

Electrode properties of $\text{La}_{1-x}\text{Sr}_x\text{CuO}_{2.5-\delta}$ as new cathode materials for intermediate-temperature SOFCs

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Abstract

Oxygen-deficient perovskite type oxides $\text{La}_{1-x}\text{Sr}_x\text{CuO}_{2.5-\delta}$ (LSCu) have been synthesized in the composition range: $0.15 \leq x \leq 0.3$. Due to their high oxygen vacancy concentration and good electrical conductivity, these materials are characterized as new positive electrode (cathode) materials for intermediate-temperature solid oxide fuel cells (IT-SOFCs). The valence state of copper ions, thermal expansion, cathodic overpotential, reactivity with yttria-stabilized zirconia (YSZ) and polarization resistance (R_p) of the LSCu|YSZ interface are examined. At 800 °C, the sample with the composition of $\text{La}_{0.7}\text{Sr}_{0.3}\text{CuO}_{2.5-\delta}$ exhibits the lowest overpotential of about 10 and 12.6 mV at a current density of 150 and 200 mA cm⁻², respectively. LSCu show no reaction against yttria-stabilized zirconia (8YSZ) at 800 °C for 1000 h. Reaction between LSCu and YSZ occurs, however, at 900 °C for 10 h. The formation of SrZrO_3 is observed.

Based on the results of ac impedance analyses, the polarization resistance of LSCu decreases from 0.85 to 0.25 Ω at 800 °C when the fraction of Sr is increased from 20 to 30%. The reduction of polarization resistance is improved by the presence of oxygen vacancies in LSCu. These oxygen vacancies provide numerous pathways for the diffusion of oxygen ions electrode surface to the triple phase boundary (TPB) and the electrode|electrolyte interface. Therefore, LSCu may be a very attractive cathode material for IT-SOFCs.

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Keywords: Intermediate-temperature solid oxide fuel cell; Oxygen-deficient perovskite; Polarization resistance; Positive electrode material

1. Introduction

Owing to their high electrical conductivities in an oxygen-containing atmosphere, a number of doped perovskite oxides, $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ (LSM), $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ (LSC), $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ (LSF), $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_3$ (LSCF), etc. [1–3], have received much attention as positive electrode (cathode) materials for solid oxide fuel cells (SOFCs). Currently, yttria-stabilized zirconia (YSZ) is the state-of-the-art electrolyte material for SOFCs. A higher operation temperature (1000 °C) is needed to provide sufficient mobility of oxygen ions [2]. Such high-temperature operation may, however, cause a degradation of performance due to the formation of second phase, sintering of the electrode and interfacial diffusion between electrode and electrolyte. Recently, intermediate temperature SOFCs (IT-SOFCs) operating at 500–800 °C and using thin-film electrolytes have been widely investigated [4,5].

When a SOFC operates at an intermediate temperature, the rate of reduction of molecular oxygen at the cathode has a

major influence on cell performance. In earlier studies [6,7], it was realized that the possible cathodic reaction pathways for oxygen reduction and diffusion into electrolyte include: (i) reduction of molecular oxygen on the electrolyte surface; (ii) desorption–adsorption of oxygen molecules and surface diffusion to the triple phase boundary (TPB); (iii) surface reaction followed by dissolution and the diffusion of oxygen ions towards the cathode|electrolyte interface. Therefore, the cathode material should have high electrical conductivity and high oxygen-ion mobility. To date, the state-of-the-art material used for cathodes in SOFCs has been Sr-doped LaMnO_3 (LSM). Since LSM is a poor ionic conductor. It is to be expected that the diffusion of oxygen ions to the electrode|electrolyte interface via the bulk LSM electrode does not make a significant contribution to the overall oxygen flux [7]. On the other hand, mixed conducting electrode material may increase the TPB, and reduce the area specific polarization resistance, R_p , at the electrode|electrolyte interface [8]. Hence, the performance of SOFC can be enhanced. To search for a good electrode material with desired properties, Sr-doped lanthanum copper oxide with a perovskite-based structure has been found to be a candidate cathode material for an IT-SOFC [9], due to its oxygen-deficient char-

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acteristics and low resistivity of $4.8 \times 10^{-4} \Omega \text{ cm}$ at 300 K [10,11].

In this study, the thermal expansion, electrochemical properties and the structural stability of LSCu against YSZ at 800 and 900 °C has been investigated.

