**548e Mesoscale Simulations of Hydrated Nafion Membranes**

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We report mesoscale simulations of hydrated Nafion using dissipative particle dynamics (DPD) method. Nafion was presented as a branched sequence of beads. Because the size of the bead is relatively small, the skeleton needs some rigidity that was achieved by connecting atoms separated by 3 “normal” bonds by very weak bonds. Therefore, the minimum of the energy of a fluorocarbon chain in vacuum always corresponds to a stretched conformation. There were 2 types of water beads: (i) pure water (ii) water with K+ counterion inside. We accepted the effective bead diameter of 0.76nm at the reduced density of 3. Such a model cannot represent the conformations of long Nafion olygomers from atomistic simulation [1] because of the absence of long-range interactions in DPD. However, conformations of short (18 to 48 carbon atoms) n-fluorocarbons were fitted very reasonably. Water-skeleton dissipative interactions were fitted in order to represent the conformation of n-fluorocarbon in a water bath. The charges were “smeared out” over the effective spherical bead and the electrostatic forces were calculated as derived in ref [2]. At large distances the interactions of charged spheres are identical to those of two point charges. Ewald summation was applied in order to account for long-range electrostaic interactions.

We performed 3 simulations with the water content of 3, 6, 12, and 17 wt %. 12% wt approximately corresponds to the saturation. The total number of beads was about 67,000. At the water content of 3 wt%, we observed formation of separated hydrophilic clusters, containing water and sidechains. At higher water contents, a continuous hydrophilic subphase was formed. No particular segregation morphology in any of the systems was detected. However, the tessellation analysis shows that the hydrophilic subphase is comprised of a three-dimensional network of irregular channels of the average diameter of 2, 2.5 and 3 nm at 6, 12 and 17 wt% of water, respectively. With the increase of the water content a percolation-type transition from the system of isolated hydrophilic clusters to the three dimensional network of irregular channels forming a hydrophilic subphase. The modeling allows one to estimate the structural parameters (volume fraction or porosity, surface area, channel diameter) and the transport coefficients (permeability, conductivity) in the hydrophilic subphase. Also, it is possible to mimic SAXS, SANS, and NMR experiments to discriminate the structural models used for interpretation of the experimental data.

(1) VISHNYAKOV A.; NEIMARK A. V. Molecular simulation study of Nafion membrane solvation in water and methanol J. Phys. Chem. B 2000, 104, 4471. (2) GROOT R. D. Electrostatic interactions in dissipative particle dynamics-simulation of polyelectrolytes and anionic surfactants J. Chem. Phys. 2003, 118, 11265.