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WSRC-TR-2005-00310, REV. 0

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Characterization Testing of H_2O-SO_2 Electrolyzer at Ambient Pressure

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

REPORT DATE: AUGUST 1, 2005

Westinghouse Savannah River Company
Savannah River Site
Aiken, SC 29808

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REVIEWS AND APPROVALS

J. L. Steimke, Author, Engineered Equipment & Systems Dept. Date

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D. B. Burns, Level 4 Manager, Engineered Equipment & Systems Dept. Date

S. T. Wach, Level 3 Manager, Engineered Equipment & Systems Dept. Date

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LIST OF ACRONYMS

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

1.0 EXECUTIVE SUMMARY

This document reports work performed at the Savannah River National Laboratory (SRNL) that resulted in a major 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 major 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, that is sent to the acid decomposition portion of the cycle. The focus of this work was to conduct single cell electrolyzer tests in order to prove the concept of SO_2-depolarization and to determine how the results can be used to evaluate the performance of key components of the HyS Process.

A test facility for conducting SO_2-depolarized electrolyzer (SDE) testing was designed, constructed and commissioned. The maximum cell current is 50 amperes, which is equivalent to a hydrogen production rate of approximately 20 liters per hour. 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 simple 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 electrocatalyst 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.

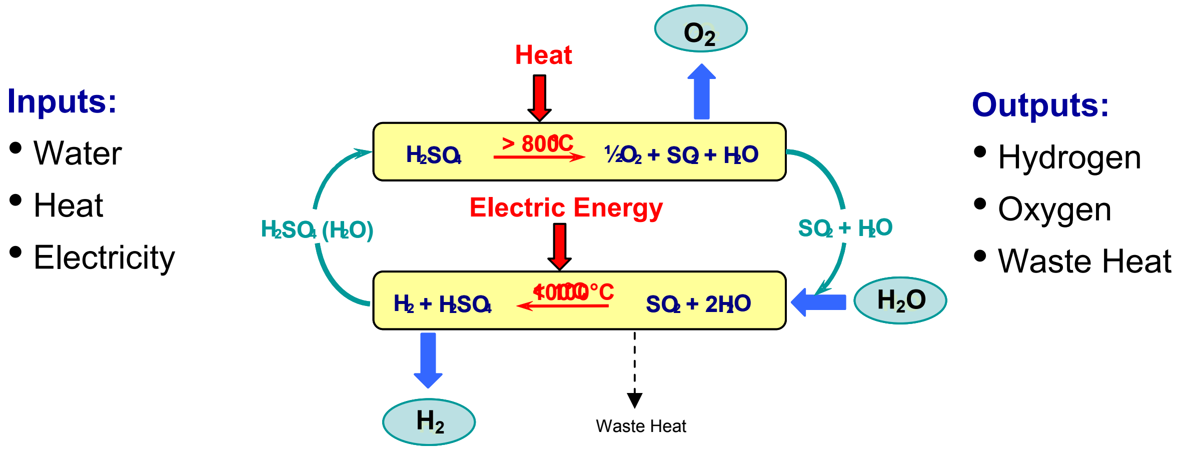
2.0 INTRODUCTION

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

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

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

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



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

The research documented in this report had three goals,

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

3.0 DISCUSSION

3.1 BACKGROUND

3.1.1 Previous Work

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

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

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

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

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

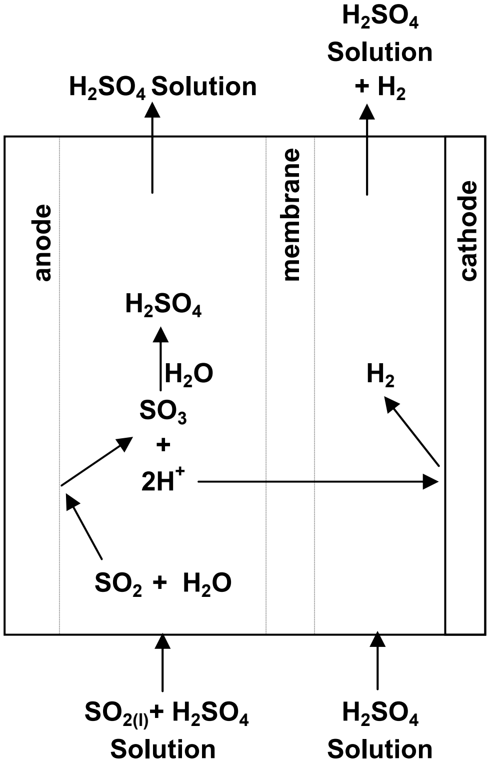


Figure 1 **SO_2-Depolarized Electrolyzer for Hydrogen Production**

In the Westinghouse tests, separate liquid streams fed the electrolyzer and are referred to as the catholyte and the anolyte. The catholyte was a solution of sulfuric acid and water and the anolyte was a solution of sulfuric acid, water, and dissolved sulfur dioxide (SO_2). Sulfur dioxide was oxidized at the anode to produce sulfuric acid and protons (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 2. Lu improved his cells and measured generally decreasing voltages during his research. Figure 2 also shows Lu's (1983) prediction for operation at 100°C, 20 atm and 30 wt% sulfuric acid.

Testing by the Westinghouse Electric Company indicated that the anode overpotential decreased with increased temperature, indicating that higher electrical efficiency might occur at higher operating temperature. However, there was little or no improvement in the limiting current with increased temperature at atmospheric pressure [Lu, 1983]. The lack of improvement in the limiting current arises primarily from the reduced solubility of SO_2 at the higher temperatures. To overcome the effects of reduced SO_2 solubility at higher temperature, Lu recommended operating the electrolyzer at elevated pressure. At elevated pressure (e.g., 20 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 1.0 volt, for a current density of 20 mA/cm^2. The sulfuric acid product would be used in the copper refining process.

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

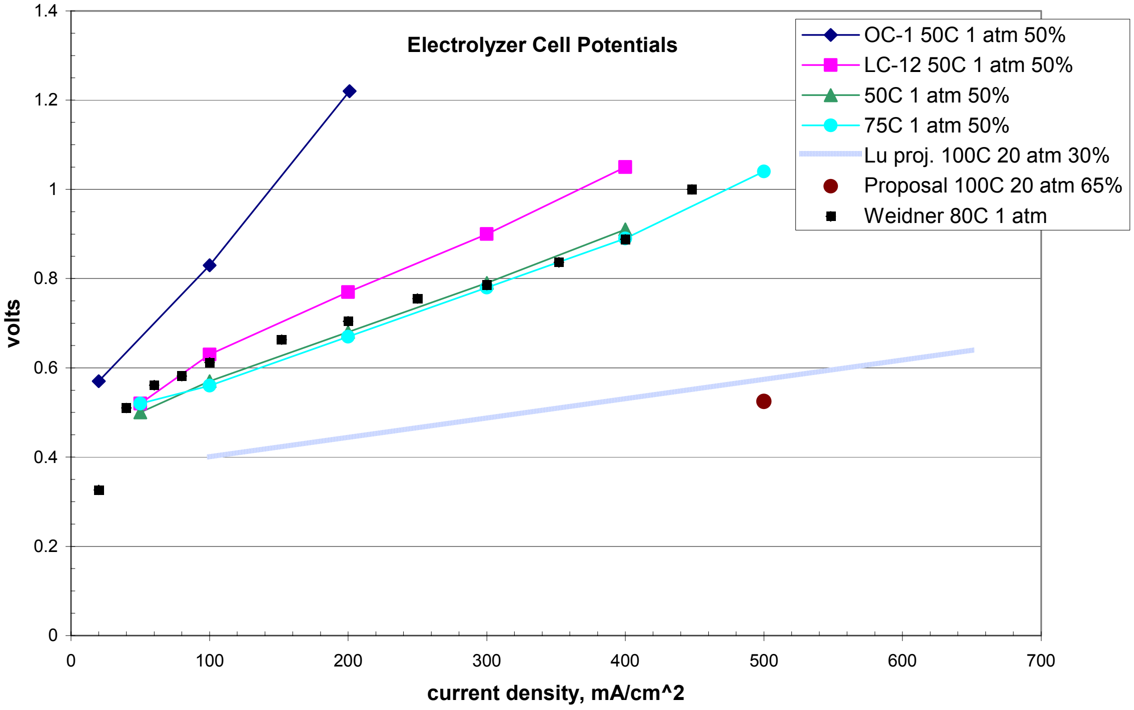


Figure 2 Cell Potentials Measured in Previous Work

3.1.2 Conduct of Engineering at SRNL

SRNL follows a formal procedure for planning and conducting all experimental work performed at the laboratory. A Task Technical and Quality Assurance Plan (Appendix 1) was written for the work documented in this report. Then all steps of Manual L1, Procedure 7.02, “Administration of Conduct of Research and Development in SRTC” were followed and documented. A formal Job Hazard Analysis committee was chaired by Mark Fowley of SRNL. A peer reviewed Work Instruction (Appendix 2) was prepared and followed for this work.

3.1.3 Analysis

An important component of commercial development of the HyS Process is optimization of an electrolyzer design that features low cell fabrication cost and operates at high current density 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.

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

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

Cell voltage $E = E_{rev} + \eta_a + \eta_c + \eta_{ohm} + \eta_{hw}$ [4]

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

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

η_c , cathode overpotential, is smaller than anode overpotential and is a function of catalyst surface area and type. It increases with increasing current density.

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

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

3.2 HARDWARE AND PROCEDURE

3.2.1 Overview of Test Facility

A test facility capable of testing sulfur dioxide depolarized electrolyzers at pressures up to two bar was designed and constructed. The facility is capable of operating with electrolyzer currents up to 50 amperes, 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 could easily be 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. The DAS has additional voltage inputs available for use with future cells with provisions to measure individual components of the overall cell voltage.

3.2.2 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.

A photograph of the PES cell is shown in Figure 3. Each of the twelve long bolts in the photograph holds a stack of Belleville washers to keep the assembly in compression. The protruding copper tab is the anode electrical connection. The 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.

Figure 3 **Photograph of Proton Energy Systems Cell**

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 shown in the center of Figure 4 and 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 as shown in Figure 5. 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 shown in Figure 6, 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.

