

## Transport in Polymer Electrolytes for Fuel Cells: Physical Chemistry

Thomas Kalapos, Berryinne Chou, Hossein Ghassemi and Tom Zawodzinski Jr

Department of Chemical Engineering, Case Western Reserve University, Cleveland, OH-44106

### Introduction

One of the main components of a Polymer electrolyte membrane fuel cell (PEMFC) is the proton exchange membrane. It plays the dual role of separating the fuel from the oxidant and providing proton conduction from the anode to cathode. Issues related to water, heat and pressure management have stimulated interest in higher operating temperatures, necessitating low relative humidity. The current state of the art proton exchange membrane is Nafion® which belongs to the class of perfluorosulfonic acid polymer membranes. This class of membranes is unable to maintain proton conductivity at  $T > 100^{\circ}\text{C}$  and low RH. The main reason for loss in conductivity is due to the decreased water uptake at high temperatures. This has led to interest in developing membranes with high proton conductivity with limited or no dependence on humidity.

Recent work has shown that certain types of interactions and structures in composite and phase-separated membranes contribute to enhanced conductivity with relatively little water present. To further understand this phenomenon, the thermodynamics and mobility of water present in such membranes have been studied. Thermal analysis has been deployed to assess the energetics of water uptake by these materials. NMR relaxation and diffusion measurements have been used in several different ways to access information. Comparison of mobility at different length scales associated with relaxation and diffusion measurements allows us to separate tortuosity and chemical interaction effects. Dilution of  $^1\text{H}$  nuclei with  $^2\text{H}$  allow us to assess the intermolecular dipolar interactions amongst water molecules, giving us clues to water structure. Finally, these data are interpreted in light of morphological aspects of the polymers and composite.

### Experimental

**Materials** Nafion® 117 was obtained from Ion Power Inc (Bear, Delaware) and was pretreated in accord with previously described methods<sup>[i]</sup>. BPSH 35 membranes were synthesized in house according to the previously published procedure<sup>[ii]</sup>. The multiblock polymer (MB-150) was synthesized in house according to a published procedure<sup>[iii]</sup>. The inorganic / organic composite membrane (I/O) was prepared in house by blending PVDF or BPSH-x ( $x = 0$  to 60) with sulfonated silica particles. After cleaning, and before equilibration, the membranes were stored immersed in DI water for 12 hours. The final product was precipitated in water. This was then filtered and dried for characterization.

**Characterization** Water uptake of the membranes was determined gravimetrically. First, the membranes were equilibrated at  $30^{\circ}\text{C}$  in the vapor space of vials that contained solutions of LiCl that corresponded to specific activities of water vapor ( $a_w = 0.25, 0.75, 0.9, 1.0$ ) and hence, different relative humidity values. The equilibrated samples were weighed and then dried in a vacuum oven and weighed again to determine the amount of water that was held at the respective humidity levels. Samples that were equilibrated under the same conditions, though not weighed nor dried, were used for the DSC measurements.

Differential scanning calorimetry was performed with a Mettler Toledo DSC822e configured with an intra cooler capable of reaching

temperatures of  $-70^{\circ}\text{C}$ . Sampling pans were 40 $\mu\text{l}$  aluminum with pins on the bottom for consistent placement on the heating stage. Sample pan lids were either the standard type or those with a 50 micron pinhole that were found to allow a sufficient relief of pressure without prematurely drying out the membrane.

Before applying differential scanning calorimetry to water-saturated polymer membranes, scans were run with only water in the pan. This was to test the accuracy of the measurement of the specific heat of fusion and that of vaporization. In particular, there is a concern with using a hermetically sealed pan in the vaporization region of a volatile component, i.e., water. The concern is that the pan would pressurize and thereby elevate the boiling point and also at some point burst open and expel water mass and the heat content associated with it, thereby giving a false measurement of the specific heat of vaporization. To address this concern, we ran DSC of water in three pan configurations: (a) closed pan, (b) pan with a 50  $\mu\text{m}$  pinhole in the lid, (c) open pan.

### Results and Discussion:

#### *Water Uptake and DSC*

For the analysis of DSC data for the subject membranes, we distinguish two temperature regions of interest, the 'water vaporization' region and the 'water melting' region.

*Water vaporization region.* Figure 1 shows DSC thermograms of the tested membranes ( $-50$  to  $300^{\circ}\text{C}$ ). In Table 2, results of the DSC studies of water vaporization from the membranes are summarized. An important aspect to note is the experimentally determined specific heat of vaporization of water ( $\Delta H_v$ ) from the membrane. In comparison to liquid water ( $\Delta H_v = 2257 \text{ J/g}$ ), the values for water vaporization from the membranes differ by only 3 to 11%, which we consider to be within experimental error. This tells us that the water expected to be in the membrane from the isopiestic measurements and subsequently expected to be driven off under the experimental conditions, is all accounted for.

