

Short Communication

Synthesis of 5 mol% Ga³⁺-doped SnP₂O₇/KPO₃ composite electrolyte for intermediate temperature fuel cells

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In this study, 5 mol% Ga³⁺-doped SnP₂O₇ / corresponding metaphosphate composite electrolyte was prepared. Synthesis and intermediate temperature electrical properties of Sn_{0.95}Ga_{0.05}P₂O₇/KPO₃ were investigated. The X-ray diffraction result showed that the composite electrolyte had a pyrophosphate structure. Conductivities of the composite electrolyte indicated that it had a good linear Arrhenius relationship in the whole test temperature range. The highest conductivity of Sn_{0.95}Ga_{0.05}P₂O₇/KPO₃ was 3.4×10⁻² S·cm⁻¹ at 700 °C.

Keywords: Composite; X-ray diffraction; Conductivity; Electrolyte; Fuel cell

1. INTRODUCTION

Fuel cells are electrochemical devices which directly transform chemical energy into electrical energy with high energy conversion efficiency and low environmental pollution [1–6]. In recent years, low temperature fuel cells with operating temperature lower than 150 °C, such as proton exchange membrane fuel cells (PEMFCs), and high temperature fuel cells with operating temperatures higher than 700°C, such as solid oxide fuel cells (SOFCs), have been widely studied [7–11]. However, there have been few reports on medium temperature SOFCs with operating temperatures in the range of 150–700 °C [12–17].

Electrolytes as the key materials of fuel cells have been the focus of all kinds of research. Recent studies showed that stannic pyrophosphate based solid electrolytes had high conductivities in the range of 150–400 °C. Typical examples included electrolytes of Sn_{1-x}Ga_xP₂O₇, Sn_{1-x}In_xP₂O₇ and Sn_{1-x}Al_xP₂O₇ etc [18–20]. Ma et al. synthesized Sn_{1-x}Ga_xP₂O₇ (x = 0.00-0.15) and found that Sn_{0.91}Ga_{0.09}P₂O₇ had the highest conductivity of 4.6×10⁻² S·cm⁻¹ in wet hydrogen at 175 °C [18]. Hibino et al. investigated the intermediate temperature electrical properties of Sn_{1-x}In_xP₂O₇ [19]. However, the chemical stability of

stannic pyrophosphate was low. It has been reported that composite electrolytes can not only improve the strength of SnP_2O_7 , but also increase the conductivities [21–23]. Sato et al. synthesized dense SnP_2O_7 - SnO_2 composite ceramics by reacting H_3PO_4 with SnO_2 substrates [22]. The Ga^{3+} (0.062 nm) ionic radius was close to Sn^{4+} (0.069 nm). Therefore, it is necessary to investigate Ga^{3+} -doped stannic pyrophosphate composite electrolyte.

In this study, 5 mol% Ga^{3+} -doped SnP_2O_7 / corresponding metaphosphate composite electrolyte was prepared. Synthesis and intermediate temperature electrical properties of $\text{Sn}_{0.95}\text{Ga}_{0.05}\text{P}_2\text{O}_7/\text{KPO}_3$ were investigated.

2. EXPERIMENTAL

Pure raw materials of 2.7642 g K_2CO_3 , 8.5905 g SnO_2 , 13 mL 85 % H_3PO_4 and 0.2812 g Ga_2O_3 were weighed respectively with an electronic analytical balance. The raw materials were put into the crucible and heated until they became solid. After crushing, the obtained powder was fired at 500 °C for 1 h. The solid sample was ground into powder and pressed into a disc, then sintered at 700 °C for 1 h to obtain a $\text{Sn}_{0.95}\text{Ga}_{0.05}\text{P}_2\text{O}_7/\text{KPO}_3$ pellet (thickness: 1.2 mm).

