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Electrical conduction of dense Ga^{3+}-doped SnP_2O_7–SnO_2 composite ceramic at intermediate temperatures

Hongtao Wang*, Lin Sun, Jitang Chen, Chunhua Luo, Suhua Fan

College of Chemistry and Chemical Engineering, Fuyang Teachers College, Anhui Provincial Key Laboratory for Degradation and Monitoring of Pollution of the Environment, Fuyang 236041, China

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Abstract

A dense Ga^{3+}-doped SnP_2O_7–SnO_2 composite ceramic (9 mol% Ga^{3+}) was prepared by reacting a porous 9 mol% Ga^{3+}-doped SnO_2 substrate with an 85% H_3PO_4 solution at 600 °C. The XRD result confirmed that an SnP_2O_7 phase grows on the internal surface of the SnO_2 substrate. The highest conductivity was observed in dry air atmosphere at 350 °C to be 2.26×10^{-2} S cm^{-1} and in wet air atmosphere at 275 °C to be 3.79×10^{-2} S cm^{-1},. The lg $\sigma \sim$ lg (p_{O_2}) plot result indicated that the composite ceramic was almost a pure ionic conductor under high oxygen partial pressure and a mixed conductor of ion and electron under low oxygen partial pressure.

Keywords: Tin pyrophosphate; Composite ceramic; Conductivity; Electrolyte

1. Introduction

Solid oxide fuel cells (SOFCs) can convert directly fuels to electrical power with high energy efficiency and little pollution [1–3]. The most commonly used electrolyte for SOFCs was yttria-stabilized zirconia (YSZ) [1]. However, YSZ requires high temperature operation, which can lead to complex problems such as electrode sintering, interfacial diffusion between electrolyte and electrodes, and the stability of bonding materials at elevated temperatures. Thus, great efforts of research activities were dedicated to develop new electrolyte with high ionic conductivities in the temperature range of 100–600 °C [4–6]. In recent papers, a new type intermediate temperature protonic conductor, metal pyrophosphates (MP_2O_7, M=Sn, Ti, Si, Ce, Ge and Zr), have been proposed [7–11]. As compared to YSZ, the use of MP_2O_7-based electrolytes present the advantages of high ionic conductivities, leading to the reduction of the operating temperature of the cell. Among the reported metal pyrophosphates, the acceptor doped SnP_2O_7 has the highest proton conductivity ($> 10^{-2}$ S cm^{-1}) and potential applications in fuel cell, direct oxidation of methane to methanol, and gas sensors, etc. [12–15].

Unfortunately, in previous reports, the acceptor doped SnP_2O_7 was almost prepared by merely pressing SnP_2O_7 powder into pellet and the heat-treating temperature was below 700 °C. It may be ascribed to phosphates were transformed to other forms of phosphates by hydrolysis and dehydration reactions at elevated temperatures [16]. On the other hand, the relative densities of obtained SnP_2O_7 pellets were much lower than traditional ceramics, e.g. YSZ, doped CeO_2, etc. A new process for preparing the dense composite ceramic was proposed [17–19]. Recently, Hibino et al. prepared dense SnP_2O_7–SnO_2 composite ceramics doped with different divalent and trivalent cations (5 mol% Y^{3+}, In^{3+}, La^{3+}, Sm^{3+}, Er^{3+}, Gd^{3+}, Mg^{2+}, Sc^{3+} and Ga^{3+}), which exhibited relatively high proton conductivities in the temperature range of 100–600 °C [17,18]. Performance of H_2/air fuel cell in Mg^{2+}-doped SnP_2O_7–SnO_2 composite ceramic (5 mol% Mg^{2+}) was also reported by Ma et al. [19]. Ma et al. also reported the overall conductivity of $Sn_{1-x}Ga_xP_2O_7$ and the highest conductivities were observed for the sample of $x=0.09$ to be 4.6×10^{-2} S cm^{-1} in wet H_2 and 2.9×10^{-2} S cm^{-1} in dry air at 175 °C, respectively [20].

Therefore, it is necessary to investigate Ga^{3+}-doped SnP_2O_7–SnO_2 composite ceramic (9 mol% Ga^{3+}). In this report, we demonstrated successful low temperature synthesis of the composite ceramic by reacting a porous 9 mol% Ga^{3+}-doped

*Corresponding author. Tel.: +86 558 2596249; fax: +86 558 2596703.
E-mail address: hongtaoking3@126.com.cn (H. Wang).

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SnO_2 substrate with an 85% H_3PO_4 solution at 600 °C, investigated the morphological and structural characteristics of the composite ceramic using SEM and XRD. Its electrochemical properties were investigated using some electrochemical methods at intermediate temperatures (100–400 °C).

