

Preparation of Nafion-sulfonated clay nanocomposite membrane for direct menthol fuel cells via a film coating process

Tae Kyoung Kim^a, Myeongsoon Kang^a, Yeong Suk Choi^{b,*}, Hae Kyung Kim^b,
Wonmok Lee^b, Hyuk Chang^b, Doyoung Seung^b

^a Research Institute of Chemical & Electronic Materials, Cheil Industries Inc., Uiwang-si 437-711, Republic of Korea

^b Energy & Materials Research Lab, Samsung Advanced Institute of Technology (SAIT) P.O. Box 111, Suwon 449-600, Republic of Korea

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Abstract

Nafion sulfonated clay nanocomposite membranes were successfully produced via a film coating process using a pilot coating machine. For producing the composite membranes, we optimized the solvent ratio of *N*-methyl-2-pyrrolidinone (NMP) to *N,N'*-dimethylacetamide (DMAc), the amount of sulfonated montmorillonite (S-MMT) in composite membranes and the overall concentration of composite dispersions. Based on the optimized viscosity and composition, the composite dispersions were coated on a poly(ethylene terephthalate) (PET) substrate film. The distance between a metering roll and a PET film and the ratio of metering roll speed versus coating roll speed of the pilot coating machine were varied to control membrane thickness. The film coated composite membrane exhibited enhanced properties in the swelling behavior against MeOH solution, ion conductivity and MeOH permeability, compared to the cast Nafion composite membrane due to the higher dispersion state of S-MMT in Nafion matrix and the uniform distribution of small-size ion clusters. These properties influenced a cell performance test of a direct methanol fuel cell (DMFC), showing the film coated composite membrane had a higher power density than that of Nafion 115. The power density was also related with the higher selectivity of the composite membrane than Nafion 115.

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1. Introduction

Proton exchange membranes (PEMs) are considered as crucial materials for DMFC applications, because the membranes segregate both sides of electrodes, maintaining electrical potential and provide DMFCs with ion conductivity, transferring proton ions from anodes to cathodes through ionic clusters formed by aggregation of ionic functional groups [1]. Nafion, a perfluorinated membrane, is one of the most commonly used membranes for DMFCs, because of excellent electrochemical stability, high ion conductivity, and good mechanical property [2–4]. In spite of the advantages of Nafion, great deals of efforts have been concentrated on Nafion clay nanocomposite membranes to solve the drawbacks of neat Nafion membranes, such as high swelling behavior in methyl alcohol (MeOH) aqueous solu-

tions and high MeOH permeability. The high swelling behavior and the MeOH permeability cause poor mechanical strength in alcoholic environments and reverse potentials of circuits resulting in diminution of power density, respectively [5–9].

So far, most of the Nafion clay nanocomposite membranes were prepared by solution-casting methods [10] and hot-pressing methods [11]; casting low concentrations of composite dispersions on glass dishes followed by careful drying procedures, pressing Nafion organoclay composite materials near the glass transition temperature of the Nafion. However, the batch-processes are not suitable for mass production due to time-consuming procedures for removal of solvents and fluctuation of mechanical and electrochemical properties of each batch. Therefore, mass production methods, which have advantages in low production costs and uniform qualities, are required for PEMs.

A film coating process is one of the effective mass production methods for producing films or membranes, if coating dispersions and coating machines are available. Obtaining stable coating dispersions is a prominent problem in applying the film

* Corresponding author. Tel.: +82 31 280 9326; fax: +82 31 280 9359.
E-mail address: Yeongsuk.choi@samsung.com (Y.S. Choi).

coating process for producing membranes. Acid-form Nafion dispersions in isopropyl alcohol (IPA) and water are commercially available, so the dispersions can be used for producing composite membranes via film coating processes. However, producing Nafion clay composite membranes through the coating methods using the acid-form Nafion dispersions is not easily controllable due to high viscosity with low solid contents. Especially, IPA is too volatile to coat the Nafion dispersions on substrate films, because the rapid vaporization of IPA causes viscosity variation of the as-prepared dispersions after mixing Nafion and clays. Another potential problem is that residual water hinders uniform thickness and/or profile of coated membranes. Therefore, Nafion clay composite dispersions need to have stable viscosities during coating process. To obtain stable dispersions, the Nafion clay dispersions should be prepared with less volatile solvents.

In this paper, we developed a film coating process for producing Nafion organoclay (S-MMT) composite membranes. The relation of physical/electrochemical properties and membrane formation conditions was explained by varying the ratios of co-solvents, the S-MMT loading amounts, and the concentrations of composite dispersions in the lab scale. With controlling the distances between the metering roll and the substrate film, the optimized composite dispersion was applied for the film coating process. Efficiency of the film coating process was elucidated by comparing mechanical and electrochemical properties of the coated composite membrane and the lab scale membrane using scanning transmission electron microscopy (STEM), X-ray diffraction pattern (XRD), Universal Test Machine (UTM), MeOH permeability, and proton conductivity. The performance tests of DMFCs with the nanocomposite membranes were studied for evaluation of the composite membranes.

2. Experimental

2.1. Preparation of S-MMT and composite membranes

The Aldrich Co. supplied the K-10 MMT for this experiment; it had 95 mequivalents for each 100 g of cation exchange capacity. Sulfonated clay, S-MMT, was prepared as follows. The MMT was treated with dilute sulfuric acid aqueous solution to convert Na^+ -MMT into H^+ -MMT. The H^+ -MMT was washed with deionized water to remove residual sulfuric acid and dried under high vacuum at 100°C . The dried H^+ -MMT was treated with 1,3-propane sultone through refluxing H^+ -MMT in toluene at 110°C for 24 h followed by filtrating, washing and drying processes to obtain S-MMT [10].

