A Final Report for 03/13/06-03/12/09

1. DOE award number

Award number: DE-FC07-06ID14752

2. The project title and name of the project director/principal investigator

Project title: HIGH PERFORMANCE ELECTROLYZERS FOR HYBRID
THERMOCHEMICAL CYCLES

Name of the project director: Dr. John W. Weidner, Principal Investigator

3. Date of report and period covered by the report

Date of report: May 10, 2009

Period covered by the report: March 13, 2006 to March 12, 2009

4. Comparison of the actual accomplishments with the goals and objectives established for the period and reasons why the established goals were not met

Overall goals for the period of March 13, 2006 to March 12, 2009: Optimize the hybrid sulfur electrolyzer, develop novel catalysts for SO₂ oxidation, and test alternative membranes.

Actual accomplishments with the goals established: Optimized the hybrid sulfur electrolyzer by developing a mathematical model to predict and understand water transport, which affects cell voltage, membrane resistance via sulfuric acid concentration, and SO₂ crossover. The model was validated with experimental data. Catalysts were synthesized and characterized in the electrolyzer, and membranes developed by Sandia National Laboratory (SNL) were tested.

5. A discussion of what was accomplished under these goals during the reporting period, including major activities, significant results, major findings or conclusions, key outcomes or other achievements.

Major activities:

Extensive electrolyzer testing was performed at the University of South Carolina (USC). Emphasis was given to understanding water transport under various operating (i.e., temperature, membrane pressure differential and current density) and design (i.e., membrane thickness) conditions when it became apparent that water transport plays a deciding role in cell voltage. A mathematical model was developed to further understand the mechanisms of water and SO₂ transport, and to predict the effect of operating and design parameters on electrolyzer performance.

Major findings:

The major findings are outlined below. Full results and detailed discussions are provided in Appendix A at the end of this report.

- Water management in the cell is critical in electrolyzer operation. Water is needed:
 - As a reactant at the anode.
 - To keep the membrane hydrated and provide adequate proton conductivity.
 - To control sulfuric acid concentration.
 - To control the adverse effects of SO₂ crossover.
 - Water transport across the membrane is significantly influenced by membrane type, membrane thickness, temperature, pressure differential across the membrane, and current.
 - A mathematical model for water management was developed to account for the effects of water transport stated above. The model was used to accurately predict cell performance over a wide range of design (e.g., membrane type, membrane thickness) and operating conditions (e.g., temperature, pressure differential across the membrane, current).
 - Sulfuric acid concentration affects cell voltage via the reaction equilibrium and membrane conductivity via membrane water content. Detailed equilibrium calculations were performed at Savannah River National Laboratory using OLI equilibrium software. Membrane conductivity measurements were performed at USC.
 - Low membrane conductivity at low water content (i.e., high sulfuric acid concentration) is the present limitation of the Nafion membrane. A membrane is needed that has significant conductivity at high acid concentrations.
 - SO₂ crossover can limit cell performance if not properly managed. A model was developed, and verified experimentally, to understand and control the detrimental effects of SO₂ crossover.
 - Alternative membranes (SDAPP) were developed at SNL and tested at USC to limit SO₂ crossover. These membranes are capable of operation at higher temperature than Nafion membranes, but their conductivity still depends on water content.
 - Catalyst loading is not a factor in electrolyzer performance based on how the membrane-electrode assembly (MEA) is currently fabricated,. However, the large anode overpotential indicates that a well-designed MEA would significantly improve electrolyzer performance.
6. Cost status: Money spent.
 7. Schedule status: Tasks completed.
 8. Any change in approach or aims and reasons for change: No changes made.

9. Actual or anticipated problems or delays and actions taken or planned to resolve them
No problems and delays.
10. Any absence or changes of key personnel or changes in consortium/teaming arrangement: No changes.
11. A description of any product produced or technology transfer activities accomplished during this reporting period:

Publications:

1. John A. Staser and John W. Weidner, "Quantifying Individual Voltage Contributions of the Hybrid Sulfur Electrolyzer," *J. Electrochem. Soc.*, submitted.
2. John A. Staser and John W. Weidner, "Sulfur Dioxide Crossover During the Production of Hydrogen and Sulfuric Acid in a PEM Electrolyzer," *J. Electrochem. Soc.*, in press, May 2009.
3. John A. Staser, Kirsten Norman, Cy H. Fujimoto, Michael A. Hickner and John W. Weidner, "Transport Properties and Performance of Polymer Electrolyte Membranes for the Hybrid Sulfur Electrolyzer," *J. Electrochem. Soc.*, in press, May 2009.
4. Maximilian B. Gorenssek, John A. Staser, Thomas G. Stanford and John W. Weidner, "A Thermodynamic Analysis of the SO₂/H₂SO₄ System in SO₂ – depolarized Electrolysis," *Int. J. Hydrogen Energy*, submitted.
5. John A. Staser and John W. Weidner, "Effect of Water Transport on the Production of Sulfuric Acid in a PEM Electrolyzer," *J. Electrochem. Soc.*, **156**, B16 (2009).
6. John Staser, Ramaraja P. Ramasamy, Premkumar Sivasubramanian and John W. Weidner, "Electrochemical Oxidation of SO₂ in a PEM Electrolyzer for H₂ Production," *Electrochem. and Sol. St. Let.*, **10**, E17 (2007).

Presentations:

1. John A. Staser and John W. Weidner, "Effect of SO₂ Crossover on Hydrogen and Sulfuric Acid Production in a PEM Electrolyzer," Presented at the 215th Meeting of the Electrochemical Society, May 2009.
2. John W. Weidner, "Electrochemical Production of Hydrogen," Tulane University, New Orleans, LA, *Invited*, April, 2009.
3. Maximilian B. Gorenssek, John A. Staser and J.W. Weidner, "Hybrid Sulfur Cycle Flowsheets for PEM Electrolyzers with SO₂ Vapor Feed," The American Institute of Chemical Engineering, Philadelphia, PA, November, 2008.
4. John A. Staser and John W. Weidner, "Effect of Water Management on the Operation of a Hybrid-Sulfur PEM Electrolyzer for Hydrogen Production," Presented at the 214th Meeting of the Electrochemical Society, October 2008.
5. John W. Weidner, "Hydrogen Production Technologies Using Nuclear Energy," f-cell, Stuttgart, Germany, *Invited*, September, 2008.

6. John A. Staser and John W. Weidner, "Modeling Water Transport for the Production of Hydrogen via the Hybrid-Sulfur Process The 3rd Annual Korea-USA Joint Symposium on Hydrogen & Fuel Cell Technology, Seoul, South Korea, *Invited*, May, 2006.
7. John W. Weidner, "Electrochemical Generation of Hydrogen via Thermochemical Cycles," Florida Solar Energy Center, *Invited*, May 2008.
8. John W. Weidner, "Electrochemical Generation of Hydrogen via Thermochemical Cycles," University of Delaware, Newark, DE, *Invited*, October 2007.
9. John W. Weidner, "Electrochemical Generation of Hydrogen via Thermochemical Cycles," Paul Scherrer Institute, Villigen, Switzerland, *Invited*, September 2007.
10. John A. Staser and John W. Weidner, "Electrocatalysts for the Production of Hydrogen via the Hybrid-Sulfur Process," Presented at the 211th Meeting of the Electrochemical Society, May 2007.
11. John A. Staser and John W. Weidner, "Electrochemical Generation of Hydrogen via Thermochemical Cycles," Presented at the AIChE Annual Meeting, November 2006.
12. John A. Staser and John W. Weidner, "H₂ Production in a PEM Electrolyzer from SO₂ Oxidation," Presented at the 58th Southeast Regional Meeting of the American Chemical Society, November 2006.
13. John W. Weidner, Prem Sivasubramanian, John A. Staser, and Charles E. Holland, "Electrochemical Generation of Hydrogen via Thermochemical Cycles," Fuel Cells Science & Technology 2006, Turin, Italy, September, 2006.
14. John W. Weidner, Prem Sivasubramanian, and John A. Staser, "Electrochemical Generation of Hydrogen via Thermochemical Cycles," The 1st Annual Korea-USA Joint Symposium on Hydrogen & Fuel Cell Technology, Daejeon, South Korea, *Invited*, May, 2006.
15. Maximilian B. Gorenssek, William A. Summers and J.W. Weidner, "Hybrid Sulfur Cycle Flowsheets for Hydrogen Production from Nuclear Energy," The American Institute of Chemical Engineers Spring Meeting, Orlando, FL, April, 2006.

Appendix A.

A I. Abstract

It is proposed to study and optimize the operation of a hybrid-sulfur type electrolyzer for the efficient production of clean hydrogen. The goal of this work is to understand the parameters that affect electrolyzer efficiency, leading to better designs and a higher current efficiency for hydrogen production. Performance has been evaluated from polarization data. The rate of hydrogen production has been estimated to obtain current efficiency and the concentration of sulfuric acid byproduct and production rate have been measured to determine the rate at which sulfuric acid may be sent back to the thermal decomposition unit. The effect of temperature has been measured by varying the temperature from $\sim 60^{\circ}\text{C}$ to $\sim 90^{\circ}\text{C}$ for the proton exchange membrane (PEM) electrolyte.

Realizing that water management is an important aspect of electrolyzer performance because it affects sulfuric acid concentration and thus cell voltage, a mathematical model has been developed to determine the effects of operating and design parameters on water transport. The model has been extended to determine the effects of water transport on SO_2 crossover to the cathode.

Further addressing the problem of SO_2 crossover to the cathode, alternative PEM electrolytes have been developed at Sandia National Laboratories. These membranes have been optimized to resist sulfur dioxide crossover, and have been tested in our electrolyzer system.

