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Polymer Electrolyte Membrane (PEM) Electrolyzer Operation with Varying Inlet Water Feed

Configurations

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Proton Exchange Membrane (PEM) electrolysis is a potential alternative technology to crack water in specialty applications where a dry gas stream is needed, such as isotope production. One design proposal is to feed the cathode of the electrolyzer with vapor phase water. This feed configuration would allow isotopic water to be isolated on the cathode side of the electrolyzer and the isotope recovery system could be operated in a closed loop. Tests were performed to characterize the difference in the current-voltage behavior between a PEM electrolyzer operated with a cathode water vapor feed and with an anode liquid water feed. The cathode water vapor feed cell had a maximum limiting current density of 100 mA/cm^2 at 70°C compared to a current density of 800 mA/cm^2 for the anode liquid feed cell at 70°C. The limiting current densities for the cathode water vapor feed cell were approximately 3 times lower than predicted by a water mass transfer model. It is estimated that a cathode water vapor feed electrolyzer system will need to be between 8-14 times larger in active area or number of cells than an anode liquid feed system.

Commercially available PEM electrolyzers can generate H_2 pressures of up to 200psi and have production rates from 400-7900 kg/yr [1]. These units have the advantages of producing high purity hydrogen (99.999%) at high conversion efficiency (95%). Fast response time as well the ability to accept variations in load make the technology desirable for on-demand delivery and photovoltaic power sources [2]. Disadvantages of operation include high capital cost and the hydrogen production costs being largely dependent on the cost of electricity. A large energy supply is often needed due to high anode overpotentials [3]. In certain specialty applications, such as isotope separation, a dry gas supply is needed and the capital and energy costs have less effect on the relative efficiency of the system.

One of the technological issues with the use of a PEM electrolyzer in isotope separation is the development of an overall system design that will maintain the oxygen and hydrogen streams separate, maintain a closed loop hydrogen system, and allows easy integration of the electrolyzer. One design option for the isotope recovery system that would meet these criteria is to feed water vapor to the PEM electrolyzer on the cathode side of the membrane. To keep the hydrogen contained in a closed loop, hydrogen gas would be used as the carrier for the isotopic water vapor. Oxygen gas would be produced at the cathode and be exhausted by natural convection or be removed by a sweep gas. A proposed operating configuration, using tritiated water, is shown in Figure 10. The water vapor would diffuse across the membrane and be oxidized at the anode to produce oxygen gas. The protons and isotopic nuclei produced by the reaction would be conducted back to the cathode and reduced to form isotopic hydrogen gas. When an electrolyzer in this configuration is operated such that it electrolyzes all the isotopic water that crosses the membrane, the isotopic water and hydrogen gas should be confined to the

cathode side of the electrolysis cell. Operating the cathode water vapor feed in this mass transport limited condition will limit the reaction rate in the cell to the rate of water diffusion across the membrane. The cathode water vapor feed configuration is significantly different than traditional PEM electrolyzer operation with a feed of liquid water to the anode [4]. With a liquid feed of water to the anode, the reaction rates in the cell at a given cell voltage are limited more by the kinetics of the reactions and the ohmic losses in the membrane and are not significantly limited by mass transfer.

This work focuses on the experimental comparison of a cathode water vapor feed electrolyzer with a traditional anode liquid feed system. These experimental results are compared with a model for mass transfer in a cathode water vapor feed electrolyzer was developed in previous work [5]. Polarization (current-voltage) testing of a single electrolysis cell is performed to compare the steady-state performance of a cathode water vapor feed cell with an anode liquid feed cell for design purposes. The polarization of a cathode water vapor feed electrolyzer was characterized for different cell temperatures at 100% relative humidity for the cathode feed gas. For comparison, an identical cell was operated with an anode liquid water feed at different cell temperatures and water flow rates.

Experimental

Cathode Water Vapor Feed Operation- A bench scale PEM electrolyzer in cathode water vapor feed configuration was tested to determine the electrochemical performance of the cell. Nitrogen was used as the carrier gas for water vapor to the cathode. The dry flow rate of nitrogen for all cathode water vapor feed experiments was 1000 sccm. The nitrogen was humidified using a Nafion tube humidifier from Fuel Cell Technologies. The humidifier temperature and water level were controlled throughout the experiments. The humidifier temperature was set to the

desired dewpoint for each experiment. All experiments cathode water vapor feed experiments were performed at 100% Relative Humidity (RH). To prevent condensation, a heated transfer line carried the gas from the humidifier to the electrochemical cell. Before entering the cell, the dewpoint of the inlet gas was measured using a humidity sensor from Vaisala HMT 334 humidity sensor. The humidity sensor was mounted in a heated and insulated T fitting that was thermostated at 75°C. The outlets of the cell were at atmospheric pressure. The cell exhaust was vented into a fume hood with adequate ventilation to maintain the atmospheric concentration of hydrogen well below 1%. The cathode water vapor feed equipment described above was integrated and assembled by Giner Electrochemical Systems, Inc. and operation of the system was controlled using a LabView program.

Anode Liquid Feed Operation- In the anode liquid feed configuration, water was fed to the anode of the electrolyzer from a temperature controlled water reservoir. A Thermo Scientific NESLAB 7 constant temperature bath was used as the water reservoir. Water was pumped from the reservoir to the cell using a Watson-Marlow 403U/R1 peristaltic pump. Flexible tubing with a 1/16" bore was used for delivery of the water to the cell. With this size tubing, the pump accurately delivered water flow rates between 2 ccm and 11 ccm per the manufacturer's directions. During anode liquid water feed experiments, nitrogen with a 25°C dewpoint was flowed through the cathode. The dry nitrogen flow rate during these experiments was 500 sccm. The heated transfer line was heated to 75°C to keep water from condensing.