2. Experimental

2.1. Preparation and characterization of the composite ceramic

The Ga^{3+}-doped SnP_2O_7–SnO_2 composite ceramic (9 mol% Ga^{3+}) was prepared through a route analogous to that reported by Ma [19] and Hibino et al. [17,18]. SnO_2 (Luoyang Ship Material Research Institute, 50–70 nm), Ga_2O_3 (99.9%) and additional 1.5 mol% CuO as a sintering aid [21] were fully mixed. After agitation for a given time, 10 wt% starch was added as the pore former. The mixture was ground with agate balls at 150 rpm for 6 h. Further heat treatment at 1150 °C in air for 5 h was applied to form a porous 9 mol% Ga^{3+}-doped SnO_2 substrate. Finally, a dense Ga^{3+}-doped SnP_2O_7–SnO_2 composite ceramic (9 mol% Ga^{3+}) was synthesized by reacting concentrated phosphoric acid with porous Ga^{3+}-doped SnO_2 substrate and heat-treating at lower temperature (600 °C).

X-ray diffraction (XRD) was measured with a Panalytical X' Pert Pro MPD diffractometer with Ni filter using Cu K_α radiation ($\lambda = 0.15418$ nm) after polishing the composite ceramic surface. The micrograph of the composite ceramic was taken by a scanning electron microscope (SEM).

2.2. Electrochemical measurements

For the electrochemical determinations, the dense composite ceramic was made into thin disc of 16.1 mm in diameter and a thickness of 1.2 mm. Platinum paste was smeared on both sides (area: 0.5 cm^2) of the composite ceramic which acted as electrodes, then, heated at 400 °C for 30 min. The conductivity was measured by an AC impedance method over the frequency range from 1 Hz to 3 MHz in dry and wet air atmospheres using electrochemical workstations (Zahner IM6ex) in the temperature range of 100–400 °C. The conductivity as the function of oxygen partial pressure (p_{O_2}) was measured in the p_{O_2} range of $1–10^{-20}$ atm. The p_{O_2} was accommodated by commixing O_2, air, N_2, H_2O and H_2 in proper ratio, and measured using an oxygen sensor on line.

3. Results and discussion

3.1. Structure of the composite ceramic

The XRD pattern of the composite ceramic was shown in Fig. 1. In Fig. 1, diffraction peaks of SnO_2 (JCPDS 01-077-0452) and SnP_2O_7 (JCPDS 00-029-1352) were obvious. The diffraction peaks at 19.4°, 22.5°, 25.2°, 27.6°, 32.0° and 37.7° for SnP_2O_7 in the composite indicated that 9 mol% Ga^{3+}-doped SnO_2 substrate partially reacted with concentrated phosphoric acid, leading to the formation of SnP_2O_7 in the internal of the substrate [17–19].

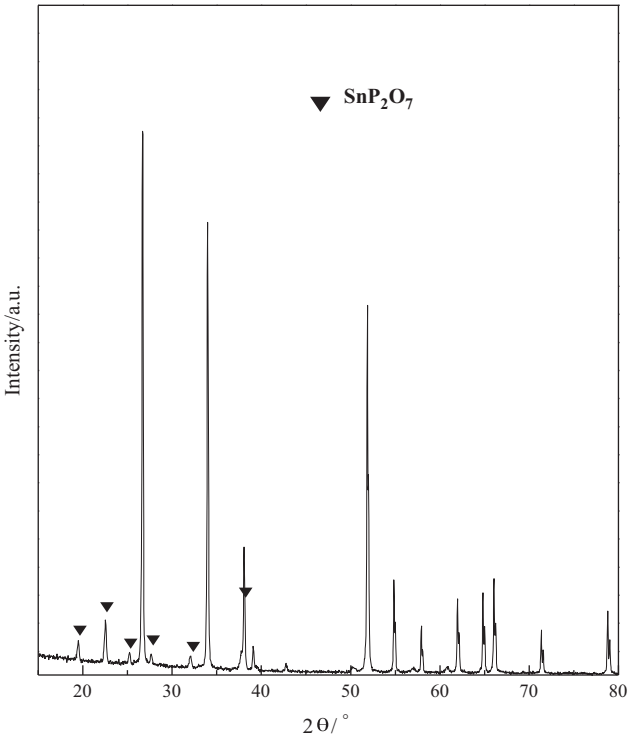

Fig. 1. XRD pattern of the composite ceramic.

