Investigation of $\text{La}_{1-x}\text{Sm}_x\text{Sr}_y\text{CoO}_{3-\delta}$ cathode for intermediate temperature solid oxide fuel cells

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Abstract: $\text{La}_{1-x}\text{Sm}_x\text{Sr}_y\text{CoO}_{3-\delta}$ (LSSC; $x=0.475, 0.650, 0.825, y=0.35, 0.40, 0.45$) compounds, which have the same compositions as the $\text{La}_{0.7}\text{Sr}_{0.3}\text{CoO}_{3-\delta}$ (LSC) and $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ (SSC) mixture (corresponding mole ratio is 3:1, 1:1 and 1:3, respectively), are synthesized through a conventional solid-state reaction and characterized by X-ray diffraction, thermal expansion coefficient, X-ray photoelectron spectrometer and electrical conductivity measurement, as well as the electrochemical impedance spectra and single cell performance measurement. Interestingly, the experimental results reveal that with the linear increase of y in LSSC, the conductivity of the corresponding samples does not alter linearly but reaches a peak when $y=0.35$, namely, the maximum electrical conductivity enhancing from 2148 S cm^{-1} (LSC, $y=0.30$) and 1802 S cm^{-1} (SSC, $y=0.50$) to 2750 S cm^{-1} ($y=0.35$). In addition, this turning point coincidentally corresponds to the structure transition from hexagonal ($y=0.35$) to orthorhombic ($y=0.40$). Furthermore, comparing with LSC and SSC, the cathode polarization resistance (R_p) decreases by about 50% and 38%, respectively, after employing the LSSC ($y=0.40$) compound as cathode at 800°C and $0.21 \text{ atm p(O}_2\text{)}$, which also leads to an increment

of 49% and 31% respectively in peak power density. These results imply promising applications of such effective cathodes for intermediate temperature solid oxide fuel cells.

Key words: solid oxide fuel cell; electrical conductivity; electrochemical performance; lanthanum strontium cobaltite; samarium strontium cobaltite

1. Introduction

Over the past years solid oxide fuel cells (SOFCs) have drawn extensive attention as highly efficient power generators with low emissions and fuel flexibility [1]. A continuous effort has been made to diminish the operating temperature of SOFCs for long-term stability in a cost effective way. However, reducing the operating temperature results in a decline in cell performance, which is largely due to a significant increment in cathode polarization resistance (R_p) [2]. Therefore, mixed ionic and electronic conductors (MIECs) such as $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) [3-5], $Sm_{0.5}Sr_{0.5}CoO_{3-\delta}$ (SSC) [6-8], $La_{0.7}Sr_{0.3}CoO_{3-\delta}$ (LSC) [9-11], and $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) [12-15] have been extensively explored as potential materials to improve the electrocatalytic activity on the cathode side at low operating temperatures. In addition, the mixed conductivity extends oxygen reduction reaction (ORR) zone from the conventional gas-electrode-electrolyte triple-phase boundary (TPB) to the whole cathode surface, hence significantly diminishing R_p on the cathode side at lower temperature [16].

Extensive studies have focused on combining or infiltrating a second phase or doping other elements to make property of the cathode material intermediate between the attributes of the parent components, occasionally superior to both. Zhou et al. [17] demonstrated that $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$

+ LaCoO₃ (BSCF+LC) composite cathode exhibited better electrical conductivity than the pure BSCF, resulting in attractive cathode performance for intermediate temperature solid oxide fuel cells (IT-SOFCs). Jung et al.[18] showed that the R_p of Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.1}Zn_{0.1}O_{3-δ} - La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} (BSCFZ-LSCF) composite cathode was ~64% lower than that of BSCFZ cathode and one order of magnitude lower than that of LSCF cathode. Zhu et al. [19] indicated that BSCF-30 wt% SSC composite cathode displayed much higher conductivity (176 S cm⁻¹ at 500 °C) than BSCF (26 S cm⁻¹ at 500 °C), while the R_p value of BSCF-30 wt% SSC was only one seventh of that of BSCF at 550 °C. Lou et al. [20] revealed that the infiltration of SSC onto the porous structure of LSCF cathodes could dramatically decline the R_p of the cathode and maintain the stability of LSCF cathodes, increasing the peak power densities by ~22%. Li et al. [21] synthesized (Ba_{0.5}Sr_{0.5})_{1-x}Sm_xCo_{0.8}Fe_{0.2}O_{3-δ} (BSSCF) compounds and discovered that the electrical conductivity of BSSCF was greater than that of BSCF, rising with the incremental content of Sm. Furthermore, electrochemical impedance spectra (EIS) disclosed that the electrochemical performance of BSSCF was better than that of BSCF. The total resistance of (Ba_{0.5}Sr_{0.5})_{0.9}Sm_{0.1}Co_{0.8}Fe_{0.2}O_{3-δ} was 2.98 Ω cm² at 500 °C, which was only about half of that of BSCF.

