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Nafion/Sulfonated Montmorillonite Composite: A New Concept Electrolyte Membrane for Direct Methanol Fuel Cells

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An organic species bearing an organic sulfonic acid (HSO_3-) was grafted onto the surface of montmorillonite (MMT) by silane condensation, and the composite membranes were cast together with Nafion. The performance of the Nafion/HSO_3−MMT composite membranes for direct methanol fuel cells (DMFCs) was evaluated in terms of methanol permeability, proton conductivity, and cell performance. The methanol permeability of the composite membrane decreased dramatically with increasing content of HSO_3−MMT in the composite membrane. By rendering proton conductivity to MMT by functionalization with an organic sulfonic acid, the proton conductivity of the composite membrane was lowered only slightly from that of pristine Nafion 115. The combination of these effects led to a significant improvement in the performance of DMFCs made with Nafion/HSO_3−MMT composite membranes.

Introduction

Among various fuel cells, direct methanol fuel cells (DMFCs) are suited for portable devices or transportation applications owing to their high energy density at low operating temperatures and the ease of handling a liquid fuel.[1] Yet they have major technical drawbacks, i.e., slow oxidation kinetics of methanol and high methanol crossover from the anode to the cathode.[2−4] In particular, high methanol permeation through Nafion membranes significantly lowers 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 provide proton conduction from the anode to the cathode and effective separation of the anode (methanol) and cathode (oxygen) reactants. The Nafion membrane is by far the most studied proton electrolyte membrane for DMFCs as well as for polymer electrolyte membrane (PEM) fuel cells. However, current Nafion membranes cannot meet the requirements for practical DMFC applications.

Nafion membranes are chemically inert in both the oxidizing and reducing atmospheres of the fuel cell, have demonstrated a long-term stability under fuel cell operating conditions, and have an excellent proton conductivity (0.07−0.23 S cm^{-1}).[5] Yet, the high methanol permeability rate across the membrane poses a critical problem in realization of DMFCs for practical use.[6] This phenomenon is caused by the protonic drag of methanol, similar to electro-osmotic drag of water. Methanol is easily transported together with solvated protons by means of the electro-osmotic drag as well as by diffusion through the water-filled ion channels within the Nafion structure and through the Nafion itself. Methanol transported across the membrane is chemically oxidized to CO_2 and water at the cathode, and causes a loss in Coulombic efficiency for methanol consumption as much as 20% under practical operation conditions.[7]

There have been many attempts to reduce the methanol permeability through the polymer electrolyte membranes: (i) to modify the surface of the membranes to block the methanol transport, (ii) to control the size of the proton transport channels using different block copolymers and cross linkages, (iii) to develop new types of electrolyte polymers, and (iv) to introduce a winding pathway for a methanol molecule by making a composite with inorganic materials. The composite membranes have been mostly prepared by addition of a nonconductive ceramic oxide such as silica, titania, zirconia, mixed silicon−titanium oxides, zeolites, silicon−aluminum oxides, and montmorillonite in the Nafion membrane.[8−15] Zirconium phosphates[16−21] have also been examined, which have a moderate proton conductivity when

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humidified (∼10^{-3} S cm^{-1}).[16] Among the reported zirconium phosphate fillers, γ-layered zirconium phosphates containing sulfophenyl groups had the highest conductivity (∼0.05 S cm^{-1}) at 373 K and 95% relative humidity (RH).[19] The main focus in these works was to obtain an electrolyte membrane operating at higher temperatures over 373 K. When applied to DMFCs, these composite membranes containing inorganic moieties indeed reduced the methanol crossover, yet this effect did not always lead to a desired improvement in the performance of the membrane−electrode assembly (MEA), mainly because the proton conductivity of the composite membranes mixed with these less proton-conductive oxides was markedly lowered compared with that of pristine Nafion membrane.

