Characterization and electrical properties of a novel Sn_{0.9}Cu_{0.1}P_{2}O_{7}/KPO_{3} composite electrolyte for intermediate temperature solid oxide fuel cells

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In this study, 10 mol% Cu^{2+}-doped SnP_{2}O_{7} was compounded with K_{2}CO_{3} to prepare Sn_{0.9}Cu_{0.1}P_{2}O_{7}/KPO_{3} composite electrolyte. The structure, morphology and medium temperature electrical properties of Sn_{0.9}Cu_{0.1}P_{2}O_{7}/KPO_{3} were investigated. The Raman spectrometer result showed that Sn_{0.9}Cu_{0.1}P_{2}O_{7}/KPO_{3} was composed of pyrophosphate and metaphosphate groups. The maximum conductivity of Sn_{0.9}Cu_{0.1}P_{2}O_{7}/KPO_{3} reached 6.6×10^{-2} S·cm^{-1} at 700 °C. The maximum power density of Sn_{0.9}Cu_{0.1}P_{2}O_{7}/KPO_{3} reached to 131 mW·cm^{-2} at 700 °C.

Keywords: Pyrophosphate; Composite; Electrolyte; Conductivity; Fuel cell

1. INTRODUCTION

A fuel cell is a device which can convert the energy generated by the reaction between a fuel and oxidant into electric output in one step [1–6]. In recent years, solid oxide fuel cells (SOFCs) have attracted much attention [7–11]. Yttria doped zirconia has been widely studied and applied in solid oxide fuel cells (SOFCs). However, it must be operated at high temperatures (800–1000 °C) to obtain excellent performance. Therefore, it has become a research hotspot to explore the material systems which have superior conductivities at medium (400–700 °C) and low (100–300 °C) temperatures [12–17].

Doped pyrophosphates are considered to be appropriate materials because of their good ionic conductivities at 100–300 °C [18–20]. Singh et al. synthesized Ce_{1-x}Sr_{x}P_{2}O_{7} and analyzed conductivity at 90–230 °C [18]. Hibino et al. found that M^{n+}-doped SnP_{2}O_{7} had the highest conductivity among RP_{2}O_{7} (R = Sn, Ce and Ti) materials [19–20]. Due to the low mechanical strength of single M^{n+}-doped tin pyrophosphate, composite electrolytes made of SnP_{2}O_{7}-based materials and other compounds have been developed [21–23]. Jin et al. combined Sn_{0.95}Al_{0.05}P_{2}O_{7} with polybenzimidazole or polystyrene-b-poly(ethylene/propylene)-b-polystyrene to synthesize a composite membrane [21–22]. Singh et al.
synthesized new RP$_2$O$_7$ (R = Sn and Zr) / alkali carbonate composite electrolytes and found that Sn$_{0.9}$In$_{0.1}$P$_2$O$_7$-Li$_2$CO$_3$ had a maximum conductivity of 5.5×10$^{-2}$ S·cm$^{-1}$ at 630 °C [23]. Therefore, composite electrolytes can increase applied temperature ranges of SnP$_2$O$_7$-based materials. The ionic radius of Cu$^{2+}$ (0.073 nm) is close to that of Sn$^{4+}$ (0.069 nm). Cu$^{2+}$ doped SnP$_2$O$_7$ composite electrolyte is an interesting research area.

In this study, a novel composite electrolyte Sn$_{0.9}$Cu$_{0.1}$P$_2$O$_7$/KPO$_3$ was prepared. The structure, morphology and medium (400–700 °C) temperature electrical properties of Sn$_{0.9}$Cu$_{0.1}$P$_2$O$_7$/KPO$_3$ were investigated.

2. EXPERIMENTAL

The calculated 2.7642 g K$_2$CO$_3$, 8.1389 g SnO$_2$, 13 mL 85 % H$_3$PO$_4$ and 1.8756 g Cu(NO$_3$)$_2$ were weighed out by analytical balance. The mixture was heated until it became gray and sticky. The primary powders were pre-fired and sintered at 500 °C and 700 °C for 1 h, respectively, to obtain the Sn$_{0.9}$Cu$_{0.1}$P$_2$O$_7$/KPO$_3$ composite electrolyte.

The crystal structure of Sn$_{0.9}$Cu$_{0.1}$P$_2$O$_7$/KPO$_3$ was determined by X-ray diffraction (XRD) and Raman spectrometer. A scanning electron microscope was used to characterize the morphology of the sintered sample. In order to analyze the conductivities, Pd-Ag paste was coated on both sides of the sintered sample and it was treated at 600 °C for 0.5 h. The AC impedance spectra of Sn$_{0.9}$Cu$_{0.1}$P$_2$O$_7$/KPO$_3$ were measured by a CHI660E electrochemical analyzer with Ag wires as the conductors. The test temperature range was 400–700 °C. Finally, hydrogen and oxygen were used as fuel and oxidant to test the fuel cell performance of Sn$_{0.9}$Cu$_{0.1}$P$_2$O$_7$/KPO$_3$.

