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## Effect of Water on the Electrochemical Oxidation of Gas-Phase SO<sub>2</sub> in a PEM Electrolyzer for H<sub>2</sub> Production

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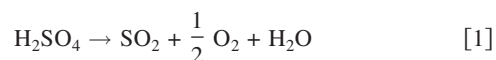
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Water plays a critical role in producing hydrogen from the electrochemical oxidation of SO<sub>2</sub> in a proton exchange membrane (PEM) electrolyzer. Not only is water needed to keep the membrane hydrated, but it is also a reactant. One way to supply water is to dissolve SO<sub>2</sub> in sulfuric acid and feed that liquid to the anode, but this process results in significant diffusion resistance for the SO<sub>2</sub>. Alternatively, we have developed a process where SO<sub>2</sub> is fed as a gas to the anode compartment and reacts with water crossing the membrane to produce sulfuric acid. There was concern that the diffusion resistance of water through the membrane is as significant as SO<sub>2</sub> diffusion through water, thus limiting the benefit of a gas-phase anode feed. We show here that water diffusion through the membrane is not as limiting as liquid-phase SO<sub>2</sub> diffusion. Therefore, we can control the cell voltage, the limiting current, and the sulfuric acid concentration by varying the diffusion resistance of the membrane via thickness or temperature. Catalyst loading, however, has a negligible effect on cell performance.  
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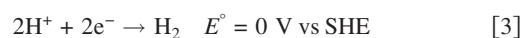
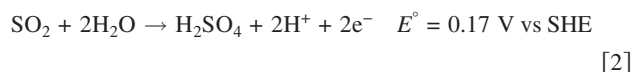
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New, highly efficient methods for large-scale hydrogen production are needed for the development of the hydrogen economy. Current methods of hydrogen production include reforming of hydrocarbons, coal gasification, biological processes, water electrolysis, and water splitting via thermochemical cycles using a high-temperature thermal source (e.g., nuclear or solar energy).<sup>1-6</sup> Using water as the source of hydrogen rather than hydrocarbons results in highly pure hydrogen and zero emissions. The disadvantage is that extracting hydrogen from water is very energy intensive. For example, electrolyzers can achieve electrical efficiencies of 71–79% based on the higher heating value (HHV) of hydrogen.<sup>7</sup> However, factoring in an optimistic thermal-to-electrical efficiency of 50% for advanced nuclear reactors, the overall efficiency from thermal energy to the HHV of hydrogen is still less than 40%.<sup>8</sup> Thermochemical cycles offer the advantage over water electrolysis in that thermal-to-hydrogen efficiencies can exceed 50%.<sup>8-11</sup>

Although there are hundreds of possible thermochemical cycles that can produce hydrogen from water, the leading candidates are the sulfur-based cycles.<sup>5,6</sup> In these cycles, oxygen is generated from the decomposition of H<sub>2</sub>SO<sub>4</sub> in the temperature range of 850–1000°C via the reaction



The sulfur dioxide that is generated must be converted back to H<sub>2</sub>SO<sub>4</sub> to produce hydrogen and complete the cycle. In the sulfur-iodine cycle, this is accomplished via a two-step process involving iodine. The distillation of HI from solution and concurrent decomposition to iodine is the most difficult processing issue for the iodine-containing portion of the cycle.<sup>5,6</sup> In the 1970s, Westinghouse Electric Corporation developed the hybrid sulfur process, which eliminated the use of iodine completely.<sup>9,10</sup> They electrochemically oxidized SO<sub>2</sub> to H<sub>2</sub>SO<sub>4</sub> from a liquid-phase anode stream via the following reactions at the anode and cathode

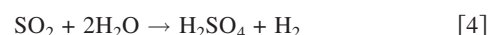


Thus, the overall reaction in the electrolyzer is represented as

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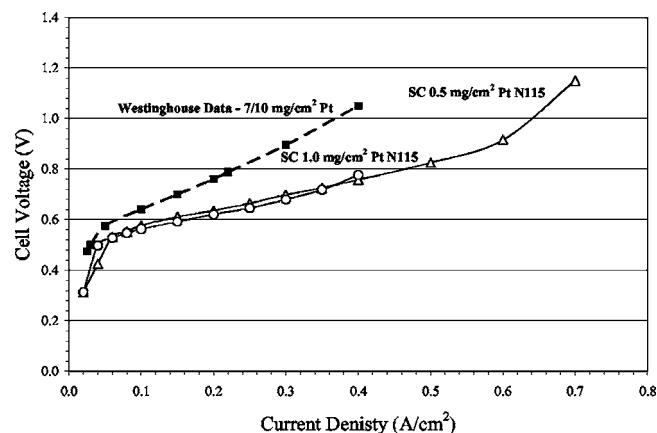


which, when coupled with Reaction 1, completes the cycle. Westinghouse demonstrated this process on a scale of 150 L/h of hydrogen in 1976, and a conceptual plant design was developed.<sup>5</sup> However, limitations in the electrolytic cell (e.g., high voltages and low current densities) prevented this process from being commercialized.

