Hybrid Sulfur Electrolyzer Development

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ABSTRACT

The proof of concept of SO2 electrolysis for the hybrid sulfur (HyS) process is the second priority research target of the DOE Nuclear Hydrogen Initiative's thermochemical program for FY07. The proof of concept of the liquid-phase option must be demonstrated at the single cell level for an extended run times (>100 hours). The rate of development of HyS will depend on the identification of a promising membrane or an alternative means for controlling sulfur formation. Once successful long-duration operation has been demonstrated, SRNL will develop a multi-cell stack that can be connected to the H2SO4 decomposer being developed by SNL for the S-I ILS for a Hybrid Sulfur Integrated Laboratory-Scale Experiment during FY 2008.

During the first quarter of FY07, SRNL continued the component development and membrane development activities with the goal of identifying and characterizing improved electrodes, electrocatalysts, membranes and MEA configurations which could then be tested at larger scale in the SDE test facility. A modified glass cell was fabricated to allow measurements of sulfur dioxide (SO2) transport across membrane samples at elevated temperatures (up to 70 °C). This testing also includes evaluating SO2 transport in different sulfuric acid concentrations (30 - 70 wt%). A new potentiostat/frequency analyzer was installed for determining ionic conductivity of membranes. This instrument enhances our capabilities to characterize membrane, electrocatalyst and MEA properties and performance.

Continuing work from FY06, evaluations were preformed on various commercial and experimental membranes and electrocatalyst materials for the SDE. Several different types of commercially-available membranes were analyzed for sulfur dioxide transport as a function of acid strength including perfluorinated sulfonic acid (PFSA), sulfonated poly-etherketone-ketone, and poly-benzimidazole (PBI) membranes. Experimental membranes from the sulfonated diels-alder polyphenylenes (SDAPP) and modified Nafion® 117 were evaluated for SO_2 transport as well. These membranes exhibited reduced transport coefficient for SO_2 transport without the loss in ionic conductivity.

A composite perfluorinated sulfonic acid (PFSA) membrane was received from Giner Electrolchemical. This membrane features deposited platinum within a Nafion 115 membrane. The membrane was tested for SO2 transport and exhibited reduced SO2 transport compared to the unmodified Nafion membrane. It will also be tested for ionic conductivity to determine if the platinization increases ionic conductivity compared to the standard Nafion membrane. SRNL also completed initial testing of an SNL-prepared (Mike Hickner, PI) polyphenylene-based membranes for sulfur dioxide (SO2) transport characteristics. Results in 30 wt% sulfuric acid solutions at ambient laboratory temperature indicates these materials exhibit similar characteristics to those exhibited by the PBI family of membranes. This indicates a substantial reduction in SO2 transport compared to that for the standard Nafion membranes. We recommend further testing of the SDAPP-family of membranes, membranes modified by the incorporation of Pt nano-particles (i.e. Giner membranes) and the SNL membranes. By modifying membranes like new generation of SDAPP with Pt nano-particles we expect to be able to meet the target of SO_2 reduction by a factor of 100 compared with that measured with the PFSA-family of membranes.

Testing of platinum and palladium catalyst activity as the electrocatalyst for the SDE was conducted at different acid concentrations (30 - 70 wt%) and elevated temperatures (20 - 70 °C). Cyclic and linear sweep voltammetry revealed that platinum provided better catalytic activity with much lower potentials and higher currents than palladium. Palladium exhibited poorer catalytic activity and chemical stability than platinum, and, therefore, is not recommended for use as the anode catalyst in the SDE. Testing also showed that the catalyst activity is strongly influenced by concentration of the sulfuric acid. We recommend further testing to determine if binary and ternary alloys of noble and transition metals will provide increased reaction kinetics and good chemical stability in concentrated sulfuric acid solutions. The primary driver for consideration of alloy catalysts is a reduction in capital costs for electrolyzer catalyst.

Various cell configurations were examined with respect to the membrane electrode assembly (MEA) chemistry and preparation. The MEAs tested that did not perform well were analyzed by using scanning electron microscope (SEM). These analyses revealed that the poorly performing MEAs suffered from delamination of the cathode catalyst layer and that sulfur deposited on the hydrogen side of the membrane and catalyst layer.

Modifications were made to the SDE test facility to permit higher temperature operation over a broader range of flow conditions for planned single cell testing. This necessitated changing from the electrolyzer block heaters to an anolyte water jacket heating concept. The design was completed and safety approvals obtained for modification of the water jacket heating system. The necessary new equipment was procured and installed. Checkout testing will be completed late this quarter or in early January.

Tests were performed using the SRNL pressurized electrolyzer test facility on an electrolyzer cell with an MEA comprised of a PBI membrane. Testing was frequently interrupted by electrical shorts in the cell. However, we were able to make two important observations. First, using hydrogen production as an indication, the PBI membrane passed less sulfur dioxide than previous Nafion membranes. Second, the cell potential for the PBI membrane increased significantly with time, possibly indicating a loss of phosphoric acid, a component of the membrane. This may remove PBI as a candidate for the SDE membrane. By contrast, the two best Nafion membranes showed no degradation in performance. Further testing will be performed.

Long term operation of the electrolyzer was prevented in the latter part of the reporting period due to a reoccurring short between the copper anode terminal block and the grounded anode side SS pressure plate. The short is due to a small leak that allows two or three drops of the highly conductive sulfuric acid/SO2 anolyte to bridge through a fiberglass insulator at the gap around the flow connector. This electrolyzer design was used for several months without problems prior to the current series of leaks, which coincided with the replacement of the graphite block backing plate. The replaced graphite block was made from graphite supplied by a different vendor than that of the original block. We now suspect that the leak is either due to slight permeability of the graphite block itself, or to tiny ridges in the surface of the new graphite block where the o-ring seals. We are in the process of both resurfacing the graphite block and redesigning the connector fitting to eliminate the potential leak path.

Subcontract efforts with Giner Electrochemical Systems and Isotron Corporation were initiated and kickoff meetings were held. Giner will assist SRNL in both electrolyzer design/scale-up and in membrane development. Isotron is pursuing a unique electrolyzer design approach that could eliminate SO2 crossover problems.

Dr. William A. Summers, PI, traveled to Johannesburg, South Africa in early October and presented a paper of the Hybrid Sulfur development program at the Third International Topical Meeting on High Temperature Reactor Technology (HTR-2006). Two papers, one on component development results and one on electrolyzer testing, were presented at the Southeastern Regional Meeting of the American Chemical Society in Augusta, Georgia on November 2, 2006. A paper on the HyS development program was also presented at the AIChE 2006 Annual Meeting in San Francisco on November 13-16, 2006. A summary of SRNL development work in 2006 was presented at the NHI Semiannual Program Review in Germantown on October 31 – November 1, 2006.

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LIST OF ACRONYMS

BAS	Bioanalytical Systems
CCE	Catalyst Coated Electrode
CCM	Catalyst Coated Membrane
CV	Cyclic Voltammogram
DI-water	Deionized water
DMFC	Direct Methanol Fuel Cell
EDAX	Energy Dispersive Spectroscopy
EIS	Electrochemical Impedance Spectroscopy
EW	Equivalent Weight
GES	Giner Electrochemical Systems
HyS	Hybrid Sulfur
LSV	Linear Sweep Voltammogram
MEA	Membrane Electrode Assembly
OCP	Open Circuit Potential
OPM	Oxford Performance Materials
PA	Phosphoric acid
PAFC	Phosphoric Acid Fuel Cell
PBI	Poly-Benzimidazole
PEM	Proton Exchange Membrane and Polymer Electrolyte Membrane
PEMFC	Polymer Electrolyte Membrane Fuel Cell
PFSA	Perfluorinated Sulfonic Acid
RT	Room Temperature, 25 °C
SCUREF	South Carolina Universities Research and Education Foundation
SDAPP	Sulfonated Diels-Alder Polyphenylenes
SDE	Sulfur Dioxide-depolarized Electrolyzer
SEM	Scanning Electron Microscopy
SHE	Standard Hydrogen Electrode
SNL	Sandia National Laboratory
SPEK	Sulfonated Poly-Etherketone
SPEKK	Sulfonated Poly-Etherketone-ketone
SRNL	Savannah River National Laboratory
SRS	Savannah River Site

1.0 INTRODUCTION

Water-splitting processes are being developed to provide global-scale quantities of hydrogen by combining electrolysis or thermochemical hydrogen production technologies with advanced nuclear reactors that can deliver high temperature process heat. Thermochemical water splitting cycles, with the greatest effort being given to the sulfur-based cycles, offer a highly efficient route for the production of hydrogen. A variant on sulfur-based thermochemical cycles is the Hybrid Sulfur (HyS) Process, which uses a sulfur dioxide depolarized electrolyzer (SDE) to produce the hydrogen. In FY05, testing at the Savannah River National Laboratory (SRNL) explored the use of a low temperature proton-exchange-membrane design concept for the SDE [1]. The advantages of this design concept include high electrochemical efficiency and small footprint, both of which are crucial for successful implementation on a commercial scale.

The electrolyzer oxidizes sulfur dioxide to form sulfuric acid at the anode [r1] and reduces protons to form hydrogen at the cathode [r2]. The overall electrochemical cell reaction consists of the production of H_2SO_4 and H_2 [r3].

Anode: $SO_2 + 2H_2O \rightarrow H_2SO_4 + 2H^+ + 2e^-$ [r1]
Cathode: $2H^+ + 2e^- \rightarrow H_2$ [r2]

Overall: $SO_2 + 2H_2O \rightarrow H_2SO_4 + H_2$ [r3]

The proof of concept of SO2 electrolysis for the hybrid sulfur (HyS) process is the second priority research target of the DOE Nuclear Hydrogen Initiative's thermochemical program for FY07. Technical options must be better defined and the challenges better understood and the current status of electrolyzer performance established by a long duration run (>100 hours) before a commitment can be made to an ILS demonstration in FY08. Two process options are being explored: gas-phase and liquid-phase SO2 feed. The University of South Carolina is exploring the gas-phase option under a NERI project. Savannah River National Laboratory (SRNL) is pursing the liquid-phase option, which is the main focus of the NHI work under Work Package N-SR07TC301. The SRNL liquid-phase SDE development program is the subject of this report.

The proof of concept of the liquid-phase option must be demonstrated at the single cell level for an extended run times (>100 hours). Additionally, membrane development work will be performed by Sandia National Laboraotry and an industrial partner to address sulfur crossover control. The rate of development of HyS will depend on the identification of a promising membrane or an alternative means for controlling sulfur formation. Once successful long-duration operation has been demonstrated, SRNL will develop a multi-cell stack that can be connected to the H2SO4 decomposer being developed by SNL for the S-I ILS for a Hybrid Sulfur Integrated Laboratory-Scale Experiment during FY 2008.

The research being conducted under NHI Work Package N-SR07TC0301 has been divided into the following major work tasks:

Task 1. Perform single cell electrolyzer development and conduct performance testing.

- 1.1 Conduct component development
- 1.2 Conduct single cell electrolyzer tests
- 1.3 Perform membrane development
- 1.4 Perform 100 hour Longevity tests

Task 2. Perform multi-cell stack electrolyzer design based n expected ILS experiment operating requirements

- 2.1 Prepare multi-cell stack design
- 2.2 Construct multi-cell electrolyzer

Task 3. Determination of critical process chemical and physical properties, including H2O/SO2/H2SO4 mixture properties

Task 4. Project management and reporting

During the first quarter of FY07 efforts were directed primarily at Task 1. Task 2 and Task 3 were initiated near the end of the quarter, and this work will be reported in the second quarter report. Work on Tasks 1.1 and 1.2 during the first quarter is reported in Section 2. Work on Task 1.2 is reported in Section 3. Task 4 is discussed in Section 5.

Subcontract efforts have also been initiated with two commercial companies to provide industrial support for the program. This work is reported in Section 4.

