TEOM: A novel technique for investigating sorption in proton-exchange membranes

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Abstract

A new technique, namely, the tapered element oscillating microbalance (TEOM) is successfully utilized to investigate the equilibrium water and methanol vapor phase sorption and desorption in Nafion® membrane at different relative humidity (RH) and temperatures. The water sorption was found to increase with temperature from 30°C to 90°C. This is explained by the increase in the flexibility of polymer chains via a decrease in Young’s modulus of membrane with temperature. The effect of various pretreatments, e.g., heating, vacuum treatment, and hot pressing on the water sorption properties is also investigated. It is observed that the water sorption for Nafion® membrane depends both on the pretreatment of the membrane and on the temperature of sorption. The desorption isotherm exhibits a hysteresis with respect to sorption for both water and methanol. This hysteresis behavior may be attributed to the relaxation or viscoelastic properties of Nafion® membrane. In summary, TEOM appears to be an attractive technique for characterizing sorption–desorption behavior of proton exchange membranes.

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1. Introduction

Recently there has been much interest in polymer electrolyte membrane fuel cells (PEMFC). An important factor determining the performance of the PEM fuel cells is the hydration level of the proton-exchange membrane (PEM) [1–3]. A common PEM is Nafion®, a polymer consisting of a polytetrafluoroethylene (PTFE) backbone with side-chains culminating in SO3⁻H⁺ groups. It exhibits excellent chemical, mechanical, and thermal stability along with low gas permeability and high proton conductivity when adequately hydrated. The amount of water sorbed in the membrane is critical as the proton conductivity directly depends upon the water content of the membrane [4–6]. The main factors that affect the extent of water sorption in a PEM are the nature of polymer backbone, temperature, ion-exchange capacity, pretreatment, as well as the physical state of external water, i.e., whether it is in liquid or vapor form. Water basically dissociates the acid groups and provides a medium for conduction of protons.

In the operation of a typical PEM fuel cell, the reactant feed gases are prehumidified to provide adequate hydration levels in the membrane. This is supplemented by the water produced at the cathode due to the electrochemical reaction, which also results in a gradient in the activity of water across the membrane causing water to diffuse back from cathode to anode [7]. Further, water is transported from anode to cathode along with the protons, i.e., via the electro-osmotic drag. Thus, water management is critical to successful working of a PEMFC, which necessitates an understanding of water sorption characteristics of PEMs.

Many investigators have studied the uptake of water in PEMs. Several investigations have been done on the hydration, swelling, and drying under different conditions for Nafion®, based on spectroscopic, gravimetric and other methods [7–11]. The adsorption from liquid phase is quicker as compared to that from vapor phase. Further, Nafion® adsors around 22 water molecules per acid site from liquid water, while it adsors around 14 water molecules from saturated
vapor [7,8], i.e., the so-called Schroeder’s Paradox recently explained by Choi and Datta [12].

An important variable is the pretreatment of a PEM that affects its water sorption. In an early study, the following nomenclature was used to describe pretreatment of Nafion®, namely, “E-form” for a membrane swollen and expanded in high-temperature water, and “S-form” for a membrane shrunk in vacuum at high temperatures [13]. The normal membranes were termed “N-form”. It was found that the E-form membrane becomes rubbery when the temperature increases, with a tendency to adsorb more water. However, in S-form membranes, the ionic clusters shrink and the water uptake drops. Kawano et al. [14] studied the stress–strain characteristics of Nafion® membrane for various pretreatments (boiling, soaking in other solvents, heating, etc.). They observed that the slope of stress–strain, i.e., Young’s modulus (E) of the membrane, decreased for a membrane boiled in water, making them more pliable for higher water uptake.

