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## Characterization and evaluation of Ba-doped $\text{Ba}_x\text{Sr}_{1-x}\text{Co}_{0.9}\text{Sb}_{0.1}\text{O}_{3-\delta}$ as cathode materials for $\text{LaGaO}_3$ -based solid oxide fuel cells

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### ABSTRACT

$\text{Ba}_x\text{Sr}_{1-x}\text{Co}_{0.9}\text{Sb}_{0.1}\text{O}_{3-\delta}$  (BSCSbx,  $x = 0.0-0.8$ ) are investigated as cathodes for intermediate temperature solid oxide fuel cells (IT-SOFCs). BSCSbx oxides are crystallized in a tetragonal structure with s.g.  $P4/mmm$ . XPS analysis shows that Ba doping reduces valence state of Co ions: Co in  $\text{SrCo}_{0.9}\text{Sb}_{0.1}\text{O}_{3-\delta}$  is prone to  $\text{Co}^{4+}$ , while Co in Ba doped  $\text{SrCo}_{0.9}\text{Sb}_{0.1}\text{O}_{3-\delta}$  becomes more prone to  $\text{Co}^{3+}$ . Oxygen deficiency  $\delta$  increases with Ba doping even at high temperatures. Conductivity is found to decrease with Ba doping. Thermal expansion coefficient (TEC) decreases from  $20.6 \times 10^{-6} \text{ K}^{-1}$  for  $x = 0.0$  to  $18.4 \times 10^{-6} \text{ K}^{-1}$  for  $x = 0.6$  at 30–1000 °C. With increasing  $x$  from 0.0 to 0.6, polarization resistance ( $R_p$ ) decreases monotonously, and then increases with further increasing  $x$ . The lowest  $R_p$  of  $0.081 \Omega \text{ cm}^2$  at 700 °C is obtained for BSCSb0.6 cathode. At 700–850 °C, the  $R_p$  of BSCSb0.6 is mainly contributed from electron charge transfer; however, below 700 °C, ion charge transfer plays a more important role in  $R_p$ . Maximum power densities of the cell with BSCSb0.6 cathode on 300- $\mu\text{m}$  thick  $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$  (LSGM) electrolyte attain 306–944  $\text{mW cm}^{-2}$  at 700–850 °C. These results indicate that BSCSb0.6 is a promising cathode for application in IT-SOFC.

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### Introduction

SOFCs are electrochemical power generation devices with the advantages of all solid-state, high efficiency and low emission. SOFCs have attracted more and more attentions as a promising technique for future power generation [1,2]. In

traditional SOFCs, pure electronic conductor  $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$  is usually used as cathode material and then the oxygen reduction reaction (ORR) is limited to the cathode/electrolyte/air triple phase boundary [3]. Then high temperatures, typically above 1000 °C, are needed for the operation of traditional SOFCs. However, too high temperatures can result in a series

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of issues, such as deterioration of cell performance because of poor chemical/thermal compatibility among the cell components, increment of SOFC system cost, and limited choice of both the electrode and electrolyte materials [4]. However, lowering operating temperature to the 600–850 °C range increases the cell overpotential, which is mainly due to increased activation energy for the ORR [5–7]. Thus one of the main goals for IT-SOFC application is to develop new cathode materials with excellent electrochemical catalytic activity for the ORR [8–11].

Up to now, development of mixed ionic and electronic conductors for IT-SOFC cathodes is mainly concentrated on cobalt-based perovskites because of their high ionic diffusion fluxes and excellent catalytic activity for oxygen reduction [12–14]. The high temperature  $\text{SrCoO}_{3-\delta}$  phase shows a cubic structure with high oxygen permeability; however, at room temperature, the  $\text{SrCoO}_{3-\delta}$  oxide with a hexagonal structure has been demonstrated to possess poor oxygen permeability. Thus a phase transition takes place when the  $\text{SrCoO}_{3-\delta}$  oxide is heated. This transition will result in an abrupt change in the TEC, which is not beneficial for good contact between electrode and electrolyte and then limits its application in SOFCs. A common method for this problem is to dope proper cations into either Sr or Co sites of  $\text{SrCoO}_{3-\delta}$  oxide to stabilize the cubic structure down to room temperature [13,15]. Recently, Aguadero et al. [16,17] reported that doping the  $\text{SrCoO}_{3-\delta}$  system with proper amount of Sb cations at Co sites could stabilize the  $\text{SrCoO}_{3-\delta}$  from a hexagonal to a subtle tetragonal distorted perovskite phase and greatly improve the electrical conductivity, thermal stability and oxygen transport properties. Using this Sb doped  $\text{SrCoO}_{3-\delta}$  materials as SOFC cathodes, the greatly improved electrochemical performances characterized by polarization resistance ( $R_p$ ) were obtained, e.g., the  $R_p = 0.009\text{--}0.23 \Omega \text{ cm}^2$  at 900–600 °C for  $\text{SrCo}_{0.95}\text{Sb}_{0.05}\text{O}_{3-\delta}$  (SCSb) cathode on  $\text{Ce}_{0.8}\text{Nd}_{0.2}\text{O}_{1.9}$  (NDC) electrolyte reported by Aguadero et al. [17] and the  $R_p = 0.13 \Omega \text{ cm}^2$  at 650 °C for SCSb cathode on  $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$  (SDC) electrolyte reported by Lin et al. [18]. In our and other groups' experience, the partial substitution of  $\text{Sr}^{2+}$  in strontium cobaltite-based perovskites, such as  $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$  and  $\text{SrCo}_{0.9}\text{Nb}_{0.1}\text{O}_{3-\delta}$ , by larger cation  $\text{Ba}^{2+}$  has been demonstrated to promote the release of lattice oxygen and then the reduction of  $\text{Co}^{4+}$  to  $\text{Co}^{3+}$  [12,19,20]. It is reasonable to consider that the introduction of  $\text{Ba}^{2+}$  into the Sr sites of SCSb may be a possible way to improve the oxygen transport properties because of the increased concentration of oxygen vacancy; furthermore, the reduction of the oxidation state of Co cation due to the introduction of a larger cation  $\text{Ba}^{2+}$  is beneficial to reducing the chemical expansion resulting from the thermal reduction of  $\text{Co}^{4+}$  to lower oxidation state in 300–500 °C temperature range [20,21], which is favorable to thermal expansion compatibility between the electrode and electrolyte.

