Stability of SPEEK-Triaminopyrimide Polymer Electrolyte Membrane for Direct Methanol Fuel Cell Application
(Kestabilan Polimer Membran Elektrolit SPEEK-Triminopyrimidine untuk Aplikasi Sel Bahan Api Metanol Terus)

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ABSTRACT
Modification of sulfonated poly (ether ether ketone) (SPEEK) membrane was conducted by incorporating Cloisite 15A® clay and 2,4,6-triaminopyrimidine (TAP) via solution intercalation method. The effect of the Cloisite and TAP introduction was evaluated in terms of the membrane’s physicochemical and hydration properties. The membrane’s properties were compared among the SPEEK based membranes, including parent SPEEK, SPEEK/Cloisite and SPEEK/Cloisite 15A®/TAP. The uniform dispersion of Cloisite 15A® particles in SPEEK polymer matrices was confirmed by SEM analysis. The stability in water; in terms of dimensional change and dissolution, of the modified membrane was investigated and compared to the parent SPEEK membrane. SPEEK/Cloisite 15A®/TAP nanocomposite membrane exhibited the highest selectivity by means of the ratio of proton conductivity to methanol permeability. Owing to its higher proton conductivity and significantly lower methanol permeabilities and high stability in water environment, SPEEK/Cloisite 15A®/TAP nanocomposite membrane was found to be a potential alternative polymer electrolyte membrane for DMFC applications.

Keywords: Cloisite; direct methanol fuel cell; nanocomposite membranes; sulfonated poly (ether ether ketone); triaminopyrimidine

INTRODUCTION
Direct methanol fuel cells (DMFCs) have recently received lots of attention due to their high-energy density and their low emission of pollutants. Nafion (Du Pont), a commercially proton-conducting polymer membrane has been used in DMFCs, because this perfluorinated ionomer membrane has excellent chemical, mechanical and electrochemical properties as well as high proton conductivity at ambient temperature and high humidity condition. However, its high methanol permeabilities restrict its capability to be used in DMFCs. The methanol permeation not only causes loss of fuel but also forms a mixed potential at the cathode and leads to a lower electrochemical performance (ca. at over 40% methanol loss) of the DMFC (Akiba et al. 2006).

These drawbacks have prompted research on proton-conducting polymer membranes aimed at decreasing the methanol permeability, mainly by using different kind of aromatic polymers such as sulfonated poly (ether ether ketone) (SPEEK) (Li et al. 2003). Its water uptake, proton conductivity and methanol permeability of this potential SPEEK aromatic polymer can be controlled via sulfonation process. However, at high degree of sulfonation (DS) SPEEK membrane give a beneficial effect on the proton conductivity but it tends to swell in water thus resulting in high methanol permeability. Therefore, preparation of SPEEK incorporating with impermeable inorganic filler towards polar molecules such as water and methanol is crucial in order to fulfill the requirement of DMFCs. Nevertheless, poor compatibility between
aromatic polymer and inorganic filler will produce severe agglomeration of fillers in the polymer base matrices thus terminated the filler’s advantages itself. This behavior will deteriorate the barrier properties of the composite membrane system (Kim et al. 2007).

Due to this awareness, efforts to eliminate these unselective gaps produced from the incompatibility of the polymer and fillers often focused on the use of organic-surfactant by chemically or physically linking the two components to introduce a favorable interaction between the polymer and inorganic filler or by modifying the nanocomposite formulation method to prepare the intercalated/exfoliated nanocomposite membranes (Chuang et al. 2007; Genne et al. 1996). While recently, the study on the eliminating the presence of gaps between the polymer and inorganic filler by introducing a kind of compatibilizer such as Irganox 1010 and 2,4,6-triaminopyrimidine (TAP) was conducted for gas application (Frounchi et al. 2006; Song et al. 2004). Nevertheless, up to now there is scarce information on the study of the effect of compatibilizer incorporation in polymer matrix for direct methanol fuel cell (DMFC) application. Therefore, in the present study the beneficial effect of incorporating 2,4,6-triaminopyrimidine (TAP) as a compatibilizer to enhance the compatibility between SPEEK base polymer and Cloisite 15A nanoclays which resulting to a better Cloisite 15A particles dispersion and less agglomerations was discussed in terms of the nanocomposite membranes long term stability in water environment.

