



# Hydrogen bonding in narrow protonated polymer electrolyte pores

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## ABSTRACT

Proton conductivity in fuel cell membrane materials such as Nafion<sup>®</sup> decreases dramatically with decreasing water content. At very low water content proton transport is thought to occur through narrow necks, which can be either static or fluctuatively formed temporarily. In the present work we investigate the properties of hydrogen bonding and protons in a one-dimensional narrow model pore by using ab initio Car–Parrinello molecular dynamics. The pore consists of eight suitably arranged CF<sub>3</sub>–CF<sub>2</sub> and four CF<sub>3</sub>–SO<sub>3</sub>H entities and is filled with water at varying water content  $\lambda$  (the ratio between the number of water molecules and the number of sulfonic acid groups) between 2.5 and 4.5. Proton mobilization in this pore occurs in two steps. First, around  $\lambda = 3$  sulfonic acid groups dissociate to form sulfonate groups and hydronium ions which form mostly contact ion pairs. Second, increasing the water content to  $\lambda = 4.5$  leads to an increase of the population of Zundel-like H<sub>5</sub>O<sub>2</sub><sup>+</sup> configurations with more or less symmetrically shared protons. Simultaneously, the number of hydrogen bonds increases and the hydrogen bond network becomes more liquid-like.

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## 1. Introduction

Proton exchange membranes are essential components of fuel cells. The proton conducting properties of polymer electrolyte membranes such as Nafion<sup>®</sup> by DuPont are based on the dissociation of protons from the highly acidic sulfonic acid (SO<sub>3</sub>H) groups which are located at the terminus of the pendant side chains of a perfluorinated polymer backbone (see, e.g., [1–11] for recent reviews). The current picture of proton conductance in these polymer electrolyte membranes is based on the view that the conducting protons migrate through aqueous clusters and channels, which form in the material once it contains sufficient water, in an analogous way to that in water and aqueous acidic solutions [12–19]. Namely, the actual transport coefficient depends on the interplay between classical H<sub>3</sub>O<sup>+</sup> ion diffusion and structural diffusion via proton hops according to the Grotthuss mechanics (discussed in much detail for water, e.g., in Refs. [20,21]). At high water content, the channels and clusters become interconnected and macroscopic proton transport can occur. The channel walls are formed by the hydrophobic polymer chains and the sulfonate groups are either on the surface or stick into the aqueous phase, which thus forms, after dissociation of the protons from the sulfonic acid groups, a medium of high ionic strength.

At low water content  $\lambda$ , which is defined as the ratio between the number of water molecules and the number of sulfonate groups as  $\lambda = n_{\text{H}_2\text{O}}/n_{\text{SO}_3}$ , proton transport is significantly reduced, and there appears to be a percolation threshold around  $\lambda \approx 3$ –4, below which proton conductivity drops to zero. Proton conduction in the vicinity of the percolation threshold is thought to occur through narrow necks or pores which might fluctuatively open and close on some time scale (an idea put forward in Ref. [22]) and which may or may not reflect some intrinsic structure of the polymer [23]. In all scenarios the transport through these narrow necks should become rate-determining, and it has been experimentally established that the activation energy increases for very low water content [24].

Many challenging questions arise for theorists in connection with fuel cell operation of such membranes. Two aspects of the structure–activity relation in a fuel cell stand out as fundamentally important. The first aspect is polymer morphology. What is the morphology of a Nafion membrane? How does it change with water content? Can we learn how to influence this morphology and keep it sufficiently stable during fuel cell operation? In recent years substantial simulation efforts have been made by various groups to understand these phenomena on the atomic level [22,25–45].

The second theoretically intriguing aspect is the elucidation of the elementary steps of proton conductivity in Nafion membranes on the molecular scale. This aspect has also recently been studied intensely by several research groups. Computer simulation studies in this context were often based on the use of reactive molecular

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force fields, typically of the empirical valence bond (EVB) type (e.g., [31,35,46–48]). At very low water content, such force field calculations cannot give reliable answers, and quantum mechanical methods have to be used. Paddison and Elliott [49–52] studied by ab initio quantum chemistry methods the interactions between two side chains and investigated the influence of side chain length and water content on the dissociation of the  $\text{SO}_3\text{-H}$  bond. They found that protons start dissociating from the sulfonic acid group for  $\lambda \approx 3$ . Eikerling and coworkers [53–55] investigated a periodic surface layer of  $\text{CF}_3\text{-SO}_3\text{-H}$  and  $\text{CF}_3\text{-O-CF}_2\text{-CF}_2\text{-SO}_3\text{H}$  entities; they specifically addressed questions regarding the optimum sulfur–sulfur distance for the proton dissociation step. This distance was found to be between 6 and 7 Å and depends somewhat on the length of the chain

In the present work, we present first results of Car–Parrinello molecular dynamics (CPMD) modeling [56] of the behavior of water and protons inside a cylindrical pore composed of  $\text{CF}_3\text{-SO}_3\text{H}$  and  $\text{CF}_3\text{-CF}_3$  molecules. This system setup can be regarded as a simple (and presumably overly symmetric) model of the narrow necks thought to exist at low water content in a Nafion membrane. The pore system is studied with varying water content  $\lambda$  between 2.5 and 4.5. We specifically investigate the question how the mobilization of the protons progresses with increasing number of available water molecules.

Section 2 briefly summarizes the model and simulation parameters. Results are presented in Section 3 and discussed in Section 4.

