



## Hydrophilic Domain Contribution on the Proton Transport Properties of Sulfonated Polysulfone Based Blend Membranes

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The application of sulfonated polysulfone (SPSF) as a charged membrane is limited by its degree of substitution due to its high water solubility that affects the membrane mechanical strength. However, this type of polymer also has a high effective charge that can increase the proton conductivity of the membrane. To optimize these properties, SPSF was blended with its unmodified polymer, polysulfone (PSF), to form a blend membrane consisting of hydrophilic domain from SPSF and hydrophobic domain from PSF. The blend membranes were synthesized by mixing the polymers at 1:1 and 1:2 weight compositions of SPSF and PSF in dimethylacetamide (DMAc), respectively, and casting to form a thin polymer film by evaporation. In order to maintain the mechanical strength, the SPSF polymer chains were ionically cross-linked using Ba<sup>2+</sup> ions. The presence of cross-link agent is crucial, but it can also reduce the effective charge. Thus only a small amount of BaCl<sub>2</sub> was introduced to the blend. The concentration of cross-link agent (BaCl<sub>2</sub>) from 0.1 to 0.5 % w/w was varied to study its effect on membrane effective charge and proton conductivity. The resulting membranes were characterized to determine the ionic exchange capacity (IEC) by titration, the water content by gravimetry, hydrophilicity of the surface by contact angle meter, the ionic transport properties by membrane potential measurements, and the proton conductivity by conductivity measurements using Wheatstone bridge at 50 Hz. In this study, the physicochemical properties of blend membranes are compared with the SPSF one and then discussed, focusing on the formation of hydrophilic domain by blending, the effect of cross-link agent, and its contribution on the proton conductivity.

Penerapan *sulfonated polysulfone* (SPSF) sebagai membran bermuatan terbatas oleh tingkat substitusi karena kelarutan air yang tinggi akan mempengaruhi kekuatan mekanik membran. Namun, polimer jenis ini juga memiliki muatan efektif tinggi yang dapat meningkatkan konduktivitas proton membran. Untuk mengoptimalkan sifat-sifat ini, SPSF dicampur dengan polimernya yang tidak dimodifikasi, *polysulfone* (PSF), untuk membentuk membran *blend* yang terdiri dari domain hidrofilik SPSF dan domain hidrofobik PSF. Membran *blend* disintesis dengan mencampurkan polimer dengan komposisi 1:1 dan 1:2 antara SPSF dan PSF dalam larutan *dimethylacetamide* (DMAc), yang kemudian dicetak membentuk film polimer tipis dengan cara penguapan. Untuk menjaga kekuatan mekanik, ion Ba<sup>2+</sup> ditambahkan untuk membentuk *ionically cross-linking* diantara rantai-rantai polimer SPSF. Kehadiran agen *cross-link* sangatlah penting, tetapi juga dapat mengurangi muatan efektif membran. Oleh karena itu hanya sejumlah kecil BaCl<sub>2</sub> yang boleh ditambahkan ke dalam campuran. Konsentrasi agen *cross-link* (BaCl<sub>2</sub>) divariasikan dari 0,1 hingga 0,5 % w/w untuk mempelajari pengaruhnya terhadap muatan efektif membran dan konduktivitas proton. Membran yang dihasilkan dikarakterisasi untuk menentukan kapasitas penukar ion (IEC) dengan cara titrasi, kadar air dengan metode gravimetri, hidrofilitas permukaan dengan pengukuran sudut kontak, sifat transportasi ionik dengan pengukuran potensial membran dan konduktivitas proton melalui pengukuran konduktivitas menggunakan jembatan Wheatstone pada frekuensi 50 Hz. Dalam penelitian ini, sifat fisikokimia membran *blend* dibandingkan dengan membran SPSF, yang kemudian dibahas dengan fokus pada pembentukan domain hidrofilik dalam proses *blending*, efek agen *cross-link*, serta kontribusinya pada konduktivitas proton.

