Experiment and simulation studies on SPEEK PEM with different sulfonation degrees

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Abstract. Effects of degrees of sulfonation (DS) on the cluster aggregation, proton conductivity and mechanical properties of sulfonated poly ether ether ketone (SPEEK) proton exchange membranes (PEMs) were investigated by experiment and simulation studies. SPEEK materials with different DS and the corresponding PEMs had been prepared by sulfonation and solution casting. The water uptake, swelling ratio, proton conductivity and mechanical properties of SPEEK PEMs were greatly affected by DS. And the hydrophilic cluster aggregation in SPEEK of different DS was revealed by molecular simulation. The relationship between structure and performance of SPEEK membrane provides theoretical guidance for the preparation of high performance proton exchange membranes.

1. Introduction
Because of high efficiency and zero emission, proton exchange membrane fuel cell (PEMFC) is believed to be alternative energy conversion devices in mobile vehicles and power generations [1]. Proton exchange membrane (PEM) acts as a key component of PEMFC, which will directly dominate the performance and lifetime of the PEMFC [2].

Compared with other commonly used PEM materials in PEMFC, sulfonated poly ether ether ketone (SPEEK), a kind of non-fluorinated material, possesses good chemical stability and thermal stability, low cost, and high mechanical stability. However, as is the case with most non-fluorinated material, SPEEK PEMs are limited by poor hydrophilic cluster morphology and insufficient proton conductivity, resulting from low hydrophilic/hydrophobic difference and rigidity of the polymer backbone [3]. It’s well known that the increase of degrees of sulfonation (DS) would improve the hydrophilic cluster morphology and the proton conductivity as well. Nevertheless, serious deterioration in swelling and mechanical properties will be yielded by high DS. This study aim to investigate the effects of DS on the cluster aggregation, proton conductivity and mechanical properties of SPEEK PEMs by experiment and simulation studies.

2. Experiment and simulation detail

2.1. Preparation of SPEEK material and SPEEK membranes
According to our previous work [4], sulfonation preparation of SPEEK from PEEK was carried out from Poly(ether ether ketone) (PEEK) powder (Degussa, VESTAKEEP 4000 P: density 1.30 g cm\(^{-3}\)). SPEEK material with different DS was obtained by tuning the reaction time from 0.3 h to 1.5 h at 50 °C. Solution casting method was applied to fabricate SPEEK membranes.
2.2. Simulation

SPEEK chain composing of 10 monomers was adopted. The DS values of prepared SPEEK samples were determined by titration and adopted in molecular simulation. Due to chain rigidity and stiffness of SPEEK, initial density of 0.4 g cm\(^{-3}\) is set for the periodic cell to avoid ring spearing and catenation [5]. Table 1 exhibits the composition of each periodic cell of SPEEK with different DS. Annealing strategy used in this study was shown in figure 1.

Table 1. Construction of periodic cells of SPEEK with different DS.

| DS  | Number of SPEEK chain | Number of H\(_2\)O | Number of H\(_3\)O\(^+\) |
|-----|-----------------------|--------------------|--------------------------|
| 30% | 5                     | 30                 | 15                       |
| 40% | 5                     | 40                 | 20                       |
| 50% | 5                     | 50                 | 25                       |
| 60% | 5                     | 60                 | 30                       |
| 70% | 5                     | 70                 | 35                       |
| 80% | 5                     | 80                 | 40                       |

[Image: Amorphous Cell construction]

3. Results and discussion

3.1. Properties of SPEEK membranes

The DS values of SPEEK mentioned in this research were according to NaCl titration results. As the sulfonation time increased from 0.3 h to 1.5 h, the DS values of SPEEK samples varied from 20% to 70%. This proves that the DS of SPEEK polymers could be easily controlled by sulfonation time.

Figure 2 shows the water uptake, swelling ratio, proton conductivity and XRD spectra of SPEEK membranes with different DS. Enhanced proton conductivity was observed with increasing DS. However, SPEEK sample with a DS of 54% exhibited excessive swelling (as high as 40%) at 80 °C, indicating a decline in dimensional stability of the SPEEK membranes with higher concentrations of sulfonic acid groups. Moreover, as reported in our previous publication [4], tensile strength and modulus of SPEEK samples decreased with increasing DS. When the DS of SPEEK increase from 35% to 54%, tensile strength and modulus of SPEEK membranes gradually decrease from 33.20 MPa and 1156.89 MPa to 23.79 MPa and 564.24 MPa.
Figure 2. Water uptake (a), swelling ratio (b), proton conductivity (c) and XRD spectra (d) of SPEEK membranes with different DS.

3.2. Molecular simulation results
To explore hydrophilic cluster morphology of SPEEK membranes with different DS, MD simulation was performed. The dispersion of H$_2$O and H$_3$O$^+$ was investigated by molecular dynamic simulation. The result was shown in figure 3. With increasing DS, H$_2$O content increases proportionally. Consequently, the hydrophilic clusters, composed of H$_2$O and H$_3$O$^+$, become expanded and connected, resulting in wide and connected proton conducting channels.

![Final snapshot of H$_2$O and H$_3$O$^+$ in SPEEK matrix. Red, oxygen in H$_2$O and H$_3$O$^+$; white, hydrogen in H$_2$O and H$_3$O$^+$; other atoms were set as invisible.](image)
Mean square displacement (MSD) analysis at 300 K was carried out to study the effects of such cluster morphology on the mobility of H$_3$O$^+$ according to equation (1) [6],

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

where $r_i(0)$ and $r_i(t)$ denote the coordinates of atom i at specific time $t=0$ and $t=t$ respectively, and the bracket represents the ensemble average. Figure 4 reveals the mean square displacements of H$_3$O$^+$ in SPEEK matrix at 300 K. As shown in figure 4, with the increasing of DS, the MSD of H$_3$O$^+$ at 300 K was improved gradually. With enhanced H$_3$O$^+$ mobility, a higher proton transfer is expected, which is consistent with the result of proton conductivity in figure 2c.

![Figure 4. Mean square displacements of H$_3$O$^+$ in SPEEK matrix at 300 K.](image)

4. Conclusion
Enhanced water uptake and proton conductivity of SPEEK membranes are observed with increasing DS. However, SPEEK sample with a DS of 54% exhibits excessive swelling (as high as 40% at 80 °C) and poor mechanical properties, indicating a decline in dimensional stability and mechanical stability. Furthermore, MD simulation was conducted to explore the cluster morphology of SPEEK membranes with different DS. With increasing DS, the hydrophilic clusters are developed to be wide and connected proton conducting channels, and H$_3$O$^+$ mobility is enhanced as well. Therefore, a higher proton transfer is expected, which is consistent with the result of proton conductivity.

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