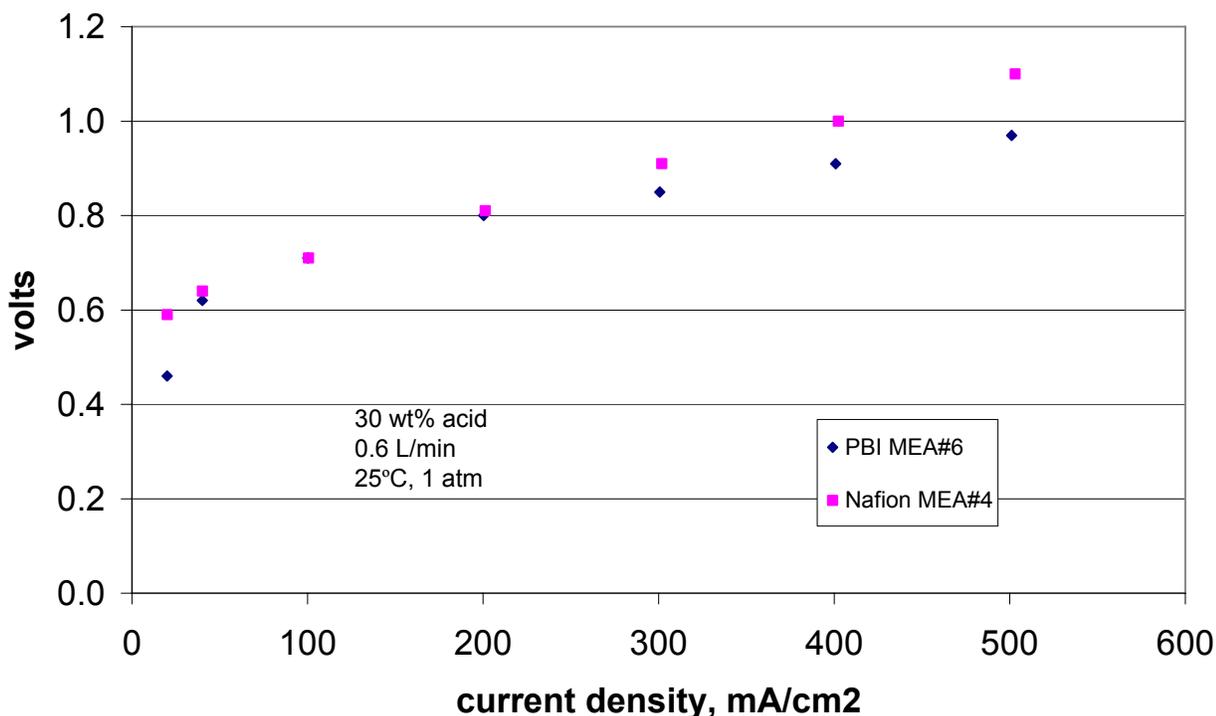## Comparison of Cell Voltages for Nafion and PBI

Figure 3 Comparison of Cell Potentials for MEA #6 and MEA #4
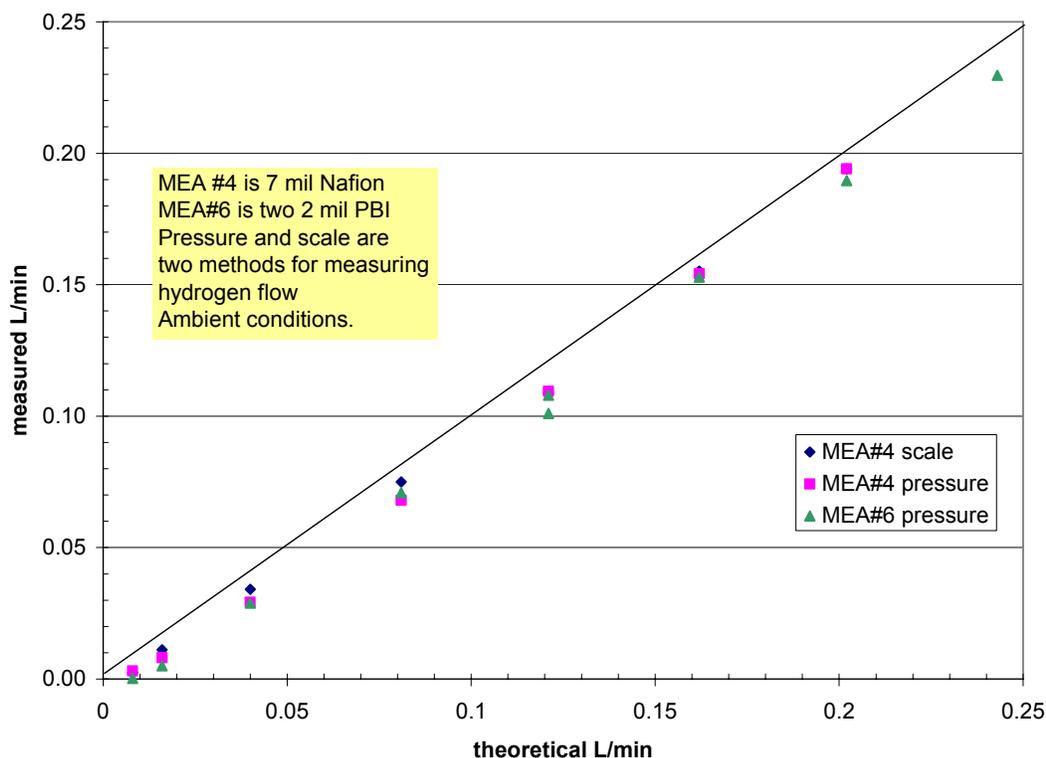
Hydrogen Flow Comparison

