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NEW PROTON EXCHANGE MEMBRANES FOR FUEL CELLS

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EVALUATION OF THE HUMIDIFICATION REQUIREMENTS OF NEW PROTON EXCHANGE MEMBRANES FOR FUEL CELLS

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ABSTRACT

Measurements of PEM fuel cell device performance were made with different gas inlet temperatures and relative humidity using a newly-designed test fixture. Significant improvement in device performance was observed when the fuel inlet temperature was increased above the operating temperature of the cell. These measurements were then correlated to a model to describe energy and mass transport processes.

INTRODUCTION

Fuel cells are energy conversion devices, forming electricity from chemical energy. The design challenge is to form rugged, reliable designs that yield high voltage efficiency. Historically fuel cells have been classified by the nature of the ionic conductor, the active element separating the two electrode layers. A range of ionic conductors have been developed, designed for low ionic resistance at the operating cell temperature. Hydrogen-oxygen fuel designs for low temperature ($< 100^{\circ}\text{C}$) ionic conductor designs focus on aqueous solutions, because ionic rates in solutions remain sufficiently rapid. Alkaline fuel cells, used in NASA space hardware, utilize a concentrated KOH solution. Proton exchange membrane (PEM), fuel cells—the focus of this study—use an ion conducting polymer, especially polyperfluorosulfonic acid materials. These polymer materials, when imbibed with water, exhibit solution-like properties, but because the anions are chemically bound to the polymeric structure, the electrolyte is contained. Importantly, product water removal is simplified, as electrolyte dilution is not a concern. However, the proton transport rate is a function of the polymer geometry, which is set, in part, by the polymer water content. [1] Consequently, dynamics of water flow are essential to understand the design of efficient conversion devices.

The electrochemical electrode layers, positioned onto the two opposite membrane faces, are composites, designed for electronic and ionic conductivity to active catalytic sites. Water dynamics also influence transport processes within these layers. Gaseous reactants also must permeate the electrode layers so they are formed with considerable porosity. Product liquid water must drain promptly to assure that gas transport structures are not obstructed.

Analyses of the various transport processes is complicated, and the absence of sensible tools has lead to only limited understanding of these fuel cell devices. This paper describes improved analytical techniques that are important to diagnose device designs.

EXPERIMENTAL

Experiments are made to interrogate the success of device fabrication technologies. One way to form these layered devices is to build each of the two electrode layers as thin films on transfer sheets (decals) and then laminate the two layers, fuel and air, to an ion conducting sheet. As formed on the transfer sheets, the electrode layers are thermally processable under conditions that membrane materials otherwise could be degraded. As an example, electrode layers are 0.004 cm thick while ionic conducting membrane sheets are 0.006 cm thick. Considerable art is involved in this processing, and diagnostics serve as an important guide to illustrate effects of process variations.

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The experimental test fixture used to control the fuel cell is shown schematically in Fig. 1. The fuel cell device is clamped into a flowing chemical reactor between two electrically conductive plates. The plates include milled features that direct flow along the 46 cm^2 active test area. The reactant gas is metered with a mass flow meter and mixed with liquid water (fed at a known rate from a HPLC pump) into a humidifier unit heated to 160°C . This temperature is high enough to ensure that all the liquid water is injected as vapor into the reactant gas. The temperature of the gas water vapor mixture is maintained as it passes through heated tubing to the fuel cell inlet. A separate gas-water mixing fixture is used for both the air and fuel feeds, although only one is shown. The inlet gas temperature is measured just prior to the active fuel cell area entrance (approximately 2 mm from the active area of the fuel cell). The entrance relative humidity is calculated, based on this temperature, and knowing the gas and water feed rates, and gas pressure. The temperature of the feed stream is controlled by adjusting the temperature of the transfer tubing.

Figure 1: PEM Test Fixture: Known flow rates of water are pumped into flowing reactant streams to generate 2-phase mixtures. Test devices are clamped into a electrically conductive fixture.

The temperature of the gas exiting the fuel cell active area is measured also within 2 mm from the active area to assure assessment of actual reactant gas phase temperature. Water dynamics are complicated because the membrane transports water between the two compartments. Inlet water feed rates are known, and to those flows electrochemical product water flow is added. The resulting flow is partitioned between the two device exhaust streams. Two-phase water flow is involved in both sides of the device. The water in the exhaust stream is then cooled to 5°C and then the condensate continuously weighed to monitor exit water flow rate. Some non-condensed water leaves the system in exhaust streams. This small quantity is assumed to correspond to 100% RH at the temperature measured following water collection.

