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Closeout Report for Hybrid Sulfur Pressurized Button Cell Test Facility

Generation IV Nuclear Energy Systems Initiative (Gen IV) Program
FY10 Work Package G-SR10VH0301

Author: T. J. Steeper

REPORT DATE:
SEPTEMBER 15, 2010

Savannah River National Laboratory
Savannah River Nuclear Solutions
Savannah River Site
Aiken, SC 29808

Prepared for the U.S. Department of Energy Under
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REVIEWS AND APPROVALS

T. J. Steeper, Author, Process Science and Engineering

J. L. Steimke, Reviewer, Process Science and Engineering

W. A. Summers, Program Manager, Alternate Energy Programs

B. J. Giddings, Level 4 Manager, Process Science and Engineering

S. L. Marra, Environmental & Chemical Process Technology Research Programs

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LIST OF ACRONYMS

atm	atmospheres
DAS	data acquisition system
FEP	fluorinated ethylene propylene
HyS	Hybrid Sulfur Cycle
MEA	membrane electrode assembly
NHI	Nuclear Hydrogen Initiative
PEM	proton exchange membrane
PFA	perfluoroalkoxy
PPS	polyphenylene sulfide
PTFE	polytetrafluoroethylene
PVDF	polyvinylidene fluoride
SDE	SO_2 depolarized electrolyzer
SRNL	Savannah River National Laboratory
SS	stainless steel
Viton	DuPont trade name for Vinylidene fluoride/hexafluoropropylene copolymer, or FKM

1.0 EXECUTIVE SUMMARY

This document is the Close-Out Report for design and partial fabrication of the Pressurized Button Cell Test Facility at Savannah River National Laboratory (SRNL). This facility was planned to help develop the sulfur dioxide depolarized electrolyzer (SDE) that is a key component of the Hybrid Sulfur Cycle for generating hydrogen. The purpose of this report is to provide as much information as possible in case the decision is made to resume research. This report satisfies DOE Milestone M3GSR10VH030107.0.

The HyS Cycle is a hybrid thermochemical cycle that may be used in conjunction with advanced nuclear reactors or centralized solar receivers to produce hydrogen by water-splitting. The HyS Cycle utilizes the high temperature (>800ºC) thermal decomposition of sulfuric acid to produce oxygen and regenerate sulfur dioxide. The unique aspect of HyS is the generation of hydrogen in a water electrolyzer that is operated under conditions where dissolved sulfur dioxide depolarizes the anodic reaction, resulting in substantial voltage reduction. Low cell voltage is essential for both high thermodynamic efficiency and low hydrogen cost. Sulfur dioxide is oxidized at the anode, producing sulfuric acid that is sent to the high temperature acid decomposition portion of the cycle. Sulfur dioxide from the decomposer is cycled back to electrolyzers.

The electrolyzer cell uses the membrane electrode assembly (MEA) concept. Anode and cathode are formed by spraying a catalyst, typically platinized carbon, on both sides of a Proton Exchange Membrane (PEM). SRNL has been testing SDEs for several years including an atmospheric pressure Button Cell electrolyzer (2 cm^2 active area) and an elevated temperature/pressure Single Cell electrolyzer (54.8 cm^2 active area).

