Short communication

Montmorillonite functionalized with perfluorinated sulfonic acid for proton-conducting organic–inorganic composite membranes

Youngkwon Kim[a], Jae Sung Lee[a,b,*], Chang Houn Rhee[c],
Hae Kyung Kim[d], Hyuk Chang[d]

[a] *School of Environmental Science and Engineering, Pohang University of Science and Technology, Pohang 790-784, Republic of Korea*
[b] *Department of Chemical Engineering, Pohang University of Science and Technology, Pohang 790-784, Republic of Korea*
[c] *Corporate R&D, Research Park, LG Chem Ltd., Daejeon 305-380, Republic of Korea*
[d] *Materials and Device Laboratory, Samsung Advanced Institute of Technology, Suwon 440-600, Republic of Korea*

Abstract

Organic sultones and a perfluorinated sultone are grafted on the surface of montmorillonite (MMT) to render the organic sulfonic acid (HSO_3-) functionality. Organic–inorganic composite proton-conducting membranes are cast together with Nafion® using these functionalized MMTs as inorganic fillers. Grafting with the perfluorinated sultone is more efficient on the surface of MMT than with non-fluorine organic sultones. Montmorillonite functionalized with the perfluorinated organic sulfonic acid also shows higher ion exchange capacity and ion conductivity, which are desired attributes to serve as an effective filler for a proton-conducting composite membrane. The composite membrane reduces the relative permeability of methanol in 3 M solution by about 40%, while maintaining comparable ionic conductivity relative to pristine Nafion membrane. This leads to much enhanced performance of a direct methanol fuel cell employing the Nafion®/sulfonated MMT composite membrane. The current density of a membrane-electrode assembly (MEA) fabricated with a composite membrane containing MMT functionalized with perfluorinated organic sulfonic acid is about 24% higher than that of a MEA fabricated with a composite membrane containing MMT functionalized with non-fluorine organic sulfonic acids, and about 40% higher than that with pristine Nafion®.
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1. Introduction

Direct methanol fuel cells (DMFCs) are expected to find major application in powering portable devices and to replace batteries in the near future because of their simple system design and the ease of handling storable liquid methanol [1,2]. They do, however, have major technical drawbacks, i.e., slow oxidation kinetics of methanol and high methanol crossover rates from the anode to the cathode [3–5]. In particular, the high methanol crossover rate has been one of the main issues impeding the wide application of DMFCs. It is dictated by polymer electrolyte membranes (most commonly Nafion®) which are employed to provide proton conduction from the anode to the cathode and to

give effective separation of the anode (methanol) and cathode (oxygen) reactants.

There have been many attempts to reduce methanol permeability through polymer electrolyte membranes, namely: (i) treatment of the surface of the membranes to block the methanol transport; (ii) control of the size of the proton transport channels using different block copolymers and cross linkage; (iii) development of new types of electrolyte polymers; (iv) introduction of a winding pathway for a methanol by making a composite with inorganic fillers. The composite membranes have been mostly prepared by addition of non-conductive ceramic oxides such as silica, titania, zirconia, mixed silicon–titanium oxides, zeolites, silicon–aluminum oxides and montmorillonite to the Nafion® membrane [6–13]. These composite membranes containing inorganic moieties indeed reduced methanol crossover. Yet the effect did not always lead to the desired improvement in the performance of the membrane-electrode assembly

* Corresponding author. Tel.: +82 54 279 2266; fax: +82 54 279 5528.
E-mail address: jlee@postech.ac.kr (J.S. Lee).

(MEA), mainly because the proton conductivity of the composite membranes containing these less-proton-conductive oxides was markedly lowered compared with that of pristine Nafion® membrane. In previous work, we modified the surface of montmorillonite (MMT) or TiO_2 with an organic sulfonic acid group and formed composite membranes with Nafion® in order to minimize the loss of proton conductivity caused by adding the inorganics while reducing the methanol permeability [14,15]. Indeed, MEA containing MMT functionalized with organic sulfonic acid groups demonstrated much improved performance of DMFCs compared with MEA containing the pristine Nafion membrane and the composite membranes made with unmodified MMT. This functionalization method is commonly employed to render strong acidity to minerals like kaolinite, magadiite and montmorillonite [16–19].

