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Competition between side chain length and side chain distribution: Searching for optimal polymeric architectures for application in fuel cell membranes

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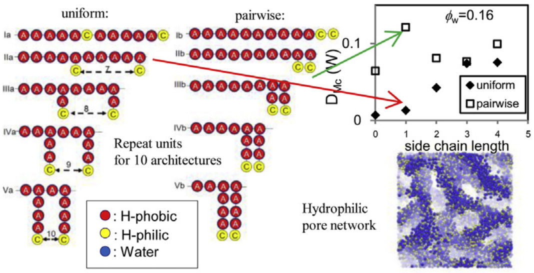
HIGHLIGHTS

- Microphase separation is simulated for various amphiphilic polymeric membranes.
- Side chains are distributed uniformly or pairwise along hydrophobic polymer backbones.
- Water diffusion through hydrated membranes is modeled.
- For a uniform side chain distribution long side chains reveal the highest diffusion.
- For a pairwise side chain distribution short side chains reveal the highest diffusion.

GRAPHICAL ABSTRACT



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ABSTRACT

Microphase separation within 10 polymeric membranes of similar ion exchange capacity is studied by dissipative particle dynamics (DPD). The polymers consist of hydrophobic A and hydrophilic C fragments. For 8 grafted architectures, the side chains ([C], [AC], [AAC], or [AAAC]) are distributed uniformly or pairwise along the hydrophobic backbone. For the other 2 (block type) architectures the C fragments are uniformly and pairwise distributed within the backbone, respectively. For the water containing pore networks the following trends are found: For the uniform architectures, the pore size is lowest for the block- and increases further for the grafted architectures with increase of side chain length, while for the pairwise architectures the reverse trend is observed. Water diffusion through the hydrophilic pore networks is deduced from Monte Carlo tracer diffusion calculations (through 800 snapshots). Among the uniform architectures diffusion is highest for the grafted architecture with long [AAAC] side chains. Interestingly, for the pairwise architectures diffusion is highest for the grafted polymers with the short ([C]) side chains. Side chain length and side chain distribution are thus predicted to be interesting design parameters in order to optimize proton and or solvent transport within flexible amphiphilic polymeric membranes.

1. Introduction

Nafion is usually used as a polymer electrolyte membrane (PEM) in fuel cells, its chemical formula is given in Fig. 1. Its purpose is to

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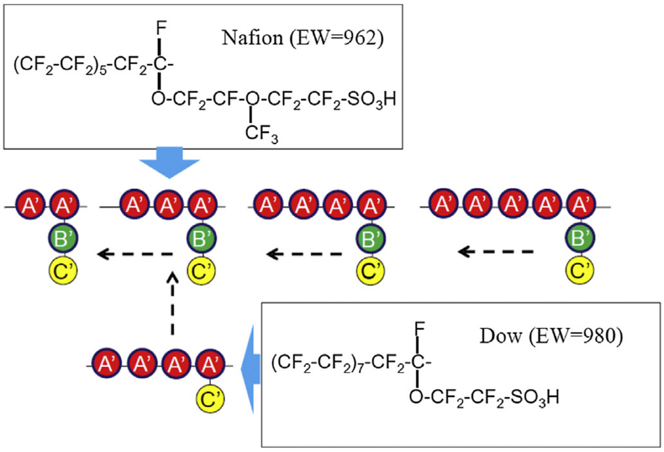

Fig. 1. Chemical formula of Nafion and Dow repeat units and bead representations of molecular fragments proposed in Ref. [30]: A′:$-CF_2-CF_2-CF_2-CF_2-$, B′:$-O-CF_2-CF(CF_3)-O-$, C′:$-CF_2-CF_2-SO_3H$. Dashed arrows are directed towards architectures for which in Ref. [31] water diffusion was predicted to increase for water volume fractions fixed between $\phi_w = 0.1$ and $\phi_w = 0.3$.

separate the anode from the cathode, and simultaneously to allow protons to flow from the anode to the cathode. Nafion is composed of a hydrophobic ($-CF_2-CF_2-$) backbone to which side chains are attached that have a pendant hydrophilic SO_3H group. Since Nafion membrane takes up water [1–9] when exposed to humid environments this results in micro phase separation with the acidic sites and water forming a hydrophilic pore network. The pores, which are a few nm in diameter, provide the diffusive pathway for protons and water [6–8]. One route to optimize proton transport in polymer electrolyte membranes (PEM) might be to optimize the phase separated pore morphology.

