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The Effect of Nanoclay Loading on Physico-chemical Properties of SPEEK Electrolyte Membrane

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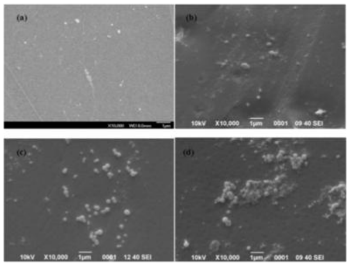
Graphical abstract



Abstract

Nanocomposite of SPEEK membrane was prepared by incorporating Cloisite15A® via solution interaction method to improve the physical-chemical properties of parent SPEEK membrane. Various weight of Cloisite15A® clays were added into SPEEK matrices. The physico-chemical properties of the SPEEK nanocomposites were studied based on morphological structure, liquid uptake, proton conductivity and methanol permeability as respect to the SPEEK with 63% of degree of sulfonation (DS). The distribution of Cloisite15A® particles in SPEEK matrices was confirmed by SEM analysis. The methanol permeability of the SPEEK nanocomposite membranes declined as the Cloisite15A® weight loading increased. The proton conductivity of SPEEK with 2.5 wt. % of Cloisite15A® loading exceeded that of parent SPEEK membrane. The influence of water behavior on the proton conductivity and methanol permeability was critically discussed. Owing to high proton conductivity and low methanol permeability SPEEK/Cloisite15A® nanocomposite membrane performed essentially improved selectivity with nine-fold higher than that of parent SPEEK.

Keywords: SPEEK; modified SPEEK membrane; Cloisite15A®; nanocomposite membrane; DMFC

■1.0 INTRODUCTION

Direct methanol fuel cell (DMFC) is considered as one promising environmental friendly, reliable and highly efficient power generation technology due to its low weight, high energy density, simplicity, low emission and the ease of handling their liquid fuel, are suitable for portable electronic devices and transportation applications.[1]

The crucial part of DMFCs is proton exchange membrane (PEM). The role of PEM is to provide proton conduction from the anode to the cathode and indeed it acts as an effective separator of the anode (methanol) and cathode (oxygen) reactants.[2] In such an application, perfluorosulfonic polymers such as Nafion® by DuPont show optimal characteristics as solid electrolytes for polymeric electrolyte fuel cells.[3] This unique polymer fulfils mechanical strength and chemical/thermal stability as well as high proton conductivity. In spite of these desirable properties, high methanol crossover and high cost are its critical limitations for DMFCs commercialization.[4]

Due to this awareness, there has been an intensive research effort towards the development of alternative membranes with potentially lower costs and better processability. Many polymers, such as sulfonated poly(ether sulfones), sulfonated poly(arylene ether sulfone), and various other polymeric systems have been described in the open literature.[5-8] However, the methanol permeability, in many cases, is still relatively high.

Due to limits in polymeric membrane performance, many research efforts have been focused on developing membranes with selective inorganic fillers. One such system is a nanocomposite membrane, which typically incorporates nanoscale filler such as montmorillonite (MMT) clays into a polymer matrix. The intent of this type of membrane is to take advantage of the good processability of polymers, remarkable barrier properties performance of MMT and low cost of overall systems.[9-12] The significant performance in terms of the MMT barrier properties towards methanol in polymer electrolyte membranes is always sacrificed by the poor compatibility between the MMT and polymer matrix. This reduced the selectivity performance of the nanocomposite membrane relative to the parent polymer.[13]

Therefore, rather than modifying the MMT in the lab scale, commercially available organically modified MMT (Cloisite15A®) was selected in the present research to prepare high-performance, cost-effective and easy to prepare hydrocarbon based nanocomposite membranes to achieve reduced methanol permeability. Subsequently the Cloisite15A® loadings dependency of the proton conductivity and methanol permeability properties of the fabricated membranes was investigated to evaluate the SPEEK/ Cloisite15A® membranes for DMFC applications.