Nafion powder was prepared by precipitation of Nafion dispersion of DuPont (a solid content of 20 wt%, 1100 E. W.) from methylene chloride. DMAc and NMP were used as organic solvents for dispersing S-MMT and the Nafion powder instead of water and IPA, because DMAc and NMP are good solvents for Nafion with high boiling temperatures. The Nafion powder was dissolved in co-solvents with various ratios of DMAc to NMP. S-MMT was added into the Nafion solutions and stirred the mixtures until uniform composite dispersions were obtained. The

concentrations of the composite dispersions were adjusted by addition of solvents.

The lab scale membranes were prepared with a doctor blade. On the other hand, for pilot scale production, Nafion S-MMT composite membrane was produced using an Inokin 2 roll reverse die coater, equipped with a slot die, a coating roll, a metering roll, and a floating dryer. The coated composite membrane was delaminated from the PET substrate film before evaluation of membrane properties and DMFC performances.

2.2. Characterization and measurements

XRD patterns were obtained by using a Philips X'pert Pro X-ray diffractometer, equipped with a $\text{Cu K}\alpha$ source ($\lambda = 0.15406 \text{ nm}$) at 30 kV and 30 mA. The diffractograms were scanned with a scanning rate of 2° min^{-1} in a 2θ range of 1.2° – 10° at a room temperature.

For observing ion clusters, STEM images were obtained using a FEI Tecnai F20 G2 scanning transmission electron microscope at an accelerating voltage of 200 kV. Each membrane was stained with 0.5 M silver nitrate aqueous solution by the procedure described in other paper [21]. The stained membranes were molded with epoxy resin, sliced to yield about 90 nm thicknesses using a RMC microtome PowertomeXL and placed on copper grids.

Tensile strength of membrane was measured using a Tinius Olsen UTM H5K-T universal tensile test machine. Each membrane was prepared in a size of 5 mm (width) \times 30 mm (length). The distance between two grips of UTM was fixed at 10 mm and the drawing speed of grips was set at 50 mm min^{-1} .

Viscosity measurements were performed using a TA Instrument AR-2000 rheometer, equipped with a planner plate and a cone plate (diameter of 60 mm, cone angle of 2°) under a steady state flow mode. A dispersion of 2 ml was placed on a planner plate. The gap between the cone plate and the planar plate, temperature and shear rate range were set up as $54 \mu\text{m}$, 25°C and 0.1 – 10 s^{-1} , respectively.

Swelling behavior measurements of membranes in MeOH aqueous solution were carried out as follows. The membranes were dried under high vacuum at 110°C for 12 h. After being dried, the length, width and thickness of the membranes were measured and then immersed in a MeOH aqueous solution of MeOH (1 mol, 32 g) and water (1 mol, 18 g) for 24 h at room temperature. The sizes (length, width, and thickness) of the swollen membranes were re-measured after removing the MeOH solution from membrane surfaces. Swelling ratio of each membrane (%) was calculated using the size variation of the membrane in wet and dried states.

Ion conductivity was evaluated using a 4-point probe method using a Solartron 1260 ac impedance analyzer with amplitude of 20 mV and a frequency range of 1 Hz–500 kHz. Each membrane (1.5 cm \times 4.0 cm) was fixed in a Teflon conductivity test cell consisted of two Pt wires (a counter electrode and a working electrode) and two Pt foils (reference electrode 1 and reference electrode 2). The Teflon test cell was immersed in a deionized water bath to maintain constant humidity and temperature of membrane. The resistance of membrane could be obtained using

the intercepting value of a real axis (Z') in the complex plane composed of a real axis (Z') and an imaginary axis (Z''). Ionic conductivity was calculated using the following equation:

$$\alpha = \left(\frac{1}{R}\right) \left(\frac{L}{A}\right) \quad (1)$$

where R is the resistance of a membrane, L the length of a membrane, and A is the cross-sectional area of a membrane [10].

MeOH permeability measurements of membranes were performed using a diffusion cell consisted of two reservoirs. A membrane with a transporting area of 10 cm^2 was placed between a MeOH reservoir and a water reservoir. The internal volume of each reservoir was 35 ml. MeOH permeability was calculated using the following equation describing the relations between MeOH concentrations and elapsed times [12–15]:

$$P = \left(\frac{\Delta C_B}{\Delta t}\right) \left(\frac{1}{C_{Ai}}\right) \left(\frac{L}{A}\right) V_B \quad (2)$$

where P is the permeability of a membrane, $\Delta C_B/\Delta t$ the slope of the molar concentration variation of MeOH in the water reservoir as a function of time, C_{Ai} the initial concentration of MeOH in the MeOH reservoir, L and A are the thickness and the area of a membrane, respectively. V_B is the volume of deionized water in the water reservoir.

