A Systematic Survey of the Effect of Proton Exchange Membrane Cavity Shapes on Conductivity

Mai-Anh Ha, Erin A. Pierce, Lara A. Patel, and Maria A. Gomez
Department of Chemistry, Mount Holyoke College, South Hadley, MA

Inspired by experimental and theoretical studies of water filled cavities in polymer exchange membranes, a systematic survey of various, probable cavity shapes is conducted and the effect of shape on conductivity investigated. Recently, the majority of experimental and theoretical research has probed the likelihood of the parallel channel network model, the bimodal network model, and Gierke's cluster network model and therefore will both guide and provide a comparative set of data for construction of differently shaped cavities and their properties.[1,2,3,4,5] The conductivity of these shapes will be probed both by Molecular Dynamics through the extraction of diffusion constants as well as by Monte Carlo using graph theory techniques to consider the impact of shape on hydrogen bonding networks.[6] Following the construction of a shape, water is added with random orientations and a fixed density. Subsequent configurations are generated using Monte Carlo until the system has equilibrated at a specific temperature and density. The radial distribution of distances between hydrogen-hydrogen, oxygen-hydrogen, and oxygen-oxygen atoms confirms expected water molecule interactions.[6] Starting from the energetic and physical snapshots of water within a cavity provided by Monte Carlo, graph theory techniques will find hydrogen-bonding networks within water in the cavity and their equilibrium fluctuations. Diffusion constants calculated from time dependent Molecular Dynamics trajectories will compliment the time-independent equilibrium picture provided by the graph theory analysis of equilibrium snap shots provided by Monte Carlo. Comparison of the diffusion constants, a direct measure of conductivity, with the hydrogen bonding network fluctuations will help assess possible correlations between hydrogen bonding and proton conductivity.

[1] X. Kong and K. Schmidt-Rohr. Polymer **52**, 1971 (2011).
[2] G.S. Hwang, M. Kaviany, J.T. Gostick, B. Kientiz, A. Z. Weber, M.H. Kim. Polymer **52**, 2584 (2011).
[3] Q. Duan, H. Wang, J. Benziger. J. Membr. Sci. **392-393**, 88 (2012).
[4] T. Ohkubo, K. Kidena, N. Takimoto, A. Ohira. J. Mol. Model. **17**, 739 (2011).
[5] T. Ohkubo, K. Kidena, N. Takimoto, A. Ohira. J. Mol. Model. **18**, 533 (2012).
[6] B. C. Wood, N. Marzari. Phys. Rev. B: Condens. Matter **76**, 134301 (2007).