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Nano-structured Materials for Fuel Cells

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The need for clean and reliable renewable energy is widely recognized throughout the world. Polyelectrolyte membrane fuel cells have attracted interest as one of the most promising nonpolluting power sources capable of producing electrical energy with high thermodynamic efficiency. A vital component of PEM fuel cells is a selectively conductive polymer electrolyte membrane; such membranes allow the charge separation that is harvested as useful voltage at the device level. The industry standard is Nafion, developed and produced by DuPont (see Figure 1).

Nafion membranes absorb water, which creates a network of selective water pores in the membranes; typically, the pores are a couple of nanometers in diameter. The pore network is thus an example of a self-assembled nano-structure.

Clearly, the structural organization of the water pores in Nafion is of great importance for the performance of the membrane. Nafion morphology was extensively studied during the past 30 years via a host of experimental and molecular-level computational approaches. These different approaches have given rise to various contradictory models of Nafion morphology, e.g., cylindrical pores vs. clustered chain structures (Figure 2).

Figure 1. *A Nafion membrane.*

Model for Self-assembling Pore Networks

We have adapted a non-intuitive, highly nonlinear reformulation of the Cahn–Hilliard energy to model the energetic landscape presented by charged polymers interacting with solvent (Figure 3).

Nafion consists of a stiff backbone polymer with attached side chains. The side chains are hydrophilic, i.e., their interaction reduces the energy by quenching the electrostatic field. The energetics of Nafion/water interaction, therefore, reflect a balance of the tendencies to maximize the polymer/water interface and to minimize the bending of the stiff backbone polymer; see Figure 4. A sharp-interface reduction of the model leads to a higher-order Ricci-curvature flow, which gives the motion of the interfaces in terms of their curvatures and the structure of the interface in the transverse direction.

Figure 2. *Suggested Nafion pore morphologies. Left, cylindrical pores (Rubatat et al.,* Macromolecules, *2004); right, clustered chains (Gierke et al.,* Journal of Membrane Science, *1983).*

$$E(u) = \int_\Omega \frac{1}{2}\left(\varepsilon^2 \Delta u - W'(u)\right)^2 - \varepsilon\left(\frac{\varepsilon^2 \eta_1}{2}|\nabla u|^2 + \eta_2 W(u)\right),$$

Figure 3. *In our model, interfacial energy is derived through an unfolding of the DiGiorgi energy, the square of the variational derivative of the Cahn–Hilliard energy E_{CH}, balanced against unfolding parameters η_1, η_2, which incorporate the solvation energy of the charged groups and the elastic energy of the polymer.*

GPU Computational Study

Simulation of the self-assembly process is a demanding numerical problem: The high-order, three-dimensional PDE to be solved is characterized by sharp variations in the solution near the pores and couples fast processes and very slow transients. We apply a suite of techniques to overcome these difficulties, including convex–concave operator-splitting to gain numerical stability and adaptive timesteps to overcome time stiffness; see Figure 5. Nevertheless, with a typical runtime of a week, this numerical scheme is too slow to allow efficient study of self-assembled networks.

To speed up the computation, we use a general-purpose graphical processing unit (GP-GPU). GPUs, with hundreds of weak processors, as opposed to the few strong processors in a CPU core, are well suited for problems that can be split into many small parts and computed in parallel. Using a GPU, we exploit existing parallelizations of the FFT to obtain a typical speedup factor of ten, shortening runtime from a week to overnight.

Verification with Experimental Data

The Nafion nano-structure is typically studied by small-angle X-ray scattering (SAXS) experiments, in which an X-ray beam is shot at a Nafion sample. The scattered beam is detected on a screen located a few meters from the sample, so that only small-angle scattering is detected.

We validate our model by simulating the scattering curve for the pore network obtained numerically. Along with the network of water pores, however, we must take into account the crystalline network also known to exist in Nafion (Figure 6). This crystalline network, which is crucial to the mechanical stability of Nafion, is observed in scattering experiments. Combining models for the crystalline and solvent-phase pore networks, we obtain an excellent fit between experimental and numerical scattering data up to a length of 25 nm.
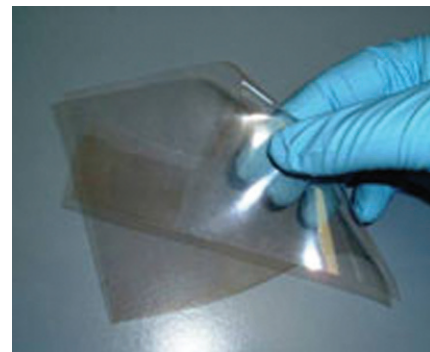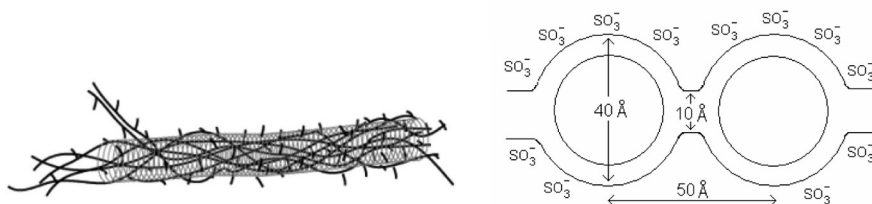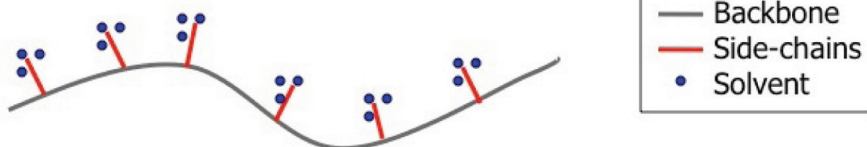

