La_{0.4}Bi_{0.4}Sr_{0.2}FeO_{3-δ} as Cobalt-free Cathode for Intermediate-Temperature Solid Oxide Fuel Cell

Mei Li^a, Yuyu Ren^a, Zhesheng Zhu^a, Shiyue Zhu^a, Fanglin Chen^b, Yanxiang Zhang^{c*},
Changrong Xia^{a*}

^a Key Laboratory of Materials for Energy Conversion, Chinese Academy of Sciences ,
Department of Materials Science and Engineering & Collaborative Innovation Center
of Suzhou Nano Science and Technology,

University of Science and Technology of China, No. 96 Jinzhai Road, Hefei, Anhui
Province, 230026, P. R. China

^bDepartment of Mechanical Engineering, University of South Carolina, Columbia, SC
29208, USA

^cNational Key Laboratory for Precision Hot Processing of Metals, School of
Materials Science and Engineering, Harbin Institute of Technology, Harbin 150001,
China

*Corresponding author. Tel: ++86-551-63607475, Fax: ++86-551-63601696,

E-mail: xiacr@ustc.edu.cn; Tel: +86-451-86418617, Fax: +86-451-86413922,

Email: hitzhang@hit.edu.cn

Abstract

$\text{La}_{0.4}\text{Bi}_{0.4}\text{Sr}_{0.2}\text{FeO}_{3-\delta}$ (LBSF) has previously been demonstrated to show the highest electrochemical performance in a series of bismuth doped lanthanum strontium ferrite $\text{La}_{0.8-x}\text{Bi}_x\text{Sr}_{0.2}\text{FeO}_{3-\delta}$ where $0 \leq x \leq 0.8$ as the cathode for intermediate-temperature solid oxide fuel cells. The cobalt-free electrocatalyst LBSF is further investigated in the present study using thermogravimetric analysis, oxygen temperature-programmed desorption method, iodometric titration and high-temperature X-ray diffraction refinement methods to reveal its structural properties including oxygen non-stoichiometry coefficient (δ), valence state of Fe, and lattice parameters at the different temperatures. In addition, the oxygen reduction process on the single phase LBSF is explored using the distribution of relaxation time method based on the electrochemical impedance spectroscopy measurements conducted in oxygen partial pressure from 0.01 to 1.0 atm. The LBSF cathode electrochemical performance is effectively improved by cooperating $\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$ (SDC), an oxygen ion conductor, resulting in interfacial polarization resistance less than $0.1 \, \Omega \, \text{cm}^2$ at $700 \, ^\circ\text{C}$ when SDC is used as the electrolyte.

KEYWORDS: solid oxide fuel cell, bismuth doped lanthanum strontium ferrite, oxygen reduction process, cathode, oxygen non-stoichiometry

1. Introduction

Solid oxide fuel cell (SOFC) has been paid a lot of attention as a novel energy conversion technology due to its high fuel utilization, modularity, and excellent fuel flexibility.¹⁻³ Unfortunately, the current SOFC systems are still too expensive for broad commercialization. To promote the SOFC development, the operating temperature must be sufficiently reduced so that much less expensive materials could be used.⁴ Although improvements in intermediate-temperature SOFCs have been achieved, their performance is still typically limited by electrochemical oxygen reduction reaction (ORR) at the cathodes. Therefore, it is critical to explore materials and/or optimize cathode structures to improve the cathode performance.

In the past decade, ferrite-based perovskites have been studied as potential cathode materials for intermediate temperature SOFCs. The ferrite electrocatalysts have shown much higher catalytic activity for ORR than the conventional manganite based materials, typically strontium-doped lanthanum manganite (LSM).⁵⁻⁷ For example, the chemical surface oxygen exchange coefficient (K_{chem}) is $3.0 \times 10^{-5} \text{ cm s}^{-1}$ for $\text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_{3-\delta}$, much higher than $1.0 \times 10^{-9} \text{ cm s}^{-1}$ for $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3-\delta}$ at the same temperature, 700 °C.⁸⁻⁹ In addition, the ferrite materials are much more cost effective and have exhibited higher durability than the cobalt-containing mixed ionic and electronic conductors such as $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF) and $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$,¹⁰⁻¹⁴ which have been extensively investigated as the cathodes

for intermediate-temperature SOFCs. The cobalt-containing perovskite oxides often suffer problems such as high thermal expansion coefficients, easy reduction, evaporation of cobalt and the high cost of cobalt element, thus limiting further applications.¹⁵ However, the ferrite oxides have shown lower catalytic activity than the cobalt materials. For example, at 700 °C, $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ has a K_{chem} of $2.0 \times 10^{-4} \text{ cm s}^{-1}$, much higher than that of $\text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_{3-\delta}$.^{8, 16} Recently, Bi^{3+} is proposed to dope to the A-site in the ferrite to increase the catalytic activity due to the existence of highly polarizable $6s^2$ lone pair electrons for Bi^{3+} .^{8, 17-19} In a series of components $\text{La}_{0.8-x}\text{Bi}_x\text{Sr}_{0.2}\text{FeO}_{3-\delta}$ ($x = 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7$, and 0.8), we have demonstrated that the composition $\text{La}_{0.4}\text{Bi}_{0.4}\text{Sr}_{0.2}\text{FeO}_{3-\delta}$ (LBSF) has exhibited the promising properties for ORR. The K_{chem} at 700 °C for LBSF is $9.5 \times 10^{-4} \text{ cm s}^{-1}$, even higher than $2.8 \times 10^{-4} \text{ cm s}^{-1}$ for LSCF in the oxygen partial pressure range from 0.05 bar to 0.21 atm.²⁰ As a result, the interfacial polarization resistance for a single phase LBSF supported on SDC ($\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$) electrolyte is $0.12 \Omega \text{ cm}^2$ at 700 °C. The resistance is lower than that for the typical single phase LSCF such as $0.18 \Omega \text{ cm}^2$ at 700 °C when GDC (gadolinia doped ceria) is used as the electrolyte.²¹ Further, a cell based on SDC electrolyte with the single phase LBSF cathode generates a peak power density of 480 mW cm^{-2} at 600 °C. The cell performance is comparable to those obtained with composite cathodes such as $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ -SDC and LSCF-GDC.²²⁻²³