Electrochemical Cell- The cells tested had a 50 cm^2 circular active area cell and was prepared by Giner Electrochemical Systems, Inc. The cell housing was made out of aluminum and was

heated by silicone heating pads placed on the outside of the cell. The heating pads were circular and of similar size as the active area. The temperature of the cell was monitored by a thermocouple within the cell housing. The Membrane Electrode Assembly (MEA) in the cell had 2 mg/cm^2 of Pt catalyst at the cathode and a 2 mg/cm^2 of PtIrO$_2$ catalyst at the anode. The membrane in the cell was Pt-treated Nafion$^®$ 117 (1100 equivalent weight, 7 mils in thickness). Porous titanium gas diffusion media were used for mass transport and electrical contact. The cell used for cathode water vapor feed experiments only had an anode oxygen outlet port and thus did not allow for testing with an anode sweep gas. The cell used for anode liquid water experiments had water inlet and outlet ports on the cathode. Both the cathode water vapor feed cell and the anode liquid feed cell were assembled by Giner Electrochemical Systems, Inc.

Polarization Testing- The cell polarization was tested using a Bio-Logic HCP-803 high-current potentiostat capable of applying currents up to 80A and voltages of ± 3 V. The anode of the cell was connected to the potentiostat as the working electrode and the cathode of the cell was connected as the counter and reference electrodes. After setting the flows and temperatures for an experiment, the cell was allowed to come to thermal equilibrium for 15-20 minutes with no electrochemical load. At the start the electrochemical testing, the cell voltage was held at 1.8 V for 30 minutes to allow concentration gradients in the cell to fully develop. The cell voltage was changed in a stepwise fashion between 1.80 V and 1.20 V with between 2 and 12 minutes given for the cell to achieve steady-state. In general, longer step times were used in the cathode water vapor feed configuration because humidifier transients occasionally caused data fluctuation. The hold times at each cell voltage for both cathode vapor and anode liquid feed test configurations are given in Appendix A.

Results and Discussion

An important consideration in cathode water vapor feed experiments is the relative humidity of the cathode feed gas. The humidity from the Fuel Cell Technologies humidifier is measured by a dewpoint meter to monitor its variability. Representative samples of the transient gas dewpoint data collected at humidifier temperatures between 30°C and 70°C are shown in
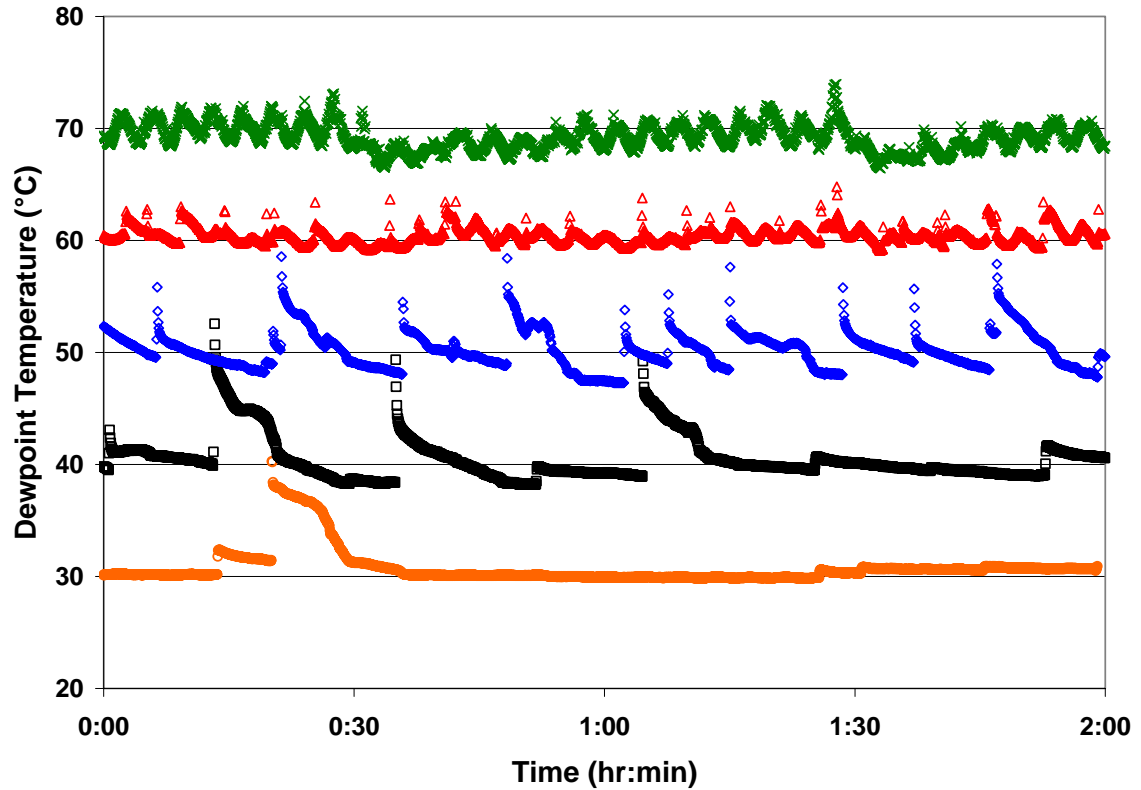

Figure 11. The flow rate of nitrogen through the humidifier was 1000 sccm for all cases.

