

# Preparation and properties of high performance nanocomposite proton exchange membrane for fuel cell

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## Abstract

Various spatially enlarged organoclays were prepared by using poly(oxypropylene)-backboned quaternary ammonium salts of various molecular weights  $M_w$  230, 400 and 2000 as the intercalating agents for  $\text{Na}^+$ -montmorillonite. The modified MMT was utilized to improve the compatibility with Nafion<sup>®</sup>. Sufficient interaction of the modified MMT with Nafion<sup>®</sup> was studied by using X-ray diffraction (XRD) and X-ray photoelectron spectra (XPS). The performance of the Nafion<sup>®</sup>/*m*-MMT composite membranes for direct methanol fuel cell (DMFCs) was evaluated in terms of water uptake, ion exchange capacity (IEC), methanol permeability, proton conductivity, and cell performance. The methanol permeability of the composite membrane decreased with the increasing of *m*-MMT content. The proton conductivity of the membrane was lowered slightly from that of pristine Nafion<sup>®</sup> membrane. These results led to an essential improvement in the single-cell performance of DMFCs.

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**Keywords:** Fuel cell; Montmorillonite; Poly(oxypropylene); X-ray; Membrane electrode assembly

## 1. Introduction

Recently, direct methanol fuel cells (DMFCs) exhibit the most promising alternative for various portable electronic devices and transportation applications. They offer the advantages of compactness, lightweight, high power density and low temperature operation. The potential commercial applications include cellular phones, PDAs, laptop computers, military back power packs, etc. [1–4].

Nowadays, perfluorosulfonate ionomer (PFSA), such as Nafion<sup>®</sup>, has been tested with some success. However, Nafion<sup>®</sup> membrane has major technical drawbacks, such as slow oxidation kinetics of methanol and high methanol crossover from the anode to the cathode [5–7]. In particular, it has been reported that over 40% of the methanol can be wasted in DMFCs through Nafion<sup>®</sup> membrane [8]. This phenomenon lowers the fuel efficiency and cell performance, and thus impedes the commercial development of DMFCs. The methanol crossover is dictated by the polymer electrolyte membrane, which is employed to

the effective separation of the anode (methanol) and cathode (oxygen) reactants and provides proton conduction from the anode to the cathode. However, current Nafion<sup>®</sup> membranes cannot completely meet the requirements for practical DMFC applications.

Methanol is easily transported together with solvated protons by means of the electro-osmotic drag as well as by diffusion through the water-filled ionic channels within the Nafion<sup>®</sup> structure and through the Nafion<sup>®</sup> itself. In order to reduce the methanol permeability through the membrane, many approaches have been conducted: (i) modifying the surface of the membranes to block the methanol transport, (ii) developing new models of electrolyte polymers, (iii) controlling the size of proton transport channels by using different block copolymers and cross linkages, and (iv) introducing a winding pathway for a methanol molecule by preparing a composite with inorganic materials [19].

Recently, the composite membranes have been prepared by the addition of ceramic oxide such as silica, titania, zirconia, mixed silicon–titanium oxides, zeolites, silicon–aluminum oxides, and montmorillonite in the Nafion<sup>®</sup> membrane [9–20]. Rhee et al. reported that the ion channel size of Nafion<sup>®</sup> composite membranes with 3 wt% HSO<sub>3</sub>-MMT loading were reduced

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from 3.84 to 2.94 nm [19]. In this case, the methanol permeability was reduced by 50% comparing to that of pristine Nafion<sup>®</sup>. They pointed out that the size of ion channel has a direct effect on the methanol permeability in the membrane. Indeed, maximization of the balance between proton conductivity (C) and methanol permeability (P), i.e. the *C/P* ratio ( $\Delta$ ), is still a challenging task, since hydrated proton and methanol have similar properties.

Montmorillonite (MMT) is a layered aluminosilicate mineral which has large surface areas (220–270 m<sup>2</sup> g<sup>-1</sup>, specified by Aldrich) and a negative layer charge. Its proton form (H<sup>+</sup>-MMT) possesses a proton conductivity of 10<sup>-4</sup> S cm<sup>-1</sup> at room temperature [21]. Since silicate clays are hydrophilic and lack the affinity for hydrophobic polymers, an organic modification is required to enhance their compatibility with polymeric materials. The effect of MMT on the barrier properties of polymer matrices could be utilized to improve the performances of membranes for use in DMFCs.

In the present work, nanocomposite membranes with various contents of Na<sup>+</sup>-MMT, modified montmorillonite (*m*-MMT) have been prepared by using poly(oxypropylene)-backboned quaternary ammonium salts of various molecular weights *M<sub>w</sub>* 230, 400 and 2000 as the intercalating agents for Na<sup>+</sup>-MMT. The modified MMT was analyzed by X-ray diffraction (XRD) and thermogravimetric analysis (TGA). The composite membranes were characterized by using X-ray diffraction (XRD), X-ray photoelectron spectra (XPS). Methanol permeability and proton conductivity of the composite membranes have been measured as criteria to estimate the beneficial effect of the *m*-MMT on the barrier properties of Nafion<sup>®</sup>. The performance of these composite membranes in DMFC has been evaluated and the results will be discussed.