A II. Introduction to Hybrid Sulfur Process

To use hydrogen as a renewable energy carrier on a large scale, a method must be developed which provides efficient production of clean hydrogen. The scale of the production required is large when considering the likely demand for hydrogen. For example, with vehicles in the United States consuming more than 350 million gallons of gasoline per day, and allowing for 1% of vehicles to be powered by hydrogen fuel cells, the increased hydrogen production capacity would be 80 000 kg/day.¹ The methods existing today for large-scale production of hydrogen typically involve hydrocarbon reforming of natural gas or coal gasification. Not only is hydrocarbon reforming nonrenewable, but the hydrogen produced is often contaminated with trace impurities such as carbon monoxide and sulfur compounds.²⁻¹⁰

Much attention has been given in the past to the so-called UT-3 hydrogen production cycle, which was based on two sets of reactions.¹¹⁻¹⁶ The first two reactions (first set) involve the formation of hydrobromic acid while producing oxygen, and the second two reactions (second set) involve the reduction of water with a bromide compound, producing hydrogen.

In an attempt to better understand the intricacies of this process, several authors have recently reported on a thermodynamic study of each governing reaction.¹¹ They performed simple experiments to check the conclusions reached by the thermodynamic analysis, focusing on the hydrolysis of CaBr_2 and FeBr_2 , which they had previously concluded to be the limiting steps in the overall process.

They found that in the first experiment (hydrolysis of CaBr_2), sintering was a problem and the reaction progress reached only 11%. In the second experiment (hydrolysis of FeBr_2), the reaction progressed to 87%.

They concluded that the process reactions lead to significant sintering of the catalyst bed, which reduces the reactivity and leads to passivation. The passivated film limits diffusion of the reactants and products through the catalyst bed. In addition, the low reaction progress hinders process efficiency. The authors estimated an overall process efficiency from 15-22%, assuming electricity generated at 35% efficiency.¹¹

Another disadvantage of the UT-3 process is that the hydrogen produced is in a stream of HBr , and separation may be difficult and cost-intensive. Electrolysis of water has the advantage in that the hydrogen produced is highly pure and there are zero emissions from the process. However, low temperature electrolysis is relatively inefficient due to the thermal to electrical energy efficiency of current power plants (< 30%) and the efficiency of the alkaline electrolyzer (40%).^{17,18} Hence, the overall thermal efficiency of low temperature electrolysis can be less than 10%.¹⁷ In addition, the traditional alkaline electrolyzers use KOH as the electrolyte, which is a corrosive material and not conducive to long-term operation.¹⁹ Low temperature electrolysis has advantages for small, distributed hydrogen generation, but the low efficiency eliminates it as a practical choice for large-scale hydrogen production.

High-temperature electrolysis, especially when coupled with advanced nuclear reactors expected to meet thermal to electric efficiencies of 70%⁷, are expected to approach overall efficiencies of 50%.²⁰ Two issues remain, however, that make the future of this technology uncertain. The achievable current densities are low (i.e., 0.2 A/cm^2 at 1.25 V and 830°C)²¹ and much progress must be made in the development of materials suitable for long-term operation at high temperatures in corrosive environments.

Work is being conducted on alternative methods to achieve water electrolysis, including the development of zero-gap cells and the addition of an activator to reduce energy consumption.²² Focus has also been afforded in recent years on utilizing solar electricity for water electrolysis, but some limitations of solar receivers remain, and the electrolysis step of the process still has a low efficiency, hindering the feasibility of the overall process for large-scale production.²³⁻³⁰

Proton exchange membrane (PEM) electrolyzers have seen interest recently because they can be operated at low temperature ($\sim 80^\circ\text{C}$) and do not use corrosive media. Several disadvantages with this method for water electrolysis do exist, however. In this process, oxygen is produced at the anode. This reaction has a small exchange current density, even on Pt, leading to high cell overpotentials. In addition, the electrolyzer efficiency decreases as the current density increases, a trait not desirable since high operating current densities lead to the highest hydrogen production rate.³¹

Overall, water electrolysis has distinct disadvantages in efficiency and required materials. A recent Department of Energy (DOE) Energy Information Administration reported that electrolyzers can potentially reach efficiencies of 60-63%, but the inefficiencies in electricity generation for this process to supply the energy for the electrolysis step drastically reduce the overall process efficiency.³²

Thermochemical cycles have recently received attention as an alternative to high temperature electrolysis for large-scale, efficient production of hydrogen because the

electrolysis step is carried out at low temperature (<100°C) and the operating voltage is often significantly lower, which would reduce the energy requirement for the electrolysis step. This eliminates the materials concern present in high-temperature electrolysis and may potentially lead to higher efficiency.

One such thermochemical cycle involves the electrolysis of anhydrous HCl coupled with a reverse Deacon reaction at 450-500°C to recover HCl for the electrolysis step.²⁴ The authors chose this cycle because the energy sum of all reactions must equal the energy required for the decomposition of water. They chose a more energy-intensive electrolysis step in order to lower the temperature required for the HCl recovery step (the reverse Deacon reaction). In this way, they hope to avoid the high-temperature gas-cooled nuclear reactor required for other thermochemical processes.³³⁻³⁵

The authors chose to electrolyze anhydrous HCl instead of hydrous HCl due to decreased diffusion limitations in the gas-phase feed.³⁵ The lower diffusion limitations lead to higher electrolyzer efficiency. They estimated that the overall process utilized energy from a nuclear reactor more efficiently than water electrolysis by about 15%. Even so, given 40% efficiency for electricity generation at 500-550°C, the process efficiency is lower than that which can be achieved by utilizing high-temperature nuclear reactors.

The leading candidate for the thermochemical water splitting cycle, because of its use of high-temperature nuclear reactors which will achieve significantly higher efficiency for electricity generation, is the sulfur-based process.³⁶⁻⁴⁰ This process requires energy at high temperature (nuclear or solar energy >850°C) for the recovery step, which makes it a good candidate to be coupled with next-generation nuclear reactors and solar power towers.⁴¹⁻⁴⁵

In the sulfur-based thermochemical cycles, the high-temperature step involves the decomposition of H₂SO₄ to produce oxygen and sulfur dioxide via the following reaction:

The sulfur dioxide that is generated from Reaction 1 is converted back to H₂SO₄ in the electrolyzer, with the production of hydrogen balancing the reaction. In the sulfur-iodine (S-I) process, this is accomplished by reacting SO₂ with iodine to produce H₂SO₄ and HI. The difficulty arises when separating HI from the water and iodine before decomposition to hydrogen. In addition to the energy-intensive separation step, serious materials problems are encountered owing to the corrosive nature of HI.^{36,37}

In an alternative process, Westinghouse Corporation developed the hybrid-sulfur process, eliminating the iodine step in a liquid-phase process in which SO₂ dissolved in sulfuric acid is oxidized at the anode:^{39,46,47}

The protons produced at the anode migrate through the porous separator and reduce to hydrogen at the cathode. The reaction at the cathode is the hydrogen evolution reaction (HER):

Overall, the hybrid-sulfur electrolyzer consumes sulfur dioxide and water and produces sulfuric acid at the anode and hydrogen at the cathode. The overall electrolyzer reaction is given:

Combining Reactions 1 and 4, the overall thermochemical process is water and energy (heat and electricity) converted to hydrogen and oxygen.

In addition, a potential parasitic reaction may occur at the cathode due to the crossover of SO_2 through the membrane that results in the reduction of SO_2 to sulfur at the cathode.

Reaction 5 consumes current that would otherwise be used for the production of hydrogen, produces oxygen in the hydrogen stream and produces sulfur deposits that may increase cell resistance over time.

In our process, pure gaseous SO_2 (as opposed to SO_2 dissolved in sulfuric acid) is fed to the electrolyzer anode, while liquid water is fed to the cathode. The water required for Reaction 2 diffuses through a proton exchange membrane (PEM) to the anode (see Figure 1). The rate of water flux to the anode is slowed by electro-osmotic drag toward the cathode. The flux of water can be further influenced by hydraulic permeation due to a pressure differential across the membrane. Hence, the net water flux is equal to the combined effects of diffusion, permeation and electro-osmotic drag.

The objective of this work is to determine the effects of operating (current density, operating temperature and membrane pressure differential) and design (membrane thickness) parameters on water transport and its influence on electrolyzer performance.

A III. Hybrid Sulfur Experimental Setup

The Nafion® membranes were prepared by spraying the desired loadings of Pt catalyst onto each side of an ELAT® carbon cloth diffusion backing and hot-pressing the catalyst-coated backing to the Nafion® membrane.^{46,48} The catalyst was 40 wt% Pt on carbon purchased from E-TEK. The N115 and N212 MEAs with Pt-black were purchased from Lynntech and no modification was required. The electrolyzer experiments were conducted in a 10 cm² cell purchased from Fuel Cell Technologies, Inc. The cell was maintained at the required temperature by inserting heating rods into the aluminum endplates and inserting a thermocouple near the carbon flowfield blocks. The water was heated to a temperature 8°C higher than the desired cell temperature to allow for some cooling before reaching the cell inlet. The electrolyzer reactants and products were passed through Kynar plates situated between the aluminum endplates and the carbon blocks because concentrated sulfuric acid will corrode the aluminum endplates.

The cell was operated at 80°C unless otherwise noted, and the conversion of SO_2 was 20%. The conversion was increased to 80% without significant loss of performance. The pressure differential across the membrane was maintained by the use of a globe valve

behind the cathode. The pressure gradient was maintained with the cathode at high pressure relative to the anode.

A IV. Hybrid Sulfur Results

A. Electrolyzer Experiments on Nafion® Membranes

Previous work on the hybrid sulfur electrolyzer was conducted with a 40cm² cell hardware.⁴⁶ The hardware was difficult to assemble and handle and the large electrode area led to excessive use of materials like Nafion and expensive catalyst inks. Instead of having carbon flow channels in direct contact with the MEA, carbon plates were hollowed out and a high-flow carbon cloth was used as the flow field. After each experiment, the cathode carbon flow fields were disposed because it was thought that sulfur deposition at the cathode (via Reaction 5) damaged the carbon during the experiments.⁴⁶

The first electrolyzer experiment with standard 10 cm² fuel cell hardware was conducted to determine if sulfur reduction damaged the carbon blocks, and to see if performance comparable to that of the 40 cm² cell could be achieved. The results of this first experiment compared to the best 40 cm² data are shown in Figure 1:

Figure 1. 40 cm² vs. 10 cm² electrolyzer data. The membrane ΔP was 600 kPa and the catalyst loading was the same (1.0 mg/cm² Pt).

