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Nano structure of NAFION: a SAXS study

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Abstract

We performed small angle scattering experiments with synchrotron radiation to study the nano structure and the swelling behavior of NAFION polymer membranes in water–methanol under in situ measurement conditions, which are relevant for their use in direct methanol fuel cells. To retrieve structural information from the scattering data, we propose a model with discrete sandwich like structure elements for the nano structure of the cross-linked channel system within the membrane. They consist of a shell region and an embedded core region, the latter being either empty or flooded by water–methanol. In summary, the scattering data indicate, that this simple structure model is able to describe the swelling behavior of NAFION on a nanometer scale. During swelling we find a shrinking of the core region and a swelling of the shell region, which contains the side-chains of the NAFION molecule. © 2001 Elsevier Science Ltd. All rights reserved.

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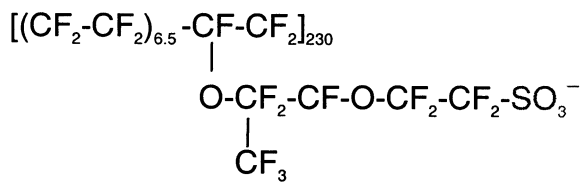
1. Introduction

NAFION™ is the best-known ionomer membrane for use as a solid, proton conducting electrolyte in electrochemical technology. In low temperature direct methanol fuel cells (DMFC), it combines the roles of a solid polymer electrolyte and a separator between the methanol–water mixture on one side of the membrane and air on the opposite side.

NAFION has a copolymer molecular architecture. The molecule is characterized by a hydrophobic polytetrafluoroethylene backbone chain and regularly spaced shorter perfluorovinyl ether side-chains, each terminated by a strongly hydrophilic sulfonate ionic group.

The molecular structure of the studied NAFION 117 membrane from the DuPont company is



Schematically, its nano structure is illustrated in Fig. 1.

The mechanical strength of NAFION membranes arises from the interaction of the perfluorinated backbone chains. For its use as a protonic conductor, the porous membrane contains about 20 wt% water forming hydration shells around the fixed covalently bonded anionic sulfonic acid groups. The conductivity is assigned to hydrated protons (H_3O^+) as protonic charge carriers. For the charge passage through the membrane, a percolated sponge-like microstructure supplies the transport channels.

Numerous neutron and X-ray small angle studies have been performed to study the nano structure and the 10–20% swelling behavior of NAFION membranes

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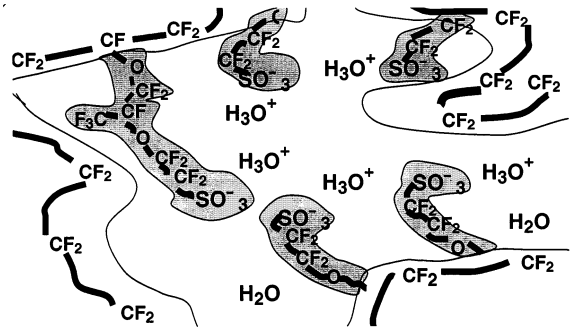

Fig. 1. Phenomenological sketch of the nano structure in NAFION solid polymer electrolytes. Phase separation into three cross-linked regions: Perfluorinated hydrocarbon backbone, side-chains with fixed sulfonic end groups and water–methanol region.

after water uptake, which is necessary for its proton conductivity. Several structure models have been proposed for the interpretation of the scattering patterns. The details of these models are still under discussion, see Refs. [1,2] for review articles.

2. Experimental

We used small angle X-ray scattering with synchrotron radiation to study the nano structure of NAFION 117™ membranes and performed in situ experiments under working conditions as in DMFC: dry, in water, in water–ethanol mixtures and in pure methanol.

The NAFION was available as a 175 μm thick membrane (NAFION 117 from the DuPont Company). The molecular weight of the copolymer was 250 000 with 8 wt% sulfonic acid groups. After cleaning in hot H_2O_2 and water, the membrane was mounted inside a flow cell and in situ small angle scattering measurements were carried out at room temperature in air with the dry membrane, in water, in water–methanol mixtures with 10–90 vol% methanol and in pure methanol.