We have developed a modification to the hybrid-sulfur process by carrying out Reaction 3 in a proton exchange membrane (PEM) electrolyzer by feeding SO<sub>2</sub> as a gas to the anode and liquid water to the cathode.<sup>12</sup> The water required at the anode in Reaction 2 is supplied from the cathode via transport across the membrane. The potential advantage of feeding SO<sub>2</sub> as a gas is the improved transport rate of this reactant to the electrode surface. Although we demonstrated that gas-phase SO<sub>2</sub> can be converted to sulfuric acid in a PEM electrolyzer via Reaction 2,<sup>12</sup> the current drawn from the cell was limited by water transport across the membrane. Here we investigate the effect of membrane thickness, temperature, and platinum catalyst loading to see if electrolyzer performance can be influenced in ways the liquid-phase process cannot.

### Experimental

The N115 SC membrane electrode assemblies (MEAs) 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.<sup>12</sup> 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 cm<sup>2</sup> cell purchased from Fuel Cell Technologies, Inc. The cell was maintained at the requisite temperature with heating rods and thermocouples inserted into the endplates. The water was preheated to 8°C above the cell temperature and sent to the cathode at 100 mL/min. These flow conditions were found to best keep the cell at the desired temperature. The SO<sub>2</sub> was fed at flow rates necessary to maintain a constant conversion based on the current passed. For the data reported here, the conversion was maintained at 20% (i.e., five times the SO<sub>2</sub> flow rate needed to sustain Reaction 2). However, the cell was operated with conversions ranging from 20 to 80% with no noticeable effect on performance. The cell was operated at 1.0 atm on both sides of the membrane so that water transport through the membrane was due solely to diffusion and electro-osmotic drag. The sulfuric acid produced at the anode was collected in a knock-out vessel at the bottom of the cell. The sulfuric acid concentration was analyzed by an Orion 4 Star pH meter from the Thermo Electric Corporation.



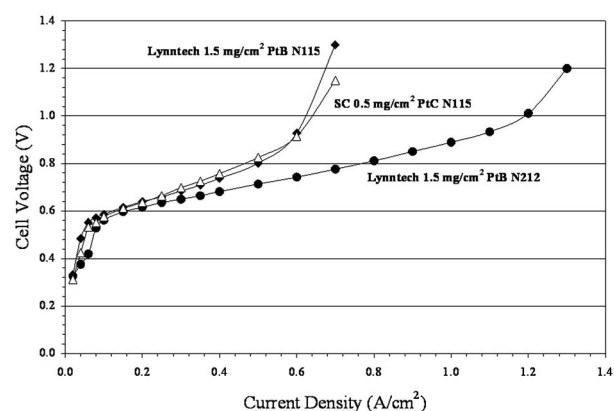
**Figure 1.** *V-I* response of the PEM electrolyzer at 80°C with our N115 MEAs: 0.50 ( $\Delta$ ) and 1.0 ( $\circ$ ) mg/cm<sup>2</sup> Pt-carbon, respectively. The Westinghouse data ( $\blacksquare$ ) was obtained at 1.0 atm and 50°C, with a catalyst loading of 7 and 10 mg/cm<sup>2</sup> on the anode and cathode, respectively.<sup>9</sup>

