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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. Unfortunately, perfluorosulfonic acid polymers (e.g., Nafion) studied previously in SO2-depolarized electrolyzers for the HyS process suffer from poor proton conductivity at high acid concentrations. Therefore, alternative membranes are needed to obtain high efficiency in the electrolyzer used in the HyS process. Recent studies have shown that the HyS electrolyzer can operate with sulfuric acid-doped polybenzimidazole membranes, which have good proton conductivity when in contact with concentrated acid. Here we show model results that indicate s-PBI membranes can operate at up to 160°C at similar acid concentrations, which can reduce kinetic resistance and should improve overall system efficiency.

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.[1-5] The HyS electrolyzer depends on a two-step thermochemical process which involves the high temperature 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.[5, 6] 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.[2] In the electrolyzer, SO_2 is oxidized at the anode and produces sulfuric acid according to the following reaction:

$$SO_2 + 2H_2O \rightarrow H_2SO_4 + 2H^+ + 2e^- \quad U^0_{SO2} = 0.158 \text{ V vs. SHE} \qquad [1]$$

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The protons produced in Reaction 1 are transported across the membrane and reduce to hydrogen at the cathode via the following reaction:

$$2H^+ + 2e^- \rightarrow H_2 \qquad U^0_{H2} = 0 \text{ V vs. SHE} \qquad [2]$$

This process was developed by Westinghouse[7] in the late 1970s. Liquid sulfuric acid saturated with SO_2 was fed to the anode and liquid sulfuric acid was fed to the cathode. However, limitations in SO_2 solubility and diffusion resulted in low operating currents and high cell voltages (i.e., low energy efficiencies). To eliminate the limitations of a liquid feed, dry SO_2 was fed to the anode and water was supplied by diffusion across the membrane.[6] 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 and high currents.[6] However, this operation yielded low acid concentrations due to the need to fully humidify Nafion in order to promote membrane conductivity.[8, 9] This creates a challenge when using a PEM electrolyzer in the HyS process. That is, the production of concentrated sulfuric acid is desired to improve the efficiency of the high-temperature decomposition step, but has the adverse effect of dehydrating the membrane and reducing the efficiency of the electrolysis step of the cycle.[6]

Acid-doped polybenzimidazole (PBI) membranes represent an alternative to Nafion because they do not rely on water for their proton conductivity, and therefore they offer the possibility of operating at high acid concentrations and/or elevated temperatures to minimize voltage losses. PBIs are a class of aromatic heterocyclic polymers with high thermal and chemical stabilities.[10, 11] PBI membranes have these exceptional performance characteristics in various electrochemical devices due to their high ionic conductivity when imbibed with various acid electrolytes.[12, 13] PBI is a basic polymer and possesses both proton donor and acceptor sites. This property induces a specific interaction between the proton acceptor and donor sites and polar solvents, which allows for the direct acid incorporation into the polymer matrix.[14-16] To date, a large variety of PBI polymers have been synthesized and studied, however, a sulfonated polybenzimidazole was found to be best suited for HyS electrolyzer applications due to its stability in the sulfuric acid environments in the HyS electrolyzer[1].

A process for casting and doping the PBI membranes, termed the PPA process, was recently developed for the synthesis of sulfonated PBI (s-PBI) membranes. Here we report the use of s-PBI membranes in the HyS electolyzer at elevated temperatures. The prepared s-PBI membranes were characterized in regards to molecular weight, membrane composition, ionic conductivity, and mechanical integrity. Performance evaluations were conducted under various operating parameters over temperatures ranging from 90°C to 160°C.