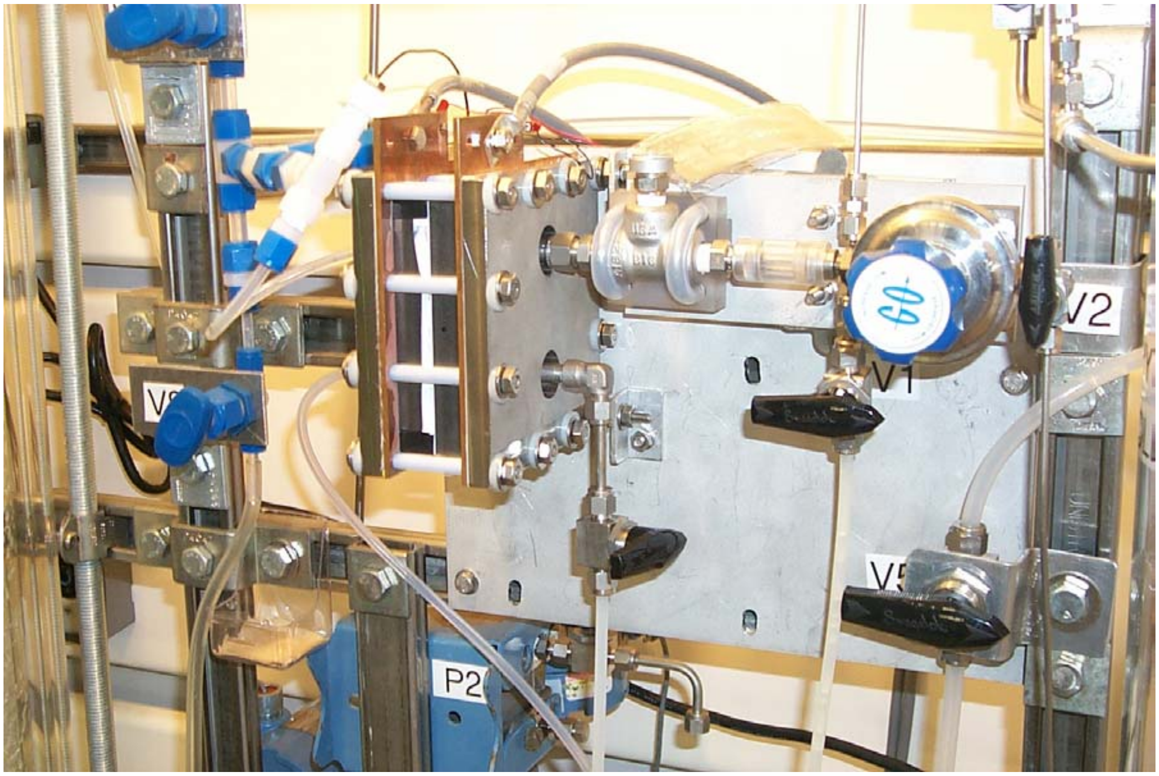


Figure 4 Photograph of USC Cell

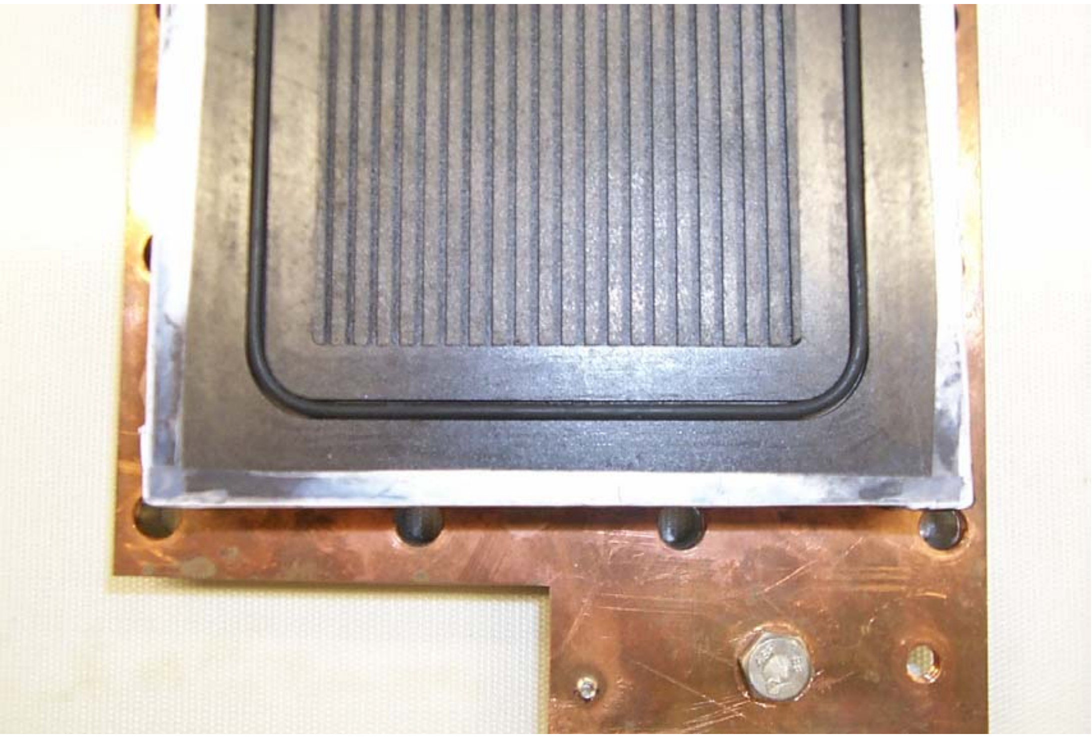


Figure 5 Photograph of Graphite Block, Grooved Wafer and Copper Connector

Figure 6 **Photograph of Membrane Electrode Assembly from Anode Side**

The facility was located in a large chemical hood as shown in Figure 7. Air flow was maintained whenever hydrogen or sulfur dioxide was present in the hood. The hood was effective, no sulfur dioxide odor leaked out. In Figure 7, the 100 lb. cylinder of sulfur dioxide was on the left. To the right of it was the SO_2 Absorber. In the upper middle of the picture is the electrolyzer cell. Below it is the Anolyte flowmeter and below that is the Anolyte Pump. Further to the right is the Hydrogen Collector.

Figure 7 **Photograph of Electrolyzer Test Facility**

Figure 8 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.

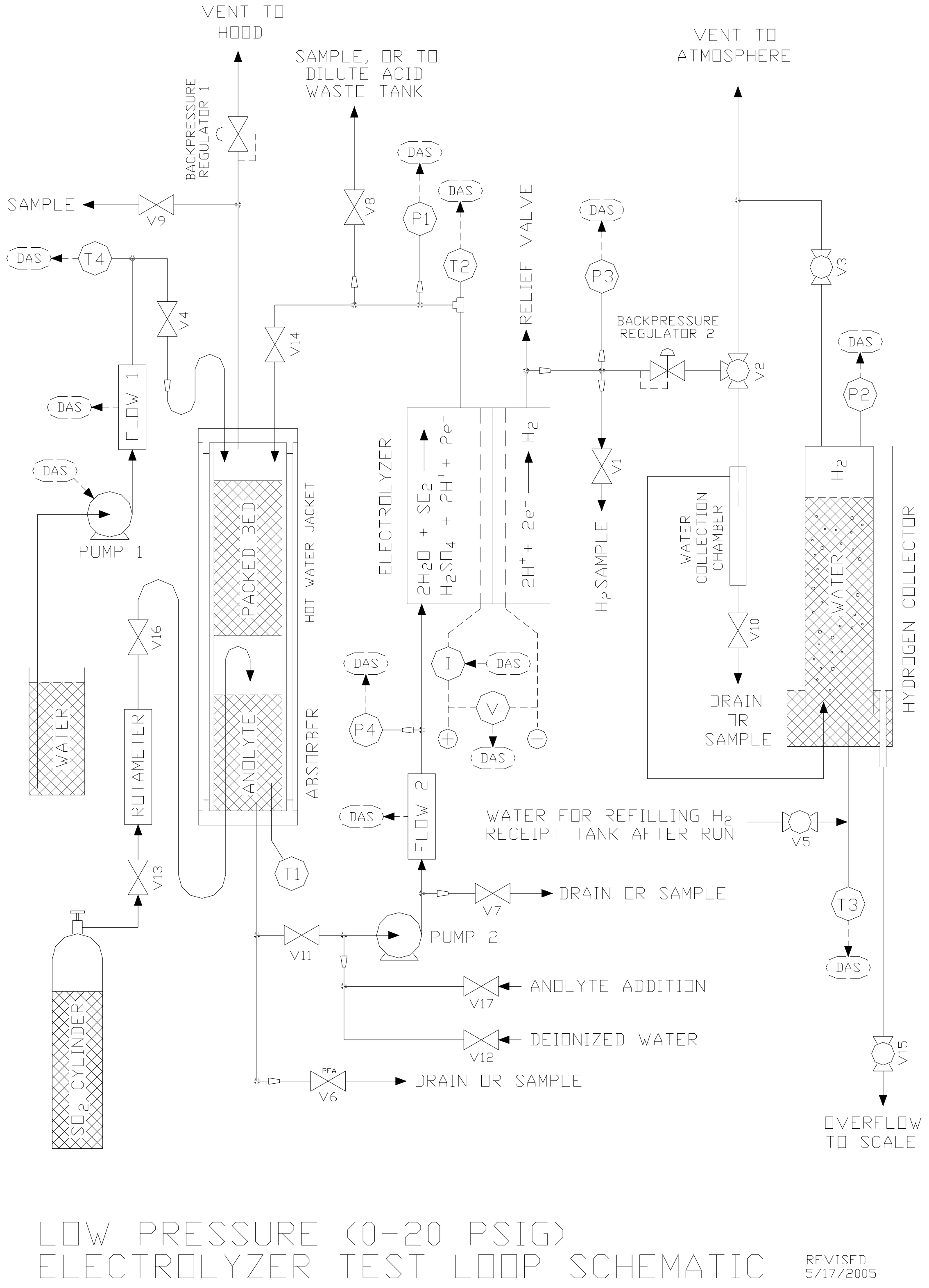


Figure 8 Schematic of Electrolyzer Test Facility

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 (instrument # 3-2937) was connected to the output of the power supply to allow for independent measurement of current. Voltage taps independently connected to the cell electrodes were connected to the DAS.

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

Table 1 Instrument List for Hydrogen Electrolyzer Test Facility

instrument	number	lower range	upper range	units	location
P1	TR-03540	0	20	psig	cell anolyte outlet pressure
P2	TR-03604	-75	25	in. H_2O	Hydrogen Collector pressure
P3	TR-20263	0	20	psig	cell hydrogen outlet pressure
P4	TR-03761	0	50	psig	cell anolyte inlet pressure
T1	TR-03763	0	100	°C	Anolyte tank temperature
T2	TR-03764	0	100	°C	cell anolyte outlet temperature
T3	TR-02812	0	100	°C	hydrogen collector temperature
T4	TR-02808	0	100	°C	makeup water temperature
flow1	TR-03760	0	10	mL/min	makeup water flow
flow2	TR-03562	0	2	L/min	anolyte flow
rotameter	s/n 41568	0	0.54	L/min	SO_2 gas flow
scale	TR-30074	0	100	lb	weight of water displaced from H_2 collector
voltage		0	20	volts	total voltage across cell
current		0	50	amps	reads as 0 - 5 volts
current	3-2937	0	50	amps	shunt

3.2.3 Test Matrix

The Test Matrix 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.

3.2.4 Abbreviated Procedure for Operation with Acid and Sulfur Dioxide

The following is a summary of the Work Instruction (Appendix 2) 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, as shown in Figure 9. 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. The slopes of the pressure data are 1.57 and 1.42, for the anode and cathode, respectively. The expected slope for laminar flow is 1.0, for sudden expansions and contractions or for very rough pipe the slope is 2.0 and for hydraulically smooth pipe in turbulent flow the slope is about 1.75. Therefore, the nature of the flow most nearly resembles smooth pipe in turbulent flow. This information was provided as some insight into the interval flow passages of the PES cell, which we could not disassemble.

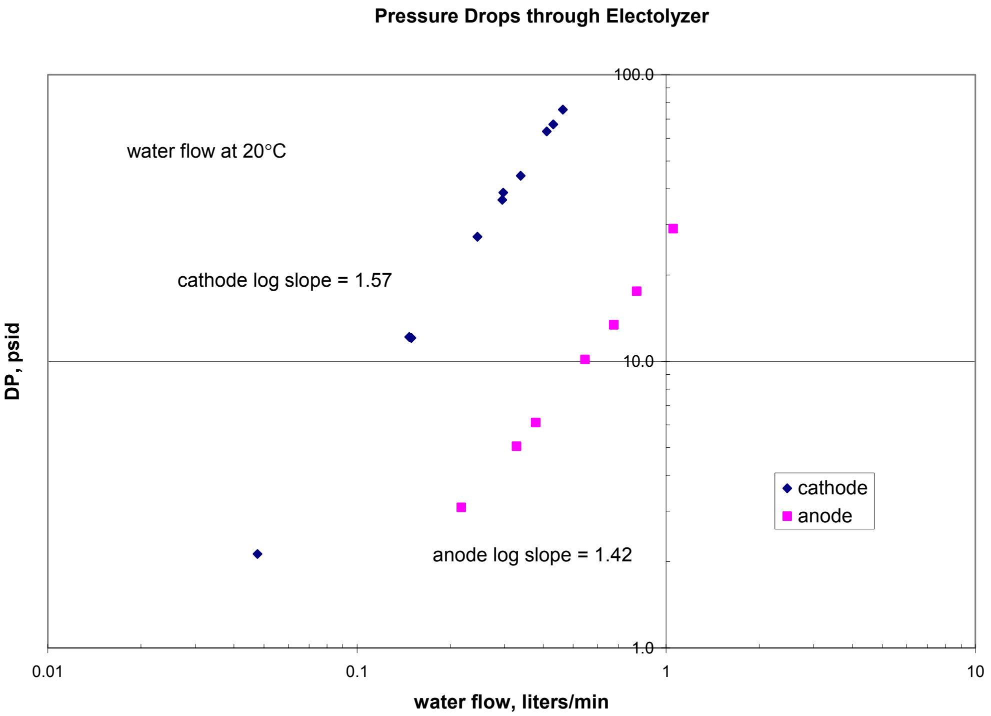


Figure 9 Pressure Drops for Anolyte and Catholyte Sides of PES Cell

Plots of cell potential vs. current density, called Polarization curves or Tafel Plots, for water electrolysis are shown in Figure 10. Tabular data are listed in Appendix 4. 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 the other terms in Equation 1. 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.

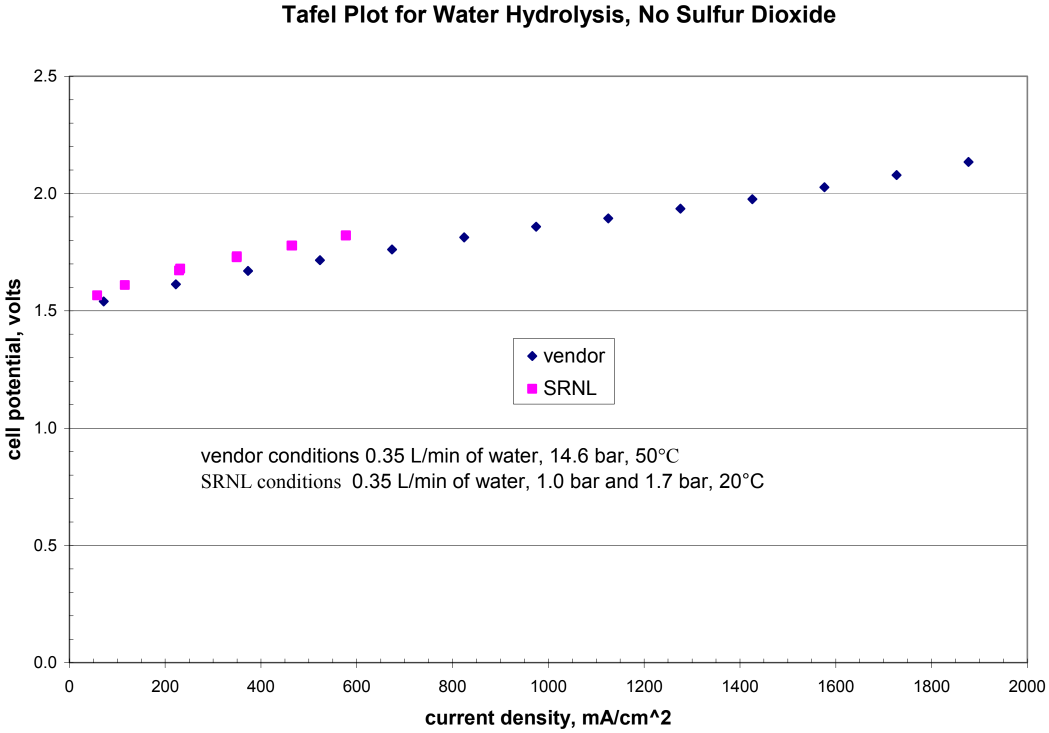


Figure 10 Tafel Plot for Water Electrolysis, No Sulfur Dioxide

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. Figure 11 shows hydrogen flow measurements 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.