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## Introduction

In the proton-exchange membrane fuel cell (PEMFC) applications, Nafion is the most widely used as the membrane electrolyte component due to its advantages, such as good mechanical and thermal stability and high proton conductivity (0,08 S cm<sup>-1</sup>).<sup>1-3</sup> However, regardless of its excellent properties, Nafion has some drawbacks, in-

cluding high production cost, high methanol permeability, and dehydration process in a high-temperature operation that has to be overcome for broad applications and commercialization of PEMFC.<sup>2-4</sup> One of the solutions is to find an alternative material that suitable as a membrane electrolyte to replace Nafion.

Sulfonated polysulfone (SPSF), commonly used as a negatively charged membrane in electrodialysis, is one of the alternative materials for membrane electrolyte in fuel cell applications. Polysulfone (PSF) as a backbone polymer has some advantages among other polymers, such as good mechanical strength, high thermal stability, low price, and ease of processing.<sup>3-5</sup> Moreover, introducing sulfonate groups into polymer chains to form SPSF, a strong negatively charged polyelectrolyte, leads to decrease the methanol permeability with respect to Nafion.<sup>4</sup> Thus, it also becomes a potential candidate as the membrane electrolyte in the direct methanol fuel cell (DMFC).

The application of SPSF as a charged membrane is naturally limited by its degree of substitution due to its high water solubility. The degree of substitution affects the membrane mechanical strength. An extensive sulfonation leads to swell the polymers and, even to some extent, can convert them into a water-soluble polymer.<sup>5</sup> Thus, the membrane made of this type of polymer, is only suitable for applications that require low mechanical strength. However, this type of polymer also has a high effective charge that might play important role to increase the proton conductivity of the membrane.

To optimize those properties, the degree of sulfonation must be high, while maintaining the strong interaction between polymer chains to keep the membrane in a solid form. One of the solutions is by blending the polymer with another compatible polymer and/or by adding a cross-linking agent. In this study, SPSF was blended with its unmodified polymer (PSF) to form a blend membrane that consists of hydrophilic domains from SPSF and hydrophobic domains from PSF. In order to maintain the mechanical strength, the SPSF polymer chains were ionically cross-linked using Ba<sup>2+</sup> ions. Here, we focused on the effects of cross-link agent concentration and the mass ratio of SPSF/PSF on the membrane ionic transport properties and hydrophilicity.

## Experimental Methods

### Materials

Udel PSF (MW=35.000 Da) was obtained from Union carbide. Chloroform, chlorosulfonic acid, hydrochloric acid, sulfuric acid, barium chloride, sodium hydroxide, and N,N-dimethylacetamide (DMAc) were purchased from Merck with analytical grade and used without further purification.

### Methods

#### Sulfonation of Polysulfone

The PSF was sulfonated according to the procedure previously described by Nagarale et al.<sup>6</sup> Ten grams of PSF pellets are dissolved in 100 mL Chloroform. Each solution was kept in an ice bath at 0 °C. Chlorosulfonic acid in chloroform with concentration of 10 % v/v is added dropwise to the PSF solution, with the temperature kept constant at 0 °C. The resulting reaction mixture was stirred for 30 minutes. After the complete addition of the mixed solution, the po-

lymer was precipitated in 500 mL methanol, which then washed with methanol until it was free of acid and dried in an oven at 60 °C.

### Membrane Preparation

The SPSF/PSF blend membranes were cast from SPSF/PSF solution via phase inversion technique by evaporation. The SPSF/PSF solution was prepared by dissolving the polymers with a total mass fraction of 25 % in DMAc. Here, two types of blend membranes were prepared with different SPSF/PSF mass ratio of 1:1 and 1:2, respectively. Further, the cross-link agent (BaCl<sub>2</sub>) was added into the polymer solution at various concentrations from 0.1 to 0.5 % w/w and stirred vigorously. The blend solution was spread over a glass surface and dried at ambient before later dried in the oven at 60 °C to remove the residual solvent completely.