LSC and SSC are known to possess considerably high oxide ion conductivity and high electronic conductivity over a wide temperature range since the divalent strontium dopant (Sr²⁺) partially substitutes for the trivalent samarium (Sm³⁺) or lanthanum (La³⁺) [22]. Moreover, both of them are perovskite type complex oxides, which can undergo broad adjustments of their composition and show various notable properties [15, 16]. The A and/or B-site cations can partially be substituted for the purpose of improving chemical and physical features such as catalytic activity, electrical conductivity, thermal and mechanical stability or electrode-electrolyte compatibility, which would

lead to wide application in industrial and scientific fields [9]. However, there is little published information relating combination of LSC and SSC so far. In this work, the perovskite type $\text{La}_{1-x}\text{Sm}_x\text{Sr}_y\text{CoO}_{3-\delta}$ (LSSC) compounds with $x=0.475$ when $y=0.35$, $x=0.650$ when $y=0.40$ and $x=0.825$ when $y=0.45$ were synthesized and characterized as the cathode materials for IT-SOFCs.

2. Experimental

2.1. Powder preparation

The conventional solid-state reaction method was applied to synthesize the $\text{La}_{1-x}\text{Sm}_x\text{Sr}_y\text{CoO}_{3-\delta}$ (LSSC) powders. Stoichiometric amounts of La_2O_3 (99.5%), Sm_2O_3 (99.99%), SrCO_3 (99.0%) and Co_2O_3 (99.9%), which could react to generate LSC and SSC respectively with the mole ratio (LSC: SSC = 3:1, 1:1 and 1:3, i.e. $x=0.475$ when $y=0.35$, $x=0.650$ when $y=0.40$, $x=0.825$ when $y=0.45$), were mixed together in deionized water and then milled for 8h. After drying and grinding, the mixed powders were calcined at 900-1300 °C for 6 h in air. The samples were named according to their concentration of Sr^{2+} and firing temperatures, $\text{La}_{1-x}\text{Sm}_x\text{Sr}_y\text{CoO}_{3-\delta}$ (where $x=0.475$ when $y=0.35$, $x=0.650$ when $y=0.40$, $x=0.825$ when $y=0.45$) calcined at 1200 °C, denoted as LSSC35-1200, LSSC40-1200 and LSSC45-1200. In addition, a mixture consisting of pure-phase LSC and SSC in the weight ratio of 1:1 is denoted as LSC+SSC to make a comparison.

2.2. Sample preparation

The mixed powders consisting of raw materials were pressed at a pressure of 50 MPa to shape a bar with dimensions of 3 mm × 5 mm × 50 mm, and then heated at 1200 °C for 6 h in air for thermal expansion and electrical conductivity measurements.

$\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$ (SDC) was employed as the electrolyte substrate to fabricate symmetric cells for

impedance studies. NiO-SDC (weight ratio of 6:4) was employed as the anode material to form electrolyte-supported fuel cells. The synthesis process was reported in our previous paper [23].

2.3. Characterization

The crystal structures of the synthesized compounds at room temperature were identified by X-ray diffraction (XRD) with Cu K α radiation. The device ARL X'TRA diffractometer was used and operated at 40 kV and 35 mA in the 2θ range of 20° - 70° . Measurements of thermal expansion coefficient (TEC) were analyzed by a dilatometer (RPZ-01, Luoyang, China). The TEC values were calculated in air from 40 to 800 $^\circ\text{C}$ at a heating rate of 5 $^\circ\text{C min}^{-1}$. The porosity of the sintered bars was measured by Archimedes' principle. Electrical conductivity measurement was performed from 200 to 800 $^\circ\text{C}$ at intervals of 50 $^\circ\text{C}$ in air using DC four-probe method. X-ray photoelectron spectroscopy (XPS) was conducted using an X-ray photoelectron spectrometer (ESCALAB 250 Xi, Thermo Scientific, USA) with AlK α radiation at room temperature. The morphology of the cathode was observed by scanning electron microscopy (SEM, JEOL, JSM-5900) analysis. The electrochemical performance of the symmetric cells with different cathodes was investigated using electrochemical workstation (CHI 604e) in the frequency range of 0.01 Hz to 100 kHz with an AC amplitude of 10 mV at various $p(\text{O}_2)$ values ranging from 0.05 to 1 atm (mixing O_2 and N_2) and 800 $^\circ\text{C}$. The EIS were fitted with the equivalent circuit by Zview software. The cathodic polarization measurement was conducted on a three-electrode system at 800 $^\circ\text{C}$ in air. For single cell performance measurement, the current-voltage (I-V) plots and the EIS were measured at 800 $^\circ\text{C}$ employing 3% humidified H_2 as the fuel at a flow rate of 50 ml min^{-1} and stationary air as the oxidant [24].

