

Composite Membrane Containing a Proton Conductive Oxide for Direct Methanol Fuel Cell

Dong-Hyun Peck*, Sung-Yong Cho, Sang-Kyung Kim, Doo-Hwan Jung, and Jeong-Soo Kim[†]

Korea Institute of Energy Research (KIER), Yuseong, Daejeon 305-343, Korea

[†]Dept. of Polymer Eng., Chungnam National University, Daejeon 305-764, Korea

(Received October 26, 2007 : Accepted December 7, 2007)

Abstract : The composite membrane for direct methanol fuel cell (DMFC) was developed using $\text{H}_3\text{O}^+-\beta''\text{-Al}_2\text{O}_3$ powder and perfluorosulfonylfluoride copolymer (Nafion) resin. The perfluorosulfonylfluoride copolymer (Nafion) resin was mixed with $\text{H}_3\text{O}^+-\beta''\text{-Al}_2\text{O}_3$ powder and it was made to sheet form by hot pressing. The electrodes were prepared with 60 wt% PtRu/C and 60 wt% Pt/C catalysts for anode and cathode, respectively. The morphology and the chemical composition of the composite membrane have been investigated by using SEM and EDXA, respectively. The composite membrane and $\text{H}_3\text{O}^+-\beta''\text{-Al}_2\text{O}_3$ were analyzed by using FT-IR and XRD. The methanol permeability of the composite membranes was also measured by gas chromatography (GC). The performance of the MEA containing the composite membrane (2 wt% $\text{H}_3\text{O}^+-\beta''\text{-Al}_2\text{O}_3$) was higher than that of normal pure Nafion membrane at high operating temperature (e.g. 110°C), due to the homogenous distribution of $\text{H}_3\text{O}^+-\beta''\text{-Al}_2\text{O}_3$, which decreased the methanol permeability through the membrane and enhanced the water contents in the composite membrane.

Keywords : Composite membrane, Beta-alumina, Nafion, Direct methanol fuel cell (DMFC).

1. Introduction

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 (DMFC).¹⁾ Methanol permeability through 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.^{2,3)} The fuel permeability through the composite membranes made by casting a polymer solution is much higher than that through the commercial membranes.^{2,3)} It is also reported recently that the composite membranes can be prepared by addition 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.⁴⁻⁷⁾ The ionic conductivity of the composite membranes mixed with non-conductive oxides is lower compared with normal membranes.

$\text{H}_3\text{O}^+-\beta''\text{-Al}_2\text{O}_3$ ($\text{H}_3\text{O}^+-\beta''\text{-alumina}$) is a protonic conductor with reported ionic conductivities of 1×10^{-5} , 2×10^{-4} and 5×10^{-3} S/cm at 25°C, 150°C and 300°C, respectively.⁸⁻¹⁰⁾ $\text{H}_3\text{O}^+-\beta''\text{-Al}_2\text{O}_3$ can be prepared conventionally by an ion-exchange reaction using sodium- $\beta''\text{-alumina}$ ($\text{Na}-\beta''\text{-Al}_2\text{O}_3$) with concentrated sulfuric acid.⁸⁾

In the present work, a preparation method of composite

membrane was developed using perfluorosulfonylfluoride copolymer resin (a precursor material for a perfluorosulfonated polymer) and $\text{H}_3\text{O}^+-\beta''\text{-Al}_2\text{O}_3$ powder. The morphology, the chemical composition and the methanol permeability of the composite membrane have been investigated by SEM, FT-IR and gas-chromatography analyses. $\text{H}_3\text{O}^+-\beta''\text{-Al}_2\text{O}_3$ powder was analyzed with XRD. The performance of the MEA (Membrane Electrode Assembly) with composite membrane for DMFC was evaluated, and the results are discussed.