2.0 COMPONENT DEVELOPMENT

Original work on the development of a SDE featured a parallel-plate electrolyzer with a separator or membrane to keep the anolyte and catholyte compartments separate [2]. Since this work was completed in the early 1980s, significant advances have occurred in electrolyzer technology principally in the area of hydrogen fuel cells. Advanced hydrogen fuel cells employ proton conductive membranes with catalyst layers deposited on either side of the membrane, forming the respective anode and cathode of the electrochemical cell. This electrochemical cell type is known as a proton-exchange-membrane (PEM) cell, and the combination of membrane and electrode catalyst layers is referred to as the membrane electrode assembly (MEA).

SRNL has selected the PEM cell and MEA design concept for the SDE in the HyS process [3]. The MEA concept provides a much smaller cell footprint than conventional parallel plate technology. The smaller footprint is a major benefit in scaling the electrolyzer to the size that will be required for commercial production. Key attributes of the SDE are high energy efficiency and long operating lifetime. To achieve high energy efficiency, the electrolyzer must exhibit rapid reaction kinetics at each electrode, little crossover of reagent and products across the membrane, and excellent chemical stability of each of the components to concentrated sulfuric acid solutions.

SRNL established the proof-of-concept of the PEM/MEA cell approach for SDE operation in FY05 using modififed commercially available water electrolyzer cells [1]. A custom-design SDE cell was developed during FY06, and it remains as the primary development approach. During the FY06 HyS Project we focused on identifying electrolyzer component materials and cell configurations that promote high energy efficiency and long operating lifetimes. Specific testing focused on evaluating commercially-available membranes for ionic resistance and sulfur dioxide transport characteristics, evaluating different electrocatalyst materials and evaluating different cell configurations. This work is continuing in FY07.

Task 1.1 of the FY07 HyS Project focused on identifying electrocatalysts and cell configurations that promote high energy efficiency and long operating lifetimes. Task 1.3 focuses on evaluating commercially-available and experimental membranes for ionic resistance and sulfur dioxide transport characteristics at different acid concentrations and temperatures. Each of these tasks is discussed in the following sections.

2.1 Experimental

2.1.1 Membrane Preparation

A list of the tested membranes is shown in Table 1 and Table 2. During the selection process of commercially available and experimental membranes, an array of thicknesses, equivalent weights (EWs), chemistry, and reinforcements were considered. Preparation procedures of the membranes before testing were conducted according to the supplier's recommendations. Commercial membranes include perfluorinated sulfonic acid (PFSA) membranes and nonfluorinated membranes such as Fumatech sulfonated poly-etherketone (SPEK), which were conditioned by washing in 0.5 M H_2SO_4 at 80 ºC for one hour and rinsing in deionized water (DI-water) at 80 ºC for another hour. Once treated, the membranes were stored in water until ready to use. Commercial Poly-benzimidazole type membranes (PBI) from Celtec and sulfonated poly-etherketone-ketone (SPEKK) from Oxford Performance Materials (OPM) were rinsed with DI-water before use.

Table 2 shows the experimental membranes prepared exclusively to reduce the transport of inert species such as dissolved SO_2. The membranes include Sandia National Laboratories (SNL) hydrated sulfonated Diels-Alder polyphenylenes (SDAPP) and Giner Electrochemical Systems (GES) hydrated platinized Nafion® 117. These membranes were used as received.

Table 1. Commercial Membranes

ID	Manufacturer	Classification	Thickness (mm)	Equivalent Weight (g/eq.)
Nafion® 117	DuPont	PFSA	180	1100
Nafion® 112	DuPont	PFSA	50	1100
F-1460	Fumatech	PFSA	60	1400
Celtec-V	PEMEAS	PBI with immobilize electrolyte	50	----
Celtec-L	PEMEAS	PBI	50	----
FKB	Fumatech	PEK	80	----
OXPEKK	OPM	SPEK	25	N/A
E-750	Fumatech	SPEK	50	700

Table 2. Experimental Membranes

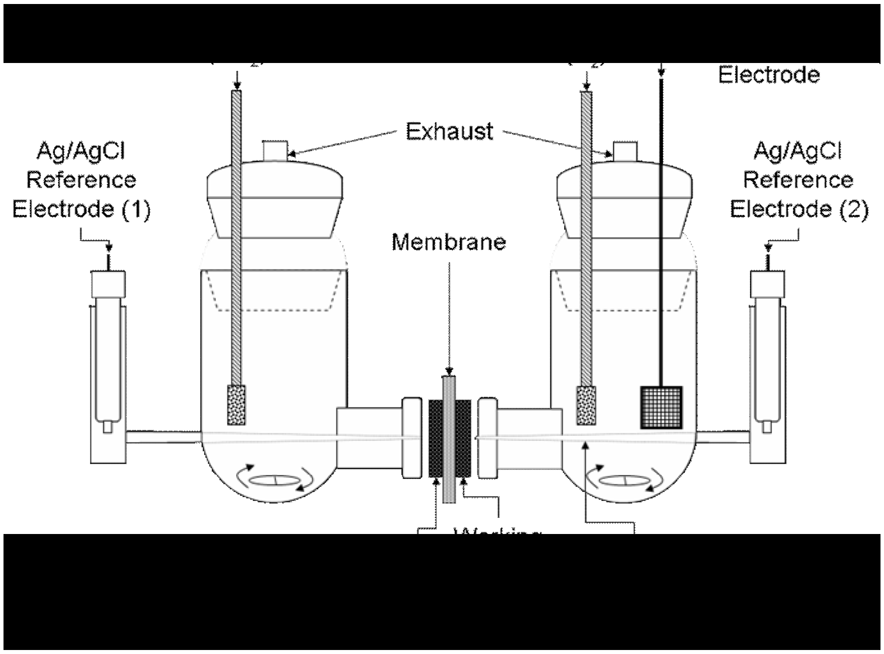
ID	Manufacturer	Classification	Thickness (mm)	Equivalent Weight (g/eq.)
Platinized	GES	PFSA	180	1100

Nafion® 117				
SDAPP-2.2	SNL	SDAPP	50	N/A
SDAPP-1t	SNL	SDAPP	25	N/A
SDAPP-4t	SNL	SDAPP	50	N/A
SDAPP-1.6	SNL	SDAPP	76	N/A

2.1.2 Membrane Characterization

The membrane ionic resistivity and SO_2 transport were evaluated using a custom made permeation cell; a schematic of the cell is shown in Figure 1. The cell consists of two glass chambers joined by a Teflon™ bridge where the membrane is secured. During measurements both chambers were filled with the concentrated acid of interest and purged of oxygen by flowing nitrogen. A three electrode system, which included a silver-silver chloride reference electrode (Ag/AgCl, 196 mV vs. standard hydrogen electrode (SHE)), a platinum flag as the counter electrode, and a platinum mesh as the working electrode, was used during measurements.

[redacted]



[redacted]

Figure 1. Simplified schematic of the membrane characterization cell

The Electrochemical Impedance Spectroscopy (EIS) technique was used to evaluate the ionic resistivity (ρ) as a function of acid concentration. For this measurement, the working electrode and reference electrode were placed in position (1). After allowing several minutes for the membrane to equilibrate in the sulfuric acid solution, a 10 mV vs. OCP (open circuit potential) sinusoidal voltage was imposed across the membrane at frequencies between 100 kHz and 200 Hz. The resulting response was plotted in the form of Nyquist plots. The resistance was calculated from the value of the real impedance when the imaginary response is zero. The resistivity was calculated with the following equation,

$$r = \frac{Z_{real} A}{L} \qquad \text{[eq1]}$$

where 'L' is the thickness of the membrane, 'A' is the area available for proton conduction, and 'Z_{real}' is the real part of the impedance response when the imaginary impedance is zero. A potentiostat/frequency analyzer from Gamry was used for this measurement.

The SO_2 transport was monitored by measuring the current as a function of time while a constant potential is applied. For the SO_2 transport, the reference and working electrodes were rearranged in position (2). The cell was filled with 30 wt% or 50 wt% H_2SO_4 and purged with N_2. A constant potential of 1040 mV vs. SHE was applied on the working electrode while the current was measured as a function of time. Once the background current became close to zero, the flowing of SO_2 was started on the left chamber. The SO_2 permeating through the membrane was oxidized to sulfuric acid by the working electrode. A Bioanalytical Systems (BAS) B/W electrochemical analyzer was used to measure the current responses as a function of time.

2.1.3 Catalyst Characterization

The catalyst activity and stability was evaluated using the three-electrode cell shown in Figure 2. The cell consists of a glass vial with a Teflon cap and a water jacket. The three electrodes, which included a silver-silver chloride reference electrode, a platinum wire as the counter electrode, and a glassy carbon disk electrode, were inserted through the Teflon cap. Catalysts were deposited onto the glass carbon disk electrode by spraying suspensions of the catalyst onto the electrode. Catalyst materials tested included platinum (Pt) and palladium (Pd).

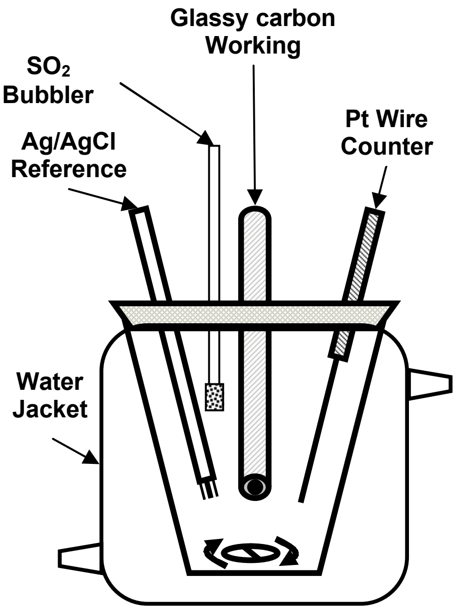


Figure 2. Simplified schematic of the catalyst characterization cell

During measurements the vial was filled with concentrated acid and purged of oxygen by flowing nitrogen. The catalyst's electrochemical characterization consisted of cyclic voltammograms (CVs) in the solution purged with nitrogen and linear sweep voltammograms (LSVs) in SO_2 saturated sulfuric acid solutions. The CVs were performed at a scan rate of 50 mV/sec and in a potential window between 1004 mV and -100 mV vs. Ag/AgCl. The LSVs were performed in the potential window between 804 mV and 104 mV vs. Ag/AgCl at a scan rate of 5 mV/sec. The experiments were carried out at temperatures ranging from 30 ºC up to 60 ºC and at different acid concentrations. The curves were repeated until a stable performance was obtained. Both measurements were performed starting from the anodic potential and going in the cathodic direction.

2.2 Results and Discussions

2.2.1 Membrane development - Sulfur Dioxide Transport

In a perfectly efficient SDE, all of the SO_2 is oxidized to sulfuric acid [r1]. In practice, the cell is not 100% efficient and some of the SO_2 migrates from the anolyte side through the membrane into the catholyte side of the cell. Migration of the neutral SO_2 species largely arises by diffusion driven by the concentration gradient from the anolyte to the catholyte. Upon reaching the cathode, SO_2 can be reduced to produce sulfur and sulfides. Reduction of the SO_2 decreases the electrical efficiency of the cell. The SO_2 transport to the cathode not only affects the purity of the hydrogen being produced, but the long term effects of these impurities incorporated in the membrane, cathode catalyst, or diffusion layer are not yet known.

Thus, a separator with high ionic conductivity, low minimal SO_2 transport, and long term stability is needed. The current design for the SDE is based on a polymer electrolyte membrane fuel cell (PEMFC). The Nafion® family of perfluorinated sulfonic acid membranes is an attractive candidate membrane due to its relatively high ionic conductivity and chemical stability in strong acid solutions. However, previous testing indicated fairly high SO_2 transport across this membrane to the cathode.

A review of the literature revealed a number of commercially available membranes that may be suitable for use in the SDE. Table 1 provides the list of commercial membranes that were selected for testing the SO_2 transport. The first group of membranes selected was the PFSA family membranes which have been developed for PEM fuel cells for operation at low temperatures (80 °C). The properties of the PFSA type membrane with an equivalent weight (EW) of 1100 is considered in this work as the baseline to which all other membranes were compared.

