

Elucidating Structure/Function Relations in PEMs with Multiscale Simulations

Stephen J. Paddison

Department of Chemical and Biomolecular Engineering
University of Tennessee, Knoxville, Tennessee 37996

The need to operate proton exchange membrane (PEM) fuel cells at temperatures above 100 °C with an electrolyte that exhibits high mechanical and thermal stability coupled with resistance to chemical degradation has propelled the pursuit to develop high performance materials. Success in this effort requires a molecular-level understanding of structure-function relations. The archetypical PEMs are ionomers that when hydrated possess a complex phase-separated morphology with the water and solvated ions confined to domains with dimensions of only a few nanometers by the strongly hydrophobic and semi-crystalline polymer backbones. The efficient operation of a fuel in diverse applications (i.e., vehicular, portable, and stationary) demands that the PEM exhibit high proton conductivity ($\approx 10^{-1} \text{ Scm}^{-1}$) under low humidity conditions (25-50% relative humidity). Elucidating the connections between the chemical structure and the transport properties has motivated extensive research including computational and theoretical work performed during the past 15 years.¹⁻⁵

Characterizing the local and long range structure and connecting it with the transport properties has remained elusive despite extensive experimental studies. This talk will review theoretical effort to understand structure property relationships over length scale from a few angstroms to tens of nanometers. Several distinct methodologies have been employed in these PEMs including: electronic structure calculations and ab initio molecular simulations of systems involving no more than a few hundred atoms of the hydrated ionomers, through all atom classical molecular dynamics simulations of several thousand atoms, to coarse-grained classical simulations of several million atoms, to phenomenological models employing statistical mechanics.

Simulations of PEM morphology and proton transport take many forms and cover many different orders of magnitude of both time and distance. The possible simulation sizes increase as one moves up from electronic structure calculations (a few hundred atoms or less) to course grained simulations (millions of atoms are represented), and the possible amount of time simulated increase as one moves to the right from ab initio molecular dynamics (tens of picoseconds) to course grained (tens of microseconds) to statistical mechanics (infinite time limit). These large discrepancies in system sizes and simulation times are due to the approximations and computational algorithms involved. The most computationally intensive, and accurate, calculations are electronic structure and ab initio dynamics. In these simulations, the potential due to the electrons is explicitly calculated, which is very computationally demanding. As one moves to classical molecular dynamics, the electronic potential is describe by empirical potentials for the interactions of neighboring atoms, which is significantly less computationally intensive. Thus, classical molecular dynamics can access up to one million atoms, tens of nanoseconds of simulation time, and domains tens of nanometers in size. Course graining the individual atoms into beads or particles greatly increases simulation times

and the representative number of atoms, but at the cost of losing all atomic scale resolution. Statistical mechanical representations are similar to the phenomenological models examined previously, however, the atomic structure of the morphology may be investigated explicitly through the a priori assumptions of the model. All of the simulation techniques for investigating PEMs have limiting assumptions, drawbacks and advantages. PEMs are very heterogeneous systems with ordering over many nanometers, as well as proton migration occurring via interactions of only a few Å. As such, it will require contributions from all the mentioned techniques, with their varying resolution, time and length scales, to truly understand proton transport in PEMs.

In this talk we will review the various methodologies that have been utilized during the past 2 decades to understand both structure and transport relations in PEMs.

References

1. K. D. Kreuer, S. J. Paddison, E. Spohr, and M. Schuster, *Chem. Rev.* 2004, **104**, 4637.
2. S. J. Paddison, *Annu. Rev. Mater. Res.* 2003, **33**, 289.
3. J. A. Elliott and S. J. Paddison, *Phys. Chem. Chem. Phys.* 2007, **9** 2602.
4. *Device and Materials Modeling in PEM Fuel Cells*; Paddison, S. J., Promislow, K. S., Eds.; Springer-Verlag Berlin: Berlin, 2008, **113**, pp. 1-588.
5. B. F. Habenicht and S. J. Paddison, *Polymer Science: A Comprehensive Reference*, Matyjaszewski K., Möller, M., Eds.; Vol. **10: Polymers for Sustainable Environment and Energy**, Elsevier, 2012, Chapter 39, pp. 777-810.