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## V.P.3 Theory, Modeling, and Simulation of Ion Transport in Ionomer Membranes

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### Objectives

It is our objective to develop new theoretical and computational techniques to investigate the structure and transport properties of hydrated ionomer membranes, and thereby to enable the development of new and more useful materials for use in polymer electrolyte membrane fuel cells. Specifically, our aim is to produce a tool to predict both the nanophase structure and the proton transport properties for any given membrane material and level of hydration. In this way we hope to develop a deeper understanding of the dominant factors affecting the nature and magnitude of the proton transport.

### Technical Barriers

One of the most significant technical barriers to the improvement of polymer-electrolyte fuel cells lies in our lack of understanding of the formation of the continuous hydrophilic pathways necessary for proton conduction. Another serious obstacle is the difficulty of achieving high proton conductivities in a low-humidity environment. In our research, we face the obstacle of the extremely large computer resources required for an accurate simulation of large volumes of membrane electrolyte material. This necessitates our use of a combination of theoretical analysis with united-atom simulation techniques to reach viable conclusions in reasonably short computation times.

### Abstract

We have used a combination of analytical theory and molecular-dynamics simulations to investigate the effect of various material parameters on the structure and proton conductivity of Nafion<sup>®</sup>-like ionomer membranes. This has included the effects of varying the

length of the molecular side chains and their spacing along the polymer backbone, as well as membrane stretching, membrane poling by the application of strong electric fields, and inclusion of hydrophilic nanoparticles. Most recently we have studied the effects of confining the ionomer inside cylindrical pore channels penetrating an inert membrane.

### Progress Report

During the past year we have used molecular-dynamics simulations to explore the consequences of modifying an ionomer membrane in numerous ways [1,2]. We have extended and solidified our previous preliminary results on the effects of strong electric fields on a Nafion<sup>®</sup>-like ionomer, and have confirmed that an aligned structure consisting of a hexatic array of one-dimensional ion channels is thermodynamically stable. This structure has enhanced proton conductivity through the membrane, as the channels follow the direction of the applied poling field. We determined the role of some ionomer structural parameters in the formation of this 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 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. The number of cylindrical clusters in this case is thus 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

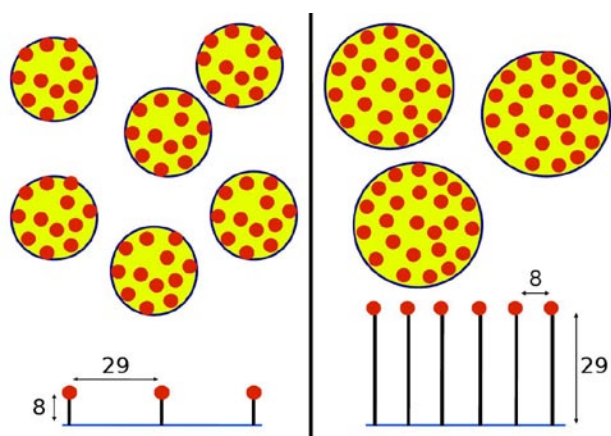
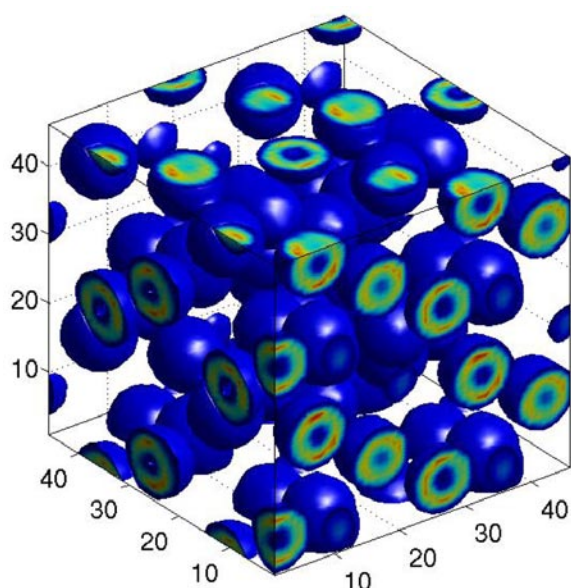
aggregates are highly tortuous, and this inhibits the diffusion of protons along the poled pathways.

