Short communication

A novel composite membranes based on sulfonated montmorillonite modified Nafion® for DMFCs

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Abstract

A novel functional organoclay was prepared using POP-backboned quaternary ammonium salts that contained sulfonic acid (–SO₃H) to improve the performance of Nafion® membranes used in direct methanol fuel cells. Modified layered silicate clays were cast with Nafion®. The performance of the Nafion®/MMT-POPD400-PS composite membranes was evaluated in terms of methanol permeability, proton conductivity and cell performance. The methanol permeability of the composite membrane declined as the MMT-POPD400-PS content increased. The MMT was functionalized using organic sulfonic acid to enhance proton conductivity. The proton conductivity of the composite membrane exceeded that of pristine Nafion®. These effects essentially improved the single-cell performance of DMFC.

1. Introduction

Direct methanol fuel cells (DMFCs) have great potential in generating electricity owing to their high efficiency and lightness [1]. However, two major technical limitations restrict the commercialization of the DMFC. They are the slow oxidation kinetics of methanol and the high methanol crossover from the anode to the cathode [2–4]. Nafion® (perfluorosulfonic acid) membranes are commonly adopted as electrolytes, because of their long-term stability under fuel cell operating conditions and excellent proton conductivity. However, the high methanol permeability rates across such membrane represent a serious obstacle to the realization of DMFCs for practical use [5].

Composite membranes have been used in DMFCs to reduce the permeability of methanol as compared to pristine Nafion® [6–12]. Most composite membranes have been prepared by the addition of nonconductive ceramic oxide, such as silica [6], titania [7] and montmorillonite [8–12]. However, improving the cell performance of DMFCs by incorporating inorganic moieties into the Nafion® membrane has not been very successful. Ion-conducting inorganics, such as MMT-SO₃H and MMT-COOH,

have also been investigated without much success, although these materials may reduce the methanol permeability and proton conductivity of composite membranes [11–12].

A modified montmorillonite with an organic sulfonic acid group (MMT-SO₃H) was prepared and a composite electrolyte membrane with Nafion® was fabricated to increase proton conductivity and reduce the methanol permeability as compared to pristine Nafion®. Since silicate clays are hydrophilic and have little affinity for hydrophobic polymers, an organic modification is required to enhance their compatibility with polymeric materials [13]. In this investigation, a sulfonated intercalating agent was synthesized by the ring-opening condensation reaction of 1,3-propane sultone (PS). Modified montmorillonites were prepared from poly(oxyproplene)-backboned (POP) quaternary ammonium salts of POPD400-PS as intercalating agents for Na⁺-MMT. Such composite membranes in DMFCs are synthesized, characterized and evaluated.

2. Experimental

2.1. Materials synthesis

The adduct of amine/1,3-propane sultone was synthesized using poly(propylene oxide)-backboned diamines of M_w 400 as the starting material and was abbreviated as POPD400. The

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diamine was commercially available from the Huntsman Chemical Co., Philadelphia, Pennsylvania, U.S.A. The preparation of diamine bearing one sulfonic acid (–SO$_3$H), abbreviated as POPD400-PS was carried out in a glass reactor equipped with a stirrer. The designated amount of 1,3-propane sultone (12.2 g, 100 mmol) was slowly added to a reactor charged with POPD400 (40 g, 100 mmol). The progress of the reaction was characterized by FT-IR to confirm that the diamine bears one sulfonic acid (–SO$_3$H) successfully. Organoclay has been prepared by cation exchange between Na$^+$ in clay galleries and poly(oxyproplene) (POP)-backboned diamines cations in aqueous solution [14]. In this present work, a total of 10 g of Na$^+$-MMT (cation exchange capacity CEC = 1.45 mequiv g^{-1}) was dispersed homogeneously in 1 L deionized water at 80 °C. The slurry was added with the POPD400-PS (7.6 g, 14.5 mmol) and the equivalent 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.

To prepare a composite membrane, a desired amount of prepared MMT/organoclay was added to a 5 wt% Nafion® solution, and then stirred and degassed by ultrasonication. The contents of functionalized MMT in the mixture were varied in 1–6 wt% based on Nafion®. 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 crevice of 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 fabricating the composite membrane.