Experimental

Polymerization of s-PBI Membranes

This version of polybenzimidazole is synthesized with a pre-sulfonated monomer, mono-sodium 2-sulfoterephthalate. Using a presulfonated monomer allows for the controlled placement of the sulfonate group in every repeat unit of the polymer. The s-PBI was synthesized similar to a previously reported procedure.[16] In the typical polymerization procedure seen here, 3,3',4,4'-tetraaminobiphenyl is reacted with mono-

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sodium-2-sulfoterephthalate in polyphosphoric acid on a 15mM scale. Monomers were then added to a 100 mL reactor. The reactor was equipped with a three neck reactor head, a stir rod attached to an overhead stirrer, and a nitrogen inlet/outlet. Nitrogen flow was established and monitored through and oil filled bubbler. The reactor was then placed in a silica oil bath which was thermally regulated using a thermal controller with ram/soak features. The reaction follows a procedure in which the solution is heated from room temperature to a final polymerization temperature of 220°C in a stepwise manner. The ramp/soak profile was performed as follows:

From an initial ambient temperature, the solution was heated to 120°C over a period of two hours. This temperature was then held for an additional two hours before it was increased to 150°C over three hours. The solution temperature was held at 150°C for three and a half hours and then heated to 170°C over a period of one hour. The solution then remained at this temperature for three hours, at which point it was increased to 190°C over a one hour period. The solution was then held at 190°C for ten to fifteen hours to reach desired viscosity and finally increased to 220°C over a period of one hour. The solution was held at 220°C for one to four hours to adjust viscosity for casting.

Membrane Formation

Polymer solutions were directly cast at 220°C onto heated class plates for membrane formation. A heated metal casting blade with a casting thickness of 508 micrometers was used. Once the solution was cast, the glass plates were placed in a humidification chamber at 55%RH to hydrolyze for approximately 24 hours. Hydrolysis of the polyphosphoric acid into phosphoric acid induced a sol-to-gel transition resulting in a Flory Type III gel membrane. The resulting membranes were then sealed in polyethylene bags until further analysis or testing was conducted.

Imbibing Procedure

The hydrolyzed polymer membranes directly cast from PPA solution were soaked in a de-ionized water bath for phosphoric acid removal. The pH of the water baths were monitored and water was replaced as needed until a neutral pH was obtained over a period of 5 days. The PBI membranes were then immersed for 3 days in a 20 wt% H_2SO_4 bath for sulfuric acid imbibing. Titration analyses were conducted at each stage of the acid exchange process.

Titrations were conducted using a Metrohm 716 DMS Titrino automated titrater and a standardized sodium hydroxide solution. The acid exchange was confirmed using the difference in pKa and equivalence points between sulfuric acid and phosphoric acid. Moverover, titration across the full spectrum revealed only two equivalence points, verifying that only sulfuric acid remained in the membrane.

Membrane Electrode Assembly Fabrication

Membrane electrode assemblies (MEAs) were constructed by hot-pressing gas diffusion electrodes obtained from BASF to each side of the s-PBI membranes as described previously.[17] The MEAs were loaded into a single cell purchased from Fuel Cell Technologies, Inc. The cell was 10 cm^2 and consisted of graphite blocks with flow channels machined into them sandwiched between two aluminum endplates to provide compression. Teflon tubing was passed through the face of the aluminum endplates directly into the graphite blocks for the reactants and products in order to minimize corrosion.

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Electrolyzer Setup

In the electrolyzer, contact between the aluminum endplates and sulfuric acid was prevented. The cell was heated by heating rods obtained from Omega that were inserted into the aluminum endplates. Gaseous SO_2 was fed into the anode compartment via a mass-flow controller at a rate corresponding to 25% conversion at each current. The conversion of SO_2 was kept low to ensure a sufficient amount of water entered the cell. The setup used here differs from the setup used for the Nafion membranes as discussed previously.[1] When Nafion membranes were used, dry SO_2 gas was fed to the anode and liquid water was 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.

