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X^+ - β "-aluminas /Nafion (X = H₃O, NH₄) hybrid membranes for high-temperature PEMFCs

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Hybrid membranes as an electrolyte for high-temperature proton exchange membrane fuel cells (PEMFCs) were prepared from a Nafion polymer matrix with $NH_4^+/H_3O^+-\beta^*$ -aluminas as an inorganic filler that has fast proton conductivity. The membranes, containing 5-20 wt% of filler, were obtained with a fairly uniform thickness of about 80 µm. The properties of the hybrid membranes - such as thermal stability, water uptake, proton conductivity, methanol crossover, and proton selectivity - were measured in the 25-120 °C temperature range and compared to those of Nafion[®]. The hybrid membranes became more thermally stable, showing a mere 2 wt% of water loss at 120 °C; they also had advantages over Nafion[®] in terms of water uptake, methanol crossover, and selectivity. The proton conductivities of the hybrid membranes generally lowered compared to Nafion[®]; however, they were maintained sufficiently for an electrolyte, representing 1.6 × 10⁻¹ and 1.8 × 10⁻¹ S/cm at 100 and 120 °C in the H₃O⁺-\beta^{*}-aluminas/Nafion[®] hybrid membrane, respectively.

Key words : Hybrid membrane, β"-alumina, High-temperature PEMFCs.

Introduction

Polymers that possess ion-conducting properties are used with membrane materials as a solid electrolyte in various electrochemical devices. In the field of proton exchange membrane fuel cells (PEMFCs), DuPont's Nafion[®] is a conventional proton-conducting polymer electrolyte membrane that is widely used because of its high proton conductivity and its chemical, mechanical, and thermal stability [1, 2]. However, this material has some shortcomings that must be addressed such as those relating to water management, excessive use of novel metal catalyst, and CO-poisoning at the anode, because they normally operate at relatively low temperatures, *i.e.*, ~ 80 °C . In the case of direct methanol fuel cells (DMFCs), especially, the high methanol crossover and slow methanol oxidation kinetics at the anode catalyst appear to be major problems. Therefore, the development of new proton-conducting membranes or structural modifications to conventional electrolytes - for example, hybrid membranes that can work with PEMFCs at higher temperatures and retard methanol crossover in DMFCs - seem to be the key to solving the aforementioned significant problems in fuel cells that use polymer membranes [3, 4].

To improve the electrolyte properties at higher temperatures, numerous recent studies describe the synthesis of Nafion[®] composite recast membranes modified by incorporating inorganic fillers. As examples, nano-composite membranes were prepared by incorporating non-conductive ceramic oxides such as ZrO₂, TiO₂, and SiO₂ via an in situ sol-gel technique [5, 6]. These nano-composite membranes exhibit better thermomechanical properties, even though their ionic conductivities were lower than those of Nafion[®] [7]. The incorporation of inorganic solid acids into Nafion® to increase additional acidic sites was also reported [8]. The composite membrane from $Zr(HPO_4)_2$ as a proton-conducting solid acid and perfluorosulfonate ionomer (PFSI) was synthesized via an *in situ* precipitation technique, electrically and chemically [9, 10]. In addition, Nafion[®] membranes containing hygroscopic ceramic oxides reportedly operated above 100 °C in DMFC and PEMFC [11, 12]. Cesium hydrogen sulfate, a low-temperature proton conductor, was incorporated onto a porous glass support and prepared for membranes in a hydrogen fuel cell; however, cesium hydrogen sulfate membranes were not able to produce an appreciable current and showed poor stability and low conductivity in fuel cells [13]. In any case, approaches based on solid-state composite or hybrid materials have been attempted for many years with high-temperature PEMFCs.

