Effect of Polyethylene Glycol on Sulfonated Polyether Imide (SPEI) for Fuel Cell Applications1

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Abstract—The sulfonated polyetherimide (sPEI) was synthesized by direct sulfonation method using chlorosulfonic acid as a sulfonating agent. Different sulfonation degrees of sPEI was obtained by varying the ratio of PEI to chlorosulfonic acid and reaction time. Then, sulfonated polyetherimide was blended with polyethylene glycol (PEG) and thermally cross-linked in order to achieve high performance proton exchange membrane. It was found that the addition of PEG resulted in a significant increase in porosity and water uptake of the membranes, which favored proton transport at low temperature. The maximum proton conductivity was 11 mS/cm at 75°C for the blend membrane containing 20% PEG. The sulfonation and blend modification of PEI were characterized by attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy.

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INTRODUCTION

Proton exchange membrane fuel cells (PEMFC) are one of the promising energy sources because of their high power conversion and environmentally friendly system [1–3]. Proton exchange membrane is the critical part of the fuel cell which provides the continuous ion transport channels. Consequently, characteristic optimization of the proton exchange membrane is one of the research priorities of PEMFC’s researchers [4, 5]. Perfluorinated polymer membranes such as Nafion on account of their excellent chemical and thermal stability and high proton conductivity in the hydrated state have been widely used as the proton exchange membrane in PEMFCs [6]. However, the high cost of these polymers still hinders the widespread application and commercialization of PEMFCs [7].

For this reason, extensive attempts have been made to consider alternative sulfonated aromatic polymers (SAPs) such as sulfonated poly(ether ether ketone) (SPEEK) [8–10], sulfonated poly(ether sulfone) (SPES) [11–13], sulfonated poly(ether sulfone ketone) [14], sulfonated poly phenyl sulfone (SPPSU) [15], and sulfonated poly benzimidazole (SPBI) [16–18]. However, the polyaromatic backbone rigidity and the acidic groups anchored on their main chain prevent the continuous ion transport channels from forming distinct phase-separated structures, thereby decreasing transport of protons. Thus, it should be noted that formation of water mediated pathways for proton transport is also required in these polymers [19]. Therefore, it is expected that proton conductivity of the membranes enhances by increasing their water uptake and sulfonic acid concentration.

Different methods have been followed to introduce new polymeric membrane using nanofiller [20–24], blend modification [25, 26] and cross-linking treatment [27–32]. The blending of polymers is a simple method to enhance polymer electrolyte membrane (PEM) performance. The hydrophilic polymer such as PEG was commonly used as a cross-linker agent for blending with some sulfonated polymer such as sulfonated polyimide and sulfonated polyether ketone [16, 18, 33]. In fact, PEG as a cross-linker agent can be placed between the sPEI chains and improve their hydrophilicity. In related studies, Bai et al. introduced diamine terminated PEG to modify properties of sulfonated polyimide membrane (sPI) [34–36]. There are a few researchers that have investigated thermal cross-linking treatment of blend membrane. Liu et al. reported thermal cross-linking treatment of poly(aryl ether ketone) with carboxylic acid groups [37].

1The article is published in the original.
over, Mikhailenko et al. investigated properties of cross-linked sulfonated poly(ether ether ketone). Heat treatment of sPEEK in the presence of ethylene glycol or glycerol and properties of the prepared membrane was also investigated by Mikhailenko and co-workers [28, 35].

The present work describes the development of blend modification and cross-linking treatment to modify proton exchange membrane properties. In this study, we utilized chlorosulfonic acid to synthesize sulfonated polyetherimide (sPEI). PEG with molecular weight of 400 g/mol was used as a hydrophilic polymer and a cross-linker agent in the preparation and modification of proton exchange membrane based on PEI. We have tried to investigate the effect of PEG content on water uptake and proton conductivity behavior of PEI-based membrane.

EXPERIMENTAL

Materials

Polyetherimide (PEI, Ultem1000) was dried under vacuum oven at 90°C before use. Polyethylene glycol 400 (PEG, P3265), chlorosulphonic acid (CSA), dichloroethane (DCE), dimethyl acetamide (DMAc), isopropanol, deionized water (DI water), sodium chloride (NaCl), phenolphthalein (pH indicator) were used as received. All these chemicals were purchased from Aldrich.

