V.B.6 Multiscale Modeling of Fuel Cell Membranes

Adam Weber (Primary Contact), Andrew Crothers
Lawrence Berkeley National Laboratory
1 Cyclotron Road, Mailstop 70R0108B
Berkeley, CA 94720
Phone: (510) 486-6308
Email: azweber@lbl.gov

DOE Manager: Donna Ho
Phone: (202) 586-8000
Email: Donna.Ho@ee.doe.gov

Project Start Date: September 2014
Project End Date: Project continuation and direction determined annually by DOE

Overall Objectives

- Develop multiscale model of ion and solvent transport through fuel-cell membranes.

- Propose material optimization strategies and explore design criteria for ion-conducting membranes across multiple length scales.

Fiscal Year (FY) 2016 Objectives

- Develop detailed nanoscale model of ion transport in the membrane.

- Develop upscaling methodology to predict macroscopic properties.

- Identify limiting aspects of membrane performance.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cell section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan:

(C) Performance

Technical Targets

The aim of this project is modeling and validation of a model of transport in fuel cell membranes. Insights gained from these studies will be applied toward the design and synthesis of fuel cell membranes and membrane electrode assemblies that meet the following DOE hydrogen storage targets:

- Membrane electrode assembly performance: 300 mA/cm^2 at 0.8 V

- Membrane electrode assembly performance: 1,000 mW/cm^2 at rated power

- Membrane area specific proton resistance: 0.02 ohm cm^2 at maximum operating temperature and water partial pressures from 40–80 kPa

FY 2016 Accomplishments

- Modeled transport within the ionomer network using a resistor network approach.

- Developed an energy balance framework for the electrochemical potential of cations based on atomistic simulations.

- Validated the model using experimental measurements and atomistic simulations.

- Identified areas to improve membrane conductivity through material design.

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INTRODUCTION

Ionomer membranes are a critical component of fuel cell operation because they ensure efficient operation by separating hydrogen and oxygen reactants while allowing proton transport between the anode and cathode. To improve fuel cell performance by increasing proton conduction between the anode and cathode, DOE has identified a target for the reduction of the membrane specific area resistance to 0.02 ohm cm^2 at maximum operating temperature and water partial pressure from 40 kPa to 80 kPa. The membrane consists of a structural hydrophobic phase surrounding conducting nanoscale hydrophilic domains that are connected to form a conductive network across the membrane. Despite the broad use of ionomer membranes in fuel cells, there is not a clear and quantitative understanding of how the nano- and network-scales inherent in transport in ionomers affect macroscopic properties, such as ionic resistance. Moreover, transport at these multiple length scales in membranes have associated time scales, which impact dynamic operando behavior. The complexity of this multiscale problem presents a challenge for rational design of improved membranes. The goal of this project is to develop a model that can predict transport behavior across lengthscales and determine how each scale impacts macroscopic properties. This model will be used to identify limitations in current membranes and propose strategies for designing materials with improved performance. Under this work, a detailed and predictive nanoscale model for proton conductivity has been developed. The model was upscaled to predict membrane conductivity and identify sources of ion transport resistances.

APPROACH

The general approach of this project is to model each length scale relevant for transport in ionomers and connect these models through a generalized upscaling methodology. The nanoscale was modeled using a mean field physics model. The network-scale was modeled using a resistor network methodology. The results of the simulations are validated with molecular dynamics simulations at the nanoscale and experimental conductivity measurements at the macroscale. The material properties that are critical for membrane performance can be elucidated by analyzing the results of the model at each length scale.

RESULTS

The methodology was developed to model proton conductivity in ionomer membranes individually at both the nanoscale and network-scale, and communicate between these scales to predict macroscopic conductivity. This framework was then used to understand sources of resistance for proton conduction and identify potential avenues to improve performance.

The nanoscale model was developed and simulations were performed. The results at the nanoscale were upscaled to predict macroscopic properties by using a bundle of capillaries methodology. The model was shown to be predictive of experimental membrane conductivity for both lithium- and proton-form membranes, as shown in Figure 1.

The nanoscale model provides a fundamental understanding of molecular interactions that can be leveraged to elucidate potential avenues for improved material design. Protons in the ionomer are either solvated and mobile or bound to the ionomer and immobile. The fraction of the population in either of these states is the result of an interplay between solvation and electrostatic forces. By tuning the membrane properties (e.g., delocalizing the negative charges of the ionomer and making the membrane more acidic), more protons dissociate from the ionomer and participate in ion transport, thus increasing membrane conductivity, as shown in Figure 2.