3. Results and discussion

3.1. Crystal structure

The solid-state reaction among the raw materials is first investigated. Fig. 1(a) displays the XRD patterns of the LSSC compounds calcined at various temperatures. For comparison, the XRD patterns of pure LSC and SSC are also exhibited. Both LSC and SSC oxides demonstrate a pure-phase perovskite structure, and their diffraction peaks can be indexed well according to hexagonal and orthorhombic lattice symmetry, respectively. After calcinations at 900 °C for 6 h under air, the mixed powder of LSSC40-900 sample displays noticeable perovskite peaks with some impurity phases remained. With increasing calcination temperature to 1100 °C, relatively complete diffraction peaks of a perovskite-structured oxide are observed. With further improving the firing temperature to 1200 °C, formation of the perovskite phase for LSSC40 is completed as the crystallinity of the sample calcined at 1300 °C continues to grow. All of the diffraction peaks of LSSC40-1200 can be readily indexed depending on a pure-phase perovskite with orthorhombic lattice symmetry and the unit cell constant is similar to that of SSC. Fig. 1(b) shows the X-ray diffraction patterns for the LSSC powders with varied ratio, all of which have been fired at 1200 °C for 6 h from raw materials. XRD peaks of LSSC40-1200 and LSSC45-1200 show an orthorhombic perovskite structure without any impurity peaks, which is similar to that of SSC. However, LSSC35-1200 exhibits a hexagonal structure with a similar lattice parameter to that of LSC. It is well known that perovskite structure is adaptable enough to take up an extensive scale of metal ions in its A and B sites. According to their ionic radius sizes, La^{3+} ($r = 0.136$ nm), Sm^{3+} ($r = 0.124$ nm) and Sr^{2+} ($r = 0.144$ nm) may take over the A-site of the perovskite while cobalt ions may occupy the B-site [17, 25]. Table 1 shows the structure type and cell parameters of the five samples calculated by using the whole pattern matching. The calculated data of LSC and SSC are consistent with the results

reported by Gwon et al. [26] and Tu et al. [27] respectively.

Fig. 1 XRD patterns of (a) LSC, SSC, LSC+SSC and LSSC40 calcined at various temperatures; (b)

LSC, LSSC35, LSSC40, LSSC45 and SSC calcined at 1200 °C

Table 1

Structure and lattice parameters of LSC, SSC and LSSC

	Structure	a (Å)	b (Å)	c (Å)	V (Å ³)
La _{0.7} Sr _{0.3} CoO _{3-δ}	Hexagonal	5.443	5.443	13.206	338.8
LSSC35-1200	Hexagonal	5.431	5.431	13.156	336.0

LSSC40-1200	Orthorhombic	5.392	7.600	5.381	220.5
LSSC45-1200	Orthorhombic	5.397	7.595	5.403	221.5
Sm _{0.5} Sr _{0.5} CoO _{3-δ}	Orthorhombic	5.404	7.579	5.368	219.8

3.2. Thermal expansion

Fig. 2 shows thermal expansion results of sintered **LSC**, **SSC** and **LSSC** samples acquired after continuous rate heating from 40 to 800 °C. The dependence on varied content of the elements, i.e. La, Sm and Sr, is not distinguishable, with the TEC values between 17.47 and $19.88 \times 10^{-6} \text{ K}^{-1}$ from 40 to 800 °C. Though effected by escalating temperature, the expansion behavior is chiefly assumed to derive from chemical alterations within the material and is thus mentioned as the stoichiometric expansion coefficient [28, 29].

Fig. 2 Thermal expansion curves for **LSC**, **SSC** and **LSSC** calcined at 1200 °C

3.3. Electrical conductivity

The electrical conductivity of **LSC**, **SSC** and **LSSC** heated at 1200 °C for 6 h in air is displayed in Fig. 3. The measured porosity of the sintered bars is around 2%. All the samples exhibit a

metallic-like behavior, conductivities decreasing as temperature grows. This may be attributed to the loss of oxygen from the lattice as reported in the literature [9, 30], and could be expressed in Kröger-Vink notation:

In the equation, $\text{Co}_{\text{Co}}^{\square}$ denotes a tetravalent cobalt ion (Co^{4+}) on a normal Co-site while $\text{Co}_{\text{Co}}^{\times}$ denotes a trivalent cobalt ion (Co^{3+}) with no surplus charge. $\text{O}_{\text{O}}^{\times}$ refers to an oxygen ion on an oxygen site and $\text{V}_{\text{O}}^{\square\square}$ refers to an oxygen vacancy. As temperature increases, the sample loses oxygen, leading to the generation of oxide ion vacancies and reduction of Co^{4+} to Co^{3+} . This, in turn, brings about a decrease in the electronic charge carrier concentration, which is responsible for the electrical conductivity of the sample.