2. Experimental

2.1. Preparation of composite membranes

The composite membrane for a DMFC was prepared by mixing $\text{H}_3\text{O}^+-\beta''\text{-Al}_2\text{O}_3$ and perfluorosulfonylfluoride copolymer resin (Nafion[®] R-1100 resin, DuPont Fluoroproducts, USA) in Internal Mixer (RHEOMIX R600, HAAKE, Germany) at 200-250°C. $\text{H}_3\text{O}^+-\beta''\text{-Al}_2\text{O}_3$ powder was easily mixed with copolymer resin, due to the melt-fabricable property of the copolymer resin. The starting material Na- $\beta''\text{-alumina}$ was prepared using Al_2O_3 (Junsei Chem., Japan), Na_2CO_3 (Oriental Chem., Korea) and $(\text{MgCO}_3)_4 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$ (Kanto Chem.) by solid state reaction at 1250°C for 2 hours. Fully hydrated $\text{H}_3\text{O}^+-\beta''\text{-Al}_2\text{O}_3$ powder was obtained by treating in hot concentrated sulfuric acid and subsequent washing with deionized water at 90°C for several times.¹¹⁾ The crystal-phase of the prepared powder was analyzed with X-ray diffractometer (RINT 2000 ULTIMA PLUS, RIGAKU, Japan). The mixture of $\text{H}_3\text{O}^+-\beta''\text{-Al}_2\text{O}_3$ powder and copolymer resin was pulverized with a universal grinder (M20, IKA

*E-mail: dhpeck@kier.re.kr

Labortechnik, Germany). The contents of $\text{H}_3\text{O}^+-\beta''-\text{Al}_2\text{O}_3$ powder in the mixture were varied in 2, 5 and 10 wt%. To compare the properties of membrane, the membranes were prepared with and without $\text{H}_3\text{O}^+-\beta''-\text{Al}_2\text{O}_3$ powder.

The mixed material was taken in a stainless steel frame (100 mm \times 100 mm, $t = 0.14$ mm), and pre-formed as a sheet shape by hot pressing between 200°C and 250°C. The perfluorosulfonylfluoride copolymer membrane was transformed into Na^+ -form of perfluorosulfonate membrane by immersing in a solution of 20 wt% NaOH/methanol (2 : 1 in ratio of volume) at 90°C for 7hr and washed with de-ionized water. This membrane was converted into the H^+ -form by immersing in 1M H_2SO_4 solutions for several hours at 90°C, and rinsing repeatedly with de-ionized water.¹²⁾

2.2. Characterization of composite membrane

The morphology of the composite membrane was investigated by SEM (Philips, XL30 SFEG). The distribution of chemical elements in the composite membrane was obtained from the energy dispersive X-ray analysis (EDXA). The sample of the composite membrane was freeze-fractured in liquid N_2 , so it exposed a fresh cross-sectional surface. The infrared spectra of the composite membrane were obtained using FT-IR spectrometer (ZnSe ATR Prism, MAGNA 560, FT-IR NICOLET, USA).

Fig. 1 shows the equipment for measuring methanol permeability of the membranes. The polymer membrane sample (16 cm^2) was inserted between vessel 1 and vessel 2 by a ground down O-ring joint. 60 ml methanol solution (2M or 2.5 M) and 60 ml deionized water was filled in vessel 1 and vessel 2, respectively. After a fixed period of time, the amount of methanol that crossed the membrane and appeared on the other side (vessel 2) was determined by gas chromatography (GC 17A, Shimadzu). The gas chromatography was equipped with a capillary column (14% cyano propyl phenyl methyl poly siloxane, 30 m \times 0.25 mm \times 1.0 mm) and a flame ionization detector (FID). Water from vessel 1 was removed and analyzed for methanol at fixed intervals of time and various concentration of $\text{H}_3\text{O}^+-\beta''-\text{Al}_2\text{O}_3$ in the membrane.

