Effect of Dispersion State of Cloisite15A® on the Performance of SPEEK/Cloisite15A Nanocomposite Membrane for DMFC Application

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ABSTRACT: The introduction of 2,4,6-triaminopyrimidine (TAP) into sulfonated poly(ether ether ketone) (SPEEK)/Cloisite15A® nanocomposite membranes were investigated for the purpose of maintaining low methanol permeability and suppressing swelling in direct methanol fuel cell (DMFC). SPEEK with 63% of degree of sulfonation (DS) was prepared by sulfonation of PEEK. Cloisite15A (7.5 wt %) along with various weight loading of TAP was incorporated into SPEEK matrix via solution intercalation method. The effect of TAP loading on the SPEEK/Cloisite15A/TAP morphology was studied. The beneficial impact of the SPEEK/Cloisite15A/TAP morphology on the physicochemical properties of the membrane was further discussed. Swelling behavior, ion exchange capacity (IEC), proton conductivity, and methanol permeability of the resultant membranes were determined as a function of Cloisite15A and TAP loadings. Uniform distribution of Cloisite15A particles in the SPEEK polymer matrix in the homogenous SPEEK/Cloisite15A/TAP nanocomposite membranes was confirmed by scanning electron microscopy and X-ray diffraction. The water uptake of the SPEEK nanocomposite membranes decreased dramatically in the presence of TAP. The significant selectivity of SP/7.5/7.5 nanocomposite membranes could indicate a potential feasibility as a promising electrolyte for DMFC. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 969–977, 2012

Key words: membranes; nanocomposites; compatibility; inorganic materials; clay

INTRODUCTION

Direct methanol fuel cells (DMFCs) is a promising green technology that has been widely researched in the recent years on account of their high efficiency, compact structure, and ease in refueling (methanol fuel).[1] Polymer electrolyte membrane (PEM) as proton conductive material is the heart component of DMFC; high proton conductivity and low methanol permeability are expected to be obtained.[2] Nafion® membranes are, by far, the most studied and widely used PEM material. Upon hydration, Nafion membranes tend to show an increase in proton conductivity. However, high methanol permeability and large dependence of proton conductivity upon water content limit its application.[3] Therefore, great efforts have been devoted on the development of the substitutes for Nafion. One of the most well-known PEM based on nonperfluorinated polymer for DMFC under accelerated research is sulfonated poly(ether ether ketone) (SPEEK).

SPEEK has been considered to be one of the best alternatives, which offers the attribute of adjustable proton conductivity, excellent chemical, and thermal stability.[4–6] SPEEK was generally prepared by SPEEK with concentrated sulfuric acid.[7] Proton conductivity of SPEEK is mostly dependent on the degree of sulfonation (DS), and DS can be adjusted by sulfonation conditions, such as reaction time, temperature, and concentration of sulfuric acid.[8,9]

It was reported that the SPEEK membrane has lower methanol permeability than that of Nafion.[10] However, methanol permeability varied largely with DS; therefore, it is hard to maintain high methanol barriers at high DS. To address this problem, several studies have been conducted by adding inorganic fillers such as montmorillonite (MMT) into SPEEK polymer matrix.[11–15]

MMT is a well-known layered silicate, which is very promising to decrease the methanol permeability in polymeric membranes due to its high aspect ratio that contributes to the winding diffusion pathway for methanol.[16] The most popular approach to modify MMT microstructure to enhance its compatibility with SPEEK polymer base is by modifying the

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formulation preparation method and MMT surface modification with organoclay.[17] However, a new approach such as filling the interface spacing between the polymer and the inorganic filler to improve the methanol barrier properties of the polymer–inorganic membranes is scarcely reported.

Therefore, in this work, SPEEK membrane is modified by incorporating Cloisite15A (commercial modified MMT) with the presence of 2,4,6-triaminopyrimidine (TAP) as a compatibilizer. The choice of TAP as the compatibilizer was inspired by the fact that TAP can induce strong hydrogen bonding with SPEEK and Cloisite15A due to the presence of NH_2 functional groups in its chemical structure.[18] This advantage could enhance the compatibility of the mixtures and thus reveal the unique features possessed by both SPEEK and Cloisite15A to improve the performance of the parent polymer. Considering the advantages of each material, the composite membranes consist of SPEEK, Cloisite15A, and TAP were prepared, and their properties as a PEM for DMFC were investigated by measuring the ionic exchange capacity (IEC), swelling behavior, proton conductivity, methanol permeability, and DMFC performance.

