

Proton Conducting Properties of Hydrates of Tin Dioxide and Zirconia under High Water Vapor Pressure

Shinji Hara, Masaru Miyayama and Tetsuichi Kudo

Institute of Industrial Science, University of Tokyo, 4-6-1 Komaba, Meguro-ku, Tokyo 153-8505

Fax +81-3-5452-6341, e-mail: shara@iis.u-tokyo.ac.jp

As the proton conductive solid electrolytes for fuel cells operated up to 150°C, hydrates of tin dioxide ($\text{SnO}_2 \cdot n\text{H}_2\text{O}$) and zirconia ($\text{ZrO}_2 \cdot n\text{H}_2\text{O}$) were chosen and their proton conductivities were evaluated. Both hydrates showed high proton conductivities above 10^{-2}Scm^{-1} at 150°C under high water vapor pressures. The conductivities decreased with a decrease in water vapor pressure at 130–150°C, but the decrease of conductivity in hydrated tin dioxide was smaller than that in hydrated zirconia. Hydrated tin dioxide could recover high conductivity after drying at 150°C, and thermally-stable hydrogen-bonded water was suggested to cause the reproducible proton conducting property. The hydrated tin dioxide was found to be a promising candidate for the proton-conductive electrolyte.

Key words: fuel cell, hydrated tin dioxide, hydrated zirconia, high proton conductivity, intermediate temperature

1. INTRODUCTION

Recently fuel cells (FCs) are being developed enthusiastically all over the world as a power source of next generation. Some FCs, which are utilized for electric vehicles or a home electric generator, are expected to be operated under relative low temperature (below 300°C). Thus, Polymer Electrolyte Fuel Cells (PEFCs), using high proton-conductive polymers as the electrolyte are investigated generally. However, these types of polymers, such as perfluorinated ionomer Nafion, have heat-resistance limitations, so that the operating temperature of PEFCs is suppressed below 100°C. The operation under intermediate temperatures (100–300°C) increases the reaction efficiency on electrodes and the thermal efficiency of fuel-reforming system. Furthermore, the severe poisoning of platinum-based catalyst in the electrodes by carbon monoxide included in reformed fuel gas can be depressed, so that hydrogen gas of low purity can be used. However, useful electrolytes have never been found at intermediate temperature at present. Thus, we aimed to search for new inorganic materials exhibiting high proton conductivity at intermediate temperature and to evaluate them. Hydrated zirconia and hydrated tin dioxide are known to show relatively high proton conductivity even at room temperature [1]. In the present study, proton conducting properties of these hydrates were examined at 100–150°C under high water vapor pressure.

2. EXPERIMENTAL

Hydrated zirconia was prepared by a method similar to that reported by Clearfield [2-5]. After boiling zirconium oxychloride solution ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$) for 2h, 25% ammonia solution (NH_4OH) was dropped gradually into the $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ solution. Obtained white precipitate was boiled in 20% KOH solution to remove excess chloride ion, and washed using centrifuge with distilled water till chloride ion was not detected by silver nitrate. White powder of hydrated zirconia was obtained by drying.

Hydrated tin dioxide was prepared by adding NH_4OH into tin (IV) chloride solution ($\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$), following the method described by Giesekke et al. [6]. After washing and drying the precipitate in the same way with the hydrated zirconia, white powder of hydrated tin dioxide was obtained.

The powders were pressed into pellets, 4mm in diameter 1–3mm in thickness, at 140MPa uniaxially. Electrodes were deposited onto pellets with Au sputtering.

Electrical conductivity was measured by an AC impedance method at 5Hz to 13MHz at 25–150°C for the samples placed in a stainless vessel, which is pressure-resistant to 0.7 MPa. Water vapor pressure was controlled by heating vessel and by adjusting leak valve ($P_{\text{H}_2\text{O}} = 0.0\text{--}0.5 \text{ MPa}$).

X-ray diffraction (XRD) profiles of these hydrates were observed with a powder diffractometer system using $\text{CuK}\alpha$ radiation under 40kV and 20mA at room temperature.