In K⁺- β "-aluminas, the K⁺ ion acts as a charge carrier; because of its structural characterization, the alkali ion(K⁺) in the internal conduction plane can be exchanged with other comparable ions and converted to ceramic ionic conductors with various electrical functions. Consequently, these K⁺- β "-aluminas are expected to be a very good host material for the ion-exchange of K⁺ ions to other protonic ions such as NH₄⁺ or H₃O⁺. The NH₄⁺- or

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 H_3O^+ - β "-aluminas can be used as proton conducting ceramics that are stable over a wide temperature range, and to as high as 350 °C [14, 15]. These protonic β "aluminas constitute a fast ion conductor, having 5 × 10⁻³ and 1.0 × 10⁻² S/cm of proton conductivity at 100 °C and 150 °C, respectively.

In the present study, hybrid membranes for hightemperature PEMFCs were synthesized from Nafion[®] with protonic β "-aluminas acting as an inorganic filler; their properties as an electrolyte were evaluated. For that purpose, NH₄⁺- and H₃O⁺- β "-aluminas powders were synthesized via ion-exchange reactions from a K⁺- β "alumina precursor and homogeneously mixed with a Nafion[®] ionomer dispersion, and the membranes were prepared from the mixture by a solution casting method. Their properties as an electrolyte were compared with those of a commercial Nafion[®] membrane in terms of thermal stability, water uptake, proton conductivity, methanol permeability, and proton selectivity.

Experimental Methods

To prepare inorganic fillers, a K⁺- β "-alumina precursor was synthesized by a solid-state reaction with a molar ratio of [K₂O] : [Al₂O₃] = 1 : 6 [16]. From the precursor, H₃O⁺- and NH₄⁺- β "-aluminas were prepared via ionexchange reactions by a hydrothermal process in an autoclave, using acetic acid (10 wt%) as the ion-exchange medium, and by immersing the K⁺- β "-aluminas in molten ammonium nitrate (NH₄NO₃) at 180 °C for several hours, respectively [17, 18].

The ultrafine-milled H_3O^+ - and NH_4^+ - β "-aluminas powder was incorporated into a Nafion[®] dispersion (20 wt%, DE2021, DuPont, United States), consecutively, and the mixture was ultrasonically treated for 1 h; it was then placed in a shaking incubator for 3 h. The suspension was then vigorously homogenized within a homogenizer for 1 h and spread onto a glass substrate. After drying the solvent for 24 h at 40 °C, the cast membrane was heated in a vacuum oven to evaporate residual solvent for 2 h at 135 °C. The thickness of the membranes obtained was 80-100 µm; β "-alumina contents in the hybrid membranes were chosen as 5, 10, 15, and 20 wt %.

As a standard sample, a commercial Nafion[®] membrane was selected. For the measurement of membrane properties, the following chemical treatment was conducted for each membrane: (1) immersing in a 3% H₂O₂ solution for 1 h at 80 °C, to remove organic impurities; (2) rinsing in boiling, deionized water for 1 h; (3) removing residual impurities from the membrane with 0.5 M H₂SO₄ for 1 h at 80 °C; and (4) finally, rinsing in boiling, deionized water for 1 h, to remove any metallic impurities or residual H₂SO₄.

The phase formation of the β "-aluminas was analyzed using an X-ray diffractometer (D/max 2200, Rigaku, Japan); the hybrid membrane morphology was observed by SEM (Model JSM-6380, JEOL, Japan), to estimate the size of the β "-alumina fillers and the uniformity of particle dispersion in the polymer matrix. For observation, the samples were fractured in liquid nitrogen and sputter-coated with Au.

The high-temperature propertis of the membranes were ascertained via a TGA (TA Instruments 2050 system, New castle, United States), in the temperature range of 30-130 °C. Additionally, the thermal stability and water-management properties were analyzed by examining the sample weight loss. The water uptake of each of the hybrid membranes was measured by the difference in the weight before and after soaking. For the weight in the hydrated state (W_{wer}), the membranes were soaked for 24 h in deionized water at room temperature. The weight in the a dried state (W_{dry}) was measured after drying in a vacuum oven at 80 °C for 24 h. The water uptake content was calculated by:

Water uptake content(%) =
$$\frac{W_{wet} - W_{dry}}{W_{wet}} \times 100$$
 (1)

The proton conductivity was determined with a complex impedance analyzer (IM-6, Zahner, Germany), using a four-probe AC technique. The samples were held in an autoclave, to measure the proton conductivity at 100% relative humidity; the temperature was varied between 25 °C and 120 °C. Proton conductivity was calculated by:

$$\sigma = \frac{L}{R_x W_x D} \tag{2}$$

Where σ , L and R denote proton conductivity; distance between the electrodes, to measure the potential; and impedance of the membrane, respectively. W and D are the width and thickness of the membrane, respectively.

The methanol permeability - which is an especially important factor with respect to DMFCs - was measured using a permeation cell that consisted of two compartments, at 25 °C , 40 °C , and 60 °C. One compartment of the cell, having a volume of $V_A = 43$ ml, was filled with a solution of methanol (5 wt%); the other was filled only with deionized water. The two compartments were continuously stirred using a magnetic stirrer during the taking of measurements. The concentration of methanol fluxing from compartment A to B, across the membrane, was detected over time using a refractive index detector (RID-10A, Shimadzu, Japan) [19]. The methanol permeability (P = DK) was calculated by:

$$C_B(t) = \frac{S}{V_B} \times \frac{DK}{L} C_A(T - T_0)$$
(3)

 C_A and C_B are the concentrations of methanol in compartments A and B, respectively, under a methanol flow from A to B. S and L are the surface area and the thickness of the membrane, D and K are the methanol diffusivity and the solubility, respectively; $(t - t_0)$ is the permeation time. The methanol permeability (P) is defined as the product of diffusivity and solubility.



Fig. 1. X-ray diffraction patterns of X^+ - β "-alumina powder. (a) K^+ (precoursor), (b) H_3O^+ , (c) NH_4^+ .



Fig. 2. X-ray diffraction patterns of (a) Nafion[®] and hybrid membrane containing 20 wt% of (b) H_3O^+ - β "-alumina and (c) NH_4^+ - β "-alumina.

Results and Discussion

The K⁺- β "-alumina, used as a precursor for H₃O⁺and NH₄⁺- β "-alumina inorganic fillers, has XRD characteristic peaks at the planes (2 0 <u>10</u>), (2 2 0) and (0 1 2). As shown in Fig. 1, H₃O⁺- and NH₄⁺- β "-aluminas that had been ion-exchanged at the rate of 90 wt% sustained thoroughly the primary structure of the K⁺- β "-alumina. Fig. 2 shows the XRD patterns of the hybrid membranes containing 20 wt% of β "-alumina fillers, compared to that of Nafion[®]. This proves that inorganic fillers are incorporated unchanged into the Nafion[®] dispersion.

Fig. 3 shows the SEM images of H_3O^+ - β "alumina particles and a cross-section of the hybrid membrane containing 20 wt% of H_3O^+ - β "-alumina. The average diameter of the inorganic filler particle was measured to be about 0.3-0.5 µm and the membranes were obtained with a fairly uniform thickness of about 80 µm. All



(a)



Fig. 3. SEM images of (a) H_3O^+ - β "-alumina powder and (b) cross-section of hybrid membrane containing 20 wt% of H_3O^+ - β "-alumina.

membranes appeared to have a quite homogenous distribution and the β "-alumina fillers were uniformly dispersed in the polymer matrix. In the case of NH₄⁺- β "-alumina as an inorganic filler, features similar to those in Fig. 3 were observed.

The thermal stabilities of the hybrid membranes were analyzed from the TGA results (Fig. 4). Actually, the chemical transformation for all the components comprising the membranes did not occur at temperature lower than 130 °C, so there existed the possibility of dehydration and physical absorption, but only on the surface of the membranes. Nafion[®] showed a rapid weight loss of about 6 wt%, up to 70 °C and a continuous loss of about 2.5 wt% more, up to 130 °C. On the other hand, the hybrid membranes containing 10 wt% of H₃O⁺- or NH₄⁺- β "aluminas indicated a continuous and gentle slope of weight loss of about 2.5 and 3.0 wt%, up to 130 °C, respectively. The thermal stability of the hybrid membranes greatly increased because the dehydration around the



Fig. 4. TGA results of (a) Nafion[®] and hybrid membrane containing 10 wt% of (b) $H_3O^+-\beta$ "-alumina and (c) $NH_4^+-\beta$ "-alumina.