EXPERIMENTAL

Materials

Poly(ether ether ketone) (PEEK) with average molecular weight of 3.92×10^4 and density $1.30/g^3$ was obtained from Vitrex, USA. Concentrated sulfuric acid (95–97%) purchased from QRex was used as the sulfonating agent for sulfonation process. Cloisite15A was obtained from Southern Clay Products and was used as received. The typical dry particle sizes of Cloisite15A are 10% less than 2 μm, 50% less than 6 μm, and 90% less than 13 μm. The cation exchange capacity value of Cloisite15A is 1.25 meq g^{-1}. Dimethylsulfoxide (DMSO) and TAP were obtained from Sigma-Aldrich and used as the solvent and as the compatibilizer, respectively. Nafion 211 (NR-211) membrane with equivalent weight of 1100 and thickness of 25.4 μm was obtained from Ion Power, USA and was used as received. Nafion 211 was used as a reference membrane.

Preparation of nanocomposite membrane

Sulfonation of PEEK was carried out according to the method described elsewhere.[19] About 10 wt % of SPEEK solution was first prepared by dissolving SPEEK in 50 mL of DMSO. Desired amounts of Cloisite15A and TAP (as summarized in Table II) were added to 40 mL 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. 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°C to evaporate the DMSO solvent. This preparation method was known as solution intercalation method. The polymer dope was then cast according to the method described elsewhere.[18]

Nuclear magnetic resonance spectroscopy

Hydrogen-nuclear magnetic resonance (^{1}H-NMR) spectroscopy was used to determine the DS of parent SPEEK membrane. Based on the DS obtained, the ion exchange capacity (IEC) can be determined as well. ^{1}HNMR spectra were recorded on a Varian Unity Inova spectrometer at a resonance frequency of 399.961 MHz at room temperature. For each analysis, 3 wt % polymer solutions were prepared in deuterated dimethyl sulfoxide (DMSO-d_6). The DS was determined by comparative integration of distinct aromatic signals. The IEC and DS of SPEEK in hydrogen form are related to each other by the following equation.

$$\mathrm{DS}\% = \frac{288(\mathrm{IEC})}{1000 - 80(\mathrm{IEC})} \times 100\% \quad (1)$$

It should be mentioned that the unit molecular weight of SPEEK in hydrogen form and PEEK is 368 and 288, respectively. The number (80) resulted from the difference between these two unit molecular weights.[20]

Once the IEC of parent SPEEK obtained from the ^{1}H-NMR analysis, the IEC of the composite membranes can be estimated by the following equation.

$$\mathrm{IEC}_{\mathrm{composite}} = \frac{[(\mathrm{IEC}_{\mathrm{SPEEK}} * m_{\mathrm{SPEEK}}) + (\mathrm{IEC}_{\mathrm{additive1}} * m_{\mathrm{additive1}}) + (\mathrm{IEC}_{\mathrm{additive2}} * m_{\mathrm{additive2}})]}{m(\mathrm{SPEEK} + \mathrm{additives})} \quad (2)$$

where m_{SPEEK} is the weight load of SPEEK and m_{additive} is the weight load of additives incorporated into the SPEEK formulation.

Morphological and dispersion state characterization

For observation of the dispersion of Cloisite15A in the SPEEK/Cloisite15A/TAP membrane, the JSM-6390LV scanning electron microscopy (SEM) and X-ray diffraction (XRD) were used. The details parameters used in XRD analysis were described elsewhere.[18] The d-spacing of Cloisite15A in nanocomposites was calculated using Bragg's equation based on XRD results:

$$d = \frac{n\lambda}{2\sin\theta} \quad (3)$$

where d is the spacing between layers of the clay, λ the wave length of X-ray equal to 0.154056 nm, θ the angle at the maximum point of the first peak (lowest θ) in the spectra, and n is a whole number, representing the order of diffraction $n = 1$ in our calculation.

Swelling behavior measurement

Membrane samples were dried in an oven at 60°C for 48 h. The weighed films were then soaked in deionized water overnight at room temperature and at elevated temperature, before being blotted dry with absorbent paper to remove any surface moisture and then reweighed. Later, the water uptake was calculated as follows:

$$\text{Water uptake} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100\% \quad (4)$$

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

Proton conductivity measurement

The proton conductivity of the membrane was measured by AC impedance technique using a Solartron impedance-gain phase analyzer. Films having 13 mm diameter that were sandwiched between two stainless steel block electrodes with $\sim$ 3 kg/cm^2 pressure were placed in an open, temperature-controlled cell. The most crucial step before proton conductivity measurements is that all samples must be soaked in water at room temperature for hydration. 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, σ (S m^{-1}), was calculated according to eq. (5).

