

Ionic conduction in undoped SnP₂O₇ at intermediate temperatures

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ABSTRACT

Tin pyrophosphate, SnP₂O₇, is prepared with various initial molar ratios of phosphorus vs. metal ions, P_{ini}/Sn, and different heat-treating temperatures from 573 to 923 K. The preparation conditions are optimized giving consideration to the influence of H₃PO₄ concentration, P_{ini}/Sn molar ratio and heat-treating temperature. The ionic conduction behaviors are investigated by means of electrochemical methods including ac impedance spectroscopy, hydrogen and water vapor concentration cells, etc. in the temperature range of 323–523 K. The results indicate that the samples obtained from 85% H₃PO₄ and SnO₂ nanopowders with P_{ini}/Sn ≥ 2.4 are a single cubic phase, and that in wet hydrogen atmosphere, the samples are almost pure ionic conductors, the ionic conduction is contributed mainly by proton and partially by oxide ion. An ionic conductivity of 2.17 × 10⁻² S cm⁻¹ is achieved for the sample prepared from P_{ini}/Sn = 2.8 under wet hydrogen atmosphere at 448 K.

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1. Introduction

Fuel cells have attracted increasing attention because they cleanly and high efficiently convert chemical energy directly to electrical energy, etc. The presently most favored electrolyte is yttria stabilised zirconia (YSZ) with operating temperature in the range 1073–1273 K [1–6]. However, for practical applications, such high temperatures present a number of problems, such as sealing, degradation and selection of cell materials. Therefore, considerable effort has recently been devoted for searching and developing appropriate proton conducting electrolytes toward the intermediate temperature fuel cells (ITFCs) in the temperature range of 373 to 873 K [3].

Recently, a kind of novel solid state proton conductors, Sn_{1-x}R_xP₂O₇ (R = Al³⁺, Ga³⁺, In³⁺, Sb³⁺, Mg²⁺), have been attracting considerable interests due to their potential applications in some electrochemical devices such as fuel cells, gas sensors, etc. at intermediate temperatures (373–573 K) [7–20]. Hibino et al. reported that SnP₂O₇ and Sn_{0.9}In_{0.1}P₂O₇ exhibit high protonic conductivities of above 10⁻² S cm⁻¹ from 348 to 573 K and above 10⁻¹ S cm⁻¹ from 398 to 573 K under unhumidified conditions, respectively [7,8]. A fuel cell using Sn_{0.9}In_{0.1}P₂O₇ electrolyte membrane with 0.35 mm thickness yielded a power density of 264 mW cm⁻² under unhumidified H₂/air conditions at 523 K [8]. Chen et al. reported that Sn_{0.9}In_{0.1}P₂O₇ can conduct both protons and oxide ions at low temperatures (403–503 K) [15].

However, there are few reports dealing with influence of preparation conditions on phase purity of SnP₂O₇. Moreover, little atten-

tion has been focused on protonic and oxide-ionic conduction of SnP₂O₇. In this paper, the ionic conduction behaviors are investigated in the temperature range of 323–523 K, and we try to make estimation of the proton and oxide ion transport properties from the concentration cells of water vapor and hydrogen [15,21,22].

2. Experimental

Tin pyrophosphate, SnP₂O₇, is prepared as follows. The required amounts (P_{ini}/Sn molar ratios = 2.0–3.0) of SnO₂ (Luoyang Ship Material Research Institute, 50–70 nm) and H₃PO₄ (85% and 28%) are fully mixed and held with stirring at 573 K until they became powders, then heat-treated from 773 to 923 K for 2 h to obtain SnP₂O₇ products.

The crystalline structure of the obtained powders is determined at room temperature by X-ray diffraction analysis (X' Pert-pro MPD). The final molar ratios of phosphorus vs. metal ions, P_{fin}/Sn, in the powders are evaluated through X-ray fluorescence (XRF) measurement. The powders are pressed into pellet (diameter 20 mm, thickness 2.4–2.6 mm) at hydrostatic pressure of 300 MPa. Platinum paste is coated on both sides of the pellet and heated at 523 K for 30 min. The as-obtained pellet is sealed between two alumina tubes, and then placed in an electric furnace for electrochemical measurements. The conductivities are measured in dry air, wet air and wet H₂ atmospheres at 323–523 K by an AC impedance method using electrochemical workstations (Zahner IM6ex) over the frequency range from 1 Hz to 3 MHz. The wet gases are obtained by saturating water vapor at 298 K and the dry gases are obtained by using a cold trap based on low temperature nitrogen gas (ca. 153 K determined by a thermo-couple temperature sensor). In order to study the ionic conduction in

