Morphology and Diffusion Behaviour of Nafion and SPEEK

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Abstract. Phase separation morphology and diffusion properties of Nafion and SPEEK were investigated in this study. Nafion and SPEEK PEMs had been prepared by solution casting procedure. TEM image of Nafion membrane shows a preferable continuous proton conductive channels with 3-5 nm width distributed in hydrophobic matrix, while SPEEK exhibits poor phase separation morphology with isolated clusters (1 nm in width) morphology. Radial distribution function of S-S for Nafion exhibits a much more intensive S-S peak than that of SPEEK, suggesting that the agglomeration of hydrophilic domains, represented by sulfonate groups, in SPEEK is worse than that in Nafion matrix, which might be attributed to the lower electronegativity of H than that of F and higher steric hindrance of SPEEK backbone. The corresponding hydrophilic cluster morphology of Nafion and SPEEK membranes with different hydration level were explored by MD simulation. SPEEK possessed much smaller hydrophilic channels than that of Nafion especially at low hydration level. And consequently, much lower mobility of H_2O and H_3O^+ are revealed for SPEEK.

1. Introduction

Proton exchange membrane fuel cell (PEMFC) has drawn increasing attention for their high efficiency and zero emission [1, 2]. Acting as a key component of PEMFC, proton exchange membrane (PEM) has been intensively investigated [3].

Perfluorosulfonated ionomers (PFSI), in particular Nafion with equivalent weight (EW) of 1100, are the most widely used proton-exchange membrane (PEM) materials because of good stability and proton conductivity. However, low operation temperature, high cost and high fuels crossover limited its further application. As one of the promising alternatives for Nafion, sulfonated polyetheretherketone (SPEEK) possesses good chemical stability and thermal stability, low cost, high mechanical stability, but poor hydrophilic cluster morphology and insufficient proton conductivity [4-6].

It's well known that the inherent proton diffusion of PEM is dominated by the chemical configuration, hydrophilic/hydrophobic phase separation and water content [7-9]. It's crucial to explore the difference in the morphologies and properties between Nafion and SPEEK materials. Molecular dynamic (MD) simulation is a powerful tool to investigate the structure and diffusion information in molecular scale that could not be easily obtained using experimental methods. Recently, MD simulation has been successfully applied to explore the membrane structure, water cluster distribution and transport of proton and water in PEMs [10-13]. In spite of the significant experimental and theoretical attempts performed, the comparison on the structure and diffusion

Wang, R., Li, M., Liu, C., He, X. and You, X.
Morphology and Diffusion Behaviour of Nafion and SPEEK.
In *Proceedings of the International Workshop on Materials, Chemistry and Engineering (IWMCE 2018)*, pages 552-557
ISBN: 978-989-758-346-9

properties of perfluoro-based Nafion and hydrocarbon-based SPEEK have not been implemented in previous efforts, and the detailed mechanism of proton transport in PEMs is still unclear. Therefore, the morphology and diffusion behavior of Nafion and SPEEK were investigated experimentally and theoretically.

Nafion (EW=1100) was adopted in this study. SPEEK with higher degree of sulfonation (DS) shows better hydrophilic cluster morphology and higher proton conductivity. However, excessive hydrophilic characteristic results in swelling and poor mechanical properties. Our preliminary study confirmed that EW 632 SPEEK obtained good stability and performance [14]. This study aims to investigate the phase separation morphology and diffusion behavior of Nafion and SPEEK under different water state in terms of experiment and molecular dynamic (MD) simulation.

2. Experiment and molecular simulation

2.1. Preparation of Nafion and SPEEK membranes

Nafion solution (20 wt. %, EW=1100) was provided by Aldrich. Poly (etheretherketone) (PEEK, VESTAKEEP4000P with density of 1.30 g cm^3) powder was supplied by Degussa. SPEEK (EW=632, DS=50%) was prepared from poly (etheretherketone) (PEEK) according to our previous work [5]. Solution casting method was applied to fabricate Nafion and SPEEK membranes [7, 14].

2.2. Characterization methods

Nafion and SPEEK membranes were characterized on a FEI Tecnai G2-TF30 transmission electron microscope (TEM).

