

Preparation and performance of a Nafion[®]/montmorillonite nanocomposite membrane for direct methanol fuel cell

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Abstract

Direct methanol fuel cells (DMFC) have major technical problems, e.g. slow methanol oxidation kinetics and high methanol crossover, to use as power sources for several applications. To overcome these problems it has been proposed to increase the fuel cell operating temperature to over 100–150 °C and to reduce the methanol permeability.

In this work, we made Nafion[®]/montmorillonite (MMT) nanocomposite membranes and carried out diverse tests. The nanocomposite membranes were produced by direct melt intercalation of perfluorosulfonylfluoride copolymer resin (Nafion[®] resin) into the montmorillonite and modified montmorillonite (m-MMT) which was organized by dodecylamine. The membrane–electrode assembly (MEA) has been made using a hot pressing method and the electrode prepared using PtRu black and Pt black catalysts for anode and cathode, respectively.

The morphology of the nanocomposite membranes has been investigated using SEM and TEM. The nanocomposite membranes and MMT and m-MMT were analyzed using by FT-IR and X-ray diffraction (XRD). The thermal and mechanical properties of those membranes were also investigated and the methanol permeability was measured by gas chromatography (GC). The performance of the MEA using the nanocomposite membrane was evaluated by single cell test. The results show that the performance of the MEA using the nanocomposite membrane was higher than that of a commercial Nafion[®] membrane at high operating temperature.

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1. Introduction

Direct methanol fuel cells (DMFCs) using polymer electrolyte membrane are promising candidates for the application of portable power sources, electric vehicle and transport applications because they do not require any fuel processing equipment and can be operated at low temperature of 25–130 °C [1]. However, commercialization of the direct methanol fuel cell is inhibited by two major technical problems. One of that is slow methanol oxidation kinetics of the anode catalyst. The second is methanol diffusion from the anode to the cathode side, across the polymer electrolyte membrane. Nafion[®] (perfluorosulfonic acid) membrane are commonly used as electrolytes, owing to good chemical and thermal resistance and high ionic conductivity. However, it has been found that over 40% of the methanol can be wasted in DMFCs across such membrane [2]. That causes loss of fuel, reduced fuel efficiency, reduced cathode voltage and excess thermal load in the cell. Recently, perfluorosulfonate ionomer membranes such as Nafion[®]

(DuPont), Flemion[®] (Asahi Glass Co.), Aciplex[®] (Asahi Chem.) and Dow XUS (Dow Chemical) are used as polymer electrolyte membrane for direct methanol fuel cell [3]. Methanol permeability of these membranes is high. For the reduction of the methanol permeability through the membrane, composite membranes were also used in DMFC. The composite membranes were prepared by recasting of a Nafion[®] solution to which oxide colloids were previously added. The gas permeability of the so obtained composite membranes made by casting of a polymer solution is much higher than that of the commercial membranes [4,5]. It is also reported recently that the composite membranes can be prepared by permeation of non-conductive ceramic oxide such as silicon oxide, titanium oxide and zirconium oxide, mixed silicon-titanium and silicon-aluminum oxides in the Nafion[®] membrane [6–9]. The ionic conductivity of the composite membranes mixed with non-conductive oxides is lower compared with normal membranes. H⁺-montmorillonite (MMT) is a protonic conductor with reported ionic conductivities of 1×10^{-4} S/cm at room temperature [10].

In the present work, we made a nanocomposite membrane with various contents of MMT, modified montmorillonite

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(m-MMT) by melt intercalation method using internal mixer. The thermal stability and physical properties of the composite membrane was characterized with TGA, FT-IR and X-ray diffraction (XRD). Methanol permeability and conductivity of the composite membrane mixed with MMT and m-MMT was examined by gas-chromatography and impedance analyzer, respectively. The effects of composite membrane on the performance of DMFC at various temperatures were evaluated and the results are discussed.