$$\sigma = \frac{d}{RS} \quad (5)$$

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

Methanol permeability measurement

To conclude the barrier properties of the membranes, measurement was made of the permeability of methanol in tested membranes. The compartment A (VA = 50 cm^3) of the permeation cell was filled with methanol with concentration of CA = 1M. All the tested membranes were first immersed into the water for 24 h. The membrane ($A = 5.7256$ cm^2) was clamped between the two compartments. The methanol molecules diffused along the concentration gradient through the membrane into the opposite compartment of the permeation cell. Both compartments were continuously stirred. The concentration of the methanol permeation at about 1 mL from compartment A to water compartment B was measured using Waters 410 Refractometer. The methanol permeability test of SPEEK and its nanocomposite membranes was carried out for 3 h at room temperature.

The methanol permeability, P, value was calculated using the following equation,

$$P = \alpha \times \frac{V_B}{A} \times \frac{L}{C_A} \quad (6)$$

where P is methanol permeability, $\alpha = \alpha = \frac{C_B(t)}{(t-t_o)}$ 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.

Single PEM fuel cell test

Preparation of membrane electrode assembly

The membrane electrode assembly (MEA) was prepared by hot pressing the anode and cathode to the membrane at 80 kg cm^{-2} pressure and 80°C for 2 min. The active surface area of the MEA was 5.0 cm^2 and was composed of PtRu-supported carbon catalyst (1.0 mg/cm^2 as Pt amount) with binder of Nafion DE1021CS (Binder/Carbon = 1) and PtRu-supported carbon catalyst (1.0 mg/cm^2 as Pt amount) with binder of Nafion DE1021CS (Binder/Carbon = 0.75) in cathode and anode, respectively.

Single DMFC performance

The single DMFC performance was evaluated by recording the cell voltage versus current density curves using a fuel cell analyzer test system (PRO200F, PRO-POWER communication Co., USA). Air (100% RH) with flow rate 100 cc min^{-1} and methanol (3M) with flow rate 1 cc min^{-1} were supplied to the cathode and anode, respectively. Constant current measurement of 50 mA cm^{-2} for 20 min was performed and repeated two times after cell temperature became 60°C. Once the temperature became 60°C, the DMFC performance measurement

TABLE I
Physicochemical Properties of SPEEK with Various Degree of Sulfonation (DS) and SPEEK with Different Cloisite15A® Loadings

Membrane	Proton conductivity (mS cm^{-1})	Methanol permeability × 10^7 (cm^2 s^{-1})	Membrane selectivity × 10^{-3} (Ss cm^{-3})
SP50	1.96	3.56	5.51
SP63	6.46	5.59	11.6
SP77	7.76	20.3	3.82
SP88	8.70	*Soluble*	*Soluble*
SP63/1.0Cl	4.24	3.26	13.0
SP63/2.5Cl	7.88	0.899	87.7
SP63/5.0Cl	4.02	0.803	50.1
SP63/7.5Cl	1.94	0.489	39.7

was conducted three times, and the results were presented as the average data.

RESULTS AND DISCUSSION

SPEEK/Cloisite15A/TAP nanocomposite membrane

Various weights of Cloisite15A were loaded into the sulfonated poly(ether ether ketone) (SPEEK) with 63% of DS (SP63) to study the effect of the filler loading on the membrane morphological structure. The performance of SPEEK with various DSs and that of SP63 with different Cloisite15A loadings are shown in Table I. It was a typical phenomenon to obtain low methanol permeability for polymer–inorganic composite membrane, but it is difficult to have high proton conductivity at the same time. Therefore, it is crucial to further emphasize in preparation of a polymer–inorganic composite membrane with improved proton conductivity. From Table I, it was observed that SP63 with 7.5 wt % of Cloisite15A loading exhibited the lowest proton conductivity. This was probably due to the worst agglomeration of Cloisite15A particles in the SPEEK matrices as depicted in the SEM micrograph in Figure 1(a), which will be discussed further in the next section. Therefore, it is crucial to further study the effect of TAP (compatibilizer) loading on the morphological structure of SP63 with 7.5 wt % of Cloisite15A loading. The composition of the membrane samples used for this study is tabulated in Table II.