This work extends our previous research on LBSF by investigating its structural and oxygen non-stoichiometry at high temperatures. Its electrochemical performance is

further improved by incorporating SDC to form composite electrodes consisting of various amounts of LBSF and SDC. Adding an ionically conducting phase to the electronically conducting electrocatalyst can provide more active sites for ORR.²⁴ In the cathode, doped ceria such as SDC and GDC are common ionically conducting components, which can enlarge the three-phase boundary region for the electrode reaction by providing sufficient paths to transport the oxygen ions.

2. Experimental

2.1 Materials Preparation and Synthesis

$\text{La}_{0.4}\text{Bi}_{0.4}\text{Sr}_{0.2}\text{FeO}_{3-\delta}$ (LBSF) powder was synthesized using a combustion process and the specific fabrication details were previously reported.⁸ All chemicals used in this work were from Sinopharm Chemical Reagent Co. Ltd. The combustion agents were ethylenediaminetetraacetic acid (EDTA, 99.5%) and citric acid (99.5%) while the precursors were La_2O_3 (99.99%), $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (99.0%), $\text{Sr}(\text{NO}_3)_2$ (99.5%), and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (98.5%). The resulted ashes were collected and heated at 800 °C for 2 h to obtain the perovskite structure. $\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$ (SDC) powder was prepared via the glycine–nitrate method.²⁵ Stoichiometric amount of $\text{Sm}(\text{NO}_3)_3$ (99.95%) and $\text{Ce}(\text{NO}_3)_3$ (99%) were dissolved in distilled water to form an aqueous solution with a total metal concentration of 0.1 M. The combustion agent (glycine, 99.5%) was subsequently added to the nitrate solution. The molar ratio of metal ion to glycine was 2 : 1. The solution was stirred for 2 h with magnetic stirring apparatus, and then

heated on a hot plate until self-combustion occurred, resulting in pale yellowish ashes.

The as-prepared ashes were heated at 600 °C for 2 h to form fluorite structured SDC powders.

2.2 Cell Fabrication

Symmetrical cells supported on SDC electrolytes were fabricated for electrochemical measurement. The SDC powder was uniaxially pressed into disk-shaped pellets at 250 MPa with a 13mm diameter stainless steel die, and then sintered at 1400 °C for 5 h to form dense SDC pellets as the electrolyte substrates, which were about 10 mm in diameter and 0.5 mm thick. LBSF-SDC mixed powders with various SDC contents were prepared by ball milling the two powders for 12 hours. The SDC content in weight percentage was varied from 0% to 50%. In this study, a composite with x wt. % SDC was labeled as LBSF-SDCx. For example, LBSF-SDC30 represented the composite containing 30 wt. % SDC. The composite powder was mechanically mixed with 60 wt. % organic additives (α -terpineol and ethyl cellulose) to form a cathode slurry. The slurry was then printed onto both sides of the SDC pellets using the screen-printing technique to form the symmetrical cells. The cells were subsequently heated to 850 °C with the heating rate of 3 °C min⁻¹ and calcined at 850 °C for 2 h in air to form porous composite electrodes for electrochemical characterization. Meanwhile, the symmetrical cells of bare LBSF were calcined at 900 and 1000 °C to reveal the sintering effect on electrochemical performance.

2.3 Oxygen Non-stoichiometry

The oxygen non-stoichiometry coefficient and average valence of Fe in LBSF at room temperature were measured by the iodometric titration.⁵ Approximately 5g LBSF powder was dissolved with about 0.2 M HCl solution, and then the pH was adjusted to ~ 6 with distilled water to avoid the possible side reaction between I_2 and $Na_2S_2O_3$. Sufficient KI solution with a concentration of 100 g L^{-1} was added to the LBSF solution. The $Na_2S_2O_3$ solution, whose concentration was titrated by a standard $K_2Cr_2O_7$ solution with a concentration of $0.02344\text{ mol}\cdot\text{L}^{-1}$, was then added dropwise to the LBSF solution with the burette to reduce Fe^{4+}/Fe^{3+} to Fe^{2+} , and starch indicator was used to show the end point. The oxygen non-stoichiometry coefficients and the valence states of Fe at high temperatures were determined by thermogravimetric analysis (TGA, SDT Q600). The test was performed from room temperature to $800\text{ }^\circ\text{C}$ with a heating rate of $10\text{ }^\circ\text{C}/\text{min}$ in air.

2.4 O₂-TPD

The change of oxygen content with temperature was further revealed using oxygen temperature-programmed desorption (O₂-TPD) analysis. To conduct the O₂-TPD experiment, about 200 mg LBSF powder was deposited into the U-type quartz reactor. The testing process generally consisted of two steps, the pretreatment and analysis. The sample in the reactor was pretreated in dilute O₂ (5% O₂ in He) at a flow rate of 20 ml min^{-1} in an oven heated from room temperature to $400\text{ }^\circ\text{C}$ with a ramp rate of

20 °C min⁻¹, and kept for 30 min at 400 °C. Subsequently, the reactor was cooled down to 30 °C in the same atmosphere. Prior to running the O₂-TPD analysis, He, which was used for desorption, was fed to the reactor at a 20 ml/min flow rate and kept for 30 min at 40 °C to purge out any excess oxygen molecule. The sample was then heated to 850 °C with a constant ramp rate of 10 °C/min with flowing He (flow rate of 20 ml/min). The TCD signal of the thermal conductivity coefficient for freed O₂ and He was recorded as a function of temperature.

