—Communication—

Proton Conductivity of Some Hydrated Compounds at Intermediate Temperature up to 150°C under High Water Vapor Pressure

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Proton conductivity of some hydrated compounds such as $\text{ZrO}_2 \cdot n\text{H}_2\text{O}$, $\text{SnO}_2 \cdot n\text{H}_2\text{O}$, and $\text{Ce}(\text{HPO}_4)_2 \cdot n\text{H}_2\text{O}$ were investigated in the temperature range of 25°C ~ 150°C under saturated water vapor pressure ($p_{\text{H}_2\text{O}}/p_s = 1$, p_s : equilibrium pressure). They showed high proton conductivity in the order of 10^{-2} S cm⁻¹ at 150°C. The activation energies of conduction were small (0.16-0.19 eV), suggesting the surface adsorbed water mechanism. A composite of $\text{Ce}(\text{HPO}_4)_2 \cdot n\text{H}_2\text{O}$ with ethylene oxide/propylene oxide random copolymer (P(EO/PO)) was prepared and tested from a practical interest. It showed relatively high proton conductivity in the order of 10^{-3} S cm⁻¹, though the fraction of $\text{Ce}(\text{HPO}_4)_2 \cdot n\text{H}_2\text{O}$ was as small as 7% in weight.

Key Words : Proton Conductor, Hydrate, Fuel Cell, Saturated Vapor Pressure

1 Introduction

Proton conductors show their great importance as a key material for their potential application as solid electrolyte in the devices such as fuel cell, batteries, electrochromic glasses and sensors *etc.*^{1, 2)} At present polymer electrolyte membrane fuel cells (PEMFC) have gained more and more interests as a promising power source for environmentally acceptable electric buses and cars. Up to now perfluorinated ionomer Nafion has been applied nearly exclusively as proton conductor in membrane fuel cell³⁻⁶⁾. Due to the high price of Nafion and low operating temperature below 100°C, there is a huge need for substitute materials. For reformed fuel gas produced from carbon-containing sources such as methanol, the higher operating temperature is desired to reduce the severe poisoning of platinum-based catalysts by carbon monoxide. At the same time, the polarization at the oxygen electrode, a major part of the total voltage drop, could be reduced to a lower level and the water balance control in the fuel cell system would also be easier at elevated temperatures. One of promising candidates replacing Nafion may be organic/inorganic composite materials.⁷⁻⁹⁾ Thus, we have initiated a study to develop a membrane composed of inorganic proton conductors and heat-resistive polymer applicable for fuel cell operated at the intermediate temperature range (100~300°C) as a final target.

In this communication, we report proton conductivity of hydrated compounds such as $\text{ZrO}_2 \cdot n\text{H}_2\text{O}$, $\text{SnO}_2 \cdot n\text{H}_2\text{O}$ and $\text{Ce}(\text{HPO}_4)_2 \cdot n\text{H}_2\text{O}$ in the temperature range of 25°C ~ 150°C under saturated water vapor pressure ($p_{\text{H}_2\text{O}}/p_s = 1$, p_s : equilibrium pressure). To date those material have only been evaluated as a proton conductor at near-room temperature. We also report preliminary results obtained with a polymer composite electrolyte of $\text{Ce}(\text{HPO}_4)_2 \cdot n\text{H}_2\text{O}$.

2 Experimental

2.1 Sample preparation

$\text{ZrO}_2 \cdot n\text{H}_2\text{O}$ was prepared by a method similar to that reported by Clearfield.¹⁰⁾ 2.4 ml of 25% NH_4OH was dropped slowly into a stirred ZrOCl_2 solution (25 ml of 25 m mol) until the pH reached 2~3. White precipitate thus obtained was washed using a centrifuge with pure water for three times. Then it was boiled in a 20% KOH solution at 100°C for 1 hour, and washed with pure water thoroughly in a centrifuge till free Cl^- was not detected. White powder of $\text{ZrO}_2 \cdot n\text{H}_2\text{O}$ ($n \sim 3$) was obtained by drying at a desiccator for 2 days.

$\text{SnO}_2 \cdot n\text{H}_2\text{O}$ was produced similar manner as described by Giesekke *et al.*¹¹⁾ 11 ml of 25% NH_4OH was added into 25 ml of 25 m mole SnCl_4 solution to pH~8, to produce white precipitate. Then it was washed with pure water thoroughly in a centrifuge. After confirming no free Cl^- , the resultant was dried at a desiccator for 2 days. White powder of $\text{SnO}_2 \cdot n\text{H}_2\text{O}$ ($n \sim 2$) was obtained.

Both $\text{ZrO}_2 \cdot n\text{H}_2\text{O}$ and $\text{SnO}_2 \cdot n\text{H}_2\text{O}$ are poorly crystalline matter with very broad peaks observed from XRD as the same as reported by England *et al.*¹²⁾

$\text{Ce}(\text{HPO}_4)_2 \cdot n\text{H}_2\text{O}$ was produced on the base of the reports by Alberti *et al.*¹³⁾ 3 g of $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ was dissolved into 100 ml H_2O , and mixed with 100 ml of 1 M H_2SO_4 . The solution was added by 200 ml 42.5 wt% of H_3PO_4 while stirring. Light yellow precipitate was observed. After being boiled at 90°C for 6 hours, it was washed with pure water thoroughly in a centrifuge to pH ~ 4. Then it was dried at a desiccator for 2 days. Microcrystalline of $\text{Ce}(\text{HPO}_4)_2 \cdot n\text{H}_2\text{O}$ ($n \sim 4$) was thus obtained.