In this work, we report a new type of sulfonated MMT (HSO_3-MMT) functionalized with perfluorinated sulfonic acid groups, which was employed to form composite electrolyte membranes with Nafion®. The terminal perfluorinated sulfonic acid functional groups containing the strongly-electron-withdrawing fluorine atoms increase the acid strength of the terminal sulfonic acid groups giving superacidity, and thus increase the proton conductivity through the membrane [20,21]. They are structurally analogous to Nafion® itself. Thus, the organic species bearing the perfluorinated sulfonic acid functional group is grafted on MMT to make a filler for the proton-conducting organic–inorganic composite membrane with Nafion®. For comparison, composite membranes are prepared containing MMT fillers decorated with non-fluorine organic sulfonic acid groups. The characteristics of the membrane are studied in terms of methanol crossover, proton conductivity and spectroscopic properties, and the performance of the MEA fabricated from these membranes is evaluated for a DMFC.

2. Experimental

2.1. Fabrication of functinonalized MMT and composite membrane

Raw MMT (Aldrich, Montmorillonite-K10) was treated with 1 M H_2SO_4 at 338 K to convert Na^+-MMT into H^+-MMT. The surface functionalization of H^+-MMT was performed by dehydration with 1,4 butane sultone (1,4-BS), 1,3 propane sultone (1,3-PS) and 1,2,2-tri-fluoro-hydroxy-L-trifluomethylethane sulfonic acid sultone (FMES) as sulfonic acid precursors. The reactions were carried out at the refluxing temperature of toluene (383 K) for 24 h with the molar ratio of H^+-titanate, sulfonic acid precursor and toluene of 1:0.5:15. The prepared samples were separated by filtration, washed with toluene and dried at 383 K in vacuum oven. To prepare a composite membrane, 5 wt% HSO_3-MMT based on Nafion was added to 5 wt% Nafion solution (DuPont), and then stirred mechanically and degassed by ultrasonication. The prepared mixture was poured into a glass dish, and dried by slowly increasing the temperature from 353 to 403 K to prevent a crevice in the composite polymer membrane. Finally, the residual solvent in the composite membrane was fully removed by evacuation at 403 K for 12 h.

2.2. Physical characterization

X-ray diffraction (XRD) patterns were obtained on a MAC Science Co, M18XHF diffractometer with Cu Kα radiation (40 kV, 200 mA). Thermogravimetric analysis (TGA, TGS-2) was operated in the range of 323–1073 K at a heating rate of 10 K min^{-1} under air flow of 40 ml per min. X-ray photoelectron spectra (XPS) were acquired with a VG-Scientific ESCALAB 220 iXL spectrometer equipped with a hemispherical electron analyzer and a Mg Kα (1253.6 eV) X-ray source. ^{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 5.0 kHz. The spectra of ^{29}Si MAS NMR were measured at a frequency of 59.590 MHz. Transmission electron microscopy (TEM) image was taken on a Hitachi 7600 operated at 80 kV. The TEM sample was prepared by using an Ultra-microtome (RMC MT 7000) with a 45° diamond knife and mounted on a 200-mesh copper grid.

2.3. Ion exchange capacity measurements

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

2.4. 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 in flowing air (500 ml min^{-1}) and the opposite side was wetted by flowing 2 M methanol/water solution (30 ml min^{-1}). The amounts of methanol and water that crossed through the membrane were determined by a gas chromatography (GC, HP 6890) equipped with a packed column (Porapak Q) and a thermal conductivity detector.

2.5. Ionic conductivity measurements

The ionic conductivity of the composite membranes was measured by a four-point probe method using an AC impedance analyzer. The composite membrane was fixed in a measuring cell comprised 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 ionic conductivity (σ) was calcu-

lated by $\sigma = L/(A \times R)$, where L and A are the distance between the two inner Pt-probes and the cross-sectional area of the membrane, respectively.

2.6. Performance tests for a single cell

The catalyst slurries for the cathode and the anode were prepared by mixing Pt black or Pt–Ru black with 5 wt% Nafion solution, respectively. For fabrication of the MEA, the catalyst slurry was coated on carbon paper. The catalyst loading was approximately 8 mg cm^{-2} for both the anode and the cathode and the effective electrode area of the single cell was 16 cm^2. The MEA was fabricated by hot pressing at 398 K and 6000 psi for 3 min. Experiments on the passive DMFC were undertaken at the ambient temperature with 5 ml of 3 M methanol/water solution and an air-breathing system was used [22].