2.5 Electrochemical Properties of the Electrodes

Electrochemical impedance spectra of the symmetrical cells were recorded using a Solartron 1260 Frequency Response Analyzer combined with a Solartron 1287 potentiostat. The measurement was conducted in a frequency range of 0.01 Hz to 1 MHz, with a bias voltage of 10 mV, and at temperature from 500 to 800 °C. All the symmetrical cell impedances have been divided by two to account for the fact that two identical electrodes were measured. Silver wires were attached to both sides of the symmetrical cells with silver paste (Sina-Platinm Metals Co., Ltd.) for current collection. The measurements were conducted in a two-electrode setup, and no reference electrode was used. The effect of oxygen partial pressure on electrode performance was studied by mixing O₂ and N₂ in the desired ratios. The oxygen partial pressure was set to be 0.01, 0.1, 0.21, and 1.0 atm. The measurement was started from the low oxygen partial pressure and low temperature. The sample was

allowed to equilibrate for 30 minutes in each atmosphere before the impedance measurement was conducted.

2.6 Characterizations

The phase structures at various temperatures were investigated using X-ray diffraction (XRD, SmartLab, 9 kW) with a temperature control unit (Anton Paar, TCU 1000N).

The XRD patterns for Rietveld refinement were measured in a temperature range of 30 to 600 °C. The patterns were collected by scanning between 20-80° with a step size of 0.02° and a scan speed of 3 °·min⁻¹ at 40 kV and 200 mA. The α_2 component of the filtered radiation was stripped-off. The crystalline parameters in different temperatures were calculated with the XRD data using the Rietveld refinement method considering the oxygen non-stoichiometry coefficients that were determined by the TGA and iodometric titration measurements. To evaluate the chemical compatibility between LBSF and SDC at fuel cell operation and electrode fabrication temperatures, LBSF-SDC50 mixtures were heated at 850 °C for 5 h, forming LBSF-SDC composites for XRD measurement. The microstructures were characterized using scanning electron microscopy (SEM, JSM-6700F). The Pore size of bare LBSF electrodes which were sintered at the different temperatures, were measured using mercury injection apparatus (PM60GT-17).

3. Results and Discussion

3.1 Oxygen Non-stoichiometry at Different Temperatures

The lattice oxygen releasing behavior is investigated with TGA analysis. Figure 1 shows the weight loss versus temperature up to 800 °C. The loss below 235 °C is mainly caused by physical and chemical absorbed water. Lattice oxygen begins to be released at 310 °C. The oxygen loss results in the formation of oxygen vacancies. This process is further explored with the O₂-TPD analysis in a temperature range of 40 - 850 °C, Figure 2. As reported in the literatures for the ABO₃ perovskite materials,²⁶⁻²⁸ there are always two peaks in the O₂-TPD profile, which are corresponding to two types of chemisorbed oxygen species. In the low temperature range from about 300 to 600 °C, the peak is named as α , which is ascribable to the nominal valence changed from tetravalent (Fe⁴⁺) to trivalent (Fe³⁺) and strongly depends on the concentration of surface oxygen vacancies. In the high temperature range of about 600 – 900 °C, the β peak is associated with the nature of the B ion and its occurrence is strictly linked to the further reduction of B cation to the lower valence, i.e. Fe³⁺ to Fe²⁺. Figure 2 clearly presents the α peak with the onset temperature of about 310 °C and extending up to 800°C, suggesting the existence of the β peak, which overlaps with the α peak. Consequently, the O₂-TPD in Figure 2 is mainly attributed to the reduction of Fe⁴⁺ to Fe³⁺.¹⁹

The oxygen stoichiometry (3- δ) in La_{0.4}Bi_{0.4}Sr_{0.2}FeO_{3- δ} at room temperature is 2.96 as determined from the iodometric titration method. Based on the TGA result, the oxygen non-stoichiometry coefficient (δ) and average valence of Fe (n) at various temperatures are calculated, Table 1. The oxygen non-stoichiometry δ increases with

the temperature while the average valence n decreases, mainly because the tetravalent state of Fe shows lower stability compared to the trivalent, and the conversion of tetravalent Fe to trivalent causes the formation of oxygen vacancies in accordance with the charge neutrality.²⁹

3.2 Phase Structures

Figure 3 shows the XRD patterns for SDC, LBSF, and LBSF-SDC50. The pattern for the composite can be attributed to either LBSF or SDC. No unexpected peaks can be obviously found. In addition, the peak position is not shifted. Therefore Figure 3 demonstrates that LBSF is chemically compatible with SDC when they are co-heated at 850 °C for 5 h. Consequently, LBSF is stable as the cathode for intermediate-temperature SOFC based on doped ceria electrolytes and those using doped ceria as the cathode interlayers.

Figure 4 shows the typical fractured cross-sectional microstructures of the LBSF-SDC composite cathodes, which are calcined at 850 °C for 2h. Fig.4a indicates that the average size of the LBSF particle is about 120 nm. When SDC is cooperated, smaller particles are found, which should be SDC particles, while the LBSF particle size is almost not changed, Fig.4b and 4c.

The LBSF structural change with temperature is probed using the high-temperature-XRD, Figure 5a. LBSF presents a cubic (Pm-3m) perovskite phase from room temperature to 600 °C. The XRD peaks shift toward smaller angles with

increasing temperature, indicating the expansion of lattice volume at high temperatures, Figure 5b.