The MEA used in both experiments was a Nafion 115 membrane with gas diffusion electrodes hot-pressed at 150°C and 500 psi for 5 minutes to form the assembly. The gas diffusion electrodes in each case were ELAT 1400 carbon cloth with ink consisting of 40 wt% Pt on carbon sprayed to a loading of 1 mg/cm².⁴⁶

The results in Figure 1 indicate that neither the size of the electrode nor the type of fuel cell hardware used significantly affects the cell performance. Several consecutive experiments were run with the 10 cm² without performance degradation or corrosion of the carbon block. Hereafter all electrolyzer data reported will be for the 10 cm² cell.

Commercial MEAs from Lynntech were purchased and tested as electrolyzers in an attempt to reduce the time required to prepare MEAs. The Lynntech MEAs have a catalyst loading of 1.5 mg/cm² Pt using a Pt-black catalyst. Two membrane thicknesses were purchased, N212 (2 mil dispersion cast) and N115 (5 mil extrusion cast) to determine the effect of membrane thickness on electrolyzer performance. Also, because the Lynntech MEAs have a higher catalyst loading than our in-house MEAs (0.5 and 1.0 mg/cm² Pt using a Pt-carbon catalyst) the effect of catalyst loading on electrolyzer performance was determined.

Figure 2 below shows electrolyzer data for MEAs of three catalyst loadings (0.5, 1.0 and 1.5 mg/cm² Pt) compared to data provided by Westinghouse. The Westinghouse cell used a porous membrane separator and a liquid anode feed:^{39,40}

Figure 2. Nafion® 115 data at different catalyst loadings vs. Westinghouse data. The Westinghouse cell used a porous diaphragm separator, and used SO₂ dissolved in sulfuric acid as the anode reactant, which introduced an extra mass transport limitation. The ΔP of the gas-fed cell (with Nafion 115) was 600 kPa. The catalyst loading does not affect electrolyzer performance.

The results of Figure 2 indicate that the gas-phase electrolyzer used at South Carolina allows for a significant performance improvement over the liquid-based Westinghouse cycle. For example, for the highest current density reported by Westinghouse (0.4 A/cm²), the liquid-phase electrolyzer cell voltage is 1.05 V vs. 0.760

V for the gas-phase South Carolina electrolyzer, an improvement of 0.250 V. In addition, the liquid-phase electrolyzer had a significantly higher catalyst loading of 7 mg/cm², which was as much as 14 times higher than the catalyst loading used for the gas-phase electrolyzer.

The improvement in performance over the Westinghouse design is the result of several factors. First, the resistance of Westinghouse's porous diaphragm separator is higher than that of Nafion. Second, the liquid anode feed introduces a mass transport barrier in the solubility limit of SO₂ in sulfuric acid, with the solubility of SO₂ decreasing as the concentration of sulfuric acid increases. Third, the concentration of sulfuric acid affects the cell performance, with more concentrated sulfuric acid leading to an increase in the cell voltage by the Nernst equation.^{49,50} The sulfuric acid concentration was controlled in the Westinghouse cell and was the same at every current density. In the gas-phase cell the sulfuric acid concentration is determined by the water management properties and the current density.⁴⁹

In addition, the data in Figure 2 also indicate that catalyst loading does not affect electrolyzer performance for the gas phase cell.

The effect of membrane thickness on electrolyzer performance was determined by testing the N117 (7 mil extrusion cast), N115 (5 mil extrusion cast) and N212 (2 mil dispersion cast) films.

Figure 3. Effect of membrane thickness. $\Delta P = 600$ kPa. The thinner membrane exhibits the best performance due to lower resistance and increased water transport to the anode, which reduces the concentration of sulfuric acid and results in lower cell voltage.

The results presented in Figure 3 indicate that membrane thickness does have an effect on electrolyzer performance. The operating cell voltage is lower for the thinner (2 mil) membrane than the thicker (5 mil and 7 mil) membranes at all current densities. In addition, the thinner membrane (N212) is able to achieve higher current densities than the thicker N115 membrane (1.3 A/cm^2 vs. 0.7 A/cm^2) and the N117 membrane (1.3 A/cm^2 vs. 0.4 A/cm^2) and also exceeds the Westinghouse projection at current densities greater than 0.4 A/cm^2 . This is due to a higher rate of water diffusion through the thinner membrane. Because water is only fed to the cathode but must participate in the reaction at the anode, all water used for the anode reaction must diffuse through the membrane from the cathode. A higher rate of water diffusion leads to lower sulfuric acid concentration and a lower cell voltage.

So far the effects of catalyst loading and membrane thickness have been investigated. Next the effect of operating temperature will be discussed. Figure 6 shows the effect of operating temperature on the Lynntech N212 MEA.⁴⁸

Figure 4. Effect of temperature on Nafion 212. $\Delta P = 600 \text{ kPa}$. Increasing the cell temperature affects electrolyzer performance in two ways. The membrane resistance decreases as the temperature increases, and the water flux to the anode increases with temperature. The lower membrane resistance leads to lower cell voltage, as does the lower sulfuric acid concentration.

The results in Figure 4 show that increasing the operating temperature leads to lower cell voltage. The performance increases due to lower Ohmic resistance with increased temperature, as well as a higher rate of water flux to the anode, which lowers the sulfuric acid concentration and decreases the cell voltage.

From the electrolyzer experimental results presented thus far, it is clear that water management strongly influences the electrolyzer performance. A coupled mathematical and experimental model has been developed to predict water management as a function of membrane thickness, cell temperature, operating current density and membrane pressure differential.

B. Water Transport and H₂SO₄ Production

B1. Water Transport Model

The electrolyzer operates as shown in Figure 5. Gaseous SO₂ fed to the electrolyzer reacts with water at the anode via Reaction 2, forming H₂SO₄ (i.e. sulfuric acid) and producing protons that migrate to the cathode. The rate of H₂SO₄ production is constant at each current density and determined by Faraday's law. Since the current density is the same at every point on the electrode, the production rate of H₂SO₄, the water flux, and hence the concentration of sulfuric acid is uniform throughout the electrolyzer. Therefore, the model is one-dimensional in the x-direction (through the membrane).

Figure 5. Schematic of the model system under consideration. Dry SO₂ gas and liquid water are fed to the anode and cathode, respectively. Water diffuses across the Nafion® membrane from the cathode to the anode due to a gradient in the water activity. Water also moves to the anode with a pressure gradient and is transported back to the cathode via electro-osmotic drag.

The protons produced by the oxidation of SO₂ migrate through the membrane to the cathode, where they are reduced to form hydrogen. Water crosses the membrane from the cathode to the anode due to a concentration gradient. Additional water crosses the membrane if a pressure differential is maintained between the cathode and the anode. In addition, water will cross the membrane from the anode to the cathode due to electro-osmotic drag.

The water flux model is similar to that developed previously for hydrogen production from anhydrous HCl.⁵¹ The key difference in the model presented here is that

liquid sulfuric acid is the product, and hence the water activity is fixed by the concentration. The water flux is determined by several factors. Diffusion is driven by a concentration gradient, water is carried from the anode to the cathode via electro-osmotic drag and water is driven in the direction of a pressure differential. The sum of these contributions comprises the net water flux:

$$N_w = \frac{\rho_M}{M_M \delta_M} \int_{\lambda_a}^{\lambda_c} D_w d\lambda - \frac{\xi \lambda i_{H_2SO_4}}{\lambda_c F} + \frac{P_M}{\delta_M} (P_c - P_a) \quad [6]$$

The first term on the right side of Eq. 6 is the flux due to diffusion across the membrane, and is a function of temperature, the second term is the flux through the membrane due to the electro-osmotic drag and the third term is the water transport rate due to a pressure differential across the membrane. The parameter P_M is the water permeability of the membrane. The electro-osmotic drag coefficient, ξ , has been estimated previously and found to have a value of 2.5.⁵¹ The integration limits, λ_a and λ_c , are the limits at the anode and cathode, respectively, and correspond to the water content of the membrane at these two interfaces. The water content changes as a function of the water mole fraction.^{52,53} The integration limit at the cathode is held constant, since it is the water content of the membrane in contact with pure water, which was measured to be 22 and 18 at 30 and 80°C, respectively.⁵⁴

The expression for D_w was given previously as:⁵¹

$$D_w = A_1 \lambda_a (1 + e^{-0.28\lambda}) \exp\left[\frac{-2436}{T}\right] \quad [7a]$$

(for $0 < \lambda_a \leq 3$)

$$D_w = A_2 \lambda_a (1 + 161e^{-\lambda_a}) \exp\left[\frac{-2436}{T}\right] \quad [7b]$$

(for $3 < \lambda_a \leq 17$)

The pre-exponential factors A_1 and A_2 depend on the membrane type but not the thickness. As demonstrated previously,⁵¹ the water content at the cathode, λ_c , is constant and equal to the water content of the membrane in contact with pure water, which was measured to be 22 and 18 at 30 and 80°C, respectively.⁵⁴

The water content at the anode, λ_a , (and hence the water transport in the membrane) has been investigated in several papers.^{52,55-73} An equation has been developed to predict λ_a as a function of water activity at 30°C.⁵² That equation, however, does not predict λ when the membrane is in contact with pure water ($a_w = 1.0$). In this case, the real value at 80°C has been measured to be 18.0; the equation presented in Ref. 53 yields a value of 14.0.