2. Experimental

2.1. Preparation of nanocomposite membrane

Perfluorosulfonylfluoride copolymer resin (Nafion[®] R-1100 resin) used in this study is supplied by DuPont Ind. Co. The cation exchange capacity of montmorillonite (Cloisite Na, Southern Clay Product Co.) is 100 meq/100 g. Dodecylamine-exchanged montmorillonite (m-MMT) was synthesized from dodecylamine (Aldrich) by a cation exchange reaction.

The protonated form of $\text{CH}_3-(\text{CH}_2)_{11}-\text{N}_2\text{H}$ was formed by dissolving 0.047 mol of dodecylamine in 100 ml of a 0.048N HCl solution at 80 °C, and 20 g of MMT was thoroughly dispersed in the 400 ml deionized water. Then the ion exchanged MMT was made by mixing the two solutions for 1 h at 80 °C. The ion exchanged MMT was separated from the aspiration and washed with deionized water. Aspiration and washing were repeated till white AgCl precipitate was not observed when some drops of 0.1 N AgNO₃ were added to the solution. After removal of the ion exchanged MMT from the solutions, the ion exchanged MMT were dried in oven for 24 h. The dried ion exchanged MMT was then passed through the sieve (<325 mesh). Equivalent ion exchange reactions were used to prepare NH⁺- and H⁺-exchanged forms of the MMT.

The composite membranes were synthesized using the following procedure. A perfluorosulfonylfluoride copolymer resin and MMT, m-MMT were mechanically mixed by internal mixer (HAAKE, Rheomix 600). The mixture of MMT, m-MMT and copolymer resin was pulverized using by universal grinder (M20, IKA Labortechnik, Germany). The contents of MMT and m-MMT in the mixture were varied in 3, 5 and 7 wt.%. The mixed composite material was take in a stainless steel frame (100 mm × 100 mm, $t = 0.14$ mm), and pre-formed as a sheet shape of 130–140 μm by hot pressing between 200 and 230 °C at 6000 psi. The composite membranes were accomplished by annealing the membrane at temperatures greater than the glass transition temperature ($T_g \sim 230$ °C) of perfluorosulfonylfluoride copolymer resin.

To prepare H⁺-form of the composite membrane, the composite membrane was transformed into Na⁺-form of perfluorosulfonate membrane by immersing in a solution of 20% NaOH/methanol (2:1 in ratio of volume) at 90 °C for 2 h and washed with deionized water. This membrane was

converted into the H⁺-form by immersing it in 1 M H₂SO₄ solutions for several hours at 90 °C, and rinsed repeatedly with deionized water [11]. The ion exchanged MMT was easily mixed with copolymer resin, due to the melt-fabricable property of the copolymer resin. To compare the properties of membranes, the membranes were prepared with and without MMT.

2.2. Thermal stability of a composite membrane

To investigate the thermal properties of the composite membrane, the composite membranes with various MMT, m-MMT contents were analyzed by TG/DSC (SETARAM, TG-DSC 92). The thermal analyzer system was programmed to heat the samples from 30 to 600 °C at the heating rate of 10 °C/min under N₂.

2.3. IR spectroscopy

Infrared spectroscopic experiment on modified MMT by dodecylamine was performed with FT-IR spectrometer (MAGNA 560, Nicolet Co.). The FT-IR spectra for modified MMT were recorded in the wave number range from 500 to 4000 cm⁻¹. The KBr pellet method was used.

2.4. X-ray diffractometer

An X-ray diffractometer (Rigaku Co., D-MAX 2000-Ultima Plus) was adopted to measure the change in d -spacing of montmorillonite crystal before and after the intercalation with perfluorosulfonylfluoride copolymer resin. Cu K α ($\lambda = 1.54$ Å) was used as an X-ray source at d generator voltage of 45 kV and current of 100 mA. The 2θ scanning rate was 2°/min. The repeat distance in the silicate, d , was calculated using the Bragg's law, $d = \lambda/2 \sin \theta_{\max}$, where θ_{\max} is the position of the (0 0 1) peak in the XRD pattern.

