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Preparation of High Performance SPEEK/Cloisite 15A Nanocomposite Membrane via Advanced Membrane Formulation Method

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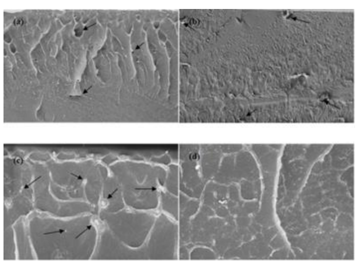
Graphical abstract



Abstract

Sulfonated poly (ether ether ketone) (SPEEK)/Cloisite 15A® nanocomposite membranes were prepared via solution intercalation method. For better dispersion of nanoclay in the polymer matrix, the solution intercalation method was modified and a compatibilizer was introduced. The state of nanoclay dispersion was determined by FESEM. The effect of the solution formulation preparation method and compatibilizer on the performance properties such as proton conductivity and methanol permeability of all membranes was studied. FESEM analysis confirmed that SPEEK/Cloisite 15A® nanocomposite membrane prepared via modified solution intercalation method and in the presence of compatibilizer was the best membrane in terms of its morphological structure. Due to its well nanoclay distribution in polymer matrix, this kind of membrane exhibited the highest selectivity owing to its high proton conductivity and low methanol permeability. SPEEK/Cloisite 15A® with compatibilizer prepared via modified solution intercalation method was found to be the best membrane.

Keywords: SPEEK; Cloisite 15A®; 2,4,6-triaminopyrimidine; nanocomposite; DMFC

■1.0 INTRODUCTION

Polymer-inorganic nanocomposite materials have been extensively investigated for direct methanol fuel cell (DMFC), and have the potential to provide a solution to the trade-off problem of polymeric membranes. For instant, many polymer-inorganic nanocomposite membranes show much lower methanol permeability but similar or even improved proton conductivities compared to the corresponding pure polymer membranes and even commercial Nafion® membranes [1-3]. The nanocomposite materials may combine the advantages of each material, i.e., the flexibility and processability of polymers, and the selectivity and thermal stability of the inorganic fillers.

The performance of a DMFC is always pronounce by the ratio of proton conductivity to methanol permeability or so called membrane selectivity. Thus, adding inorganic nanofillers may affect the membrane cell performance in two ways, i.e., the uniform nanosized distribution of inorganic filler particles produces a winding diffusion pathway towards methanol to migrate through the nanocomposite membrane and the complete exfoliation morphology allows more cations to mobile and available for conduction [4].

Therefore, a number of studies have been focused on the type of modification of Nafion® and aromatic polymers using different kinds of approaches and preparation methods for producing exfoliated nanocomposite membranes for DMFC applications [5-7]. Due to the difference in polarity between the aromatic polymers (non-polar) and the filler (polar), different methods can be followed to improve the compatibility between the clay and the polymer [8]. Among the available aromatic polymers, sulfonated aromatic poly(ether ether ketone) (SPEEK) is a promising candidate for its functional group (sulfonic acid) reactivity in which could provide a good contact between its polymer backbones and the fillers. Instead of using natural silicate clays such as montmorillonite (MMT), the commercially organically modified MMT clay, i.e., Cloisite 15A® was used. However, from the preliminary study, it was found that there was still lack of compatibility between them [9]. Other approaches that have the potential in producing exfoliated polymer-inorganic nanocomposites were via formulation preparation method such as solution intercalation, in situ polymerization and sol-gel [10-12].

In the present study, solution intercalation process was used and was modified to intercalate SPEEK and Cloisite 15A® clays. Due to its beneficial effect on the methanol crossover problem owing to its high impermeability towards methanol and its special features (high aspect ratios) that can provide a winding diffusion pathway for methanol; it is worth taking any possible efforts to pronounce this high potential. Therefore, the introduction of functional compounds such as 2,4,6-

triaminopyrimidine as a compatibilizer was also employed along with the modified solution intercalation method for preparation of a homogenous SPEEK/Cloisite 15A® polymer-inorganic nanocomposite membrane. The prepared nanocomposite membranes were characterized in terms of their morphologies and performance properties.

