

Short communication

Thermal studies of the state of water in proton conducting fuel cell membranes

T.L. Kalapos, B. Decker, H.A. Every, H. Ghassemi,
T.A. Zawodzinski Jr.*

*Department of Chemical Engineering and Case Advanced Power Institute,
Case Western Reserve University, Cleveland, OH 44106, USA*

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Abstract

The thermodynamics of acid group hydration was studied for different membranes (including Nafion[®] and sulfonated poly(arylene ether sulfone) (BPSH)) and model systems (including an organic/inorganic composite (I/O) and a multiblock polymer (MB-150)). Experiments were carried out with the membranes exposed to different activities of water corresponding to different levels of membrane hydration. Isopiestic sorption shows a significantly greater uptake in water for the multiblock polymer as compared to the others. Differential scanning calorimetry (DSC) was used to study thermal properties to elucidate the state of water in the membranes. A comparison is made of various modes of collecting data using DSC. Based on these data, we discuss the overall understanding of water interactions with these membranes as well as the limitations of thermodynamic data in describing microenvironments within the membrane.

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1. Introduction

In optimizing performance of polymer electrolyte fuel cell technology for applications, one must consider material performance in light of the entire fuel cell and power system. For example, though the optimal conditions for the present leading fuel cell membrane (i.e., Nafion[®]) are at full hydration and 80 °C, there are system advantages to operating at higher temperatures (>100 °C) and lower levels of hydration (~25% relative humidity) in transportation applications. At higher temperatures, there is a greater driving force for heat rejection, requiring less exchanger surface area for heat removal. Raising the cell temperature can also significantly lower the poisoning affects of CO in certain hydrogen (reformate) feed streams by affecting the equilibrium constant for CO adsorption [1]. However, at temperatures approaching and greater than 100 °C (while maintaining atmospheric pressure), proton conductivity in polymer electrolyte membranes is typically lower than expected (based

on thermal activation) [2] due to the accompanying decrease in water content.

Several aspects of the proton conduction mechanism are responsible for the decrease in conductivity. At higher water contents, the protons exhibit higher mobility, perhaps using a well-developed water network to ‘hop’ between neighboring water molecules in what is referred to as a Grotthuss mechanism [3]. On the other hand, at low water contents, proton conduction predominantly occurs via a vehicular mechanism—the protons and associated water move as a single entity [4]. This latter mechanism is a less effective means of proton transport, thus leading to a decrease in proton conductivity and corresponding decrease in cell performance. A higher water content is also desired as the presence of more water substantially screens the field associated with the negatively charged counterions, decreasing the ‘restraining force’ on protons and water, again enabling more facile transport.

Finally, in some cases the connectivity of the long-range conduction network may be improved by the swelling of the membrane that accompanies the higher water contents. Thus, the overall mobility of water and protons increases substantially with increasing water content. Though this increased mobility

* Corresponding author. Tel.: +1 216 368 5547; fax: +1 216 368 3016.
E-mail address: taz5@case.edu (T.A. Zawodzinski Jr.).

improves conductivity, it is a liability in direct methanol fuel cell (DMFC) operation where a high electro-osmotic drag of water in a swollen membrane can lead to greater methanol crossover. This motivates us to better understand and even tune the tightness of water binding in a fuel cell membrane.

The amount and properties of water present in the membrane are largely dependent on the nature of the interaction between the water and the ionic groups as well as on the mechanical properties of the polymer [5]. The latter is a key relevant parameter in determining the swelling of the polymer, while the former drives water uptake at relative humidity less than $\sim 75\%$ [6].

Toward understanding the effects of water in the membrane, several workers have posited the existence of three ‘states’ of water in the membrane, corresponding to various non-freezing and freezing fractions of water as observed via DSC [7–12]. The freezing fraction of water is identified as loosely bound, or ‘free’ water and ‘bound-freezable’ water while the (non-observable) non-freezing fraction is identified with ‘tightly bound’ water. Similar distinctions have long been discussed in the context of porous media, such as porous glass and rocks and in the hydration of proteins [13,14]. In this mental construct, the transport properties of water and protons would be dependent on the population of the different environments.