Model

This electrochemical system was analyzed using Aspen Plus equipped with an electrolyte interface to obtain the activities of each component at varying solution compositions similar to the method used by Gorensek[18]. These values were then used with the Nernst equation,

$$E_T = E_T^0 - \frac{RT}{nF} \ln Q_T \qquad [3]$$

where

$$Q_T = \frac{(a_{SO_2})(a_{H_2O})^2}{(a_{SO_4^-})(a_{H_2})10^{-2\,pH}} \qquad [4]$$

and

$$E_T^0 = E^0 + (T - 298.15)\left(\frac{dE^0}{dT}\right) \qquad [5]$$

to obtain the reversible cell potential as a function of species concentration, temperature, and pressure. The activities of the solutes are calculated on a molar basis using the results from the Aspen Plus simulation.

Sensitivity analysis were conducted in which the cell current, temperature, and pressure were varied, and the reversible cell potential and sulfuric acid concentration were calculated. The compositions of the liquid and vapor phases were also calculated using the Aspen Plus simulation.

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Results and Discussion

Figure 1 shows the ionic conductivity measured for s-PBI over a range of temperatures. The conductivity of this material is very desirable; however, the conductivity of s-PBI experiences a significant decline above 160°C. This is indicative of the breakdown of the membrane due to the polymer solubility in sulfuric acid at high temperatures. Although there is a temperature limit on s-PBI due to solubility at higher temperatures, the membrane has very desirable proton conductivity and is capable of operational temperatures well above that of Nafion. Due to this, s-PBI was chosen as an ideal candidate to replace the traditional Nafion membrane for use as a polymer electrolyte membrane in the HyS electrolyzer.

Figure 2 shows the model results for the concentration of sulfuric acid collected from the exit of the electrolyzer over a range of operating temperatures at two current densities and at a constant humidification rate and SO_2 feed rate. The acid concentration (mol/L) was calculated using the results from the Aspen simulation. For operation at atmospheric pressure, a sharp increase in acid concentration is seen as the cell temperature increases past 100°C. For operation at a pressure of 2 atm, acid concentrations start very high (<13 mol/L) and increase as a function of temperature. This indicates that pressure and temperature have a significant effect on the acid concentration produced by the electrolyzer, and that high temperature and pressures should be used in order to maximize the acid concentration leaving the electrolyzer. However, an economic analysis should be performed to determine if the small increase in acid concentration is worth the extra cost of cell operation at elevated pressures.

Figure 3 shows the model results for the reversible cell potential as a function of cell temperature and humidification rate at constant current operation and constant SO_2 feed rate. The reversible potential is calculated using Eq. 3. The activities and pH used in Eq. 4 are calculated from the Aspen simulation. As the cell temperature increases at a constant humidification temperature, the reversible cell potential increases, primarily due to the shift in water from the liquid to the gas phase. At temperatures less than 100°C, the reversible potential decreases as the humidification rate, and therefore the water concentration in the liquid phase, increases. However, at temperatures greater than 100°C, the opposite effect is seen. Due to the fact that s-PBI does not need to be hydrated to facilitate proton conduction, when operating the electrolyzer at elevated temperatures (<100°C), the amount of water fed to the cell should be as close to the stoichiometric requirement as possible in order to minimize the reversible cell potential.

Figure 4 shows a plot of the reversible cell potential as a function of acid concentration at 5 different current densities and at a constant humidification rate and constant and SO_2 feed rate. It is clear than an increase in the acid concentration increases the reversible cell potential. This indicates that the concentration of sulfuric acid in the electrolyzer has a significant effect on the electrolyzer operation due to the increase of the minimum operating cell potential. This is also seen in Figure 5, where an increase in cell temperature, and therefore an increase in acid concentration, causes a significant increase in the reversible cell potential. Figure 6 again confirms this, where an increase in the current density, and therefore an increase in the acid concentration, affects an increase in the reversible cell potential at constant temperature and relative humidity. These results should be taken into consideration when operating the electrolyzer, and an economic analysis should be performed due to the tradeoff between producing a high acid

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concentration in the electrolyzer at a high voltage vs. producing a lower acid concentration in the electrolyzer and concentrating the acid stream in further steps.

