V.N.5 Water Nanochannels in Nafion®: Quantitative Scattering Analysis and NMR

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Objectives

We develop and apply advanced solid-state nuclear magnetic resonance (NMR) methods, as well as novel quantitative analyses of scattering data, to elucidate the composition, supramolecular structure, and dynamics of polymer-based nanostructured materials. Our studies of Nafion® and Nafion®-based materials are an important component of this project. We have determined the shape and size of the water clusters and crystallites in hydrated Nafion®, elucidated the chain conformation and packing, and will investigate the water-polymer interface. We will also characterize Nafion®-based materials such as its nanocomposites with silica particles.

Technical Barriers

Nafion® has many favorable properties but also several limitations, including its limited temperature range of operation, significant cost (currently thousands of dollars for the amount of film needed in a fuel-cell powered car), and poor performance in direct-methanol fuel cells due to methanol cross-over. Any rational design of improved Nafion®-based materials, for instance its nanocomposites with silicates and other inorganic nanoparticles, will have to rely on knowledge of the supramolecular structure of Nafion®, which we can provide.

Abstract

The structure of the Nafion® ionomer used in the proton exchange membrane of H_2/O_2 fuel cells has long been contentious. Many different models of differently shaped water clusters or polymer domains have been proposed to explain the characteristic "ionomer peak" and small-angle upturn observed in small-angle scattering of hydrated Nafion®. Using a new algorithm recently developed by us, we have quantitatively simulated small-angle scattering data of hydrated Nafion®. The "ionomer peak" arises from parallel, but otherwise randomly packed water channels surrounded by a polymer shell, forming inverted-micelle cylinders. At 20 vol% of water, the water channels have an average diameter of 2.4 nm, with a distribution between ~1.8 and 3.5 nm. The crystallites (~ 14%) in Nafion®, which form physical crosslinks crucial for mechanical properties, are elongated and parallel to the water channels, with cross sections of ~(5 nm)^2. Simulations for previous models of Nafion®, including Gierke's cluster and the polymer-bundle model, do not match the scattering data. The considerable stiffness of the Nafion® backbone derived from NMR confirms these findings by excluding various models that would require tightly folded or randomly coiled chains, while stabilizing long cylindrical structures. The new model explains several important features of Nafion®, in particular the fast diffusion of water in Nafion and its persistence at low temperatures.

Progress Report

The proton-exchange membrane (PEM) is a central, and often performance-limiting, component of all-solid H_2/O_2 fuel cells. Nafion®, the most widely used PEM, consists of a perfluorinated polymer that combines a hydrophobic Teflon-like backbone with hydrophilic ionic side groups, see Figure 1(a). It stands out among polymer materials for its high, selective permeability to water and small cations.

High-resolution ^{13}C NMR of Fluoropolymers. In spite of the technological significance of perfluorinated polymers such as Nafion®, or poly(tetrafluoroethylene), PTFE/Teflon®, no ^{13}C solid-state nuclear magnetic resonance (NMR) spectra of these temperature- and solvent-resistant materials could be found in the literature prior to 2001. The standard ^{13}C spectra of Nafion® and Teflon® are broadened due to the large ^{19}F chemical-shift anisotropy, which prevents on-resonance ^{19}F decoupling.