We have developed a different equation, using equilibrium water uptake values measured for different sulfuric acid concentrations at 80°C. This method assumed that the weight change after equilibrating with sulfuric acid was due to water uptake, and that H_2SO_4 uptake was minimal. In fact, Nafion membranes have been used to concentrate

sulfuric acid for the hybrid sulfur thermochemical cycle.⁷⁴ This equation is used in the model to determine the water content at the anode, λ_a :

$$\lambda_a = 123.8y_w^3 - 224.01y_w^2 + 134.14y_w - 16.35 \quad [8]$$

where a_w is the water activity, determined by the mole fraction of water in the flux:

$$a_w = \frac{N_w - \frac{i_{H_2SO_4}}{F}}{\left(N_w - \frac{i_{H_2SO_4}}{F}\right) + \frac{i_{H_2SO_4}}{2F}} \quad [9]$$

The sulfuric acid flux is the sum of the H_2SO_4 flux obtained via Faraday's law and the water flux obtained via Eq. 6:

$$N_{\text{sulfuric acid}} = \left(N_w - \frac{i_{H_2SO_4}}{F}\right) + \frac{i_{H_2SO_4}}{2F} \quad [10]$$

The sulfuric acid concentration is determined by a relationship between the H_2SO_4 weight percent and the molarity. The H_2SO_4 weight percent is determined from the flux values predicted by the model.

$$y_{H_2SO_4} = \frac{\frac{i_{H_2SO_4}}{2F}}{\frac{i_{H_2SO_4}}{2F} + \left(N_w - \frac{i_{H_2SO_4}}{F}\right)} \quad [11]$$

where $y_{H_2SO_4}$ is the weight percent of H_2SO_4 and M_i is the molecular weight of species i . The weight percent, $y_{H_2SO_4}$, is used to determine the sulfuric acid density from tabulated data.⁷⁵ The moles of H_2SO_4 , determined by Faraday's law, are used with the solution density to calculate the concentration.

B2. Water Transport and H_2SO_4 Production Results

The polarization curves for the electrolyzers with Nafion 117, 115, and 212 run with a differential pressure ($\Delta P = P_c - P_a$) of 600 kPa are given in Figure 6, and are the same results shown in Figure 3 and published previously.⁴⁸ Also included in this figure are the results from the Nafion 212 membrane run with zero differential pressure. The symbols are experimental data and the lines are smooth curve fits to the data.

Figure 6. Polarization curve data for the Nafion® 117, 115 and 212 electrolyzers. The water transport to the anode influences cell voltage. Water flux is higher for thinner membranes, and increases with the pressure gradient across the membrane. Unless noted in the figure, ΔP was 600 kPa. The cell temperature was 80°C.

As expected, the cell voltage decreases as the membrane thickness decreases. The results from the N212 electrolyzer run with a zero pressure differential further illustrate the effect of water flux on the cell voltage. The data in Figure 6 show that the cell voltage increases as the pressure differential decreases (about 0.20 V at 0.5 A/cm²). The electrolyzer also could not be operated at current densities above 0.6 A/cm² with a zero pressure differential. The cell voltages for the N212 operated with a zero pressure differential are comparable to those of N117 operated with a 600 kPa pressure differential.

It was previously concluded that the differences in the V-I curves for the three different membranes were due to different membrane resistances at moderate current densities.⁴⁶ It was speculated that the voltage was not sensitive to water transport as long as sufficient water crossed the membrane to sustain Reaction 2. However, the N212 membrane at $\Delta P = 0$ more closely matches the N117 membrane at $\Delta P = 600$ kPa, even though the resistance of the membranes are not a function of differential pressure. Hence, the effect of water transport on the cell voltage must be related to the concentration of sulfuric acid formed at the anode.

This is clear when the voltage is plotted versus sulfuric acid concentration for the two different N212 cases, as shown in Figure 7. Again, the points are experimental data and the lines are smooth curve fits to the data.

Figure 7. Comparison of cell voltage for Nafion® 212 for $\Delta P = 0$ kPa and 600 kPa as a function of sulfuric acid concentration. Because the two cell voltages at the same sulfuric acid concentrations are equal, the increased cell voltage for the $\Delta P = 0$ kPa electrolyzer in Figure 2 is due to the increased sulfuric acid concentration. The cell temperature was 80°C.

These two curves are virtually identical; the voltage penalty for producing H₂ at 700 kPa is approximately 0.025 V. Therefore, a key factor influencing the cell voltage is the sulfuric acid concentration. As a result, accurately predicting, and ultimately controlling, water transport as a function of design (e.g., membrane thickness and type) and operating (e.g., temperature, pressure, current) parameters is critical for the efficient operation of the electrolyzer.

To accurately predict sulfuric acid concentration as a function of the pressure differential, the variables P_M in Eq. 6 and A_1 and A_2 in Eqs. 7a and 7b must be determined for each membrane as a function of pressure differential. The molar flux of water across the membrane at 80°C is given in Figure 8 as a function of the pressure differential across the membrane. The cell was run with N₂ as the carrier gas at the anode and at open circuit voltage. The symbols are experimental data and the lines are least-squared fits to these data. As expected, the water flux increases with increasing pressure differential. This experiment was repeated at 50°C and 65°C, and no measurable difference in the water flux was measured. The resulting permeability value for Nafion was $P_M = 1.1 \times 10^{-10}$ mol/(cm s kPa).

Figure 8. Experimental data (symbols) and model predictions (lines) for the effect of pressure differential on water flux for Nafion® 115 and Nafion® 212. Nitrogen was fed to the anode at 100 sccm, and water was fed to the cathode. The cell temperature was 80°C. The nitrogen pressure was maintained at 101 kPa, and the pressure difference across the membrane was controlled by a globe valve on the cathode side.

The variables A_1 and A_2 were determined from the $\Delta P = 600$ kPa case for the Nafion 212 to correspond to the experimental data at 0.30 A/cm^2 . The values of A_1 and A_2 were found to be 2.2×10^{-3} and $8.3 \times 10^{-4} \text{ cm}^2/\text{s}$, respectively, and were not a function of thickness or temperature.

After the values of P_M and A_1 and A_2 were determined, it was possible to employ the model over the entire range of operating current densities, pressure differentials, temperature and membrane thickness, and provide insight into the operation of the electrolyzer without any adjustable parameters. Figure 9 shows data (symbols) and model simulations (lines) for the production of sulfuric acid for the Nafion 212 electrolyzer at 80°C and $\Delta P = 600$ kPa.

Figure 9. Contribution of water and H₂SO₄ to the total sulfuric acid flux of the Nafion® 212 electrolyzer. The points are experimental data and the lines are model predictions. After 0.5 A/cm², the water flow rate begins to decrease due to electro-osmotic drag. The total volumetric flow rate continues to increase due to the increased production of H₂SO₄. ΔP was 600 kPa. The cell temperature was 80°C.

The errors in measuring the sulfuric acid production rate are more pronounced at low current density, where the production rate is low, but are negligible. The sulfuric acid is separated into the H₂SO₄ and water. These results confirm that the electrolyzer is not limited by water reaching the anode to participate in Reaction 2. There is excess water crossing the membrane to participate in the reaction. In fact, the amount of water available for the reaction increases with current density.

To better understand why the amount of water crossing the membrane increases with current, the model predictions of the contributions to the total water flux are plotted in Figure 10.

Figure 10. Contributions of diffusional flux and electro-osmotic drag to the net water flux in Nafion® 212. The lines are model predictions. The diffusion and pressure effects work to offset the electro-osmotic drag effect. ΔP was 600 kPa. The cell temperature was 80°C.

The experimental data for the total water flux (symbols) have been plotted along with the model simulations (lines). At low current densities, the molar flux of water increases with increasing current density due to an increase in the amount of H_2SO_4 produced at the anode. The presence of H_2SO_4 reduces the water activity and leads to an increase in concentration-driven diffusion from the cathode. As the current density increases, however, this phenomenon is increasingly offset by the electro-osmotic drag, which pulls water back across the membrane to the cathode. A situation then exists in which the flux due to diffusion competes with electro-osmotic drag. The pressure-driven flux is the same over all current densities.

The experimental data (symbols) and model simulations (lines) for the production rate of sulfuric acid as a function of current and membrane thickness (Nafion 117, 115 and 212) are shown in Figure 11.

Figure 11. Experimental data (symbols) and model predictions (lines) for sulfuric acid production rate as a function of current density for the three PEM electrolyzers. The model shows good agreement with the experimental data, with a prediction that the total molar flow rate increases with increasing current density. ΔP was 600 kPa. The cell temperature was 80°C.

As expected, the production rate of sulfuric acid increases with current since water transport and H_2SO_4 production increase. It also increases with decreasing membrane thickness because more water is transported across the thinner membranes at each current. The sulfuric acid production rates at 0.5 A/cm² are 1.89×10^{-5} and 2.75×10^{-5} mol/cm² s for the Nafion 115 and 212 electrolyzers, respectively. Nafion 117 cannot operate at this current density. For Nafion 117 at 0.3 A/cm², the production rate of sulfuric acid is 1.41×10^{-5} mol/cm² s.

Since the sulfuric acid concentration affects cell voltage, it is desirable to study sulfuric acid concentration as a function of membrane thickness, current density and pressure differential. The experimental concentration data (symbols) and model simulations (lines) for $\Delta P = 600$ kPa are given in Figure 12.

Figure 12. Experimental data (symbols) and model predictions (lines) for the concentration of H_2SO_4 leaving the electrolyzer. The sulfuric acid concentration increases with current density because a) the rate of H_2SO_4 production increases with current density and b) the electro-osmotic drag of water back to the cathode increases with current density. Also, decreasing the pressure gradient increases the sulfuric acid concentration. Unless noted in the figure, ΔP was 600 kPa. The cell temperature was 80°C.

Again, there is good agreement between the model and the data; the data more closely agree with the model at current densities above 0.2 A/cm² because of the difficulty in accurately measuring the pH of the sulfuric acid produced at very low current densities. At 0.5 A/cm², the experimental concentrations are 5.88 M and 4.33 M for the Nafion 115 and Nafion 212 electrolyzers, respectively. The model predictions for these two electrolyzers are 5.72 M and 4.46 M. For the Nafion 117 electrolyzer at 0.3 A/cm², the experimental and model predictions for the H_2SO_4 concentration are 5.14 M and 5.15 M, respectively. As expected, the sulfuric acid concentration decreases as membrane thickness decreases. The increased water flux through the thinner membranes dilutes the sulfuric acid.

The sulfuric acid concentration data for N212 with $\Delta P = 0$ kPa are also presented in Figure 12. These sulfuric acid concentration values are very close to those of N117 with $\Delta P = 600$ kPa. This result is expected when one considers Figure 2, in which it was shown that the cell voltages were very similar for N212 at $\Delta P = 0$ kPa and N117 at $\Delta P = 600$ kPa. Sulfuric acid concentration can be closely correlated to cell voltage.