Figure 6 also illustrates the need to operate the cell closest to the stoichiometric requirement for water in order for the reaction to proceed. An increase in water in the cell, not used in the reaction or to facilitate the hydration of the membrane, only serves to increase the reversible cell potential, thereby increasing the amount of energy necessary to operate the cell.

Analysis of the model results indicates that the amount of excess water in the electrolyzer has the greatest effect on the final acid concentration as well as the reversible cell potential. Therefore, the humidification rate should be adjusted to closely match the stoichiometric requirement of water. An economic analysis should also be performed to compare the energy requirement of producing high acid concentrations in the electrolyzer vs. removing water after electrolysis and increasing the acid concentration downstream of the electrolyzer.

Conclusion

We have successfully operated the HyS electrolyzer using sulfuric acid-doped s-PBI membranes at increased operational temperatures and performed a model analysis on the operational parameters at these elevated temperatures. This is a significant step towards HyS systems capable of high temperature operation. Future work will include elevated temperature operation at different pressures to compare the effect of pressure on the HyS cell to the model results, as well as perform further model analysis to determine the most thermodynamically and energy efficient operating conditions. Eventually, the ideal operating parameters will be incorporated into a commercially viable system.

Notation

a_x	Activity of species x
E_T	Reversible cell potential, V
E_T^0	Temperature specific standard cell potential, V
E^0	Standard Cell Potential, V
F	Faraday constant, 96485 C/mol
Q_T	Reaction quotient
T	Temperature, K

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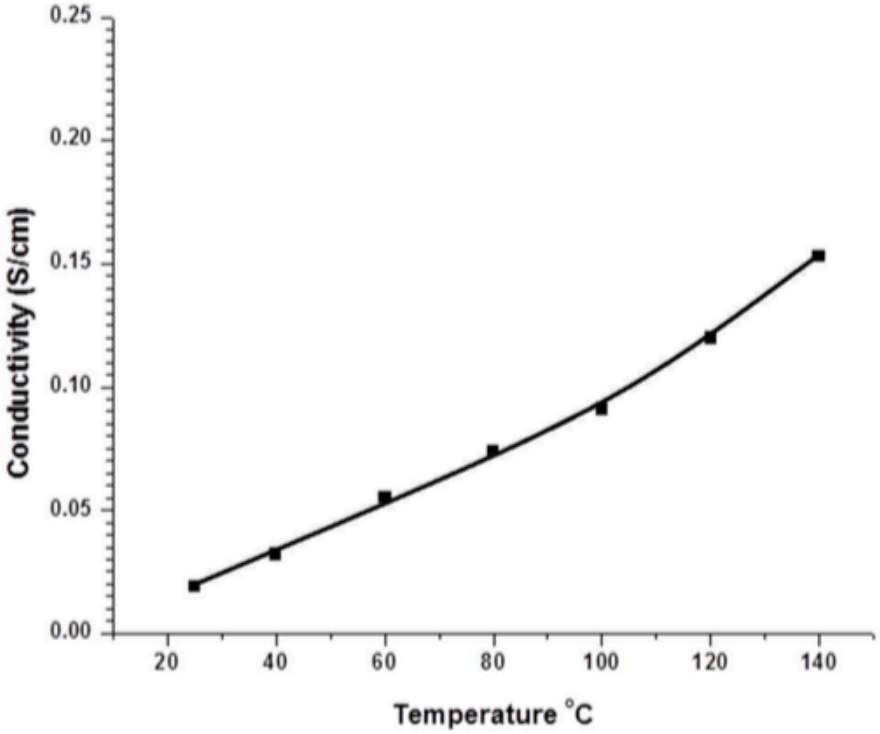

Figure 1. Anhydrous conductivity for s-PBI doped with sulfuric acid for temperatures ranging from 30°C to 140°C.