Membranes developed for Direct Methanol Fuel Cells (DMFC) such as SPEKK and SPEK are studied in this work due to their improved properties to reduce the crossover of methanol and their ability to operate at higher temperatures (up to 140 °C). Finally membranes originally developed for Phosphoric Acid Fuel Cells (PAFC) from the PBI family were selected for their ability to operate at temperatures up to 200 °C under dry conditions. Unlike the sulfonated type of membranes (PFSA, SPEKK or SPEK) that employ sulfonic acid groups to transport hydrated protons, these PBI membranes employ a hopping mechanism in which immobilized anions (such as PA) act as proton solvents and provide a path for rapid proton exchange. As a result, protons are conducted without the creation of water channels that transport water and other inert molecules.

Table 2 provides the list of experimental membranes that are being develop to decrease the transport of neutral species such as SO_2. The first membrane consists of the use of platinum nano-particles embedded in the pores of a Nafion® 117 membrane to reduce the transport of neutral species. A similar approach has been considered for the development of methanol-blocking membranes without adverse effects on the proton conductivity [4]. The other set of membranes consist of SDAPP which provide a good proton conductivity with reduced water transport.

The permeation rate of SO_2 species through the membranes was monitored by an electrochemical technique (see experimental section). The flux profile contains three distinct regions. Initially, the currents are flat indicating that the system is building up SO_2 concentration in the chamber and membrane. As SO_2 passes through the membrane, it is oxidized by the working electrode resulting in a measurable permeation. The permeation current increases with time until steady-state conditions (i.e., third region) are reached and no change in the flux is observed. By assuming that all SO_2 transported reacts according to [r1] we can obtain the SO_2 flux, J_{SO_2}, from the electrical response using Faraday's Law,

$$J_{SO_2} = \frac{i}{nF} \qquad \text{[eq2]}$$

where '*i*' is the current density in A/cm^2, '*F*' is Faraday's constant (96,487 C/eq.), and '*n*' is the number of electrons transferred.

The effect of the acid concentration on the SO_2 flux through the commercial membrane samples is observed in Figure 3. At low acid concentration, the SO_2 transport is highest (see Figure 3a) and decreases when the acid concentration is increased from 30 wt% to 50 wt% (see Figure 3b). This behavior can be explained by the change in water concentration on the polymer matrix. At low acid concentrations the membrane hydration level is higher, as a result the polymer swells increasing the polymer pore diameter. As the acid concentration increases, the hydration level of the polymer decreases causing the polymer matrix and the pores to shrink. The shrinkage of the pores results in smaller channels that reduce the amount of inert species permeating through the water channels. Although beneficial in reducing the SO_2 transport, the decrease in water also affects the proton transport resulting in a decrease in ionic conductivity. Such decrease in ionic conductivity as a function of acid concentration has been observed by Junginger et al. [5].

The dependence on the thickness on membranes with same polymer chemistry can be observed in the figure by comparing the flux through Nafion® 112 (N112) and Nafion® 117 (N117). As expected, N112 exhibited the highest flux followed by N117, which follows the order of thickness for the Nafion® membranes (see Table 1). The concentration of sulfonic acid groups (i.e., equivalent weight) in the membrane also affects the transport of sulfur dioxide. As observed above, when the membranes hydrate, especially PFSA polymers, water binds to the ionic groups to produce a fully separate phase with concentrated ionic domains. This domain contains channels where neutral species that dissolve in water can diffuse. As a consequence, a membrane with the same thickness but higher EW will transport less SO_2 than a material with lower EW as the number of domains is decreased. The effect of the amount of conductive groups on the flux can be observed by comparing Nafion® 112 (EW= 1100 g/eq) and F-1460 (1400 g/eq). For the PFSA type membranes, the lowest flux is observed for F-1460 and followed by Nafion® 117 (which the decrease in transport is attributed to the increase in thickness).

The polymer backbone can also affect the SO_2-transport characteristics of the polymer. For example, polymers from the polyether ketone (PEK and SPEK) and polybenzimidazole (PBI) families exhibited much lower SO_2 transport than those from the PFSA family. We attribute the reduced SO_2-flux to the stiffer backbones of the PEK and PBI polymers, which prevent phase separation and formation of ionic acid domains [6]. Among the membranes tested, OXPEKK showed the lowest flux followed closely by the FKB and Celtec-L membranes.

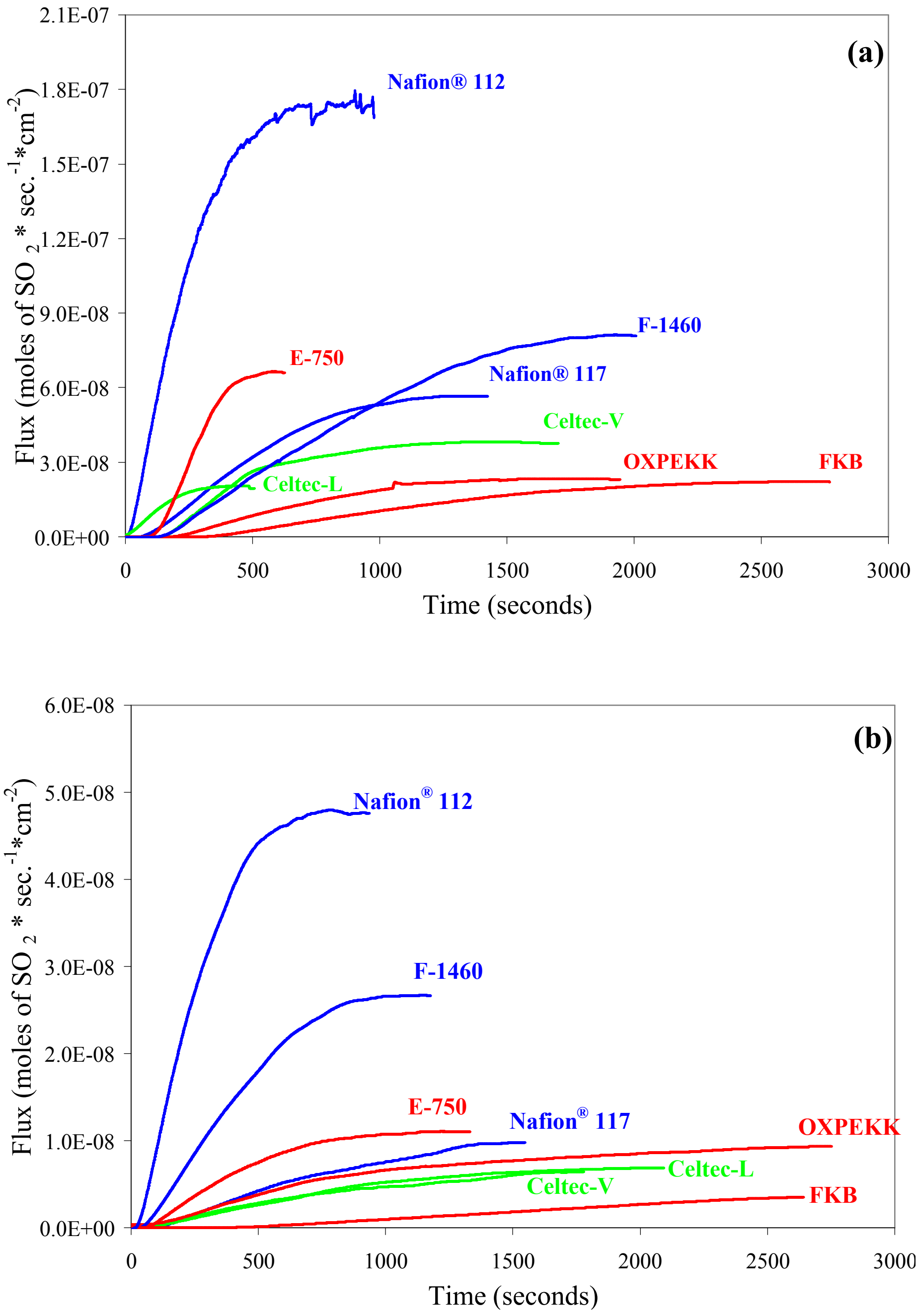


Figure 3. **SO_2 transport through commercial membranes immersed in (a) 30 wt% and (b) 50 wt% H_2SO_4 saturated with SO_2 at room temperature. Working electrode set at 1040 mV vs. SHE**

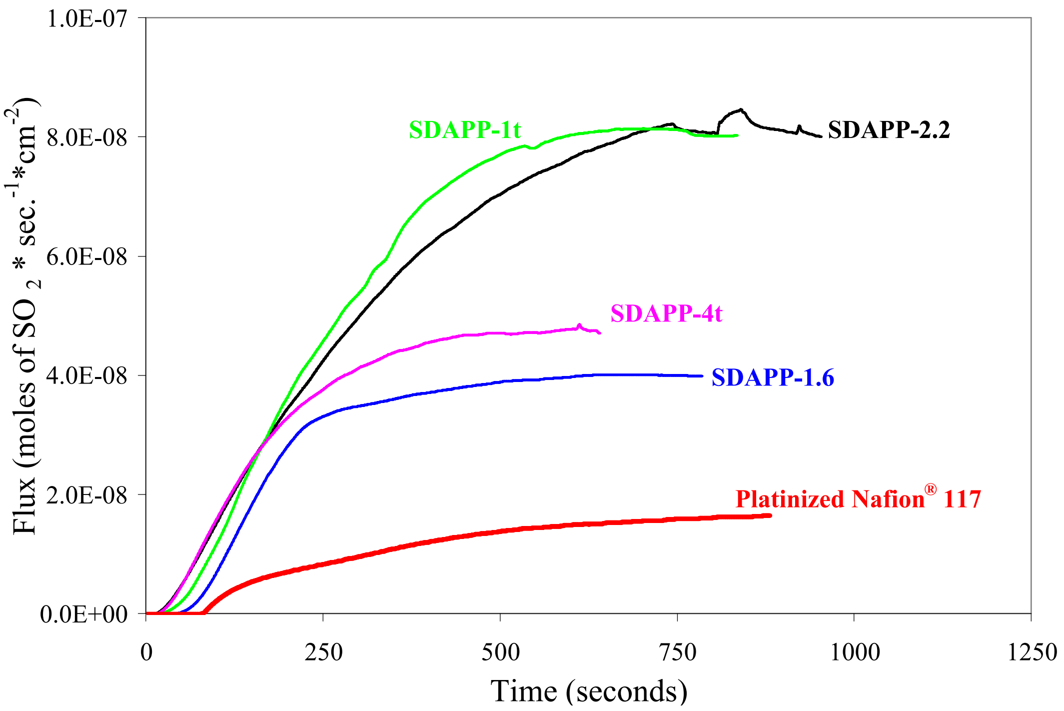


Figure 4: SO_2 transport through experimental membranes immersed in 30 wt% H_2SO_4 saturated with SO_2 at room temperature. Working electrode set at 1040 mV vs. SHE

SNL provided four sulfonated polyphenylene-based membranes (SDAPP) that feature a very strong polymer backbone and good conductivity. GES provided a platinized-PFSA membrane for evaluation that features a Nafion® 117 membrane embedded with Pt nano-particles in the membrane pores. SO_2-transport characteristics of these experimental membranes are plotted in Figure 4.

The SO_2 flux, J_{SO_2}, through a membrane can be described by the modified Fick's law of diffusion, where the thickness, '*L*', of the membrane and the transport coefficient, '*D*', will play an important role on the flux. At steady state conditions and assuming that all SO_2 transported through the membrane is oxidized at the membrane surface, Fick's first law of diffusion can be simplified and used to calculate '*D*',

$$J_{SO_2} = \frac{DC_0}{L} \qquad \text{[eq3]}$$

where 'C_0' is the bulk concentration of SO_2 (estimated value 1.09 M in 30 wt% H_2SO_4 and 0.9523 M in 50 wt% H_2SO_4) and '*L*' is the thickness of the membrane.

Table 3 provides a summary of the measured SO_2 transport coefficient for all the commercial and experimental membranes. Transport coefficients were determined for the commercial membranes in both 30 and 50 wt% H_2SO_4. Transport coefficients for the experimental membranes have been determined only in 30 wt% H_2SO_4 at this time.

