

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

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Abstract. The $\text{PrBaCo}_2\text{O}_{5+\delta}$ cathode powder was prepared by solid-state reaction using Pr_6O_{11} , BaCO_3 , Co_2O_3 and Fe_2O_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 $\text{PrBaCo}_2\text{O}_{5+\delta}$. The equal amount of $\text{PrBaCo}_2\text{O}_{5+\delta}$ calcined at optimal temperature and $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$ 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 $\text{PrBaCo}_2\text{O}_{5+\delta}$ is about 1300°C, $\text{PrBaCo}_2\text{O}_{5+\delta}$ is chemically stable with $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$, and the medium diameter D_{50} of $\text{PrBaCo}_2\text{O}_{5+\delta}$ - $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$ 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_2O 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, $\text{LnBaCo}_2\text{O}_{5+\delta}$ ($\text{Ln}=\text{La, Pr, Gd, Sm, Y, et al}$) have received widespread investigation as potential cathodes for IT-SOFCs [15-18]. The structure can be represented by $\text{CoO}_2|\text{LnO}_8|\text{CoO}_2|\text{BaO}$ 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 $\text{PrBaCo}_2\text{O}_{5+\delta}$ cathode powder and investigate the chemical compatibility between $\text{PrBaCo}_2\text{O}_{5+\delta}$ and $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$ electrolyte powder. The particle size distribution of $\text{PrBaCo}_2\text{O}_{5+\delta}$ - $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$ composite cathode powder was identified by laser particle size analyzer.

2. Experimental

$\text{PrBaCo}_2\text{O}_{5+\delta}$ powder was synthesized by the conventional solid-state reaction method. The raw materials of Pr_6O_{11} , BaCO_3 , Co_2O_3 and Fe_2O_3 were calculated and weighted according to the stoichiometry of $\text{PrBaCo}_2\text{O}_{5+\delta}$ 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°C, 1100°C, 1200°C and 1300°C for 2h in air, respectively. The crystal structures were determined by XRD using the diffractometer (D8 ADVANCE, Bruker, Germany) with Cu K α radiation to obtain the optimal temperature of solid-state reaction. The diffraction angle was 20 ° to 80 ° with a step size of 0.05 °.

$\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$ electrolyte powder was synthesized by the same method with commercially available chemicals of Sm_2O_3 and CeO_2 , and calcined at 1200°C for 2h in air.

The $\text{PrBaCo}_2\text{O}_{5+\delta}$ powder calcined at optimal temperature and $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$ powder in the same weight ratio were ball-milled for 8 h. After dried and screened, the mixed powder was calcined to prepare $\text{PrBaCo}_2\text{O}_{5+\delta}$ - $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$ 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 $\text{PrBaCo}_2\text{O}_{5+\delta}$ and same impurity peaks were identified when the calcination temperatures are 1000°C and 1100°C 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°C, a slight increase in the peak intensity of the $\text{PrBaCo}_2\text{O}_{5+\delta}$ phase was observed and the impurity peaks intensity is lower than that at 1000°C and 1100°C, indicating that the solid-state reaction is not finished. It can be seen from the pattern that a pure-phase oxide of $\text{PrBaCo}_2\text{O}_{5+\delta}$ was identified without any detectable impurity phases when calcined at 1300°C for 2h in air. The $\text{PrBaCo}_2\text{O}_{5+\delta}$ formed the double-layered perovskite structure after the calcinations at 1300°C for 2h, and the optimal temperature of solid-state reaction for $\text{PrBaCo}_2\text{O}_{5+\delta}$ is about 1300°C.

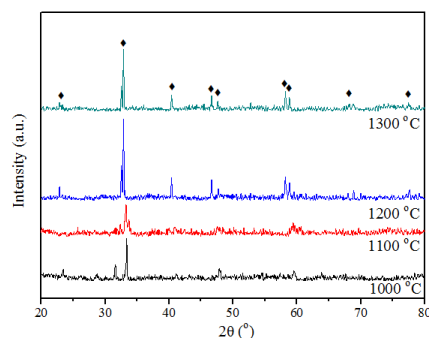


Figure 1. XRD patterns of powder calcined at 1000°C, 1100°C, 1200°C and 1300°C for 2h.

