

## DEVELOPMENT OF A COMPOSITE MEMBRANE CONTAINING A PROTON- $\beta''$ - $\text{Al}_2\text{O}_3$ POWDER

S.Y. Cho\*, D.H. Peck, D.H. Jung, B.D. Lee, D.R. Shin, and J.S. Kim\*

\*Dept. of Polymer Eng., Chung Nam Nat'l University, Taejon, 305-764, Korea

Korea Institute of Energy Research (KIER), P.O. Box 103, Yusong, Taejon 305-343, Korea

To whom correspondence should be addressed. Fax: +82-42-860-3739; E-mail: [dhpeck@kier.re.kr](mailto:dhpeck@kier.re.kr)

### 1. INTRODUCTION

Perfluorosulfonate ionomer membranes such as Nafion<sup>®</sup> (DuPont), Flemion<sup>®</sup> (Asahi Glass Co.), Aciplex<sup>®</sup> (Asahi Chem.), and Dow XUS (Dow Chemical) are used as polymer electrolyte membrane for direct methanol fuel cell (DMFC)[1]. Methanol permeability of these membranes is high. Reduction of the methanol permeability in the membrane, the composite membrane was used in DMFC and PEMFC. The composite membranes were prepared by recasting of a Nafion<sup>®</sup> solution to which oxide colloids were added previously. The gas permeability of a composite membranes made by casting of a polymer solution is much higher than that of commercial membrane [2, 3]. 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<sup>®</sup> membrane [4-7].

$\text{H}_3\text{O}^+$ - $\beta''$ - $\text{Al}_2\text{O}_3$  ( $\text{H}_3\text{O}^+$ - $\beta''$ -alumina) is a protonic conductor with reported ionic conductivities of  $1 \times 10^{-5}$ ,  $2 \times 10^{-4}$  and  $5 \times 10^{-3}$  S/cm at 25°C, 150°C and 300°C, respectively [8, 9, 10].  $\text{H}_3\text{O}^+$ - $\beta''$ - $\text{Al}_2\text{O}_3$  can be prepared conventionally by an ion-exchange reaction using sodium- $\beta''$ -alumina ( $\text{Na}-\beta''$ - $\text{Al}_2\text{O}_3$ ) with concentrated sulfuric acid.

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 compositions and the methanol permeability of the composite membrane have been investigated using by SEM, FT-IR and GC-chromatography.  $\text{H}_3\text{O}^+$ - $\beta''$ - $\text{Al}_2\text{O}_3$  powder was analyzed with XRD. The effects of composite membrane on the performance of DMFC were evaluated, and the results are discussed.

### 2. EXPERIMENTAL

#### 2.1. Preparation of composite membrane

The composite membrane for a direct methanol fuel cell (DMFC) was prepared by mixing of a  $\text{H}_3\text{O}^+$ - $\beta''$ - $\text{Al}_2\text{O}_3$  and perfluorosulfonylfluoride copolymer resin (DuPont Fluoroproducts, USA) in Internal Mixer (HAAKE, Germany) at 200-250°C. A  $\text{H}_3\text{O}^+$ - $\beta''$ - $\text{Al}_2\text{O}_3$  powder was easily mixed with copolymer resin, due to the melt-fabricable property of the copolymer resin. A starting material Na- $\beta''$ -alumina was prepared using  $\text{Al}_2\text{O}_3$  (Junsei Chem., Japan),  $\text{Na}_2\text{CO}_3$  (Oriental Chem., Korea) and  $(\text{MgCO}_3)_4\text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$  (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 heating this material with concentrated sulfuric acid and this powder was washed with deionized water at 90°C for several times [8]. The crystal-phase of the prepared powder was analyzed using by 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 using by Universal grinder (IKA 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 composite material was take in a stainless steel frame (100mm x 100mm, t = 0.14mm), and pre-formed as a sheet shape by hot pressing between 200°C and 250°C. This membrane was converted into the  $\text{H}^+$ -form by immersing it in 1M  $\text{H}_2\text{SO}_4$  solutions for several hours at 90°C, and rinsed repeatedly with de-ionized water [9].

## 2.2. Characterization of composite membrane

The morphology of the composite membrane was investigated using SEM (Philips, XL30 SFEG). The distribution of chemical element in the composite membrane was determined using the energy dispersive X-ray analysis (EDXA). The composite membrane was freeze-fractured in liquid  $\text{N}_2$ , exposing 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).