Table 1. Designation of sPEI samples

<table>
<thead>
<tr>
<th>Sample designation</th>
<th>Mole ratio of CSA/PEI repeat unit</th>
<th>Reaction time, h</th>
</tr>
</thead>
<tbody>
<tr>
<td>sPEI-1</td>
<td>0.6</td>
<td>2</td>
</tr>
<tr>
<td>sPEI-2</td>
<td>0.6</td>
<td>4</td>
</tr>
<tr>
<td>sPEI-3</td>
<td>0.6</td>
<td>8</td>
</tr>
<tr>
<td>sPEI-4</td>
<td>1.2</td>
<td>2</td>
</tr>
<tr>
<td>sPEI-5</td>
<td>1.2</td>
<td>4</td>
</tr>
<tr>
<td>sPEI-6</td>
<td>1.2</td>
<td>8</td>
</tr>
<tr>
<td>sPEI-7</td>
<td>1.8</td>
<td>2</td>
</tr>
</tbody>
</table>

Table 2. Composition of the sPEI-based blend membranes

<table>
<thead>
<tr>
<th>Sample designation</th>
<th>sPEI, wt %</th>
<th>PEG, wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>sPEI</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>sPEI-5PEG</td>
<td>95</td>
<td>5</td>
</tr>
<tr>
<td>sPEI-10PEG</td>
<td>90</td>
<td>10</td>
</tr>
<tr>
<td>sPEI-15PEG</td>
<td>85</td>
<td>15</td>
</tr>
<tr>
<td>sPEI-20PEG</td>
<td>80</td>
<td>20</td>
</tr>
</tbody>
</table>

Preparation of Sulfonated PEI (sPEI)

Briefly, this modification was performed in a 250 mL lab reactor which was equipped with a constant-pressure dropping funnel containing diluted chlorosulphonic acid. The PEI (5 g) was dissolved in dichloroethane (30 mL) and chlorosulphonic acid was added slowly to the solution under N₂ atmosphere at room temperature. The solution was stirred strongly at 30°C. Finally, the obtained sulfonated PEI was precipitated in isopropanol and washed several times with distilled water. The sulfonated PEI was dried under reduced pressure at 90°C. Different sulfonation degree of sPEI was obtained by varying the ratio of PEI to chlorosulfonic acid and reaction time. Designation of the samples and the detailed conditions of each sample are summarized in Table 1.

Preparation of Membrane

Designation of the samples and the detailed composition of all membranes are summarized in Table 2. sPEI-6 was selected and dissolved in DMAc solvent in order to prepare a 20 wt % polymer/solvent solution. A desired amount of PEG was dissolved in DMAc and stirred strongly at room temperature. Then, PEI solution was added to the PEG solution, and the mixture was stirred at room temperature for 24 h. The mixture of sPEI/PEG was then casted onto a glass plates and drying at 80°C for 12 h. Finally, the prepared membranes were heat-treated in vacuum oven at 60, 80, 100, and 120°C for 2 h and 135°C for 8 h in order to induce thermal cross-linking reaction. The thickness of all membranes were measured with a digital micrometer in the range of 65 to 85 microns.

Characterization

ATR-FTIR. Chemical structure of the sPEI membranes were characterized by a Bruker Tensor 27 attenuated total reflectance–Fourier transform infrared spectroscopy (Bruker Instruments, Darmstadt, Germany). Field emission scanning electronic microscopy (FESEM) (Zeiss SUPRA 35VP) was used to examine the morphology of PEI-based blend membranes. Cross cuts of the membrane were prepared by breaking them under liquid nitrogen. The FESEM micrographs of cross-section of the membrane were taken at various magnifications.

Water uptake (WU). The hydrophilicity of the prepared membranes was determined by water uptake measurements at room temperature. The dry membranes were firstly weighted and then immersed in deionized water for three days to obtain a well-wet membranes. The water uptake of membrane was then calculated according to the following Eq. (1):

\[
WU = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100, \tag{1}
\]
where $W_{\text{dry}}$ is the weight of dried membrane and $W_{\text{wet}}$ is the weight of the wet membrane [27].

**Ion-exchange capacity (IEC).** The ion-exchange capacity of membranes was calculated by titration. As the first step, the sPEI membranes were soaked in saturated NaCl solution for 12 h in order to exchange their protons with sodium ions. Then, this solution was titrated with 0.01 M NaOH solution and phenolphthalein as an indicator [28]. The IEC was calculated according to the following Eq. (2):

$$\text{IEC} = \frac{V \times M}{m},$$

where $V$ is volume of the NaOH consumed in the titration; $M$ is the molar concentration of the NaOH; and $m$ is the weight of dried membranes.