As discussed previously, we observed that the SO_2 transport coefficients of the commercial membranes decreased by a factor of between 2 and 5 times upon an increase in the sulfuric acid concentration from 30 wt% to 50 wt%. In general, the lower the equivalent weight of the polymer, the greater the effect of H_2SO_4 concentration on the SO_2 transport coefficient.

Interestingly, the platinized-Nafion® 117 membrane exhibited a SO_2 transport coefficient at about a factor of three lower than the un-modified Nafion® 117 membrane. We will continue to evaluate the characteristics of platinized Nafion® membranes to determine if further reduction in SO_2 transport can be realized without loss in ionic conductivity and overall performance of the membrane in the SDE.

Initial results with the SDAPP family of experimental membranes indicate lower SO_2 transport compared to the PFSA class of membranes. In general, the SDAPP membranses are comparable to the PBI membranes in SO_2 transport. Thus, these membranes are attractive candidates for further development for use in the SDE.

Table 3: SO_2 transport coefficient through the tested membranes immersed in 30 wt% and 50 wt% H_2SO_4 saturated with SO_2 at room temperature. Working electrode set at 1040 mV vs. SHE.

	Transport Coefficient (cm^2/s)	
Membrane	**30 wt. % H_2SO_4**	**50 wt. % H_2SO_4**
Nafion® 117	9.33E-07	1.85E-07
F-1460	4.45E-07	1.67E-07
Celtec-V	6.76E-07	3.44E-07
Celtec-L	7.24E-07	2.30E-07
OXPEKK	5.28E-08	2.46E-08
FKB	1.61E-07	2.94E-08
E-750	3.03E-07	5.77E-08
SDAPP-2.2	3.85E-07	-----
SDAPP-1t	3.68E-07	-----
SDAPP-4t	1.11E-07	-----
SDAPP-1.6	2.79E-07	-----
Platinized Nafion® 117	2.71E-07	-----

2.2.2 Catalyst Characterization

Selecting the right catalyst will have an impact on the electrical efficiency by allowing the SDE to operate at conditions closer to the reversible potential (0.17 V vs. SHE) and will have an influence in helping achieve a long-term stable performance. Two types of catalysts will be needed, one for the anode and one for the cathode. At the cathode, the electrochemical reaction [r2] occurs at higher rates than reaction [r1] and at the reversible potential of 0 V vs. SHE. The current catalyst of choice for both electrodes is platinum supported on carbon.

Compared to the cathode, the kinetics of the electrochemical oxidation of SO_2 at the anode are very slow. Consequently, most of the inefficiencies of the electrolyzer arise from the low kinetics for reaction [r1]. Furthermore, this anode catalyst is subject to a harsher chemical environment (concentrated H_2SO_4 solutions) compared to the cathode. Chemical stability of the catalyst is an important attribute in order to develop an electrolyzer with high operational lifetime. Thus, we undertook an examination of the role of the electrocatalyst to identify a more active and stable anode catalyst.

Catalyst activity and stability was evaluated using cyclic voltammetry (CV) using the electrochemical cell shown in Figure 2. In a CV experiment a potential on the working electrode containing the catalyst is applied momentarily and the current measured. The potential is then changed by a small amount and a new current measured. This is continued until the potential is swept through a range of potentials reflecting both anodic and cathodic conditions. Increased catalytic activity is noted by increased current.

Information as to the stability of the catalyst derives from repeated CV scans. Stable electrocatalysts exhibit no change in the oxidation and reduction currents after repeated CV scans. Unstable electrocatalysts will exhibit reduced oxidation and reduction currents after repeated CV scans. Figure 5 shows the typical consecutive CVs for Pt supported on carbon (Pt/C, 45 wt% Pt) and Pd supported on carbon (Pd/C, 40 wt% Pd) measured at room temperature in 30 wt% H_2SO_4 and in the absence of SO_2.

The high potential peak shows the monolayer oxide formation-reduction of the catalyst layer in 30 wt% H_2SO_4 is observed at around 0.75 V vs. SHE for Pd and 0.8 V vs. SHE for Pt. As the acid concentration is increased, the peak intensity for the oxide formation decreases indicating the formation of oxides is more limited. The low potential peak in the potential region between 0.24 and 0.1 V vs. SHE corresponds to the hydrogen adsorption-desorption on the catalyst surface. Contrary to the metal oxidation peak at high potentials, as the acid strength increases the intensity of the hydrogen adsorption-desorption peak increases.

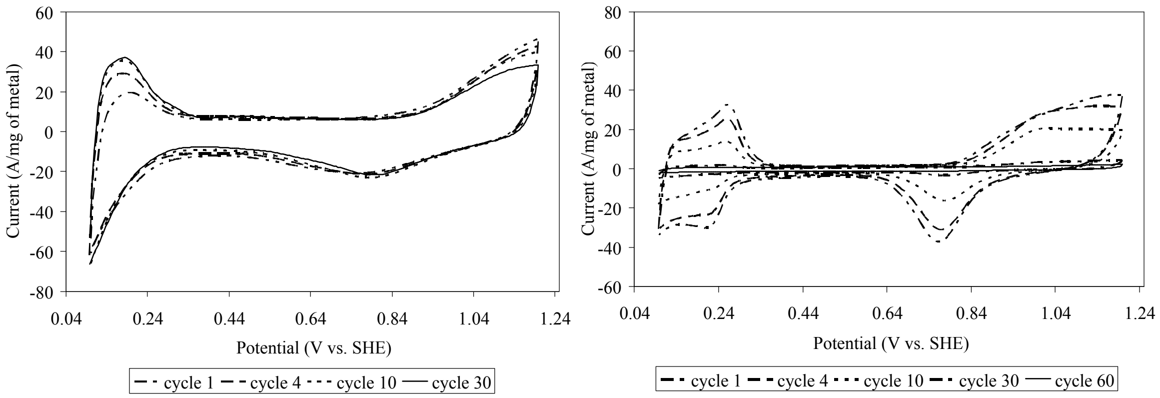
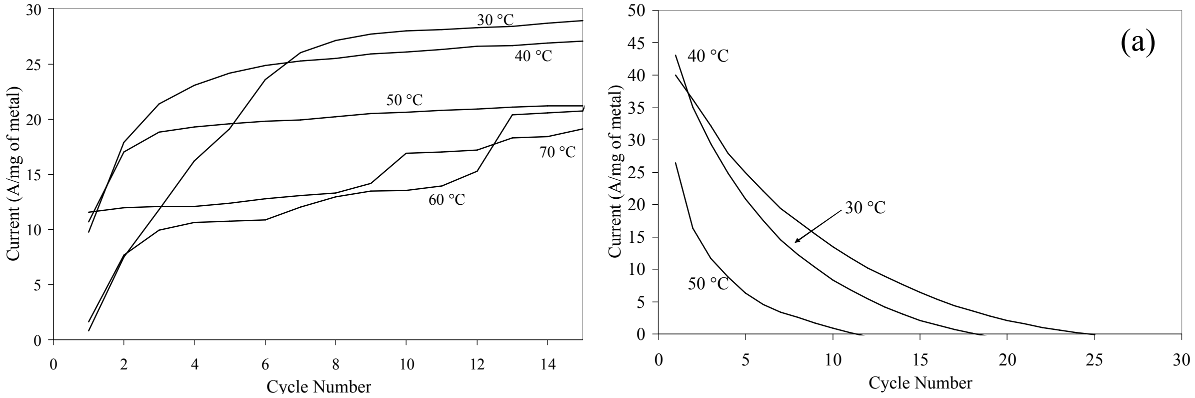


Figure 5. Typical cyclic voltammograms after consecutive cycling for Pt/C (left) and Pd/C (right) in 30 wt% with N_2 at room temperature.

In general, the area under the hydrogen adsorption-desorption peak gives an idea of the electrochemically active surface area available for reaction. A reduction in the surface area indicates that the metal particles are either agglomerating on the carbon surface or the metal catalyst is not stable in the solution and is dissolving. The difference in the hydrogen desorption peak height after consecutive cycling is shown in Figure 6.

In the case of the Pt/C catalyst, the peak tends to increases until it stabilizes. This initial increase corresponds to the initial wetting by the electrolyte of the catalyst surface. For the Pt case, the hydrogen adsorption peak is highest at low temperatures and decreases as temperature increases.

In the case of Pd the surface area tends to decrease with each cycle until no peaks are observed. The degradation of the Pd catalyst is enhanced by temperature and acid strength, therefore making it impossible to get reliable data for the Pd catalyst at temperatures higher than 50 ºC.



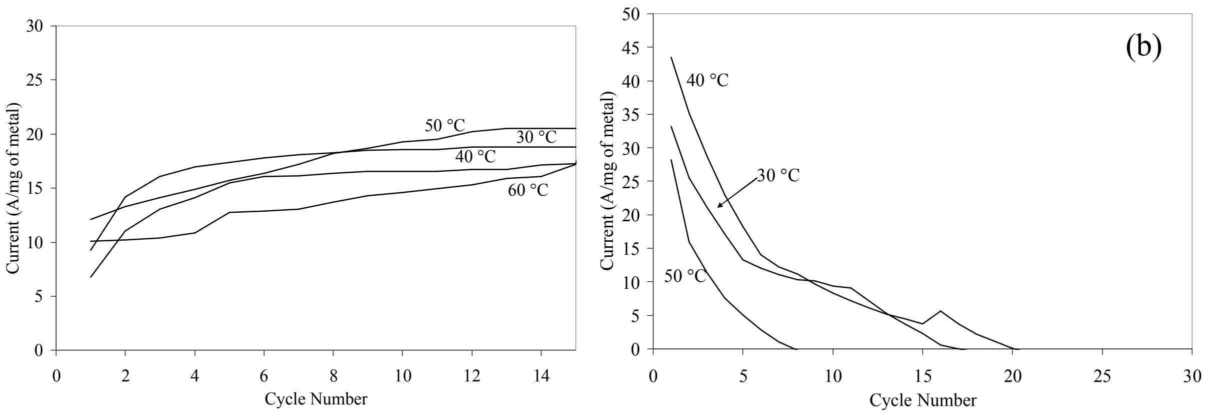
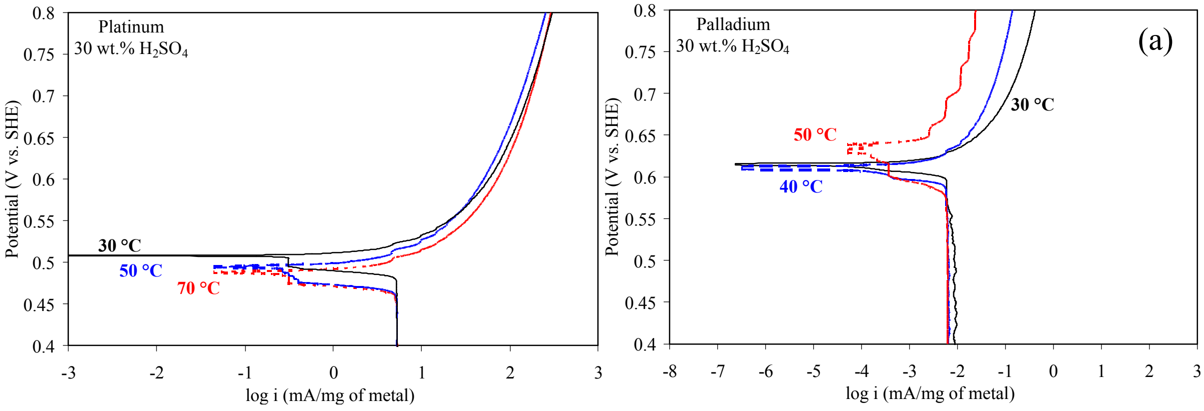


Figure 6. Hydrogen desorption peak height after consecutive cycling (see Figure 5) for Pt/C (left) and Pd/C (right) in (a) 30 wt% and (b) 50 wt% H_2SO_4 purged with N_2 at room temperature.

The electrocatalytic activity of the Pt/C and Pd/C catalysts was also investigated for the oxidation of SO_2 in sulfuric acid solutions and at different temperatures. The potential-current relationship is shown in Figure 7 in the form of Tafel plots. It can be seen from the plots how the open circuit voltage increases as the acid strength increases; for example for Pt/C and Pd/C at 30 wt% H_2SO_4 at room temperature a potential of 0.50 V and 0.59 V vs. SHE is observed while a potential of 0.56 V and 0.66 V vs. SHE in 50 wt% H_2SO_4 respectively.