To minimize the loss of proton conductivity caused by adding the inorganics while reducing the methanol permeability, we modified a clay (montmorillonite) with an organic sulfonic acid group (HSO_3−MMT) and formed a composite electrolyte membrane with Nafion. The evaluation of the electrochemical activities of the DMFC was accomplished for a single cell fabricated with the cast composite membranes. Although the proton conductivity was still slightly lowered, the composite membranes tested in DMFC exhibited substantially improved performance by reducing the methanol crossover drastically compared with the pristine Nafion membrane. The composite membrane developed here has been successfully adopted to build a prototype DMFC to generate 100 Wh electricity from 100 mL of methanol solution, sufficient enough to power a notebook PC for 10 h of continuous operation.[22]

Montmorillonite (MMT) is an abundant and inexpensive layered alumino-silicate mineral that has large surface areas (220−270 m^2 g^{-1}, specified by Aldrich) and a negative layer charge. Its proton form (H^+-MMT) has a proton conductivity of 10^{-4} S cm^{-1} at room temperature,[23] and a cationic exchange capacity (CEC) of 0.95 meq g^{-1}. An organic species bearing the functionality (HSO_3-group) was grafted on the surface of MMT by silane condensation, which had been previously employed to render strong acidity to minerals such as kaolinite, magadiite and montmorillonite.[24−27]

Experimental Section

Preparation of Materials. *Functionalized MMT*. Raw MMT (Aldrich, Montmorillonite-K10) was treated with 1 N H_2SO_4 at 300 K to convert Na^+-MMT into H^+-MMT. The surface functionalization of H^+-MMT with 3-mercaptopropyltrimethoxy silane (3-MPTMS) was performed at the refluxing temperature of toluene (383 K) for 24 h with weight ratio of H^+-MMT, 3-MPTMS, and toluene of 1:0.2−2:5−20. Then thiol (−SH) grafted onto MMT was oxidized into sulfonic acid ($-SO_3H$) with 10 wt % hydrogen peroxide at 333 K. The prepared sample was then treated with 1 N H_2SO_4 at ambient temperature for complete protonation. The treated MMTs were separated by filtration, washed with deionized water and ethanol, and dried at 353 K in a vacuum oven.

Fabrication of Composite Membrane. To prepare a composite membrane, a desired amount of prepared HSO_3-MMT was added into a 5 wt % Nafion solution (DuPont), and then stirred mechanically and degassed by ultrasonication. The contents of functionalized MMT in the mixture were varied in 3, 5, 10, and 15 wt % based on Nafion. The prepared mixture was slowly poured into a glass dish in an amount that would give 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 353 to 403 K to prevent crevice of composite membrane. Finally, the residual solvent in the composite membrane was fully removed by evacuation at 403 K for 12 h. The diagram in Scheme 1 describes the procedure of making a composite membrane.

Characterization Methods. *Physicochemical Characterization.* X-ray diffraction (XRD) patterns were obtained on a MAC Science Co. M18XHF diffractometer with Cu Kα radiation (40 kV, 200 mA). The thermal properties of functionalized (HS- and HSO_3-) MMT were analyzed by thermogravimetric analysis (TGA, TGS-2). The TGA analyzer was operated in the range of 50 to 800 °C at a heating rate of 10 K/min under air flow of 60 mL/min. The degree of oxidation of thiol (HS-) to sulfonic (HSO_3-) groups was 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 ($h\nu = 1253.6$ eV) X-ray source. The ^{27}Al and ^{29}Si solid-state NMR measurements were performed on a Varian Unity Inova 300 MHz spectrometer (7.4 T) equipped with a 7-mm Chemagnetics MAS probe head using a sample rotation rate of 5.5 kHz. The chemical shifts for ^{27}Al and ^{29}Si were referenced to the positions of $Al(H_2O)_6^{3+}$ from $AlCl_3$ aqueous solution and tetramethylsilane (TMS), respectively. The spectra of ^{27}Al and ^{29}Si MAS NMR were collected at frequencies of 78.156 and 59.590 MHz, respectively.

Ion-Exchange Capacity Measurements. The ion-exchange capacity (IEC) (mmol of sulfonic acid/g of HSO_3-MMT) of each sample was determined by the back-titration method. Thus, 0.5 g of the sample was soaked overnight in 50 mL of distilled water containing 5 mL of 0.1 N NaOH to exchange sodium ions with the protons in the inorganic. Back-titration was accomplished by titrating the remaining NaOH in solution with 0.1 N HCl solutions. The IEC values were obtained by subtracting the added volume of 0.1 N HCl from the initial 0.1 N NaOH volume.

Methanol Permeability Measurements. The methanol permeability of the composite membranes was measured at 300 K in a single cell without electrodes. The membrane permeate side was dried by flowing air (500 mL/min) and the opposite side was wetted by flowing 2 M methanol/water solution (30 mL/min). The amounts of methanol and water that crossed through the membrane were determined by a gas chromatograph (GC, HP 6890) equipped with a packed column (Porapak Q) and a thermal conductivity detector (TCD).

