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Charge transport in the electrospun nanofiber composite membrane's three-dimensional fibrous structure

Matthew B. DeGostin [a], Aldo A. Peracchio [a], Timothy D. Myles [b], Brice N. Cassenti [a], Wilson K.S. Chiu [a], *

[a] Department of Mechanical Engineering, University of Connecticut, 191 Auditorium Road, Storrs, CT 06269-3139, USA
[b] Center for Clean Energy Engineering, University of Connecticut, 44 Weaver Road, Unit 5233, Storrs, CT 06269, USA

HIGHLIGHTS

- A Fiber Network Model was developed to predict conductivity of Electrospun membranes.
- Conductivity trends compared well with limited in-plane experimental conductivity data.
- Further validation resulted by comparison to Effective Medium and Porous Media theory.

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ABSTRACT

In this paper, a Fiber Network (FN) ion transport model is developed to simulate the three-dimensional fibrous microstructural morphology that results from the electrospinning membrane fabrication process. This model is able to approximate fiber layering within a membrane as well as membrane swelling due to water uptake. The discrete random fiber networks representing membranes are converted to resistor networks and solved for current flow and ionic conductivity. Model predictions are validated by comparison with experimental conductivity data from electrospun anion exchange membranes (AEM) and proton exchange membranes (PEM) for fuel cells as well as existing theories. The model is capable of predicting in-plane and thru-plane conductivity and takes into account detailed membrane characteristics, such as volume fraction, fiber diameter, fiber conductivity, and membrane layering, and as such may be used as a tool for advanced electrode design.

1. Introduction

Electrospinning of polymeric ion conducting nanofibers has recently gained attention as a promising means of constructing membranes for electrochemical applications that exhibit desirable transport properties and enhanced structural stability. The electrospun membranes resulting from this fabrication technique have unique fibrous structures whose transport characteristics may be highly dependent on the geometry of the underlying fiber network [1]. Recently, fuel cells, in particular anion exchange membrane (AEM) [2–4] and proton exchange membrane (PEM) [5–8] fuel cells, have been targeted by researchers as systems that could benefit from the electrospinning technique. In many of these studies, ion exchange membranes (IEM) are fabricated by spinning a highly conductive ionomer nanofiber (such as Nafion) with an inert, hydrophobic fiber and processing the membranes to produce inter-connected three-dimensional networks of ion conducting fibers completely surrounded by a mechanically supportive uncharged insulating matrix [6].

The main function of IEMs is to allow the flow of ions (protons for PEM and hydroxide ions for AEM, typically) between electrodes in a membrane electrode assembly (MEA), while simultaneously resisting the flow of electrons and gases. To aid in developing these technologies, significant experimental and modeling efforts have been directed at predicting ion flow and transport processes in existing ionomer membranes relevant to PEM and AEM fuel cells [9–17]. In many of these studies, conductivity of ions through membranes is predicted using a simple analytical model such as percolation theory [10], or via inclusion of a dust species in a Dusty Fluid model [10,12]. Such volume averaged approaches yield a

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* Corresponding author.
E-mail address: wchiu@engr.uconn.edu (W.K.S. Chiu).

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Nomenclature

A	Cross-sectional area m^2
D	Distance between electrodes m^2
d	Diameter m
f	Volume fraction of conducting fiber
I	Total current A
L	Coupon length m
l	Individual length of a fiber, m
l_c	Distance between neighboring contact points, m
L_f	Total length of fiber in a coupon, m
n	Number of layers in a coupon
n_{FL}	Number of fibers in a layer
n_{IP}	Number of in-plane conducting paths
n_{TP}	Number of thru-plane conducting paths
R	Resistance, Ω
SF	Swelling scale factor
T	Total coupon thickness, m
V	Volume, m^3
w	Coupon width, m

Greek

ΔV	Potential difference, V
δ	Layer thickness, m
ε	Porosity
ρ	Density, $g\ m^{-3}$
σ	Ionic conductivity, $S\ m^{-1}$
τ	Tortuosity