*Water melting region.* Figure 2 shows the DSC thermograms of the tested membranes in the range of  $-50$  to  $50^{\circ}\text{C}$ . In Table 1, results of the DSC studies of water melting in the membranes are summarized. An important aspect to note here is the experimentally determined specific heat for the melting of water ( $\Delta H_f$ ). The comparison to liquid water ( $\Delta H_f = 333 \text{ J/g}$ ) reveals significant deviations that we can interpret in several ways. First, the mean heat of fusion of water in the membrane could be different from that of liquid water, indicating stronger or weaker enthalpies of interaction between water and the membrane/water system than the enthalpy of interaction of water in water. Second, not all of the water present was frozen, even at  $-50^{\circ}\text{C}$ , the beginning of the DSC scan, indicating stronger enthalpies of interaction. In this second case, the entire mass of water cannot be divided into the total amount of heat represented by the melting endotherm. Third, the water expected to be present was incorrectly stated.

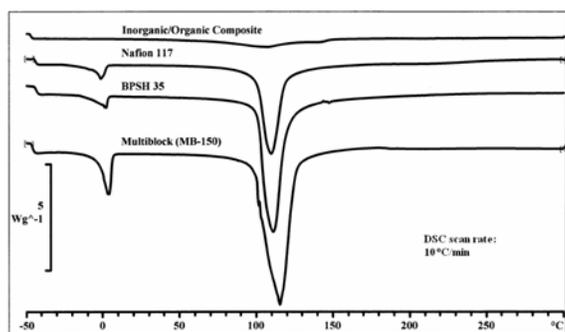


Fig. 1: DSC Thermograms of select membranes (-50 to 300°C).

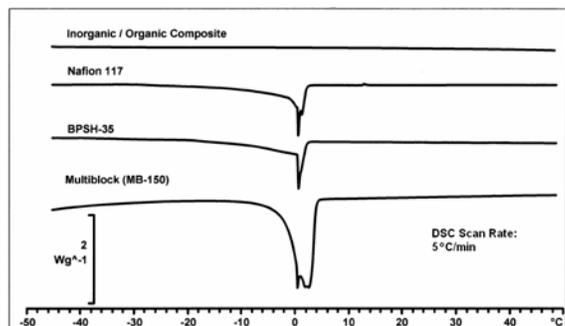


Fig. 2: Typical DSC thermograms of PEFC membranes in the water melting region. Here, MB-150 shows a significantly greater amount of “freezable” water as compared to Nafion® 117 and BPSH-35

The third interpretation is refuted, within experimental error, when we consider that the expected amount of water is entirely revealed in the vaporization region, and therefore, would have also been present in the melting region. This leaves us with the possibility of a lower enthalpy of water fusion and the presence of nonfreezing water, both due to interactions of water with the membrane.

In fact, at water contents below complete saturation, there is generally not much evidence for a ‘freezing’ fraction of water. The absence of additional peaks in the water melting region, in conjunction with the low heat of melting and normal heat of vaporization, is generally interpreted as indicating that the water is ‘non-freezing.’ From the isopiestic data, water does indeed interact strongly with the membrane at low relative humidity or water content. However, water sorbed into the membrane in the ‘swelling’ region (above ~ 6 waters per sulfonic acid) also does not contribute a freezing peak, even though its interaction with the membrane is not strong (based on the  $\ln(a_w)$  versus  $\lambda$  plot).

Table 1. Summary of DSC, water melting region

sample	wt% water	$T_m$ (°C)	$\Delta H_f$ (J/g)	$\Delta H_f$ per mass water (J/g water)	$H_2O$ (f) ( $\lambda$ )	$H_2O$ (nf) ( $\lambda$ )
Nafion® -117	19.9	-0.4	35.21	176.9	8.3	7.2
BPSH- 35	32.8	0.4	32.53	99.2	5.3	12.4
MB150	35.7	3.7	84.07	235.5	14.6	6
I/O	6.97	-	--	--	--	11.9

### Transport Results

Recent studies in our lab have focused on studies of BPSH composites with sulfonated silica nanoparticles. The sulfonated silica particles have interactions with the polymer binders, as indicated by changes in glass transition temperature observed by DSC in the composite relative to that of the starting materials. Shifts in positions of sulfonate IR bands are also observed in the composites. The effect of membrane fabrication conditions on observed morphology and overall performance was also investigated. Membranes were tested for their proton conductivity and other related properties, such as water up-take. The conductivity was higher than  $10^{-2} \text{ Scm}^{-1}$  at 90°C and 20% relative humidity. Furthermore, the change in conductivity with water content is much less than that for Nafion or BPSH membranes. Similar behavior was observed for phase-segregated multiblock copolymers. These results have been interpreted as indicating that small amounts of water in structured environments (interfacial zones) are effective in providing conductive pathways. Further spectroscopic investigation of these phenomena are currently in progress.

### References:

- <sup>i</sup> T. A. Zawodzinski, and J. E. McGrath, *J Membrane Science*, **197**, 231 (2002).
- <sup>ii</sup> F. Wang, M. Hickner, Y. S. Kim, T. A. Zawodzinski, and J. E. McGrath, *J Membrane Science*, **197**, 231 (2002).
- <sup>iii</sup> H. Ghassemi, W. Harrison, T.A. Zawodzinski, Jr., J. E. McGrath, *Polymer Preprints* (American Chemical Society, Division of Polymer Chemistry), **45**, 68 (2004).