The profiles show that the humidifier does not produce a steady dewpoint and that the transient spikes seen in the dewpoint of the cathode feed gas depends on the humidifier temperature. It is believed that the variability in the dewpoint temperature is related to the construction of the humidifier. In the humidifier, the dry gas flows through a long coil of Nafion tubing submerged in heated water. As the gas travels through the tube, water diffuses through the Nafion and saturates the gas. The saturated gas then flows out of the humidifier and to the cell. The thermocouple for monitoring the humidifier temperature is placed in the gas space of the humidifier near the gas exit. The location of the thermocouple in the humidifier may be one

possible cause of the dewpoint instability. If there are temperature differences between the liquid temperature and the temperature of the gas in the humidifier then the humidity transients may result. The spikes in the cathode inlet dewpoint temperature cause corresponding spikes in the cell current. The spikes in the cell current are caused because the membrane water content is increases with relative humidity and as the membrane water content increases more water diffuses across the membrane to react at the anode. These results show that maintaining good control of the inlet gas humidification in a cathode water vapor feed electrolyzer is important to achieve a constant reaction rate.

The variation of the inlet dewpoint also led to difficulties in interpreting the polarization data collected during cathode water vapor feed experiments. The polarization curves were performed in using fixed voltage control. For experiments at 30°C and 40°C, the points on the polarization curve were taken where the current density was stable. For the 50°C to 70°C data, the points on the polarization curve were determined from average current density values at each voltage.

Figure 12 shows the current/voltage behavior (i.e. – polarization) of the electrolysis cell at temperatures between 30°C and 70°C. The polarization for the cell was tested in the range between 1.20 V and 1.80 V. In the voltage range below approximately 1.4 V the cell is kinetically limited and the current increases exponentially with the cell potential. Between 1.4 V and 1.7 V the cell is transitioning to a mass transfer limited mode of operation. Above 1.7 V, the cell current is completely limited by the diffusion rate of water across the membrane and further increases in the cell voltage do not result in higher cell current. The steady state current that is reached above 1.7 V is known as the mass transfer limited current density. At the mass transfer

limiting current density, the rate of water diffusion across the membrane is equal to the reaction rate of water at the anode.

As the cell temperature is increased in cathode water vapor feed experiments, the current density of the reaction increases in both the kinetically limited region and the mass transfer limited region. The increase in current density in the kinetically limited region is due to the dependence of the exchange current density on temperature. The increase in the limiting current with temperature is due to the dependence of the membrane water diffusion coefficient on temperature. One exception to the general trends in the data is that the limiting current density for the cell at 60°C and 70°C are nearly identical. The temperature dependence of the limiting current density is shown in Figure 13. The limiting current density increases linearly for cell temperatures between 30°C and 50°C and this linear trend also explains the limiting current at 70°C, however, the 60°C limiting current is larger that the linear trend predicts. The reason for the change in the trend of limiting current with temperature is not clear, but one possible explanation is it could be that it is an artifact of data interpretation methods at higher temperatures. Also shown in Figure 13 are limiting current density predictions from a 1-D mass transfer model[5]. The experimental limiting current densities are approximately 3 times smaller than those predicted by the mass transfer model. The differences between the mass transfer model and the experimental data may be due inaccurate assumptions for model parameters or may be due to insufficient experimental data. The mass transfer model requires values for the water diffusion coefficient in Nafion, the water electroosmotic drag coefficient in Nafion, and the gradient in membrane water content across the membrane. Literature values for these quantities were used in the model and may not be accurate for running the cell in a cathode water vapor feed configuration. It must also be acknowledged that the cathode water vapor feed

polarization experiments were only performed on a single MEA. Multiple MEA tests should be conducted to ensure that polarization results are reproducible.

For comparison with the cathode water vapor feed polarization data, anode liquid feed testing of a similar PEM electrolyzer was conducted at temperatures between 30°C and 70°C. Figure 14 shows the results of polarization testing of the liquid feed electrolyzer for temperatures in this range. The current densities generated in the anode liquid feed cell were significantly larger than in the cathode water vapor feed cell. At 1.8 V, the current densities for the anode liquid feed cell were all above 500 mA/cm^2 compared to less than 110 mA/cm^2 for the cathode vapor feed cell. Also, in the anode liquid feed system, a mass transfer limiting current was never reached. In the kinetically limited region of the curve, the current density produced by the cell does not vary with temperature as much as for the water vapor feed cell. Also, a limiting current density was not reached in the voltage range tested. At cell voltages between 1.4 and 1.8 V, the polarization was mostly linear. The linear polarization is due to the ohmic losses in the Nafion membrane. These ohmic losses decrease as the temperature increases. This is consistent with the fact that the conductivity of Nafion increases with temperature[6]. The anode liquid water feed during the experiments in Figure 14 was 10 ccm. The 10 ccm water flow rate was large enough that at all experimental conditions there was more than 30 times the amount of water reacted flowing to the cell. The relationship of the stoichiometric excess ratio to the cell current density for water flow rates of 10 ccm and 2 ccm are shown in Figure 15.

The cell polarization for a liquid water feed of 2 ccm is shown in Figure 16. The cell polarization with the 2 ccm water flow rate was nearly identical to the 10 ccm case. A comparison case illustrating the similarity in polarization with varying water flow rate at 70°C is shown in Figure 17.