Since the oxygen non-stoichiometry coefficients (δ) have been determined using the TG analysis and iodometric titration method, the lattice parameters (a , b , and c) at the different temperatures can be calculated from the HT-XRD patterns using Rietveld refinement method,³⁰ which has been widely used for the perovskite oxides such as $\text{Bi}_{0.5}\text{Sr}_{0.5}\text{FeO}_{3-\delta}$, $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_{3-\delta}$,¹⁹ $\text{BaZr}_{1-x}\text{Co}_x\text{O}_{3-\delta}$,³¹ $\text{Ca}_{0.9}\text{Y}_{0.1}\text{TiO}_{3+\delta}$,³² $\text{Na}_{0.9}\text{Zr}_{2.9}\text{Mo}_{0.1}\text{O}_{12}$,³³ and $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$.³⁴ The reliability factors of R_p and R_{wp} as listed in Table 1 indicate the good quality of the simulation. Figure 6 also demonstrates the good agreement between the calculated and experimental XRD profiles at different temperatures. Lattice parameters ($a = b = c$) increase with the temperature, which can be used to determine the expansion behaviors. As suggested by McIntosh *et al.*,³⁴ the average thermal expansion coefficient (α) can be defined as,

$$\alpha = (a - a_0) / (a_0 \Delta T) \quad (1)$$

Where a is the lattice parameter and a_0 is the lattice parameter at the reference state, ΔT is the temperature difference between the two states. The average thermal expansion coefficient is $13.89 \times 10^{-6} \text{ K}^{-1}$ as calculated from the HT-XRD results. The value is smaller than that of $14.8 \times 10^{-6} \text{ K}^{-1}$ as determined from the thermal expansion curves,⁸ and the slight difference between the two values mainly dues to the different temperature range.

3.3 Oxygen Reduction Processes on LBSF Cathode

To explore the oxygen reduction processes on the LBSF electrodes, four different oxygen partial pressures from 0.01 to 1.0 atm are applied for the electrochemical measurement on the symmetrical cells at temperatures of 550, 600 and 650 °C. Figure 7a shows the electrochemical impedance spectra measured at 600 °C. The impedance spectrum is analyzed with the distribution of relaxation time (DRT) method³⁵⁻³⁸ to reveal the effect of oxygen partial pressure. The results are shown in Figure 7b, where τ is the relaxation time which is defined as a function of the frequency f , *i.e.* $\tau = 1/2\pi f$, $F(\tau) = \tau G(\tau) \ln 10$ in which $G(\tau)$ is the DRT of the impedance.³⁷ Each peak of the DRT profile is an indication of a sub-process in the oxygen reduction reaction. The area under the peak is the polarization resistance corresponding to the sub-process. The peak at the low relaxation time, *i.e.* the high frequency peak P_1 , is not changed in either peak position or peak area by the oxygen partial pressure, suggesting that P_1 corresponds to the sub-process of oxygen-ion transportation. The others are obviously changed when P_{O_2} is decreased. The change is featured by shifting to the low frequency, increasing in peak area and even peak splitting. It is noted that the low-frequency peak (P_3) is the largest, implying that this sub-process dominates the oxygen reduction reaction. The peak splitting in the intermediate-frequency range exhibits an additional sub-process at the low P_{O_2} of 0.10 and 0.01 atm. However, these peaks are much smaller than the low-frequency one. They are thus grouped as P_2 , corresponding to the sub-processes at the intermediate frequency range.

Based on the DRT analysis, three arcs are proposed to fit the impedance spectra using the ZView software, and the equivalent circuit ($LRb(RiCPEi)$) is shown in Figure 7c. Here L is the inductance arising from the measurement apparatus, Rb is the resistance of the electrolyte, and ($RiCPEi$) is the description of a sub-step in the cathode reaction process. The fitting results shown in Figure 7a indicate a good agreement between the experimental data and the fitting lines. Note that the first intercept on the real axis corresponding to Rb has been subtracted for better comparison of the interfacial polarization resistance.

To get more insight into the oxygen reduction processes, the equation of $R_i = kP_{O_2}^{-n}$ is used to illustrate the relationship between the resistance R_i and oxygen partial pressure P_{O_2} , where k is a constant, and n is the parameter related to the rate-determining step.³⁹⁻⁴⁰ Figure 8 shows the dependence of the resistance R_i for the high-, medium- and low-frequency arcs on the oxygen partial pressure. As shown in Figure 8a, the values of n for R_1 ascribed to the resistance at the high frequency are almost 0, indicating R_1 is independent of P_{O_2} . This phenomenon agrees well with oxygen ion-transfer process occurring on the electrode/electrolyte interface. In addition, this result is consistent with the DRT analysis. The corresponding sub-process can be expressed as,⁴¹⁻⁴²

The value of n for R_2 , the resistance at the medium-frequency shows obvious dependence on the temperature, Figure 8b. It is about 0.25 at 550 °C and increases to 0.63 at 650 °C. The difference in n value indicates the complex sub-processes to the medium-frequency responses, which can also be seen from Figure 7b. The sub-process is possibly related to charge transfer at 550 °C (Eq. 3) and changes to oxygen dissociation at high temperatures (Eq. 4).³⁹⁻⁴⁰

The impedance response of the low frequency (R_3) is found to have a dependence of about 0.25 on the oxygen partial pressure, Figure 8c, relating to the diffusion of intermediate oxygen species (Eq. 5).⁴³⁻⁴⁴

The sum of R_2 and R_3 represents most of R_p , dominating the electrode reaction of the composites. As shown in Figure 8d, the value of n for R_2+R_3 increases from about 0.26 to 0.36 with temperature, suggesting that the electrode reaction process is the competition of oxygen dissociation and the diffusion of intermediate oxygen species. Meanwhile, the process will be dominated by Eq. 4 as temperature increases.

