

Final Report

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Summary of accomplishments

Our research program was aimed at elucidating the nature of proton transport in ionomer membranes by means of a combination of analytical theory and molecular modeling. There were two broad thrusts. The first of these was directed towards understanding the equilibrium structure of Nafion and related polymers at various levels of hydration. The second thrust was concerned with the transport of protons through a membrane of this type. The research on structure proceeded 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 lead to the equilibrium structure, which turns out to be qualitatively different at different levels of hydration. The use of a carefully formulated dielectric function was necessary to achieve accurate results.

The work on transport of protons in Nafion-like membranes also involved a combination of theory and simulation. Atomistic molecular-dynamics simulations were employed to determine some of the characteristic parameters for the diffusion of hydronium in hydrated membranes. These results were used in a theoretical model of non-linear diffusion to predict transport coefficients. Among our results was the discovery that treatment with strong electric fields may enhance the properties of the polymer membranes. Our computer simulations showed that the vigorous application of a stretching force or an electric field can modify the structure of the ionomer that lies at the heart of a polymer-electrolyte-membrane fuel cell. If these predictions are verified experimentally, then it should be possible to produce fuel cells capable of delivering much higher currents than those currently available.

Final Report on Completed Research

A number of interesting and unexpected results emerged from the research performed in this project. Some of these are related to our discovery of the effects of stretching [1, 2], or application of a strong electric field [3, 4, 5], on the structure of a Nafion-like ionomer as modeled in our simulations. Our observation of the formation of thread-like structures [4] capable of supporting proton transport has now been extended to find that an ionomer constrained within a cylindrical cavity will self-organize in such a way that direct pathways for proton transport can be formed [6]. Other results relate to the central role that the length of side chains can play in determining ionomer morphology [7].

General considerations

One of the characteristic features of ionomers is the partial phase separation of the material into separate regions, one rich in the hydrophobic backbone segments and one rich in the hydrophilic charged end-groups of the side chains. In Nafion-like polymers it is the electrostatic forces acting between the polar hydrophilic ends of the perfluorosulfonic vinyl ether side chains that lie at the root of the phase separation process. The forces acting between the polar end groups drive the segregation to a point at which the constraints due to the side-chain attachment to the polytetrafluoroethylene backbone prevent further separation.

Significant experimental and theoretical efforts have been put into the characterization of the microstructure of dry and swollen Nafion membranes. Although the fact of microphase segregation and its influence on the thermodynamic and transport properties of Nafion membranes are well established, some uncertainty regarding the morphology of the subphases in swollen Nafion remains. It has been generally assumed that the hydrophilic phase is continuous, in accord with the experimental evidence of high conductivity and water permeability. The conventional model of microphase segregation in Nafion membranes, put forward by Gierke *et al.* [8, 9], where the protons and water diffuse between globular clusters through cylindrical narrow channels, was further modified by Mauritz and Rogers [10] and Eikerling *et al.* [11]. Also, Ioselevich *et al.* [12] developed a lattice-based micelle-channel model to describe a connecting structure of water bridges between the cages of the micelles. However, there is as yet no direct experimental evidence for the existence of the channels connecting the clusters in Gierke's model. Other models explaining the properties of hydrated Nafion exploit bilayer, lamellar, and sandwich-like structures for nanophase separation in PEM membranes. Gebel [13] describes the Nafion membrane as an aggregation of polymeric chains forming elongated objects (simplified as cylinders), embedded in a continuous ionic medium. At larger scales, those aggregates form bundles with definite orientational order. This new picture of multi-scale structure can explain membrane swelling as a continuous process from the dry state to a colloidal suspension.

Scanning calorimetry experiments on cast Nafion films [14] led to the conclusion that a

continuous water phase exists only when the relative humidity of the membrane exceeds 90%. This conclusion contradicts the simulation results of Khalatur *et al.* [15], where formation of continuous channels at very low hydration, and even in almost dry membranes, is reported. This is certainly consistent with conductivity measurements in Nafion films with very little water present [16]. In contrast to all the above-mentioned network models, Vishnyakov *et al.* [17] showed that the water clusters do not form a continuous hydrophilic subphase. Instead, the cluster-size distribution evolves in time as a consequence of the formation and rupture of temporary bridges between clusters.

