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Layered perovskite $LnBa_{0.5}Sr_{0.5}Cu_2O_{5+\delta}$ (Ln = Pr and Nd) as cobalt-free cathode materials for solid oxide fuel cells

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ABSTRACT

Cobalt-free layered perovskite $LnBa_{0.5}Sr_{0.5}Cu_2O_{5+\delta}$ (Ln = Pr and Nd, PBSC and NBSC) powders are prepared using combined citrate and EDTA complexing method. The performance of PBSC and NBSC cathode materials are evaluated for solid oxide fuel cells (SOFCs). Two oxidation states (Cu^{2+}/Cu^{+}) for Cu ions exist in $LnBa_{0.5}Sr_{0.5}Cu_2O_{5+\delta}$ oxides. The main valence of Pr ions in PBSC is 3+. The average thermal expansion coefficients (TECs) of PBSC and NBSC are 14.2 and 14.6 × 10^{-6} K^{-1} between 30 and 950 °C, which are similar to the TECs of $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ (LSGM) intermediate-temperature electrolyte. The electrical conductivity of PBSC is slightly higher than that of NBSC. At 800 °C, the polarization resistance (R_p) values of the PBSC and NBSC cathodes on the LSGM electrolyte are 0.043 and 0.057 Ω cm^2, respectively. The electrolyte-supported single cells were prepared by using PBSC and NBSC as cathode, LSGM as electrolyte (300 μm thickness), $Ce_{0.9}Sm_{0.1}O_{1.95}$ (SDC) as interlayer and Ni/SDC as anode. At 850 °C, the maximal power densities are obtained as 681 and 651 mW cm^{-2} for PBSC and NBSC cathodes.

Introduction

In the current scenario of rapid depletion of fossil fuels and the increasing demand of energy globally, exploration of new type of green energy is the most popular and urgent topic of research [1]. As a power generation technology, solid oxide fuel cell (SOFC) system is a promising device by converting fuels directly into electrical energy in an environmentally friendly way [2]. However, high operation temperatures (850–1000 °C) of conventional SOFC are disadvantageous for their commercial application, which is mainly due to serious interface reaction, high-cost and significant performance degradation. Therefore, the main efforts turn to promote SOFC by lowering the working temperatures [3]. However, the cathode electrochemical properties will decrease rapidly when the operating temperature decreases. Thus it's critical to

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find potential cathode materials with high electrocatalytic activity and low polarization loss.

In recent years, layered perovskite-type $LnBaCo_2O_{5+\delta}$ (Ln = rare earth) mixed ionic and electronic conductors (MIEC) are deemed to the potential cathodes of intermediate temperate (IT) fuel cell. The crystal structure of $LnBaCo_2O_{5+\delta}$ oxides can be theoretically regarded as the consecutive layers $\ldots CoO_2|LnO_\delta|CoO_2|BaO\ldots$ [4,5]. Compared to the cubic perovskite structure, the oxygen bonding strength of Ln-O layer can be reduced in the layered structure and disorder-free channels for oxygen ion motion can be provided. Therefore, oxygen diffusivity is remarkably enhanced in layered perovskite-type oxides [6,7]. Kim and Manthiram have reported that the different ion radii of lanthanides have different influence on the performance of the $LnBaCo_2O_{5+\delta}$ perovskites [8]. The oxygen content (5+δ), electrical conductivity and thermal expansion coefficient (TEC) increase with the ionic radius of lanthanide metal ions increased. Among these $LnBaCo_2O_{5+\delta}$ components, $PrBaCo_2O_{5+\delta}$ cathode shows excellent electrochemical performance. For example, Zhang et al. measured the polarization resistance (R_p) of $PrBaCo_2O_{5+\delta}$ cathode on SDC electrolyte, and the value of R_p was 0.213 Ω cm^{-2} at 600 °C [7]. Nevertheless, the cobalt-based layered perovskite cathodes often encounter some problems such as high cost of cobalt element and high thermal expansion coefficients (TECs), which limits the application of cobalt-based oxide as cathode materials for SOFC.

Obviously, it is significant to develop cobalt-free cathodes with lower TECs and sufficient catalytic activity at reduced temperatures for IT-SOFCs. Several perovskite-type compounds have been reported as intermediate-temperature SOFC cathodes such as $BaFe_{0.85}Cu_{0.15}O_{3-\delta}$ [9], $Ba_{0.5}Sr_{0.5}Zn_{0.2}Fe_{0.8}O_{3-\delta}$ [10], $La_{2-x}Sr_xCuO_{4-\delta}$ [11], $Sr_2Fe_{1.5}Mo_{0.5}O_{6-\delta}$ [12] and $PrBaCuFeO_{5+\delta}$ [13]. Among of them, cobalt-free oxides with layered perovskite structure have attracted much attention because their A-sites are ordered. As mentioned earlier, the ordering A-sites are recognized to be able to greatly enhance the diffusivity of oxygen-ion in the bulk of the material by orders of magnitude, and consequently improve cathode performance. Kong et al. has reported that the average TEC for $SmBaCu_2O_{5+\delta}$ is 14.6 × 10^{-6} K^{-1}, which is much lower than that of $SmBaCo_2O_{5+\delta}$ (21.2 × 10^{-6} K^{-1}) in the same temperature range [14]. Ding et al. has synthesized layered perovskite oxide $PrBaFe_2O_{5+\delta}$, and examined as a novel cathode for proton-conductor IT-SOFCs [15]. Although these materials have shown good thermal and chemical stabilities, they have a relatively low conductivity and electrocatalytic activity for the oxygen reduction reaction (ORR) at intermediate temperatures. Therefore, further improving the electrochemical performance of cobalt-free layered perovskite cathodes is important for the successful development of IT-SOFCs.

