



Short communication

Modelling the Nafion[®] diffraction profile by molecular dynamics simulation

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ABSTRACT

A diffraction profile is here derived from classical Molecular Dynamics (MD) simulation for the hydrated perfluorosulphonic acid fuel-cell membrane material Nafion[®] at 363 K using a $76 \text{ \AA} \times 76 \text{ \AA} \times 76 \text{ \AA}$ box. The MD simulation reproduces the phase-separated nanoscale structure of Nafion[®] and water channels. No specific structural features, such as a characteristic channel diameter, could be distinguished. Nevertheless, the envelope of the simulated diffraction profile based on 6000 MD “snapshots” reproduced well the key features of the experimental SAXS profile. This draws into questions previous interpretations of diffraction data for the Nafion[®] system which involve simplistic notions of channel- and cluster-diameter.

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1. Introduction

The polymer electrolyte membrane fuel cell (PEMFC) is today the most common fuel-cell concept for low power and low temperature applications. At the heart of the fuel cell is a proton-conducting polymer electrolyte membrane (PEM), with the role of separating the electrodes and maintaining high intrinsic proton conductivity. A PEM material must satisfy severe demands: good mechanical strength, chemical stability in a highly acidic and oxidizing environment, and low fuel permeability [1,2].

The prototype PEMFC membrane materials have been perfluorosulphonic acids (PFSAs). These have now been studied intensely for several decades [3]. The most established PFSAs membrane material is Nafion[®] (Fig. 1). It was developed by DuPont in the 1960s, but several alternatives now exist, e.g., Flemion[®], Aciplex[®] and the more recently developed Hyflon[®] [4–11]. Their common structural feature is hydrophilic sulphonic acid side-chains attached to a hydrophobic perfluorinated $-\text{CF}_2-$ backbone.

Though many thousands of papers have now reported the Nafion[®] morphology, its structure is still widely debated. There exists an overall consensus that the hydrated PFSAs form phase-separated morphologies in the nanometer regime, where water and sulphonic acid groups form spherical regions separated by water channels spheres embedded in the fluorocarbon matrix. The size and nature of these regions are subjects of continuous discussion. Several models have been suggested based on diffraction

studies: small-angle X-ray scattering (SAXS), small-angle neutron scattering (SANS) and wide-angle X-ray diffraction (WAXD). Some models of the hydrophilic domains involve dispersed spherical objects with characteristic repeat distances between the particle centres, while others maintain that the dominant structural features are individual local clusters. The shape and morphology of the ionic domains have also been disputed: spherical clusters [12], lamellae [13], rods [14] and ribbon-like [15] structures have been proposed. Perhaps the most widely accepted nanoscale structural model has been suggested by Gierke [12] (the “cluster-network model”), where spherical ionic clusters (diameter: 4–5 nm) are interconnected by narrow water channels (diameter: 1 nm; length: 4–5 nm). This model has recently been challenged, however, by Schmidt-Rohr and Chen [16], who claim that elongated parallel but otherwise randomly packed water channels are surrounded by partial hydrophilic side-chains to form inverted-micelle cylinders.

This whole controversy has its origin in the basic difficulty of interpreting the diffraction data, which is very diffuse for hydrated polymers like Nafion[®], whose SAXS profile displays only one broad peak at smaller angles; its precise location is dependent on the level of hydration, but would appear to correspond to a distance of 4–5 nm [16,17].

Atomic-level simulations can give some useful insights which can shed further light on these structural issues. An earlier MD study has focused on different PFSAs-based polymer materials—Hyflon[®]/Dow[®], Nafion[®] and Aciplex[®] [18]. However, the limited size of the simulation box used has made it impossible to address phase-separation and water-channel nanostructural issues. Other groups have also modelled Nafion[®] using classical or EVB-based MD techniques [19–36]. However, these also use limited MD-box sizes.