Because it was shown in Figure 12 that the pressure differential influences the sulfuric acid concentration, one would expect that the sulfuric acid production rate would change with the pressure differential. This is indeed what is observed in Figure 13 for

sulfuric acid production in the N115 electrolyzer operated at 0.2 A/cm^2 and the N212 electrolyzer operated at 0.5 A/cm^2 . As expected, the sulfuric acid production rate increases with pressure differential.

Figure 13. Experimental data (symbols) and model predictions (lines) for sulfuric acid production as a function of ΔP for Nafion® 115 and Nafion® 212. Sulfuric acid concentration increases with ΔP due to the increase in water flux to the anode. The cell temperature was 80°C . The pressure gradient was controlled by a globe valve.

Again, the model simulations (lines) closely follow the experimental data (symbols). For example, at $\Delta P = 400 \text{ kPa}$ the experimental sulfuric acid production rate for N115 at 0.2 A/cm^2 is $1.37 \times 10^{-5} \text{ mol/cm}^2 \text{ s}$ and the model prediction is $1.33 \times 10^{-5} \text{ mol/cm}^2 \text{ s}$. For N212 at 0.5 A/cm^2 the experimental rate is $2.15 \times 10^{-5} \text{ mol/cm}^2 \text{ s}$ and the model prediction is $2.22 \times 10^{-5} \text{ mol/cm}^2 \text{ s}$.

We have already seen in Figures 12 and 13 that increasing the pressure differential decreases the sulfuric acid concentration and increases the sulfuric acid production rate. Continuing this investigation, the sulfuric acid concentration for the N115 and N212 electrolyzers are presented as a function of pressure differential in Figure 14.

Figure 14. Experimental data (symbols) and model predictions (lines) for sulfuric acid concentration as a function of pressure for Nafion® 115 and Nafion® 212. The sulfuric acid concentration decreases with ΔP due to the increase in water flux to the anode. The cell temperature was 80°C. The water pressure at the cathode was controlled by a globe valve.

At $\Delta P = 400$ kPa the experimental (point) sulfuric acid concentration for N115 at 0.2 A/cm² is 3.52 M and the model prediction (line) is 3.73 M. For N212 at 0.5 A/cm² the experimental sulfuric acid concentration is 5.45 M and the model prediction is 5.25 M. The N212 was operated at 0.5 A/cm² versus 0.2 A/cm² for N115 in Figures 13 and 14 simply because N115 could not reach 0.5 A/cm² at $\Delta P = 0$ kPa.

The sulfuric acid production rate data (points) for N212 at two different temperatures (50°C and 80°C) and two different pressure differentials (0 kPa and 600 kPa) are presented in Figure 15, along with the model predictions (lines). The highest rate is observed at 80°C and $\Delta P = 600$ kPa due to the increased rate of diffusion flux at high temperature and the increased pressure-driven flux at a high pressure differential.

Figure 15. Experimental data (symbols) and model predictions (lines) for sulfuric acid production rate for Nafion® 212 at different temperatures and cathode water pressures. The temperature and pressure gradients were varied for each test. The sulfuric acid flux increases with temperature and pressure gradient.

At 50°C and $\Delta P = 600$ kPa, the experimental sulfuric acid production rate at 0.5 A/cm² is 2.12×10^{-5} mol/cm² s and the model prediction is 2.00×10^{-5} mol/cm² s. At 80°C and 0 kPa pressure differential, the experimental sulfuric acid production rate at 0.5 A/cm² is 1.35×10^{-5} mol/cm² s and the model prediction is 1.38×10^{-5} mol/cm² s.

From Figure 15 we can see that increasing the pressure differential has a greater effect on sulfuric acid production rate than increasing the temperature. That is, the sulfuric acid rate increases more with pressure differential than with temperature. This is due to the greater increase in pressure-driven flux of water through the membrane with increasing pressure differential than diffusion flux due to an increase in the temperature.

In addition, the sulfuric acid concentration changes with temperature as well as pressure due to the increased water flux to the anode at higher temperature. For example, at 80°C and $\Delta P = 0$ kPa, the sulfuric acid concentration at 0.5 A/cm² is 7.42 M. At 50°C and $\Delta P = 600$ kPa, the sulfuric acid concentration at 0.5 A/cm² is 5.77 M. At 80°C and $\Delta P = 600$ kPa, the sulfuric acid concentration at 0.5 A/cm² is 4.03 M.

C. Water Transport and SO₂ Crossover

C1. SO₂ Crossover Model

The water flux N_w and the λ profile, both found in Eq. 6, can be used to calculate the flux of SO₂ via the following equation:⁷⁶

$$N_{SO_2} = \frac{C_{SO_2} M_M}{\lambda \rho_M} N_w - D_{SO_2} \frac{dC_{SO_2}}{dx} \quad [12]$$

with the boundary conditions $C_{SO_2} = C_{SO_2}^*$ at $x = 0$ (gas anode side) and $C_{SO_2} = 0$ at $x = \delta_M$ (liquid cathode side). The flux of SO_2 is a combination of convective transport with the water toward the anode (first term on the right) and diffusional flux to the cathode due to a concentration gradient (second term on the right).

When the water flux obtained via Eq. 6 is zero (i.e., no pressure differential, open circuit conditions) Equation 12 reduces to the following form:

$$N_{SO_2} = -D_{SO_2} \frac{dC_{SO_2}}{dx} \quad [13]$$

Equation 13 is Fick's first law. Combining Eq. 13 with the differential material balance gives Fick's second law:

$$\frac{\partial C_{SO_2}(x,t)}{\partial t} = -D_{SO_2} \frac{\partial^2 C_{SO_2}(x,t)}{\partial x^2} \quad [14]$$

Equation 14 can be solved with the following initial and boundary conditions:⁷⁷

$$C_{SO_2} = 0 \quad @t = 0 \quad [15a]$$

$$C_{SO_2} = C_{SO_2}^* \quad @x = 0 \quad [15b]$$

$$C_{SO_2} = 0 \quad @x = \delta_M \quad [15c]$$

to render the following equation for SO_2 crossover current as a function of time:

$$i_{SO_2}(t) = \frac{2FD_{SO_2}C_{SO_2}^*}{\delta_M} \left(\frac{2}{\sqrt{\pi\tau}} \sum_{j=0}^{\infty} \exp \left[-\frac{(2j+1)^2}{4\tau} \right] \right) \quad [16]$$

The electrochemical monitoring technique is used to calculate the parameters D_{SO_2} and $C_{SO_2}^*$ via a least-square fit method at conditions under which Eq. 13 is valid (i.e., $N_w = 0$).¹⁸ The current achieved during the electrochemical monitoring technique is small enough that water flux due to electro-osmotic drag is assumed to be negligible. The τ in Eq. 16 is defined as:

$$\tau = \frac{tD_{SO_2}}{\delta_M^2} \quad [17]$$

The SO_2 flux is converted to a crossover current density by the following relationship:

$$i_{SO_2} = 2FN_{SO_2} \quad [18]$$

The SO_2 diffusion coefficient and solubility (D_{SO_2} and $C_{SO_2}^*$) needed for the solution of Eq. 12 can be determined by a least-square fit of Eq. 16 to the current-time response from the electrochemical monitoring technique. A list of model parameters is given at the end of this appendix.

C2. SO_2 Crossover Results

From the discussion of the model above, it is clear that the SO_2 crossover is a strong function of the water transport in the membrane. Thus, any discussion of SO_2 crossover must begin with an investigation of water flux in the membrane. Solving Eq. 6, along with parameters given previously,⁷⁶ gives the flux of water through the membranes as a function of current density at differential pressures of 600 kPa and 0 kPa; these values are shown in Figure 16.

Figure 16. Model predictions from Eq. 4 (lines) and experimental data (points, N115 •, N212 ○) for the molar flux of water as a function of current density at different ΔP . The cell temperature was 80°C.

The two pressure differentials were chosen to highlight the extreme cases of high and low pressure differentials. The points are data and the lines are model predictions. The water flux to the anode increases with current density. For the conditions shown in Figure 16, the water flux to the anode increases with current density up to approximately 0.5 A/cm². At current densities higher than 0.5 A/cm², the electro-osmotic drag to the

cathode is high enough to offset the diffusion and pressure-driven flux to the anode. Under these conditions, the water flux to the anode begins to decrease. The model predicts a decrease in the water flux to the anode at current densities above 0.5 A/cm^2 for the $\Delta P = 0 \text{ kPa}$ case. However, due to the more concentrated sulfuric acid^{49,50} at $\Delta P = 0 \text{ kPa}$, the electrolyzers could not be run past 0.5 A/cm^2 .

The water flux values shown in Figure 16 are used in conjunction with D_{SO_2} and $C_{\text{SO}_2}^*$ values obtained from the electrochemical monitoring technique and Eq. 12 to determine the SO_2 flux via Eq. 12. The data obtained from the electrochemical monitoring technique for N115 are shown in Figure 17.

Figure 17. Electrochemical monitoring technique on N115. The cell voltage and temperature were 0.31 V and 80°C, respectively. The limiting current is the SO_2 crossover current density, i_{SO_2} .

Initially, N_2 is sent to the gas side (cathode) and liquid water to the other (anode), with $\Delta P = 0 \text{ kPa}$. At time $t = 0 \text{ s}$, a step voltage of 0.31 V is applied. The current density immediately increases due to double-layer charging, and then begins to decay. Once the current reaches the steady-state value at $t = t^*$, the gas at the cathode is switched to SO_2 . The voltage at the anode ($\sim 0.31 \text{ V}$) is such that any SO_2 crossing the membrane to the water side is oxidized to H_2SO_4 . This operation is opposite of normal electrolyzer operation; during the electrochemical monitoring technique, the water side serves as the anode, and SO_2 crossing the membrane is oxidized to H_2SO_4 . Thus, the anode voltage must be above 0.158 V, and the limiting current indicates that all SO_2 crossing the membrane is oxidized. The limiting current density reached at t_f is the SO_2 crossover current, i_{SO_2} . The membrane pressure differential, ΔP , is subsequently increased to 100

kPa and then to 150 kPa, resulting in a lower value for i_{SO_2} . The decrease in i_{SO_2} as ΔP increases is indicative of the convective flux of SO_2 toward the gas side due to water flux.