3.4 Electrochemical Performance for the LBSF-SDC Composite

Previous investigation shows that $\text{La}_{0.4}\text{Bi}_{0.4}\text{Sr}_{0.2}\text{FeO}_{3-\delta}$ has demonstrated the highest electrochemical performance in a series of single phase $\text{La}_{0.8-x}\text{Bi}_x\text{Sr}_{0.2}\text{FeO}_{3-\delta}$ ($0 \leq x \leq 0.8$) electrodes.⁸ This work explores the effect of SDC incorporation to further increase the electrochemical performance. Figure 9a shows the interfacial polarization resistance as a function of the LBSF-SDC composition at various temperatures. When the SDC content increases, R_p generally decreases to a lowest value and then increases. The lowest R_p is obtained with the LBSF-SDC30 composite. At 600°C, R_p for LBSF-SDC30 is $0.64 \Omega\text{cm}^2$, which is about 1/2 of $1.23 \Omega\text{cm}^2$ for the single phase LBSF electrode. The performance is comparable with those reported for cobalt-containing electrodes such as LSCF-GDC30 composite.⁴⁵ In some cases, LBSF-SDC composites are even better than those for LSCF based composites. For example, at 700°C, R_p is $0.093 \Omega\text{cm}^2$ for LBSF-SDC30 composite. The resistance is 50% of $0.184 \Omega\text{cm}^2$ reported for a LSCF cathode infiltrated with $\text{La}_{0.4875}\text{Ca}_{0.0125}\text{Ce}_{0.5}\text{O}_{2-\delta}$.⁴⁶ R_p is $0.209 \Omega\text{cm}^2$ for the LBSF-SDC50 composite, which is much smaller than $0.306 \Omega\text{cm}^2$ reported for a LSCF-SDC50 composite electrode, noting that the two electrodes have similar composition.⁴⁷ The activation energy (E_a) of R_p for LBSF-SDC is presented in Figure 9b. It clearly shows that E_a decreases first and then increases with the SDC content.

Figures 10a and 10b show typical Nyquist plots and the fitting results, obtained at 600 °C in the air ($P_{\text{O}_2} = 0.21 \text{ atm}$). The impedance spectra show good agreement with the equivalent circuit (LRb(RiCPEi)) shown in Figure 7c. To further explore the

specific effect of SDC incorporation on the electrochemical performance, the impedance spectrum is analyzed using the DRT method, Figure 10c. The areas for the low-, medium-, and high-frequency peaks (P_3 , P_2 , P_1) are reduced by adding SDC up to 30 wt. %. Therefore, all the reaction sub-processes are accelerated when 30 wt. % SDC is added, especially the diffusion of the intermediate oxygen species (Eq.5). SDC can enlarge the three-phase boundary region for the electrode reaction and provide sufficient paths to transfer the oxygen ions.⁴⁸ Since the lowest peak areas are obtained for the composite with 30 wt. % SDC, a percolated ionic conduction network is possibly formed at this composition as suggested by the percolation models for the composite electrodes.⁴⁵ However, excessive SDC could hinder the reactions related to the charge transfer processes as well as slow down the electronic conduction as suggested by the appearance of an extra peak in the high frequency, which may be ascribed to the bulk electron transfer process from the current collector to the electrocatalyst.

DRT results indicate that the areas under P_3 of LBSF-SDC composites are smaller than that for the bare one, Figure 10c. Therefore, the energy barrier for the diffusion of intermediate oxygen species decreases with incorporation of SDC. However, the areas corresponding to P_2 and P_1 increase sharply with SDC when $x \geq 30$ wt. %. Consequently, the energy barrier for charge transfer processes increases SDC is added to LBSF. The result of E_a for LBSF-SDC is the competition of the diffusion of intermediate oxygen species and the charge transfer processes, Figure 9b.

3.5 Electrochemical Performance of LBSF electrodes heated at different temperature

The microstructure effect on electrochemical performance is investigated with LBSF electrodes. Figure 11a shows the EIS measured at 650 °C with symmetrical cells, and the lines fitted using the equivalent circuit shown in Figure 7c. The polarization resistance for the sample heated at 850 °C is slightly higher than that at 900 °C, which shows the lowest R_p value of 0.291 $\Omega \text{ cm}^2$. Meanwhile, it is much lower than that at 1000°C. The heating temperature affects the microstructure, the adhesion of the electrode to the electrolyte, and the active sites with respect to the oxygen reduction process in the cathode. The microstructures comparison can be found in Figure 4a, Figure 11b, and 11c, which are typical cross-sectional SEM pictures for LBSF electrodes heated at 850 °C, 900 °C and 1000 °C, respectively. The particle size increases with the heating temperature. Figure 11d shows their pore size distributions. Generally, the pore size increases while the pore volume (porosity) decreases with the heating temperature. So, heating at high temperature causes a loss of porosity, which might limit gas transportation to and from the reaction sites. In addition, the increase in particle size exhibits a loss of surface area for the cathode reaction. However, the resistance for the electrode heated at 850 °C is slightly higher than that at 900°C. It might be that 900°C sintering results in better adherence between the electrolyte and the cathode, leading to a lower charge transfer resistance.⁴⁸⁻⁵⁰

4. Conclusions

In this work, we have extended the previous research to characterize the properties of the promising $\text{La}_{0.4}\text{Bi}_{0.4}\text{Sr}_{0.2}\text{FeO}_{3-\delta}$ cathode material. The oxygen non-stoichiometry coefficient δ is 0.04 at room temperature as determined with the iodometric titration method, and increases with temperature up to 0.11 at 790 °C as calculated with the TGA results. $\text{La}_{0.4}\text{Bi}_{0.4}\text{Sr}_{0.2}\text{FeO}_{3-\delta}$ is cubic structured perovskite and its lattice parameter increases with temperature, resulting in an average expansion coefficient of $13.89 \times 10^{-6} \text{ K}^{-1}$ as determined with the HT-XRD analysis. The oxygen reduction reaction is limited by oxygen dissociation and the diffusion of intermediate oxygen species processes as determined using the distribution of relaxation time method for the electrochemical impedance spectra measured at different oxygen partial pressure. Incorporation with SDC can effectively enhance the electrochemical reaction processes and consequently reduce the interfacial polarization.