3. RESULTS AND DISCUSSION

3.1 Temperature dependence of conductivity of hydrates under saturated water vapor pressure

Figure 1 shows the temperature dependence of conductivity of hydrated zirconia and hydrated tin dioxide in air and under saturated water vapor pressure. On both hydrates, the conductivity in air did not increase above 90°C, however, that under saturated water vapor pressure continued to increase with increasing temperature. At 150°C, $P_{H_2O} = 0.49\text{MPa}$ (Relative Humidity RH = 100%), the conductivity of hydrated zirconia and hydrated tin dioxide reached up to $2.3 \times 10^{-2}\text{Scm}^{-1}$ and $1.4 \times 10^{-2}\text{Scm}^{-1}$, respectively. These values of conductivity are comparable to that of Nafion at 100°C under saturated water vapor pressure. It was confirmed with thermogravimetry (TG) that the amount of hydrated water of both hydrates began to decrease

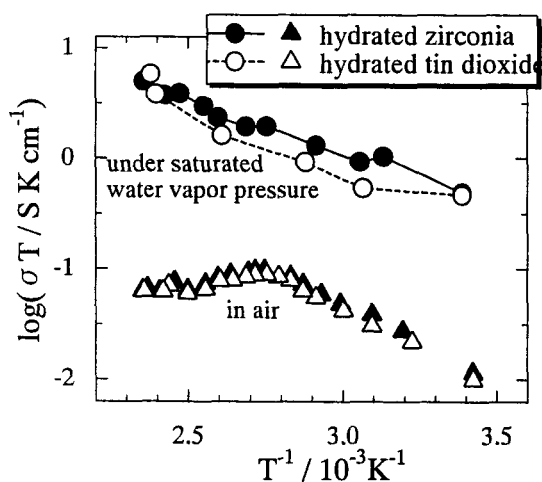


Fig.1 Temperature dependence of conductivity for hydrated zirconia and hydrated tin dioxide

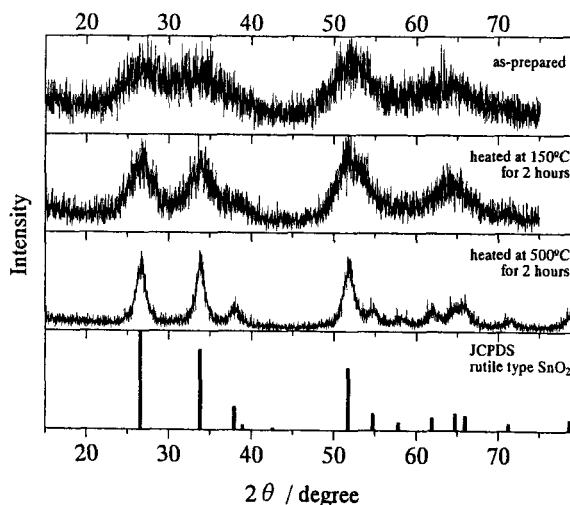


Fig.2 XRD patterns of hydrated tin dioxide

below 100°C with increasing temperature in air. This desorption of hydrated water will be responsible for that conductivity did not increase above 90°C in air.

The activation energies (E_a) are estimated as 24kJmol^{-1} and 32kJmol^{-1} for hydrated zirconia and hydrated tin dioxide, respectively. These values are not far from the reported one (23kJmol^{-1}) for hydrated zirconia between 0 and 40°C [2]. According to the same reference, the surface liquid-like water mechanism (quasi-liquid) 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.

Figure 2 shows XRD patterns of hydrated tin dioxide. The broad peaks of as-prepared sample indicate their amorphous-like state. The sharpness of the peaks increased with increasing heating temperature. However, the peak positions did not move and was in accordance with those of rutile-type SnO_2 . About hydrated zirconia, same result was observed. These results indicate that there are no structural changes in these hydrates by heating. Accordingly, the changes of proton

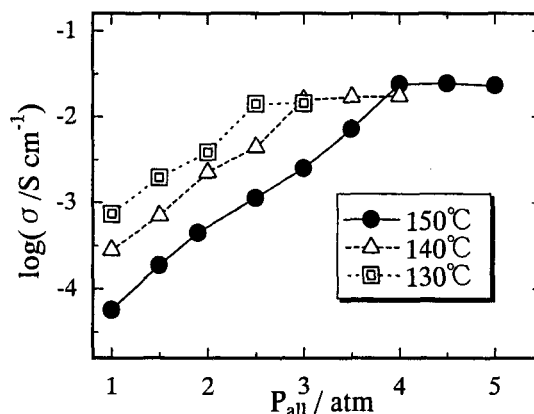


Fig.3 Conductivity vs. water vapor pressure for hydrated zirconia at 130-150°C

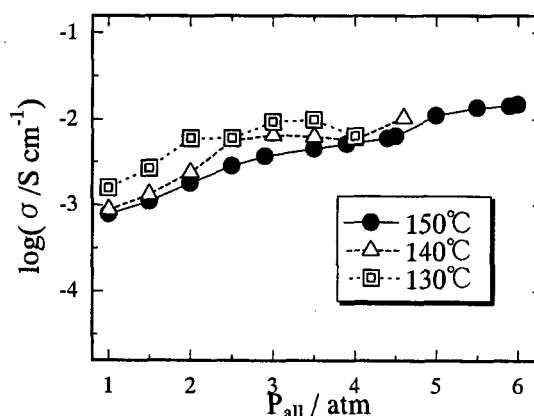


Fig.4 Conductivity vs. water vapor pressure for hydrated tin dioxide at 130-150°C

conductivity in air are attributed to that of hydrated water amount.

