Generation of Hydrogen Using Electrolyzers with Sulfur Dioxide Depolarized Anodes

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1.0 EXECUTIVE SUMMARY

This document reports work performed at the Savannah River National Laboratory (SRNL) that resulted in an accomplishment by demonstrating the proof-of-concept of the use of a proton exchange membrane or PEM-type electrochemical cell to produce hydrogen via SO_2-depolarized water electrolysis. For the first time, sulfur dioxide dissolved in liquid sulfuric acid was used to depolarize water electrolysis in a modern PEM cell. The use of such a cell represents a step 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, which 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 tested. The maximum cell current is 50 amperes, which is equivalent to a hydrogen production rate of approximately 20 liters per hour. The test facility was designed for operation at room temperature with pressures up to 2 bar. Feed to the anode of the electrolyzer can be water, sulfuric acid of various concentrations, or sulfuric acid containing dissolved sulfur dioxide. Provisions are included to allow variation of the operating pressure in the range of 1 to 2 bar. Hydrogen generated at the cathode of the cell can be collected for the purpose of flow measurement and composition analysis. The test facility proved to be easy to operate, versatile, and reliable.

Two slightly different SDE's were designed, procured and tested. The first electrolyzer was based on a commercially available PEM water electrolyzer manufactured by Proton Energy Systems, Inc. (PES). The PES electrolyzer was built with Hastelloy B and Teflon wetted parts, a PEM electrolyte, and porous titanium electrodes. The second electrolyzer was assembled for SRNL by the University of South Carolina (USC). It was constructed with platinized carbon cloth electrodes, a Nafion 115 PEM electrolyte, carbon paper flow fields, and solid graphite back plates. Proof-of-concept testing was performed on each electrolyzer at near-ambient pressure and room temperature under various feed conditions. SDE operation was evidenced by 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 conventional water electrolysis (1.23 V). Cell performance at low currents equaled or exceeded that achieved in the two-compartment cells built by Westinghouse Electric Corporation during the original development of the HyS Process. Performance at higher currents was less efficient due to mass transfer and hydraulic issues associated with the use of cells not optimized for liquid feed. Test results were analyzed to determine performance trends, improvement needs, and long-term SDE potential.

The PES cell failed after several days of operation due to internal corrosion of the titanium electrodes in the presence of sulfuric acid. Although it was anticipated that the titanium would react in the presence of acid, the rapid deterioration of the electrodes was unexpected. The USC cell was constructed of carbon-based components and had excellent corrosion resistance. However, it was a modified design originally based on gaseous reactants, and it had poor mass transfer characteristics when using liquid sulfuric acid feed with dissolved sulfur dioxide. This resulted in substantially increased polarization losses at higher current densities. Future work will focus on operation at higher temperature and pressure, as well as improved cell designs specifically considering the unique flow conditions for SDE operation.

The membranes in both cells permitted the transport of some sulfur dioxide from the anode to the cathode, where it reacted with hydrogen gas to form elemental sulfur. However, the sulfur did not appear to poison the cathode catalyst and it was easily washed out 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 Nafion 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.

Both test cells were able to achieve water electrolysis with SO2-depolarization of the anode at cell voltages of less than 0.8 volts at low current densities. The cell voltages increased at higher currents due to the limitations mentioned above. The results of these tests indicate that improved versions of these cells have the potential to meet the commercial operating conditions necessary to make the HyS Process a viable hydrogen production option. The effects of various cell operating conditions, such as sulfuric acid concentration, temperature and pressure, were modeled, but further testing is required to determine their actual impact on cell performance.

2.0 INTRODUCTION

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. Thermo-chemical 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. Thermo-chemical 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 thermo-chemical 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 thermo-chemical 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 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 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 $$\mathrm{SO_2(aq) + 2H_2O(aq) \leftrightarrow H_2SO_4(aq) + 2H^+(aq) + 2e^-} \qquad [1]$$

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

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

The Westinghouse researchers used parallel plate cells and a porous rubber membrane that allowed hydraulic communication between the two parallel flow channels. A small 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.

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 (actually hydronium ions). 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 1. Lu improved his cells and measured generally decreasing voltages during his research. Figure 1 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 bar) 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 bar 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 one 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 1. 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.