The lack of variation in cell polarization with liquid water flow rate demonstrates that the cell is capable of operating at low anode flow rates without mass transfer limitations. Maintaining a low water feed rate during the operation of a PEM electrolyzer allows the amount of water recirculation in the system to be minimized. Future testing could investigate using anode water flow rates to near stoichiometric flow rates.

The mass transfer model presented in previous work [5] predicted that the current for an anode liquid water feed electrolyzer would be around 8 times larger than the limiting current in a cathode water vapor feed electrolyzer. The difference in the cell polarization between these two feed configurations is shown in Figure 18.

The mass transfer limiting current density for the cathode water vapor feed system is around 100 mA/cm^2 while the current for the cathode water vapor feed system is near 800 mA/cm^2 at 1.8V. This current density could most likely be increased to 1000-1400 mA/cm^2 if the a higher current density is desired and if it was determined that the higher voltage did not significantly affect the lifetime of the MEAs. Therefore, the cell current density produced by the anode liquid water feed system and thus the water reaction rate could be between 8-14 times larger than a similarly sized cathode water vapor feed system. To get an equivalent water processing rate between the two systems, either the reaction area of the cathode water vapor feed system or the number of cells used for processing the water would need to be increased proportionally to the difference in current density. If it is assumed that the tritium system the needs to process 190 kg of tritiated water per year, this means that a single electrolysis cell would need to operate at an average current of 65 A to meet this demand. Theoretically, all of this water could be processed by a single 50 cm^2 cell if the at 1300 mA/cm^2 if the cell operated continuously with an anode liquid water feed. More likely, is that several cells would be needed

in order to handle a more transient water processing rate. In contrast, a cathode water vapor feed system would require 8-14 cells operating continuously to process the 190 kg/year of tritiated water and this would be increased if the processing rate were transient.

Conclusions

Experiments have been conducted to characterize the current-voltage (i.e. polarization) operating characteristics for a Polymer Electrolyte Membrane (PEM) electrolyzer. As predicted by a mass transfer model, a PEM electrolyzer fed by a cathode water vapor feed reaches a limiting current at potentials above 1.6 V. Tests performed on a single Nafion 117 MEA showed that the limiting current could be as high as 100 mA/cm^2 at 70°C. The experimental values for the limiting current density were 3 times lower than predicted by a mass transfer model for a PEM electrolyzer that was previously published. The differences between predictions and the experimental data are hypothesized to be due to lack of consideration for other significant mass transfer limitation sources or inapplicability of fuel cell operating parameters such as the electroosmotic drag coefficient. Experiments with an anode liquid water feed with a similar cell showed that the current density was not limited by mass transfer up to 1.8 V. At 1.8 V, the current density was 800 mA/cm^2 and was still in the ohmic region where current increases linearly with voltage. The 50 cm^2 cell could possibly reach current densities of 1200-1400 mA/cm^2 before mass transfer limitations occur.

Acknowledgments

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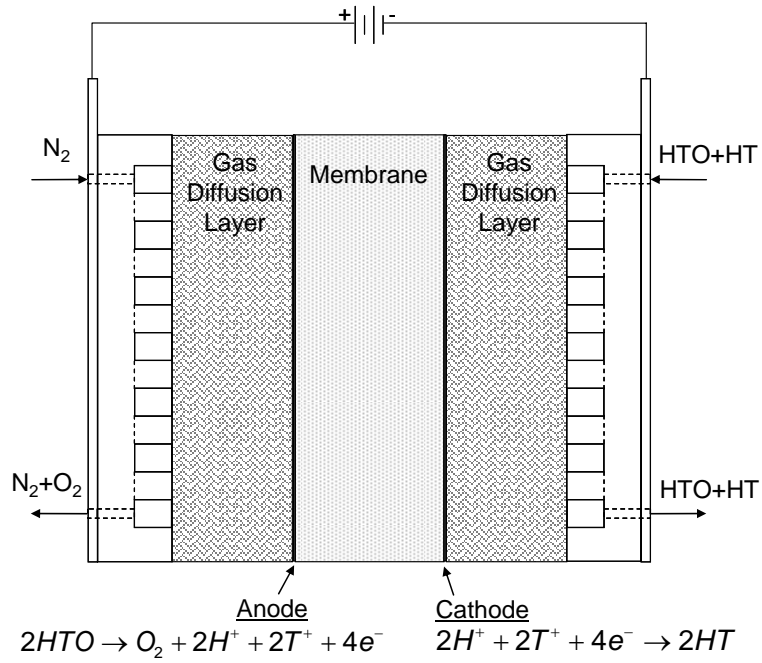
Figure 1.   Illustration of a cathode water vapor feed PEM electrolyzer.

Figure 2.   Cathode humidifier dewpoint temperature profiles with time. Humidifier set point

($\diamondsuit$) 30°C ($\square$) 40°C ($\bigcirc$) 50°C ($\triangle$) 60°C ($\times$) 70°C

Figure 3.   Cathode water vapor feed electrolyzer cell polarization at 100% RH for

temperatures between 30°C and 70°C. ($\diamondsuit$) 30°C ($\square$) 40°C ($\triangle$) 50°C ($\bigcirc$) 60°C ($\times$) 70°C

Figure 4.   Temperature dependence of the mass transfer limiting current density for a

cathode water vapor feed PEM electrolyzer and comparison to model predictions. ($\diamondsuit$) Exp.

limiting current densities ($-$) Model predictions

Figure 5.   Anode liquid water feed electrolyzer polarization at temperatures between 30°C

and 70°C with a liquid water flow rate of 10 ccm. ($\diamondsuit$) 30°C ($\square$) 40°C ($\triangle$) 50°C ($\bigcirc$) 60°C ($\times$)