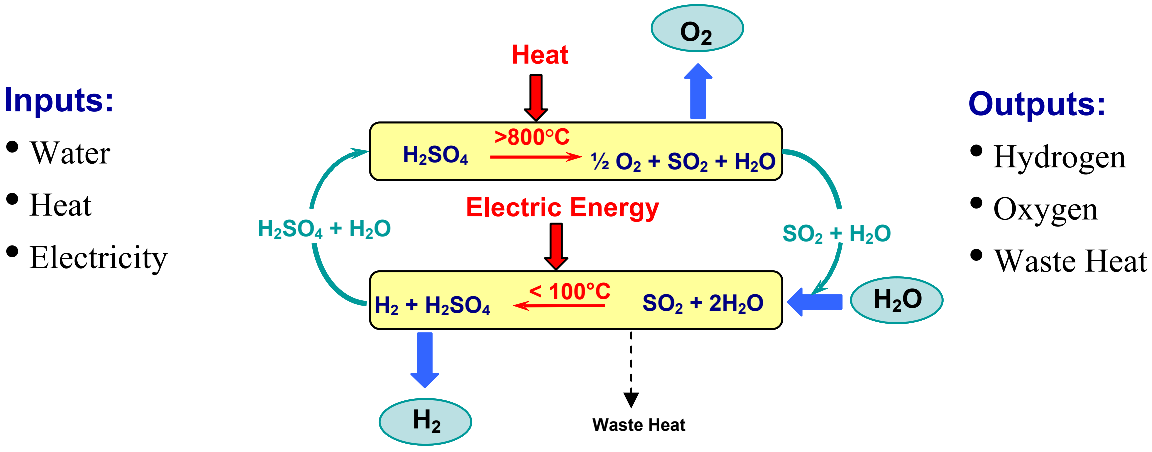
SRNL tested 37 MEAs in the Single Cell electrolyzer facility from June 2005 until June 2009, when funding was discontinued. An important result of the final months of testing was the development of a method that prevents the formation of a sulfur layer previously observed in MEAs used in the Hybrid Sulfur Cycle electrolyzer. This result is very important because the sulfur layer increased cell voltage and eventually destroyed the MEA that is the heart of the cell. Steimke and Steeper [2005, 2006, 2007, 2008] reported on testing in the Single Cell Electrolyzer test facility in several periodic reports. Steimke et. al [2010] issued a final facility close-out report summarizing all the testing in the Single Cell Electrolyzer test facility. During early tests, significant deterioration of the membrane occurred in 10 hours or less; the latest tests ran for at least 200 hours with no sign of deterioration. Ironically, the success with the Single Cell electrolyzer meant that it became dedicated to long runs and not available for quick membrane evaluations.

Early in this research period, the ambient pressure Button Cell Electrolyzer test facility was constructed to quickly evaluate membrane materials. Its small size allowed testing of newly developed membranes that typically were not available in sizes large enough to test in the Single Cell electrolyzer. The most promising membranes were tested in the Single Cell Electrolyzer as soon as sufficient large membranes could be obtained. However, since the concentration of SO_2 gas in sulfuric acid decreases rapidly with increasing temperature, the ambient pressure Button Cell was no longer able to achieve the operating conditions needed to evaluate the newer improved high temperature membranes. Significantly higher pressure operation was required to force SO_2 into the sulfuric acid to obtain meaningful concentrations at increased temperatures. A high pressure (200 psig), high temperature (120 ^{o}C) Button Cell was designed and partially fabricated just before funding was discontinued in June 2009.

SRNL completed the majority of the design of the test facility, including preparation of a process and instrument drawing (P&ID) and preliminary designs for the major components. SRNL intended to complete the designs and procure or fabricate the specialized equipment, including all wetted-parts for handling the SO_2/sulfuric acid reactants. The portion of the P&ID that included commercial equipment, standard tubing, controls, and structural systems was procured from a commercial partner (Giner Electrochemical Systems LLC). This report summarizes the objectives, preliminary design, and status of the test facility. At the time of this report, SRNL was continuing discussions with potential partners for transfer of the technology for use under other programs.

2.0 INTRODUCTION

HyS is conceptually the simplest of the thermo-chemical cycles for splitting water as it involves only sulfur chemistry. In the HyS Cycle shown below 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^+). 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 allows hydrogen ions to pass through but blocks 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 standard cell potential for conventional water electrolysis is 1.23 volts at 25˚C. However, commercial electrolyzers typically require higher voltages ranging from 1.8 V to 2.6 V [Kirk-Othmer, 1991]. The oxidation of sulfur dioxide instead of water in the HyS electrolyzer occurs at a much lower potential. For example, the standard cell potential for sulfur dioxide oxidation at 25˚C in 50 wt % sulfuric acid is 0.29 V [Westinghouse, 1980]. Since power consumption by the electrolyzers is equal to voltage times current, and current is proportional to hydrogen production, a large reduction in voltage results in a large reduction in electrical power cost per unit of hydrogen generated.