2. Experimental procedure

Samples of $\text{La}_{1-x}\text{Sr}_x\text{CuO}_{2.5-\delta}$ ($x = 0.15, 0.2, 0.25$ and 0.3) powder were synthesized by a conventional solid-state reaction. La_2O_3 , SrCO_3 and CuO were mixed in an appropriate ratio and ball-milled in ethanol solution for 24 h. The powder mixtures were then calcined at 800 °C for 20 h in air. The calcined powders were cold isostatically pressed at 200 MPa and then sintered at 1000 °C in air for 20 h. The crystal structure of the samples was analyzed by X-ray diffraction (XRD) at room temperature with $\text{Cu K}\alpha$ radiation at a rate of 2° min^{-1} . The oxidation state of the Cu ions was determined by the two-step iodometric titration technique [12,13]. The structural stability of LSCu against YSZ electrolyte was examined by co-firing of 8YSZ and LSCu powder at 800 and 900 °C in a 1:1 weight ratio.

The overpotential of oxygen reduction of the cathode was determined by a current-interruption technique, as shown in Fig. 1. The steady-state residual voltage (overpotential) between the working and reference electrodes was measured at a constant current density in the range $10\text{--}300 \text{ mA cm}^{-2}$, and at 600–900 °C.

The electrode polarization resistance, R_p , of the LSCu/YSZ interface was determined by ac impedance spectroscopy. The same analyses were also conducted on the LSM ($\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$)/YSZ samples. Impedance analyses were taken over the frequency range 0.1–100 kHz under an applied amplitude of 20 mV. The overall electrode polarization resistance was determined from the difference between the high- and low-frequency intercept on the impedance spectra.

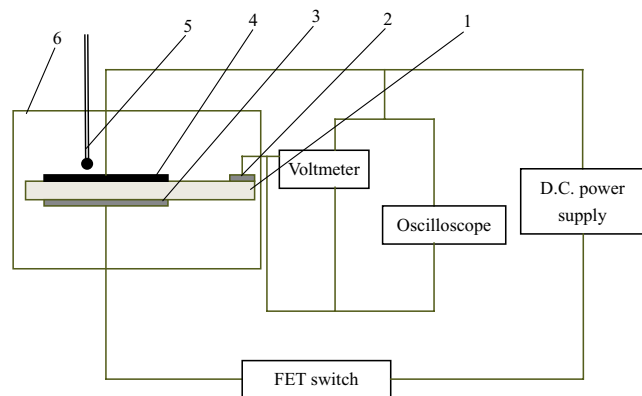


Fig. 1. Schematic diagram for cathodic overpotential measurements: (1) YSZ electrolyte, (2) Pt reference electrode, (3) Pt counter electrode, (4) working electrode (LSCu), (5) thermocouple and (6) furnace.

For the overpotential and impedance analyses, dense disks of 8YSZ (20 mm diameter and 0.6 mm thick) were used as the electrolyte. The cathode powder was mixed with binder prepared from α -terpineol and ethyl-cellulose, and applied on the YSZ disc by a screen-printing method. Platinum paste was painted on the other side as the counter electrode, and on the edge of the cathode side as the reference electrode. The samples were then heat-treated at 850 and 1150 °C for LSCu and LSM, respectively, for 5 h. The morphologies and the microstructures of the tested samples were observed by scanning electron microscopy (SEM).

3. Results and discussion

3.1. Crystal structure of LSCu

The crystal structure of lanthanum copper oxide is highly dependent on Sr addition. For lanthanum copper oxide with 15 wt.% Sr addition, a single perovskite-based orthorhombic structure is found. With increase in strontium content, the stability of the perovskite structure is enhanced. Based on the XRD analyses, a single tetragonal structure is formed when the strontium content is in the range 20–30 wt.%. The structural parameters of LSCu with various amounts of strontium are listed in Table 1. The relationships of $a \approx 2\sqrt{2}c$ and $b \approx \sqrt{2}c$ suggested that both orthorhombic and tetragonal LSCu are essentially superlattices of standard perovskite. It is known that a superlattice is commonly found in a structure with excess charge defects. In this case, the formation of the superlattice is caused by the presence of numerous oxygen vacancies [14].

