Microporous and Mesoporous Materials 177 (2013) 17–24

Contents lists available at SciVerse ScienceDirect

Microporous and Mesoporous Materials

journal homepage: www.elsevier.com/locate/micromeso

Intrinsic relationships between proton conductivity and nanopore size and functionalization

Marshall T. McDonnell [a], David J. Keffer [b,*]

[a] Department of Chemical and Biomolecular Engineering, University of Tennessee, Knoxville, TN 37996-2200, United States
[b] Department of Material Science and Engineering, University of Tennessee, Knoxville, TN 37996-2200, United States

ARTICLE INFO

Article history:
Received 12 February 2013
Received in revised form 5 April 2013
Accepted 12 April 2013
Available online 18 April 2013

Keywords:
Proton
Conductivity
Nanopore
Proton exchange membranes
Diffusivity

ABSTRACT

A fundamental understanding of the relationship between the nanoscale structure of proton exchange membranes (PEMs) and their proton conductivity would be exceedingly useful in optimizing existing and designing new materials. In this work, a set of structural descriptors, accounting for nanopore size, functionalization and connectivity are employed to predict proton conductivities in PEMs. The model reproduces experimentally determined conductivities in two PEMs. The model is applied to water-filled cylindrical nanopores functionalized on their interior surface with acid groups. It is demonstrated that for cylindrical nanopores of a given radius there is an optimal surface coverage of acid groups. The optimum can be sharply peaked, indicating that non-optimal surface coverages (either too low or too high) drastically reduce the conductivity of the pore. The theoretical maximum conductivity through a cylindrical nanopore is calculated to be about 0.70 S/cm at 300 K.

1. Introduction

Materials discovery can be accelerated by guidance based on a fundamental understanding of the relationship between molecular-level structure and macroscopic properties [1]. Computer modeling plays an important role in contributing to the understanding of structure/property relationships. The abundance of data produced by molecular simulations, positions and velocities of every atom as a function of time, must be distilled into a set of structural descriptors that characterize the material. The structural descriptors are chosen to comprise a necessary and sufficient set from which the properties of interest can be functionalized. Once generated, these functions which provide the value of the property at a given set of structural descriptors should be able to reproduce experimental measurements for known materials and predictively estimate values for new materials. In this paper, this approach is applied to nanostructured proton exchange membranes.

There is significant interest in high temperature (>80 °C) proton exchange membrane (PEM) fuel cells because of the potential reduction in catalyst content, which represents a significant fraction of the fuel cell cost [2]. The current platinum or platinum alloy catalysts have higher activities and are less susceptible to CO poisoning with increased temperature, lowering stringent requirements on fuel purity. The primary obstacle toward high temperature PEM fuel cells lies in the fact the PEM must be hydrated to conduct protons from the anode to the cathode. At increased temperatures, the PEM dries out and the conductivity drops dramatically [3]. Thus there is significant interest in developing a predictive understanding of the relationship between the nanoscale structure of the hydrated PEM and the resulting conductivity.

The industry standard for PEMs is Nafion, a perfluorosulfonic acid (PFSA) polymer electrolyte. When hydrated, Nafion undergoes a nanoscale phase segregation into hydrophobic regions composed of the polymer backbone and aqueous domains containing water, the side chains terminated in the sulfonate group and hydronium ions [4]. Nafion is a member of a class of PEMs in which the transport of charge is strongly correlated with the transport of water, as is also the case in bulk acid solutions. Experimental observations of the self-diffusivity of charge and water in Nafion show them to respond in qualitatively similar manners to changes in the structure of the membrane induced either by changes in hydration or polymer chemistry [5]. There are other classes of PEMs in which the transport of water and charge are decoupled. One such class relies primarily on the introduction of dopants in the aqueous domain which enhance diffusion of charge through the structural mechanism and typically slow down the diffusion of water [6]. Another class of PEMs achieves proton transport without the presence of water, either by substitution of water with a different proton solvent or relying solely on the proton-conductivity of the polymeric backbone that makes up the PEM [7]. This work focuses on the class of hydrated PEMs including Nafion, in which water and charge transport are strongly correlated.

In a previous work, we postulated a set of three structural descriptors from which the self-diffusivity of water and the proton

---

* Corresponding author.
E-mail address: dkeffer@utk.edu (D.J. Keffer).

1387-1811/$ - see front matter © 2013 Elsevier Inc. All rights reserved.
http://dx.doi.org/10.1016/j.micromeso.2013.04.007

conductivity in this first class of PEMs could be estimated [8]. The descriptors include (1) acidity, a measure of the number of excess protons per unit volume of the aqueous domain, (2) confinement, a measure of the interfacial surface area between the polymer and aqueous domains per unit volume of the aqueous domain and (3) connectivity, a measure of the nature of the network of aqueous clusters through which transport of water and charge occurs. These three structural descriptors, while themselves coarse-grained, require a molecular model of the hydrated membrane in order to estimate the volume, surface area and distribution of the aqueous domain within the polymer. These three structural descriptors are again invoked in this work to provide an approximate characterization of the structure from which transport properties can be estimated.

The remainder of this paper is organized as follows. The approach used to generate conductivity as a function of these structural descriptors is given. The approach is then validated for Nafion and other systems. The approach is then used to predict the conductivity of new proton exchange membranes.