■2.0 EXPERIMENTAL

Sulfonation process of poly (ether ether ketone) (PEEK) (Vitrex Inc., USA) was carried out according to the previously reported procedure.[14] Four sets of Sulfonated poly (ether ether ketone) (SPEEK) nanocomposite membranes with different additives loading were formulated via solution intercalation method and were namely as SP/1.0, SP2.5, SP/5.0 and SP/7.5 based on the Cloisite loading (wt. %). SPEEK with 63 % of DS was dissolved in Dimethylsulfoxide (DMSO) (Sigma-Aldrich) to produce a 10 wt. % solution. Various amounts of Cloisite15A® clays (Southern Clay Products, Inc.) and 2,4,6-triaminopyrimidine (TAP) (Sigma-Aldrich) were added to a small amount of DMSO in another container and the mixture was vigorously stirred for 24 h at room temperature. The latter mixture was then added to the SPEEK solution so that the total amount of DMSO becomes 90 mL. The SPEEK containing mixture was again vigorously stirred for 24 h at room temperature to produce a homogeneous solution. Before proceeding to the casting process, the mixture was heated to 100 ºC to evaporate the DMSO solvent. The casting process of the SPEEK nanocomposite was conducted according to the previously reported procedure.[14]

For observing the dispersion of Cloisite15A® in SPEEK/Cloisite15A®/TAP membrane, the JSM-6390LV Scanning Electron Microscopy (SEM) was used. The liquid uptake (water and methanol) measurement was performed according to the procedure as detailed elsewhere.[15] The water/methanol uptake was calculated as follows,

$$\text{Water/methanol uptake} = \frac{Wwet - Wdry}{Wdry} \times 100\% \qquad \textbf{(2.1)}$$

where, W_{wet} is the weight of the wet membrane and W_{dry} the weight of the dry membrane.

For hydrophilicity measurement, the contact angle (CA) of the membrane surface was measured using a VCA Optima Surface Analysis System (AST Products Inc., Billerica, MA) to determine the surface wettability of the membrane. Sample coupons with an area of about 5 cm x 1.5 cm were prepared by cutting pieces at random locations within the membrane sheet. The sample was placed on a glass plate and fixed with masking tape. Then, a drop of distilled water was placed on the sample surface using a micro syringe (Hamilton Company, Reno, NV). The contact angle was measured within a 30 second period after the water drop was placed. The CA was measured at three different spots on each membrane sample coupon and the results were presented as average data.

The proton conductivity measurement was conducted as described elsewhere.[14] The proton conductivity of membrane, σ (Scm^{-1}), was calculated according to the following equation:

$$\sigma = \frac{d}{RS} \qquad \textbf{(2.2)}$$

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.[16] Equation (2.3) 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,

$$P = \alpha \times \frac{VB}{A} \times \frac{L}{CA} \qquad \textbf{(2.3)}$$

where, P is methanol permeability, $\alpha = \frac{CB\quad t}{t\text{-}t_o}$ 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

Table 1 depicts the physical properties of SPEEK membranes with various levels of sulfonation. It can be seen that as the DS increases, the water uptake increase. This is because the introduction of sulfonic acid groups in PEEK polymer structure increases its solubility in polar solvent such as water. [17] Sulfonation is also gives a positive impact on proton conductivity.[7] As can be seen in Table 1, increasing the DS increase the proton conductivity but an undesirable effect on methanol permeability is obtained, whereby, methanol permeability declines with DS increment. Both properties are very closely related to the membrane selectivity which was expressed as the ratio of proton conductivity to methanol permeability. From Table 1, the highest membrane selectivity was 10.8 × 10^3 achieved by SP63. Owing to its sufficient water absorbed, higher proton conductivity and outstanding lower methanol permeabilities as compared to other SPEEK membranes prepared, SPEEK at 63 % of DS was found to be the optimum membrane to be further developed. Consequently, in this study, SPEEK nanocomposites formulation was prepared by incorporating various weight of Cloisite15A® to SP63. In order to determine the optimum Cloisite15A® weight loading in SPEEK matrix, a set of four SP63 samples incorporated with different weight loading of Cloisite15A® were prepared. Table 2 shows the sample designation of SPEEK with various loading of Cloisite15A®.

