Key Words:
electrolysis
hydrogen
nuclear

Retention:
Permanent

Design and Performance Objectives of the Single Cell Test System for SO_2 Depolarized Electrolyzer Development

Author: J. L. Steimke

This work was conducted for the DOE
Nuclear Hydrogen Initiative
NHI Work Package N-SR07TC0301

REPORT DATE: JANUARY 15, 2007

Westinghouse Savannah River Company
Savannah River Site
Aiken, SC 29808

Prepared for the U.S. Department of Energy
Under Contract Number DEAC09-96-SR18500

SRNL™
SAVANNAH RIVER NATIONAL LABORATORY

DISCLAIMER

This report was prepared for the United States Department of Energy under Contract No. DE-AC09-96SR18500 and is an account of work performed under that contract. Neither the United States Department of Energy, nor WSRC, nor any of their employees makes any warranty, expressed or implied, or assumes any legal liability or responsibility for accuracy, completeness, or usefulness, of any information, apparatus, or product or process disclosed herein or represents that its use will not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, name, manufacturer or otherwise does not necessarily constitute or imply endorsement, recommendation, or favoring of same by Westinghouse Savannah River Company or by the United States Government or any agency thereof. The views and opinions of the authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Printed in the United States of America

Prepared For
U.S. Department of Energy

Abstract

The single cell test system development for the SRNL sulfur dioxide-depolarized electrolyzer has been completed. Operating experience and improved operating procedures were developed during test operations in FY06 and the first quarter of FY07. Eight different cell configurations, using various MEA designs, have been tested. The single cell test electrolyzer has been modified to overcome difficulties experienced during testing, including modifications to the inlet connection to eliminate minute acid leaks that caused short circuits. The test facility was modified by adding a water bath for cell heating, thus permitting operation over a wider range of flowrates and cell temperatures. Modifications were also identified to permit continuous water flushing of the cathode to remove sulfur, thus extending operating time between required shutdowns. This is also expected to permit a means of independently measuring the rate of sulfur formation, and the corresponding SO_2 flux through the membrane.

This report contains a discussion of the design issues being addressed by the single cell test program, a test matrix being conducted to address these issues, and a summary of the performance objectives for the single cell test system. The current primary objective of single cell test system is to characterize and qualify electrolyzer configurations for the following 100-hour longevity tests. Although the single cell test system development is considered complete, SRNL will continue to utilize the test facility and the single cell electrolyzer to measure the operability and performance of various cell design configurations, including new MEA's produced by the component development tasks.

Background

The Hybrid Sulfur Process is being developed as a technology to generate hydrogen for the proposed Hydrogen Economy. A key part of the technology is the development of sulfur dioxide depolarized electrolyzers to generate hydrogen gas. The anode of the electrolyzer is bathed in a sulfuric acid solution saturated in sulfur dioxide. Sulfur dioxide is oxidized to sulfuric acid at the anode. Hydrogen ions cross a membrane to the cathode where they are reduced to hydrogen gas. Sulfur dioxide depolarized electrolyzers require a much lower voltage than conventional electrolyzers and so the cost of electrical power is correspondingly lower. A separate high temperature step using heat from a nuclear reactor decomposes sulfuric acid to sulfur dioxide, water and oxygen. Oxygen is a product and sulfur dioxide and water are recycled.

Previous Work at SRNL

Research on sulfur dioxide depolarized electrolyzers began at Savannah River National Laboratory (SRNL) in FY2005. During 2005 two electrolyzer cells were tested [Steimke and Steeper, 2005] in the facility shown in Figure 1. The first was a commercial cell designed for conventional water electrolysis. The second cell was built at the University of South Carolina (USC) and was originally designed to have sulfur dioxide introduced to the anode as a gas. The commercial cell initially functioned well and demonstrated sulfur dioxide depolarized operation as evidenced by relatively low voltages and generation of sulfuric acid rather than oxygen at the anode. However, it failed as the result of corrosion. The carbon based USC cell resisted corrosion but its operation was limited by mass transfer. Elemental sulfur was found at the cathodes of both cells, indicating that sulfur dioxide had crossed the Nafion membranes and reacted with product hydrogen. Sulfur was readily flushed from both cathodes with no evidence of catalyst poisoning.

Figure 1 Test Facility in 2005

For FY 2006 [Steimke and Steeper, 2006] the test loop was improved and the electrolyzer cell shown in Figure 2 was designed and built. The new carbon based cell was corrosion resistant and had good mass transfer characteristics.