The sorption of methanol in Nafion® is also of interest in context of the direct methanol fuel cells (DMFC) [15–17]. The two main obstacles that currently limit DMFC performance are the low activity of methanol electro-oxidation catalysts and the crossover of methanol through the polymer electrolyte membrane. It has been observed that methanol crossover to the cathode not only lowers the fuel utilization but also adversely affects the oxygen kinetics at the cathode, resulting into lower cell performance [18,19]. Consequently, there is a strong motivation to systematically study the water/methanol sorption isotherms for Nafion® and other polymer electrolyte membranes. Experiments with the conventional gravimetric methods are slow, providing data of low accuracy. The sorption data are affected by the flow patterns, bypassing, and incomplete contact of the gas with the sample [20]. Further, the equipment has limited temperature and pressure range. There is also significant reduction in mass resolution at high temperatures. Here, the use of a novel and relatively fast technique, namely the tapered element oscillating microbalance (TEOM) is described to accurately measure equilibrium water/methanol sorption–desorption isotherms for PEMs. The effects of solvent activity or relative humidity (RH), temperature, and various pretreatment protocols on sorption behavior of Nafion® are investigated. Further, this technique can also be utilized to study the sorption behavior of inorganic powder additives in our efforts to develop high temperature proton-exchange membranes by improving water retention at elevated temperatures [21,22].

2. Description of the TEOM

The tapered element oscillating microbalance (TEOM) Series 1500 Pulse Mass Analyzer (PMA) purchased from Rupprecht & Patashnick Co., Inc., Albany, NY, was utilized to study the equilibrium solvent sorption–desorption behavior for Nafion® membranes. This offers a novel means of analyzing real-time mass change of sample in a fixed-bed while the gases pass through the sample. It includes a tapered element oscillating microbalance, which is based on inertial forces rather than gravity, to measure the mass change of sample [23]. The TEOM possess certain advantages over conventional gravimetric techniques in measuring sorption in polymer electrolyte membranes:

1. The steady flow of gas through the sample provides complete contact with the test material.
2. High mass resolution (1 × 10⁻⁸ g) and a low standard deviation.
3. The experiments can be performed over a wide range of temperatures (25–500 °C) and pressures (vacuum to 60 atm).
4. The microbalance employs a resonant cantilever to measure changes in inertia rather than weight, hence the data obtained is not influenced by flow patterns of gas streams, buoyancy and other aerodynamic factors.

However, there are some limitations in using TEOM. It cannot be used for volatile or fragile samples, which may alter the natural oscillating frequency of the test bed. Also, liquid phase studies cannot be performed using this technique.

The heart of the TEOM is an oscillating tapered test bed in which the sample is packed. This tube containing the sample vibrates constantly at its natural frequency of oscillation. There is a feedback system, which maintains the oscillation in which the sample is packed. This tube containing the sample is packed.

The motion of TEOM test bed may be approximated as free undamped vibrations of a cantilever in one of the principle planes of the beam [25,26]. The effects of rotatory inertia and of transverse shear deformation are neglected. The equation of motion for beam of uniform cross section is

\[ E I \frac{d^4y}{dx^4} + \rho A \frac{d^2y}{dt^2} = 0 \]  

where \( E \) is the Young’s modulus, \( I \) the second moment of area of the cross section, \( \rho \) the density, \( A \) the beam cross sectional area, \( y \) the displacement from the centerline of the beam at any section \( x \), and \( t \) the time.

For free undamped vibration, the solution is of the form

\[ y(x, t) = Y(x) \sin(\omega t + \alpha) \]

where \( \omega \) is the frequency of vibration, and or \( \alpha \) is the phase angle.

Substituting this in Eq. (1),

\[ \frac{d^4y}{dx^4} - \kappa y = 0 \]  

(3)
\[ \kappa = \frac{\rho A \omega^2}{EI} \]  

The solution for Eq. (3) is of the form,

\[ Y = B \exp(\kappa x) \]  

Now, the frequency of vibration \( f \) is defined as \( \omega / 2\pi \). Thus,

\[ f^2 = \frac{\omega^2}{4\pi^2} = \frac{sEI}{\rho A \kappa x} = \frac{\kappa_o m}{m} \]  

where \( m = \rho A \) is the dynamic mass of the system and \( \kappa_o \) is the effective spring constant for the tapered element. Thus, the change in mass of system \( \Delta m \) for the corresponding change from initial frequency \( f_i \) to final frequency \( f_f \) is

\[ \Delta m = \kappa_o \left( \frac{1}{f_i^2} - \frac{1}{f_f^2} \right) \]  

