Characterization of layered double perovskite LaBa_{0.5}Sr_{0.25}Ca_{0.25}Co_{2}O_{5+δ} as cathode material for intermediate-temperature solid oxide fuel cells

Chuangang Yao^{a,*}, Haixia Zhang{^a}, Xiaojuan Liu^{b}, Junling Meng{^b}, Xiong Zhang^{b}, Fanzhi Meng^{c,*}, Jian Meng{^b}

^{a} School of New Energy, Bohai University, Jinzhou 121007, PR China
^{b} State Key Laboratory of Rare Earth Resources Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, PR China
^{c} School of Materials Science and Engineering, Changchun University of Science and Technology, Changchun 130022, PR China

**A R T I C L E  I N F O**

Keywords: Solid oxide fuel cell Cathode Layered perovskite Electrical conductivity Electrochemical performance

**A B S T R A C T**

Layered perovskite oxide LaBa_{0.5}Sr_{0.25}Co_{2}O_{5+δ} (LBSCO) is studied as a potential cathode material for intermediate temperature solid oxide fuel cells (IT-SOFCs). Ca-free sample LaBa_{0.5}Sr_{0.25}Co_{2}O_{5+δ} (LBSCO) is also investigated for comparison. The thermal expansion coefficient (TEC) value is reduced from 26.2 × 10^{-6} K^{-1} to 20.0 × 10^{-6} K^{-1} by Ca doping. The electrical conductivity of LBSCO is above 500 S cm^{-1} at room temperature to 800 °C. Substitution of Sr by Ca can effectively enhance the electrochemical performance. The area specific resistance (ASR) values of LBSCO and LSCO are 0.075 Ω cm^{-2} and 0.084 Ω cm^{-2} at 800 °C, respectively. Moreover, LBSCO cathode achieves an excellent outputting of 662 mW cm^{-2} at 800 °C. Based on these results, Ca doped layered perovskite LBSCO can be a cathode candidate material for IT-SOFC application.

**1. Introduction**

Solid oxide fuel cells (SOFCs) have been widely researched as the next generation energy conversion device with high efficiency, light pollution and multi-fuel adaptability [1–3]. Currently, the research emphasis of SOFC technology is on the intermediate temperature (IT) application. The reduction of operating temperature can effectively improve the long-term stability of SOFC [4]. However, a lower operating temperature also has some drawbacks for SOFC, such as slow down the process of oxygen reduction and increase the over-potential of the cathode [5]. Hence, the development of new alternative SOFC cathode materials with excellent electrochemical characteristics is the key for the application of IT-SOFC. Considering this fact, mixed ionic and electronic conductors (MIECs) are widely researched, such as Ba_{0.5}Sr_{0.5}Co_{2}O_{4}Fe_{2}O_{3} (BSCF) [6] La_{0.4}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3} (LSCF) [7], and Sm_{0.5}Sr_{0.3}Co_{2}O_{3} (SSC) [8].

Recently, layered double perovskites LnBaCo_{2}O_{5+δ} (LnBCO, Ln = La, Pr, Nd, Sm, and Gd) have also attracted a great deal attention as the next generation alternative IT-SOFC cathode materials due to their excellent chemical diffusion and surface exchange coefficients [9–14]. This family of layered perovskite compounds have a general formula AA'B_{2}O_{5+δ} (A': lanthanides or Y; A': Ba or Sr; B: Co, Fe or Mn). [BO_{2}]^{−}\quad [A'O]^{−}\cdot [BO_{2}]^{−}\quad [A'O]^{−}\cdot

⁎ Corresponding authors.

E-mail addresses: yaochuangang@bhu.edu.cn (C. Yao), mengtiantang0527@gmail.com (F. Meng).

https://doi.org/10.1016/j.jssc.2018.05.028
Received 28 February 2018; Received in revised form 17 May 2018; Accepted 18 May 2018
Available online 21 May 2018
0022-4596/ © 2018 Elsevier Inc. All rights reserved.
important to find a compromise way to keep the good electrocatalytic activity of the Co-rich SOFC cathodes and reduce the formation of impurity phase (e.g., SrCO₃) simultaneously. Lee et al. [29] recently claimed that the smaller size difference between the host and dopant, the less dopant segregation will be, which is an efficient way to enhance the stability of the cathode surface and meanwhile retain the excellent electrical and electrochemical performance of Co-rich SOFC cathodes. Therefore, in this work, Co-based layered double perovskite LaBaₓSrₓCo₂O₅₋𝛿 (LBSCO) is chosen as the starting material for comparison. We focus on the effects of Ca doping on the crystal structure, thermal behavior, electrical properties and electrochemical performance of LaBaₓSrₓCaₓCo₂O₅₋𝛿 (LBSCaCO) in order to assess its potential application as SOFC cathode.