2.3. Fabrication of membrane-electrode-assembly (MEA) and cell performance test

For the fabrication of MEA, cathode catalyst ink was prepared by dispersing a commercial Pt black catalyst (HiSpec 1000 from Johnson Matthey Fuel Cells) in alcohol solution with Nafion dispersion. The catalyst ink was coated onto the gas diffusion layer to form a cathode catalyst layer with 5 mg cm^{-2} Pt. The anode catalyst layer was prepared by the same way as the cathode and loaded with 5 mg cm^{-2} PtRu black catalyst (HiSpec 6000 from Johnson Matthey Fuel Cells, Pt/Ru ratio = 1/1). Both electrodes and membranes were hot-pressed to fabricate MEA with a reaction area of 10 cm^2 . Semi-passive DMFC single cell tests were conducted at 30°C with 1 M MeOH aqueous solution and air as fuels for the anode and the cathode, respectively. The MeOH solution was fed into the anode using a microflow pump at 3 stoichiometry MeOH flow rate. Air was furnished to the cathode through an air-breathing method of a natural convection. The single cell performance of the scaled-up composite membrane was compared to that of Nafion 115 membrane from the evaluation of polarization curves.

3. Results and discussions

3.1. Effect of solvent ratios on membrane properties

Solvents generally affect physical properties of films, so the determination of solvent ratios without S-MMT is a preliminary step for producing composite membranes. DMAc and NMP are widely used solvents for producing polymer electrolyte

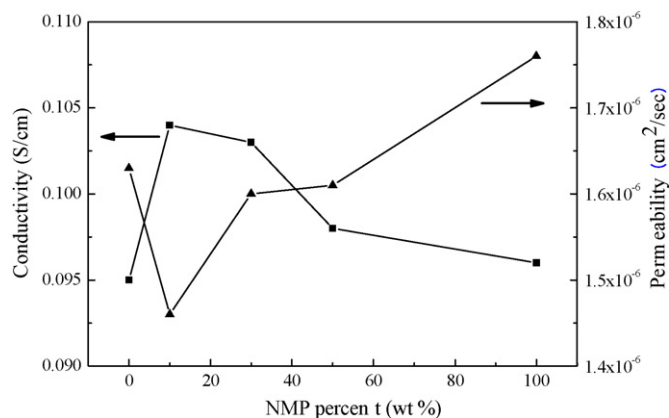


Fig. 1. Proton conductivity and MeOH permeability of cast Nafion membranes prepared with various ratios of NMP to DMAc. S-MMT was not added into the membranes.

membranes, because the solvents have various interactions, e.g. hydrogen bondings or van der Waals forces, with polymer chains influencing morphologies and properties of membranes [16,17]. The DMAc and NMP also have several merits in the fabrication of Nafion clay composite membranes: dispersing the primary particles of clays, expanding the basal spacings of clays, and intercalating Nafion polymer chains into the basal spacings. Fig. 1 represents the effect of solvent ratio on conductivity and permeability of cast Nafion membranes dispersing with S-MMT. As the ratio of NMP in the co-solvent increased, the proton conductivity values increased from 0.095 S cm^{-1} for the membrane prepared with 100 wt% DMAc to a maximum value of 0.104 S cm^{-1} for the membrane with 10 wt% NMP in the solvents. Then the conductivity decreased to 0.096 S cm^{-1} with the high NMP ratio ranges (>10 wt%).

The solvent ratio also affected MeOH permeability values of membranes. The MeOH permeability of these membranes was improved within a NMP ratio of 10 wt%, decreasing from 1.63×10^{-6} to $1.46 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, but the permeability was deteriorated with high NMP ratio ranges (>10 wt%). The proton conductivity and the MeOH permeability values of the cast Nafion membranes could be explained as follows. Small amount of high boiling point solvent (NMP) might make the membranes dense through azeotropic vaporization of two solvents and reorganization of the sulfonic acids to form ion clusters, but, with large amounts of NMP, vaporization of the solvents might be retarded, remaining NMP droplets in the drying membranes and forming coarse membranes. As the DMAc/NMP ratio of 90:10 (wt%) showed the best conductivity and permeability values, the solvent ratio was chosen for further process.

3.2. Effect of S-MMT amounts on membrane properties

As clay loading amounts were reported to affect mechanical properties of composite membranes, e.g. tensile strength, elongation and toughness [18,19], we evaluated the influence of S-MMT amount on permeability and conductivity of cast composite membranes. Various amounts of S-MMT were added to the Nafion dispersion prepared with a fixed DMAc/NMP ratio

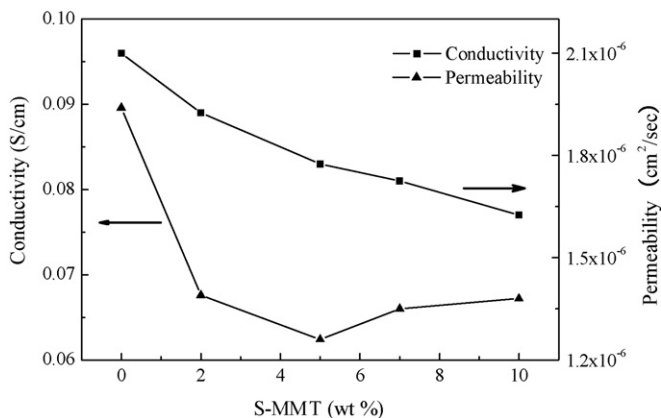


Fig. 2. Effect of S-MMT amounts on proton conductivity and MeOH permeability of cast Nafion S-MMT composite membranes (lab scale composite membranes).

of 90:10 (wt%). As given in Fig. 2, the proton conductivity decreased linearly from 0.096 to 0.077 S cm⁻¹ as the content of S-MMT increased from 0 to 10 wt%. The composite membranes are expected to have proton conductivity values of 0.08 S cm⁻¹ or more at room temperature to reduce the current loss occurred by the ohmic resistance of S-MMT in the cell performance test. As composite membranes containing S-MMT within 7 wt% had ion conductivity values of more than 0.081 S cm⁻¹, we infer that the suitable S-MMT loading amounts were within 7 wt%.