To the best of our knowledge, the performance of  $\text{Ba}^{2+}$  doped SCSb oxides as IT-SOFC cathodes has not been reported to date. In this article, we systematically investigated the effect of Ba doping level on micro-structure, valence states of transition metal cations, oxygen deficiency  $\delta$ , electrical conductivity, TEC and interfacial polarization resistance of  $\text{Ba}_x\text{Sr}_{1-x}\text{Co}_{0.9}\text{Sb}_{0.1}\text{O}_{3-\delta}$  (BSCSbx) with  $x = 0.0\text{--}0.8$ . The rate-

limiting step for the ORR of BSCSb0.6 cathode at 650–850 °C has also been analyzed and discussed. In the end, the cell performance and the long-term stability of LSGM-supported single cell with BSCSb0.6 as cathode were tested.

## Experimental data

### Sample preparation

The BSCSbx oxides with  $x = 0.0, 0.2, 0.4, 0.6$  and  $0.8$  were prepared by a solid-state reaction method.  $\text{BaCO}_3$ ,  $\text{SrCO}_3$ ,  $\text{Co}_2\text{O}_3$  and  $\text{Sb}_2\text{O}_5$  were used as the raw materials. All materials used here were of analytical grade. Stoichiometric amounts of  $\text{BaCO}_3$ ,  $\text{SrCO}_3$ ,  $\text{Co}_2\text{O}_3$  and  $\text{Sb}_2\text{O}_5$  were thoroughly ground for 1 h, and then pressed into pellets and calcined at 900 °C for 10 h in air. The calcined pellets were pulverized and reground. Subsequently, the obtained powders were pressed into pellets (diameter of 13 mm) and cylinders (diameter of 6 mm) at 220 Mpa for the measurements of electrical conductivity and thermal expansion, respectively. The final sintering temperatures for the pellets and cylinders were 1100 °C for the  $x = 0.0\text{--}0.4$  and 1050 °C for the  $x = 0.6\text{--}0.8$ . The nanosized SDC, LSGM and NiO powders were prepared by a glycine nitrate method. The dense LSGM pellets used for electrolyte supported SOFCs were obtained by sintering at 1450 °C for 10 h. The anode consisted of the SDC and NiO powders in a weight ratio of 60:40.

### Characterization

The micro-structure were determined by a Rigaku D/Max- $\gamma$ A X-ray diffractometer using Cu K $\alpha$  radiation ( $\lambda = 0.15418 \text{ nm}$ ). The valence states of the transition metal ions in BSCSbx were determined by XPS using the VG Scientific ESCALAB MK II X-ray photoelectron spectrometer. This spectrometer used a monochromatized microfocussed Al K $\alpha$  (1486.6 eV) radiation source. Thermogravimetric analysis (TGA) was performed using a thermal analyzer (HENVEN HCT-3) in air at a flow rate of 50 mL  $\text{min}^{-1}$ . Oxygen deficiency  $\delta$  in the BSCSbx is determined by the iodometric titration method. The temperature program desorption (TPD) was conducted to detect the thermal desorption of lattice oxygen with increasing temperature, using a chemisorption analyzer (PCA-1200, Builder, China) with heating rate of 10 °C  $\text{min}^{-1}$  and flowing rate of 30 mL  $\text{min}^{-1}$  in He. A dc four-probe method was used for electrical conductivity measurements of the BSCSbx samples. A horizontal dilatometer (Netzsch DIL 402C) was used for the thermal expansion measurement for the BSCSbx samples.

Symmetrical cells with the configuration of BSCSbx/LSGM/BSCSbx were used for the measurement of interfacial polarization resistance, The BSCSbx paste was screen-painted onto both sides of LSGM pellet, followed by sintering at 950 °C for 2 h to obtain the symmetrical cell. Impedance spectra were performed on an electrochemical analyzer (CHI 604D, Chenhua) by using three-electrode method.

LSGM electrolyte-supported single cells with the configuration of BSCSbx/LSGM/SDC/NiO-SDC ( $x = 0.0$  and  $0.6$ ) were also fabricated by a screen-printing method. The thickness of the LSGM pellet was controlled to be around 300  $\mu\text{m}$ . The

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