ACKNOWLEDGMENT

We gratefully acknowledge the financial support of the Ministry of Science and Technology of China (2012CB215403), the National Nature Science Foundation of China (51372239), and the U.S. National Science Foundation (DMR-1210792). We thank Wanqun Zhang for the assistance for the HT-XRD measurement.

References

1. Minh, N. Q.; Takahashi, T. *Science and Technology of Ceramic Fuel Cell*. Elsevier: The Netherlands, **1995**.
2. Steele, B. C. H. Material science and engineering: The Enabling Technology for the Commercialisation of Fuel Cell Systems. *J. Mater. Sci.* **2001**, *36*, 1053-1068.
3. Ormerod, R. M. Solid Oxide Fuel Cells. *Chem. Soc. Rev.* **2003**, *32*, 17-28.
4. Steele, B. C.; Heinzl, A., Materials for Fuel-Cell Technologies. *Nature* **2001**, *414*, 345-352.
5. Niu, Y.; Sunarso, J.; Zhou, W.; Liang, F.; Ge, L.; Zhu, Z.; Shao, Z. Evaluation and Optimization of $\text{Bi}_{1-x}\text{Sr}_x\text{FeO}_{3-\delta}$ Perovskites as Cathodes of Solid Oxide Fuel Cells. *Int. J. Hydrogen Energy* **2011**, *36*, 3179-3186.
6. Simner, S. P.; Bonnett, J. R.; Canfield, N. L.; Meinhardt, K. D.; Shelton, J. P.; Sprenkle, V. L.; Stevenson, J. W. Development of Lanthanum Ferrite SOFC Cathodes. *J. Power Sources* **2003**, *113*, 1-10.
7. Ralph, J. M.; Rossignol, C.; Kumar, R. Cathode Materials for Reduced-Temperature SOFCs. *J. Electrochem. Soc.* **2003**, *150*, A1518-A1522.

8. Li, M.; Wang, Y.; Wang, Y.; Chen, F.; Xia, C. Bismuth Doped Lanthanum Ferrite Perovskites as Novel Cathodes for Intermediate-Temperature Solid Oxide Fuel Cells. *ACS Appl. Mater. Interfaces* **2014**, *6*, 11286-11294.
9. Souza, R. A. D.; Kilner, J. A.; Walker, J. F.; Adler, S. A SIMS Study of Oxygen Tracer Diffusion and Surface Exchange in $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3+\delta}$. *Mater. Lett.* **2000**, *43*, 43-52.
10. Beckel, D.; Muecke, U.; Gyger, T.; Florey, G.; Infortuna, A.; Gauckler, L. Electrochemical Performance of LSCF Based Thin Film Cathodes Prepared by Spray Pyrolysis. *Solid State Ionics* **2007**, *178*, 407-415.
11. Tietz, F.; Haanappel, V. A. C.; Mai, A.; Mertens, J.; Stöver, D. Performance of LSCF Cathodes in Cell Tests. *J. Power Sources* **2006**, *156*, 20-22.
12. Nie, L.; Liu, M.; Zhang, Y.; Liu, M. $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ Cathodes Infiltrated with Samarium-Doped Cerium Oxide for Solid Oxide Fuel Cells. *J. Power Sources* **2010**, *195*, 4704-4708.
13. Shao, Z.; Haile, S. M. A High-Performance Cathode for the Next Generation of Solid-oxide Fuel Cells. *Nature* **2004**, *431*, 170-173.
14. Liu, B.; Chen, X.; Dong, Y.; Mao, S. S.; Cheng, M. A High-Performance, Nanostructured $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ Cathode for Solid-Oxide Fuel Cells. *Adv. Energy Mater.* **2011**, *1*, 343-346.

15. Wei, B.; Lü, Z.; Huang, X.; Liu, Z.; Miao, J.; Li, N.; Su, W.
Ba_{0.5}Sr_{0.5}Zn_{0.2}Fe_{0.8}O_{3-δ} Perovskite Oxide as a Novel Cathode for
Intermediate-Temperature Solid-Oxide Fuel Cells. *J. Am. Ceram. Soc.* **2007**, *90*,
3364-3366.
16. Egger, A.; Bucher, E.; Yang, M.; Sitte, W. Comparison of Oxygen Exchange
Kinetics of the IT-SOFC Cathode Materials La_{0.5}Sr_{0.5}CoO_{3-δ} and La_{0.6}Sr_{0.4}CoO_{3-δ}.
Solid State Ionics **2012**, *225*, 55-60.
17. Wang, L. Y.; Wang, D. H.; Huang, H. B.; Han, Z. D.; Cao, Q. Q.; Gu, B. X.; Du,
Y. W. The Magnetic Properties of Polycrystalline Bi_{1-x}Sr_xFeO₃ Ceramics. *J. Alloys
Compd.* **2009**, *469*, 1-3.
18. Wedig, A.; Merkle, R.; Stuhlhofer, B.; Habermeier, H. U.; Maier, J.; Heifets, E.
Fast Oxygen Exchange Kinetics of Pore-Free Bi_{1-x}Sr_xFeO_{3-δ} Thin Films. *Phys. Chem.
Chem. Phys.* **2011**, *13*, 16530-16533.
19. Niu, Y.; Sunarso, J.; Liang, F.; Zhou, W.; Zhu, Z.; Shao, Z. A Comparative Study
of Oxygen Reduction Reaction on Bi- and La-Doped SrFeO_{3-δ} Perovskite Cathodes. *J.
Electrochem. Soc.* **2011**, *158*, B132-B138.
20. Zhao, L.; Hyodo, J.; Chen, K.; Ai, N.; Amarasinghe, S.; Ishihara, T.; Jiang, S. P.
Effect of Boron Deposition and Poisoning on the Surface Exchange Properties of

LSCF Electrode Materials of Solid Oxide Fuel Cells. *J. Electrochem. Soc.* **2013**, *160*, F682-F686.