2.2. Characterization

The structure of the synthesized POPD400-PS was characterized with infrared spectroscopy using a Nicolet Avatar 320 FT-IR instrument (WI, U.S.A.) in the range of 4000–400 cm^{-1}. The d-spacing of MMT/POPD400 and MMT/POPD400-PS organoclays were scanned at a rate of 1° min^{-1} by using a Shimadzu XD-5 X-ray diffraction Instrument (XRD; 45 kV, 30 mA) with copper target and Ni filter. The basal spacing (n = 1) was calculated according to Bragg's law, $n\lambda = 2d \sin \theta$. 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^{-1} in nitrogen atmosphere.

2.3. Proton conductivity

Proton conductivities of membranes were measured at room temperature by AC impedance method, using a Solartron Inter-
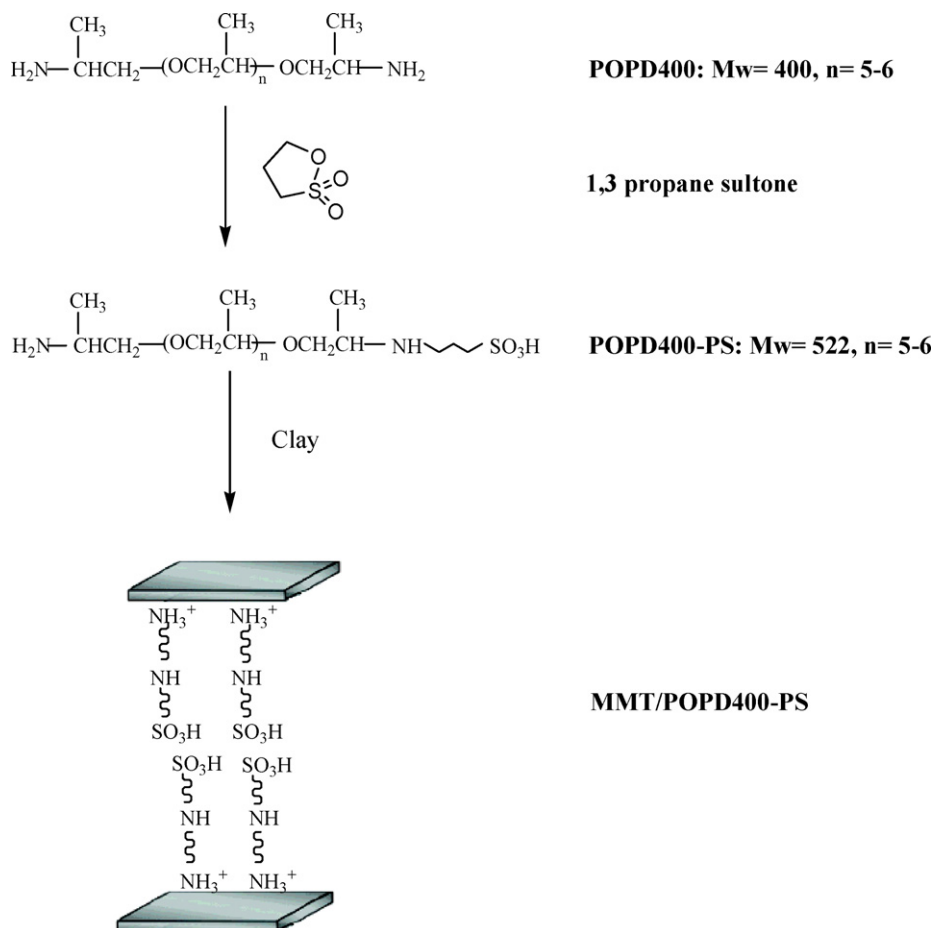
Scheme 1. Synthesis scheme of POPD400 bearing sulfonic acid side group and the process of preparing POPD400-PS intercalated MMTs.

face 1260 gain phase analyzer, Hampshire, U.K. over the frequency range of 1 Hz–10 kHz. The sample was place sandwiched between two circular platinum electrodes of 1.0 mm diameter in an open cell. The conductivity was calculated from the following equation: $\sigma = L/RA$, where L is the membrane thickness, A the surface area of the electrodes and R is the resistance.