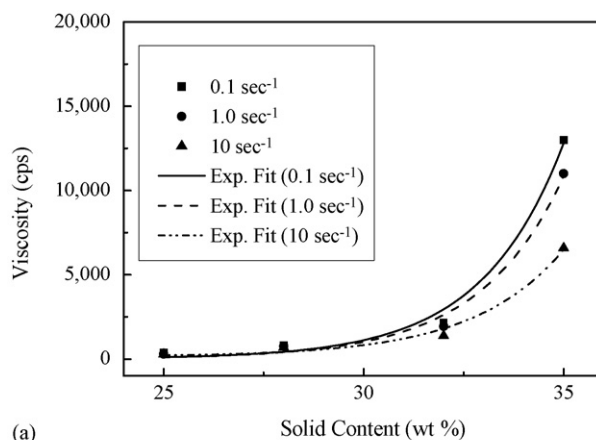
MeOH permeability of composite membranes specified the S-MMT amount for best performance. The MeOH permeability decreased from $1.95 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ to the minimum value of $1.26 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ as the S-MMT amounts increased to 5 wt%, and then the permeability value increased to $1.38 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ with the S-MMT amounts over 5 wt%. Based on the proton conductivity and MeOH permeability, the composite membrane prepared with 5 wt% S-MMT loading amount was selected for film coating process because the composite membrane had the lowest permeability value with an allowable conductivity value of 0.083 S cm⁻¹.

3.3. Concentration of Nafion and S-MMT in composite dispersions

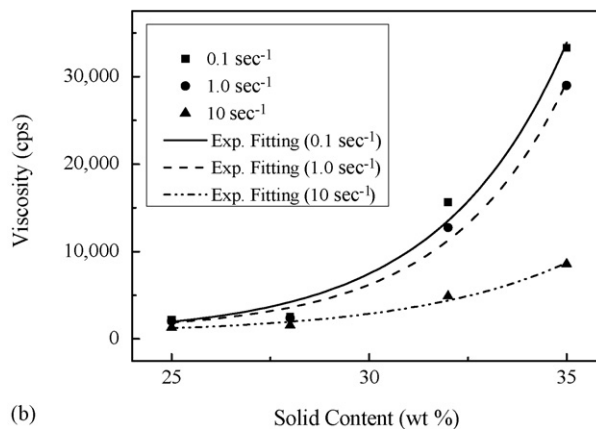
Proper concentration ranges need to be set up for extruding composite dispersions from the slot die and coating the dispersions on the PET substrate. Fig. 3 represents the relation of viscosity and concentrations of Nafion and S-MMT in the composite dispersions. To extrude Nafion S-MMT composite dispersions with a film coating machine, the composite dispersions should have viscosity values less than 5000 cps at a shear rate of 10 s⁻¹, and the viscosity values should be higher than 1000 cps at a shear rate of 0.1 s⁻¹ to sustain the coated form on a PET substrate after coating the composite dispersions. Exponential fitting was applied to investigate the viscosity behavior with respect to solid concentrations. As shown in Fig. 3(a), the viscosity values of composite dispersions with solid concentrations above 32 wt% exponentially increased up to a value of 6600 cps under a shear rate of 10 s⁻¹. The vis-

cosity value above 5000 cps impedes the composite dispersion to be coated onto PET substrate. From the viscosity values of the composite dispersions, the optimized concentration range of the composite dispersion was determined as 30–32 wt%. While Nafion S-MMT composite dispersions with 100 wt% DMAc had higher viscosity values than those of the dispersions prepared with co-solvents composed of DMAc and NMP under the same solid concentration and the shear rate, showing viscosity values over 5000 cps with a solid concentration of 32 wt%, as given in Fig. 3(b). The viscosity data indicate that the composite dispersions prepared with a DMAc/NMP ratio of 90:10 (wt%) and a solid concentration of 32 wt% had a suitable viscosity range of 1000–2000 cps for extruding the dispersions onto PET substrate film.

In addition to viscosity range, the width variation of composite dispersions after coated on PET substrate should be considered, because the width variation causes fluctuation of film thickness. The composite dispersions with a concentration range of 25–28 wt% showed 3–5% width expansion in 1 min after cast, but the composite dispersions with a concentration range of 32–35 wt% showed no expansion. The width variation data indicates that optimized concentration range (30–32 wt%) was reasonable for applying the film coating method.



(a)



(b)

Fig. 3. (a) The relation of viscosity and solid contents of Nafion S-MMT composite dispersions prepared with a DMAc/NMP ratio of 90:10 (wt%) and 5 wt% S-MMT. (b) The relation of viscosity and solid contents of cast Nafion S-MMT composite dispersions prepared with 100 wt% DMAc and 5 wt% S-MMT.