21. Liu, Z.; Liu, M.; Yang, L.; Liu, M. LSM-Infiltrated LSCF Cathodes for Solid Oxide Fuel Cells. *J. Energy Chem.* **2013**, *22*, 555-559.

22. Xia, C.; Chen, F.; Liu, M. Reduced-Temperature Solid Oxide Fuel Cells Fabricated by Screen Printing. *Electrochem. Solid-State Lett.* **2001**, *4*, A52-A54.

23. Leng, Y.; Chan, S.; Jiang, S.; Khor, K. Low-Temperature SOFC with Thin Film GDC Electrolyte Prepared in Situ by Solid-State Reaction. *Solid State Ionics* **2004**, *170*, 9-15.

24. Adler, S. B. Factors Governing Oxygen Reduction in Solid Oxide Fuel Cell Cathodes. *Chem. Rev.* **2004**, *104*, 4791-4843.

25. Wang, Y.; Zhang, H.; Chen, F.; Xia, C. Electrochemical Characteristics of Nano-Structured $\text{PrBaCo}_2\text{O}_{5+x}$ Cathodes Fabricated with Ion Impregnation Process. *J. Power Sources* **2012**, *203*, 34-41.

26. Teraoka, Y.; Honbe, Y.; Ishii, J.; Furukawa, H.; Moriguchi, I. Catalytic Effects in Oxygen Permeation Through Mixed-Conductive LSCF Perovskite Membranes. *Solid State Ionics* **2002**, *152*, 681-687.

27. Fino, D.; Russo, N.; Saracco, G.; Specchia, V. The Role of Suprafacial Oxygen in Some Perovskites for the Catalytic Combustion of Soot. *J. Catal.* **2003**, *217*, 367-375.

28. Teraoka, Y.; Yoshimatsu, M.; Yamazoe, N.; Seiyama, T. Oxygen-Sorptive Properties and Defect Structure of Perovskite-Type Oxides. *Chem. Lett.* **1984**, 893-896.
29. Tu, H.; Takeda, Y.; Imanishi, N.; Yamamoto, O. $\text{Ln}_{0.4}\text{Sr}_{0.6}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (Ln= La, Pr, Nd, Sm, Gd) for the Electrode in Solid Oxide Fuel Cells. *Solid State Ionics* **1999**, 117, 277-281.
30. Larson, A. C.; Von Dreele, R. B. General Structure Analysis System (GSAS). *Los Alamos Natl. Lab. Rep. LAUR* **1994**, 86-748.
31. Rao, Y.; Zhong, S.; He, F.; Wang, Z.; Peng, R.; Lu, Y. Cobalt-Doped BaZrO_3 : A Single Phase Air Electrode Material for Reversible Solid Oxide Cells. *Int. J. Hydrogen Energy* **2012**, 37, 12522-12527.
32. Chourasia, R.; Shrivastava, O. P. Structure Refinement of Polycrystalline Orthorhombic Yttrium Substituted Calcium Titanate: $\text{Ca}_{1-x}\text{Y}_x\text{TiO}_{3+\delta}$ ($x = 0.1-0.3$). *Bull. Mater. Sci.* **2011**, 34, 89-95.
33. Chourasia, R.; Shrivastava, O. P.; Wattal, P. K. Synthesis, Characterization and Structure Refinement of Sodium Zirconium Molibdo-Phosphate: $\text{Na}_{0.9}\text{Zr}_2\text{Mo}_{0.1}\text{P}_{2.9}\text{O}_{12}$ (MoNZP). *J. Alloys Compd.* **2009**, 473, 579-583.

34. McIntosh, S.; Vente, J. F.; Haije, W. G.; Blank, D. H. A.; Bouwmeester, H. J. M. Oxygen Stoichiometry and Chemical Expansion of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ Measured by in Situ Neutron Diffraction. *Chem. Mater.* **2006**, *18*, 2187-2193.
35. Hayd, J.; Ivers-Tiffée, E. Detailed Electrochemical Study on Nanoscaled $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ SOFC Thin-Film Cathodes in Dry, Humid and CO_2 -Containing Atmospheres. *J. Electrochem. Soc.* **2013**, *160*, F1197-F1206.
36. Zhang, Y.; Chen, Y.; Chen, F. In-Situ Quantification of Solid Oxide Fuel Cell Electrode Microstructure by Electrochemical Impedance Spectroscopy. *J. Power Sources* **2015**, *277*, 277-285.
37. Zhang, Y.; Chen, Y.; Yan, M.; Chen, F. Reconstruction of Relaxation Time Distribution from Linear Electrochemical Impedance Spectroscopy. *J. Power Sources* **2015**, *283*, 464-477.
38. Sumi, H.; Yamaguchi, T.; Hamamoto, K.; Suzuki, T.; Fujishiro, Y. High Performance of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3\text{--Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ Nanoparticulate Cathode for Intermediate Temperature Microtubular Solid Oxide Fuel Cells. *J. Power Sources* **2013**, *226*, 354-358.
39. Takeda, Y.; Kanno, R.; Noda, M.; Tomida, Y.; Yamamoto, O. Cathodic Polarization Phenomena of Perovskite Oxide Electrodes with Stabilized Zirconia. *J. Electrochem. Soc.* **1987**, *134*, 2656-2661.