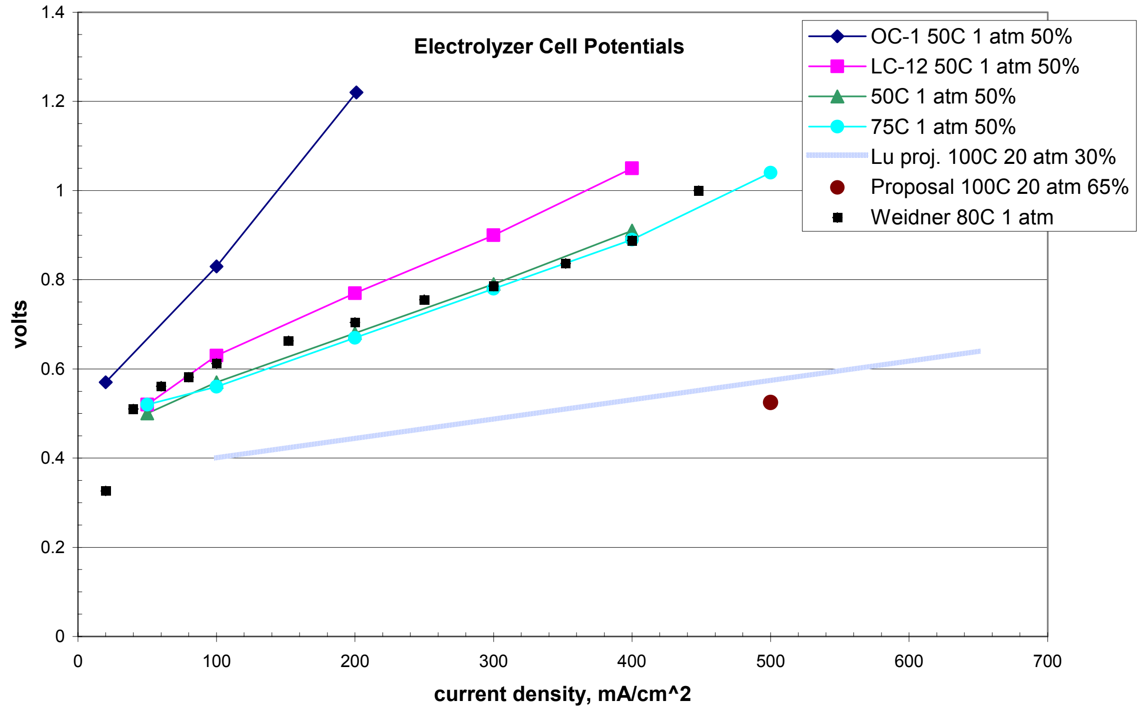

Figure 1 Cell Potentials Measured in Previous Work

3.1.2 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 and low cell voltage. 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. 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.

3.2 HARDWARE AND PROCEDURE

3.2.1 Apparatus

Two electrolyzers with sulfur dioxide depolarized anodes were tested in this work. The first was a HOGEN® PEM Water Electrolyzer Test Cell built by Proton Energy Systems (PES) of Wallingford CT. Due to limited funding and a tight schedule, it was believed desirable to do the initial testing with a modern, commercially available electrolyzer rather than design and build our own. The PES cell was chosen after discussions with a number of electrochemical cell vendors. PES is experienced in making water electrolyzers and they believed that their cell would withstand our harsh chemical conditions. Their cell was also rated at 200 psig, which exceeded our needs for preliminary testing.

The PES electrolyzer has an active area of 86 cm^2 and uses the concept of a membrane electrode assembly (MEA). The membrane is made from Nafion® and pressed against it are an anode and a cathode made from porous titanium with platinum black catalyst on the titanium. The catalyst loading on the electrodes is 4 mg/cm^2 and the specific area for the catalyst is 25 m^2 /g.

The inside of the electrolyzer has passages for the flow of anolyte and catholyte. The wetted surfaces of the inside of the electrolyzer (except for the titanium electrodes) are normally made from 316 stainless steel and Teflon. The PES normally uses deionized water as the anolyte and the catholyte is water that soaks through the membrane from the anolyte. With the intended operation, oxygen gas is generated at the anode and hydrogen gas is generated at the cathode. SRNL changed the operation of the electrolyzer so that the anolyte was a solution of sulfuric acid, water and sulfur dioxide or just water and sulfur dioxide. The pertinent chemical reactions are Equations 1 – 3.

The purchase agreement between SRNL and PES specified that the electrolyzer internals were proprietary, and SRNL could not take it apart or reverse engineer it in any way. PES would not disclose the type of Nafion membrane or its pre-treatment.

After initial discussions with the electrolyzer manufacturers and the decision to purchase the PES electrolyzer, a literature search by SRNL on sulfuric acid resistant materials determined that both 316 stainless steel and titanium were marginal materials with up to 0.050” corrosion per year. SRNL requested the base plate be changed from the 316 stainless steel usually used by PES to Hastelloy B. This material was chosen for its chemical resistance to the harshest reagent, sulfuric acid solutions in the range from 30 wt% to 70 wt% saturated with sulfur dioxide and at temperatures up to 80°C. SRNL deemed this change to be essential since the base plate was one of the primary pressure containing components. PES agreed to this change for a cost increase covering the material and additional machining difficulty. SRNL also requested that PES consider substituting graphite electrodes, which have greater corrosion resistance, for the normally used titanium. PES stated that change would require significant redesign and testing that they were not prepared to do for a single purchase. SRNL proceeded with the order from PES believing the titanium electrodes would last through the planned short testing period, and since the electrodes are internal and not pressure containing components.

The PES electrolyzer is designed to operate with up to 160 amperes at 1 to 2 volts. For our initial testing, the anode and cathode were connected to an available direct current power supply capable of supplying up to 50 amperes at up to 20 volts.

The second cell, the USC cell is a nearly square sandwich. The outer layer of the sandwich is two ½” (12.7 mm) thick pieces of stainless steel for structural strength. Next are two thin fiberglass insulators. Next are two copper terminal plates with large tabs to bolt the power supply cables and voltage taps to. Next are two 0.8” (20.3 mm) thick solid graphite blocks. Each has an O-ring groove machined in it to provide a seal. Each graphite block also has a nearly square recess machined in it. The recesses are 3.0” x 3.0” by 0.10” (76.2 mm x 76.2 mm x 2.54 mm). Each graphite block also has two holes with pipe threads to allow inlet and outlet of fluid. A porous graphite wafer, 0.104” (2.64 mm) thick, fit snugly in each recess. The anode wafer has thin grooves 0.070” (1.78 mm) deep and 0.063” (1.6 mm) wide machined in it to facilitate flow of anolyte. There are no grooves in the cathode wafer. The last and innermost layer was the MEA consisting of a sheet of Nafion 115, which looks like heavy duty plastic wrap, and a slurry of powder consisting of 40 wt% of platinum on carbon and Nafion hot pressed onto the Nafion sheet. The total thickness of the MEA was 0.030” and the active area was 40 cm^2. The platinum loading for both the anode and cathode was 0.5 mg/cm^2, one-eighth the platinum loading of the PES cell.

The facility was located in a large chemical hood. Air flow was maintained whenever hydrogen or sulfur dioxide was present in the hood. The hood was effective, no sulfur dioxide odor leaked out. Also in the hood were a 100 lb. cylinder of sulfur dioxide, the SO_2 Absorber, the electrolyzer cell, the Anolyte flowmeter, the Anolyte Pump and the Hydrogen Collector.