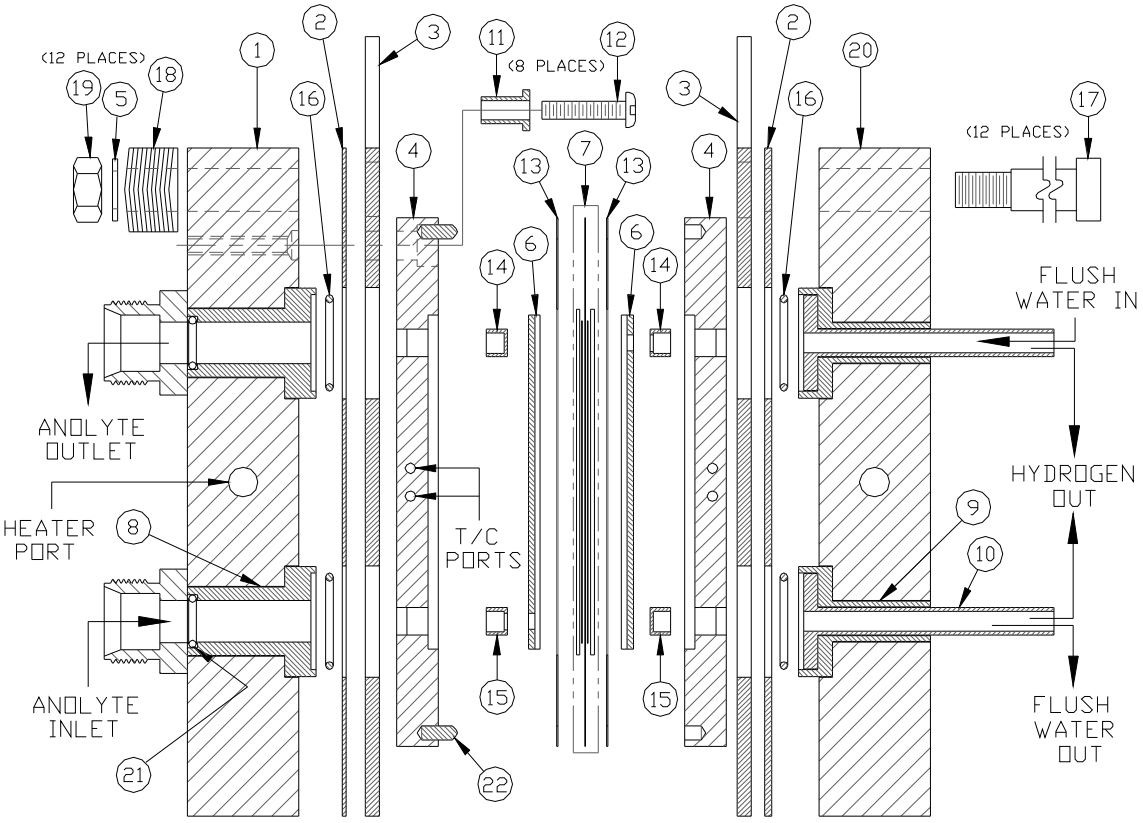

Figure 2 Electrolyzer Cell Used in 2006

Six different membrane electrode assemblies (MEA) were tested in the 2006 cell. The primary results of testing in 2006 are as follows.

1. The cell had excellent corrosion resistance.
2. The cell had better mass transfer and pressure drop characteristics than the previously tested USC cell, but still required at least 200 mL/min of anolyte flow to avoid mass transfer limitation. Flowrates this large correspond to a low conversion of sulfur dioxide to sulfuric acid on each pass through the cell, less than 2%. Higher conversions are necessary for cost effective commecial operation.
3. Increasing the concentration of sulfuric acid in the anolyte higher than 30 wt% increased cell voltage for four reasons.
    a. Dehydrated the membrane which reduced its ionic conductivity.
    b. Increased anolyte viscosity which increased resistance to mass transfer
    c. Decreased electrical conductivity of the anolyte.
    d. Decreased concentrations of the two reactants, water and sulfur dioxide.
4. Increasing temperature decreased cell voltage for four reasons.

a. Increased reaction rate
b. Increased anolyte electrical conductivity
c. Decreased anolyte viscosity.
d. Increased ionic conductivity of membrane
e. Note: Increasing temperature also decreased equilibrium concentration of sulfur dioxide but this negative effect was smaller than the positive effects on reaction rate, conductivity and viscosity.

5. Increasing pressure of sulfur dioxide in the anolyte absorber decreased cell voltage because this increased the concentration of sulfur dioxide, a reactant.
6. Once again sulfur was found at the cathode, but there was no evidence of catalyst poisoning.