Molecular dynamics (MD) studies, using both classical force fields and an *ab initio* approach, appear to support the idea of irregularly shaped ionic clusters of sulfonic groups connected by smaller channels of similar composition embedded in the hydrophobic covalent matrix. However, the characteristic length scales of the morphological conformations suggested by experimental data are currently inaccessible to atomistic modeling. Despite the rich variety of experimental findings and theoretical predictions for a nanophase morphology of a cluster formation in PEM materials, numerical experiments have not so far found any ordered structure for cluster formation in hydrated membranes [15, 18]. The main reason for this lack of evidence is the small system size accessible to simulations, a size comparable to the experimentally defined structural lengths of nanophases. The size of individual ionic clusters and the average distance between them, about 2-5 nm clusters separated by a 12-15 nm, in the various morphological models, are problematic for atomistic modeling. Thus it is impossible to treat the entire polymer in an *ab initio* manner (i.e. a full electron treatment with a molecular orbital theory). To probe the morphology at the nanometer scale, a mesoscale model is required.

There are several commonly used approaches to simulating macromolecular structures. In one family of methods (molecular dynamics) the system is allowed to equilibrate following Newton's laws of motion while the temperature is maintained at a constant value [19]. Because there may be significant potential barriers between local potential-energy minima, a speedier approach (Monte Carlo) is to allow transitions from one conformation to some other distant conformation by random selection, but to accept only those transitions that would be realizable at the chosen temperature, were energy alone to be the determining factor.

We have developed a hybrid version that combines some of the advantages of the two approaches. The side chains are from time to time detached from the polymer backbone and allowed to move dynamically, but are subject to constraints that are equivalent to requiring adequate volume to be available to accommodate the amount of backbone material corresponding to one side chain. The side chains are then re-attached to the backbone material, and further equilibration permitted. This has the disadvantage that the dispersion of side chain units along the backbone is altered in this procedure, but has the advantage of speed while maintaining the most important characteristics of the material.

We now list some of the topics addressed in our completed research.

1. The role of the ionomer structural architecture

We have analyzed the effect of changing the length of the side chains, and the spacing between them along the polymer backbone, on the shape of the hydrophilic network of sulfonate clusters created by their partial phase separation from the hydrophobic backbone material. Various modifications of a Nafion-like ionomer have been studied. These include ionomers having a backbone spacing up to twice that of Nafion and those having side chains with a length up to three times that of Nafion. We showed in detail how two membranes with the same equivalent weight but different detailed architectures, as in Figure 1, can have completely different morphologies [7]. In ionomers having longer sidechains, we find that larger sulfonate aggregates with a higher sulfonate population are formed. In ionomers with shorter side chains, the ion diffusion in small clusters is mostly based on an ion-hopping mechanism between adjacent sulfonates. Inside the larger clusters found in ionomers having longer sidechains, however, the proton transfer has additional contributions from vehicular and Grotthuss dynamics. In membranes with higher sulfonate concentration and longer sidechains, the nearest-neighbor distance between clusters becomes small enough for temporary inter-cluster bridges to be formed, and this facilitates overall proton diffusion in the membrane.

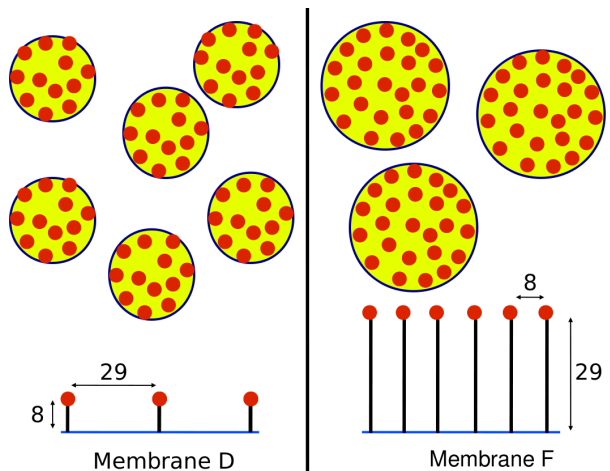


Figure 1: Schematic illustration of two ionomers with the same equivalent weight but different structure

2. Stretching-induced ionomer ordering

We have investigated the effect of stretching-induced structure orientation on the proton conductivity of Nafion-like polymer electrolyte membranes [1]. Our simulations show that uniaxial stretching causes the hydrophilic regions to become elongated in the stretching direction. This change has a strong effect on the proton conductivity, which is enhanced along the stretching direction, while the conductivity perpendicular to the stretched polymer backbone is reduced. In a humidified membrane, stretching also causes the perfluorinated side chains to tend to orient perpendicular to the stretching axis. This in turn affects the distribution of water at low water contents. The water forms a continuous network with narrow bridges between small water clusters absorbed in head-group multiplets. In a dry membrane the side chains orient along the stretching direction.