2. Experimental

2.1. Sample preparation

The LBSCO and LBSCaCO powders were synthesized via Pechini method [20]. Stoichiometric amounts of La₂O₃ (99.99%, Sinopharm Chemical Reagent Co. Ltd, abbreviated as SCRC) was dissolved into nitric acid solution. Ba(NO₃)₂ (≥ 99.5%, SCRC), Sr(NO₃)₂ (99.9%, SCRC), Co(NO₃)₂·6H₂O (99%, SCRC), Ca(NO₃)₂·4H₂O (99%, SCRC) were sequentially added in distilled water. Solid citric acid monohydrate and polyethylene glycol were added as complexing agent. Then the solutions were water bathed at 70 °C for 24 h. Subsequently, the resulting gels were calcined at 600 °C in air for 3 h. The obtained powders were fully ground and followed by a sintering of 10 h at 1000 °C in air to form the pure phase.

2.2. Characterizations

The phase structures of LBSCO and LBSCaCO samples were determined by the X-ray diffraction (XRD, Rigaku D/Max 2500 diffractometer) measurement. The XRD data were obtained over 10°–20° with a scanning rate of 0.02° s⁻¹. The Rietveld refinements were accomplished by using the GSAS + EXPGUI program.

The valence states of metal elements in LBSCO and LBSCaCO were confirmed by X-ray photoelectron spectroscopy (XPS, Thermo- Electron ESCALAB 250 spectrometer) at room temperature in air.

The thermal stability of LaBaₓSrₓCaₓCo₂O₅₋𝛿 (x = 0, 0.25) were examined by thermogravimetric analysis (TGA, NETZSCH STA 449F3) from 30 °C to 800 °C in air atmosphere.

LBSCO and LBSCaCO powders were pressed into pellets (diameter × thickness = 12 mm × 1 mm) and bars (length × width × height = 5 mm × 5 mm × 25 mm) under 260 MPa for 15 min with a hydrostatic pressing instrument. The samples with pellet and bar types were sintered at 1000 °C for 10 h to form high density samples (> 90%, measured by Archimedes method). LBSCO and LBSCaCO dense pellets were used for the measurement of electrical conductivity by a DC four-terminal method from 30 °C to 800 °C in air.

The microstructures of the symmetrical cells were observed using the scanning electron micrographs (SEM, Hitachi S-4800) at 10 kV.

2.3. Electrochemical performance

Symmetrical cells consists of electrode | Sm₂₀₃Ce₆₀₋₅O₁₉ (SDC) | electrode were prepared for electrochemical performance analysis. The SDC pellets were fabricated via Sol-gel method according to ref. [30]. Electrode slurries were prepared by mixing the LBSCO and LBSCaCO powders with moderate amounts of binder (ethylene cellulose and α-terpineol in a weight ratio of 3:97). Then the ready-made slurries were coated on both sides of the SDC pellets symmetrically. Then, the prepared symmetrical cells were calcined for 2 h at 1000 °C in air. The electrochemical impedance spectroscopy (EIS) was tested via Autolab Electrochemical Instruments (PGSTAT302) during the frequency region of 0.1 Hz to 1 MHz with a perturbation of 10 mV in air.

The performances of single cells with NiO-SDC as anode were tested via Autolab Electrochemical Instruments (PGSTAT302). The measurement is from 650 °C to 800 °C with H₂ as the fuel gas and ambient atmosphere as oxidizing agent, respectively.

3. Results and discussion

3.1. Crystal structure and chemical compatibility

The Rietveld refined XRD patterns of LaBaₓSrₓCo₂O₅₋𝛿 (LBSCO) and LaBaₓSrₓCaₓCo₂O₅₋𝛿 (LBSCaCO) powders are shown as Fig. 1. The observed XRD patterns are well consistent with the calculated patterns. Both samples are single phase without any impurities and can be retrieved to cubic structure with Pm 5m (No.221) space group, indicating a lack of long-range ordering of cations in the lattice. The lattice parameters of LBSCO and LBSCaCO are a = b = c = 3.896(7) Å and a = b = c = 3.880(6) Å. The lattice parameters are reduced with the replacement of Sr by Ca in LBSCO due to the relatively small ionic radius of Ca²⁺ (r = 1.34 Å, coordination number = 12) compared with that of Sr²⁺ (r = 1.58 Å, coordination number = 12).

The chemical compatibility between LaBaₓSrₓ₋₅₋₅CaₓCo₂O₅₋𝛿 (x = 0, 0.25) samples and SDC electrolyte were investigated by XRD. The XRD patterns of LBSCO-SDC (volume ratio = 1:1) mixture and LBSCaCO-SDC (volume ratio = 1:1) mixture that sintered for 6 h at...