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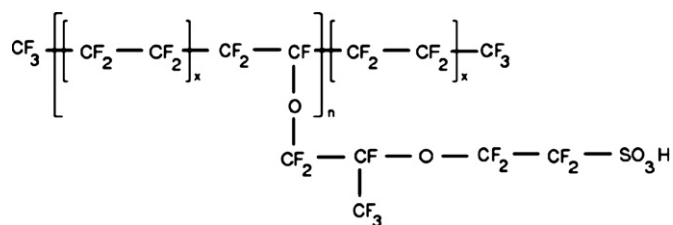


Fig. 1. A schematic representation of the Nafion® molecular structure; $n=10$ and $x=6$ in the systems simulated.

In this present work, we use a *ca.* $76 \text{ \AA} \times 76 \text{ \AA} \times 76 \text{ \AA}$ cubic MD-box, making this one of the largest all-atom force-field Nafion® simulations ever made. The MD simulation data obtained has thereafter served as input for simulating the corresponding diffraction pattern and comparing it with experimental data, *cf.* [37,38].

2. Molecular dynamics simulation

In an MD simulation, a number of atoms are placed in a simulation box (the MD-box) and all interactions between these atoms are described by classical forces. Repeated solution of Newton's equations of motion for the atoms in the box generates an atomic-scale "movie" of the material over a limited time interval. Electrons are not treated explicitly, but are taken into account in developing the force-field used as input data for the simulations. Here, the modified DREIDING force-field [39] was used. This is the same as that used in our previous MD study [18]. A similar force-field has also been used in other MD simulations of Nafion® [19–21].

A cubic MD-box was constructed with side-lengths of $\sim 80 \text{ \AA}$ to contain Nafion® along with ~ 20 wt% water molecules and hydronium ions. This was accomplished by duplicating the final configurations in our previous work [18] in all the three orthogonal directions. The MD-box side-lengths shrank to $\sim 76 \text{ \AA}$ during the preliminary relaxation process.

The molecular structure of our system was chosen to achieve the commonly used Nafion® 117 membrane. The MD-box contained 32 independent oligomers, each with 10 side-chains separated by 14 $-\text{CF}_2-$ monomers, and with 4800 H_2O molecules and 320 H_3O^+ ions to make the systems charge neutral, resulting in a total of 37504 atoms and an effective level of hydration (λ) of 15.

The Nafion® MD-box was first relaxed in an NVT ensemble for 5 ps at 363 K, followed by a 3.5 ns simulation in NPT at the same temperature. The temperature was chosen to correspond to Nafion® operating conditions in a PEMFC. Data sampling was performed during the last 3 ns of this time period, during which the system was in equilibrium. The simulations were made using the DL.POLY software [40], where periodical boundary conditions were imposed on our cubic MD-box. An Ewald summation routine was used to calculate long-range electrostatic forces with a relative precision of 10^{-5} in the calculation of forces. The simulation was run at normal pressure; time-steps of 1 fs were used, and data were sampled every 0.5 ps (500 steps). Other simulation details are as follows:

- NVT Nose-Hoover thermostat relaxation time parameter: 1.0 ps;
- NPT Nose-Hoover thermostat relaxation time parameter: 0.1 ps;
- NPT Nose-Hoover barostat relaxation time parameter: 0.3 ps;
- Verlet neighbour list cut-off: 20 \AA ;
- Verlet neighbour list border width: 0.5 \AA ;
- Multiple time-step interval: 5;
- Primary cut-off for multiple time-step algorithm: 6 \AA .