3.2 Water vapor pressure dependence of conductivity of hydrates

Figures 3 and 4 shows the water vapor pressure dependence of conductivity at 130~150°C measured on decreasing water vapor pressure, for hydrated zirconia and hydrated tin dioxide, respectively. Decreases in conductivity with a decrease in water vapor pressure were observed for both materials, however the decrease and its temperature dependence were smaller in hydrated tin dioxide than in hydrated zirconia. Weight decrease due to desorption of hydrated water on heating in air was also smaller in hydrated tin dioxide than that in hydrated zirconia. This result indicates the conductivity of both hydrates is strongly related to the amount of hydrated water.

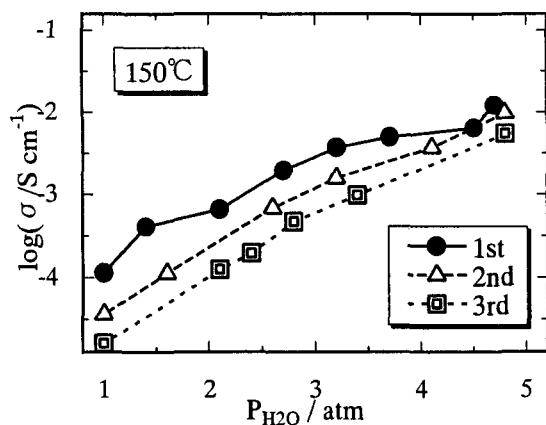


Fig.5 Conductivity vs. water vapor pressure for hydrated zirconia on repeated measurements

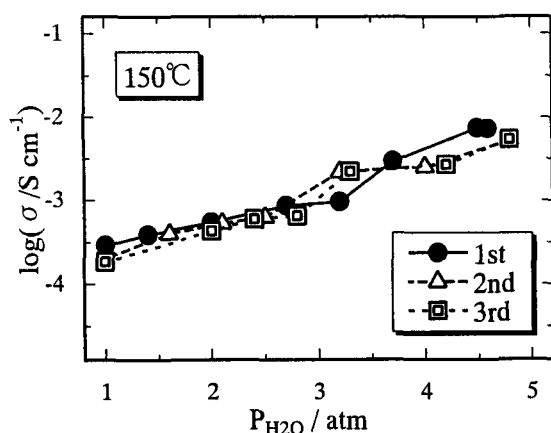


Fig.6 Conductivity vs. water vapor pressure for hydrated tin dioxide on repeated measurements

The variations of conductivity of both hydrates were determined after repeated drying (at 150°C, RH = 20%). After that operation, the conductivity of hydrated zirconia under low water vapor pressure markedly dropped irreversibly as shown in figure 5, whereas the conductivity of hydrated tin dioxide was kept unchanged as shown in figure 6.

At the practical operation of FCs, it is preferable to use electrolytes that have high and stable proton conductivity under low water vapor pressure. In this point of view, hydrated tin dioxide is more suitable for practical use than hydrated zirconia.

3.3 The elimination behavior of hydrated water

It has been reported that hydrated water of hydrated tin dioxide can be classified into three classes; structural water, bonded water and absorbed water, in order of bonding strength [7]: structural water refers to hydroxyl groups condensed and is released at a temperature above 400°C; bonded water refers to the hydrogen-bonded water and is released gradually from 200°C up to 400°C; absorbed water is defined as the water physisorbed to the bonded water and released below 200°C.

