



Proton conductivity and microstructures of the core-shell type solid electrolytes in the $\text{MO}_2\text{-In}_2\text{O}_3\text{-P}_2\text{O}_5$ (M=Ti, Sn, Zr) systems

Takaaki Shirai^a, Shunsuke Satou^a, Morihiro Saito^a, Jun Kuwano^{a,*}, Hidenobu Shiroishi^b

^a Department of Industrial Chemistry, Faculty of Engineering, Tokyo University of Science, 12-1 Ichigayafunagawara-machi, Shinjuku-ku, Tokyo 162-0826, Japan

^b Department of Chemical Science and Engineering, Tokyo National College of Technology, 1220-2 Kunugida-machi, Hachioji-shi, Tokyo 193-0997, Japan

ARTICLE INFO

Article history:

Received 18 January 2008

Received in revised form 31 July 2008

Accepted 18 November 2008

Keywords:

Proton
Electrolyte
Conductivity
Core-shell
Diphosphate

ABSTRACT

The proton conducting $0.9\text{MO}_2 \cdot 0.05\text{In}_2\text{O}_3 \cdot 1.3\text{P}_2\text{O}_5$ (M=Ti, Sn, Zr) electrolytes based on a core-shell structure were synthesized by a ball milling method. The core-shell type electrolytes showed the proton conductivities ranging from a higher value than those of Nafion membranes to 10^{-5} Scm^{-1} at intermediate temperatures of 150–200 °C, depending on the heat-treatment conditions. The samples with high conductivity were proved to adopt a core-shell structure by SEM observation, powder XRD analysis and ^{31}P MAS-NMR measurements.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Polymer electrolyte membrane fuel cells have the potential to be a clean and efficient means of electrical energy generation. However, they also have the following problems to be solved for their widespread use: (1) cost and CO-poisoning of Pt catalysts, (2) depletion of Pt resource, (3) cost, long-term durability and thermal properties of perfluoro-sulfonated polymer electrolytes, (4) humidity control, and (5) low-quality thermal source. As one of the solutions of these problems, extensive efforts have been devoted to develop intermediate temperature fuel cells that operate at temperatures of 150–300 °C. A key component of the fuel cells is the electrolyte. Inorganic proton (H^+) conducting solid electrolytes (HCEs) [1] such as CsH_2PO_4 [2,3], NH_4PO_3 [4–6] are the promising candidates, taking into account the low production cost and thermal durability.

We have recently developed the core-shell type HCEs in the $\text{TiO}_2\text{-In}_2\text{O}_3\text{-P}_2\text{O}_5$ system, which shows the high proton conductivity (σ_{H^+}) of $10^{-1}\text{-}10^{-2} \text{ Scm}^{-1}$ at intermediate temperatures around 100 °C–200 °C [7,8]. They are among the best inorganic HCEs for intermediate-temperature fuel cells. We have proposed the “core-shell model” that the electrolyte consists of the core particles of non-conductive crystalline diphosphate MP_2O_7 or its solid solutions and the shells of an amorphous phosphate phase around the cores. Fig. 1 shows the schematic image of the core-shell structure. Protons transport in the shells (or along the surface of the shells) connected with each other. They were easily prepared at low cost by a ball milling [7] or a sol-gel

method [8]. On the other hand, Nagao and co-workers have recently discovered the crystalline $\text{Sn}_{1-x}\text{In}_x\text{P}_2\text{O}_7$ ($x=0.1$) electrolytes [9–11]. High conductivities of over 10^{-1} Scm^{-1} at temperatures of 150–300 °C were reported even in a dry atmosphere. They have insisted that the proton conductivity results from hoppings of protons introduced into the bulk of $\text{Sn}_{0.9}\text{In}_{0.1}\text{P}_2\text{O}_7$ through a reaction between water vapor, and electron holes and oxygen vacancies, as with the case of the densified sintered bodies of high temperature proton conducting ceramics (ex. Yb-doped SrCeO_3) [12]. The powdered $\text{Sn}_{0.9}\text{In}_{0.1}\text{P}_2\text{O}_7$ sample was prepared by a low temperature sol-gel process, and the green compact, which presumably had a rather low density, was used without densification (sintering) for the conductivity measurements. As far as we know, such a high conductivity has never been found in any green compact of hard ceramic oxide powders without sintering. In addition, amorphous materials sometimes tend to remain in samples prepared through the sol gel process of phosphate-containing ceramics. More recently, Nagao et al. [11] have also reported that the P-excess, non-stoichiometric composition $\text{Sn}_{0.9}\text{In}_{0.1}\text{P}_{2.4}\text{O}_7$ (the charge is not balanced) shows a much higher conductivity than the stoichiometric composition $\text{Sn}_{0.9}\text{In}_{0.1}\text{P}_2\text{O}_7$; however they have not yet explained the mechanism for the enhancement, the role of the excess P content and the unbalanced charge. Thus, the proton conduction mechanism has been not yet fully elucidated.

