



Dependence of pore morphology and diffusion on hydrophilic site distribution within hydrated amphiphilic multi block co-polymer membranes



G. Dorenbos

Knowledgegenet Co., Lofty Chuo Bldg. (9F), 1-17-24, Shinkawa, Chuo-ku, Tokyo 104-0033, Japan

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ABSTRACT

Dissipative particle dynamics (DPD) combined with Monte Carlo (MC) tracer diffusion calculations are used to study phase separation and diffusion within hydrated (amphiphilic) alternating multi block co-polymer membranes. The co-polymers are composed of hydrophobic (A) and hydrophilic (C) fragments. The hydrophobic A block length is alternating short (x A fragments) and long (y A fragments). One repeat unit is represented as A_xC_y , with $y \geq x$. The phase separated morphologies that were generated for 18 architectures by DPD at a water content of 25 percent by volume reveal that water is contained within a pore network with hydrophilic C fragments located near the pore boundary. The morphologies are mapped onto a cubic grid on which MC (tracer) trajectory calculations are performed in which particle movement is restricted to the water containing pore networks. For architectures for which the hydrophilic fragment fractions are the same (same ion exchange capacity), an increase in difference of hydrophobic block lengths (or $y - x$) result in a linear increase in inter pore distance and a significant increase in long-range diffusion through the pore networks.

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1. Introduction

Currently Nafion[®] is mostly applied as a proton exchange membrane (PEM) in fuel cells. Its purpose is to separate the cathode from the anode while simultaneously acting as a conductor for protons. Nafion[®] is a per-fluorinated sulfonic acid (PFSA) polymer composed of a hydrophobic Teflon backbone to which side chains are grafted with a pendant hydrophilic SO_3H group (Fig. 1(a)). The water uptake, expressed as the number of water molecules λ per sulfonic site, increases with relative humidity [1–8]. Phase separation results in a water containing pore network with pores a few nm in diameter surrounded by polymer phase [6–8]. Since these pores are the diffusive pathways for water and protons this makes their degree of connectivity essential for obtaining high proton conductivities. Because at low humidity the proton conductivity decreases rapidly [1–4,6,9,10], this requires a fuel cell design strategy that provides sufficient hydration of the PFSA membranes during operating conditions. The development of membranes with good connected pore networks would be an important step toward wide scale application of fuel cells.

In order to find alternative polymers that can provide sufficient proton conductivity and mechanical strength at working conditions several alternative grafted or block polymer membranes have been synthesized. As for the PFSA membranes, these alternatives have acidic, hydrophilic, sites located within the backbones of the block polymers or within the side chains of the grafted polymer. Examples are the block polymers poly-benzimidazole (PBI) [11], sulfonated poly-ether-ether-ketone (SPEEK) [12,13], sulfonated styrene/ethylene-butylene/styrene (SSEBS) [9] sulfonated poly aryl ether ketones (SPAES) [14] and BPSH [15], sulfonated polyimide (SPI) [16], and the grafted [bis] (perfluoroalkyl) sulfonyl imide perfluorinated ionomers [17]. Due to the presence of hydrophilic (acidic) sites within the molecular architectures, membranes composed of these ionomers swell and phase separate under humid conditions, resulting in water containing pore networks.

The extent to which the pores are connected may, besides the hydration level, depend on several parameters like the molecular architecture, acidic site density, side chain length, side chain distribution, backbone and/or side chain stiffness, etc. Theoretical approaches such as molecular dynamics (MD) [18–30], coarse grained MD [31,32] and meso scale methods such as dissipative particle dynamics (DPD) [33–45] may be helpful to gain insight in how the pore size and their connectivity is affected by these parameters. With respect to fuel cell membranes MD has frequently been applied

E-mail address: dorenbos@ny.thn.ne.jp.

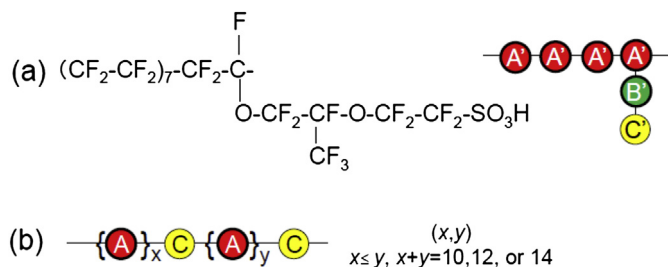


Fig. 1. (a) Repeat unit of the grafted Nafion® (EW = 1143) polymer and bead parameterization determined in previous work [39] A': $\text{CF}_2\text{-CF}_2\text{-CF}_2\text{-CF}_2$, B': $\text{O-CF}_2\text{-CF}(\text{CF}_3)\text{-O}$, C': $\text{CF}_2\text{-CF}_2\text{-SO}_3\text{H}$. (b) DPD representation of a repeat unit of the model multi-block co-polymers considered here which are composed of two hydrophobic blocks that contain x and y A beads, respectively, covalently bonded by a hydrophilic C bead.

to model phase separation within the grafted (PSFA) [18–30] membranes and predicts indeed water clustering in agreement with experiment. From MD diffusion constants can be obtained by sampling mean square displacements of water and/or protons during a period of at most several ns. During this time only the local environment of the diffusing species can be probed and obtained diffusion constants do not represent experimentally obtained long range diffusion constants. For this reason simulation of long range diffusion requires a meso scale probing of the pore connectivity. This essentially means that the system size should be significantly larger than the characteristic distance of the pore network. As an example, for the PFSA membranes the characteristic distance as estimated from the Bragg spacing is around 5 nm [6–8,10], and therefore the obstructions (bottlenecks) in the diffusion pathways can only be probed for system volumes of the order of 10^4 nm or more.

