Statistical Physics and Computer Modeling of Ionomers: Fundamentals and Application to Proton-conducting Membranes

Alexei R. Khokhlov
Physics Department, Moscow State University, Moscow 119899, Russia

Although recent years have witnessed an impressive confluence of experiments and theories, there are controversial opinions concerning the morphology of ionomer membranes used in polymer electrolyte fuel cells. For this problem, numerical mesoscopic simulations in conjunction with simple models provide a rather detailed answer. We discuss, with examples from our own and other studies, some applications of the analytical approaches and mesoscopic simulation techniques, including dissipative particle dynamics (DPD), cellular-automaton-based (CA) method,[1] integral-equation (RISM)[2] and field-theoretic (SCMF)[3] methods, and integrated multiscale modeling strategies. The main question addressed in this talk is what role do the competing hydrophobic/polar interactions play for the structural properties and behavior of hydrated Nafion membranes. The results demonstrate the important predictive capability of the mesoscopic simulations to Nafion membranes with different hydrated morphologies. We check against simulation data the existing phenomenological models used in the literature to describe the structural features of water-swollen ionomer membranes. In particular, our SCMF calculations predict distinct morphological changes in the material upon alteration of temperature and water content.[3] We find that the hydration level corresponding to the microphase segregation depends on the temperature of the system. Spherical clusters constituting the hydrophilic microphase of the membrane at relatively low water content (but above the transition point) grow in size, coalesce and form a network of channels responsible for the ionic transport at higher hydration levels. This hydrophilic phase is shielded from the hydrophobic matrix by the sidechains of Nafion, their end-groups being turned towards the water clusters. The results obtained are similar to those reported from RISM and CA studies and support the "cluster-network" model for the low hydration levels and the "sponge" model at higher hydration levels.

References

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