40. Escudero, M. J.; Aguadero, A.; Alonso, J. A.; Daza, L. A Kinetic Study of Oxygen Reduction Reaction on La_2NiO_4 Cathodes by Means of Impedance Spectroscopy. *J. Electroanal. Chem.* **2007**, *611*, 107-116.
41. Chen, X. J.; Khor, K. A.; Chan, S. H. Identification of O_2 Reduction Processes at Ytria Stabilized Zirconia|Doped Lanthanum Manganite Interface. *J. Power Sources* **2003**, *123*, 17-25.
42. Adler, S. B. Limitations of Charge-Transfer Models for Mixed-Conducting Oxygen Electrodes. *Solid State Ionics* **2000**, *135*, 603-612.
43. Heuvein, F. H. v.; Bouwmeester, H. J. M. Electrode Properties of Sr-Doped LaMnO_3 on Ytria-Stabilized Zirconia II. Electrode Kinetics. *J. Electrochem. Soc.* **1997**, *144*, 134-140.
44. Kenney, B.; Karan, K. Impact of Nonuniform Potential in SOFC Composite Cathodes on the Determination of Electrochemical Kinetic Parameters. *J. Electrochem. Soc.* **2006**, *153*, A1172-A1180.
45. Dusastre, V.; Kilner, J. A. Optimisation of Composite Cathodes for Intermediate Temperature SOFC Applications. *Solid State Ionics* **1999**, *126*, 163-174.
46. Liu, M.; Ding, D.; Blinn, K.; Li, X.; Nie, L.; Liu, M. Enhanced Performance of LSCF Cathode through Surface Modification. *Int. J. Hydrogen Energy* **2012**, *37*, 8613-8620.

47. Fu, C.; Sun, K.; Zhang, N.; Chen, X.; Zhou, D., Electrochemical Characteristics of LSCF–SDC Composite Cathode for Intermediate Temperature SOFC. *Electrochim. Acta* **2007**, *52*, 4589-4594.
48. Xia, C. R.; Rauch, W.; Chen, F. L.; Liu, M. L. $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ Cathodes for Low-Temperature SOFCs. *Solid State Ionics* **2002**, *149*, 11-19.
49. Jorgensen, M.J.; Primdahl, S.; Bagger, C.; Mogensen, M. Effect of Sintering Temperature on Microstructure and Performance of LSM–YSZ Composite Cathodes. *Solid State Ionics* **2001**, *139*, 1-11.
50. Sasaki, K.; Wurth, J.P.; Gschwend, R.; Godickemeier M.; Gauckler, L.J. Microstructure-Property Relations of Solid Oxide Fuel Cell Cathodes and Current Collectors. *J. Electrochem. Soc.* **1996**, *143*, 530-543

Figure Captions

Figure 1. TGA curves for the LBSF powder measured from room temperature to 800 °C.

Figure 2. O₂-TPD curve for the LBSF powder measured from 40 to 850 °C.

Figure 3. Room temperature XRD patterns for the powders of (a) SDC heated at 600 °C for 2 h, (b) LBSF-SDC50 heated at 850 °C for 5 h, and (c) LBSF heated at 800 °C for 2h.

Figure 4. Cross-sectional microstructures of composite cathodes, (a) LBSF, (b) LBSF-SDC30, (c) LBSF-SDC50.

Figure 5. (a) High-temperature XRD patterns recorded at 30-600 °C and (b) the magnified view for the (110) peak for the LBSF powder.

Figure 6. Rietveld refinement plots for the LBSF powder measured at various temperatures.

Figure 7. (a) Electrochemical impedance spectra measured at 600 °C under different oxygen partial pressures for a symmetrical cell with the LBSF electrodes, (b) DRT analysis of the EIS data shown in Figure 7a, and (c) equivalent circuit as suggested from Figure 7b for fitting the impedance spectra in Figure 7a.

Figure 8. Dependence of the resistance for the high-, medium- and low-frequency arcs on the oxygen partial pressure. (a) R_1 , (b) R_2 , (c) R_3 , (d) R_2+R_3 .

Figure 9. (a) Interfacial polarization resistance (R_p) measured from 500 to 800 °C for the LBSF-SDC composites with various SDC contents. (b) Activation energy (E_a) of R_p for LBSF-SDC.

Figure 10. (a-b) Electrochemical impedance spectra measured at 600 °C for symmetrical cells with LBSF-SDC composite electrodes at various compositions, (c) DRT analysis of the EIS data shown in Figure 10(a-b).

Figure 11. (a) EIS of LBSF symmetrical cells measured at 650 °C. (b-c) Cross-sectional microstructures of LBSF electrodes heated at 900 °C and 1000 °C, respectively. (d) Pore size distributions of LBSF electrodes measured at room temperature.

Table 1. Lattice Parameters (a, b, and c), Oxygen Non-stoichiometry Coefficient (δ) and Average Fe Valence (n) for $\text{La}_{0.4}\text{Bi}_{0.4}\text{Sr}_{0.2}\text{FeO}_{3-\delta}$ at the Different Temperatures (T)

T (°C)	a =b=c (Å)	R _{wp} (%)	R _p (%)	Δ	n
30	3.9292	5.37	4.18	0.04	3.120
100	3.9324	5.36	4.20	0.04	3.120
200	3.9414	5.42	4.22	0.04	3.120
300	3.9440	5.37	4.22	0.04	3.120
400	3.9475	5.34	4.20	0.0539	3.092
500	3.9540	5.42	4.24	0.0612	3.078
600	3.9603	5.45	4.25	0.0725	3.055
700	-	-	-	0.0938	3.012
790	-	-	-	0.1114	2.977

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11