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David W. Gerlach
United Technologies Research Center

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Experimental Verification of Electroosmotic Dehumidification with Nafion and Plaster-Silica Gel Membranes

David W. GERLACH

United Technologies Research Center,
East Hartford, CT, USA
860-610-7695, fax: 860-622-6482, gerlacdw@utrc.utc.com

ABSTRACT

In electroosmotic dehumidification, a membrane composed of a desiccant material removes moisture from air to be conditioned. Then, electroosmotic pumping driven by the application of voltage moves the moisture across the membrane and rejects it on the other side. A bench top experiment was developed to screen promising membrane materials. Two sealed humidity chambers were separated by a membrane. The changes in the humidity of the chambers were measured as current was applied to the membrane. The most successful inorganic membrane tested was a silica gel concrete using Plaster of Paris as the cement and silica gel particles as the aggregate. Nafion membranes were also tested and showed a higher current, mass flow rate, and water vapor partial pressure differential. However, the electroosmotic flux is significantly smaller than predicted. Further research is needed to reconcile the experimental data and modeling in order to determine feasibility.

1. INTRODUCTION

Electroosmosis has been proposed for dehumidification in air conditioning systems (Mina, 2003 and Gerlach, 2006). In electroosmosis, water is pumped through channels or pores in solid material by the application of a voltage. A membrane composed of a desiccant material removes moisture from air to be conditioned. Then, electroosmotic pumping moves the moisture across the membrane and rejects it on the other side. This allows the sensible and latent loads to be handled separately and may lead to improvements in energy efficiency and comfort control.

Although water is a neutral molecule, ions produced in surface reactions with the membrane move under the application of an electrical field. The ions have a solvation shell of bound water molecules that moves with them. In the presence of bulk water, the movement of the solvated ions can move more water due to viscous forces.

This report details the use of membranes made of a plaster-silica gel composite and of Nafion®, a sulfonated tetrafluoroethylene copolymer produced by DuPont. Because of Nafion's chemical resistance and ability to conduct protons (H+ ions), it is commonly used as the membrane in polymer electrolyte membrane (PEM) fuel cells. Nafion is also used in diffusion driven membrane dryers for gases (Ye, 2003). These operate in a similar manner to total enthalpy exchangers, but usually have much smaller flow rates. Electroosmotic flow in Nafion is primarily due to the water in the solvation sheath.

Electroosmosis has been studied extensively for a variety of applications such as pumping single-phase water in microsystems (e.g. Razunguzwa, 2004), characterizing the surface properties of materials (e.g. Vernhet, 1994), and pumping to remove groundwater contaminants (e.g. Paillat, 2000). However, its application for dehumidification processes is relatively new and there is very little literature directly on this topic.

Mina (2003 and 2004) has performed the most extensive study of electroosmotic dehumidification. Electroosmotic flow in flooded pores is analyzed. The performance of an electroosmotic membrane with a desiccant layer coupled to it was analyzed. A generalized coefficient of performance for conditioning of moist air was used to analyze the performance gains achievable with electroosmosis. Mina studied fairly simple low cost materials such as plaster, kaolin, and concrete.

Electroosmosis has been used in commercial basement dewatering systems (e.g. Hamatrol, Drytronic websites). The US Army Corps of Engineers has found these systems to be effective in not only preventing water seepage, but in reducing the humidity in basements (Hock, 1998).

Researchers at the European Aeronautics Defense and Space Company have investigated electroosmosis for removing sweat from the seats of luxury cars. They were not able to produce an electroosmotic flow using sodium chloride solution in glass capillaries and frit. They did produce measurable flow using a non specified clay membrane. A variety of polymer membranes were tested with distilled degassed water and an artificial sweat solution with pH of 5.5. The "best" membrane was Nafion. All tests were done with the membrane materials submerged (Godula-Jopek, 2004).