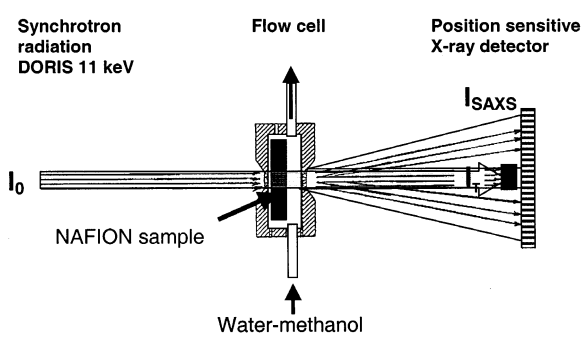

Fig. 2. Schematic experimental set-up for in situ measurements with synchrotron radiation.

The experiments were performed at our JUSIFA beamline [3] with synchrotron radiation from the DORIS synchrotron source (HASYLAB).

The small angle scattering experiments were performed with monochromatic 11.5 keV X-rays. As it is shown schematically in Fig. 2, the small angle scattering studies were performed with the membrane in a flow cell. The small angle scattering intensity was recorded with a two-dimensional position sensitive detector, corrected for instrumental background the usual way and finally radial averaged around the center of the primary beam.

As an example, the radial averaged scattering cross section is given in Fig. 3 as a function of the scattering vector for a membrane, swollen in 10 vol% methanol. As shown, the scattering from the empty cell contributes a background and has to be subtracted. Due to the unfavorable background situation at very low scattering vectors, reliable data are achieved in the range $Q > 0.02$ Å^{-1}. A constant background contribution arises from the molecular structure of the NAFION itself (wide angle background) and is also subtracted previous to the final fitting procedure.

3. Results and discussion

In situ results for NAFION in air (dry), water and methanol are given in Fig. 4. A common feature is the appearance of a relative maximum at $Q \approx 0.15$ Å^{-1} ('ionomer peak'), which corresponds to an interplanar distance $d = 2\pi/Q \approx 40$ Å. The Porod Q^{-4} scattering contribution at the smallest scattering vectors arises from very large structures in the NAFION membrane, which are not in the scope of this study.

To retrieve more detailed structural information from the scattering data, we apply a model for the nano structure. Central for the understanding of this model is that phase separation is assumed to occur in the polymer into a hydrophobic backbone fluorocarbon phase and a region with the side-chains, see Fig. 5. Their fixed hydrophilic SO_3^- end groups form adjacent aqueous domains for the proton conductivity. We propose a basic structure element, as shown in Fig. 6. It is a sandwich structure, consisting of a shell region with the side-chains and an embedded core region, either empty or flooded by water–methanol.

We propose, that the complex structure of cross-linked channels can be described by a composition of these basic structure elements, see Fig. 7 and assume their random distribution inside the volume of the membrane.

A scattering theory with randomly distributed particles in a homogeneous matrix can then be applied. For simplicity, equally sized particles are used in our model. The scattering cross section $d\Sigma/d\Omega$ is proportional to the structure factor of the particles:

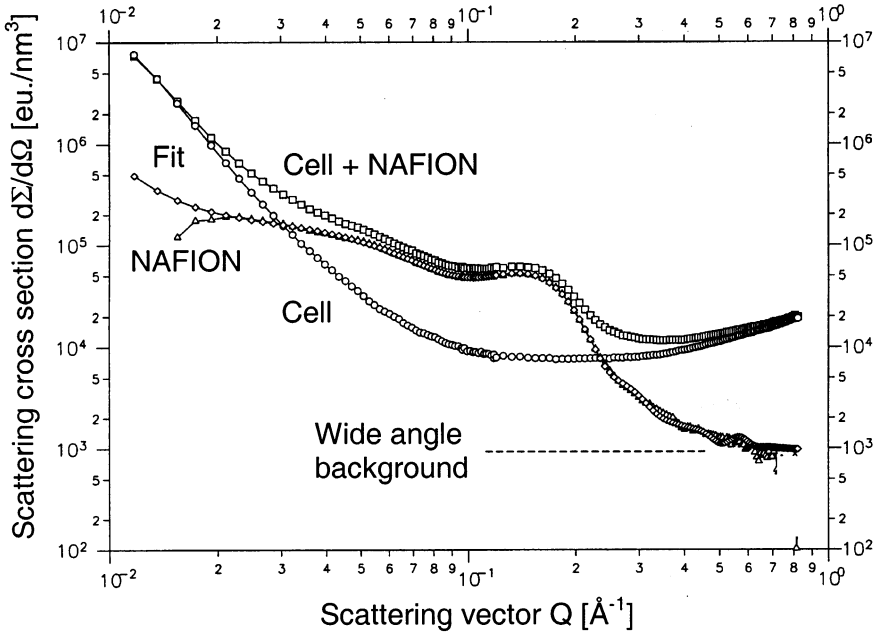

Fig. 3. Small angle scattering from NAFION in 10 vol% methanol in water and from the empty cell. The data can be fitted with the proposed sandwich-like structural model.

$$\frac{d\Sigma}{d\Omega} \sim \Delta n_p^2 S^2(\vec{Q}) \tag{1}$$

where $\Delta n_p = n_p - \langle n \rangle$ is a measure for their scattering contrast and is given by the difference of the electron densities within the particle n_p and the surrounding matrix $\langle n \rangle$. The particle structure factor for a parallelepiped of dimensions $(x, y, z) = (a, b, c)$ is given by

$$S^2(Q) = \left(\frac{\sin(Q_x a/2)}{Q_x a/2} \frac{\sin(Q_y b/2)}{Q_y b/2} \frac{\sin(Q_z c/2)}{Q_z c/2} abc \right)^2 \tag{2}$$

Here, Q_x, Q_y, Q_z are the Cartesian components of the scattering vector $\vec{Q}$, $|\vec{Q}| = Q = 4\pi \sin(\varepsilon/2)/\lambda$. λ is the wavelength of the X-rays and ε the scattering angle.

In the case of a sandwich type particle with electron density differences Δn_c for the core and Δn_s for the shell region (Fig. 7), particles with a core thickness c along the z-direction, thickness $s/2$ for each of the upper and lower shell regions and a total thickness $t = c + s$ yield a scattering cross section

$$\frac{d\Sigma}{d\Omega} \sim \left(\frac{\sin(Q_x a/2)}{Q_x a/2} \frac{\sin(Q_y b/2)}{Q_y b/2} ab \right)^2 [\Delta n_s (S(Q_z, t) - S(Q_z, c)) + \Delta n_c S(Q_z, c)]^2 \tag{3}$$

where

$$S(Q_z, t) = \frac{\sin(Q_z t/2)}{Q_z t/2} t, \quad S(Q_z, c) = \frac{\sin(Q_z c/2)}{Q_z c/2} c \tag{4}$$

For a random orientation of these particles in the sample, we have to take the average over all possible orientations of the particles with respect to the scattering vector. It is convenient to transform the Cartesian components of $\vec{Q}$ into spherical coordinates with orientation angles θ and ϕ, since it is mathematically irrelevant whether the particle is rotated relatively to the scattering vector or vice versa.

$$\begin{aligned} Q_x &= Q \sin\Theta \cos\phi \\ Q_y &= Q \sin\Theta \sin\phi \\ Q_z &= Q \cos\Theta \end{aligned} \tag{5}$$

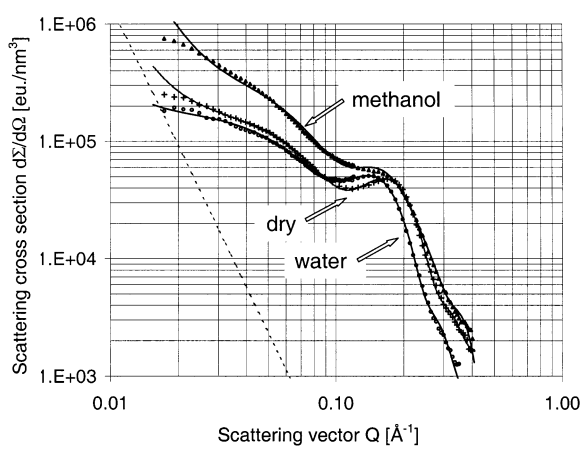

Fig. 4. Small angle scattering from dry NAFION and after equilibration in water and pure methanol.