The presence of oxygen vacancies in the samples was also verified by the titration results of copper ions. As shown in Table 1, the concentration of Cu^{3+} ions increase with increasing strontium content and reaches a maximum value at about 30 wt.% of strontium [8]. Since Sr-doped lanthanum copper oxide crystallizes in an ABO_3 (perovskite) lattice, the stoichiometry of oxygen (or the fraction of oxygen vacancies), is determined from the total valences of the cations La, Sr and Cu. Apparently, the fraction of oxygen vacancies is at least 16.67%. The presence of concentrated oxygen vacancies may cause strong electrostatic repulsion from surrounding cations and thus will destabilize the perovskite structure. To increase the stability of this highly defective perovskite lattice, oxygen vacancies in LSCu are orderly distributed. Thus, crystallization of superlattices is observed. As the addition of Sr exceeds 20 wt.%, more trivalent copper ions are created. Consequently, a more stable and symmetrical tetragonal lattice is obtained.

3.2. Structure stability of perovskite LSCu against 8YSZ

To examine the structure stability of $\text{La}_{1-x}\text{Sr}_x\text{CuO}_{2.5-\delta}$ ($x = 0.15, 0.2, 0.25$ and 0.3) against 8YSZ (which is the most commonly used electrolyte for SOFCs), powders of

Table 1
Structure parameters of $\text{La}_{1-x}\text{Sr}_x\text{CuO}_{2.5-\delta}$ with different compositions

Composition	Structure	a (Å)	b (Å)	c (Å)	$\text{Cu}^{3+}/(\text{Cu}^{2+} + \text{Cu}^{3+})$ (%)	$2.5-\delta$
$\text{La}_{0.85}\text{Sr}_{0.15}\text{CuO}_{2.5-\delta}$	Orthorhombic	5.5040	10.6011	3.8785	7.2	2.461
$\text{La}_{0.8}\text{Sr}_{0.2}\text{CuO}_{2.5-\delta}$	Tetragonal	10.8666	–	3.8570	14.2	2.471
$\text{La}_{0.75}\text{Sr}_{0.25}\text{CuO}_{2.5-\delta}$	Tetragonal	10.8586	–	3.8568	17.4	2.462
$\text{La}_{0.7}\text{Sr}_{0.3}\text{CuO}_{2.5-\delta}$	Tetragonal	10.8513	–	3.8514	19.6	2.448

LSCu and 8YSZ were mixed and then co-fired at 800 and 900 °C. The XRD patterns of powder mixtures after being annealed at 800 °C for 1000 h are given in Fig. 2. The decomposition of orthorhombic $\text{La}_{0.85}\text{Sr}_{0.15}\text{CuO}_{2.5-\delta}$ into La_2CuO_4 and tetragonal LSCu is observed. When unmixed $\text{La}_{0.85}\text{Sr}_{0.15}\text{CuO}_{2.5-\delta}$ powder is annealed at 800 °C for 1000 h, a similar phase decomposition takes place. Therefore, the appearance of La_2CuO_4 and tetragonal LSCu in the LSCu/YSZ mixture is caused by self-decomposition of orthorhombic LSCu. By contrast, no second phase is found in lanthanum copper oxide containing 20, 25 and 30 wt.% Sr. When more than 20 wt.% of Sr is added to LSCu, more trivalent copper ions are induced, as seen in Table 1. Consequently, improved structural stability is expected. Thus, the tetragonal structure of these samples remain stable at 800 °C.

The XRD pattern of a LSCu and 8YSZ mixture heated at 900 °C for 10 h is shown in Fig. 3. For $\text{La}_{0.85}\text{Sr}_{0.15}\text{CuO}_{2.5-\delta}/8\text{YSZ}$, in addition to orthorhombic LSCu and

8YSZ, a La_2CuO_4 phase and a small amount of SrZrO_3 are detected. In comparison to the annealing results at 800 °C (Fig. 2), the formation of SrZrO_3 is due to the reaction at 900 °C. As discussed previously, the formation of a perovskite structure in the LSCu system is greatly affected by the strontium content. $\text{La}_{0.85}\text{Sr}_{0.15}\text{CuO}_{2.5-\delta}$, however, reacts with YSZ and forms SrZrO_3 at the higher temperature. Furthermore, the formation of SrZrO_3 also destabilizes both orthorhombic and tetragonal perovskite due to the consumption of Sr in LSCu. Thus, decomposition is also observed in the sample of $\text{La}_{0.8}\text{Sr}_{0.2}\text{CuO}_{2.5-\delta}$.