2. MEMBRANE MATERIALS

The material to be used for the electroosmotic membrane is the main determinant of the device's performance and therefore will determine the efficiency, cost, size, etc. of the final device. An electroosmotic dehumidification membrane must be hydrophilic and hygroscopic to capture and hold moisture. In order for the material to allow forward electroosmotic flow, it must have mobile and stationary ions at the pH and composition of condensed humidity. It is preferable that the mobile ions be produced by a surface chemical reaction with water so that the ions are continuously produced and not depleted by current flow. The material needs to be porous, but the pores or holes can not be large enough to allow backward pressure driven flow or bulk air flow. It must be possible to fabricate thin but durable membranes of the material. The material should not crack or degrade with repeated moisture content changes. This could be accomplished by having a low volume change with change in moisture content or by the material being sufficiently flexible that it does not crack. In addition, the material must be sufficiently inexpensive that the final electroosmotic dehumidification is not eliminated from use on a first cost basis.

3. SIMPLIFIED MEMBRANE MODEL

The total mass flux of water through the membrane ($\dot{m}''_{total}$) is the sum of the forward flow of water by electroosmotic pumping ($\dot{m}''_{bulk}$) and the backward flow of water by diffusion ($\dot{m}''_{diffusion}$):

$$\dot{m}''_{total} = \dot{m}''_{bulk} + \dot{m}''_{diffusion} \tag{1}$$

At steady state the total mass flux is constant through each layer. However, the diffusive and electroosmotic fluxes vary with position (Figure 1). The moisture transport in the air was not modeled.

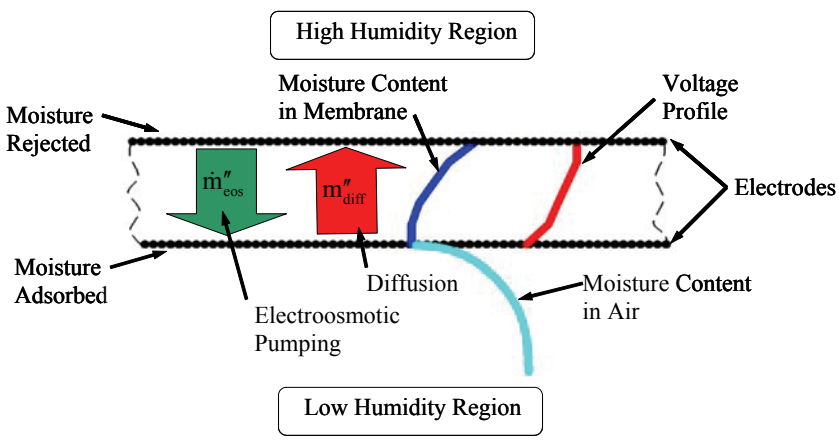

Figure 1: Schematic of electroosmotic dehumidification process. Water is pumped from a region of low humidity to a region of high humidity.

In general, the electroosmotic mass flux ($\dot{m}''_{eos}$) is proportional to the electrical potential gradient (∇E):

$$m''_{eos} = C_{eos} \nabla E \tag{2}$$

coefficient C_{eos} is a function of the membrane material, pore geometry (porosity and tortuosity), and the water content of the membrane. The important factors and functional form of C_{eos} can be determined by a combination of calculations and/or experiment. Because the electroosmotic flux sets up a concentration gradient, a diffusional flux

flows in the opposite direction. The mass flux due to diffusion (m''_{diff}) is generally proportional to the gradient of the water content (∇W):

$$m''_{diff} = -D\nabla W \tag{3}$$

The effective diffusion constant D is dependent on similar properties to those that determine C_{eos} and is usually empirically measured. The surface water content of the membrane can be calculated from equilibrium with the moisture content of the air.

Gerlach (2006 and 2008) gives a description of the method used to calculate C_{eos} and D for silica gel and Nafion membranes.

Model Predictions

The model predictions for Nafion membranes are in a range that is realistic for practical use. The current densities are on the order of tens of milliamps per square centimeter. The voltage is also in the range of tens of millivolts across a single membrane. A real system may electrically connect membranes in parallel in order to increase the voltage required. The mass fluxes are on the order of 10^{-9} kg/s-cm^2. At a flux of 5×10^{-9} kg/s-cm^2, a 5 ton air conditioning unit with a sensible heat ratio of 0.60 will require a 57 square meters of membrane. Although this would be cost prohibitive with Nafion at current prices, the surface area could easily be handled in an arrangement similar to crossflow total enthalpy exchangers.