### Characterization

#### 1. Ion-exchange capacity (IEC)

The ion exchange capacity (IEC) was determined by the titration method according to the previously described procedure by Smitha et al.<sup>3</sup> Here, the value of IEC is calculated using the following equation:

$$IEC = \frac{(B-P) \times 0.01 \times 5}{m} \quad (1)$$

where IEC is the ion exchange capacity (meq g<sup>-1</sup>), B is the required volume of sulfuric acid to neutralize the blind sample soaked in NaOH (mL), P is the required volume of sulfuric acid to neutralize the sulfonated membrane soaked in NaOH (mL), 0.01 is the normality of the sulfuric acid solution, 5 is the factor that corresponds to the ratio between the amount of NaOH taken to dissolved the polymer and the amount that used for titration and m is the mass of sample (g).

#### 2. Contact Angle Measurement

The contact angle of the membrane surface against water was measured by a contact angle meter, model Cam-plus Micro (Tantec Inc.). Here, deionized water was dropped onto the surface of the membrane using a microliter syringe and then the contact angle was measured.

#### 3. Water Uptake

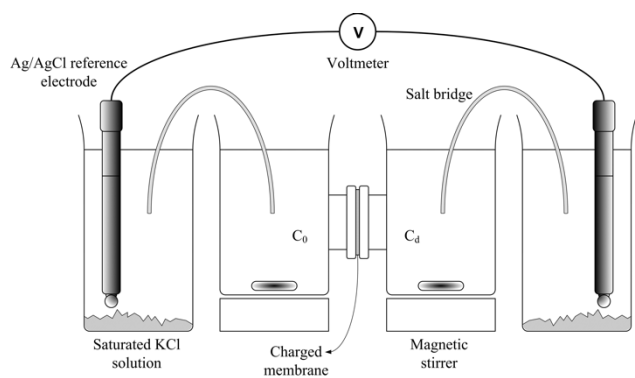
The membranes were dried in the oven at 60 °C for at least 18 h before weighing to obtain the dry sample weight. The membranes were soaked in deionized water at least 18 h. The excess water on the surface of the wetted membrane was removed using tissue paper before weighing. The water uptake can be calculated by the following equation:<sup>7</sup>

$$W_U(\%) = \frac{w_b - w_d}{w_d} \times 100\% \quad (2)$$

where w<sub>b</sub> and w<sub>d</sub> are the masses of wet and dried samples, respectively.

#### 4. Membrane Potential Measurement

The measurement setup of the membrane potential is shown in Figure 1. The membrane was placed between two compartments. In the left compartment, the concentration of KCl solution was kept constant at 0.001 M. In contrast, in the right compartment, the concentration of KCl solution were varied from 0.001 M to 2 M. Ag/AgCl glass reference electrodes connected to digital multimeter (Sanwa CD800a) were used to measure the membrane potential.<sup>8</sup>



**Figure 1.** The schematic of membrane potential measurement setup.

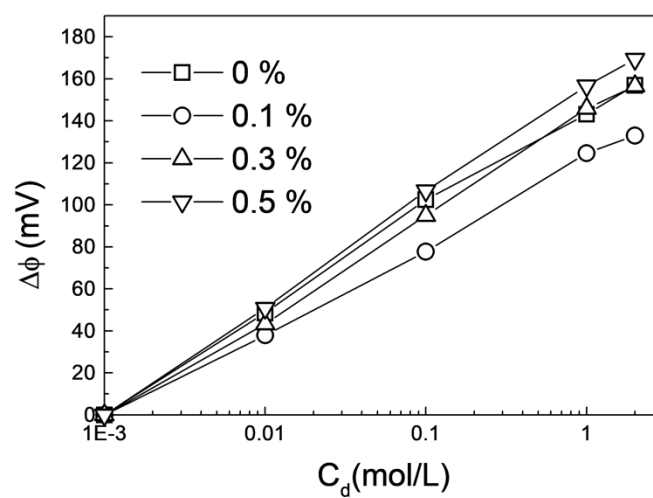
### 5. Proton Conductivity Measurement

The membranes were soaked in HCl 1 M solution for one night and then washed with deionized water until neutral. The membranes were later cut in the same size as the electrodes of the conductivity meter. In wet conditions, the membrane was clipped between the electrodes and the conductivity was measured with the conductivity meter bridge model 31 at 50 Hz.

