V.N.19 Theory, Modeling, and Simulation of Ion Transport in Ionomer Membranes

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Objectives

The scientific objective of our research effort is the development of new theoretical tools whereby the use of atomistic and molecular simulations that are run for modest lengths of time can lead to realistic and useful predictions of the structure and properties of the polymer membranes used in fuel cells. In particular it is our goal to understand the nanophase separation process that allows the formation of channels through which proton transport can occur. We hope that the search for new and more effective membranes for efficient fuel cells may receive some useful assistance from the development of these new theoretical tools.

Technical Barriers

Significant technical barriers to the successful operation of polymer electrolyte fuel cells include the conflicting requirements of higher temperature operation and high water content in the membranes, as well as the chemical degradation that can occur in a fuel cell environment. By developing a deeper understanding of structure and proton transport in fuel cell membranes we hope to guide the design of materials that will retain the essential property of high current flow while avoiding the need for large water content and exposed vulnerable chemical bonds. New nanoscale morphologies may be needed to achieve this goal.

Abstract

This project comprises a research program aimed at elucidating the nature of proton transport in ionomer membranes by means of a combination of analytical theory and molecular modeling. There are two broad thrusts. The first of these is directed towards understanding the equilibrium structure of Nafion® and related polymers at various levels of hydration. The second thrust is concerned with the transport of protons through a membrane of this type.

The research on structure is proceeding by building on existing work, but with the introduction of some novel techniques, among which is a hybrid Molecular Dynamics--Monte Carlo approach. This method permits rapid computations by temporarily decoupling the motion of the polar side chains from that of the perfluorinated backbone, while still retaining the essential aspects of the constraint that phase separation can only continue to a very limited degree. Competition between an elastic energy due to this constraint and the tendency to phase separation leads to the equilibrium structure, which will be qualitatively different at different levels of hydration. The use of a carefully formulated dielectric function will help achieve accurate results.

The work on transport of protons in Nafion®-like membranes also involves a combination of theory and simulation. Atomistic molecular-dynamics simulations are being employed to determine some of the characteristic parameters for the diffusion of hydronium in hydrated membranes. These results will be used in a theoretical model of non-linear diffusion to predict transport coefficients. The inclusion of the Grøtthus mechanism for charge transport is being considered in a related set of simulations with the objective of formulating a general diffusion equation capable of describing proton transport involving both hydronium and water diffusion, and charge transfer by other more complex mechanisms.

The goal of the research is the development of new theoretical tools whereby the use of atomistic simulations that are run for modest lengths of time can lead to realistic and useful predictions. The search for new and more effective membranes for efficient fuel cells may receive some useful assistance from the development of these new theoretical tools.

Progress Report

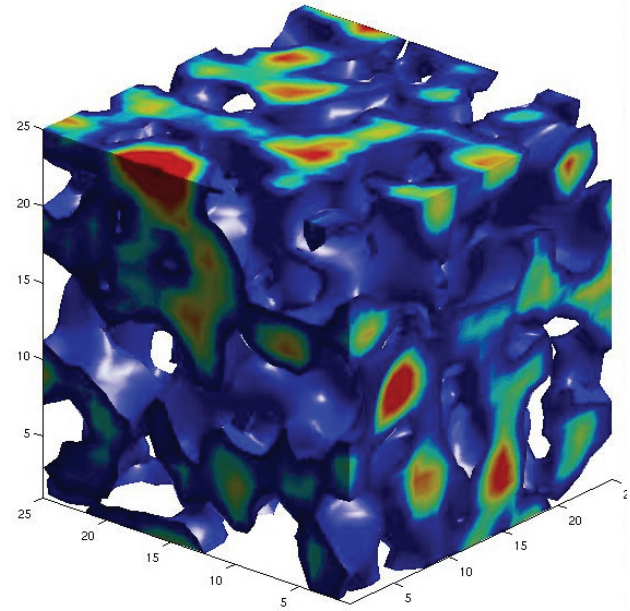
The principal achievements at this time involve the identification of the detailed role of electrostatic interactions in determining the structure of ionomers. The difficulties that are typically encountered in attempts to simulate the structure of polymer membranes composed of materials similar to the widely adopted Du Pont material, Nafion®, lie in the immense amount of computer time necessary to run fully atomistic molecular-dynamics simulations. It is thus necessary to adopt some kind of composite model in which some

of the groupings of atoms are treated as a single entity. The challenge lies in maximizing the simplification while retaining the essential elements of the problem.

The properties of these materials are largely determined by the tendency to ionization of the hydrophilic groups in water-like liquids. The specificity of the interaction between the ion and the polymer in the ionomer makes it possible for these materials to be used as permselective membranes and films for micro-encapsulation and coating. A significant interest in ionomer materials stems from their growing application as the polymer electrolyte membrane (PEM) or proton exchange membrane in fuel-cell technologies. A typical membrane consists of a polytetrafluoroethylene backbone and regularly spaced perfluorovinyl ether pendant side chains. The side chains are terminated by strongly acidic sulfonic groups such as SO_3H. When exposed to humidity, the membrane takes up large amounts of water, leading to a bi-continuous nanophase-separated network of aqueous pores and polymer. At the same time the sulfonic acid groups ionize, the SO_3H groups dissociating to SO_3^- and H^+, and the material becomes proton conducting. The ionomer morphology determines the network connectivity of the membrane and strongly influences its conductivity and mechanical performance. The self-assembly of ionomers into a large variety of microstructures is mainly governed by the charged end groups of side chains. It is commonly assumed that the cluster-like structure created by hydrophilic side chain groups preexists in dry membranes [1].