2.4. Methanol permeability

Methanol permeability was determined and calculated by using two connected compartment cells. In the beginning, one compartment was filled with 10 M methanol solution, and the other compartment was filled with deionized water. Each of the compartment was kept stirring during experiment to ensure the uniformity of the cell concentration. The refractive index of methanol solution was recorded with time and was converted to the methanol concentration. Methanol permeability was obtained by analyzing the methanol concentration with time.

2.5. DMFC single-cell test

The membranes were immersed in 2 M sulfuric acid for 1day 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^2 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^{-2} for anode and cathode, respectively.

3. Results and discussion

Scheme 1 displays the synthesis of POPD400 with a sulfonic acid side group via a ring-opening reaction between the primary amine of POPD400 and 1,3-propane sulfone. Scheme 1 also depicts an idealized preparation of the MMT-SO$_3$H organoclay. Fig. 1 shows the FT-IR spectra of POPD400 and POPD400-PS. In the spectra, infrared bands appear at 824, 860, 924, 1015 and 1106 cm^{-1}. After modification by POPD400, the IR bands that are produced by the POPD400-PS appeared at 607, 671, 730, 790, 824, 924, 1015, 1040, 1065, 1106 and 1175 cm^{-1}. Table 1 compares the infrared absorptions of POPD400 and POPD400-PS. The new IR bands of the intercalating agents demonstrate that C−S (607, 671 cm^{-1}) and species that contain C−C−C (1065 cm^{-1}) and CH−N−C (1175 cm^{-1}) are generated. FT-IR was used to characterize the progress of the reaction, and confirm that the POPD400-PS had been synthesized successfully (Fig. 2).

In the conventional method for Na$^+$-MMT intercalation, the incorporated organics are typically quaternary ammonium salts that can be formed by treating the precursor amines with hydrochloric acid. The ionic exchange reaction between the quaternary ammonium salts (−NH$_3$Cl$^-$) and sodium ions
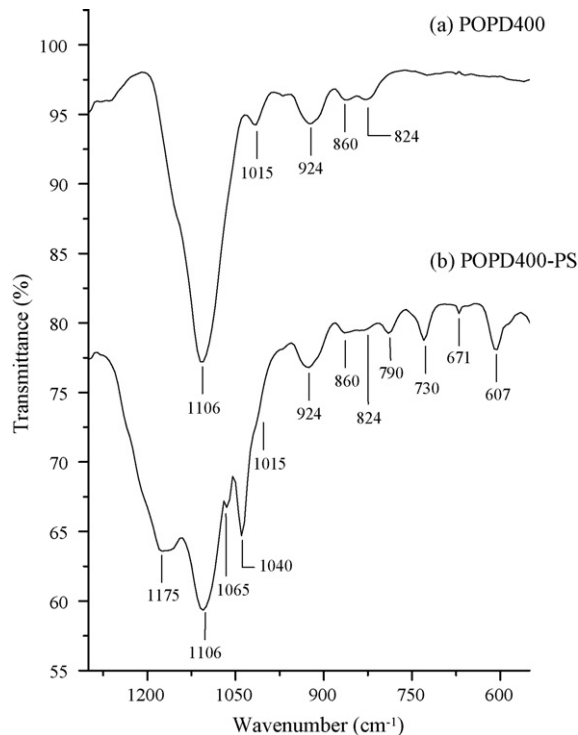

Fig. 1. FT-IR spectra of: (a) POPD400 and (b) POPD400-PS.

Table 1
Comparison of infrared frequencies (cm^{-1}) of POPD400 and POPD400-PS[a]

POPD400 (this work)	POPD400-PS (this work)	Assignment [15]
	607, 671	ν (C−S)
	730	ρ (−CH$_2$−CH$_2$−CH$_2$−)
	790	ω (secondary amine, −NH−)
824, 860	824, 860	ν (primary amine −NH$_2$)
924	924	ν (C−O−C)
1015	1015	ν (C−N)
	1040	ν (−SO$_3$H)
	1065	ν (C−C−C)
1106	1106	ν (CH−NH$_2$)
	1175	ν (CH−NH−C)

ν, stretching; ρ, rocking; ω, wagging.