Fig. 5. Water uptake of (a) Nafion[®], (b) $H_3O^+-\beta^{"}$ -alumina/Nafion[®] and (c) $NH_4^+-\beta^{"}$ -alumina/Nafion[®] membrane, as a function of filler content.

 Table 1. Numerical values of water uptake, proton conductivity, methanol permeability, and selectivity of hybrid membranes, according to filler type, filler content, and temperature

Membranew type	Contents (wt.%)	Water uptake(%) at 25 °C	$\begin{array}{c} Conductivity \\ (\Omega^{-1} cm^{-1}) \end{array}$	Methanol permeability (cm ² s ⁻¹)	Selectivity $(\Phi \cdot 10^{-3}/\Omega^{-1} \text{cm}^{-3} \cdot \text{s}) \text{ at } 25 ^{\circ}\text{C}$
- H₃O⁺-β"-alumina / Nafion- -	5	30.06	7.32×10^{-2} at 25 °C		49.6
			9.30×10^{-2} at 40 °C		
			11.58×10^{-2} at 60 °C	1.47×10^{-6} at 25 $^{\rm o}C$	
			13.63×10^{-2} at 80 °C	1.85×10^{-6} at 40 $^{\rm o}C$	
			15.58×10^{-2} at 100 °C	2.38×10^{-6} at 60 $^{\rm o}C$	
			17.60×10^{-2} at 120 °C		
	10	31.73	6.94×10^{-2} at 25 °C	1.35×10^{-6} at 25 °C	51.7
	15	34.9	6.17×10^{-2} at 25 °C	1.22×10^{-6} at 25 °C	50.4
	20	26.17	5.84×10^{-2} at 25 °C		59
			7.53×10^{-2} at 40 $^{\rm o}{\rm C}$		
			9.68×10^{-2} at 60 °C	9.95×10^{7} at 25 $^{\rm o}C$	
			11.30×10^{-2} at 80 $^{\rm o}C$	$1.74 \times 10^{\text{-6}}$ at 40 $^{\rm o}C$	
			12.81×10^{-2} at 100 °C	$2.30\times10^{\text{-6}}$ at 60 $^{\circ}\mathrm{C}$	
			14.51×10^{-2} at 120 °C		
- NH ₄ -β"-aluminas / Nafion- -	5	25.40	6.63×10^{-2} at 25 °C		51.8
			8.35×10^{-2} at 40 °C	1.31×10^{-6} at 25 $^{\rm o}C$	
			10.33×10^{-2} at 60 °C	1.94×10^{-6} at 40 °C	
			12.13×10^{-2} at 80 °C	2.58×10^{-6} at 60 °C	
			13.71×10^{-2} at 100 °C		
			16.23×10^{-2} at 120 °C		
	10	25.86	5.67×10^{-2} at 25 °C	1.27×10^{-6} at 25 °C	46.2
	15	26.17	5.23×10^{-2} at 25 °C	1.25×10^{-6} at 25 °C	42.8
	20	25.40	4.58×10^{-2} at 25 °C	1.25×10^{-6} at 25 °C	38.2
			5.61×10^{-2} at 40 °C	2.14×10^{-6} at 40 $^{\rm o}C$	
			6.98×10^{-2} at 60 $^{\rm o}{\rm C}$	2.72×10^{-6} at 60 $^{\rm o}C$	
			8.33×10^{-2} at 80 $^{\rm o}C$		
			9.58×10^{-2} at 100 °C		
			10.98×10^{-2} at 120 °C		

ion-clustered channel and the sulfuric group in the Nafion[®] matrix was hindered by the incorporation of inorganic fillers. H_3O^+ - β "-alumina filler, which preserves abundant water in the internal conduction plane of itself, was found

to be more effective in this respect.

