

Gel-type shell contributing to the high proton conductivity of pyrophosphates



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ARTICLE INFO

Article history:

Received 20 January 2016

Received in revised form

9 March 2016

Accepted 11 March 2016

Available online 12 March 2016

Keywords:

Pyrophosphate

Calcination temperature

Proton conductivity

Gel-type shell

Phosphorus /metal ratio

ABSTRACT

Metal pyrophosphates have attracted considerable interests due to their high proton conductivity and potentially wide applications in the temperature range of 100–400 °C. However, great difference in conductivity was reported by different groups on the same pyrophosphates. The reason for the huge difference is still in debate up to now, and there is no coherent standpoint in literatures on the proton conduction mechanism. In this study, we chose $\text{Fe}_{0.4}\text{Nb}_{0.5}\text{P}_2\text{O}_7$, which was reported showing high proton conductivity recently, as an example to disclose the reason inducing the divergence in proton conductivity and conduction mechanism. We found that the as-prepared pyrophosphate grains have three layers, i.e. crystalline pyrophosphate core, amorphous phosphate shell in the middle and gel-type shell composed of amorphous phosphorus species as the outermost layer. The content of amorphous phosphorus species decreases with the increase of the calcination temperature of pyrophosphates, and the calcination temperature-dependent residual soluble phosphorus curve extremely coincides with the conductivity curve. Thus, the proton conduction of pyrophosphates is realized via a gel-type shell formed by residual amorphous phosphorus species on surfaces of pyrophosphate grains. We suggested that the phosphorus content is the key factor to explain the great difference in conductivity of pyrophosphates prepared by different groups.

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1. Introduction

Ceramic materials with high and pure proton conductivity are candidates as electrolytes in hydrogen sensors, batteries, fuel cells, electrolytic cells, hydrogen pumps, and membrane reactors, etc [1–4]. Recently, a kind of novel solid state proton conductors, metal pyrophosphates MP_2O_7 , attracts considerable interests due to their high proton conductivity in a temperature range of 100–400 °C. Kwon et al. [5] firstly reported that SnP_2O_7 exhibits high proton conductivities of above $10^{-2} \text{ S cm}^{-1}$ from 75 to 300 °C under unhumidified conditions. The proton conductivity of SnP_2O_7 could be increased as high as $10^{-1} \text{ S cm}^{-1}$ through partial substitution of Sn^{4+} cations with low valence cations, such as In^{3+} , Sb^{3+} , Sc^{3+} and Ga^{3+} [6–10], in the temperature range of 200–400 °C at low humidity. However, some researchers reported quite different results about the proton conductivity of pyrophosphates. For example, Singh et al. [11] reported that the conductivity of $\text{Sn}_{1-x}\text{Ce}_x\text{P}_2\text{O}_7$ samples was only 10^{-8} – $10^{-6} \text{ S cm}^{-1}$ in 300–550 °C range in the ambient air. Phadke et al. [12], found that

$\text{Zn}_{0.1}\text{Sn}_{0.9}\text{P}_2\text{O}_7$ shows the highest conductivity of $2.84 \times 10^{-6} \text{ S cm}^{-1}$ at 600 °C in the temperature range of 300–600 °C. These conductivity values were several orders of magnitude lower than the previously reported conductivity for acceptor doped pyrophosphates.

Table S1 summarizes the proton conductivity of pyrophosphates reported by different groups [6,7,10–17]. It can be found that the calcination temperature has great influence on the proton conductivity, i.e. samples calcined at higher temperatures (1000–1400 °C) show much lower proton conductivity (10^{-5} – $10^{-9} \text{ S cm}^{-1}$), while those calcined at lower temperatures (450–650 °C) show higher proton conductivity (10^{-3} – $10^{-1} \text{ S cm}^{-1}$). The crystal structure of pyrophosphates does not change with the increase of calcination temperature according to XRD patterns shown in references [11,15,18,19]. Except calcination temperature, initial P/M (M: metal elements) ratio [6,9,10,20–25] has great influence on proton conductivity though pyrophosphates were calcined at lower temperatures (Table S2). Other factors such as preparation methods [22], as well as chemical precursors [11,23] are attributed to the huge difference in proton conductivity. The reason for the huge difference in proton conductivity is still in debate up to now.

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Two mechanisms were proposed to explain the proton conduction of pyrophosphates. One is bulk conduction, i.e. proton conduction is realized via bulk migration [7,24,26,27], and another is the surface conduction, i.e. proton conduction is related to an amorphous phosphate layer covered on non-conductive pyrophosphate particles [12,15,22,28]. Hibino et al. [8,29] attributed the low conductivity of low P/M ratio samples to the phosphate deficiency resulting in a partial disconnection of the P-O-P network for proton migration in the pyrophosphate bulk, i.e. following the bulk migration mechanism. However, other researchers found that amorphous phosphate layer covering the pyrophosphate grains facilitates the proton migration [25,28]. For example, in the investigation of the influence of P/(Sn+In) ratio on proton conductivity, Kreller et al. [25], deduced the existence of the amorphous phosphate layer for the rapid proton diffusion. Therefore, there are no coherent standpoints in literatures on the proton conduction mechanism and the primary reason leading to the great divergence in proton conductivity.