Phase analysis of $\text{Sn}_{0.95}\text{Ga}_{0.05}\text{P}_2\text{O}_7/\text{KPO}_3$ was measured by X-ray diffractometer (XRD, X-D-3, China). The microstructure of composite electrolyte was characterized by scanning electron microscope (SEM, Sigma 500). The electrochemical workstation (CHI660E, Chenhua, Shanghai) was used to measure the AC impedance spectra of $\text{Sn}_{0.95}\text{Ga}_{0.05}\text{P}_2\text{O}_7/\text{KPO}_3$ and calculate corresponding conductivity in the temperature range of 400–700 °C. An oxygen concentration discharge cell was made up to determine the oxide ionic conduction of the composite electrolyte. A hydrogen-oxygen fuel cell was constructed which was coated with Pd-Ag paste (area: 0.5 cm^2) in the center of both sides of $\text{Sn}_{0.95}\text{Ga}_{0.05}\text{P}_2\text{O}_7/\text{KPO}_3$.

3. RESULTS AND DISCUSSION

Fig. 1 shows the XRD diagram of $\text{Sn}_{0.95}\text{Ga}_{0.05}\text{P}_2\text{O}_7/\text{KPO}_3$. $\text{Sn}_{0.94}\text{Ga}_{0.06}\text{P}_2\text{O}_7$ is listed for comparison [18]. After comparison, the composite electrolyte $\text{Sn}_{0.95}\text{Ga}_{0.05}\text{P}_2\text{O}_7/\text{KPO}_3$ was mainly consistent with the literature [18], besides, signs of KH_2PO_4 and SnO_2 were found. This may be because K_2CO_3 reacts with H_3PO_4 and SnP_2O_7 in the preparation process: $2\text{H}_3\text{PO}_4 + \text{K}_2\text{CO}_3 = \text{H}_2\text{O} + \text{CO}_2\uparrow + 2\text{KH}_2\text{PO}_4$ and $\text{SnP}_2\text{O}_7 + \text{K}_2\text{CO}_3 = \text{SnO}_2 + 2\text{KPO}_3 + \text{CO}_2\uparrow$. At the same time, most of K_2CO_3 reacts with SnP_2O_7 to form KPO_3 .

