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Proton conducting composite membranes from Nafion and $NH_4^+/H_3O^+-\beta^{"}$ -alumina for high temperature PEMFC

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Composite membranes as an electrolyte for high-temperature PEMFCs (proton exchange membrane fuel cells) were prepared by mixing a Nafion polymer matrix and proton- β "-aluminas (H₃O⁺- β "-Al₂O₃ and NH₄⁺/H₃O⁺- β "-Al₂O₃) as inorganic fillers with fast proton conductivity. From the K⁺- β "-alumina precursor, the aforementioned proton- β "-aluminas were prepared via ion-exchange reactions by a hydrothermal process using an acetic acid solution and ammonium nitrate solution, respectively. Water contact angles of the composite membranes were measured, and the electrical properties of the PEMFCs were analyzed at 80~100 °C under atmospheric pressure. As the filler content increases, the contact angle becomes smaller and thus more hydrophilic. Also, some prepared composite membranes showed a higher cell performance than Nafion[®] 115 membrane at 80~100 °C.

Key word: β"-alumina, Solid electrolyte, Composite membrane, High-temperature PEMFCs.

Introduction

Fuel cells and solar cells have been proposed as a solution to problems such as environmental pollution and depletion of fossil fuels. Among them, proton exchange membrane fuel cells (PEMFCs) have desirable properties, which make them potentially applicable to cars, homes, and portable power generators. Such advantages can make PEMFCs a leading alternative to internal combustion and diesel engines for transportation as well as for power generation [1]. In the field of PEMFCs, DuPont's Nafion[®] is a conventional protonconducting polymer membrane electrolyte that is widely used because of its high proton conductivity and chemical, mechanical, and thermal stability. However, this material has some shortcomings, such as water management, excessive use of a novel metal catalyst, and CO-poisoning at the anode, because PEMFCs normally operate at relatively low temperatures of about 80 °C. To improve the electrolyte properties at higher temperatures, Nafion is modified by incorporating inorganic fillers. The following are expected to result from the development of high-temperature PEMFCs [2, 3]:

(1) Faster reaction rates, decreasing or even eliminating the need for novel metal catalysts.

(2) Greater tolerance to CO poisoning at the anode.

(3) Higher proton mobility, decreasing membrane resistivity.

(4) Water evaporation, mitigating the "flooding" problem at the cathode.

There are several PEMFC studies using Nafion-based composite membranes that operate at high temperature or low humidity [4-8].

In this study, composite membranes that can be applied to high-temperature PEMFCs were prepared from a Nafion[®] solution and two types of proton- β "-alumina ceramics; that is, H₃O⁺- β "-alumina and NH₄⁺/H₃O⁺- β "-alumina, the latter of which has been used as an inorganic filler that is stable over a wide temperature range, to as high as 350 °C, and has fast proton conductivity values of 5×10^{-3} and 1.0×10^{-2} S/cm at 100 °C and 150 °C, respectively [9].

Experimental

To prepare inorganic fillers, a K^+ - β "-alumina precursor was synthesized in the ternary system K₂O-Li₂O- Al_2O_3 . The molar ratio was $[K_2O] : [Al_2O_3] = 1 : 5$, to which was added 0.2 wt.% Li₂O as a stabilizer. The K^+ - β "-alumina precursor was attrition-milled after being ball-milled to maximize the surface area and minimize the particle size. Characteristics of the K^+ - β^- alumina powder were determined using an X-ray diffractometer (Rigaku Rint 2000, Cu Ka-radiation scanning range 5 to 70 ° 20, step width 0.08 °, scanning speed 10 °/minute⁻¹), scanning electron microscopy (SEM, JEOL JSM-6308, Japan) and particle size analysis (PSA, Brookhaven Instruments Co.). From the K^+ - β "-alumina, H_3O^+ - β "-alumina and NH_4^+/H_3O^+ - β "alumina were prepared via ion-exchange reactions by a hydrothermal process using an acetic acid solution

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(CH₃COOH) and ammonium nitrate solution (NH₄NO₃) with various reaction times, temperatures and concentrations of the ion-exchange medium. After that, the ion-exchange rate of each specimen was measured with an inductively coupled plasma (ICP, Spectro Modular EOP). A similar process had been conducted before in the same laboratory [10].