The improvement in the SO_2 oxidation kinetics upon an increase in temperature is readily observed by the change in open circuit potential and the change in the Tafel slope. In the case of Pt, as the temperature increases the open circuit potential decreases. In the case of Pd the same is true at temperatures below 40 ºC. Once the system approaches 50 ºC, the deterioration of the Pd catalyst is so great that the activity drops drastically. In view of the kinetic results, we conclude that the Pt catalyst is superior to that of the Pd catalyst. It is also apparent that the use of acid concentrations higher than 50 wt% H_2SO_4 will decrease the SDE power efficiency by increasing the SO_2 oxidation overvoltage.



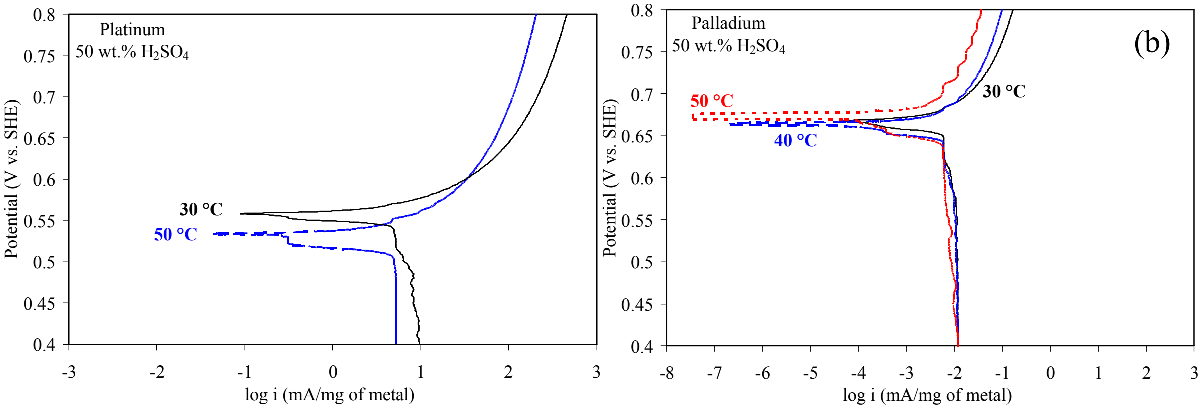


Figure 7. Tafel plots for SO_2 oxidation on Pt/C (left) and Pd/C (right) in (a) 30 wt% and (b) 50 wt% H_2SO_4 saturated with SO_2 at different temperatures.

Figure 8 shows the Arrhenius plots used to calculate the Arrhenius activation energy, 'E_a', for the oxidation of SO_2. The graphs were prepared by plotting the logarithm of the exchange current density, 'log i_o', which was obtained from the Tafel plots versus the inverse of temperature, 1/T. In the case of Pt, the plot results in two parallel lines where the linear slope corresponds to the activation energy as described by the formula at the top of Figure 8. In the case of Pd, the plots result in two intersecting lines. This result suggests that Pd dissolution occurs resulting in reduced exchange current density. Note also, that Pd requires at least twice the activation energy of Pt for the oxidation of SO_2. Thus, we conclude that Pt is a superior material to Pd as an elctrocatalyst

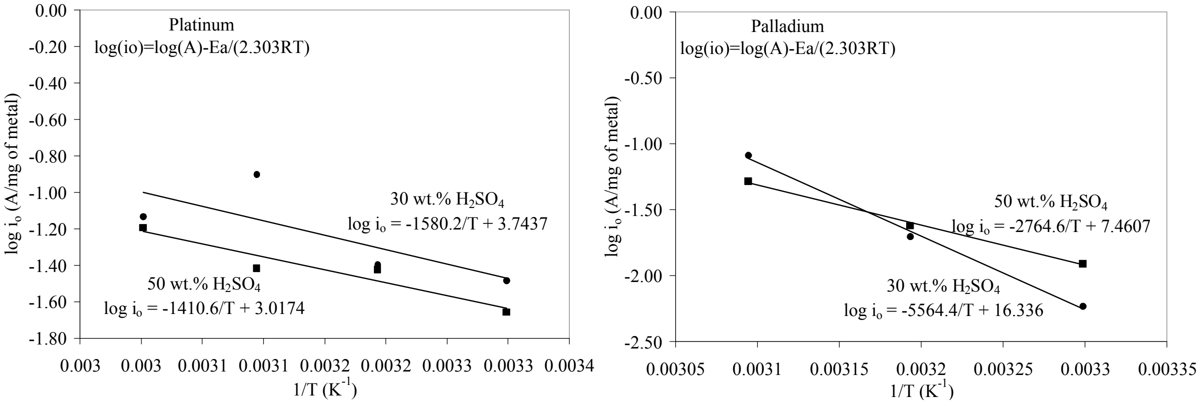


Figure 8. Arrhenius plots for SO_2 oxidation on Pt/C (left) and Pd/C (right) in 30 wt% and 50 wt% H_2SO_4 saturated with SO_2 at different temperatures.

2.2.3 Cell Design

An important factor in the development of a successful SDE is the way the individual components are incorporated. An improper assembly will lead to an electrolyzer with high electrical inefficiencies. The simplest electrolyzer design will consist of three basic components. Figure 9 (a) shows a simplified schematic of the basic units in the SDE. Starting on both extremes the flow fields are encountered. The flow field's role is to collect the electrons and to allow easy access of the reactants and products to all parts of the electrolyzer. The flow field will also play an important role in the heat management in order to avoid hot or cold spots.

Next to the flow fields is the diffusion medium. The diffusion medium is one of the most critical components in achieving good performance in the SDE; its duties include current collector, transport media and support for the catalyst layers. Generally the diffusion media consists of two layers. The first layer, or the backbone of the diffusion layer, consists of a conductive paper or cloth that provides structural integrity and macro-pores to aid in the diffusion of reactants and products. The second layer or micro-porous layer refines the surface of the first layer by using a thin smooth carbon layer that decreases the contact resistance between the catalyst layer and the first layer while allowing the diffusion of species in and out of the catalyst layer.

The micro-porous layer finds its use in gas phase feeds; however when the reactants are liquid the micro-porous layer adds a mass transfer resistances to the system. In the heart of the electrolyzer the MEA is found. The MEA consists of a membrane coated with a catalyst layer on both sides. Figure 9 (b) shows a scanning electron microscope (SEM) image of an MEA. The catalyst layer composition consists of the catalyst powder bonded with solid electrolyte. The solid electrolyte can be either of the same MEA membrane material or any other electrolyte with high ionic conductivity and high reactant diffusivity. According to the results in sections 4.1 and 4.2 Nafion® shows the desired properties for the catalyst layer binder/electrolyte.

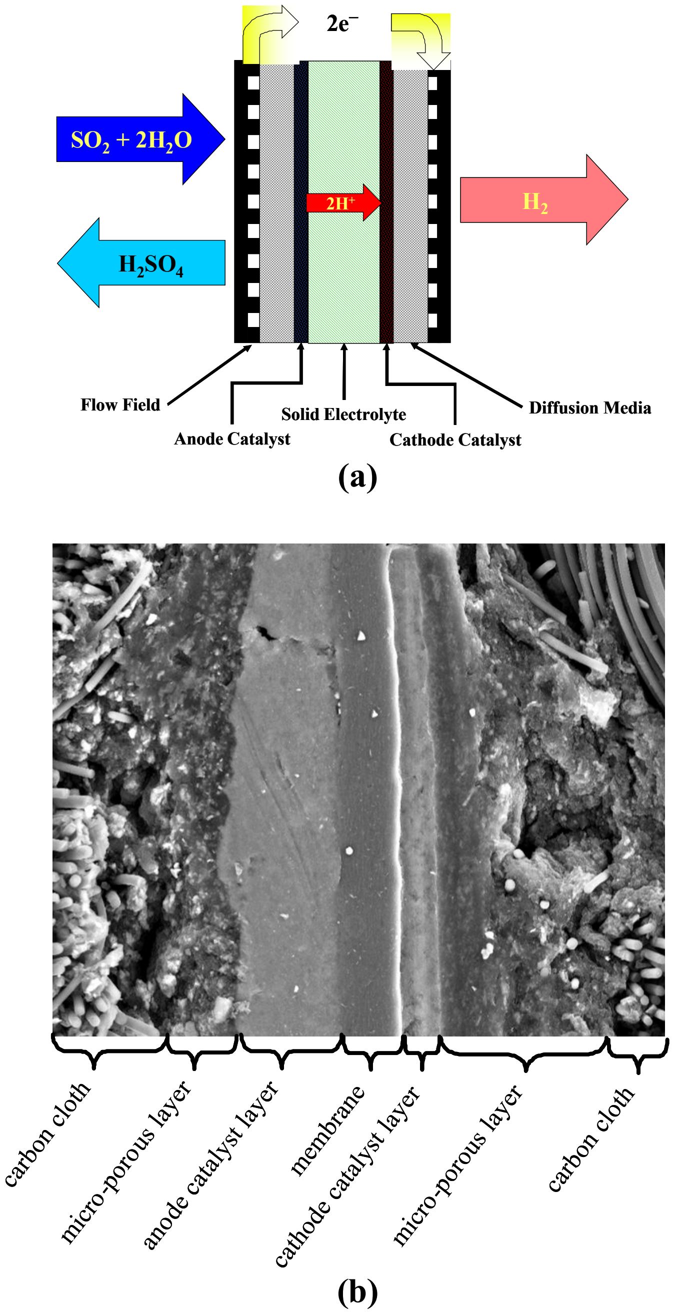


Figure 9. Simplified schematic of the SDE and the processes taking place (a) and SEM image of the MEA (b).

For the MEA to have a maximum catalyst utilization and minimal contact resistance, the catalyst layer must be bonded to the membrane. There are two current methods used to create this bond, which are referred to as catalyst coated electrode (CCE) and catalyst coated membrane (CCM). For the CCE preparation, a catalyst ink (catalyst powder, liquid polymer electrolyte and solvent) is deposited on the micro-porous layer of the diffusion layer. After allowing the ink to dry, the electrode is bonded on to the membrane using a heated press.

The CCE process requires the use of a diffusion layer with a micro-porous layer, which reduces the flexibility of the diffusion layers that can be studied. Because of the way the MEA is prepared by the CCE method, the catalyst layer is more strongly bonded to the diffusion layer than to the membrane. In systems where the reactants are liquid and the membrane tends to swell, delamination of the catalyst layer tends to occur.

In the CCM preparation method, the catalyst ink is deposited directly onto the membrane. This method allows for a wider variety of diffusion layers with or without the micro-porous layer. Usually the catalyst layer deposited with this method tends to be more compact, the catalyst utilization is higher, and the catalyst layer is bonded more strongly to the membrane.

The general descriptions of the MEAs prepared during this task are listed on Table 4. A total of five different types of MEAs were prepared. The 1st type was considered as the baseline and its design was identical to that used in a PEM fuel cell. The MEA was prepared using the CCE method by which N115 membrane was heat pressed with the catalyst layer (Nafion and Pt/C) loaded on the carbon cloth's micro-porous layer.

After observing performance deterioration and catalyst delamination, the 2nd MEA was prepared by the CCM method. The 2nd MEA design was an improvement of the first according to the feed back received from the testing engineers. On the 2nd design, the amount of catalyst was increased and the catalyst layer (Nafion and Pt/C) was deposited directly on N117, a thicker membrane. This design showed improvement in the performance of the SDE, however the performance deteriorated due to some operation problems.

The 3rd MEA design was a repeat of the 2nd MEA with the only difference being a slightly higher catalyst loading. The performance and stability were improved. In the 4th MEA the catalyst loading was decreased from 1.4 mg of Pt/cm^2 to 0.88 mg of Pt/cm^2. No loss in performance was observed. This fourth MEA showed a great improvement in performance and stability from the 1st and 2nd MEA tested.

