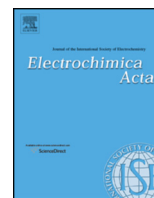




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Resistor–Network Modeling of Ionic Conduction in Polymer Electrolytes

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ABSTRACT

A resistor- and pore-network methodology is used to examine transport of ions in various ion-conducting polymers. The model is used to examine ion conduction in random and correlated (at the mesoscale) distributions of high and low conductive domains showing the impact that defects or different conduction modes have on overall effective conductivity and percolation. The specific case of Nafion is modeled where swelling is accounted for as well as a spatially varying conductivity within the nanodomains. The model is also used to investigate conduction in thin-films, where a substantial drop in conductivity is witnessed for films less than 50 nm thick. The model shows good agreement with experimental data and provides a methodology for efficient multiscale modeling of transport in ion-conducting polymers from the nanoscale morphology through the mesoscale transport pathways to the observable macroscale properties.

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1. Introduction

Transport of ionic species through ion-conducting polymers, or ionomers, is a major consideration in the design of polymer-electrolyte fuel cells (PEFCs), redox flow cells, solar–fuel generators, and batteries. Ionic conduction, or lack thereof, is usually a significant source of efficiency loss in these devices, especially as one endeavors to simplify or scale systems [1]. For example, it is desired to operate PEFCs at low humidities and temperatures above 100 °C to decrease system complexity and water management; however, an ionomer has yet to be developed that can conduct efficiently under such conditions. To minimize the overall cell ohmic resistance, the ionomer is made as thin as possible so that the effective conductance, a function of intrinsic conductivity and geometry, is sufficiently high. Such a strategy has a minimum threshold due to the need for mechanical stability and chemical durability of the membranes. The search for materials with high intrinsic conductivity and/or better mechanical properties is an ongoing task, including the development of composite structures composed of conductive and nonconductive elements [2–7].

Transport of ions within ionomers is inherently multiscale, where ions are traversing the length of the membranes and

interacting with dynamic nanophase separated domains that coalesce into transport pathways at the mesoscale [8]. Mathematical modeling is ideally suited for exploring ionomers due to their complexity and nonlinearity in their transport phenomena and even structural data. For PEFCs specifically, the proton-exchange membrane (PEM) plays an integral role in controlling the cell's ohmic losses. In addition, the PEM is a critical component in PEFC water management as it transports water and normally requires hydration for efficient proton conduction, thereby setting minimal cell humidity requirements. While there are efforts to develop PEMs that conduct efficiently at higher temperatures (>100 °C) and/or lower humidities, these are still in the laboratory setting [9].

The polymer of choice, Nafion[®], a random copolymer of polytetrafluoroethylene and polysulfonyl fluoride vinyl ether, serves as a benchmark material due to its remarkable proton conductivity and thermo-mechanical stability [10]. Absorption of water by the ionic groups creates nanodomains in the semi-crystalline polymer matrix through which ion and water transport occurs. Nanophase separation and water-uptake capacity are affected by the backbone rigidity and ion interactions which control the reorganization and inter-connectivity of the domains [11–13]. The water uptake is characterized by a primary hydration of around $\lambda = 6$ (i.e., 6 water molecules per sulfonic acid site), followed by a secondary swelling of the polymer matrix to a $\lambda = 14$ (saturated vapor) and $\lambda = 22$ (liquid water) [14,15]. Water uptake has been modeled by various means, mainly using an

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energy-balance approach wherein the chemical energies related to dissolution are countered by the mechanical energies related to swelling and backbone deformation [16–23]. While these models have shown significant insight into the quasi-equilibrium water content, their use as models of transport have been limited since they inherently neglect the connectivity between the water domains. To complicate matters, it is also known that a PEM exhibits significantly different water uptake and physical properties depending on the phase of water in contact with the surface, namely liquid or vapor [15,24–26]. Such a change in uptake is thought to perhaps be due to surface morphological changes of the PEM when exposed to the different environments as discussed by Kreuer [14], Freger [26,27], and explored by Weber and coworkers [24,28–31]. What is known for certain is that the domain sizes change with liquid versus vapor equilibration as measured by x-ray scattering and macroscopic property measurements [32]. Overall though, the modeling and understanding of transport properties such as ion conductivity are not nearly as developed as that of bulk water uptake.