3. Humidity effects on Nafion structure

We have found that, in a departure from the results of many previous theories of cluster swelling, sulfonate multiplets split into smaller components at the onset of membrane hydration. Our simulations show that the location of water inside low-sulfonate membranes depends strongly on the membrane’s sulfonate concentration [20]. When the concentration is low, nearly all sulfonates are in multiplet formations, and the average water loading per multiplet thus perfectly matches the water content of the membrane. However, when the sulfonate concentration is at about the percolation limit of terminal groups, the water loading per multiplet is consistently larger than the water content of the membrane. In this case, a fraction of the bridging sulfonates can no longer retain their solvation shell in the hostile environment of the hydrophobic backbones. The excess water molecules, stripped from these ‘narrow-bridge’ sulfonates, are redistributed between the sulfonate clusters. This results in excess water shells around the sulfonate multiplets, giving a ‘water encapsulation’ of the cluster.

4. External-field-induced nanophase separation

Our simulations have revealed an interesting consequence of the partial phase separation that occurs in Nafion-like membranes exposed to a strong external electric field. A *dc* electrostatic field induces the formation of a new morphology of the type shown in Figure 2. The sulfonate clusters, initially of a spherical or oblate form, transform into cylindrically shaped aggregates along the *x*-axis. These cylindrical clusters form a hexatic array across the *yz* plane with a lattice constant of roughly 2-3 nm. Each rod consists of distinctive ‘wire-like’ chains of oxygens and sulfurs and accompanying protons.

The mean spacing between sulfonate groups along the chains is about 6.5–8 Å, close to the separation distances expected for Nafion-like membranes [21]. This ordering of the sulfonates into chain-like structures is also evident from the sharp maxima in the sulfonate structure factor $S_{SS}(k_x)$.

5. Poling of Ionomers with Long/Short Sidechains

We have now determined the role of some ionomer structural parameters in the formation of the ordered hexatic phase in poled membranes. We found that it is the length of the side chains that effectively controls the two-dimensional density of the cylindrical rod-like

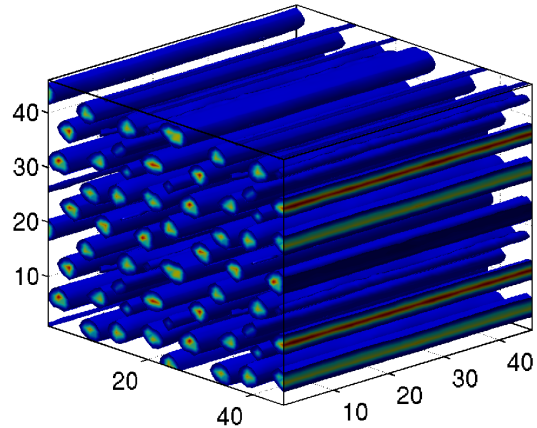


Figure 2: Distribution of protons at high fields

sulfonate clusters. In membranes with shorter side chains, the lattice constant of the hexatic phase is about twice the length of the sidechain. In this case the backbone matrix does not hinder the formation of rod-like clusters, and there is negligible elastic stress. However, in membranes with longer sidechains, which would give rise to larger cluster formations in an unpoled membrane, the sidechain-polymer entanglements restrict the clustering of sulfonates in the poled material. Thus, the number of cylindrical clusters in this case is controlled by a delicate balance between the effective sulfonate-sulfonate attraction and the elastic forces resisting backbone deformation. The latter makes the formation of larger clusters unfavorable, thereby making the two-dimensional density of induced cylindrical aggregates in poled ionomers higher than expected from theoretical predictions. We have also shown that ion diffusion in poled membranes is strongly anisotropic, and depends on the structural parameters of the hexatic phase. When the backbone segment length in homologous membranes (membranes with constant sidechain length) is decreased, thicker ionic cylinders with shorter sulfonate separations in them are formed. In this case the diffusion of protons both along the poled structures and perpendicular to them increases as an inverse function of the backbone segment length. Thick cylinders are also formed in constant equivalent-weight membranes with longer sidechains and shorter backbone segments. However, in this case the cylindrical aggregates are highly tortuous, and this inhibits the diffusion of protons along the poled pathways.