## 2. Experimental

### 2.1. Materials and chemicals

Na<sup>+</sup>-MMT, a Na<sup>+</sup> type of smectite clay (trade name: PGV<sup>®</sup>) with a cation exchange capacity of 1.45 mequiv g<sup>-1</sup>, was supplied by Nanocor Co. (U.S.A.). Poly(oxyalkylene)amines were purchased from the Huntsman Chemical Co., Philadelphia, Pennsylvania, U.S.A. The POP-backboned diamines with different molecular weight, *M<sub>w</sub>* 230, 400 and 2,000 g mol<sup>-1</sup> were used as the intercalants and denoted as POP230, POP400 and POP2000, respectively. Perfluorosulfonylfluoride copolymer resin (Nafion<sup>®</sup> R-1100 resin) used in this study is supplied by E.I. DuPont Co.

### 2.2. Preparation of MMT/POP-diamines organoclay

Organoclay was prepared by cation exchange between Na<sup>+</sup> in clay galleries and POP-backboned diamines cations in aqueous solution [22]. A total of 10 g of Na<sup>+</sup>-MMT was dispersed homogeneously in 1 L of deionized water at 80 °C. The slurry was added to amine salts prepared from poly(propylene glycol)-bis(2-aminopropyl ether) with a molecular weight of 2000 g mol<sup>-1</sup> (designated as POP2000, 22.8 g, 11.4 mmol) and

the equivalents of hydrochloric acid in water. After being stirred at 80 °C for 5 h, the precipitate was collected at ambient temperature, then was washed thoroughly with deionic water/ethanol three times and dried under vacuum.

### 2.3. Preparation of composite membrane

To prepare a composite membrane, a desired amount of prepared MMT/POP-diamines organoclay was added to a 5 wt% Nafion<sup>®</sup> solution, and then stirred and degassed by ultrasonication. The contents of functionalized MMT in the mixture were varied in 1–7 wt% based on Nafion<sup>®</sup>. The prepared mixture was slowly poured into a glass dish in an amount that would provide a thickness of ca. 120 μm of the formed composite membrane. The filled glass dish was placed on the leveled plate of a vacuum-dry oven, and then was dried by slowly increasing the temperature from 300 to 323 K to prevent forming crevice in composite membrane. Finally, the residual solvent in the composite membrane was completely removed by evacuation at 393 K for 12 h. Scheme 1 describes the procedure of preparing the composite membrane.

### 2.4. Instrumental characterization

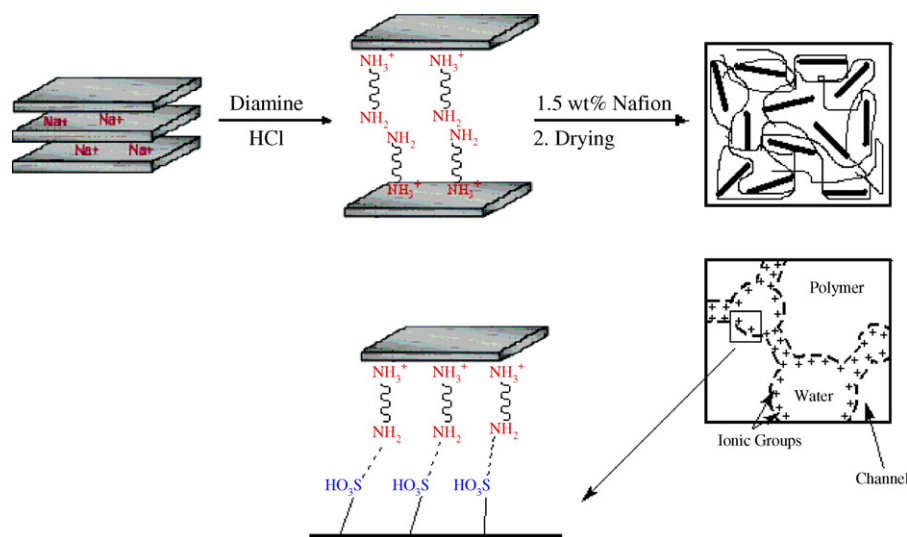
The d-spacing of MMT/POP-diamines organoclays and the ionic channel size of composite membranes were scanned at a rate of 1° min<sup>-1</sup> by using Shimadzu XD-5 X-ray diffraction (XRD; 45 kV, 30 mA) with copper target and Ni filter. The basal spacing (*n* = 1) and ionic channel size were calculated according to Bragg's law,  $n\lambda = 2d \sin \theta$ , through the observed peaks of *n* = 2, 3, . . . , etc. Thermogravimetric analysis (TGA) was conducted utilizing a DuPont-TGA951 by heating the samples from ambient temperature to 800 °C with a heating rate of 10 °C min<sup>-1</sup> in nitrogen atmosphere. The interaction between amine (–NH<sub>2</sub>) and sulfonic (–SO<sub>3</sub>H) groups were analyzed by X-ray photoelectron spectra (XPS) acquired with a VG-Scientific ESCALAB 220 iXL spectrometer equipped with a hemispherical electron analyzer and an Mg Kα (*hν* = 1253.6 eV) X-ray source.