Nafion has been modeled by initio methods [10–12], Molecular Dynamics (MD) [12–24], Coarse Grained MD (CGMD) [25,26], Bond Fluctuation Model (BFM) [27], self-consistent approaches [28,29] and Dissipative Particle Dynamics (DPD)) [30–36]. Atomistic simulation of the phase separation for large system size is at present not achievable due to limited computer power. Large scale atomistic simulations for system size ~2.7 × 10^4 nm^3 (2 × 10^6 atoms) on hydrated Nafion were performed recently, but required special assumptions in the studies of Knox and Voth [24]. Since for such large size it is impossible to simulate the evolvement from random configurations towards equilibrated morphologies, their aim was to study the time evolvement for pre-assumed pore networks. Komarov et al. [12] reported on a MD study involving more than 4 million atoms. To obtain hydrated Nafion morphologies of that system size they created equilibrium morphologies for a system containing ~6.5 × 10^4 atoms. By repeatedly creating periodic images that were again subjected to equilibration the system could be scaled up by factor 64 to a system volume of ~2.7 × 10^4 nm^3. Yamamoto and Hyodo [30] used DPD to calculate for system size ~2.3 × 10^4 nm^3 Nafion1200 morphologies (1200 means the equivalent weight (EW) of 1200 gr polymer per sulfonic site). They coarse grained molecular fragments into beads and by Fourier transformation of the pair correlation function of the water containing beads they calculated X-ray scattering profiles for the equilibrated morphologies. The wave factor q_{max}, at which a maximum in the scattering occurs, was found to decrease with water uptake, in agreement with experiment.

Based on the parameterization in Ref. [30], Dorenbos et al. [31] also modeled hydrated Nafion with side chains uniformly distributed along the polymer backbones (see Fig. 1). They analyzed the connectivity of DPD pore morphologies for several EW Nafion membranes. Water diffusion within the morphologies of various EW Nafion membranes was studied by means of Monte Carlo (MC) tracer diffusion calculations. By mapping the pore phase onto a cubic grid, and by restricting tracer particles to move solely through the hydrophilic phase, diffusion constants could be derived from the particles' mean square displacement (MSD). The obtained diffusion constants matched well experimental values when the water mobility within the pores was assumed to be equal to that in pure water. Such an assumption is clearly an oversimplification. But it was indeed concluded from quasi elastic neutron scattering studies [37,38] on hydrated Nafion membranes that within the pores the water diffusion constant is close to that of pure water. For example, at a water volume fraction of ~14 vol% ($\phi_w = 0.14$) (or $\lambda \sim 5$ when hydration level is expressed as the number of water molecules per SO_3H site) Pivovar and Pivovar [37] measured a local water mobility of ~1.6 × 10^{-5} cm^2/s, which is around 70% of the pure water value of 2.3 × 10^{-5} cm^2/s.

In Ref. [31] reproduction of the experimental water diffusion constant within Nafion at various water volume fractions could only be achieved when tracer water particles were allowed to move freely within the phase that contains both water and the hydrophilic pending side chain fragments. When the particle movement was restricted to within the static pore network that only contained water, the diffusion constants turned out to be too low as compared to experiments. Water diffusion through Nafion was predicted in a recent DPD-MC study [34] to increase significantly when the side chains are non-uniformly distributed. Also the best agreement between simulation and experiment for liquid water diffusion and O_2 gas permeation through hydrated Nafion was obtained when the side chains were assumed to be statistically distributed along the backbones [34].

The trend obtained for Nafion was also found for model polymers with side chains distributed at various locations along the backbones. Those studies [34,39] assumed a bimodal distribution of side chain placement with intervals between successive branching points being alternatingly small (x backbone bond lengths) and large (y A backbone bond lengths). By systematically varying x and y while keeping $x + y$ (or EW) constant it was found that at fixed water volume fraction of $\phi_w = 0.16$ [34] and $\phi_w = 0.17$ [39] for uniform side chain distributions ($x = y$) diffusion is lower as compared to a non-uniform side chain distribution. Moreover, the inter cluster spacing and diffusion increased approximately linear with asymmetry parameter y/x. Since these trends were obtained for various water contents, the percolation thresholds for diffusion also decreased with increase of y/x [39].

Within a Dow membrane, whose side chains are shorter than that of Nafion (see Fig. 1) water diffusion was predicted to be less than that of Nafion of the same EW for $\phi_w = 0.1$–0.3 [31], consistent with experiment. This suggested that longer side chains are capable of providing better connected pore networks that result in higher diffusion. This was confirmed in a later DPD study [40] were ~40 polymeric architectures with uniformly distributed side chains were systematic screened. For fixed EW diffusion increased with side chain length. In Ref. [41] it was found that this trend persists to low water contents, resulting in longer side chain architectures revealing the lowest percolation thresholds for diffusion. Noteworthy is that the above is in accordance with results from a MD study obtained by Allahyarov and Taylor [26] who also found that for similar EW the architectures with longer side chains revealed the highest water diffusion.

From the above DPD studies [31,34,39–41] the obtained trend are summarized as follows: For grafted polymers of the same EW and fixed ϕ_w water diffusion can be enhanced by the following two procedures: (1) for uniform side chain distributions the side chain lengths are increased [31,40,41] or (2) for fixed side chain lengths