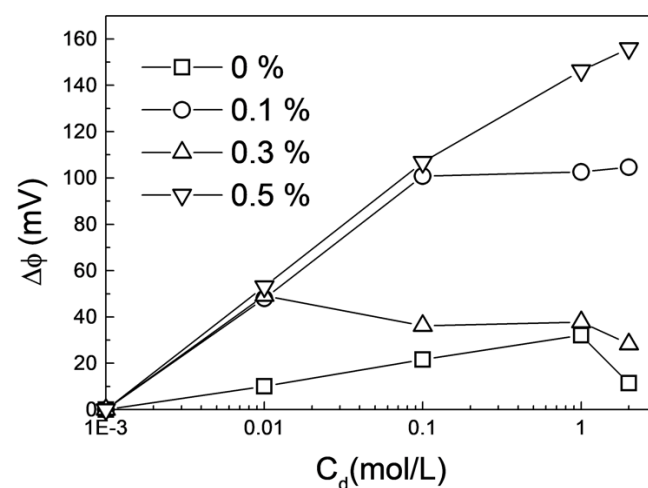
### Result and Discussion

Figure 2 shows the membrane potential of SPSF/PSF blend membranes for two different weight ratios of SPSF/PSF at various cross-link agent concentrations. If we compare the behaviour shown in Figure 2a and 2b, we can see the effect of PSF concentration in the membrane blend. The increase of PSF concentration might perturb the membrane structure then leads to the decrease of membrane potential. However, the introduction of  $Ba^{2+}$  ions that act as ionic bridges improves the membrane potential, especially in the membrane with low SPSF content.

The introduction of  $Ba^{2+}$  ions improves the membrane surface hydrophilicity, as shown by the decrease of contact angle (Figure 3a). On the other hand, they show different behaviour in bulk hydrophilicity, as reflected from the water uptake measurements (Figure 3b). In the case of SPSF/PSF 1:1, the small amount of  $Ba^{2+}$  ions decreases the water uptake significantly, while further addition increases it. This might occur due to the charge neutralization that leads the membrane to become more hydrophobic. Still, the further increase of cross-link agents might induce a more homogeneous hydrophilic cluster formation that increases the bulk hydrophilicity of the membrane. The membrane with lower SPSF content (SPSF/PSF 1:2) shows a slight increase in water uptake before follows the same behaviour as membranes with SPSF/PSF 1:1. The same behaviour between these two types of membranes at high concentration of  $Ba^{2+}$  proves that the cross-linking agent plays an important role in membrane bulk hydrophilicity.



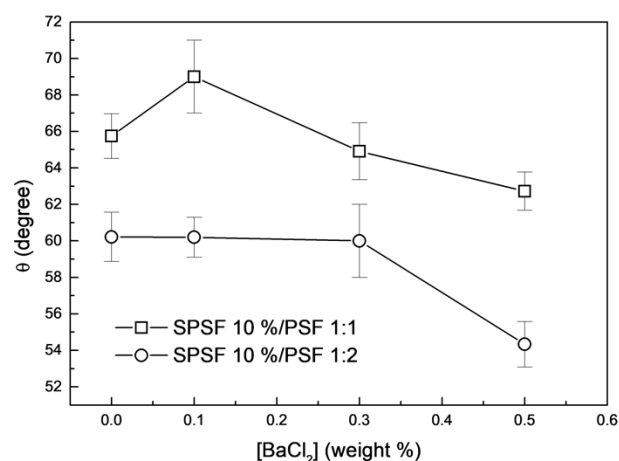
(a)