Subscripts

A	Anisotropic swelling
$bulk$	Bulk property
eff	Effective property
f	Fiber
I	Isotropic swelling
IP	In-plane
L	Layer
P	Supporting matrix
t	Property of total coupon
TP	Thru-plane
w	After swelling

quick, homogenized performance estimation for a membrane but they often require the application of ambiguous parameters that are difficult to obtain (such as tortuosity), or are insensitive to topological effects of microstructural networks and local membrane morphology. In addition, the dominant ion transport mechanisms in polymeric membranes are not yet fully understood [12,13,18]. As discussed by Grew et al. [12], several H^+ transport mechanisms in the PEM have been proposed including the Grotthuss mechanism, convective processes, mass diffusion, and migration. Hydroxide ion (OH^-) transport in AEMs may exhibit similar mechanisms [3,12], however experimental studies have shown that lower conductivities may result in the presence of CO_2 due to conversion of OH^- to the less mobile carbonate and bicarbonate species [13].

Electrospun membranes are an unique class of IEMs due to the microstructural properties that can result from the fabrication process. In addition to the versatility in using a variety of polymeric materials in the process [1,19,20], researchers are afforded control over membrane volume fraction [2,6,7], nanofiber diameter [6,21–23], fiber alignment and orientation [1], and the detailed structure of the fiber such as the presence of pores or surface nanoparticles [1,21]. Based on the interplay between charge transport and underlying membrane structure in traditional polymeric fuel cell membranes [12], membranes fabricated via electrospinning could exhibit distinct charge transport behavior based on their underlying microstructural morphologies [24], and therefore react uniquely to adverse conditions such as the presence of CO_2. In order to support further development of advanced membranes (fabricated by e.g., electrospinning), it is warranted to develop and utilize computational and theoretical models that are sensitive to these distinct microstructural morphologies for predicting membrane performance under a wide range of conditions.

In the present work, a Fiber Network (FN) model was developed to predict ionic conductivities of polymeric composite membranes produced by electrospinning. This model relies on the solution of random resistor networks that represent the conducting fiber morphology of the membrane via application of an existing analytical electrochemical fin theory [25]. The model can accommodate a range of fibrous membrane morphologies and can be readily combined with more detailed physical models that, for instance, model the effects of CO_2 absorption on OH^- conductivity in AEMs [26]. Here, ion transport occurs via simple diffusive mechanism in the case of an applied electrical potential gradient [3]. To aid in development of the model, the works of Park et al. [2] and Ballengee et al. [7] are used as references for describing the electrospinning approach and resulting membrane morphologies, and providing conductivity data for AEMs and PEMs, respectively. The model is then used to predict membrane ion conductivities for an electrospun AEM composed of chloromethylated polysulfone (CMPSF) nanofibers and poly(phenylsulfone) PPSU supporting matrix and a PEM composed of Nafion nanofibers and PPSU matrix, after calculating the fiber conductivity to match a single experimental conductivity data point for each material. The model predictions agree well with experimental measurements for ionic conductivities, showcasing the FN model as a viable means of modeling charge transport behavior in fibrous ionomeric membranes. Results from a recently developed Effective Medium theory (EMT) are also presented for validation of the FN model predictions of electrospun AEM conductivity. Based on insight gained from the FN model, simple resistor-based closed-form analytical solutions have been developed to predict conductivity of electrospun membranes given easily obtained structural parameters relevant to the electrospinning process and fitting a constant (accounting for nanofiber conductivity and fiber layering) to one experimental data point. Finally, conductivity predictions using an existing transport model from Porous Media Theory (PMT) are compared to FN model predictions for an electrospun PEM. To apply PMT, estimates of tortuosity for various electrospun membranes are obtained via outputs from the FN model. The combination of the models developed in this paper with other transport models accounting for effects of CO_2 will be considered for future work. In the following section, the FN model and other models used in this work will be described. Comparison with experimental data and validation of the models is shown in a separate Results and Discussion section.

2. Methodology

2.1. Fiber network model

The goal of this model is to approximate the 3-D morphology of electrospun nanofiber composite membranes including membrane swelling in the presence of water, and compute resulting transport properties such as in-plane and thru-plane ionic conductivities.