On the other hand, LSCu tetragonal perovskite with a high strontium content ($x = 0.25$ and 0.3) still exhibits higher stability than the other samples at 900 °C, and there is no formation of La_2CuO_4 , as seen in Fig. 2. The formation of AZrO_3 (A: Sr or Ca) has been found in some other divalent-doped perovskite oxides, i.e., $\text{La}_{1-x}\text{A}_x\text{MO}_3$ (M: Co, Mn, Fe, etc.), on reaction with YSZ [1,15–17]. Thus, the formation of SrZrO_3 is simply caused by the diffusion of Sr ions in LSCu towards YSZ [18].

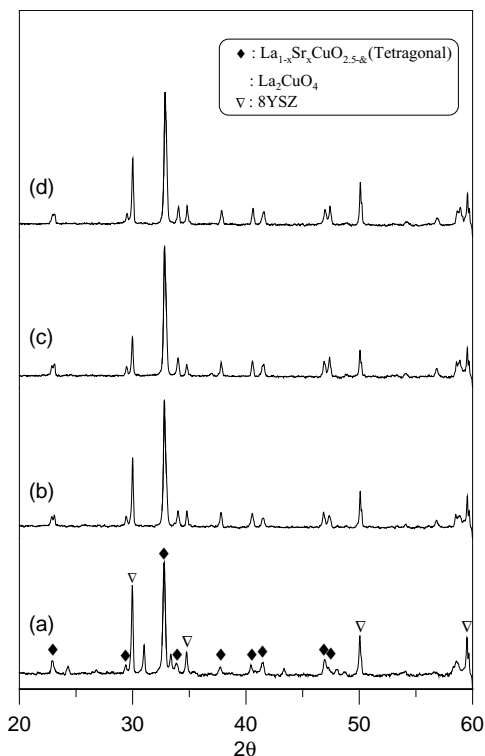


Fig. 2. XRD patterns for various LSCu/YSZ powder mixtures annealed at 800 °C for 1000 h: (a) $\text{La}_{0.85}\text{Sr}_{0.15}\text{CuO}_{2.5-\delta}/8\text{YSZ}$, (b) $\text{La}_{0.8}\text{Sr}_{0.2}\text{CuO}_{2.5-\delta}/8\text{YSZ}$, (c) $\text{La}_{0.75}\text{Sr}_{0.25}\text{CuO}_{2.5-\delta}/8\text{YSZ}$ and (d) $\text{La}_{0.7}\text{Sr}_{0.3}\text{CuO}_{2.5-\delta}/8\text{YSZ}$.

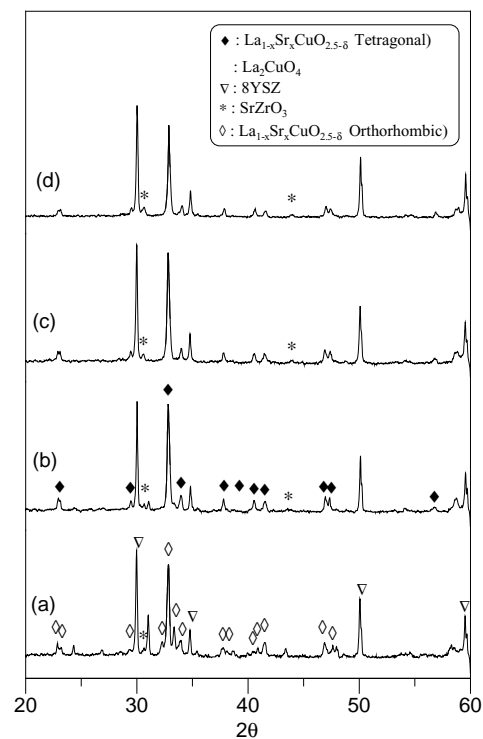


Fig. 3. XRD patterns of LSCu/YSZ powder mixture annealed at 900 °C for 10 h (a) $\text{La}_{0.85}\text{Sr}_{0.15}\text{CuO}_{2.5-\delta}/8\text{YSZ}$, (b) $\text{La}_{0.8}\text{Sr}_{0.2}\text{CuO}_{2.5-\delta}/8\text{YSZ}$, (c) $\text{La}_{0.75}\text{Sr}_{0.25}\text{CuO}_{2.5-\delta}/8\text{YSZ}$ and (d) $\text{La}_{0.7}\text{Sr}_{0.3}\text{CuO}_{2.5-\delta}/8\text{YSZ}$.