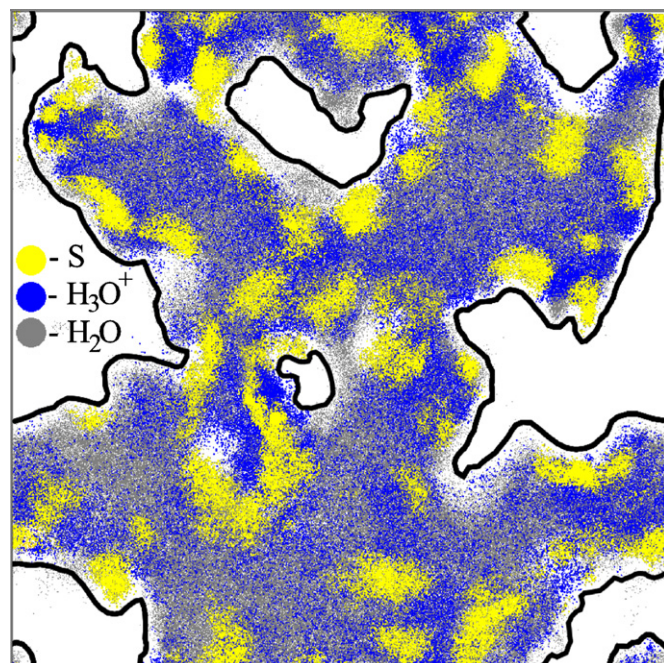


Fig. 2. A projection of a $76 \text{ \AA} \times 76 \text{ \AA} \times 5 \text{ \AA}$ slice through the Nafion® MD-box. Empty regions represent the polymer backbone, while coloured points represent the accumulated coordinates of sulphur and water- and hydronium-oxygen atoms during the simulation.

3. Simulated diffraction profile

The theoretical X-ray diffraction pattern for effectively a *ca.* 76 \AA primitive "crystalline" cubic unit-cell of Nafion® was calculated by accumulating the calculated scattered intensity contributions from 6000 MD-generated "snapshots" of the positions of all 37,504 atoms in the MD-box. This was done using the program DISCUS [41]. The radiation used for the simulation was $\text{CuK}\alpha$, and the instrumental resolution parameter was set to 0.1. The effect of thermal broadening is achieved implicitly by summing together the scattered intensities for the 6000 MD-snapshot structures, and allowing the unit-cell dimensions to vary during the simulations. *Note:* no symmetry constraints are applied within the MD-box during the simulation. The DISCUS program treats the entire MD-box as a primitive (space group: P1) unit-cell. The apparent "noise" in the calculated diffraction profile (see later) is thus a direct result of the overlap of a large number of calculated individual reflections arising from the finite size of the MD-box "unit-cell". The "real" Nafion® system has an effectively amorphous structure (an infinite unit-cell), resulting in a smooth experimental diffraction profile.

4. Results and discussion

Density is a key factor for controlling the quality of any MD simulation in the NPT ensemble. For the water content used in this study ($\lambda = 15$), the experimental density of Nafion® (1100 EW) is given as $\sim 1.75 \text{ g cm}^{-3}$ at 300 K [42,43]. In our simulations, the density of the equilibrated system was found to be a little lower—around 1.73 g cm^{-3} . However, we consider our density values to be reliable, since a temperature increase of 50 K has earlier been found to result in a density decrease of 0.02 – 0.04 g cm^{-3} [23].

Fig. 2 shows a projection through a 5 \AA thick slice through the simulation box, illustrating the spatial distribution of water, hydronium ions and sulphonate groups. Other atoms are not shown; the polymer Teflon backbone appears as empty regions, and the hydrophobic/hydrophilic interface as a thick black line. The elon-