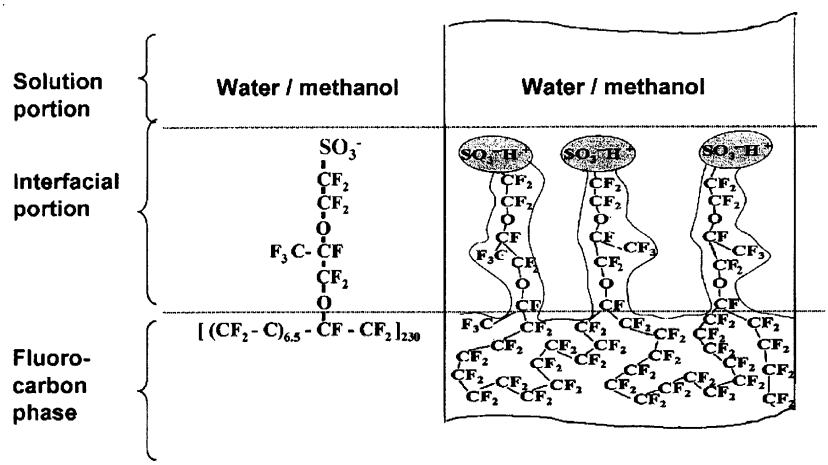

Fig. 5. Separation of hydrophobic fluoro-carbon backbone polymer and hydrophilic side-chains.

Hence, the averaged scattering cross section for randomly oriented particles

$$\left\langle \frac{d\Sigma}{d\Omega} \right\rangle = \frac{1}{4\pi} \int_0^{2\pi} \int_0^{\pi} \frac{d\Sigma}{d\Omega}(Q, \Theta, \phi) \sin\Theta \, d\Theta \, d\phi \tag{6}$$

then yields with $u = \cos\Theta$

$$\left\langle \frac{d\Sigma}{d\Omega} \right\rangle \sim \int_0^1 \frac{2}{\pi} \int_0^{\pi/2} S^2(a, b, \phi, u) \, d\phi [\Delta n_s (S(t, u) - S(c, u)) + \Delta n_c S(c, u)]^2 \, du \tag{7}$$

with

$$S(a, b, \phi, u) = \frac{\sin(Qa \cos(\phi)\sqrt{1-u^2}/2)}{(Qa \cos(\phi)\sqrt{1-u^2}/2)} \cdot \frac{\sin(Qb \sin(\phi)\sqrt{1-u^2}/2)}{(Qb \sin(\phi)\sqrt{1-u^2}/2)} ab \tag{8}$$

$$S(t, u) = \frac{\sin(Qtu/2)}{(Qtu/2)} t, \quad S(c, u) = \frac{\sin(Qcu/2)}{(Qcu/2)} c \tag{9}$$

Fitted parameters of the proposed model are: core thickness c, total shell thickness s, scattering contrasts Δn_c and Δn_s from the core and shell regions and their