The importance of the resistance at each length scale was investigated using the model. As shown in Figure 3, conductivity in the ideal limit actually decreases with increasing water content because the water dilutes the concentration of protons. However, as the membrane fills with water, a greater fraction of the nanodomains becomes conductive, which results in the observed increased conductivity with increasing water content. Moreover, as the water content increases, the protons at the nanoscale are mobilized, which further increases conductivity. Finally, as the water content of the membrane increases, there is increased connectivity across the network and its tortuosity decreases, thus facilitating increased conductivity. Figure 3
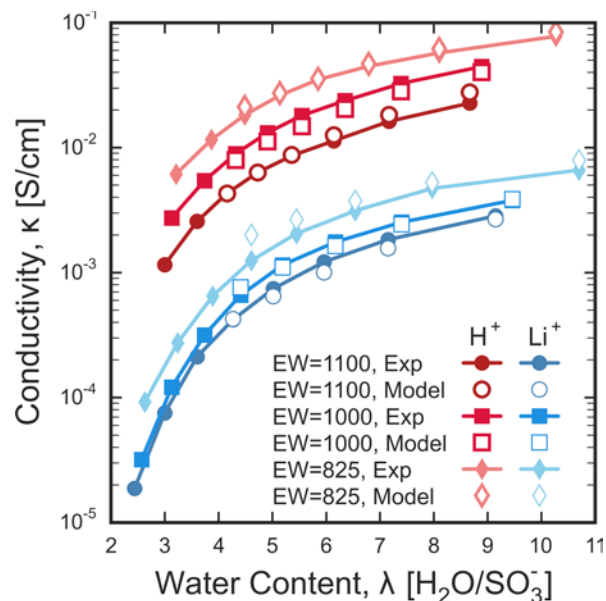

FIGURE 1. 3M membrane conductivity of lithium- and proton-form membranes as a function of water content as determined from the model (open) and experiments (filled, with red and blue lines to guide the eyes for proton- and lithium-form membranes, respectively) for different equivalent weights (EWs) of 1,100 (circles), 1,000 (squares), and 825 g/mol (SO_3^-) (diamonds).
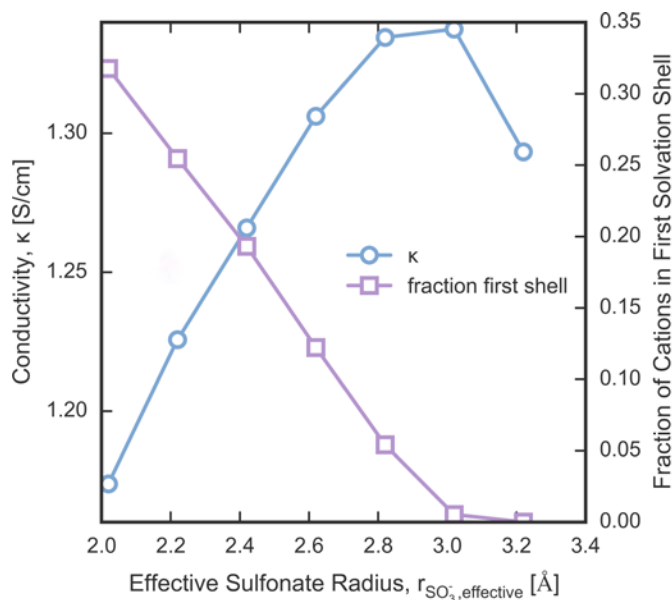

FIGURE 2. Proton conductivity (circle, left axis) and fraction probability of protons in the primary solvation shell of sulfonate groups (square, right axis) at λ = 9 [H_2O/SO_3^-] for a varying size of the effective volume of the negatively charge side-chain moiety. Lines are guides to the eyes only.

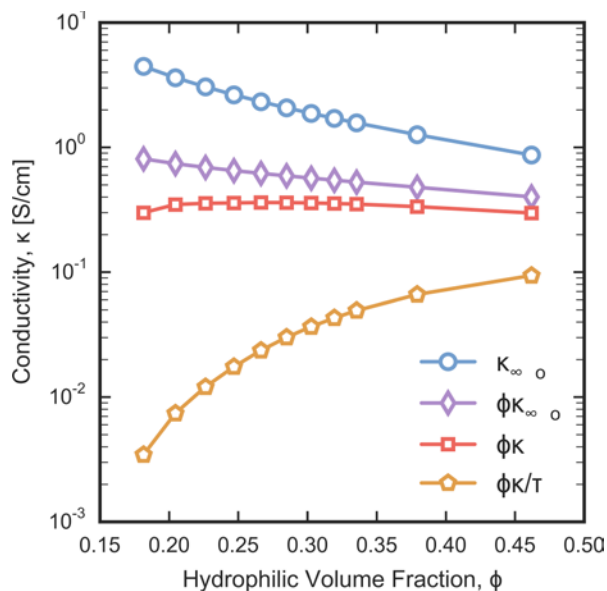provides a quantitative framework for strategies to improve membrane conductivity to achieve the goal of a specific

FIGURE 3. Breakdown of contributors to proton conductivity as a function of hydrophilic volume fraction. κ_∞ (circles) is the conductive ideal limit in a nanodomains (which changes due to nanodomains size), $\phi\kappa_\infty$ (diamonds) accounts for the presence of the volume fraction of the nanodomains, $\phi\kappa$ (squares) accounts for the local interactions as well, and $\phi\kappa/\tau$ (pentagons) also accounts for the network tortuosity. Lines are guides to the eyes only.