Morphological structural study

Figure 1(a–c) showed the SEM micrograph surfaces of SP/7.5, SP/7.5/7.5, and SP/7.5/10.0 membranes, and Figure 1(d–e) showed the SEM micrograph for the cross sections of SP/7.5 and SP/7.5/7.5 membranes. It is observed that, SP/7.5/7.5 membrane shows better Cloisite15A dispersion on the membrane surface than that of SP/7.5 with the size of the particle agglomeration less than 1 μm. As expected, SP/7.5 membrane shows severe agglomeration of Cloisite15A particles whose size is as large as ~ 5 μm. Black arrows in Figure 1(d) show gaps between Cloisite15A particles and SPEEK matrices for SP/7.5 membrane cross section, whereas white arrows in Figure 1(e) show the good adhesion of Cloisite15A particles with SPEEK matrices for SP/7.5/7.5 membrane.

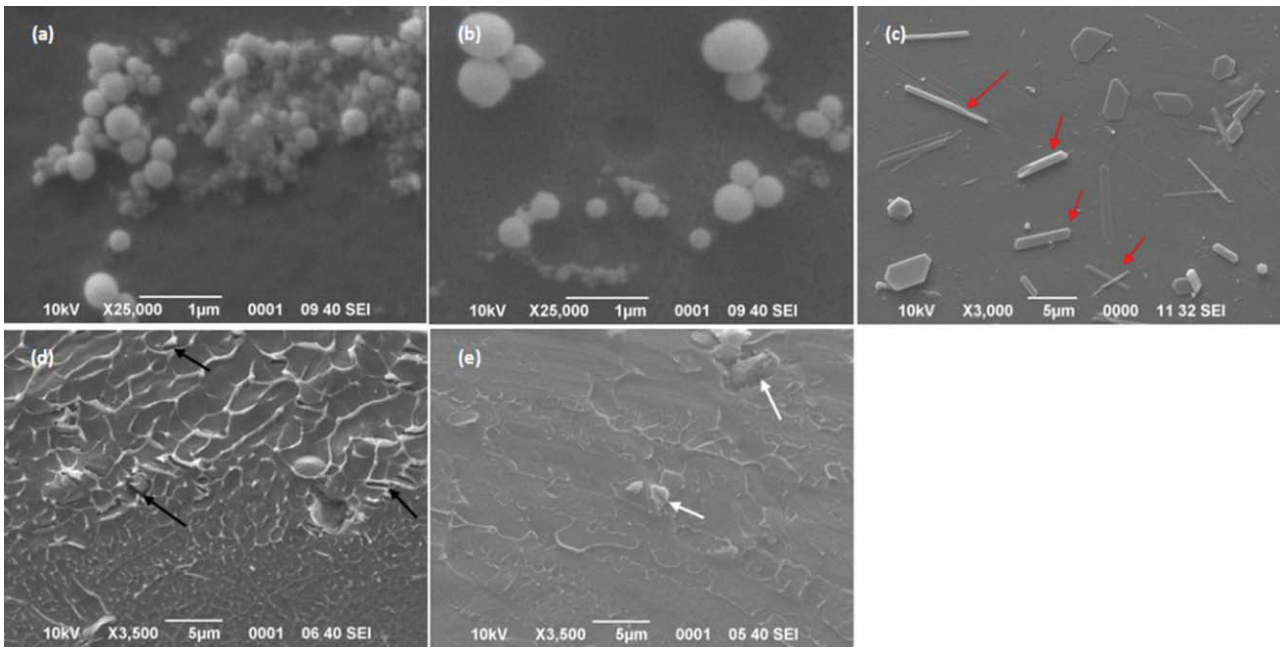

Figure 1 SEM images of membrane surface of (a) SP/7.5; (b) SP/7.5/7.5; (c) SP/7.5/10.0; and membrane cross section of (d) SP/7.5; (e) SP/7.5/7.5. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE II
Composition and Physicochemical of SPEEK Nanocomposite Membranes

Sample designation	SPEEK (g)	Cloisite15A® (g)	TAP (g)	IEC (meq g^{-1})	Water uptake (wt %)	Proton conductivity (mS cm^{-1})	Methanol permeability × 10^7 (cm^2 s^{-1})
SP63	10	–	–	1.8617	29.7 ± 0.01	6.46	5.59
SP/7.5	10	0.75	–	1.8190	47.58 ± 0.06	1.94	0.489
SP/7.5/1.0	10	0.75	0.10	1.8023	25.82 ± 0.65	2.28	0.159
SP/7.5/2.5	10	0.75	0.25	1.7686	25.34 ± 1.89	3.80	0.112
SP/7.5/5.0	10	0.75	0.50	1.7382	18.26 ± 0.54	4.97	0.0603
SP/7.5/7.5	10	0.75	0.75	1.7004	17.83 ± 0.62	6.40	0.0489
SP/7.5/10.0	10	0.75	1.00	1.6642	23.88 ± 2.78	5.95	0.0699
Nafion®211 (NR-211)	–	–	–	–	25.18 ± 1.75	23.06	15.7

It is also important to investigate the performance of the SP/7.5/10 membrane to confirm that addition of TAP above 1 : 1 (Cloisite15A/TAP) mass ratio is not applicable when Cloisite15A loaded to SPEEK is high. This might be because some of the sulfonic acid groups in SPEEK were interacted directly by the hydroxyl group of Cloisite15A, and TAP was not fully functioning as a compatibilizer. This was proved by the appearance of TAP particles (as shown by red arrows) in SP/7.5/10.0 image in Figure 1(c).

