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Water induced phase segregation in hydrocarbon proton exchange membranes

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ABSTRACT

Proton exchange membranes (PEMs) are a key material for proton exchange membrane fuel cells (PEMFCs). Non-fluorinated hydrocarbon PEMs are low-cost alternatives to Nafion, but limited by the low proton conductivity, because of the weak phase segregation structure and narrow ion-transport channels. Various efforts have been taken to improve the performance of hydrocarbon PEMs, but mostly with complex methodologies. Here we demonstrate a simple, yet very efficient method to create phase segregation structure inside a typical hydrocarbon PEM, sulfonated poly(ether ether ketone) (SPEEK). By simply adding appropriate amounts of water into the DMF solvent, the resulting SPEEK membrane exhibits widened ion-transport channels, with the phase size of 2.7 nm, as indicated by both molecular dynamic (MD) simulations and transmission electron microscope (TEM) observations, and the proton conductivity is thus improved by 200%. These findings not only further our fundamental understanding of hydrocarbon PEMs, but are also valuable to the development of low-cost and practical fuel cell technologies.

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Proton exchange membrane fuel cells (PEMFCs) are one of the most promising energy conversion devices with zero emissions and high efficiency [1–3]. After decades of development, PEMFCs are approaching commercialization, but the high manufacture cost of key components is still a barrier to widespread applications [1]. One of the key components is the proton exchange membranes (PEMs) [1,3–6]. Up to now, Nafion is a benchmark of PEMs owing to its excellent chemical stabilities and high proton conductivity [7]. However, the manufacture of perfluorocarbon polymers makes it very difficult to reduce its cost [5].

To address this issue, much effort has been devoted to developing non-fluorinated PEMs with stable hydrocarbon backbones, such as sulfonated poly(ether ether ketone) (SPEEK), sulfonated poly(arylene ether sulfone) (SPAES), and sulfonated poly(phthalazinone ether sulfone ketone) (SPPEK) [8]. Although cost has been reduced, the proton conductivity of these PEMs is relatively low, mostly because the phase segregation structure (ion conduction channels) cannot be efficiently formed inside the polymer [9].

Several strategies have been taken to build appropriate phase segregation structures for sulfonated hydrocarbon PEMs. One strategy is to design multi-block copolymers or flexible side chains [10–12]. For example, McGrath et al. designed a 6FK-BPSH multi-block copolymer possessing a higher proton conductivity than Nafion 112 over a wide range of relative humidity (RH) and temperature [10], the ionic groups were located closer to each other in the multi-block copolymer than in random copolymer, facilitating the phase segregation and resulting in larger domains and greater differences in topography. Also, Pang et al. introduced a flexible tetra-sulfonated side chain to the poly(aryl ether ketone) membrane (TS-PAEK-25) [12], resulting in a quite clear phase-segregated morphology. The small-angle X-ray scattering (SAXS) result showed that the morphology of the membrane has a phase size of 8.17 nm, which was larger than that of Nafion (3.53 nm). This unique phase-segregated structure resulted in an excellent proton conductivity of 151 mS/cm at 100 °C. Another strategy is to use additives, which seems to be a simpler method in comparison to the synthesis of complex structures. Some additives, such as PTFE, SiO₂, and heteropolyacid, have been reported to be beneficial to the proton conductivity, durability and mechanical stability [13]. For example, Dong reported an SPEEK/PANTs (poly vinylphosphonic acid functionalized silica nanotube) composite membrane which showed a high proton conductivity of 103 mS/cm at low temperature (30 °C) [14]. The nanotubes (1240 nm in length) distributed evenly within the SPEEK matrix and constructed

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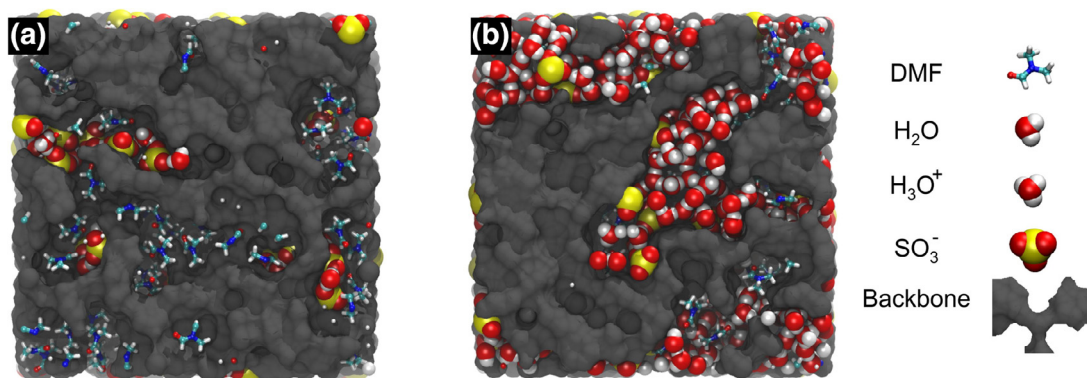


Fig. 1. Atomistic MD simulation results for SPEEK membranes containing DMF (a) or H₂O/DMF (b) with a volume ratio of 1:1.

continuous pathway that facilitates proton transportation along the nanostructure. Although introducing additives to PEMs is considered as a facile way to increase the phase segregation and proton conductivity, there is always a compatibility issue between the polymers and the additives, and additives may also aggregate in the membrane and result in inhomogeneous membranes [13,14].