Figure 4 Hydrogen Flow Comparison for Nafion and PBI

Effect of Acid Concentration on Cell Potential

Testing quantified the effect of acid concentration on cell potential for MEA #4 and for 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.

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. 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.

Effect of Pressure on Net Hydrogen Production Rate

Figure 5 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.
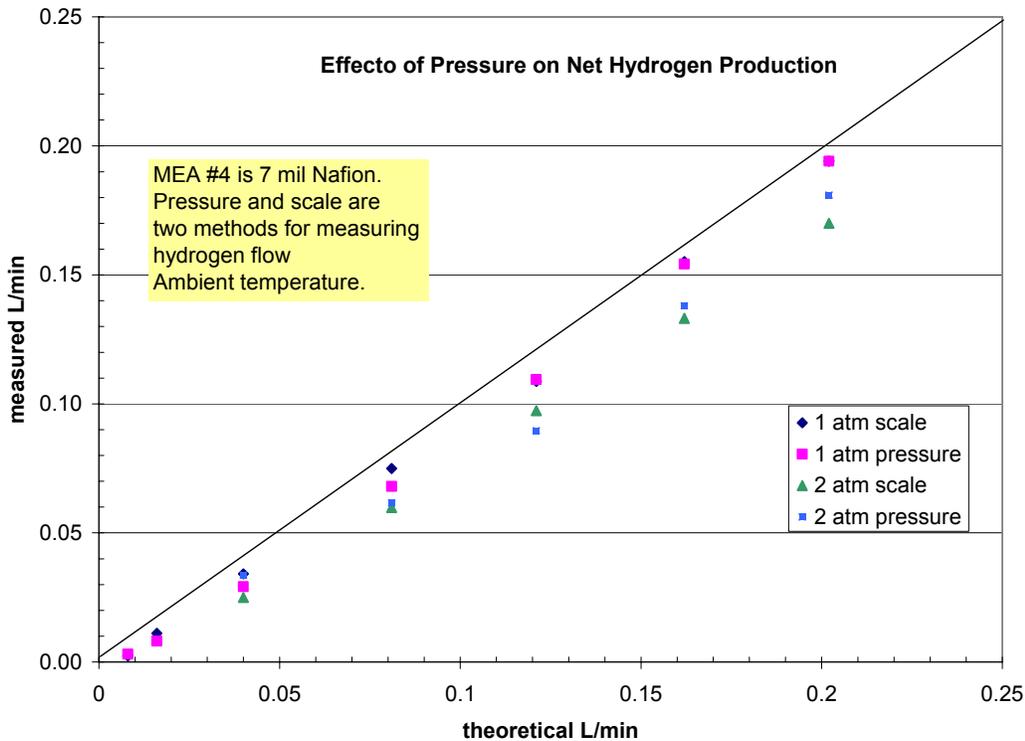

Figure 5 Net Hydrogen Production as Function of Pressure

CONCLUSIONS

The primary conclusions resulting from this work are as follows.
1. The electrolyzer designed, contructed 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 SO_2 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.

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 SO_2 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.

REFERENCES

Colon-Mercado, H. R., D. T. Hobbs, D. B. Coleman and A. A. Ekechukwu, "Initial Component Test Results for an SO_2 Depolarized Electrolyzer Cell Design, WSRC-STI-2006-00064, August 2006.

Steimke, J. L. and T. J. Steeper, "Characterization Testing of H_2O-SO_2 Electrolyzer at Ambient Pressure", WSRC-TR-2005-00310, Rev. 0, August 2005.