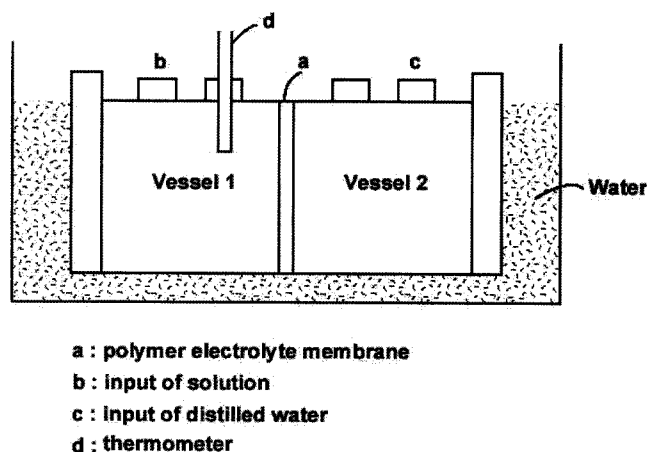


Fig. 1. Schematic diagram of the cell for measurement of methanol permeability of the membranes.

2.3. Fabrication of the MEA, and measurement of single cell performance

The catalyst slurry was prepared by mixing Nafion solution (DuPont), and 60 wt% Pt/C for cathode ink and 60 wt% PtRu/C for anode ink. For fabrication of the MEA, the catalyst slurry was coated on carbon paper substrate. The content of catalyst loading was controlled to be approximately 3 mg/cm^2 and the effective electrode area of the single cell was 7.6 cm^2 . The previous prepared composite membrane was used to form the MEA. The MEA was obtained by hot pressing at 135°C and 100 kg/cm^2 for 2 min.

The procedures for the cell assembly and the measurements of cell performance were described in detail in a previous paper.¹³⁾ 2 M Methanol/water-solution was pumped into the anode channel of the cell, and oxygen gas was supplied into the cathode channel at ambient condition. Cell performances were evaluated over the range of 90-125°C with methanol concentrations of 2 M and 2.5 M. 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. Result and Discussion

3.1 Composite membrane

Fig. 2 shows the XRD pattern of the ion-exchanged $\text{H}_3\text{O}^+-\beta''-\text{Al}_2\text{O}_3$. The XRD pattern of the exchanged $\text{H}_3\text{O}^+-\beta''-\text{Al}_2\text{O}_3$ (Fig. 1) was nearly identical with NaAl_5O_8 ($\text{Na}-\beta''-\text{Al}_2\text{O}_3$) (JCPDS file-No. 19-1173). Further EDXA evidences that sodium is not present in the ion-exchanged $\text{H}_3\text{O}^+-\beta''-\text{Al}_2\text{O}_3$ powder. This proves that the structure has been retained after the ion exchange.

Fig. 3 shows the SEM photograph of the cross-section of the composite membrane (2 wt% $\text{H}_3\text{O}^+-\beta''-\text{Al}_2\text{O}_3$). The thickness of the composite membrane is approximately 130-140 μm . A homogenous distribution of the mixed $\text{H}_3\text{O}^+-\beta''-\text{Al}_2\text{O}_3$ particles in the composite membrane was detected using EDXA (Al K α mapping). The agglomerated particles were observed in some region of composite membrane containing 10 wt% of $\text{H}_3\text{O}^+-\beta''-\text{Al}_2\text{O}_3$.

Fig. 4 shows the FT-IR spectra recorded in the wave num-

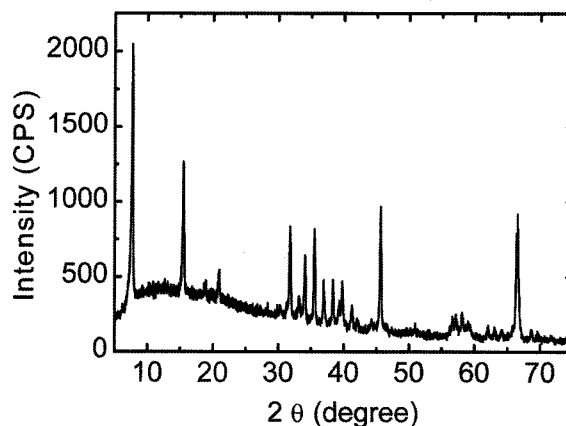


Fig. 2. XRD pattern of the ion-exchanged $\text{H}_3\text{O}^+-\beta''-\text{Al}_2\text{O}_3$ powder obtained from ion exchange process.

