ECS Transactions, 61 (28) 11-17 (2014)
10.1149/06128.0011ecst ©The Electrochemical Society

Polybenzimidazole Membranes for Hydrogen Production in the Hybrid Sulfur Electrolyzer

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The hybrid sulfur (HyS) thermochemical cycle has been studied as a means to produce large quantities of clean hydrogen at higher efficiencies than those possible from water electrolysis. Recent studies have shown that the HyS electrolyzer can be operated at with sulfuric acid-doped s-PBI membranes as opposed to traditional Nafion membranes. Our research has shown that s-PBI membranes provide the option of operating the cell at significantly elevated temperatures in order to reduce kinetic resistance.

Introduction

In the recent decade, the hybrid sulfur (HyS) thermochemical cycle has gained considerable attention because of its ability to produce clean hydrogen at higher efficiencies than water electrolysis. The HyS electrolyzer depends on a two-step thermochemical process which involves the decomposition of H_2SO_4 to SO_2, O_2, and H_2O, as well as an electrochemical oxidation of SO_2 in the presence of water to produce H_2SO_4 and H_2.(1, 2) Because the sulfur compounds are recycled, the overall process is the decomposition of water into hydrogen and oxygen. This process is of interest because the high temperature decomposition of sulfuric acid could be coupled to next-generation nuclear power plants or high temperature solar arrays.

The HyS process was developed by Westinghouse in the late 1970s. That design incorporated a liquid fed anode, however, limitations in SO_2 solubility, diffusion, and the use of thick membranes resulted in low operating currents and high efficiencies.(3) Weidner patented a gas-phase process in which dry SO_2 was fed to the cell and water was supplied by diffusion across the membrane.(1, 2) These studies were able to characterize water transport with different membrane thicknesses, predict the current, voltage, and acid concentration, and concluded that operation of the HyS electrolyzer with Nafion could give low voltages at high currents.(2) However, this operation yielded lower acid concentrations due to the need to fully humidify Nafion in order to promote membrane conductivity.(4, 5)

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The goals of the work were to increase the operational temperatures and determine the optimal parameters of operation at these elevated temperatures.

Experimental

The s-PBI used for evaluation was synthesized following a previously reported procedure.(6) The resulting polymer solution was cast resulting in a phosphoric acid doped membrane. To achieve the sulfuric acid doped analogue of the membrane, an acid exchange procedure was conducted. The acid exchange was verified using titration noting only two equivalence points corresponding with sulfuric acid. Once this process was complete, the conductivity of the membrane was determined using a previously reported procedure.(7)

After preparation, membrane electrode assemblies (MEAs) were prepared using s-PBI. The MEAs were then loaded into a single cell obtained from Fuel Cell Technologies, Inc. The area of the cell was 10 cm^2, and consisted of graphite plates with flow channels etched into them which were compressed between two aluminum endplates to achieve an airtight seal. Teflon tubing was placed through the aluminum face of the cell and attached directly to the graphite plate in order to avoid exposing the aluminum in the cell assembly to the SO_2 and sulfuric acid. The cell was heated using heating rods inserted into the aluminum endplates. Omega scientific process controllers were used to control the heating rods. Gaseous SO_2 was supplied to the anode using a mass-flow controller at a rate corresponding to 4 times the stoichiometric requirement for each current. It was previously reported that the percent conversion of SO_2 had little effect on the cell performance.(8) An excess flow of SO_2 ensured that an adequate amount of water entered the anode during the reaction.

The setup used for evaluating the s-PBI membranes differs from the setup used for the Nafion membranes as discussed previously.(2) When Nafion membranes are used, dry SO_2 gas is fed to the anode and liquid water is fed to the cathode, however, when using a s-PBI membrane, liquid water contacting the membrane could accelerate the leeching of acid and reduce performance, therefore, the cathode is kept dry and humidified SO_2 is fed to the anode. The humidifier temperature and cell temperature were varied during the experiments to study the effect of humidity and temperature on s-PBI membrane performance. During the operation of the cell, the sulfuric acid was collected at the exit of the anode and titrated with sodium hydroxide in order to determine the concentration.