2.5. Methanol permeability measurement

The methanol permeability of the membranes was performed in the permeability measuring device. The polymer membrane (16 cm²) was inserted between vessels 1 and 2. Sixty milliliters methanol solution (2 M) and 60 ml deionized water was filled in each vessels 1 and 2, respectively. After a fixed period of time, the amount of methanol that crossed through the membrane and diffused on the other side of the vessel (vessel 2) was determined by gas chromatography (GC 17A, Shimadzu). The gas chromatography equipped with a capillary column (14% cyano propyl phenyl methyl poly siloxane, 30 m × 0.25 mm × 1.0 μm) and a flame ionization detector (FID).

2.6. Proton conductivity measurement

The proton conductivity of the hybrid composite membranes was measured by using impedance analyzer.

The composite membrane was fixed in a four-point probe cell. This cell was consisted of two platinum wire outer current-carrying electrodes (distance 3 cm) and two platinum wire inner potential-sensing electrodes (distance 1 cm). The structure of the cell was fabricated from PTFE (Teflon) material.

The conductivities of the membranes were measured in the longitudinal direction, and were calculated using the following equation:

$$\rho = \frac{L}{RS}$$

where ρ , L , R and S denote the ionic conductivity, distance between reference electrodes, the resistance of the membrane and the cross-sectional area of the membrane, respectively.

The impedance measurements were carried out in the frequency region from 10 mHz to 10^5 Hz and in the ac current amplitude of 0.01 mA using a frequency-response analyzer (Solatron SI 1260, impedance/gain-phase analyzer) and potentiostat (Solatron SI 1287, electrochemical interface). The conductivities of the composite membranes were measured at various temperatures.

2.7. Fabrication of the MEA and measurement of single cell performance

The catalyst slurry was prepared by mixing Nafion[®] solution (5%, DuPont), and Pt black for cathode ink and PtRu black for anode ink. For fabrication of the membrane-electrode assembly (MEA), the catalyst slurry was coated on carbon paper for electrode substrate. The content of catalyst loading was approximately 3 and 5 mg/cm² for anode and cathode, respectively. The effective electrode area of the single cell was 7.6 cm².

The procedures for the cell assembly and the measurements of cell performance were described in detail in the paper [12]. The fabricated composite membrane was used as a membrane for MEA. MEA was fabricated by hot pressing at 135 °C and 130 kg/cm² for 10 min. Two molar methanol/water solution and oxygen gas was supplied into the anode and cathode sides of the single cell. The performances of the single cell were evaluated over the range of 60–125 °C at 1/1.6 atm (anode/cathode). An electronic load with a maximum capability of 0.1 kW (EL-1010D, Dae-Jin Instrument, Korea) was used to evaluate the performance of the single cell.

3. Results and discussion

Fig. 1 shows the FT-IR spectra of the modified MMT containing dodecylamine. The transmittance bands at 3630, 1050, and those between 600–400 cm⁻¹ can be associated, respectively, with –OH stretching of the lattice water, Si–O stretching, and Al–O stretching, and Si–O bending. Concurrently, those bands at 3200–2400 (NH⁺ stretching),

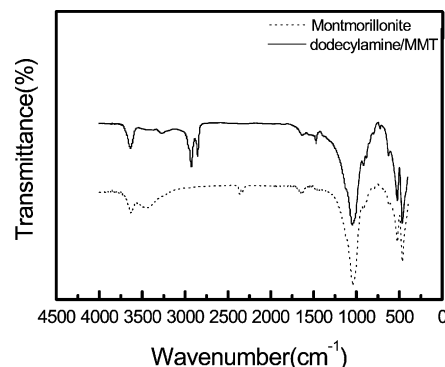


Fig. 1. Infrared spectra of MMT and m-MMT in the wave number range from 500 to 4000 cm⁻¹.

1550–1300 cm⁻¹ (CH₃, stretching) are the consequence due to the characteristic frequencies of dodecylamine. It is shown that the organization of Na-MMT is accomplished successfully.