While such a distinction may be a convenient mental picture, it has several limitations as a descriptive hypothesis. First, it is important to realize that the residence time of water in the various environments in a system at any temperature above the freezing point is such that only average properties of all water molecules are observed at timescales longer than a few tens of picoseconds. All *thermodynamic* or experimentally slow measurements then provide average values over all populations. Also, the inherent range of environments present in a polymer tends to blur any quantitative use of these distinctions. Nonetheless, the description of water in these environments is a qualitatively useful guide for broad correlations of properties. Our discussion in this context serves primarily as a caution to realize that the true situation represents a balance of different variables and that the existence of different micro-environments for water is more effect than cause.

It is the aim of this work to investigate and describe the thermodynamics of acid group hydration for different membranes

and model systems. Isoopiestic measurements were carried out with membranes that had been exposed to different activities of water corresponding to different levels of membrane hydration, providing access to free energy of water uptake. Differential scanning calorimetry (DSC) was performed with membranes that had been exposed to an activity of water of unity in order to examine the condition of water in the membranes, as either freezing or non-freezing. The enthalpic nature of the solvation interaction allows it to be readily characterized thermodynamically. This can be done through analysis of isopiestic data, i.e., the measurement of the sorption of water as a function of water activity in the vapor state, and, of course, using the DSC data.

2. Experimental

Nafion[®] 117 was obtained from Ion Power Inc. (Bear, Delaware). BPSH-35 membranes were synthesized in house according to the known procedure [15]. The membrane is a poly(arylene sulfone) polymerized from 3,3'-sulfonated and non-sulfonated 4,4' dichlorodiphenylsulfone monomers with bisphenol A by a condensation reaction. The designation ‘35’ refers to the percent sulfonation of the polymer. The multiblock polymer (MB-150) was synthesized in house by condensation polymerization of oligomeric blocks of BPSH-100 and oligomers formed from bisphenol A and decafluorobiphenyl according to a published procedure [16]. The structures of the BPSH and MB-150 polymers are shown in Fig. 1. The inorganic/organic composite membrane (I/O) was prepared by casting a composite film of poly(vinylidene difluoride) and silica particles that were surface modified with silylhexacanesulfonate from a dimethylacetamide solution. Surface modification of the silica was carried out by reacting silica particles with 11-bromo-undecyltrichoro silane in bicyclohexane at 80 °C for one day, followed by further reaction with potassium thioacetate in ethanol. The product was oxidized in a hydrogen peroxide/acetic acid mixture. Table 1 details the treating and cleaning procedures to yield the H⁺ form of the membranes. After cleaning, and before equilibration, the membranes were stored immersed in DI water.

For isopiestic determinations, water uptake of the membranes was determined gravimetrically. First, the membranes

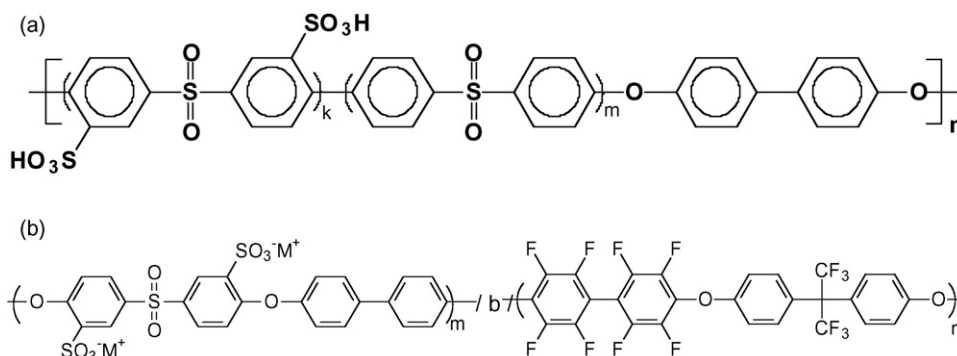


Fig. 1. Structures of: (a) BPSH-35 and (b) MB-150 used in this study.

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