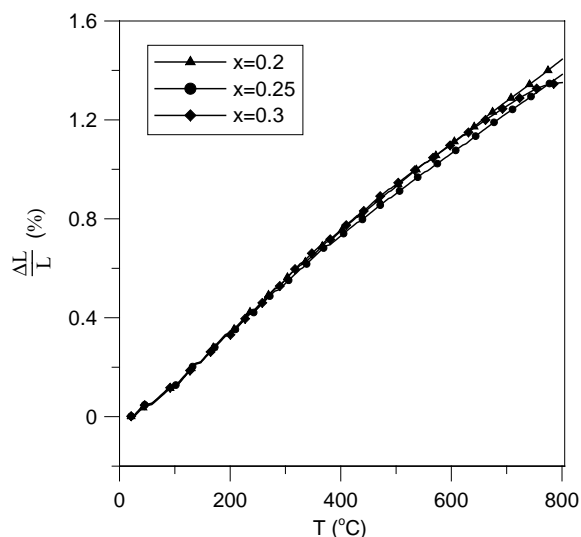


Fig. 4. Dilatometric curves of $\text{La}_{1-x}\text{Sr}_x\text{CuO}_{2.5-\delta}$ ($x = 0.2, 0.25$ and 0.3) as function of temperature.

In summary, in order to use LSCu as the cathode in a IT-SOFC and prevent the phase decomposition of LSCu and the reaction of LSCu/YSZ, addition of strontium between 20 and 30 wt.% is necessary.

3.3. Thermal expansion

Dilatometric curves of $\text{La}_{1-x}\text{Sr}_x\text{CuO}_{2.5-\delta}$ discs sintered at 1000°C are shown in Fig. 4. The thermal expansion of these samples increases almost linearly with increasing temperature from room temperature to 800°C . The thermal expansion coefficients (TECs) of LSCu ($x = 0.2, 0.25$ and 0.3), calculated by fitting the dilatometric curves, are in the range of 1.68×10^{-5} to $1.79 \times 10^{-5} \text{ K}^{-1}$ from 25 to 800°C . These values are larger than that of the commonly used electrolyte material, YSZ ($\text{TEC} = 1.05 \times 10^{-5} \pm 5\% \text{ K}^{-1}$). The TEC mismatch of LSCu and YSZ may cause delamination and material fracture at the electrode|electrolyte interface, and thereby reduce the performance when operating at high

temperature for a long period of time. A similar problem has been observed in other cathode materials such as LSC, LSF-based perovskite, etc. [19–21].

To minimize TEC mismatch, LSCu may be applied as a thin-layered cathode on the electrolyte surface or the SOFC operated at lower temperatures. In the latter case, the thermal expansion mismatch will become less critical. Furthermore, according to the theory of thermal expansion developed by Ruffa [22,23], TEC mismatch is inversely proportional to the metal-oxide bond length (A–O and B–O bond). TEC mismatch can be reduced by doping with aliovalent ions (for example, Mn ions) to increase the metal-oxide bond length. For instance, the TEC mismatch of $\text{Pr}_{1-x}\text{Sr}_x\text{CoO}_3$ has been successfully reduced by Mn doping [24]. Therefore, the TEC mismatch of the LSCu system may also be modified by aliovalent cation doping. Further investigations are required to confirm this suggestion.

3.4. Cathodic overpotential measurement

The cathodic overpotential of LSCu was carried out using a LSCu|YSZ|Pt cell. Typical electron micrographs of the top and cross-section of a $\text{La}_{0.75}\text{Sr}_{0.25}\text{CuO}_{2.5-\delta}$ porous cathode on YSZ electrolyte after firing at 850°C for 5 h are presented in Fig. 5. The thickness of the $\text{La}_{0.75}\text{Sr}_{0.25}\text{CuO}_{2.5-\delta}$ porous layer is about $10 \mu\text{m}$ and the grain size is about $1\text{--}2 \mu\text{m}$. Appropriate necking with a homogeneous and continuous pore distribution are also observed. Typical cathodic overpotential curves for $\text{La}_{0.75}\text{Sr}_{0.25}\text{CuO}_{2.5-\delta}$ as a function of current density at $600, 700, 800$ and 900°C are shown in Fig. 6(a). The cathodic overpotential of these electrodes decreases with increasing temperature. Although, LSCu/YSZ exhibits the best overpotential behaviour at 900°C , the secondary phase, SrZrO_3 , is formed at 900°C after annealing for a few hours (as shown in Fig. 3). The formation of SrZrO_3 may cause degradation of electrode performance [25].