The 5th MEA was prepared according to the method of the 4th MEA substituting a Celtec-L membrane for the Nafion® 117. The 6th MEA consist of 2 Celtec-L membranes, each coated on one side only. The 7th MEA was similar to that of the 5th MEA except we used a Celtec-V membrane in place of the Celtec-4 membrane. Catalyst loadings were also lower. The 8th MEA was prepared according to the method of the 4th MEA substituting the thinner Nafion® 115 membrane for Nafion® 117 and with lower catalyst loadings.

Table 4. Description of the prepared MEAs

MEA Number	Preparation Procedure	Membrane Type	Anode Loading (mg of Pt/cm^2)	Cathode Loading (mg of Pt/cm^2)
1	CCE/carbon cloth with micro-porous layer	Nafion® 115	0.68	0.65
2	CCM	Nafion® 117	1.1	1.1
3	CCM	Nafion® 117	1.4	1.3
4	CCM	Nafion® 117	0.9	1.0

5	CCM	Celtec-L	1.0	1.2
6	CCM	2 x Celtec-L	2.2	1.5
7	CCM	Celtec-V	0.8	0.8
8	CCM	Nafion® 115	0.8	0.6

MEAs #1 and #6 inititally performed well in the SDE. However, after a few hours both of these MEAs exhibited much degraded performance. Post SDE testing, we analyzed cross-sections of these MEAs by scanning electron microscopy (SEM) to identify changes that could be correlated to the degraded performance.

Figure 10 provides SEM images and sulfur content within each region of the two MEAs. MEA #1 consists of a Nafion® membrane heat bonded to micro-porous layers coated with Pt catalyst. We observed no change in the anode side of this MEA. On the cathode side, there is a large increase in the sulfur content (24%) compared to that in the membrane and anode catalyst layer (3%). The increased sulfur content is attributed to formation of elemental sulfur due to the chemical reduction of SO_2 by H_2 that is being produced at the cathode side. Also, we observed delamination of the cathode catalyst layer from the membrane, which is evident by the dark regions at the membrane and cathode catalyst interface. .We believe the delamination of the cathode catalyst layer is the principle cause for the degradation in performance of this MEA since delamination would increase the resistance across the MEA resulting in an increase cell potential to maintain a constant cell current.

MEA #6 featured two Celtec-L membranes each coated with catalyst only one side. The two membranes were then assembled in the SDE such that the catalyst coated surfaces faced outward. MEA #6 also exhibited delamination of the cathode catalyst layer as evidence by the dark region between the membrane and cathode catalyst layer. We believe the delamination was caused by the weak bond between the catalyst layer and the membrane. The preparation of all MEAs included hot pressing at 140 ºC to bond the catalyst layers to the membrane. This temperature is adequate for MEAs constructed with Nafion® membranes as the glass transition temperature (T_g) of this membrane is ~120 ºC. PBI polymers have a much higher T_g of about 400 ºC. Thus, the hot press temperature we used to prepare this MEA, is likely not optimal to ensure a good bond between the catalyst layer and the membrane.

There was increased sulfur concentration in the cathode catalyst layer compared to the membrane which is consistent with the formation of elemental sulfur. Note that the amount of sulfur in the catalyst layer of MEA #6 is much lower than that in MEA #1. This finding is consistent with previous tests that indicate PBI-based membranes exhibit reduced SO_2 transport compared to Nafion®-based membranes. Note also the appearance of some deposit in the region in between the two membranes, which contains a slightly elevated sulfur level. The formation of the deposit between the two membranes also likely contributed to the increased cell voltage in the SDE..

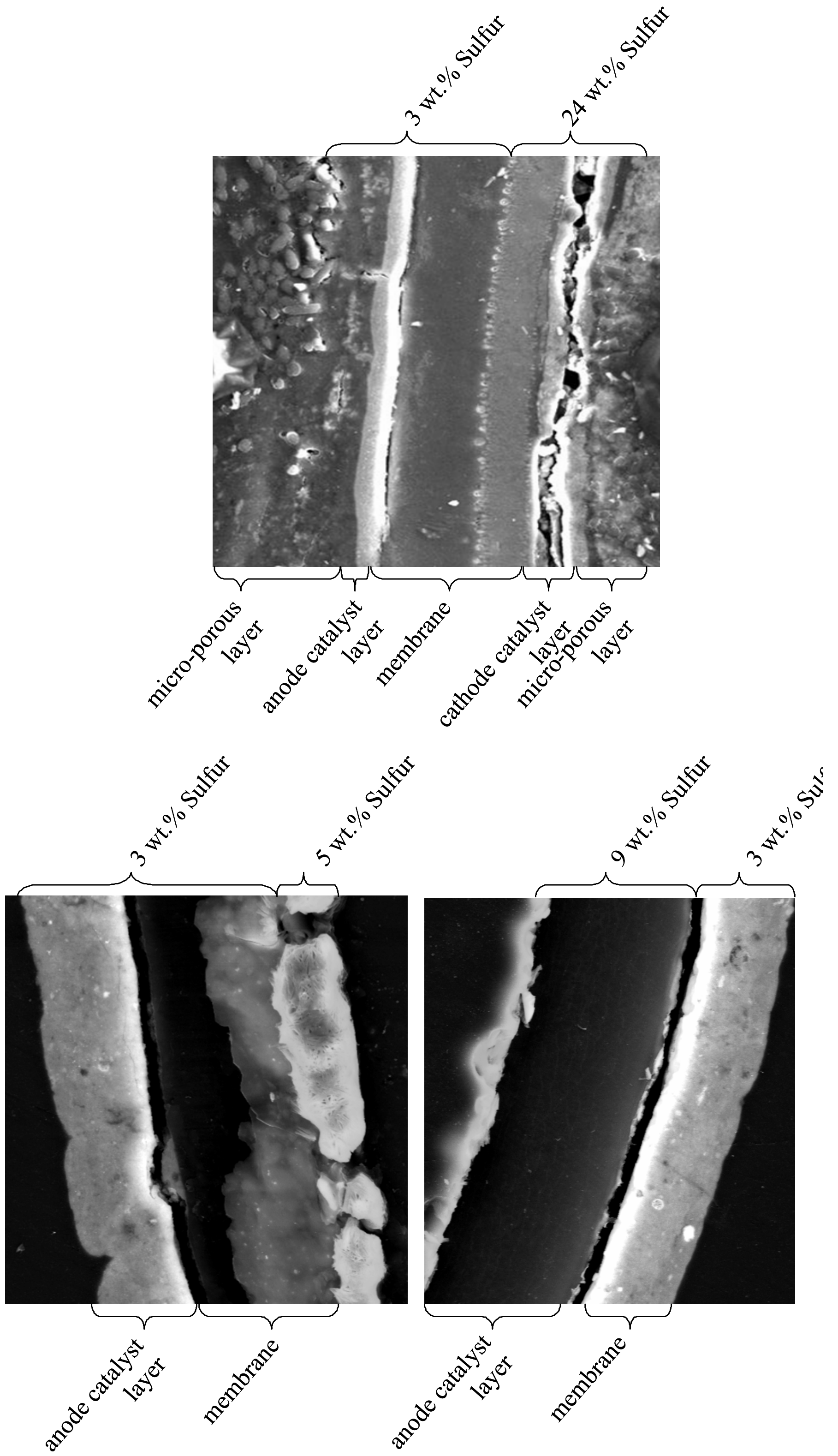


Figure 10. Back-scattering SEM image for 1st MEA (top) and 6th MEA (bottom)

2.3 Conclusions

Several different types of commercially-available membranes were analyzed for sulfur dioxide transport as a function of acid strength including perfluorinated sulfonic acid (PFSA), sulfonated poly-etherketone-ketone, and poly-benzimidazole (PBI) membranes. Experimental membranes from the sulfonated diels-alder polyphenylenes (SDAPP) and a platinized-Nafion® 117 were evaluated for SO_2 transport as well. These membranes exhibited reduced transport coefficient for SO_2 transport without a loss in ionic conductivity. We recommend further testing of the SDAPP-family of membranes as well as membranes modified by the incorporation of Pt nano-particles.

Testing examined the activity and stability of platinum and palladium as electrocatalysts for the SDE in sulfuric acid solutions. Cyclic and linear sweep voltammetry revealed that platinum provided better catalytic activity with much lower potentials and higher currents than palladium. Testing also showed that the catalyst activity is strongly influenced by concentration of the sulfuric acid. We recommend further testing to determine if binary and ternary alloys of noble and transition metals will provide increased reaction kinetics and good chemical stability in concentrated sulfuric acid solutions.

In consideration of possible cell configurations and the results from membrane and electrocatalyst testing, we prepared 8 different MEAs for testing in the 50-cm^2 electrolyzer. Preparation of these MEAs explored the effects of catalyst loading, membrane type, and preparation procedure. Post-test analysis of the two MEAs showed sulfur deposits on the cathode side of the MEA and delamination of the cathode catalyst layer. We attribute the predominant cause for the loss in performance of these MEAs is a result of delamination of the cathode catalyst layer.

3.0 SINGLE CELL TESTING

Task 1.2 of the FY07 HyS program consists of continuation of single cell electrolyzer tests with liquid electrolyte. Initial proof-of-concept tests were conducted on a PEM/MEA type SDE in FY05 using a modified commercial water electrolyzer operating at room temperature and atmospheric pressure. During FY06, the electrolyzer test facility was modified to permit operation at conditions of temperatures up to 70 °C and pressures to 6 bar (90 psia). A single cell electrolyzer was also designed and constructed to meet the specific requirements of liquid anolyte sulfur-dioxide depolarized operation.

During the first quarter of FY07, SRNL continued testing a sulfur dioxide depolarized electrolyzer cell in support of the Hybrid Sulfur Program. The cell has a proton exchange membrane (PEM), against which is pressed an anode, a cathode and flow fields. A sulfuric acid solution saturated with sulfur dioxide is pumped past the anode and hydrogen is generated at the cathode. Prior to the first quarter of FY 2007 testing has been almost exclusively with Nafion 117 membranes. Nafion, which is a fluorocarbon produced by DuPont Corporation and used extensively in PEM fuel cells, has the advantages that it is durable, well characterized and its performance does not degrade during testing. It has the disadvantages that it passes a significant amount of sulfur dioxide from the anode to the cathode, and it has a higher ionic resistance than desired. Sulfur dioxide reacts with product hydrogen at the cathode to form elemental sulfur, which must be periodically flushed from the cell. The relatively high ionic resistance of Nafion makes it more difficult to achieve our target cell voltage of 600 mV at a current density equal to 500 mA/cm^2.

Component development efforts conducted under tasks 1.1 and 1.3 (reported above) indicated that polybenzimidizole (PBI) membranes have both lower sulfur dioxide permeability and lower ionic resistance than Nafion 117. Therefore, in the first quarter of FY 2007 we tested MEA #7, which used a PBI membrane. The anode, cathode and flow fields were the same as for the Nafion membranes. Testing with the PBI membrane was frequently interrupted by electrical shorts in the cell caused by internal acid leaks (discussed in more detail below). This shorts/leaks seem to be unrelated to the PBI membrane. We made two important observations concerning the use of the PBI membrane in the electrolyzer cell. First, at least initially, the cell potential for the PBI membrane was significantly less than for Nafion membranes, as predicted. Second, the cell potential for the PBI membrane increased significantly with time. By contrast, the two best Nafion membranes showed no degradation in performance. The degradation of performance of the PBI cell may be related to a loss of phosphoric acid (a component of the membrane). Unless the degradation can be prevented, it will probably remove PBI from further consideration as a preferred SDE membrane.

Figure 11 compares the cell voltages for a Nafion membrane (MEA #4) and a fresh PBI membrane (MEA #7) for ambient conditions and approximately 30 wt% sulfuric acid. For the current density range of most interest, the PBI cell voltage is 200 mV less, which was very encouraging. However, Figure 12 shows the degradation in performance of the PBI membrane with time at ambient conditions. The final data on the plot represent only about thirty hours of running time. The observed rate of degradation is unacceptable.