3. Results and discussion

Three types of sulfonated montmorillonite (HSO$_3$-MMT) were prepared by functionalizing the surface hydroxyl group of MMT by dehydration with 1,4-butane sultone (1,4-BS), 1,3-propane sultone (1,3-PS) and FMES as sulfonic acid precursors. This one-step functionalization process is shown in Scheme 1 and represents a significant advancement over the two-step process that we reported previously [14,15]. The original process employed silanes as starting materials and involved thiol group intermediates. The oxidation of the thiol group to sulfonic acid is particularly troublesome due to the large exothermicity of the oxidation reaction and a substantial amount of the grafted surface sulfur species is lost during this process. Thus, the new one-step process simplifies significantly the surface functionalization of MMT.

The IEC (mmol of sulfonic acid per g of HSO$_3$-MMT) is an important determinant of ion conductivity. Thus, the IEC of each sample was obtained by the back-titration method [14,15]. The results are shown in Fig. 1. The H$^+$-MMT treated with 1 M
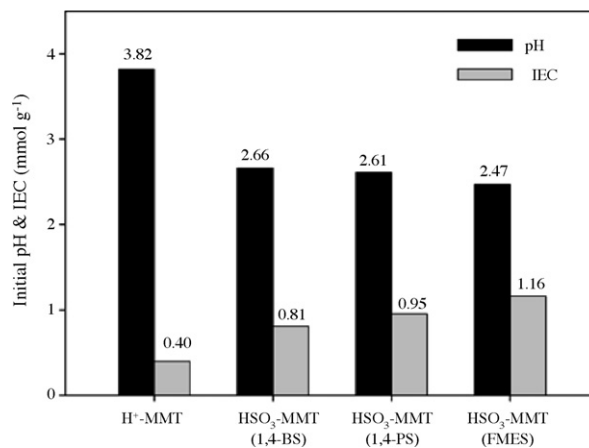

Fig. 1. pH and ion exchange capacities (IEC) of montmorillonites upon grafting precursors.

H$_2$SO$_4$ had a pH of 3.82 and an IEC of 0.40 mmol g^{-1}, which indicates that Na$^+$ in the interlayer of montmorillonite has been exchanged with H$^+$. When using FMES as a grafting precursor, the resulting HSO$_3$-MMT (FMES) has a lower pH and a higher IEC value than the others. This sample notation with the precursor noted in the parenthesis will be used hereafter. The HSO$_3$-MMT (1,3-PS) has slightly lower pH and higher IEC values than HSO$_3$-MMT (1,4-BS). However, both HSO$_3$-MMT (1,4-BS) and HSO$_3$-MMT (1,3-PS) samples have IEC values that are at least twice that of H$^+$-MMT without organic functionalization. Notably, HSO$_3$-MMT (FMES) has an IEC that is three-times that of unmodified H$^+$-MMT.