Membrane Thickness

As the membrane thickness increases the electrical resistance increases. At the same time the back diffusion of water decreases. Therefore a thicker membrane can maintain a larger vapor pressure difference, but at a reduced pumping efficiency than a thinner membrane. Alternatively total mass flux through a membrane increases with increasing membrane thickness when the humidity conditions on each side of the membrane are held constant (Figure 2).

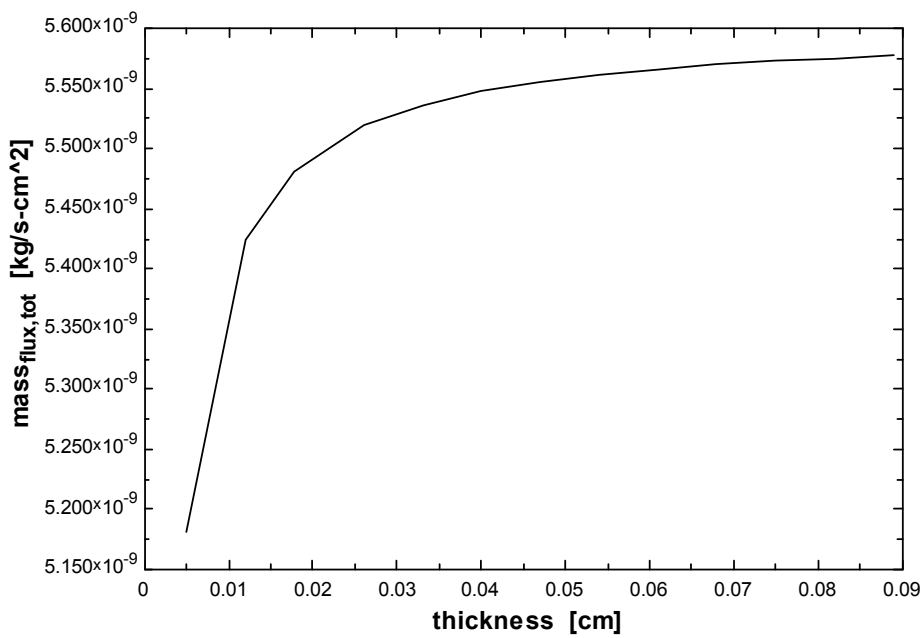

Figure 2: The total water mass flux through the Nafion membrane increases with increasing thickness for set humidity conditions (relative humidities of 0.775 and 0.715 current density of 30mA/cm^2)

Because this model uses the average water content of the two sides to calculate the conductivity, the membrane resistance increases linearly with membrane thickness for constant humidity conditions. Consequently, the voltage increases linearly with thickness for a set current flow and the energy required per unit mass to pump the water is linearly related to membrane thickness

4. MEMBRANE EXPERIMENT

A bench top experiment was developed to screen promising membrane materials and to provide data for model validation (Figure 3). Two chambers, of 0.002 m^3 volume each, were separated by a test membrane held in a ½ or 3/8 inch thick acrylic frame. The frame was bolted between flanges on the boxes, so that the test membrane could be easily replaced. The joints between the flanges and the frame were sealed by closed cell foam gaskets. The humidity levels and temperature were recorded every five minutes by humidity and temperature transducers. The transducers accuracies were 2.5% relative humidity and 0.6 ºC for temperature. In addition the temperature was measured in each test chamber with type T thermocouples with an accuracy of 1 ºC. A standard DC power supply applied either a constant voltage or constant current to the electrodes on each side of the membrane.