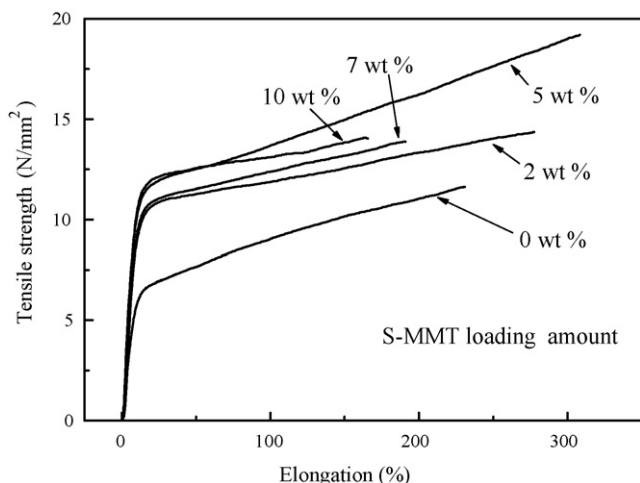


Fig. 4. Tensile strength dependence on S-MMT loading amount in cast Nafion S-MMT composite membranes prepared with a DMAc/NMP ratio of 90:10 (wt%).

3.4. Tensile strength measurement of membranes

Mechanical properties such as elongation, tensile strength and toughness should be taken into account to develop composite membranes with flexibility, processibility, and durability under harsh operation conditions of DMFCs, including fabrication of MEAs. Fig. 4 exhibits the tensile strength and elongation tendency of cast Nafion composite membranes. As the content of S-MMT increased up to 5 wt%, the composite membranes had the higher tensile strength value than that of Nafion without S-MMT. Then, the tensile strength values decreased with the S-MMT amounts over 5 wt%. Elongation degree of the composite membranes had the same results, showing the maximum elongation value of 308% with 5 wt% S-MMT. The toughness of composite membranes exhibited the following order: 5 wt% (461 kJ m^{-2}) > 2 wt% (339 kJ m^{-2}) > 7 wt% (228 kJ m^{-2}) > 0 wt% (209 kJ m^{-2}). The Nafion S-MMT composite membrane with 5 wt% S-MMT loading amount had a maximum tensile strength, elongation, and toughness. As shown in the XRD data and photograph images (refer to Figs. 5 and 6), the S-MMT in the composite membranes sustained the layered structures and formed particles due to the aggregation of S-MMT, indicating that the interfacial area between S-MMT and Nafion matrix did not increase with respect to S-MMT amounts. Therefore, S-MMT aggregation particles would become defects (or weak points) in the elongation of samples and deter the expansion of samples. That is why the composite with 5 wt% S-MMT had the maximum values in elongation and toughness measurements.

3.5. Fabrication of Nafion S-MMT composite membranes via a film coating process

Scale-up production of Nafion S-MMT composite membrane was performed using the optimized composite dispersion consisted of the DMAc/NMP ratio of 90:10 (wt%), the S-MMT loading amount of 5 wt%, and the solid concentration of 32 wt%,

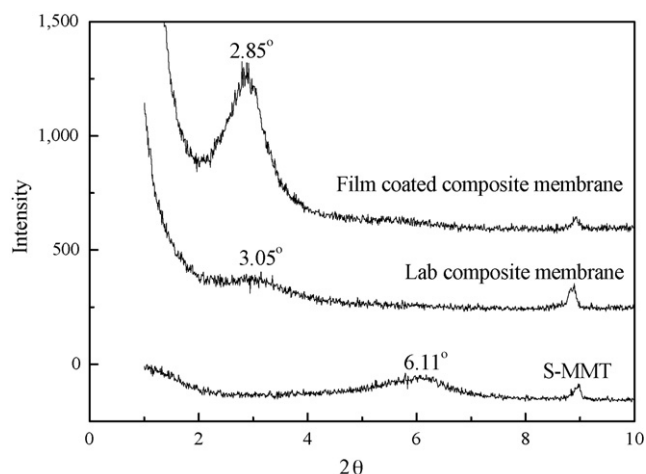


Fig. 5. XRD patterns of S-MMT and composite membranes prepared with a DMAc/NMP ratio of 90:10 (wt%) and 5 wt% S-MMT.

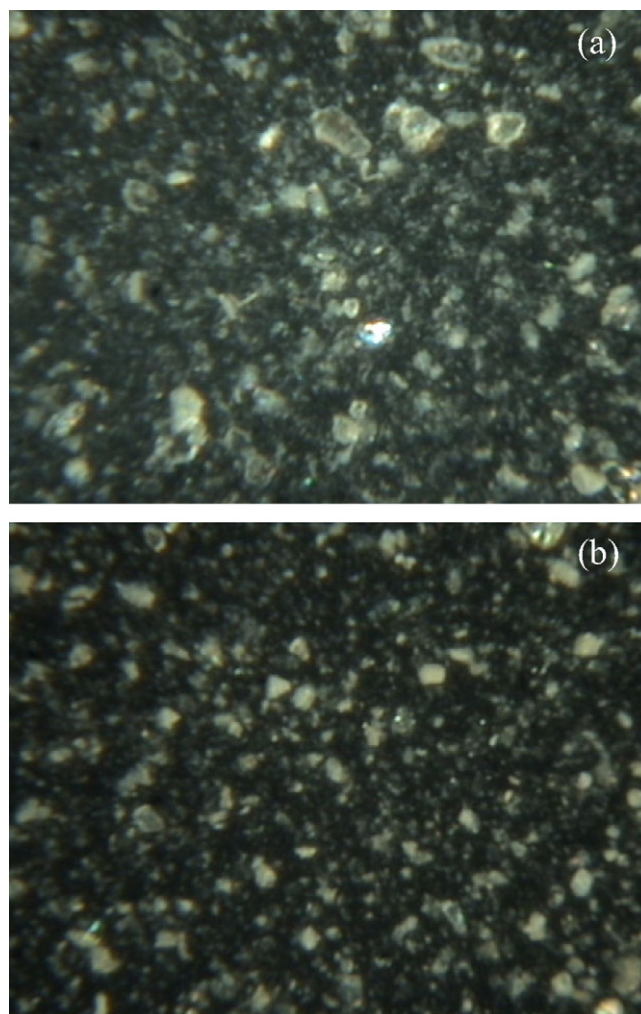


Fig. 6. Photograph images of (a) lab scale composite membrane and (b) film coated composite membrane taken by a co-axial type microscopy with a contact lens of 500 times. The composite membranes were fabricated with 5 wt% S-MMT and a DMAc/NMP ratio of 90:10 (wt%).

