Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Antimony doped barium strontium ferrite perovskites as novel cathodes for intermediate-temperature solid oxide fuel cells



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ARTICLE INFO

Article history: Received 2 November 2015 Received in revised form 30 December 2015 Accepted 17 January 2016 Available online 19 January 2016

Keywords: Solid oxide fuel cells Barium strontium ferrite Antimony doping Defect chemistry analysis Interfacial polarization resistance

ABSTRACT

Antimony was doped to barium strontium ferrite to produce ferrite-based perovskites with a composition of $Ba_{0.5}Sr_{0.5}Fe_{1-x}Sb_xO_{3-\delta}$ (x = 0.0, 0.05, 0.1) as novel cathode materials for intermediatetemperature solid oxide fuel cells (IT-SOFCs). The perovskite properties including oxygen nonstoichiometry (δ), mean valence of B-site, tolerance factors, thermal expansion coefficient (TEC) and electrical conductivity (σ) are explored as a function of antimony content. By defect chemistry analysis, the TECs decrease since the variable oxygen vacancy concentration is decreased by Sb doping, and σ decreases with *x* due to the reduced charge concentration of Fe⁴⁺ content. Consequently, the electrochemical performance was substantially improved and the interfacial polarization resistance was reduced from 0.213 to 0.120 Ω cm² at 700 °C with Sb doping. The perovskite with x = 1.0 is suggested as the most promising composition as SOFC cathode material.

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1. Introduction

To overcome the increasing energy demands and environmental challenges, solid oxide fuel cells (SOFCs) have attracted remarkable attention as one of the promising future green energy conversion devices with fuel flexibility, high efficiency and low emissions [1,2]. The traditional SOFCs with yttria stabilized zirconia electrolyte (YSZ) and La_{1-x}Sr_xMnO₃ (LSM) cathode need to operate at high temperature of 800–1000 °C, thus limiting the commercial use due to the cost of the materials and maintenance of the cell without significant loss of the cell efficiency [3]. One effective way is to reduce the operating temperature of the SOFCs to an intermediate temperature range of 500–800 °C. However, the performance of intermediate-temperature solid oxide fuel cells (IT-SOFCs) is strongly dependent on cathode materials, since cathode polarization resistance usually dominates in the total cell resistance [4–13].

Many mixed ionic and electronic conductors (MIECs) such as $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ [5], $Sm_{0.5}Sr_{0.5}CoO_{3-\delta}$ [6], $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$

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(LSCF) [7], Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3- δ} (BSCF) [8,9] and LnBaCo₂O_{5+ δ} [10–12] have been extensively studied as potential cathode materials owing to their excellent catalytic activities for the oxygen reduction reaction. Among these MIEC materials, BSCF has been given much more attention in consideration of its fast oxygen-ion transport properties for low temperature application [8,9]. However, the structural instability of BSCF greatly limited further application [14–17]. In addition, cobalt-based cathode materials often encountered some problems like high thermal expansion coefficient (TEC), high cost of cobalt element and easy evaporation and reduction of cobalt [18,19]. Therefore, it is desirable to develop cobalt-free cathodes with good electrocatalytic activity for IT-SOFCs.

Fe-based perovskite oxides as promising cathodes for IT-SOFCs attracted much attention as possible alternatives to cobaltites because of the less flexible redox behavior of iron such as Sm_{0.5}Sr_{0.5}FeO_{3- δ} [20], La_{0.8}Sr_{0.2}FeO_{3- δ} [21], and Ba_xSr_{1-x}FeO_{3- δ} [22]. Meanwhile, B-site substitution in perovskite oxides by antimony can effectively improve structural stability and present good electrochemical performance [23–26]. In this work, antimony is doped to the B-site of Ba_{0.5}Sr_{0.5}FeO_{3- δ} to form a series of ferritebased perovskites with a general formula of



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Ba_{0.5}Sr_{0.5}Fe_{1-x}Sb_xO_{3- δ} (BSFSb, x = 0.0, 0.05, 0.10). These compounds are prepared using a combustion process and their oxygen nonstoichiometry (δ), mean valence of B-site, tolerance factors, thermal expansion coefficient (TEC), electrical conductivity (σ) are systematically evaluated as a function of the Sb content. The effects of Sb contents on the electrochemical performances are also evaluated using samaria doped ceria (SDC) as the electrolyte.