Unlike using the solid additives aforementioned, in this study, we are interested in the influence of water to the phase segregation of sulfonated hydrocarbon PEMs. Water is abundant, environmental friendly, and easy to remove from membranes without causing any inhomogeneous issue. We focused on the influence of water to the phase segregation of SPEEK, a promising proton-exchange membrane with stable backbone but weak phase segregation structure [9,15].

Atomistic MD simulations were first applied to study the morphology of a SPEEK membrane containing DMF or H₂O/DMF mixture solvents. To determine the ratio between SPEEK and solvent molecules in a simulation box, the SPEEK membrane was first simulated under a fully wet state, namely, with a hydration level $\lambda = 10$ (where λ denotes the number of water molecules per H₃O⁺) [16]. The volume of all ion channels formed in such a simulated wet membrane was taken as the space to be fully filled with solvent molecules in the following simulations.

The simulations were then started with the box containing SPEEK chains and solvent molecules (DMF or H₂O/DMF mixture) with above-determined volume ratio. After 30 ns of equilibration, phase segregation morphologies were generated. As demonstrated in Fig. 1, the resulting ionic channels in the DMF-containing SPEEK membrane seems to be narrow, and the DMF molecules were

squeezed to line up in a wire state in the channels. By contrast, the ionic channels formed in the H₂O/DMF-containing SPEEK membrane are wide, inside which water molecules aggregate together with the sulfonate groups and hydronium ions. These results indicate that, after solvent evaporation, the H₂O/DMF-containing SPEEK membrane may solidify with a structure of enhanced phase segregation.

Although the atomistic MD simulations are informative, the box is too small to identify any long-ranged structural pattern possibly generated by phase segregation. Coarse grained (CG) simulations were thus employed to extend the space and time scales. Martini CG force field [17] was used for simulating $3 \times 3 \times 3$ systems. After equilibration, the CG systems were transformed back to atomistic configurations and further equilibrated. The simulation results are present in Fig. 2. Charged particles are not shown so as to have a clear view of the ion channels. Stronger phase segregation with wider ion channels in the membrane can be clearly observed in SPEEK containing H₂O/DMF mixture (Fig. 2(b)) than that with DMF (Fig. 2(a)), which is consistent to the atomistic MD simulation results.

To obtain structural information of the ion channels, DMF molecules were removed from both configurations, and water molecules were added to the channels to make the final hydration level $\lambda = 10$. The refilled systems were then equilibrated. Structure factors (SFs) of the hydrophilic species (H₂O, H₃O⁺, and -SO₃⁻) were then calculated based on their radial distribution functions (RDFs) [18,19]. As shown in Fig. 2(c), the SF peak for the SPEEK membrane formed with H₂O/DMF appears at $q = 2.3 \text{ nm}^{-1}$, with a greater intensity than the SF peak for the membrane formed with

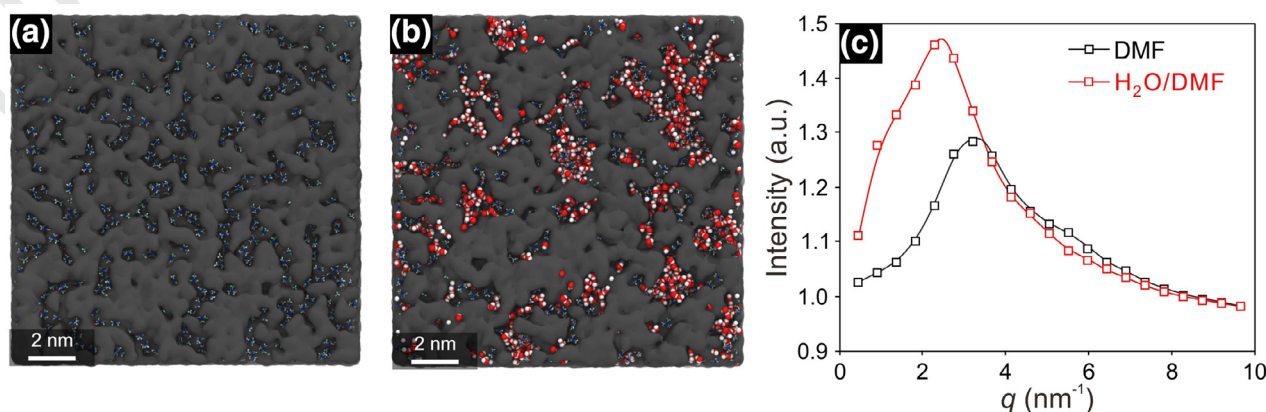


Fig. 2. CG simulation results for SPEEK membranes containing DMF (a) or H₂O-DMF (b) in nanometer scale. The hydrophobic parts are presented in grey. Structure factors (c) of hydrophilic species (H₂O, H₃O⁺, -SO₃⁻) was calculated to quantify the phase segregation structures.

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