The evidence for the intercalation on interlayer of MMT can be obtained from the XRD patterns of the composite. Fig. 2a and b shows XRD patterns of copolymer resin/MMT and copolymer resin/m-MMT, respectively. As shown in Fig. 2a, all the composites contain those diffraction peaks characteristic of the pristine Na⁺-MMT. It is considered that polymer chains are not intercalated on interlayer of MMT. This composite shows up the phase separated morphology.

Fig. 2b shows XRD patterns for the intercalated composite with various contents of the m-MMT. As shown in

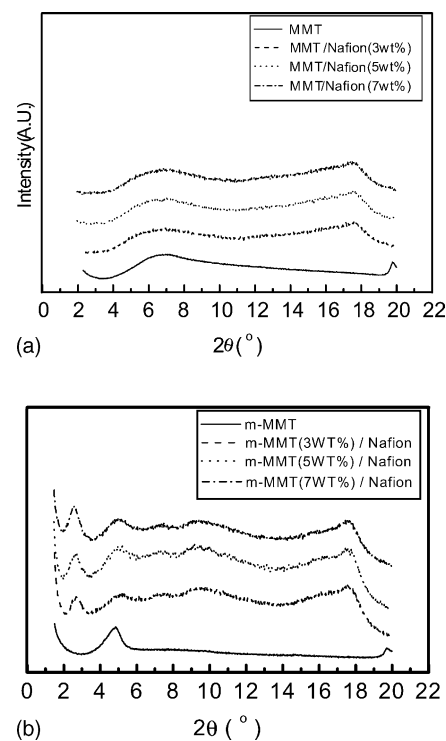


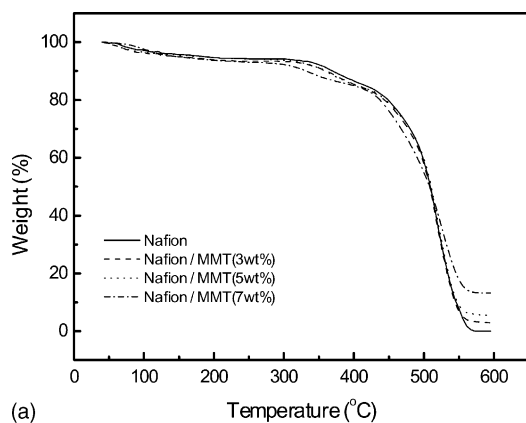
Fig. 2. X-ray diffraction patterns of (a) MMT and (b) m-MMT/Nafion[®] composite membrane with various content of MMT.

Table 1
Interlayer distance (d_{100}) of MMT, m-MMT and the intercalated composites

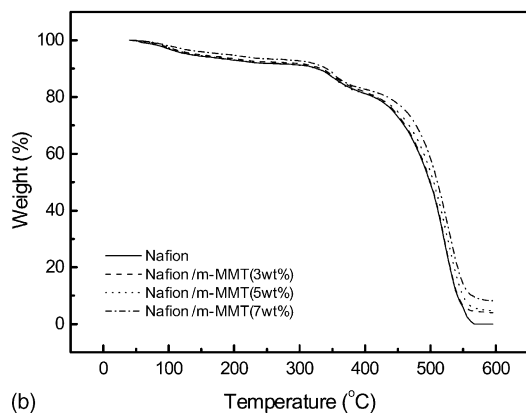
Samples	Interlayer distance	
	d (Å)	Δ (Å)
MMT	12.56	0
m-MMT	18.24	5.68
Copolymer resin/3% m-MMT	32.76	20.2
Copolymer resin/5% m-MMT	32.76	20.2
Copolymer resin/7% m-MMT	34.22	22.42

Fig. 2b, the d -spacing of (0 0 1) plane in the composites were found to be changed in height. The d_{100} value are calculated and summarized in Table 1. XRD pattern of $2\theta = 17.5^\circ$ appear to the crystalline peak scattering from the polyfluorocarbon chains of perfluorosulfonylfluoride copolymer resin. It is clear that the polymer matrix is intercalated into interlayer of the m-MMT. But the d -spacings are not increased with the increments of the m-MMT with the polymer matrix.

