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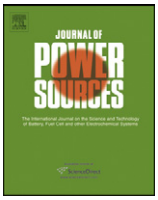

Cobalt-site cerium doped $Sm_xSr_{1-x}CoO_{3-\delta}$ oxides as potential cathode materials for solid-oxide fuel cells

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ABSTRACT

A series of new oxides with the nominal composition of $Sm_xSr_{1-x}Co_{1-y}Ce_yO_{3-\delta}$ ($x = 0.1, 0.3, 0.5$; $y = 0.05, 0.1$) were synthesized. Their crystal structure, morphology, thermal expansion and electrochemical properties were systematically investigated. A phase-pure perovskite-type $Sm_{0.3}Sr_{0.7}Co_{0.95}Ce_{0.05}O_{3-\delta}$ oxide is obtained, while the other samples are actually composed of B-site cation deficient $Sm_xSr_{1-x}Co_{1-y}Ce_{y-z}O_{3-\delta}$ ($0 < z < y$) and CeO_2 mixed phases. These two-phase samples exhibit larger oxygen nonstoichiometry (δ) and higher average thermal expansion coefficients (TEC), while the single-phase $Sm_{0.3}Sr_{0.7}Co_{0.95}Ce_{0.05}O_{3-\delta}$ oxide shows a smaller δ and a lower TEC as compared to $Sm_{0.3}Sr_{0.7}CoO_{3-\delta}$. The introduction of cerium also effectively suppresses the chemical expansion and the growth of grain particles. The smaller grain size is beneficial in improving the electrode surface area. In addition, the electrical conductivities of Ce-doped $Sm_xSr_{1-x}CoO_{3-\delta}$ are all higher than $200\,S\,cm^{-1}$. EIS tests demonstrate that partially substituting Co with Ce and the B-site deficiency improve the cathode performance. $Sm_{0.3}Sr_{0.7}Co_{0.95}Ce_{0.05}O_{3-\delta}$ shows the lowest area specific resistance (ASR) among the others. Through proper cobalt-site cerium doping, the $Sm_xSr_{1-x}CoO_{3-\delta}$ related oxides could be developed into promising cathode materials for SOFC.

1. Introduction

Solid-oxide fuel cells (SOFCs) have several advantages over conventional power generation system, including higher energy efficiency and environmental friendliness [1]. Cathode is an important component of SOFCs and development of high-performance cathode is one of the key steps towards the wide spread of SOFC technology. In recent years, the application of perovskite-type oxides as cathode materials of intermediate-temperature (IT)-SOFCs has received increasing attentions [2–4] because of their high thermal stability as well as good thermal and chemical compatibility with solid electrolytes. Some perovskite oxides possess mixed oxygen ionic and electronic conductivity, which successfully extend the active oxygen reduction sites from the typical triple phase boundary (TPB) to the entire exposed cathode surface. As a result, an obvious reduction in electrode polarization resistance at low operation temperature is frequently observed. Among the many perovskites, $(LnSr)CoO_{3-\delta}$ (Ln: La, Pr, Sm, Gd) [3,5–7], $(LaSr)MnO_{3-\delta}$ [8], $(LaSr)(CoFe)O_{3-\delta}$ [9] and $(BaSr)(CoFe)O_{3-\delta}$ [10] have been the most widely investigated. It has been reported that Co-based perovskite oxide with relatively high ionic conductivity exhibited higher electrochemical performance than the conventional Co-free materials such as $(LaSr)MnO_{3-\delta}$ at intermediate temperature. However, the average thermal expansion coefficients (TEC) of the Co-based perovskite-type materials are typically high, which limit their practical applications.

Strontium-doped samarium cobaltite with the compositions of $Sm_xSr_{1-x}CoO_{3-\delta}$ (SSC) show high electrical conductivity over a wide range of temperatures and have been extensively investigated as potential cathodes of IT-SOFCs recently. However, these materials have much larger TEC than the typical electrolytes such as samarium doped ceria (SDC) [6,11]. Several ways have been exploited to improve their compatibility with the electrolytes. Doping Fe or Mn into the B-site could lower the TEC. However, it also leads to a decrease in the electrical conductivity and an increase in the electrode polarization resistance [12]. The formation of a composite electrode by introducing an ionic conducting phase, typically with the same composition to that of electrolyte, is frequently adopted. Xia et al. [3] and Zhang et al. [13] demonstrated that the electrochemical performance of SSC was greatly improved when it formed composite with doped ceria. It is believed that introducing doped ceria to the SSC cathode could also decrease the TEC and improve the thermal compatibility with doped ceria electrolyte.