Owing to the incorporation of hydrophilic fillers, water uptake in all hybrid membranes containing 5-20 wt% of fillers increased in comparison to Nafion[®]. As shown in Table 1 and Fig. 5, $H_3O^+-\beta^{"}$ -alumina that is more hydrophilic and able to maintain abundant water in the internal conduction plane increased the water uptake of the hybrid membranes fairly adequately, up to 34 wt% at 15 wt% of filler content. At a higher level of filler (*i.e.*, over ≈ 20 wt%), however, water uptake suddenly decreased, because $H_3O^+-\beta^{"}$ -alumina particles agglomerate around the sulfuric group of the polymer matrix and strongly prevent water absorption. In the case of $NH_4^+-\beta^{"}$ -alumina as a filler, the water uptake increased only slightly in comparison to Nafion[®].

The proton conductivities of the hybrid membranes containing 5-20 wt% of the filler were measured in the temperature range of 25-120 °C, with 100% relative humidity. Fig. 6 indicates the influence of the ion type and the filler content on proton conductivity, at room temperature. All hybrid membranes showed lower conducti-vities in comparison to Nafion[®] of which the con-ductivity was measured to be 8.3×10^{-2} S/cm at room temperature. The conductivity generally lowered with an increase in filler content, because the free volume and size of the ion clusters incorporated into the β "-alumina particles both diminished owing to a decrease in dipole-dipole interaction of the side chain in Nafion®; as a result, the migration of protons around the ion-clustered channels was prevented. For the filler type, the H_3O^+ - β "-aluminas/ Nafion hybrid membrane-which maintains a fast proton migration with an abundance of water in the internal conduction plane-exhibited higher conductivities than did NH_4^+ - β "-alumina/Nafion[®]. Figs. 7-1 and 7-2 show Arrhenius plots of proton con-ductivity as a function of temperature, from 25 to 120 °C, for the hybrid membranes containing 5 wt% and 20 wt% of filler, respectively. The conductivities increased stably with rising temperature; in the case of the H_3O^+ - β "-aluminas/Nafion[®] hybrid membrane containing 5 wt% filler, the conductivity at 120 °C appears to be 1.76×10^{-1} S/cm (Table 1). Accordingly, it is expected that the proton conductivities of the H_3O^+ - β "-



Fig. 6. Proton conductivity of (a) Nafion[®], (b) H_3O^+ - β ''-alumina/Nafion and (c) NH_4^+ - β ''-alumina/Nafion[®] membrane, as a function of filler content at 25 °C with 100% of relative humidity.



Fig. 7. 7-1 Proton conductivity of (a) Nafion[®], (b) H_3O^+ - β "-alumina/Nafion and (c) NH_4^+ - β "-alumina/Nafion[®] membrane containing 5 wt% of filler as a function of temperature, with 100% relative humidity. 7-2 Continued, containing 20 wt% of filler.

aluminas/Nafion[®] hybrid membranes would be higher than those of Nafion[®] at high temperatures (*i.e.*, above 100 °C) with a low-humidity atmosphere.

The methanol permeabilities of the hybrid membranes containing 5-20 wt% of filler were measured in the temperature range of 25-60 °C; they were then compared, on this basis, to Nafion[®]. Fig. 8 shows the concentration of permeated methanol as a function of filler contents, at room temperature; the methanol permeability of Nafion[®] is 1.55×10^{-6} cm²/s, at room temperature [20]. Within the measured range, the methanol permeabilities of hybrid membranes appeared to be lower than those of Nafion[®], owing to a definite block-effect (Table 1). In particular, the H₃O⁺- β "-aluminas/Nafion hybrid membrane containing 20 wt% of filler exhibited a decrease of about 35%, compared to Nafion[®], with a value of 9.95 × 10⁻⁷ cm²/s. In the H₃O⁺- β "-aluminas/Nafion[®] hybrid membrane, the methanol permeability diminished with an increase in



Fig. 8. Methanol pemeability of (a) Nafion[®], (b) H_3O^+ - β "-alumina/Nafion[®] and c) NH_4^+ - β "-alumina/Nafion[®] membrane, as a function of filler content at 25 °C.