The methanol permeability of the membranes was determined by gas chromatography (GC 17A, Shimadzu). The gas chromatography equipped with a capillary column (14% cyano propyl phenyl methyl poly siloxane, 30mx0.25mmx1.0 $\mu\text{m}$ ) and a flame ionization detector (FID).

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

The catalyst slurry was prepared by mixing Nafion solution (DuPont), and 60% Pt/C for cathode ink and 60% PtRu/C for anode ink. For fabrication of the membrane/electrode assembly (MEA), the catalyst slurry was coated on carbon paper substrate. The content of catalyst loading was approximately 3 mg/cm<sup>2</sup> and the effective electrode area of the single cell was 7.6cm<sup>2</sup>. The composite membrane was used as a

membrane for MEA. MEA was fabricated by hot pressing at 135°C and 100kg/cm<sup>2</sup> for 2min.

The procedures for the cell assembly and the measurements of cell performance were described in detail in the previous paper [10]. 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.

### 3. RESULT AND DISCUSSION

#### 3.1 Composite membrane

Fig. 2 shows the XRD pattern of the ion-exchanged H<sub>3</sub>O<sup>+</sup>-β"-Al<sub>2</sub>O<sub>3</sub>. The XRD pattern of the exchanged H<sub>3</sub>O<sup>+</sup>-β"-Al<sub>2</sub>O<sub>3</sub> (Fig. 1) was nearly identical with NaAl<sub>5</sub>O<sub>8</sub> (Na-β"-Al<sub>2</sub>O<sub>3</sub>) (JCPDS file-No. 19-1173). There was no evidence of sodium containing region in the exchanged H<sub>3</sub>O<sup>+</sup>-β"-Al<sub>2</sub>O<sub>3</sub> powder by EDXA. This proves that the structure has been retained after the ion exchange.

Fig. 3 shows the SEM photography of the cross-section of the composite membrane (2 wt.% H<sub>3</sub>O<sup>+</sup>-β"-Al<sub>2</sub>O<sub>3</sub>). The thickness of the composite membrane is approximately 130-140μm. A homogenous distribution of the mixed H<sub>3</sub>O<sup>+</sup>-β"-Al<sub>2</sub>O<sub>3</sub> particles in the composite membrane was detected using EDXA (Al Kα mapping). The agglomerated particles were observed in some region of composite membrane containing 10 wt.% of H<sub>3</sub>O<sup>+</sup>-β"-Al<sub>2</sub>O<sub>3</sub>.

Fig. 4 shows the FT-IR spectra recorded in the wave number range from 500 to 4000 cm<sup>-1</sup> of the protonated composite membrane containing 5 wt.% of H<sub>3</sub>O<sup>+</sup>-β"-Al<sub>2</sub>O<sub>3</sub>. The Absorption bands around 3400 and 3500 cm<sup>-1</sup> were observed which corresponds to hydroxyl groups. The above band confirms the evidence of H<sub>2</sub>O molecules bound with proton. The stretching modes of AlO<sub>4</sub> were observed in the absorption bands around 950 cm<sup>-1</sup> regions. The stretching modes of AlO<sub>6</sub> were observed in the absorption bands around 600-800 cm<sup>-1</sup> regions. The band at 1400-1500cm<sup>-1</sup> is due to CF<sub>2</sub> bond. The symmetric stretching vibration modes of SO<sub>3</sub>H<sup>+</sup> were observed in the bands around 990-1090cm<sup>-1</sup> regions.

Table 1 showed the methanol permeability rate of the composite membrane with various contents of H<sub>3</sub>O<sup>+</sup>-β"-Al<sub>2</sub>O<sub>3</sub> particle at different methanol concentration. The methanol permeability rate of the membrane was higher at high concentration of methanol. The methanol permeability rates of the composite membranes with 0 wt.% and 10 wt.% of H<sub>3</sub>O<sup>+</sup>-β"-Al<sub>2</sub>O<sub>3</sub> powder were 6.9 and 6.78 μmol/cm<sup>2</sup>s, respectively. It was found that the methanol permeability rate decreased slightly with increasing the contents of H<sub>3</sub>O<sup>+</sup>-β"-Al<sub>2</sub>O<sub>3</sub> powder in the composite membrane. Thus, the methanol permeability rate of the composite membrane was lower than that of normal pure membrane as electrolyte.

Table 1. Methanol permeability rates of the composite membrane with various contents of  $\text{H}_3\text{O}^+-\beta''-\text{Al}_2\text{O}_3$  particles at different methanol concentration.