As shown in Fig. 3, LSC reaches a maximum conductivity of $\sim 2148 \text{ S cm}^{-1}$ at about 200°C , while that of SSC is $\sim 1802 \text{ S cm}^{-1}$ at about 300°C , both similar to the previous reports [9, 26, 27]. Interestingly, all the conductivity of LSSC compounds is higher than that of the pure-phase LSC and SSC from 200 to 800°C , with LSSC35-1200 showing the highest conductivity at all temperatures. This could be understood by considering the variation in Sr-doping content. The replacement of La^{3+} or Sm^{3+} by Sr^{2+} breaks the electroneutrality, which could be compensated either by oxidation of Co^{3+} to Co^{4+} (electronic compensation) or by the generation of oxygen vacancies (ionic compensation) [31, 32]. According to the viewpoint of Petrov et al. [9], the amount of Co^{4+} in the $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ system goes through a maximum at $x \sim 0.4$ and decrease with higher content of Sr^{2+} . This indicates that the charge imbalance is adjusted mainly by the formation of Co^{4+} for $x < 0.4$ in $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ while at $x > 0.4$ oxygen vacancies are formed at the expense of Co^{4+} . In this study, XPS measurement was carried out to investigate the charge states of cobalt ions. As shown in Fig. 4(a), there are two peaks

located near 780 and 795 eV, which can be associated with Co 2p_{3/2} and Co 2p_{1/2}, respectively. The Co 2p_{3/2} peaks are deconvoluted into three peaks in Fig. 4b-d, and the peaks corresponding to the higher, medium and lower binding energy are attributed to Co²⁺, Co³⁺ and Co⁴⁺, respectively[23, 33]. According to the peak area ratios presented in Table 2, the Co⁴⁺ content in LSSC35-1200 is higher than those in the other two samples, indicating that the compound LSSC35-1200 have more electronic charge carriers, thus enhancing the electrical conductivity[34]. Therefore, it is possible to infer that in LSSC series, the electronic compensation mechanism prevails over the ionic compensation at $y \leq 0.35$, while the formation of oxygen vacancies is dominant compared to the generation of Co⁴⁺ at $y > 0.35$.

In addition, given the various contents and ionic radii of La³⁺, Sm³⁺ and Sr²⁺, as well as the oxidation of the larger Co³⁺ ions to the smaller Co⁴⁺ ions, the unit cell parameters of each sample changes as summarized in Table 1, which may lead to the result that the inflection point (where $x=0.475$ when $y=0.35$) of electrical conductivity coincidentally corresponds to the structure transition from hexagonal to orthorhombic.

Fig. 3 The conductivity of La_{1-x}Sm_xSr_yCoO_{3-δ} samples

Fig. 4 (a) XPS results for Co ions of the LSSC series cathodes; (b-d) Deconvoluted results of Co 2p_{3/2} for the three LSSC samples.