Dispersion state of Cloisite15A

Figure 2(a,b) illustrates the XRD patterns of Cloisite15A (as reference) and SPEEK composite namely SP/7.5 and SP/7.5/7.5. The analysis of the pure Cloisite15A shows the corresponding basal distance of planes 001 at $2\theta = 7.1^\circ$ with the gallery distance of 1.24 nm. Similar corresponding peak was recorded by SP/7.5 sample. This indicates that an ordinary composite SP/7.5 is obtained. According to SP/7.5/7.5 sample, the corresponding peak was shifted to $2\theta = 6.9^\circ$ at 1.28 nm. In addition, the particular diffraction peak of SP/7.5/7.5 membrane seemed broader and had lower intensity when compared with the peak of the original Cloisite15A. Therefore, SP/7.5/7.5/membrane can be considered as intercalated or partial exfoliated composite membrane.[14] This finding confirmed the SEM images that showed a better dispersion of Cloisite15A particles in the presence of TAP in SP/7.5/7.5 membrane. This observation also suggested that an appropriate amount of TAP loading may enhance the dispersion state of Cloisite15A fillers in the base polymer.

Water uptake behavior

Table II shows the effect of TAP loading on water uptake and IEC when the DS of SPEEK and Cloisite15A loading were fixed to 63 and 7.5 wt %, respectively. Generally speaking, in the presence of filler, SO_3^- groups in the polymer chains were decreased per unit volume, and the water uptake in the sulfonated polymers should be strongly dependent upon the amount of sulfonic acid groups.[21] According to Table II, this expectation is fulfilled for all the SPEEK composite membranes except SP/7.5 and SP/7.5/10.0 membranes.

The increase in TAP loading from 1.0 to 7.5 wt % decreased the water uptake. This might be due to the good interaction between SPEEK and Cloisite15A with the TAP assistance. It was suggested that the high water uptake in SP/7.5 was due to the water molecules that were absorbed by the ionic clusters had occupied the interfacial voids between the SPEEK polymer matrices and the agglomerated Cloisite15A fillers. However, when TAP is introduced, the gap between SPEEK and Cloisite15A had become narrower or even disappeared due to the good distribution of Cloisite15A particles throughout the membrane microstructure. This contributed to a more manageable water uptake activity in SPEEK/Cloisite15A/TAP nanocomposite membranes. Figure 3 could describe the water molecules transport occurred in SPEEK nanocomposite membranes.

Nevertheless, upon 10 wt % addition of TAP, the water uptake is increased although it is still lower than that of SP63 and SP/7.5 membranes. It was suggested that the excess of TAP loading has increased the water uptake of the membrane due to an increased in free amine (NH_2) groups, which assisted the membrane to absorb more water.[18]

Performance of SPEEK nanocomposite membranes

In general, it is known that the proton conductivity does not directly correlate to either water uptake or IEC for any of the polymers applicable in fuel cell technology.[9] This is also supported by our experimental data on proton conductivity and its relationship to water uptake and IEC. Table II summarizes the proton conductivity and methanol permeability of Nafion® 211 membrane and for the membranes made of SP/7.5 and TAP incorporated SP/7.5.

