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# NdBaCu<sub>2</sub>O<sub>5+δ</sub> and NdBa<sub>0.5</sub>Sr<sub>0.5</sub>Cu<sub>2</sub>O<sub>5+δ</sub> layered perovskite oxides as cathode materials for IT-SOFCs

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## ARTICLE INFO

### Article history:

Received 19 June 2015

Received in revised form

13 August 2015

Accepted 3 September 2015

Available online 11 November 2015

### Keywords:

SOFCs

Cathodes

Thermal expansion

Electrochemical performance

## ABSTRACT

Cobalt-free perovskite oxides NdBaCu<sub>2</sub>O<sub>5+δ</sub> (NBCO) and NdBa<sub>0.5</sub>Sr<sub>0.5</sub>Cu<sub>2</sub>O<sub>5+δ</sub> (NBSCO) has been investigated as cathode materials in intermediate-temperature solid fuel cells (IT-SOFCs). The crystal structure, thermal expansion, electrical conductivity and electrochemical properties have been characterized by X-ray diffraction (XRD), dilatometer, four-probe dc method, electrochemical impedance spectroscopy (EIS) and cathodic polarization examinations. The average thermal expansion coefficients (TEC) values of NBCO and NBSCO are  $13.0 \times 10^{-6}/^{\circ}\text{C}$  and  $14.5 \times 10^{-6}/^{\circ}\text{C}$ , which are more desirable on combining with the electrolytes than cobalt-based cathodes. The partly substitution of Sr on B-site increases the electron hole concentration and improves the conductivity. The polarization resistances values of NBSCO are 0.205  $\Omega\text{cm}^2$ , 0.200  $\Omega\text{cm}^2$  and 0.135  $\Omega\text{cm}^2$ , whereas the polarization resistances values of NBCO are 8.61  $\Omega\text{cm}^2$ , 3.18  $\Omega\text{cm}^2$  and 0.83  $\Omega\text{cm}^2$  at 600  $^{\circ}\text{C}$ , 700  $^{\circ}\text{C}$  and 800  $^{\circ}\text{C}$ , respectively. The improved electrochemical performance of NBSCO should be ascribed to the higher conductivity as well as the improved oxygen adsorption/desorption and oxygen ions diffusion processes.

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## Introduction

Solid oxide fuel cells (SOFCs) have received considerable interest in recent years due to their less pollution than traditional energy conversion devices and their high energy efficiency. However, conventional high operating temperatures (800–1000  $^{\circ}\text{C}$ ) cause some problems, such as the serious interface reaction, the thermal expansion mismatch among the components and the limitations in the choice of

electrode and interconnect materials and so on [1]. Reducing the operating temperatures to the intermediate range from 500  $^{\circ}\text{C}$ –800  $^{\circ}\text{C}$  is the fundamental solution in the development of SOFCs. However, the electrochemical activity of cathode decreases dramatically at the intermediate operating temperatures. Traditional cathode materials such as La<sub>1-x</sub>Sr<sub>x</sub>MnO<sub>3</sub> [2] show poor oxide-ion conductivity and inadequate catalytic activity. Developing new mixed conductors of IT-SOFCs materials with high catalytic activity are the hotspot and focus at present.

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<http://dx.doi.org/10.1016/j.ijhydene.2015.09.006>

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Layered perovskite oxides, a kind of mixed ionic and electronic conducting (MIEC) oxides, have acquired immense attention as cathodes for IT-SOFCs recently years. Among various MIEC oxides,  $\text{LnBaCo}_2\text{O}_{5+\delta}$  ( $\text{Ln}$  = lanthanide) have drawn much attention due to the wide variations in oxygen contents ( $5+\delta$ ) and the promising MIEC properties. Layered perovskite oxides can be attributed with general formula  $\text{AA}'\text{B}_2\text{O}_{5+\delta}$  of which A-site being rare earth elements, A'-site being alkaline earth element and B-site being transition elements. Layered perovskite oxides consist of consecutive layer  $[\text{BO}_2]\text{-}[\text{AO}]\text{-}[\text{BO}_2]\text{-}[\text{A}'\text{O}]$  stacked along the c-axis [3]. Such layer structure reduces the oxygen bonding strength in  $[\text{AO}]$  layer and provides order channel for ion motion which enhance oxygen diffusivity [4]. Taskin et al. investigated the chemical diffusion coefficient  $D$  and the surface exchange coefficient  $K$  in layered perovskite oxides and found they were much higher than that of simple  $\text{ABO}_3$ -type perovskite [5]. The cathode performance and thermal expansion coefficient (TEC) of  $\text{LnBaCo}_2\text{O}_{5+\delta}$  oxides are decreased with ion radius of lanthanide decreasing [6]. Although the  $\text{LnBaCo}_2\text{O}_{5+\delta}$  samples have better cathode performance comparable to that of  $\text{La}_{0.5}\text{Ba}_{0.5}\text{CoO}_{3-\delta}$  disordered perovskite [1], some urgent problems still exist in the commercial use. On the one hand, the average thermal expansion coefficients values of  $\text{LnBaCo}_2\text{O}_{5+\delta}$  are too high. The TECs of  $\text{NdBaCo}_2\text{O}_{5+\delta}$  and  $\text{SmBaCo}_2\text{O}_{5+\delta}$  are  $23.1 \times 10^{-6} \text{ K}^{-1}$  and  $20.8 \times 10^{-6} \text{ K}^{-1}$  at 300–1370 K [7] which are much higher than that of SDC electrolyte ( $12.2 \times 10^{-6} \text{ K}^{-1}$ ).  $\text{LnBaCo}_2\text{O}_{5+\delta}$  cathodes suffer the high thermal strain and the poor adhesion with the electrolytes which reduce the using time. The reason of the abnormally high TEC of cobalt-based perovskite is the low-spin to high-spin transition of the  $\text{Co}^{3+/4+}$  ions with the increasing temperature [6]. On the other hand, the high price of cobalt element also will raise the manufacture cost. The substitution of other cheaper irons to cobalt would further reduce the manufacture costs [8]. Therefore, developing novel Cobalt-free layered perovskite cathodes with acceptable TEC and adequate catalytic activity is the desirable for the development of IT-SOFCs.