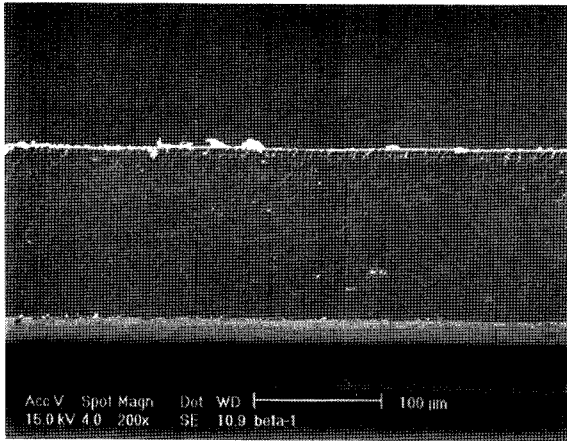


Fig. 3. SEM photograph of the cross-section of the Nafion/H₃O⁺-β''-Al₂O₃ composite membrane (2 wt% H₃O⁺-β''-Al₂O₃).

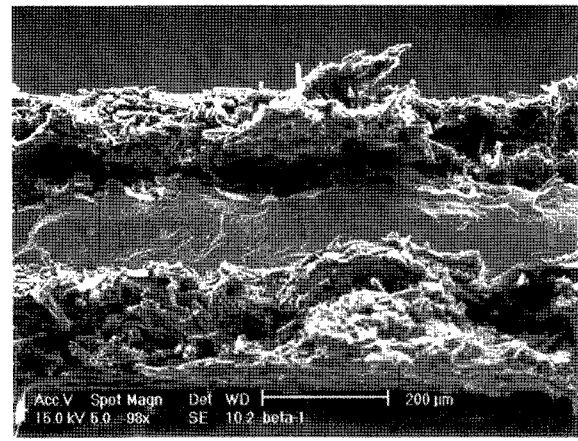


Fig. 5. SEM photograph of cross section of the MEA made with the composite membrane and the coated electrocatalysts on carbon paper.

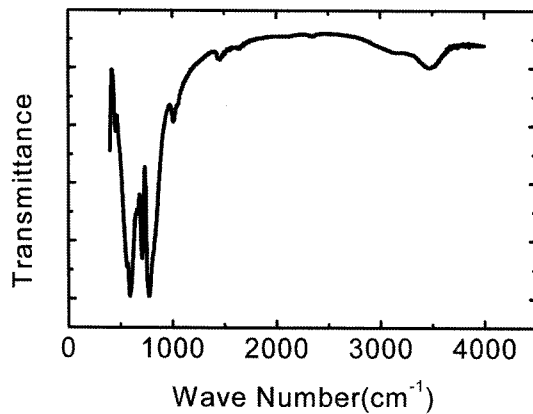


Fig. 4. Infrared spectra of the protonated composite membrane (Nafion/5 wt% of H₃O⁺-β''-Al₂O₃) in the wave number range from 500 to 4000 cm⁻¹.

ber range from 500 to 4,000 cm⁻¹ of the protonated composite membrane containing 5 wt% of H₃O⁺-β''-Al₂O₃. The Absorption band observed around 3,400 cm⁻¹ corresponds to hydroxyl groups. The above band confirms the evidence of H₂O molecules bound with proton. The stretching modes of AlO₄ were observed in the absorption bands around 950 cm⁻¹ regions. The stretching modes of AlO₆ were observed in the absorption bands around 600-800 cm⁻¹ regions. The band at 1400-1500 cm⁻¹ is due to CF₂ bond. The symmetric stretching vibration modes of SO₃⁻H⁺ were observed in the bands around 990-1090 cm⁻¹ regions.