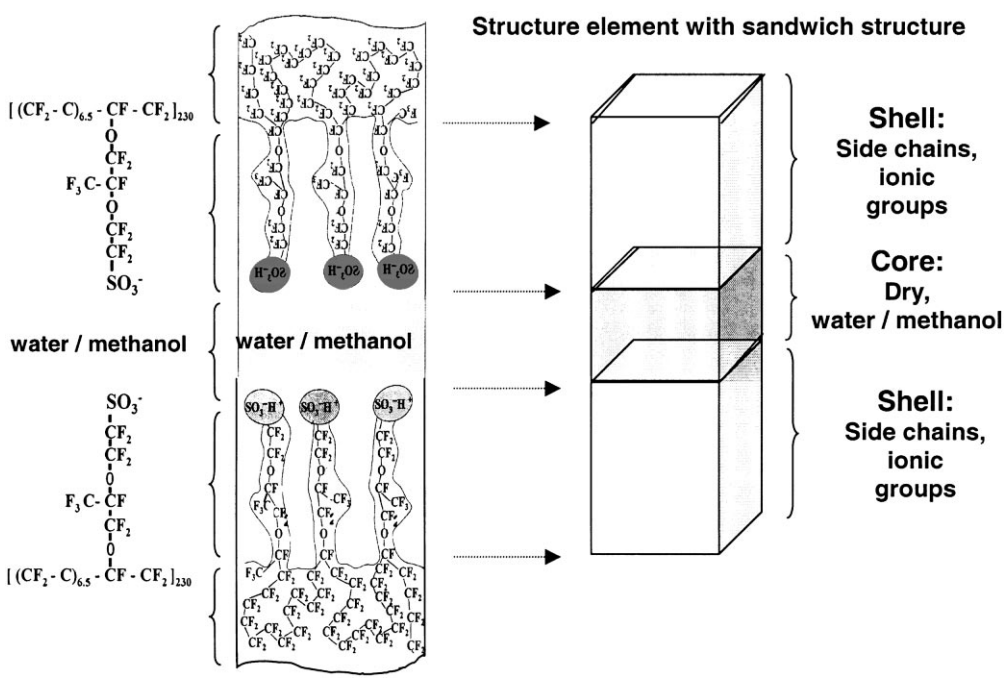

Fig. 6. Proposed discrete structure elements as particles in a homogeneous matrix.

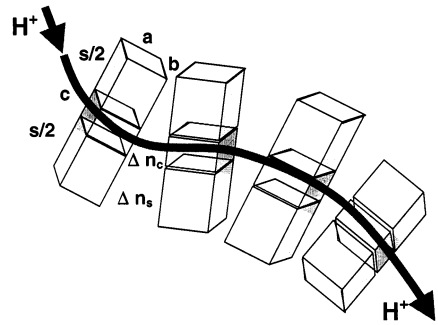

Fig. 7. Composition of basic structure elements to complex channel structures.

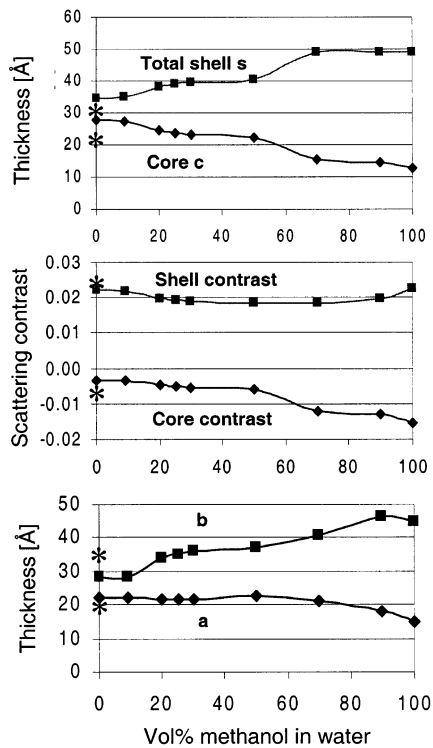

Fig. 8. Results from least squares fits applying the core-shell sandwich model to dry and swollen NAFION. Data for the dry membrane are marked by * symbols.

lateral dimensions a and b. The results from a least-squares fit with the proposed sandwich like particles for the dry membrane and after equilibration in water and pure methanol are given in Fig. 8.

The particle scattering is found to arise from rather small particles with lateral dimensions a and b between 15 and 45 Å and total thickness $(c+s)$ of about 60 Å. The core and shell thickness varies and depends strongly on the volume concentration of the methanol. In methanol swollen membranes, the core region becomes smaller whereas the side-chains in the shell region extent strongly. For the dry sample, core and shell are somewhat smaller than in the water equilibrated membrane. This reflects its macroscopic swelling behavior in water.

The scattering contrast is a measure for the difference in electrons relative to the average value in the membrane. Consistent with the underlying assumptions of the model, the core contrast for dry NAFION is about twice as high as in the water flooded membrane, whereas the shell region with the side-chains is not affected by water.

Swelling in methanol leaves the side-chains nearly unaffected; the core contrast, however, becomes larger according to the lower electron density in methanol. Inside the core region, methanol contributes an electron density of approximately 0.26 e $Å^{-3}$, water in the water equilibrated sample a density of 0.33 e $Å^{-3}$. The mean density of NAFION is slightly higher than in water. Therefore, the scattering contrast increases when the water is replaced by methanol.

4. Conclusion

The experimental finding indicates that pure methanol replaces the water and dehydrates the ionic shell. In addition, side-chain swelling is observed at the cost of available volume for the core region. In summary, we have shown that simple structure models with sandwich-like, anisotropic structure units can be applied successfully to describe the nanostructure of ionomers like NAFION.

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