Table 2

Peak area ratios of Co²⁺, Co³⁺ and Co⁴⁺ arising from the results of XPS analysis

	Co ²⁺ (%)	Co ³⁺ (%)	Co ⁴⁺ (%)
LSSC35-1200	33.7	42.2	24.1
LSSC40-1200	34.5	41.8	23.7
LSSC45-1200	36.6	40.7	22.7

3.4. Electrochemical characterizations

Fig. 5 shows the impedance spectra of the LSC, SSC as well as the LSSC cathodes as it changes with respect to oxygen partial pressure $p(\text{O}_2)$ at 800 °C. The equivalent circuit model shown in Fig. 5f is utilized to fit the impedance arcs. R_{ohm} represents the overall ohmic resistance mainly related to the electrolyte. $R_{\text{HF}}/\text{CPE}_{\text{HF}}$, $R_{\text{MF}}/\text{CPE}_{\text{MF}}$ and $R_{\text{LF}}/\text{CPE}_{\text{LF}}$ are associated with process in the electrodes at high-, medium-, low-frequency regions, respectively [35-37]. To clearly present the differences in the electrode polarization behavior, R_{ohm} in the EIS was subtracted, showing only the electrode polarization impedance. Table 3 summarizes the values of R_{HF} , R_{MF} and R_{LF} fitted by the model, as well as those of the corresponding capacitances. Generally, the high-frequency (HF) arc is assigned to charge transport processes, such as conduction of oxygen ions either in the bulk electrode or at the interface between the electrode and the electrolyte. A careful scrutiny of literature revealed that the middle-frequency (MF) arc could be attributed to electrode process, such as the ionization of the adsorbed oxygen molecule, the dissociative adsorption of oxygen, or the surface diffusion of the adsorbed oxygen. The low-frequency (LF) arc can be related to non-charge transfer processes, either adsorption of a gas phase oxygen molecule to the cathode surface or gas phase diffusion through the porous cathode layer [30, 35, 38]. The choice of three R/CPE elements mirrors the fundamental description of the way a MIEC cathode works, by assuming the three rate-determining steps which summarized by Fukunaga et al. [8] in the overall oxygen reduction reaction. Since these reaction steps have different time constants, each reaction is expected to occur in a diverse characteristic frequency range. As shown in the fitting results, the LSSC cathodes display better electrochemical performance than LSC and SSC. The pure LSC and SSC cathodes exhibit R_{P} (i.e. the sum of R_{HF} , R_{MF} and R_{LF}) values of 0.166 and 0.134 $\Omega \text{ cm}^2$ at 800 °C and 0.21 atm $p(\text{O}_2)$, respectively, similar to

those reported in the literature [39]. In contrast, R_p values as low as 0.092, 0.083 and 0.097 $\Omega \text{ cm}^2$ are obtained at 800 °C and 0.21 atm $p(\text{O}_2)$ for LSSC35-1200, LSSC40-1200 and LSSC45-1200, respectively. In addition, it can be seen that R_p is governed by R_{LF} at low $p(\text{O}_2)$ values of 0.1 and 0.05 atm, while at 1 and 0.21 atm R_p is dominated by R_{MF} . It is reasonable that all the low-frequency circles clearly change as the value of $p(\text{O}_2)$ increases because the oxygen diffusivity of MIEC is sufficiently high (typically $D_k > 10^{-7}$ to $10^{-8} \text{ cm}^2 \text{ s}^{-1}$ above 800 °C for 0.7-1atm) at high temperatures and high $p(\text{O}_2)$ values [40, 41]. Furthermore, it is noted that the fitted capacitance for HF and MF is relatively large compared with the values reported for other cathodes. This may be the consequence of the mechanical stress in the film caused by mismatches in the lattice constant or thermal expansion, and the contribution of oxygen nonstoichiometry in the electrolyte layer as well as experimental factors [10].

Fig. 6a-c present R_p and $p(\text{O}_2)$ values for LSC, SSC and LSSC cathodes in the high-, medium- and low-frequency regions at 800 °C, respectively. The change of R_p with $p(\text{O}_2)$ can be described by an expression given below:

$$R_p \propto P(\text{O}_2)^{-n} \quad (2)$$

According to literature [37, 42], the overall ORR could be separated into several dissimilar elementary steps. Different reaction orders n represent various elementary steps.

$$n=1/10, \text{O}_{\text{TPB}}^{2-} + \text{V}_{\text{O}}^{\square\square} \rightleftharpoons \text{O}_{\text{O}}^{\times} \quad (8)$$

The slopes for **LSC**, **SSC** and LSSC cathodes in each frequency region are similar as presented in Fig. 6a-c, and this indicates that all the cathodes examined show analogous reaction behavior throughout the frequency range. Slopes between 0.10 and 0.13 in the high-frequency region are found for **LSC**, **SSC** and LSSC. This feature suggests that the electrode reaction in the high frequency may be mainly limited by the process of oxygen ion transfer from TPBs to the electrolyte [30, 36]. In the case of medium-frequency arc, the reaction orders fall between 0.19 and 0.27, which denotes the charge transfer process at the TPBs may be the rate limiting steps. Low-frequency arcs offer n-value of ~ 1 , implying that gas phase diffusion of oxygen molecules is a limiting factor in non-charge transfer process. These results are similar to those of S.-W. Baek et al [35].

Comparing LSSC series with **LSC and SSC**, the most viable improvement in R_p may contribute to R_{HF} and R_{MF} , as shown in Table 3 and Fig. 6. However, the enhancement in R_{LF} , related to the non-charge transfer process, is insignificant. These results suggest that the decrease in R_p values could be ascribed mainly to the enhancement of electrical conductivity as discussed above. Because of the improved electronic conduction paths, there would be more electrons transferring to the active ORR site, thus facilitating the formation and conduction of oxygen ions, leading to lower R_{HF} and R_{MF} values.