(≡Si−O$^-$Na$^+$) in the layered MMT is the main driving force for the intercalation of MMT. For example, the poly(propylene oxide)diamine of M_w 400 (POPD400) was treated with one equivalent amount of hydrochloric acid to produce monoammonium salts, which could intercalate with Na$^+$-MMT. Therefore, the modified silicates expand from 12.4 to 17.3 Å because of the aforementioned controlling factor of Na$^+$-MMT intercalation. The intercalating profile was further studied using organic intercalants that comprised a POP-backbone structure with the mono-tethering functionality of a quaternary ammonium salt. The reaction in Scheme 1 describes the synthesis intercalating agent POPD400-PS. The starting poly(alkylene oxide)diamine with Mw 400 was allowed to react with one equivalent amount of 1,3-propane sultone (PS) to synthesize sulfonated intercalating agents. The intercalation of POPD400-PS with Na$^+$-MMT produced a d-spacing of 17.7 Å in the silicate as indicated in Fig. 2.

Table 2
Basal spacing and solvophilicity of Na$^+$-MMT intercalated by POPD400 and POPD400-PS

Intercalating agent	d-Spacing (Å)[a]	Weight fraction (w/w, %)[b]	Solvophilicity[c]		
			Toluene	Ethanol	Water
None	12.4	0/100	−	−	+
POPD400	17.3	27/73	−	+	−
POPD400-PS	17.7	35/65	−	+	−

[a] Basal spacing was determined by X-ray diffraction.
[b] Weight fraction: organic composition/clay (measured by TGA).
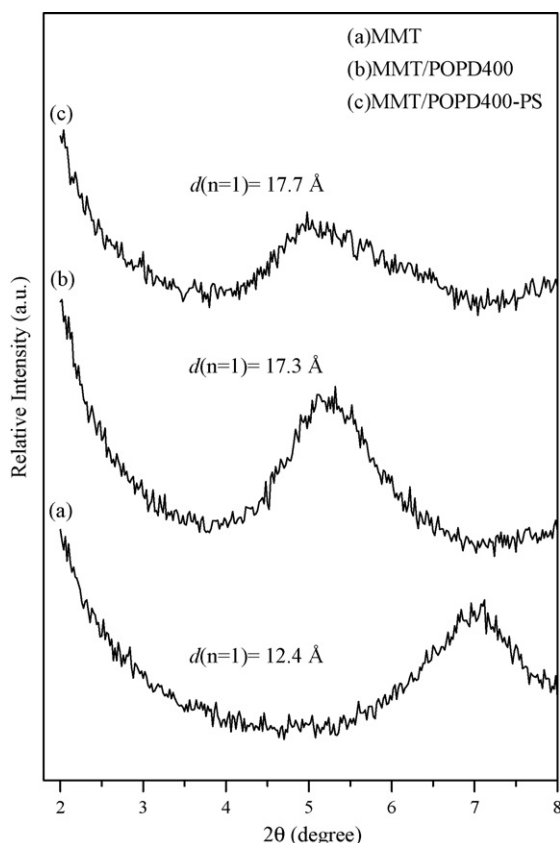[c] +, dispersible; −, aggregated.

Fig. 2. X-ray diffraction patterns of: (a) original MMT, (b) MMT/POPD4000 and (c) MMT/POPD400-PS.

The intercalated silicates were analyzed by thermogravimetric analyses (TGA), revealing that the percentage of the organic encapsulated is 35% as shown in Table 2.

Fig. 3 presents the methanol permeability and proton conductivity of membranes fabricated with various proportions (0–6 wt%) of MMT-POPD400-PS in Nafion®. The methanol permeability decreased rapidly as the amount of MMT-POPD400-PS added to Nafion® increased. Indeed, several studies have demonstrated that adding montmorillonite nanofiller can improve the barrier properties of Nafion® membrane towards methanol, because the length-to-width ratio of the additive is high [8–12]. The methanol permeability of the composite membranes that contained 6 wt% MMT-POPD400-PS was 1.2×10^6 cm^2 S^{-1}, 60% of that of pristine Nafion®. The proton conductivity of the composite membranes increased

with added MMT-POPD400-PS. The proton conductivity of the composite membranes generally declined from that of pristine Nafion® membrane as the inorganic filler content increased [6–12]. However, the cause may involve various mechanisms of proton transportation. We suggest two mechanisms that improve proton transportation in the composite membrane: (i) hopping mechanism is promoted by the intercalating agent (POPD400-PS) with a long chain and (ii) the vehicle mechanism is accelerated on the surface of the introduced clay network oxide [16]. Three to five weight percent MMT-POPD400-PS is tentatively concluded to be the optimum level of inorganic filler in the composite electrolyte membrane for DMFCs.