### Results and Discussion

Figure 1 shows the voltage-current (*V-I*) response of the PEM electrolyzer for the anodic oxidation of gas-phase SO<sub>2</sub> to H<sub>2</sub>SO<sub>4</sub> and the cathodic reduction of protons to H<sub>2</sub>. The data were collected on two N115 MEAs (0.5 and 1.0 mg/cm<sup>2</sup> Pt on carbon) at 80°C. For comparison, Fig. 1 also shows the Westinghouse data for SO<sub>2</sub> bubbled through liquid sulfuric acid at 50°C.<sup>9</sup> Their platinum loadings were 7 and 10 mg/cm<sup>2</sup> on the anode and cathode sides, respectively. Our data show better performance than Westinghouse's liquid SO<sub>2</sub> cell. That is, we achieved 0.40 A/cm<sup>2</sup> at 0.76 V compared to their 1.05 V at this current. At 1.05 V we achieved 0.66 A/cm<sup>2</sup>. The large increase in voltage for the liquid-phase SO<sub>2</sub> electrolyzer between 0.050 and 0.40 A/cm<sup>2</sup> is due to the relatively poor conductivity of the diaphragm separator. The lower resistance of the PEM electrolyzer is evident from the smaller slope in the *V-I* curve between 0.050 and 0.60 A/cm<sup>2</sup>. The liquid-phase electrolyzer is limited to a maximum current density of 0.4 A/cm<sup>2</sup> due to mass-transfer limitations resulting from the solubility of SO<sub>2</sub> in water. The gas-phase electrolyzer does not face these solubility limitations. Instead, the increase in voltage for the gas-phase electrolyzer beyond 0.60 A/cm<sup>2</sup> is due to the limited rate at which water can diffuse through the PEM.

Gorensek<sup>8</sup> performed a preliminary process flow-sheet analysis for making hydrogen from the hybrid sulfur process. To achieve a thermal-to-hydrogen efficiency of 50%, and for the cost of hydrogen to be competitive with that made from natural gas, the target operating condition was 0.50 A/cm<sup>2</sup> at 0.60 V. The gas-phase electrolyzer meets the current density, and hence cost, target but is still 200 mV above the efficiency target at that current density. Based on his analysis, a cell voltage of 0.80 rather than 0.60 V would lower the efficiency from 50 to 44%. This, however, is still an improvement over water electrolysis. Although this was a preliminary analysis, it does indicate that the electrolyzer performance shown here is encouraging. The Pt loading, however, had a negligible effect on electrolyzer performance.

To further investigate the effect of water transport on electrolyzer performance, the cell was run with two membranes of different thickness: N115 and N212. The N115 and N212 membranes are 5 mils (125  $\mu$ m) and 2 mils (50  $\mu$ m) thick, respectively, and each has a polymer molecular weight of 1100 g/mol. The two MEAs were purchased from Lynntech with a Pt-black catalyst loading of 1.5 mg/cm<sup>2</sup>. The *V-I* curves for these two MEAs are shown in Fig. 2, and improved performance for the thinner N212 MEA is observed. That is, there was both significant decrease in the voltage up to 0.6 A/cm<sup>2</sup> and an increase in the limiting current. The 100 mV



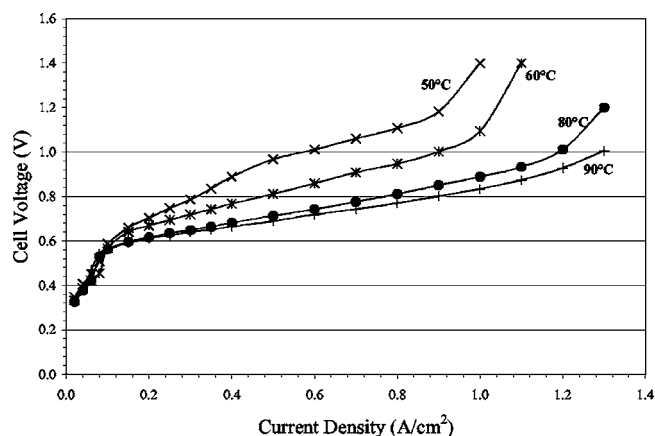
**Figure 2.** *V-I* response of the PEM electrolyzer at 80°C with Lynntech MEAs: 1.5 mg/cm<sup>2</sup> Pt-Black on N115 ( $\diamond$ ) and N212 ( $\bullet$ ). The data for a Pt-carbon loadings of 0.50 mg/cm<sup>2</sup> ( $\Delta$ ) from Fig. 1 are shown for comparison.

decrease in the voltage at 0.50 A/cm<sup>2</sup> increases the estimated efficiency from 44 to 47%. The electrolyzer was able to reach 1.0 A/cm<sup>2</sup> before the slope in the *V-I* curve started to rise. A doubling in the current density from the targeted value of 0.50 A/cm<sup>2</sup> set by Gorensek<sup>8</sup> to 1.0 A/cm<sup>2</sup> reduces the cost of the electrolyzers by 50%, which is a substantial reduction in the capitol costs for this process.

