MAR09-2008-002620

Abstract for an Invited Paper
for the MAR09 Meeting of
the American Physical Society

The Nanostructure of Nafion for Fuel-Cell Membranes from Small-Angle Scattering and NMR Analysis[1]

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We have investigated the long contentious nanometer-scale structure of the Nafion ionomer used in proton exchange membranes of H_2/O_2 fuel cells. Using a simple algorithm based on 3D numerical Fourier transformation, we have quantitatively simulated previously published small-angle scattering data of hydrated Nafion. The characteristic "ionomer peak" arises from long, parallel but otherwise randomly packed water channels surrounded by the partially hydrophilic sidebranches, forming inverted-micelle cylinders. The channels are stabilized by the considerable stiffness of the Nafion backbones, detected by ^{13}C and ^{19}F NMR. An upper limit of 300 nm to the persistence length of the water channels has been estimated from ^{2}H NMR of $^{2}H_2O$ in the channels. At 20 vol% water, the water channels have diameters between 1.8 and 3.5 nm, with a 2.4-nm average. The hydration-induced changes in small-angle scattering patterns and in the surface-to-volume ratio have also been analyzed in quantitative detail. Nafion crystallites ($\sim$10 vol%), which form physical crosslinks crucial for the mechanical properties of Nafion films, are elongated and parallel to the water channels, with cross sections of $\sim(5\ \mathrm{nm})^2$. Simulations for a dozen other models of Nafion, including Gierke's cluster and the polymer-bundle model, do not match the scattering data. The water-channel model is the first without constrictions of $\sim$1.2 nm diameter; it can explain important features of Nafion, including fast diffusion of water and protons through Nafion and its persistence at low temperatures.

[1]This work was supported by the U.S. Department of Energy - Basic Energy Sciences under Contract No. DE-AC02-07CH11358