During operation, performance evalutions were conducted over a range of current densities at a constant 30 SCCM SO_2 flow rate. Three humidification temperatures were used: 90°C, 95°C, and 98.5°C. The electrolyzer parameters were adjusted, then sufficient time elapsed to ensure stable device operation was reached prior to data collection.

Results and Discussion

The conductivity of s-PBI was measured over a range of temperatures, which can be seen below.

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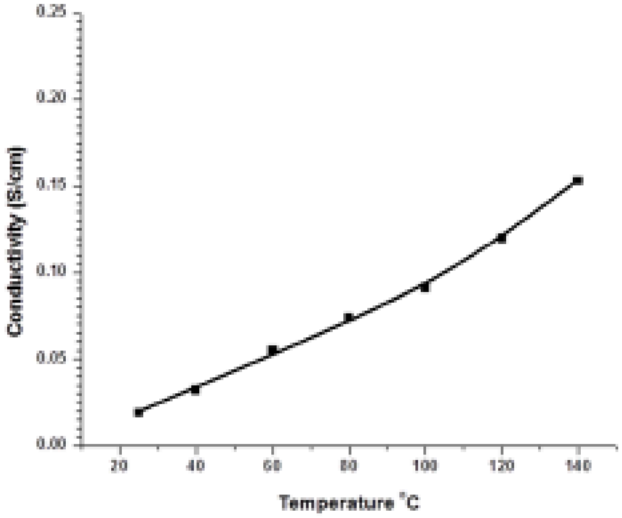

Figure 1. Anhydrous conductivity for s-PBI doped with sulfuric acid.

As seen in Figure 1, the conductivity of the s-PBI increases linearly as a function of temperature well above the operating temperature of Nafion (< 100°C). Due to this, s-PBI was chosen as an ideal candidate to replace Nafion for use as a polymer electrolyte membrane in the HyS electrolyzer.

Figure 2 shows the effect of current density and temperature on the sulfuric acid concentration. It can be seen when both temperature and current density are increased, the sulfuric acid concentration increases.

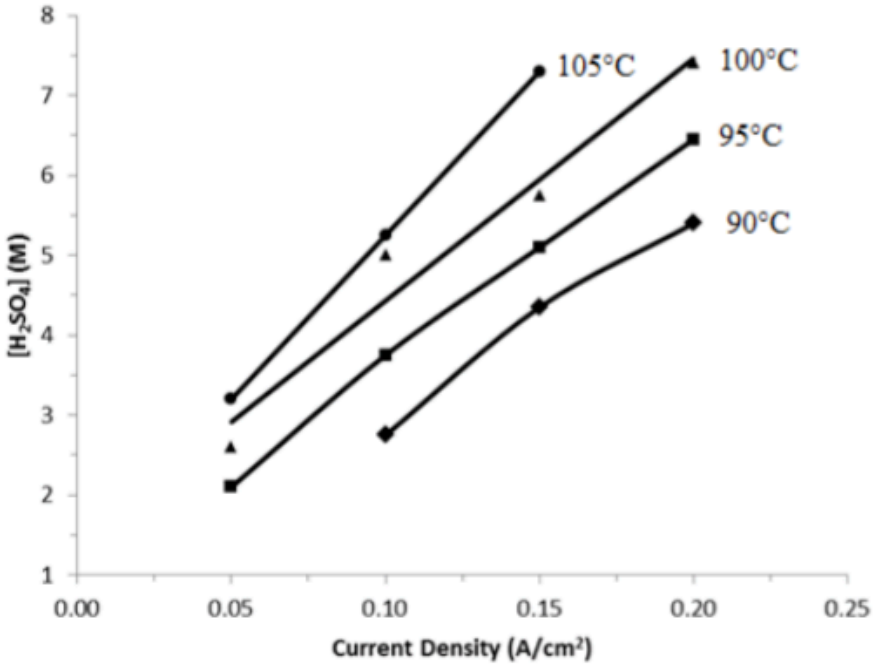

Figure 2. Sulfuric acid concentration as a function of current density for various temperatures.