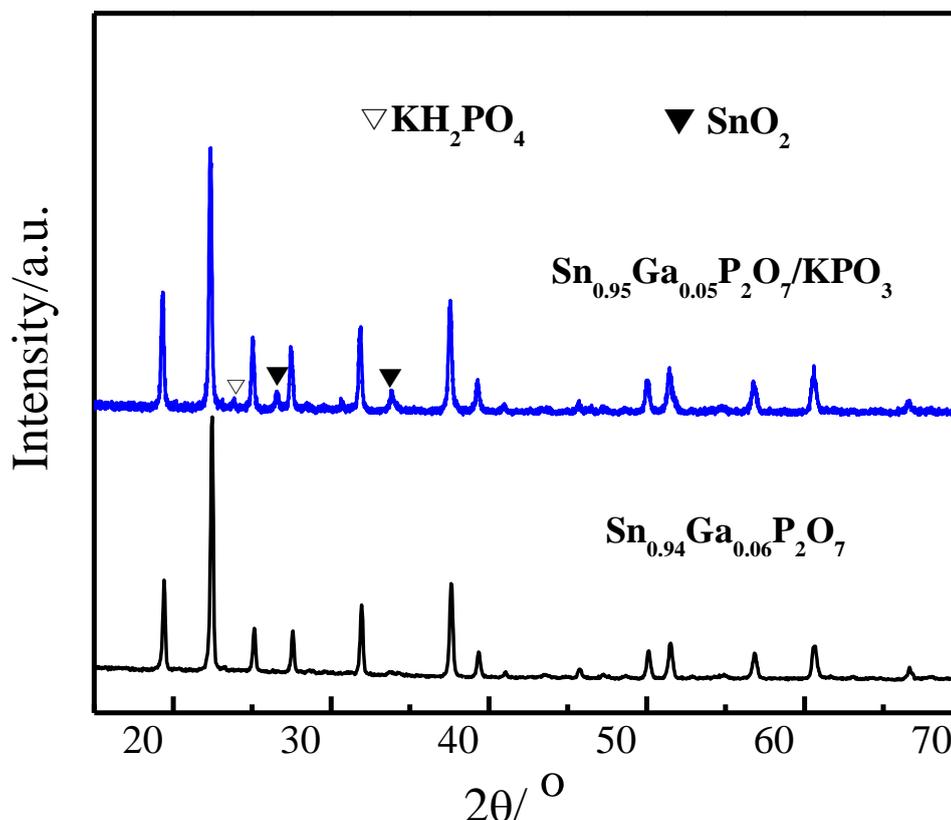


Figure 1. XRD pattern of $\text{Sn}_{0.94}\text{Ga}_{0.06}\text{P}_2\text{O}_7$ [18] and $\text{Sn}_{0.95}\text{Ga}_{0.05}\text{P}_2\text{O}_7/\text{KPO}_3$.

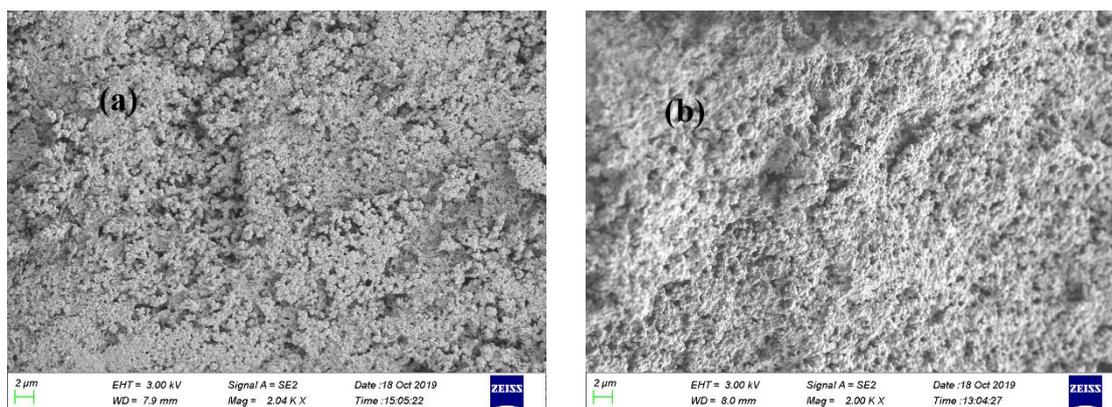


Figure 2. The external and cross-sectional SEM photos of $\text{Sn}_{0.95}\text{Ga}_{0.05}\text{P}_2\text{O}_7/\text{KPO}_3$ (a, b).

The morphology of $\text{Sn}_{0.95}\text{Ga}_{0.05}\text{P}_2\text{O}_7/\text{KPO}_3$ is shown in Fig. 2. Fig. 2(a, b) show that the external and cross-sectional surfaces of the composite electrolyte are compact, without obvious pores, and the grain size is small. To some extent, the grains gather together in Fig. 2(b) under sintering by mechanical mixing method.

Fig. 3 shows the $\log(\sigma T) \sim 1000 T^{-1}$ plots of $\text{Sn}_{0.95}\text{Ga}_{0.05}\text{P}_2\text{O}_7/\text{KPO}_3$ in air at 400–700 °C and the reported samples from 50 °C to 300 °C [18–19]. From Fig. 3, the conductivities of $\text{Sn}_{0.94}\text{Ga}_{0.06}\text{P}_2\text{O}_7$ and $\text{Sn}_{0.95}\text{In}_{0.05}\text{P}_2\text{O}_7$ at 50–200 °C increase with the change of temperature because the formed oxygen vacancies promote the migration of ions. The conductivities decrease at 200–300 °C, which shows the stability is weakened in $\text{Sn}_{0.94}\text{Ga}_{0.06}\text{P}_2\text{O}_7$ and $\text{Sn}_{0.95}\text{In}_{0.05}\text{P}_2\text{O}_7$ [18–19]. It can be seen from Fig. 3 that the

