Multiscale Modeling of Water and Proton Diffusion in Self-Assembled Polymer Electrolyte Membranes

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Polyelectrolyte membranes composed of hydrophilic and hydrophobic fragments segregate upon solvation and form mesoscopic structures with interpenetrating hydrophilic and hydrophobic subphases. A typical example is Nafion polymer with sulfonate sidechains attached to perfluorinated backbone [1]. Water concentrates around the sulfonate groups in nanometer size clusters, which grow and coalesce into a 3-dimentional network of water channels as the degree of hydration increases. This segregated morphology determines the transport properties of Nafion membranes that are widely used as compartment separators in fuel cells and other electro-chemical devices, as well as permselective diffusion barriers in protective fabrics. We introduce a coarse-grained soft-core model of Nafion membrane, which accounts explicitly for polymer rigidity and electrostatic interactions, and is matched to atomistic molecular dynamics simulations. By means of dissipative particle dynamics (DPD) and Monte Carlo (MC) simulations, we explore geometrical, transport, and sorption properties of hydrated membranes of various composition. Molecular diffusion of water and proton in hydrophilic subphase of solvated membrane is studied with two methods: random walk in digitized 3D static replicas of the segregated membrane and in the course of dynamic DPD simulations. Novel methodology will be presented for coarse-grained modeling of proton transport accounting for vehicular and hopping mechanisms [2]. One of the interesting conclusions is the importance of the dynamics percolation effects related to the merge and rapture of water bridges between water clusters due to thermal fluctuations [3].

References

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