Content of $\text{H}_3\text{O}^+-\beta''-\text{Al}_2\text{O}_3$ (wt.%)	Methanol permeability rate ( $\mu\text{mol}/\text{cm}^2 \text{ s}$ )			
	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

### 3.2 Performance of single cell

Fig. 6 shows the performance of the MEA made from normal pure membrane and electrocatalyst at various operating temperatures (90-125°C) with 2M methanol and oxygen in 1/1.6 atm. It can be seen that the current densities are 500mA/cm<sup>2</sup>, 550mA/cm<sup>2</sup>, and 160mA/cm<sup>2</sup> (at a potential of 0.3V) 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 and showed very low performance.

Fig. 7 shows the effects of cell temperatures (90°C, 110°C, and 125°C) on the performance of the MEA made from composite membrane (2 wt.% of  $\text{H}_3\text{O}^+-\beta''-\text{Al}_2\text{O}_3$ ) with 2M methanol and oxygen in 1/1.6 atm. The current densities of the single cell using composite membrane with 2 wt.% of  $\text{H}_3\text{O}^+-\beta''-\text{Al}_2\text{O}_3$  are 380mA/cm<sup>2</sup>, 600mA/cm<sup>2</sup>, and 410mA/cm<sup>2</sup> at 90°C, 110°C, and 125°C at 0.3V, respectively. The highest performance was observed at the temperature of 110°C.

Comparing the 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  $\text{H}_3\text{O}^+-\beta''-\text{Al}_2\text{O}_3$ , which enhanced the proton conductivity in the composite membrane. As shown in Table 1, although 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 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  $\text{H}_3\text{O}^+-\beta''-\text{Al}_2\text{O}_3$  can be used as electrolyte membrane at low and high operating temperatures for DMFCs.

Fig. 8 shows the effects of the contents of  $\text{H}_3\text{O}^+-\beta''-\text{Al}_2\text{O}_3$  powder in the composite membrane on the performance of the MEA at 110°C. It can be seen that at a potential of 0.3V, the current densities are 550mA/cm<sup>2</sup>, 600mA/cm<sup>2</sup>, 430mA/cm<sup>2</sup>, and 440mA/cm<sup>2</sup>. The contents of  $\text{H}_3\text{O}^+-\beta''-\text{Al}_2\text{O}_3$  in the composite membrane are 0 wt.%, 2 wt.%, 5 wt.%, and 10 wt.%, respectively. The MEAs containing 0 wt.% and 2

wt.% of  $\text{H}_3\text{O}^+-\beta''\text{-Al}_2\text{O}_3$  in the composite membrane show higher performance as than that of 5 wt.% and 10 wt.%. This is due to non-homogenous distribution of  $\text{H}_3\text{O}^+-\beta''\text{-Al}_2\text{O}_3$  particles in the composite membrane. It can be considered that the non-homogenous distributed  $\text{H}_3\text{O}^+-\beta''\text{-Al}_2\text{O}_3$  particles affect to the reduction of charge transfer from the anode side to the cathode side.

#### 4. CONCLUSION

A fabrication method of composite membrane for direct methanol fuel cell (DMFC) was developed using a  $\text{H}_3\text{O}^+-\beta''\text{-Al}_2\text{O}_3$  powder and perfluorosulfonylfluoride copolymer resin. A  $\text{H}_3\text{O}^+-\beta''\text{-Al}_2\text{O}_3$  was easily mixed with the copolymer resin, due to the melt-fabricable property of the copolymer resin. The thickness of the composite membrane is approximately 130-140 $\mu\text{m}$ .

The methanol permeability rate of 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 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 and showed very low performance. 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 2 wt.% of  $\text{H}_3\text{O}^+-\beta''\text{-Al}_2\text{O}_3$  can be used as electrolyte membrane at low and high operating temperatures for DMFCs.

#### ACKNOWLEDGMENTS

This work was supported by the Ministry of Commerce, Industry and Energy, Korea.

#### REFERENCES

1. O. Savadogo, J. New Materials for Electrochemical systems, 1, 47-66 (1998).
2. J.-S. Jiang, D.B. Greenberg, and J.R. Fried, J. Membrane Science, 132, 273-276 (1997).
3. K.M. Nouel and P.S. Fedkiw, Electrochimica Acta, 43 (16-17), 2381-2387 (1998).
4. K.A. Mauritz et.al. J. Appl. Polymer Sci., 55, 181 (1995)
5. R.V. Gummaraju, R.B. Moore, K.A. Mauritz, J. Polymer Sci., B Polymer Phys., 34, 2383 (1996)
6. W. Apichatachapan, R.B. Moore, K.A. Mauritz, J. Appl. Polymer Sci., 62, 417 (1996)
7. O.L. Shao, K.A. Mauritz, R.B. Moore, Chem. Mater., 7, 192 (1995)
8. Ph. Colomban, et.al. J. Chemical Phys., 67(11), 5244-5251 (1977)
9. C.S. Kim, Y.G. Chun, D.H. Peck, and D.R. Shin, Int. J. Hydrogen Energy, 23(11), 1045-1048 (1998)
10. D.H. Jung, C.H. Lee, C.S. Kim, and D.R. Shin, Journal of power sources, 71, 169-173 (1998)