The thermal stability for perfluorosulfonylfluoride copolymer resin and MMT, m-MMT with various contents were studied by TGA. The TGA analysis of perfluorosulfonylfluoride copolymer resin/MMT is shown in Fig. 3a. As shown in Fig. 3a, the weight loss of perfluorosulfonylfluoride



(a)



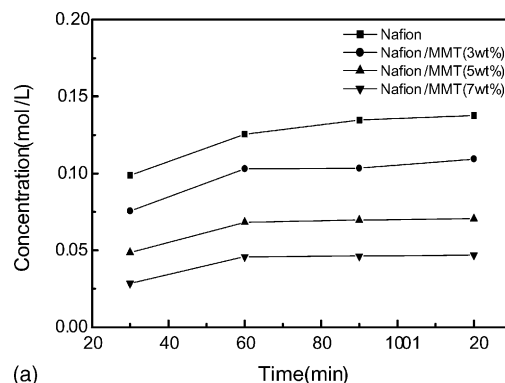
(b)

Fig. 3. TGA thermodiagrams of (a) MMT and (b) m-MMT/Nafion[®] composite membrane with various content of MMT.

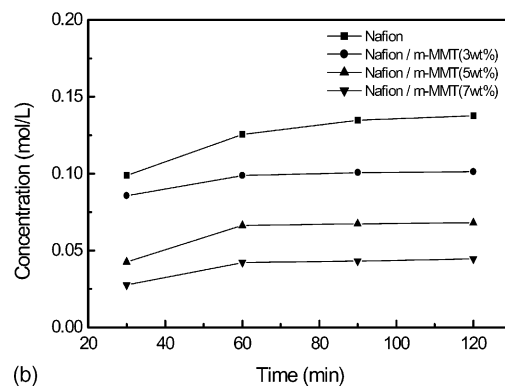
copolymer resin/MMT composite in the temperature range from 25 to 280 °C are about 6 wt.%. It is reported that the gases are H₂O, SO₂ and CO₂. A weight loss of 8% is recorded between 270 and 380 °C because the evolution of SO₂ and CO₂ increase throughout this region, and also occurs SF₄, CO, HF and CF [13]. At the highest temperatures, 355–560 °C, 86% of the sample volatilizes. As a result, thermal resistance of perfluorosulfonylfluoride copolymer resin/MMT composite was lower than that of pure copolymer resin in the all stage. Also the thermal resistance of 5 and 7% MMT in polymer matrix was lower than that of 3% MMT. This is because unmodified MMT works as the defect rather than the retardant filler in polymer matrix.

For the perfluorosulfonylfluoride copolymer resin/m-MMT nanocomposite system, the TGA curves behaved slightly different as shown in Fig. 3b. As shown in Fig. 3b, perfluorosulfonylfluoride copolymer resin/m-MMT nanocomposite displayed higher thermal resistance than that of pure copolymer resin. The thermal resistance of the perfluorosulfonylfluoride copolymer resin/m-MMT nanocomposite was also increased slightly with increasing the contents of m-MMT in the nanocomposite membrane. It is considered that the presence of MMT distributed homogeneously on the polymer matrix affect good thermal property.

The Fig. 4a shows the methanol permeability weight of perfluorosulfonylfluoride copolymer resin and MMT with



(a)



(b)

Fig. 4. Methanol concentration of (a) MMT and (b) m-MMT/Nafion[®] composite membrane with various content of MMT as a function of time.

various contents by GC, as function of time. The methanol permeability weight of the composite membrane decreased slightly with increasing the contents of MMT in the composite membrane, as shown in Fig. 4a. The methanol permeability weight of the composite membranes with 0 and 7 wt.% of MMT were 0.13 and 0.045 mol/l at 1 h, respectively.

