Technical note

Measuring moisture sorption and diffusion kinetics on proton exchange membranes using a gravimetric vapor sorption apparatus[☆]

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Abstract

The understanding of water sorption and diffusion properties of proton exchange membranes is crucial to the fuel cell's ultimate performance. In this study, a dynamic gravimetric vapor sorption (DVS) instrument was used to measure the water vapor sorption properties of three Nafion® based fuel cell membranes: N-117 (extruded film, 183 μm thick); N-112 (extruded film, 51 μm thick); and NR-112 (dispersion cast film, 51 μm thick). Water sorption characteristics were studied between 0 and 95% relative humidity (RH) at 30, 40, 50, 70, and 80 °C. The thicker dispersion cast, N-117, film had a lower water vapor sorption capacity (based on percentage weight gain) than the thinner, N-112 sample. The dispersion cast, NR-112, film had a lower percentage water uptake than the extruded, N-112, film. Below 80% RH, the water sorption capacity increases with temperature for all three samples. Above 80% RH, the moisture sorption capacity increases from 30 to 50 °C, but decreases at 70 and 80 °C compared to the lower temperature data. Moisture diffusion coefficients were also calculated over the humidity and temperature range studied. In general, maximum diffusion coefficients were measured at intermediate humidities. Water heat of sorption calculations at low coverages yielded higher values for the extruded (N-112) film compared to the dispersion cast (NR-112) film indicating a higher affinity for water.
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1. Introduction

Proton exchange membrane fuel cells (PEMFC) are an expanding area of research for use as low pollution power generators for mobile and stationary applications. The PEMFC is composed of a membrane electrode assembly consisting of several layers. There are typically two carbon cloth gas-diffusion layers that allow concurrent transport of gases and water while collecting current and two carbon-supported Pt based catalyst layers where the electrochemical reactions take places. These layers are sandwiched between a proton exchange membrane that permits proton transfer from anode to cathode [1].

A critical parameter affecting the performance of these proton exchange membranes is the water content. Water is typically supplied to the fuel cell by humidifying the gas feed stream. The level of hydration within the proton exchange membrane is vital to its performance. If the hydration level is too low, the polymers exhibit greatly reduced ionic conductivity [2]. Membrane dehydration is a well-known fuel cell failure mechanism. On the contrary, if hydration level is too high, excess water can flood the pores in the gas diffusion layer and block off reaction sites or impede mass transport within the electrode structure [3,4]. In addition, the water vapor diffusion coefficients as a function of water content are important parameters in characterizing the performance of proton exchange membranes [4].

Related to the water content is the operating temperature of the proton exchange membrane. Increasing the operating temperature above room temperature improves the electrode kinetics of the oxygen reduction reaction [5]. However, if the temperature is above the boiling point of water, the water content in the polymer decreases leading to a decrease in conductivity [6]. Additionally, if the temperature is above the glass transition for the polymer, then polymer chain rearrangement can occur and cause structural changes in the membrane, lower membrane sta-

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bility, and reduce performance [5]. For the above reasons, it is important to study the behavior of these films over wide temperature and humidity ranges.

In this study, the water content and diffusion kinetics were studied on three different Nafion® based membranes over a range of temperatures. Nafion® is a commercially available perfluorosulfonic acid polymer often used as an exchange membrane in PEMFCs. Nafion® is an ideal choice for PEMFC applications due to its high chemical and electrochemical stability, sufficient mechanical strength, low permeability to reactant species, selective and high ionic conductivity, and electronic insulation properties [7]. Nafion® has further applications as a novel clothing materials for protection from chemical warfare agents, separators in chloro-alkali cells, and as super acid catalysts [8,9]. For the above reasons, Nafion® films were used in this study as model proton exchange membranes.

2. Experimental

Dynamic gravimetric vapor sorption (DVS) is a well-established method for the determination of vapor sorption isotherms. The DVS-1000 instrument (Surface Measurement Systems, London, UK) used for these studies measures the uptake and loss of vapor gravimetrically using a recording ultra-microbalance with a mass resolution of $\pm 0.1\,\mu g$. The high mass resolution and baseline stability allow the instrument to measure the adsorption and desorption of very small amounts of probe molecule. The vapor partial pressure around the sample is controlled by mixing saturated and dry carrier gas streams using electronic mass flow controllers. The temperature is maintained constant $\pm 0.1\,°C$, by enclosing the entire system in a temperature-controlled incubator.