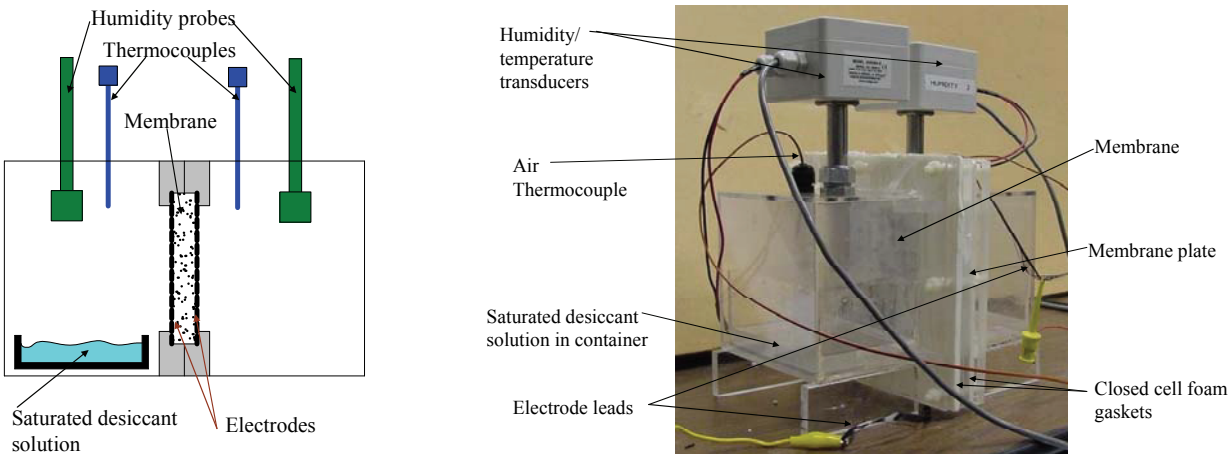

Figure 3: Left: Schematic of free convection membrane experiment Right: Free convection setup with silica gel concrete membrane

The humidity on one side of the membrane was kept constant with saturated NaCl solution (RH~ 75%). The humidity in the other chamber was allowed to vary to demonstrate the electroosmotic dehumidification effect. The water flow rate was determined from the change in humidity of the side without the salt solution. Because the flow rate in the tests was low, no liquid water was observed exuding from the membrane. The water simply evaporated off of the membrane backside and entered the air.

For the Nafion tests, a small fan (4.5 cfm) was added to each chamber to reduce the convective mass transport resistance. The fans were attached at the vertical midpoint of the back wall and pointed down. After the addition of fans, the humidity equilibrated faster at the level determined by the salt solution. However, no improvement in the rate of electroosmotic transport was noted, implying that the convective resistance was not significant.

5. INORGANIC MEMBRANE EXPERIMENTS

A variety of membrane materials based on silica gel, Plaster of Paris, or zeolites were investigated. These will be termed inorganic materials, although some of the membranes contained polymers such as agar. The most successful inorganic membrane was a silica gel concrete using Plaster of Paris as the cement and silica gel particles as the aggregate.

A container of saturated NaCl solution in the chamber on one side of the membrane maintained the air at 73% relative humidity. Without any forced convection, the time for diffusion through the air to reach equilibrium is on the order of days (Figure 4). The water diffused through the membrane and caused the other side to also trend towards this equilibrium value.

