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Evaluation of $Pr_{1+x}Ba_{1-x}Co_2O_{5+\delta}$ ($x = 0 - 0.30$) as cathode materials for solid-oxide fuel cells

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ABSTRACT

Layered-perovskite $Pr_{1+x}Ba_{1-x}Co_2O_{5+\delta}$ (PBC, $x = 0 - 0.30$) oxides are designed and evaluated as cathode materials for solid-oxide fuel cells (SOFCs). The effect of x on structural, thermal and electrochemical properties has been systematically investigated. Analysis of X-ray photoelectron spectroscopy indicates the existence of mixed valences of Pr^{3+}/Pr^{4+} and Co^{3+}/Co^{4+}. Among the series samples, the $x = 0.10$ shows the best electrochemical performance. The conductivity reaches as high as 600 S cm^{-1} at 600 – 800 °C. As cathode materials for electrolyte-supported single cells, the maximum power densities at 800 °C are 408, 713, 732, 546 and 435 mW cm^{-2} for $x = 0$, 0.05, 0.10, 0.20 and 0.30, respectively. Our results demonstrate that the layered-perovskite $Pr_{1+x}Ba_{1-x}Co_2O_{5+\delta}$ are potential cathode materials for SOFCs, which electrochemical properties can be improved by optimizing Pr/Ba molar ratio.

1. Introduction

Solid-oxide fuel cells (SOFCs) have attracted extensive attention as economic, efficient and sustainable energy conversion systems [1,2]. Traditional SOFCs operating at high temperature around 1000 °C ask for rigorous requirements on materials and technology, which hinders the commercialization of SOFCs. Recently, great effort has been devoted to developing intermediate-temperature (600 – 800 °C) SOFCs (IT-SOFCs), which can not only extend the choice of interconnecting materials, but also reduce the cost of practical application. The reduction of operating temperature, however, obviously leads to the degradation of electrochemical performance due to electrolyte ohmic resistance and electrode polarization. Conventional perovskite-based (La, Sr)MnO_3 (LSM) cathode materials cannot meet the requirements of IT-SOFCs due to poor oxide-ion conductivity in this temperature range [3].

In recent years, layered double perovskites with general formula $AA'B_2O_{5+\delta}$ (A = rare earth, A′ = alkaline earth, B = transition metal) have received much attention [4]. These oxides have an ordered structure in which lanthanide and alkali earth ions occupy alternate (001) layers and oxygen vacancies are mainly located in the rare earth planes $[AO]_\delta$, which can enhance the oxygen-ion transport property [5]. As mixed ionic-electronic conductors (MIECs), $LnBaCo_2O_{5+\delta}$ (Ln = Y, Pr, Nd, Sm, Gd) have been employed as potential cathode materials for IT-SOFCs because of their surface exchange kinetics and rapid oxygen diffusion [6–12].

To improve the electrochemical performance, many studies on $LnBaCo_2O_{5+\delta}$ have focused on cationic substitution and microstructure fabrication. For example, porous electrode with $LnBaCo_2O_{5+\delta}$ cathode-electrolyte composites is favorable to increase the triple-phase boundary (TPB) and to lower the contact resistance [13,14]; substitution of Ba by Sr can enhance oxygen diffusion and electrical conductivity [15–18]; substitution of Co by other transition metal ions at B-sites can reduce thermal expansion coefficients (TECs) [19–22]. However, how the substitution affects the electrochemical performance of the cathodes has rarely been reported.

Some researchers have found that, in (La, Sr)(Co, Fe)$O_{3-\delta}$ and $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ perovskites, the A-site cation radius has a great effect on lattice deficiencies. The A-site cation deficiencies introduced into the lattice structure significantly affect the physical and chemical properties of the materials [23–27]. Among the $LnBaCo_2O_{5+\delta}$ oxides, $PrBaCo_2O_{5+\delta}$ has attracted tremendous interest due to its high electronic conductivity, low cathode polarization and excellent electrochemical performance [7,28–30].