XPS of the S 2p core level for the in situ outgassed samples reveal characteristic S 2p$_{3/2}$–S 2p$_{1/2}$ spin–orbital splitting, as shown in Fig. 2. The XPS analysis is useful for evaluating qualitatively the type of sulfur species and measuring quantitatively the sulfonic acid groups near the surface region [14]. The chemical properties of the samples were probed by examining the more intense component S 2p$_{3/2}$. Samples exhibit only one
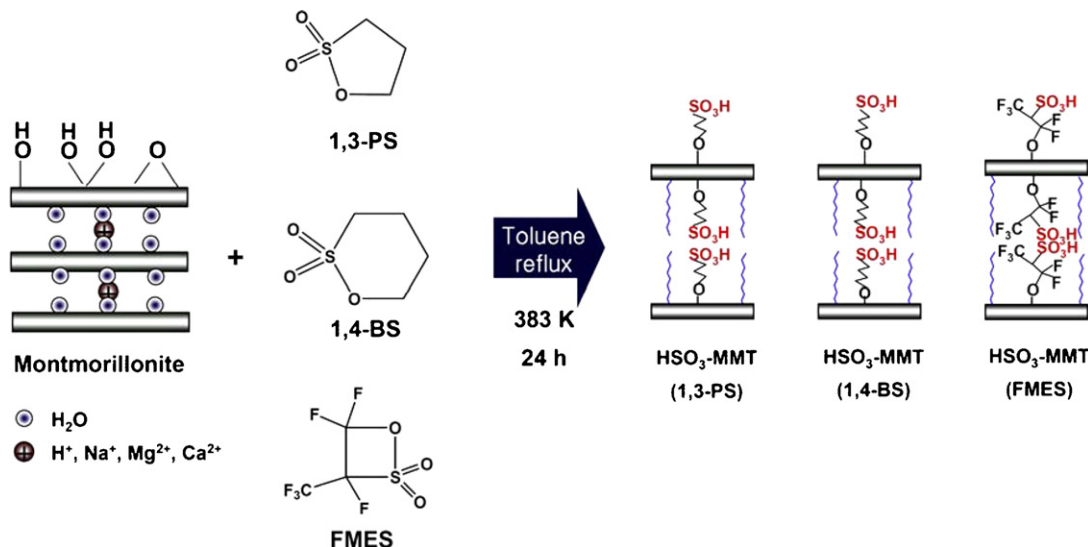
Scheme 1. Schematic representation of functionalization steps of montmorillonites.
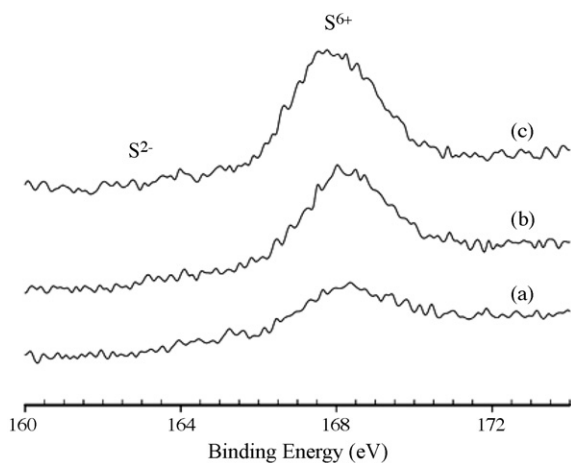
Fig. 2. X-ray photoelectron spectra (XPS) in S 2p core level region of: (a) HSO$_3$-MMT (1,4-BS), (b) HSO$_3$-MMT (1,3-PS) and (c) HSO$_3$-MMT (FMES).

type of sulfur species with a binding energy (BE) of 168.0 eV that is associated with a sulfate (S^{6+}) species due to the sulfonic (–SO$_3$H) group [23]. There is no indication of S^{2-} species (expected at a binding energy near 163 eV) which was observed when the two-step functionalization method using silanes as precursors was employed [14]. Considering the intensity of the S^{6+} peaks in Fig. 2 for each HSO$_3$-MMT sample, it can be concluded that FMES and 1,3-PS are more efficiently grafted on to the surface of MMT than 1,4-BS. For all sulfonated montmorillonites, sulfonic acid groups are directly grafted on to the surface of MMT.

The results of ^{29}Si MAS NMR spectroscopy are presented in Fig. 3. H$^+$-MMT exhibits ^{29}Si responses in the range from −75 to −120 ppm, as shown in Fig. 3(a). Each Si atom in the MMT structures has two or three Si atoms as nearest neighbours. The remaining nearest neighbouring atom is either Al or H. The Q^3 is attributed to the central Si in (Si–O–)$_2$Si(–O–A1)–OH and Q^4 to the central Si in (Si–O–)$_3$Si(–O–Al) [14,24]. The Q^4/Q^3 ratio of each HSO$_3$-MMT was 1.06 (H$^+$-MMT), 1.64 (HSO$_3$-MMT (1,4-BS)), 2.06 (HSO$_3$-MMT (1,3-PS)) and 2.37 (HSO$_3$-MMT (FMES)). After surface fuctionalization with different precursors, the increase in the Q^4/Q^3 ratio compared with
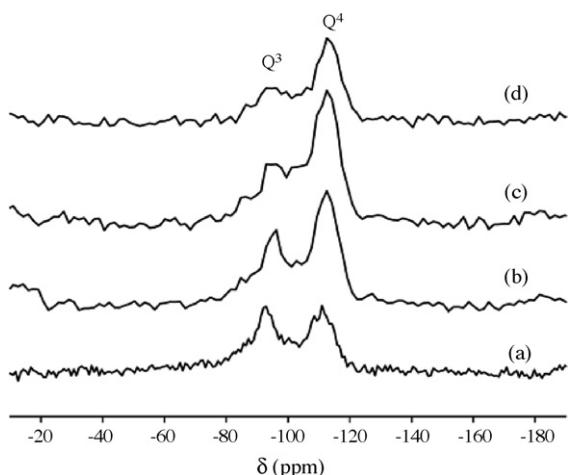