The portion of the data in Figure 17 where the N_2 feed was switched to SO_2 at $\Delta P = 0$ kPa is shown in Figure 18.

Figure 18. Comparison of experimental data (points) and the model using least-square fit (line) of the transient region. The resulting fit, obtained by the least-squares method, yielded values D_{SO_2} and $C_{SO_2}^*$ as model parameters.

The SO_2 crossover current density, i_{SO_2} , has been normalized with respect to the limiting current density. The transient data in which the SO_2 crossover current density increased to the limiting value were used in a least-squares model⁷⁷ to determine D_{SO_2} and $C_{SO_2}^*$ via Eq. 14. The diffusion coefficient at 80°C was $D_{SO_2} = 2.86 \times 10^{-6} \text{ cm}^2/\text{s}$ and the solubility in Nafion was $C_{SO_2}^* = 1.58 \times 10^{-4} \text{ mol/cm}^3$.

The electrochemical monitoring technique has been reproduced for N115 and N212 at various membrane pressure differentials. The experimental SO_2 crossover current density, i_{SO_2} , obtained from the electrochemical monitoring technique and the model predictions for i_{SO_2} obtained via Eqs. 12 and 18 are shown in Figure 19.

Figure 19. SO_2 crossover current density as a function of membrane ΔP . The lines are the model predictions and the points (N115 •, N212 ○) are experimental data. The temperature was 80°C.

The data and model predictions indicate that i_{SO_2} is higher for N212 than for N115. For example, at $\Delta P = 400$ kPa, i_{SO_2} is approximately 11.1 mA/cm² for N212 and 4.4 mA/cm² for N115. The decrease in i_{SO_2} observed in the thicker N115 membrane is due to the lower diffusion term in the convection-diffusion equation (Eq. 12).

Another trend is observed in Figure 19, namely that as ΔP increases, i_{SO_2} decreases. The decrease in i_{SO_2} as the pressure differential increases is the same trend observed during the electrochemical monitoring technique in Figure 17. One concludes that as the pressure differential is increased (and hence the water flux to the anode due to Eq. 6), the SO_2 crossover decreases due to its solubility in water (i.e. the convective term in Eq. 12 works to counter diffusion).

The solubility and diffusion coefficient of SO_2 as a function of temperature are shown in Figure 20 for N115.

Figure 20. Solubility of SO₂ in Nafion as a function of temperature. The points (N115 ● and ◆; N212 ○ and ◇) are data and the lines are smooth curve fits to the data. The membrane pressure differential was $\Delta P = 0$ kPa.

As expected the solubility of SO₂ is higher at lower temperatures.⁷⁸ For example, we have indicated in the discussion of the electrochemical monitoring technique in Figures 17 and 18 that at 80°C, $C_{\text{SO}_2} = 1.58 \times 10^{-4} \text{ mol/cm}^3$. The solubility increases as the temperature decreases; at 50°C the solubility $C_{\text{SO}_2} = 4.00 \times 10^{-4} \text{ mol/cm}^3$. The diffusion coefficient increases with temperature. The solubility and diffusion coefficient for N212 at 80°C are shown for comparison, and are within experimental error of those values reported for N115. It was determined that the solubility of SO₂ in a hydrated Nafion membrane was within 10% of the reported value for the solubility in water.⁷⁸ This result is consistent with our understanding of a hydrated Nafion membrane, in which as many as 20 moles of water can exist for each mole of sulfonate group.

We have shown that at the very low current densities (i.e. $<0.02 \text{ A/cm}^2$) achieved in the electrochemical monitoring technique, increasing the membrane pressure differential, ΔP , leads to a decrease in the SO₂ crossover current density, i_{SO_2} . This is due to the increased water flux to the anode observed in Figure 16, which increases the convective term in Eq. 12 and offsets diffusion. In addition to increasing water flux to the anode by increasing ΔP , one can also increase water flux by increasing the electrolyzer current density, as shown in Figure 16. One would expect that, just like increasing ΔP lowers i_{SO_2} , increasing the electrolyzer current density should also lower

i_{SO_2} .

This trend is observed in Figure 21. As the current density increases (increasing water flux to the anode), the convection term in Eq. 12 becomes larger, continually offsetting the diffusion term. As a result, the SO₂ crossover current density, i_{SO_2} , decreases. The decrease in i_{SO_2} as the current density increases can be quite dramatic, and i_{SO_2} actually goes to zero for N115 at sufficiently high ΔP and current density.

Figure 21. SO₂ crossover current density. The cell temperature was 80°C. The SO₂ flux decreases as current density increases due to the increase in the water flux with current density. At sufficiently high ΔP and current density it is observed that SO₂ crossover can be prevented.

Unfortunately, it is not possible to experimentally measure SO₂ crossover current, i_{SO_2} , while the electrolyzer is operated under load. For this reason, the only experimental data presented in Figure 21 are for the zero current case, determined by the electrochemical monitoring technique. The values reported at current densities above zero are model predictions via Eqs. 6 and 12. As a means to estimate SO₂ crossover under load, sulfur deposition at the cathode was correlated to water flux predicted by the model by utilizing EDX elemental analysis. N115 membranes were run under several different conditions, and cross-sections were taken of each membrane for EDX elemental analysis. The conditions, reported in Table 3, consisted of the following: $\Delta P = 600$ kPa at 0.25 A/cm² for 15 hours (Case 1), $\Delta P = 0$ kPa at 0.10 A/cm² for 16 hours (Case 2), $\Delta P = 600$ kPa at 0.10 A/cm² for 8 hours followed by $\Delta P = 0$ kPa at 0.10 A/cm² for 4 hours (Case 3), and $\Delta P = 200$ at 0.02 A/cm² for 100 hours (Case 4). The ratio of S to Pt atoms in each electrode was obtained via elemental analysis. Since the Pt loading was the same at each electrode, and the reduction of SO₂ to elemental sulfur is not possible at the

anode, the ratio of S to Pt atoms at the anode was taken as the background. Any increase in this ratio at the cathode was attributed to reduction of SO₂ to elemental sulfur. The S:Pt ratio at the cathode was divided by that at the anode to determine the extent of sulfur deposition during electrolyzer operation. The cathode to anode ratio for Case 1, S_c/S_a, is 1.1, given in Table 1. For Case 2, the ratio S_c/S_a, is 5.1; for Case 3, the ratio S_c/S_a, is 1.4, and for Case 4, the ratio is S_c/S_a 25.6. The model predicts no SO₂ crossover for the conditions realized in Case 1, as shown in Figure 6 (N115, $\Delta P = 600$ kPa, $i = 0.25$ A/cm²). The model predicts SO₂ crossover current density, $i_{SO_2} = 3.2$ mA/cm² for the conditions realized in Case 2 (N115, $\Delta P = 0$ kPa, $i = 0.10$ A/cm²), corresponding to a total sulfur crossover of 9.55×10^{-3} mol. The data obtained from elemental analysis allow us to determine the total mass of the cathode, and hence the mass of each element. Under the conditions of Case 2, 3.13×10^{-5} mol of sulfur were reduced at the cathode. Thus, only about 0.33% of the sulfur crossing the membrane was reduced to elemental sulfur at the cathode.

Similar analysis was performed for Cases 3 and 4, with very similar results. Thus, slightly less than 0.5% of the sulfur crossing the membrane is reduced to elemental sulfur at the cathode. The rest of the sulfur, in the form of SO₂, is swept out of the cathode compartment with the water. The percent of sulfur crossing the membrane, in addition to being small, is almost the same at each condition tested. Therefore, reducing the amount of sulfur crossing the membrane (SO₂ crossover), should result in a lower rate of sulfur reduction at the cathode.

	Case 1	Case 2	Case 3	Case 4
Current Density (A/cm ²)	0.25	0.10	0.10	0.02
Time (hrs.)	15	16	8/4	100
ΔP (kPa)	600	0	600/0	200
SO ₂ Crossover (mol)	0	9.55×10^{-3}	2.41×10^{-3}	5.60×10^{-2}
Sulfur Deposited in Cathode (mol)	0	3.13×10^{-5}	8.92×10^{-6}	1.96×10^{-4}
% Sulfur Reduced	0	0.33	0.37	0.35

Table 1. Ratio of sulfur at the cathode and anode after operation at various conditions measured by EDX elemental analysis. The trend indicates that SO₂ crossover can be prevented if ΔP and the current density are sufficiently high.

Even the small extent of reduction significantly modifies the electrode structure, as shown by the SEM of Case 4 in Figure 22. Here, once the sulfur has built up enough in the cathode to fill the porous structure, it continues to build up outside of the cathode. However, we have not seen a delamination of the cathode, as reported by SRNL.^{79,80}

Figure 22. SEM image of N115 run at 0.02 A/cm^2 for 100 hours with $\Delta P = 200 \text{ kPa}$. SO_2 crosses the membrane from the anode to the cathode via a concentration gradient and reduces to sulfur inside the cathode via Reaction 5.

In addition to changing the composition of the cathode, sulfur deposition via Reaction 3 consumes current that would ideally be used for the production of hydrogen. This serves to render the electrolyzer less efficient, but the current consumed by reduction to sulfur is small enough that current efficiencies are still $>99\%$. In addition, SO_2 crossing the membrane is lost to the sulfur cycle and must be added as fresh SO_2 . The SO_2 crossing the membrane could also contaminate the H_2 product stream. The reduced sulfur at the cathode results in a compositional change of the electrode. It has not been shown, however, that changing the composition of the electrode over time results in significant voltage losses, because the longest operation has only been for 100 hours. It has been shown that SO_2 crossover can be controlled by two means; namely by increasing the current density and by increasing the pressure differential. Both methods increase the water flux to the anode, which increases the convective transport of SO_2

toward the anode. Understanding the factors that affect SO_2 crossover are essential in evaluating new membranes for use in the electrolyzer.