For the DVS experiments, a small ($\sim 1\,cm^2$) section of film was placed in a stainless steel mesh sample pan. The 400 mesh pan (400 holes/in.) allowed direct vapor flow to all sides of the film. The sample pan was then placed in the DVS at the desired temperature and dried at 0% RH to establish a dry mass. After a stable, dry mass was achieved, the sample was exposed to the following relative humidity (RH) profile: 0–10% RH in 2% RH increments, 10–30% RH in 5% RH increments, 30–90% RH in 10% increments and 95% RH. The humidity was decreased in a similar manner to achieve a complete desorption profile. Mass equilibrium was reached at each humidity stage by measuring the percentage change in mass with respect to time (i.e. slope or dm/dt). Once the mass slope was below a predetermined threshold value and equilibrium was achieved; the experiment proceeded to the next programmed humidity stage. Complete sorption and desorption isotherms were collected at 30, 40, 50, 70, and 80 °C. A new sample was used for each temperature to minimize any thermal history effects.

Three different Nafion® films were obtained from DuPont: N-117, N-112, and NR-112. All three films are based on the Nafion® material, which is a perfluorosulfonic acid/TFE copolymer in the acid (H⁺) form. N-117 and N-112 are non-reinforced extruded films while the NR-112 material is a non-reinforced dispersion-cast film. The N-117 sample is 183 μm thick at 23 °C and 50% RH, while the N-112 and NR-112 samples are 51 μm

thick at the same conditions. These film thickness values were used for all diffusion calculations. The effect of film thickness for the same base material can be investigated by comparing the results from the N-117 and N-112 samples, while the effect of extruded or dispersion-cast films can be studied by comparing the N-112 and NR-112 samples.

3. Theory

From the initial vapor uptakes with each change in relative humidity, it is possible to calculate the water vapor diffusion constant into the film. The method used to calculate the diffusion constants for thin films utilizes diffusion equations first employed by Crank and Park [10]. In short, a thin film sample, with thickness d, is placed in the DVS and for a single step change in humidity the initial kinetics of sorption into the bulk for a two-sided film may be described by Eq. (1) below:

$$\frac{M_t}{M_\infty} = \frac{4}{d}\sqrt{\frac{Dt}{\pi}} \tag{1}$$

where M_t is the amount adsorbed at time t, M_∞ the amount adsorbed at thermodynamic equilibrium, and D is the diffusion constant. This equation is applied for values of $M_t/M_\infty < 0.4$, where a plot of M_t/M_∞ against $t^{1/2}/d$ should be linear. The diffusion constant D can then be calculated from the slope of this line. The only input parameter necessary for these calculations is the film thickness. Diffusion constants were calculated for each step change in humidity at each temperature. In order to monitor fast diffusion processes, data points were collected every 2 s for these experiments. For the linear fit described above, a minimum R^2 value of 99.9% was used for all diffusion calculations.

A sorption isotherm describes the equilibrium vapor or gas uptake as a function of vapor or gas partial pressure. By measuring isotherms at different temperatures, it is possible to calculate the isoteric heat of sorption, via a Clausius–Clapeyron type equation [11]:

$$\left(\frac{\partial \ln p}{\partial T}\right)_\theta = -\frac{\Delta H_s}{RT^2} \tag{2}$$

where p is the partial pressure, T the temperature, R the universal gas constant, and ΔH_s is the heat of sorption. ΔH_s values can be obtained if sorption isotherms are measured at different temperatures and assuming the heat of sorption is exclusively exothermic and independent of temperature. With $d(1/T)/dT = -1/T^2$, Eq. (2) can be rearranged to:

$$\left(\frac{\partial \ln p}{\partial (1/T)}\right)_\theta = \frac{\Delta H_s}{R} \tag{3}$$