Table 1 Physico-chemical properties of SPEEK at different level of sulfonations

Sample	**Water uptake @ *RT (%)**	**Proton conductivity (mScm^{-1})**	**Methanol permeability x 10^7 ($\mathrm{cm}^2\mathrm{s}^{-1}$)**	**Membrane selectivity x 10^{-3} (Sscm^{-3})**
SP50	10.4 ±1.84	1.93±0.03	3.57±0.05	5.42±0.54
SP63	29.7±0.10	6.23±2.06	5.76±0.38	10.8±0.08
SP77	70.3±6.85	7.57±3.29	20.32±0.25	3.28±0.33
SP88	102.2±4.38	8.15±5.27	*soluble*	*soluble*

**RT = room temperature*

3.2 Morphological Studies

Figure 1 (a)-(d) illustrates the SEM surface images of SP/1.0, SP/2.5, SP63/5.0 and SP63/7.5 membranes, respectively. Whereas, Figure 2 (a)-(d) shows the SEM cross-section images of SP/1.0, SP/2.5, SP/5.0 and SP/7.5 membranes, respectively. Both SP/1.0 and SP/2.5 membranes showed a uniform Cloisite15A® distributions. Due to the lower amount of Cloisite15A® loaded in the SPEEK matrix, SP/1.0 membrane showed less amount of Cloisite15A® distribution than that of SP/2.5 membrane. Unfortunately, agglomeration regions appeared in SP/5.0 and become worse in SP/7.5 membrane. The result shows that the content of Cloisite15A® is too much when 5.0 wt. % and 7.0 wt. % of Cloisite15A® is added. Similar observation on polybenzimidazole/montmorillonite (PBI/MMT) nanocomposite membranes was reported by Chuang *et al.*[11]

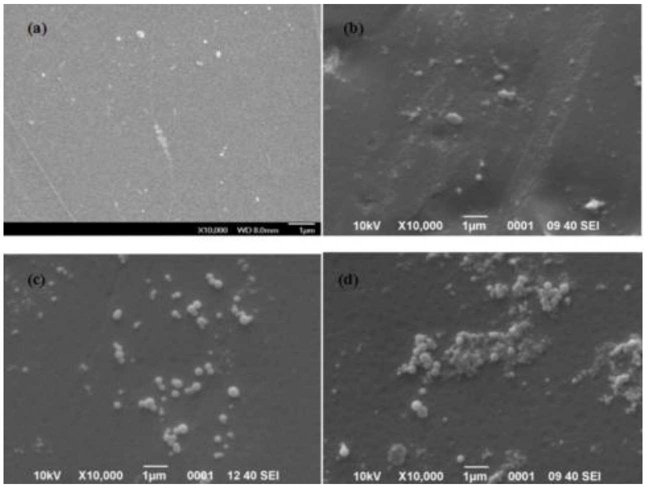


Figure 1 SEM surface image of (a) SP/1.0CL, (b) SP/2.5, (c) SP/5.0 and (d) SP/7.5 membranes

Similar observation can be seen from the SEM cross-section images of those composite membranes as showed in Figure 2 (a)-(d). SP/1.0 membrane shows uniform distribution of Cloisite particles. The largest size of Cloisite particle that can be seen is about 4µm. A number of voids also can be seen from SP/1.0 image. This indicated that the Cloisite particles were not completely attached to the SPEEK matrix. SP/2.5 shows a smoother cross-section image than that of SP/1.0. However, there is agglomeration of cloisite as large as 5µm as pointed by the white arrow. This explained that SP/2.5 was not completely exfoliated in SPEEK matrix. When 5.0 wt. % of Cloisite was added into SPEEK, more Cloisite agglomeration and voids observed. On the other hand, SPEEK with 7.5 wt. % of Cloisite indicates less voids but with worse agglomeration of Cloisite in the size of 10µm.

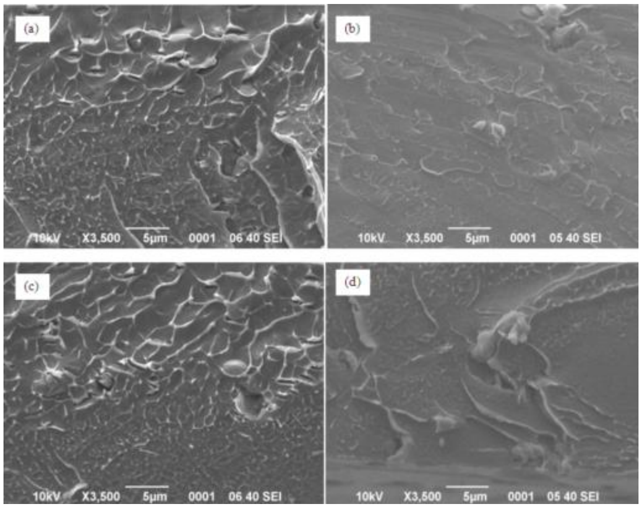


Figure 2 SEM cross-section image of (a) SP63/1.0CL, (b) SP63/2.5CL, (c) SP63/5.0CL and (d) SP63/7.5CL membranes