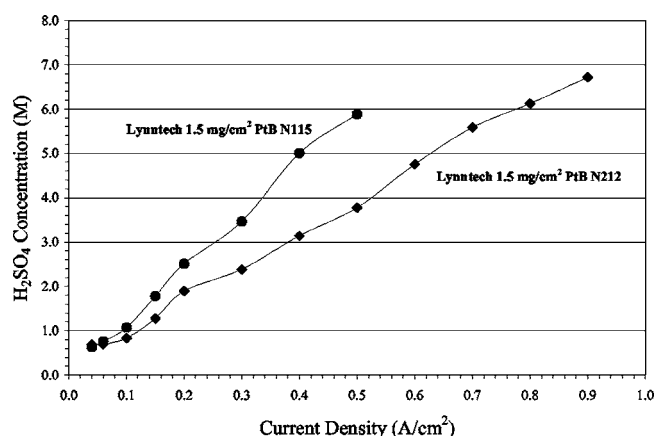
Also shown for comparison in Fig. 2 is a *V-I* curve from our MEA made from N115 with 0.50 mg Pt/cm<sup>2</sup> on carbon. Despite the higher catalyst loading (1.5 mg/cm<sup>2</sup> vs 0.5 mg/cm<sup>2</sup>), the performance of the Lynntech N115 MEA is essentially the same as our N115 MEA. This supports the conclusion drawn in Fig. 1 that catalyst loading has a negligible effect on electrolyzer performance. It suggests that further reduction in catalyst loading may be possible without a significant reduction in electrolyzer performance.

Membrane water transport is also influenced by temperature. Figure 3 shows the effect of temperature on the N212 MEA with 1.5 mg/cm<sup>2</sup> Pt-black loading. As expected, the performance improved as the cell temperature was increased from 50 to 90°C. The reason for the lower voltage at higher currents is the significantly lower membrane resistance at higher temperatures. The ohmic resistance decreases from 0.548  $\Omega$  cm<sup>2</sup> at 50°C to 0.265  $\Omega$  cm<sup>2</sup> at 90°C. Improved water transport is also evident from the decrease in the mass-transfer-limited current as the temperature is decreased.

In addition to voltage, the concentration of sulfuric acid produced by the oxidation of SO<sub>2</sub> is important in determining the over-



**Figure 3.** The effect of temperature on the *V-I* response of the PEM electrolyzer. The MEAs were N212 with 1.5 mg/cm<sup>2</sup> Pt-black.



**Figure 4.** The effect of current density on the sulfuric acid concentration in the anode drip for N115 and N212 MEAs at 80°C.

all efficiency of the hybrid-sulfur cycle. That is, the more concentrated the acid, the less water must be removed before the H<sub>2</sub>SO<sub>4</sub> is sent to the high-temperature loop (i.e., Reaction 1). Figure 4 shows the acid concentration as a function of current density for the N115 and N212 membranes. As expected, the acid leaving the electrolyzer with the N115 MEA was more concentrated than that leaving the electrolyzer with the N212 MEA for the same current density due to the more limited water diffusion across the thicker N115 membrane. Higher sulfuric acid concentrations were achieved for the N212 MEA by going to higher current densities. Lui et al.<sup>9</sup> worked in 50 wt % H<sub>2</sub>SO<sub>4</sub>, which corresponds to approximately 9.4 M. This is higher than the 6.8 M achieved at 0.9 A/cm<sup>2</sup> for the N212 MEA, but it shows that comparably high concentrations can be achieved with a gas-fed anode.

### Conclusion

Feeding SO<sub>2</sub> as a gas to a PEM electrolyzer showed improved performance over the liquid-phase process reported previously. One reason was the lower ohmic losses from a PEM cell compared to one with a diaphragm separator. The PEM resistance was further decreased by going to thinner membranes and higher temperatures. Another reason for improved performance is the enhanced SO<sub>2</sub> diffusion at the anode. Water transport across the membrane has little effect on the voltage until the cell becomes water limited. However, it may be necessary to operate close to the limiting current in order to produce sufficiently high sulfuric acid concentrations. The desired current density, voltage, and acid concentration must be determined from an overall process analysis that optimizes the capitol cost (i.e., current density) and efficiency (i.e., cell voltage and acid concentration). From this, the desired membrane properties (e.g., conductivity and water transport) can be determined to achieve this optimum. However, these results show that commercial membranes are already close to meeting the desired characteristics.

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