The SDE electrolyzer half-cell and net cell reactions are:

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

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

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

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

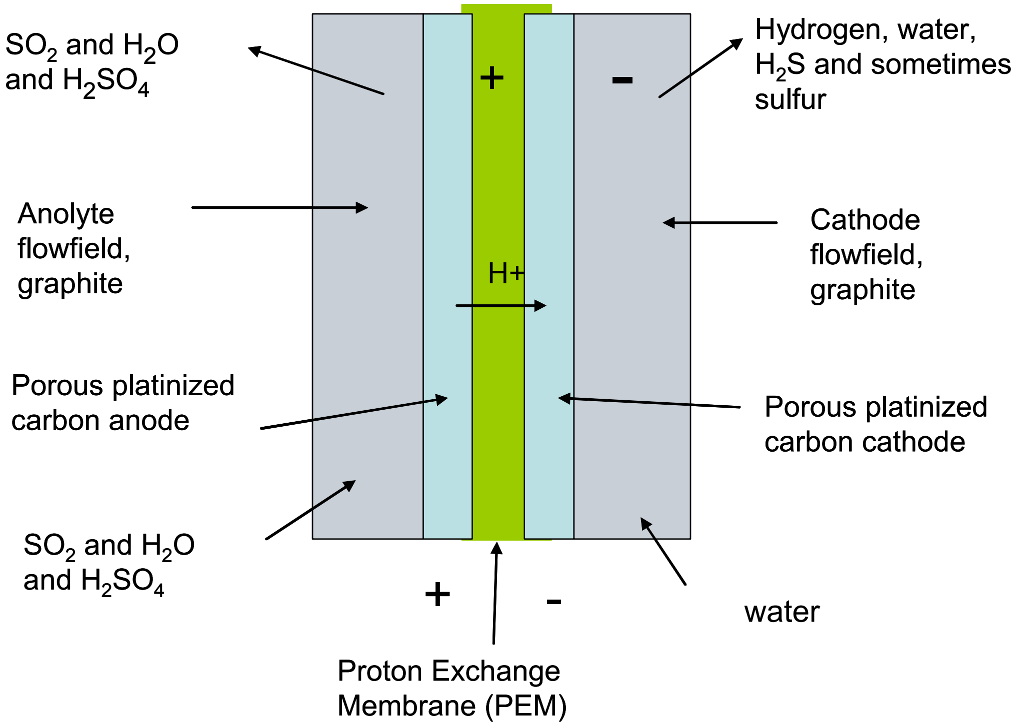


Figure 1 Schematic of Electrolyzer Cell

3.0 DISCUSSION

3.1 BACKGROUND

Steimke and Steeper [2005, 2006] tested a graphite based electrolyzer cell designed and built at SRNL with six MEAs. The cell was durable and cell voltages were similar to the lowest cell voltages measured by other researchers. Steimke and Steeper [2007] performed a 100 hour long Longevity Test in the SRNL cell. Hydrogen production efficiency was high but cell voltage slowly increased during the test. This was later determined to be the result of the formation of a sulfur layer. Steimke and Steeper [2008] continued the work on the SRNL electrolyzer (MEAs 7 through 26). Steimke and Herman [2008] tested a three cell stack. Steimke et. al [2010] continued the work on the SRNL electrolyzer (MEAs 27 through 37). A method of operation was discovered that eliminated the sulfur layer formation.