The performance of composite membranes was tested in a DMFC single cell. Fig. 4 plots cell potential versus current density and power density versus current density of the DMFC membrane-electrode assembly (MEA) with an MMT-POPD400-PS and pristine Nafion® composite membrane. Indeed, the suppression of the methanol crossover results in higher OCV at lower current densities [17]. In this work, however, the improvement at lower current densities is less, perhaps because of the concentration of the methanol fuel in the DMFCs test. Some groups have shown that the OCV change at low current densities with a low concentration of methanol fuel was too small to be distinguished [18–21]. In this work, the single cell was tested at low methanol concentration (2 M). Hence, the phenomenon exhibited by DMFCs herein may be reasonable. The composite membrane with 5 wt% MMT-POPD400-PS outperformed pristine Nafion®. The current densities measured
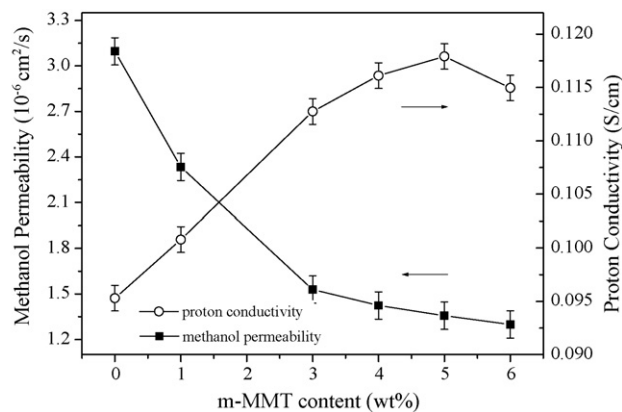

Fig. 3. The proton conductivity (–○–) and methanol permeability (–■)– of the pristine Nafion® and composite membranes fabricated with different amounts of MMT-POPD400-PS.
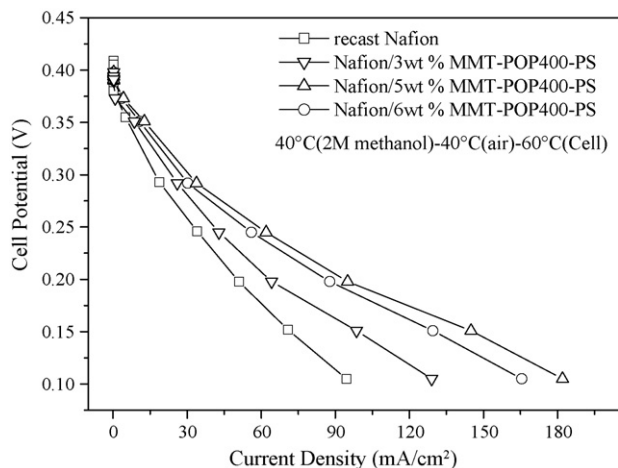
Fig. 4. Polarization curves for the MEA made with pristine Nafion® membrane and composite membranes operated at 313 K.

with composite membranes that contained 0, 3, 5 and 6 wt% MMT-POPD400-PS, were 51 and 64, 95 and 88 mA cm^{-2}, respectively, at a potential of 0.2 V. Meanwhile, the membrane with 6 wt% inorganic loading does not outperform that with 5 wt%, perhaps because the proton conductivity at 6 wt% inorganic loading is reduced, as plotted in Fig. 3. However, all of the composite membranes that contain MMT-POPD400-PS outperform pristine Nafion® at high current densities.

4. Conclusions

POP-backboned oligomers that bear an organic sulfonic acid intercalating agent can be used in the preparation of highly ordered silicates with basal spacing of up to 18 Å via a cation exchanging mechanism. The Nafion®/MMT-POPD400-PS composite membranes exhibit a higher selectivity than pristine Nafion®, perhaps because of the increased proton conductivity and decreased methanol permeability of the composite membranes. The high selectivity reveals that the composite membrane is suited to DMFC applications. The combination of these effects substantially improved the properties of Nafion®/MMT-POPD400-PS composite membranes, which are appropriate for DMFC applications.

Acknowledgment

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