**Degree of sulfonation (DS).** Degree of sulfonation was measured based on IEC, which can be calculated according to the following Eq. (3) [29]:

$$\text{DS} = \frac{M_{\text{polymer}} \times \text{IEC}}{1 - M_{\text{SO}_{2}\text{H}} \times \text{IEC}} - 1.$$

where $M_{\text{polymer}}$ is the molar mass of PEI and $M_{\text{SO}_{2}\text{H}}$ is the molar mass of the sulfonic acid group. The $\lambda$ value represents the number of water molecules per sulfonic acid site which can be calculated by the Eq. (4) [30].

$$\lambda = \frac{1000 \times W_{\text{U}}}{18 \times \text{IEC}}.$$

**Proton conductivity ($\sigma$).** The proton conductivity of the membranes was measured by an AC impedance analyzer (PARSTAT 2273). For this analysis, the membranes were cut into a 1.5 cm$^2$ rectangle samples, and were kept in DI water overnight to achieve a fully-hydrated membrane. The sample was placed between the two electrodes in the cell. The proton conductivity was calculated as [31]:

$$\sigma = \frac{D}{RA},$$

where $\sigma$ is the proton conductivity (s/cm), $R$ is the ohmic resistance of the membrane (Ω), $D$ is the thickness of the membrane sample (cm), and $A$ is the surface area of the membrane sample (cm$^2$).

**RESULTS AND DISCUSSION**

The chlorosulfonic acid is one of the most commonly used sulfonating agents and it can be used for direct sulfonation of most materials. Direct sulfonation of polymers commonly uses in order to provide sulfonic acid functionality, thereby enhancing hydrophilicity of polymers [38]. The sulfonation of PEI with chlorosulfonic acid is shown in Scheme 1. PEI with different degree of sulfonation (DS) was designed (as mentioned in section “Preparation of Sulfonated PEI (sPEI)”).

![Scheme 1](https://via.placeholder.com/150)

Table 3. Properties of sulfonated PEI samples

<table>
<thead>
<tr>
<th>Sample designation</th>
<th>IEC, meq/g</th>
<th>DS, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPEI-1</td>
<td>1.34</td>
<td>50</td>
</tr>
<tr>
<td>SPEI-2</td>
<td>1.51</td>
<td>57</td>
</tr>
<tr>
<td>SPEI-3</td>
<td>1.69</td>
<td>65</td>
</tr>
<tr>
<td>SPEI-4</td>
<td>1.48</td>
<td>56</td>
</tr>
<tr>
<td>SPEI-5</td>
<td>1.60</td>
<td>61</td>
</tr>
<tr>
<td>SPEI-6</td>
<td>1.85</td>
<td>73</td>
</tr>
<tr>
<td>SPEI-7</td>
<td>1.50</td>
<td>57</td>
</tr>
</tbody>
</table>

It has been well-known that the IEC values directly depend on the content of the sulfonic acid groups present in the membrane. Hence, this parameter can be used to obtain optimum sulfonation condition and to choose desirable sulfonated polyetherimide sample. IEC value of the prepared
Sulfonated polyetherimide was determined and presented in Table 3.

From IEC value, the sulfonation degree of all membranes was also calculated by Eq. (3) and represented in Table 3. From Tables 2 and 3, it is observed that the sulfonation degree and IEC values of the membranes increase by increasing acid concentration and reaction time. Furthermore, sulfonated polyetherimide (sPEI-6) showed higher IEC and DS values in comparison with the other samples. Because of high sulfonation degree of the sPEI-6, this sample was employed for the preparation of sPEI/PEG blend membrane.

The successful sulfonation of sPEI-6 was also confirmed by ATR-FTIR. The characteristic bands of the sulfonic group can be observed in ATR-FTIR spectrum of the sulfonated PEI (Fig. 1, curve 2). For sulfonated PEI, the bands at around 1019 and 1167 cm⁻¹ can be assigned to the symmetric vibration of the sulfonic group [8, 14]. The hydroxyl group band has also appeared at around 3300 cm⁻¹. Consequently, the ATR-FTIR spectra showed that the sPEI-6 has been successfully sulfonated.

As mentioned in introduction, the main disadvantage of polyaromatic-based membranes is their high rigidity which prevents the formation of continuous ion transport channels in membrane matrix. For this reason, PEG as a hydrophilic and cross-linker agent was used to enhance the performance of sPEI membrane for fuel cell application. As shown in Scheme 2,
PEG as a cross-linker agent can be placed between the sPEI chains. This cross-linking occurs by esterifying sulfonated PEI with PEG under heat treatment. Under such condition, it is expected that the blend modification of sPEI in the presence of PEG increases the distance between polymer chains and enhances the water absorption, thereby facilitating proton transport across sPEI-based membranes.

Scheme 2.

Presence of PEG in sPEI-based blend membrane was also detected and confirmed by ATR-FTIR analysis. For PEG, the characteristic bands of the hydroxyl and methylene groups appeared at around 3370 and 2850–2950 cm$^{-1}$, respectively (Fig. 2, curve 1). As shown in Fig. 2 (curves 2 and 3), the aliphatic C–H bands belonging to the PEG appear at about 2850–2950 cm$^{-1}$. The OH band of sulfonic group at around 3390 cm$^{-1}$ has overlapped with the OH bands of PEG.

fig. 2. ATR-FTIR spectra of (1) PEG, (2) sPEI-20PEG (before heat treatment), and (3) sPEI-20PEG (after heat treatment).
However, ATR-FTIR analysis did not show any obvious difference between the ATR-FTIR spectrum of sPEI/PEG blend membrane before and after cross-linking heat treatment.