FIGURE 4. Proton transport in a two-dimensional slice of the Nafion™ network. The lines in the figure are segments of the network connecting nodes. Segments are colored to show potential drop from high potential (red) to low (blue). Segments colored black are those with a current flux one standard deviation above the average.

area resistance of 0.02 ohm cm^2. Namely, by increasing the hydrophilic fraction of the membrane, increasing the acidity of the ionomer, or decreasing the tortuosity of the conductive network the goal can be approached.

To understand why the tortuosity of the conductive network is an important factor of membrane conductivity, an experimentally consistent resistor-network model was developed to calculate the effective conductivity of the membrane. The resistor network was obtained by analyzing three-dimensional images from cryo-transmission electron microscopy of a hydrated ionomer and extracting the conductive pathways [1]. The results of the network simulation, as shown in Figure 4, show that the membrane is heterogeneous and some pathways dominate. If the membrane were treated as a homogeneous medium, isopotential lines would be straight, vertical lines. The medium is not homogeneous, but has small nonuniformities existing across the network making isopotential lines (lines following a constant color) circuitous. There are dominant pathways in the network, as indicated by segments colored black, but these pathways do not stretch across the entire network. There are also large regions through which little current passes. The conductivity of the membrane may be increased by designing ionomers that are more homogeneous at the mesoscale, and thus less tortuous.
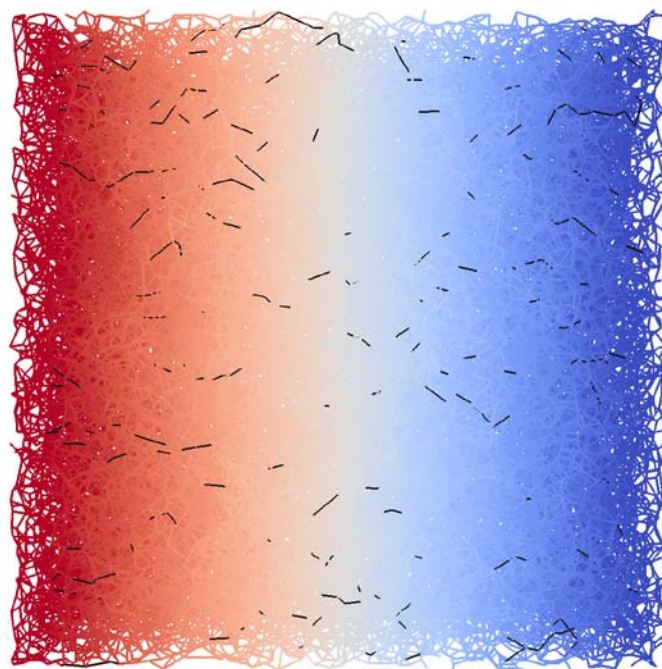
CONCLUSIONS AND FUTURE DIRECTIONS

This project has resulted in several findings that provide a deeper understanding of proton conduction in fuel cell membranes and potential avenues for further improvement.

- Resistances to proton transport in the membrane are due to molecular-scale interactions, the fraction of the membrane that is nonconductive, and the tortuosity of the conductive network.

- Reducing the fraction of protons bound to the ionomer through novel materials, such as membranes with increased acidity, would reduce membrane resistance. Reducing the tortuosity of the conductive pathway in the membrane would also reduce membrane resistance.

While these strategies for decreasing membrane resistances are valuable, the overall performance of the membrane goes beyond simply the resistance, with durability and water uptake and transport playing important roles. Future work seeks to incorporate these aspects to make a holistic understanding of the interplay of factors influencing membrane performance. Specific activities include:

- Incorporate solvent uptake and transport into the membrane model.

- Model how the conductive pathways in the membrane change under different water contents and what the response is under dynamic, operando conditions.

- Understand how contaminates and additives move through the membrane.

SPECIAL RECOGNITIONS & AWARDS/ PATENTS ISSUED

1. Adam Weber, IAHE Sir William Grove Award.

FY 2016 PUBLICATIONS/PRESENTATIONS

1. Gostick, J.T. and A.Z. Weber, Resistor-Network Modeling of Ionic Conduction in Polymer Electrolytes. *Electrochimica Acta*, 2015. **179**: p. 137–145.

2. Crothers, A.R., C.J. Radke, and A.Z. Weber, Multiscale Model of Proton Transport in Perfluorosulfonic-Acid Membrane. *ECS Transactions*, 2015. **69**: p. 731–742.

3. Crothers, A.R., C.J. Radke, and A.Z. Weber, Multiscale Model of Proton Transport in Perfluorosulfonic-Acid Membrane. 228 ECS Meeting, 2015.

REFERENCES

1. Frances I. Allen, Luis R. Comolli, Ahmet Kusoglu, Miguel A. Modestino, Andrew M. Minor, and Adam Z. Weber, "Morphology of Hydrated As-Cast Nafion Revealed through Cryo Electron Tomography," *ACS Macro Letters*, **4**, 1–5 (2015).