We have obtained the first high-resolution ^{13}C NMR spectra of solid perfluorinated polymers, see Figure 1(c), by combining 28-kHz magic-angle spinning (MAS) with rotation-synchronized ^{19}F 180°-pulses.[1] The small line width shows that most Nafion® backbone segments are helical and conformationally ordered, even though Nafion® is a more or less random copolymer with sidebranches that cannot crystallize. Conformational disorder is concentrated at the branch points.[2] Furthermore, motional narrowing of ^{13}C-^{19}F
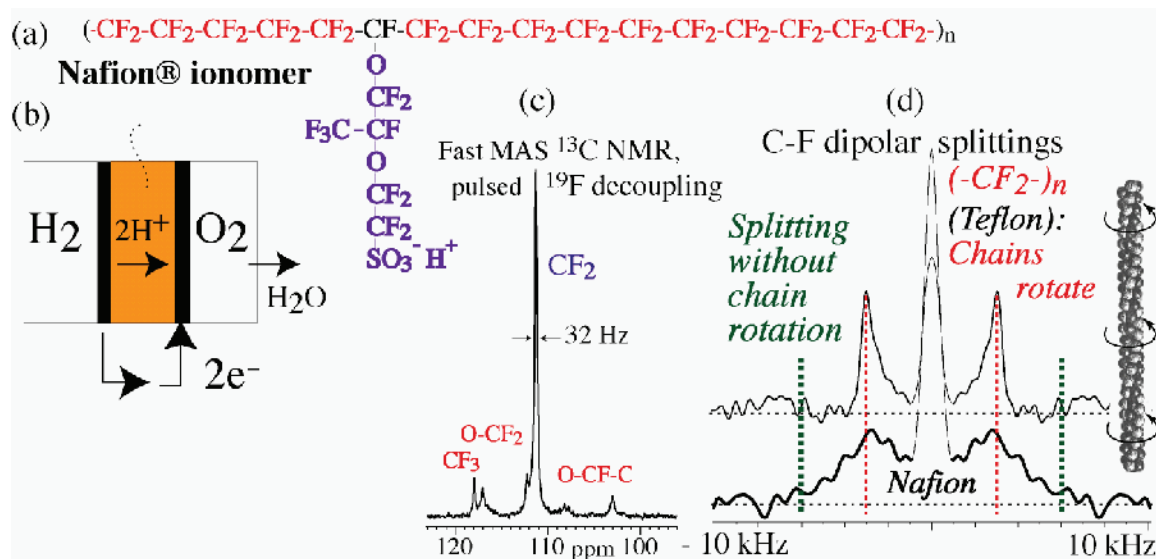
FIGURE 1. (a) Chemical structure of the Nafion® fuel cell membrane. The actual number of CF_2 groups between branch points varies along the polymer chain, around an average of 13. (b) Simple schematic of the proton-exchange membrane at the center of a H_2/O_2 fuel cell, sandwiched between catalyst-containing layers (black). (c) The sharp polymer-backbone resonance of our high-resolution ^{13}C NMR spectrum proves a uniform helical conformation of the stiff backbone between the more disordered branch points. (d) The helix segments rotate around their axes, as proven by motional narrowing of C-F dipolar splittings.

dipolar splittings, see Figure 1(d), proved that most chain segments between branch points rotate by more than 150º around their helix axes. This rigidity of the backbone excludes many models of Nafion® that are based on the assumption of random coiling. Nevertheless, the helices do not pack into well-ordered bundles, according to orientational correlation data from ^{19}F CODEX (centerband-only detection of exchange) NMR. The chain curvature probed in these experiments is in good agreement with the 2 – 5-nm persistence length of the backbone, estimated based on data for PTFE (Teflon®).

Quantitative SAXS Simulations of the Nanostructure of Nafion®. The hydrophobic Teflon®-like backbone and the hydrophilic ionic side branches of hydrated Nafion® self-organize to produce a clear peak in small-angle X-ray or neutron scattering (SAXS/SANS) at around $q^* = 2\pi/(4\text{ nm})$, where q relates to the scattering angle 2θ and the X-ray or neutron wavelength λ according to $q = 4\pi/\lambda \sin\theta$. This "ionomer peak" has been variously attributed to spherical inverted-micelle water clusters[3-7], layered structures[8-10], and polymer bundles[11-13]. While the original Gierke model[5] of a network of spherical water clusters connected by 1-nm diameter channels is still the most popular, the presence of elongated structures was clearly demonstrated by SAXS studies. First, unoriented samples show a $I(q) \sim q^{-1}$ power law typical of long cylinders at small q,[11-14] see the log-log plot in Figure 2(d) where $I(q) \sim q^{-1}$ is represented by a line of slope -1. Even more importantly, SAXS of oriented Nafion samples does

not exhibit a meridional ionomer peak of correlations along the draw direction.[15-17] It was proposed that the elongated structures were polymer bundles[11-13] or slabs[15], but without regards to volume-fraction requirements, as discussed below. Progress in the understanding of Nafion® and related PEM materials has been seriously hampered by the lack of a convincing model that helps make sense of the bewildering array of data on Nafion® and their varied interpretations.[18]