3.3 Liquid Uptake Study

Figure 3 illustrates the water and methanol uptake of parent SP63 and its composites with various weight of Cloisite15A® loading. As a rule, increasing the nanoclay inorganic material has a negative influence on liquid uptake such as water and methanol. This is because as the amount of inorganic material increased the amount of sulfonic acid groups in the polymer chain were decreased per unit volume.[18] However, some studies showed that the effect of dispersion state of fillers could enhance the wettability of the parent polymer and simultaneously contributing higher proton conductivity.[19] From the Figure 3, it was found that all SPEEK incorporated with Cloisite shows higher water uptake as compared to parent SPEEK. Based on the morphological structure images as illustrated in 2, it is most likely the wettability of the composite membranes was influenced by the dispersion state of the inorganic fillers. Hence, both excess sulfonic acid group and alkyl ammonium in SPEEK and Cloisite15A® layers, were able to coordinate with water molecules.[20]

The improvement in the hydrophilicity property of the nanocomposite material was further studied by conducting the contact angle experimental. Figure 4 illustrates the results observed from the contact angle testing. Apparently, the wettability of the SPEEK membrane was effectively improved in the presence of the Cloisite fillers. Unfortunately, at higher amount of Cloisite loading, i.e., 7.5 wt. %, the hydrophilicity of the membrane decreased dramatically. This is again must be due to the non-homogeneous of Cloisite dispersion. Compared to the results in water, the opposite influences of Cloisite on the uptake behaviors in methanol solution were obtained. The addition of Cloisite decreased the uptake of parent SPEEK membrane in methanol solution greatly. It is suggested that the existence of impermeable passive cloisite fillers has significantly limit the transportation of methanol molecules to pass through the composite membrane thus reduce the methanol uptake considerably. However, increasing the content of Cloisite continuously has no more remarkable influence on the absorption behaviors in methanol solution. The phenomena interesting us are that the uptakes of blend membranes in methanol solution are far lower than that in water in the presence of Cloisite. It was agreed that degree of swelling of polymeric membrane in solvent is proportional to the hydrogen bonding capability of solvent.[12]