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the samples in wet hydrogen atmosphere, hydrogen and water vapor concentration cells are constructed and the electromotive forces (EMFs) are measured at 373–473 K. The observed values (EMF_{obs}) of electromotive forces of the cells are given by the following Nernst equation [15,21,22].

$$\text{EMF}_{\text{obs}} = \frac{RT}{2F} \left\{ -t_{\text{ion}} \ln \left[\frac{p_{\text{H}_2(\text{A})}}{p_{\text{H}_2(\text{B})}} \right] + t_0 \ln \left[\frac{p_{\text{H}_2\text{O}(\text{A})}}{p_{\text{H}_2\text{O}(\text{B})}} \right] \right\}.$$

If the $p_{\text{H}_2\text{O}}$ in both cell compartments is the same, the EMF_{obs} of the hydrogen concentration cell with $p_{\text{H}_2\text{O}(\text{A})} = p_{\text{H}_2\text{O}(\text{B})}$ gives the sum of the proton and oxide ion contributions. The ionic transport number ($t_{\text{ion}} = t_{\text{H}} + t_{\text{O}}$) is given by $\text{EMF}_{\text{obs}}/\text{EMF}_{\text{cal}}$, where $\text{EMF}_{\text{cal}} = \frac{RT}{2F} \ln \left[\frac{p_{\text{H}_2(\text{A})}}{p_{\text{H}_2(\text{B})}} \right]$. Similarly, the EMF of the water vapor concentration cell with $p_{\text{H}_2(\text{A})} = p_{\text{H}_2(\text{B})}$ gives the oxide-ionic contribution. Therefore, the ionic transport number in wet hydrogen atmosphere may be estimated by using the following concentration cells.

$$\text{H}_2 (p_{\text{H}_2} = 1.01 \times 10^5 \text{ Pa}) (p_{\text{H}_2\text{O}} = 1.7 \times 10^3 \text{ Pa}), \\ \text{Pt}|\text{SnP}_2\text{O}_7|\text{Pt}, \text{H}_2\text{-Ar} (p_{\text{H}_2} = 1.01 \times 10^4 \text{ Pa}) (p_{\text{H}_2\text{O}} = 1.7 \times 10^3 \text{ Pa}) \text{ cell} \quad (1)$$

$$\text{H}_2 (p_{\text{H}_2} = 1.01 \times 10^5 \text{ Pa}) (p_{\text{H}_2\text{O}} = 1.7 \times 10^3 \text{ Pa}), \\ \text{Pt}|\text{SnP}_2\text{O}_7|\text{Pt}, \text{H}_2 (p_{\text{H}_2} = 1.01 \times 10^5 \text{ Pa}) (p_{\text{H}_2\text{O}} = 1.23 \times 10^4 \text{ Pa}) \text{ cell}. \quad (2)$$

The isotope effect on conductivity is applied to examine the proton conduction in water vapor-containing atmosphere.

3. Results and discussion

Fig. 1 shows XRD patterns of the obtained powders prepared from different concentrations (85% and 28%) of H_3PO_4 and SnO_2 with P_{ini}/Sn molar ratio of 2.4 at different heat-treating temperatures. When using higher concentration of H_3PO_4 (85%), the phase purity of the powders increases with increasing heat-treating temperature. The diffraction peaks of SnO_2 impurity are observed for the powders prepared at 573 K, whereas the powders prepared at 773 K or higher show a single cubic phase structure of SnP_2O_7 . On the other hand, when using lower concentration of H_3PO_4 (28%), the diffraction peaks of SnO_2 are all observed for the powders prepared at 573–923 K. The samples consist of grains of SnP_2O_7 mixed with SnO_2 on the outside of

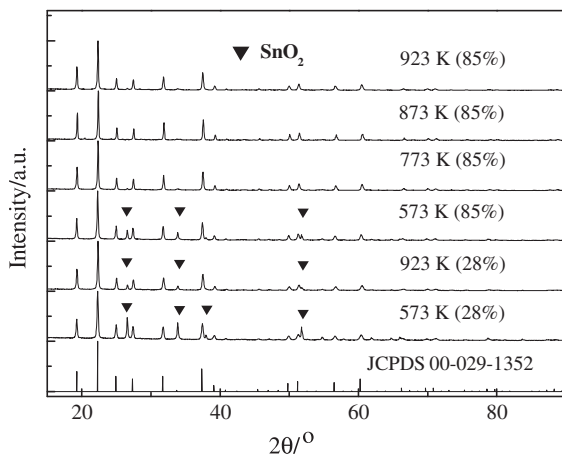


Fig. 1. XRD patterns of the powders prepared from H_3PO_4 (85% and 28%) and SnO_2 with P_{ini}/Sn molar ratio of 2.4 at different heat-treating temperatures from 573 to 923 K.