2.0 EXPERIMENTAL

Sulfonating 63% of sulfonic acid group into poly (ether ether ketone) (PEEK) polymer base (Vitrex Inc., USA) was carried out according to the previously reported procedure [13]. SPEEK nanocomposite membranes were formulated different preparation methods, i.e., conventional solution intercalation or modified solution intercalation. The SPEEK nanocomposite formulation with different methods was prepared as discussed below:

(i) Conventional solution intercalation (without 2,4,6-triaminopyrimidine, TAP)

Sulfonated poly (ether ether ketone) (SPEEK) with 63% of DS (SP63) was dissolved in dimethylsulfoxide (DMSO) (Sigma-Aldrich) to produce a 10 wt. % solution. 0.1 g amounts of Cloisite 15A® clays (Southern Clay Products, Inc.) was added to a small amount of DMSO and was then vigorously stirred at 60°C for 2 h and then added to the SPEEK solution. Finally, the mixture was vigorously stirred at 60°C for 24 h.

(ii) Conventional solution intercalation (with TAP)

SP63 was dissolved in DMSO (Sigma-Aldrich) to produce a 10 wt. % solution. 0.1 g amounts of Cloisite 15A® clays and 0.1 g of TAP were added to a small amount of DMSO, then the mixture was vigorously stirred at 60°C for 2 h. Subsequently, the mixture was added into SPEEK solution and was vigorously stirred at 60°C for 24 h.

(iii) Modified solution intercalation (without TAP)

SP63 was dissolved in DMSO to produce a 10 wt. % solution. 0.1 g amounts of Cloisite 15A® clays was added to a small amount of DMSO and was vigorously stirred for 24 h at room temperature. The Cloisite 15A® solution was added into SPEEK solution and the mixture was again vigorously stirred for 24 h at room temperature. Before proceeding to the casting process, the mixture was heated to 100ºC to evaporate the DMSO solvent.

(*iv) Modified solution intercalation (with TAP)*

SP63 was dissolved in DMSO to produce a 10 wt. % solution. 0.1 g amounts of Cloisite 15A® clays was added to a small amount of DMSO. In another container 0.1 g of TAP was added to a small amount of DMSO. Then both solutions were stirred at room temperature for 24 h, separately. The Cloisite 15A® and TAP solutions were added together and were stirred again at room temperature for 24 h. Finally, the mixture was added into SPEEK solution and was vigorously stirred for 24 h at room temperature. Before proceeding to the casting process, the mixture was heated to 100ºC to evaporate the DMSO solvent. The total DMSO solution used for all the different methods was 90 ml.

All the SPEEK nanocomposite solutions prepared were cast according to the previously reported procedure [13].

For observing the dispersion of Cloisite 15A® in SPEEK nanocompoiste membranes, the JSM-6701F Field-Emission Scanning Electron Microscopy (FESEM) was used.

The proton conductivity measurement was conducted as described elsewhere [13]. The proton conductivity of membrane, σ (Scm^{-1}), was calculated according to the following equation:

$$\sigma = \frac{d}{RS} \tag{1}$$

where, d and S are the thickness of the hydrated membrane and the area of the membrane sample, respectively.

The methanol permeability of SPEEK and its nanocomposite membranes was measured as detailed described elsewhere [14]. Equation (2) expresses the methanol permeability of the membranes. The methanol permeability test was carried out for 3 h at room temperature. The methanol permeability, P, value was calculated using the following equation,

$$P = \alpha \times \frac{VB}{A} \times \frac{L}{CA} \tag{2}$$

where, P is methanol permeability, $\alpha = \frac{CB(t)}{(t - to)}$ the slope of linear interpolation of the plot of methanol concentration in the permeate compartment, C_B (t), versus time, t, V_B is the volume of the water compartment, A is the membrane cross-sectional area (effective area), L is thickness of the hydrated membrane and C_A is the concentration of methanol in the feed compartment, t_o is time lag, related to the diffusivity.

3.0 RESULTS AND DISCUSSION

3.1 SPEEK Nanocomposite Membranes

Table 1 shows the SPEEK nanocomposite membranes formulations prepared via different methods. All prepared membranes were based on the SPEEK with 63 % of DS and were incorporated with Cloisite 15A® alone or together with TAP. The performance of the prepared nanocomposite membranes were then discussed based on their morphological structural and performance properties such as proton conductivity, methanol permeability and selectivity.