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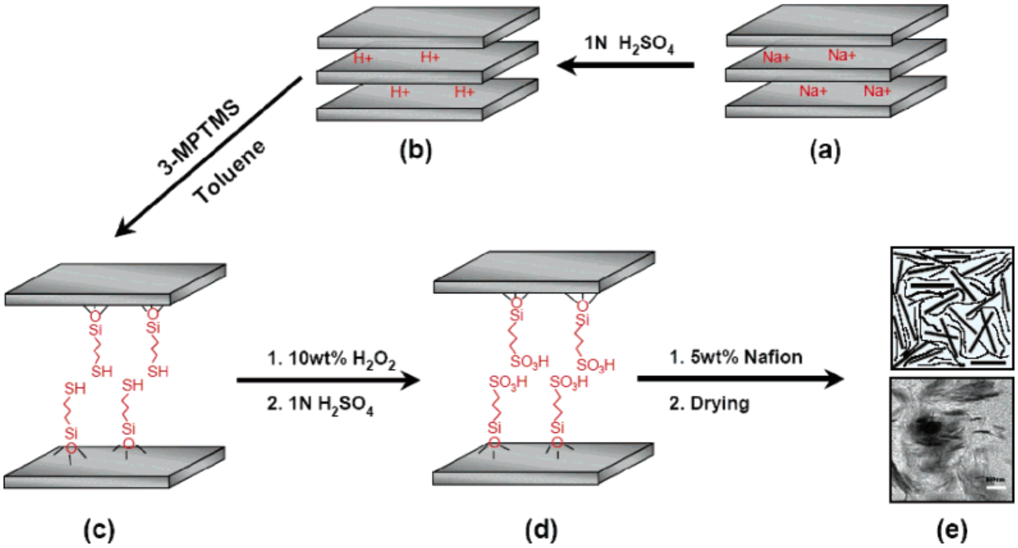
Scheme 1. Idealized Representation of the Processes of Preparing the Nafion/Sulfonated Montmorillonite Composite Membranes



(a) Na^+-MMT; (b) H^+-MMT, Na^+-MMT treated with 1 N H_2SO_4; (c) HS-MMT, H^+-MMT treated with 3-MPTMS; (d) HSO_3-MMT, HS-MMT treated with 10 wt % H_2O_2 and 1 N H_2SO_4; (e) schematic model and TEM image of a Nafion/composite membrane casted with HSO_3-MMT.

Proton Conductivity Measurements. The proton conductivity of the composite membranes was measured by a 4-point probe method using an ac impedance analyzer. The composite membrane was fixed in a measuring cell made of two outer platinum foils and two inner platinum wires. The installed cell was placed in a chamber with controlled humidity and temperature. By applying constant currents (I) through the two outer Pt-probes and measuring voltage drops (V) across the two inner Pt-probes, the resistance (R) of the membrane was measured. The proton conductivity (σ) of the membrane was calculated by $\sigma = L/(AR)$, where L and A are the distance between the two inner Pt-probes and the cross-sectional area of the membrane, respectively. The impedance measurements were carried out in the frequency region from 1 Hz to 10^5 Hz and in the ac current amplitude of 1 mA using a Solatron electrochemical impedance analyzer with ZPLOT software.

Performance Tests for a Single Cell. The catalyst slurries for the cathode and anode were prepared by mixing Pt black or Pt−Ru black, respectively, with 5 wt % Nafion solutions. For fabrication of the membrane−electrode assembly (MEA), the catalyst slurry was coated on carbon paper as the electrode substrate. The catalyst loading was approximately 8 mg cm^{-2} for both the anode and cathode and the effective electrode area of the single cell was 10 cm^2. The MEA was fabricated by hot pressing at 398 K and 3500 psi for 5 min. The performances of the single cell were evaluated at 313 K with 2 M methanol/water solution and air supplied into the anode and cathode sides of the single cell, respectively.