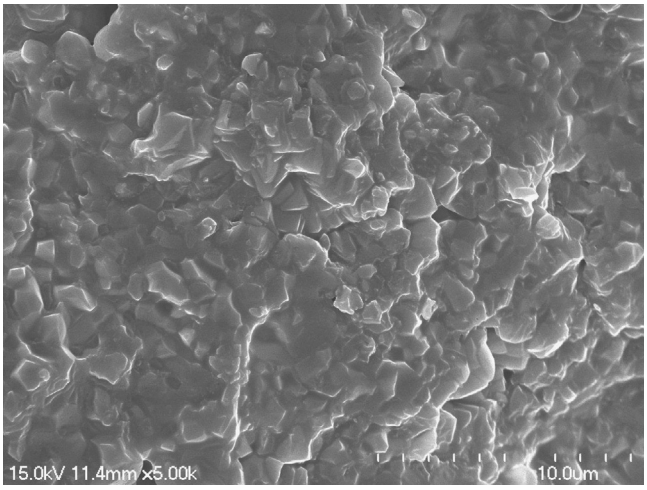

Fig. 2. The cross-sectional SEM image of the composite ceramic.

3.2. SEM image

Fig. 2 displayed cross-sectional SEM image in the center of the composite ceramic. The result of SEM analysis indicated that the composite ceramic is very dense. The density of the composite ceramic is 4.23 g cm^{-3}, which is higher than the theoretical density of SnP_2O_7 (3.79 g cm^{-3}) and lower than the theoretical density of SnO_2 (6.92 g cm^{-3}). This can be explained by two major differences of the molar volume between SnP_2O_7 (76.4 cm^3 mol^{-1}) and SnO_2 (21.6 cm^3 mol^{-1}). Since the molar

volume of SnP_2O_7 is larger than that of SnO_2, the high density of the composite ceramic is expected after porous substrate reacted with phosphoric acid. [17,18] It is evident from the XRD in Fig. 1 that it can be assigned to SnO_2 and SnP_2O_7.

3.3. Conductivity measurements

Fig. 3 showed Arrhenius plots of the total conductivities of the sample in dry and wet air atmospheres at 100–400 °C. The conductivities roughly increased from 100 to 300 °C. The highest conductivities were observed to be 2.26×10^{-2} S cm^{-1} in dry air atmosphere at 350 °C and 3.79×10^{-2} S cm^{-1} in wet air atmosphere at 275 °C which is similar to the previous reports [17,18]. It can also be seen from Fig. 3 that the conductivity in water vapor-saturated air atmosphere is higher than that in corresponding gas without water vapor. This may be interpreted in terms of defect chemistry. When water vapor is introduced, as shown in Eqs. (1) and (2), the conduction convered from electron hole and oxygen vacancy to protonic conduction. The long-range mobility of proton is much easier than oxygen ion and electron hole, thus the conductivity in wet air is higher than in dry air [22].

$$H_2O(g)+V_O+O_o^{\times}\Leftrightarrow 2OH_O^{\bullet} \quad (1)$$

$$H_2O(g)+2h^{\bullet}+2O_o^{\times}\Leftrightarrow 2OH_O^{\bullet}+1/2O_2 \quad (2)$$

The p_{H_2O} dependency of the total conductivity of the composite ceramic was carried out with the change of the water vapor concentration. Fig. 4 showed that the total conductivity increased with increasing water vapor concentration. The observation can be explained using Eqs. (1) and (2). The increase in water vapor concentration shifts the Eqs. (1) and (2) toward the right side, resulting in an increase of the proton concentration in the composite ceramic [22].

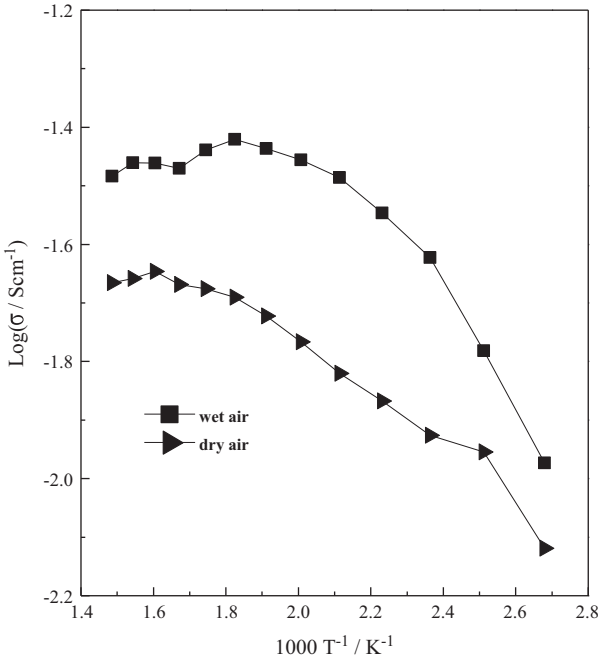

Fig. 3. Temperature dependence of electrical conductivity of the composite ceramic in dry and wet air atmospheres at 100–400 °C.