having a viscosity of 1389 cps at a shear rate of 10 s^{-1} . For producing Nafion S-MMT composite membranes with a pilot coater, the distance (D_{mrf}) between a metering roll and a substrate film, and the ratio (R_{mr}) of metering roll speed versus coating roll speed should be chosen because they are main factors influencing membrane thickness. When the coating roll speed and the metering roll sizes of the coating machine were fixed for normal operations, the R_{mr} and D_{mrf} values became significant. By varying the R_{mr} and the D_{mrf} values, an empirical formula concerning membrane thickness was induced as follows:

$$t(\mu\text{m}) = 57.2 + 0.0279D_{\text{mrf}} - 0.896R_{\text{mr}} \quad (3)$$

For producing the composite membranes with $80\ \mu\text{m}$ thickness, D_{mrf} and R_{mr} were set as $800\ \mu\text{m}$ for D_{mrf} and 1% for R_{mr} . With the D_{mrf} and R_{mr} values, the film coated composite membrane with a size of $80 \pm 5\ \mu\text{m}$ (thickness) \times $250\ \text{mm}$ (width) \times $10\ \text{m}$ (length) was successfully fabricated.

3.6. XRD patterns of S-MMT in composite membranes

Fig. 5 shows the XRD patterns of S-MMT, the lab scale composite membrane and the film coated composite membrane. The organoclay had the diffraction pattern of (00 1) plane of S-MMT at 6.11° in 2θ ranges. The diffraction pattern of S-MMT in composites shifted to low angles of 3.05° for the lab scale composite membrane and 2.85° for the film coated composite membrane. The basal spacings, calculated using the Bragg equation, were $1.45\ \text{nm}$ for S-MMT, $2.89\ \text{nm}$ for the laboratory composite membrane and $3.1\ \text{nm}$ for the film coated composite membrane, respectively. The XRD patterns indicate that the Nafion polymer chains intercalated into the interlayer spaces of S-MMT, expanding the basal spacing of S-MMT. The basal spacing expansion of S-MMT in the film coated composite membrane was larger than that of the lab scale composite membrane, elucidating that the film coated composite membrane had a high dispersion state of S-MMT in Nafion matrix compared to the laboratory composite membrane.

3.7. Property of film coated composite membrane and performance of DMFC test

Thermal and physical histories of polymers generally affect mechanical and physical properties of polymers. Consequently, film coated composite membrane might have different mechanical and electrochemical properties from the laboratory composite membrane due to change of fabrication method.

MeOH permeability of the film coated composite membrane was evaluated using a digital refractometer with 3 M MeOH aqueous solution at room temperature. The MeOH concentration in the water reservoir increased due to MeOH diffusion from the MeOH reservoir to the water reservoir. The permeability value of the film coated composite membrane was $1.14 \times 10^{-6}\ \text{cm}^2\ \text{s}^{-1}$ which is comparable with the value of Nafion 115, $1.55 \times 10^{-6}\ \text{cm}^2\ \text{s}^{-1}$.

Proton conductivity of the film coated composite membrane (wet thickness: $100\ \mu\text{m}$) was measured by a 4-point probe method at room temperature, showing the same value of $0.093\ \text{S cm}^{-1}$ as Nafion 115. Reminding that the laboratory composite membrane prepared with the same composition and concentration had a MeOH permeability value of $1.26 \times 10^{-6}\ \text{cm}^2\ \text{s}^{-1}$ and ion conductivity value of $0.083\ \text{S cm}^{-1}$, the film coated composite membrane exhibited enhancements in both ion conductivity and MeOH permeability, which are generally contrary to each other.

The swelling behaviors of composite membranes also elucidate the effect of clay, S-MMT, on dimensional stability of membranes. As listed in Table 1, the swelling degree of membranes, including Nafion 115, appeared in the following order: film coated composite (volume expansion = 93%) < lab scale composite membrane (143%) < Nafion 115 (175%). The swelling degree indicates that strong interaction between S-MMT and Nafion main chains [10] existed and the interaction retarded expansion of Nafion polymer in MeOH solution. Moreover, low expansion of the film coated Nafion S-MMT composite might be related to dispersion degree of S-MMT in Nafion matrix.

Dispersion states of S-MMT in composite membranes were examined using a Sometch SV32 co-axial type microscopy. As given in Fig. 6, the film coated composite membrane had S-MMT particles of $2\text{--}4\ \mu\text{m}$, which is smaller than that of the lab scale composite membrane, $4\text{--}10\ \mu\text{m}$. In addition to the size of S-MMT particles, the S-MMT particles were uniformly distributed in Nafion matrix, compared to the lab scale composite. The microscopy images support the discussion concerning the enhancement of permeability, conductivity and swelling behavior of the film coated composite membrane by high dispersion state of S-MMT.

