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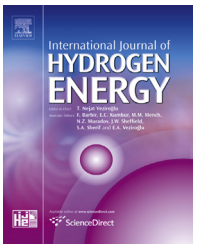

Performances of nickel-doped $SmBaCo_2O_{5+\delta}$–$Sm_{0.2}Ce_{0.8}O_{1.9}$ composite cathodes for IT-SOFC

Li-Na Xia [a,b], *Jing You* [a,b], *Zhi-Ping He* [a,b], *Xiao-Wei Huang* [a,b,*], *Yan Yu* [a,b,**]

[a] College of Materials Science and Engineering, Fuzhou University, Fuzhou 350116, PR China
[b] Key Laboratory of Eco-Materials Advanced Technology (Fuzhou University), Fujian Province University, PR China

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ABSTRACT

$SmBaCo_{1.7}Ni_{0.3}O_{5+\delta}$-x$Sm_{0.2}Ce_{0.8}O_{1.9}$ (SBCN-xSDC, x = 0–50 wt.%) composite cathodes were prepared and characterized for potential use in intermediate-temperature solid oxide fuel cells (IT-SOFCs) based on an SDC electrolyte. The electrical conductivity and the thermal expansion coefficient (TEC) decreased with an increase in the SDC content of SBCN-xSDC composite cathodes. TEC values decreased from 15.59 × 10^{-6} K^{-1} for SBCN to 13.17 × 10^{-6} K^{-1} for SBCN-50SDC. Furthermore, the addition of SDC to the SBCN cathode improved its electrochemical performance. Among others, the SBCN-20SDC showed the lowest polarization resistance of 0.0272 Ω cm^2 at 800 °C; an anode-supported single-cell configuration of Ni-SDC/SDC/SBCN-20SDC obtained a maximum power density of 628 mW cm^{-2} at 800 °C. Even when the content of SDC was raised up to 50 wt.%, the electrochemical performance of SBCN-50SDC still exceeded that of pure SBCN. These results indicated that the SBCN-xSDC composite cathode is a promising material for IT-SOFCs.

Introduction

Solid oxide fuel cells (SOFCs) are promising power generation devices with high energy efficiency, low emissions and excellent fuel flexibility [1,2]. Lowering the operating temperature to an intermediate range (600–800 °C) has been the main priority of SOFC research because it can enhance the thermal stability of SOFCs and lower the cost of production [3]. However, a major obstacle to develop intermediate-temperature solid oxide fuel cells (IT-SOFCs) is the sharp increase in the cathode polarization resistance. This is because the oxygen reduction reaction (ORR) rate at the cathode and the transport properties dramatically decrease when the operating temperature is reduced [4–6]. For example, the traditional SOFC cathode, $La_{1-x}Sr_xMnO_{3-\delta}$, is not suitable for IT-SOFCs due to its poor catalytic activity for the electrochemical reduction of oxygen in this temperature regime [7]. Therefore, the development of new cathodes with high

* *Corresponding author*. College of Materials Science and Engineering, Fuzhou University, Fuzhou 350116, PR China.
** *Corresponding author*. College of Materials Science and Engineering, Fuzhou University, Fuzhou 350116, PR China.
E-mail addresses: xwhuang@fzu.edu.cn (X.-W. Huang), yuyan@fzu.edu.cn (Y. Yu).

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electrocatalytic activity for the ORR is vital to achieving a favorable cell performance in IT-SOFCs [8].

In recent years, mixed ionic-electronic conductors (MIECs) with perovskite structures, such as $Sm_{0.5}Sr_{0.5}CoO_3$ (SSC) and $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF), have received extensive attention [9,10]. These MIECs not only show good ionic conductivity and electrocatalytic activity but also help extend the electrochemical active area from the three-phase boundary (TPB) to the whole cathode surface, which results in an improvement in electrochemical performance [9,10]. Of the current MIECs, the double-perovskite oxides $LnBaCo_2O_{5+\delta}$ (Ln = Pr, Nd, Sm, Gd …) have been thoroughly studied as promising cathode materials for IT-SOFCs because of their fast oxygen ion diffusion and interfacial oxygen exchange rate in combination with a high electrical conductivity [11,12]. For example, Zhang et al. [13] and Kim et al. [14] have reported that the double perovskite $PrBaCo_2O_{5+\delta}$ exhibited high oxygen mobility and surface exchange kinetics, when compared with $La_{0.5}Sr_{0.5}CoO_{3-\delta}$ at an intermediate temperature. Mixed conducting $NdBaCo_2O_{5+\delta}$ electrodes, as prepared by Yadav et al. [15], have shown very fast electrode kinetics. Cathodes with cobalt favor the activation of oxygen reduction and thus provide a lower activation polarization loss [16]. However, the thermal expansion coefficients (TEC) of cobalt containing cathodes are significantly higher than IT-electrolytes ($Sm_{0.2}Ce_{0.8}O_{1.9}$ and $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$) and interconnect materials. The large TEC values of cobalt-based perovskite oxides come from two factors: 1) the reduction of Co^{4+} ions to lower valence but larger sized Co^{3+} and Co^{2+} ions due to thermal-driven releasing of lattice oxygen, and 2) the transition of Co^{3+} ions from low spin to high spin [5,17,18]. For example, $PrBaCo_2O_{5+\delta}$ and $NdBaCo_2O_{5+\delta}$ exhibit TECs of more than $20 \times 10^{-6}\,K^{-1}$ [19]. The thermal expansion mismatch can cause delamination or cracks at the interface of the electrode and the electrolyte. Therefore, it is important to improve the thermal compatibility between cathodes and electrolytes [16].