In this work, we designed and prepared Pr-rich $Pr_{1+x}Ba_{1-x}Co_2O_{5+\delta}$ compounds ($0 \leq x \leq 0.30$) to serve as cathode materials for SOFCs. Changing Pr content can effectively adjust

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the Co valence and oxygen vacancy. The effects of structure, oxygen content and thermal expansion on electrochemical performances were systematically investigated.

2. Experimental

$Pr_{1+x}Ba_{1-x}Co_2O_{5+\delta}$ (PBC) series samples with $x = 0 - 0.30$ were prepared via a sol-gel process. Pr_6O_{11} (99.9%), $Sr(NO_3)_2$ (99.5%), $Ba(NO_3)_2$ (99.5%) and $Co(NO_3)_2 \cdot 6H_2O$ (99%) were used as starting materials. Pr_6O_{11} was first dissolved completely into concentrated nitric acid; $Ba(NO_3)_2$ and $Co(NO_3)_2 \cdot 6H_2O$ were dissolved into deionized water. The two solutions were mixed together, followed by addition of parallel complexants of citric acid and ethylenediaminetetraacetic acid (EDTA). The molar ratio of total metal ions, citric acid and EDTA was 1:2:1. An appropriate amount of ammonia was added to adjust pH value of the solution to 7 – 8. The precursor solution was subsequently heated at 120 °C under stirring to form a viscous gel. The gel was baked at 150 °C overnight and then calcined at 400 °C for 8 h to achieve a powder. The powder was ground, pelletized, and finally sintered in air at 1000 °C for 10 h. $La_{0.8}Sr_{0.2}Ga_{0.83}Mg_{0.17}O_{2.815}$ (LSGM) and $Ce_{0.8}Sm_{0.2}O_{1.9}$ (SDC) were synthesized via solid state reaction, as described in detail elsewhere [31,32]. The anode was the mixture of NiO and SDC with a weight ratio of 65:35.

The phase of the samples was checked with X-ray diffraction (XRD) by using Philips X'Pert PRO diffractometer operating with Cu Kα radiation. To determine the electrical conductivity, all the powders were pressed into pellets with diameter of 13 mm and thickness of 1 mm under a pressure 100 MPa, followed by sintering at 1000 °C for 10 h to become denser. The densities of the pellets, measured by Archimedes method, are 5.81, 5.89, 5.89, 5.74 and 5.71 $g\,cm^{-3}$ for $x = 0$, 0.05, 0.10, 0.20 and 0.30, respectively. The conductivity was measured on a RTS-8 digital instrument in stagnant air with a standard four-point probe method. Four silver wires were attached on the pellet surface with silver paste to obtain good electrical contact between the silver wires and the sample. Thermal expansion coefficients (TECs) were measured on rectangular-shaped bar sample (5 × 5 × 20 mm) with a dilatometer (NETZSCH STA449c/3/G) from room temperature to 900 °C at a heating rate of 5 $°C\,min^{-1}$. Thermogravimetric (TG) behavior was checked by a Stanton STA 781 instrument. Surface analysis was performed on an X-ray photoelectron spectrometer (XPS, MultiLab2000, VG). All the fitted parameters were fitted with software XPSPEAK41, and the spectra are fitted by using Shirley-type background subtraction method. The full width at half maxima (FWHM) was constrained in the range of 1.0 – 2.5 eV. 80% Gaussian and 20% Lorentz functions were used for different chemical states of the elements. The fitted standard deviations for the O 1s, Pr 3d, and Ba 3d - Co 2p core-level spectra were confined within 3.4, 3.8 and 4.0%, respectively.

The single cells were fabricated based on electrolyte-supported technique to form the configuration of NiO-SDC/SDC/LSGM/PBC. 300 μm thick LSGM served as the electrolyte. The buffer layer SDC was uniformly screen-printed onto one side of the LSGM disk, followed by baking at 1300 °C in air for 1 h. The anode ink (NiO-SDC) was subsequently printed onto the buffer layer and fired at 1250 °C in air for 2 h. The cathode slurry was screen-printed onto the other side of LSGM disk and sintered 950 °C for 2 h. The cells were tested from 650 to 800 °C with hydrogen as fuel at a flowing rate of 50 $mL\,min^{-1}$ and the static air as oxidant.