If the partial pressures (p_1 and p_2) at two temperatures (T_1 and T_2) and identical surface coverages are obtained, then the heat of sorption can be calculated directly via:

$$\Delta H_s = -R\frac{\ln(p_2/p_1)}{(1/T_2) - (1/T_1)} \tag{4}$$

Eq. (4) can be used for any vapor–sorbate system over a wide range of temperatures. Heat of sorption values were calculated
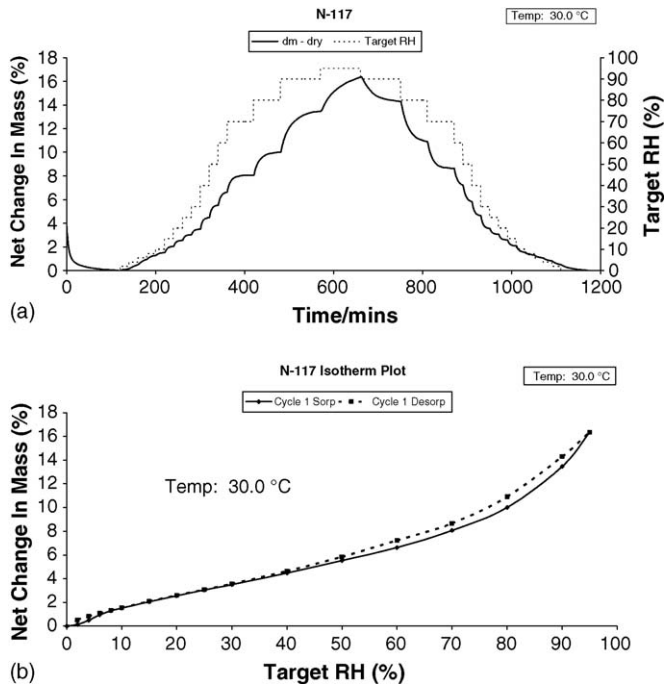
Fig. 1. Moisture sorption and desorption kinetics (a) and isotherm (b) for the N-117 sample at 30 °C. Water sorption kinetics are relatively fast as the sample rapidly approaches equilibrium with each change in humidity. Water sorption is dominated by bulk absorption.

over the entire isotherm range to determine the affinity of water vapor over a range of coverages.