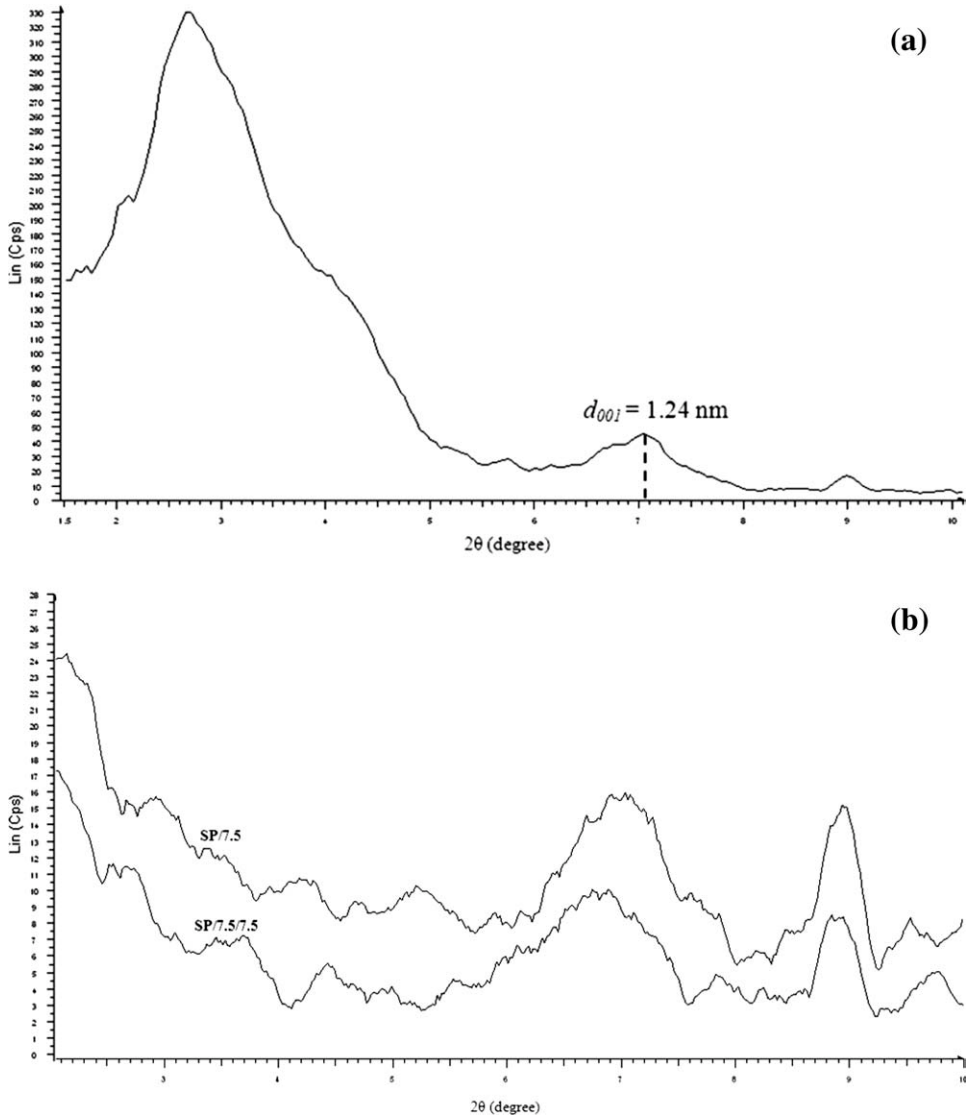

Figure 2 XRD patterns of (a) Cloisite15A® and (b) SPEEK composite membrane.

Based on Table II, it is found that, even though the water uptake value of SP/7.5 membrane was higher than other membranes, the proton conductivity of SP/7.5 membrane was the lowest. This was due to the agglomeration of Cloisite15A in the SPEEK matrices that resists proton transport across the membrane via the free space between SPEEK and Cloisite15A or even through the Cloisite15A itself. However, for SP/7.5/1.0 and SP/7.5/2.5 membranes, their proton conductivities were decreased linearly with decreased in water uptake. This behavior was extensively reported by a numbers of researchers.[12–21,23,24] Interestingly, upon loading of 5.0 and 7.5 wt % TAP, the membranes showed higher proton conductivities despite the decreased in water uptake. This in contrast phenomenon was also reported by Hande et al.[22] This phenomenon occurred was probably due to a better connected

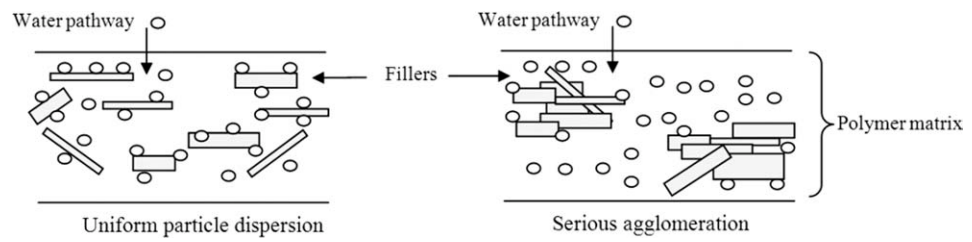

Figure 3 Transport mechanism model of water through SPEEK nanocomposite membranes.