It is noted that when the operating temperature is as low as 600°C , LSCu still exhibits a low cathode overpotential of about 70 and 80 mV at a current density of 150

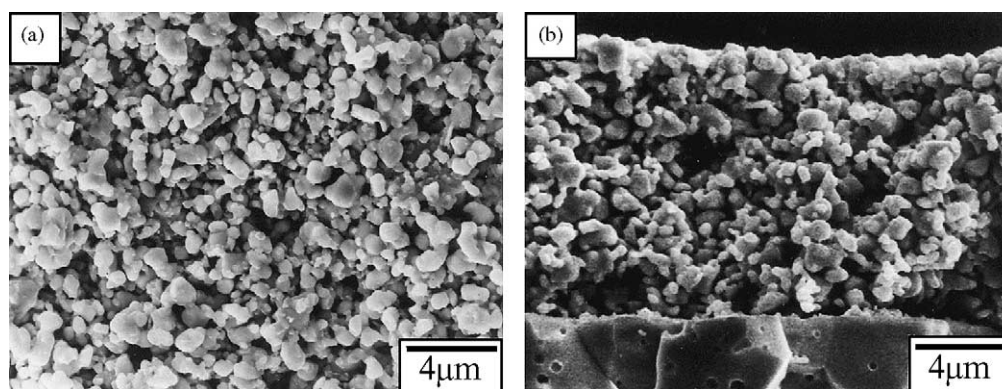


Fig. 5. Electron micrographs of $\text{La}_{0.75}\text{Sr}_{0.25}\text{CuO}_{2.5-\delta}$ porous cathode applied on YSZ electrolyte after firing at 850°C for 5 h: (a) top view and (b) cross-section.

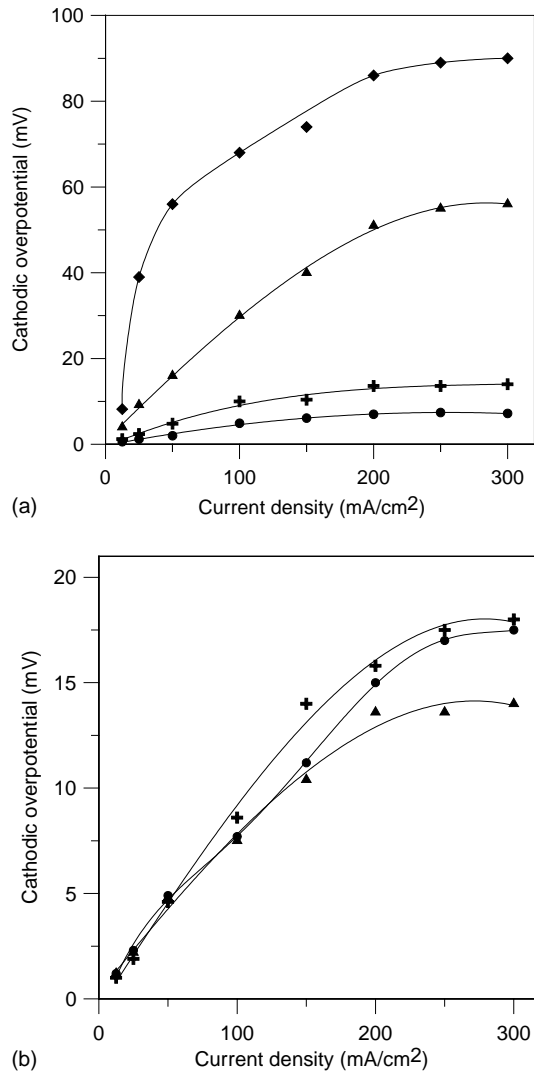


Fig. 6. Cathodic overpotential curves for: (a) La_{0.75}Sr_{0.25}CuO_{2.5-δ} measured at (◆) 600 °C, (▲) 700 °C, (+) 800 °C, (●) 900 °C; (b) LSCu with various strontium contents: (+) La_{0.8}Sr_{0.2}CuO_{2.5-δ}, (●) La_{0.75}Sr_{0.25}CuO_{2.5-δ}, (▲) La_{0.7}Sr_{0.3}CuO_{2.5-δ} measured at 800 °C.