### 2.5. Water uptake, ion exchange capacity (IEC)

Polymer membranes were dried in a vacuum oven at 80 °C for 2 h and weighted. The samples were then immersed in distilled water and isothermal oscillated at 60 °C for 2 h. The water uptake was calculated using the following equation:

$$\text{Water uptake} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100\% \quad (1)$$

The quantity of acid equivalents per gram of polymer can be obtained by the following steps. First, the membrane in the acid form was immersed in 2 M NaCl solution to convert sulfonic acid to sodium form. Next, the released H<sup>+</sup> was back titrated with a 0.01 N NaOH solution using phenolphthalein as indicator, meanwhile, the volume of NaOH and pH was recorded to determine the equivalence point. The IEC is the equivalents per gram of dry polymer.



Scheme 1. Idealized representation of the process of preparing the Nafion<sup>®</sup>/MMT-diamine composite membranes.

## 2.6. Proton conductivity

Proton conductivities of full hydration membranes were measured at room temperature by AC impedance method using a Solartron Interface 1260 gain phase analyzer, Hampshire, U.K. over the frequency range of 1 Hz–10 kHz. The sample was placed sandwiched between two circular platinum electrodes of 1.0 mm diameter in an open cell. A spring linked to one of the electrodes kept the membrane under a constant pressure, thereby providing good contact between the electrodes and the membrane. The conductivity was calculated from the following equation:  $\sigma = L/RA$ , where  $L$  is the membrane thickness,  $A$  is the surface area of the electrodes and  $R$  is the resistance.

## 2.7. Methanol permeability

Methanol permeability was determined and calculated by using two connected compartment cells as reported in our previous study [23]. In the beginning, one compartment was filled with 2 M methanol solution in deionized solution, the other compartment was filled with deionized water. Each compartment was kept stirring during experiment to ensure the uniformity of the cell concentration. The density and weight fraction of methanol were recorded with time and were converted to the methanol concentration. Methanol permeability was obtained by analyzing the methanol concentration with time.

## 2.8. DMFC single-cell test

The membranes were immersed in 2 M sulfuric acid for 1 day and then washed with distilled water to remove the remaining sulfuric acid in order to assure of the hydrogen form of the composite membranes. Fuel cell experiments were carried out in a 4 cm<sup>2</sup> self designed single cell. The single-cell was tested with 2 M methanol solution and air breathing after equilibrium at 40 °C for 4 h. A layer of 20 wt% of PtRu (1:1, a/o) on carbon black (anode) and 20 wt% of Pt on carbon black (cathode)

were applied on two gas diffusion layers. The content of catalyst loading was approximately 0.2 and 0.4 mg cm<sup>-2</sup> for anode and cathode, respectively.

## 3. Results and discussion

### 3.1. Analysis of MMT/POP-diamines organoclay

Various spatially enlarged organoclays were prepared by using POP-backed quaternary ammonium salts of various molecular weights  $M_w$  230, 400 and 2000 as the intercalating agents for Na<sup>+</sup>-MMT [22]. The wide  $d$  spacings of modified silicates were measured as 13.6, 17.3 and 54.8 Å, respectively, and were correlated to the molecular weight of the intercalating agents as summarized in Table 1. Results implicated these POP-diamines have been intercalated into the MMT interlayer spacing have a similar orientation. The XRD of MMT/POP2000 exhibited a series of Bragg peaks in the Fig. 1 from  $n = 1-5$ , indicating a more ordered gallery structure was formed comparing the pristine montmorillonite. Meanwhile, the organoclay became highly organophilic as POP-diamines molecular weight was increased [24,25]. However, POP230 and POP400 derived MMT were much easier to disperse in the polar solvent than the MMT/POP2000 organoclay (Table 1). Results showed that the modified MMT would be dispersed much better in Nafion<sup>®</sup> solu-

Table 1  
Basal spacing and solvophilicity of Na<sup>+</sup>-MMT intercalated by POP-diamines

Intercalating agent	$d$ spacing (Å) <sup>a</sup>	wt fraction (w/w%) <sup>b</sup>	Solvophilicity <sup>c</sup>		
			Toluene	Ethanol	Water
None	12.4	0/100	–	–	+
POP230	13.6	22/78	–	+	–
POP400	17.3	27/73	–	+	–
POP2000	54.8	60/40	+	+	–

<sup>a</sup> Basal spacing was determined by X-ray diffraction.

<sup>b</sup> Weight fraction: organic composition/clay (measured by TGA).

<sup>c</sup> (+) dispersible; (–) aggregated.