Fig. 6d shows the polarization overpotential curves for **LSC**, **SSC** and LSSC based cathodes at 800 °C and 0.21 atm $p(\text{O}_2)$. It can be seen that there is an obvious reduction in polarization overpotential when employing LSSC series as cathodes. The tendency corresponds to the results shown in Fig. 5 and Table 3, **LSSC40-1200** displaying the lowest overpotential. As shown in Fig. 7, the **LSSC40-1200** cathode is porous, and is approximately 30 μm in thickness. It is shown that

LSSC40-1200 cathode is properly sintered to the SDC electrolyte.

Fig. 5 Impedance spectra of (a) LSC, (e) SSC and (b-d) LSSC cathodes with variation in oxygen partial pressure $p(\text{O}_2)$ at 800 °C; (f) Equivalent circuit model used to fit the impedance spectra

Table 3

Fitting parameters for the EIS tests on the symmetric cell with LSC, SSC or LSSC cathodes at varying O_2 partial pressure at 800 °C

	$p(\text{O}_2)$	R_{HF}	$\text{CPE}_{\text{HF-T}}$	$\text{CPE}_{\text{HF-P}}$	R_{MF}	$\text{CPE}_{\text{MF-T}}$	$\text{CPE}_{\text{MF-P}}$	R_{LF}	$\text{CPE}_{\text{LF-T}}$	$\text{CPE}_{\text{LF-P}}$
	(atm)	($\Omega \text{ cm}^2$)	(F cm^{-2})		($\Omega \text{ cm}^2$)	(F cm^{-2})		($\Omega \text{ cm}^2$)	(F cm^{-2})	
LSC	1	1.58E-02	1.35E-03	0.998	7.13E-02	6.14E-02	0.840	6.3E-03	1.741	0.531

	0.21	1.92E-02	1.02E-03	0.981	0.112	3.33E-02	0.886	3.42E-02	0.877	0.571
	0.1	2.02E-02	1.32E-03	0.977	0.136	2.67E-02	0.863	7.66E-02	0.705	0.866
	0.05	2.18E-02	2.58E-03	0.979	0.161	2.94E-02	0.831	0.161	0.617	0.871
LSSC35-1200	1	4.3E-03	1.67E-02	0.987	3.54E-02	0.185	0.961	6.7E-03	4.969	0.660
	0.21	5.3E-03	1.06E-02	0.981	5.57E-02	0.162	0.919	3.09E-02	2.208	0.785
	0.1	5.9E-03	1.94E-02	0.973	6.38E-02	0.292	0.811	6.69E-02	2.98	0.793
	0.05	6.4E-03	2.37E-02	0.961	6.96E-02	0.391	0.762	0.115	2.981	0.810
LSSC40-1200	1	2.8E-03	4.85E-02	0.967	2.75E-02	0.434	0.848	8.4E-03	1.990	0.677
	0.21	3.3E-03	5.36E-02	0.927	4.02E-02	0.375	0.791	3.96E-02	2.355	0.834
	0.1	3.5E-03	5.20E-02	0.907	4.71E-02	0.391	0.767	7.40E-02	1.990	0.803
	0.05	3.8E-03	2.81E-02	0.965	5.14E-02	0.544	0.673	0.125	1.892	0.829
LSSC45-1200	1	5.9E-03	2.41E-03	0.998	3.15E-02	0.162	0.944	6.8E-03	1.716	0.748
	0.21	7.3E-03	1.54E-02	0.955	4.52E-02	0.201	0.826	4.42E-02	1.999	0.843
	0.1	7.8E-03	2.79E-02	0.912	5.39E-02	0.258	0.768	9.63E-02	1,774	0.887
	0.05	8.1E-03	4.16E-02	0.885	6.30E-02	0.203	0.776	0.181	1.589	0.870
SSC	1	1.24E-02	1.42E-02	0.861	4.83E-02	0.242	0.839	7.5E-03	4.435	0.728
	0.21	1.45E-02	4.33E-02	0.870	7.03E-02	0.301	0.746	4.95E-02	3.405	0.791
	0.1	1.60E-02	3.68E-02	0.966	7.52E-02	0.321	0.710	0.104	3.439	0.840
	0.05	1.68E-02	5.79E-02	0.893	8.68E-02	0.510	0.628	0.204	3.363	0.884

Fig. 6 LSC, SSC and LSSC symmetric cells, $T=800\text{ }^{\circ}\text{C}$. (a) dependence of the HF resistance on $p(\text{O}_2)$; (b) dependence of the MF resistance on $p(\text{O}_2)$; (c) dependence of the LF resistance on $p(\text{O}_2)$; (d) cathodic overpotential obtained at $p(\text{O}_2)=0.21\text{ atm}$