4. Results and discussion

Fig. 1 displays the typical moisture sorption and desorption kinetic results obtained. Specifically, Fig. 1a shows the moisture sorption and desorption results for the N-117 sample at 30 °C. The solid trace displays the percentage change in mass, referenced to the dry mass, versus time on the left axis while the dashed trace shows the chamber RH as a function of time on the right axis. The sample mass increases or decreases with each corresponding increase or decrease in humidity and rapidly reaches equilibrium. From these equilibrium points the isotherm can be determined. Fig. 1b displays the water vapor isotherm for this N-117 sample at 30 °C. The sorption cycle is shown in the solid line, while the desorption cycle is the dashed lines. Multiple cycle experiments (not shown) indicate there is no measurable difference between the first cycle isotherms and subsequent isotherms, indicating that water sorption under these conditions is completely reversible. The sample sorbs relatively large amounts of water. To illustrate, at 95% RH, the sample uptakes over 15% of its dry weight in water vapor. Surface water sorption, is typically limited to less than 1% changes in mass for non-porous, polymer film samples. Therefore, water sorption is most likely dominated by bulk absorption. Above 40% RH there is measurable hysteresis between the sorption and desorption isotherms. Hysteresis gaps of this type are often indicative of a bulk absorption dominated mechanism where vapor desorption is diffusion limited.
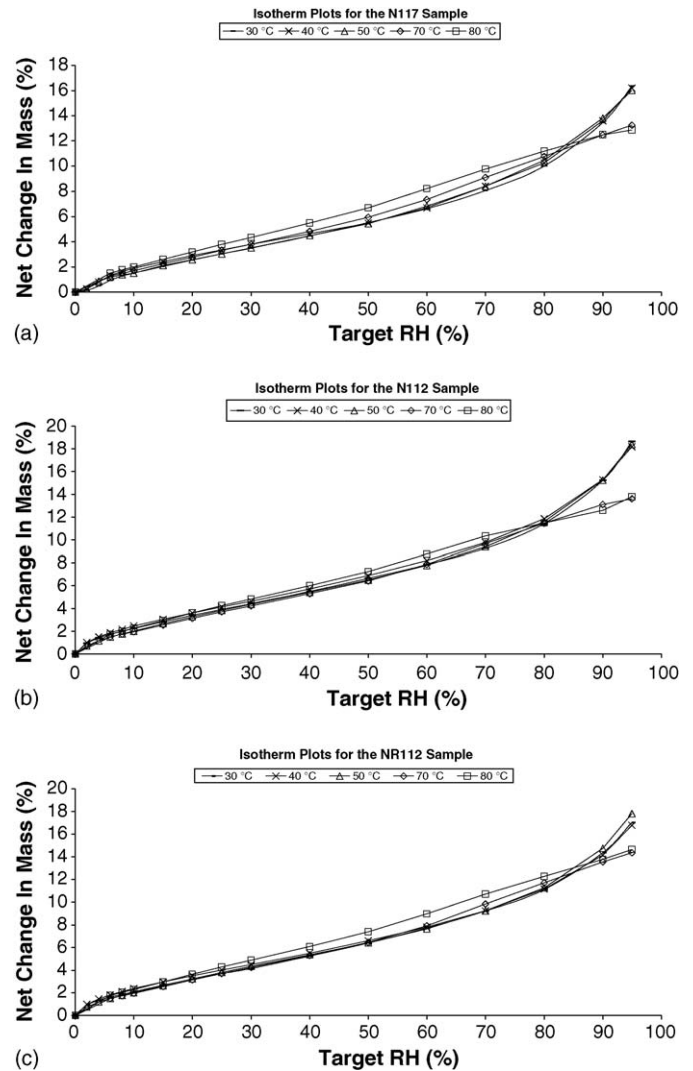

Fig. 2. Moisture sorption isotherms for the N-117 (a), N-112 (b), and NR-112 (c) samples at 30 (−), 40 (×), 50 (△), 70 (◇), and 80 °C (□). Below 80% RH, moisture uptake increases with temperature. Above 80% RH, moisture sorption capacity begins to decrease at 70 and 80 °C.

Identical experiments were performed for all three samples at 30, 40, 50, 70 and 80 °C. To illustrate the effects of temperature, Fig. 2 displays the water sorption isotherms for the N-117 (a), N-112 (b), and NR-112 (c) samples at each temperature. As the temperature increases from 30 to 50 °C, there is a slight increase in vapor sorption capacity for all three samples across the entire humidity range. This is most likely due to an increase in bulk sorption capacity. As the temperature increases, sample mobility will increase, thus allowing more water to penetrate the bulk. At 70 and 80 °C, the results are more complicated. Below 80% RH, there is an increase in water sorption capacity as with the lower temperature isotherms. However, above 80% RH, the moisture sorption capacity decreases compared to the results at 50 °C. The higher temperatures appear to limit the maximum water sorption capacity for all three films. This may be due to the high temperatures drying out the samples. Alternatively, the high temperatures and high humidities may be causing a transformation or rearrangement of the polymer. The glass transition
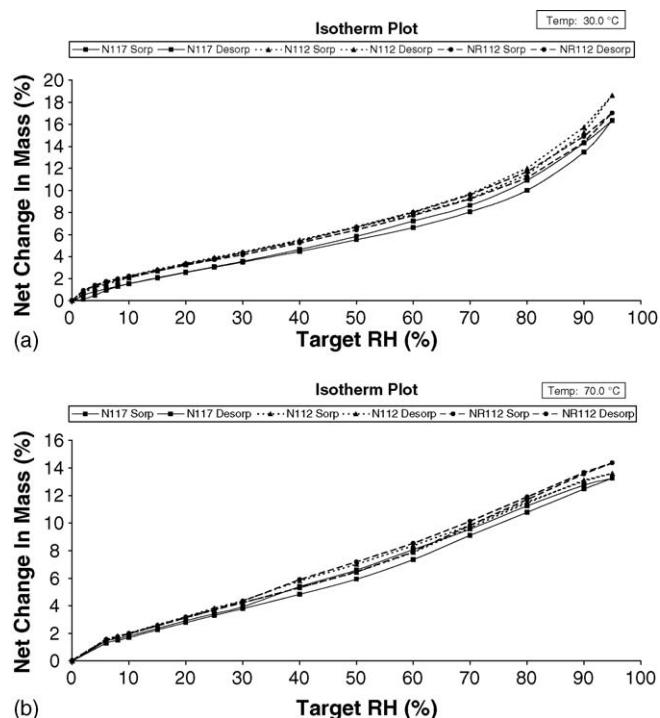
Fig. 3. Water vapor sorption and desorption isotherms for the N-117 (solid), N-112 (dashed), and NR-112 (dotted) samples at 30 (a) and 70 °C (b).
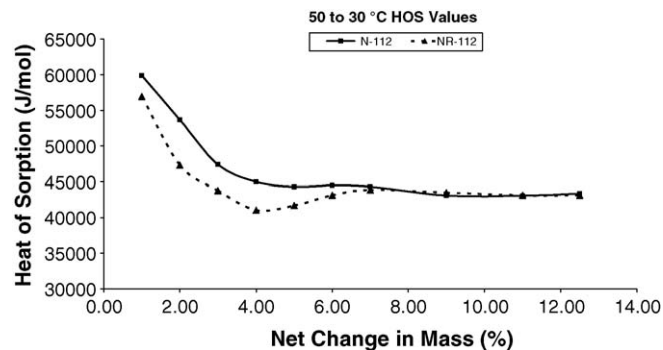