composite electrolyte has a good linear Arrhenius relationship in the whole test temperature range. This may be due to the conducting ions which could conduct through the interface and the bulk phase in the composite. The maximum conductivity of $\text{Sn}_{0.95}\text{Ga}_{0.05}\text{P}_2\text{O}_7/\text{KPO}_3$ is $3.4 \times 10^{-2} \text{ S} \cdot \text{cm}^{-1}$ at $700 \text{ }^\circ\text{C}$.

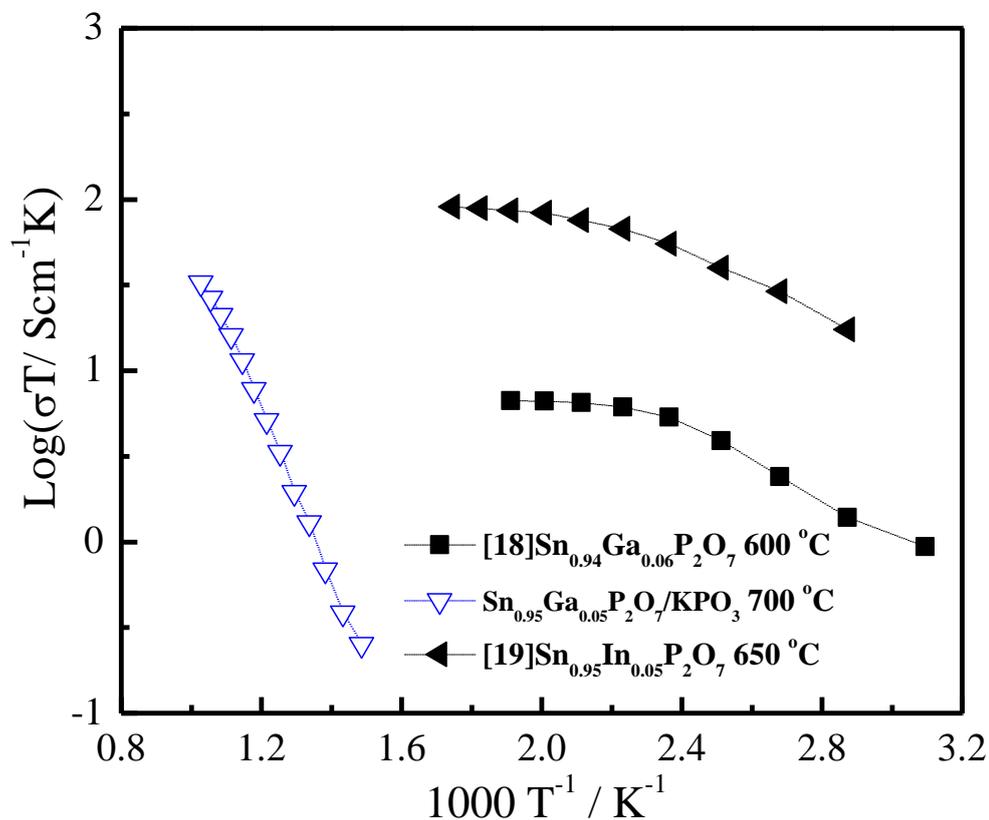


Figure 3 The $\log(\sigma T) \sim 1000 T^{-1}$ plots of $\text{Sn}_{0.94}\text{Ga}_{0.06}\text{P}_2\text{O}_7$ [18] (sintered at $600 \text{ }^\circ\text{C}$), $\text{Sn}_{0.95}\text{Ga}_{0.05}\text{P}_2\text{O}_7/\text{KPO}_3$ (sintered at $700 \text{ }^\circ\text{C}$) and $\text{Sn}_{0.95}\text{In}_{0.05}\text{P}_2\text{O}_7$ [19] (sintered at $650 \text{ }^\circ\text{C}$).