Table 1 SPEEK nanocomposite membranes prepared via different methods

Sample designation	SPEEK (g)	Cloisite 15A®,Cl (g)	TAP (g)	Formulation preparation method
SP/Cl (1)	10	0.1	0	Conventional solution intercalation
SP/Cl (2)	10	0.1	0	Modified solution intercalation
SP/Cl/TAP (1)	10	0.1	0.1	Conventional solution intercalation
SP/Cl/TAP (2)	10	0.1	0.1	Modified solution intercalation

3.2 Morphological Studies

Figure 1(a)-(d) illustrates the FESEM image of cross-section morphology of SP/Cl(1), SP/Cl(2), SP/Cl/TAP(1), SP/Cl/TAP(2), respectively. Although different magnifications were used to compare the tested membranes, the objective of this study to figure out the changes occurred when using different kind of methods was successfully achieved. From

Figure 1(a), it is clearly shows that SP/Cl prepared via conventional solution intercalation method performed the worst morphology. The arrows show large voids up to 2 µm which were produced by the abandonment of Cloisite 15A® particles that did not completely attached to the SPEEK polymer ring. When SP/Cl is prepared via modified solution intercalation method, FESEM image in Figure 1(b) shows a better Cloisite 15A® particles dispersion. It can be seen that the Cloisite 15A® particles completely attached to SPEEK polymer backbone performed no non-occupied micro-void. However, the agglomeration of the Cloisite 15A® particles was still large with up to 5 µm and there was gap between the Cloisite 15A® particles and the SPEEK polymer matrix. Therefore, TAP was introduced into SPEEK/ Cloisite 15A® formulation to enhance the compatibility between SPEEK and Cloisite 15A®. Figure 1(c) shows the SP/Cl/TAP(1) image with more uniform distribution of Cloisite 15A® compared to SP/Cl(1) and SP/Cl(2). The Cloisite 15A® particles were well connected with the SPEEK polymer matrices. However, the agglomeration size of Cloisite 15A® particles is still large which was in the range of 0.1 to 1 µm. Interestingly, the SP/Cl/TAP(2) cross-section image shows a uniform distribution of Cloisite 15A® particles throughout the SPEEK matrices. Most of the Cloisite 15A® particles that have been distributed in SP/Cl/TAP(2) membrane were less than 250 nm size. Due to its rich availability of hydrogen atoms in its chemical structure, TAP was successfully attached SPEEK and Cloisite 15A® via hydrogen bonding [9]. It was also suggested that the modified solution intercalation method that has been used to prepare SP/Cl/TAP was successfully provide a separate medium to each materials to achieve their homogeneity in their solvent before gone through further mixing process to enhance their compatibility.

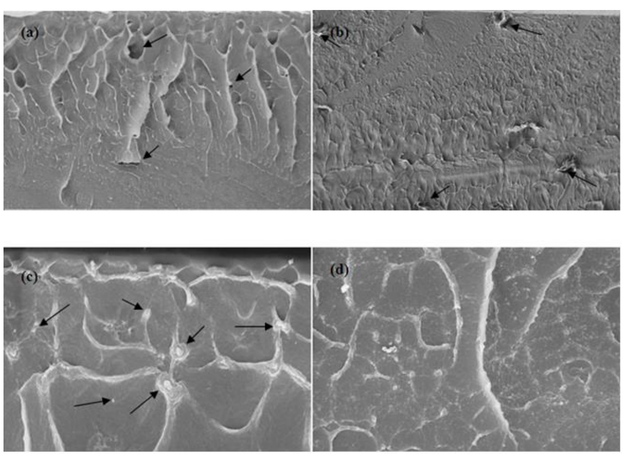


Figure 1 FESEM image of cross-section morphology of (a) SP/Cl(1), (b) SP/Cl(2), (c) SP/Cl/TAP(1) and (d) SP/Cl/TAP(2)

3.2 Proton Conductivity

Figure 2 shows the proton conductivity as a function of different methods used to prepare the nanocomposite membranes dope solution. The proton conductivities increase gradually from SPEEK/ Cloisite 15A® prepared via conventional solution intercalation method to the SPEEK/ Cloisite 15A® prepared via modified solution intercalation method in the presence of TAP. The highest proton conductivity achieved was 1.06×10^{-3} Scm^{-1} which was recorded from SP/Cl/TAP(2) membrane. This achievement was contributed by the well dispersion of inorganic fillers morphology in which could possibly yield the highest ionic conductivity since more cations could be mobile and available for conduction [4]. It was suggested that, a serious agglomeration of Cloisite 15A® particles in the SPEEK polymer matrix will limit the beneficial effect of the SPEEK and Cloisite 15A®. This is because the agglomeration of Cloisite 15A® may limit the separation of the sulfonic acid network structure from SPEEK thus reduce the conduction of proton activities [2]. This behavior consequently decrease the proton conductivity of such membrane as exhibited by SP/Cl(1).