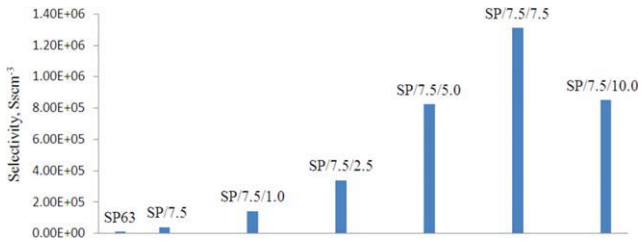

Figure 4 Selectivity of parent SPEEK and SPEEK nanocomposites with various weights of TAP loadings. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

ionic linkages in the SPEEK matrices that allowed more protons to transport via free diffusion between the SPEEK and Cloisite15A interface and due to the good conductivity of the Cloisite15A particles itself.[14,18] However, their proton conductivity values were still lower than that of SP63 membrane (6.46 m S cm^{-1}) and Nafion 211 membrane. It should be noted that the lower value of the proton conductivity of Nafion 211 than that of reported by other researcher[23] might be because of the difference in using the operating conditions during the proton conductivity measurement.

Methanol permeability is crucial in DMFC applications and is directly related to the selectivity of the membrane. Excessive swelling of PEM will transform the membrane with high methanol permeability that may result in low membrane selectivity. Therefore, the addition of inorganic filler with high barrier properties toward methanol and the good dispersion of filler particles in the polymer matrix are desirable. The results summarized in Table II indicated a decreased in methanol permeability upon addition of TAP. This suggested that the addition of TAP is favorable in preparing a homogenous SPEEK/Cloisite15A membrane to demonstrate the unique feature of Cloisite15A, that is, its high aspect ratio (length to width), which can provide longer a pathway toward methanol to cross the membrane.[16]

Selectivity of SPEEK and its nanocomposite membranes

Proton conductivity and methanol permeability are the two transport properties of a polyelectrolyte membrane, which determine its electrochemical performance.[21] The higher selectivity value leads to a better membrane performance in practical conditions. Dependency of transport properties on TAP loading, the membrane selectivity values of sulfonated poly(ether ether ketone) (SPEEK), and its nanocomposite membranes are shown in Figure 4. The maximum selectivity is achieved at 7.5 wt % of TAP loading. This observation originates from the favorable influence of increasing TAP loading on proton conductivity and its greater adverse effect on methanol permeability. Moreover, all nanocomposite membranes are shown to be more selective than the unfilled SPEEK. Figure 5 summarizes the proton conductivity and methanol permeability results from various research works reported in the literature[12,14,15,16,24,25] and compared to the SP/7.5/7.5 composite membrane prepared in this study. From the observation, it was found that SP/7.5/7.5 composite membrane exhibited the among the lowest proton conductivity value. However, the impressive improvement in methanol barrier property of the membrane compensates that weak point.

DMFC performance testing

To confirm that failure in fine and uniform distribution of inorganic particles contributes to poor performance of PEM, the DMFC performance test is essential. Therefore, in this study, the DMFC performance testing of parent SPEEK, SP/7.5/7.5 and Nafion 211 as reference was conducted.

Figure 6 shows that the DMFC experiments with Nafion 211, SP/7.5/7.5, and SP63 membranes exhibit high-open circuit potentials (OCV) of 0.68, 0.61, and 0.51 V, respectively. SP/7.5/7.5 membrane shows higher OCV than that of parent SPEEK due to its very low methanol permeability. OCV is closely

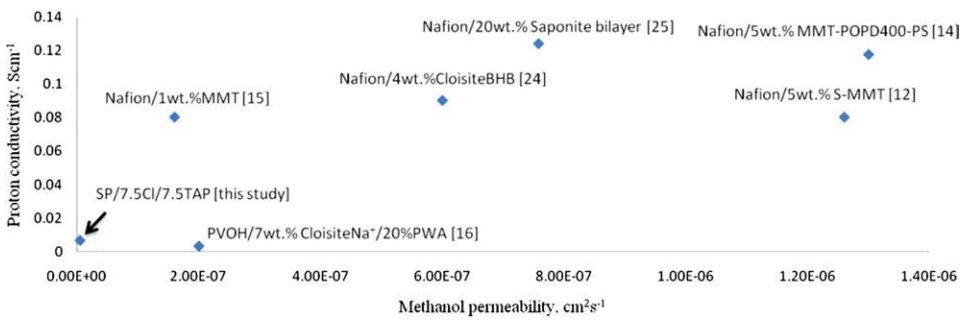

Figure 5 Review study on polymer-inorganic materials by previous researchers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