Electrochemical impedance spectra (EIS) and power output measurements of the cells were performed on electrochemical workstation (PARSTAT2273, US). The impedance was detected over a frequency range from 10 mHz to 100 kHz with an AC signal amplitude of 10 mV under open circuit voltage. The EIS fitting analysis was controlled with the program Zview from EChem Software.

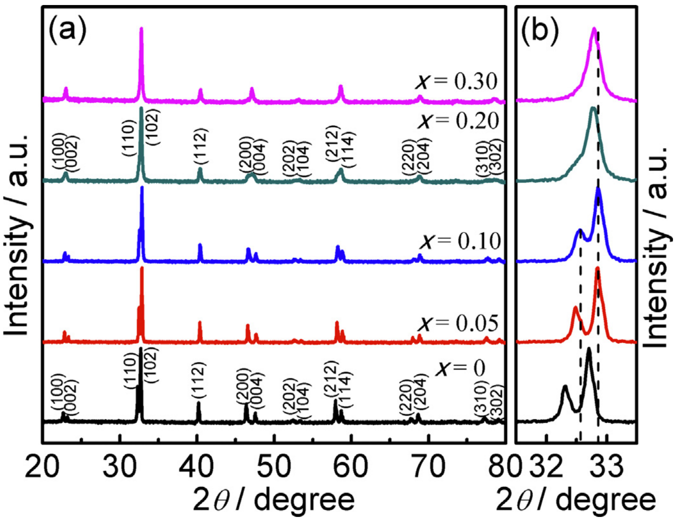

Fig. 1. X-ray diffraction patterns of PBC sintered at 1000 °C for 10 h.

3. Results and Discussion

Fig. 1a presents the XRD patterns of the PBC oxides obtained by sintering at 1000 °C for 10 h. All samples are phase-pure. The phase can be indexed well in a tetragonal structure with space group of P4/mmm for $x = 0 - 0.30$. For further evaluation of the effect of x on the structure, the XRD patterns between 31.5° and 33.5° are magnified and compared in Fig. 1b. The peaks shift gradually toward higher angles with increasing Pr/Ba ratio from $x = 0$ to 0.10, indicating the shrinkage of unit cell. This agrees well with the fact that the ionic radius of Pr^{3+} (1.30 Å) is smaller than that of Ba^{2+} (1.61 Å) [33]. The lattice parameters calculated by the Jade software are listed in Table 1. An earlier study also showed that the crystal structure of cobalt-based layered perovskite can exist in either tetragonal or orthorhombic forms [34]. The $LnBaCo_2O_{5+\delta}$ oxides with larger or smaller cation radii can be crystallized into a tetragonal structure, while those with intermediate-size cation radii are propitious to forming an orthorhombic structure [34]. However, in our case, for $0 \le x \le 0.10$, the observed split peaks are characteristic for the layered perovskite oxides with tetragonal structure. With increasing x, the characteristic double peaks incorporate into one shoulder peak for $x \ge 0.20$, indicating that the structure symmetry does not change but the lattice distortion is reduced. Such phenomenon is also identified as a specific evidence of the layered perovskites [35].

XPS technique was used to study the chemical state of the compositional elements and the surface properties of the materials. Fig. 2 displays the survey spectra, O 1s, Pr 3d, and Ba 3d - Co 2p core-level spectra for PBC. The typical survey spectra of the series PBC ($x = 0 - 0.30$) samples are shown in Fig. 2a. The five relative strong peaks are assigned to Pr 3d, Co 2p/Ba 3d, O 1s, C 1s, and Ba 4d photoelectrons, respectively. The XPS survey is in agreement with the elementary composition of the samples. The fitting result of the O 1s peak indicates that oxygen ions exist in several chemical environments. As can be seen in Fig. 2b, the O 1s core-level spectra of the PBC samples with different x show the identical feature containing three independent peaks. This implies that, for each specimen, the contribution of oxygen to the spectra originates from three different chemical environments on the oxide surface. The O 1s peak at 528.3 eV is attributed to the lattice oxygen (O_L) at normal sites of the perovskite structures [36,37], while the peak at 531.1 eV corresponds to the hydroxyl and/or carbonate form (O_H)