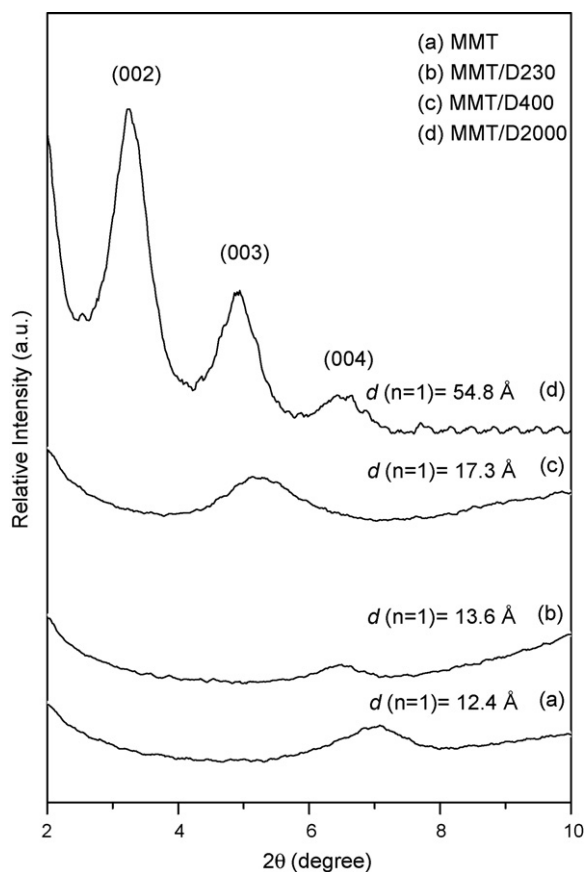


Fig. 1. XRD patterns of (a) original MMT, (b) MMT/POP230, (c) MMT/POP400, and (d) MMT/POP2000.

tion (low aliphatic alcohols) with the decreasing of the molecular weight of intercalating agent.

### 3.2. Analysis of Nafion<sup>®</sup>/m-MMT composite membranes

Up to now, the morphology of Nafion<sup>®</sup> is still not completely elucidated, and there is not a general agreement on the Nafion<sup>®</sup> structure. Nevertheless, it is generally agreed that the ionic sites can reorganize themselves depending on the hydration level of the polymer. It is also known that there is a hydrophilic path through which water and ions are transported [27]. Therefore, by controlling the ion channel size, direct effect on the methanol permeability in the membrane may be achieved. Fig. 2 shows the XRD patterns of the Nafion<sup>®</sup>/MMT-POP400 composite membranes at different loadings. From Bragg's law, it was estimated that ionic channel size of Nafion<sup>®</sup> was reduced from 3.98 to 2.34 nm with 7 wt% MMT-POP400. Furthermore, MMT displays a characteristic peak at  $2\theta = 7^\circ$ . Comparing with interlayer spacing of unmodified MMT (12.4 Å) in Fig. 1, the relatively large initial interlayer spacing of MMT-POP400 (17.3 Å) was observed and the polymer chains can intercalate into galleries much easier. The composite membranes showed featureless diffraction patterns in the region from  $2\theta = 4$  to  $8^\circ$  until the loading of MMT-POP400 reached 7 wt%. This strongly implies that a disordered and exfoliated nanocomposite was formed.

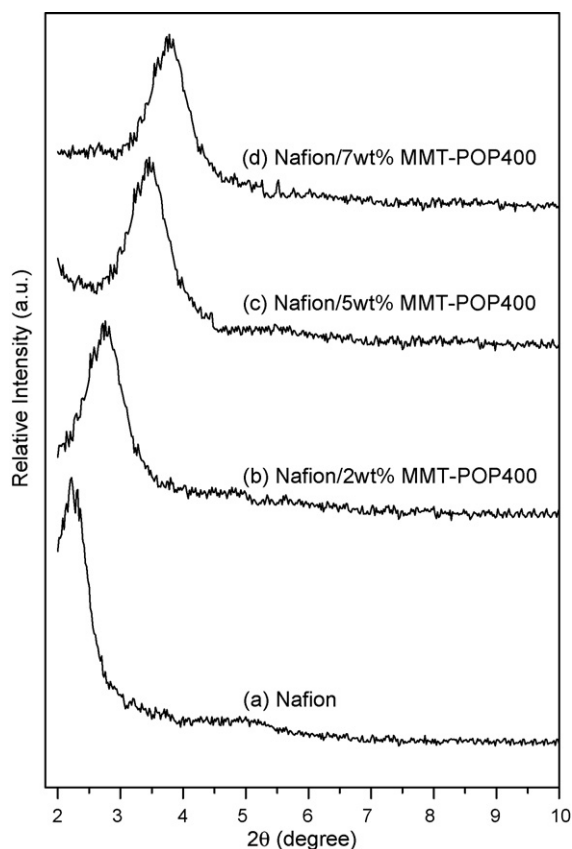


Fig. 2. XRD patterns of (a) Nafion<sup>®</sup> membrane, (b,c,d) Nafion<sup>®</sup>/MMT-POP400 composite membranes with various content of *m*-MMT.

The evidence for the change in ionic channel size of the composite membranes fabricated with equal content (5 wt%) of various modified-MMTs (*m*-MMT) can be obtained from the XRD patterns (Fig. 3). As shown in Fig. 3, comparing XRD patterns of pristine Nafion<sup>®</sup> with the composite membranes indicated that the size of ion channel in the membrane was changed by introducing *m*-MMT. According to Bragg's law, it was suggested that the size of ionic channel were reduced with increasing molecular weights of intercalating agent derived MMT. Nevertheless, the characteristics of two diffraction peaks of the Nafion<sup>®</sup>/MMT-POP2000 were observed. This phenomenon indicated that MMT-POP2000 is poorly dispersed within Nafion<sup>®</sup> as microphase-separated stacked layers, since the organoclay of MMT-POP2000 was highly organophilic and poor interaction with Nafion<sup>®</sup>. On the other hand, the broad diffraction peak of the Nafion<sup>®</sup>/MMT composite membrane was observed, most likely due to the poor compatibility with Nafion<sup>®</sup>. The smaller channel in membranes could be a factor responsible for the reduced methanol crossover through the electrolyte membrane which will be discussed later.