Fig. 7 SEM images of cross-section of **LSSC40-1200** cathode

To further confirm the enhanced performance of the LSSC cathodes, complete fuel cells of SDC electrolyte supported NiO/SDC (weight ratio of 6:4) anode with LSSC, LSC and SSC as cathode respectively were fabricated. The results of I-V curves and power densities for the cells at 800 °C are shown in Fig. 8. The open circuit voltages (OCV) of the cells in humidified H₂ at 800 °C are about 0.8 V, close to the value calculated from the Nernst equation. **The peak power density is 119.29 mW cm⁻² for the cell with pure-phase LSC as cathode, and that for the one with pure-phase SSC is 134.77 mW cm⁻². However, a peak power density as high as 176.94 mW cm⁻² is obtained for the cell with LSSC40-1200 as cathode, implying an increase of 49% and 31% respectively in cell performance.**

Fig. 8 Voltages and power densities as a function of current density for cells with LSC, SSC and LSSC cathodes measured at 800 °C

4. Conclusions

$\text{La}_{1-x}\text{Sm}_x\text{Sr}_y\text{CoO}_{3-\delta}$ (LSSC; where $x=0.475$ when $y=0.35$, $x=0.650$ when $y=0.40$, $x=0.825$ when $y=0.45$) compounds are synthesized and characterized in comparison with pure-phase LSC and SSC on thermal expansion coefficients, electrical conductivity and electrochemical properties. All compositions in the LSSC system have a perovskite-type structure, and the structure shifts from hexagonal to orthorhombic as the value of y increases from 0.35 to 0.4. The TECs of LSSC are about $18.12\sim 19.20 \times 10^{-6} \text{ K}^{-1}$ in air from 40 to 800 °C, which are similar to that of LSC and SSC. Electrical conductivity measurement exhibits LSSC has much higher conductivity than LSC and SSC. LSSC 35-1200 shows a maximum conductivity of around 2750 S cm^{-1} , leading to a growth of 29% and 53%, in contrast with that of LSC and SSC respectively. This inflection point (where $x=0.475$ when $y=0.35$) of electrical conductivity corresponds to the structure transition from hexagonal to orthorhombic coincidentally. As indicated by the XPS results, the Co^{4+} content in LSSC 35-1200 is higher than those in LSSC40-1200 and LSSC45-1200, which may lead to the enhanced electrical

conductivity. In addition, after employing **LSSC40-1200** as cathode, the cathode polarization resistance reduces by **50% and 38%** compared with that of **LSC and SSC** at 800 °C, respectively. Accordingly, LSSC series also exhibit higher power densities, with a maximum of 176.94 mW cm⁻² for **LSSC40-1200** at 800 °C, implying an increment of **49% and 31%** respectively. **According to the varied oxygen partial pressures research on the EIS, the improved electrochemical performance of LSSC cathode could be mainly explained by the high electrical conductivity resulted from electronic compensation.** These results demonstrate that LSSC could be a potential cathode material for IT-SOFCs.

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References

- [1] A.B. Stambouli, E. Traversa, *Renew. Sust. Energ. Rev.* 6 (2002) 433-455.
- [2] D.J.L. Brett, A. Atkinson, N.P. Brandon, S.J. Skinner, *Chem. Soc. Rev.* 37 (2008) 1568-1578.
- [3] Z.P. Shao, S.M. Haile, *Nature* 431 (2004) 170-173.

- [4] Z.P. Shao, W.S. Yang, Y. Cong, H. Dong, J.H. Tong, G.X. Xiong, J. Membr. Sci. 172 (2000) 177-188.
- [5] Z.P. Shao, H. Dong, G.X. Xiong, Y. Gong, W.S. Yang, J. Membr. Sci. 183 (2001) 181-192.
- [6] T.C. Yeh, J.L. Routbort, T.O. Mason, Solid State Ion. 232 (2013) 138-143.
- [7] C.R. Xia, W. Rauch, F.L. Chen, M.L. Liu, Solid State Ion. 149 (2002) 11-19.
- [8] H. Fukunaga, M. Koyama, N. Takahashi, C. Wen, K. Yamada, Solid State Ion. 132 (2000) 279-285.
- [9] A.N. Petrov, O.F. Kononchuk, A.V. Andreev, V.A. Cherepanov, P. Kofstad, Solid State Ion. 80 (1995) 189-199.
- [10] T. Kawada, J. Suzuki, M. Sase, A. Kaimai, K. Yashiro, Y. Nigara, J. Mizusaki, K. Kawamura, H. Yugami, J. Electrochem. Soc. 149 (2002) E252-E259.
- [11] A. Ringuede, J. Fouletier, Solid State Ion. 139 (2001) 167-177.
- [12] J.A. Lane, S.J. Benson, D. Waller, J.A. Kilner, Solid State Ion. 121 (1999) 201-208.
- [13] L.W. Tai, M.M. Nasrallah, H.U. Anderson, D.M. Sparlin, S.R. Sehlin, Solid State Ion. 76 (1995) 259-271.
- [14] L.W. Tai, M.M. Nasrallah, H.U. Anderson, D.M. Sparlin, S.R. Sehlin, Solid State Ion. 76 (1995) 273-283.
- [15] A. Petric, P. Huang, F. Tietz, Solid State Ion. 135 (2000) 719-725.
- [16] N. Mahato, A. Banerjee, A. Gupta, S. Omar, K. Balani, Prog. Mater. Sci. 72 (2015) 141-337.
- [17] W. Zhou, Z. Shao, R. Ran, P. Zeng, H. Gu, W. Jin, N. Xu, J. Power Sources 168 (2007) 330-337.
- [18] D.W. Jung, C. Kwak, H.J. Park, J.S. Kim, S.-J. Ahn, D.-H. Yeon, S. Seo, K.-S. Moon, S.M. Lee, Scripta Mater. 113 (2016) 59-62.