All of the prepared proton- β "-alumina powder was mixed homogeneously with 20 wt.% of Nafion solution. Then, H₃O⁺- β "-alumina/Nafion and NH₄⁺/H₃O⁺- β "-alumina/Nafion composite membranes were prepared from the mixture by a solution casting method. The contents of proton- β "-alumina in each of the composite membranes were chosen to be 2.5, 5.0, 7.5 and 10.0 wt.% [11].

After drying, the composite membranes were heated in a vacuum oven for 2 h at 135 °C to remove residual solvent. The membranes were then kept in a solution of 3% H_2O_2 , 0.5 M H_2SO_4 , and deionized water for 1 h at 80 °C.

Water contact angles were determined by a drop shape analyzer (KRUSS DSA100) using the sessile drop method, the most common method of contact angle measurement on a solid surface. After the water was removed from the surface of the swollen composite membranes, the contact angle was measured at room temperature. The water droplet was limited in volume to about 0.5 μ l.

Membrane electrode assemblies (MEAs) were made from different prepared composite membranes. Carbon cloth containing a catalyst loading of 5 g/m² was used



Fig. 1. XRD pattern of K^+ - β "-alumina



Fig. 2. SEM images of K^+ - β "-alumina: (a) after ball-milling, (b) after attrition-milling

for the electrode. The membranes were sandwiched between two electrodes and hot-pressed at 135 °C and 100 kg/cm² for 3 minute. A graphite plate was used as a gas flow-field. The testing system was designed by WonA Tech Co., Ltd. The flow rates of H₂ and O₂ were 90 cc/minute⁻¹, and the operating temperatures were 80 °C and 100 °C. The temperature of the humidifier was kept equal to each respective operating temperature.

Results and discussion

In Fig. 1, the phase analysis of K^+ - β^- -alumina from the ternary system $K_2O-Li_2O-Al_2O_3$ was compared to the reference samples (JCPDS card No. 31-960 (β alumina), 21-618 (β^- -alumina)). The results for the 2 θ values and the intensities of all peaks were in agreement with those of the reference.

Also, Fig. 2 and 3 show the particle shape and particle size of K^+ - β "-alumina powers. According to the PSA measurements, the mean particle size of the ball-milled powder was $1.0 \sim 2.0 \ \mu$ m and that of the attrition-milled powder was $300 \sim 500 \ nm$.

Table 1 and Fig. $4 \sim 6$ show the ion-exchange rates of H₃O⁺- β "-alumina after the following reactions: in 10 wt.% acetic acid solution at 150 °C for $2 \sim 4$ h, and in 10 wt.% acetic acid solution for 2 h at 150 ~170 °C. The ion-exchange rate increased in response to a longer reaction time and higher temperature. However, boehmite



Fig. 3. The particle size distributions of K^+ - β "-alumina: (a) after ball-milling, (b) after attrition-milling

Table 1. The ion-exchange rates of H_3O^+ - β "-alumina 1) in 10 wt.% acetic acid solution at 150 °C for 2 ~4 h and 2) in 10 wt.% acetic acid solution for 2 h at 150 ~ 170 °C

1) 10 wt.% acetic acid solution, $150\ ^{\rm o}{\rm C}$		2) 10 wt.% acetic acid solution, 2 h	
Time	Ion-exchange rate (%)	Temperature	Ion-exchange rate (%)
0	0	150 °C	85.8
2 h	85.8		
2.5 h	86.4	160 °C	85.51
3 h	84.65		
3.5 h	87.58	170 °C	90.49
4 h	86.82		



Fig. 4. The XRD patterns of H_3O^+ - β "-alumina in 10 wt.% acetic acid solution at 150 after (a) 2 h, (b) 2.5 h, (c) 3 h, (d) 3.5 h, (e) 4 h



Fig. 5. The XRD patterns of H_3O^+ - β "-alumina in 10 wt.% acetic acid solution for 2 h at (a) 150 °C, (b) 160 °C, (c) 170 °C



Fig. 6. The ion-exchange rates of H_3O^+ - β "-alumina in 10 wt.% acetic acid solution (a) at 150 °C for 2 ~ 4 h, (b) for 2 h at 150 ~ 170 °C

appeared after 3 h at 150 $^{\circ}$ C (Fig. 4), and also at 160 and 170 $^{\circ}$ C after 2 h (Fig. 5).