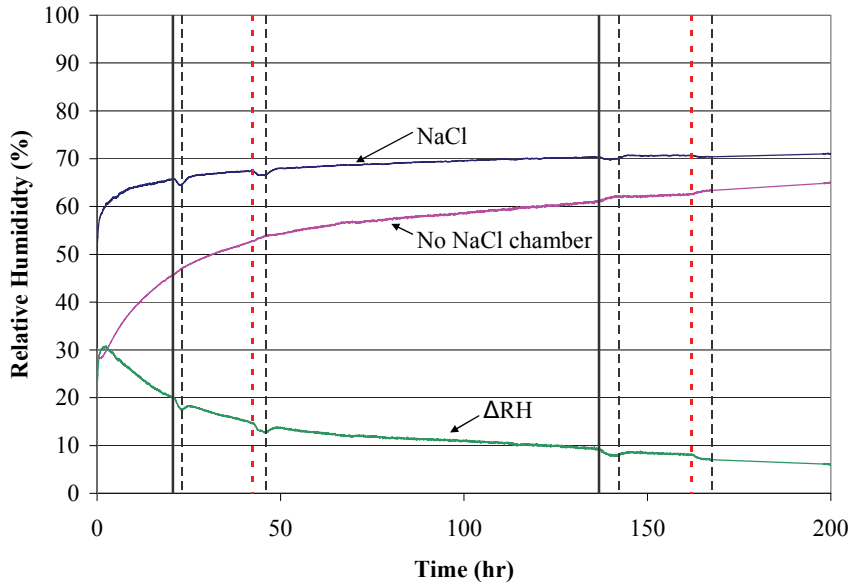

Figure 4: Time series data of Silica gel/plaster membrane experiment. Upper line is the relative humidity on the side with NaCl, middle line is the relative humidity on the side with no solution, and the lower line is the difference in the relative humidity between the two sides. Vertical lines show the times when the current was turned on with the negative electrode on the side with the NaCl chamber (solid line), turned on with the negative electrode towards the chamber with no salt (small dashes), or turned off (large dashes).

The measured humidity curve changes when voltage is applied and returns to the diffusion dominated curve when the voltage is turned off. This only occurs with the switching of the voltage, demonstrating that the humidity changes are a result of the application of voltage. However, the humidity changes are comparable to the stated instrumentation error. The measured molar flux is in the range of 10^{-7}-10^{-9}mol/s-m^2 or 10^{-13}-10^{-15} kg/s-cm^2. Contrary to the expected behavior, the direction of the humidity change was not dependent on the polarity of the applied voltage. This may be due to the combination of opposite flow directions in the membrane components. The Plaster of Paris acts as a base and the silica gel acts as an acid. Therefore the two membrane components should have opposite surface charge potentials and the flow in each component should be in opposite directions.

A number of membrane formulations using plaster, silica gel, sodium silicate, and zeolites were tested in order to improve on the performance of the plaster and silica gel membrane discussed above. None of them demonstrated any significant improvements and several shrank or crumbled during drying.

6. NAFION MEMBRANE EXPERIMENT

A 10x10cm Nafion 117 membrane electrode assembly (MEA) with commercially applied fuel cell electrodes and catalysts was tested. The Nafion membranes were mounted between acrylic frames with polyethylene sheet gaskets and mounted in the two chamber setup. Stainless steel mesh current collectors were mounted in contact with the membrane faces. The fans were on during all Nafion tests.

A regulated electrical power supply applied a constant current to the membrane. Currents of 2, 3, 5, and 10 amps were used with the flow directed towards the chamber with NaCl. A single test with a 3 amp current in the reverse direction was performed to verify the direction of flow depends on the current. These values correspond to current densities of 0.02, 0.03, 0.05, and 0.10 amp/cm^2.

The time series data from these experiments was curve fit to determine the diffusion and electroosmotic coefficients (Figure 5 and 6). The readings from the humidity transducers were calibrated with respect to the equilibrium vapor pressure of the saturated NaCl solution. The humidity ratio increased on the side of the membrane with the saturated salt solution, because the temperature increased from the ohmic heating of the membrane (Figure 5). The

electroosmotic flow is assumed to be directly proportional to the current. The diffusion rate is assumed to be directed proportional to the difference in humidity ratio across the membrane. At zero current, all flow through the membrane is assumed to be due to concentration driven diffusion.