An oxygen concentration discharge cell was made up to determine the oxide ionic conduction in $\text{Sn}_{0.95}\text{Ga}_{0.05}\text{P}_2\text{O}_7/\text{KPO}_3$. The oxygen concentration discharge cell was tested at $700 \text{ }^\circ\text{C}$, as shown in Fig.4. The open circuit voltage is close to that of theoretical electromotive force at $700 \text{ }^\circ\text{C}$. The main reason may be that the metaphosphate is uniformly coated on the surface of $\text{Sn}_{0.95}\text{Ga}_{0.05}\text{P}_2\text{O}_7$ particles after melting, which improves the compactness and forms a fast ion channel at the interface in the composite. The current density-voltage plot shows a linear relationship. The result shows that $\text{Sn}_{0.95}\text{Ga}_{0.05}\text{P}_2\text{O}_7/\text{KPO}_3$ is a good oxide ionic conductor at $700 \text{ }^\circ\text{C}$ [24].

Fig. 5 shows the I - V - P curve of $\text{Sn}_{0.95}\text{Ga}_{0.05}\text{P}_2\text{O}_7/\text{KPO}_3$ at $700 \text{ }^\circ\text{C}$. From Fig. 5, the relationship between current density and voltage is a straight line. Usually, the open circuit voltage decreases with the increase of test temperature. The open circuit voltage is 1.08 V in our test, which is slightly less than that of the theoretical value at $700 \text{ }^\circ\text{C}$. This shows that a proper amount of metaphosphate combined with $\text{Sn}_{0.95}\text{Ga}_{0.05}\text{P}_2\text{O}_7$ can not only improve the density, but also increase the fuel cell performance of

the composite. The maximum current density and power density of $\text{Sn}_{0.95}\text{Ga}_{0.05}\text{P}_2\text{O}_7/\text{KPO}_3$ are $136 \text{ mA}\cdot\text{cm}^{-2}$ and $87 \text{ mW}\cdot\text{cm}^{-2}$ at 700°C , respectively.