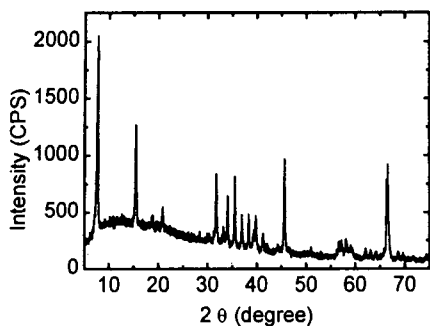


Fig. 2 XRD pattern of the ion-exchanged  $\text{H}_3\text{O}^+-\beta''-\text{Al}_2\text{O}_3$  powder obtained from ion exchange process

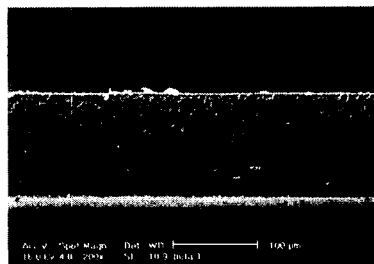


Fig. 3 SEM photography of the cross-section of the protonated composite membrane (2 wt.%  $\text{H}_3\text{O}^+-\beta''-\text{Al}_2\text{O}_3$ ).

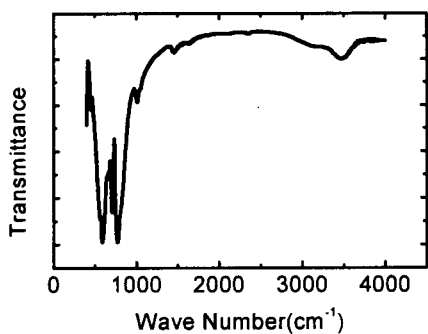


Fig. 4 Infrared spectra of the protonated composite membrane (5 wt.% of  $\text{H}_3\text{O}^+-\beta''-\text{Al}_2\text{O}_3$ ) in the wave number range from 500 to 4000  $\text{cm}^{-1}$ .

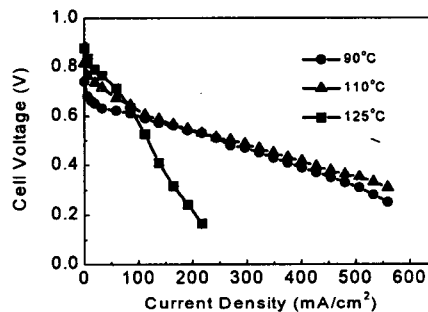


Fig. 5 Polarization curves for the MEA made from normal membrane at various operating temperatures (90-125°C) with 2M methanol and oxygen in 1/1.6 atm

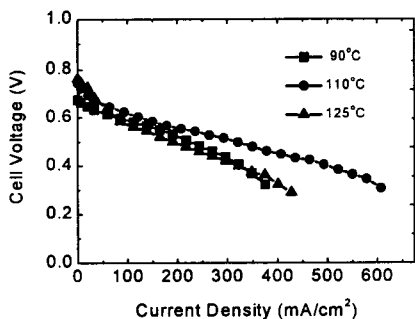


Fig. 7 Effects of the temperatures (90~125°C) on the performance of the MEA made from composite membrane (2 wt.% of  $\text{H}_3\text{O}^+-\beta''-\text{Al}_2\text{O}_3$ .) with the same condition

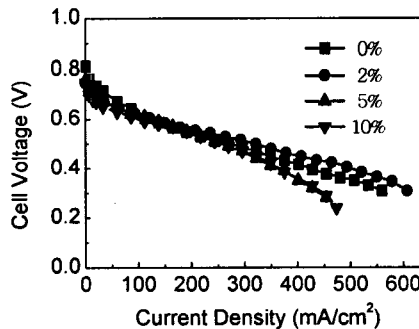


Fig. 8 Effects of the contents of  $\text{H}_3\text{O}^+-\beta''-\text{Al}_2\text{O}_3$  powder in the composite membrane on the performance of the MEA at 110°C