Figure 7 shows weight change (TG curve) and differential weight change (DTG curve) before and after a cycle of drying (at 150°C, in air) and moisturing (at 25°C, in saturated water vapor) for hydrated tin dioxide. DTG curve of hydrated tin dioxide before drying shows large peak at 25~130°C and small peak at 150~350°C; they are attributable to desorption of absorbed water and bonded water, respectively. The small peak at 150~350°C clearly observed after drying. Figure 8 shows TG and DTG curves before and after drying (at 150°C, in air) for hydrated zirconia. DTG curve of hydrated zirconia showed only one peak before and after drying, though the peak after drying became smaller and

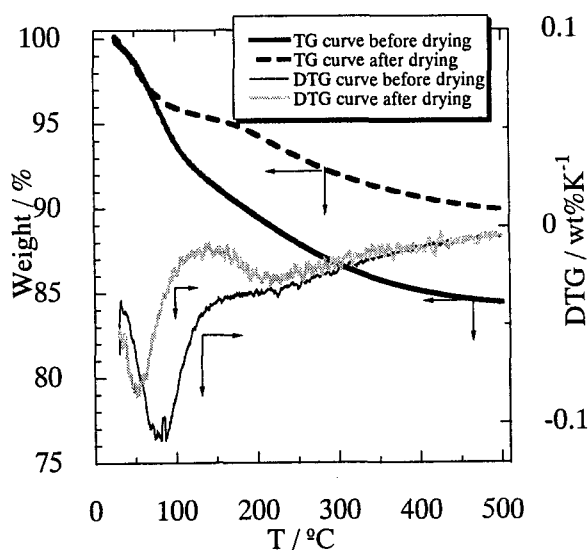


Fig.7 TG and DTG curves of hydrated tin dioxide before and after drying (150°C, RH=20%)

[7] S.Kaneko, J.Kanamori and F.Imoto, *Nihon Kagaku Kaishi*, **6**, 906, (1976)

(Received February 28, 2001; Accepted May 1, 2001)

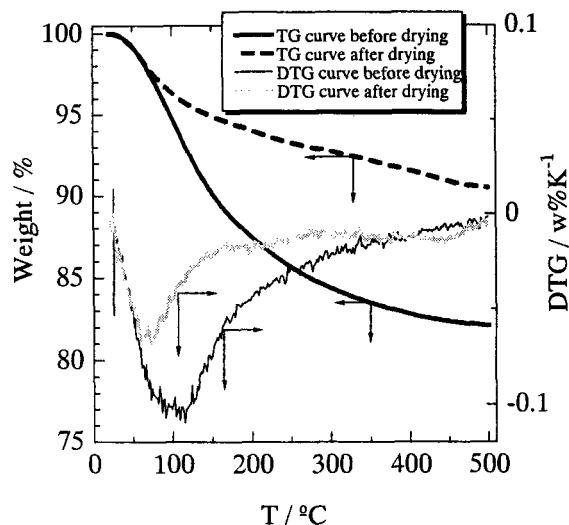


Fig.8 TG and DTG curves of hydrated zirconia before and after drying (150°C, RH=20%)

shifted to a lower temperature.

These results indicate that bonded water for hydrated tin dioxide is not released, but that for hydrated zirconia is released at 150°C. Therefore it is expected that re-absorption of desorbed water is easy for hydrated tin dioxide, but not for hydrated zirconia. Due to the thermally-stable hydrogen-bonded water of hydrated tin dioxide, it is thought that adsorption and desorption of hydrated water is reversible and the subsequent changes of conductivity is also reversible against a change in water vapor pressure at 150°C for hydrated tin dioxide.

4. CONCLUSIONS

As the proton conductive solid electrolytes, hydrates of tin dioxide and zirconia were chosen and their proton conductivities were evaluated. Both hydrates showed high proton conductivities above 10^{-2}Scm^{-1} at 150°C under high water vapor pressures. The conductivities decreased with a decrease in water vapor pressure, but the decrease of conductivities in hydrated tin dioxide was smaller than that in hydrated zirconia. Furthermore hydrated tin dioxide could recover high conductivity after drying. The hydrated tin dioxide was found to be a promising candidate for a proton-conductive electrolyte.

5. REFERENCES

- [1] W.A.England, M.G.Cross, A.Hamnett, P.J.Wiseman and J.B.Goodenough, *Solid State Ionics*, **1**, 231, (1980)
- [2] A.Clearfield, *Inorganic Chemistry*, **3**, 146, (1964)
- [3] E.Katou, and Y.Murase, *Yogyo Kyoukaishi*, **84** (10), 478, (1976)
- [4] K.Matsui, H.Suzuki, and M.Ohgai, *J. Am. Soc.*, **78** (1), 146, (1995)
- [5] K.Matsui, and M.Ohgai, *J. Am. Soc.*, **80** (8), 1949, (1997)
- [6] E.W.Giesekke, H.S.Gutowsky, P.Kirkov and H.A.Laitenen, *Inorganic Chemistry*, **6**, 1294, (1967)