Figure 3 shows data collected in 2006 with a membrane electrode assembly using a Nafion 117 membrane at temperatures up to 70ºC and pressures up to four atmospheres. The target performance of 600 mv cell potential at a current density of 500 mA/cm^2 is also shown. The figure shows that increasing temperature or pressure both decrease cell potential. We have not met the target yet, but decreasing membrane thickness or increasing ionic conductivity of the membrane should allow a significant decrease in cell voltage. Also, increasing the temperature should decrease cell voltage. The present safety analysis accounting for strength of materials in and near the cell limits us to operation at 80ºC. We may be able obtain permission to go to higher temperatures.

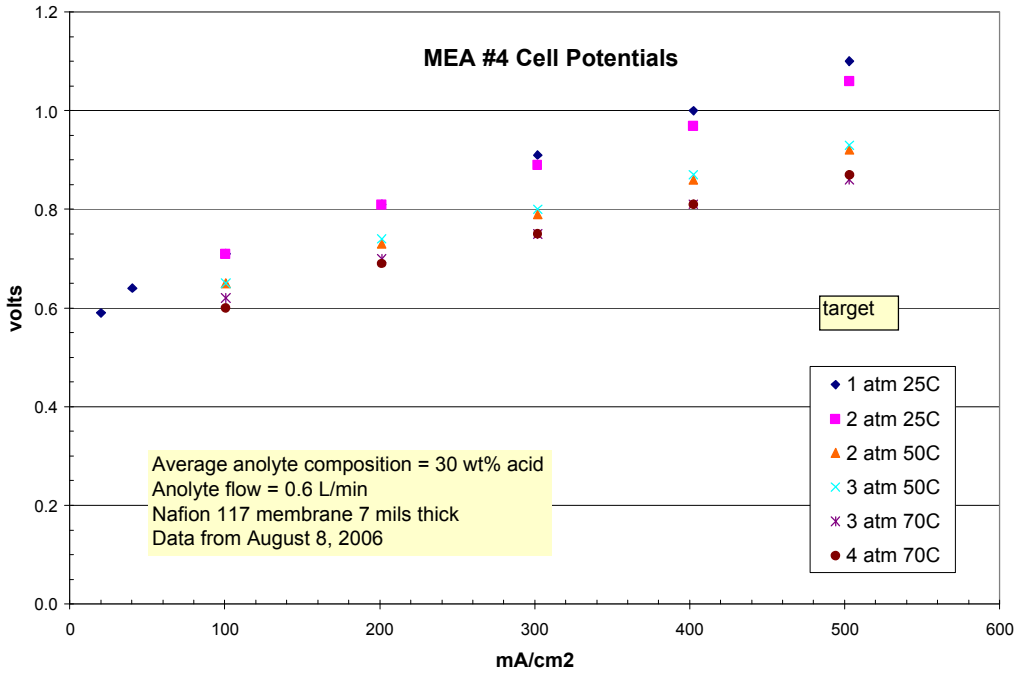

Figure 3 Electrolyzer Cell Potentials in 2006

Design Goals for FY 2007

The purpose of the Single Cell Testing is to evaluate various design aspects of the SO_2 depolarized electrolyzer and to measure the effects of the key operating parameters, including temperature, pressure, acid concentration, etc. The major design goals being addressed for FY07 include the following.

1. Improve flow field

Develop an electrolyzer cell flow field that gives good mass transfer at relatively low cell anolyte flows, such as would be used for high conversions of sulfur dioxide. The purpose of the flow field is to distribute the anolyte, containing the reactants water and sulfur dioxide, uniformly over the anode, allow intimate contact of the reactants with the catalyst and allow removal of sulfuric acid product. The 2006 flow field design was intended for high anolyte flows and low SO_2 conversions. Most of the anolyte flow passes through the porous carbon layer without coming into close contact with the catalyst layer. Numerical modeling of the entire Hybrid Sulfur loop indicated that cell conversions in the range from 10% to 50% are desirable. By contrast, for testing in FY 2006, the most frequently used flow was 600 mL/sec. For a temperature of 70ºC, a pressure of three atm and a current of 25 amperes, that flowrate corresponds to an SO_2 conversion of 1.1%. The reason for the high flowrates used in FY 2006 was the observation that cell voltage increased as the result of impaired mass transfer when the anolyte flowrate was decreased below 200 mL/min. Of course, that conclusion is specific to the 2006 flow field.

In 2007, numerical modeling will be used to design a new flow field that has less bypassing of anolyte, good mass transfer and acceptable pressure drop at lower flows and relatively high conversions. The target range of flowrates for the 50 cm^2 cell is 13 mL/min to 65 mL/min and the target pressure drop for the cell is less than 5 psid. The design should consider the ease or difficulty of manufacturing both larger numbers of units and dimensionally larger units. A commercial plant would require thousands of cells each with an area of approximately one square meter.