Fig. 4. Water vapor heat of sorption values for the N-112 sample (solid line) and NR-112 sample (dotted line) calculated from the water sorption isotherms collected at 30 and 50 °C.

temperature of Nafion® is reported to be 115 °C [12]. Additionally, the storage modulus of the dry Nafion® drops by over an order of magnitude at 111 °C [13]. Water is a strong plasticizing agent which may lower these transitions to lower temperatures at high humidities. Therefore, the drop in vapor sorption capacity at high humidities above 50 °C may due the combination of water plasticization and change in thermal and mechanical behavior of the polymer.

To illustrate the differences between the different membranes studied, Fig. 3 displays the water vapor sorption isotherms for the three samples at 30 °C (a) and 70 °C (b). Comparing the sample thickness, the thinner N-112 sample (51 μm) is able to sorb more water (based on percentage of dry mass) than the thicker N-117 sample (183 μg). The trends are consistent across the temperature range studied (see Fig. 3a and b). The thicker sample may impede water from fully penetrating the bulk, thus causing a lower percentage weight gain. Also, the thinner, N-112 sample has a greater surface to bulk ratio than the thicker, N-117 sample, thus the surface layers may be able to sorb more water vapor comparatively than the bulk.

In comparing the extruded, N-112 sample with the dispersion cast, NR-112 sample, Fig. 3a illustrates that the extruded sample is able to sorb more water, based on percentage of dry weight, than the dispersion cast film at 30 °C. The differences are not as clear at 70 °C, due to the complications above 80% RH discussed above. Any differences observed at 30 °C are minimized at 70 °C, such that the results are nearly identical at 70 °C below 80% RH. Above 80% RH at 70 °C the NR-112 sample has a higher uptake than the N-112 sample, which indicates the decrease in vapor sorption capacity at high temperatures and

humidities is not as severe for the NR-112 sample compared to the N-112 sample.