### 3.3. Analysis of chemical composition by XPS

The C1s core level spectra of the pristine Nafion<sup>®</sup> membrane and composite membranes are presented in Fig. 4a. The peak envelope shows the presence of at least two components mainly attributed to the C–C and C–H species at low binding

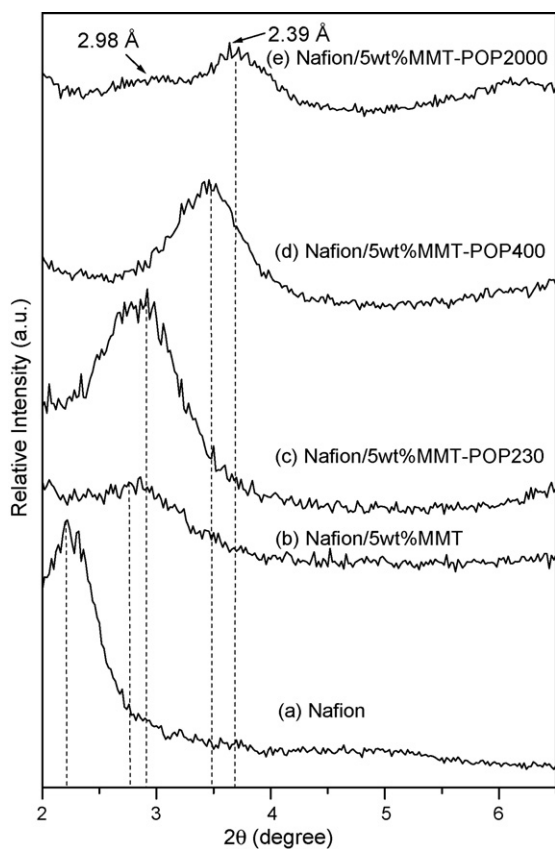


Fig. 3. XRD patterns of (a) Nafion<sup>®</sup> membrane and Nafion<sup>®</sup> composite membranes filled with 5wt% of (b) Native MMT, (c) MMT-POP230, and (d) MMT-POP400.

energy and the C–F species at high binding energy. In fact, the C1s spectrum can be fitted with at least four peaks at 282.2, 283.8, 288.9, and 290.4 eV which are illustrated in Fig. 4a. The 282.2 eV peak is attributed to the C–C environment, and the 283.8 eV may be associated with C–O. The 288.9 eV is attributed to CF<sub>2</sub> and CF–O species, and the 290.4 eV peak observed in Fig. 4a is responsible for CF<sub>3</sub> species. The resulting peak components are consistent with those reported by Huang et al. [26,27]. After introducing organoclays into Nafion<sup>®</sup>, the low binding energy component was increased and the C–F component was decreased relatively, indicating that organoclays are presented in the composition of the composite membranes. The C–N component of POP-diamine can be detected at 284.1 eV by curve fitting [28].

Since the organoclays were introduced into the Nafion<sup>®</sup>, a portion of the amine group (–NH<sub>2</sub>–) can be compensated by –SO<sub>3</sub>H groups. Indeed, when comparing the S 2p spectrum of the unmodified membrane to the S 2p spectra of the modified membranes (Fig. 4b), a shift in binding energy toward lower values in the presence of organoclays is observed. The lower binding energy values suggest the presence of interactions between the –SO<sub>3</sub>H and –NH<sub>2</sub>– functional groups [29–31]. A similar observation was noted for poly(styrene sulfonate) membranes modified with polyaniline [30]. As shown in Table 1, the weight fraction of *m*-MMT measured by TGA may explain the shift of binding energy in S 2p spectrum. Although adding the

same amount of various *m*-MMTs in the composite membrane, however, the quantities of amine functional groups generated will be different, i.e. MMT-POP230 > MMT-POP400 > MMT-POP2000. Therefore, the observation of the shift from 167.4 eV in Nafion<sup>®</sup>/MMT-POP230 will be higher than others.

The O 1s high-resolution spectrum of the unmodified Nafion<sup>®</sup> exhibits two peaks centered at 529.2 and 531.8 eV which may be attributed to oxygen atom in sulfonic acid and oxygen atom in ether, respectively as shown in Fig. 4c [32,33]. With the presence of organoclays, the shape of O 1s peak will be changed and the overall percentage of atom will be increased. This was reasonable since the oxygen atom is presented in the POP-backed diamine of intercalating agent. The O 1s peak reveals the appearance of a new component in the presence of organoclays. First, a peak appears at 531.4 eV which could be attributed to the oxygen atom of sulfonate compensated by amine groups from organoclays. As observed in the S 2p spectra of Nafion<sup>®</sup>/MMT-POP400 composite membranes, the presence of the amine groups allows stabilization of the sulfonate group which reduces the electron density around the oxygen atom and increases the electron density around the sulfur atom [29–31]. In the case of sulfur, as mentioned early in this manuscript, that the presence of organoclay lowers the S 2p peak binding energy following the increase in electron density around the sulfur atom. In the same situation, oxygen atom from the sulfonate groups may possess a higher binding energy in the presence of amine groups.