Dispersion state of S-MMT in the film coated composite membrane need to be checked with reasonable methods. STEM images of membranes stained with silver represent S-MMT effect on formation of ion clusters. The proton ions of sulfonic acid groups of Nafion were replaced with silver ions via ion exchange reactions during staining procedure. The silver-stained areas, ion clusters, had high electron densities, appearing

Table 1
Swelling behaviors of membranes in a MeOH aqueous solution

Membranes	MD expansion (%)	TD expansion (%)	Thickness expansion (%)	Area expansion (%)	Volume expansion (%)
Film coated Nafion composite membrane	23	23	27	52	93
Lab scale composite membrane	30	30	44	69	143
Nafion 115	30	43	48	86	175

The composite membranes were fabricated with 5 wt% S-MMT and a DMAc/NMP ratio of 90:10 (wt%). The composite membranes were immersed in MeOH/DI solution of 1 mol (32 g) (1 mol (18 g)) $^{-1}$ for 24 h at room temperature.

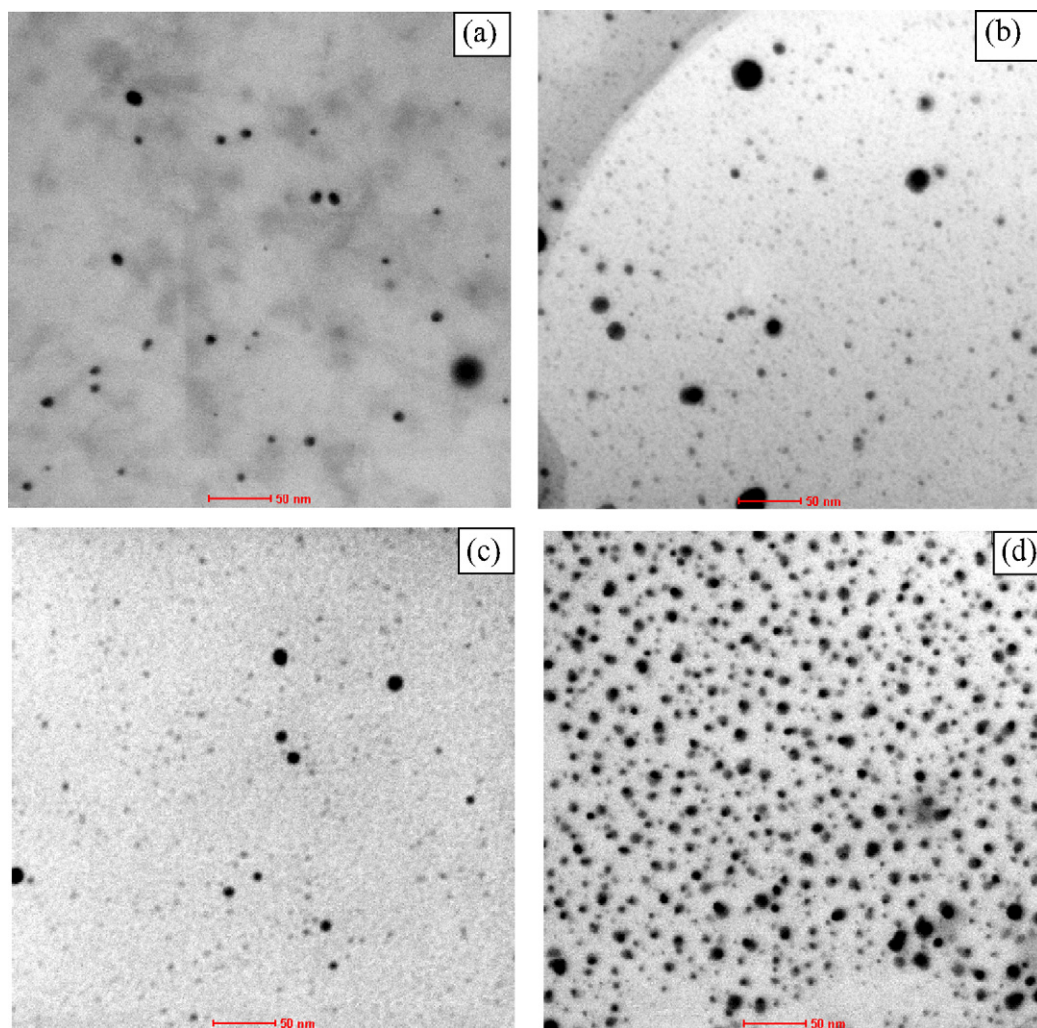


Fig. 7. STEM images of membranes. Cast Nafion membranes prepared with (a) NMP 100 wt%, (b) DMAc 50 wt%/NMP 50 wt%, (c) DMAc 90 wt%/NMP 10 wt%, and (d) film coated composite membrane fabricated with 5 wt% S-MMT and a DMAc/NMP ratio of 90:10 (wt%).