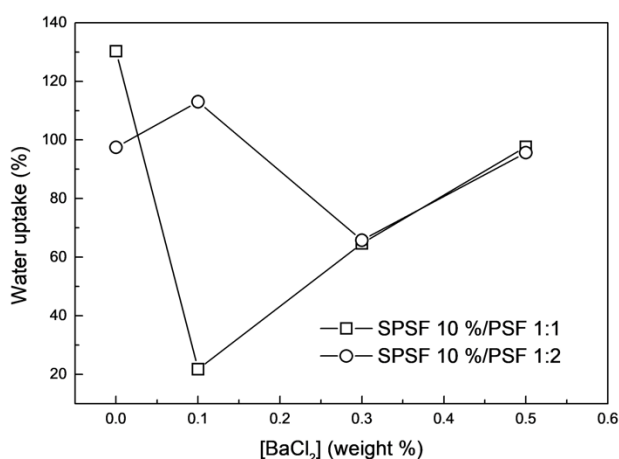
(b)

**Figure 2.** Membrane potentials of SPSF/PSF blend membranes with various cross-link agent concentration for (a) SPSF/PSF 1:1 and (b) SPSF/PSF 1:2.

Figure 4a shows the results of proton conductivity measurements. Here, the membrane with low SPSF content (SPSF/PSF 1:2) shows better performance than the membrane with high SPSF content (SPSF/PSF 1:1). This behaviour is fascinating, which is usually should be in the contrary. Moreover, the cross-link agent concentration also improves the proton conductivity until an optimum value then starts to decrease, which could be explained from the fixed charge neutralization. If we verify with those results with the IEC value, as shown in Figure 4b, we found that membranes with low SPSF content also have higher IEC value than the higher one.



(a)



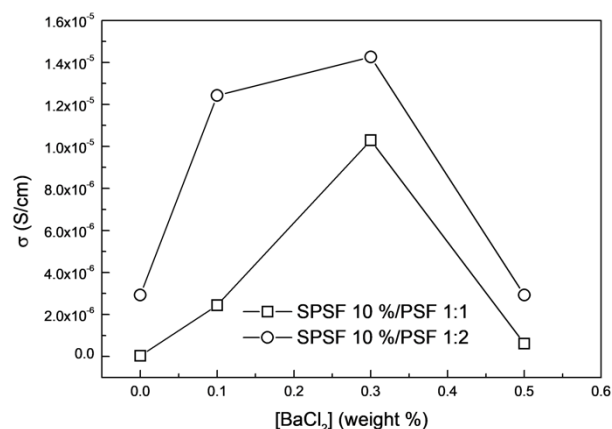
(b)

**Figure 3.** The effect of cross-link agent concentration on (a) water contact angle, and (b) water uptake of the SPSF/PSF blend membranes.

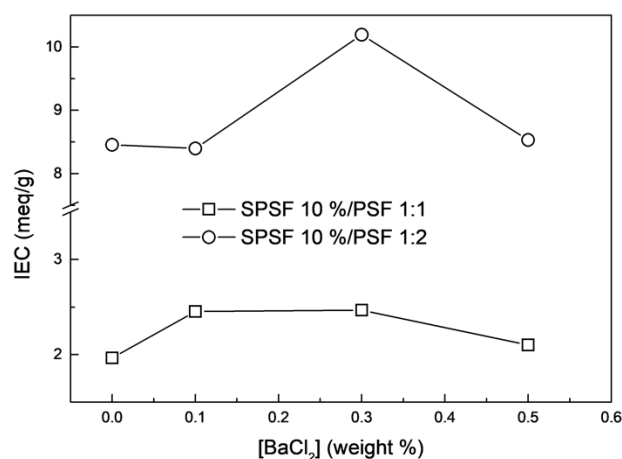
Moreover, they also show the same effect of cross-link agent concentration, where they increase the IEC value up to an optimum before start to fall. Thus, the presence of both hydrophobic domain from PSF and the cross-linking agent can induce the polymer chains to form a certain structure during membrane formation. The fixed charged groups become more active in facilitating ionic transport. This type of structure formation may due to the phase segregation of polymer mixture, where hydrophilic sub-phase percolates in the hydrophobic domains to form hydrophilic clusters that enhance the proton conductivity.<sup>9,10</sup>