2.3. Molecular Simulation

MD simulations of Nafion and SPEEK systems were conducted to investigate the difference in the hydrophilic cluster morphology and the diffusion properties between Nafion and SPEEK.

Nafion (EW=1100) and SPEEK (EW=632 EW, DS=50%) were built in this study. Nafion chain of 10 units were adopted. Each SPEEK chain consisted of 5 sulfonated PEEK monomers and 5 PEEK monomers. Periodic cell of Nafion and SPEEK at different hydration level (from 0 to 14, where λ= (H_2O, H_3O^+)/SO_3^-) were constructed. Both sulfonate groups of Nafion and SPEEK chains are undissociated when hydration level is 0. In the contrary, sulfonate groups of other systems with hydration level above 0 are dissociated. Table 1 exhibits the composition of each periodic cell of SPEEK with different hydration levels. According to literature, the initial density is set to be 2 g cm^{-3} for Nafion system. Due to chain rigidity and stiffness of SPEEK, an initial density of 0.4 g cm^{-3} is set for the periodic cell to avoid ring spearing and catenation.

Table 1. Construction of periodic cells of SPEEK with different hydration levels.

Hydration level	Number of SPEEK chain	Number of H_3O^+	Number of H_2O
0	5	0	0
1	5	25	0
2	5	25	25
4	5	25	75
6	5	25	125
8	5	25	175
10	5	25	225
14	5	25	325

After system construction, to fully equilibrate the amorphous cells, anannealing procedure were carried out on the constructed atomistic structures. Annealing strategy adopted in this study was shown in Figure 1. Finally, 1 ns NVT ensemble was further conducted at 300K, the trajectory information were recorded for structural and dynamic analysis.

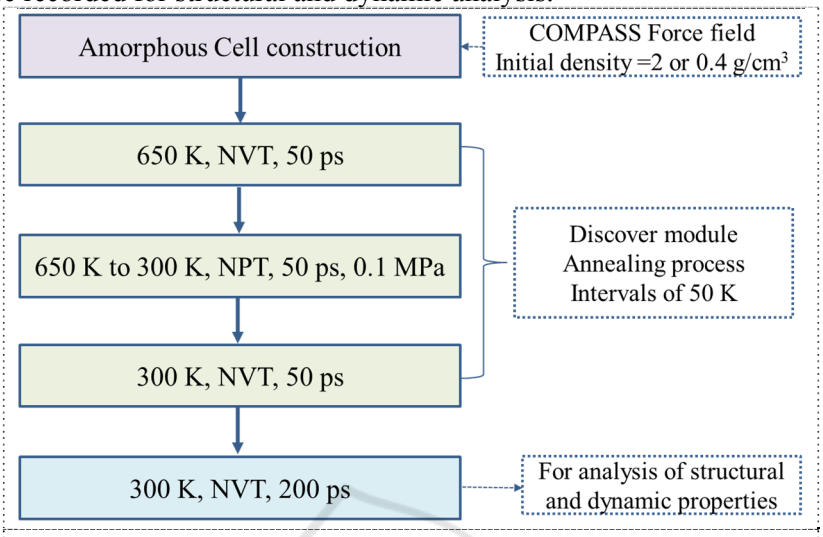

Figure 1. Simulation strategy used in this study.

3. Results and discussion

3.1. Cluster Morphology of Nafion and SPEEK membranes

Cluster morphology of PEM dominated its electrochemical behaviors. Therefore, the morphologies of Nafion and SPEEK were investigated in terms of TEM. As shown in Figure 2a, good phase separation morphology is captured in Nafion membrane. The clusters with 3-5 nm width (black spots) are distributed in hydrophobic matrix (white region), showing a preferable continuous proton conductive channels. Compared with Nafion membrane, SPEEK exhibits poor phase separation morphology in Figure 2b. The contrast between hydrophilic clusters and hydrophobic matrix is relatively low. Isolated clusters with about 1 nm width were detected for SPEEK membrane. Since the proton conduction is greatly influenced by the hydrophilic cluster morphology, a lower proton conductivity than that of Nafion is suggested for SPEEK PEM.