and 200 mA cm⁻², respectively. The cathodic overpotential curves for La_{1-x}Sr_xCuO_{2.5-δ} ($x = 0.2, 0.25$ and 0.3) as a function of current density at 800 °C are given in Fig. 6(b). The cathodic overpotential increases linearly when the current density is raised from 0 to 150 mA cm⁻², and then gradually increases at higher current density. In addition, the cathodic overpotential of LSCu decreases with increasing strontium content. La_{0.7}Sr_{0.3}CuO_{2.5-δ} exhibits the lowest cathodic overpotential of about 10 and 12.6 mV at 150 and 200 mA cm⁻², respectively. These phenomena may be due to the presence of oxygen vacancies which are increased by strontium addition. The effect of oxygen vacancies on the cathodic polarization behaviour was further examined by the following impedance measurements.

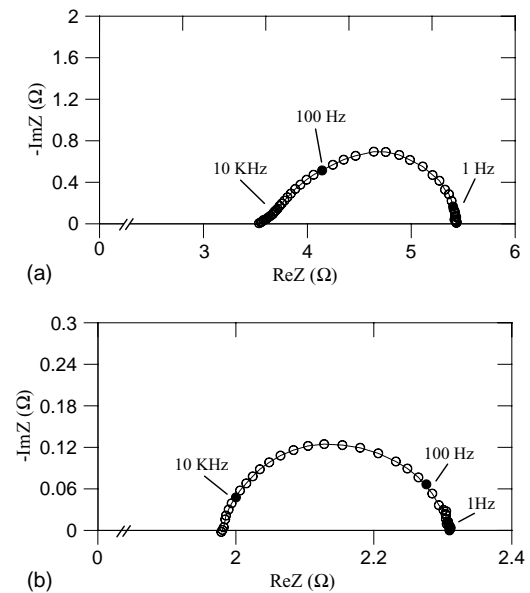


Fig. 7. Impedance spectra of La_{0.75}Sr_{0.25}CuO_{2.5-δ}/YSZ at open-circuit voltage after passing a current of 200 mA cm⁻² at (a) 700 °C and (b) 800 °C.

3.5. Impedance analyses

It has been reported [26] that the cathodic overpotential is affected mainly by the polarization at the electrode|electrolyte interface. In this section, the polarization resistance, R_p , of the LSCu|YSZ interface after passing a constant current was measured using ac impedance spectroscopy. Subsequently, the impedance analyses obtained from a LSCu|YSZ|Pt cell were adopted to study the relationship between the electrode kinetics and the presence of oxygen vacancies in tetragonal LSCu. The specific impedance spectra of La_{0.75}Sr_{0.25}CuO_{2.5-δ} taken after passing a current of 200 mA cm⁻² at 700 and 800 °C are presented in Fig. 7. The R_p of the LSCu|YSZ interface is 1.85 and 0.25 Ω at 700 and 800 °C, respectively. These values are much lower than those of La_{0.8}Sr_{0.2}MnO₃ (viz., 24.1 and 1.9 Ω at 700 and 800 °C, respectively), which was measured under the same conditions. The R_p of LSCu ($x = 0.2, 0.25$ and 0.3) as a function of strontium content at various temperatures is plotted in Fig. 8. The low R_p of LSCu and its dependence on Sr content can be rationalized by the presence of anion defects (oxygen vacancy consideration). As discussed previously, more than 16.67% of anion sites are vacant in the LSCu lattice. Such a large amount of oxygen vacancies in LSCu provide pathways for the diffusion of oxygen ions. Hence, the overall oxygen flux of the reduced oxygen ions towards the electrode|electrolyte interface can be significantly enhanced. A lower R_p at the LSCu|YSZ interface than at the LSM|YSZ interface is expected. The contribution of oxygen vacancies on the oxygen flux from the electrode surface towards the electrode|electrolyte interface is described as follows.