Various ions had been substituted in order to promote perovskite oxides electrochemical performance at intermediate-temperature. Some researchers have reported that the substitution of Sr to Ba in  $\text{LnBaCo}_2\text{O}_{5+\delta}$  can improve the conductivity and catalytic activity [9–11]. The oxygen contents are increased by Sr-doping causing an increase in the concentration of  $\text{Co}^{4+}$  which promotes electronic transport.

With the aims to reduce thermal expansion coefficient and improve electrochemical performance, we investigated the novel copper-based layered perovskite oxides  $\text{NdBaCu}_2\text{O}_{5+\delta}$  (NBCO) and  $\text{NdBa}_{0.5}\text{Sr}_{0.5}\text{Cu}_2\text{O}_{5+\delta}$  (NBSCO), including phase structure, chemical compatibility, TEC, electrical conductivity and electrochemical impedance. The effect of Sr substitution on structure and properties of NBSCO was also investigated.

## Experimental

The  $\text{NdBaCu}_2\text{O}_{5+\delta}$  (NBCO) and  $\text{NdBa}_{0.5}\text{Sr}_{0.5}\text{Cu}_2\text{O}_{5+\delta}$  (NBSCO) perovskite oxide powers were synthesized by citrate-EDTA sol-gel method.  $\text{Nd}_2\text{O}_3$  was first dissolved in nitric acid.  $\text{Cu}(\text{NO}_3)_2$ ,  $\text{Ba}(\text{NO}_3)_2$ ,  $\text{Sr}(\text{NO}_3)_2$  and  $\text{Nd}_2(\text{NO}_3)_3$  were used as the

metal sources. EDTA and citric acid were used as the complexing agent. The mole ratio of EDTA and citric acid to metal ions was 1:1.5:1. EDTA powders were dissolved in ammonia water to obtain the  $\text{NH}_4$ -EDTA solution. Stoichiometric amounts of metal nitrates were dissolved in distilled water and then were mixed in the  $\text{NH}_4$ -EDTA solution under the stirring condition at 80 °C until forming a gel. The gel then was dried to form the black porous precursor in drying cabinet. The precursor was calcined in air 1000 °C for 5 h. The NBCO or NBSCO oxide power with PVA agglomerant were pressed into a rectangular model with the size of 60 mm × 5 mm × 5 mm, and then heated at 1050 °C, 1100 °C and 1150 °C for 2 h to form specimens. The shrinkage rate of specimens was 12% when heating in 1150 °C. The specimens were tested by Archimedes displacement of water; the relative densities were greater than 90%.

The electrolyte powders of  $\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{2-\delta}$  (SDC) were synthesized by conventional solid-state reaction with  $\text{Sm}_2\text{O}_3$  and  $\text{CeO}_2$  as initial materials. The as-synthesized SDC powders were calcined in air at 1200 °C for 5 h, and then the SDC powders were pressed at 20 MPa and formed the electrolyte substrates and then sintered at 1500 °C for 2 h to obtain SDC electrolyte disks.

NBCO or NBSCO powders were mixed thoroughly with ethylcellulose – terpineol binder. The cathode slurry was applied on both sides of SDC electrolyte discs with circle pattern. The disks then were calcined at 1000 °C for 2 h in air. And Ag paste was further printed on the surfaces of electrodes. The disks were calcined at 700 °C for 0.5 h in air to form the symmetrical cells.

The phase identification of synthesized NBCO and NBSCO powder was characterized by X-ray powder diffraction (XRD) using  $\text{Cu-K}\alpha$  radiation (D/MAX-III Japan) in the range of  $20^\circ < 2\theta < 80^\circ$ . The TEC of cuboid specimens were measured by thermal dilatometer RZP-13-10P instrument in the temperature range of 100 °C–800 °C with a heating rate of 5 °C/min. The electrical conductivities of cuboid specimens were investigated with a four-probe dc method using RTS-8 four point probes meter in the temperature range of 100 °C–800 °C. Electrochemical impedance spectroscopy measurements (EIS) of the symmetrical cells were measured using CHI604D electrochemical system with the frequency range from 0.1 Hz to  $10^5$  Hz in the temperature range of 550 °C–800 °C and the amplitude potential is 10 mV. The impedance fitting analysis was performed by the ZSimpWin software. Cyclic voltammetry (CV) measurement ( $5 \text{ mV}^{-1}$ ) was performed by CHI604D. The IR drop originating from the electrolyte resistances were compensated by a postfactum correction of the CVs which using the series resistance obtained from the EIS data, in order to establish the resistance-free  $i$ - $\eta$  characteristics.

## Results and discussion

### XRD analysis

The room temperature X-Ray diffraction patterns of NBCO and NBSCO sintered 1000 °C for 5 h are shown in Fig. 1. The XRD patterns indicate that the NBCO and NBSCO specimens

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