Elvington, et. al. [2010] tested a smaller button cell electrolyzer at SRNL, which is limited to atmospheric pressure operation. Staser and Weidner [2009] at the University of South Carolina tested an alternate electrolyzer concept, in which sulfur dioxide is fed to the cell as a gas rather than first being dissolved in sulfuric acid anolyte

The ambient pressure Button Cell electrolyzer facility was constructed to quickly evaluate membrane materials. Its small size allowed testing of newly developed membranes that typically were not available in sizes large enough to test in the Single Cell electrolyzer. The most promising membranes were tested in the Single Cell electrolyzer as soon as sufficient large membranes could be obtained. However, since the concentration of SO_2 gas in sulfuric acid decreases rapidly with increasing temperature, the ambient pressure Button Cell was unable to achieve the operating conditions needed to evaluate the newer improved high temperature membranes. Significantly higher pressure operation was required to force SO_2 into the sulfuric acid to obtain meaningful concentrations at increased temperatures. A high pressure (200 psig), high temperature (120 ^{o}C) Button Cell was designed and partially fabricated just before funding was discontinued in June 2009.

The purpose of this report is to document the current design and fabrication status of the planned Pressurized Button Cell Facility. The large scale hydrogen generation research programs have a history of being started and stopped based on changing energy, economic, and political outlooks, so it seems logical to document as much information as possible in case the decision is made to resume research.

3.2 TEST FACILITY

3.2.1 Overview of Test Facility

A test facility capable of testing sulfur dioxide depolarized electrolyzers at pressures up to 20 atm (300 psig) and temperatures up to 140 ºC was originally proposed. As design progressed the design temperature was reluctantly lowered to 120 ^{o}C due to the temperature limits of available commercial equipment.

Our plan was to construct a versatile test stand for conducting research on a small sulfur dioxide depolarized electrolyzer (SDE). The SDE generates hydrogen in the Hybrid Sulfur (HyS) Process. The electrolyzer oxidizes sulfur dioxide to form sulfuric acid at the anode [r1] and reduces hydronium ions to form hydrogen at the cathode [r2]. The overall electrochemical cell reaction consists of the production of H_2SO_4 and H_2 [r3].

$$SO_2 + 2H_2O \rightarrow H_2SO_4 + 2H^+ + 2e^- \qquad [r1]$$
$$2H^+ + 2e^- \rightarrow H_2 \qquad [r2]$$
$$2SO_2 + 2H_2O \rightarrow H_2SO_4 + H_2 \qquad [r3]$$

We previously built and operated a larger electrolyzer test facility, but needed a second, smaller electrolyzer test facility to allow us to test smaller samples of membranes as they were produced. The process and instrument drawing (P&ID) for the smaller electrolyzer test facility was prepared with equipment divided into two separate sections. One portion included equipment that SRNL planned to provide directly, most of it custom designed and fabricated. The SRNL portion includes custom valves, tees, fittings, and PTFE or PFA lined SS tubing needed to handle the hot corrosive anolyte and catholyte. The valves, tees, and some specialized fittings are machined from zirconium bar stock. The remaining portion of the P&ID indicated equipment that SRNL planned to have provided by a commercial partner, mostly commercial equipment and standard tubing.

We planned to feed a liquid anolyte consisting of 30-50 wt% sulfuric acid saturated with sulfur dioxide to the electrolyzer. The anolyte was to be pumped from the bottom of a glass absorber/anolyte tank through a density meter. After the density meter, the flow was to be split with the majority (about 70 ml/min) returning through a throttle valve back to the top of the absorber/anolyte tank where it was to be distributed to trickle down through a packed bed consisting of glass Raschig rings. The remainder of the anolyte (nominal 6 ml/min) was to pass through a flowmeter to the electrolyzer. Upon leaving the electrolyzer, it was to be recombined with the bypass flow before being returned to the top of the absorber/anolyte tank. A density meter identical to the one that worked well in the Single Cell Electrolyzer test facility was purchased for this application, but is fairly large with a 16 ml internal volume. A relatively large anolyte flow was to bypass the electrolyzer to decrease the response time in the density meter, as well as provide better mixing in the anolyte tank. The larger anolyte flow also would allow this facility to use the same pump as in the Single Cell Electrolyzer test facility, eliminating the need for a difficult custom pump design/fabrication and facilitating spare parts maintenance.