Despite the rich variety of experimental findings and theoretical predictions for the nanophase morphology of cluster formation in PEM materials, numerical experiments have given few definitive results characterizing the mechanism of cluster formation in hydrated membranes. The main reason for this lack of evidence is the small system size in simulations, which is generally comparable to the experimentally determined structural scale of nanophases. The size of individual ionic clusters and the average distance between them, about 2-5 nm clusters separated by 12-15 nm, are problematic for atomistic modeling. Thus it is impossible to treat the entire polymer in an *ab initio* manner (i.e. a full electronic treatment within a molecular orbital theory). In order to overcome this obstacle we have developed a coarse-grained ionomer model in the united atom approximation, which consolidates atoms in the less important constituents but which retains smaller subunits in the more crucial hydrophilic sulfonic acid group that contains some essential membrane-specific molecular components.

We analyzed the proton-proton pair distribution function *g(r)* calculated for three different dielectric permittivities of ionomer medium in the framework of a dipolar-side-chain model. A typical result is shown in



the accompanying figure, which shows the concentration of protons (displayed as red and orange) in a typical simulation of a dry ionomer. Small permittivities facilitate the clustering of head groups, leading to well defined maxima in *g(r)* that indicate three simple cluster structures: compact and linear clusters, each created by two head groups, and a branched cluster composed of three head groups. At higher permittivity no correlations between head groups are obtained.

Completely surprising was an effective repulsion between acidic head groups at intermediate dielectric permittivities. We assume that, in the absence of strong correlations, each head-group dipole prefers to stay in the bulk of the sample in order to increase its polarization energy. A similar behavior is well documented in colloidal physics where salt pairs are effectively repulsed from the surface of neutral colloid.

We find that the dipole-dipole correlations strongly depend on the molar fraction of acidic groups. For a dilute case a strong condensation of nearly all side chains takes place. When the average interchain distance is larger than the gyration radius R_g of the side chain, the interaction between the neighboring chains is negligible. The main contribution to the Hamiltonian in this case comes from long-range dipole-dipole interaction of head groups, which acts to force the chains to aggregate. However, for a dense system, where the short-range contribution to the Hamiltonian becomes comparable with the dipolar term, the side chains start to lose their rotational entropy and thus cannot reorient themselves in order to minimize the electrostatic energy of the aggregate.

We have also numerically investigated the impact of the side chain length on the cluster formation. Our

results indicate that the length of hydrophobic tail is a strong obstacle to the head group clustering. For longer side chains the dipole-dipole attraction alone is not sufficient to cause aggregation. This conclusion is in contrast to the suggestion of Eisenberg [2] that each ionic group in the vicinity of a cluster of sulfonate groups is subject to a dipolar attraction sufficiently strong to cause a depleted zone free of charge. The phase separation can be increased if the dipole moment of the head group is increased by replacing monovalent protons with divalent positive ions.

Obviously, the effective attraction between the acidic groups of side chains cannot be solely accounted for by the sulfonate-hydrogen dipole moment. Partial charges of other side chain monomers may also contribute to the effective attraction between the head groups. To take all these contributions into account on a phenomenological level we introduced an artificial van der Waals attractive interaction between the end groups of side-chains, which is an approach that had been employed in Reference [3]. The globular micelles of diameter 3-4 nm that formed in the case of zero dipole moment evolve to percolated cluster structures for non-zero dipole moment of the head groups. Thus, an accounting for the dipole moment of sulfonate head groups changes the conformational structure of clusters from Gierke-model spherical aggregations [4] to Gebel-model elongated aggregations.

Future Directions

More work needs to be done to understand the mechanisms behind the sophisticated aggregation picture observed in experiments. Despite the fact that the shape and size distribution of aqueous pores in wet membranes are not very well known, our preliminary results for dry Nafion® side chains can be considered as a starting point for more realistic simulations with more detailed chain structures. We intend to address the issues of how the partial charges and the free protons affect the nanophase structure of the PEM materials. Our preliminary results indicate that a partial delocalization of the negative charge along the side-chain head group plays a major role in the side chain aggregation. A complete understanding of the role of head-group charges on the cluster conformations of side chains should provide helpful guidelines for understanding existing membranes and designing new membrane materials with improved characteristics.

References

1. G. Gebel and O. Diat, Fuel Cells **5**, 261 (2005).

2. A. Eisenberg, Macromolecules **30**, 7914 (1997).

3. D. G. Shirvanyanz, A. S. Pavlov, P. G. Khalatur, J. Chem. Phys., **112**, 11069 (2000).

4. W. Y. Hsu and T. D. Gierke, Macromolecules, **15** 101-105 (1982); J. Memb. Sci. **13**, 307-326 (1982).

Publications (Including Patents) Acknowledging the Grant or Contract

1. Philip Taylor and Mehdi Hamaneh, *"Structure calculations for hydrated ionomer membranes"* Bull. Am. Phys. Soc. **51** (1) Q1.00010.

2. Elshad Allahyarov and Philip Taylor *"Conformational structures in dry ionomers"* Bull. Am. Phys. Soc. **52** (1) A17.00007.

3. E. Allahyarov and Philip Taylor, *"Simple dipole model for a dry ionomer"*, in preparation for submisson to J. Phys. Chem.

4. E. Allahyarov and Philip Taylor, *"Conformational structures in dry ionomers"*, in preparation for submisson to J. Phys. Chem.