Fig. 3. ^{29}Si MAS NMR spectra of (a) H$^+$-MMT, (b) HSO$_3$-MMT (1,4-BS), (c) HSO$_3$-MMT (1,3-PS) and (d) HSO$_3$-MMT (FMES).
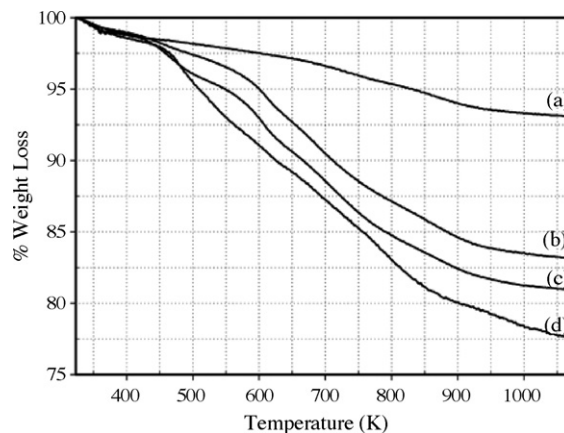

Fig. 4. Thermogravimetric analysis (TGA) curves of (a) H$^+$-MMT, (b) HSO$_3$-MMT (1,4-BS), (c) HSO$_3$-MMT (1,3-PS) and (d) HSO$_3$-MMT (FMES).

unfunctionalized MMT clearly indicates successful grafting of different sulfonic acid molecules to the surface silanol group. In particular, the higher Q^4/Q^3 values of HSO$_3$-MMT (FMES) and HSO$_3$-MMT (1,3-PS), compared with that of HSO$_3$-MMT (1,4-BS), show that FMES and 1,3-PS precursors have been more efficiently grafted on the MMT surface than the 1,4-BS precursor. These results of ^{29}Si MAS NMR spectroscopy are consistent with those described above based on XPS and IEC results.

The thermal stability of functionalized MMT with different precursors was studied by TGA. The results are given in Fig. 4. The weight losses of all samples in the temperature range from 323 to 425 K were about 2 wt%, and are probably caused by loss of water contained in the interlayers. For all sulfonated MMTs, a weight loss is recorded between 425 and 580 K, as shown in Fig. 4(b–d) because the sulfonic acid group is thermally cracked throughout this region. In any case, the thermal stability of the sulfonic acid groups will limit the allowed operating temperature of these materials. Fortunately, however, the decomposition temperatures are all much higher than the usual operating temperatures of DMFCs (<353 K) and PEMFCs (<373 K). This thermal stability is also better than HSO$_3$-MMT functionalized by the previous two-step method that showed the decomposition of the sulfonic acid group below 400 K [14].

The XRD patterns of unmodified and sulfonated MMT are compared in Fig. 5A(a and b). Composite membranes based on Nafion have now been prepared using different sulfonated MMTs as inorganic fillers. XRD patterns of the sulfonated MMT and a TEM image of a composite membrane fabricated with 5 wt% functionalized MMTs (HSO$_3$-MMT (1,3-PS)) in Nafion matrix are presented in Fig. 5A(c–f) and B. After surface functionalization of H$^+$-MMT with sulfonic acid group, the low-angle XRD peak representing the (0 0 1) plane of MMT is shifted from 6.36° to 5.90°, see Fig. 5A(a and b). From Bragg's law, its interlayer distance is estimated to have increased from 1.39 to 1.50 nm upon functionalization. Furthermore, the (0 0 1) diffraction peak of sulfonated MMT is much weaker than that of H$^+$-MMT. This indicates that this sulfonated MMT has a poor periodic layer structure compared with the original layered material [25]. Thus, the functionalization of MMT has taken place
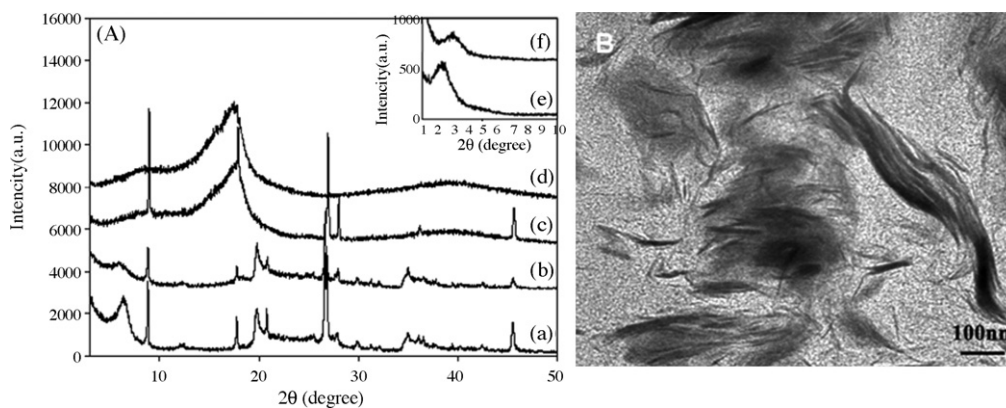
Fig. 5. (A) Wide (a–d) and small-angle (e and f) X-ray diffraction (XRD) patterns of (a) H^+-MMT, (b) HSO_3-MMT (1,3-PS), (c) Nafion/HSO_3-MMT (1,3-PS) composite membrane, (d) and (e) Nafion 115 membrane, (f) Nafion/HSO_3-MMT (1,3-PS) composite membrane (3 wt% loaded). (B) Transmission electron microscope (TEM) image of Nafion/HSO_3-MMT (1,3-PS) composite membrane.