Table 1 shows the methanol permeability rate through the

composite membrane with various contents of H₃O⁺-β''-Al₂O₃ powders at different methanol concentration. The methanol permeability rate through the membrane was higher at high concentration of methanol.¹³⁾ The methanol permeability rates through the composite membranes with 0 wt% and 10 wt% of H₃O⁺-β''-Al₂O₃ powder were 6.9 and 6.78 μmol/cm²s, respectively. It was found that the methanol permeability rate decreased slightly with increasing the contents of H₃O⁺-β''-Al₂O₃ powder in the composite membrane. Thus, the methanol permeability rate through the composite membrane was lower than that of normal pure membrane as electrolyte.

3.2 Membrane/Electrode Assembly (MEA)

Fig. 5 shows SEM photography of cross section of the MEA made with the composite membrane (2 wt% H₃O⁺-β''-Al₂O₃) and carbon paper coated with catalysts. Carbon paper coated with catalysts was observed both side of top and bottom and the composite membrane is in the center. SEM photography of cross section of the MEA indicated that the MEA is uniformly continuous and the membrane is well adhered to carbon paper coated with catalysts without any delamination. The thickness of carbon paper coated with catalysts and the composite membrane of the MEAs were approximately 130 μm and 120 μm, respectively. Carbon paper coated with catalysts has a porous structure and uniform pore-distribution.

3.3 Performance of single cell

Fig. 6 shows the performance of the MEA made from normal pure membrane and electrocatalyst at various operating

Table 1. Methanol permeability rates through the composite membrane with various contents of H₃O⁺-β''-Al₂O₃ powders at different methanol concentration.

Content of H ₃ O ⁺ -β''-Al ₂ O ₃ (wt%)	Methanol permeability rate (μmol/cm ² s)			
	in 2M methanol		in 2.5M methanol	
	1hr	2hr	1hr	2hr
0	6.90	3.53	7.09	3.64
2	6.87	3.50	7.02	3.60
5	6.82	3.44	6.96	3.56
10	6.78	3.41	6.90	3.51

temperatures (90–125°C) with 2M methanol and oxygen in 1/1.6 atm. It can be seen that the current densities are 500 mA/cm², 550 mA/cm², and 160 mA/cm² (at a potential of 0.3 V) at 90°C, 110°C, 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.

Fig. 7 shows the effects of cell temperatures (90°C, 110°C, and 125°C) on the performance of the MEA containing the composite membrane (2 wt% of H₃O⁺-β"-Al₂O₃) with 2M methanol and oxygen in 1/1.6 atm. The current densities of the single cell using composite membrane with 2 wt% of H₃O⁺-β"-Al₂O₃ are 380 mA/cm², 600 mA/cm², and 410 mA/cm² at 90°C, 110°C, and 125°C at 0.3 V, respectively. The highest performance was observed at the temperature of 110°C, and the performance was low at 90°C and 125°C.

Comparing the Fig. 6 with Fig. 7, the composite membrane improved the performance of the MEA at high operating temperature (e.g. 110°C). This is attributed to homogenous distribution of H₃O⁺-β"-Al₂O₃, which enhanced the proton conductivity in the composite membrane. As shown in Table 1, although the methanol permeability rate decreased with

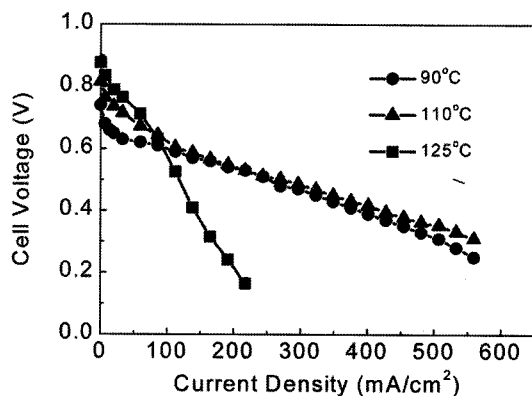


Fig. 6. Polarization curves for the MEA made from normal membrane at various operating temperatures (90–125°C) (2M methanol/oxygen = 1/1.6 atm).