## 2. Model and simulations

Fig. 1 shows the pore model used in the simulations. The pore walls consist of  $4\text{CF}_3\text{SO}_3\text{H}$  and  $8\text{CF}_3\text{CF}_3$  molecules which are arranged on a single helix. As can be seen in the top frame, this places the  $\text{SO}_3\text{H}$  groups at  $90^\circ$  from each other (left, right, top and bottom) along the approximately spherical pore perimeter. The outer C-atom positions are located equidistantly on the helical path (at a distance of 10.32 Å from the center of the pore) in such a way that

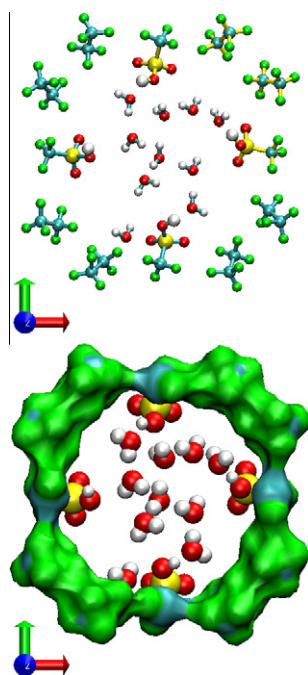


Fig. 1. Sketch of the model pore for  $\lambda = 2.5$ . The  $8\text{CF}_3\text{-CF}_3$  and the  $4\text{CF}_3\text{-SO}_3\text{H}$  entities are arranged in a helical pattern. Pore atoms are shown as a density map and water molecules as stick models. (Generated with vmd [66].)

each triflic acid entity  $\text{CF}_3\text{SO}_3\text{H}$  is followed by two hexafluoroethane entities  $\text{CF}_3\text{CF}_3$ . The  $\text{CF}_3\text{SO}_3\text{H}$  entities are shifted 2 Å towards the center of the pore in order to increase the effective exposure of the sulfonate group to the water channel. All outer C atoms are kept at fixed positions so that the channel was stable during the entire simulation run. By construction, the system fits into a box of dimensions  $(L_x, L_y, L_z) = (20 \text{ Å}, 20 \text{ Å}, 5.4 \text{ Å})$ . This pore is filled with 10, 12, 14, 16, and 18 water molecules (see Table 1), which corresponds to a water content  $\lambda := n_{\text{H}_2\text{O}}/n_{\text{SO}_3}$  ranging from 2.5 to 4.5.

We used the BLYP functional [57,58] with ultrasoft Vanderbilt pseudo potentials [59]. The cutoff was chosen as 25.0 Rydberg.

The equations of motion are integrated using the CPMD code [60] in the constant volume ensemble with a simulation time step of 4 a.u. (corresponding to 0.0967 fs). The electron fictitious mass is 400 a.u. Trajectories were integrated over  $9.2 \times 10^5$  steps, of which the first  $2 \times 10^5$  steps were discarded during equilibration. Hence the simulated trajectories last for 70 ps.

A Nosé thermostat [61] was used for the ions with target temperature 400 K and a frequency of  $3000 \text{ cm}^{-1}$ . Similarly, a Nosé thermostat for electrons was applied with frequency  $10,000 \text{ cm}^{-1}$ . The chosen target fictitious kinetic energy depended somewhat on the number of electrons and is slightly different for the five simulations, ranging from 0.011 to 0.014 a.u. At the beginning of the run the wave functions were quenched to the Born–Oppenheimer surface. The quenching procedure was repeated several times during the equilibration procedure.

## 3. Results

### 3.1. Atom distributions

Fig. 2 shows schematically the distribution of several classes of oxygen atoms projected on the  $xy$ -plane of the pore cross section. The saturation of the spots is proportional to the simulation averaged density of oxygen atoms. The semicircular regions (red; top, bottom, left, and right) represent the oxygen atoms of the 4 sulfonic acid/sulfonate groups. Green indicates the oxygen atoms belonging to protonic complexes and blue indicates the remaining water oxygen atoms.

It is apparent that the mobility of individual atoms and molecules is quite limited, most obviously for  $\lambda < 4$  (left). At these small water contents the pores are also not completely filled, as can be inferred from the empty regions. For  $\lambda = 4$  and  $\lambda = 4.5$  the empty regions vanish and the pore is now filled with water. This is accompanied by a more pronounced delocalization of the protonic oxygen atoms (green). The figures reveal, however, that the protons are still mostly confined to the outer perimeter of the pore. At the highest  $\lambda = 4.5$  about 8 green spots of different intensity can be recognized. This is consistent with fluctuations between contact ion pair, solvent separated ion pair and Zundel-like states (see below).

Table 1

Characteristic simulation data.  $n_{\text{H}_2\text{O}}$  is the total number of water molecules in the simulation cell,  $n_{\text{N}}$  the average number of O–H–O triples.  $\langle \alpha \rangle$  and  $\arccos(\cos \alpha)$  are average hydrogen bond angles computed in different ways (see text), and  $\sigma_\alpha$  is the root mean square fluctuation of the average hydrogen bond angle  $\langle \alpha \rangle$ .

$\lambda$	$n_{\text{H}_2\text{O}}$	$n_{\text{N}}$	$\langle \alpha \rangle$	$\sigma_\alpha^a$	$\arccos(\cos \alpha)$
2.5	10	15.2	168.7	5.8	170.4
3.0	12	18.5	166.6	6.9	167.6
3.5	14	22.7	165.2	8.0	165.6
4.0	16	24.8	164.0	8.5	164.3
4.5	18	29.5	163.0	9.1	163.0

$$^a \sigma_\alpha = \sqrt{\langle \alpha^2 \rangle - \langle \alpha \rangle^2}.$$

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