For this reason, changes in the color and solubility of sPEI/PEG blend membranes before and after heat treatment was done to confirm the occurrence of cross-linking reaction. The color and solubility of membranes significantly changed after heat treatment. Heat treatment of the prepared membrane resulted in an obvious color change from white to light brown [27, 28]. Insolubility of the heat-treated membranes in hot water (80°C for 48 h) further confirms that the cross-linking reaction occurs.

In fact, the ion exchange capacity and water content of membranes are very important factors that affect proton transport across membranes. In fact, the IEC value demonstrates the actual ion exchange sites available for proton conductivity [13]. The IEC values of the sPEI-based blend membranes were also determined and presented in Table 4. It can be observed that the IEC values decrease from 1.85 to 1.70 (mmol/g) with increasing PEG ratio, which can be attributed to the decreasing content of sulfonic acid group or decreasing ratio of sPEI in the membrane.

The absorbed water by the membrane as a proton carrier and proton hopping sites play a key and complex role in the proton transport phenomena. In fact, the state of absorbed water and its amount are key determinants of the predominant mechanism of proton conduction across membrane. However, the high amount of water taken up by the membranes leads to poor mechanical properties of the membrane. This case affects the performance of the proton exchange membrane in fuel cell applications [30]. The water uptake of all membranes was determined and given in Table 4. The sPEI-based blend membranes showed higher water uptake in comparison with the pure sPEI membrane. Furthermore, it is clearly realized that the water uptake of blend membranes also increases by increasing PEG content.

The cross-sections of sPEI-based blend membranes were analyzed using SEM to observe the effect of PEG content on membrane morphology. The SEM micrographs of the sPEI-based blend membranes show a tendency toward larger average pore size and a broader pore size distribution by the increase of PEG content. This result can be attributed to hydrophilcity of the PEG. From Fig. 4, it is also observed that the blend membrane containing 20% PEG absorb more water than other blend membranes. According to these results (Fig. 3 and 4), there is a good agreement between the SEM image and water uptake values. In fact, the honey comb-like structure and high porosity of these membranes can provide free volumes to absorb water molecules and thereby increasing the water uptake.

The water uptake of these blend membranes at high temperature was also determined. Figure 3 shows the water uptake as a function of temperature for all membranes after 24 hours soaking in water. A significant increase in water uptake was observed for all blend membranes by increasing temperature which can be attributed to increasing polymer chain segmental mobility and thereby enhancing water diffusion in the membrane matrix.

Proton conductivity of all membranes at 25 and 75°C was calculated by Eq. (5) and represented in Table 4. For both proposed temperatures, it is clear from this Fig. 5 that the proton conductivity was improved with increasing PEG content. In fact, the proton conductivity increased with PEG content due to the increase of absorbed water molecules which can act as proton carriers. Referring to the literatures [39], the Grotthuss mechanism and vehicular diffusion as the predominant modes of proton conduction were proposed to describe the proton conduction. In the vehicle mechanism, the proton diffusion across membrane occurs in combination with solvent molecules as proton carriers. Subsequently, it is necessary that membranes have a sufficient water uptake content to play a proton carrier role in vehicle mechanism. Since the water content of membrane increases, transport of proton together with water molecules also increases. In fact, water molecules as proton carriers can induce continuous proton transport pathways in the membrane matrix and improve the proton conductivity of proton exchange membranes. This reason led to the total increase of proton transport, whereas the IEC value of blend membranes decreases.
Fig. 4. Field emission scanning electron microscope images of the cross section of sPEI-based blend membrane with different PEG content: (A) 5, (B) 10, (C) 15, and (D) 20% with (1) low and (2) high magnification.
In this study, sulfonated polyetherimide membranes were prepared by chlorosulfonic acid as a sulfonating agent and then they were blended with PEG. The prepared blend membrane (sPEI/PEG) was heat treated to modify blend membrane in order to enhance mechanical stability and improve the efficiency of sPEI-based blend membrane in PEMFC applications. ATR-FTIR spectroscopy confirmed sulfonation of PEI. It was found that the introducing of PEG leads to the significant increase in porosity which favored the water uptake and proton transport at ambient temperature. The water uptake and proton conductivity of all blend membranes increased by increasing PEG content. However, the PEI-based blend membrane showed a decrease in IEC and DS values with increasing PEG content, which can be attributed to the decreasing sPEI ratio in the membrane. The color change and insolubility of the heat-treated membranes in hot water confirmed thermal cross-linking treatment of blend membrane.

CONCLUSIONS

Fig. 5. Proton conductivity of sPEI-based blend membranes as a function of SPEI/PEG ratio at (1) 25 and (2) 75°C.

REFERENCES