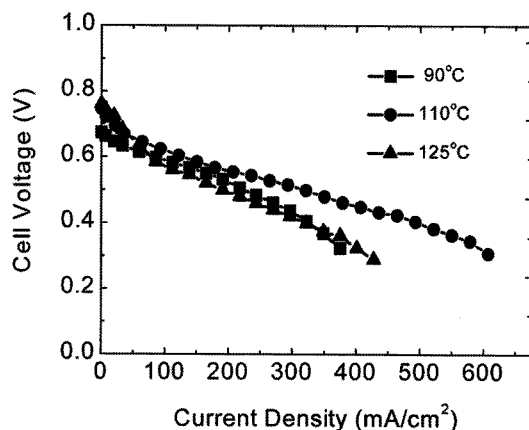


Fig. 7. Effects of the cell temperatures (90°C, 110°C, and 125°C) on the performance of the MEA made from composite membrane (2 wt% of H₃O⁺-β"-Al₂O₃) (2M methanol/oxygen = 1/1.6 atm).

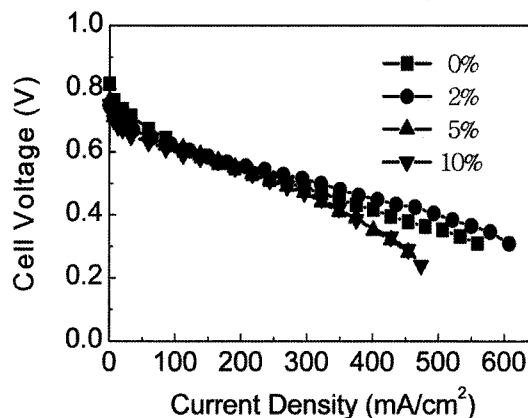


Fig. 8. Effects of the contents of H₃O⁺-β"-Al₂O₃ powder in the composite membrane on the performance of the MEA at 110°C (2M methanol/Oxygen = 1/1.6 atm).

increasing the contents of H₃O⁺-β"-Al₂O₃ powder 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. Comparing the Fig. 6 with Fig. 7, it can be seen that the composite membrane containing 2 wt% of H₃O⁺-β"-Al₂O₃ can be used as electrolyte membrane at low and high operating temperatures for DMFCs.

Fig. 8 shows the effects of the contents of H₃O⁺-β"-Al₂O₃ powder in the composite membrane on the performance of the MEA at 110°C. It can be seen that at a potential of 0.3 V, the current densities of the MEAs are 550 mA/cm², 600 mA/cm², 430 mA/cm², and 440 mA/cm² with contents of H₃O⁺-β"-Al₂O₃ in the composite membrane of 0 wt%, 2 wt%, 5 wt%, and 10 wt%, respectively. The performance of the MEA containing the composite membrane (2 wt% H₃O⁺-β"-Al₂O₃) was higher than that of normal pure Nafion membrane at high operating temperature (e.g. 110°C), due to the homogenous distribution of H₃O⁺-β"-Al₂O₃, which decreased the methanol permeability through the membrane and enhanced the water contents in the composite membrane.

The MEAs containing 2 wt% of H₃O⁺-β"-Al₂O₃ in the composite membrane show higher performance with respect to those containing 5 wt% and 10 wt%. This is due to non-homogenous distribution of H₃O⁺-β"-Al₂O₃ particles in the latter composite membranes. It can be considered that the non-homogenous distributed H₃O⁺-β"-Al₂O₃ particles affect to reduce of proton transfer from the anode side to the cathode side.

An initial approach of MEA obtained from composite membrane using perfluorosulfonylfluoride copolymer resin (Nafion) and H₃O⁺-β"-Al₂O₃ powder suggests that the present method is promising for DMFCs.

4. Conclusion

The composite membrane for direct methanol fuel cell (DMFC) was developed using a H₃O⁺-β"-Al₂O₃ powder and perfluorosulfonylfluoride copolymer resin. A H₃O⁺-β"-Al₂O₃ powder was easily mixed with the copolymer resin, due to the melt-fabricable property of the copolymer resin. The thickness

of the composite membrane was approximately 130-140 μm .