Figure 2 shows the XRD pattern of the $\text{PrBaCo}_2\text{O}_{5+\delta}\text{-Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$ powder calcined at 1300°C for 2h in air. All the diffraction peaks of mixed powder correspond to the $\text{PrBaCo}_2\text{O}_{5+\delta}$ and $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$ phases without any new phases were obtained. The $\text{PrBaCo}_2\text{O}_{5+\delta}$ and $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$ 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 $\text{PrBaCo}_2\text{O}_{5+\delta}$ and $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$ show good chemical compatibility at a temperature much higher than the working temperature of IT-SOFCs.

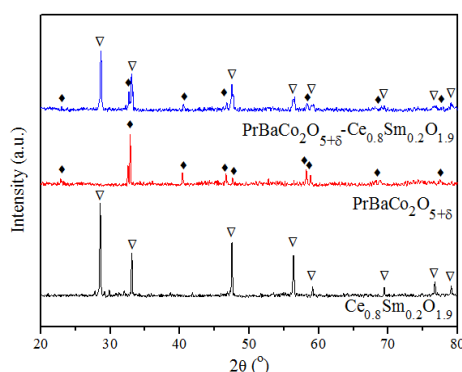


Figure 2. XRD pattern of $\text{PrBaCo}_2\text{O}_{5+\delta}\text{-Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$ powder calcined at 1300°C for 2h.

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

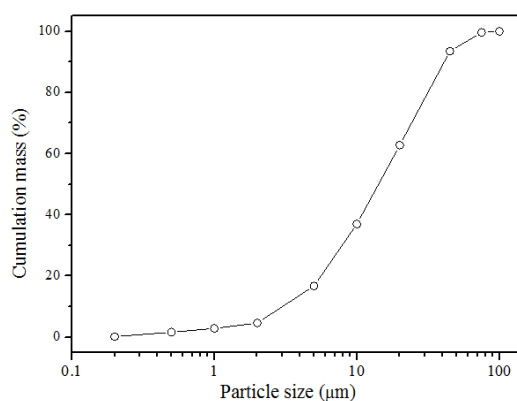


Figure 3. The particle size distribution of $\text{PrBaCo}_2\text{O}_{5+\delta}\text{-Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$ powder.

4. Conclusions

The optimal temperature of solid-state reaction for $\text{PrBaCo}_2\text{O}_{5+\delta}$ using Pr_6O_{11} , BaCO_3 , Co_2O_3 and Fe_2O_3 as starting materials is about 1300°C . The $\text{PrBaCo}_2\text{O}_{5+\delta}$ cathode powder and $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$ electrolyte powder show good chemical compatibility at a temperature much higher than the working temperature of IT-SOFCs. The $\text{PrBaCo}_2\text{O}_{5+\delta}\text{-Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$ 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 $\text{PrBaCo}_2\text{O}_{5+\delta}\text{-Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$ powder are about $14.41\mu\text{m}$ and $398.3\text{m}^2/\text{kg}$.

Acknowledgements

This project was financially supported by the Natural Science key research project of Education Department of Anhui province (KJ2018A0405) and the starting foundation of Huangshan University (2015xkj007).