During elevated temperature operation, it was determined that the humidifier temperature, and therefore the rate at which water was sent to the electrolizer, had a significant effect on the device performance. Therefore, evaluations over a range of previously mentioned operating parameters were conducted.

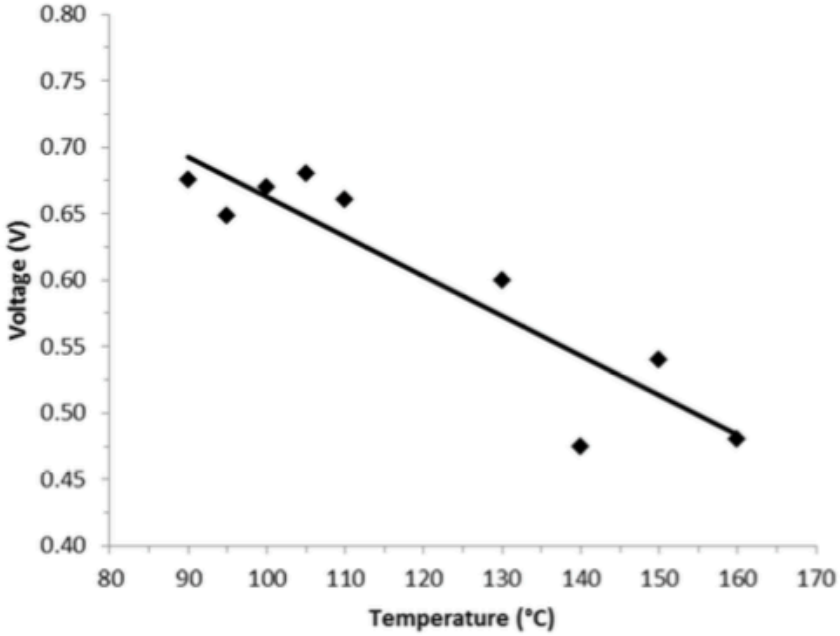

Figure 3. Voltage vs. Temperature plot for HyS electrolyzer. 0.1 A/cm^2 at 98.5°C humidification

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The humidification of the HyS electrolyzer was increased to allow for higher operating temperatures as seen in Figure 3. The voltage required to operate the electrolyzer decreased significantly as temperature was increased, which is consistent with the change in conductivity as a function of temperature as seen in Figure 1. Stable device operation was not achieved above a cell temperature of 160°C.