The methanol permeability rate through the membrane was higher at high concentration of methanol. It was found that the methanol permeability rate decreased with increasing the contents of $\text{H}_3\text{O}^+-\beta\text{-Al}_2\text{O}_3$ powder in the composite membrane.

The MEA with composite membrane containing 2 wt% of $\text{H}_3\text{O}^+-\beta\text{-Al}_2\text{O}_3$ showed better performance with respect to normal pure membrane at high operating temperature (e.g. 110°C). This composite membrane can be used as electrolyte membrane at low and high operating temperatures for DMFCs.

Acknowledgments

This work was supported by a grant from New & Renewable Energy RD&D Program funded by the Ministry of Commerce, Industry and Energy (MOCIE), Republic of Korea.

References

1. O. Savadogo, "Emerging membranes for electrochemical systems: (I) solid polymer electrolyte membrane for fuel cell systems", *J. New Mat. for Electrochem. Systems*, **1**, 47 (1998).
2. J.-S. Jiang, D. B. Greenberg, and J. R. Fried, "Preparation of a Nafion composite membrane using a porous Teflon support", *J. Membrane Science*, **132**, 273 (1997).
3. K. M. Nouel and P. S. Fedkiw, "Nafion®-based composite polymer electrolyte membrane", *Electrochimica Acta*, **43**, 2381 (1998).
4. K. A. Mauritz I. D. Stefanithis, S. V. Davis, R.W. Scheetz, R. K. Pope, G.L. Wilkes, and H.H. Huang, "Microstructural evolution of a silicon oxide phase in a perfluorosulfonic acid inomer by an in situ sol-gel reaction", *J. Appl. Polymer Sci.*, **55**, 181 (1995).
5. D. H. Jung, S. Y. Cho, D. H. Peck, D. R. Shin, and J. S. Kim, "Performance evaluation of a Nafion/silicon oxide hybrid membrane for direct methanol fuel cell", *J. Power Sources*, **106**, 173 (2002).
6. K. A. Mauritz, "Organic-inorganic hybrid materials: perfluorinated ionomers as sol-gel polymerization templates for inorganic alkoxides", *Materials Science and Engineering C*, **6**, 121 (1998).
7. P. L. Shao, K. A. Mauritz, and R. B. Moore, "Perfluorosulfonate ionomer/SiO₂-TiO₂ nanocomposites via polymer-in situ sol-gel chemistry: sequential alkoxide procedure", *Chem. Mater.*, **7**, 192 (1995).
8. G. Pourcelly and C. Gavach, "Perfluorinated membrane" in Proton conductors (solids, membranes and gels-materials and devices), 294-310, ed., P. Colomban, Cambridge Univ. Press (1992).
9. H. Ikawa, "Proton-containing β - and β' -alumina structure type compounds" in Proton conductors (solids, membranes and gels-materials and devices), 190-209, ed., P. Colomban, Cambridge Univ. Press (1992).
10. S. Chandra, "Solid state proton conductors and their applications" in Handbook of solid state batteries & capacitors, 579-600, ed., M.Z.A. Munshi, World Scientific (1995).
11. Ph. Colomban, G. Lucazeau, R. Mercier, and A. Novak, "Vibrational spectra and structure of $\text{H}^+(\text{H}_2\text{O})_n \cdot \beta\text{-alumina}$ ", *J. Chemical Phys.*, **67**, 5244 (1977).
12. C. S. Kim, Y. G. Chun, D.H. Peck, and D. R. Shin, "A novel process to fabricate membrane electrode assemblies for proton exchange membrane fuel cells", *Int. J. Hydrogen Energy*, **23**, 1045 (1998).
13. D. H. Jung, C. H. Lee, C. S. Kim, and D. R. Shin, "Performance of a direct methanol polymer electrolyte fuel cell", *J. Power Sources*, **71**, 169 (1998).