Fig. 4b shows the methanol permeability weight of perfluorosulfonylfluoride copolymer resin and m-MMT with various contents, as function of time. The methanol permeability weight of the nanocomposite membranes with 0 and 7 wt.% of m-MMT were 0.13 and 0.042 mol/l at 1 h, respectively. It was found that the methanol permeability weight decreased slightly with increasing the contents of m-MMT in the nanocomposite membrane. Thus, the methanol permeability weight of the composite membrane was lower than that of normal pure membrane as electrolyte.

The ionic conductivities of these acid-form composite membranes were measured at various temperatures, and the data are plotted in Fig. 5a and b.

Fig. 5a shows the proton conductivity of perfluorosulfonylfluoride copolymer resin and MMT membrane. All the membrane exhibits a marked increase in conductivity with increasing temperature. This is due to temperature plays a main role in the kinetics of proton motion in the polymeric membrane and mobility of polymer chains. It can be shown

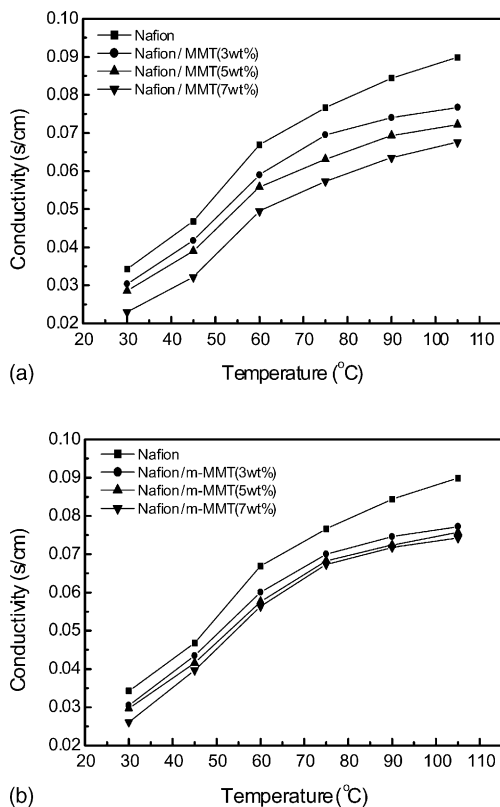


Fig. 5. Proton conductivity as a function of temperature for normal membrane and Nafion[®] resin/MMT (a) and m-MMT (b) (3, 5 and 7 wt.%) at completely humidified stage.

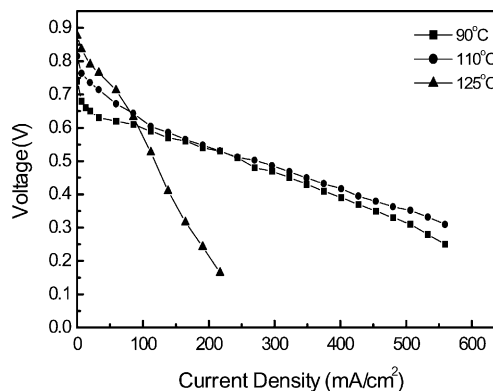
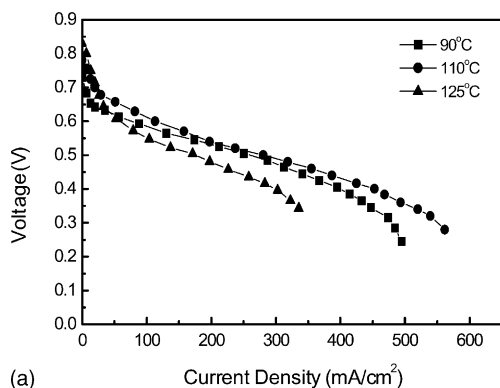


Fig. 6. Polarization curves for the MEA made from normal membrane at various operating temperatures (90–125 °C) with 2 M methanol and oxygen in 1/1.6 atm.