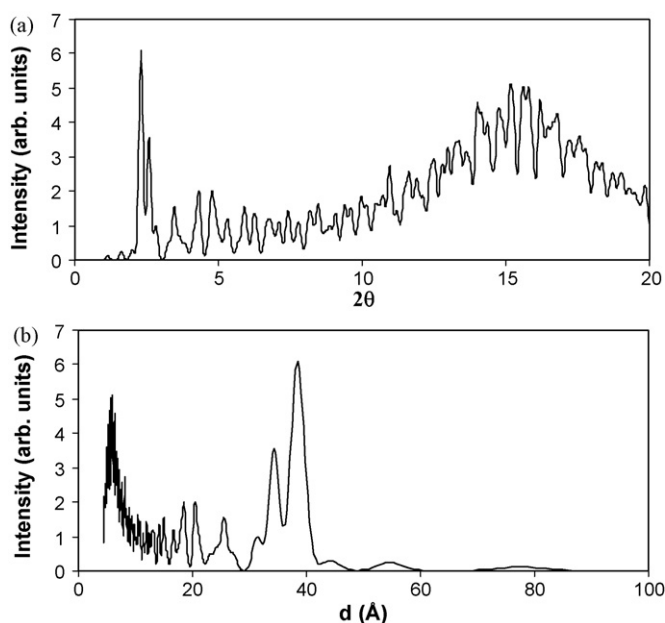


Fig. 3. Simulated X-ray diffraction profiles from 6000 time-steps in the Nafion[®] MD simulation, plotted as a function of 2θ (a) and layer-spacing d (b).

gated yellow clouds are small clusters of sulphonate groups. The typical width of a water channel is around 10 Å, but this is difficult to quantify further. The SO_3^- groups are not situated directly on the channel surface, but extended somewhat into the aqueous regions. Although H_3O^+ ions can be found throughout the channel network, they clearly collect around the sulphonate groups. There appears to be a qualitatively good agreement between our MD simulated structure and the textbook picture of the Nafion[®] nanostructure: clear phase-separation, a water-channel network and several larger water/hydronium domains.

The water-channel topology differs significantly from that enforced by the much smaller MD-box used in earlier work [18], which also indicates the importance of using a larger MD-box size. Our previous study indicated the presence of isolated hydrophilic domains containing a small number of water molecules, whose connectivity was found to be dependent on side-chain length. Here, the entire water domain is continuous, which will have a great impact on its proton transport properties.

However, it is clear that our MD-derived structure does not explicitly resemble any of the structural models discussed in the literature. The structure is clearly too complex to reduce to a number of volumetric elements of finite shape and size; *i.e.*, no “cylinders” or “spheres” can be clearly detected. This is intuitively reasonable considering the complex chemical nature of the system: highly hydrophilic sulphonate groups are covalently bonded to slightly hydrophilic side-chains which, in turn, are connected to a hydrophobic backbone which twist and turn throughout the MD-box. The formation of “cylinders” and “spheres” with well-defined hydrophobic/hydrophilic interfaces are therefore clearly an oversimplification.

It is interesting, however, that the envelope of the “noisy” simulated X-ray diffraction profile for the MD-derived structure (Fig. 3) corresponds well with that seen in experimental SAXS and SANS profiles. The main peak appears at $2\theta \sim 6^\circ$ (Fig. 3a), corresponding to the characteristic ~ 40 Å distance (Fig. 3b) often obtained from experimental SAXS data at this temperature. The pair of low-angle calculated peaks could well be an artefact of the instrumental resolution parameter used in the diffraction profile calculation; decreasing the resolution results in a single peak. An envelope of peaks is also calculated at higher angles; this corresponds to

some shorter characteristic distance occurring in the structure at $d \sim 5.6$ Å.

Interestingly, a large calculated peak appears at $d \sim 40$ Å, which is a characteristic distance emerging from a number of earlier structural studies. However, our MD study provides no obvious structural basis for this peak; the topology of our calculated structure is quite featureless. This certainly raises serious questions relating to the validity of previously proposed Nafion[®] structures. If Nafion[®] has the poorly defined topology suggested by our MD simulation, and yet this structure can still reproduce the major features of the experimental diffraction pattern, then it can only be concluded that all efforts to derive a more simplistic structural model for hydrated Nafion[®] are doomed to failure.

5. Conclusions

The topological structure of the hydrated Nafion[®] membrane has been simulated using an all-atom model and a large MD-box. The model displays the general features of the PFSA membrane – nano-phase-separated ionic domains in a hydrophobic matrix – but cannot be reduced to any of the more simplistic Nafion[®] models proposed earlier: cluster-sphere, rod-like, inverted micelle, parallel cylinders, *etc.* However, the simulated X-ray diffraction profile based on our MD-generated structure reproduces the key feature of experimental SAXS and SANS studies: a peak for $d \sim 40$ Å. This must be taken into account when interpreting diffraction data from PFSA membranes in future.

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