In this study, we prepared the core-shell type electrolytes with the composition $0.9\text{MO}_2 \cdot 0.05\text{In}_2\text{O}_3 \cdot 1.3\text{P}_2\text{O}_5$ (M=Ti, Sn, Zr) by ball milling with H_3PO_4 , followed by heat-treatments, and the sintered bodies of $0.9\text{MO}_2 \cdot 0.05\text{In}_2\text{O}_3 \cdot \text{P}_2\text{O}_5$ and $\text{TiO}_2 \cdot \text{P}_2\text{O}_5$. This research has been undertaken in connection with the following purposes: 1) The establishment of the preparation process of the core-shell type electrolytes. 2) The evaluation of the proton conductivity of the core-shell electrolytes and

* Corresponding author.

E-mail address: kuwano@ci.kagu.tus.ac.jp (J. Kuwano).

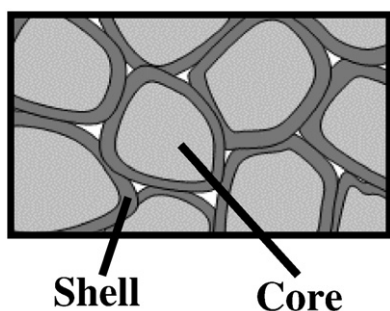


Fig. 1. Schematic image of core-shell type electrolytes.

the sintered bodies (i.e. the core parts). 3) Detailed microstructure analysis on the core-shell electrolytes by scanning electron microscopic observation, powder X-ray diffraction analysis and solid state ^{31}P NMR spectroscopy. 4) The examination of effects of the reheat-treatments on the microstructures and the conductivity to elucidate the cause of the high conductivity in the diphosphate-based electrolytes (7–11).

2. Experimental

2.1. Preparation of the $0.9\text{MO}_2 \cdot 0.05\text{In}_2\text{O}_3 \cdot 1.3\text{P}_2\text{O}_5$ ($M=\text{Ti, Sn, Zr}$) samples by the ball milling method

The calcined powder ($M_i\text{IP}1.2\text{-C}$: $M_i=\text{T, S, Z}$) with the composition $0.9\text{MO}_2 \cdot 0.05\text{In}_2\text{O}_3 \cdot 1.2\text{P}_2\text{O}_5$ was prepared by heating a stoichiometric mixture of MO_2 , In_2O_3 and $(\text{NH}_4)_2\text{HPO}_4$ on a Au-boat at 250°C for two h and then at 650°C for 12 h for $M=\text{Ti, Zr}$, and at 250°C for 1 h and then at 400°C for 1 h for $M=\text{Sn}$. The calcined powder was mixed with 85 mass% H_3PO_4 (added amount: 0.1 M in terms of P_2O_5) and CH_3OH with a planetary ball mill. The pasty mixture was dried at 100°C to expel CH_3OH and heat-treated at 500°C for 3 h. The reground powder was pressed into a pellet at 150 MPa.

Their sample names are abbreviated as " $M_i\text{IP}1.3\text{-B500}$ " ($M_i=\text{T, S, Z}$).

2.2. Reheat-treatments of the $0.9\text{TiO}_2 \cdot 0.05\text{In}_2\text{O}_3 \cdot 1.3\text{P}_2\text{O}_5$ samples

The TIP1.3-B500 pellets were reheated at 600°C , 700°C and 800°C for 1 h. The sample names are abbreviated as "TIP1.3-R(reheating temperature)" (e.g., TIP1.3-R600).

2.3. Preparation of the sintered bodies of $0.9\text{MO}_2 \cdot 0.05\text{In}_2\text{O}_3 \cdot \text{P}_2\text{O}_5$ and $\text{TiO}_2 \cdot \text{P}_2\text{O}_5$

The calcined powders were prepared by heating mixtures of MO_2 , In_2O_3 and $(\text{NH}_4)_2\text{HPO}_4$ at 250°C for 2 h, and then at 650°C for 12 h on Au-boats. A small excess of $(\text{NH}_4)_2\text{HPO}_4$ was added so that the sintered bodies had the stoichiometric compositions after being sintered. The calcined powder was cold-pressed into a pellet (12 mm in diameter, 1–2 mm in thickness) at 250 MPa, which was sintered at 1200°C for 30 min on a Pt-boat in a covered Al_2O_3 crucible. The names of the sintered $0.9\text{TiO}_2 \cdot 0.05\text{In}_2\text{O}_3 \cdot \text{P}_2\text{O}_5$ and $\text{TiO}_2 \cdot \text{P}_2\text{O}_5$ samples are abbreviated as " $M_i\text{IP-S}$ " and "TP-S".