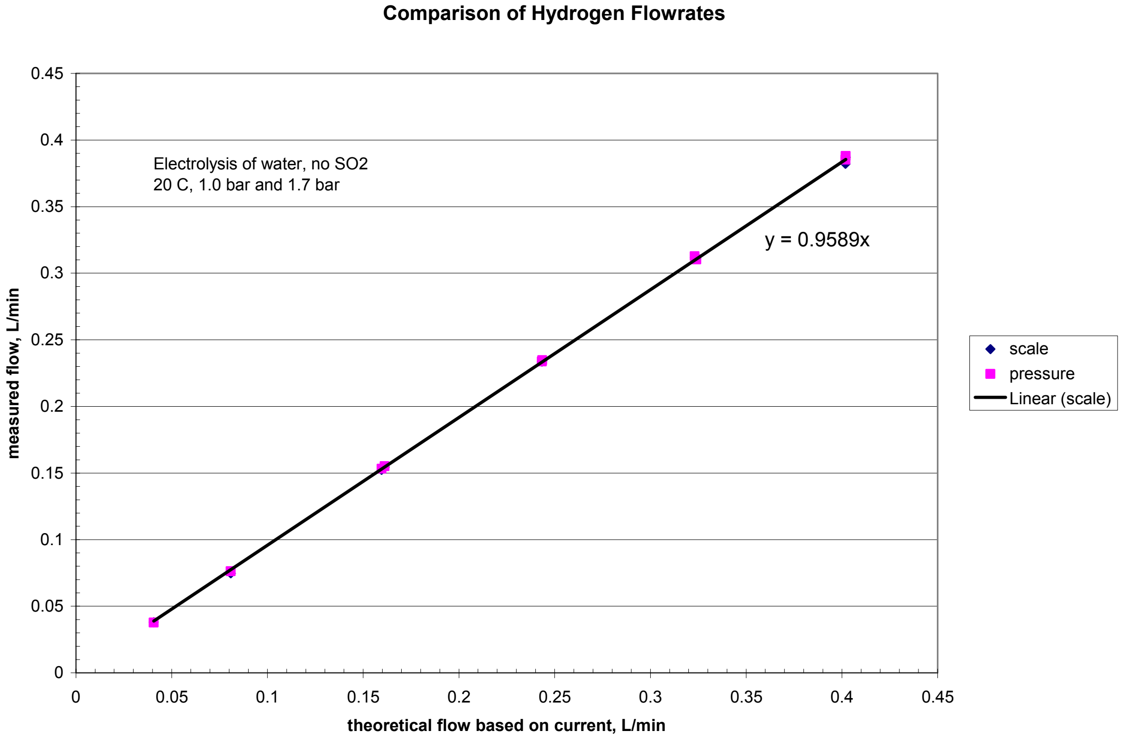


Figure 11 Hydrogen Flow Measurement for Conventional Electrolysis with PES Cell

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 12. The anolyte effluent was a two-phase mixture just as it had been for conventional electrolysis of deionized water.

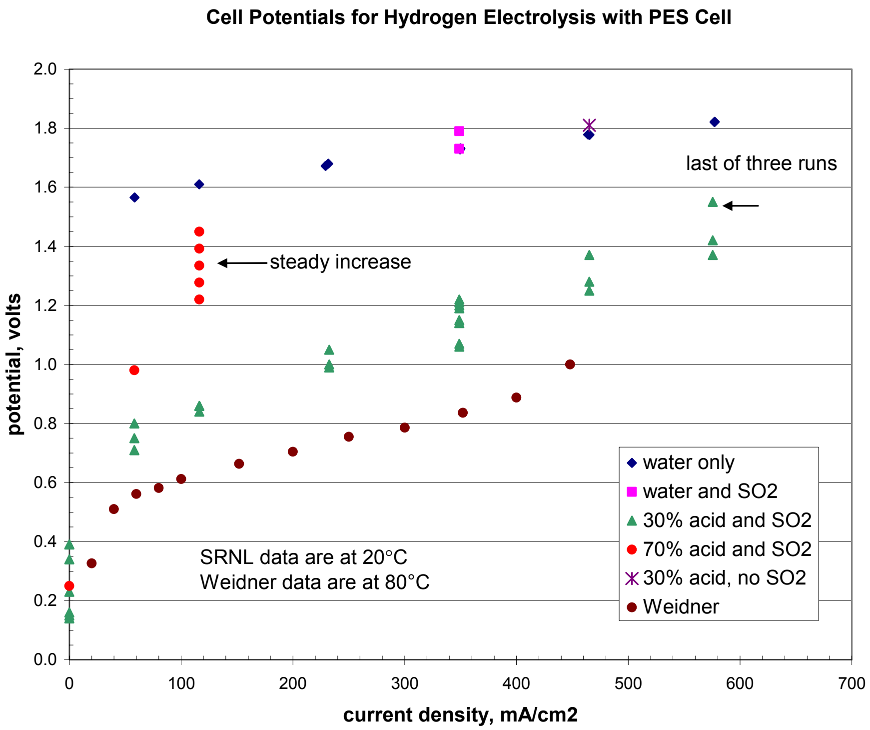


Figure 12 Cell Voltages Measured for PES Cell

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 12. 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 12. 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 13. Figure 11 previously showed that with no sulfur dioxide present, measured hydrogen rates were 96% of theoretical based on current. Figure 13 shows that the hydrogen generation rate was 96% of theoretical for anolyte consisting of sulfur dioxide and water, with no acid. After acid was introduced to the anolyte, the measured hydrogen flowrates plotted in Figure 13 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.

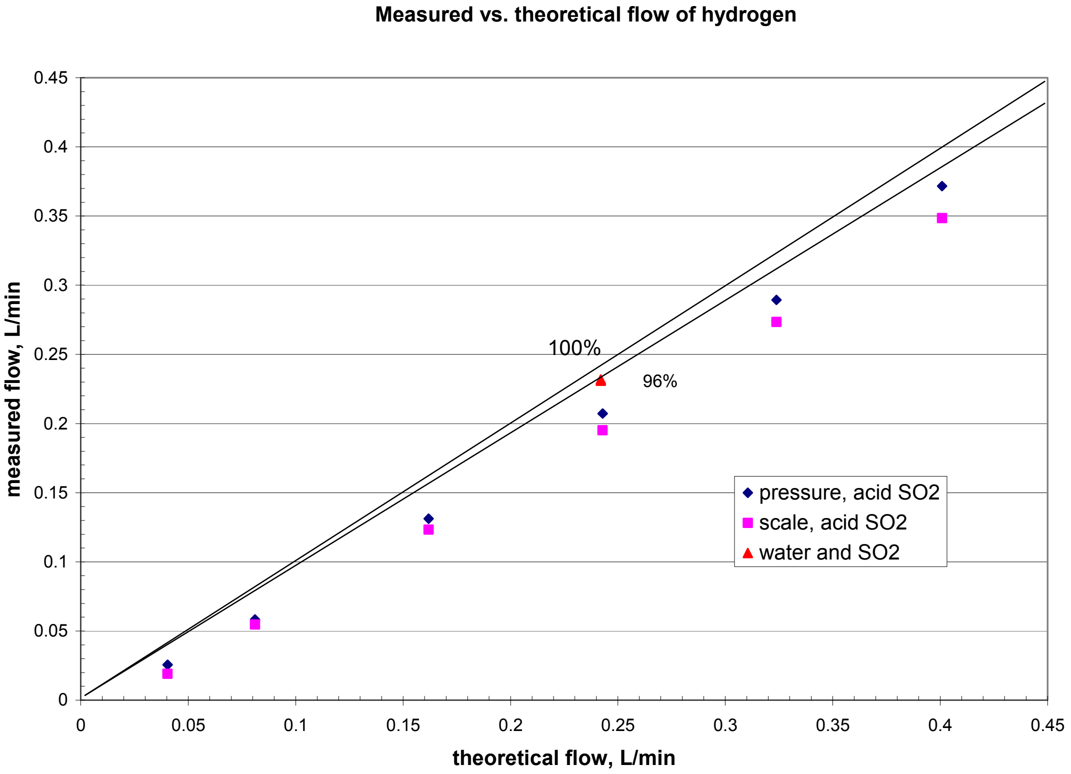


Figure 13 Hydrogen Generation Rates with PES Cell with Acid and Sulfur Dioxide

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, as shown in Figure 14.

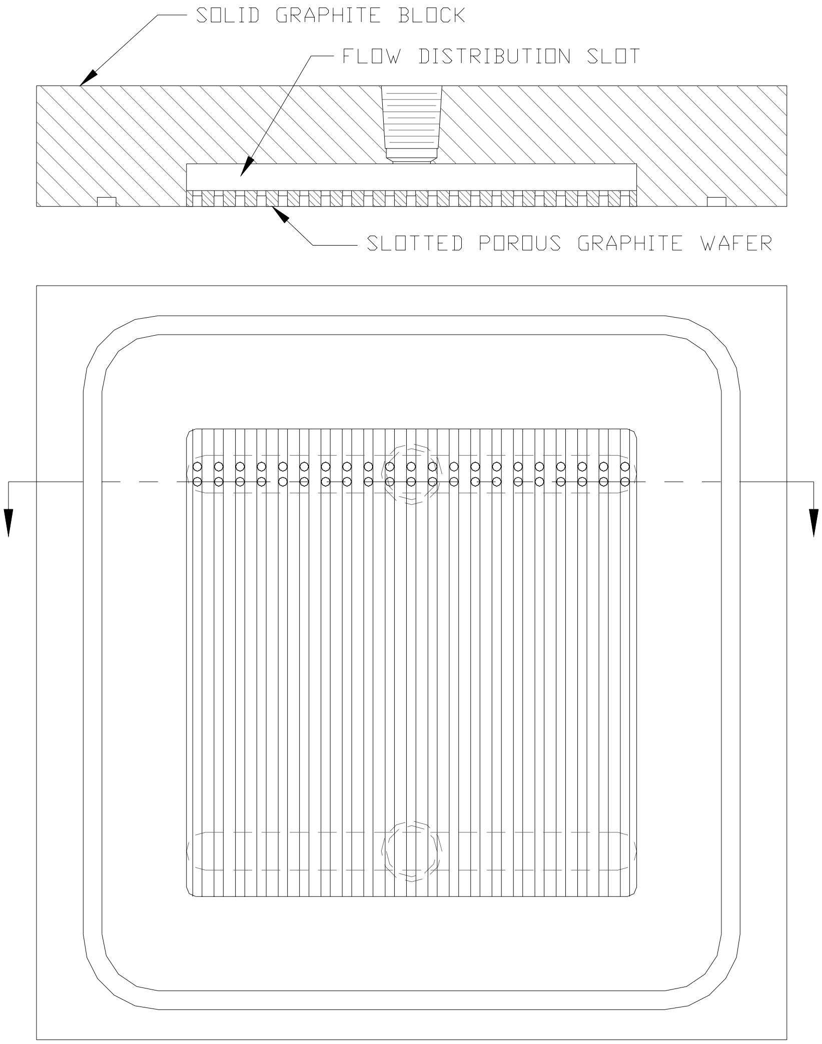


Figure 14 Details of Porous Graphite Wafer on Anode Side

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. Figure 15 plots anolyte flowrate and cell pressure drop and shows widely scattered data points. The cell was disassembled, the grooved wafer was reversed and the cell reassembled. Figure 16 plots the resulting, well behaved hydraulic data.

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 17. Tabular data are listed in Appendix 4.

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 18 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.