3. RESULTS AND DISCUSSION

Fig. 1 shows the Raman spectrum of Sn$_{0.9}$Cu$_{0.1}$P$_2$O$_7$/KPO$_3$. The vibration peaks displayed near 348–404 cm$^{-1}$ may be attributed to PO$_4$ tetrahedron in pyrophosphate and Cu-O-P vibration. The vibrations at 758 cm$^{-1}$ and 1095 cm$^{-1}$ belong to the symmetric stretching vibration of the bridged oxygen group P-O-P and the non-bridged oxygen group (PO$_2$) in pyrophosphate, respectively. The band at 692 cm$^{-1}$ belongs to the symmetric stretching vibration of P-O-P in metaphosphate. The strong band at 1160 cm$^{-1}$ belongs to the symmetric stretching vibration of the non-bridged oxygen group (PO$_2$) in metaphosphate [24]. The results show that Sn$_{0.9}$Cu$_{0.1}$P$_2$O$_7$/KPO$_3$ is composed of pyrophosphate and metaphosphate groups.
**Figure 1.** Raman spectrum of Sn$_{0.9}$Cu$_{0.1}$P$_2$O$_7$/KPO$_3$ composite.

**Figure 2.** XRD pattern of Sn$_{0.9}$Cu$_{0.1}$P$_2$O$_7$/KPO$_3$ composite.

Fig. 2 shows the XRD diagram of Sn$_{0.9}$Cu$_{0.1}$P$_2$O$_7$/KPO$_3$. Sn$_{0.9}$Cu$_{0.1}$P$_2$O$_7$ is listed for comparison. The diffraction peaks of Sn$_{0.9}$Cu$_{0.1}$P$_2$O$_7$ are consistent with Hibino et al. [19–20]. However, there are additional weak diffraction peaks of SnO$_2$. It can be inferred that high heat treatment causes the loss of P element [19, 25]. For Sn$_{0.9}$Cu$_{0.1}$P$_2$O$_7$/KPO$_3$, the extra peaks appearing at 26.36° and 33.84° are obvious and they come from crystalline SnO$_2$. These may be due to $2\text{H}_3\text{PO}_4 + \text{K}_2\text{CO}_3 = 3\text{H}_2\text{O} + 2\text{KPO}_3 + \text{CO}_2 \uparrow$. 

Sn$_{0.9}$Cu$_{0.1}$P$_2$O$_7$/KPO$_3$ composite.
and \( \text{SnP}_2\text{O}_7 + \text{K}_2\text{CO}_3 = \text{SnO}_2 + 2\text{KPO}_3 + \text{CO}_2 \uparrow \) chemical reactions in the synthesis process. Combined with the Raman spectrum results, most KPO\(_3\) exists among the grain boundaries of Sn\(_{0.9}\text{Cu}_{0.1}\text{P}_2\text{O}_7\) in amorphous form.

The morphology of Sn\(_{0.9}\text{Cu}_{0.1}\text{P}_2\text{O}_7/K\text{PO}_3\) is shown in Fig. 3. Fig. 3(a, b) shows that Sn\(_{0.9}\text{Cu}_{0.1}\text{P}_2\text{O}_7/K\text{PO}_3\) is densified and the grains in the composite are closely combined with each other and have a clear morphology. The distribution of grains is relatively uniform. In the sintering process at 700 °C, the amorphous potassium metaphosphate can flow among the Sn\(_{0.9}\text{Cu}_{0.1}\text{P}_2\text{O}_7\) particles, fill the gaps and densify the composite electrolyte.

![SEM photos of Sn\(_{0.9}\text{Cu}_{0.1}\text{P}_2\text{O}_7/K\text{PO}_3\) composite](image1)

*Figure 3.* The external and cross-sectional SEM photos of Sn\(_{0.9}\text{Cu}_{0.1}\text{P}_2\text{O}_7/K\text{PO}_3\) (a, b).