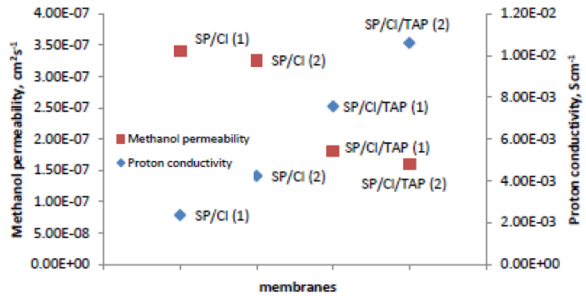


Figure 2 Proton conductivities and methanol permeabilities of SPEEK nanocomposite membranes as a function of different formulation preparation methods

3.3 Methanol Permeability

In general, incorporation of silicate layers into polyelectrolytes restricts the accessible nanometric channels for migration methanol molecules [15]. This was due to the exclusive features of silicate layers that possess higher length that its width. This uniqueness provides a longer pathway towards methanol travelling around the particles to across the membrane [1]. However, unawareness on the morphological structural of the nanocomposites may decline this benefit behavior.

Figure 2 shows the methanol permeability decreases from SP/Cl(1); SP/Cl(2); SP/Cl/TAP(1) to SP/Cl/TAP(2). It was clearly shown that the methanol permeability of SP/Cl/TAP(2) was the lowest among the tested membranes. This finding indicated that a uniform distribution of Cloisite 15A® particles pronounced the uniqueness of the impermeable inorganic particles to restrict the diffusion of methanol molecules [16]. This observation was in good agreement with the morphology study.

3.3 Selectivity

Although the presence of Cloisite 15A® has a beneficial influence on methanol permeability, it affects the proton conductivity adversely. In this regard, to determine the optimum composition among prepared membranes, their selectivity parameter was calculated. The selectivity values of SPEEK nanocomposites prepared via different methods are shown in Figure 3. Generally, higher selectivity value leads to better membrane performance. The maximum selectivity parameter among the prepared nanocomposite membranes was calculated to be about 66,300 $Sscm^{-3}$ for SP/Cl/TAP(2). This value was found to be approximately 9 times greater than SPEEK/Cloisite 15A® nanocomposite membrane prepared via conventional solution intercalation method with a selectivity parameter of about 6,920 $Sscm^{-3}$.

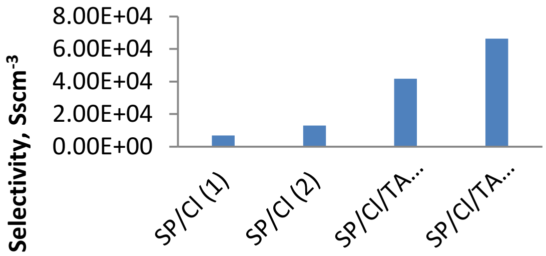


Figure 3 Membrane selectivity of SPEEK nanocomposite membranes prepared via different formulation preparation methods

4.0 CONCLUSION

A series of newly SPEEK nanocomposite membranes prepared via different formulation preparation methods have been successfully studied for DMFC applications. The modified solution intercalation method in the presence of 2,4,6-triaminopyrimidine (TAP) (SP/Cl/TAP(2) offered a good compatibility between SPEEK based polymer and Cloisite 15A® nanoclays thus demonstrated a homogenous phase with a good dispersion of Cloisite 15A® as observed by FESEM images. This good intercalation structure was thus performed acceptable proton conductivity and significantly low methanol permeability and consequently exhibited the highest membrane selectivity. Therefore, SP/Cl/TAP(2) nanocomposite membrane have the potential to be used as proton exchange membrane for DMFC applications.

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References

[1] Thomassin, J. M., Pagnoulle, C., Caldarella, G., Germain, A., Jerome, R. 2006. Contribution of Nanoclays to the Barrier Properties of a Model Proton Exchange Membrane for Fuel Cell Application. *J. Membr. Sci*. 270: 50–56.