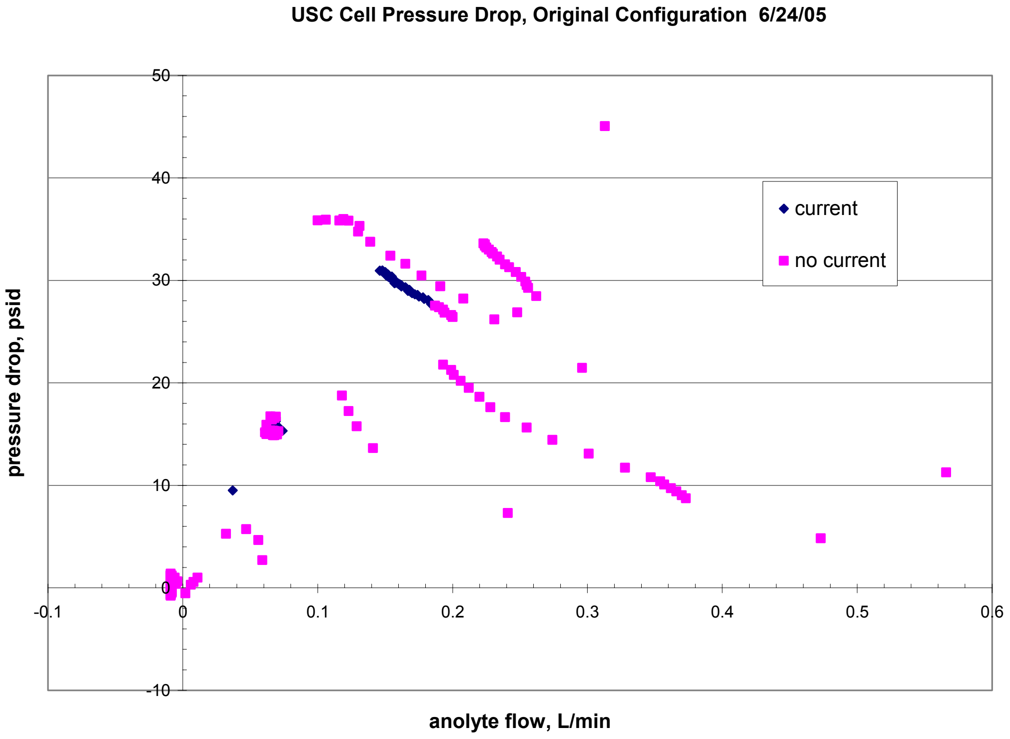


Figure 15 Hydraulic Behavior of USC Cell, As Received

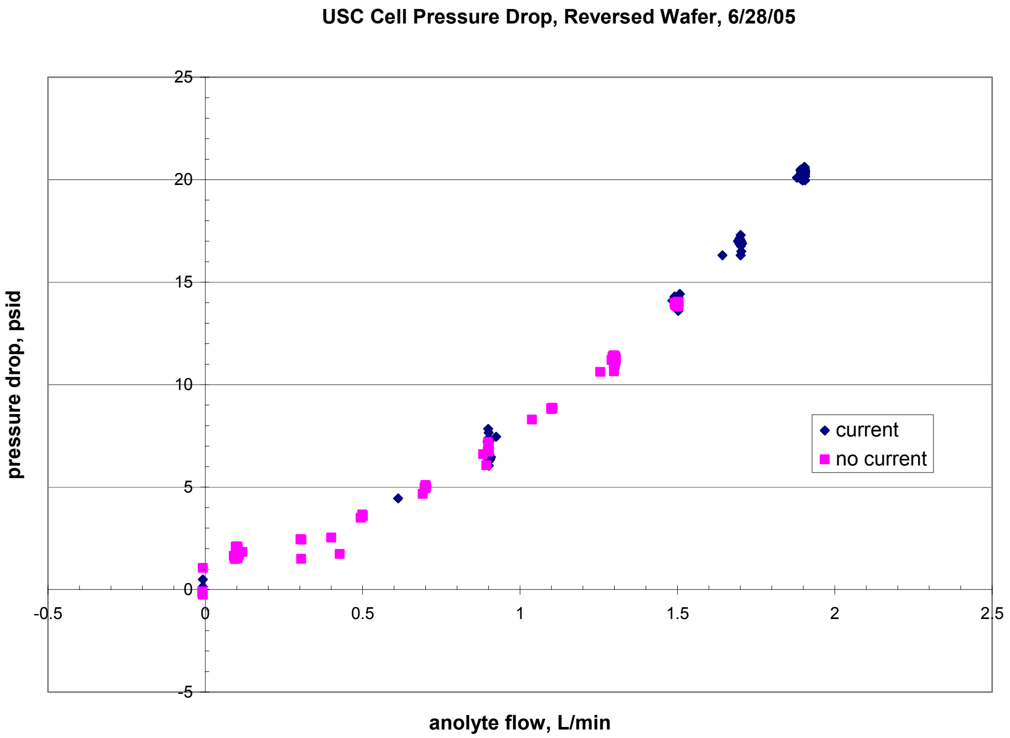


Figure 16 Hydraulic Behavior of USC Cell After Reversing the Wafer

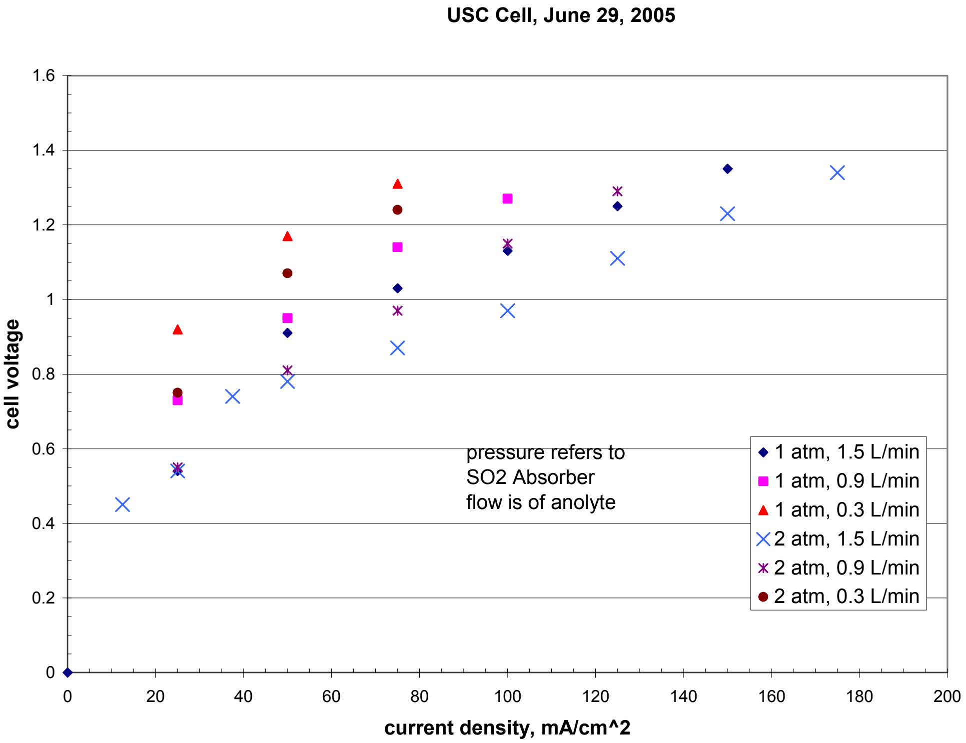


Figure 17 USC Cell Voltages

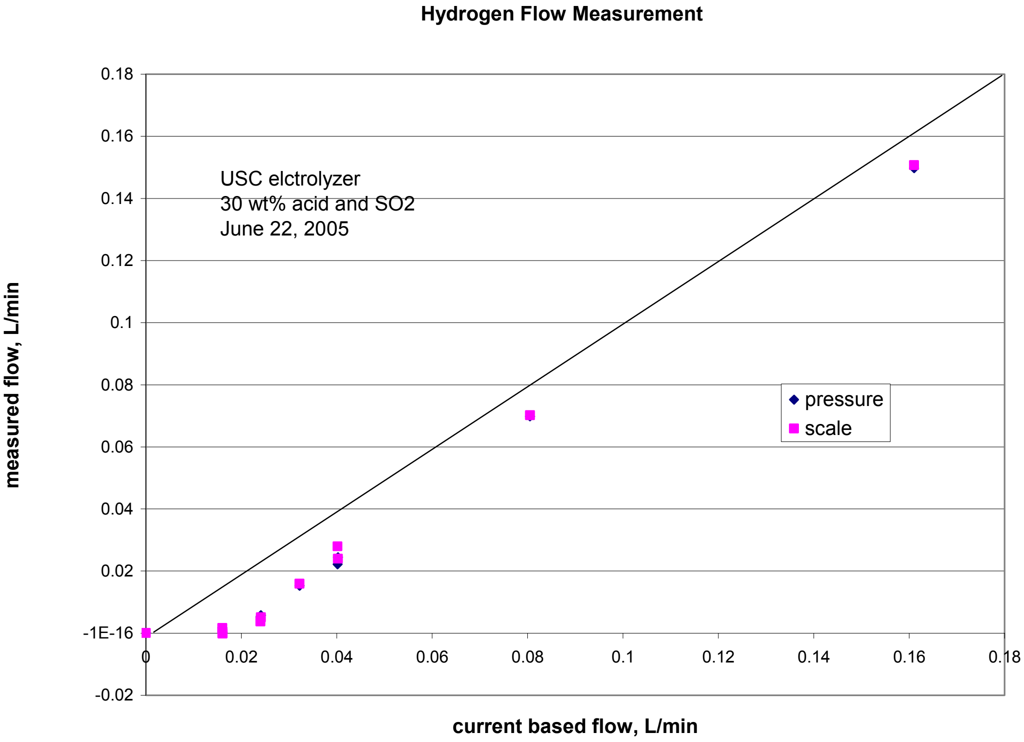


Figure 18 USC Cell Hydrogen Production Rates

3.4 IMPACT OF TEST RESULTS ON HYS PROCESS DESIGN

The SO2-depolarized electrolyzer is a major component of a complete Hybrid Sulfur (HyS) thermochemical hydrogen production process. A simplified schematic of the HyS process is shown in Figure 19. In order to optimize overall system performance and economics, tradeoffs must be made between the requirements of the electrolyzer system and the balance of the process.

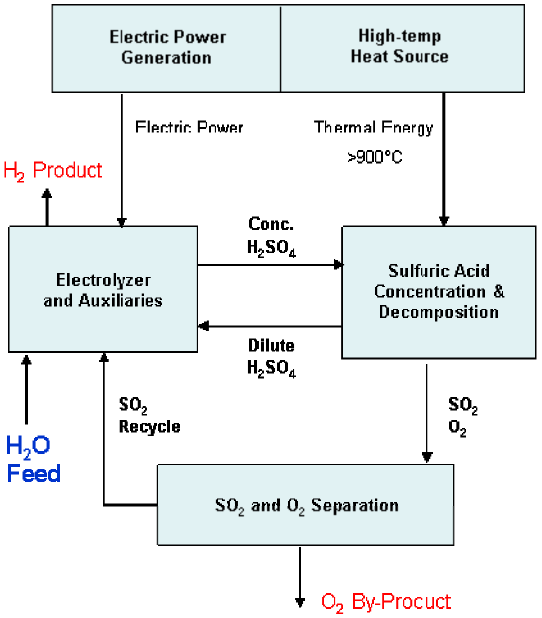


Figure 19 Hybrid Sulfur Process Block Schematic

Variables that must be optimized include the sulfuric acid concentration, temperature, pressure, and SO_2 conversion per pass in the electrolyzer. The electrolyzer voltage is reduced (i.e. higher efficiency is obtained) by operation at lower sulfuric acid concentration, but the thermal energy needed to concentrate the acid in order to perform acid decomposition is increased. Electrolyzer performance is also improved by increasing the concentration of sulfur dioxide dissolved in the acid, which increases with increasing pressure and reduces with increasing temperature. Trade-off studies performed by SRNL resulted in the following commercial operating goals for the SDE:

Operating pressure = 20 bar
Operating temperature = 100 °C
H_2SO_4 concentration = 65 wt%
Current density = 500 mA/cm2
Cell voltage = 525 mV

The purpose of the characterization tests was not to duplicate these conditions, but to establish the proof-of-concept of using a PEM-type cell to perform SO_2-depolarized electrolysis. Testing was conducted at room temperature (20-25°C) and near-ambient pressure (1-2 atmospheres) using 30 wt% and 70 wt% sulfuric acid. Future testing will seek to demonstrate operation at elevated temperature and pressure.

The most important performance measure of the electrolyzer is the cell voltage. Figure 20 shows the impact of cell voltage and SO_2 conversion per pass on the overall HyS Process thermal efficiency.