Figure 2 is a schematic of the equipment in the facility which shows the locations of the valves and instruments. There are two backpressure regulators. The first one controls the pressure in the Sulfur Dioxide Absorber. The second controls the hydrogen pressure at the cathode of the electrolyzer.

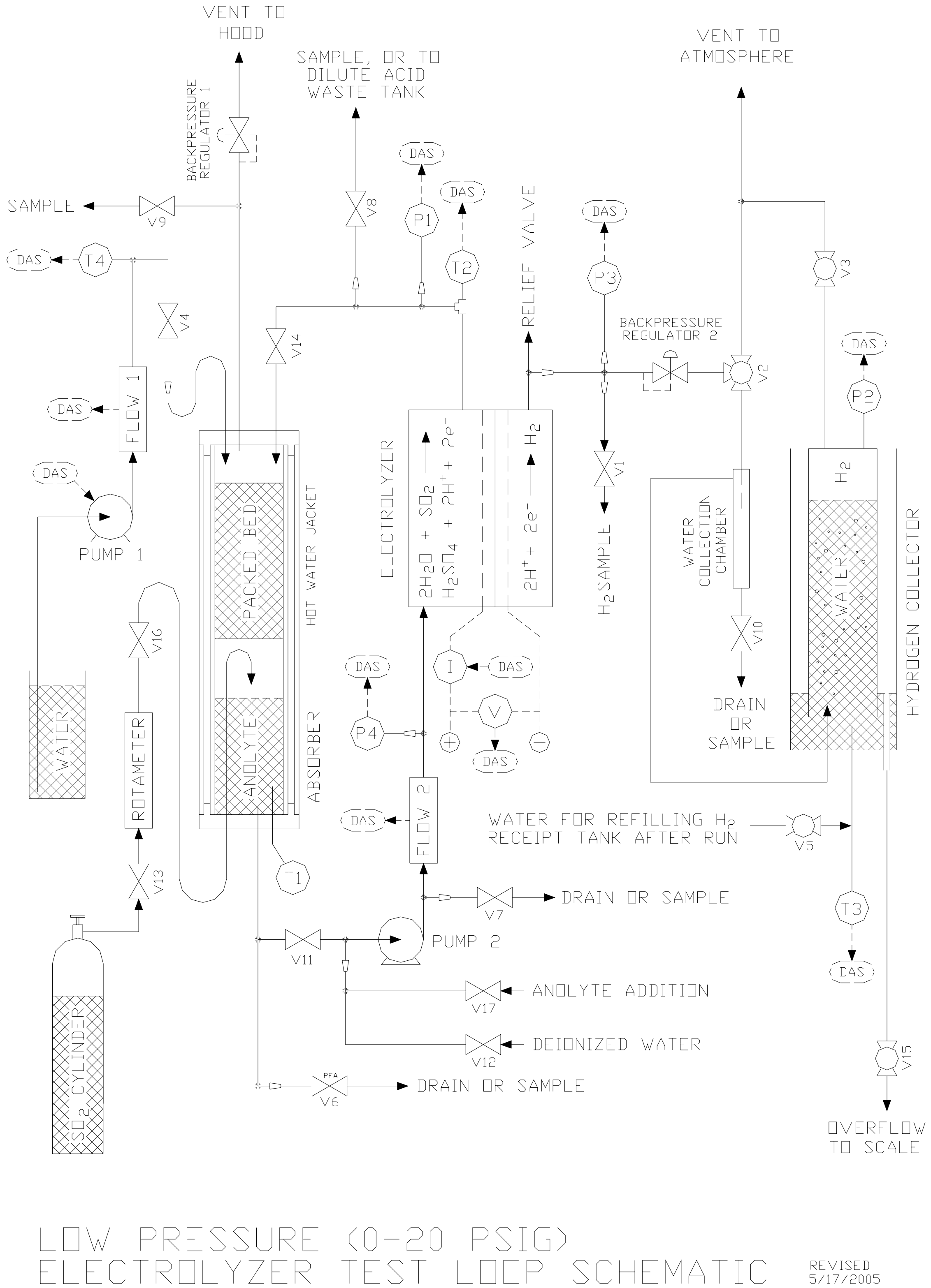

Figure 2 Schematic of Electrolyzer Test Facility

The facility includes an Absorber where sulfur dioxide gas was absorbed in either water or 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 was used and the excess gas was 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 was purchased in a 100 lb. cylinder and the flowrate was measured using a calibrated gas rotameter, Brooks R-2-15A with a glass ball. The rotameter was calibrated with air and then the calibration was extended to sulfur dioxide using the Brooks recommendation, as follows. The rotameter reading, as if the gas were air, was divided by the square root of the ratio of the densities of sulfur dioxide and air to give the volumetric flowrate of sulfur dioxide. No pressure regulator was necessary for the sulfur dioxide because the vapor pressure at room temperature is only 34 psig. The chemical reaction consumes water, so a small pump was provided to supply makeup water. Also, valves were provided so that anolyte samples or gas samples could be collected. Excess sulfur dioxide gas escaped from the Absorber through a Backpressure Regulator Valve. This was provided so the Absorber pressure could be increased, which increases the concentration of dissolved sulfur dioxide. A clear cylinder was placed around the Absorber forming a jacket through which hot water could be passed to achieve temperatures greater than ambient. However, the testing reported here was all at room temperature. All tubing, valves and connectors in the anolyte flow loop were made from fluorocarbon polymer (PTFE or PFA). The translucent tubing was useful in determining if lines were full of liquid or were passing a two-phase mixture.