**EXPERIMENTAL DETAILS**

The sulfonation process of poly (ether ether ketone) (PEEK) (Vitrex Inc., USA) to produce sulfonated poly (ether ether ketone) (SPEEK) with degree of sulfonation (DS) of 63% (SP63) was carried out according to the previously reported procedure (Jaafar et al. 2009). SP63 polymer was dissolved in Dimethylsulfoxide (DMSO) (Sigma-Aldrich) to produce a 10 wt. % solution. Two SPEEK nanocomposite formulations were prepared; i.e., SPEEK incorporated with 2.5 wt. % of Cloisite 15A® (Southern Clay Products, Inc.) alone (SP63/2.5Cl) and SPEEK incorporated with 2.5 wt. % of Cloisite 15A® and 5.0 wt. % of 2,4,6-triaminopyrimidine (TAP) (Sigma-Aldrich). The formulations were prepared via solution intercalation method in which the amount of Cloisite 15A® was added to a small amount of DMSO in one container. In another container, TAP was added to a small amount of DMSO. Both DMSO solvent used were taken from the 90 mL of the total DMSO solvent used. Both mixtures were vigorously stirred for 24 h at room temperature. Then, the mixtures were mixed together and again were stirred for 24 h at room temperature. The latter mixture was then added to the SPEEK solution and was again vigorously stirred for 24 h at room temperature. Before proceeding to the casting process, the mixture was heated to 100°C to evaporate the DMSO solvent. The casting process of the SPEEK nanocomposite was conducted according to the previously reported procedure (Jaafar et al. 2009).

For observing the dispersion of Cloisite 15A® in SPEEK/Cloisite 15A®/TAP membrane, the field emission scanning electron microscope (FESEM) (JSM-6701F, JEOL USA, Inc.) was used.

The water uptake measurement was study to determine the membrane sustainability in water at room temperature. The membranes were soaked in water at room temperature for the maximum days the membranes can sustained. The water uptake was calculated as follows:

\[
\text{Water uptake} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100%.
\]  

(1)

where, \(W_{\text{wet}}\) is the weight of the wet membrane and \(W_{\text{dry}}\) the weight of the dry membrane.

In order to determine the dimensional stability (in plane and thickness) of the membranes, similar method as water uptake measurement was implemented. However, to obtain the dimensional changes from dry to wet membrane, the dimensional change ratio in plane and dimensional change ratio in thickness defined by (2) and (3), respectively and was measured in different directions on the membrane surface and the resulting values were averaged.

\[
\text{Dimensional change ratio (plane)} = \frac{L_{\text{wet}} - L_{\text{dry}}}{L_{\text{dry}}} \times 100%.
\]

(2)

\[
\text{Dimensional change ratio (thickness)} = \frac{d_{\text{wet}} - d_{\text{dry}}}{d_{\text{dry}}} \times 100%.
\]

(3)

where, \(L_{\text{wet}}\) is the length of the wet membrane and \(L_{\text{dry}}\) the length of the dry membrane, whereas \(d_{\text{wet}}\) is the thickness of the wet membrane and \(d_{\text{dry}}\) the thickness of the dry membrane.

The proton conductivity of the hydrated membrane was measured by AC impedance technique using a Solartron impedance-gain phase analyzer, over the frequency range of 10 MHz to 10 Hz with 50–500 mV oscillating voltage. All impedance measurements were performed at room temperature and 100% relative humidity (RH). The membrane resistance, \(R\), was obtained from the intercept of the impedance curve with the real-axis at the high-frequency end. Then, proton conductivity of membrane, \(\sigma\) (Scm\(^{-1}\)), was calculated according to the following equation:

\[
\sigma = \frac{d}{RS},
\]

(4)

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 (Ismail et al. 2009). Equation (5) expresses the methanol permeability of the membranes. The methanol permeability test was carried out for 3 h at
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room temperature. The methanol permeability, \( P \), value was calculated using the following equation:

\[
P = \alpha \frac{V}{A} \times \frac{L}{C_A},
\]

where, \( P \) is methanol permeability, \( \alpha = \frac{C_B(t)}{V_B} \) 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, \( t_0 \) is time lag, related to the diffusivity.

RESULTS AND DISCUSSION

Figure 1(a) and 1(b) illustrates the FESEM surface images of SP63/2.5Cl and SP63/2.5Cl/5.0TAP nanocomposite membranes, respectively. The morphology of the SP63/2.5Cl/5.0TAP nanocomposite membranes and the SP63/2.5Cl reference is discussed.