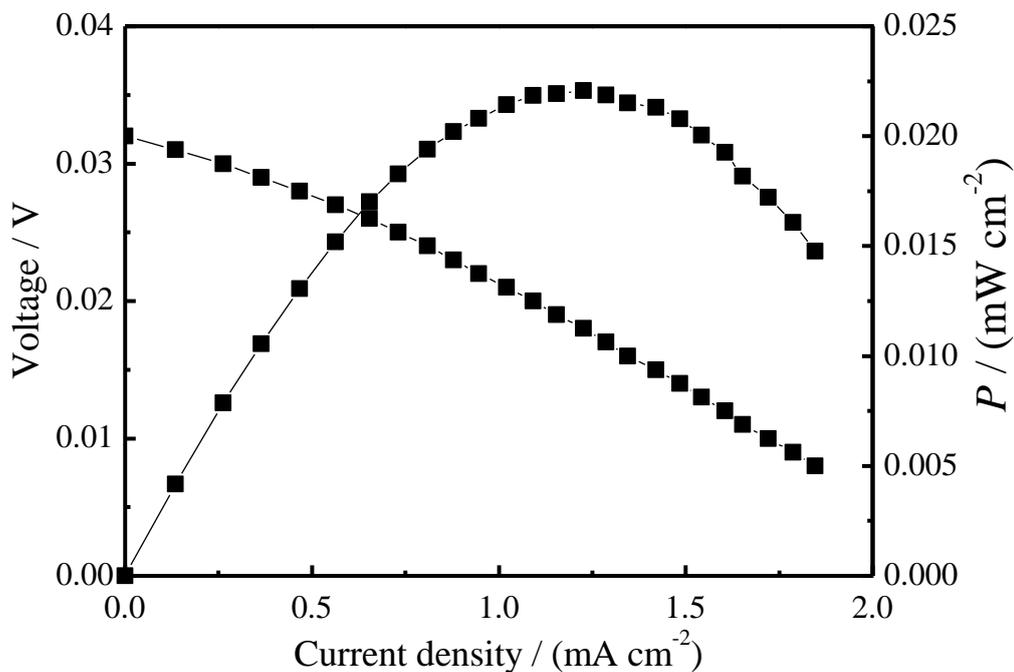


Figure 4 Oxygen concentration discharge cell of $\text{Sn}_{0.95}\text{Ga}_{0.05}\text{P}_2\text{O}_7/\text{KPO}_3$ at 700°C .

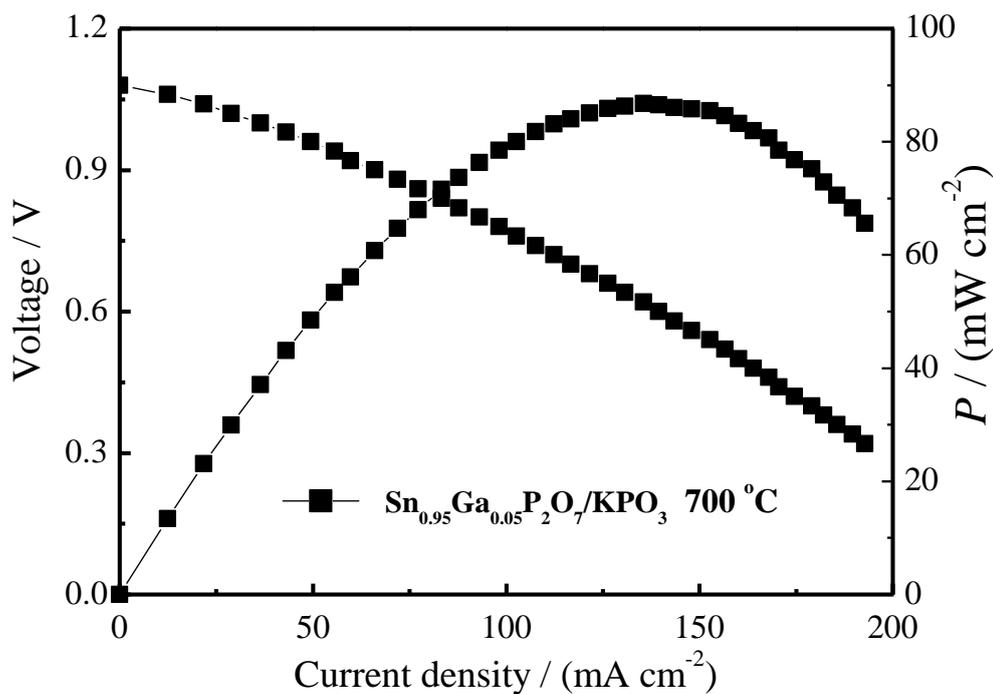


Figure 5. *I-V-P* curve of $\text{Sn}_{0.95}\text{Ga}_{0.05}\text{P}_2\text{O}_7/\text{KPO}_3$ at 700°C .

4. CONCLUSIONS

In this study, K_2CO_3 was compounded with 5 mol% Ga^{3+} -doped SnP_2O_7 to synthesize a stannic pyrophosphate / corresponding metaphosphate composite electrolyte. The SEM photos showed that the composite electrolyte was compact, without obvious pores. The oxygen concentration discharge cell result showed that $Sn_{0.95}Ga_{0.05}P_2O_7/KPO_3$ was a good oxide ionic conductor. The maximum current density and power density of $Sn_{0.95}Ga_{0.05}P_2O_7/KPO_3$ were $136 \text{ mA}\cdot\text{cm}^{-2}$ and $87 \text{ mW}\cdot\text{cm}^{-2}$ at $700 \text{ }^\circ\text{C}$, respectively.

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CONFLICTS OF INTEREST

The authors declare no conflicts of interest.

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