Results and Discussion

In Figure 1, a gradual shift of the lowest angle peak positions to smaller angles in the wide-angle X-ray diffraction (XRD) spectrum of the functionalized MMT indicated a progressive increase in the interlayer distance by fuctionalization of the surface hydroxyl groups (−SiOH) with 3-mercaptopropyltrimethoxy silane (3-MPTMS), followed by the oxidation of thiol to sulfonic acid. Thus, after surface functionalization of H^+-MMT, the low-angle XRD peak of ca. 6.2° shifted to 5.7°. From Bragg's law, its interlayer distance was estimated to increase from 1.42 to 1.55 nm, indicating that the grafted functional groups (−SH or −SO_3H) on the surface increased the interlayer distance of the MMT. Comparison of small-angle XRD patterns of pristine Nafion and the composite in Figure 1d and e indicated that the size of ion channel in the membrane was changed by the introduction of MMT. The shift of the peak in Figure 1d to a higher 2θ angle in 1e indicates that the size of the ion channel in the composite membrane was reduced by introduction of the MMT relative to that of pristine Nafion. The ion channel size has a direct effect on the methanol permeability in the membrane. From Bragg's law, it was estimated that the ionic channel size of Nafion was reduced from 3.84 to 2.94 nm. This smaller channel in the composite electrolyte membrane could be a factor responsible for the reduced methanol crossover through the electrolyte membrane as discussed below.

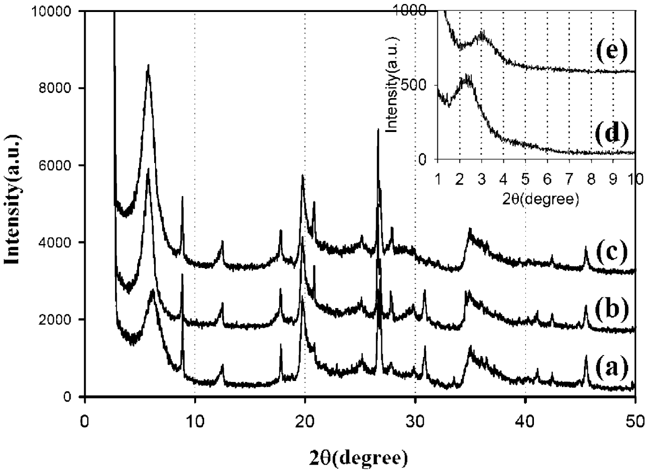


Figure 1. Wide-angle X-ray diffraction (XRD) patterns of (a) H^+-MMT, (b) HS-MMT, and (c) HSO_3-MMT; and small-angle X-ray diffraction patterns (inset) of (d) Nafion 115 membrane, and (e) Nafion/sulfonated MMT composite membrane (3 wt % loaded).

The ion-exchange capacity (IEC, mmol of sulfonic acid/g of HSO_3-MMT) is an important factor determining the ion conductivity. Thus, the IEC of each sample was determined

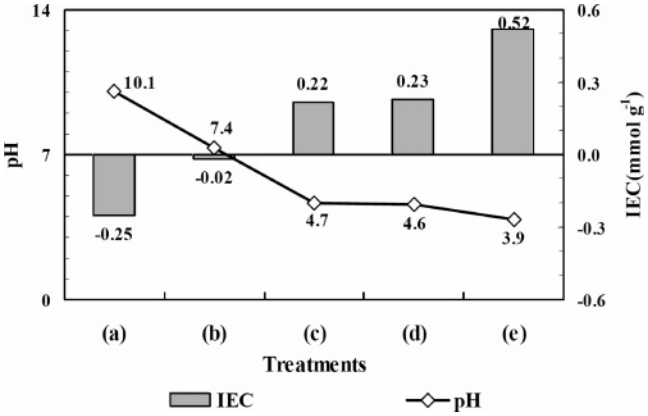


Figure 2. pH and ion exchange capacities (IEC) upon each treatment: (a) Na^+-MMT, (b) Na^+-MMT treated with 10 wt % H_2O_2, (c) H^+-MMT, (d) H^+-MMT treated with 10 wt % H_2O_2, and (e) HSO_3-MMT.