not only on the external surface of MMT, but also in its interlayer space. The wide-angle XRD pattern of the HSO_3-MMT/Nafion composite membrane is shown in Fig. 5A(c). The absence of the diffraction peak for the (0 0 1) plane suggests that the sulfonated MMT has lost the regularity of its layered structure in the Nafion matrix [26]. In comparison with the small-angle XRD pattern of pristine Nafion in Fig. 5A(e), the peak for the composite membrane in Fig. 5A(f) is shifted to a higher 2θ angle. According to a model of the structure of Nafion [27,28], the peak represents the regular chambers formed in the Nafion matrix that are connected by channels and these chambers and channels provide passages for proton transport. The shift thus indicates that the size of ion channel in the composite membrane has been reduced by introduction of MMT, relative to that of pristine Nafion. From Bragg's law, its ionic channel size is estimated to be reduced from 3.84 to 2.94 nm. The TEM image in Fig. 5B shows that the majority of the inorganic fillers still maintain the layered structure although the structural regularity has became very low. Some thin layers or plates are also seen. Thus, the interaction between MMT and Nafion is mostly intercalation in nature with a small degree of exfoliation.

Fig. 6 shows the relative permeability and proton conductivities of a pristine Nafion membrane and the composite mem-

branes. The thickness of composite membranes is maintained the same at about 150 μm by employing the same total amount of Nafion and inorganic fillers. The proton conductivity of the composite membranes was measured by the AC four-point probe method using an AC impedance analyzer. As shown in Fig. 6, the proton conductivities of composite membranes are slightly lower than that of Nafion. The ionic conductivity values of the composite membrane containing 5 wt% HSO_3-MMT (FMES) are higher than those of the other composite membranes and, in particular, the value is close to (98%) that of Nafion at 303 K and 98% relative humidity. The difference becomes more significant at 323 K. All composite membranes containing 5 wt% inorganic fillers reduce methanol crossover by 40%, which is probably caused by a tortuous passage of methanol created by the presence of MMT slabs in the Nafion matrix, as discussed in our previous report [14].

The performance under passive (no air-pumping) DMFC operating conditions [22] of a single cell with a MEA made of composite membranes of different inorganic materials and pristine Nafion 115 is presented in Fig. 7. Three molar methanol (5 ml) is used as the anode fuel and the cathode side is open to air for natural breathing. The same Pt–Ru anode and Pt cathode
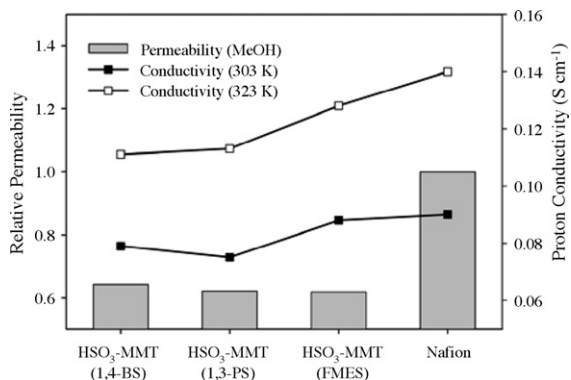