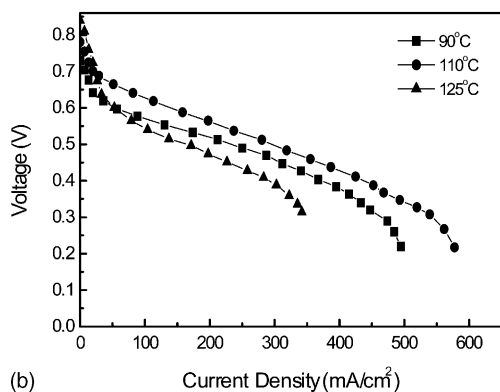
that the highest proton conductivities are 8.9×10^{-2} , 7.6×10^{-2} , 7.2×10^{-2} and 6.7×10^{-2} S/cm at 110 °C. The contents of MMT in the composite membrane are 0, 3, 5 and 7 wt.%, respectively. Fig. 5b shows the proton conductivity of perfluorosulfonylfluoride copolymer resin and m-MMT membrane. As shown in Fig. 5b, the highest proton conductivities are 8.9×10^{-2} , 7.72×10^{-2} , 7.57×10^{-2} and 7.4×10^{-2} S/cm at 110 °C. The contents of MMT in the composite membrane are 0, 3, 5 and 7 wt.%, respectively. It was found that the proton conductivity of perfluorosulfonylfluoride copolymer resin and MMT, m-MMT membranes decreased slightly with increasing the contents of MMT and m-MMT in the composite membrane and lower than normal pure membrane. But it was considered that the composite membrane containing MMT and m-MMT could be used as electrolyte membrane for DMFCs.

Fig. 6 shows the cell performance of the MEA made from normal pure membrane and electrocatalyst at various operating temperatures (90–125 °C) with 2 M methanol and oxygen in 1/1.6 atm. It can be seen that the current densities are 385, 410 and 138.1 mA/cm² (at a potential of 0.4 V) at 90, 110 and 125 °C, respectively. The performance of the MEA was increased with increasing the temperature in the range of 90–110 °C. On the other hand, the performance was rapidly decreased at the operating temperature of 125 °C and showed very low performance.

Fig. 7a and b shows the *I*-*V* characteristics of the cell using perfluorosulfonylfluoride copolymer resin and MMT, m-MMT as electrolytes that have the contents of 3% MMT (m-MMT) at various operating temperatures (90–125 °C) with 2 M methanol and oxygen in 1/1.6 atm. As shown in Fig. 7a, the cell current density using perfluorosulfonylfluoride copolymer resin and 3% MMT are 370, 452.6 and 282.8 mA/cm² (at a potential of 0.4 V) at 90, 110 and 125 °C, respectively. Fig. 7b shows the effects of cell temperatures (90, 110 and 125 °C) on the performance of the MEA made from composite membrane (3 wt.% of m-MMT) under above the same condition. It can be seen that the cell current density are 367.1, 440 and 290 mA/cm²



(a)



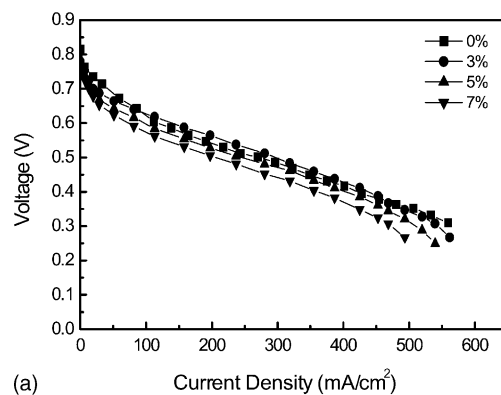
(b)

Fig. 7. Effects of the temperatures (90, 110 and 125 °C) on the performance of the MEA made from the composite membrane (3 wt.% of MMT (a) and m-MMT (b)) with 2 M methanol and oxygen in 1/1.6 atm.