Fig. 4 shows the log (\(\sigma\)T) ~ 1000 T\(^{-1}\) curves of Sn\(_{0.9}\text{Cu}_{0.1}\text{P}_2\text{O}_7/K\text{PO}_3\) in air from 400 °C to 700 °C and the reported samples [26–27]. From Fig. 4, the conductivities of Sn\(_{0.9}\text{Mg}_{0.1}\text{P}_2\text{O}_7\) (after sintered at 600 °C) at 50–250 °C are higher than those of Sn\(_{0.92}\text{In}_{0.08}\text{P}_2\text{O}_7\) (after sintered at 1000 °C) at 300–700 °C [26–27]. The result shows that high sintering temperature (1000 °C) results in the deficiency of \(\text{P}_2\text{O}_7^4\) in Sn\(_{0.92}\text{In}_{0.08}\text{P}_2\text{O}_7\) which hinders the long-range ordered conduction of ions [19]. However, there is a turning point in the Arrhenius curve of Sn\(_{0.9}\text{Mg}_{0.1}\text{P}_2\text{O}_7\) at 150 °C. This shows that the electronic conductivity increases and the stability decreases in Sn\(_{0.9}\text{Mg}_{0.1}\text{P}_2\text{O}_7\) above 150 °C. The conductivities of Sn\(_{0.9}\text{Cu}_{0.1}\text{P}_2\text{O}_7/K\text{PO}_3\) are higher than those of single Sn\(_{0.7}\text{P}_2\text{O}_7\)-based electrolytes in the temperature range of 400-700 °C [26–27]. 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 Sn$_{0.9}$Cu$_{0.1}$P$_2$O$_7$/KPO$_3$ reached 6.6×10$^{-2}$ S·cm$^{-1}$ at 700 °C.

**Figure 4.** The log (σT) ~ 1000 T$^{-1}$ curves of Sn$_{0.9}$Mg$_{0.1}$P$_2$O$_7$ (after sintered at 600 °C), Sn$_{0.9}$Cu$_{0.1}$P$_2$O$_7$/KPO$_3$ (after sintered at 700 °C) and Sn$_{0.92}$In$_{0.08}$P$_2$O$_7$ (after sintered at 1000 °C).

**Figure 5.** H$_2$/O$_2$ fuel cell performance of Sn$_{0.9}$Cu$_{0.1}$P$_2$O$_7$/KPO$_3$ at 700 °C.

Fig. 5 shows the H$_2$/O$_2$ fuel cell performance of Sn$_{0.9}$Cu$_{0.1}$P$_2$O$_7$/KPO$_3$ at 700 °C. It can be seen from Fig. 5 that the $I$-$V$ curve is basically straight, indicating that there is no electrode polarization and the microstructure of the electrode meets the requirements. The open circuit voltage is above 1.0 V,
indicating that Sn_{0.9}Cu_{0.1}P_2O_7/KPO_3 is basically airtight at 700 °C. The H_2/O_2 fuel cell using Sn_{0.9}Cu_{0.1}P_2O_7/KPO_3 as electrolyte obtains the maximum power density of 131 mW·cm^{-2} at 700 °C. The value is higher than those of Sn_{0.91}Ga_{0.09}P_2O_7 [25], Sn_{0.9}Mg_{0.1}P_2O_7 [28] and Sn_{0.94}Sc_{0.06}P_2O_7 [29] under the same conditions (Table 1). The results show that the performance of Sn_{0.9}Cu_{0.1}P_2O_7/KPO_3 is good [30].

Table 1. The highest power densities of Sn_{0.9}Cu_{0.1}P_2O_7/KPO_3 and similar electrolytes in the literatures.

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Highest power densities</th>
</tr>
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<tbody>
<tr>
<td>Sn_{0.9}Cu_{0.1}P_2O_7/KPO_3</td>
<td>131 mW·cm^{-2}, 700 °C, 1.2 mm in this work</td>
</tr>
<tr>
<td>Sn_{0.91}Ga_{0.09}P_2O_7</td>
<td>22.1 mW·cm^{-2}, 175 °C, 1.45 mm [25]</td>
</tr>
<tr>
<td>Sn_{0.9}Mg_{0.1}P_2O_7</td>
<td>105 mW·cm^{-2}, 150 °C, 1.0 mm [28]</td>
</tr>
<tr>
<td>Sn_{0.94}Sc_{0.06}P_2O_7</td>
<td>25 mW·cm^{-2}, 150 °C, 1.7 mm [29]</td>
</tr>
</tbody>
</table>

4. CONCLUSIONS

In this study, a facile K_2CO_3 salt was compounded with 10 mol% Cu^{2+}-doped SnP_2O_7 to synthesize Sn_{0.9}Cu_{0.1}P_2O_7/KPO_3. The Raman spectrometer and X-ray diffraction indicated that the main structure was SnP_2O_7 phase and most KPO_3 existed among the grain boundaries of Sn_{0.9}Cu_{0.1}P_2O_7 in amorphous form. The SEM photos showed that Sn_{0.9}Cu_{0.1}P_2O_7 and KPO_3 was densified and combined with each other during the sintering process. The maximum power density of Sn_{0.9}Cu_{0.1}P_2O_7/KPO_3 reached 131 mW·cm^{-2} at 700 °C.

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CONFLICTS OF INTEREST

The authors declare no conflicts of interest.

References


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