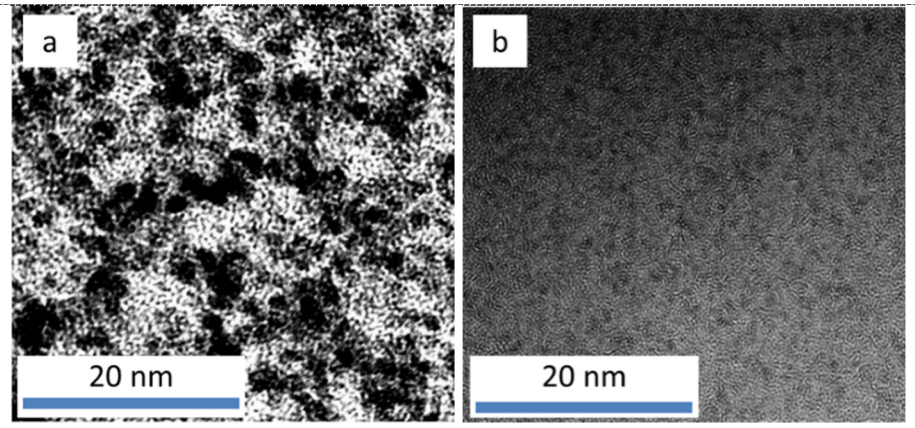

Figure 2. TEM images of Nafion and SPEEK PEMs. (a) Nafion and (b) SPEEK.

3.2. Validation of molecular dynamic simulations for Nafion and SPEEK systems

To validate the simulation result, experimental densities and simulated densities of Nafion at different hydration level are plotted in Figure 3. The experimental densities of Nafion plotted in the figure are calculated from the fitting equation [15] as follows.

$$\rho = \frac{EW + M_0\lambda}{V_m + \lambda V_0} \quad (1)$$

where M_0 represents the molecular weight of H_2O, V_m and V_0 denote the partial molar volume of the dry Nafion membrane and H_2O. V_m and V_0 could be calculated from $V_m = EW/\rho_m$ and $V_0 = M_0/\rho_0$, where ρ_m is the density of dry Nafion membrane (2.05 g/cm^3) and ρ_0 is the density of H_2O. When the hydration level increases from 0 to 14, experimental density of Nafion decreases from 2.05 g cm^{-3} to 1.71 g cm^{-3}, while the simulated values changes from 2.07 g cm^{-3} to 1.74 g cm^{-3}. Meanwhile, SPEEK share the same tendency that the simulated density decreases with increasing hydration level. Moreover, the simulated densities of SPEEK are well coincident with literature [16-18]. It could be concluded that the simulated values of Nafion and SPEEK are accordant with experimental data very well. It validates the accuracy of the molecular simulation performed in this study.

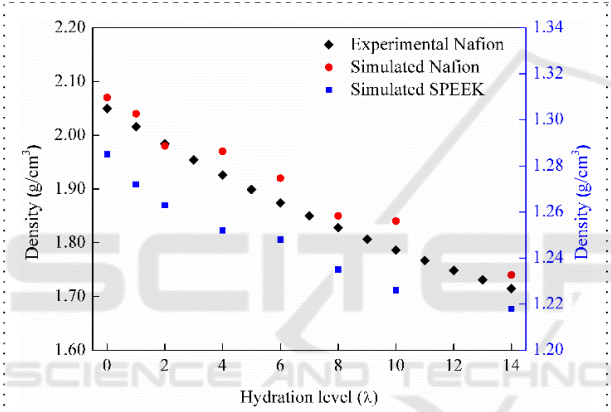

Figure 3. Experimental and simulated density of Nafion at different hydration level.

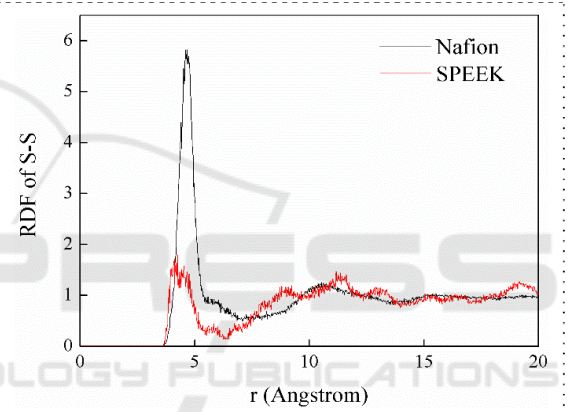

Figure 4. Radial distribution functions of S-S pair for Nafion and SPEEK system (λ=0).