The composite of $\text{Ce}(\text{HPO}_4)_2 \cdot n\text{H}_2\text{O}$ with polymer was produced as follow; Ethylene oxide/propylene oxide random copolymer (P(EO/PO))^{14, 15)} was used in this study.

Wet $\text{Ce}(\text{HPO}_4)_2 \cdot n\text{H}_2\text{O}$ (after washed by pure water, but not dried) was blended well with a liquid monomer of EO/PO on a hot plate at 50°C . The blend was molded into a sheet and polymerized by irradiating deep UV using a halogen lamp (Ushio, UXM-501MD) for 5 minutes. The fraction of $\text{Ce}(\text{HPO}_4)_2 \cdot n\text{H}_2\text{O}$ to P(EO/PO) was about 7% in weight. The decomposition temperature of this composite was confirmed to be 250°C or higher.

2. 2 Proton conductivity measurement under saturated vapor pressure

Sample green pellets with diameter of 4 mm and thickness of 1 mm to 3 mm were prepared by the cold pressing technique at about 100 MPa. Electrical conductive carbon (acetylene black) to serve as an electrode was simultaneously pressed onto both sides of the pellet. The water content of the hydrous compounds was decreased by 10-20% after cold pressing. It is considered that weakly bonded water was released, as pointed out by England *et al.* for this class of hydrates.

For the composite of $\text{Ce}(\text{HPO}_4)_2 \cdot n\text{H}_2\text{O}$ with polymer, sample pieces ($4 \times 4 \text{ mm}^2$) were cut from the UV-polymerized sheet (2 mm in thickness). Conductive carbon electrodes were pasted on both sides.

The a.c. impedance measurement was carried out using a Hewlett Packard 4192A-impedance analyzer controlled by a computer with the oscillation amplitude of 0.1 V in the frequency range of 5 Hz to 13 MHz.

A measurement system for high temperature with high water vapor pressure was specially designed with a stainless vessel resistant to 0.7 MPa. Water pressure was controlled by pressure of a separate vapor source. Sample temperature was carefully monitored using a thermocouple placed near the pellet.

3 Results and Discussion

3. 1 Proton conductivity for $\text{ZrO}_2 \cdot n\text{H}_2\text{O}$ and $\text{SnO}_2 \cdot n\text{H}_2\text{O}$

Typical Cole-Cole plots for hydrous zirconium oxide measured under $p_{\text{H}_2\text{O}}/p_s = 1$ are shown in Fig. 1. Each

Fig. 1 Typical Cole-Cole plots for $\text{ZrO}_2 \cdot n\text{H}_2\text{O}$ measured at 25°C (○), 50°C (□) and 75°C (△) under $p_{\text{H}_2\text{O}}/p_s = 1$.

Fig. 2 Plots of $\text{Log}(\sigma)$ vs. $1/T$ for $\text{ZrO}_2 \cdot n\text{H}_2\text{O}$ (△) and $\text{SnO}_2 \cdot n\text{H}_2\text{O}$ (○) under $p_{\text{H}_2\text{O}}/p_s = 1$, with their fitted lines. Activation energies are calculated from the Arrhenius equation.

plot shows a semicircle and branch due to the interfacial impedance at lower frequencies. Semicircles are not complete because of low bulk resistance. The geometrical capacity (C_g) is calculated to be in the range of 10^{-11} F, which confirmed that semicircles are corresponding to bulk resistance. The resistance of the sample was obtained from the intersection of the semicircle on the real axis. The proton conductivity (σ) was calculated from the diameter and thickness of the pellets. The Cole-Cole plots for $\text{SnO}_2 \cdot n\text{H}_2\text{O}$ are basically the same as shown in Fig. 1.

The plots of proton conductivity vs. inverse of temperature are shown in Fig. 2 for both $\text{ZrO}_2 \cdot n\text{H}_2\text{O}$ (△) and $\text{SnO}_2 \cdot n\text{H}_2\text{O}$ (○). They showed substantially the same temperature dependence of conductivity even after repeated temperature cycles between 25°C and 150°C . Each plot is linear and proton conductivity reaches a value around $2 \times 10^{-2} \text{ S cm}^{-1}$ at 150°C under $p_{\text{H}_2\text{O}}/p_s = 1$. The activation energies (E_a) are estimated as 0.19 eV and 0.16 eV for $\text{ZrO}_2 \cdot n\text{H}_2\text{O}$ and $\text{SnO}_2 \cdot n\text{H}_2\text{O}$, respectively. These values are not far from the reported one (0.24 eV) for $\text{ZrO}_2 \cdot n\text{H}_2\text{O}$ between 273 and 313 K.¹²⁾ According to the same reference, the surface liquid-like water mechanism is responsible for proton conduction of those compounds at room temperature. It is, therefore, thought that the same mechanism holds also in the intermediate temperature range to 150°C , if the water vapor pressure is sufficiently high.

