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Hydrophilic Channel Alignment Modes in Perfluorosulfonate Ionomers: Implications for Proton Transport

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What factors influence ionic conductivity in advanced polymer electrolytes? Clearly, chemically or electrically driven transport through ionic polymers depends on numerous phenomena, many of which may not even be known. Ionic polymer features such as crystallinity and ionic aggregate size have been measured using XRD, NMR, and electron microscopy,[1] but this morphological realm requires deeper exploration. If we can more completely assess morphological properties of these electrolytes, we can optimize and tailor them to suit diverse applications in polymer-electrolyte-membrane (PEM) fuel cells, reverse-osmosis membranes, and “artificial muscle” polymer actuators.

One phenomenon that has received little attention in terms of membrane design is long-range orientational order. Perfluorosulfonate ionomers such as DuPont’s Nafion exhibit a phase-separated structure, where protons conduct via ionically coordinated, water-swollen hydrophilic channels.[1] We present detailed orientational order measurements in two leading Nafion membranes using a simple and quantitative method based on deuterium NMR. We demonstrate that this channel alignment is uniform over these films but has drastically different properties for the two membrane types. If we can quantify and manipulate this order, we should be able to optimize anisotropic conductivity in, e.g., fuel cell membranes by maximizing channel alignment across the film plane.

Ionomer-based PEM fuel cells typically operate with 10−40 wt % water uptake to maximize proton conductivity.[2] Several models based on powder XRD scattering curves describe this hydrophilic phase as a network of channels and cavities that grow in size with water uptake.[3−5] Protons conduct in the acidified bath of water contained in the ion-lined channels, which provides a low activation energy environment for transport. Our initial question is, what are the alignment modes of these membrane channels?

A powerful method of determining orientational order and its dynamics in polymers lies in the use of deuterium NMR quadrupole couplings. In many cases, doping a simple deuterated probe molecule into an ordered liquid or solid provides easy access to the orientational order parameter **S** (a.k.a., the Hermann’s orientation function) as well as to higher order tensorial orientation properties.[6] This method provides quantitative, although relative, measures of **S** and other order parameters, and these can be extremely useful in characterizing ordered phase behavior and symmetries. Perfluorosulfonate ionomers present an ideal case for application of this method since they heavily absorb water, which we may replace with D_2O. Residual quadrupole splittings $\Delta\nu_Q$ of the water deuterons report on **S** via[7]

$$\Delta\nu_Q = Q_p \mathbf{S} P_2(\cos\theta) \tag{1}$$

where Q_p is the quadrupole coupling constant (∼260 kHz) and $\mathbf{S} = \langle P_2(\cos\chi)\rangle$ is the ensemble average over the second Legendre polynomial with χ the angle between a particular OD bond axis and the alignment axis of the material. θ defines the angle between the material alignment axis and the spectrometer magnetic field $\mathbf{B_0}$. In the case of nonuniaxial alignment, we may replace $\mathbf{S}P_2(\cos\theta)$ in eq 1 with appropriate tensorial equations to extract various asymmetry parameters. This temporal and spatial ensemble average gives rise to “inherited” order of the deuterated probe solute molecules as they interact with an anisotropic matrix.[6,8] Partial ordering results from biased rotations, collisions, and librations of these D_2O probe molecules. In Nafion, which consists of interconnected voids and channels, one observes a single deuterium doublet spectrum (splitting) only if there is alignment of these channels macroscopically over the membrane. Orientational distributions of domains larger than the diffusion length of D_2O on the $1/Q_p$ time scale (∼100 nm and ∼10 μs, respectively) manifest as superpositions of deuterium doublets which will broaden and provide additional structure to the observed spectrum. Previous studies using residual ^2H NMR quadrupolar interactions in perfluororsulfonate ionomers[9] did not include sufficient measurements to define membrane alignment tensor properties and included substantial dead volume in those sample cells. Our sealed and equilibrated low-dead-volume sample cell provides exquisitely reproducible and quantifiable results.