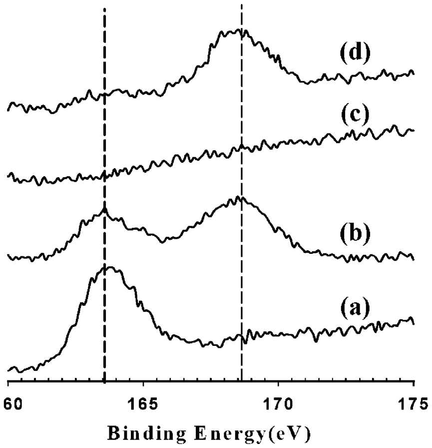


Figure 3. X-ray photoemission spectra (XPS) in the S 2*p* core level region of samples: (a) HS-MMT, (b) HSO_3-MMT (oxidation at 298K), (c) HSO_3-MMT (oxidation at over 353K, uncontrolled reaction temperature), and (d) HSO_3-MMT (oxidation at 333K). (b), (c), and (d) were obtained after the protonating reaction with 1 N H_2SO_4 at 298 K.

by the back-titration method and the results are shown in Figure 2. The IEC values were obtained by subtracting the added volume of 0.1 N HCl from the initially added amount of NaOH solution. The sign of the values (negative or positive) indicates the titration results with acid or base, respectively. Thus, Na^+-MMT with pH of 10.1 and IEC of -0.25 mmol g^{-1} indicates that alkali ions exchangeable with H^+ are present in the interlayer. Treating with 10 wt % H_2O_2 leached out the alkali ions from Na^+-MMT, and the sample became neutral with a negligible IEC value. MMTs treated with 1 N H_2SO_4 with and without the H_2O_2 treatment had similar pH and IEC values. Introduction of an organic sulfonic acid group on the surface (HSO_3-MMT) gave the highest IEC value of 0.52 mmol g^{-1} and the lowest pH of 3.9.

In Figure 3, the X-ray photoelectron spectra (XPS) of the S_{2p} core level for the in-situ outgassed samples revealed a characteristic $S_{2p3/2}-S_{2p1/2}$ spin−orbit splitting. The chemical properties of the samples should be taken from the more intense component $S_{2p3/2}$. The samples showed two types of sulfur species: one at a low binding energy (BE) (∼163.5 eV), corresponding to a thiol (−SH) group, and the other at a higher BE (∼168.5 eV), associated with the sulfonic acid ($-SO_3H$) group. This energy difference in the XPS analysis provides a useful tool for evaluating the degree of oxidation of thiol to sulfonic groups near the surface region. As shown in Figure 3b, ca. 60% of thiol groups were oxidized to sulfonic group at an oxidation temperature of 298 K. On the other hand, all functionalized sulfur groups were detached from the surface when the reaction was preformed at an uncontrolled reaction temperature as shown in Figure 3c. This points out that it is very important to control the oxidation condition to minimize the detachment of the functionalized thiol groups on interlayer surface of MMT and to accomplish complete conversion into sulfonic acid groups. As shown in Figure 3d, most of the thiol groups in the sample were converted into sulfonic groups by oxidation with 10 wt % H_2O_2 at 333 K with only 7−8% of thiol groups remaining in an unoxidized form. However, the total amount of remaining sulfur was only ca. 60% of the initial sulfur content of the sample before oxidation.

^{29}Si MAS NMR spectroscopy is an excellent method for studying silicates, silica gel, and silylated silica gel.[28−33] In general, MMT exhibits ^{29}Si resonances in the range from −75 to −120 ppm as shown in Figure 4A(a and b). Each Si atom in the MMT structures has two or three Si atoms as nearest neighbors (through bridging oxygen) with the remaining nearest neighboring atom being either Al or H. The resonance denoted as Q^3 is attributed to the central Si atom in $(Si-O-)_2Si(-O-Al)-OH$ and the Q^4 resonance represents the central Si in $(Si-O-)_3Si(-O-Al)$. As shown in Figure 4A(a and b), Na^+- and H^+-MMT had similar ^{29}Si MAS NMR spectra. After the surface fuctionalization with 3-MPTMS, two changes were noticed in Figure 4A(c): a new broad peak (T) appeared near −50 to −70 ppm, and the Q^4/Q^3 ratio increased compared with unfunctionalized MMT. This new peak (T) is due to the silane species grafted on the surface and in accord with the reported Si signal for alkyltrimethoxysilane or alkyltrichlorosilane grafted on layered silicates (near −55 to −65 ppm).[32,33] Thus, the Si atom is covalently bonded to carbon ($-O_3Si-CH_2-$ species). The increase in Q^4/Q^3 further clearly indicates the grafting of 3-MPTMS molecules to surface silanol groups. When HS-MMT was treated with hydrogen peroxide to oxidize the thiol group, the intensity of the new peak (T) decreased, indicating that a significant portion of the grafted 3-MPTMS molecules was detached from the silicate surface. This result from ^{29}Si MAS NMR was consistent with the previously described results based on XPS. There was no significant change in the Q^3, Q^4 parts of the spectrum. ^{27}Al MAS NMR (Figure 4B) showed aluminum in tetrahedral (A^{tet}) and octahedral coordination (A^{oct}), with the latter in higher intensity. In contrast to ^{29}Si MAS NMR, ^{27}Al MAS NMR did not show any variation according to the surface functionalization by