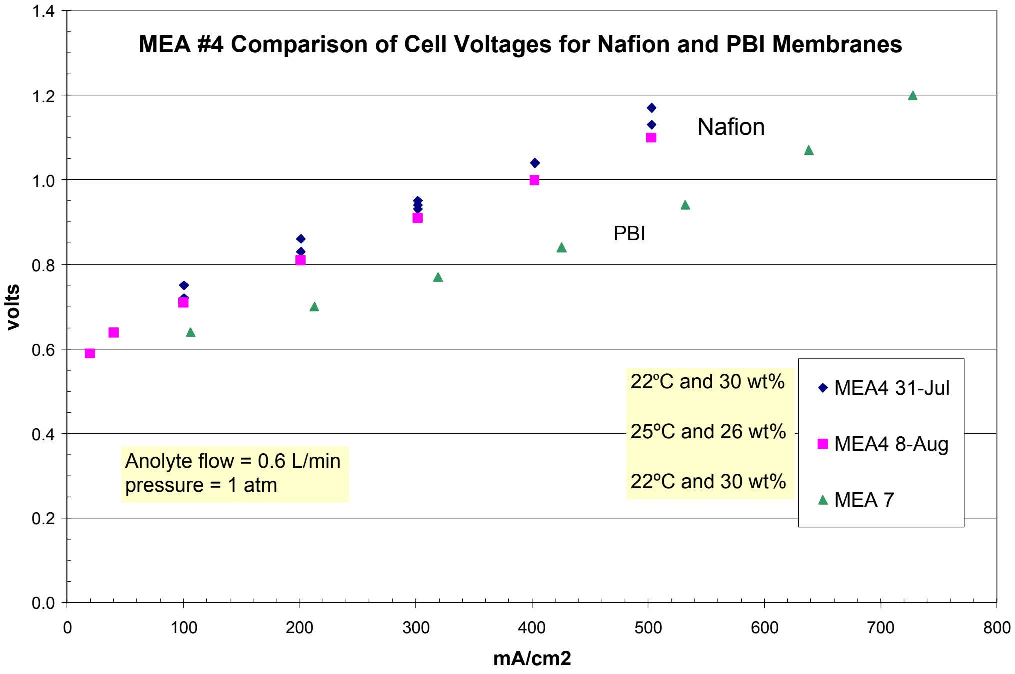


Figure 11. Comparison of PBI and Nafion MEA performance

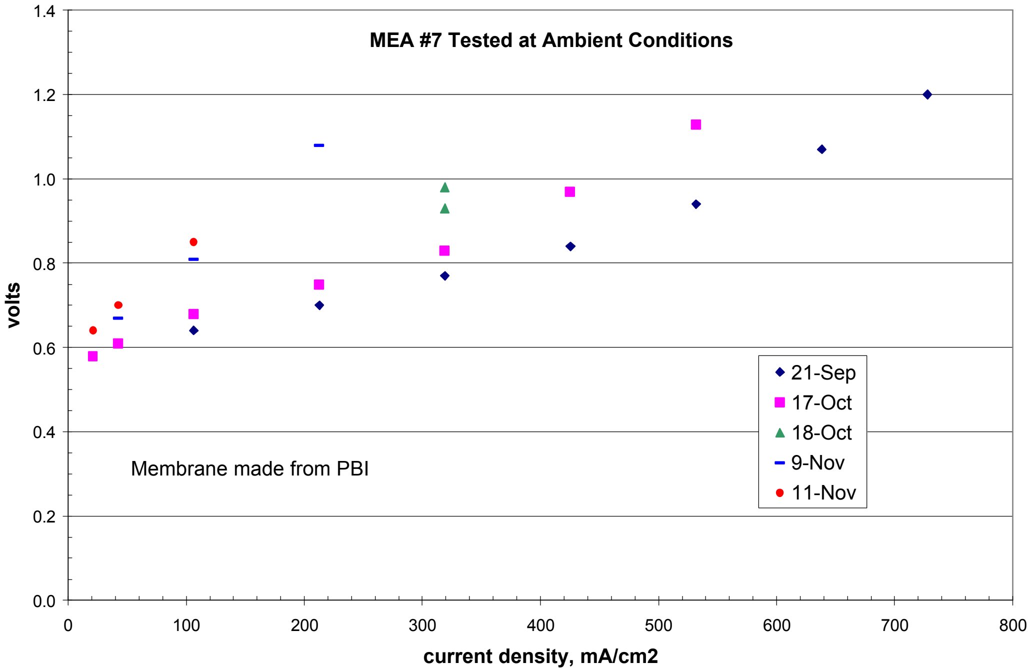


Figure 12. Degradation of Performance for PBI Membrane

During this Quarter, electrolyzer testing has been interrupted repeatedly by a recurrent short between the copper anode terminal block and the grounded anode side stainless steel pressure plate. See Figure 13. A small leak allows two or three drops of highly conductive anolyte to bridge through a fiberglass insulator at the gap around the flow connector. Sometimes the short occurs immediately upon installation, other times several hours after testing. This electrolyzer design was used for several months without problems prior to this Quarter.

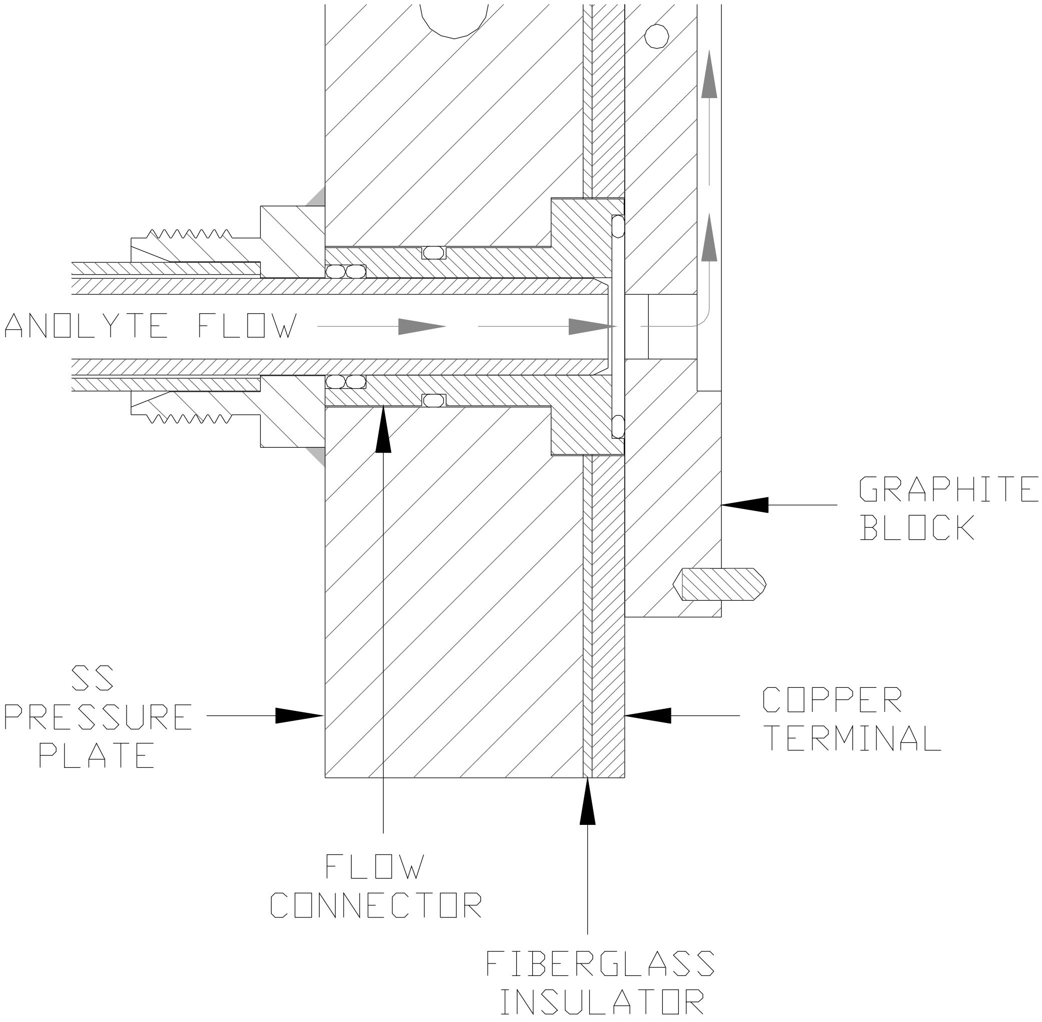


Figure 13. Side View of Electrolyzer Cell

When the first short occurred and the leak was identified, two small cracks observed in the graphite block were thought to be the cause. The block was replaced, but the leak and short reoccurred during subsequent testing. We have examined the new block with a microscope without finding any cracks. Several modifications (shown above) were made to the flow connector during attempts to eliminate this leak. The groove for the o-ring that seals to the anolyte tubing was lengthened and double o-rings were installed. An additional o-ring was installed to seal the flow connector to the stainless steel pressure plate. A thin spacer was installed between the shoulder of the flow connector and the pressure plate to remove all clearance between the flow connector and the graphite block, resulting in additional compression of the face-seal o-ring. None of these modifications have eliminated the leak.

The replaced graphite block was made from graphite supplied by a different vendor than that of the original block. We now suspect that the leak is either due to slight permeability of the graphite block itself, or to tiny ridges in the surface of the new graphite block where the o-ring seals. Both blocks were furnished by the vendors with ground surfaces, but the finish on the new graphite is not quite as smooth as the original. We plan to resurface the graphite block to eliminate the ridges.

We will also replace the fiberglass insulator with a thicker polycarbonate insulator that is o-ring sealed to longer flow connectors as shown in Figure 14. This design change should eliminate leaks as a source of electrical shorts and will permit the resumption of testing. Even if a small leak occurs with this new configuration, the anolyte can not bridge through the insulator to reach the pressure plate and cause a short. This should change a small leak to only a nuisance, not a major problem. In addition, we plan to set up a separate test with a piece of graphite from the two vendors to see if there is a permeability issue that needs to be addressed in future multi-cell stack designs.

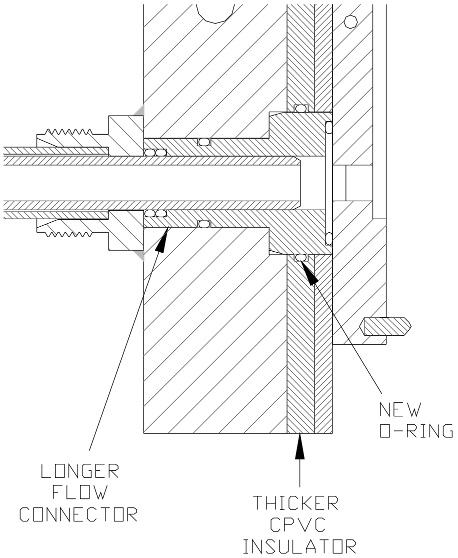


Figure 14. Side View of Electrolyzer Cell Showing Modifications

4.0 INDUSTRIAL SUPPORT

During FY06, SRNL conducted a search for industrial support in the area of electrolyzer design and manufacture. One large corporation, General Electric, proposed to become a major partner and provide cost-sharing in SDE development. Unfortunately, changes in corporate structure and strategic direction resulted in General Electric withdrawing from this proposed project. However, the efforts to seek industrial partners did result in two smaller R&D companies offering to participate in the research effort. At the end of FY06, SRNL placed subcontracts with Giner Electrochemical Systems (Newton, MA) and Isotron Corporation (Seattle, WA). Work with these industrial subcontractors was initiated during the first quarter of FY07.

Giner will assist SRNL in both electrolyzer design/scale-up and in membrane development. Isotron is pursuing a unique electrolyzer design approach that could eliminate SO2 crossover problems. Kickoff meetings were held with each company, and the progress in the 1Q are reported below.

4.1 Giner Subcontract Support

A subcontract has been placed to Giner Electrochemical Systems, LLC (Giner) to provide electrolyzer and membrane development to support the Hybrid Sulfur Program. Larry Gestaut and Tim Norman of Giner traveled to the SRNL facilities in order to participate in a program kick-off meeting. Discussions included the current status of the SRNL system design, the anticipated range of design operating conditions and testing of cell membranes. As a result of the meeting, a path forward was laid out with included the exchange of information between Giner and SRNL. SRNL was to provide the design conditions for the operation of the cell and membrane samples for evaluation. Giner agreed to provide alternative membranes for SRNL evaluation, a review of the SRNL design and testing of the provided SRNL membrane samples. Additionally, Giner will continue to support the design and testing of the single cell electrolyzer and multicell stack.