2. Experimental section

2.1. Sample preparation

 $Ba_{0.5}Sr_{0.5}Fe_{1-x}Sb_xO_{3-\delta}$ (BSFSb, x = 0.0, 0.5, 1.0) powders were synthesized by combining an EDTA-citrate complexation process and a solid state reaction. Citrate and ethylenediamine tetraacetic acid (EDTA) were employed as parallel complexing agents. $Ba(NO_3)_2$, $Sr(NO_3)_2$, and $Fe(NO_3)_3 \cdot 9H_2O$ were dissolved at the stoichiometric ratio to form an aqueous solution, and then a proper amount of citric acid was introduced, the molar ratio of EDTA: citric acid: total of metal cations was controlled around 1:1.5:1. Then Sb_2O_3 was added and the solution was heated under stirring to evaporate water until it changed into viscous gel and finally ignited to flame, resulting in a black ash. The ash was ball-milled for 24 h before calcining at 1000 °C for 3 h to form a pure perovskite oxide, and the synthesized BSFSb powders were then obtained. Powders of $Sm_{0.2}Ce_{0.8}O_{1.9}$ (SDC) electrolyte were synthesized by glycine nitrate process (GNP).

2.2. Fabrication of symmetrical electrochemical cells and the single cells with BSFSb as cathodes

Symmetrical electrochemical cells with the configuration of BSFSb/SDC/BSFSb were used for AC impedance spectroscopy (Chi604c, Shanghai Chenhua) measurements. The cathodes were screen-printed onto the dense SDC electrolyte pellets. After drying, the BSFSb cathodes were sintered at 950 °C for 3 h in air. The anodesupported SDC bilayer (ϕ 15 mm) was prepared by a one-step drypressing method. NiO+ SDC + starch mixture (60%:40%:20% in weight) was pre-pressed at 200 MPa as a substrate. Then loose SDC powder, calcined at 800 °C for 2 h to form a pure fluorite oxide, was uniformly distributed onto anode substrate, co-pressed at 250 MPa and sintered subsequently at 1400 °C for 5 h in air to densify the SDC electrolyte membrane. Fine BSFSb powders, were mixed thoroughly with a 6 wt % ethylcellulose-terpineol binder to prepare the cathode slurry, which was then painted on SDC electrolyte films, and sintered at 950 °C for 3 h in air to form tri-layer cell of NiO-SDC/SDC/BSFSb.

2.3. Characterization

The phase identification of prepared cathode powders was studied with X-ray powder diffraction by Cu-K α radiation (D/Max-gA, Japan). Iodometric titration was performed at room temperature in order to investigate the oxygen vacancy concentration, δ , for all the compositions. The variation of oxygen contents with temperature was measured by thermogravimetric analyzer (TGA) in air with a low heating rate of 2 °C/min and all samples were heated at 1100 °C for 5 h before TGA experiment. Thermal expansion of the specimen was measured from 30 to 1000 °C using a dilatometer (SHIMADZU50) at a heating rate of 10 °C min⁻¹ in air. Electrical conductivity of BSFSb was studied using the standard DC four-probe technique on H.P. multimeter (Model 34401) from 400 to 800 °C. Symmetrical electrochemical cells with the configuration of BSFSb/SDC/BSFSb applied for the impedance research were measured by AC impedance spectroscopy (Chi604c, Shanghai

Chenhua) from 500 to 750 °C. Single cells were tested from 500 to 650 °C in a home-developed-cell-testing system with humidified hydrogen (~3% H₂O) as fuel and the static air as oxidant, respectively. The flow rate of fuel gas was about 40 ml min⁻¹. The cell voltages and output current of the cells were measured with digital multi-meters (GDM-8145). A scanning electron microscope (SEM, JEOL JSM-6400) was used to observe the microstructure of the cells after testing.