### 3.4. Water uptake, ion exchange capacity

The water uptake is very crucial in DMFC because it is closely related to the proton conductivity and the mechanical strength of proton conducting membrane. The water uptake of the membranes was illustrated in Table 2. The slightly decrease in water uptake might be due to two factors: (1) introducing inorganic filler may reduce water uptake; (2) MMT-POP230 and MMT-POP400 were much more hydrophilic than MMT-POP2000. The terminal functional group (–NH<sub>2</sub>) of organoclays was hydrophilic, and then that would associate the hydrated species. Table 2 shows that the IEC values for different composition composite membranes. As shown in the Table 2, the IEC value of Nafion<sup>®</sup>/MMT-POP400 is higher than other composite membranes.

### 3.5. Proton conductivity

Fig. 5 compares the effect of the unmodified and modified MMT on the proton conductivity of the Nafion<sup>®</sup> composite membranes. The proton conductivity of the membranes tends to decrease by adding of MMT. The proton conductivity of Nafion<sup>®</sup>/MMT-POP230 was lower than that of Nafion<sup>®</sup>/MMT-POP400 since MMT-POP230 possesses higher base characteristics than others. On the other hand, introducing MMT-POP230 into Nafion<sup>®</sup> would reduce IEC value of the proton exchange membrane than that of MMT-POP400 as shown in Table 2. Therefore, it may tentatively suggest that 5 wt%

Table 2  
Physical properties of Nafion<sup>®</sup> composite membranes

	Ion channel size (Å) <sup>a</sup>	$\sigma$ (mS cm <sup>-1</sup> )	Water uptake (wt%)	IEC (mmol g <sup>-1</sup> ) <sup>b</sup>
Pristine Nafion <sup>®</sup>	3.98	100	36.0	0.89
Nafion <sup>®</sup> /5 wt% MMT	3.20	40	28.2	0.71
Nafion <sup>®</sup> /5 wt% MMT-POP230	3.02	70	32.9	0.79
Nafion <sup>®</sup> /5 wt% MMT-POP400	2.55	92	32.7	0.83
Nafion <sup>®</sup> /5 wt% MMT-POP2000	2.39, 2.98	60	32.5	0.72

<sup>a</sup> Ionic channel size was determined by X-ray diffraction.

<sup>b</sup> A base titration procedure measures the equivalents of sulfonic acid in the polymer, and the measurement was used to calculate the acid capacity or equivalent weight of the membrane.

MMT-POP400 could be the optimum level of inorganics in the composite electrolyte membrane for DMFCs.

### 3.6. Methanol permeability

Fig. 6 shows the methanol permeability of membranes fabricated with different contents of pristine MMT or modified MMT in Nafion<sup>®</sup>. The membrane thickness was maintained at 120  $\mu$ m by employing the same total amount of Nafion<sup>®</sup> and the inorganic filler. The unmodified MMT is poorly dispersed in the Nafion<sup>®</sup> membrane, the methanol permeability is only slightly increased that might be due to the lack of inter-

action between Nafion<sup>®</sup> and filler. The organoclay modified by POP-backboned quaternary ammonium salts would improve their compatibility with Nafion<sup>®</sup> and reduce the ionic channel size. The permeability of methanol decreased with increasing *m*-MMT content. This result agrees with the XRD data as shown in Fig. 3. Addition of MMT-POP400 results in a decreasing of methanol permeability by approximately 40%, which is consistent with results that Nafion<sup>®</sup>/MMT-POP400 possesses better compatibility and dispersion of organoclay. The ratio between the ion conductivity and the methanol permeability (*C/P* ratio) is actually increased by adding 5 wt% of MMT-POP400. A higher MMT-POP400 loading has no significant effect as illustrated in