2. Theory

Percolation theory describes the relationship between a transport property through a network, the connectivity and fraction of defects within the network. Analytical models of percolation, such as the effective medium approximation (EMA) [9,10], take as input the coordination (connectivity) of the network, z, the fraction of pathways that are blocked to transport, p_{EMA}, and the diffusivity through open (o) and blocked (b) paths, D_s and D_b respectively. From these inputs, one obtains the effective diffusivity, D_{eff}, from EMA. Given a bimodal distribution of open and blocked windows, we have

$$g(D) = p_{EMA}\delta(D - D_b) + (1 - p_{EMA})\delta(D - D_o) \tag{1}$$

where δ is the Dirac delta function, defined as:

$$\int_{-\infty}^{\infty} \delta(D - D_\beta)dD = 1 \tag{2}$$

EMA yields,

$$\int_0^{\infty} \frac{g(D)(D_{eff} - D)}{D + \left(\frac{z}{2} - 1\right)D_{eff}}dD = 0 \tag{3}$$

Upon integration and solving for the relevant root of D_{eff}, we have

$$\frac{D_{eff}}{D_0} = \frac{1}{2}\left[A + \sqrt{A^2 + \frac{4f}{\frac{z}{2} - 1}}\right] \tag{4}$$

where $f = D_b/D_o$ and

$$A = 1 - p_{EMA} + fp_{EMA} - \frac{f + p_{EMA} - fp_{EMA}}{\frac{z}{2} - 1} \tag{5}$$

When applied to water (w), EMA yields the effective diffusivity of water. To obtain the conductivity, EMA is applied to charge (chg) and coupled with the relation [11],

$$D_{eff}^{chg} = \left(\frac{RT}{|z|^2F^2}\right)\frac{\sigma}{c} \tag{6}$$

where σ is the conductivity, R is the gas constant, F is Faraday's constant, and T is the temperature.

The challenge lies in parameterizing percolation theory in terms of the structural descriptors. We begin with water and then proceed to charge. The self-diffusivity of water through an open pathway can be made a function of acidity and confinement by accounting for the concentration of hydronium ions, c, and the interfacial surface area, sa,

$$D_\alpha(c, sa) = f_c f_{sa} D_\alpha(c = 0, sa = 0) \tag{7}$$

where the concentration component, f_c has the functional form

$$f_c = \frac{D_\alpha(c, sa = 0)}{D_\alpha(c = 0, sa = 0)} = \begin{cases} 1 & \text{for } c \leqslant \tau_c^\alpha \\ \exp\left[k_c(c - \tau_c^\alpha)\right] & \text{for } c > \tau_c^\alpha \end{cases} \tag{8}$$

and the surface area component, f_{sa}, has a completely analogous form, where the c and sa subscripts are switched. The subscript α is set to w for water. These functional forms of an exponential decay with a rate constant, k_c^α, and a lag, τ_c^α, are suggested by both experimental observation [12] and simulation [13,14] of bulk acids and water in carbon nanotubes.

The use of exponential decay functional forms for diffusivities of both water and charge as a function of acidity is motivated by the experimental evidence from the work of Dippel and Kreuer [12]. The explanation of the decay is attributed to addition of anions breaking up the hydrogen-bond network, increasing water disorder and thus decreasing the entropic change for vehicular diffusion for the pre-exponential factor. Interestingly, the activation enthalpy decreases simultaneously with anion addition. One can infer that the entropic, exponential pre-factor is the dominant term in the decay.

The use of exponential decay functional forms to capture the effect of confinement has been motivated by simulation of water in carbon nanotubes [13]. Confinement also has a negative effect on the diffusivity where the mobility of the water decreases with decreases in the tube size.

For the self-diffusivity of charge, the total charge diffusivity must be decomposed into two separate mechanisms for diffusivity, structural and vehicular diffusivities. More details on the difference in the vehicular and structural components of self-diffusivity of charge will be discussed later.

The values of experimentally determined diffusivities in dilute bulk solutions [15,16], the factor of contribution of each type of diffusivity, the prefactor determined from the two previous values and the parameters for the rate constants and lag used in Eq. (8) are given in Table 1. By multiplying the experimental bulk water self-diffusivity and the factor given in Table 1, we compute the exponential pre-factor. The pre-factor is incorporated into the $D_\alpha(c = 0, sa = 0)$ term in Eq. (7). Importantly, no information on transport in PEMs was used in the generation of Table 1. The values of the concentration and interfacial surface area require a molecular model from which the volume and surface area of the aqueous domain can be determined. Values for Nafion are published [17]. For percolation theory, the open channel diffusivity of either water or charge is related to the component diffusivity under the corresponding conditions of acidity and confinement, $D_o = D_\alpha(c, sa)$

The MD simulations that provided the volume and surface area also provide short-time mean square displacements (MSDs) of water. By fitting these MSDs to confined random walk simulations,

Table 1
Model parameters for percolation theory for self-diffusivity using structural descriptors for acidity (c, concentration of hydronium ions) and confinement (sa, the interfacial surface area).

		Water	Charge-struct	Charge-veh
Experiment	(m^2/s)	2.26E−09[16]	9.7E−09[15,a]	9.7E−09[15,a]
Factor		1	0.621	0.379
Pre-factor	(m^2/s)	2.26E−09	6.0237E−09	3.6763E−09
k_c	(L/mol)	−0.00543	−0.459	−0.191
τ_c	(mol/L)	–	–	4.7
k_{sa}	(water molecules/Å^2)	−0.00103	−0.00715	−0.002
τ_{sa}	(Å^2)	–	–	29.5

[a] Experimental measures total charge self-diffusivity.