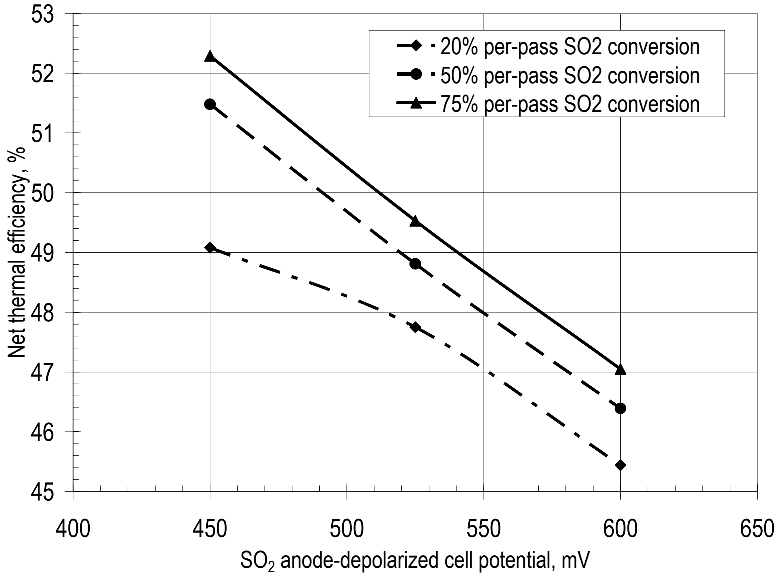


Figure 20 HyS Process Net Thermal Efficiency versus Cell Voltage

An electrolyzer cell voltage of less than 0.6 VDC per cell is desired at sufficient current density to meet commercial cost goals. Test results reported herein demonstrated cell voltages of 0.45 to 0.6 volts per cell at low current density operating at room temperature and ambient pressure with low SO_2 conversion per pass. This establishes the potential to design cells meeting the commercial performance goals when operated at increased temperature and pressure and optimized to minimize mass transfer resistance and other polarization losses. Future testing should characterize operation at these more demanding conditions, as well as assess the effects of various SO_2 conversion rates.

Another major result of the testing that impacts HyS Process design is the formation of sulfur at the cathode of the electrolyzer. This is caused by sulfur dioxide diffusing through the Nafion membrane in the PEM cell and reacting with hydrogen at the cathode to form elemental sulfur. This has three potential deleterious effects: 1) hydrogen is consumed, reducing cell efficiency; 2) sulfur may poison the cathode electrocatalyst; and 3) sulfur may block the pores of the cathode and hinder mass transfer. The test results were inconclusive as to the precise amount of current that was consumed for sulfur formation, although it was clearly substantial at low current densities. Qualitatively, it is clear that sulfur crossover must be reduced below the levels detected during the testing. However, there was no evidence that the sulfur poisoned the cathode catalyst, and it was readily washed from the cell. This may indicate that small amounts of sulfur crossover may be manageable. This should be a major focus of future SDE research.

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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8.0 APPENDIX 1 TEST PLAN

Test Plan for Small Single Cell Electrolyzer Development for the Hybrid Sulfur Cycle (U)

J. L. Steimke, 786-5A

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1. INTRODUCTION

SRNL made a proposal authored by Buckner and others to the Office of Nuclear Hydrogen Initiative to test the Hybrid Sulfur (HyS) technology for generating hydrogen. This technology uses a sulfur dioxide depolarized anode to greatly reduce the electrical energy requirement of an electrolyzer that produces hydrogen. SRNL received funding in FY05 to test an electrolyzer as part of this effort.

The electrolyzer has two sides, an anode side and a cathode side. Electrical current is passed through the electrolyzer which drives the following two reactions. Hydrogen ions cross from the anolyte to the cathode through a membrane.

Anode $SO_2 + 2\ H_2O = H_2SO_4 + 2H^+ + 2e^-$
Cathode $2H^+ + 2e^- = H_2$

The presence of sulfur dioxide at the anode greatly reduces the required cell potential to generate hydrogen as compared to electrolyzing water. The anolyte is a solution of sulfuric acid with a concentration in the range from 30 wt% to 70 wt%. Sulfur dioxide gas is dissolved in the anolyte to saturation and hydrogen gas is generated at the cathode. Peter Lu at Westinghouse Electric Corp. researched these reactions about twenty five years ago with an electrolyzer that used acid solutions as both the anolyte and catholyte. The testing described in this Task Plan will use a newer technology, using a membrane electrode assembly (MEA), in which the anode and cathode are in physical contact with the membrane. The MEA technology requires no catholyte. The electrolyzer is a key part of HyS technology. Completing the material loop for HyS requires a high temperature decomposition of sulfuric acid to generate oxygen gas and also to regenerate the sulfur dioxide gas needed for the anode reaction. The decomposition portion of the HyS Process will not be studied in this task.

1.1. Task Definition: This activity requires purchasing or building a sulfur dioxide depolarized electrolyzer with an area of approximately 100 square centimeters. The electrolyzer will be installed in a test loop. The test loop will circulate anolyte, control temperature, have hardware to saturate the anolyte with sulfur dioxide, collect hydrogen that was generated, control temperature and measure flowrates and pressures. The electrolyzer will be tested over a range of temperature, flowrate, acid concentration and current density. The results will be documented in a technical report. This work is non-baseline and R&D.

1.2. : The customer is the Office of the Nuclear Hydrogen Initiative managed out of Sandia National Laboratory.

1.3. Task Responsibilities: The EDL has overall responsibility, will design the test loop, perform the testing and document the results. The ADS will perform the analyses of chemical samples. Both sections are part of SRNL.

1.4 Task Deliverables: One technical report covering the work outlined by this Task Technical Plan (TTP) will be delivered. Laboratory notebooks will be available to the customer on request. Data and lab notebooks are handled per the QA Plan Checklist, Section 9.

2.0. Task Acceptance Criteria

none

3.0 *TASK ACTIVITIES*

3.1 Complete Conduct of R&D Process

1. R&D Hazards Checklist
2. Environmental Evaluation Checklist
3. Pressure Protection
4. Industrial Hygiene and Chemical Control
5. Fire Protection
6. Management of Safety Basis
7. Job Hazard Analysis
8. Screening Process Hazards Review

3.2 Specification of electrolyzer

1. Anolyte is sulfuric acid solution, saturated in SO_2. Range of acid concentrations is 30 wt% to 70 wt%. Anode reaction is $SO_2 + 2\ H_2O = H_2SO_4 + 2H^+ + 2e^-$.
2. Cathode reaction is $2H^+ + 2e^- = H_2$. There is no liquid catholyte, although the hydrogen gas generated is expected to contain some water vapor.
3. Temperatures range from 20° C to 80° C.
4. Wetted surfaces of the electrolyzer must withstand these solutions and temperatures.
5. Testing in 2005 will be near atmospheric pressure. Later testing will be at higher pressures. It is desirable, but not necessary, that the electrolyzer be capable of holding as much as 20 atm.
6. Active area is 100 cm^2 +/- 25 cm^2
7. Range of current densities is at least 100 mA/cm^2 to 500 mA/cm^2.
8. Maximum liquid flowrate of interest is 4.5 L/min.
9. Uses membrane electrode assembly (MEA) concept.
10. Membrane is Nafion, which passes water and hydrogen ions, but resists passing other species.
11. Anode and cathode are finely divided platinum, on porous carbon or titanium.
12. Wetted surfaces must resist the chemicals.

3.3 Procurement of electrolyzer

3.4 Design of flow loop, including instrumentation

1. Effective area for each electrode is approximately 90 cm^2.
2. Tentative current densities are 100, 200, 300, 400 and 500 mA/cm^2.
3. Maximum voltage is 2 volts.
4. Temperature range is 20° C to 80° C. Need way to control temperatures of anolyte. Need to insulate cell for higher temperatures.
5. Anolyte is sulfuric acid ranging from 30 wt% to 70 wt%. Shakedown testing with water.
6. Anolyte is saturated with SO_2. Solubility of SO_2 at 20° C is about 1 molar (64 g/L). Solubility decreases to 0.1 molar at 95° C. We will need a way to saturate sulfuric acid with SO_2. We will probably vent excess SO_2 outside building.

7. Probably want upflow for anolyte inside electrolyzer in case SO_2 bubbles come out of solution.
8. Need to measure cumulative hydrogen volume over an hour. It may not be necessary to measure instantaneous hydrogen flowrate. Must be able to sample hydrogen for chemical analysis.
9. Maximum flowrate of anolyte is 4.5 L/min. Need pump.
10. Current and voltage (potential) across cell must be measured.
11. Need capability to boost the hydrogen pressure at the cathode higher than the anolyte pressure by at least a few inches of water to stop SO_2 from diffusing to cathode.
12. May need mist eliminator on hydrogen gas because it will contain tiny droplets of water.
13. Initial testing will be for about an hour at each set of conditions. However, there will be at least one long run of 100 hours.
14. The anode reaction generates sulfuric acid, so either we run once through and then dilute the anolyte for reuse or we have continuous dilution.
15. Need to monitor acid concentration. Sampling followed by density measurement may be adequate.
16. Provide pressure protection as required.
17. All equipment will be installed in a chemical hood that vents outside.

3.4. Selection and calibration of instruments.

3.5. Construction of flow loop including electrolyzer

3.6. Shakedown testing

Using water and no current to the electrolyzer, test pumps, valves, instruments, safety devices, data acquisition system

3.7. Parametric testing

It is not known how robust the electrolyzer will be to hot concentrated sulfuric acid, so the least potentially damaging tests will be run first. First, the anolyte will be water, with power supplied to the electrolyzer, which will generate hydrogen. Then, sulfur dioxide will be added to the water, which should decrease the required cell potential. Then, the concentration of sulfuric acid will be increased in the anolyte. In the testing, vary flowrate of anolyte, temperature, current density and perhaps percent saturation of sulfur dioxide in the anolyte.

3.8. Endurance testing, 100 hours at one set of conditions.

3.9. Document work in report

3.10. Dispose of waste and dismantle any equipment that will not be used in future testing.

4.0. REPORTING

Issue report documenting testing performed in 2005.

5.0. TASK SCHEDULE:

March 1, 2005	Complete Test Plan
August 1, 2005	Complete testing at near atmospheric pressure and issue report

6. 0. RESEARCH FACILITY PLANNING: Laboratory space is available at the EDL for this task. Testing will be conducted in a large chemical hood.

7.0. PROGRAMMATIC RISK REVIEW: The following depicts the programmatic risks associated with this task and the associated mitigation, where identified.

Programmatic Risk and Mitigation

Risk Factor	Event	Mitigation
Equipment	Failure	Replacement of item
Personnel	Illness Vacation	Primary and secondary researchers and analysts identified.
Facility	Outage: Electrical Ventilation	Adjust testing intervals.

9.0. QA Plan Checklist

The following QA Procedures apply for this task (indicate Yes, No or "AR" - as required). Current revision of the procedure will be used. The QA controls are the procedures identified on the checklist. If the procedures on the matrix are changed, applicable procedures will be followed.

Yes	No	Title
		1-1 ORGANIZATION
X		1Q, QAP 1-1, Organization
X		L1, 1.02, SRTC Organization
		1-2 STOP WORK
X		1Q, QAP 1-2, Stop Work
		2-1 QUALITY ASSURANCE PROGRAM
X		1Q, QAP 2-1, Quality Assurance Program
X		L1, 8.02, SRTC QA Program Clarifications, Attachment 8.2-1
		2-2 PERSONNEL TRAINING & QUALIFICATION
X		1Q, QAP 2-2, Personnel Training & Qualification
X		L1, 1.32, Read & Sign
		2-3 CONTROL OF RESEARCH & DEVELOPMENT ACTIVITIES
X		1Q, QAP 2-3, Control of Research & Development Activities
X		L1, 8.02, SRTC QA Program Clarifications, Attachment 8.2-3
X		L1, 7.10, Control of Technical Work
X		L1, 7.16, Laboratory Notebooks and Logbooks
X		E7, 2.31, Engineering Calculations
		2-4 AUDITOR/LEAD AUDITOR QUALIFICATION & CERTIFICATION
	X	1Q, QAP 2-4, Auditor/Lead Auditor Qualification & Certification
		Not anticipated
		2-5 QUALIFICATION & CERTIFICATION OF INDEPENDENT INSPECTION PERSONNEL
	X	1Q, QAP 2-5, Qualification & Certification of Independent Inspection Personnel
		Not anticipated
		2-6 QA MANUAL REVISION
	X	1Q, QAP 2-6, QA Manual Revisions

Yes	No	Title
		Not anticipated
		2-7 QA PROGRAM REQUIREMENTS FOR ANALYTICAL MEASUREMENT SYSTEMS
		3-1 DESIGN CONTROL
	X	1Q, QAP 3-1, Design Control
	X	L1, 7.10, Control of Technical Work
		4-1 PROCUREMENT DOCUMENT CONTROL
X		1Q, QAP 4-1, Procurement Document Control
X		E7, 3.10, Determination of Quality Requirements for Procured Items
		Not anticipated
		5-1 INSTRUCTIONS, PROCEDURES & DRAWINGS
X		1Q, QAP 5-1, Instructions, Procedures & Drawings
X		E7, 2.30, Drawings
X		L1, 1.01, SRTC Procedure Administration
		6-1 DOCUMENT CONTROL
X		1Q, QAP 6-1, Document Control
		7-2 CONTROL OF PURCHASED ITEMS & SERVICES
X		1Q, QAP 7-2, Control of Purchased Items & Services
X		7B, Procurement Management Manual (for reference)
X		3E, WSRC Procurement Specification Manual (for reference)
		Not anticipated
		7-3 COMMERCIAL GRADE ITEM DEDICATION
	X	1Q, QAP 7-3, Commercial Grade Item Dedication
	X	E7, 3.46, Replacement Item Evaluation/Commercial Grade Item Dedication
		Not applicable
		8-1 IDENTIFICATION & CONTROL OF ITEMS
X		1Q, QAP 8-1, Identification & Control of Items
X		L1, 8.02, SRTC QA Program Clarifications, Attachment 8.8-1
		Not applicable
		9-1 CONTROL OF PROCESSES
	X	1Q, QAP 9-1, Control of Processes
		Not applicable
		9-2 CONTROL OF NONDESTRUCTIVE EXAMINATION
	X	1Q, QAP 9-2, Control of NDE
		Not applicable