6. Nafion in Cylindrical Pores

Some recent experiments have drawn attention to the possibility that enclosing Nafion in cylindrical pores penetrating an impervious membrane could lead to interesting new properties [22, 23]. In our most recent work we have analyzed the nano-morphology of low-water-content ionomers contained within cylindrical pores of this type. Our results reveal a strong enhancement of ion diffusion. We find that when the pore diameter D is larger than the length d that characterizes the typical sulfonate cluster size in a bulk ionomer, the protons accumulate near the pore surface and in the central area of the pore. When $D \approx d$, the protons cluster mostly in the vicinity of the pore axis. For $D < d$, the continuity of the proton distribution along the pore axis is disrupted to such an extent that water-ion aggregations form a network of separate clusters aligned along the pore axis. There is also positional correlation between the ion and sulfonate radial distributions. The calculated proton diffusion coefficients for ionomers contained in nanopores of various diameters show a nonlinear dependence on the pore diameter. We show that the ion diffusion at first decreases, and then experiences a steep increase when the pore becomes narrower. This enhancement of the diffusion is associated with a correlated movement of individual ion-water clusters, such that at any given time all ion clusters move in the same direction. This unexpected result could be of significance if it proves feasible to manufacture membranes with this particular geometry.

List of Publications Attributable to the Grant

1. E. Allahyarov and P. L. Taylor, “*Simulation Study of the Correlation between Structure and Conductivity in stretched Nafion*” J. Phys. Chem. **113** 610 (2009)
2. Y. Chen, P. L. Taylor, and D. A. Scherson, “*Electrochemical and In-Situ Optical Studies of Supported Iridium Oxide Films in Aqueous Solutions*” J. Electrochem. Soc. **156** (1) F14-F21 (2009)
3. E. Allahyarov and P. L. Taylor, “*Predicted field-induced hexatic structure in an ionomer membrane*” Phys. Rev. E. **80** 020801 (2009)
4. E. Allahyarov, P. L. Taylor, and H. Löwen, “*Simulation study of sulfonate cluster swelling in ionomers*”, Phys. Rev. E. **80** 061802 (2009)
5. P. L. Taylor and E. Allahyarov, “*Simulation study of proton transport in stretched nanocomposite ionomer fuel-cell membranes*”, Bull. Am. Phys. Soc. **54** (1) D20.00001 (2009)
6. E. Allahyarov and P. L. Taylor, “*The role of nanoparticle-membrane coupling in nanocomposite ionomers*”, Bull. Am. Phys. Soc. **54** (1) D20.00002 (2009)
7. P. L. Taylor, E. Allahyarov, K. Brinker, and Z. Tobin, “*Theoretical and simulation study of charge distribution and transport in ionomers*”, Bull. Am. Phys. Soc. **55** (1) Q16.00002 (2010)
8. Elshad Allahyarov and Philip Taylor, “*Simulation study of proton transport in a cylindrically confined ionomer channel*”, Bull. Am. Phys. Soc. **55** (1) Q16.00003 (2010)
9. E. Allahyarov and P. L. Taylor, “*Simulation study of field-induced morphological changes in a proton-conducting ionomer*” Phys. Rev. E. **81** 031805 (2010)
10. E. Allahyarov and P. L. Taylor, “*Simulation study of the equilibrium morphology in ionomers with different architectures*” J. Polym. Sci. B, Pol. Phys. **49** 368 (2011)
11. E. Allahyarov and P. L. Taylor, “*Simulation study of field-induced proton-conduction pathways in dry ionomers*” J. Phys.: Condens. Mat. **23** 234105 (2011)
12. E. Allahyarov, P. L. Taylor, and H. Löwen, “*Simulation study of poled low-water ionomers with different architectures* J. Phys.: Condens. Matter **23** 455102 (2011)

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