2. Make measurements to allow minimization of the total voltage drop across the electrolyzer cell.

The electrical power cost of a commercial plant is directly proportional to the cell voltage. An important part of this minimization is to measure, or at least estimate, the components of total voltage. One component is the voltage loss due to mass transfer resistance. This may be measured by comparing the cell voltages at high anolyte flowrate and at the flowrate of interest. Another component of interest is the voltage drop through the membrane which can be estimated by measuring cell voltages for different thicknesses of the same type of membrane.

3. Develop and test method to purge sulfur from cathode

In previous testing it has been observed that sulfur forms at the cathode. Therefore, test a method for removing the sulfur that does not interfere with electrolyzer operation.

4. Develop and test method for capturing and weighing the cathode sulfur.

All sulfur that forms at the cathode over an interval of time in the range of fifteen minutes to one hour should be collected, dried and weighed. At 25 amps and 1% loss of hydrogen the rate of sulfur formation is 0.3 g/hr. In the past we inferred the flux of sulfur dioxide by calculating the discrepancy between theoretical hydrogen production rate and actual measured production rate and assumed that the discrepancy was solely due to reaction of hydrogen with sulfur dioxide. However small hydrogen leaks can confuse the measurement, especially because the leak is different each time that the cell is rebuilt. Even without a leak, the measurement accuracy is comparable to 0.5 ampere of hydrogen.

5. Test membranes and/or methods to reduce the flux of sulfur dioxide crossing the membrane from the anode side to the cathode side.

There are two problems with sulfur dioxide crossover. First, the sulfur dioxide reacts with product hydrogen, so that net hydrogen is reduced. Second, elemental sulfur collects at the cell cathode and must be flushed periodically from the cell. In a commercial plant, this sulfur would be oxidized back to sulfur dioxide for reuse. In Task 1.1 and Task 1.4 of the SRNL HyS Research Program, we are screening promising membrane materials to reduce sulfur dioxide crossover, the most promising of which will be tested in the Single Cell Test System.

Test Matrix

In order to address these design goals the following Single Cell Test Matrix will be followed.

1. Test different membrane materials, one of which will be Nafion.
2. Test different thicknesses of the same material, for example, Nafion is available in thicknesses of 2 mils, 5 mils and 7 mils.
3. Test at different cell temperatures, typically ambient temperature, 50ºC and 80ºC.
4. Test at different cell pressures from 1 atm up to as much as six atm.
5. Test sulfuric acid concentrations ranging from 25 wt% to 70 wt%.
6. Test over a range of anolyte flowrates, the magnitude of which will depend of the design of the flowfield.
7. Test at a range of cell currents ranging from 1 ampere up to 50 amperes. For a cell with an area of 50 cm^2, this corresponds to 20 mA/cm^2 to 1000 mA/cm^2. However, do not run any currents that would cause the cell voltage to exceed 1.2 volts as damaging oxidation of the graphite can occur at higher voltages.
8. Most testing will be conducted with the power supply in current control mode. A small amount of testing will be conducted in voltage control mode.
9. Test different water flowrates to the cathode to flush out sulfur.
10. Test method of capturing and weighing sulfur. At 25 amps and 1% loss of hydrogen the rate of sulfur formation is 0.3 g/hr.
11. Test a flowfield designed for efficient performance for low anolyte flowrates.

Longevity Test

Following the Single Cell Testing, the most promising cell configuration will be adopted for use in the 100 Hour Longevity Test. Modifications to the test facility will be prepared to permit continuous, 24 hour per day, testing.

Performance Objectives

The performance objectives for the Single Cell Tests include the following.

1. Operation in the SO_2 Depolarized Electrolysis Mode using an anolyte consisting of liquid sulfuric acid solution saturated with sulfur dioxide.
2. Demonstration of the use of a Proton Exchange Membrane (PEM) and an MEA cell configuration.
3. Cell performance yielding polarization curves demonstrating low voltage (less than 900 mV) for a current density of 500 mA/cm^2.
4. Operation over the temperature range 25ºC to 80ºC and absolute pressures from 1 to 6 atmospheres.
5. Steady operation with continuous sulfur removal for the cathode.
6. Measurement of sulfur dioxide flux for various MEA configurations.

References

J. L. Steimke and T. J. Steeper, "Characterization Testing of H_2O-SO_2 Electrolyzer at Ambient Pressure", WSRC-TR-2005-00310, rev. 0, August 1, 2005

J. L. Steimke and T. J. Steeper, "Characterization Testing and Analysis of Single Cell SO_2 Depolarized Electrolyzer", WSRC-STI-2006-00120, rev. 1, September 15, 2006.