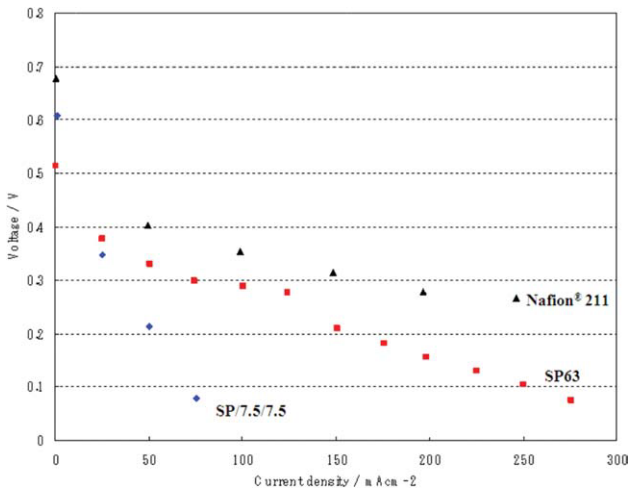

Figure 6 DMFC performance test at 60°C, voltage versus current density. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

related to the methanol permeation and it increased when the methanol crossover is decreased. Methanol crossover hinders oxygen reduction at the anode and consequently leads to a drastic decrease in OCV. The higher OCV clearly indicates that the incorporated Cloisite15A into SPEEK membrane significantly decreases the rate of methanol crossover.[26] This feature is very desirable for high output power, if the morphological structural of SP/7.5/7.5 membrane is further improved, and the MEA structure is optimized. However, the voltage of SP/7.5 membrane started to decrease dramatically as the current density increased and only performed satisfactorily until 75 mA cm^{-2} of current density. As can be seen, both SP63 and Nafion 211 membranes showed the maximum current density of 275 and 250 mA cm^{-2}, respectively. The low current density of SP/7.5/7.5 membrane was due to the low proton conductivity.

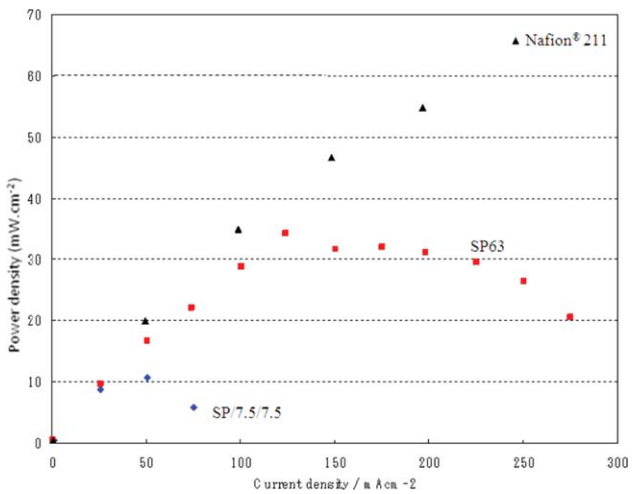

Figure 7 DMFC performance test at 60°C, power density versus current density.

Figure 7 shows the power density versus current density of SP63, SP/7.5/7.5, and Nafion 211 membranes. The maximum power density of the SP/7.5/7.5 membrane was measured to be 10.8 m W cm^{-2}, whereas the highest power density achieved by the reference SP63 and Nafion 211 membranes were 34.4 and 65.4 m W cm^{-2}, respectively. This observation indicated that agglomeration of inorganic particles in the polymer matrix does indeed deteriorate the DMFC performance.

CONCLUSIONS

Membranes were prepared from the SPEEK nanocomposite material in which Cloisite15A and TAP are incorporated. The physicochemical properties and performance in DMFC of the prepared nanocomposite membranes were studied. Experimental data on water uptake showed that the addition of TAP could significantly reduce excessive swelling of parent SPEEK and SPEEK with Cloisite15A. Although the addition of Cloisite15A as high as 7.5 wt % in SPEEK has not necessarily enabled proton conductivity as high as the commercially available membrane such as Nafion 211, the low methanol permeability could compensate the low proton conductivity to achieve high-membrane selectivity values. For example, a membrane (SP/7.5) of poor performance could be transformed to a potentially useful membrane (SP/7.5/7.5) for DMFC application with an increase in membrane selectivity by 97%. Owing to higher proton conductivity and lower methanol permeability when compared with the tested membranes, it would be worth subjecting the SP/7.5/7.5 nanocomposite membrane to further study as an alternative PEM for DMFC. It is important to optimize the MEA structure that will be compatible with the SP/7.5/7.5 membrane in the near future to obtain better performance in DMFC than the parent SPEEK membrane or even Nafion 211 membrane.

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