The cathode side of the electrolyzer being tested was connected to the hydrogen handling side of the facility. For safety, a pressure relief valve was connected to the hydrogen outlet of the electrolyzer. For testing the PES cell the pressure relief valve was set at 200 psig. For testing the USC cell the pressure relief valve was set at 35 psig. The reduction in pressure setting was necessary because the USC cell was not designed for as high a pressure as the PES cell. Downstream of the relief valve was a Backpressure Regulator 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 was to displace water 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. The water temperature, hydrogen gage pressure in the inverted cylinder, and atmospheric pressure were measured to allow for volume correction. The inner cylinder of the Hydrogen Collection Cylinder was 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 protected the glass cylinder and facilitated 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 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 was connected to the output of the power supply to allow for independent measurement of current. Voltage taps independently connected to the cell electrodes were connected to the DAS.

The instruments used in the test were thermocouples, pressure gages, flowmeters and a scale. The instrument signals were connected to the data acquisition system, a Dell computer with special acquisition boards and Labview software. Observations and some data were recorded in a laboratory notebook.

3.2.2 Test Matrix

The Test Matrix was designed with safety in mind. This was important because the testing involved pressures as high as 50 psig, potentially flammable gas mixtures, sulfur dioxide, and solutions of sulfuric acid which can cause serious chemical burns. The philosophy of testing was to introduce one new hazard at a time. The first testing was Shakedown with water and air to verify the operation of the instruments, valves and pumps and also to check for leaks. Next was electrolysis of water only, the operation originally intended by PES. One reason for this step was to verify the electrolyzer performance measured by PES. The next step added one hazard, sulfur dioxide. Water with dissolved sulfur dioxide was electrolyzed. It was expected that this mixture would demonstrate sulfur dioxide depolarized anode behavior. The final step was electrolysis of sulfur dioxide dissolved in sulfuric acid solutions.

3.2.3 Abbreviated Procedure for Operation with Acid and Sulfur Dioxide

The following is a summary of the Work Instruction prepared for this work. Any previous contents of the facility were drained. A liter of the desired acid solution was mixed in a bottle. A tube was attached to valve V17 and inserted into the bottle of acid solution. The pump was used to draw the acid into the absorber. The acid solution was circulated through the cell and absorber at flowrates ranging from 0.3 L/min to 1.5 L/min and sulfur dioxide gas was passed through the Absorber at 1 L/min. After about 20 minutes the sulfur dioxide flow was reduced to 0.5 L/min and current was passed through the cell. At the end of the day of testing, the cell was drained and both sides of the cell were flushed with deionized water. The cell was filled with deionized water for overnight and weekends

3.3 TEST RESULTS

3.3.1 Test Results for PES Cell, Water Only, No Sulfur Dioxide

Pressure drops for water flow were measured for the anode side and cathode side of the electrolyzer. The pressure drop for the cathode side is about fifteen times as large as for the anode side, so the cathode flow passages are more restrictive. The anode pressure drop was measured to allow estimation of the maximum flowrate with acid solutions. The cathode flowrate was measured as a baseline value to track any sulfur fouling of the cathode flow passages.

Data of cell potential vs. current density, called Polarization curves or Tafel Plots, were measured for conventional water electrolysis for the PES electrolyzer. Both the SRNL data and vendor data were measured for a water flowrate of 0.35 L/min. The SRNL data were measured for a cell temperature of 20°C and for hydrogen pressures of both 1.0 bar and 1.7 bar. The vendor data were measured at 50°C and 14.6 bar. The potential increased linearly from 1.55 volts at very low current density to 1.82 volts for SRNL and 1.74 volts for vendor data at about 600 mA/ cm^2. The minimum possible cell voltage is the reversible cell voltage for conventional electrolysis, which is 1.23 volts at 25°C so the excess voltage is the result of electrical resistances and overvoltages. The SRNL voltages are somewhat higher than the vendor voltages, which may be the result of the higher temperature of the vendor tests. Tafel plots usually show a region of sharply increasing voltage beyond some current density. Apparently the vendor did not run a high enough current density to encounter that region. When the cell performs conventional electrolysis of water, the anolyte effluent contains a two-phase mixture of water and oxygen. Even with no current flow, there was a small voltage, the residual voltage, of about 0.10 volt.

3.3.2 Measurement of Hydrogen Flowrates

The SRNL Facility measured hydrogen flowrates by displacement of water from a cylinder. There were actually three possible measurements. 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 bar and 20°C. The first method was to use the ruler on the side of the Hydrogen Collector to measure the height of the gas-water interface and adjust for 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 the water was displaced by hydrogen the water level dropped, and the pressure approached atmospheric. The volume was adjusted for temperature and absolute pressure for the gas. 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. Hydrogen flow measurements were made for electrolysis of water with no sulfur dioxide at cathode pressures of 1.0 bar and 1.7 bar. In this mode of operation, oxygen is generated at the anode and hydrogen is generated at the cathode. The second and third methods agreed well with each other and there was no difference between the data for the two pressures. The two methods measured hydrogen flows that were 96% of the theoretical flow, where two moles of electrons generate one mole of hydrogen gas. Three possible reasons for a measured hydrogen production rate of less than 100% of theoretical are current leakage, side reactions that consume electrons and the slight solubility of hydrogen in water.

3.3.3 PES Cell, Electrolysis of Water and Sulfur Dioxide

The first chemical testing was conducted with water and sulfur dioxide. One reason was to introduce new hazards one at a time. However, it was expected that these tests would show sulfur dioxide depolarized operation and actually demonstrate lower cell voltages than with acid solutions. Initially, the loop contained only water. Circulation was started and a current of 30 amps (349 mA/cm^2) was applied to the cell. Sulfur dioxide was gradually added to the loop. It was anticipated that the cell voltage would decrease as the concentration of sulfur dioxide increased, however, the cell voltages were nearly the same as with no sulfur dioxide a shown in Figure 3. The anolyte effluent was a two-phase mixture just as it had been for conventional electrolysis of deionized water.