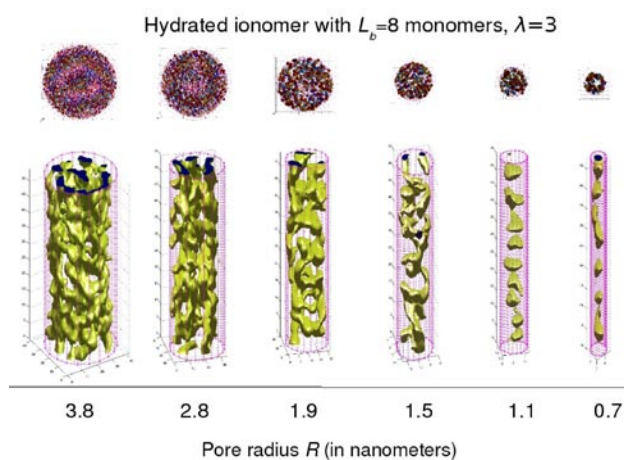
Another area of our research concerned the effects of nanoparticle inclusions in ionomer membranes [3,4]. We first analyzed the distribution of conducting ions in these nanocomposite membranes. Our simulations showed that, in the case of neutral particles, the proton distribution is almost unperturbed. This reflects the fact that the hydrophilic channels are homogeneously distributed in the membrane. When the particle-membrane interaction is hydrophilic, however, all the conducting ions accumulate near the nanoparticle surfaces [3]. When the surface area of a single nanoparticle is insufficient to accommodate the accumulated ions, a second layer of ions is formed. We found that such ‘surface assisted’ proton clustering can drastically affect the membrane conductivity, sometimes increasing it by as much as an order of magnitude. In the case of a hydrophobic particle-membrane interaction, the diffusion pathways formed by the hydrophilic ions are repelled from the nanoparticle surface. Thus proton transport across a membrane can be optimized with the right combination of nanoparticle size and concentration.

We have also 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<sup>®</sup>-like ionomer have been studied. These include ionomers having a backbone spacing up to twice that of Nafion<sup>®</sup> and those having side chains with a length up to three times that of Nafion<sup>®</sup>. We showed in detail how two membranes with the same equivalent weight but

different detailed architectures can have completely different morphologies. 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 the overall proton diffusion in the membrane.

In our most recent work we have analyzed the nano-morphology of low-water-content ionomers contained within cylindrical pores [5]. Our results reveal a strong enhancement of ion diffusion [6]. 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 wall. 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. In narrow pores the ions mostly occupy the central pore area. There is also positional correlation between the ion and sulfonate radial distributions. In smaller pores the central area is predominantly occupied by conducting ions. The calculated proton diffusion coefficients for ionomers contained in nanopores of various diameters show a nonlinear dependence on the pore diameter. We have shown that the ion diffusion at first drops and then experiences a step increase when the pore becomes narrower. This enhancement of the diffusion is associated with the correlated movement of individual ion-water clusters: at any given time all ion clusters move in the same direction. This unexpected result





could be of great significance if it proves possible to manufacture membranes with this particular geometry.

### Future Directions

The goal of our work is to use simulation methods to lead us to the discovery of new morphologies of ionomer membranes that may give enhanced proton transport and robust structures in fuel-cell applications. To achieve this we will pursue several different avenues.

First, we will extend our study of the influence of nanoparticle inclusions on the structure and transport properties of ionomer membranes. We will investigate how spherical inclusions with different sulfonate and water interaction potentials change the ionomer morphology. It is expected that in the case of hydrophilic inclusions their surface can serve as a bridging pathway for facilitated proton transfer between neighboring ionomer clusters. Alternatively, hydrophobic inclusions will most probably accumulate PTFE-rich polymer backbone material on their surfaces, and could distort the shape of ionic clusters towards a more connected topology with branching channels. We intend to calculate how the proton diffusion depends on the size, hydrophilicity, and concentration of inclusions. We also plan to investigate the ionomer reaction to the charge and surface potential of nano-inclusions. It is natural to assume that inclusions with tailored surface groups capable of releasing protons into a hydrated membrane can have the potential to increase its proton conductivity.

Another area of great interest is the structure produced by taking an inert membrane that is pierced by cylindrical holes, which are then filled with ionomer. Our recent results on nanopore-constrained ionomers include the finding that ion diffusion can be strongly enhanced in narrow tubes, and so we intend to put this study on a firmer footing by extending our simulation studies to a wider variety of systems. This is important

from a technical point of view, since the ionomer-filled nanopore matrix is a robust and durable platform, and has the capacity to reinforce the ionomer membrane's mechanical stability against damage from swelling and cracking in operating fuel cells. To understand the physics behind the transition from spherical clusters of sulfonates to wire-like clusters in narrow pores is important for devising new nanocomposite materials with extremely high ion conductivities. We will also analyze how the side-chain flexibility, the length of side chains, and the nanopore-ionomer interaction parameters affect the overall ion diffusion along the nanopore axis.

Finally, we remark that all our poling and stretching molecular-dynamics simulations have so far been carried out at room temperature. We plan to extend our studies to higher temperatures and pressures to explore any possible new phases that might be formed.

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