Table 2 and Fig. $7 \sim 9$ also show the ion-exchange rates of H_3O^+/NH_4^+ - β "-alumina after the following reactions: in 4 M NH₄NO₃ solution at 150 °C for $2 \sim 4$ h,

Table 2. The ion-exchange rates of $H_3O^+/NH_4^{+}-\beta^{"}$ -alumina 3) in 4 M NH₄NO₃ solution at 150 °C for 2 ~ 4 h, and 4) at 150 °C for 2 h in 3 ~ 5 M NH₄NO₃ solution

3) 4M NH ₄ NO ₃ solution, 150 °C		4) NH ₄ NO ₃ solution, 150 °C, 2 h	
Time	Ion-exchange rate (%)	Concentration	Ion-exchange rate (%)
0	0	3 M	92.15
2 h	93.18		
2.5 h	93.33	4 M	93.75
3 h	93.08		
3.5 h	93.70	5 M	93.97
4 h	93.70		



Fig. 7. The XRD patterns of H_3O^+/NH_4^+ - β "-alumina in 4 M NH₄NO₃ solution at 150 after (a) 2 h, (b) 2.5 h, (c) 3 h, (d) 3.5 h, (e) 4 h



Fig. 8. The XRD patterns of H_3O^+/NH_4^+ - β "-alumina after 2 h at 150 °C in various concentrations of NH_4NO_3 solution: (a) 3 M, (b) 4 M, (c) 5 M

and at 150 °C for 2 h in $3 \sim 5$ M NH₄NO₃ solution. Under both sets of conditions, the ion-exchange rate similarly reached 93%, but boehmite reappeared after 4 h.

As a result, the ion-exchange rates of proton- β "aluminas in the above mentioned reactions using 10 wt.% acetic acid solution and 4 M ammonium nitrate solution at 150 °C for 2 h were 85% for H₃O⁺- β "-alumina and 93% for NH₄⁺/H₃O⁺- β "-alumina. These proton- β "-alumina powders were used as a filler



Fig. 9. The ion-exchange rates of H_3O^+/NH_4^+ - β^* -alumina at 150 °C (a) in 4 M NH₄NO₃ solution for 2 ~ 4 h, (b) for 2 h in 3 ~ 5 M NH₄NO₃ solution



Fig. 10. Water contact angles of composite membranes as a function of filler content: (a) H_3O^+ - β^- -alumina/Nafion composite membranes, (b) NH_4^+/H_3O^+ - β^- -alumina/Nafion composite membranes

for the composite membrane.

Besides proton conductivity, hydration of the electrolyte membrane is an important factor in determining the cell performance, because the PEMFC is expected to be operated at a high temperature. Fig. 10 shows the water contact angles of composite membranes with various filler contents; (a) and (b) indicate H_3O^+ - β "-alumina/Nafion and NH_4^+/H_3O^+ - β "-alumina/Nafion composite membranes, respectively. As the content of filler is increased, the contact angle becomes smaller. This shows that the hydrophilicity of the membranes is improved by addition of proton- β "-aluminas.

Fig. 11 shows the cell performance of MEAs using H_3O^+ - β "-alumina/Nafion composite membranes, as compared to Nafion®115, as a function of filler content and temperature. The MEA using 7.5 wt.% H_3O^+ - β "-alumina filler shows the best cell performance, with 54% and 19% higher current density and power density, respectively, than those of the MEA using Nafion®115 at 100 °C. With the composite membranes, the cell performance is generally improved in the



Fig. 11. Cell perfomances of MEAs using H_3O^+ - β^- -alumina/ Nafion composite membranes, as compared to Nafion[®]115, as a function of various filler contents at (a) 80 °C and (b) 100 °C

temperature range between 80 and 100 °C, except for the membrane containing 10.0 wt.% of H_3O^+ - β "alumina filler. This is explained by the fact that fillers of β "-alumina were uniformly dispersed in the polymer matrix and powder particles agglomerate around the sulfuric acid group of the polymer matrix, strongly preventing water loss. But excessive filler addition, such as a 10 wt.% content, causes a decrease in cell performance because the ion conduction of the H_3O^+ - β "-alumina filler is not so sufficiently activated as Nafion within these temperatures, which disturbs the proton conduction.