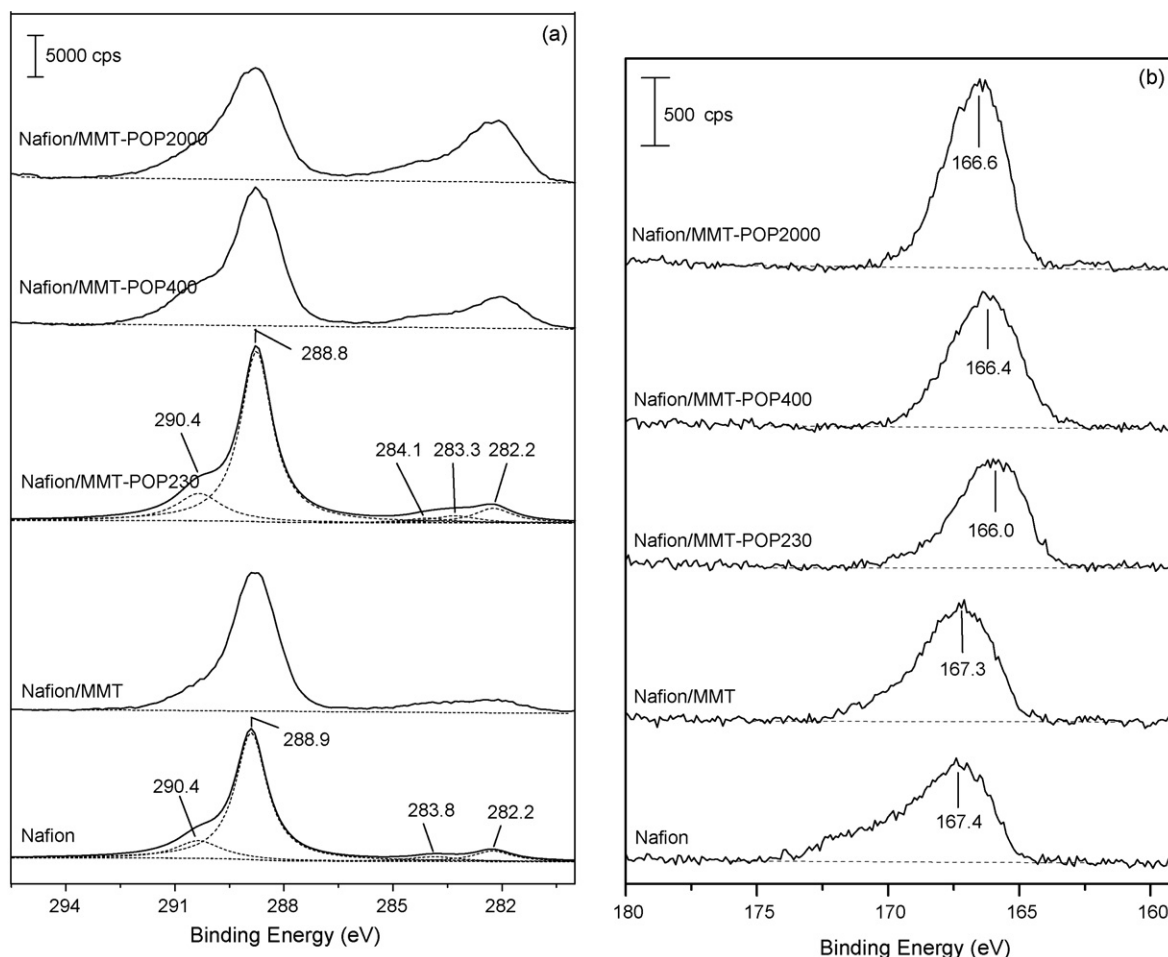


Fig. 4. High-resolution XPS spectra of the surface of Nafion<sup>®</sup> and Nafion<sup>®</sup> composite membranes: (a) C 1S, (b) S 2P, and (c) O 1S.

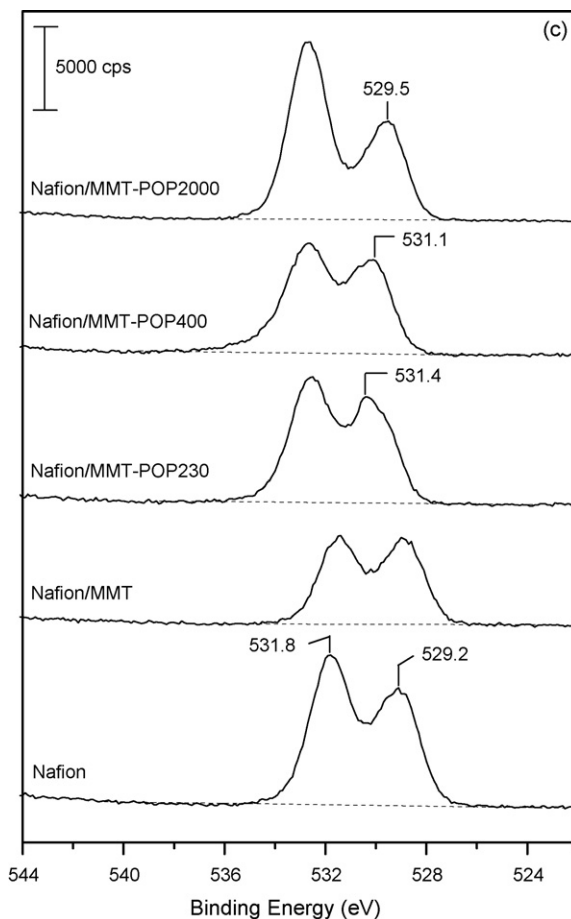


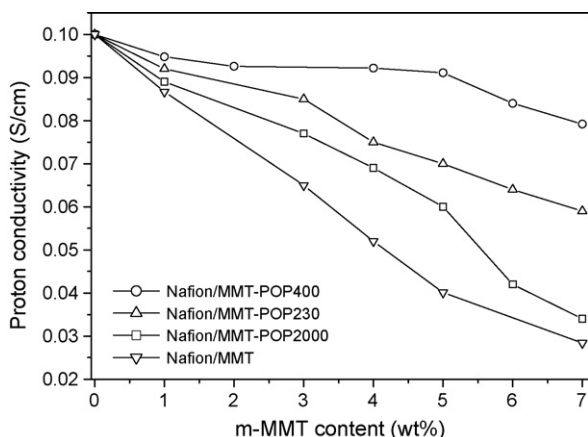
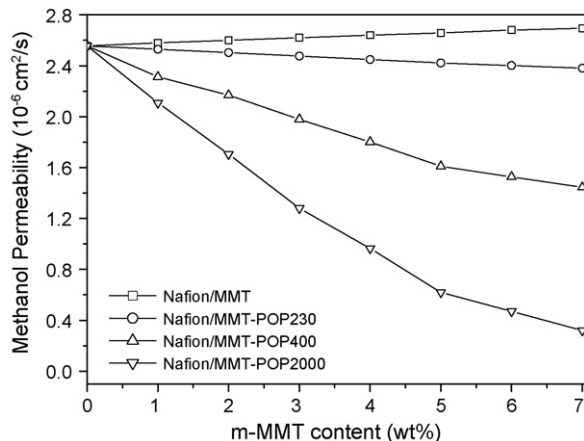
Fig. 4. (Continued).