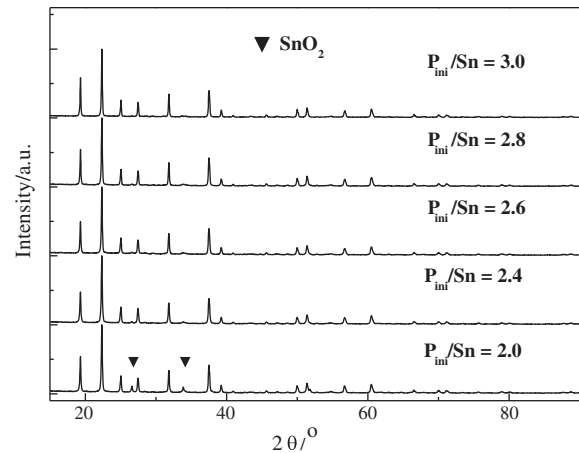
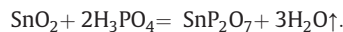


Fig. 2. XRD patterns of samples prepared from H_3PO_4 (85%) and SnO_2 with different P_{ini}/Sn molar ratios at a heat-treating temperature of 773 K.

SnP_2O_7 crystal surface [14]. As can be seen from Fig. 1, the intensities of SnO_2 peaks decrease with increasing H_3PO_4 concentration at the same heat-treating temperature. This means that the excess H_2O may affect the synthetic process. Therefore, to obtain a single cubic phase structure of SnP_2O_7 , the heat-treating temperatures above 773 K and concentrated phosphoric acid (85%) are a requisite. This is because properly high temperature and concentrated phosphoric acid are favorable to form the SnP_2O_7 as indicated by the following equation [23]:



In order to observe the influence of P/Sn molar ratio on phase purity of SnP_2O_7 products, we prepared a series of samples from H_3PO_4 (85%) and SnO_2 with $P_{\text{ini}}/\text{Sn} < 2, = 2$ and > 2 at 773 K. As shown in Fig. 2, the single cubic phase of samples is obtained when $P_{\text{ini}}/\text{Sn} = 2.4, 2.6, 2.8$ and 3.0 , corresponding to $P_{\text{fin}}/\text{Sn} = 2.02, 2.16, 2.28$ and 2.50 , respectively. The results suggest that when $P_{\text{fin}}/\text{Sn} > 2$, excess P as amorphous P_{mO_n} , which may improve proton conduction significantly [14] as discussed later, existed in the grain boundary of SnP_2O_7 crystal. On the other hand, when $P_{\text{ini}}/\text{Sn} = 2.0$, except cubic structure of SnP_2O_7 as a main phase, a SnO_2 impurity phase also is observed. Therefore, in order to obtain a single cubic phase of SnP_2O_7 , P_{ini}/Sn should be controlled to be 2.4 or more (i.e. P_{fin}/Sn should be

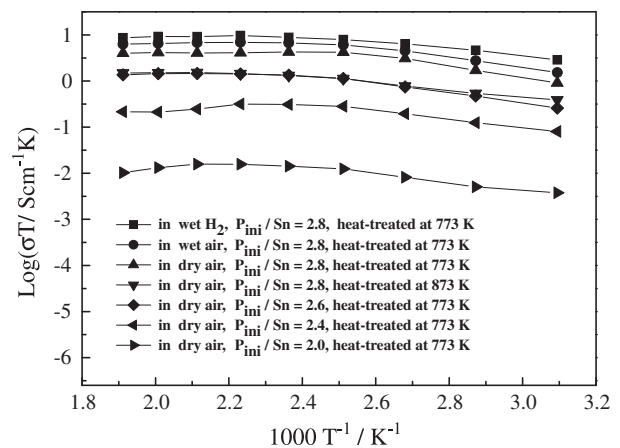


Fig. 3. Temperature dependence of the conductivity of SnP_2O_7 prepared from different P_{ini}/Sn molar ratios and heat-treating temperatures in wet H_2 , wet air and dry air.

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