Thus, with an increase in the mass, the frequency decreases, and vice versa. In TEOM apparatus, spring constant \( \kappa_o \) depends weakly on temperature. For instance, change in the spring constant for a temperature range of 30–250 °C corresponds to a mass change of \( 1 \times 10^{-5} \text{g} \) [24]. In the present study, the temperature range investigated is 30–90 °C. Hence, the effect of temperature on the effective spring constant is neglected.

3. Experimental section

3.1. TEOM apparatus

The TEOM experimental set up is shown schematically in Fig. 1. Helium gas is bubbled through water kept in a bottle (saturator) and is combined with another stream of dry helium gas downstream for obtaining the desired relative humidity. All the gas flows are controlled by means of mass flow controllers (MKS Model No. 1179A22CS1BV-S, Andover, MA). A preheated bath of ethylene glycol–water (50:50 by volume) is circulated around saturator to maintain the desired temperature, in the range of 25–115 °C. The temperature of water in the saturator is monitored via a thermocouple connected to a digital multimeter. As shown in Fig. 1, a purge helium stream is used to avoid condensation at the external surface of the test bed and back flow of exiting gas stream from the test bed.

The real-time dynamic mass change of the sample in the TEOM test bed can be analyzed graphically using LabView 5.0 program, purchased from National Instruments Corporation. Inside the TEOM, there are two temperature-controlled zones. The pre-heat zone controls the inlet gas stream temperature and the other zone controls the temperature of the tapered element and the sample bed. The TEOM performance is quantified in terms of the normalized standard deviation (NSD). The NSD is an indicator of any noise in the test bed and depends upon how well the sample is packed, and whether there is other disturbance. For the equilibrium sorption experiment, a 10 s average time with 12 recording values (approximate gate time of 0.8 s) gives a typical value of NSD below \( 3 \times 10^{-6} \text{ppm} \) [24]. More structural details of TEOM can be obtained from the company’s website (http://www.rpco.com).

Since the real-time mass change of the sample can be monitored, TEOM can be utilized for studying both dynamic and equilibrium sorption. Although the present study is focused on equilibrium sorption–desorption process, the diffusion coefficients may also be determined from dynamic sorption and desorption.

3.2. Membrane preparation

The Nafion® 112 membrane was purchased from Aldrich and then subjected to a pretreatment procedure as described in the literature [27,28]. It was boiled in 3% \( \text{H}_2\text{O}_2 \) for half an hour. Then it was heated at 60 °C in 0.5 M sulfuric acid solution for half an hour. Finally, it was heated at 60 °C.
in deionized water for 1 h. After boiling the membrane, it was washed thoroughly with DI water to remove any acid residues. It was finally dried at room temperature by leaving the membrane untouched. To study the effect of pretreatments on water sorption behavior for Nafion®, the membrane synthesized was then subjected to different treatments, as explained later on.

3.3. Sorption–desorption measurements

A known dry mass of vacuum heated membrane sample was cut into small pieces (1.5 mm × 1.5 mm) using a doctor blade and loaded carefully in the test bed. Quartz wool, purchased from Rupprecht & Patashnick Co., Inc., was used as filler material to keep the sample firmly packed, which is necessary so that the sample does not rattle around affecting the oscillations of the bed. The best way to ensure this is to check the NSD. If it is below 3 × 10⁵ ppm then, it implies that the sample was properly loaded. Typically, about 20 mg of membrane sample was packed in the test bed to get best reproducibility.