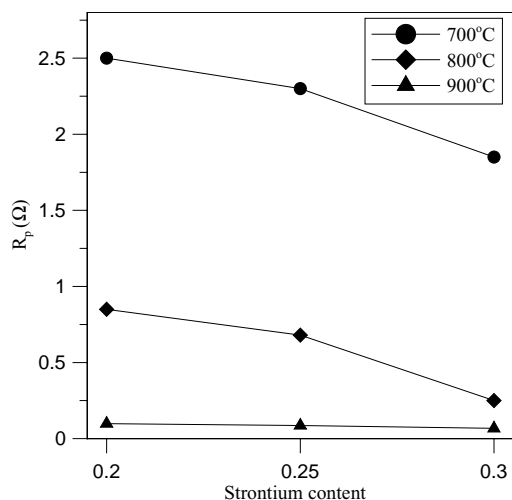


Fig. 8. R_p of LSCu as function of strontium content at various temperatures: (●) 700 °C, (◆) 800 °C and (▲) 900 °C.

For the reduction of molecular oxygen, oxygen vacancies on the electrode surface provide reaction sites for the reduction of molecular oxygen ($(1/2)O_2 + 2e^- \rightarrow O^{2-}$), and also enhance the mobility of oxygen ions to the TPB [27–29]. In addition, oxygen vacancies in the electrode provide avenues for the diffusion of reduced oxygen ions from the electrode surface to the electrode|electrolyte interface. As a result, the presence of oxygen vacancies activates the cathodic electrochemical reaction and then reduces the polarization resistance at the electrode|electrolyte interface.

On the other hand, it is well-known that LSM is a poor ionic conductor [9]. Thus, diffusion of oxygen ions towards the electrode|electrolyte interface is difficult. The difference between poor and a good oxygen-ion conductivity in the cathode material in a SOFC illustrated in Fig. 9. When the electrode material exhibits an appropriate amount of oxygen

vacancies, the diffusion of these vacancies through the bulk electrode from the surface towards the electrode|electrolyte interface can be enhanced. Consequently, the TPBs are extended inside the cathode grains, as shown in Fig. 9(a). For an electronic conductor with poor ionic conductor such as LSM, the electrochemical reaction only takes place at the TPB zone shown in Fig. 9(b). Therefore, the new cathode material, LSCu, not only activates the cathodic reaction at the TPB, but also extends the TPB.

4. Conclusions

$La_{1-x}Sr_xCuO_{2.5-\delta}$ with a perovskite structure has been obtained when 15–30 wt.% of strontium is added to the La-cation sub-lattice. Tetragonal LSCu ($0.2 \leq x \leq 0.3$) perovskite provides better structure stability against 8YSZ than the orthorhombic variety ($x = 0.15$). After heating the LSCu/YSZ powder mixture at 800 °C for 1000 h, tetragonal LSCu exhibits good stability and no phase decomposition is observed. When the same perovskite mixture is heated at 900 °C for 10 h, a small amount of $SrZrO_3$ is observed. In electrochemical measurements of LSCu/YSZ, the tetragonal $La_{0.7}Sr_{0.3}CuO_{2.5-\delta}$ displays a minimal cathodic polarization of 10 mV, which is better than that of LSM/YSZ, at a current density of 150 mA cm^{-2} at 800 °C. In addition, the polarization resistance (R_p) of the $La_{0.7}Sr_{0.3}CuO_{2.5}$ /YSZ interface is as low as 0.25Ω at 800 °C. These phenomena can be explained by the presence of oxygen vacancies in LSCu that enhance the transportation of reduced oxygen ions from the electrode surface to the electrode|electrolyte interface. Consequently, the TPB is extended inside the LSCu grain, and thus activates the cathodic reaction. Therefore, LSCu is a promising cathode material for IT-SOFCs.

Acknowledgements

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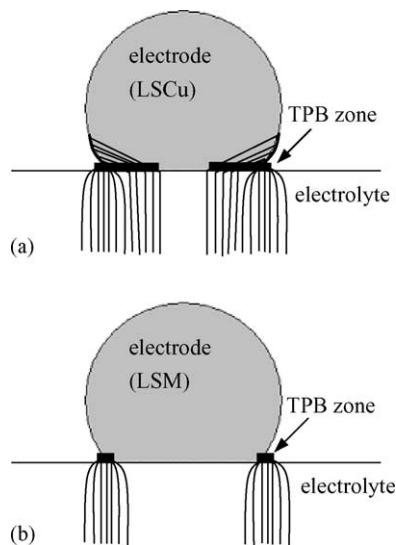


Fig. 9. Schematic of reaction pathways of oxygen flux from cathode to electrolyte for (a) mixed conductor and (b) poor ionic conductor.

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