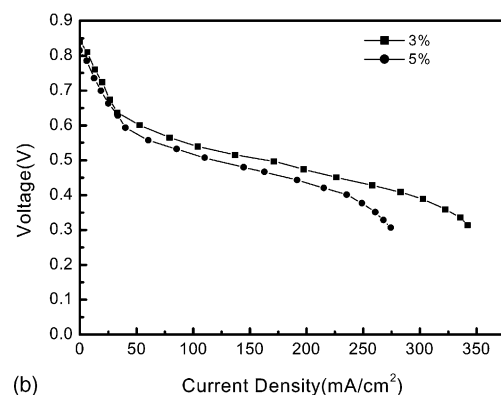
(at a potential of 0.4 V) at 90, 110 and 125 °C, respectively. At high temperature of 90 and 110 °C, the high performance is attributed to the combined effects of a reduction of ohmic resistance and polarization. But in above 125 °C, it is considered that the low performance is due to more high dehydration of the membrane than effect of a reduction of ohmic resistance and polarization.

Comparing Fig. 6 with Fig. 7, the composite membrane improved the performance of the MEA at high operating temperature (e.g. 125 °C). This is attributed to homogenous distribution of MMT and m-MMT, which enhanced the proton conductivity in the composite membrane. As shown in Fig. 4, although the methanol permeability rate decreased with increasing the contents of MMT and m-MMT in the composite membrane, the open-circuit-voltages (OCVs) of the MEA with composite membranes are lower than that of pure membrane. An exact explanation for this behavior has yet to be found. Also, it can be seen that the composite membrane containing 3 wt.% of MMT and m-MMT can be used as electrolyte membrane at low and high operating temperatures for DMFCs.

Fig. 8a and b shows the effects of the contents of m-MMT in the composite membrane on the performance of the MEA at 110 and 125 °C. It can be seen that the current densities are 410, 452, 425 and 386 mA/cm² at a potential of 0.4 V



(a)



(b)

Fig. 8. Effects of the contents of m-MMT in the composite membrane and normal membrane on the performance of the MEA at (a) 110 °C, (b) 125 °C (2 M methanol/oxygen, 1/1.6 atm).

(Fig. 8a). The contents of m-MMT in the composite membrane are 0, 3, 5 and 7 wt.%, respectively. The MEAs containing 7 wt.% of m-MMT in the composite membrane show lower performance than that of the others (0, 3 and 5 wt.%). It can be considered that the more much distributed m-MMT in the composite membrane affect to the reduction of charge transfer from the anode side to the cathode side. As shown in Fig. 8b, the current density of cell containing 3 and 5 wt.% of m-MMT are 290 and 235.3 mA/cm² (at 0.4 V) at 125 °C, respectively.

An initial approach of MEA obtained from composite membrane using perfluorosulfonylfluoride copolymer resin and MMT, m-MMT suggests that the present method is promising for DMFCs.

4. Conclusion

A fabrication method of composite membrane for direct methanol fuel cell was developed using a MMT, m-MMT and perfluorosulfonylfluoride copolymer resin. By thermal stability, methanol permeability, ionic conductivity and the cell performance, the performance of perfluorosulfonylfluoride copolymer resin and MMT, m-MMT membrane for direct methanol fuel cell was evaluated.

The methanol permeability of the composite membrane decreased slightly with increasing the contents of MMT and m-MMT in the composite membrane.

The proton conductivity of the composite membrane with MMT and m-MMT was lower than that of normal pure membrane. But it was considered that the composite membranes could be used sufficiently as electrolyte membrane for DMFCs.

The performance of the MEA made from normal pure membrane was increased with increasing the temperature in the range of 90–110 °C. However, the performance was rapidly decreased at the operating temperature of 125 °C. The composite membrane improved the performance of the MEA at high operating temperature (e.g. 125 °C). It can be seen that the composite membrane containing 3 and 5 wt.% of MMT and m-MMT can be used as electrolyte membrane at high operating temperatures for DMFCs.

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