dark areas in the STEM images. Fig. 7(a–c) exhibits the STEM images of cast Nafion membranes prepared with various solvent ratios in the absence of S-MMT. As seen in Fig. 7(a), the membrane prepared with 100 wt% NMP showed bimodal circular ionic clusters whose sizes were about 25 nm for large clusters, and 5–12 nm for relatively small clusters. The cast membrane prepared with a DMAc/NMP ratio of 50:50 (wt%) exhibited decreased bimodal cluster sizes of 15–25 nm for large clusters and 2–5 nm for small clusters, as given in Fig. 7(b). The cast membrane prepared with a DMAc/NMP ratio of 90:10 (wt%) exhibited further decreased cluster sizes of 12 nm and 2–5 nm, as given in Fig. 7(c). The ion cluster size had the proportional relation with NMP contents in the co-solvent, upholding the discussion in Section 3.1 regarding the relation of the solvent ratios and permeability and conductivity of membranes; small amounts of high boiling point solvent (NMP) might make the films dense but large amounts of NMP might retard the vaporization of the solvents, remaining NMP droplets in the drying films and forming coarse films. The STEM image of Fig. 7(d) shows the S-MMT effect on the cluster size and distribution. A large quantity of ion clusters with relatively small uniform sizes of

2–10 nm were observed in entire area of the image. The STEM image of Fig. 7(d) indicates two things; S-MMT had strong influence on the size and distribution of ion clusters in composite membranes, leading to the best conductivity and permeability of film coated composite membrane, and the dispersion state of S-MMT was uniformly distributed in Nafion matrix.

The enhanced conductivity due to high dispersion state of S-MMT in Nafion matrix was proved with single cell performances of DMFC applications. Single cell performances were carried out using semi-passive cells fabricated with the film coated composite membrane and Nafion 115. Fig. 8 represents the polarization curves obtained from the scanning voltage tests at 30 °C. The cell fitted with the film coated composite membrane showed a higher power density of 30 mW cm^{-2} than that of Nafion 115 membrane (25 mW cm^{-1}) at a cell voltage of 0.35 V. The MeOH permeability of the film coated composite membrane had a 26% decreased value compared to that of Nafion 115 membrane. The proton conductivity of the former was the same as the latter as shown in Table 2. Furthermore the selectivity of the film coated composite membrane had a higher value by 37% than that of Nafion 115. The high per-

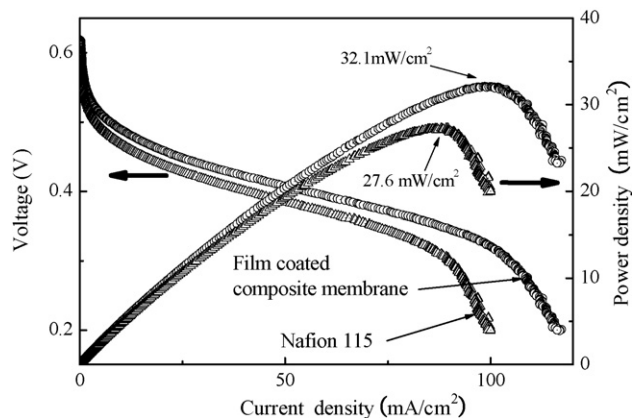


Fig. 8. Polarization curves of DMFC single cells consisted of film coated Nafion S-MMT composite membrane and Nafion 115. The single cell test was performed using 1 M MeOH solution for the anode (3 stoichiometry) and air-breathing for the cathode at 30 °C.

Table 2

Properties of scaled-up Nafion S-MMT composite membrane compared to Nafion 115

Membranes	Proton conductivity (S cm ⁻¹)	Permeability (cm ² s ⁻¹)	Selectivity ^a
Film coated composite membrane (scale-up)	0.093	1.14 × 10 ⁻⁶	8.2 × 10 ⁴
Nafion 115	0.093	1.55 × 10 ⁻⁶	6.0 × 10 ⁴

^a The selectivity is defined as the ratio of conductivity to permeability of a membrane [20].

formances of the film coated composite membrane could be elucidated by the decrease of ohmic resistance in MEA part and MeOH cross-over from anodes to cathodes. The decrease of ohmic resistance of the MEA with the film coated composite membrane was attributed to a higher conductance (defined as ‘conductivity/thickness’) of thin composite membrane (dry thickness: 80 μm) than that of the thick Nafion 115 (dry thickness: 124 μm). The interface resistance between electrodes and membranes in the MEA might be decreased for the composite membrane because the stronger adhesion between electrodes. The resistance of semi-passive cell, measured by an impedance analyzer (Hioki 3560, HiTester) with the frequency of 1 kHz at the cell voltage of 0.35 V, was 35 mΩ for the composite membrane which is a lower value than that of Nafion 115 (48 mΩ). The low resistance of semi-passive cell with the film coated composite membrane reflects the enhancement of overall cell conductance as well as high dispersion state of S-MMT.

4. Conclusions

For the production of composite membranes via a film coating process, several factors were optimized by investigating

the physical/mechanical properties. In the lab scale, we found that two factors strongly affected MeOH permeability as well as conductivity: the solvent ratio of co-solvents and the S-MMT amount. Small amount of high boiling point solvent (NMP) might make the membranes dense through azeotropic vaporization of two solvents and reorganization of the sulfonic acids to form ion clusters. S-MMT loading amounts influenced the permeability and conductivity of Nafion composite membranes, improving MeOH permeability with slight decrease of conductivity. Viscosities and width variations, associated with processability and quality of composite membranes, of composite dispersions on PET substrate were considered to obtain the desired membrane thickness. The cell performance of DMFC fitted with the composite membrane was superior to Nafion 115 membrane. The prominent cell performance might result from the enhancement of selectivity, dispersion state of S-MMT and small uniform ion cluster induced by S-MMT. This result suggests that proper factors should be considered and controlled, when production methods were changed.

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