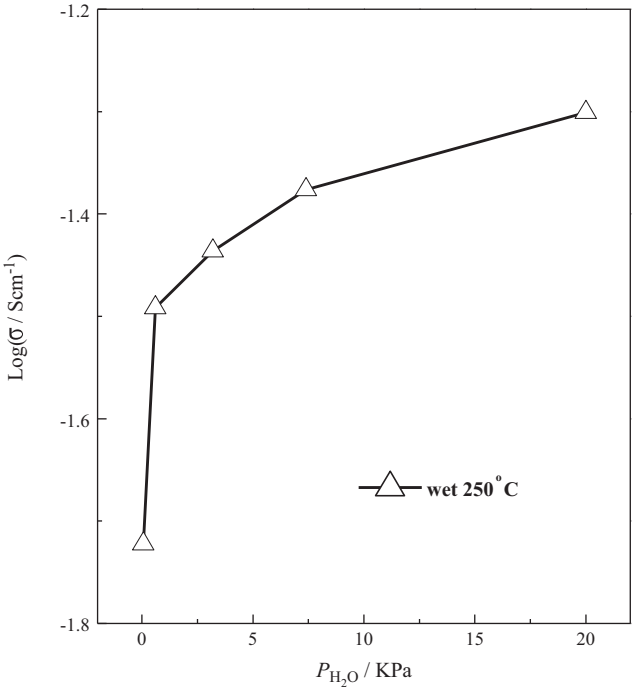

Fig. 4. The total conductivity of the composite ceramic as a function of p_{H_2O} in wet air atmosphere at 250 °C.

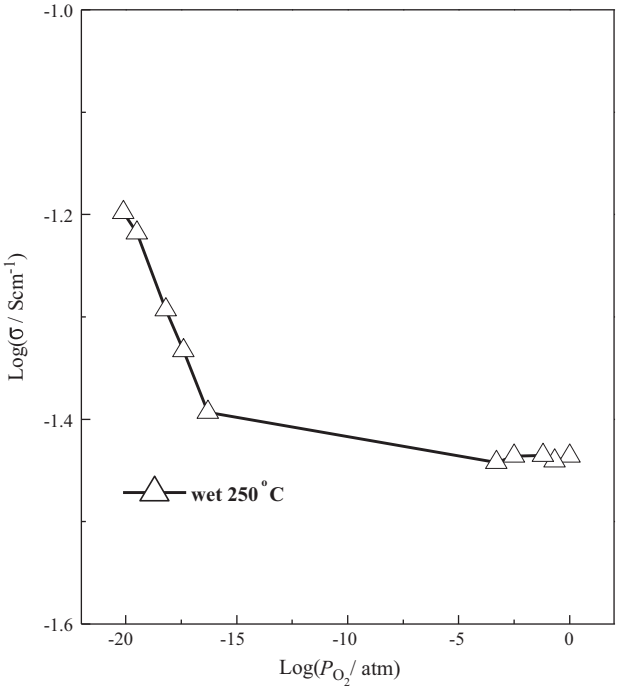

Fig. 5. Dependence of conductivity of the composite ceramic on oxygen partial pressure.

In order to investigate the ionic conductivity of the composite ceramic, the relationship between the conductivity and the oxygen partial pressure ($p_{O_2}=10^{-20}\sim$ atm) was

measured. Fig. 5 showed the plot of lg $\sigma \sim$ lg (p_{O_2}) in wet air atmosphere at 250 °C. It is clear that the conductivity is almost independent of p_{O_2}, confirming that the composite ceramic is almost a pure ion conductor at high oxygen partial pressure range. At low oxygen partial pressure range, the total conductivity increased with the increasing oxygen partial pressure, indicating that it is a mixed conductor of ion and electron. This may be due to the reduction of Sn^{4+} to Sn^{2+} to a certain extent at low oxygen partial pressure range [23].

4. Conclusions

In this study, a dense Ga^{3+}-doped SnP_2O_7–SnO_2 composite ceramic (9 mol% Ga^{3+}) was prepared by reacting a porous 9 mol% Ga^{3+}-doped SnO_2 substrate with an 85% H_3PO_4 solution at 600 °C, The heat-treated temperature is much lower than the conventional sintering temperature (about 1200 °C). The result of SEM image indicated that the composite ceramic is very dense. The lg $\sigma \sim$ lg (p_{H_2O}) plot result showed that the total conductivity increased with increasing water vapor concentration. The lg $\sigma \sim$ lg (p_{O_2}) plot result indicated that the composite ceramic was almost a pure ionic conductor under high oxygen partial pressure and a mixed conductor of ion and electron under low oxygen partial pressure.

Acknowledgments

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