70°C

Figure 6.   Relationship of the stoichiometric excess ratio and current density for a 50 cm^{2}

cell for liquid water feeds of 2 ccm and 10 ccm. ($\square$) 2 ccm ($\triangle$) 10 ccm

Figure 7.   Anode liquid water feed electrolyzer polarization at temperatures between 30°C

and 70°C with a liquid water flow rate of 2 ccm. ($\diamondsuit$) 30°C ($\square$) 40°C ($\triangle$) 50°C ($\bigcirc$) 60°C ($\times$)

70°C

Figure 8.   Anode liquid water feed electrolyzer polarization at 70°C with flow rates of 2 ccm and 10 ccm. (◇) 2 ccm (□) 10 ccm.

Figure 9.   Cell polarization comparison for anode liquid feed and cathode vapor feed PEM electrolyzer cells at 70°C. (□) Anode liquid feed (△) Cathode vapor feed

Figure 10. **Illustration of a cathode water vapor feed PEM electrolyzer.**

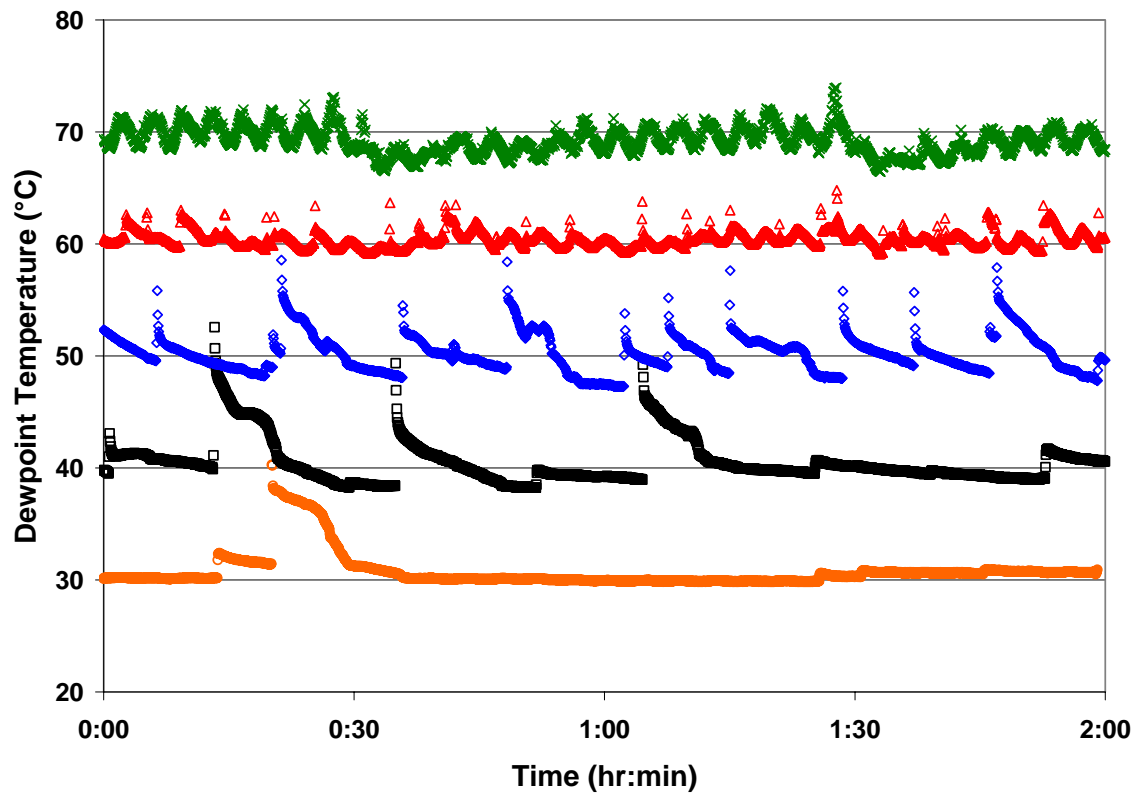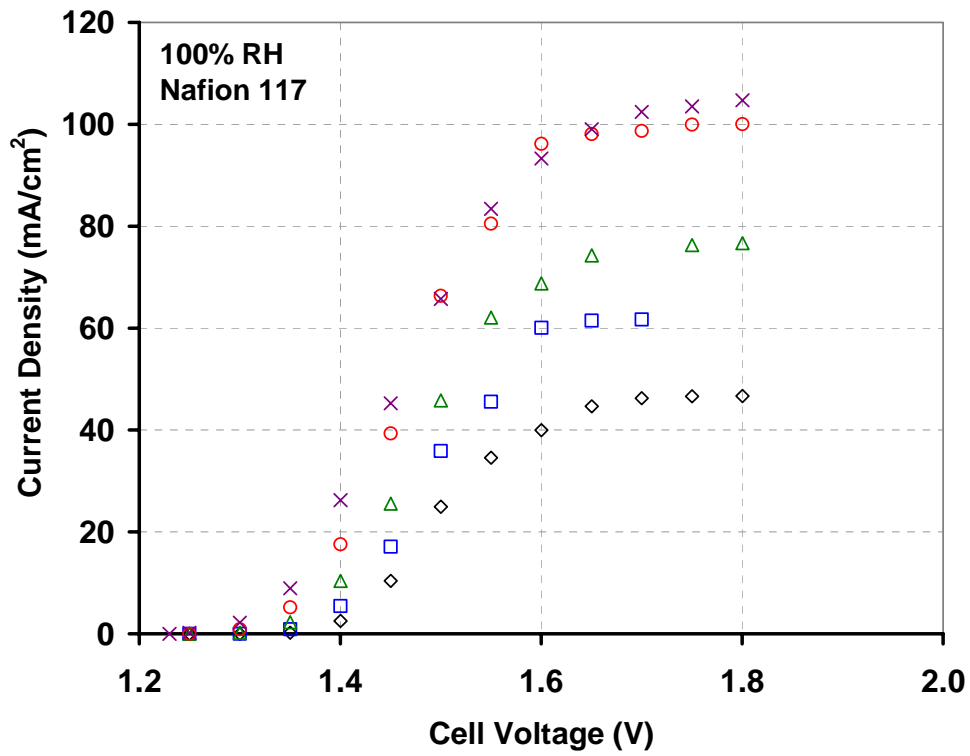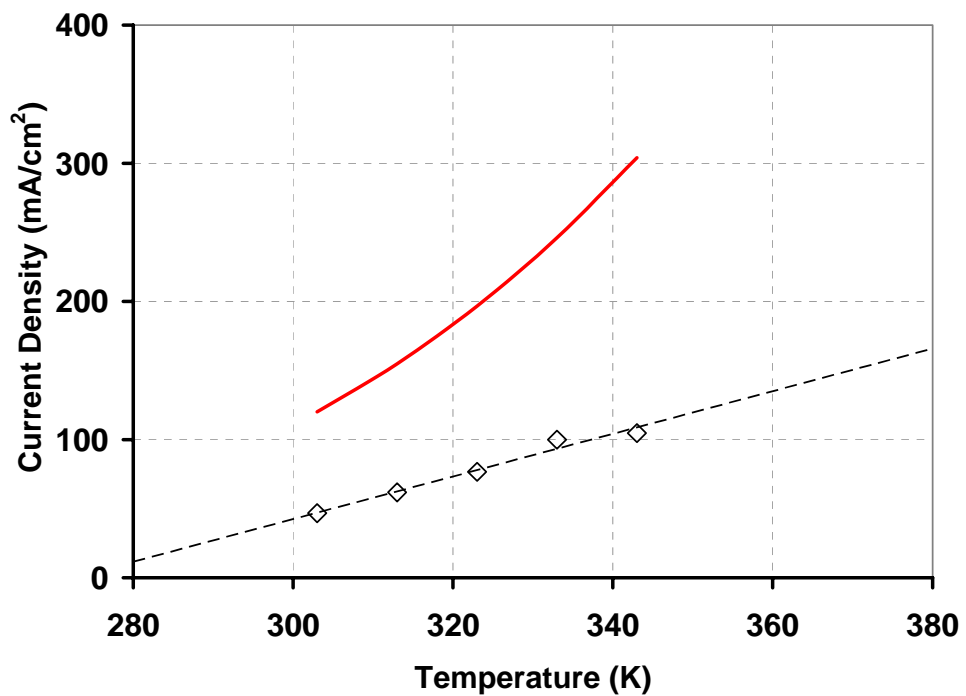**Figure 11.**　　　Cathode humidifier dewpoint temperature profiles with time. Humidifier set point (◇) 30°C (□) 40°C (○) 50°C (△) 60°C (×) 70°C