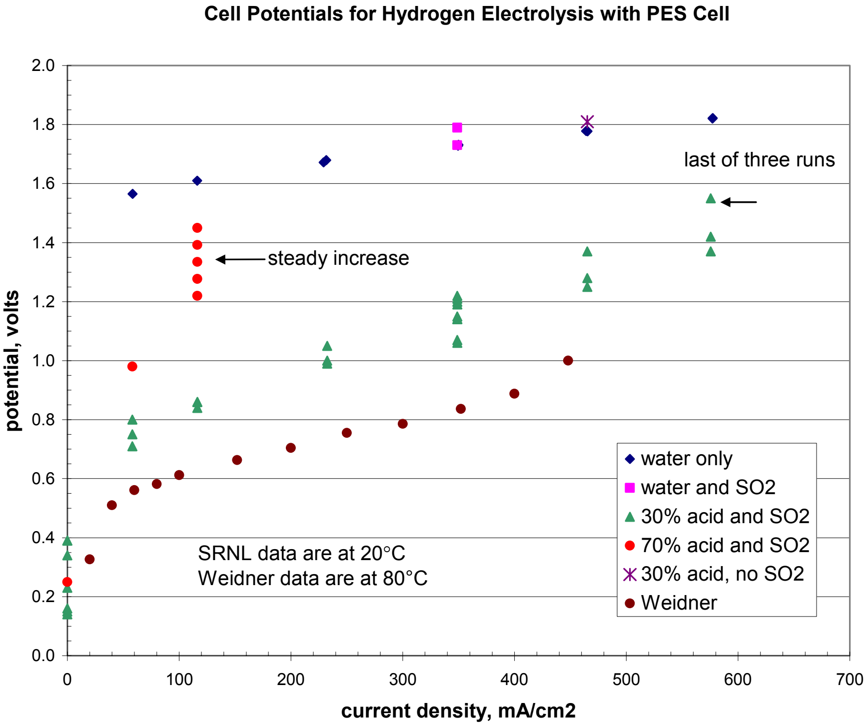

Figure 3 Cell Voltages Measured for PES Cell

A sample of anolyte was collected and titrated. Assuming divalent sulfur compounds, the molarity was 0.5, so the absorber was performing as expected. The anolyte had an unusual odor, not sulfur dioxide or hydrogen sulfide. Peter Lu mentioned the formation of dithionic acid ($H_2S_2O_6$), so that may have been the source of the odor. The Absorber was temporarily bypassed and deionized water was flowed through the cell. Dark liquid was observed to pass through the translucent effluent line. The dark liquid was collected in a sample jar, but within an hour the color had faded. Water was briefly electrolyzed and then the current was stopped. With no current there was a residual voltage initially equal to 1.37 volts that decreased with time. The cell was intentionally shorted but a residual voltage of 0.77 volt returned. The loop and cell were drained and flushed with deionized water. The test was repeated, but the second time, current was not applied until the water was saturated with sulfur dioxide. The results were similar and there was no reduction in cell voltage. The source of the residual voltages may have been the formation of compounds like dithionic acid (Ephraim, 1954) that temporarily formed a voltaic cell. The proposed reactions follow

$$SO_2 + H_2O = H_2SO_3 \qquad [4]$$

$$2H_2SO_3 = H_2S_2O_6 + 2H^+ + 2e^- \qquad [5]$$

When the power supply is de-energized the second reaction reverses, generating a residual voltage.

3.3.4 PES Cell, Testing with Sulfuric Acid Solutions and Sulfur Dioxide

The contents of the cell and loop were drained, but the loop was not rinsed. One liter of 30 wt% sulfuric acid was charged to the loop. It was intended to briefly electrolyze the acid solution with no sulfur dioxide and then add sulfur dioxide to the solution. However, it was initially observed that the cell voltage was significantly lower than for conventional water electrolysis and the anolyte effluent was single phase liquid flow. However, after eight minutes of electrolysis, the voltage increased by about 0.5 volts and gas bubbles reappeared in the anolyte effluent. Apparently, residual sulfur dioxide in the loop was sufficient to initially permit sulfur dioxide depolarized anode operation. When the sulfur dioxide was depleted, cell operation reverted to conventional electrolysis. The anolyte was then saturated with sulfur dioxide at 20°C and atmospheric pressure and electrolysis was performed. The cell voltages are plotted in Figure 3. Cell voltages were 0.6 volt to 0.8 volt less than conventional water electrolysis. Voltages generally increased slightly over the course of testing, which may have been the result of loss of catalyst. The residual voltage varied from 0.14 volt to 0.23 volt. At the conclusion of testing with 30 wt% sulfuric acid the residual voltage was 0.16 volt.

An hour after acid was introduced to the anolyte, black coloring was observed in the Hydrogen Collector, which is downstream of the cathode. The black liquid smelled of sulfur dioxide and titrated to 0.01 molar concentration assuming divalent sulfur compounds. The cathode was flushed with deionized water and yellow sulfur slurry washed out. After a couple of days, solids settled out of the black liquid from the Hydrogen Collector. An analysis of the solids showed the following elements, Fe, S, Cr and Ni, in that order of abundance, but no Ti. That is a puzzling result. Stainless steel 316 has Fe, Cr and Ni, in that order of abundance, matching the solids. Proton Energy Systems was asked to replace stainless steel 316 with Hastelloy B, which is heavily Ni and has almost no Fe or Cr. However, the valves, fittings, and connecting tubing between the electrolyzer and hydrogen collector were all either 304 or 316 stainless steel, and may have been the source of the contaminants in the hydrogen collector. It was originally believed that these lines would contain only relatively pure hydrogen, so special materials were not provided.

