Preparation, Chemical Compatibility and Particle Size of PrBaCo$_2$O$_{5+\delta}$-Ce$_{0.8}$Sm$_{0.2}$O$_{1.9}$ Composite Cathode Powder

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Abstract. The PrBaCo$_2$O$_{5+\delta}$ cathode powder was prepared by solid-state reaction using Pr$_6$O$_{11}$, BaCO$_3$, Co$_2$O$_3$ and Fe$_2$O$_3$ as starting materials, and calcined at 1000°C, 1100°C, 1200°C and 1300°C for 2h in air, respectively. Their crystal structures were analyzed to obtain the optimal temperature of solid-state reaction for PrBaCo$_2$O$_{5+\delta}$. The equal amount of PrBaCo$_2$O$_{5+\delta}$ calcined at optimal temperature and Ce$_{0.8}$Sm$_{0.2}$O$_{1.9}$ electrolyte powder were ball-milled and then calcined to prepare composite cathode powder for intermediate-temperature solid oxide fuel cells. Crystal structure was identified by X-ray diffraction, to investigate the chemical compatibility between them. According to the experimental results, the optimal temperature of solid-state reaction for PrBaCo$_2$O$_{5+\delta}$ is about 1300°C, PrBaCo$_2$O$_{5+\delta}$ is chemically stable with Ce$_{0.8}$Sm$_{0.2}$O$_{1.9}$, and the medium diameter D$_{50}$ of PrBaCo$_2$O$_{5+\delta}$-Ce$_{0.8}$Sm$_{0.2}$O$_{1.9}$ powder is about 14.41 μm.

1. Introduction

As an all solid-state power conversion device with high efficiency and environmental compatibility, solid oxide fuel cells (SOFCs) produce electrical energy and heat by electrochemically combining fuel gas and oxidizing gas without involving the fuel’s combustion [1-3]. Intermediate-temperature SOFCs (IT-SOFCs) have several advantages compared with conventional SOFCs operated at up to 1000°C, such as extending the selection of electrode and electrolyte materials, improving compatibility of components and reducing fabrication cost, and represent the research mainstream in the realm of SOFCs [4-8].

Cathode is the main component of IT-SOFCs operated in oxidizing environment and participates in the process of oxygen reduction reaction [9, 10]. Oxygen at porous cathode reacts with electrons to form oxygen ions, and then oxygen ions diffuse in the cathode to cathode-electrolyte interface and migrate to the anode through the oxide-ion conducting and dense electrolyte. At the anode, oxygen ions combine with fuel gas to form H$_2$O and/or CO$_2$ and release electrons. The electrons flow through external circuit to the cathode [1, 11-13]. Since cathode losses dominate the performance of cell [1, 14], the development of high performance cathode remains a main research hotspots.

Mixed electronic-ionic conducting and double-layered perovskite structural oxides, LnBaCo$_2$O$_{5+\delta}$ (Ln=La, Pr, Gd, Sm, Y, et al) have received widespread investigation as potential cathodes for IT-SOFCs [15-18]. The structure can be represented by CoO$_2$[LnO$_3$CoO$_2$]BaO based on the ABO$_3$...
perovskite-type structure. The replacing of A-sites with lanthanide and alkaliearth planes transform the original simple cubic perovskite to a layered crystal, which reduce the strength of oxygen binding and improve the oxygen ion transport ability and catalytic activity for oxygen reduction compared with the ABO$_3$ perovskite-type oxides [19, 20].

This study aims to obtain the optimal temperature of solid-state reaction for PrBaCo$_2$O$_{5+\delta}$ cathode powder and investigate the chemical compatibility between PrBaCo$_2$O$_{5+\delta}$ and Ce$_{0.8}$Sm$_{0.2}$O$_{1.9}$ electrolyte powder. The particle size distribution of PrBaCo$_2$O$_{5+\delta}$-Ce$_{0.8}$Sm$_{0.2}$O$_{1.9}$ composite cathode powder was identified by laser particle size analyzer.

2. Experimental
PrBaCo$_2$O$_{5+\delta}$ powder was synthesized by the conventional solid-state reaction method. The raw materials of Pr$_6$O$_{11}$, BaCO$_3$, Co$_2$O$_3$ and Fe$_2$O$_3$ were calculated and weighted according to the stoichiometry of PrBaCo$_2$O$_{5+\delta}$ and then ball-milled for 8h (the milling speed is 400r/min) in the distilled water, using silicon dioxide ball as milling media (Raw materials, distilled water and ball with mass ratio of 1:2:2). After dried and screened, the mixed powders were calcined at 1000℃, 1100℃, 1200℃ and 1300℃ for 2h in air, respectively. The crystal structures were determined by XRD using the diffractometer (D8 ADVANCE, Bruker, Germany) with Cu Ka radiation to obtain the optimal temperature of solid-state reaction. The diffraction angle was 20° to 80° with a step size of 0.05°.

Ce$_{0.8}$Sm$_{0.2}$O$_{1.9}$ electrolyte powder was synthesized by the same method with commercially available chemicals of Sm$_2$O$_3$ and CeO$_2$, and calcined at 1200℃ for 2h in air.