References

- [1] N.Q. Minh, Ceramic fuel cells, *J. Am. Ceram. Soc.* 76(1993):563-588.
- [2] A.B. Stambouli, E. Traversa, Solid oxide fuel cells (SOFCs): a review of an environmentally clean and efficient source of energy, *Renew. Sustain. Energy Rev.* 6(2002):433-455.
- [3] R. M. Ormerod, Solid oxide fuel cells, *Chem. Soc. Rev.* 32(2003):17-28.
- [4] Y. Leng, S.H. Chan, Q. Liu, Development of LSCF–GDC composite cathodes for low-temperature solid oxide fuel cells with thin film GDC electrolyte, *Int. J. Hydrogen Energy* 33(2008):3808-3817.
- [5] S. Yoo, S. Choi, J. Kim, J. Shin, G. Kim, Investigation of layered perovskite type $\text{NdBa}_{1-x}\text{Sr}_x\text{Co}_2\text{O}_{5+\delta}$ ($x=0, 0.25, 0.5, 0.75$, and 1.0) cathodes for intermediate-temperature solid oxide fuel cells, *Electrochim. Acta* 100(2013):44-50.
- [6] Y. Cao, H. Gu, H. Chen, Y. Zheng, M. Zhou, L. Guo, Preparation and characterization of $\text{Nd}_{2-x}\text{Sr}_x\text{CoO}_{4+\delta}$ cathodes for intermediate-temperature solid oxide fuel cell, *Int. J. Hydrogen Energy* 35(2010):5594-5600.
- [7] J. Molenda, K. Świerczek, W. Zajac, Functional materials for the IT-SOFC, *J. Power Sources* 173(2007):657-670.
- [8] E.D. Wachsman, K.T. Lee, Lowering the Temperature of Solid Oxide Fuel Cells, *Science* 334(2011):935-939.
- [9] S.B. Adler, Factors Governing Oxygen Reduction in Solid Oxide Fuel Cell Cathodes, *Chem. Rev.* 104(2004):4791-4843.
- [10] H. Gu, H. Chen, L. Gao, Y. Zheng, X. Zhu, L. Guo, Electrochemical characterization of Co-doped $\text{Sr}_{0.8}\text{Ce}_{0.2}\text{MnO}_{3-\delta}$ cathodes on $\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$ -electrolyte for intermediate-temperature solid oxide fuel cells, *Electrochim. Acta* 54(2009):3532-3537.
- [11] Z. Gao, X. Liu, B. Bergman, Z. Zhao, Investigation of oxygen reduction reaction kinetics on $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ cathode supported on $\text{Ce}_{0.85}\text{Sm}_{0.075}\text{Nd}_{0.075}\text{O}_{3-\delta}$ electrolyte, *J. Power Sources* 196(2011):9195-9203.
- [12] B. Liu, Y. Zhang, L. Zhang, Oxygen reduction mechanism at $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ cathode for solid oxide fuel cell, *Int. J. Hydrogen Energy* 34(2009):1008-1014.
- [13] J. Fleig, SOLID OXIDE FUEL CELL CATHODES: Polarization Mechanisms and Modeling of the Electrochemical Performance, *Annu. Rev. Mater. Res.* 33(2003):361-382.
- [14] N.P. Brandon, S. Skinner, B.C.H. Steele, Recent Advances in Materials for Fuel Cells, *Annu. Rev. Mater. Res.* 33(2003):183-213.
- [15] E. Chavez, M. Mueller, L. Mogni1, A. Caneiro, Study of $\text{LnBaCo}_2\text{O}_{6-\delta}$ ($\text{Ln} = \text{Pr}, \text{Nd}, \text{Sm}$ and Gd) double perovskites as new cathode material for IT-SOFC, *J. Phys.: Conf. Ser.* 167(2009):1-6.
- [16] Q. Zhou, F. Wang, Y. Shen, T. He, Performances of $\text{LnBaCo}_2\text{O}_{5+x}\text{-Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$ composite cathodes for intermediate-temperature solid oxide fuel cells, *J. Power Sources* 195(2010):2174-2181.
- [17] W. Wang, T.S. Peh, S.H. Chan, T.S. Zhang, Synthesis and Characterization of $\text{LnBaCo}_2\text{O}_{5+\delta}$ Layered Perovskites as Cathodes for Intermediate-Temperature Solid Oxide Fuel Cells, *ECS Transactions* 25(2009):2277-2281.
- [18] J.H. Kim, A. Manthiram, $\text{LnBaCo}_2\text{O}_{5+\delta}$ Oxides as Cathodes for Intermediate-Temperature Solid Oxide Fuel Cells, *J. Electrochem. Soc.* 155(2008):B385-B390.
- [19] H. Gu, H. Chen, Y. Zheng, L. Guo, Effect of chromium poisoning on the electrochemical properties of $\text{NdBaCo}_2\text{O}_{5+\delta}$ cathode for IT-SOFCs, *Int. J. Hydrogen Energy* 35(2010):2457-2462.

- [20] K. Zhang, L. Ge, R. Ran, Z. Shao, Shaomin Liu, Synthesis, characterization and evaluation of cation-ordered $\text{LnBaCo}_2\text{O}_{5+\delta}$ as materials of oxygen permeation membranes and cathodes of SOFCs, *Acta Materialia* 56(2008):4876-4889.