The 30 wt% acid was drained from the loop and cell. The loop and both sides of the cell were flushed three times with deionized water. One liter of 70 wt% sulfuric acid was loaded to the loop. The electrolyzer was run briefly with no sulfur dioxide to establish a baseline. The voltages were higher than for standard water electrolysis and are plotted in

Figure 3. After current was stopped, the residual voltage was high, 1.26 volts. Therefore, operating the cell with either sulfur dioxide or sulfuric acid, but not both, leads to high residual voltages. Enough sulfur dioxide was added to the anolyte to achieve a sulfur dioxide concentration of 0.2 molar, but the voltage remained high. Both sides of the cell were rinsed with deionized water and the residual voltage was 0.51 volt.

Twenty four hours later the residual voltage had decreased to 0.26 volt. The 70 wt% anolyte was saturated with sulfur dioxide. The cell voltage at 5 amps was 0.98 volts. However, increasing the current to 10 amps caused the voltage to increase. The current was stopped when the voltage passed 1.45 volts. At this point the cell was believed to be damaged irreparably by corrosion and it was used no further. There was no point in continuing with the planned test matrix since the cell performance was clearly compromised.

Hydrogen generation rates were measured using the two methods and are plotted in Figure 4. Previous showed that with no sulfur dioxide present, measured hydrogen rates were 96% of theoretical based on current. After acid was introduced to the anolyte, the measured hydrogen flowrates plotted in Figure 4 decreased and were less than the theoretical flowrates by about 0.04 L/min. The very fine suspended black solids in the Hydrogen Collector may have interfered with the measurement by holding up bubbles of hydrogen. In clean water the gas bubbles rise rapidly. One could not see what was happening to the gas bubbles in the black liquid. The gas bubbles may have attached themselves to solid particles.

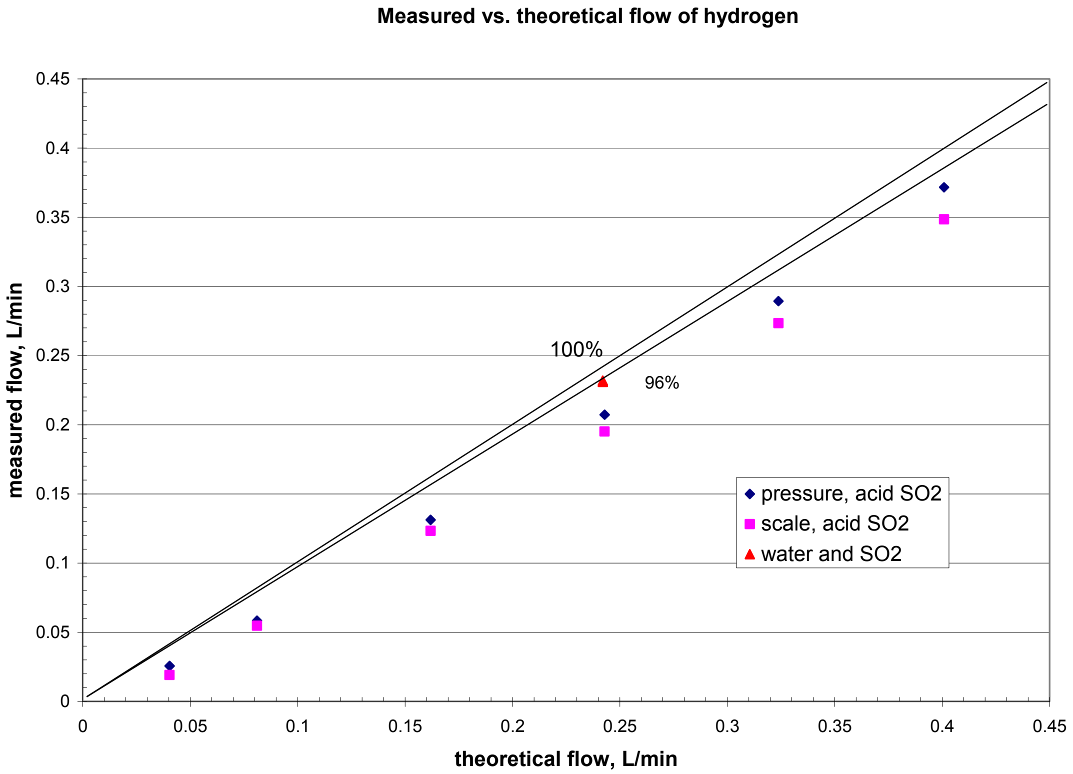

Figure 4 Hydrogen Generation Rates with PES Cell with Acid and Sulfur Dioxide

3.3.5 Testing with USC Cell

The USC cell initially had a small leak that was repaired by the use of a thicker O-ring at a sealing surface. While disassembled for correction of the leak, it was noted that the grooves in the anode side porous graphite wafer faced the MEA and were aligned vertically. In this configuration the inlet anolyte flow had to pass from a horizontal distribution slot at the bottom of the solid graphite block through the porous wafer to enter the grooves. It then flowed upward along the surface of the MEA to the top of the wafer. A series of holes was provided at the top of the wafer to let the anolyte flow easily out of the grooves through the porous wafer into the top horizontal collection slot at the top of the solid graphite block.

The USC cell was installed in the test facility. As part of the conversion to the USC cell, a different pressure relief valve with a 35 psig set point was installed in the hydrogen effluent line connected to the cell. The USC cell was initially tested with 30 wt% sulfuric acid solution, saturated with sulfur dioxide at 20°C. However, the flow resistance was erratic and changed greatly with time, therefore it was difficult to control flow. The cell was disassembled, the grooved wafer was reversed and the cell reassembled. The resulting hydraulic data were well behaved.