The PrBaCo$_2$O$_{5+\delta}$ powder calcined at optimal temperature and Ce$_{0.8}$Sm$_{0.2}$O$_{1.9}$ powder in the same weight ratio were ball-milled for 8h. After dried and screened, the mixed powder was calcined to prepare PrBaCo$_2$O$_{5+\delta}$-Ce$_{0.8}$Sm$_{0.2}$O$_{1.9}$ composite cathode powder. Crystal structure was identified by XRD using the diffractometer, to investigate the compatibility between them. The particle size distribution was identified by laser particle size analyzer (BT-9300H, Dandong, China).

3. Results and discussion
Figure 1 shows the XRD patterns of ball-milled powder calcined at different temperatures in air. The diffraction peaks of PrBaCo$_2$O$_{5+\delta}$ and same impurity peaks were identified when the calcination temperatures are 1000℃ and 1100℃ and their peak intensity was relatively low. The impurity peaks can be attributed to the raw materials and intermediate phases during the solid-state reaction, proving that the reaction is still ongoing. When the calcination temperature increased to 1200℃, a slight increase in the peak intensity of the PrBaCo$_2$O$_{5+\delta}$ phase was observed and the impurity peaks intensity is lower than that at 1000℃ and 1100℃, indicating that the solid-state reaction is not finished. It can be seen from the pattern that a pure-phase oxide of PrBaCo$_2$O$_{5+\delta}$ was identified without any detectable impurity phases when calcined at 1300℃ for 2h in air. The PrBaCo$_2$O$_{5+\delta}$ formed the double-layered perovskite structure after the calcinations at 1300℃ for 2h, and the optimal temperature of solid-state reaction for PrBaCo$_2$O$_{5+\delta}$ is about 1300℃.

![Figure 1. XRD patterns of powder calcined at 1000℃, 1100℃, 1200℃ and 1300℃ for 2h.](attachment:figure1.png)
Figure 2 shows the XRD pattern of the PrBaCo$_2$O$_{5+\delta}$-Ce$_{0.8}$Sm$_{0.2}$O$_{1.9}$ powder calcined at 1300°C for 2h in air. All the diffraction peaks of mixed powder correspond to the PrBaCo$_2$O$_{5+\delta}$ and Ce$_{0.8}$Sm$_{0.2}$O$_{1.9}$ phases without any new phases were obtained. The PrBaCo$_2$O$_{5+\delta}$ and Ce$_{0.8}$Sm$_{0.2}$O$_{1.9}$ remained their structures unchanged, and the absence of peaks shift was observed. It seems reasonable to conclude that there was no serious interface reaction appeared between them and the PrBaCo$_2$O$_{5+\delta}$ and Ce$_{0.8}$Sm$_{0.2}$O$_{1.9}$ show good chemical compatibility at a temperature much higher than the working temperature of IT-SOFCs.

Figure 2. XRD pattern of PrBaCo$_2$O$_{5+\delta}$-Ce$_{0.8}$Sm$_{0.2}$O$_{1.9}$ powder calcined at 1300°C for 2h.

Figure 3 shows the particle size distribution of PrBaCo$_2$O$_{5+\delta}$-Ce$_{0.8}$Sm$_{0.2}$O$_{1.9}$ composite powder. It can be seen that the cumulation mass is 4.65% when the particle size is 2.0μm, and the cumulation mass increased with increasing particle size. The cumulation mass is 62.81% and 92.52% when the particle size reached 20.0μm and 45.0μm, respectively. The particle size distribution is narrow and within the range of 2μm to 25μm. The medium diameter $D_{50}$ and specific surface area of PrBaCo$_2$O$_{5+\delta}$-Ce$_{0.8}$Sm$_{0.2}$O$_{1.9}$ powder are about 14.41μm and 398.3m$^2$/kg.

Figure 3. The particle size distribution of PrBaCo$_2$O$_{5+\delta}$-Ce$_{0.8}$Sm$_{0.2}$O$_{1.9}$ powder.

4. Conclusions

The optimal temperature of solid-state reaction for PrBaCo$_2$O$_{5+\delta}$ using Pr$_6$O$_{11}$, BaCO$_3$, Co$_2$O$_3$ and Fe$_2$O$_3$ as starting materials is about 1300°C. The PrBaCo$_2$O$_{5+\delta}$ cathode powder and Ce$_{0.8}$Sm$_{0.2}$O$_{1.9}$ electrolyte powder show good chemical compatibility at a temperature much higher than the working temperature of IT-SOFCs. The PrBaCo$_2$O$_{5+\delta}$-Ce$_{0.8}$Sm$_{0.2}$O$_{1.9}$ composite cathode powder were prepared by mechanical mixing method, and its particle size distribution is narrow. The medium diameter $D_{50}$ and specific surface area of PrBaCo$_2$O$_{5+\delta}$-Ce$_{0.8}$Sm$_{0.2}$O$_{1.9}$ powder are about 14.41μm and 398.3m$^2$/kg.
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