- [19] W. Zhu, Z. Lü, S. Li, B. Wei, J. Miao, X. Huang, K. Chen, N. Ai, W. Su, *J. Alloys Compd.* 465 (2008) 274-279.
- [20] X. Lou, S. Wang, Z. Liu, L. Yang, M. Liu, *Solid State Ion.* 180 (2009) 1285-1289.
- [21] S. Li, Z. Lü, B. Wei, X. Huang, J. Miao, G. Cao, R. Zhu, W. Su, *J. Alloys Compd.* 426 (2006) 408-414.
- [22] H. Ullmann, N. Trofimenko, F. Tietz, D. Stover, A. Ahmad-Khanlou, *Solid State Ion.* 138 (2000) 79-90.
- [23] S. Yu, S. He, H. Chen, L. Guo, *J. Power Sources* 280 (2015) 581-587.
- [24] S. He, H. Chen, R. Li, L. Ge, L. Guo, *J. Power Sources* 253 (2014) 187-192.
- [25] Y. Guo, H. Shi, R. Ran, Z. Shao, *Int. J. Hydrog. Energy* 34 (2009) 9496-9504.
- [26] O. Gwon, S. Yoo, J. Shin, G. Kim, *Int. J. Hydrog. Energy* 39 (2014) 20806-20811.
- [27] H.Y. Tu, Y. Takeda, N. Imanishi, O. Yamamoto, *Solid State Ion.* 100 (1997) 283-288.
- [28] P. Hjalmarsson, M. Sogaard, A. Hagen, M. Mogensen, *Solid State Ion.* 179 (2008) 636-646.
- [29] X.Y. Chen, J.S. Yu, S.B. Adler, *Chem. Mat.* 17 (2005) 4537-4546.
- [30] A. Donazzi, R. Pelosato, G. Cordaro, D. Stucchi, C. Cristiani, G. Dotelli, I.N. Sora, *Electrochim. Acta* 182 (2015) 573-587.
- [31] K.T. Lee, A. Manthiram, *J. Electrochem. Soc.* 153 (2006) A794.
- [32] S. Park, S. Choi, J. Shin, G. Kim, *J. Power Sources* 210 (2012) 172-177.
- [33] Y. Huang, B. Zhao, R. Ang, S. Lin, Z. Huang, S. Tan, Y. Liu, W. Song, Y. Sun, *J. Phys. Chem. C* 117 (2013) 11459-11470.
- [34] Y. Kim, H. Schlegel, K. Kim, J.T.S. Irvine, J.H. Kim, *Appl. Surf. Sci.* 288 (2014) 695-701.
- [35] S.-W. Baek, J. Bae, Y.-S. Yoo, *J. Power Sources* 193 (2009) 431-440.

- [36]P. Guo, X. Huang, X. Zhu, Z. Lü, Y. Zhou, L. Li, Z. Li, B. Wei, Y. Zhang, W. Su, Fuel Cells (2013) 666-672.
- [37]Y. Li, R. Gemmen, X. Liu, J. Power Sources 195 (2010) 3345-3358.
- [38]S. Adler, X. Chen, J. Wilson, J. Catal. 245 (2007) 91-109.
- [39]H. Lv, Y. Wu, B. Huang, B. Zhao, K. Hu, Solid State Ion. 177 (2006) 901-906.
- [40]S.B. Adler, J.A. Lane, B.C.H. Steele, J. Electrochem. Soc. 143 (1996) 3554-3564.
- [41]D. Garcés, A.L. Soldati, H. Troiani, A. Montenegro-Hernández, A. Caneiro, L.V. Mogni, Electrochim. Acta 215 (2016) 637-646.
- [42]A.P. Khandale, S.S. Bhoga, Electrochimica Acta 130 (2014) 439-445.

Intensity (a.u.)