The USC cell was then tested with 30 wt% sulfuric acid saturated with sulfur dioxide at 1 bar and 2 bar and for anolyte flows of 0.3, 0.9 and 1.5 L/min. The concentrations of sulfur dioxide at the two pressures are estimated to be 5 wt% and 10 wt%. The results for cell voltage are plotted in Figure 5.

1. The lowest cell voltages were for the higher sulfur dioxide concentration and the highest anolyte flowrate.
2. Voltage increased fairly rapidly with increasing current density and was generally higher than voltages measured with the PES cell.
3. Decreasing either sulfur dioxide concentration or anolyte flowrate increased cell voltage, indicating mass transfer limitations.
4. Figure 6 plots measured hydrogen generation rates. At currents below 1.5 amperes all or nearly all of the hydrogen was consumed reacting with sulfur dioxide to form sulfur. At higher currents, the reaction with sulfur dioxide consumed between 10 mL/min and 20 mL/min of hydrogen.

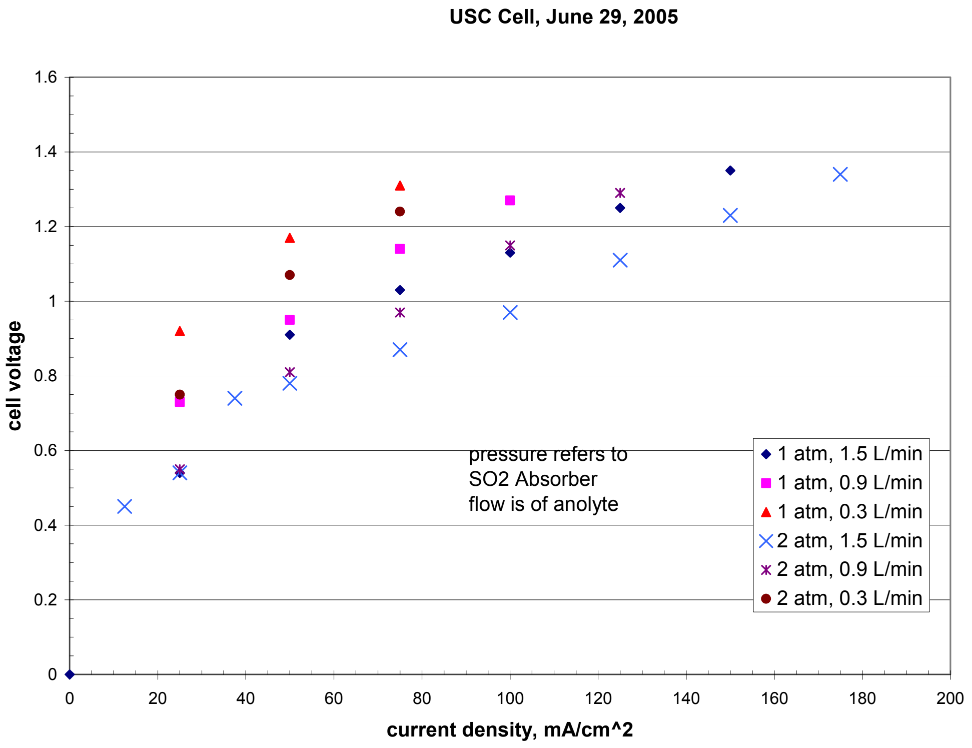

Figure 5 USC Cell Voltages

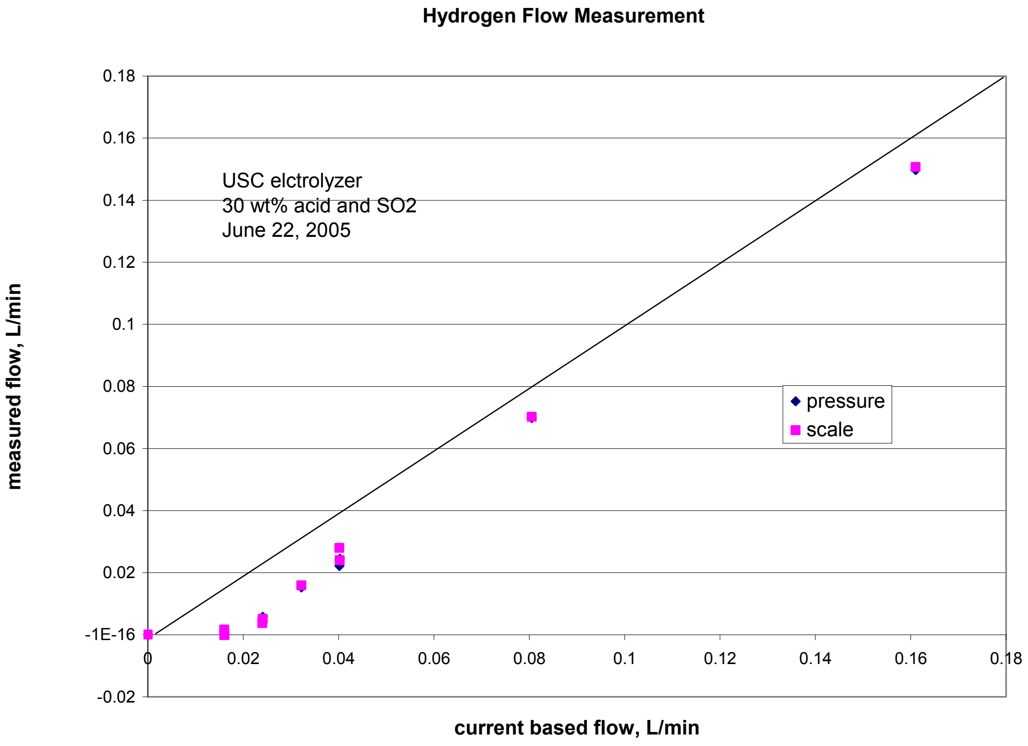

Figure 6 USC Cell Hydrogen Production Rates

4.0 CONCLUSIONS

The primary conclusions resulting from this work are as follows.