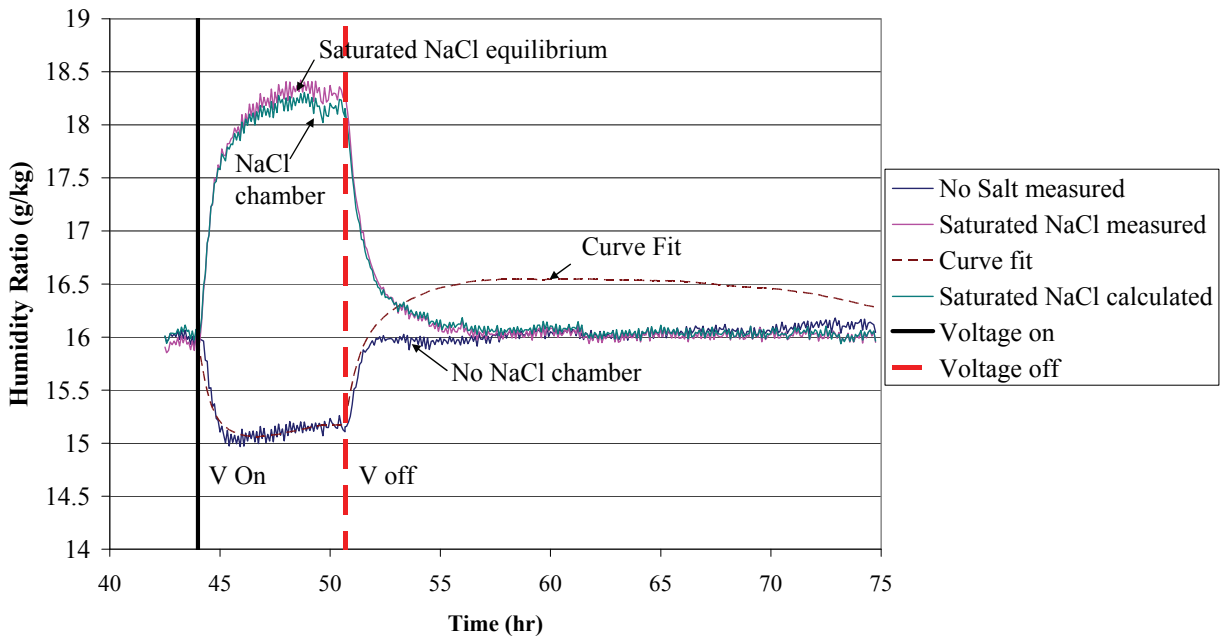

Figure 5: Time series data of humidity ratios for test at 3 amp current. Top solid: Humidity ratio on the side of the membrane with saturated salt solution, Middle solid: Humidity ratio on membrane side without salt, Bottom solid: Equilibrium humidity ratio of saturated salt solution calculated from the air temperature. Dashed: Humidity ratio on side of membrane with no salt as calculated by the curve fit.

The proportionality constants are used as fitting parameters. The instantaneous diffusional flux is calculated from the measured humidity ratio values (ω_1 and ω_2) and the total effective diffusion coefficient (D_{eff}):

$$m''_{diffusion} = D_{eff}(\omega_1 - \omega_2) \tag{4}$$

The convective resistance from the bulk flow to the surface is also included in the measured diffusion coefficient. The electroosmotic flux (m''_{eos}) is calculated by:

$$m''_{eos} = C_{eos} I \tag{5}$$

where C_{eos} is the effective electroosmotic coefficient and I is the total current flow through the membrane. The total flow through the membrane is calculated by:

$$m''_{total} = m''_{eos} + m''_{diffusion} \tag{6}$$

The time series of the humidity on the side without the NaCl was calculated from these formulas. The initial value for the humidity was taken from the experiment shortly before the current was turned on, when the humidity levels on both sides of the membrane had reached diffusion equilibrium and were steady. The predicted humidity value at the next time step (ω_{j+1}) is predicted from the value at the current time step (ω_j) by:

$$\omega_{j+1} = \omega_j + \Delta t \cdot m''_{total} \tag{7}$$

where Δt is the time between measurements. The electroosmotic and diffusion coefficients were determined through a combination of minimizing the sum of the squared errors and subjective manual fitting to the graphs.