In general, there are two effective methods for improving the thermal compatibility between cathodes and electrolytes. One method is replacing Co with transition metals with small ionic radii (e.g., Fe and Ni) to reduce the TEC [3]. For instance, Kim et al. [20] studied the effect of Ni doping in layered $NdBaCo_{2-x}Ni_xO_{5+\delta}$ perovskite oxides and found that it provides a combination of low thermal expansion and sufficiently high catalytic activity for the ORR. Another approach is introducing an ionic conducting electrolyte into the cathode to form composite cathodes, such as $La_{0.8075}Sr_{0.1425}MnO_{3-\delta}$-$(ZrO_2)_{0.92}(Y_2O_3)_{0.08}$ (LSM-YSZ), $Sm_{0.5}Sr_{0.5}CoO_{3-\delta}$-$Gd_{0.2}Ce_{0.8}O_{1.9}$ (SSC-GDC), $GdBaCo_2O_{5+\delta}$-$Ce_{0.9}Gd_{0.1}O_{1.95}$ (GBCO-GDC) and $LaBaCo_2O_{5+\delta}$–$Sm_{0.2}Ce_{0.8}O_{1.9}$ (LBCO-SDC). This is because the expanding active region of triple-phase boundaries (TPBs) enhances the electrochemical performance [3,4,21–24]. Moreover, the addition of the electrolyte to the cathode can also reduce the TEC difference between the cathode and electrolyte [24].

More recently, our group found that $SmBaCo_{1.7}Ni_{0.3}O_{5+\delta}$ (SBCN) exhibited a good electrochemical performance and a relatively low TEC ($15.59 \times 10^{-6}\,K^{-1}$) [25]. Unfortunately, the TEC of SBCN remains slightly higher than that of many electrolytes. To further improve electrochemical performance and reduce the TEC mismatch between the cathode and the electrolyte, the effects of SDC weight ratio in the composite cathode SBCN-xSDC (x = 0–50 wt.%) are systematically investigated through the X-ray diffraction (XRD), scanning electron microscopy (SEM), electrical conductivity measurements, thermal expansion coefficient determinations and electrochemical characterizations.

Experimental

Powder synthesis and fuel cell preparation

Powders of $SmBaCo_{1.7}Ni_{0.3}O_{5+\delta}$ (SBCN) were fabricated via a modified EDTA-glycine method with $Sm(NO_3)_3$, $Ba(NO_3)_2$, $Co(NO_3)_3{\cdot}6H_2O$ and $Ni(NO_3)_3{\cdot}6H_2O$ as the precursors [25,26]; $Sm_{0.2}Ce_{0.8}O_{1.9}$ (SDC) was prepared by a glycine-nitrate combustion method [27]. The composite cathodes SBCN-xSDC were prepared by ball-milling of SBCN and SDC powders in a liquid ethanol medium for 8 h. The composite cathodes were identified by the weight of added SDC (0–50 wt.% at intervals of 10 wt.%) and noted as SBCN-xSDC (x = 0, 10, 20, 30, 40, 50).

SBCN-xSDC rectangular-shaped bars (50 mm × 7 mm × 5 mm) were pressed at 200 MPa and sintered at 1100 °C for 5 h in air. The bars were used to measure the electrical conductivities and determine the thermal expansion coefficient (TEC). To obtain dense SDC electrolyte pellets, the SDC powder was pressed (200 MPa) into a pellet with a diameter of 13 mm and a thickness of 0.7 mm, followed by calcination at 1400 °C for 5 h in air.

Symmetrical half-cells with a SBCN-xSDC/SDC/SBCN-xSDC configuration were constructed for impedance studies. The cathode slurry was prepared by mixing the corresponding composite powder with an organic binder (terpineol and ethyl cellulose) in an appropriate ratio. Then, the slurries were screen-printed onto both sides of a dense SDC electrolyte pellet and sintered at 950 °C for 2 h in air to form an effective cathode with a surface area of 0.25 cm^2.

For the anode powder, 70 wt.% NiO and 30 wt.% SDC were ball-milled in ethanol for 10 h. The anode NiO-SDC and electrolyte SDC were pressed into pellets that contained two layers, followed by sintering at 1400 °C for 5 h in air. The cathode was printed on the opposite side of the SDC and was followed by calcination at 950 °C for 2 h. The single cells were fabricated by the anode-supported technique with a configuration of SBCN-xSDC/SDC/NiO-SDC.

Characterizations

The phase identification of synthesized powders and the phase reaction between cathode and electrolyte were obtained from X-ray diffraction (XRD, Ultima III) with a step size of 0.01° in 2θ over an angular scanning range from 10 to 90°. Electrical conductivity was measured by a four-terminal DC arrangement with a multimeter (UI52) from 100 to 850 °C at intervals of 50 °C in air. The TEC was determined with an electronic dilatometer (NETZSCH DIL402C) from 25 to 800 °C at a heating rate of 5 °C min^{-1} in air.

The microstructure of symmetrical half-cells was examined with a scanning electron microscope (FRI Nova Nano SEM 230). The electrochemical impedance spectra of half-cells

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