Figure 12. Cathode water vapor feed electrolyzer cell polarization at 100% RH for temperatures between 30°C and 70°C. (◇) 30°C (□) 40°C (△) 50°C (○) 60°C (×) 70°C

Figure 13. Temperature dependence of the mass transfer limiting current density for a cathode water vapor feed PEM electrolyzer and comparison to model predictions. ($\diamond$) Exp. limiting current densities ($-$) Model predictions
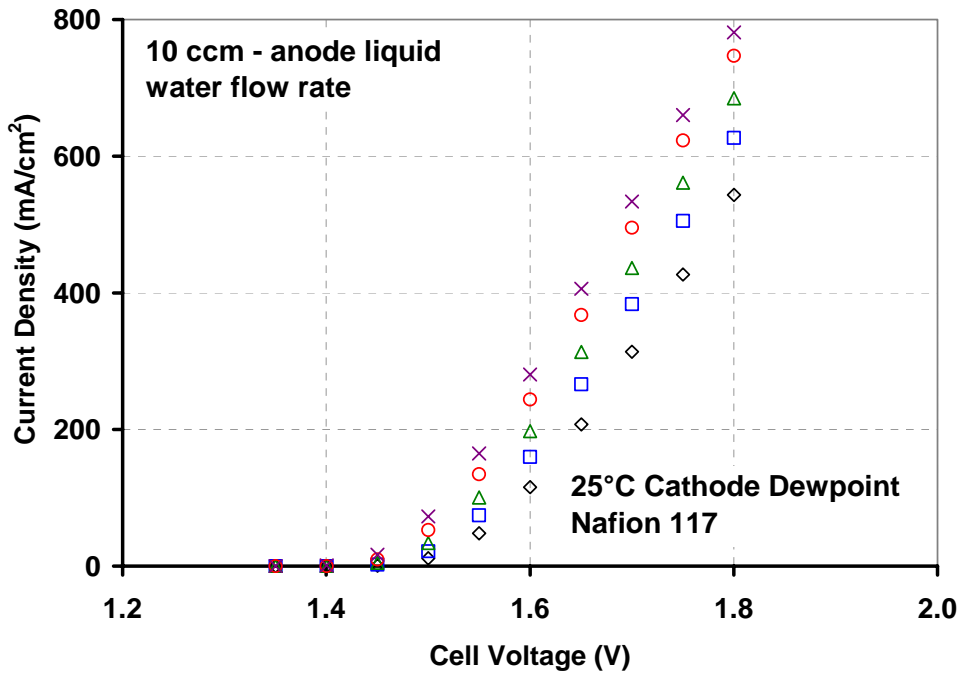
Figure 14. Anode liquid water feed electrolyzer polarization at temperatures between 30°C and 70°C with a liquid water flow rate of 10 ccm. (◇) 30°C (□) 40°C (△) 50°C (○) 60°C (×) 70°C
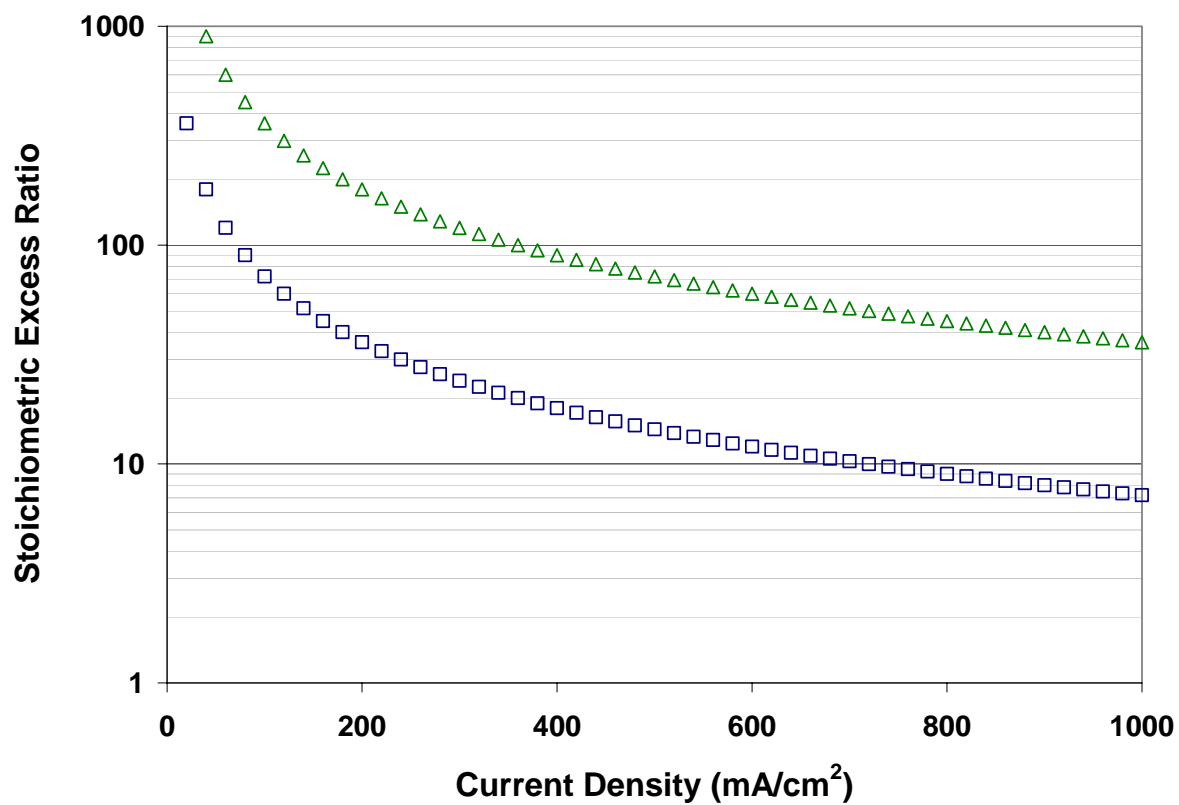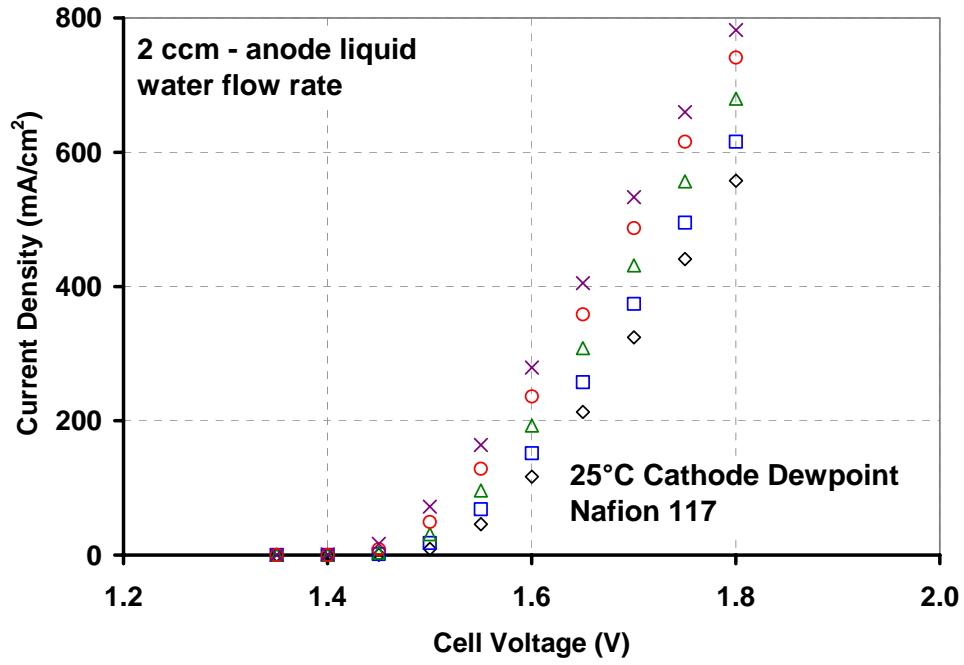
Figure 15. **Relationship of the stoichiometric excess ratio and current density for a 50 cm^2 cell for liquid water feeds of 2 ccm and 10 ccm. ($\square$) 2 ccm ($\triangle$) 10 ccm**