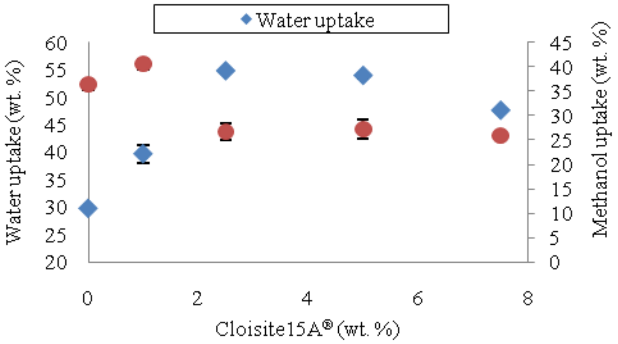


Figure 3 Water and methanol uptake of parent SP63

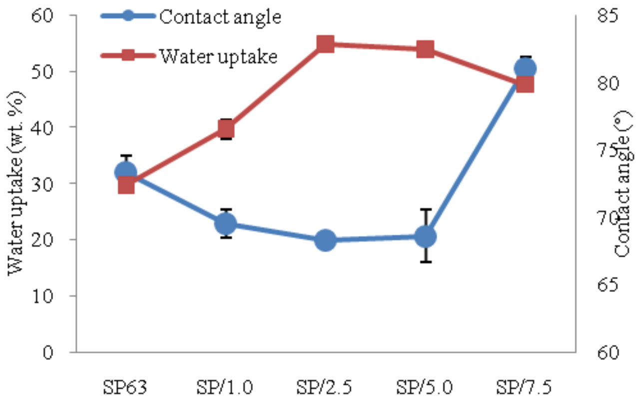


Figure 4. Contact angle of SPEEK nanocomposite membranes

3.4 Proton Conductivity

The ratio of conductivity to membrane thickness demonstrates the conductance of the membrane.[10] Table 2 compares the proton conductivity of SPEEK nanocomposites as a function of the membrane conductance (conductivity/thickness) as respected to the SP63. The thickness of membranes tested was in the range of 0.0040 cm to 0.0069 cm. As shown in Table 2, it seems that the membrane resistance does not show the dependency on the film thickness thus it can be deduced that the proton conductivities was mainly determined by the membrane area resistance. The proton conductivity is decreases with the increasing in membrane area resistance. This observation was in good agreement with the morphological study in which the membrane area resistance increases when the agglomeration of Cloisite15A® particles become worse. As expected SP/2.5CL membrane shows the highest conductance value. It was believed that the better dispersion of an adequate amount of Cloisite15A® in SPEEK provided a better ionic network cluster throughout the membrane to assist proton transport across the membrane. It was also suggested that the highly polar molecules such as protons take the advantages of migration not only via the interfacial space between SPEEK backbone and Cloisite15A® particles but also through the highly conductive of Cloisite15A® particles in which was also drives by the presence of water molecules absorbed by the Cloisite15A® particles.[20]

Table 2 Proton conductivity and its properties of SPEEK nanocomposite membranes

Membrane	**Thickness,d (μm)**	**Proton Cond,σ (mScm^{-1})**	**Resistance (Ω)**	**Conductance , σ/d (S)**
SP63	60	6.46	0.7	1.08
SP/1.0	40	4.24	0.71	1.06
SP/2.5	68	7.88	0.65	1.16
SP/5.0	69	4.02	1.29	0.58
SP/7.5	60	1.94	2.33	0.32

3.5 Methanol Permeability

The diffusion of methanol molecules in polymeric inorganic material is always depending on the water uptake behavior. [18] From Table 3 it was observed that methanol permeability decreased with increasing Cloisite15A® loading. This was due to the unique structure of the Cloisite15A® particle itself in which its length was far longer than that of its width.[13] If an intercalation or exfoliation microstructure arrangement is achieved, the unique Cloisite15A® structure could prolong the methanol permeation rate across the membrane. This advantage which was possesses by SP/2.5CL nanocomposite membrane was more pronounced than the water uptake effect that facilitate the methanol to across the membrane. This was found true because even though SP/2.5CL membrane showed the highest water uptake value, its methanol permeability still declined with the property. It was suggested that highly polar molecule such as water tend to migrate not only along the interfacial space between SPEEK and Cloisite15A® particles but also via the highly conducting pathway offered by the Cloisite15A® particles.[20] Fortunately, the impermeable Cloisite15A® particles refused to provide a mediate pathway towards a smaller polar molecule such as methanol.[21] This behavior significantly reduce the methanol permeability of the SP/2.5CL nanocomposite membrane thus performed a promising polymer electrolyte membrane for DMFC use. Table 3 also demonstrates that SP/2.5CL nanocomposite membrane exhibits the highest selectivity owing to its higher proton conductivity and lower methanol permeability than that of tested membrane. In particular, the selectivity of SP/2.5CL membrane increased the above ratio by 87% from the SP63 membrane. This achievement was contributed by the combination of the good proton conductor (SPEEK) and the impermeable highly crystalline Cloisite15A®.[22]

Table 3 Methanol permeability and selectivity of SPEEK nanocomposite membranes

Membrane	**Methanol permeability,P (cm^{2}s^{-1}) x10^8**	**Selectivity, (Sscm^{-3}) x10^{-4}**
SP63	55.9	1.16
SP/1.0	32.6	1.30
SP/2.5	8.99	8.77
SP/5.0	8.03	5.01
SP/7.5	4.89	3.97

■4.0 CONCLUSION

In the present work, a study of the influence of the addition of Cloisite15A® nanoclay on the properties of SPEEK polymer electrolyte membrane for DMFC application was successfully carried out. Conductivity and permeability characterization of SPEEK nanocomposite membranes revealed that the presence of Cloisite15A® has led to a drastic reduction of methanol crossover and higher conductivity in comparison with parent SPEEK membranes with similar degree of sulfonation. It is proposed that observed performance enhancement could be due to the unique features of the Cloisite15A® particle itself, i.e., good conductive material and highly impermeable towards methanol molecules. These behaviors were significantly assist the advantages possessed by SPEEK such as enriched with highly ionic groups (sulfonic acid) and the flexibility of its backbones in order to further enhance the performance properties of the membranes. Therefore, SPEEK/ Cloisite15A® nanocomposite membranes, due to their high proton conductivity, low methanol permeability and acceptable swelling stability, could be considered as promising polyelectrolyte membranes for DMFC applications.

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