- Backbone
- Side-chains
- Solvent

Figure 4. *Building blocks of a self-assembling pore network.*

Ongoing Challenge

The excellent agreement between experimental and numerical scattering data is clearly encouraging. This agreement is obtained for Nafion with a water intake of 20%–30%, however. Lowering the water content results in a peak shift in the SAXS data that is not duplicated in our model.

We conjecture that at low water volumes, Nafion organizes as a clustered-chain network (Figure 7). To incorporate this into our model, we are moving beyond a binary mixture model for Nafion to a three-phase model that accounts for accumulation of charge groups on the pore boundary as the water phase is depleted. We hypothesize that the accumulation of excess charge drives the morphological reorganization.

Driving our system toward a network of three-dimensional clustered-chain networks turns out to be a somewhat delicate process. Complications include the inherent coexistence of multiple competitors for minimizing states, system hysteresis, and the poorly understood influence of network junctions. This is, therefore, an ongoing project characterized by a constant interplay of modeling, numerics, analysis, and experiments.

This article describes joint work of Keith Promislow, Nir Gavish, Andrew Chrieslieb, Zhengfu Xu, and Jaylan Jones, all of Michigan State University, and James Elliot of the Materials Science Department at Cambridge University.

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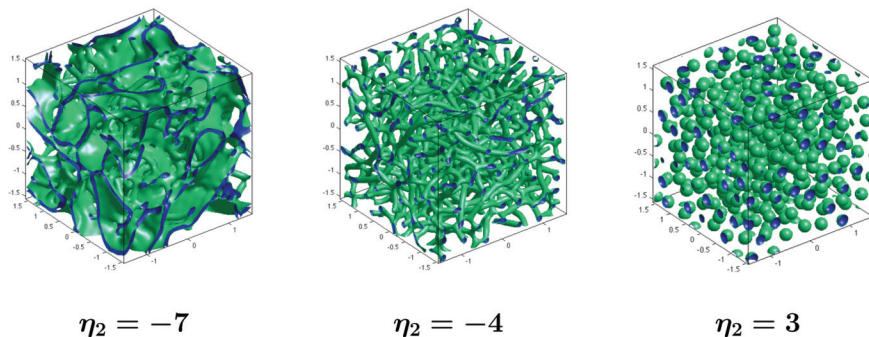
$$\eta_2 = -7 \qquad \eta_2 = -4 \qquad \eta_2 = 3$$

Figure 5. *Simulation results for the self-assembling network model. The three different parameters lead to different network morphologies. All the simulations start with random initial data.*
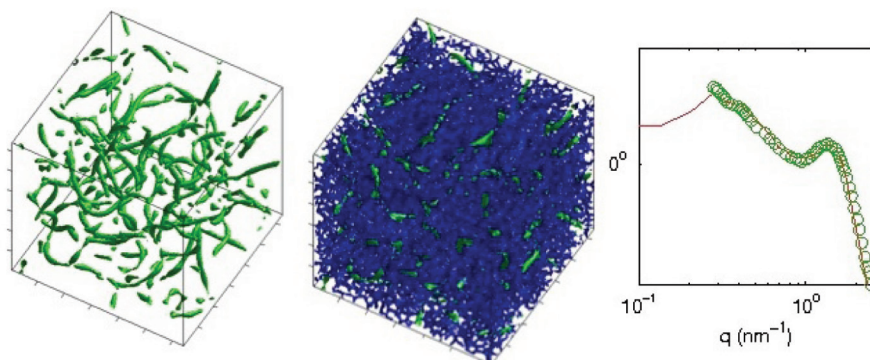

Figure 6. *Crystalline (left) and water pore (center) networks. Right, a simulated scattering curve (red) is shown with experimental scattering data (green circles). From Rubatat et al., 2004.*
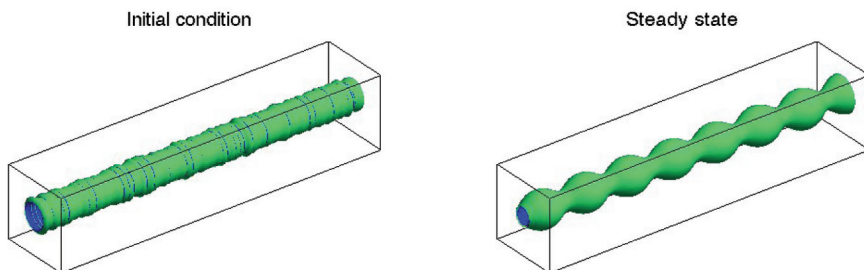

Initial condition   Steady state

Figure 7. *The initial state (left) leads, via a numerical simulation, to a single 3D clustered-chain pore (right). Obtaining a network of similar pores is an ongoing project.*