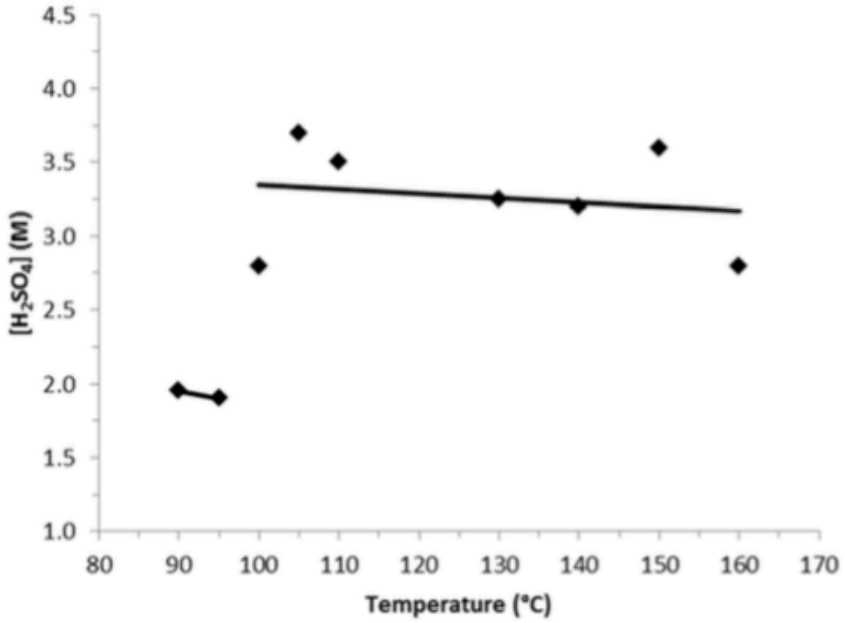

Figure 4. Sulfuric acid concentration as a function of temperature at 0.1A/cm^2 and 98.5°C humidification.

Figure 4 shows the sulfuric acid concentration as a function of temperature, corresponding to the data points seen in Figure 3. Below 100°C, the concentration of sulfuric acid produced by the HyS electrolyzer was relatively stable, was seen to be equivalent to the acid concentration reported previously for Nafion 117, and was almost twice the concentration previously reported for s-PBI at 90°C.(5) Above 100°C, the concentration of sulfuric acid as a function of temperature is relatively stable, and is much higher than sulfuric acid concentrations previously reported for both Nafion 117 and s-PBI at 80°C.(5)

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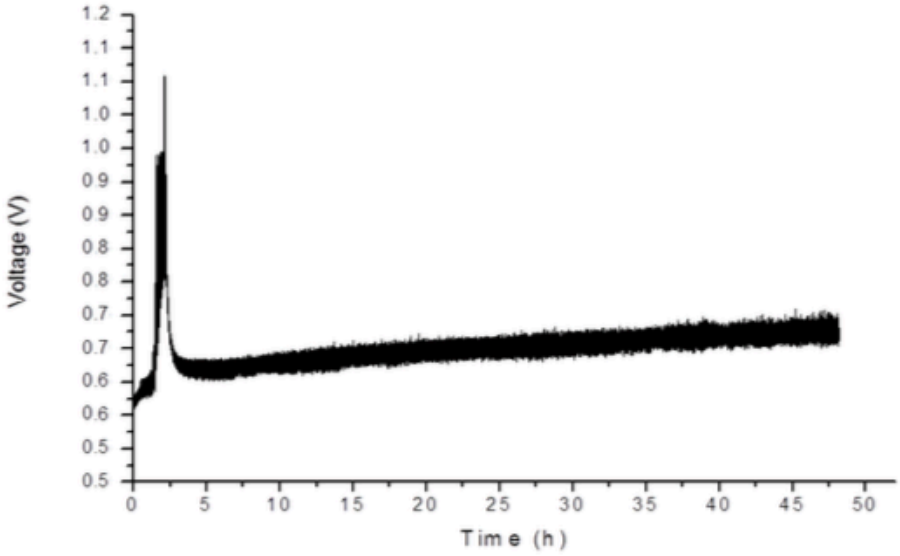

Figure 5. Stability test of the HyS electrolyzer. Operation at 120°C and 0.2 A/cm^2. Humidification temperature was 95°C.

Figure 5 shows the stability test for a one cell HyS electrolyzer setup. The open circuit potential seen at ~2.5 hours was due to a loss of water in the humidification system. Once the humidification system resumed operation, the HyS electrolyzer returned to normal operation. The cell voltage remained relatively stable thoughout the 50 hour lifetime test.

Conclusion

We have successfully increased the operational temperatures, determined the optimal parameters of operation at these elevated temperatures, and evaluated the long-term device stability. This is a significant step towards HyS systems capable of high temperature operation. Future work will include elevated temperature operation at different pressures to determine the effect of pressure on the HyS cell. Eventually, the operating parameters will be incorporated into a commercially viable system.

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