To further study the differences between the extruded, N-112 sample and the dispersion cast, NR-112 sample, the water vapor heat of sorption values were calculated using Eq. (4) over a range of water uptakes. The results are displayed in Fig. 4. The heat of sorption values were calculated using the sorption isotherms collected at 30 and 50 °C. At high water uptakes (above 6% change in mass), the heat of sorption values for both samples are nearly identical and are approximately 43 kJ mol^{-1}. The water heat of vaporization/condensation is 43.8 kJ mol^{-1} at 30 °C and 42.9 kJ mol^{-1} at 50 °C [14]. It is expected that the heat of sorption values for both films approach the heat of condensation at higher water uptakes, because the water vapor is interacting with a water covered surface at these conditions. At lower uptakes, the heat of sorption increases for both samples. At these conditions, the heat of sorption values are more indicative of the interaction with the polymer surface, as it is not completely covered by water. There are significant differences between the two samples. The extruded N-112 sample has a consistently higher heat of sorption value than the dispersion cast, NR-112 sample at low coverages. These results indicate the N-112 surface has a higher affinity for water vapor molecules. This is supported by the isotherms at 30 °C (see Fig. 3a), where N-112 sample shows a higher water uptake than the NR-112 sample.

Water vapor transport properties were investigated by calculating diffusion coefficients using Eq. (1) at each step-change in humidity and each temperature. Fig. 5 summarizes these results at 30 °C (a) and 80 °C (b). These values were calculated from the initial uptakes at each step change in humidity during the water sorption cycle. The diffusion coefficients at 30 °C range from 1×10^{-8} to 2.5×10^{-7} cm^2 s^{-1}. Previous researchers have measured vapor diffusion coefficients of Nafion® polymers at high humidities and obtained results ranging from 2.0×10^{-8} to 2.6×10^{-8} cm^2 s^{-1} [13,15]. The high humidity diffusion data at 80% RH for all three samples is approximately 2.5×10^{-8} cm^2 s^{-1}, which agrees quite well with the literature data.

Fig. 5a shows a general trend for the diffusion coefficients. There is a maximum diffusion coefficient at intermediate humidities (10–60% RH) and the values decrease at very low humidities and very high humidities. At low humidity values
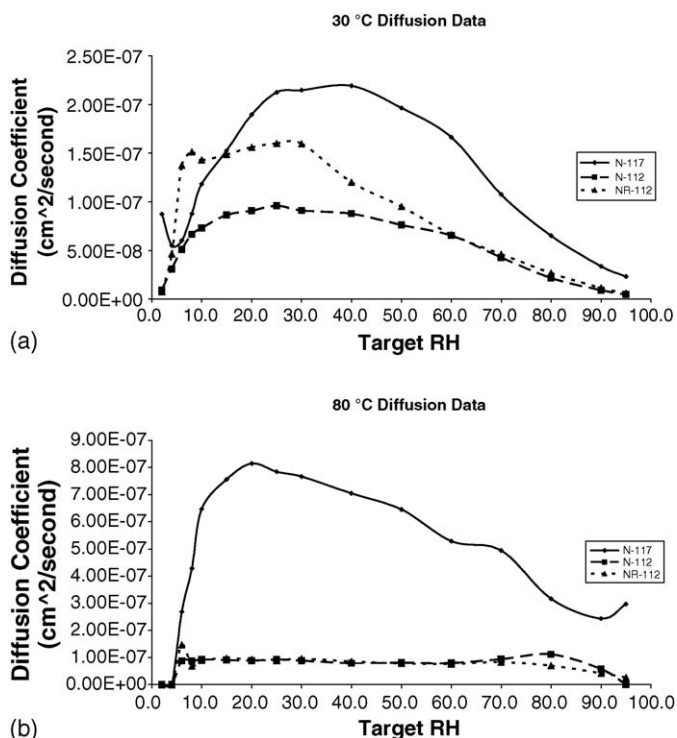
Fig. 5. Moisture diffusion values for the N-117 (solid), N-112 (dashed), and NR-112 sample (dotted) at 30 °C (a) and 80 °C (b). Diffusion values are calculated from initial uptakes at each step change in humidity.

diffusion may be limited because the sample is too dry, while at high humidities diffusion may be slowed, because the sample becomes saturated. At high humidities there is also a measurable hysteresis between sorption and desorption isotherm as shown in Fig. 1b. The hysteresis in this range further supports slower diffusion rates in this regime. The diffusion data suggests there may be an optimal water content to maximize water vapor diffusion rates. Note, the diffusion coefficients at each temperature were calculated using the same sample thickness (measured at 23 °C and 50% RH) for each humidity step. In reality, the polymer film thickness will change as a function of temperature and humidity due to different degrees of swelling.