Fig. 9. 9-1 Methanol pemeability of (a) Nafion[®], (b) $H_3O^+-\beta^{"-alumina/Nafion}$ and (c) $NH_4^+-\beta^{"-alumina/Nafion[®]}$ membrane containing 5 wt% of filler, as a function of temperature. 9-2 Continued, containing 20 wt% of filler.



Fig. 10. Transport selectivity of (a) $Nafion^{\$}$, (b) $H_3O^+-b^-$ alumina/Nafion[®] and (c) $NH_4^+-b^-$ -alumina/Nafion[®] membrane, as a function of filler content.

filler content, while it maintained comparatively fixed in the NH₄⁺- β "-alumina/Nafion[®] membrane. Figs. 9-1 and 9-2 show Arrhenius plots of methanol permeability as a function of temperature, from 25 °C to 60 °C, for the hybrid membranes containing 5 wt% and 20 wt% of filler, respectively. The methanol per-meabilities in all membranes increased with rising temperature. At 5 wt% of filler, the H₃O⁺- and NH₄⁺- β "alumina/Nafion membrane maintained an almost similar level of methanol permeability (Fig. 9-1); it appeared to be more favorable, however, with the H₃O⁺- β "-aluminas/Nafion hybrid membrane at 20 wt% of filler (Fig. 9-2).

The proton selectivity of the hybrid membranes was calculated by the parameter Φ which is defined as the ratio of proton conductivity to methanol permeability [21]. Fig. 10 shows the selectivity values of the hybrid membranes and Nafion[®], at room temperature. The selectivity of the H₃O⁺- β "-aluminas/Nafion[®] hybrid membrane appeared to be generally higher than that of the NH₄⁺- β "-alumina/Nafion[®] membrane, and it is even superior to Nafion[®] at 20 wt% of filler, in this respect.

Conclusions

In the present study, hybrid membranes that can be applied to high-temperature PEMFCs and DMFCs were prepared from a Nafion[®] matrix and $H_3O^+/NH_4^+-\beta^{"}$ alumina ceramics, the latter of which have been used as an inorganic filler that has fast proton conductivity. The fundamental properties required of an electrolyte for PEMFCs or DMFCs were analyzed and compared with those of Nafion[®]. $H_3O^+/NH_4^+-\beta^{"}$ -alumina powders were successfully synthesized with a 90 wt% ion exchange rate via a hydrothermal process from the K⁺- $\beta^{"}$ -alumina precursor. It is believed that this rate can be improved by preparing the precursor on the nano scale, as well as by searching for a more effective exchange medium or by finding an optimal reaction condition. The hybrid membranes could be made uniformly by using the mixture with a solution casting method, in which the H_3O^+/NH_4^+ β"-alumina filler is homogeneously incorporated into the Nafion[®] dispersion. The hybrid membranes enhanced the thermal properties, water uptake, methanol permeability, and proton selectivity, in comparison to Nafion[®]; there was no enhancement of proton conductivity, as expected. The proton conductivity of the hybrid membranes, however, was maintained sufficiently for an electrolyte, showing a value in excess of 1.3×10^{-1} S/cm above 100 °C. Among the hybrid membranes, the H_3O^+ - β "-aluminas/Nafion[®] hybrid membrane appeared to be more favorable as an electrolyte than the NH_4^+ - β "-alumina/Nafion[®] at higher temperatures. This can be explaned by the fact that the H_3O^+ - β "-alumina has an abundance of water on the internal conduction plane and fast proton migration owing to its high hygroscopicity and high acidity.

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