To saturate the anolyte, liquid sulfuric dioxide at a nominal 0.0137 ml/min was to be pumped from a cylinder into the vapor space below the packed bed where it would flash into gas and rise up through the packed bed to saturate the acid. To deliver liquid SO_2, the cylinder would either need a dip tube as shown on the P&ID, or the cylinder will have to be inverted so the connection is on the bottom. Since the room temperature vapor pressure of sulfur dioxide is about 34 psig the sulfur dioxide cylinder must be heated to raise its pressure to about 60 psig to ensure the pump fills with liquid rather than gas. Likewise, the SO_2 backpressure regulator would be set at about 60 psig to ensure that the sulfur dioxide inside the pump will remain liquid and not boil off at an uncontrolled rate when the cell was operated at low pressures.

Water would be pumped into the top of the packed bed at about 0.0112 ml/min to both furnish the water for the reaction in the electrolyzer [r1], and to dilute the sulfuric acid generated in the electrolyzer [r1] to maintain a constant wt% acid in the anolyte. During electrolyzer operation the anolyte quantity would continuously increase due to the production of H_2SO_4 at the anode [r1], and a portion would have to be periodically drained from the absorber/anolyte tank. We initially planned to provide conductivity probes at high and low operating levels, and high and low alarm levels, inside the absorber/anolyte tank. The conductivity probes would have to be made of highly corrosion resistant materials (zirconium or platinum), be reliability insulated on the lower portions, and represent multiple possible leak sites. Shortly before shutting the Single Cell Electrolyzer test facility down, laser diode/photo cell detectors were placed on the exterior of its absorber/anolyte tank and worked well to detect the high and low operating levels and alarm levels. A similar installation should be considered for use instead of the conductivity probes as they are commercially available and cannot leak. In either case, the control system must interface with the level indicators to open a drain valve as needed to control the anolyte level. The control system should also provide visible and audible alarms if the level control should fail for some reason and the level reaches either the high or low alarm levels.

The catholyte would be water pumped at about 0.33 ml/min through the electrolyzer. Some of the water would pass through the membrane in the electrolyzer to the anode furnishing some of the reactant and diluent water, but most of it would simply serve to hydrate the membrane and flush any trace sulfur dioxide and other sulfur compounds that may appear on the cathode side of the electrolyzer. Hydrogen generated in the electrolyzer [r2] would exit along with the flush water. Hydrogen and sulfur contaminated flush water would flow to a simple vertical cylinder water separator. Water saturated hydrogen gas would be discharged through a backpressure regulator and flowmeter to the atmosphere at about 0.149 liter/hr. The remaining sulfur contaminated flush water would periodically be discharged from the water separator and be discarded after sampling. The P&ID shows a float switch installed in the water separator to control the discharge valve. In the Single Cell Electrolyzer test facility the float switch was replaced by a laser diode/photo cell detector which worked well. Such an installation should be considered for the Pressurized Button Cell test facility as well.

The design operating range for the electrolyzer is from normal room temperature and pressure up to 21 atm (300 psig) and 120 ^{o}C. The deionized water would be supplied by a low pressure header. It was anticipated that positive displacement piston type pumps would be needed to inject against 300 psig at low flow rates from the fairly low pressure sources. The sulfur dioxide and water reactant flows could be stopped for a short time to refill piston type pumps when necessary. However, the cathode flush water flow should be relatively continuous so two pump heads operating together would be needed.

The nominal flow rates stated above are based on the currently planned electrolyzer size and nominal current. We planned to have the ability to measure and control the flow rates in the range of 10%-400% of the nominal values to allow for lower/higher current testing levels and larger cells.

3.2.2 Data Acquisition System

SRNL has partnered with an electrolyzer development company, Giner Electrolchemical Systems, LLC., in Newton, MA, on other aspects of the HyS research. The decision was made to purchase the chemical feed and control portion of the Pressurized Button Cell Facility from them. We worked closely with Simon Stone of Giner as the design of the facility matured. Several revisions to the P&ID drawing were made as responsibilities for the various components of the facility were negotiated. Giner's portion of the facility was delivered and being checked out just as funding was discontinued. It was apparent that the hardware that Giner delivered was capable of meeting all the needs of the facility; however some reprogramming of the control software was going to be needed for full implementation of the desired automatic controls. Unfortunately, funding was stopped abruptly and these changes were not completed.