Yes	No	Title
▨	▨	9-3 CONTROL OF WELDING & OTHER JOINING PROCESSES
	X	1Q, QAP 9-3, Control of Welding & Other Joining Processes
		Not applicable
▨	▨	9-4 WORK PROCESSES
	X	1Q, QAP 9-4, Work Processes
	X	**1Y, 8.20, WORK CONTROL PROCEDURE**
		Not applicable
▨	▨	10-1 INSPECTION & VERIFICATION
	X	1Q, QAP 10-1, Inspection & Verification
	X	L1, 8.10, Inspection
		No inspections
▨	▨	11-1 TEST CONTROL – (R&D Test activities are controlled by 1Q, QAP 2-3)
	X	1Q, QAP 11-1, Test Control
		Not applicable
▨	▨	12-1 CONTROL OF MEASURING & TEST EQUIPMENT
X		1Q, QAP 12-1, Control of Measuring & Test Equipment
▨	▨	12-2 CONTROL OF INSTALLED PROCESS INSTRUMENTATION
	X	1Q, QAP 12-2, Control of Installed Process Instrumentation
		Not applicable
▨	▨	12-3 CONTROL & CALIBRATION OF RADIATION MONITORING EQUIPMENT
	X	**1Q, QAP 12-3, CONTROL OF RADIATION MONITORING EQUIPMENT**
		No radiation
▨	▨	13-1 PACKAGING, HANDLING, SHIPPING & STORAGE
X		1Q, QAP 13-1, Packaging, Handling, Shipping & Storage
X		L1, 8.02, SRTC QA Program Clarifications, Attachment 8.13-1
		No shipping
▨	▨	14-1 INSPECTION, TEST & OPERATING STATUS
X		1Q, QAP 14-1, Inspection, Test & Operating Status
X		L1, 8.02, SRTC QA Program Clarifications, Attachment 8.14-1
		No inspection
▨	▨	15-1 CONTROL OF NONCONFORMING ITEMS
X		1Q, QAP 15-1, Control of Nonconforming Items
X		L1, 8.02, SRTC QA Program Clarifications, Attachment 8.15-1
		Not anticipated
▨	▨	15-2 CONTROL OF NONCONFORMING ACTIVITIES
X		1.01, MP 5.35, Corrective Action Program

Yes	No	Title
X		1B MRP 4.23 Site Tracking Analysis and Reporting
		Not anticipated
		16-3 CORRECTIVE ACTION SYSTEM
X		1Q, QAP 16-3, Corrective Action Program
X		1.01, MP 5.35, Corrective Action Program
X		1B MRP 4.23 Site Tracking Analysis and Reporting
		Not anticipated
		17-1 QA RECORDS MANAGEMENT
X		1Q, QAP 17-1, QA Records Management
X		**L1, 8.02, SRTC QA PROGRAM CLARIFICATIONS, ATTACHMENT 8.17-1**
		18-2 QUALITY ASSURANCE SURVEILLANCES
X		1Q, QAP 18-2, Quality Assurance Surveillance
		18-3 QUALITY ASSURANCE EXTERNAL AUDITS
	X	1Q, QAP 18-3, Quality Assurance External Audits
		Not anticipated
		18-4 MANAGEMENT ASSESSMENTS
	X	1Q, QAP 18-4, Management Assessments
	X	12Q, Assessment Manual
		Not anticipated
		18-6 QUALITY ASSURANCE INTERNAL AUDITS
	X	1Q, QAP 18-6, Quality Assurance Internal Audits
		Not anticipated
		18-7 QUALITY ASSURANCE SUPPLIER SURVEILLANCE
	X	1Q, QAP 18-7 Quality Assurance Supplier Surveillance
		Not applicable
		19-2 QUALITY IMPROVEMENT
X		1Q, QAP 19-2, Quality Improvement
X		L1, 8.02, SRTC QA Program Clarifications, Attachment 8.19-2
		20-1 SOFTWARE QUALITY ASSURANCE
	X	1Q, QAP 20-1, Software Quality Assurance
	X	L1, 8.20, Software Management & Quality Assurance
		No softwatre
		21-1 ENVIRONMENTAL QUALITY ASSURANCE
	X	1Q, QAP 21-1, QA Requirements for the Collection & Evaluation of Environ. Data
		No environmental data
		In addition to procedures noted above, if RW-0333P requirements are

Yes	No	Title
		invoked, the following procedures apply. These procedures may also apply at the discretion of the Task Leader to non-RW-0333P tasks.
	X	**L1, 8.21, SUPPLEMENTAL QA REQUIREMENTS FOR RW-0333P**
X		L1, 7.15, Obtaining Analytical Support
	X	L7.7, 1.16, Radioactive Sample Receiving, Labeling, & Tracking
X		L1, 7.16, Laboratory Notebooks and Logbooks

10. Identify any exceptions or additions to the procedures listed in the QA Matrix.

WSRC-IM-2002-00011, “Technical Report Design Check Guidelines,” will be used to help ensure the quality and consistency of the technical review process for technical reports produced by SRNL.

11. N/A, no software will be developed for this task

12. Document Approval

Document	**Management**		**Customer**		**CQF**	
	Yes	**No**	**Yes**	**No**	**Yes**	**No**
Technical & QA Plan	**X**			X	**X**	
Final Report	X		X			X

13.Anticipated Records:
The following records are anticipated from this task.

Yes	**No**	**Description**
X		Task Technical & QA Plan
X		Technical Notebooks
X		Task Technical Reports
X		Supporting Documentation

9.0 APPENDIX 2 WORK INSTRUCTION FOR HYDROGEN ELECTROLYZER

Author: John Steimke	Manager: Dan Burns

Reviewer: Mark Fowley

Purpose: To allow safe and effective operation of the Hydrogen Electrolyzer in 786-A.

Scope: This pertains only to the Electrolyzer Test Facility in 786-A.

Background:

SRNL made a proposal by Buckner and others to the Office of Nuclear Hydrogen Initiative to test the Hybrid Sulfur (HyS) technology for generating hydrogen. This technology uses a sulfur dioxide depolarized anode to greatly reduce the electrical energy requirement of the electrolyzer that produces hydrogen. SRNL received funding in FY05 to test an electrolyzer as part of this effort. A Task Plan [Steimke] was prepared for this work.

The electrolyzer has two sides, an anode side and a cathode side. Electrical current is passed through the electrolyzer which drives the following two reactions. Hydrogen ions cross from the anolyte to the cathode through a membrane.

Anode $SO_2 + 2\ H_2O = H_2SO_4 + 2H^+ + 2e^-$
Cathode $2H^+ + 2e^- = H_2$

The presence of sulfur dioxide at the anode greatly reduces the required cell potential as compared to traditional electrolysis. The anolyte is a solution of sulfuric acid with a concentration in the range from 30 wt% to 70 wt%. Sulfur dioxide gas is dissolved in the anolyte and hydrogen gas is generated at the cathode. Peter Lu at Westinghouse Electric Corp. researched these reactions about twenty five years ago with an electrolyzer that used acid solutions as both the anolyte and catholyte. The testing described in this Task Plan will use a newer technology, using a membrane electrode assembly (MEA), in which the anode and cathode are in physical contact with the membrane. The MEA technology requires no catholyte. The electrolyzer is a key part of HyS technology. Completing the material loop for HyS requires a high temperature decomposition of sulfuric acid to generate oxygen gas and also to regenerate the sulfur dioxide gas needed for the anode reaction.

Hazards and Precautions

1. The electrolyzer will have an electrical potential of no more than two volts across it. This voltage itself is not hazardous, but if a metal tool shorted across it a spark would be generated that could burn a person. Therefore, no metal tools may be used in the hood when the electrolyzer is energized.
2. Sulfur dioxide gas will be used in these tests. Sulfur dioxide is toxic and can cause burns to eyes and other tissues. Sulfur dioxide has the odor of a freshly lit match. The primary protection is the chemical hood. Sulfur dioxide can not be used unless the hood is operating and the sashes are in the proper positions as indicated by arrows marked on the front of the hood.
3. It is possible that hydrogen sulfide will be formed in the electrolyzer by reduction of sulfur dioxide. This gas is more toxic than sulfur dioxide and has the odor of rotten eggs.

Hydrogen sulfide can only be formed when sulfur dioxide is being used. Therefore, sulfur dioxide can not be used unless the hood is operating and the sashes are in the proper positions as indicated by arrows.

4. Sulfuric acid solutions at concentrations up to 70 wt% will be used in these tests. These solutions can cause serious chemical burns to tissues. Use chemically resistant gloves, safety glasses, faceshield and chemical apron when handling it.
5. Liquid and hardware temperatures will reach as much as 80°C, which can cause burns. Therefore, use thermally resistant gloves when working in the vicinity of hot surfaces.
6. The testing will generate hydrogen gas which is flammable and potentially explosive. The primary protection is the chemical hood. Hydrogen can not be generated unless the hood is operating and the sashes are in the proper positions as indicated by arrows.
7. This testing is designed to incrementally add risk factors. The first testing will involve air and water, but no electricity. Then electricity will be added, then sulfur dioxide and finally sulfuric acid.
8. Unplug the power supply whenever the test facility is expected to be shut down for more than one night.
9. At the end of every workday relieve the two backpressure regulators and verify using P1 and P3.
10. At the end of every workday deenergize the two pump controllers.
11. Deenergize the 220 volt power in the hood for the duration of this testing.
12. The PFA needle valves do not typically exhibit the same positive shutoff feel as metal valves. Overtightening of PFA valves may damage them.

Personal Protective Equipment

1. Safety glasses are always worn in the lab.
2. To mix, handle, clean up or dispose of sulfuric acid solutions wear face shield, apron and disposable chemical resistant gloves.
3. To connect the sulfur dioxide cylinder wear face shield, apron and disposable chemical resistant gloves.
4. To turn a valve after sulfuric acid has been introduced wear disposable chemical resistant gloves.

Accident Scenarios and Responses

1. Hood ventilation fails
    a. Turn off power supply
    b. Valve off sulfur dioxide cylinder
    c. Turn off pumps at the DAS
    d. Reestablish hood ventilation.
2. Sulfur dioxide leak is smelled or otherwise observed
    a. Valve off sulfur dioxide cylinder
    b. Turn off power supply
    c. Turn off pumps at the DAS
    d. Wait for gas to be drawn out of hood, then repair leak
3. Acid leak or spray
    a. Turn off both pumps at the DAS and valve off sulfur dioxide
    b. Clean up spill and repair leak.

Checkout of Power Supply

The purposes of this section are to check function of the power supply and to verify that the Data Acquisition System is correctly logging voltage and current. Refer to Figure 1.

1. Unplug the power supply. Connect the cables of the power supply to a calibrated shunt capable of measuring 50 amperes. Connect the voltage and current analog signals at the back of the power supply to the DAS.
2. Connect a calibrated voltmeter with a millivolt range across the shunt.
3. Start a DAS log with a 5 second period. Turn on the power supply and set the current at 5, 10, 15, 20, 30, 40 and 50 amperes. Manually record the voltmeter readings.
4. Set the power supply to zero current, turn off and unplug.
5. Remove the shunt and connect the two cables to a calibrated voltmeter capable of measuring 20 volts.
6. Plug in the power supply, turn it on and set voltages of 0.2, 0.4, 0.6, 0.8, 1.0, 1.5, 2.0, 3, 5, 10, 15 and 20 volts. Manually record the voltmeter readings.
7. Turn the power supply to maximum voltage and determine the maximum voltage, which should not be much more than 20 volts.
8. Stop the DAS log, turn off the power supply and unplug it.

Hydraulic Shakedown of Anolyte Flow Loop

The purposes of this section are to verify operation of two pumps, two flowmeters, thermocouples and pressure gages, to check for leaks and valve operation. Shakedown will be performed with air and water. Refer to Figure 1.