2.4. Characterizations

Conductivity cells were assembled by dc-sputtering gold onto the opposite faces of the sample pellets prepared as described above. The ac-impedance data of the cells were collected in air with an ac-impedance analyzer (Solartron 1260) in a frequency range of 1 Hz–32 MHz and analyzed on the complex impedance diagram to estimate the bulk conductivities. Crystalline and amorphous phases present in the samples were examined by powder X-Ray diffraction (XRD)

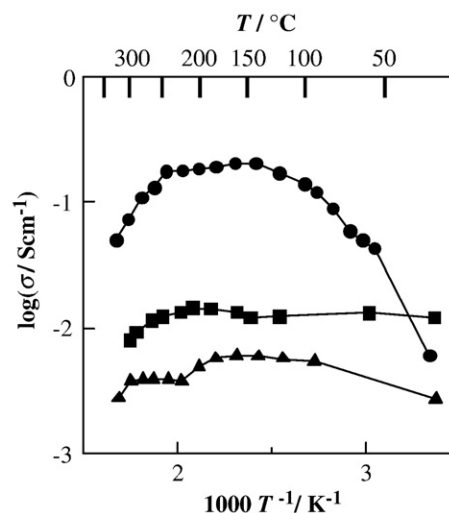


Fig. 2. Temperature dependence of conductivity for (●) TIP1.3-B500, (■) ZIP1.3-B500 and (▲) SIP1.3-B500.

analysis (Rigaku RINT 2500 system, Cu-K α , Bragg-Brentano diffractometer with a graphite monochromator, step width: 0.02° , time per step: 0.3 s). The morphologies of the samples were observed under a scanning electron microscope (SEM: Hitachi, S-5000).

Solid state magic-angle-spinning (MAS) ^{31}P NMR spectra were measured at 121.6 MHz on a CMX 300 spectrometer with a single pulse sequence (pulse width: $4\ \mu\text{s}$, acquisition delay: $5\ \mu\text{s}$, receive delay: $7.5\ \mu\text{s}$, pulse delay: 240 s) and externally referenced to the solid secondary standard $(\text{NH}_4)_2\text{HPO}_4$ (1.3 ppm from 85% H_3PO_4 standard). The sample in a 4 mm zirconia rotor was spun at 12 kHz in a Chemagnetic probe.

3. Results and discussion

Temperature dependence of the bulk conductivities were shown for $M_i\text{IP}1.3\text{-B500}$ in Fig. 2. Maximum conductivities of $2.0 \times 10^{-1}\ \text{Scm}^{-1}$ at

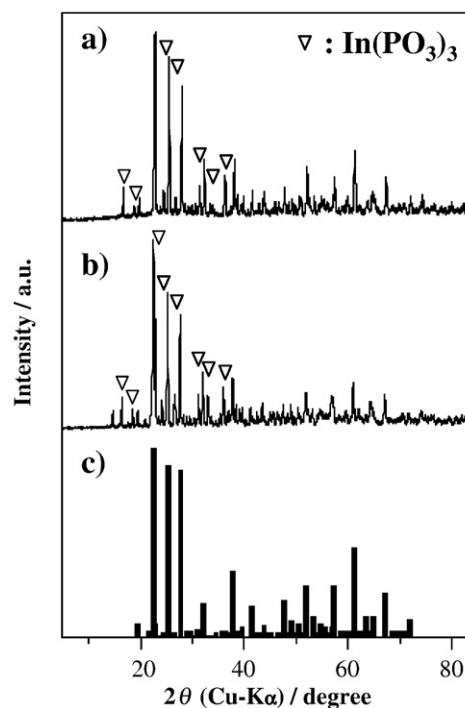


Fig. 3. XRD patterns of (a) TIP1.3-B500, (b) TIP1.2-C and (c) TiP_2O_7 (ICDD card: 38-1468).

Download English Version:

<https://daneshyari.com/en/article/1297879>

Download Persian Version:

<https://daneshyari.com/article/1297879>

[Daneshyari.com](https://daneshyari.com)