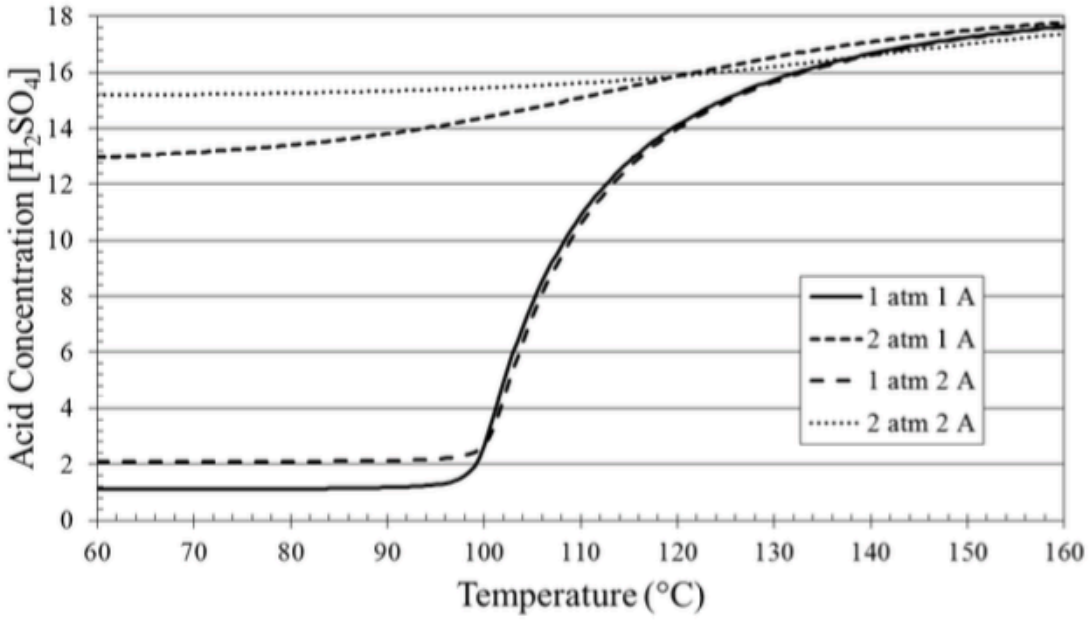

Figure 2. Sulfuric acid concentration as a function of temperature at a constant humidification rate, constant current densities, and at a constant SO_2 feed rate of 30 SCCM.

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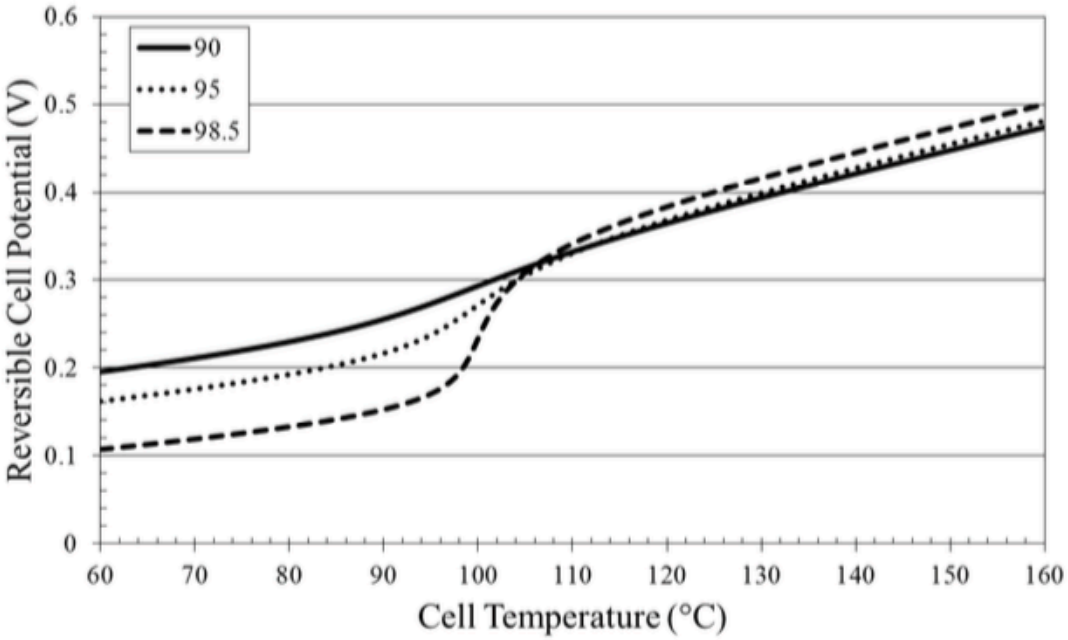