1. Install the electrolyzer in the facility hydraulically, but not electrically.
2. Close V13 and V16. Where the SO_2 cylinder would ordinarily be connected, connect an air line from a pressure regulator set at 15 psig to the inlet of the gas rotameter.
3. Close all valves.
4. Fill the Water Resupply Tank with deionized water. Label the tank accordingly on the figure.
5. Open V8 to vent the loop and open V11, V12 and V14 to fill the anolyte chamber of the Absorber to 17” of deionized water, which requires about 2.4 liters. A ruler is taped to the side of the absorber. Close V12.
6. Start logging with the DAS at a rate of once every 15 seconds.
7. Open V4 and set a flow of 5 mL/min for a few minutes with Pump 1 and Flow1 to verify function and also to verify proper logging by the DAS. Stop that flow and close V4.
8. Close V8, open V14 and set Backpressure Regulator #1 to 10 psig.
9. Use Pump 2 to set flows of 0.25, 0.5, 0.75, 1.0, 1.25, 1.5, 1.75 and 2.0 L/min, but do not exceed a pressure of 30 psig at P4. Maintain each flow for a few minutes to attain steady state.
10. Observe water flow down through the packed bed. Verify that Flow2, P1, P4, T1 and T2 are responding appropriately at the DAS. Reduce water flow to 1.0 L/min.
11. Open V16 and use V13 to set an air flow reading of 0.5 L/min at the gas rotameter. Verify that pressure P1 increases to the backpressure setpoint of 10 psig and then remains there.
12. Visually verify that flooding does not occur in the Packed Bed. Flooding is the situation where liquid backs up above the packing.
13. Briefly open V8 to collect a practice liquid sample. Then discard the liquid, which is just water.
14. Briefly open V7 to collect a practice liquid sample. Then discard the liquid, which is just water.
15. Briefly open V9 to collect a practice gas sample using a 5 mL syringe with a lock. Then discard the gas, which is just air.

16. Stop Pump2 and stop the DAS log. Stop the air flow and close V13 and V16. Set the Backpressure Regulator 1 to zero to relieve the pressure in the Absorber. Read P1 at the DAS to verify that pressure has been relieved.

Shakedown of Hydrogen Piping and Hardware

The purposes of this section are to check the operation of the Hydrogen Collector with air and to check operability of valves. Refer to Figure 1.

1. Temporarily connect the gas rotameter in the anolyte loop to the point of hydrogen generation of the electrolyzer. This is just upstream of the pressure relief valve. The electrolyzer is still not in the facility. The gas rotameter is still connected to air.
2. Place a bucket and a scale under the Hydrogen Collector.
3. Close V1, V2, V5, V10 and V15. V2 is a three-way valve, so turn it half way between the up and down positions. Open V3.
4. Set Backpressure Regulator 2 at 10 psig.
5. Open V5 to add water to the basin of the Hydrogen Collector, until water completely fills the Hydrogen Collector. Close V5 and V3.
6. Open V15 to drain the basin of the Hydrogen Collector. When draining ceases, record the scale reading. Leave V15 open.
7. Turn V2 down to the Hydrogen Collector.
8. At the end of every workday and first thing the next morning, record the water levels in the Hydrogen Collector to verify that no gas leakage has occurred.
9. Start a log with the DAS with an increment of 15 seconds.
10. Start a flow of 0.3 L/min with the gas rotameter, immediately record the time and liquid level in the Hydrogen Collection Cylinder.
11. Verify that P3 increases to 10 psig, the Backpressure Regulator 2 setting, and then holds steady.
12. Collect a practice 25 mL gas sample at V1. Then discard the gas, which is just air.
13. Verify that air bubbles into the Hydrogen Collector. Verify that P2 increases and that the liquid level in the Hydrogen Collector decreases. A tape measure is attached to side of the Hydrogen Collector. Verify that the scale reading increases. One liter is equal to 0.358”.
14. After about 10 minutes, turn V2 up to the hood vent to verify operation, then stop the air flow. Turning V2 up bypasses the Hydrogen Collector.
15. Stop the DAS log.
16. Close V1, V2, V5, V10 and V15. V2 is a three-way valve, so turn it half way between the up and down positions. Open V3.
17. Open V5 to add water to the basin of the hydrogen collector, until water completely fills the Hydrogen Collector. Close V5 and V3.
18. Open V15 to drain the basin of the Hydrogen Collection Cylinder. When draining ceases, record the scale reading. Leave V15 open.
19. Open V2 down to the Hydrogen Collector.
20. Set Backpressure Regulator 2 to zero to relieve the pressure and verify with P3.
21. Reconnect the gas rotameter to its proper location and disconnect the air supply from it.
22. Review the data collected in this section and verify that the rate of pressure increase at P2 agrees with both the observed rate of level decrease in the hydrogen collector and also with the rate of increase of the scale reading.

Electrolysis with water only, no sulfur dioxide

The purposes of this section are to verify that the performance of the electrolyzer is the same as measured by the vendor and to test collection of hydrogen. Refer to Figure 1.

1. Close V4, V6, V7, V8, V9, V11, V12, V13, V14 and V16.
2. Remove the temporary tubing that replaced the electrolyzer.
3. Close V13 and V16 and remove the temporary air line connected to the gas rotameter.
4. Install the electrolyzer in the facility. Orient the hydrogen outlet and anolyte outlet pointed upward. Connect V8 at the anolyte outlet to a hose that goes to a collection jug. Note: the anode side of the electrolyzer will be delivered full of water to prevent drying of the membrane. Connect the anode to the positive side of the power supply. Connect the cathode to the negative side of the power supply. Install the rubbery red electrode cover. This cover must be in place before the electrolyzer is energized.
5. Connect the current and voltage outputs from the power supply to the DAS. Verify that the DAS reads zero voltage and zero current. Reset the power supply coulometer to zero.
6. Verify that the Hydrogen Collector is full of water. If not, perform the following Steps 7 - 10. If it is full, proceed to Step 12.
7. Close V1, V2, V5, V10 and V15. V2 is a three-way valve, so turn it half way between the up and down positions.
8. Open V5 to add water to the basin of the Hydrogen Collector. When the water level in the annular space of the Hydrogen Collector is higher than the level in the inner cylinder open V3. Continue until water completely fills the Hydrogen Collector. Close V5 and V3.
9. Open V15 to drain the basin of the Hydrogen Collector. When draining ceases, record the scale reading. Leave V15 open.
10. Verify that V1, V5 and V10 are closed. Open V2 down to the Hydrogen Collector and set Backpressure Regulator 2 to 10 psig.
11. At the end of every workday and first thing the next morning, record the water levels in the Hydrogen Collector to verify that no gas leakage has occurred
12. Start the DAS logging at once every 15 seconds.
13. Open V11 and V14 and use Pump 2 and Flow 2 to set a flow of 350 mL/min.
14. Set a current of 9 amps and note the initial water level in the Hydrogen Collector using the tape measure attached to the side of it.
15. Verify that bubbles appear in the Hydrogen Collector. Monitor the voltage across the electrolyzer. Run until the voltage becomes steady, or for thirty minutes, whichever occurs first. Before changing or stopping the current, note the time and the level in the Hydrogen Collector. Then collect a labeled gas sample at V1. Also collect a 10 mL labeled anolyte sample at V7. The Hydrogen Collector may be bypassed by turning V2 to the up position. This sends hydrogen directly to the hood vent.
16. Periodically observe the Water Collection Chamber, which may collect condensate. Before it fills, slightly open V10 and collect the condensate in a labeled bottle. Then close V10.
17. Repeat steps 15 and 16 for currents of 18, 27, 36 and 45 amps. If necessary, use steps 10 through 13 to remove gas from the Hydrogen Collector and refill it with water.
18. Stop Pump 2, stop the DAS log, and close V12 and V8. Set Backpressure Regulator 2 to zero to relieve the pressure and verify with P3.
19. Archive a sample of the water collected at V8 and dispose of the rest of that water.

Electrolysis with water and sulfur dioxide

The primary purpose of this section is to add one risk factor, sulfur dioxide gas, to the testing before adding another risk factor, sulfuric acid. In addition, the data are expected to be useful in understanding the mechanisms of the hydrogen generation using a sulfur dioxide depolarized anode.

The reaction generates sulfuric acid, which will slowly accumulate because the anolyte will be recycled. The theoretical production of sulfuric acid will be computed. If the computed anolyte acid concentration exceeds 5 wt%, the test will be stopped and the contents of the anolyte loop will be replaced with fresh deionized water. Refer to Figure 1.

1. The Anolyte Packed Bed should still contain 17" of water from Hydraulic Shakedown. If not, refill it using Step 5 from the Hydraulic Shakedown portion of this Work Instruction.
2. Close V13 and V16. Connect a cylinder of sulfur dioxide to the gas rotameter. No pressure regulator will be necessary on the gas cylinder because the vapor pressure of SO_2 at 20°C is only about 20 psig. Set Backpressure Regulator 1 at 5 psig.
3. Set Backpressure Regulator 2 at 5 psig.
4. Close V4, V6, V7, V8, V9, V12. Open V11 and V14.
5. Verify that there is no gas at the top of the Hydrogen Collector and the basin around it is full to the overflow pipe. If not, perform Steps 7 – 10 of Electrolysis with Water, No Sulfur Dioxide. Open V15.
6. At the end of every workday and first thing the next morning, record the water levels in the Hydrogen Collector to verify that no gas leakage has occurred.
7. Verify that V1, V3, V5 and V10 are closed. V2 should be the up position and open to the Hydrogen Collector. Set Backpressure Regulator to 10 psig.
8. Start the DAS logging at once every 15 seconds. Set the power supply coulometer to zero.
9. Use Pump2 and Flow2 to start an anolyte flow of 1.0 L/min. Note the Absorber anolyte level in the laboratory notebook.
10. Set the power supply at 9 amps and note the time and level in the Hydrogen Collector. Verify that bubbles appear in the hydrogen collector.
11. Open V16. Adjust V13 to set a sulfur dioxide flow of 0.537 L/min at one bar and 20°C on the gas rotameter or 7.0 cm on the rotameter scale. This is sufficient to provide a 50% excess of SO_2 at 45 amperes. Verify that flooding does not occur in the absorber.
12. Divide the water inventory of the absorber, initially 2.4 liters, by the anolyte flowrate at FLOW2 to determine the residence time. Wait three residence times, then collect a liquid sample at the outlet of the electrolyzer and note the time and level in the Hydrogen Collector.
13. Monitor the voltage across the electrolyzer. Run until the voltage becomes steady, or for thirty minutes, whichever occurs first. Before changing or stopping the current, note the level in the Hydrogen Collector. Then collect a labeled gas sample.
14. Periodically observe the Water Collection Chamber, which may collect condensate. Before it fills, slightly open V10 and collect the condensate in a labeled bottle. Then close V10.
15. Repeat Steps 12 through 14 for currents of 18, 27, 36 and 45 amps. If necessary, stop between runs and remove the gas from the Hydrogen Collector using Steps 7 – 10 of Electrolysis with Water, No Sulfur Dioxide. Then, open V15. Keep track of the computed acid concentration in the anolyte. If it exceeds 5 wt%, stop and replace the anolyte with deionized water.
16. Reduce the anolyte flow to 0.75 L/min and repeat the run at 45 amps.
17. Relieve both Backpressure Regulators and verify with P1 and P3.
18. Turn off the power supply and unplug it.
19. Stop the flow of SO_2 by closing V13 and V16, stop Pump 2 and stop the DAS log.
20. Do not allow the electrolyzer to remain overnight with sulfur dioxide in it. At the end of the day, close V11, open V6 and V8 and drain the anolyte into a jug for later reuse. Then close V14, open V8 and V12 and use Pump 2 to pump a total of 2 liters of water through the cell and into a collection jug to flush the sulfur dioxide from the cell. Make sure that the anode side of the electrolyzer remains full of water.

Electrolysis with Sulfuric Acid Solutions and Sulfur Dioxide

The purpose of this section is to run with the chemical conditions expected in a hydrogen plant using electrolyzers with sulfur dioxide depolarized anodes. Refer to Figure 1.

1. Set Backpressure Regulator 1 at 5 psig.
2. Set Backpressure Regulator 2 at 5 psig.
3. Close V7, V8, V11, V12 and V14 and open V9 to vent the Absorber. Drain the contents of the Absorber, which is dilute, less than 5%, sulfuric acid solution, from the Absorber and the anode side of the electrolyzer by opening V6. Archive a 100 mL sample with the date and properly dispose of the rest. Close V6.
4. In a plastic jug, mix 10 liters of 30 wt% sulfuric acid solution using deionized water. Disconnect the supply of deionized water from V12 and connect a hose to it. Run the hose into the bottom of the acid jug.
5. Open V12 and V14 and use Pump2 to pump about 2.4 liters or 17” of acid solution through the electrolyzer to the Absorber. Close V4, V9 and V12.
6. Verify that there is no gas at the top of the Hydrogen Collector. If necessary, remove gas by performing Steps 7 – 10 of the section Electrolysis with Water Only, no Sulfur Dioxide. Open V15.
7. At the end of every workday and first thing the next morning, record the water levels in the Hydrogen Collector to verify that no gas leakage has occurred.
8. Start the DAS logging at once every 15 seconds and reset the power supply coulometer to zero.
9. Use Pump2 to start a flow of 1.0 L/min.
10. Divide the liquid inventory of the absorber by the liquid flowrate to determine the residence time. Wait three residence times, then set the current at 9 amps and note the time and initial water level in the Hydrogen Collector. Verify that bubbles appear in the hydrogen collector.
11. Set a sulfur dioxide flow of 0.537 L/min at one bar and 20°C on the gas rotameter or 7.0 cm on the rotameter scale by opening V16 and adjusting V13. This is sufficient to provide a 50% excess of SO2 at 45 amperes. Verify that flooding does not occur in the absorber.
12. Wait three additional residence times, then collect a liquid sample at V8 at the outlet of the electrolyzer. Note the time and hydrogen level.
13. The chemical reaction at the anode generates sulfuric acid, which will be removed by blowdown at V7 twice every day of operation using this section of the Work Instruction. Keep track of the number of minutes that have elapsed since the last blowdown. Look up the correct blowdown rate from Table 1 and multiply by the number of minutes to get the volume of blowdown. Collect that much liquid at V7. Measure the density of the blowdown and discard it as waste.
14. Open V4 and use Pump1 and Flow1 to add deionized water to the Absorber to compensate for the water consumed in the chemical reaction and also lost by evaporation and blowdown. At least twice a day, adjust the rate of water addition so that liquid level in the bottom of the absorber remains constant.
15. Monitor the voltage across the electrolyzer. Run until the voltage becomes steady, or for thirty minutes, whichever occurs first. Before changing or stopping the current, note the level in the Hydrogen Collector. Then collect a labeled gas sample.
16. Periodically observe the Water Collection Chamber, which may collect condensate. Before it fills, slightly open V10 and collect the condensate in a labeled bottle. Then close V10.
17. Repeat steps 12 through 16 for currents of 18, 27, 36 and 45 amps. Note that the rate of makeup water supplied by Pump1 will increase with increasing current. If necessary, stop between runs and remove the gas from the Hydrogen Collector using Steps 7 – 10 of Electrolysis with Water, No Sulfur Dioxide. Then, open V15.
18. Reduce the anolyte flow to 0.75 L/min and repeat the run at 45 amps.