3. Results and discussion

Fig. 1(a) shows the X-ray diffraction patterns for the Ba_{0.5}Sr_{0.5}Fe_{1-x}Sb_xO_{3- $\delta}$ (BSFSb, x = 0, 0.05, 0.10) powders, which have been heated at 1000 °C for 3 h. The XRD patterns exhibited well-crystallized perovskite structure without any observable secondary phases. Fig. 1(b) shows the magnified view of the XRD patterns for (020) lattice plane. With the increase antimony content, the corresponding XRD peaks shift toward smaller angles, indicating the expansion of the lattice volume within the same crystal structure, possibly caused by the relatively larger Sb³⁺ (0.76 Å) than Fe³⁺ (0.645 Å) and Fe⁴⁺ (0.585 Å).}

The oxygen contents and the average oxidation state values for the transition metal ions on the B-site of $Ba_{0.5}Sr_{0.5}Fe_{1-x}Sb_xO_{3-\delta}$ are determined by iodometric titration at room temperature as shown in Fig. 1(c). It is well note that the oxygen vacancy concentration increases with increasing Sb content, indicating that the oxidation state of Sb in BSF tends to trivalent state (Sb³⁺). Since Ba and Sr have a fixed valence state of +2 in the BSFSb perovskite oxides, partial Fe iron need to form a trivalent state according to the charge neutrality. Generally, a structural instability of perovskites can be avoided by regulating the Goldschmidt tolerance factor (*t*) using appropriate substitutions, which can be defined by the following mathematical expression,

$$t = \frac{r_{\rm A} + r_{\rm O}}{\sqrt{2}(r_{\rm B} + r_{\rm O})} \tag{1}$$

where r_A , r_B , and r_O are the radii of cation A, cation B, and oxygen, respectively. If the t values of perovskites tend to be closer to 1, meaning forming the cubic structure is much more possibility [27]. Taking into account the changeable valence of transition metal Fe ion, thus t should be carefully calculated with consideration of the various ionic radii of transition metals. Assuming that r_B varies depending on the valence state of the B-site ions, the t value can be calculated from the following equation:

$$t = \frac{0.5r_{Ba^{2+}}0.5r_{Sr^{2+}} + r_{O}}{\sqrt{2}\left[(1-x)\left(\left[Fe^{3+}\right]r_{Fe^{3+}} + \left[Fe^{4+}\right]r_{Fe^{4+}}\right) + xr_{Sb^{3+}} + r_{O}\right]}$$
(2)

where *x*, $[Fe^{3+}]$ and $[Fe^{4+}]$ are the mole fraction of antimony, the trivalent Fe ions and quadrivalent Fe ions, respectively, and the ionic radii involved in this equation are taken from Shannon's results [28]. As seen in Fig. 1(d), the *t* values of BSFSb are reducing and much closer to 1 with substitution of larger Sb³⁺ into B-site, suggesting that the structure of BSFSb has a smaller deformation of cubic symmetry than that of BSF. Besides, the oxygen vacancies can increase with temperature increasing, indicating that a smaller *t* values can be obtained at intermediate temperature.

To estimate the variation of oxygen contents of BSFSb at intermediate temperature range, thermogravimetric analyzer (TGA) was used in air with a low heating rate and all samples were heated at 1100 °C for 5 h before TGA experiment, suggesting that the observed weight change results from the loss of lattice oxygen on heating. The oxygen contents $(3-\delta)$ as a function of temperature in BSFSb oxides determined from the iodometric titration (room Download English Version:

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