Figure 3. Reversible cell potential as a function of electrolyzer temperature at a constant humidification rate (90°C, 95°C, and 98.5°C) and a constant current density of 0.1 A/cm^2. A constant SO_2 feed rate of approximately 30 SCCM was supplied to the electrolyzer.

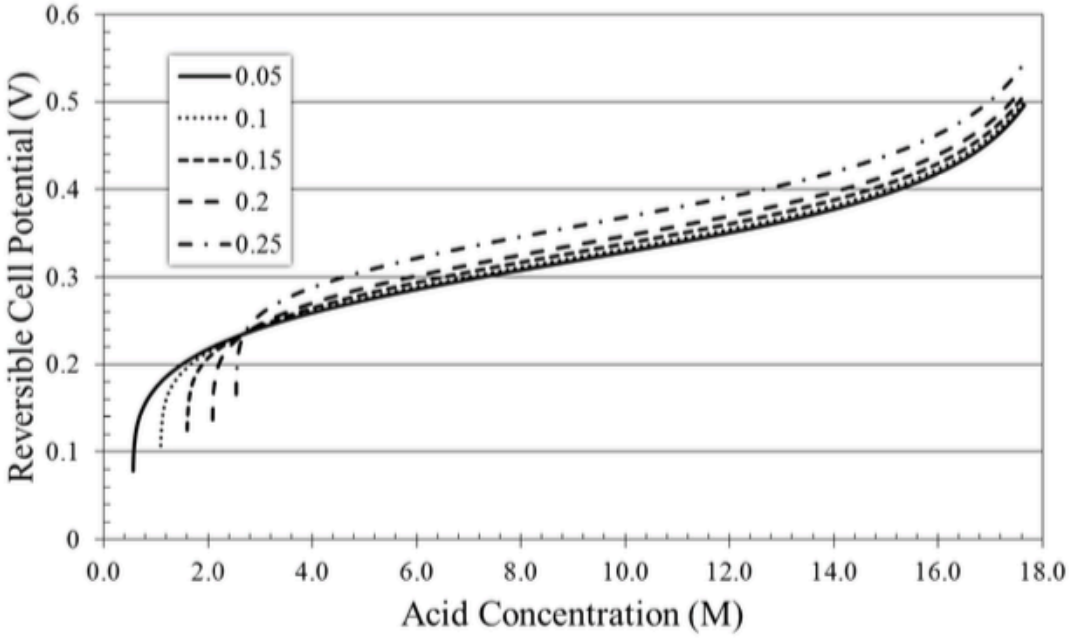

Figure 4. Reversible cell potential as a function of acid concentration at various current densities.