SP63/2.5Cl/5.0TAP nanocomposite membranes exhibited a homogeneous Cloisite 15A® particles distribution with smaller Cloisite 15A® particles sizes than that of SP63/2.5 membrane. It was suggested that the addition of 5.0 wt. % of TAP to compatibilize 2.5 wt. % of Cloisite 15A® particles in SPEEK matrices is desirable.

Absorbed water in membrane films is crucial for DMFC applications because it affects their mechanical properties, proton conductivity and barrier properties. Water absorbed by the hydrophilic sulfonic acid groups in the SPEEK membrane films results in some swelling and facilitates proton and methanol transport from the anode to the cathode. However, too much water absorption results in excessive swelling may contributed to unfavorable influence on the membrane dimensional, mechanical fragility and morphological instability of the membrane films (Gao et al. 2003). The dimensional changes in plane for instance can weaken the contact between electrolyte membrane and catalyst, which will reduce the membrane performance (Yang 2008). The water uptake, swelling ratio and solubility (to represent long term stability of the tested membranes) of parent SPEEK and its nanocomposite membranes were determined by measuring the changes in the mass, length (plane) and thickness and soluble period respectively, before and after hydration and durability in water environment. Figure 2 demonstrates the water uptake and solubility time for SP63, SP63/2.5Cl and SP63/2.5/5.0TAP membranes while Figures 3 and 4 illustrate the swelling ratio of SPEEK and its nanocomposites in the directions of plane and thickness, respectively.

It was observed that the water uptake of SP63/2.5Cl is the highest throughout the experimental period compared with SP63 and SP63/2.5/5.0TAP. It can be suggested that the non-uniformly distribution of Cloisite 15A® particles allowed the sulfonic acid group in SPEEK polymer matrix to absorb water. However, when 5.0 wt. % of TAP was added to assist the homogeneity of the polymer-inorganic mixture, the water uptake of SP63/2.5Cl/5.0TAP decreased dramatically from SP63/2.5Cl membrane. It was suggested that, when TAP is available and clutch the SPEEK and Cloisite 15A® at the possible functional groups such as carbonyl, ethers and sulfonic acid, the functional of these groups will less pronounce. This behavior therefore, caused the sulfonic acid group less functioned to absorb more water thus performed lower water uptake membrane as compared with SP63 and SP63/2.5Cl. However, when time reached up to 288 h, the water uptake value of SP63/2.5Cl/5.0TAP started to exceed the water uptake value of parent SP63 membrane. It can be seen that the water uptake of both SP63 and SP63/2.5Cl/5.0TAP membranes was leveled off started from 768 h and further up. It was also observed that up to 960 h, both membranes structure still tough and seem to maintain their mechanical stability even the time was further increased. On the contrary, SP63/2.5Cl membrane still shows gradual increase until 960 h and the membrane tend to swell much more than SP63 and SP63/2.5Cl/5.0TAP membranes.

![Figure 1. SEM images of membrane surface for (a)SP63/2.5Cl and (b)SP63/2.5Cl/5.0TAP](image)
From Figures 3 and 4, it was observed that the swelling ratios in plane and thickness of SP63/2.5Cl membrane were the highest than that of SP63 and SP63/2.5Cl/5.0TAP membranes. It was found that the swelling ratio in plane of SP63/2.5Cl/5.0TAP starts to surpass the SP63 swelling ratio at 240 h. This observation indicated that SP63/2.5Cl/5.0TAP become more fragile as time increased and its mechanical stability in water was slightly decreased compared to parent SPEEK. However, all the tested membranes showed the swelling ratio in thickness was much higher than that in plane. Similar observation was reported by Yang et al. (2008) on SPEEK/polyvinylalcohol (PVA) membranes. This suggested all the tested membranes are highly potential for DMFC potential use.

In general, incorporation of silicate layers into polyelectrolytes restricts the accessible nanometric channels for migration of polar molecules such as hydrogen ions, water and methanol molecules (Hasani-Sadrabadi et al. 2010). However, at appropriate Cloisite 15A® (2.5 wt. %) loading and the formation of a homogenous nanocomposite membrane with TAP assistance, acceptable proton conductivity and low methanol permeability have been obtained. Table 1 summarizes the performance properties such as proton conductivity and methanol permeability and the percentage of improvement in the performance properties of SPEEK nanocomposites as respect to the SP63 membrane.