The Data Acquisition System (DAS) must collect and log data as shown on the schematic, control the pump speeds, system temperatures, electrolyzer current and voltage, and provide safe shutdown under off normal conditions. We planned to use a PC based DAS running Labview software since we had numerous systems running that platform. The DAS must allow for the creation of programmable protocols for the automatic operation of the system. We planned to have some equipment, such as the independent over temperature shutdown, stand alone to reduce the cost without significantly impacting ease of use.

The control system would accept the following operator inputs:

1. Anolyte flow rate
    a. Desired flow rate
    b. Maximum allowable anode pressure drop
    c. Calibration constants for flow meter
2. Catholyte flow rate
    a. Desired flow rate
    b. Maximum allowable cathode pressure drop
3. Temperature
    a. Maximum allowable rate of temperature increase or decrease
    b. Desired anode temperature
    c. Desired cathode temperature
    d. Maximum allowable cathode temperature
    e. Desired heater/chiller circulating bath temperature
    f. Maximum heater/chiller temperature
4. SO_2 addition rate
    a. Maximum allowable flowrate
    b. Manual/automatic control
    c. Desired flowrate for manual control
    d. Desired operating pressure for automatic control
    e. Calibration constants for pressure gauges

5. Water reactant addition rate
    a. Maximum allowable flowrate
    b. Manual/automatic control
    c. Desired flowrate for manual control
    d. Desired density for automatic control
    e. Calibration constants for density meter
6. Power supply
    a. Maximum voltage for voltage control
    b. Maximum current for current control
7. Maximum allowed pressure differential across electrolyzer (absolute value of [P1+P2]/2-[P3+P4]/2)

The DAS would provide the following control functions:

1. If hood exhaust is lost for some reason or a leak is detected the electrolyzer power should be turned off and all of the reagent feeds should be stopped.
2. Anolyte flow rate needs to be controlled to the desired flow rate, or to the flow rate that causes the maximum allowable anode pressure drop (P1-P2) to be reached, whichever is less. An audible alarm with visual indication should be provided if the flow rate is limited to prevent exceeding the maximum allowable anode pressure drop. A 4-20 mA signal needs to be generated to control the anolyte circulation pump speed to set the flow. The pump speed can be varied sufficiently to produce a flow rate in the range of 40 ml/min at 4 mA to about 3000 ml/min at 20 mA. (Note that we have operated this pump reliability for long periods at about 80 ml/min.) The flow rate will be indicated by a 4-20 mA signal from the flowmeter. The flowmeter will be calibrated to provide 4 mA output at 0 ml/min to 20 mA output at 24 ml/min.
3. The catholyte flow rate needs to be controlled to the desired flow rate, or to the flow rate that causes the maximum allowable cathode pressure drop (P3-P4) to be reached, whichever is less. An audible alarm with visual indication should be provided if the flow rate is limited to prevent exceeding the maximum allowable cathode pressure drop.
4. The anode, cathode, and heater/chiller circulating bath heaters must be controlled to reach and hold the desired temperatures. Most often these temperatures will all be the same. However, it is possible that for some tests we may want the temperature of the anode, cathode, or heater/chiller circulating bath to be a few degrees above or below the nominal system temperature. Rapid changes in temperatures are usually undesirable as the differential pressure across the electrolyzer may become difficult to control, so the rate of temperature increases and decreases should be limited as specified by the operator. In addition, all heaters should be shut off by an independent shutdown system if any temperature exceeds the maximum allowable system temperature. In that event, an audible alarm with visible indication of the triggering temperature should be provided.
5. Initially, the system will be filled with air at room temperature. Frequently there will be some SO_2 still absorbed in the anolyte from previous tests. Normally the power supply will be placed in voltage control mode and the SO_2 addition rate will be set manually at some low flow. The backpressure regulator downstream of the SO_2 pump will be set manually to prevent boiling but allow venting as the system is