Many efforts have been devoted to enhance the performance of layered perovskite cobalt-free cathodes by substituting with various ions. He et al. synthesized $Sm_{1-x}La_xBaFe_2O_{5+\delta}$ (SLBFO, x = 0–0.5) oxides as cobalt-free cathodes for IT-SOFCs [16]. The results showed that the electrical conductivity of SLBFO is enhanced with substituting in La. However, the polarization resistance increased with increasing La-doping content. Recently, Kong and co-workers [17] reported a novel layered $NdBa_{0.5}Sr_{0.5}Cu_2O_{5+\delta}$ (NBSC) perovskite, which shows advanced electrochemical properties in doped ceria electrolyte settings, and could be potentially employed as cathode material for IT-SOFC applications. However, the previous investigations of $NdBa_{0.5}Sr_{0.5}Cu_2O_{5+\delta}$ are still insufficient, especially for its single-cell performance as cathode material in SOFC settings. In addition, to date, there appears to be no published study on the application of $PrBa_{0.5}Sr_{0.5}Cu_2O_{5+\delta}$ layered perovskite materials. In this work, cobalt-free layered perovskite $LnBa_{0.5}Sr_{0.5}Cu_2O_{5+\delta}$ (Ln = Pr and Nd, PBSC and NBSC) was examined as new cathodes for SOFCs based on oxide ion conductor of $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ (LSGM). Moreover, a performance comparison of the PBSC and NBSC cathodes was also carried out.

Experimental

Sample preparation

The layered perovskite $LnBa_{0.5}Sr_{0.5}Cu_2O_{5+\delta}$ (Ln = Pr and Nd, PBSC and NBSC) powders were prepared by a combined complexing method, using citrate and EDTA as complexing agent. Firstly, Pr_6O_{11} and Nd_2O_3 were dissolved in nitric acid to form a nitrate solution. $Ba(NO_3)_2$, $Sr(NO_3)_2$ and $Cu(NO_3)_2\cdot 6H_2O$ were of analytical grades. Citric acid and EDTA–$NH_3\cdot H_2O$ were added in the mixture of nitrate solution. The molar ratio of citric acid: EDTA: total metal ions was 2:1:1. After heating and stirring for some time, an atramentous viscous gel was obtained. The resulting viscous gel was baked at 150 °C for 3 h to form the dried gel. The dried gel was ground and finally calcined at 1000 °C for 6 h in air. $LnBa_{0.5}Sr_{0.5}Cu_2O_{5+\delta}$ (Ln = Pr, Nd) oxide powders were then pressed into the pellets of about 13 mm (diameter) × 0.60 mm (thickness), and then heated at 950 °C for 2 h for electrical conductivity testing. $LnBa_{0.5}Sr_{0.5}Cu_2O_{5+\delta}$ oxide powders were also pressed into cylindrical samples of about 6 mm in diameter and 4.9 mm in height, and then calcined at 950 °C for 2 h for TEC measurement. The glycine-nitrate combustion method was used to prepare the $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ (LSGM) electrolyte, $Ce_{0.9}Sm_{0.1}O_{1.95}$ (SDC) and NiO powders [18].

Cell fabrication

The symmetrical cells with the configuration of PBSC/LSGM/PBSC and NBSC/LSGM/NBSC were used for impedance studies. The appropriate organic solvent was prepared by using 10% ethyl cellulose +90% terpineol. The PBSC powders were mixed thoroughly with the organic solvent to form cathode slurry. The NBSC cathode slurry was prepared with the same method. The PBSC and NBSC cathode slurries were applied on either side of LSGM electrolyte pellets, and then the pellets were calcined at 950 °C for 2 h.

The single cells were prepared with LSGM as the electrolyte. The thickness of LSGM ceramic disks was controlled to 300 μm. NiO + SDC mixture (65:35 by weight) was used as the anode. At first, the SDC slurry was painted on one side of the LSGM electrolyte, and then calcined at 1300 °C for 1 h to obtain an interlayer. After that NiO + SDC anode was painted on the SDC interlayer, and sintered subsequently at 1250 °C for 4 h in

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