Fig. 7. Although the proton conductivity was still slightly low, the composite membranes tested in DMFC exhibited substantially improved performance by reducing the methanol crossover drastically compared with the pristine Nafion<sup>®</sup> membrane.

### 3.7. Fuel cell performances

The performance of composite membranes was tested in a DMFC single cell. Fig. 8 shows the plots of cell potential ver-

sus current density and power density versus current density for the DMFC membrane-electrode assembly (MEA) with composite membrane of 5 wt% MMT-POP400 and pristine Nafion<sup>®</sup>. The composite membrane with 5 wt% MMT-POP400 showed an improved performance comparing with pristine Nafion<sup>®</sup> itself. The current densities were measured as 51 and 56 mA cm<sup>-2</sup> at a potential of 0.2 V with the composite membrane containing 0 and 5 wt% MMT-POP400 contents, respectively. The

Fig. 5. Proton conductivity of native and modified MMT in Nafion<sup>®</sup> membranes.Fig. 6. The methanol permeability on the content of native and modified MMT in Nafion<sup>®</sup> membrane.

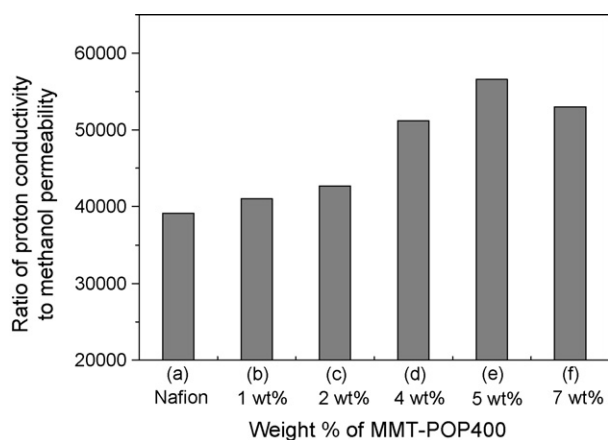


Fig. 7. Ratio of the proton conductivity to the methanol permeability for Nafion<sup>®</sup> composite membranes filled with various contents of MMT-POP400.

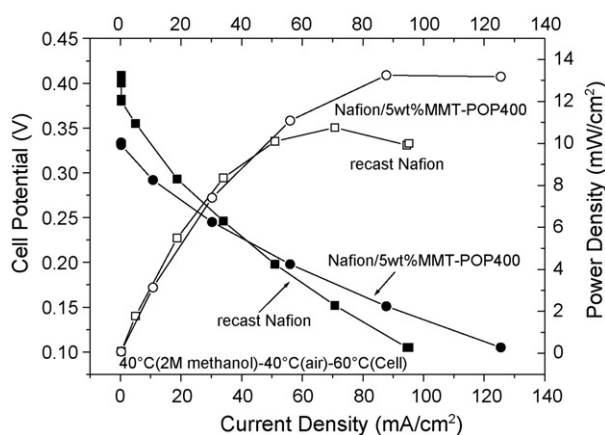


Fig. 8. Polarization curves for the MEA made with pristine Nafion<sup>®</sup> membrane and composite membranes operated at 313 K.

performance of the DMFC was improved by introducing of *m*-MMT. The maximum power density of  $13.3 \text{ mW cm}^{-2}$  was obtained for the composite membrane with 5 wt% of MMT-POP400.

The present system of Nafion<sup>®</sup>/MMT-POP-diamine provides promising results by two factors: (i) the improved compatibility of MMT-POP-diamine compared to other inorganic fillers employed previously [20]; and (ii) the highly anisotropic morphology of the MMT platelets that could be more effective in blocking the passage of methanol than materials with other geometries [14,15]. Yet, the proton conductivity of the composite membrane is still substantially lower than that of Nafion<sup>®</sup> itself.

#### 4. Conclusions

An organic species bearing an organic amine functional group ( $-\text{NH}_2$ ) was grafted on the surface of MMT by using POP-backboned quaternary ammonium salts of various molecular weights  $M_w$  230, 400, and 2000 as intercalating agents. The performance of these Nafion<sup>®</sup>/*m*-MMT composite membranes was evaluated for DMFCs in terms of methanol permeability,

proton conductivity, and cell performance. The proton conductivity of Nafion<sup>®</sup>/MMT-POP400 composite membrane was decreased slightly by adding MMT-POP400. The methanol permeability of the composite membrane decreased dramatically with increasing content of MMT-POP-diamine in the composite membrane. The Nafion<sup>®</sup>/5 wt% MMT-POP400 membrane showed higher selectivity (*C/P* ratio) than that of recasting Nafion<sup>®</sup>. The high selectivity indicates that the composite membrane is suitable for DMFC application. The current densities were measured with the composite membrane containing 0 and 5 wt% MMT-POP400 contents, respectively, as 51 and  $56 \text{ mA cm}^{-2}$  at a potential of 0.2 V. The combination of these effects led to a significant improvement of Nafion<sup>®</sup>/5 wt% MMT-POP400 composite membranes in the performance of the DMFCs.

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