1. HyS cells should be constructed of corrosion resistant materials like graphite and Teflon, like the USC cell.
2. The porous titanium electrodes used in the PES cell have inadequate corrosion resistance for the HyS conditions.
3. The PES cell had good mass transfer characteristics, while the USC cell was strongly limited by mass transfer. As a result the USC required more time to reach steady state.
4. Sulfur formed at the cathode by the reaction of hydrogen with sulfur dioxide that diffused through the membrane of both cells. We saw no evidence that the sulfur poisoned the platinum catalyst. The sulfur formed at the cathode was easily flushed out using a flow of deionized water. This conclusion is important because it indicates that sulfur will be a tractable problem in commercial scale electrolyzers.

Other observations and conclusions include the following.

1. A mixture of sulfuric acid, water and sulfur dioxide at the anode of an electrolyzer cell decreased the cell voltage for hydrogen generation for both cells by as much as 0.8 volts compared to conventional water electrolysis, which requires in the range from 1.6 volts to 2.1 volts. This important result means that a sulfur depolarized electrolyzer can produce the same amount of hydrogen at only about half the electrical energy input
2. Water and sulfur dioxide alone as an anolyte or water and sulfuric acid alone as an anolyte in the PES cell did not result in decreased cell voltages. However, these anolytes did result in large residual cell voltages, the voltage that remains after the electrical current is stopped. Residual voltages as large as 1.4 volts were measured in the PES cell. The residual voltages may be the result of the formation of dithionic acid.
3. Residual voltages diminish as the cell is allowed to remain inactive.
4. A visual indication of sulfur dioxide depolarized operation in the electrolyzer is the absence of oxygen bubbles in the anolyte effluent. With conventional water electrolysis, oxygen bubbles are easy to see.
5. With the USC cell, increasing the flowrate of anolyte and increasing the concentration of sulfur dioxide in the anolyte usually reduced the cell voltage.
6. The PES cell was only briefly checked for mass transfer limitation. An increase in anolyte flow did not reduce cell voltage.
7. The USC cell voltage increased faster with increases in current density than the PES cell. This may be partially the result of a catalyst loading that is a factor of eight lower for the USC cell.
8. Initially, the USC cell was assembled so that a graphite wafer with grooves machined in it to provide a flow path was pressed with the grooves against the MEA. This led to time varying, relatively high and unpredictable flow resistance. Turning the grooves away from the MEA gave lower and reproducible pressure drops.
9. Sulfur dioxide crossed the Nafion membrane in both the PES cell and the USC cell as evidenced by the odor of sulfur dioxide in the water flowing out of the Hydrogen Collector. The solution is to develop a membrane with less permeability for sulfur dioxide, then periodically flush out the sulfur and oxidize it back to sulfur dioxide.

5.0 SUMMARY

Successful proof-of-concept testing of sulfur dioxide depolarized electrolyzers in a PEM-type cell was conducted. As part of this effort a versatile facility for testing electrolyzer cells was designed and constructed. The test facility worked well and will be used in future testing of improved cell designs. Two electrolyzer cells were tested, a commercial cell from Proton Energy Systems and a research cell from the University of South Carolina. Both cells used a Nafion membrane which was not tested by the Westinghouse researchers during the period 1975-1982. Sulfur dioxide depolarized operation was demonstrated for both cells and the cell voltage was as much as 0.8 volts less than for standard water electrolysis. This important result means that a sulfur depolarized electrolyzer can produce the same amount of hydrogen at only about half the electrical energy input.

The commercially available PES cell was designed to withstand relatively high pressure, it had relatively low fluid resistance and it had good mass transfer characteristics. However, the PES cell failed after a short period of operation due to internal corrosion of titanium electrodes in the presence of sulfuric acid. The USC research cell was constructed of carbon-based components and had excellent corrosion resistance. However, it was a design originally based on gaseous feed, and it had poor mass transfer characteristics when using liquid feed with dissolved sulfur dioxide. This resulted in substantially increased polarization losses at higher current densities. Future work will focus on improved cell designs and operation at higher temperature and pressure.

The membranes in both cells passed substantial quantities of sulfur dioxide, some of which reacted with hydrogen gas to form elemental sulfur. Fortunately, the sulfur did not appear to poison the catalyst and it was easily washed out of the cells. Future designs should eliminate or minimize sulfur dioxide crossover, or should be designed to mitigate its effects on long term performance.

6.0 FUTURE WORK

1. The Nafion membranes used in this work passed significant quantities of sulfur dioxide. The sulfur dioxide reacted with product hydrogen to form sulfur, which tended to clog the cathode. The reaction consumed as much as 20 mL/min of hydrogen at 20°C and 1 bar. Therefore, the sulfur dioxide leakage rate was 10 mL/min. Research is needed to develop a membrane that passes less sulfur dioxide while still readily passing hydronium ions. The membrane must also tolerate the corrosive conditions and mechanical stresses.
2. The porous titanium electrodes in the PES cell had relatively low resistance to flow and good mass transfer characteristics. Also, any sulfur formed in the cathode was readily flushed out. However, the titanium was quickly damaged by the corrosive environment. The graphite electrodes in the USC cell had excellent corrosion resistance, but high resistance to flow and poor mass transfer characteristics. Research is needed to develop new electrodes that incorporate the best characteristics of both.
3. The MEA in the USC cell may have had insufficient catalyst. Tests should be conducted to optimize catalyst loading.

4. The platinum catalyst used in both cells appears to be effective and resistant to corrosion, however platinum is expensive. Literature research and testing should be conducted to find a cheaper, but still effective, catalyst.

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