The sorption–desorption data were obtained by a stepwise increase or decrease of the flow rate of humidified inlet gas stream, which changes the RH or activity of the feed gas at fixed temperatures. During the experiments, the He purge gas was kept at around 120–150 sccm, while the carrier gas through saturator was maintained at 10–15 sccm, with the dry He gas varying from 0 sccm to 100 sccm depending on RH required in the test bed. The RH was calculated from the gas flow rates and the saturator temperature. To further confirm this calculation, the inlet stream of gas entering the sample test bed was connected to a humidity probe purchased from Vaishala Inc. For various temperatures of saturator and flow of helium gas, the RH was measured. The experimental observations were in good agreement with the calculations. After loading the sample, the inlet flow was set to the desired value and sufficient time was allowed for the sample to reach steady state, typically 10–30 min. After waiting for sufficient period, if the mass of the test bed did not change for more than 1%, then the equilibrium was assumed. This was good enough for such vapor phase experiments. Thus, the change in sample mass for the set condition was recorded and then the inlet flow was adjusted to get next desired RH. The real-time sample mass variation in TEOM is shown in Fig. 2 for step changes to 10%, 20% and 30% RH conditions. The total mass of sample increases as it adsorbs solvent. The mass change corresponds to the amount of solvent adsorbed. The increase in mass represents the dynamic changes of the test bed, and hence this data can be utilized to study the kinetic parameters for sorption and desorption process. In the present set up, both sorption and desorption experiments were done in a similar fashion by stepping the RH up and down, respectively. The vapor phase equilibrium sorption data is reported here as λe, defined as the ratio of moles of absorbed solvent per mole of sulfonic acid groups within Nafion®. Alternatively, the data can be presented as ratio of mass of absorbed solvent to mass of dry polymer. Both these representations are useful depending on the objective of study.

4. Results and discussion

4.1. Water sorption

The equilibrium water sorption isotherm for 1100 EW Nafion® membrane at 30 °C is shown in Fig. 3 along with data available in the literature [10,13,30,34] for similar EW membrane. The sorption curve is typical of the swelling membrane, with an extended region of gradually increasing slope that turns sharply higher above water activity of 0.7. At the origin, the isotherm had a sharp initial slope, rapidly lev-
eling off at activity of 0.2, corresponding to the weight uptake of 0.04 g/g and about two water molecules. Our data obtained with TEOM are in good agreement with published results from different laboratories, thus validating the accuracy of the technique. The room temperature water sorption isotherm was reproduced and the error bar for each RH condition is shown, confirming that the data are reproducible. The added advantage of the TEOM is that the data are obtained rapidly as compared to other gravimetric techniques and are highly reproducible. This is important because of the efforts in laboratory on developing high temperature proton conducting membranes that require accurate measurements of water sorption. The sorption data also agrees with our water sorption model developed recently based on a physicochemical understanding of how the water molecules interact with the PEM [31,32].

The data were also obtained at different temperatures ranging from 30 °C to 90 °C. Fig. 4, thus, shows the effect of temperature on water sorption isotherm for Nafion membrane. The amount sorbed increases gradually with temperature, especially with high water activity. Kawano et al. [14] have studied the stress–strain characteristics of Nafion membrane at different temperatures and found that the initial slope of the curves, i.e., the Young’s modulus ($E$) decreases with increasing temperature, thus softening the membrane and allowing higher water uptake. A lower $E$ reduces the swelling pressure on the imbibed liquid thus equilibrating at higher sorbed amount. We have also recently investigated the effect of water activity and temperature on $E$ for Nafion membrane, using the technique of optoelectronic holography (OEH) [31]. Fig. 5 shows the variation in $E$ versus water activity at two different temperatures. Thus, $E$ decreases both with water activity and temperature. A thorough investigation of the effects of temperature on physicochemical behavior of polymer is important, since water management and performance of PEMFC depends on operating temperature. Also, the durability of the membrane depends upon the thermomechanical properties.