D. Alternative Membranes

Researchers at Sandia National Laboratories have developed a series of alternative proton exchange membranes for fuel cell applications.^{81,82} These highly-stable, sulfonated Diels-Alder poly(phenylene) (SDAPP) membranes were developed for use in direct methanol fuel cells to reduce methanol crossover compared to Nafion membranes.⁸¹ They have an advantage over Nafion in that they are capable of operating at higher temperatures due to stiffer polymer backbones and superior mechanical properties.⁸² The one major flaw of these materials, as in many other non-poly(perfluorosulfonic acid) PEMs, is that their conductivity suffers greatly at low membrane water content. Since the SO_2 electrolyzer in this work is fed with a liquid water stream at the cathode, there are no significant conductivity concerns. Moreover, the presence of liquid water at the cathode (under pressure in the cases where the reactor is run at temperatures above 100°C) presents a problem for Nafion in that the mechanical properties of the membrane are compromised to a greater extent when in contact with a liquid phase due to water plasticization.⁸³

The parameters in Eq. 6 (water flux equation described earlier) were determined in the same manner as the previous discussion. The functional form of D_w was the same, except the pre-exponential factors were modified so that $A_1 = 2.2 \times 10^{-3}$ and $A_2 = 8.7 \times 10^{-4} \text{ cm}^2/\text{s}$, respectively. For lack of contrary evidence, the electro-osmotic drag coefficient, ξ , remained the same at 2.5. The membrane permeability was $P_M = 9.0 \times 10^{-11} \text{ mol/cm}^2 \text{ s/kPa}$, which was determined by the slope of the water flux at zero current (open circuit) with respect to the membrane pressure differential, ΔP . This method is identical to that outlined in our previous paper,⁴⁹ but the permeability value for SDAPP was found to be lower than that of Nafion ($1.1 \times 10^{-10} \text{ mol}/(\text{cm}^2 \text{ s kPa})$).

The polarization curves for SDAPP 4 and N115 at 80°C and 120°C and $\Delta P = 300 \text{ kPa}$ are shown in Figure 23. The points are data and the lines are smooth curve fits to the data. The cell voltage is higher for the SDAPP4 membrane at 80°C , indicating lower performance than N115 at these conditions.⁸⁴

Figure 23. Polarization curves for SDAPP4 and N115. The points (N115 at 80°C ○, N115 at 120°C ●, SDAPP4 at 80°C ◇, SDAPP4 at 120°C ◆) are data and the lines are smooth curve fits to the data. The membrane pressure differential was $\Delta P = 300$ kPa.

The SDAPP4 membrane exhibits better performance than N115 when the temperature is raised to 120°C. At 80°C and 0.40 A/cm², the operating voltage for SDAPP4 is 1.01 V, while the operating voltage for N115 is 0.862 V. When the temperature is increased to 120°C, the operating voltage for SDAPP4 at 0.40 A/cm² is 0.75 V vs. 0.776 V for N115.

We have shown previously⁴⁹ that water flux to the anode has a significant effect on electrolyzer performance. The water flux to the anode is shown in Figure 24 for the same conditions as the polarization curves given in Figure 23.

Figure 24. Water flux to the anode. The points (N115 at 80°C ○, N115 at 120°C ●, SDAPP4 at 80°C ◇, SDAPP4 at 120°C ◆) are data and the lines are model predictions (Eq. 6). The membrane pressure differential was $\Delta P = 300$ kPa.

The points are experimental data and the lines are model predictions via Eq. 6. The results indicate that SDAPP4 exhibits a higher water flux to the anode at all current densities. For example, at 80°C and 0.20 A/cm², the water flux for SDAPP4 is 0.84×10^{-5} mol/cm² s, while the water flux for N115 at the same temperature and current density is 0.75×10^{-5} mol/cm² s. Thus, despite a slightly lower water permeability, as discussed above, SDAPP4 has a higher water flux. This is due to the SDAPP4 membranes being slightly thinner than N115 (4 mil vs. 5 mil).

The sulfuric acid production rates of SDAPP 4 and N115 at 80°C and 120°C and $\Delta P = 300$ kPa are shown in Figure 26.

Figure 26. Sulfuric acid production rates. The points (N115 at 80°C ○, N115 at 120°C ●, SDAPP4 at 80°C ◇, SDAPP4 at 120°C ◆) are data and the lines are model predictions (Eq. 7). The membrane pressure differential was $\Delta P = 300$ kPa.

The points are data and the lines are model predictions. As expected, the sulfuric acid production rate increases with current density due to the increased water flux to the anode at higher current density. The production rate for the SDAPP4 membrane is higher than that of the N115 membrane because SDAPP4 is thinner (4 mil vs. 5 mil) than N115 while having nearly the same water transport characteristics,⁸⁵ allowing for increased water transport to the anode at all current densities.

When the temperature is increased to 120°C, the sulfuric acid production rate increases at all current densities. The increase in acid production was due to increased water transport to the anode with temperature as well as increased current density.⁴⁹ For example, the sulfuric acid production rate of SDAPP4 at 80°C and 0.40 A/cm² is 1.00×10^{-5} mol/cm² s. When the temperature increases to 120°C, the sulfuric acid production rate increases to 1.38×10^{-5} mol/cm² s. The increase in the sulfuric acid production rate is a weak function of temperature, as already reported.⁴⁹ Membrane pressure differential and membrane thickness have a more pronounced effect.

The analysis of the sulfuric acid production rate leads to a discussion of the resulting acid concentration at the anode. The sulfuric acid concentrations at 80°C and 120°C and $\Delta P = 300$ kPa for SDAPP 4 and N115 are shown in Figure 27.

Figure 27. Sulfuric acid concentration for SDAPP 4 and N115. The points (N115 at 80°C ○, N115 at 120°C ●, SDAPP4 at 80°C ◇, SDAPP4 at 120°C ◆) are data and the lines are model predictions. The membrane pressure differential was $\Delta P = 300$ kPa.

The points are data and the lines are model predictions. The concentration increases as the current density because of the increased production rate of H_2SO_4 at higher current density. The sulfuric acid concentration of SDAPP 4 is lower than that of N115 due to the increased water transport to the anode for the thinner membrane.

The sulfuric acid concentration decreases as the temperature increases due to the increased water flux to the anode at elevated temperatures. For example, the sulfuric acid concentration of SDAPP 4 at 80°C and 0.40 A/cm² is 7.94 M. When the temperature is raised to 120°C, the sulfuric acid concentration decreases to 6.03 M.

We have shown that the operating voltages can be compared as a function of sulfuric acid concentration.^{49,76} It was determined that, for the same membrane operated with a different ΔP , the cell voltage at each ΔP corresponded to the sulfuric acid concentration at each current density. This analysis indicated that the operating voltage was a strong function of the sulfuric acid concentration, which is determined by the water flux to the anode. The water flux is controlled by the current density, temperature, membrane thickness and pressure differential.

Examining the sulfuric acid concentration data in Figure 27 once more, one concludes that the concentration for N115 at 120°C is similar to that of SDAPP 4 at 80°C. If the membrane resistance for N115 and SDAPP4 were identical, then one would expect the polarization curves to be nearly identical in Figure 24 for N115 at 120°C and SDAPP 4 at 80°C. This is clearly not the case, however, and the difference is due to the higher membrane electrode assembly resistance when SDAPP4 is used as the membrane.

SDAPP has an intrinsically higher conductivity than Nafion in liquid water (200 mS/cm vs. Nafion at 180 mS/cm at 80°C),⁸² but exhibits a higher MEA resistance due to the increased interfacial resistance of Nafion-based electrodes with a non-Nafion membrane.⁸⁶ When the MEA resistance is accounted for, and the increase in cell voltage is subtracted (iR corrected), the curves are nearly identical at the two different temperatures (80°C and 120°C), as shown in Figure 28.

Figure 28. Voltage as a function of sulfuric acid concentration. The voltage has been corrected for membrane resistance. The points (N115 at 80°C ○, N115 at 120°C ●, SDAPP4 at 80°C ◇, SDAPP4 at 120°C ◆) are data and the line is a fit through the data points. The membrane pressure differential $\Delta P = 300$ kPa.

In addition to better operation at higher temperature, SDAPP4 membranes have received attention for use in the hybrid sulfur electrolyzer due to the possibility of lower SO₂ crossover than Nafion. With the water flux known via Eq. 6, we can use the data obtained from the electrochemical monitoring technique to determine the SO₂ crossover in the same manner as our previous paper.⁷⁵ The SO₂ crossover current density, i_{SO_2} , as a function of ΔP is shown in Figure 29 at 80°C. As expected, the crossover current decreases as ΔP increases due to the increased water transport to the anode.

Figure 29. SO_2 crossover current density as a function of ΔP . The points (N115 $\circ$, SDAPP4 $\diamond$) are data and the lines are the model predictions based on the calculated water flux values. The cell temperature was 80°C .

The results of Figure 29 indicate that the SO_2 crossover can be reduced by increasing the water flux to the anode. The water flux, as described already, is a function of membrane pressure differential, temperature, current density and membrane thickness. Thus, any operating conditions under which the net flux of water to the anode should increase would result in a decrease in SO_2 crossover.

The solubility of SO_2 in each PEM is shown in Figure 30 as a function of temperature, along with the diffusion coefficient values. These results quantify the extent to which the solubility of SO_2 decreases as the temperature is increased. The diffusion coefficient increases with temperature.

Figure 30. SO₂ solubility and diffusion coefficient in SDAPP4 and N115 as a function of temperature. The points (N115 ○, SDAPP4 ◇) are data and the lines are smooth curve fits to the data.