Herein, in order to make $Sm_xSr_{1-x}CoO_{3-\delta}$ cathodes more compatible with SDC electrolyte and improve the cathode performance, the cobalt-site doping with cerium was exploited. A new series

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of oxides with the nominal composition of $Sm_xSr_{1-x}Co_{1-y}Ce_yO_{3-\delta}$ ($x = 0.1, 0.3, 0.5$; $y = 0.05, 0.1$) were synthesized. The effect of x and y on the crystal structure, morphology, thermal expansion, electrical conductivity, oxygen nonstoichiometry and electrochemical performance were systematically investigated.

2. Experimental

2.1. Sample preparation

Oxide powders with the nominal compositions of $Sm_xSr_{1-x}Co_{1-y}Ce_yO_{3-\delta}$ (SSCC) ($x = 0.1$, 0.3 and 0.5; $y = 0.05$ and 0.1) were prepared by a citric-EDTA complexing sol–gel method. The nitrates of Sm, Sr, Co and Ce were used (99.9% or higher) as the cation sources. EDTA was dissolved in $NH_3 \cdot H_2O$ at first and citric acid and stoichiometric nitrates were added afterwards. The molar ratio of EDTA, citric acid and metal ions was 1:1.5:1. $NH_3 \cdot H_2O$ was added to adjust the pH value to 6–7 and then a clear solution was obtained. After a drying process at 200 °C and with a combustion reaction, the water was removed and a spongy solid was formed. Finally, the obtained products were calcined at 950 °C for 5 h in air with the same heating and cooling rate of 2 °C min^{-1} to prepare the SSCC oxides. The powder samples were subjected to X-ray diffraction (XRD), iodometric titration and thermogravimetry (TG) characterization. The abbreviations of $Sm_xSr_{1-x}Co_{1-y}Ce_yO_{3-\delta}$ series are listed in Table 1.

The SSCC powders were grinded, sieved (300 meshes), and then uniaxially pressed at 400 MPa to prepare the green bars. After sintered at 1200 °C for 5 h in air with a heating and cooling rate of 2 °C min^{-1}, dense SSCC bars with the dimensions of ~18 mm × 4 mm × 5 mm were obtained, which were adopted for the electrical conductivity and thermal expansion measurement.

The preparation procedures for the powder and green disk of $Sm_{0.2}Ce_{0.8}O_{1.9}$ (SDC) are similar to that of SSCC. After sintering the green disks at 1400 °C for 5 h in air, dense SDC electrolytes with a diameter of ~13.0 mm and thickness of ~0.5 mm were obtained. To fabricate the cathode layers, SSCC powder was dispersed in a mixture of ethylene glycol, ethanol and isopropyl alcohol with the help of high-energy ball mill (Fritsch Pulverisette 6). The obtained suspension was deposited onto the both surfaces of SDC using the spray coating method. Symmetric SSCC-SDC-SSCC cells were obtained by calcined at 1000 °C for 2 h.

2.2. Characterization

The crystal phases of samples were determined by XRD with Cu Kα radiation (Bruker, model D8 Advance). The diffraction patterns were collected at room temperature in the range of $20^\circ \le \theta \le 80^\circ$ with the step width of 0.02° and scan rate of 0.5 s $step^{-1}$. The morphologies of porous cathodes were examined by scanning electron microscopy (SEM) (FEI, QUANTA-2000). The electrical conductivity of sintered specimens was measured in the stagnant air by a four-probe DC instrument (Keithley, model 2440 5A), where the Ag paste and Ag wires were used to connect the sample and instrument. The thermal expansion behaviors of sintered specimens were measured using the apparatus of dilatometer (Netzsch, model DIL 402C). The heating rate was 5 °C min^{-1}. The weight changes of the samples were investigated up to 1100 °C with a heating rate of 10 °C min^{-1} in air atmosphere (50 ml min^{-1}) using a TG apparatus (NETZSCH STA 449 F3).