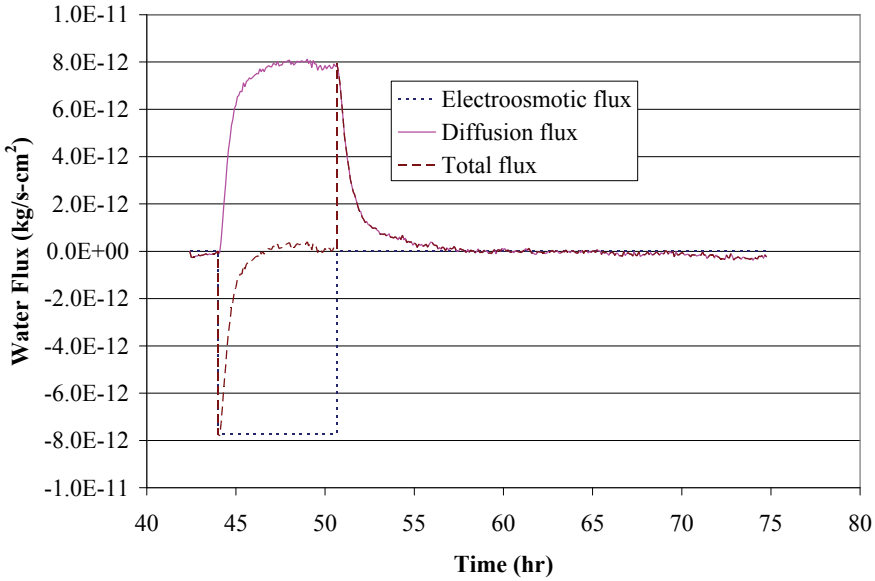

Figure 6: Electroosmotic and diffusion flows at 3 amp current as determined by a curve fit to experimental data.

Jeon (2006) reported long term degradation in membrane performance with increasing current density in direct methanol fuels cells. At current densities of 100, 150, and 200 mA/cm^2 after a period of 145 hours, the fuel cell power densities were 93.9, 79.9, and 55.1% of the initial value. Consequently, the maximum current density used in the experimental tests was set at 100 mA/cm^2 or 10 amps total for the test setup. However, the membrane performance dropped dramatically (Figure 7) after this test and the membrane may have been damaged. A least square curve fit through the origin for the 0.02 and 0.03 A/cm^2 tests performed before the 10 amp test has a slope of 0.94 (g/kg)/(A/cm^2) (R^2=0.94). For the 0.1 A/cm^2 test and the following 0.05 and -0.03 A/cm^2, the slope is significantly reduced to 0.19 (g/kg)/(A/cm^2) (R^2=0.99).

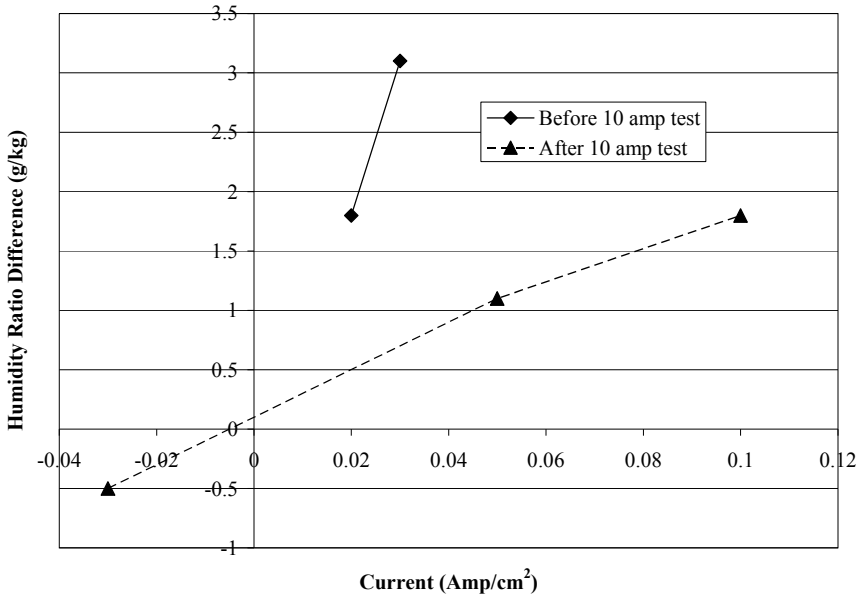

Figure 7: Humidity ratio sustained across Nafion membrane as a function of applied current density.

Comparison of Experiment to Model

The diffusion flux is similar in magnitude to that predicted by the model. The electroosmotic flux is three orders of magnitude smaller than that predicted. However, the raw humidity measurements were of similar magnitude to the measurement accuracy. In addition, the results of the curve fitting technique are very sensitive to the data.

5. CONCLUSIONS

The Nafion membranes showed a higher current, mass flow rate, and water vapor partial pressure differential than the plaster-silica gel membrane. However, many of the parameters measured in the membrane experiments are several orders of magnitude different than that predicted by the model implying that a real system would have performance considerably less than that predicted. However, the experimental error in the experiments was so large that it is unclear how much of a difference from the predictions could be expected.

Using a thicker Nafion membrane should demonstrate a larger humidity change, allowing a greater certainty about the magnitude of the results.

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