The solubility of SO₂ is slightly lower in SDAPP4 than in N115; for example, at 80°C, the solubility of SO₂ in SDAPP4 is $1.40 \times 10^{-4} \text{ mol/cm}^3$, and it is $1.58 \times 10^{-4} \text{ mol/cm}^3$ for N115. The difference in solubility between the two membranes is small, and may not be significant. In fact, the solubility in both membranes is very close to that of SO₂ in water, which is understandable given our knowledge of hydrated membrane electrolytes.⁷⁶

Due to the lower solubility at elevated temperatures and the increased water flux to the anode, the SO₂ crossover current density, i_{SO_2} , decreases with increasing temperature, as shown in Figure 31. In addition, the crossover current is lower for SDAPP4 at all temperatures reported due to the increased water flux to the anode for the thinner membrane. The points in Figure 31 correspond to crossover currents measured by the electrochemical monitoring technique.

Figure 31. SO₂ crossover current density as a function of temperature. The points (N115 ○, SDAPP4 ◇) are data and the lines are smooth curve fits to the data.

The results shown in Figures 30 and 31 indicate that the difference in SO₂ crossover between Nafion and SDAPP4 membranes is due to the lower diffusion coefficient of SO₂ in the SDAPP membranes. For example, Figure 30 shows that the solubility is nearly the same, and is close to the solubility of SO₂ in water. The water transport properties of the two membranes are similar, but the diffusion coefficient of SO₂ in SDAPP4 is significantly lower than that in Nafion.

In addition to increasing water flux, and hence the convective term in Eq. 12 by increasing the temperature, the water flux increases as the current density increases.^{49,76} Thus, the SO₂ crossover current decreases as the current density is increased, as shown in Figure 32.

Figure 32. SO₂ crossover current density as a function of current density at different temperature. The points (N115 at 80°C ○, N115 at 120°C ●, SDAPP4 at 80°C ◇, SDAPP4 at 120°C ◆) are data and the lines are model predictions (Eq. 12). The pressure differential was $\Delta P = 300$ kPa.

The only experimental data points are at zero current, because, as reported previously, it is impossible to measure i_{SO_2} while the electrolyzer is under load.⁷⁶ However, the model predictions show that i_{SO_2} decreases as the water flux to the anode increases (with increased current density). As reported already, only about 0.5% of the sulfur crossing the membrane is reduced to elemental sulfur in the cathode. The rest is swept out of the cathode compartment with the water.

E. Thermodynamic Analysis

A thermodynamic analysis of the hybrid sulfur system has been developed at Savannah River National Laboratory using the Mixed Solvent Electrolyte model of Aspen Plus.⁵⁰ The Aspen-OLI interface was used to solve the Nernst equation:

$$U_{eq} = U_{eq}^o - \frac{RT}{2F} \cdot \ln Q_T \quad [19]$$

for the species activities:

$$Q_T = \frac{(a_{SO_2}) \cdot (a_{H_2O})^2}{(a_{SO_4^{2-}}) \cdot (a_{H_2}) \cdot 10^{-2pH}} \quad [20]$$

and

$$U_{eq}^o = E^o + (T - 298.15) \left(\frac{dE^o}{dT} \right) \quad [21]$$

The model has been used to determine the solubility of SO₂ in sulfuric acid as a function of temperature, pressure and acid concentration. It has also been used to determine the reversible potential as a function of temperature, pressure and acid concentration.

The solubility of SO₂ in sulfuric acid at 101 kPa and 80°C is shown in Figure 33 as a function of sulfuric acid concentration.

Figure 33. Solubility of SO₂ as a function of sulfuric acid concentration. The temperature is 80°C and the system pressure is 101 kPa.

In general, the solubility of SO₂ decreases as the sulfuric acid concentration increases. This phenomenon may affect the operation of the hybrid sulfur electrolyzer; concentrated sulfuric acid is desired for the thermal decomposition step, but increasing the sulfuric acid concentration in the electrolyzer may lead to mass transfer limitations.

The reversible potential at 101 kPa and 80°C as a function of sulfuric acid concentration is shown in Figure 34.

Figure 34. Reversible potential (U_{eq}) as a function of sulfuric acid concentration. The temperature is 80°C and the system pressure is 101 kPa.

The reversible potential increases as the sulfuric acid concentration increases. Just as the solubility of SO₂ in sulfuric acid may affect the operation of the electrolyzer, the reversible potential may also affect the electrolyzer. Again, concentrated sulfuric acid is desired for the decomposition step, but increased sulfuric acid concentration in the electrolyzer increases the reversible potential via the Nernst equation.

F. Consideration of Voltage Contributions

The thermodynamic analysis performed at SRNL has allowed for the development of an equation to predict the reversible potential as a function of sulfuric acid concentration at 101 kPa and 80°C:

$$U_{eq} = 0.048 \ln[H_2SO_4] + 0.301 \quad [22]$$

where $[H_2SO_4]$ is the concentration of sulfuric acid in mol/liter.⁸⁷

The reversible potential is one component of the cell voltage. The resistance component, as a function of current density and membrane resistance, must be measured at each operating condition. For example, the membrane resistance has been measured at each current density (corresponding to a certain sulfuric acid concentration) and this membrane resistance has been used to determine the iR losses.

The other voltage component is the surface overpotential, and is due to catalyst activity. A relationship between the surface overpotential and the current density has been developed:

$$\eta_s = 0.0382 \ln(i_{\text{H}_2\text{SO}_4}) + 0.300 \quad [23]$$

The three components that make up the cell voltage are thus:

$$V = U_{\text{eq}} + iR + \eta_s \quad [24]$$

The membrane resistivity as a function of sulfuric acid concentration is shown in Fig. 35.

Figure 35. Membrane resistivity as a function of membrane thickness. The cell temperature was 80°C. The points (N212 current interrupt (○), N212 four-point (◇), N115 current interrupt (●)) are experimental data. The lines are current interrupt data corrected for thickness based on N115 data.

The resistivity was measured by the current interrupt method during electrolyzer operation for the N115 membrane. The current interrupt data were then scaled with thickness to obtain resistivity values for N117 and N212.

To confirm the current interrupt data, the resistivity was also measured by the four-point method, in which the membrane was equilibrated with sulfuric acid of different concentrations and the resistivity was measured. The results obtained for the four-point method are only valid for a membrane equilibrated with sulfuric acid; in the operating electrolyzer, the water content of the membrane is not constant throughout the

membrane. Thus, the results obtained from the four-point method have been integrated to obtain an effective resistivity, which is shown in Figure 35.

Now that the voltage contributions can be calculated, an investigation of the individual contributions can be performed. The contributions of the N115 electrolyzer are shown in Figure 36.

Figure 36. Voltage components for N115. The membrane pressure differential was $\Delta P = 600$ kPa and the temperature was 80°C .

As shown in Figure 36, the iR losses (resulting from the increase in membrane resistivity with sulfuric acid concentration) are responsible for the large increase in voltage observed past about 0.5 A/cm^2 . The results indicate that the surface overpotential is about 0.35 V , and can possibly be reduced through development of a more active catalyst, either with novel electrocatalysts or by better utilization using novel supports.

Finally, the model can be used to predict cell voltage. This is shown in Figure 37 for the three membranes investigated here. The model predictions are given by Eq. 24. The empirical relationship between the surface overpotential, η_s , and the current density results in good agreement between the model and the experimental data.

It must be noted that thus far, only an empirical relationship obtained from the data has been used to simulate the surface overpotential, η_s , due to the activity of the catalyst toward SO_2 oxidation. A more detailed analysis requires a more comprehensive evaluation of the Pt catalyst loading (or a novel catalyst) on electrolyzer performance, and is beyond the scope of the work outlined here.

Figure 37. Experimental data (N212 (○), N115 (●) and N117 (◆)) and model predictions (lines) for the polarization curves. The membrane pressure differential was $\Delta P = 600$ kPa and the temperature was 80°C .

A V. Hybrid Sulfur Conclusions

We have developed a mathematical model, in conjunction with experimental data, to predict water transport in a PEM electrolyzer fed with gaseous SO_2 . We predicted the combined effects of diffusion, permeation and electro-osmotic drag, and show how these influence cell performance. We now understand how water transport affects the sulfuric acid concentration, which influences the cell voltage. There is a tradeoff between low voltages (large water transport) and high sulfuric acid concentrations (low water transport) in that a higher sulfuric acid concentration is desired for downstream decomposition, but concentrated sulfuric acid increases the cell voltage and hence the power required to drive the electrolyzer. The model reveals how the water transport rate can be manipulated by independently varying design (e.g., membrane thickness), and operating conditions (e.g., temperature, current, pressure differential). The model also indicates how water transport affects the rate at which SO_2 crosses the membrane. The SO_2 crossover can result in sulfur reduction at the cathode, which modifies the composition of the electrode. It can also introduce SO_2 into the hydrogen stream, and wastes SO_2 that must be replaced in the electrolyzer system. In addition, the model can be combined with a thermodynamic analysis to predict cell voltage, and leads to insight into areas in which performance improvements can be achieved. (i.e., catalyst design). In addition, the significant reduction in conductivity of Nafion membranes in the presence of concentrated sulfuric acid indicates that a different polymer electrolyte membrane is needed in which the conductivity is not adversely affected by concentrated sulfuric acid.

A VI. Model Parameters

A_1, A_2	pre-exponential factors for diffusion coefficient
a_i	activity of species i
C_i	concentration of species i , mol/cm ³
D_i	diffusion coefficient of species i , cm ² /s
E°	standard reduction potential, V
F	Faraday's constant
i	current density, A/cm ²
j	region in electrolyzer
M_M	molecular weight of membrane, g/mol
N_i	flux of species i , mol/cm ² s
P_j	pressure in region j , kPa
ΔP	pressure gradient across the membrane ($P_c - P_a$), kPa
P_M	membrane permeability, mol/(cm s kPa)
R	ideal gas constant, membrane resistivity, Ω -cm
t	time, s
T	temperature, K
x	distance into membrane, cm
U_{eq}	reversible cell potential, V
δ_M	thickness of the catalyst coated membrane, cm
λ	water content of the membrane, mol H ₂ O/mol SO ₃ ⁻
λ_k	water content of the membrane at interface k , mol H ₂ O/mol SO ₃ ⁻
κ	membrane conductivity, S/cm

η_s	surface overpotential, V
ρ_M	density of the membrane, g/cm ³
τ	dimensionless time
ξ	electro-osmotic drag coefficient, H ⁺ /H ₂ O

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