The proton conductivity can be increased further if the fixed charged groups inside the membrane are delocalized.<sup>11</sup> Here, the fixed charges delocalization will induce a formation of less interacting water clusters that resemble the free water with the highest proton conductivity through the Grotthuss mechanism.<sup>10</sup> In our case, the presence of PSF in membrane provides the hydrophobic domains for the formation of hydrophilic clusters. At the same

time, the addition of  $Ba^{2+}$  ions might help the fixed charges delocalization besides forming the ionic bridges to improve the mechanical strength.



(a)



(b)

**Figure 4.** The effect of cross-link agent concentration on (a) proton conductivity and (b) Ion exchange capacity of SPSF/PSF blend membranes.

## Conclusion

The introduction of PSF into SPSF to form a blend membrane is observed to activate the function of fixed charged groups inside the membrane, thus facilitate transport of ions. The presence of  $Ba^{2+}$  ions as ionic cross-link bridges improves the membrane transport properties, especially the proton conductivity and its function as an ionic barrier. Moreover,  $Ba^{2+}$  ions also make the membrane becomes more hydrophilic as deduced from their contact angle and water uptake. However, the information concerning phase segregation and hydrophilic clusters formation has to be verified and studied further.

## Conflicts of Interest

There are no conflicts to declare.

## Acknowledgments

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## References

- 1 R. Souzy and B. Ameduri, Functional fluoropolymers for fuel cell membranes, *Prog. Polym. Sci.*, 2005, **30**, 644–687.
- 2 B. Smitha, S. Sridhar, and A.A. Khan, Solid polymer electrolyte membranes for fuel cell applications—a review, *J. Memb. Sci.*, 2005, **259**, 10–26.
- 3 B. Smitha, S. Sridhar and A.A. Khan, Synthesis and characterization proton conducting polymer membrane for fuel cell, *J. Memb. Sci.*, 2003, **225**, 63–76.
- 4 Y.-Z. Fu and A. Manthiram, Synthesis and characterization of sulfonated polysulfon membranes for direct methanol fuel cells, *J. of Power Sources*, 2006, **157**, 222-225.
- 5 J.A. Kerres, Development of ionomer membrane for fuel cells, *J. Memb. Sci.*, 2001, **185**, 3–27.
- 6 R.K. Nagarale, G.S. Gohil, V.K. Shahi, and R. Rangarajan, Preparation and electrochemical characterization of sulfonated polysulfone cation-exchange membranes: Effects of the solvents on the degree of sulfonation, *J. Appl. Polym. Sci.*, 2005, **96**, 2344–2351.
- 7 J. Won, H.H. Park, Y.J. Kim, S.W. Choi, H.Y. Ha, I.-H. Oh, H.S. Kim, Y.S. Kang, and K.J. Ihn, Fixation of nanosized proton transport channels in membranes, *Macromolecules*, 2003, **36**, 3228–3234.
- 8 V. Suendo, M. Minagawa, and A. Tanioka, Membrane potential of bipolar membrane: the effect of concentration perturbation of the intermediate phase around a certain value, *J. Electroanal. Chem.*, 2002, **520**, 29–39.
- 9 S.S. Jang, V. Molinero, T. Cagun, and W. A. Goddard III, Nanophase-segregation and transport in Nafion 117 from molecular dynamics simulations: Effect of monomeric sequence, *J. Phys. Chem. B*, 2004, **108**, 3149–3157.
- 10 E. Spohr, P. Commer, and A.A. Kornyshev, Enhancing proton mobility in polymer electrolyte membranes: Lessons from molecular dynamics simulations, *J. Phys. Chem. B*, 2002, **106**, 10560–10569.
- 11 B. Piluharto, V. Suendo, T. Ciptati, C. L. Radiman, Strong correlation between membrane effective fixed charge and proton conductivity in the sulfonated polysulfone cation-exchange membranes, *Ionics*, 2011, **17**, 229–238.