In comparing the data at 30 and 80 °C, diffusion coefficients for all three samples are higher at 80 °C. The increased temperature most likely increases mobility within the polymers, thus increasing water vapor diffusion into the film. At 30 °C, there are some differences between the extruded, N-112 and dispersion cast, NR-112 samples. At intermediate humidities, the NR-112 sample has higher diffusion coefficients, while at low and high humidities the N-112 and NR-112 samples have similar values. At 80 °C, there is almost no difference between the N-112 and NR-112 samples. Therefore, the preparation method appears to have an effect on water diffusion coefficients at low temperatures, but not at high temperatures. At high these conditions, diffusion may be dominated by temperature effects and not sample morphology. At both temperatures, the thicker, N-117 sample has faster diffusion rates than the thinner, N-112 sample. At the present time, these results are not fully understood. One expects

a thicker sample would lead to slower bulk diffusion rates, which is contrary to the current results. Perhaps the orientation of the polymers differs depending on the thickness of the films, which would affect vapor diffusion rates.

5. Conclusions

Water sorption properties were measured on three Nafion® based films over a range of temperature and humidity conditions. Water sorption was completely reversible and there was no sample history with respect to sorbed water. Increased temperatures lead to increased water sorption capacity up to 80% RH. Above 80% RH and 50 °C, vapor sorption capacity decreased compared to lower temperature data. The thicker N-117 sample had a lower percentage uptake than the thinner N-112 sample. The extruded N-112 sample had a higher percentage uptake compared to the dispersion cast NR-112 sample. Heat of sorption calculations showed a higher sorption energy for the N-112 compared to the NR-112 sample. Diffusion coefficients were calculated at each step change in humidity and each temperature. Diffusion coefficients increased with increasing temperature. Also, there appeared to be a maximum diffusion regime at intermediate humidity values. Future experiments are planned to include a range of vapors (i.e. methanol and ethanol) and a wider range of sample chemistries and morphologies.

References

[1] P. Choi, R. Datta, J. Electrochem. Soc. 150 (2003) E601.
[2] T.V. Nguyen, N. Vanderborgh, J. Membr. Sci. 143 (1998) 235.
[3] W.-k. Lee, S. Shimpalee, J.W. Van Zee, J. Electrochem. Soc. 150 (2003) A341.
[4] T.A. Zawodzinski, M. Neman, L.O. Sillerud, S. Gottesfeld, J. Phys. Chem. 95 (1991) 6040.
[5] C. Yang, S. Srinivasan, A.B. Bocarsly, S. Tulyani, J.B. Benziger, J. Membr. Sci. 237 (2004) 145.
[6] F. Damay, L.C. Klein, Solid State Ionics 162/163 (2003) 261.
[7] O. Savadogo, J. New Mater.: Electrochem. Syst. 1 (1998) 47.
[8] D. Rivin, G. Meermeier, N.S. Schneider, A. Vishnyakov, A.V. Neimarck, J. Phys. Chem. B 108 (2004) 8900.
[9] M. Legras, Y. Hirata, Q.T. Nguyen, D. Langevin, M. Metayer, Desalination 147 (2002) 351.
[10] J. Crank, G.S. Park, Diffusion in Polymers, Academic Press, New York, 1968.
[11] P.W. Atkins, Physical Chemistry, 6th ed., W.H. Freeman and Company, New York, 1998.
[12] S.H. DeAlmeida, Y. Kawano, J. Therm. Anal. Calorimetry 58 (1999) 569.
[13] J.T. Uan-Zo-li, The effects of structure, humidity, and aging on the mechanical properties of polymeric ionomers for fuel cell applications, Masters' Thesis, Virginia Polytechnic Institute and State University, 2001.
[14] D.R. Lide (Ed.), CRC Handbook of Chemistry and Physics, 80th ed., CRC Press, New York, 1999.
[15] T. Takamatsu, M. Hashiyama, J. Appl. Polym. Sci. 24 (1979) 2199.