Proton conducting composite membranes from Nafion and \( \text{NH}_4^+/\text{H}_3\text{O}^+ - \beta^\prime\prime\)-alumina for high temperature PEMFCs

Ki-Moon Lee, Min-Ho Jang, Choon-Soo Han, Sung-Tae Lee, Jun-Hee Lee and Sung-Ki Lim*
Department of Materials Chemistry and Engineering, Konkuk University, 1 Hwayang-dong, Gwangjin-gu, 143-701 Seoul, South Korea

Composite membranes as an electrolyte for high-temperature PEMFCs (proton exchange membrane fuel cells) were prepared by mixing a Nafion polymer matrix and proton-\( \beta^\prime\prime\)-aluminas (\( \text{H}_2\text{O} - \beta - \text{Al}_2\text{O}_3 \) and \( \text{NH}_4^+ /\text{H}_3\text{O}^+ - \beta - \text{Al}_2\text{O}_3 \)) as inorganic fillers with fast proton conductivity. From the \( \text{K} - \beta - \text{alumina} \) precursor, the aforementioned proton-\( \beta^\prime\prime\)-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: \( \beta^\prime\prime\)-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 proton-conducting 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-\( \beta^\prime\prime\)-alumina ceramics: that is, \( \text{H}_2\text{O} - \beta - \text{alumina} \) and \( \text{NH}_4^+ /\text{H}_3\text{O}^+ - \beta^\prime \)-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 \( 5 \times 10^{-3} \) and \( 1.0 \times 10^{-2} \text{ S/cm} \) at 100 °C and 150 °C, respectively [9].

Experimental

To prepare inorganic fillers, a K-\( \beta\)-alumina precursor was synthesized in the ternary system \( \text{K}_2\text{O} - \text{Li}_2\text{O} - \text{Al}_2\text{O}_3 \). The molar ratio was \( [\text{K}_2\text{O}] : [\text{Al}_2\text{O}_3] = 1 : 5 \) to which was added 0.2 wt% \( \text{Li}_2\text{O} \) as a stabilizer. The K-\( \beta\)-alumina precursor was attrition-milled after being ball-milled to maximize the surface area and minimize the particle size. Characteristics of the K-\( \beta\)-alumina powder were determined using an X-ray diffractometer (Rigaku Rint 2000, Cu Kα radiation, scanning range 5 to 70 °, 20 step width 0.08 °, scanning speed 10 °/minute), scanning electron microscopy (SEM, JEOL JSM-6308, Japan) and particle size analysis (PSA, Brookhavien Instruments Co.). From the K-\( \beta\)-alumina, \( \text{H}_2\text{O} - \beta - \text{alumina} \) and \( \text{NH}_4^+ /\text{H}_3\text{O}^+ - \beta^\prime \)-alumina were prepared via ion-exchange reactions by a hydrothermal process using an acetic acid solution.
(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, H₂O-β”-alumina/Nafion and NH₄/H₂O-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% H₂O₂, 0.5 M H₂SO₄, 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 μl.

Membrane electrode assemblies (MEAs) were made from different prepared composite membranes. Carbon cloth containing a catalyst loading of 5 g/m² was used 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 K₂O·Li₂O·Al₂O₃ was compared to the reference samples (ICPDS card No. 31-960 (β̈-alumina), 21-618 (β”-alumina)). The results for the 2θ 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 powders. According to the PSA measurements, the mean particle size of the ball-milled powder was 1.0 ~ 2.0 μm and that of the attrition-milled powder was 300 ~ 500 nm.

Table 1 and Fig. 4 ~ 6 show the ion-exchange rates of H₂O-β”-alumina after the following reactions: in 10 wt.% acetic acid solution at 150 °C for 2 ~ 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

<table>
<thead>
<tr>
<th>Time</th>
<th>Ion-exchange rate (%)</th>
<th>Temperature</th>
<th>Ion-exchange rate (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 h</td>
<td>0</td>
<td>150 °C</td>
<td>85.8</td>
</tr>
<tr>
<td>2 h</td>
<td>85.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.5 h</td>
<td>86.4</td>
<td>160 °C</td>
<td>85.51</td>
</tr>
<tr>
<td>3 h</td>
<td>84.65</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.5 h</td>
<td>87.58</td>
<td>170 °C</td>
<td>90.49</td>
</tr>
<tr>
<td>4 h</td>
<td>86.82</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Fig. 1.** XRD pattern of K⁺-β”-alumina

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

**Fig. 3.** The particle size distributions of K⁺-β”-alumina: (a) after ball-milling, (b) after attrition-milling
Proto n conducting com posite m em branes f rom Nafion a nd NH$_4$$^+$/$H_3$$^+$O$^-$β"-alum ina for h igh tem perature PEMFC

appeared after 3 h at 150 °C (Fig. 4), and also at 160 and 170 °C after 2 h (Fig. 5).