Fig. 12 shows the results of the NH_4^+/H_3O^+ - $\beta^{"-}$ alumina/Nafion composite membranes. In the case of the membrane containing 2.5 wt.% NH_4^+/H_3O^+ - $\beta^{"-}$ alumina filler, the cell had the best performance of 11% and 32% improvements in current density and power density, respectively, at 80 °C, as compared to Nafion[®]115. Above 7.5 wt.% of filler, however, the cell performance was lowered compared with Nafion[®]115. At 100 °C, moreover, all the MEAs using NH_4^+/H_3O^+ - β "-alumina/Nafion composite membranes indicated a



Fig. 12. Cell perfomances of MEAs using $NH_4^+/H_3O^+-\beta^{"}$ -alumina/ Nafion composite membranes, as compared to Nafion[®]115, as a function of various filler contents at (a) 80 °C and (b) 100 °C

lower performance than Nafion[®]115. This can be explained by using the results of a previous study, in which it was found that the water uptake of $NH_4^+/H_3O^+-\beta^{"-}$ alumina is lower than that of $H_3O^+-\beta^{"-}$ -alumina and also that $NH_4^+/H_3O^+-\beta^{"-}$ -alumina has a lower proton conductivity than $H_3O^+-\beta^{"-}$ -alumina at high temperature [11].

Conclusions

 H_3O^+ - β "-alumina and NH_4^+/H_3O^+ - β "-alumina as proton conductive solid electrolytes were prepared successfully

by an ion-exchange reaction from a K^+ - β "-alumina precursor. Ion-exchange rates of 85% for H_3O^+ - β "alumina and 93% for NH_4^+/H_3O^+ - β "-alumina were measured, without the formation of secondary phases such as boehmite. The proton- β "-alumina/Nafion composite membranes were maintained sufficiently as an electrolyte for PEMFC at about 80 ~ 100 °C, because H_3O^+ - and NH_4^+/H_3O^+ - β "-alumina fillers with an internal protonic conduction plane effectively maintain the presence of water, causing the hydrophilic property of the composite membrane to improve. These results show the high potential of the proton- β "-alumina containing composite membrane as an electrolyte for operating fuel cells at higher temperatures.

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References

- J. Larminie and A. Dicks, "Fuel Cell Systems Explained", John Wiley & Sons Ltd. 2003.
- T.A. Zawodzinski, J. Kavey, J. Valerio and S. Gottesfeld, Electroch. Acta. 40, (1995) 297-302.
- R.F. Silva, S. Passerini and A. Pozio, Electroch. Acta. 50, (2005) 2639-2645.
- 4. S. Vengatesan, H.J. Kim, S.Y. Lee, E. Cho, H.Y. Ha, I.H. Oh, S.A. Hong and T.H. Lim, Int. J. Hydr. Ener. 33, (2008) 171-178.
- 5. W.K. Chao, C.M. Lee, D.C. Tasi, C.C. Chou, K.L. Hsueh and F.S. Shieu, J. Pow. Sour. 185, (2008) 136-142.
- U.H. Jung, K.T. Park, E.H. Park and S.H. Kim, J. Pow. Sour. 159, (2006) 529-532.
- J. Tian, P. Gao, Z. Zhang, W. Luo and Z. Shan, Int. J. Hydr. Ener. 33, (2008) 5686-5690.
- H.L. Lin and T.J. Chang, J. Memb. Sci. 325, (2008) 880-886.
- P.S. Nicholson, M.Z.A. Munshi, G. Singh, M. Sayer, and M.F. Bell, Sol. Sta.Ion. 18-19, (1986) 699-703.
- S.J. Kim, H.M. Kim, W.S. Kim, and S.K. Lim, J. Cer. Proc. Res. 9, (2008) 271-277.
- S.J. Kim, H.M. Kim, Y.T. Yoo, J.R. Haw, S.G. Kim, M.H. Jang and S.K. Lim, J. Cer. Proc. Res. 10, (2009) 176-182.