Table 1 shows the increment in proton conductivity is small for SP63 membrane incorporated with Cloisite 15A® alone, in which the proton conductivity increases by only 18%. When TAP is introduced, the increment in the proton conductivity was approximately 47%. This significant improvement in proton conductivity value was suggested rely on the well distribution of Cloisite 15A® particles in the membranes that was assisted by TAP. As being said by Wang & Dong (2007), a well dispersion of inorganic fillers morphology is expected to yield the highest ionic conductivity since more cations could be mobile and available for conduction. This expectation was found true by Kim et al. (2007) who suggested that smaller size and uniform distribution of ionic clusters leading to a better proton conductivity value. Other than that, it was suggested that the well dispersion of Cloisite 15A® particles will perform a highly ion transportation that took the opportunity to hop from one Cloisite 15A® particle to another in the ionic clusters because the Cloisite 15A® itself is a good proton conducting material due to the presence of the high polar cations (quaternary ammonium) in the clay layers thus performing high proton conductivity (Cervantes-Uc et al. 2007; Nagarale 2010).

As given in Table 1, SP63/2.5Cl nanocomposite membranes with different loading of TAP do not show the dependency of conductivity value with the film thickness because it was mainly determined by membrane surface resistivity. It was suggested that the surface resistivity is closely dependence with membrane morphological structural. The better the Cloisite 15A® particles dispersion the lower the surface resistivity of membrane will be thus performed higher proton conductivity value.

Table 1 also shows the dependency of the methanol permeability of SPEEK membranes filled with Cloisite 15A® on TAP loading. A significant reduction in methanol permeabilities of both SP63/2.5Cl and SP63/2.5Cl/5.0TAP; i.e. 84% and 98%, respectively, was observed. The well dispersion of Cloisite 15A® particles in the SPEEK matrices as shown in Figure 1, have successfully activated the Cloisite 15A® particles functions as the methanol barrier that contributed the winding diffusion effects towards methanol molecules thus resulted decreased in the methanol permeability (Gaowen & Zhentao 2005).
A parameter to compare membranes with respect to possible application in direct methanol fuel cell and to identify the optimum membrane from the tested membranes is the selectivity of proton conductivity to methanol permeability (Roelofs et al. 2010). From the observation of this study, it can be concluded that the addition of Cloisite 15A® and TAP to SPEEK has an important influence on both the proton conductivity and methanol permeability. Cloisite 15A® has a beneficial impact on the methanol permeability, whereas TAP has the positive impact on the morphological structure of the nanocomposite membrane to enhance the proton conductivity. Figure 5 illustrates the selectivity of SP63, SP63/2.5CI and SP63/2.5CI/5.0TAP nanocomposite membranes. Figure 5 shows that the selectivity was dramatically increase from SP63 to SP63/2.5CI/50TAP nanocomposite membrane. The selectivity shows a maximum value SP63/2.5CI/50TAP, i.e. $9.03 \times 10^5$ Sccm$^{-3}$. This result was in good agreement with
the SEM image result that showed the smoothest dispersion of Cloisite 15A® particles in the SPEEK matrices for SP63/2.5Cl/5.0TAP samples performed the most promising polymer electrolyte membrane for DMFC used.

CONCLUSION

In the present work, a study of the influence of the addition of Cloisite 15A® nanoclay and 2,4,6-triaminopyrimidine (TAP) on the properties of SPEEK polymer electrolyte membrane for DMFC application was successfully carried out. Since that clays commonly used are not able to disperse well in polymer matrix, 2,4,6-triaminopyrimidine (TAP) was introduced as a compatibilizer to enhance the compatibility between SPEEK and Cloisite 15A® nanoclay. Measurement of the physicochemical and hydrolytic properties of the tested membranes showed that the incorporation of Cloisite 15A® and TAP has significantly improved the proton conductivity and methanol barrier properties of parent SPEEK. The selectivity of the membrane was thus largely increased by the addition of the compatibilizer that clearly has a beneficial impact on the performances of the polymer electrolyte membrane for DMFC. However, it was found that SP63/2.5Cl/5.0TAP has to sacrifice its mechanical steadiness for long term stability in water environment. However, this weakness was compensate with its higher selectivity as compared to other tested membranes, which makes the SP63/2.5Cl/5.0TAP membrane as the optimum polymer electrolyte membrane that is a very valuable target for improving the performances of direct methanol fuel cell.

REFERENCES


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