3.3. Hydrophilic clusters of hydrated Nafion and SPEEK systems

Radial distribution function of S-S for Nafion and SPEEK system presented are shown in Figure 4. Both radial distribution functions exhibit a clear first peak at about 4.5Å. Nafion exhibits a much more intensive peak than that of SPEEK. It proves that the agglomeration of hydrophilic domains, represented by sulfonate groups, in SPEEK is worse than that in Nafion matrix, suggesting smaller hydrophilic clusters and lower phase separation morphology in SPEEK. This is consistent with TEM observations.

Hydrophilic cluster morphology of Nafion and SPEEK membranes with different hydration level were explored by MD simulation. As typical representatives of hydrophilic groups, $-SO_3^-$ (or $-SO_3H$ when hydration value=0), H_2O and H_3O^+ were carefully investigated and are presented in Figure 5. A lower degree of phase separation of SPEEK, compared with that of Nafion, is observed, especially at low water content. Moreover, the cluster sizes of SPEEK are smaller than that of Nafion for each hydration level. This might be caused by the lower electronegativity of H than that F and higher steric hindrance of SPEEK backbone. With increasing hydration level, H_2O content increases proportionally. Consequently, the hydrophilic clusters, composed of $-SO_3^-$, H_2O and H_3O^+, become expanded and connected, resulting in wide and connected proton conducting channels.

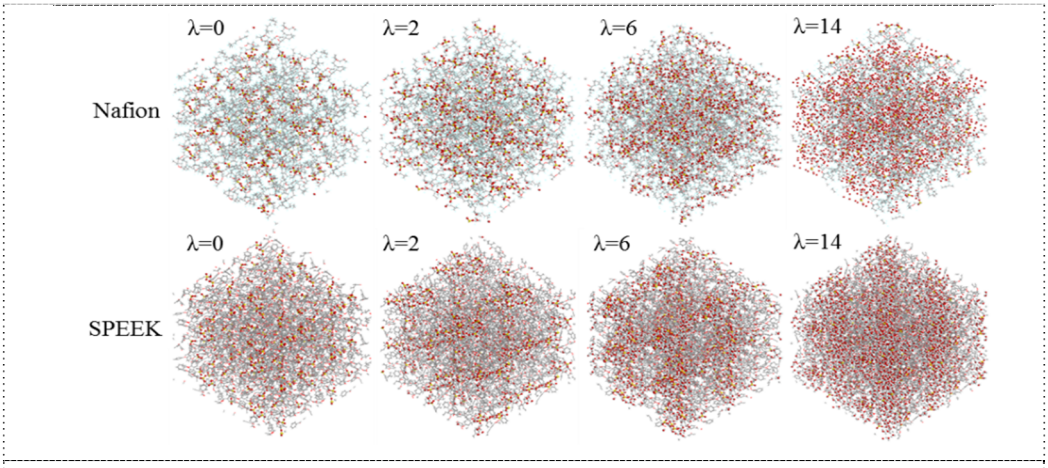

Figure 5. Final snapshots of $-SO_3^-$, H_2O and H_3O^+ in Nafion and SPEEK matrix at 300 K. Red balls, oxygen in $-SO_3^-$, H_2O and H_3O^+; white balls, hydrogen in H_2O and H_3O^+; Yellow balls, sulfur in $-SO_3^-$; other atoms were set in line mode.

3.4. Diffusion properties of Nafion and SPEEK

To investigate the effects of such cluster morphology on the mobility of H_2O and H_3O^+, mean square displacement (MSD) analysis was performed at 300 K according to equation (2) [19],

$$MSD = \langle [r_i(t) - r_i(0)]^2 \rangle \tag{2}$$

where r_i(t) and r_i(0) are the coordinates of atom i at specific time t=t and t=0, and the bracket represents the ensemble average. Figure 6 exhibits the mean square displacements of H_2O and H_3O^+ in Nafion and SPEEK matrix at 300 K.