Figure 16. Anode liquid water feed electrolyzer polarization at temperatures between 30°C and 70°C with a liquid water flow rate of 2 ccm. (◇) 30°C (□) 40°C (△) 50°C (○) 60°C (×) 70°C
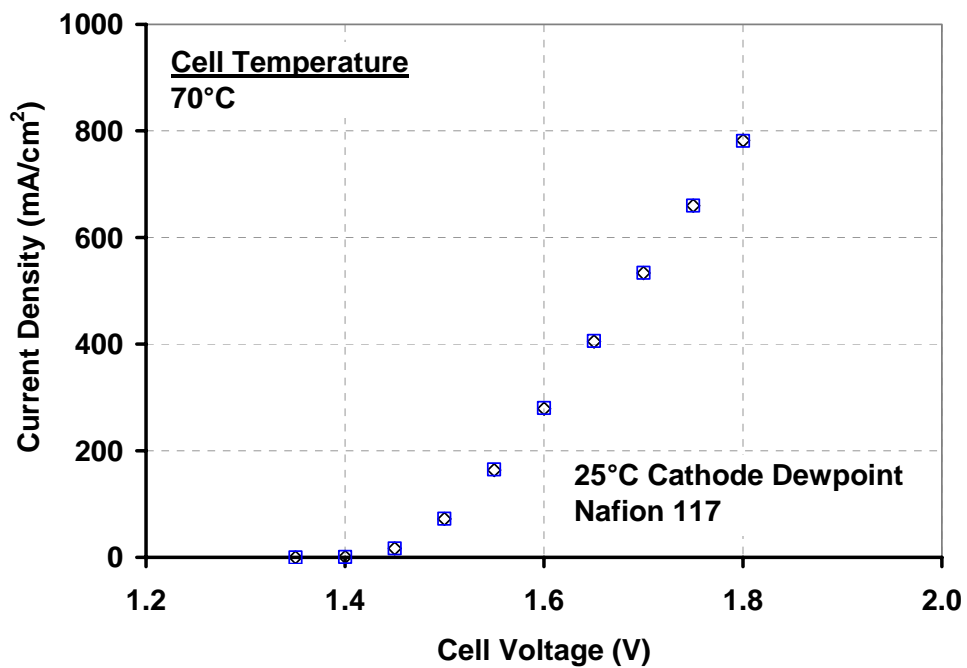
Figure 17. Anode liquid water feed electrolyzer polarization at 70°C with flow rates of 2 ccm and 10 ccm. (◇) 2 ccm (□) 10 ccm.
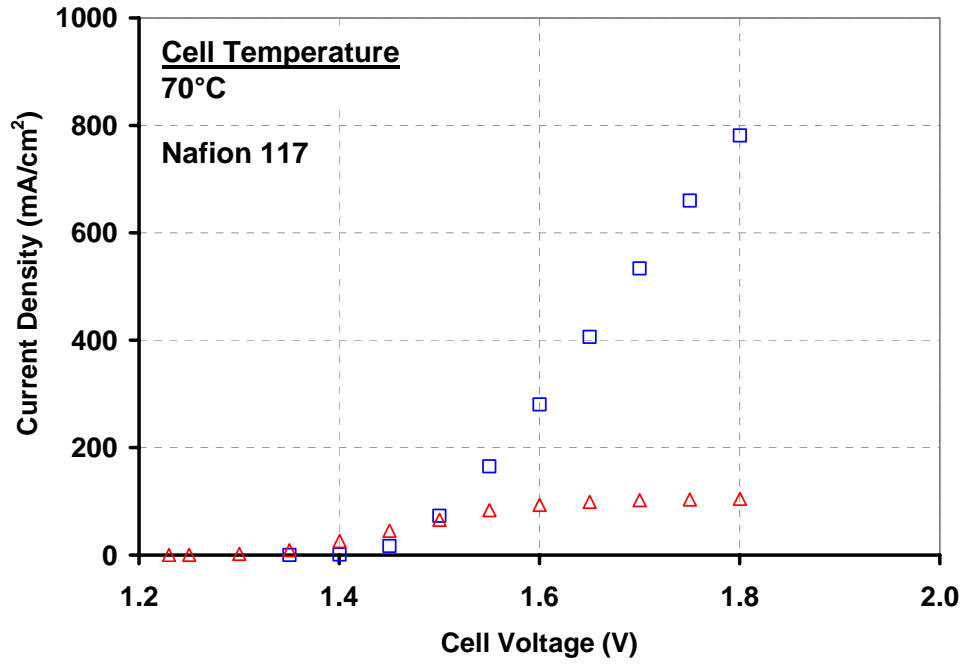
Figure 18. Cell polarization comparison for anode liquid feed and cathode vapor feed PEM electrolyzer cells at 70°C. (□) Anode liquid feed (△) Cathode vapor feed