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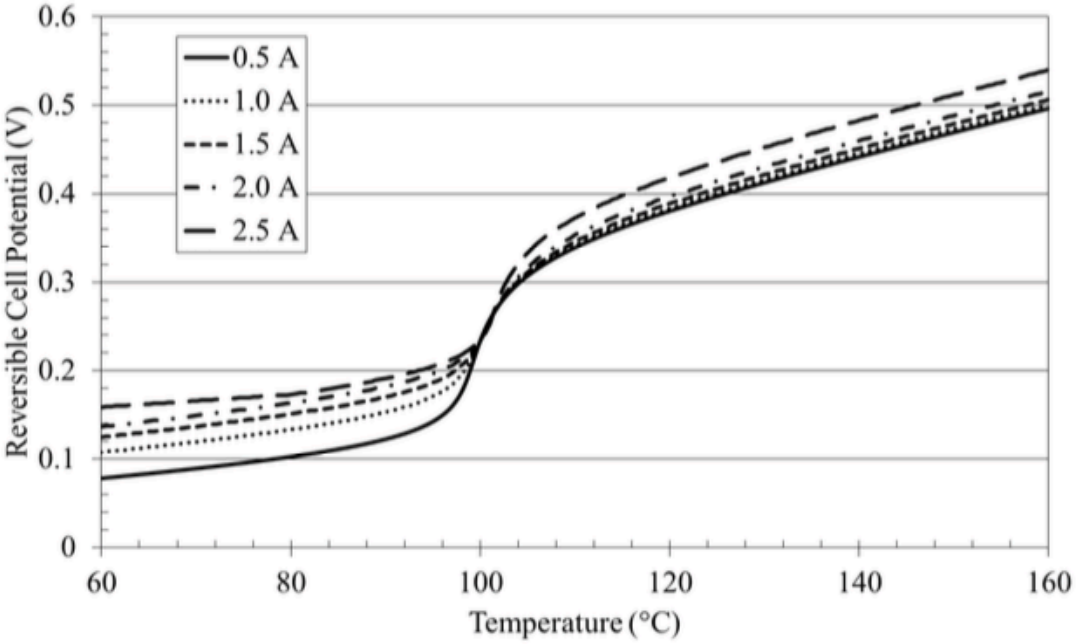

Figure 5. Reversible cell potential as a function of cell temperature at a constant humidification rate and a constant SO_2 feed rate of approximately 30 SCCM.

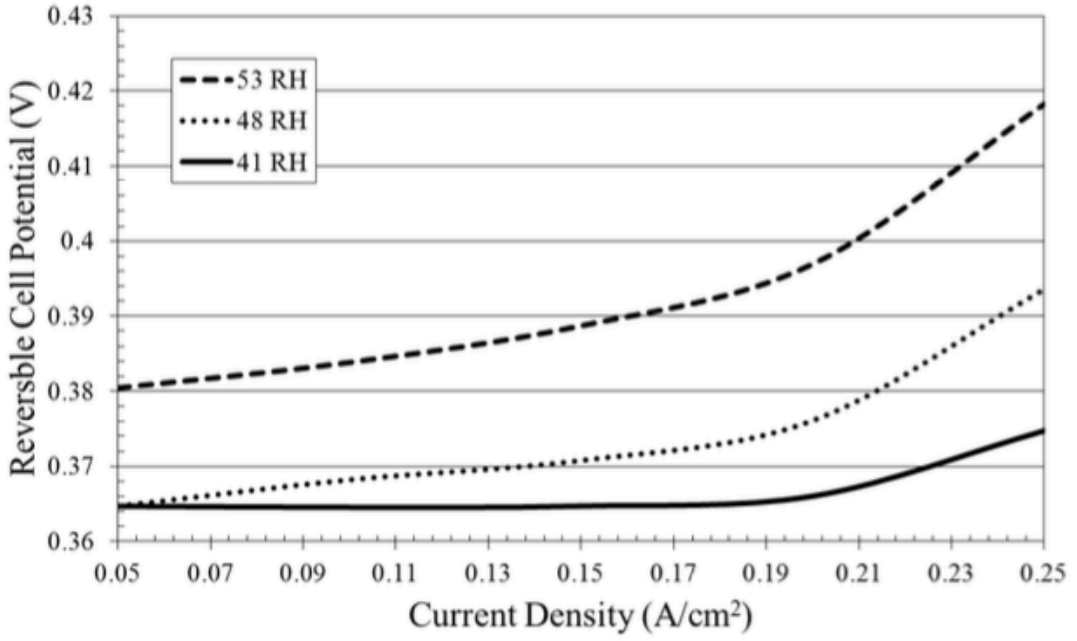

Figure 6. Reversible cell potential as a function of relative humidity at a constant SO_2 feed rate of approximately 30 SCCM and at a constant temperature of 120°C.

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