2.3. Iodometric titration

The room-temperature oxygen contents of SSCC were determined by iodometric titration method. In this method, approximate 50 mg of the sample were dissolved in 1 M HCl solution (~100 ml) containing an excess of KI (~2 g), resulting in the reduction of tri- and tetra-metal (Co^{4+}, Co^{3+}, Ce^{4+} to Co^{2+}, Ce^{3+}) and oxidation of I^- to I_2. The product I_2 was then titrated with sodium thiosulfate solution using starch as indicator. The whole process can be generally written as

$$\begin{aligned}&2AB_{1-z}O_{3-\delta}\cdot zCeO_2+(12+8z-4\delta)H^+\\&+[2(m-2\delta)+2z(7-n-m)]I^-=2A^{n+}+2(1-z)B^{(6-n-m)+}\\&+2zCe^{3+}+(6+4z-2\delta)H_2O+[m-2\delta+z(7-n-m)]I_2\end{aligned} \tag{1}$$

$$I_2+2S_2O_3{}^{2-}=2I^-+S_4O_6{}^{2-} \tag{2}$$

where δ is the oxygen nonstoichiometry; z is the ratio of second phase in perovskite phase; n is the average oxidation state of A-site ions and m is the reduction amount of the oxidation state of B-site ions ($1 \le n \le 5$ and $1 \le m \le 6-n$). For $(Sm_xSr_{1-x})(Co_{1-y}Ce_{y-z})O_{3-\delta}\cdot zCeO_2$, Sm^{3+}, Sr^{2+} and O^{2-} take fixed valence while Co and Ce were reduced to bivalent and trivalent, respectively. Therefore the oxygen nonstoichiometry can be written as:

$$\delta=\frac{CVM-[m+z(7-n-m)]w_0}{16CV-2w_0} \tag{3}$$

where w_0 is the mass of sample, M is the molar mass of $Sm_xSr_{1-x}Co_{1-y}Ce_{y-z}O_3\cdot zCeO_2$, C is the molar concentration of $Na_2S_2O_3$ and V is the consumption of volume of the $Na_2S_2O_3$ solution.

2.4. Electrochemical impedance measurement

The polarization resistance and area specific resistance (ASR) of SSCC cathodes were characterized by the electrochemical impedance spectra (EIS) (Solartron 1287 potentiostat + Solartron 1260 frequency response analyzer). Silver paste (pre-diluted silver paste by alcohol) was painted to the electrode surfaces as current collectors. The applied frequency was in the range of 10 mHz to 10 kHz with a signal amplitude of 10 mV. Samples were tested under open circuit voltage condition in air atmosphere.

Table 1
Phase constituents, second phase CeO_2 content and evolution of peak $(1\,1\,0)_p$ in SSCC series.

Sample[a]	Symbol	Phases constituents	Ce ($y \times 10^2$ mol%)	CeO_2[b] ($z \times 10^2$ mol%)	2θ[c] $(1\,1\,0)_p$
$Sm_{0.5}Sr_{0.5}CoO_{3-\delta}$	SSCC55-10	Single-phase	0	0	33.36
$Sm_{0.5}Sr_{0.5}Co_{0.95}Ce_{0.05}O_{3-\delta}$	SSCC55-9505	Two-phase	5	1.25	33.08
$Sm_{0.5}Sr_{0.5}Co_{0.9}Ce_{0.1}O_{3-\delta}$	SSCC55-91	Two-phase	10	3.07	33.21
$Sm_{0.3}Sr_{0.7}CoO_{3-\delta}$	SSCC37-10	Single-phase	0	0	33.10
$Sm_{0.3}Sr_{0.7}Co_{0.95}Ce_{0.05}O_{3-\delta}$	SSCC37-9505	Single-phase	5	0	32.90
$Sm_{0.3}Sr_{0.7}Co_{0.9}Ce_{0.1}O_{3-\delta}$	SSCC37-91	Two-phase	10	2.42	32.83

[a] For convenient, using the nominal expression $Sm_xSr_{1-x}Co_{1-y}Ce_yO_{3-\delta}$ to represent the actual composition $Sm_xSr_{1-x}Co_{1-y}Ce_{y-z}O_{3-\delta}\cdot zCeO_2$ of two-phase samples.

[b] CeO_2 constituent in $Sm_xSr_{1-x}Co_{1-y}Ce_{y-z}O_{3-\delta}\cdot zCeO_2$ oxides.

[c] Diffraction angle 2θ of the characteristic peak $(1\,1\,0)_p$ of the perovskite phase.