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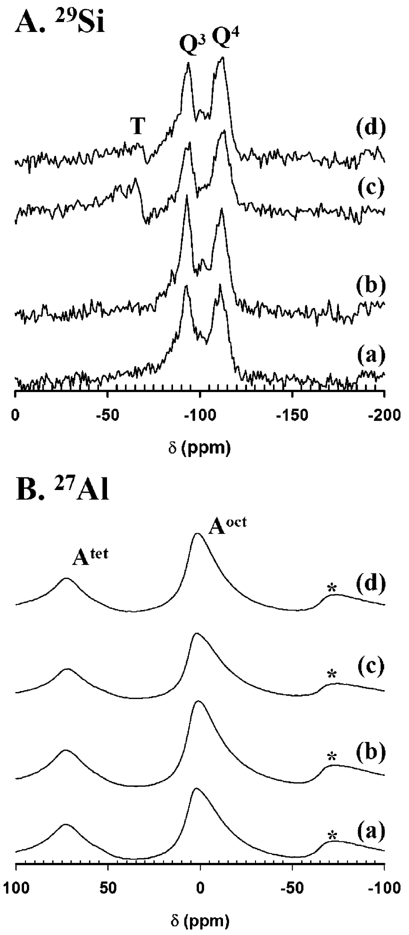

Figure 4. (A) ^{29}Si and (B) ^{27}Al MAS NMR spectra of MMT samples: (a) Na^+-MMT, (b) H^+-MMT, (c) HS-MMT, and (d) HSO_3-MMT (oxidation at 333K). (b) and (d) were obtained after the protonation reaction with 1 N H_2SO_4 at 298 K. (*) represents the sidebands by magic angle spinning at 5.5 kHz.

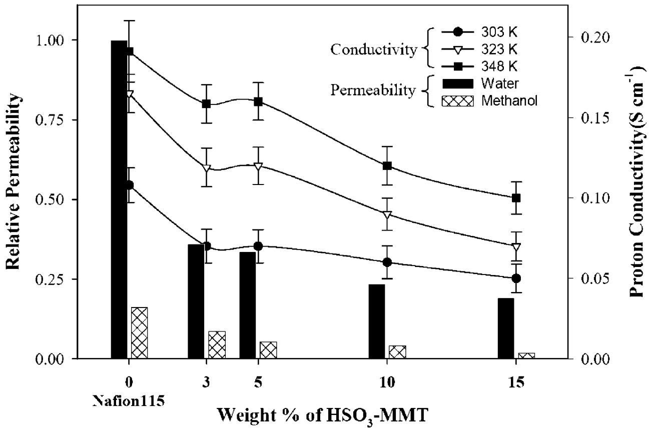

Figure 5. Relative permeability (bar graph) and proton conductivity (open marked line) of Nafion 115 and composite membranes fabricated with different amounts of HSO_3-MMT. All composite membranes had the same membrane thickness of ca. 120 μm.

3-MPTMS or the oxidation by hydrogen peroxide. Throughout the whole process, aluminum appeared to remain only a spectator of the surface functionalization.

Figure 5 shows the relative permeability and proton conductivity of membranes fabricated with different wt % (0−15 wt %) of HSO_3-MMT (IEC ~0.52) in Nafion. The relative permeability of methanol and water decreased rapidly with increasing amounts of HSO_3-MMT added to Nafion. The membrane thickness was maintained the same at ca. 120 μm by employing the same total amount of Nafion and the inorganic filler. In the case of the membrane containing 15 wt % HSO_3-MMT, its permeability of methanol and water (relative to the permeability of water through pristine Nafion 115) was 0.017 and 0.19, respectively, indicating reduction by 90% and 80% relative to pristine Nafion 115.