More recently, a series of $A_{0.5}^{III}B_{0.5}^V P_2 O_7$ compounds exhibiting extremely high proton conductivities in the temperature range of 200–400 °C was reported by Hibino et al. [17]. Among these metal pyrophosphates, $Fe_{0.4}Nb_{0.5}P_2 O_7$ (FNPO) and $Fe_{0.4}Ta_{0.5}P_2 O_7$ show the highest proton conductivity. For example, the proton conductivity of FNPO reaches to $\sim 0.2 \text{ S cm}^{-1}$ at 300 °C in unhumidified air. They attributed the high proton conductivity to that the charge-compensation of the deficient A^{III} or B^V cations is realized through the incorporation of protons into pyrophosphates, i.e. bulk migration mechanism. Therefore, in this communication FNPO was chosen as an example to disclose the reason which induces the great divergence in proton conductivity of pyrophosphates reported by different groups, and discuss the possible proton migration mechanism for pyrophosphates. Here, we presented strong experimental evidences to show that the high proton conductivity of pyrophosphates is related to a gel-type shell composed of residual amorphous phosphorus species on surfaces of pyrophosphate grains.

2. Experimental section

2.1. Synthesis of the FNPO powders

FNPO powder was prepared as follows. 0.80 g of $Fe_2 O_3$ (0.005 mol) and 1.66 g of $Nb_2 O_5$ (0.00625 mol) were mixed with 8.07 g of $H_3 PO_4$ (0.07 mol) and 100 g of deionized water, and then the mixture was stirred at 300 °C until a high-viscosity paste was formed. A fraction of the $H_3 PO_4$ is lost in the subsequent calcination process via vaporization; therefore, an excess of $H_3 PO_4$ was used for the solid-state reaction. The paste was calcined in an alumina crucible at calcination temperature of 450–700 °C with 50 °C interval for 2 h. The resultant powders were ground in an agate mortar with a pestle.

2.2. Synthesis of FNPO-700/450 powder

The FNPO powder calcined at 700 °C was firstly synthesized according to the above steps. And then the 700 °C FNPO powder was mixed with extra 2.30 g of $H_3 PO_4$ (0.02 mol) and 100 g of deionized water, and the mixture was stirred at 300 °C until a high-viscosity paste was formed. The paste was calcined at 450 °C for 2 h.

2.3. Proton conductivity tests

The proton transport number of FNPO is very close to 1, so the total conductivity is almost equal to its proton conductivity [17].

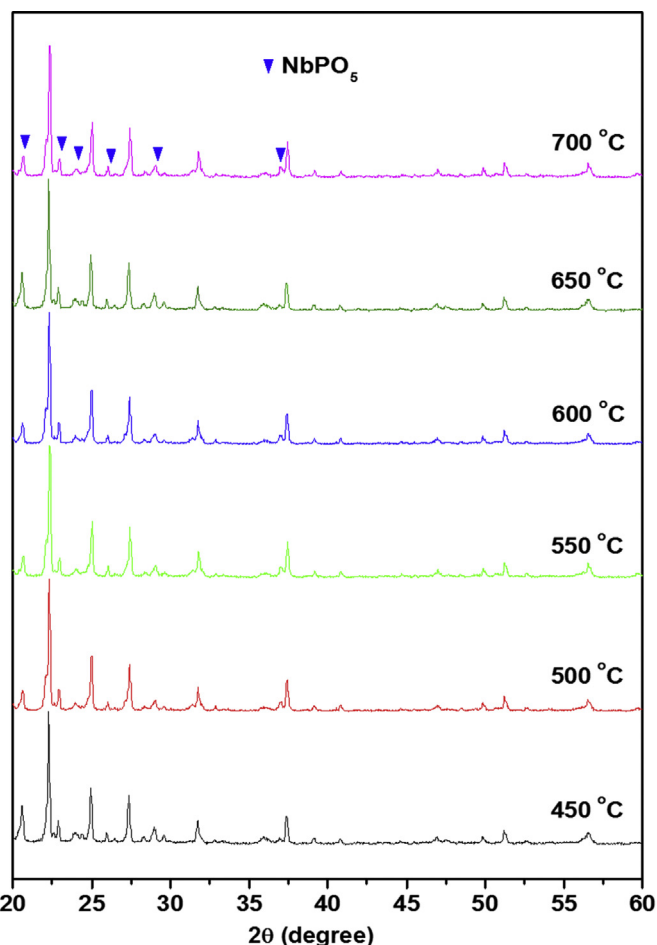


Fig. 1. XRD patterns of the FNPO samples calcined in the temperature range of 450–700 °C.

The total conductivities were measured in various atmospheres on bar-shaped samples with two-probe methods. The bar-shaped samples were prepared as follows: the as-prepared powders were pressed into bars under a pressure of ~ 200 MPa in a stainless steel mold and then calcined in 400 °C for 2 h. Although the impedance in the two-probe method reflects many impedance components, in the pathway that the current flows, such as the lead inductance, the lead resistance, and the stray capacitance between two leads the other impedance components could all be disregarded with relatively low values when the sample materials have a high impedance. In this study, the impedances of samples are larger than 1000 Ω . Thus lead inductance, lead resistance and the stray capacitance can be ignored without inducing remarkable errors. The resistances were recorded by a multimeter (Keithley 2000). The final proton conductivity was calculated by the following equation:

$$\sigma = L/RS \quad (1)$$

where R is the resistance of the bar-shaped sample, L is the distance between the two electrodes, S is the cross sectional area of the bar-shaped sample.

2.4. Characterization of the FNPO materials

The final molar ratios of phosphorus vs. metal ions, $P/(Fe+Nb)$, in the powders were evaluated by using Inductively coupled plasma (ICP-AES, ICPS-8100) analysis and X-ray fluorescence (XRF) measurements. Phase structures of the materials were determined

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