The test fixture includes features to measure DC performance, either under potential or current control. Likewise, instrumentation is provided to measure AC impedance, a useful

diagnostic of ionic conductivity. (Electronic conductivity is generally not influenced by discrete moisture levels, while ionic conductivity is a strong function of that parameter.) The test fixture is fully automated so that pressure, reactant and product flow, temperature, and electronic measurements are controlled.

RESULTS

Gas inlet temperatures and water content are important parameters to fuel cell performance. Fig. 2 shows calibration data that illustrates that the fixture delivers steam at 100% RH to the experiment. Fuel gas inlet temperature is plotted as a function of the fuel water feed rate, using a constant H_2 feed of 0.5 SLPM at 180 kPa. The solid line shows calculated inlet gas temperature required to achieve 100% RH. Inlet temperatures are controlled so that the gas entered the fuel cell active area at the temperatures indicated by the dots in Fig. 2, following the 100% RH trace. Temperatures above the line are < 100 % RH, while measured temperatures below the line indicate the initiation of two phase flow.

Experiments are done to vary the steam content under constant water flow conditions. Some test data are shown in Fig. 3. As shown the air feed is 2.5 SLPM with 25% RH at 95 °C, and 180 kPa. Fuel feed was 0.5 SLPM H_2 at 180 kPa with 0.82 g/min. of water. Using this fixed combination of H_2 feed rate, water feed and gas pressure, the inlet temperature of 105 °C provides 100% RH in the inlet. The bulk of the cell hardware was maintained, using high flow water at a constant temperature at 95 °C. However, gas phase temperatures are not necessarily controlled once inside the fuel cell active area. Data for cell voltage and fuel electrode-to-air electrode water transport rates are all determined at 1 amp/cm² current density conditions. When inlet temperatures are lowered below the 100% RH condition, two phase water is injected. At temperatures in excess of 105 °C, the feed stream is less than 100% RH. Data show voltage performance that improves until the 100% RH condition is achieved and then remains flat

Figure 2: Anode gas inlet temperature controlled to the dew point temperature. Line shows required inlet temperature to achieve 100% RH in the anode feed stream.

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Figure 3: Effect of Two-phase Water Flow on Device Voltage Performance: Example of performance of PEM device with constant anode water content, as the steam/liquid water ratio is varied.

These data are compared to analytical calculations that solve the coupled flow equations for these devices. [2] Calculations (Figure 4) show the same trend as with experimental data. Voltage increases with temperature of the fuel feed, up to the point where 100% RH is achieved. This voltage performance is the result of either localized cooling, driven by evaporation of water within the fuel channel, or by liquid condensation within the fuel electrode layer. This example is not given to suggest optimum operational conditions, for these are set by a variety of design factors. Rather it is given as an illustration of the type of analysis available by this test fixture.

A second illustration of test fixture performance is the ability to diagnose devices as the relative humidity is changed. Figure 6 plots cell voltage and ionic resistance through a period of time as the air and inlet water feeds are independently changed. Voltage degradation can result from several factors including excessive water in the electrode layers (flooding) or by drying of either or both the membrane and the electrode layers. Drying leads to increased resistance, a parameter followed by the resistance measurement.

Fuel water feed (Figure 6) is initially held constant with no air water feed. Air conditions are sufficient to maintain high voltage. However, when the air pressure decreases, water partial pressure drops and voltage loss is apparent. This voltage loss is obviously the result of high device resistance. Increasing the air water feed rate quickly corrects the resistive loss. At time 1.5 hr the fuel water feed rate is lowered, again causing a high measured resistance, but nowhere near as high as shown earlier. Voltage remains quite constant, showing real differences in water requirements for the fuel and air. In this case, around 2 hr, increasing the air water feed corrects the cell resistance, but really has no impact of the device voltage.

In summary, the cell voltage is strongly dependent on the water content and temperature of the fuel and air feed streams. The optimization of the fuel water feed and the air water feed need to be done simultaneously for each device design, since they are coupled parameters.

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Figure 4: Model Predictions of PEM Device Performance. Model replicates conditions of Figure 3, showing voltage variation caused by changing the steam/water ratio.

Figure 5: Transient Data During Dynamic Input Transients. PEM device data showing effects of pressure, fuel and air water feed changes on voltage output and high frequency (ionic) resistance.

CONCLUSIONS

This paper describes a new test fixture that simultaneously measures fuel cell electrochemical parameters, including cell resistance, while controlling the flow and gas compositions of fuel and air reactant streams. It has been shown that the cell performance can be strongly dependent on the gas inlet temperature at a fixed water feed rate. A PEM fuel cell heat and water management model predicts the observed trends in cell voltage as a function of gas inlet temperature.

ACKNOWLEDGMENT

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