Figure 1 shows ^2H NMR spectra as a function of membrane angles with respect to $\mathbf{B_0}$ for DuPont extruded Nafion 112 and the latest dispersion-cast Nafion 212 membranes. Dramatic features of Nafion morphology become apparent due to these data. Both membranes show nearly uniform order, but in perpendicular directions, and with different symmetries. Part

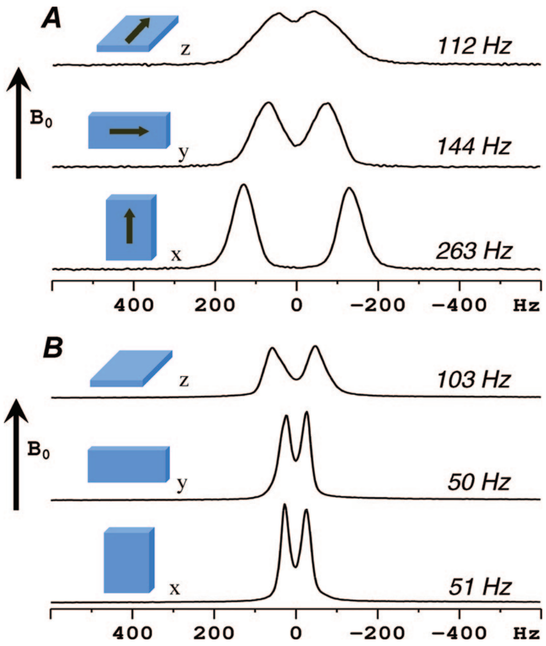

Figure 1. Room temperature ^2H NMR spectra of two Nafion membranes swollen with 13 wt % D_2O. (A) Extruded Nafion 112. The arrows indicate the extrusion direction. (B) Dispersion-cast Nafion NRE212. The rectangular blocks in blue indicate different membrane directions (*x*, *y*, *z*) with respect to the spectrometer $\mathbf{B_0}$ field, where the membrane *z*-axis is perpendicular to the plane. The splitting values $\Delta\nu_Q$ at right result from nonlinear least-squares fits to each spectrum.

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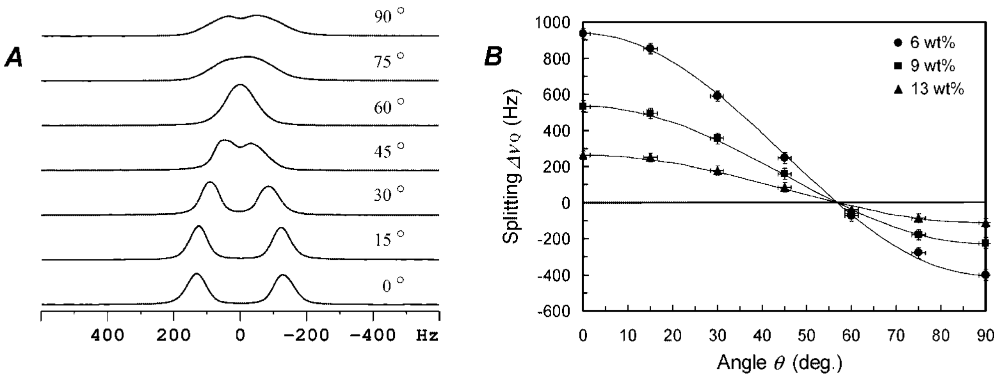

Figure 2. (A) ^{2}H NMR spectra versus rotation angle of Nafion 112 with 13 wt % D_2O. (B) Plots of quadrupole splitting $\Delta\nu_Q$ vs angle θ of the extrusion direction relative to the spectrometer field $\mathbf{B}_0$ over a range of D_2O uptake. Solid lines are fitted curves using eq 2, where $\eta = 0.12$ provides best fits for all curves and is the only adjustable fit parameter after specifying $\Delta\nu_0$, the spectral splitting at $\theta = 0$. The error estimate for η based on all our data fits is ±0.02.

A shows that extruded Nafion 112 channels align along the extrusion direction, as expected due to extrusion and shear forces, and we further observe that this membrane is biaxially aligned with asymmetry parameter $\eta = 0.12 \pm 0.02$ given by $\eta = |\Delta\nu_Q{}^y - \Delta\nu_Q{}^z|/\Delta\nu_Q{}^x$. The superscripts x, y, or z given on $\Delta\nu_Q$ here denote splittings with the noted membrane axis relative to $\mathbf{B_0}$. Part B shows that, somewhat surprisingly, the dispersion-cast 212 channels uniformly align across the membrane plane and with uniaxial symmetry ($\eta = 0$). We propose that this alignment arises from casting solvent flow during evaporation and conceivably other annealing processes. Dispersion-cast Nafion from other sources (Gas Hub Inc., see Supporting Information) also show uniform uniaxial through-plane alignment. Prominently featured in these nominally chemically equivalent systems, which differ only by processing, we observe a factor of >2.5 better alignment in the extruded case, indicating that we may substantially improve through-plane order of dispersion-cast films.