4.2 Methanol sorption

The methanol sorption isotherm is shown in Fig. 6 together with water sorption isotherm for comparison. These data are of interest in connection with DMFC [17]. The experimental procedure to measure methanol sorption was similar to that of water sorption. Methanol was filled in saturator and methanol activity in the TEOM test bed was measured. The sorption isotherm for methanol follows a pattern similar to that of water. Also the initial slopes of both curves are similar. There is an extended region of gradually increasing slope for both solvents, as well as a marked upturn for high activities. The mass uptake of 0.106 g for methanol at an activity of 0.4 corresponds to about three methanol molecules per sulfonyl...
acid site, as compared to five molecules in the case of water sorption. For similar solvent activity, thus, fewer number of methanol molecules are associated with sulfonic acid group as compared to water.

4.3. Sorption–desorption measurements

Fig. 7 shows the water and methanol vapor phase sorption and desorption isotherm of a Nafion® membrane at 30 °C. This exhibits a hysteresis for both the solvents. The desorption curve was obtained after the sorption measurements for both the solvents. The sorption experiments were completed for the sample by stepping up the RH, followed by stepping down of RH for desorption. While stepping down, sufficient time was provided to the sample to reach equilibrium. Typically 10–40 min were required at each RH condition. The desorption exhibits enhanced water and methanol uptake as compared to sorption for activity range of 0.2–0.9. This might suggest the Nafion® membrane underwent swelling during the sorption process that had not fully relaxed during desorption process. According to Rivin et al. [30], the hysteresis during the desorption process can be explained by the slow volume relaxation of the hydrophilic clusters in response to the change in vapor activity, resulting in higher swelling of membrane at a given activity. This slow relaxation may be determined by the viscoelastic properties of Nafion®. Nguyen and Vanderborgh [35] attributes the hysteresis between absorption and desorption to an effect known as “skin effect”. This is due to collapse of pore structure during desorption process, which causes more water to be trapped within the pores of Nafion membrane. Future work includes studying this phenomenon at a more fundamental level and obtain similar curves at different temperatures.

4.4. Membrane pretreatment effect

Fig. 8a and b show the effect of four different pretreatments on water sorption characteristic of the Nafion® membrane at 30 °C and 90 °C, respectively. Thus, the equilibrium sorption isotherm was obtained for (a) untreated Nafion® sample, (b) sample heated at 30 °C, (c) 110 °C for 24 h in vacuum, and (d) sample hot pressed at 170 °C. The hot press pretreatment is very important especially during MEA preparation for fuel cell testing. Also, the vacuum treatment ensures that the membrane is as dry as possible. The other pretreatment effects were selected as common conditions for synthesizing membranes for high-temperature operation. The pretreatment of the Nafion® membrane substantially affects the water sorption behavior. For sorption at 30 °C (Fig. 8a), the sorption amount for both untreated and sample vacuum heated at 30 °C is rather similar. The hot pressed membrane exhibited the lowest sorption, which is significant in that the procedure
for preparing MEA might result in reduced performance. Further, vacuum heating the sample at 30 °C was similar. The hot pressed membrane again showed the lowest sorption isotherm. Hence, the water sorption for Nafion® membrane depends both on the pretreatment procedure and the sorption temperature. The physical structure of Nafion® polymer changes with pretreatment and affects the sorption behavior. Also, for the similar pretreatment procedure, the sorption amount is remarkably different when the sorption temperature is varied. An example of variation of membrane properties at different humidification and temperature is already shown in Fig. 5, wherein the E decreases both with water activity and temperature. Thus, a rigorous study of the effect of pretreatments on the thermomechanical properties of Nafion® membrane is called for to further elucidate the observed results.

5. Conclusions

From the results obtained, TEOM seems to be a novel technique for investigating sorption−desorption behavior of Nafion® membrane for various solvents. Further, the pretreatment study allows determining processing steps to be considered while synthesizing membranes to obtain best fuel cell performance. The results obtained are accurate and reproducible. Future work includes utilizing TEOM to screen various candidates, both polymer and inorganic powders, for higher water uptake to design high temperature proton exchange membrane. Overall, TEOM can be an effective tool in studying both dynamic and equilibrium behavior of Nafion® membrane, in particular, for fuel cell applications.

References