Table 2 and Fig. 7 ~ 9 also show the ion-exchange rates of H$_2$O'/NH$_4$'-β"-alumina after the following reactions: in 4 M NH$_4$NO$_3$ solution at 150 °C for 2 ~ 4 h, and at 150 °C for 2 h in 3 ~ 5 M NH$_4$NO$_3$ 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 H$_2$O'/β"-alumina and 93% for NH$_4$'/H$_2$O'-β"-alumina. These proton-β"-alumina powders were used as a filler.

<table>
<thead>
<tr>
<th>Time</th>
<th>Ion-exchange rate (%)</th>
<th>Concentration</th>
<th>Ion-exchange rate (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>3 M</td>
<td>92.15</td>
</tr>
<tr>
<td>2 h</td>
<td>93.18</td>
<td>4 M</td>
<td>93.75</td>
</tr>
<tr>
<td>2.5 h</td>
<td>93.33</td>
<td>4 M</td>
<td>93.75</td>
</tr>
<tr>
<td>3 h</td>
<td>93.08</td>
<td>5 M</td>
<td>93.97</td>
</tr>
<tr>
<td>3.5 h</td>
<td>93.70</td>
<td>5 M</td>
<td>93.97</td>
</tr>
<tr>
<td>4 h</td>
<td>93.70</td>
<td>5 M</td>
<td>93.97</td>
</tr>
</tbody>
</table>

Fig. 4. The XRD patterns of H$_2$O'-β"-alumina in 10 wt.% acetic acid solution at 150 °C 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$_2$O'-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$_2$O'-β"-alumina in 10 wt.% acetic acid solution (a) at 150 °C for 2 ~ 4 h, (b) for 2 h at 150 ~ 170 °C.

Fig. 7. The XRD patterns of H$_2$O'/NH$_4$'-β"-alumina in 4 M NH$_4$NO$_3$ solution at 150 °C 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$_2$O'/NH$_4$'-β"-alumina after 2 h at 150 °C in various concentrations of NH$_4$NO$_3$ solution: (a) 3 M, (b) 4 M, (c) 5 M.
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$_2$O$^+$$\beta^{-}$-alumina/Nafion and NH$_4^+$/H$_3$O$^+$$\beta^{-}$-alumina/Nafion composite membranes, respectively. As the content of filler is increased, the contact angle becomes smaller. This shows that the hydrophilicity of the membranes is improved by addition of proton-$\beta^{-}$-aluminas.

Fig. 11 shows the cell performance of MEAs using H$_2$O$^+$$\beta^{-}$-alumina/Nafion composite membranes, as compared to Nafion®115, as a function of various filler contents at (a) 80 °C and (b) 100 °C. The MEA using 7.5 wt.% H$_2$O$^+$$\beta^{-}$-alumina filler shows the best cell performance, with 54% and 19% higher current density and power density, respectively, than those of the MEA using Nafion®115 at 100 °C. With the composite membranes, the cell performance is generally improved in the temperature range between 80 and 100 °C, except for the membrane containing 10.0 wt.% of H$_2$O$^+$$\beta^{-}$-alumina filler. This is explained by the fact that fillers of $\beta^{-}$-alumina were uniformly dispersed in the polymer matrix and powder particles agglomerate around the sulfuric acid group of the polymer matrix, strongly preventing water loss. But excessive filler addition, such as a 10 wt.% content, causes a decrease in cell performance because the ion conduction of the H$_2$O$^+$$\beta^{-}$-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$_3$O$^+$$\beta^{-}$-alumina/Nafion composite membranes. In the case of the membrane containing 2.5 wt.% NH$_4^+$/H$_3$O$^+$$\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^+$/H$_3$O$^+$$\beta^{-}$-alumina/Nafion composite membranes indicated a
Proton conducting composite membranes from Nafion and NH₄⁺/H₃O⁻-β"-alumina for high temperature PEMFC

Fig. 12. Cell performances of MEAs using NH₄⁺/H₃O⁻-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.

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 NH₄⁺/H₃O⁻-β"-alumina is lower than that of H₃O⁻-β"-alumina and also that NH₄⁺/H₃O⁻-β"-alumina has a lower proton conductivity than H₃O⁻-β"-alumina at high temperature [11].

Conclusions

H₃O⁻-β"-alumina and NH₄⁺/H₃O⁻-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 H₃O⁻-β"-alumina and 93% for NH₄⁺/H₃O⁻-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 H₃O⁻ and NH₄⁺/H₃O⁻-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.

Acknowledgement

This paper was supported by Konkuk University in 2010.

References