19. Turn off the power supply and stop the DAS.
20. Drain the acid solution from the anolyte loop at V6 and archive a 100 mL sample.
21. Repeat Steps 5 through 19 with a 70 wt% solution of sulfuric acid.
22. If time permits, repeat Steps 5 through 19 with a 50 wt% solution of sulfuric acid.
23. Repeat Steps 5 though 21 at a temperature at T1 of 80°C.
24. Stop the flow of SO_2, stop Pump 2 and stop the DAS log.
25. Relieve both Backpressure Regulators and verify with P1 and P3
26. Turn off the power supply and unplug it.
27. Do not allow the electrolyzer to remain overnight with sulfur dioxide in it. At the end of the day, open V6 and drain the anolyte into a jug for later reuse. Then close V14, open V8 and V12 and pump water through the cell and into a collection jug to flush the sulfur dioxide from the cell. Make sure that the anode side of the electrolyzer remains full of water.

Table 1 Acid Blowdown Rates in mL/min

amperes	30 wt% acid	50 wt% acid	70 wt% acid
9	0.72	0.45	0.23
18	1.43	0.90	0.46
27	2.15	1.35	0.70
36	2.86	1.80	0.93
45	3.58	2.25	1.16

10. APPENDIX 3 TYPICAL RAW DATA

DATE	TIME	T 1	T 2	T 3	T 4	P 1	P 2	P 3	P 4	FM 1	FM 2	SCALE	ICELL	ECELL
		°C	°C	°C	°C	psig	Inch H2O	psig	psig	L/min	L/min	lb	amps	volts
6/29/2005	7:22:35	22.488	22.531	22.434	23.162	1.581	47.79	-0.646	3.915	-0.043	0.501	3.324	0	0.004
6/29/2005	7:22:50	22.498	22.541	22.445	23.158	1.606	47.793	-0.629	3.964	-0.043	0.505	3.325	0	0.004
6/29/2005	7:23:05	22.509	22.562	22.445	23.153	1.629	47.793	-0.614	3.951	-0.043	0.5	5.624	0	0.004
6/29/2005	7:23:20	22.539	22.577	22.45	23.128	1.659	47.79	-0.595	3.976	-0.043	0.499	5.621	0	0.004
6/29/2005	7:23:35	22.544	22.572	22.45	23.143	1.695	47.793	-0.572	4.027	-0.043	0.501	5.622	0	0.004
6/29/2005	7:23:50	22.568	22.596	22.465	23.142	1.72	47.79	-0.549	4.05	-0.043	0.5	5.622	0	0.004
6/29/2005	7:24:05	22.589	22.612	22.465	23.128	1.748	47.79	-0.53	4.08	-0.043	0.5	5.624	0	0.004
6/29/2005	7:24:20	22.599	22.632	22.465	23.289	2.79	47.79	-0.522	13.58	-0.043	1.474	5.626	0	0.007
6/29/2005	7:24:35	22.599	22.672	22.475	23.233	2.803	47.79	-0.505	13.679	-0.043	1.496	5.624	0	0.008
6/29/2005	7:24:50	22.639	22.697	22.475	23.294	2.856	47.79	-0.49	13.845	-0.042	1.502	5.627	0	0.009
6/29/2005	7:25:05	22.659	22.712	22.47	26.264	2.911	47.787	-0.505	13.993	-0.042	1.5	5.627	1.026	0.506
6/29/2005	7:25:20	22.69	22.748	22.476	26.235	2.962	47.79	-0.574	13.833	-0.042	1.502	5.627	1.001	0.509
6/29/2005	7:25:35	22.71	22.768	22.481	26.25	2.996	47.79	-0.62	14.032	-0.042	1.499	5.627	0.999	0.513
6/29/2005	7:25:50	22.725	22.793	22.486	26.275	3.062	47.79	-0.69	14.199	-0.042	1.495	5.624	0.997	0.515

11.0 APPENDIX 4 DATA SUMMARY

date	cell	anolyte	SO2 absorber pressure, bar	Anolyte flowrate, L/m	Current density, mA/cm^2	Cell voltage
23-May	PES	water	na	0.35	58	1.57
23-May	PES	water	na	0.35	116	1.61
23-May	PES	water	na	0.35	229	1.67
23-May	PES	water	na	0.35	349	1.73
23-May	PES	water	na	0.35	465	1.78
23-May	PES	water	na	0.35	577	1.82
23-May	PES	water	na	0.35	577	1.82
23-May	PES	water	na	0.35	464	1.78
23-May	PES	water	na	0.35	350	1.73
23-May	PES	water	na	0.35	232	1.68
1-Jun	PES	water and SO2	1	0.35	349	1.73
1-Jun	PES	water and SO2	1	0.35	349	1.79
3-Jun	PES	water	1	0.35	0	0.26
3-Jun	PES	water	1	0.35	116	1.65
3-Jun	PES	water	1	0.35	233	1.74
3-Jun	PES	water	1	0.35	349	1.83
3-Jun	PES	water	1	0.35	465	1.9
3-Jun	PES	water	1	0.35	576	1.96
3-Jun	PES	water	1	0.35	465	1.89
3-Jun	PES	water	1	0.35	349	1.82
3-Jun	PES	water	1	0.35	233	1.75
3-Jun	PES	water	1	0.35	116	1.66
3-Jun	PES	water	1	0.35	0	1.45
3-Jun	PES	water	1	0.35	0	1.41
3-Jun	PES	water	1	0.35	0	0.31
6-Jun	PES	30 wt% H2SO4	residual SO2	0.35	116	0.87
6-Jun	PES	30 wt% H2SO4	residual SO2	0.35	233	1.11
6-Jun	PES	30 wt% H2SO4	residual SO2	0.35	349	1.32
6-Jun	PES	30 wt% H2SO4	residual SO2	0.35	465	1.81
6-Jun	PES	30 wt% H2SO4	1	0.35	0	0.23
6-Jun	PES	30 wt% H2SO4	1	0.35	349	1.07
6-Jun	PES	30 wt% H2SO4	1	0.35	116	0.86
6-Jun	PES	30 wt% H2SO4	1	0.35	233	1
6-Jun	PES	30 wt% H2SO4	1	0.35	465	1.25
6-Jun	PES	30 wt% H2SO4	1	0.35	576	1.37
6-Jun	PES	30 wt% H2SO4	1	0.35	0	0.39
6-Jun	PES	30 wt% H2SO4	1	0.35	58	0.8
6-Jun	PES	30 wt% H2SO4	1	0.35	0	0.15
6-Jun	PES	30 wt% H2SO4	1	0.35	58	0.75
6-Jun	PES	30 wt% H2SO4	1	0.35	116	0.84
6-Jun	PES	30 wt% H2SO4	1	0.35	233	0.99

DATA SUMMARY

date	cell	anolyte	SO2 absorber pressure, bar	Anolyte flowrate, L/m	Current density, mA/cm^2	Cell voltage
6-Jun	PES	30 wt% H2SO4	1	0.35	349	1.14
6-Jun	PES	30 wt% H2SO4	1	0.35	465	1.28
6-Jun	PES	30 wt% H2SO4	1	0.35	576	1.42
7-Jun	PES	30 wt% H2SO4	1	0.35	0	0.14
7-Jun	PES	30 wt% H2SO4	1	0.35	58	0.71
7-Jun	PES	30 wt% H2SO4	1	0.35	116	0.86
7-Jun	PES	30 wt% H2SO4	1	0.35	233	1.05
7-Jun	PES	30 wt% H2SO4	1	0.35	349	1.22
7-Jun	PES	30 wt% H2SO4	1	0.35	465	1.37
7-Jun	PES	30 wt% H2SO4	1	0.35	576	1.55
7-Jun	PES	30 wt% H2SO4	1	0.35	0	0.39
7-Jun	PES	30 wt% H2SO4	1	0.35	0	0.34
7-Jun	PES	30 wt% H2SO4	1	0.35	349	1.06
7-Jun	PES	30 wt% H2SO4	1	0.35	349	1.14
7-Jun	PES	30 wt% H2SO4	1	0.6	349	1.15
7-Jun	PES	30 wt% H2SO4	1	0.15	349	1.21
7-Jun	PES	30 wt% H2SO4	1	0.35	349	1.2
7-Jun	PES	30 wt% H2SO4	1	0.6	349	1.19
7-Jun	PES	30 wt% H2SO4	1	0.35	0	0.16
7-Jun	PES	70 wt% H2SO4	1	0.35	0	0.25
7-Jun	PES	70 wt% H2SO4	1	0.35	58	0.98
7-Jun	PES	70 wt% H2SO4	1	0.35	116	1.22
7-Jun	PES	70 wt% H2SO4	1	0.35	116	1.28
7-Jun	PES	70 wt% H2SO4	1	0.35	116	1.34
7-Jun	PES	70 wt% H2SO4	1	0.35	116	1.39
7-Jun	PES	70 wt% H2SO4	1	0.35	116	1.45
29-Jun	USC	30 wt% H2SO4	1	1.5	0	0
29-Jun	USC	30 wt% H2SO4	1	1.5	25	0.54
29-Jun	USC	30 wt% H2SO4	1	1.5	50	0.91
29-Jun	USC	30 wt% H2SO4	1	1.5	75	1.03
29-Jun	USC	30 wt% H2SO4	1	1.5	100	1.13
29-Jun	USC	30 wt% H2SO4	1	1.5	125	1.25
29-Jun	USC	30 wt% H2SO4	1	1.5	150	1.35
29-Jun	USC	30 wt% H2SO4	1	0.9	25	0.73
29-Jun	USC	30 wt% H2SO4	1	0.9	50	0.95
29-Jun	USC	30 wt% H2SO4	1	0.9	75	1.14
29-Jun	USC	30 wt% H2SO4	1	0.9	100	1.27
29-Jun	USC	30 wt% H2SO4	1	0.3	25	0.92
29-Jun	USC	30 wt% H2SO4	1	0.3	50	1.17
29-Jun	USC	30 wt% H2SO4	1	0.3	75	1.31
29-Jun	USC	30 wt% H2SO4	2	1.5	25	0.54

DATA SUMMARY

date	cell	anolyte	SO2 absorber pressure, bar	Anolyte flowrate, L/m	Current density, mA/cm^2	Cell voltage
29-Jun	USC	30 wt% H2SO4	2	1.5	50	0.78
29-Jun	USC	30 wt% H2SO4	2	1.5	75	0.87
29-Jun	USC	30 wt% H2SO4	2	1.5	100	0.97
29-Jun	USC	30 wt% H2SO4	2	1.5	125	1.11
29-Jun	USC	30 wt% H2SO4	2	1.5	150	1.23
29-Jun	USC	30 wt% H2SO4	2	1.5	175	1.34
29-Jun	USC	30 wt% H2SO4	2	1.5	12.5	0.45
29-Jun	USC	30 wt% H2SO4	2	1.5	37.5	0.74
29-Jun	USC	30 wt% H2SO4	2	0.9	25	0.55
29-Jun	USC	30 wt% H2SO4	2	0.9	50	0.81
29-Jun	USC	30 wt% H2SO4	2	0.9	75	0.97
29-Jun	USC	30 wt% H2SO4	2	0.9	100	1.15
29-Jun	USC	30 wt% H2SO4	2	0.9	125	1.29
29-Jun	USC	30 wt% H2SO4	2	0.3	25	0.75
29-Jun	USC	30 wt% H2SO4	2	0.3	50	1.07
29-Jun	USC	30 wt% H2SO4	2	0.3	75	1.24