brought up to the desired basic system operating temperature. After the air in the absorber/anolyte tank is purged to the operator's satisfaction the backpressure regulator setting will be increased manually to several psig above the desired operating pressure. The power supply will be placed in the current control mode and the SO_2 flow rate will be placed in automatic control. The DAS will then need to adjust the sulfur dioxide flow rate so P2 reaches and then is held at the desired operating pressure. The DAS should adjust the SO_2 addition rate to ensure the maximum allowable differential pressure across the electrolyzer is not exceeded. The operator specified maximum SO_2 flow rate is intended to help facilitate control of the differential pressure across the electrolyzer.

6. The outputs from the density meter are anolyte density and temperature in digital format. In this application the density meter will have a 12 second response time because of its internal volume (16 ml) and low anolyte flow rate (80 ml/min. Fortunately, concentrations in the anolyte will not change rapidly because of small reaction rates and relatively large anolyte volume in the system. In automatic control the DAS will control the water addition rate to the anolyte to maintain a constant anolyte density. Water is added both as a reactant and as a diluent to prevent increasing acid concentration. Anolyte density of the anolyte is a function of acid concentration, wt% SO_2 absorbed and anolyte temperature. Initially in a run, the water addition rate to the anolyte may be set to manual control to avoid a large windup in the proportional integral differential (PID) control.

3.2.3 General Materials of Construction

Polytetrafluoroethylene (PTFE, DuPont trade name Teflon®), perfluoroalkoxy (PFA), and fluorinated ethylene propylene (FEP) all were used at various places in the Single Cell Electrolyzer test facility without problems. The planned 120 ^{o}C maximum operating temperature is well within their service temperature but these plastics are soft and their resistance to wear and creep is low. Because of superior creep behavior, glass filled PTFE was tried as an insulator at the discharge of the cathode in the Single Cell Electrolyzer, but leaked slightly through the material. This was possibly caused by H_2S corrosion but not confirmed. Polyphenylene sulfide (PPS, Phillips Chemical trade name Ryton®) worked well for the gears in the various anolyte pumps with no sign of problems. Polyvinylidene fluoride (PVDF) was used for gaskets and an insulator in the Single Cell Electrolyzer without problems and is specified for gaskets in the Pressurized Button Cell Elecrtrolyzer. It should be able to handle the planned 120 ^{o}C operating temperature, but not much more.

Polyetheretherketone (PEEK) tubing is available that can handle the design pressure/temperature of the Pressurized Button Cell test facility. However, some PEEK parts were used in the construction of the three cell stack that was operated briefly in the Single Cell Electrolyzer test facility. Some attack by the anolyte was noted, so PEEK is not recommended for long term use.

The SO_2 saturated sulfuric acid anolyte was found to be quite corrosive based on experience in the Single Cell Electrolyzer test facility. Stainless steel (SS) was attacked rapidly so PFA lined SS was substituted. A Hasteloy® B2/PPS gear pump failed after a fairly short time because of pitting of the Hasteloy® B-2. The pump was replaced with a custom designed and fabricated PFTE lined pump. When that pump started working poorly due to wear at the PTFE/gear interface, an Alloy 20 pump was tried. Although the Alloy 20 pump worked reasonably well for a while, the relatively massive body of the pump was appreciably pitted and the thin can on the pump magnet was completely gone after about a year. It was expected that the higher temperature planned for the Pressurized Button Cell test facility would aggravate the corrosion problem and make Alloy 20 unacceptable. Zirconium grounding tubes in the flowmeter performed very well with no evidence of corrosion throughout years of operation, so we planned to use a custom zirconium pump and fittings with PTFE or PFA lined SS tubing for handling the anolyte.