[2] Lin, Y. F., Yen, C. Y., Hung, C. H., Hsiao, Y. H., Ma, C. C. M. 2007. A Novel Composite Membranes Based on Sulfonated MMT Modified Nafion for DMFC. *J. Power Source*. 168: 162–166.

[3] Chuang, S. W., Hsu, S. L. C., Hsu, C. L. 2007. Synthesis and Properties of Fluorine-containing Polybenzimidazole/Montmorillonite Nanocomposite Membranes fFor Direct Methanol Fuel Cell Applications. *J. Power Sources*. 168: 172–177.

[4] Wang, M., Dong, S. 2007. Enhanced Electrochemical Properties of Nanocomposite Polymer Electrolyte Based on Copolymer with Exfoliated Clays. *J. Power Sources*. 170: 425–432.

[5] Gosalawit, R., Chirachanchai, S., Shishatskiy, S., Nunes, S. P. 2008. Sulfonated Montmorillonite/sulfonated Poly(ether ether ketone) (SMMT/SPEEK) Nanocomposite Membrane f0or Direct Methanol Fuel Cells (DMFCs). *J. Membr. Sci*. 323: 337–346.

[6] Hasani-Sadrabadi, M. M., Dashtimoghadam, E., Ghaffarian, S. R., Hasani Sadrabadi, M. H., Heidari, M., Moaddel, H. 2010. Novel High-performance Nanocomposite Proton Exchange Membranes Based on Poly (ether sulfone). *Renewable Energy*. 35: 226–231.

[7] Tripathi, B. P., Kumar, M., Shahi, V. K. 2009. Highly Stable Proton Conducting Nanocomposite Polymer Electrolyte Membrane (PEM) Prepared by Pore Modifications: An Extremely Low Methanol Permeable PEM. *J. Membr. Sci.* 327: 145–154.

[8] Villaluenga, J. P. G., Khayet, M., Valentin, J. L., Seoane, B., Mengual, J. I. 2007. Gas Transport Properties of Polypropylene/clay Composite Membranes. *Eur. Polym. J.* 43: 1132–1143.

[9] Jaafar, J., Ismail, A.F., Matsuura, T. 2009. Preparation and Barrier Properties of SPEEK/Cloisite 15A®/TAP Nanocomposite Membrane For DMFC Application. *J. Membr. Sci.* 345: 119–127.

[10] Kim, T. K., Kang, M., Choi, Y. S., Kim, H. K., Lee, W., Chang, H., Seung, D. 2007. Preparation of Nafion-sulfonated Clay Nanocomposite Membrane for Direct Methanol Fuel Cells via a Film Coating Process. *J. Power Sources*. 165: 1–8.

[11] Nunes, S. P., Ruffmann, Rikowski, B. E., Vetter, S., Richau, K. 2002. Inorganic Modification of Proton Conductive Polymer Membranes for Direct Methanol Fuel Cells. *J. Membr. Sci.* 203: 215–225.

[12] Iwata, M., Adachi, T., Tomidokoro, M., Noble, R. D. 1996. Organic-Inorganic Gas Separation Membranes: Preparation and Characterization. *J. Membr. Sci.* 116: 211–220.

[13] Jaafar, J., Ismail, A. F., Mustafa, A. 2007. Physicochemical Study of Poly(Ether Ether Ketone) Electrolyte Membranes Sulfonated with Mixtures of Fuming Sulfuric Acid and Sulfuric Acid for Direct Methanol Fuel Cell Application. *Mater. Sci. Eng., A.* 460–461: 475–484.

[14] Ismail, A. F., Othman, N. H., Mustafa, A. 2009. Sulfonated Polyether Ether Ketone Composite Membrane Using Tungstosilicic Acid Supported on Silica–aluminium Oxide for Direct Methanol Fuel Cell (DMFC). *J. Membr. Sci.* 329: 18–29.

[15] Cervantes-Uc, J. M., Cauich-Rodr´ıguez, J. V., Torres, H. V., Garfias-Mes´ıas, L. F., Paul, D. R. 2007. Thermal Degradation of Commercially Available Organoclays Studied by TGA-FTIR. *Thermochim. Acta.* 457: 92–102.

[16] Libby, B., Smyrl, W. H., Cussler, E. L. 2003. Polymer-zeolite Composite Membrane for Direct Methanol Fuel Cells. *AIChE J.* 49: 991–1001.