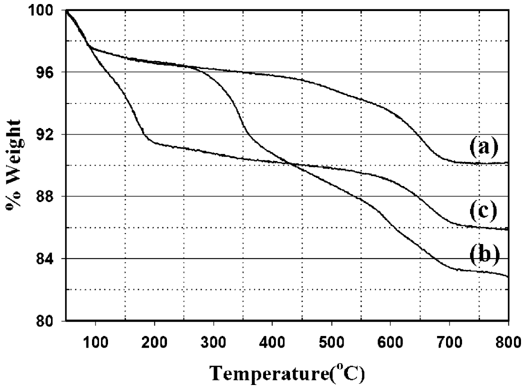

Figure 6. Thermogravimetric analysis (TGA) diagrams of (a) H^+-MMT, (b) HS-MMT, and (C) HSO_3-MMT.

The proton conductivity of the composite membranes was measured with the 4-point probe method using an ac impedance analyzer at three different temperatures. The marked error bar in Figure 5 originated mainly from the thickness variation along the composite membranes. In general, the proton conductivity of the composite membranes decreased with an increase in the content of inorganic filler from that of the pristine Nafion membrane.[14] The rate of proton conductivity drop was slow with HSO_3-MMT content up to 5 wt %, but became more rapid at higher loadings. This trend was consistent for the three different temperatures tested. A relatively coarse distribution of inorganics in the Nafion matrix for composite membranes of high inorganic contents might be responsible, as observed qualitatively by TEM. All of the composite membranes exhibited a marked increase in proton conductivity with increasing temperature, indicating that temperature played a main role in the kinetics of proton motion in the polymer membrane and mobility of polymer chains. It was tentatively concluded that 3−5 wt % HSO_3-MMT could be the optimum level of inorganics in the composite electrolyte membrane for DMFCs.

The thermal stability of functionalized MMT's was studied by thermogravimetric analysis (TGA), as shown in Figure 6. The weight loss of untreated and HSO_3-MMT in the temperature range from 50 to 100 °C was ca. 2.5 wt %, and probably caused by water contained between interlayers. As shown in Figure 6b, a weight loss of ca. 5 wt % was recorded between 260 and 400 °C because the surface functionalized thiol group was thermally decomposed through this region and eventually the sample lost 17% of its initial weight at 800 °C. For HSO_3-MMT, a weight loss of ca. 6 wt % shown in Figure 6c was recorded between 100 and 180 °C because the sulfonic acid group was thermally cracked in this temperature region and the eventual weight loss was ca. 14%. Here, we could estimate the amount of the functional group loaded on MMT from the TGA thermograms. With unmodified MMT as the baseline, the amounts of thiol and sulfonic functionalized group in MMT could be estimated to be ca.

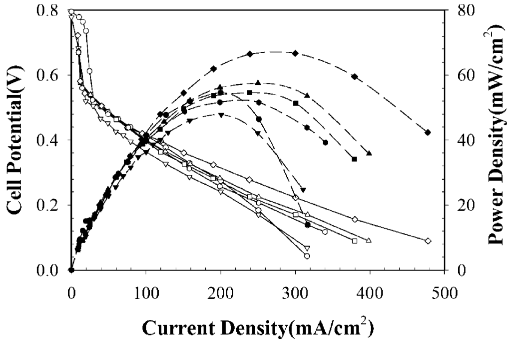

Figure 7. Polarization curves for the MEA made with Nafion115 and composite membranes operated at 313 K (2 M methanol/air flow rate: 2× stoichiometric): ●, Nafion 115; ▼, Nafion + 3 wt % unfunctionalized MMT; ■, Nafion + 3 wt % HSO_3-MMT; ◆, Nafion + 5 wt % HSO_3-MMT; ▲, Nafion + 10 wt % HSO_3-MMT; ⬢, Nafion + 15 wt % HSO_3-MMT. The same symbols (but open ones) denote cell potentials for corresponding samples.

7 and 4 wt %, respectively. These values represent the loadings of organic functions on MMT and agree with the sulfur contents of 1.95 and 0.88 wt %, respectively, obtained by chemical analysis. Although the formula weight of functional groups is increased by oxidation of the thiol groups to sulfonic acid, the percent weight loss was reduced from 7 to 4 wt %. This indicates that ca. 45% of the thiol group grafted initially on the surface of the interlayer was detached from the surface through the oxidation and protonation steps. This number is roughly consistent with that estimated by XPS analysis (ca. 40%). The oxidation reaction of thiol with hydrogen peroxide is a highly exothermic reaction, and thus the introduced functional groups could be detached thermally from the surface of the interlayer. It is thus very important to control the oxidation temperature to prevent the detachment of functional groups. In any case, the thermal stability of the sulfonic acid group would limit the allowed operating temperature of the composite membrane below 100 °C. Yet, the material is stable at desired operating temperatures (40−70 °C) of DMFC for portable devices.