Sulfuric acid does not vaporize appreciably at the planned concentrations, so 316 SS should be able to handle the SO_2 saturated water vapor at the top of the absorber/anolyte tank. However, a pressure reduction will cause outgassing of SO_2 and possible generation of acid droplets. There is little likelihood that the drops will reach the SS tubing attached to the zirconium seal flange, and a little corrosion should not be a problem in the small diameter tubing as it has high a high pressure rating. It would be advisable to check these connections periodically until sufficient experience is obtained. The relief valve is more likely to be struck by the acid droplets. To be more conservative, we used a Hasteloy® C-276 relief valve at the top of the Absorber/Anolyte tank on the Single Cell Electrolyzer test facility.

304 SS tubing was originally used on the discharge of the electrolyzer in the Single Cell Electrolyzer test facility. Since the membrane allows some SO_2 to cross over to the cathode where part of it is reduced to H_2S, slow corrosion of the 304 SS occurred. Tubing was changed to 316 SS. This worked well until we discovered and applied the operating method that eliminated the sulfur layer formation in the MEA. A consequence of the new operating method is to nearly eliminate SO_2 gas from the catholyte. An improved membrane material that greatly reduced or eliminated the SO_2 crossover would have the same effect. Without the SO_2 to maintain oxidizing conditions and preserve the passivation layer on the SS, H_2S that forms at the cathode causes rapid corrosion of 316 SS. A float switch was originally used in the water separator of the Single Cell Electrolyzer test facility but experienced severe corrosion problems after the operating method change. That led to the change to an external laser diode/photo cell detector for level control in the water separator. A SS valve in the water drain from the water separator also failed rapidly due to corrosion of the seat. A plastic solenoid valve was purchased and worked well, but is not rated for the operating pressure planned for the Pressurized Button Cell Electrolyzer test facility. We planned to use valves and fittings with wetted parts machined from zirconium along with PTFE or PFA lined SS tubing for all the piping from the electrolyzer cathode discharge through the water drain from the water separator. The hydrogen gas discharge from the water separator in the Single Cell Electrolyzer test facility did not appear to have serious corrosion problems, and 316 SS proved to be satisfactory there.

Vinylidene fluoride/hexafluoropropylene copolymer, (FKM, DuPont trade name Viton®) was used for most of the seals in the Single Cell Electrolyzer test facility. They were affected by the SO_2 saturated sulfuric acid anolyte, but the effect appeared to be limited to enlargement by 5-10% during service and since fully contained did not leak. They could not be reused because of the size change. One of the pumps we used had perfluoroelastomer

(FFKM, DuPont trade name Kelrez®) o-rings which showed no effect from the anolyte exposure. Kelrez® is very expensive at this time though, so we planned to continue to use Viton® where fully contained. A lower cost alternative to Kelrez® is FEP encapsulated o-rings but they are fairly hard and likely to cause more creep if seating against PTFE insulators or tubing, especially at the higher temperatures planned for the Pressurized Button Cell Electrolyzer test facility.

4.0 CONCLUSIONS

The Hybrid Sulfur Process is a leading candidate for thermochemical production of hydrogen using high temperature heat from either a Generation IV nuclear reactor or a solar central receiver. A key component of the HyS process is the SO_2-depolarized electrolyzer (SDE). SRNL conducted extensive research on the SDE under the DOE-NE Nuclear Hydrogen Initiative (NHI). Unfortunately, the NHI program was terminated by DOE prior to completion of the construction of a key research facility, the Pressurized Button Cell Test Facility. This report summarizes the objectives, preliminary design, and status of the test facility. At the time of this report, SRNL was continuing discussions with potential partners for transfer of the technology for use under other programs.

5.0 ACKNOWLEDGEMENTS

This work was performed for the U.S. Department of Energy, Office of Nuclear Energy, under the Nuclear Hydrogen Initiative. Dr. William A. Summers was the program manager. Major SRNL contributors to the work included Tim Steeper, Dr. John Steimke, Dr. Hector Colon-Mercado, Dr. Mark Elvington, Dr. David Hobbs, and David Herman.

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