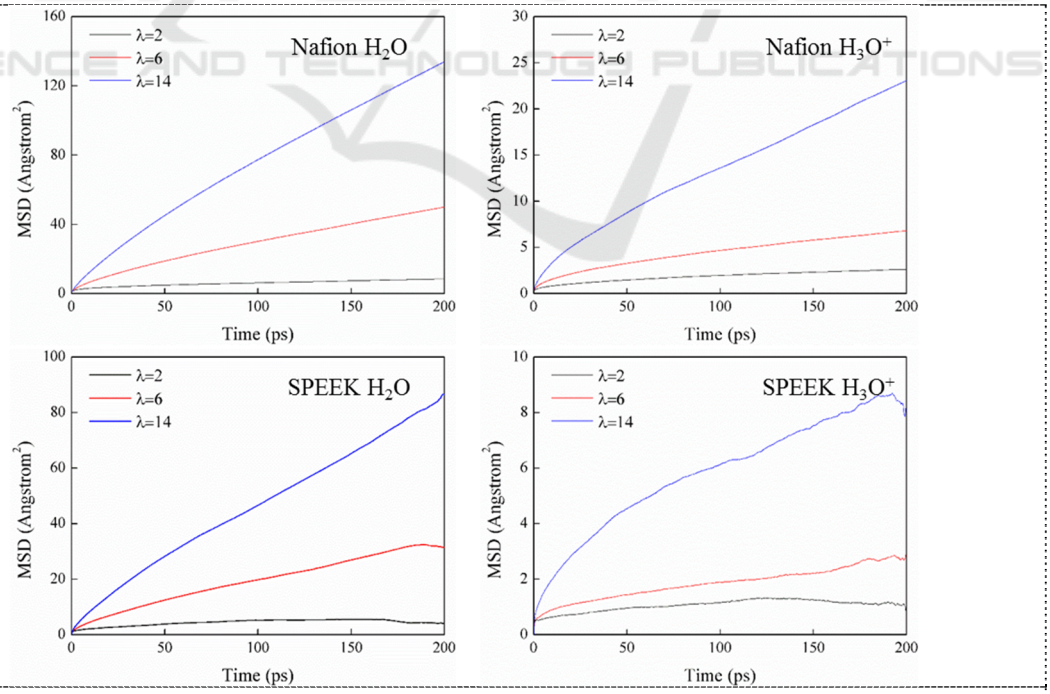

Figure 6. Mean square displacements of H_2O and H_3O^+ in Nafion and SPEEK matrix at 300 K.

With the increasing of hydration level, the MSD of H_2O and H_3O^+ increase gradually. This will lead to an increase in proton conductivity. In comparison with Nafion, SPEEK presents lower MSD of H_2O and H_3O^+, suggesting a lower proton transfer. This could be attributed to the worse phase separation morphology in SPEEK than that of Nafion.

4. Conclusions

As one of the promising alternatives for Nafion, SPEEK possesses good chemical stability and thermal stability, low cost, high mechanical stability, but poor hydrophilic cluster morphology and insufficient proton conductivity. In this study, MD was performed to investigate the hydrophilic cluster morphology and diffusion behavior of Nafion and SPEEK. SPEEK shows poorer phase separation and much smaller hydrophilic channels especially at low hydration levels. This might be caused by the lower electronegativity of H than that F and higher steric hindrance of SPEEK backbone. Consequently, much lower mobility of H_2O and H_3O^+ are revealed for SPEEK. With increasing hydration levels, the hydrophilic clusters are developed to be wide and connected proton conducting channels, and H_3O^+ mobility is enhanced as well. Therefore, a higher proton transfer is expected at higher relative humidity.

Acknowledgment

The authors thank the financial support of the Natural Science Foundation of Hebei Province (Grant no. B2018502046) and the Fundamental Research Funds for the Central Universities (Grant no. 2016MS110 and 2016MS111).

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