Fig. 6. Relative permeability (bar graph) and proton conductivity (open marked line) of recast Nafion and composite membranes fabricated with different HSO_3-MMTS. All composite membranes have the same membrane thickness of 150 μm and the same amounts of 5 wt% sulfonated MMTs.
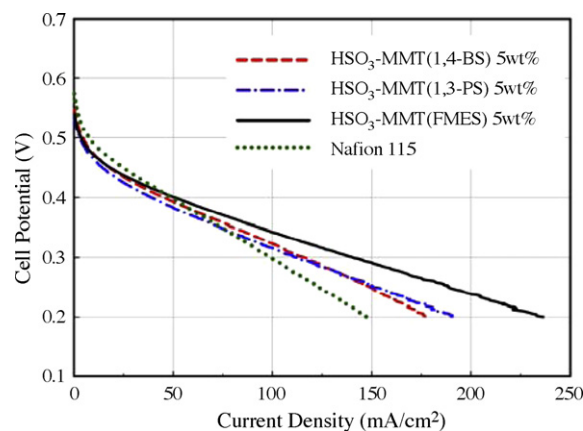

Fig. 7. Single-cell performance curves for MEA made with Nafion 115 and composite membranes (thickness = 150 μm) operated at room temperature (3 M methanol 5 ml; air-breathing system).

are employed as electrodes of MEA and the amount of each electrode catalysts is $8\,mg\,cm^{-2}$. The composite membranes with 5 wt% functionalized MMTs give a much improved performance compared with that of Nafion 115 itself, especially in the high-current region. Further, the composite membrane with 5 wt% HSO_3-MMT (FMES) shows a higher performance than membranes with 5 wt% HSO_3-MMT (1,3-PS) and 5 wt% HSO_3-MMT (1,3-BS). The current densities for the composite membranes with 5 wt% inorganic fillers such as HSO_3-MMT (1,3-BS), HSO_3-MMT (1,3-PS) and HSO_3-MMT (FMES) are 114, 113 and $140\,mA\,cm^{-2}$, respectively, at a potential of 0.3 V. By comparison, the current density measured with a Nafion 115 membrane is $99\,mA\,cm^{-2}$ at 0.3 V. Since the reduction of methanol crossover with all composite membranes is almost the same, the best performance with the HSO_3-MMT (FMES)/Nafion composite membrane should be due to its higher proton conductivity compared with the other composite membranes.

There have been many attempts to improve the efficiency of DMFCs through incorporation of inorganic moieties into the Nafion membrane [6–13]. There has not, however, been much success in meeting the expectations for these materials because of too low an ion conductivity that decreases the ion conductivity of the composite membrane to an unacceptable level. To increase the ionic conductivity of composite membranes, the surface functionalization of MMT was performed by silane condensation [14]. Relative to silane groups, sultone groups provide a simpler one-step functionalization reactiom [20]. The second advantage of the new functionalization method is higher ionic conductivities of HSO_3-MMT than those of membranes with fillers functionalized by the silane route. In particular, HSO_3-MMT (FEMS)/Nafion composite membrane has an ionic conductivity that is comparable to that of a pristine Nafion membrane, particularly at 303 K. This excellent proton conductivity appears to be due to the terminal perfluorinated sulfonic acid functional groups, in which electron-withdrawing fluorine is expected to increase the acid strength of the protons in the sulfonic acid groups [29]. Furthermore, the new version of HSO_3-modified MMT exhibits a much improved thermal stability relative to MMT modified with non-fluorine sultones.

4. Summary and conclusions

This study has demonstrated that montmorillonite functionalized with perfluorinated organic sulfonic acid serves as an effective filler for a composite membrane with Nafion. Relative to MMT decorated with non-fluoride organic acid groups, fluorine-containing MMT displays higher ion exchange capacity and ion conductivity, which are desired attributes to serve as an effective filler for a composite membrane with Nafion®. The fabricated composite membrane gives a 40% reduction in the relative permeability of methanol in 3 M solution while maintaining comparable ionic conductivity relative to pristine Nafion membrane. This promises a much enhanced performance from a DMFC-employing a composite membrane containing fluorinated MMT.

Acknowledgements

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