Various models of proton conduction in PEMs have shown the possible existence of different mechanisms of transport [33–38]. The first is a proton hopping or Grotthuss mechanism wherein the proton moves across a hydrogen-bond network mainly through concerted molecular bond rotations of the hydrated Eigen or Zundel clusters [38–40]. The second mechanism is a vehicular mechanism that is associated with movement of a hydronium ion. The first mechanism is known to be fast and the second slower. As mentioned, there are two transport modes where for the liquid-equilibrated transport mode, Grotthuss type conductivity is believed to be dominant, and for vapor-equilibrated it is thought to be more vehicular. The reason for this is that the domain sizes are larger for liquid-equilibration and subsequently there is more of a bulk-like water region [41,42]. However, there is undoubtedly a mixture of modes, wherein the connectivity becomes increasingly important, and dominant transport pathways emerge. While the two mechanisms have been explored at the atomic scale through ab-initio and molecular dynamics [42–45], or at the coarse grain scale through dissipative particle dynamics and other methods [46–48], scaling up to a macroscopically measurable quantity across the membrane has been a challenge due to the connectivity issues and disparate length scales of the phenomena; a true, efficient multiscale representation of the conductivity does not exist.

To model the connectivity between hydrophilic domains efficiently and resolve macroscopic transport properties, one can utilize a resistor-network approach similar to pore-network modeling in porous media [49,50]. While the approach is not new and demonstrates many of the experimental observations such as a percolation threshold for conduction [51], it is not fully developed for PEMs wherein transport is multiscale and occurs within a dynamic framework with varying morphology and transport properties. The most exemplary of its adoption to PEMs was accomplished by Eikerling et al. [52,53] and subsequently by Weber et al. [28,54], wherein such an approach was shown to be able to bridge the gap between the different membrane transport modes (i.e., liquid-equilibrated or vapor-equilibrated) in a physically consistent framework. Eikerling et al. and Weber et al. both utilized a framework of essentially swollen and collapsed channels and used tangential evidence to derive the effective channel-size distributions. Recently, some groups have used a more rigorous approach for modeling transport wherein they accounted for the network structure in more detail [55–58]. There is still a need to improve the techniques and fidelity of the models, as well as exercise them in terms of exploring and setting design targets. In this paper, we explore conductivity as a function of network topology and ratio of conductivities between the two modes in

order to both prove out the approach and help establish design targets and understanding for PEM development.

The outline of the paper is as follows. First, the modeling methodology is presented. Next, several test cases are explored in terms of conductivity ratio and bulk network dimensionality. Then the modeling of transport more relevant to Nafion is carried out using recently measured values for its channel size and connectivity, where the different conductivity values represent bridging or perhaps defect sites. Finally, a general discussion of the findings is made followed by the summary.

2. Modeling

Two related modeling approaches were used to calculate effective conductivities of ion-conducting polymer electrolytes. For the general case of a block co-polymer (BCP), a resistor network was used, which uses a finite-difference scheme to estimate the effective conductivity of the network. For the more specific case of ionomers like Nafion[®], a pore-network approach was used wherein the conductance values between neighboring nodes is determined from physical considerations of the specific 'pore structure'. Both of these approaches are outlined in more detail in the sections that follow.

2.1. General Solution Procedure

For both the BCP and Nafion studies, the effective conductivity of the network was found in the same manner. Using the conductivity κ of the conducting material, and the size information for the conduit connecting nodes (or pores) i and j , the conductance g_{ij} conduit can be found. The ion flow in the network follows Ohm's law, such that the flow of current I between two neighboring pores i and j is proportional to the voltage difference ΔV and the conductance between them as

$$I = g_{ij}\Delta V \quad (1)$$

The current entering and exiting each node will sum to zero for steady-state conditions with no reaction terms. Thus, a current balance around node i gives

$$0 = \sum_{k=1}^n g_{ik}(V_k - V_i) \quad (2)$$

where node i has n neighboring pores. Performing this balance on each node in a network with N nodes results in a linear system of N equations that can be easily solved to find the V in each node. The effective conductivity of the network can be found by applying voltage boundary conditions on two opposing faces of the network and solving the system of equations resulting from the application of Eq. (2) to every node. With the voltage in each node known, it is possible to calculate the total flow of current through a control surface. The key to the present resistor or pore-network simulations is to find meaningful values for g_{ik} to be used in Eq. (2).

The modeling domains used here are illustrated in Fig. 1 for the 2D and 3D cases. The inset views show a close-up of the pore-throat-pore conduit. The pores are represented by cubes and the throat are drawn as lines for clarity, although they were treated as cylinders in the simulations. In all the simulations presented below, the voltage gradient was applied in the z-direction.

2.2. Resistor Network Modeling of Block Co-Polymers

Resistor values for the BCP network were determined by assigning each node in the network to be either conducting or non-conducting. Once an assignment has been made to each node, the

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