For limited system size, water and proton diffusion through hydrated Nafion1143 (1143 is the equivalent weight (EW) and refers to 1143 g polymer/mol SO_3H) was calculated by Devanathan et al. [25]. They observed an appreciable increase in diffusion of these species near $\lambda = 5$. The size of the simulation box was at most ~ 60 nm³ (at $\lambda = 20$) containing 800 water molecules and 40 Nafion side chains. For around 3 times larger system size Cui et al. [26] obtained pore morphologies and found an increase of water and proton diffusion through Dow (EW = 977) and Nafion (EW = 1143) membranes with water uptake, in accordance with experiment. Karo et al. [27] simulated for a system size of ~ 400 nm³ water diffusion within Dow and Nafion membranes at $\lambda = 15$. They noted that the pore morphology depends strongly on system size, and therefore questioned results deduced from earlier MD simulations [28] obtained for smaller simulation box volumes.

The largest system size, comprising $\sim 2 \times 10^6$ atoms (volume $\sim 27,000$ nm³), for which MD modeling has been performed on PFSA membranes was reported by Knox and Voth [29]. They pre-assumed 5 different morphologies and a random morphology. With exception of the random morphology, each of them evolved such that the characteristic scattering peak could be reproduced. Perhaps the most interesting observation was the formation of wires containing hydronium ions, water and sulfonate side chain groups. These wires connect the hydrophilic clusters that were originally imposed on the pre-assumed morphologies. Since water and proton diffusion takes place through the thus established hydrophilic network the extent to which the water clusters are interconnected by such wires will affect the long range transport properties.

Park et al. [30] performed MD for Nafion1143 and several SPI block ionomers which differ in the length of the hydrophilic (sulfonated) blocks. Their work revealed that near a water content of 25 vol% ($\phi_w = 0.25$) for Nafion a well phase separated morphology occurs. The distribution of water within SPI membranes turned out

to be much more dispersed. This was attributed to the stiff backbone and the possibility of water molecules to form also hydrogen bonds with the ether oxygen in the hydrophobic blocks. Since such an association of water with the Teflon backbone in Nafion is absent this resulted in a much more phase separated morphology within Nafion. From experiments of Park et al. [30] it was found that above a hydrophilic block length fraction of $\phi = 0.6$ a sharp increase in water uptake (up to 45 vol% at $\phi = 0.8$) and proton conductivity occurs, suggesting that water becomes better connected. Also their MD study predicted for $\phi > 0.6$ a sharp increase in proton diffusivity at water contents comparable with experiment.

Jang et al. [31] applied coarse grained MD (CGMD) to study the effect of side chain distribution along the polymer backbones on morphology and diffusion. They found that at $\phi_w = 0.2$ for Nafion polymers with uniform side chain attachments phase separation is less pronounced and the pores are smaller than for polymers with all side chains located at one end of the backbone, but water and proton diffusion was not drastically affected by these differences in sequence design. Allahyarov et al. [32] concluded from CGMD simulations that for PFSA like polymers with similar EW those with the longer side chains form larger clusters and higher proton conductivities, in line with DPD studies [35,38] in which side chain length and density were varied.

Dorenbos et al. [33–38] combined DPD with Monte Carlo (MC) trajectory calculations and simulated the diffusion of neutral species (water O_2 , N_2 , H_2) through hydrated Nafion. The static pore networks obtained from DPD (using the parameterizations proposed by Yamamoto and Hyodo [39]) were mapped on a cubic grid on which MC trajectory calculations through the pore networks were performed. Using this strategy experimental long range water diffusion [34] and O_2 and H_2 gas permeation rates [35] could be approached. The interesting finding was the capability of predicting trends regarding diffusive transport when the EW or side chain length of the polymers is varied. Water diffusion and O_2 and N_2 permeation within hydrated Nafion membranes was expected at similar ϕ_w to decrease with increase in EW or decrease of ion exchange capacity (IEC), where IEC is the inverse of EW or mole equivalent of acidic sites per gram polymer. The explanation for these findings was that while the pore size increases with decrease of IEC, the connections between them become narrower, which act as bottlenecks for diffusion [33–35]. The same findings were deduced from theoretical studies [36,37] of model polymers similar in architecture as PFSA but in which the side chain lengths were varied. For architectures of the same IEC the ones that contain the longer side chains revealed at fixed ϕ_w the largest water clusters, largest inter cluster spacing and fastest diffusion. For architectures with same side chain lengths a decrease in IEC, due to increase in inter branching distance along the backbones, also resulted in increased cluster size and distance between them, but slower diffusion (see Fig. 8 in Ref. [37]).

DPD-MC modeling aimed to predict percolation thresholds for diffusion, revealed that, at similar IEC, for the longer side chain architectures also much lower percolation thresholds are expected than those containing short side chains [37]. This was explained due to differences in topological distance between hydrophilic sites within the architectures: An increase in topological distance allows the formation of larger and better connected pores that result in higher diffusion constants at same water content and thus a lower percolation threshold.

All of the above studies assumed idealized architectures with branching points (grafted polymers) or hydrophilic sites uniformly distributed along the backbone (block polymers). For realistic polymers for which these distributions might be non-uniform or statistical, this might affect the pore morphology. Indeed, a recent DPD-MC study [38] predicted that for grafted model ionomers,

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