Figure 2A shows NMR spectra as a function of Nafion 112 membrane angle θ with respect to $\mathbf{B_0}$, rotating about the membrane y-axis. Because of the membrane biaxiality, θ follows a dependence given by[6,7,10,11]

$$\Delta\nu_Q = \frac{1}{2}\Delta\nu_0[3\cos^2\theta - 1 + \eta\sin^2\theta] \qquad (2)$$

which we may use to fit splittings as a function of angle and wt % D_2O uptake, shown in Figure 2B. Here we note that the biaxiality of $\eta = 0.12$ is stable over a large range of hydration level (at least from 4 to 20 wt % based on further data), indicating that the degree and symmetries of alignment in these channels are stable vs hydration. A similar analysis shows that Nafion 212 exhibits $\eta = 0$.

Figure 3 depicts models for the channel morphologies in these membranes. Parts A and B show two possibilities, consistent with our data, for the extruded Nafion 112 channel morphology. Part A depicts biaxial (elliptical) channels aligned uniaxially along the extrusion direction, while part B depicts uniaxial (cylindrical) channels aligned biaxially via larger local bends in-plane vs through-plane. Distinguishing between (A) and (B) requires further structural studies. Part C shows the dispersion-cast Nafion 212 channel morphology, consisting of cylindrical channels aligned uniaxially across the plane of the film. Note that these models and our observations do not comment on whether Nafion exhibits a cluster-network model[3] or quasi-cylindrical channel models.[4,5]

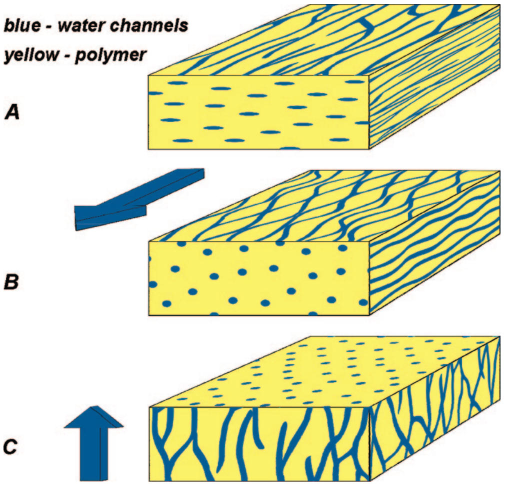

Figure 3. Proposed hydrophilic channel alignment models for Nafion 112 (A, B) and 212 membranes (C). (A) Biaxiality caused by ellipsoidal channels aligned along the extrusion direction (block arrow) in the membrane plane. (B) Biaxiality caused by cylindrical channels with directional anisotropy in the membrane plane relative to across the plane (zigzag character in film plane and perpendicular to extrusion direction). (C) Uniaxially aligned cylindrical channels perpendicular to the membrane plane (block arrow). Arrow also indicates solvent evaporation gradient direction.

Various observations of fuel cell operation and membrane behavior could sensibly depend on orientational order effects. Reports of anisotropic conductivity in Nafion,[12,13] while not a settled topic in the literature, should provide correlations with orientation if we carefully study equivalent samples. High-temperature annealing of extruded films produces increased fuel cell performance,[2,14] which might be explained due to randomization of alignment in these films, producing better through-plane conductivity than unannealed Nafion 112 films aligned in-plane. Furthermore, aging of membranes in operating fuel cells, which usually requires hours or days of operation before becoming stable,[2] could result from the evolution of flow alignment of the hydrophilic channels. Our method would allow in situ characterization of membrane order, even during cell operation.

To conclude, we quantitatively measure bulk channel alignment in Nafion membranes using ^{2}H NMR directly on residually aligned absorbed D_2O. This method of using deuterated probe molecules to interrogate order may be conducted on almost any NMR spectrometer and does not require complicated sample mounting or sectioning for film cross sections to interact with, e.g., an X-ray or neutron beam. Furthermore, we note that numerical quantification of order properties such as the biaxiality parameter is straightforward using this method, as opposed to with XRD, polarizing microscopy, or other methods. We present results for two perfluorosulfonate ionomer membranes showing that channels are biaxially oriented ($\eta = 0.12$) in the membrane plane for extruded membranes, whereas channels are uniaxially oriented perpendicular to the plane for dispersion-cast membranes. We propose that control over the direction and extent of orientational order of the hydrophilic channels will allow increased material design freedom and improvements in ionomer device performance, e.g., increased proton conductivity across the membrane plane in fuel cells. Further detailed studies of ^{2}H NMR quadrupole splittings vs D_2O uptake and temperature and direct correlations with proton conductivity anisotropy are underway.

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Supporting Information Available: Experimental details of ionomer membrane preparation and NMR acquisition. This material is available free of charge via the Internet at http://pubs.acs.org.

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