Several attempts have been made to simulate the SAXS curve[3, 11-13] of Nafion®,[4, 19] but only a limited q-range was considered and the input parameters did not correspond to realistic three-dimensional density distributions. Using a new method of calculating the small-angle scattering curve by numerical Fourier transformation from a given scattering density distribution,[20] we have shown that a new model of water channels inside cylindrical inverted micelles, see Figure 2(a-c), reproduces all the features of the published small-angle scattering curve, see Figure 2(d), at hydration levels typical in fuel-cell applications. The water channels are 1.7 – 3.5 nm in diameter, with an average of 2.4 nm, which is significantly smaller than the size $d = 4$ nm traditionally derived from $d = 2\pi/q^*$. Crystallites, which are crucial for mechanical properties, are also included in the simulations. We have simulated SAXS curves for half a dozen other models,[4-13] including Gierke's spherical-cluster model.[3] They all fail to match the experimental scattering data. The cylindrical inverted micelles are stabilized by the stiff backbones clearly seen in the NMR results. The new model
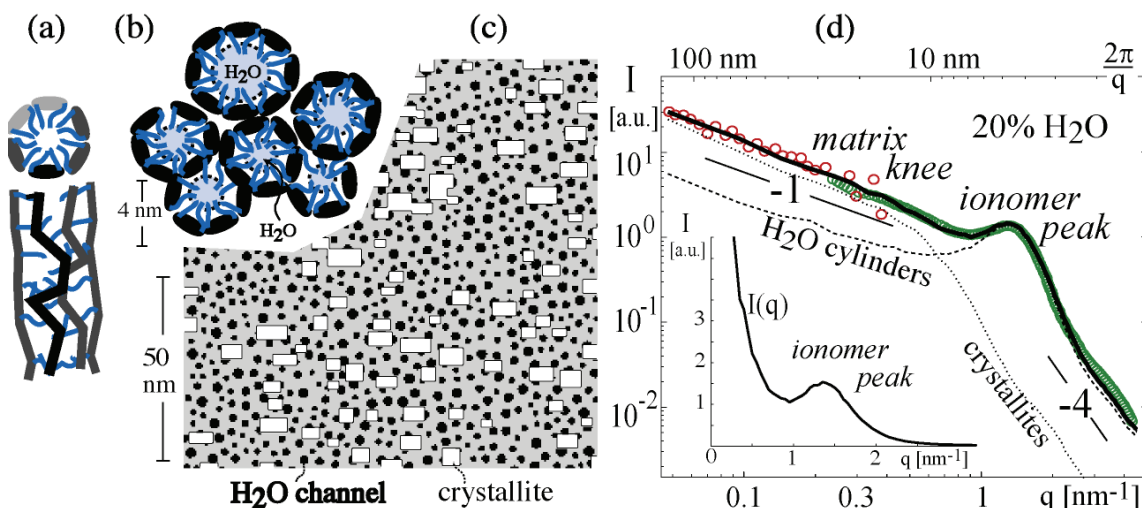
FIGURE 2. Inverted-micelle cylinder (water-channel) model of Nafion®. (a) Two views of an inverted micelle cylinder, with the polymer backbone on the outside and the ionic side groups lining the water channel. (b) Schematic of the approximately hexagonal packing of several inverted-micelle cylinders. (c) Cross sections through the cylindrical water channels (black) and the Nafion® crystallites (white) as used in the simulation of the small-angle scattering curves in d). (d) Small-angle scattering data (circles) of Rubatat et al.[12] in a log(I) vs. log(q) plot for Nafion® at 20 vol% of H_2O, and our simulated curve from the model shown in c). Simulated scattering curves from the water channels and the crystallites by themselves (in an structureless matrix) are shown dashed and dotted, respectively. The inset shows the ionomer peak in a linear plot of I(q).

explains many of the salient properties of hydrated Nafion®, such as the fast diffusion of water through Nafion® and the persistence of conduction and diffusion even below the freezing transition of the freezable water, which occurs because water in the narrower channels will not freeze.

Future Directions

Based on our insights into the segmental and supramolecular structure of Nafion®, we plan to characterize the water in the channels and the ionic groups at the water-polymer interface in more detail. We will extend our studies to Flemion, a perfluorinated ionomer membrane material that differs from Nafion® only in the end group of its side branch. It is also produced commercially and can be prepared from Nafion® by post-polymerization modification. In small-angle scattering, Flemion exhibits the ionomer peak and small-angle upturn familiar from Nafion®.[21] From the NMR perspective, it has the great advantage that the signal of its ionic group, the COO moiety, is quite easily observable in ^{13}C NMR with a distinct downfield chemical shift and relatively weak [13]C-^{19}F dipolar couplings. In contrast, the SO_3 group of Nafion® is invisible to NMR. We will also study the properties of water in Nafion®. For instance, investigations of both the freezable and nonfreezable water and their spatial relations will allow us to test our model and explain transport properties, since water in the narrower channels in our structure will not freeze and not be in contact with frozen core water.

Nanocomposites made by growing silicate or phosphate nanoparticles in the water channels or by solution-casting Nafion® with clay nanoparticles will also be studied. These materials are currently of great interest due to their increased conductivity and stability at high temperature, relative to neat Nafion®. Interestingly, the water absorption capacity increases in the silicate-containing Nafion®; silicates and phosphates adsorb water so strongly that it does not become volatile at 100°C.

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+ 6 other publications acknowledging the grant or contract