The performance of composite membranes was tested in a single cell for DMFC. Figure 7 shows the plots of cell potential vs. current density (polarization curves) and power density vs. current density for the DMFC membrane-electrode assembly (MEA) with composite membranes of different inorganic contents. The composite membrane with 3 wt % unfunctionalized MMT had a performance worse than that of Nafion 115 itself, but the composite membrane with 3 wt % HSO_3-MMT showed an improved performance, which showed that it is much more effective to introduce functionalized MMT into the composite membrane than the unfunctionalized one. The current densities measured with the composite membranes with HSO_3-MMT contents of 0, 3, 5, 10, and 15 wt %, respectively, were 244, 271, 336, 286, and 260 mA cm^{-2} at a potential of 0.2 V. Thus, the performance of the DMFC was improved initially with increasing the inorganic content, showed a maximum power density at 5 wt % loading, and then was deteriorated with further increasing the content of HSO_3-MMT. Still, all the composite membranes containing HSO_3-MMT showed better performance, particularly at high current densities, than pristine Nafion 115. As shown in Figure 5, the methanol permeability decreased monotonically with increasing content of HSO_3-MMT in the composite membrane. Yet this reduced methanol crossover is not directly translated into an improved cell performance for membranes with high inorganic loadings of 10 and 15 wt %. This might be due to the decreased proton conductivity at higher inorganic contents as shown in Figure 5 that has compensated for a part of performance gains obtained from reduced methanol crossover. In addition, the composite membranes with higher inorganic contents showed a less uniform distribution of HSO_3-MMT in the Nafion matrix, which would reduce the effective contact area for protonic conduction between the two phases. The maximum power density of 67 mW cm^{-2} was obtained for the composite membrane with 5 wt % of HSO_3-MMT. All things considered, 5 wt % loading was an optimized content of HSO_3-MMT in the Nafion matrix to trade the proton conductivity off with the methanol crossover.

As mentioned in the Introduction, there have been many attempts to improve the cell performance of DMFCs through incorporation of inorganic moieties into a Nafion membrane.[8−15] However, there has not been much success that parallels the expectations put into these materials. Many inorganic particles have a problem of too low an ion conductivity which lowers the ion conductivity of the composite membrane to an unacceptable level. Ion-conducting inorganics such as heteropolyacids and zirconium phosphates, have also been examined without significant success either, although these materials have improved performance at higher operating temperatures over 100 °C. The present system of HSO_3-MMT/Nafion provides encouraging results probably by two factors: (i) the relatively high proton conductivity of HSO_3-MMT compared to other inorganic fillers employed previously; and (ii) the highly anisotropic morphology of the MMT platelets that could be more effective in blocking the passage of methanol than materials of other geometries.[14,15] Indeed, Yano et al.[34] reported that the clay particle length had a direct effect on the permeability of water. Longer, more tortuous pathways were generated by introducing a clay with a higher aspect ratio, and thus the permeability of water was more effectively reduced. Yet, the proton conductivity of the composite membrane is still substantially lower than that of Nafion itself. Moreover, the thermal stability of the sulfonic acid group is not yet adequate for high-temperature operations (>100 °C). Work is in progress to overcome these problems.

Conclusions

An organic species bearing an organic sulfonic acid (HSO_3-) was grafted on the surface of MMT by silane condensation, and the composite membranes were cast together with Nafion. The performance of these Nafion/sulfonated MMT composite membranes was evaluated for DMFCs in terms of methanol permeability, proton conductivity, and cell performance. The methanol permeability of the composite membrane decreased dramatically with increasing content of HSO_3-MMT in the composite membrane. The relative

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(34) Yano, K.; Usuki, A.; Okada, A. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 2289.

permeabilities of methanol and water were reduced by up to 90% and 80%, respectively, relative to pristine Nafion 115. By rendering proton conductivity to MMT by functionalization with an organic sulfonic acid, the proton conductivity of the composite membrane was lowered only slightly from that of pristine Nafion 115. The combination of these effects led to a significant improvement in the performance of a DMFC made with Nafion/HSO_3-MMT composite membranes.

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