In the period after the kickoff meeting Giner has processed three membranes for evaluation at SRNL. These included:

A. One treated (platinized) Nafion 117 membrane for SO_2 crossover evaluation
B. Two Nafion 117 MEA's with different catalyst formulations for evaluation on SRNL's electrolysis cell.

The membranes have been received by SRNL and are being prepared for testing. In addition, SRNL is supplying samples of membranes to Giner for testing. Testing will involve mechanical stability and other property tests. SRNL is currently in the process of providing the membrane samples.

Giner is also consulting with SRNL on cell design and multi-cell stack development. SRNL provided drawings of the current electrolyzer design to Giner for the purpose of reviewing against their designs and experience. Giner engineers reviewed and then reported on their design assessment of the SRNL single cell test cell. Several comments regarded materials of construction and flow distribution recommendations. A concern was raised with whether adequate flow distribution will be achieved across the membrane. SRNL shared this concern and has been addressing this issue through the use of a computational hydraulic model to optimize the geometry of the system to maximize the flow distribution. The results of the modeling effort (developed under a different SRNL project) will be incorporated into the design of the electrolyzer.

Multi-cell designs used in the fuel cell and water electrolyzer industry are being evaluated to provide insight into the layout of the multi-cell stack. Early discussions with Giner centered on the issue of whether to use a mono-polar or bipolar design. The concern is the conductivity of the working fluid will require a mono-polar design. Giner has begun a preliminary design effort of a cell stack using their standard high pressure water electrolyzer as a starting point. Such a derivative design will require the identification of a suitable thermoplastic and metal for the anode compartment. They will run several samples of prospective materials of construction in SO_2 saturated sulfuric acid. Following literature searches, this testing will be the second level screen of potential construction materials before a detail design/fabrication effort is started. It does appear that Giner's polysulfone frame material and typical water electrolyzer metals of titanium, niobium, and zirconium are problematic. Giner has also identified a means by which a three cell SDE stack can be operated in a bipolar mode. This will require that each of the three cells is individually fed reactant and product fluids. The SRNL set-up must then provide fluid breaks in these fluid lines external of the Giner stack. Giner intends to present a preliminary design review meeting with SRNL participation by the end of January.

Giner also prepared a white paper describing the advantages of a gas diffusion electrode for the hybrid-sulfur electrolyzer cell under development at SRNL, and a potential three phase program to develop such a cell design. The gas diffusion electrode (or a liquid SO_2 variant of the concept) promises to decouple the sulfur dioxide depolarization from the PEM membrane, significantly decreasing cross-over issues. SRNL plans to review the proposed concept both from the standpoint of cell performance and overall HyS system performance. The baseline Giner concept would require pure gaseous SO2 feed to the electrolyzer, similar to the feed used by Dr. John Weidner in his gaseous SDE research. Since current HyS process flowsheets are based on absorbing SO2 in sulfuric acid as a means of purifying the oxygen product from the process, it is unknown what impact on plant efficiency would result for a flowsheet producing pure gaseous SO2. This is being evaluated under some related contracts in conjunction with Dr. Weidner, and the result of that work will be used to help evaluate the Giner gas diffusion electrode approach.

4.2 Isotron Subcontract Support

Isotron Corporation of Seattle, WA was granted a small subcontract to perform proof-of-concept evaluations of a novel approach that promises to minimize or eliminate sulfur dioxide crossover by unique electrochemical cell design. Isotron will develop a FEMLAB model of the design, perform optimization simulations, and modify the model for revised design approaches. If simulations establish the feasibility of the concept, Isotron will develop a test plan for follow-on Phase II development, including a detailed outline of proposed test configurations. The basic approach proposed by Isotron is described below.

4.2.1 Isotron Proposed MEA Concept

There are several possible solutions to SO2 crossover. The principal focus of SRNL's development efforts has been polymer engineering to reduce the solubility and/or mobility of SO2 in the proton exchange membrane. In the context of fuel cells, this approach is essential for conventional PEM fuel cell designs, where the catalyst is incorporated directly into the membrane itself, and fuel must necessarily contact the membrane.

Another remedy, not possible with conventional PEM-based fuel cell designs, is to reduce the concentration of fuel in the solution on the anode side of the membrane to near-zero. In this way, there would be no fuel present to diffuse, and having a proton-selective membrane would therefore be unnecessary. Returning to the present application, this ideal scenario would mean an electrolyzer could in fact be operated in serial flow-through mode, with only one inlet and one outlet, without fear of deactivating the cathode. Such a scenario is only possible if a) SO2 feed concentration is small, b) flow rate is small, or c) the anode contains a very large specific surface area. The latter alternative is preferred. Figure 15 is a schematic illustrating how a highly reactive flow-through electrode could prevent SO2 crossover. SO2 is fully reacted at the high surface area flow-through anode, resulting in an SO2-free feed to the cathode. Other configurations are possible, including a "flow-by" mode and a "flow-by" anode with a "flow-through" cathode.

High surface area electrodes have further advantages, over and above a potential to reduce or eliminate SO2 crossover. The most significant of these advantages is the ability to provide a very large current from a comparatively small electrode. In the present context, this implies that, for a given desired H2 output (measured in amps of current), the current *density* within the electrode is significantly smaller, and the required polarization is correspondingly reduced. Unfortunately, electrodes with high specific surface area are often marked by impeded mass transfer due to the tortuosity of most porous electrode materials.

Neah Power Systems of Bothell, WA has developed an innovative direct methanol fuel cell electrode design which has a high specific surface area (50-100 cm2/cm2) and near-zero tortuosity. Developed to eliminate methanol crossover and enhance cell power density, Neah's patented technology leverages well-established, silicon processing methods, employing anisotropic etching of crystalline silicon to create parallel pores through the silicon wafer. Neah coats each pore's interior with a conductive material, followed by a catalyst.

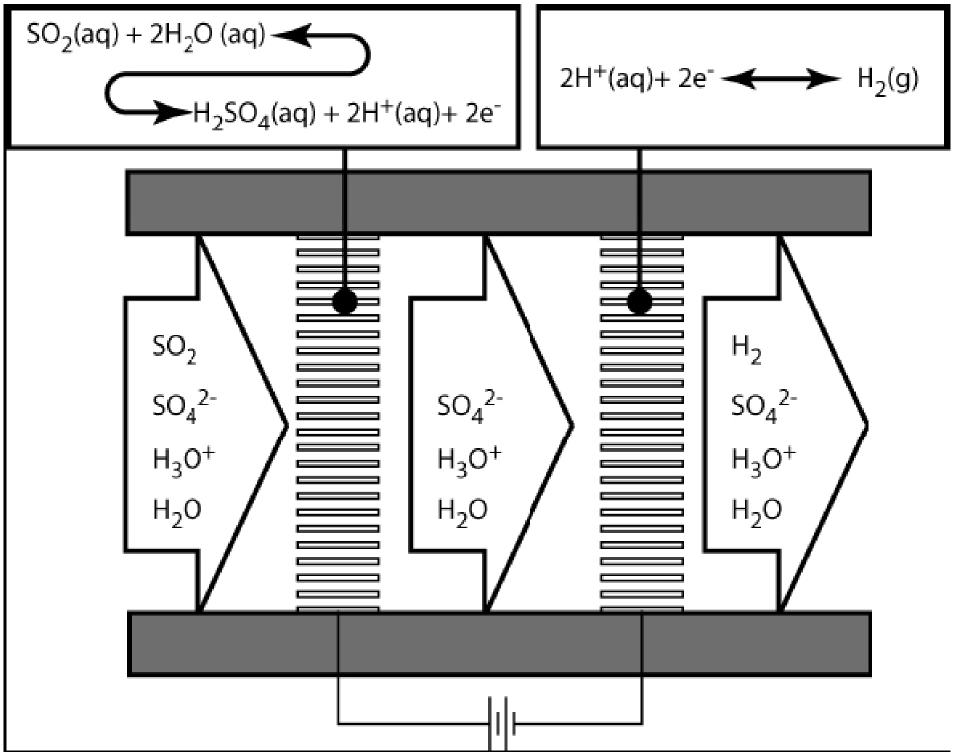


Figure 15. Isotron-proposed highly reactive flow-through electrode for SDE

Isotron, in conjunction with Neah Power, will develop a cell design model and evaluate the use of the high-surface area silicon electrode for SDE operation. A telecon kickoff discussion was held between SRNL and Isotron, and the design work was initiated this quarter.

5.0 PROJECT MANAGEMENT

Dr. William A. Summers, PI, traveled to Johannesburg, South Africa in early October and presented a paper of the Hybrid Sulfur development program at the Third International Topical Meeting on High Temperature Reactor Technology (HTR-2006). This trip also included meeting with PBMR and other organizations in South Africa who are interested in the Hybrid Sulfur Process as the hydrogen production technology for use with the Pebble Bed Modular Reactor. Visits where also made to the PBMR test and research facilities and to the North-West University.

Two papers, one on component development results (Dr. Hector Colon-Mercado) and one on electrolyzer testing (Dr. John Steimke), were presented at the Southeastern Regional Meeting of the American Chemical Society in Augusta, Georgia on November 2, 2006. A paper on the HyS development program (Dr. John Steimke) was also presented at the AIChE 2006 Annual Meeting in San Francisco on November 13-16, 2006. A summary of SRNL development work in 2006 was presented (Dr. William A. Summers) at the NHI Semiannual Program Review in Germantown on October 31 – November 1, 2006.

The overall budget for this project is planned at $1,400,000, which includes an FY06 carryover of $200,000 for the two industrial subcontracts. Spending during the first two months of FY07 totaled $104,265. Total spending for the first quarter will be available in early January. Since the NHI program is being funded under a continuing resolution, the final spendout plan has not been finalized. However, unless there are significant changes, we expect to be on track to utilize the current budget and meet all project milestone and deliverables.

6.0 FUTURE WORK

During the second quarter, work will continue on Task 1.1 (Component Development) and Task 1.3 (Membrane Development). The major milestones for these efforts include selection of the membrane for longevity testing (due 2/20/07) and the assembly of the MEA for longevity testing (due 3/21/07). Other work will include continued membrane characterization for the SNL, Giner, and other candidates and evaluation of improved electrocatalysts, including binary and ternary compounds.

A major milestone for Task 1.2, Single Cell Testing, is the completion of single cell test system development (due 1/15/07) and the preparation of a deliverable report entitled “Design and Performance Objectives of the Single Cell Test System for SO2 Depolarized Electrolyzer Development (due 1/15/07). We plan to complete single cell tests by the end of the second quarter in order to prepare for the longevity testing.

Task 1.4, Longevity Testing, was initiated near the end of the first quarter with preparation of a test plan and revised operating procedures for safety approval. We plan to complete the finalization of the Longevity Test cell design and operating conditions by 3/30/07. A major milestone is the completion of the 100 hour longevity test and issuance of a test report by 6/15/07. However, our current schedule is to initiate testing sooner, if possible, in order to provide contingency and the opportunity for longer duration operation.

Task 2, Multi-cell Stack Development, was initiated near the end of the first quarter. Conceptual design is scheduled to be completed by 4/27/07, and detailed design by 6/15/07. A Level 3 Milestone and Deliverable, Complete Multi-cell Stack Design, are due 7/1/07. A key issue being evaluated in this task is the suitability of the Giner multi-cell stack design to meet the needs of the SDE stack due in September.

Task 3, Chemical and Physical Properties, was initiated in the first quarter and scheduled for completion on 8/1/07.

Task 4, Project Management and Reporting, is ongoing. A miletone is due on 1/31/07, requiring submittal of a journal article on SO2 electrolysis. It is planned to submit one article on cell component development to Electrochemical and Solid-State Letters. Other articles to peer-reviewed journals are also planned, but they will be later in the year in order to be able to report on the research and testing progress that is planned.

6. 0 REFERENCES

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