3. 2 Proton conductivity for $\text{Ce}(\text{HPO}_4)_2 \cdot n\text{H}_2\text{O}$ and its polymer composite

The Cole-Cole plots recorded with $\text{Ce}(\text{HPO}_4)_2 \cdot n\text{H}_2\text{O}$ at various temperatures were similar to those in Fig. 1. Thus its conductivity was determined in the same way.

Previously, Barboux *et al.*¹⁶⁾ measured proton conductivity of the same compound at 290 K, and claimed that the surface water mechanism was the case, because its conductivity depended very much on water vapor pressure especially in the region near $p_{\text{H}_2\text{O}}/p_s \sim 1$. We also ob-

Fig. 3 Plots of $\text{Log}(\sigma)$ vs. temperature for $\text{Ce}(\text{HPO}_4)_2 \cdot n\text{H}_2\text{O}$ (□) and composite of $\text{Ce}(\text{HPO}_4)_2 \cdot n\text{H}_2\text{O}$ with P(EO/PO) (△) (7 wt%) under $p_{\text{H}_2\text{O}}/p_s = 1$.

Fig. 4 Typical Cole-Cole plots for composite of $\text{Ce}(\text{HPO}_4)_2 \cdot n\text{H}_2\text{O}$ with P(EO/PO) (7 wt%) measured at 25°C (○) and 50°C (□) under $p_{\text{H}_2\text{O}}/p_s = 1$.

served strong water pressure dependence of conductivity similar to that, though our sample showed higher conductivity (about $10^{-2} \text{ S cm}^{-1}$ under $p_{\text{H}_2\text{O}}/p_s \sim 1$).

In contrast to $\text{ZrO}_2 \cdot n\text{H}_2\text{O}$ and $\text{SnO}_2 \cdot n\text{H}_2\text{O}$, the $\log \sigma \cdot 1/T$ plots for $\text{Ce}(\text{HPO}_4)_2 \cdot n\text{H}_2\text{O}$ was not linear. Thus its conductivity (under $p_{\text{H}_2\text{O}}/p_s = 1$) is shown as a function of T itself in Fig. 3. Note that conductivity stays at a level of $10^{-2} \text{ S cm}^{-1}$ in the whole temperature range from room temperature to 150°C. Presumably, such a weak temperature dependence is related to its structure. According to So *et al.*¹⁷⁾, $\text{Ce}(\text{HPO}_4)_2 \cdot n\text{H}_2\text{O}$ takes a layered structure built up of "cerium planes" with HPO_4 groups in between. Water molecules are intercalated between the layers, to form a hydrogen bonding network with phosphate ions suitable for proton conduction. It is, therefore, thought that, for this material, both the intercalated structural water and the surface adsorbed water

may contribute to proton transport. As temperature is raised, proton conduction on the surface may be enhanced as is the case for $\text{ZrO}_2 \cdot n\text{H}_2\text{O}$ or its $\text{SnO}_2 \cdot n\text{H}_2\text{O}$ counterpart. However, that within the layers might be lowered, if the content of intercalated water molecules is decreased with temperature even under very humid conditions. A peculiar temperature dependence of the compound could be explained as a result of such opposite effects.

In Fig. 4, typical Cole-Cole plots measured for a composite of $\text{Ce}(\text{HPO}_4)_2 \cdot n\text{H}_2\text{O}$ with P(EO/PO) are shown. Conductivity given by those plots is shown in Fig. 3 as a function of temperature. The shape of $\log \sigma \cdot T$ curve is similar to that of $\text{Ce}(\text{HPO}_4)_2 \cdot n\text{H}_2\text{O}$ itself, though conductivity is about one order of magnitude lower. Considering a low fraction (7 wt%) of the conducting material ($\text{Ce}(\text{HPO}_4)_2 \cdot n\text{H}_2\text{O}$), a fall of conductivity to such an extent is not surprising.

4 Conclusion

Proton conductivity of $\text{ZrO}_2 \cdot n\text{H}_2\text{O}$, $\text{SnO}_2 \cdot n\text{H}_2\text{O}$ and $\text{Ce}(\text{HPO}_4)_2 \cdot n\text{H}_2\text{O}$ were investigated in a wide temperature range from 298 K to 423 K under $p_{\text{H}_2\text{O}}/p_s = 1$. There is no report concerning the proton conductivity for these hydrates evaluated at higher temperatures yet. The conductivity shows as high as $10^{-2} \text{ S cm}^{-1}$ above 100°C under $p_{\text{H}_2\text{O}}/p_s = 1$. The composite of $\text{Ce}(\text{HPO}_4)_2 \cdot n\text{H}_2\text{O}$ /polymer shows proton conductivity of $10^{-3} \text{ S cm}^{-1}$ even at very low content of $\text{Ce}(\text{HPO}_4)_2 \cdot n\text{H}_2\text{O}$ (7 wt%), which shows the potential application as polymer electrolyte membrane.

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