

# On the high temperature conductivity of ceramics

$\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$  –  $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$

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Perovskite-type ceramics  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$  (LSCF) and  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ – $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$  (LSCF–GDC) prepared by the method of solid-state reaction were tested by SEM, and their conductivity-temperature relationships were measured by the direct current four-terminal method. The activation energies of small polarons of single-phase LSCF and LSCF–GDC are  $E_{a1} = 9.92$  kJ/mol and  $E_{a2} = 12.34$  kJ/mol, respectively.

**Keywords:** Perovskite-type ceramics, conductivity-temperature, activation energies.

**Високотемпературна провідність кераміки**  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$  –  $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$ .  
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Кераміка типу перовскіту  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$  (LSCF) і  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ – $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$  (LSCF–GDC), отримана методом твердофазного синтезу, протестована з допомогою SEM. Виміряна провідність в залежності від температури чотириконтактним методом постійного струму. Енергії активації малих поляронів однофазних LSCF і LSCF–GDC складають  $E_{a1} = 9,92$  кДж/моль і  $E_{a2} = 12,34$  кДж/моль відповідно.

Кераміка типа перовскита  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$  (LSCF) и  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$  –  $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$  (LSCF–GDC), полученная методом твердофазного синтеза, протестирована с помощью SEM. Измерена проводимость в зависимости от температуры четырехконтактным методом постоянного тока. Энергии активации малых поляронов однофазных LSCF и LSCF–GDC составляют  $E_{a1} = 9,92$  кДж/моль и  $E_{a2} = 12,34$  кДж/моль соответственно.

## 1. Introduction

In recent years, materials based on mixed electron-ion conductivity (MIEC) have been widely used for cathodes and electrolytes of solid oxide fuel cells (SOFC) [1]. MIEC materials are mainly transition metal oxides with a perovskite structure. Among them, materials based on lanthanum cobalt oxides and barium cobalt oxides, which are stable and have the ability to rapidly transfer oxygen ions, are widely studied for pure academic interest and potential applications [2]. However, the performance of these compounds is not perfect and further optimization is needed for practical use.

Because the expansion coefficient of LSCF ceramics at high temperature is identical with the electrolyte of SOFC, and the electrochemical properties of LSCF ceramics above 600° need to

be further improved,  $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$  (SDC),  $(\text{ZrO}_2)_{0.9}(\text{Y}_2\text{O}_3)_{0.1}$  (YSZ) electrolyte materials are added to LSCF as cathode materials of SOFC to improve its high temperature performance [3, 4].

Generally speaking, when the mass ratio of GDC to LSCF is 3:7, electrochemical and conductive properties of the material are best [5]. Therefore, it is more important to study the synthesis, characterization and ionic conductivity of LSCF after doping.

Two kinds of ceramics, LSCF and LSCF–SDC, were synthesized and characterized by XRD and SEM. The electrical conductivity of LSCF–SDC composites and single-phase LSCF were measured during the heating process at 20–700°C. The activation energies of LSCF–SDC composites and single-phase LSCF were obtained by fitting the measured curves.

## 2. Experimental

For composite samples, 3 g of SDC powder and 7 g of LSCF powder were weighed on the electronic analytical balance and ground in an agate mortar for 40 minutes to mix them uniformly. The mixed powders were poured into a rectangular die and dry pressed for 60 s to form (20×14×0.9 mm) rectangular sheet blanks under a pressure of about 600 MPa. The LSCF samples were made according to the same method. The pressed samples were sintered in a box furnace at 1100°C for 5 hours and then cooled naturally. The samples are taken out at room temperature and cut into strips. The specifications of two strip samples are as follows: for LSCF sample, the electrode spacing is  $L = 7$  mm, the width is  $w = 2.98$  mm, the thickness is  $d = 0.8$  mm; for LSCF-SDC sample, the electrode spacing of is  $L = 6.8$  mm, the width is  $w = 3.2$  mm, and the thickness is  $d = 0.81$  mm.

Four silver wires were attached to the strip specimens with silver conductive glue. Conductivity was measured by a four-terminal method. The morphology of samples was observed by scanning probe electron microscopy (SPEM), and the information on microstructures was obtained.

Four sample electrodes were connected to a KEITHLEY 2400 digital source meter and placed in a temperature controlled tube furnace. The temperature range was 20–700°C and the temperature control speed was 2°C/min. The sample resistance was measured on heating. The experimental device is shown in Fig. 1.

## 3. Results and discussion

### 3.1 SEM microscopic morphology of two samples

Scanning microscopic images of sample sections are shown in Fig. 2. The magnification is ×5000 and the scanning voltage is 25 kV. According to the SEM images, the porosity determined using a Photoshop software was 23 % for the LSCF-SDC composite and 25 % for the LSCF sample; the average void size was about 0.4 nm as measured by micromorphology. In some mixtures, SDC segregation is observed (white areas in the figure), which may be associated with precipitation at grain boundaries during crystallization.

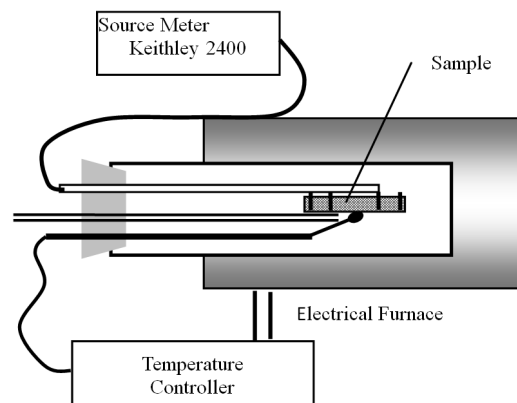


Fig. 1. Experimental device scheme.

### 3.2 Activation energies of conductivity in LSCF and LSCF-SDC

Figure 2 shows the Arrhenius curves of conductivity for LSCF and LSCF-SDC samples. It can be seen that the conductivity of both samples increases first and then decreases with increasing temperature, and a peak value of the conductivity is observed [6]. The conductivity of the LSCF-GDC sample is only 1/3 ~ 1/2 of LSCF. This is due to the fact that GDC has mainly oxygen-ionic conductivity, and its ionic conductivity is much lower than that of LSCF (mainly electronic conductivity). Therefore, the GDC particles in the LSCF-GDC composite have an obvious barrier effect on the electronic conductivity of LSCF, which results in the conductivity of the LSCF-GDC being lower than that of the LSCF. The maximum temperature of conductivity is the same, which indicates that GDC contributes little to the overall conductivity of the sample compared with LSCF in the mixed electron-ion conduction process. Therefore, the conductivity of the sample decreases with the addition of GDC, but the peak position remains unchanged. Since the LSCF conductivity at low temperatures is associated with the mechanism of small polaron jumps, the conductivity of the sample increases with temperature. The relationship between conductivity by the mechanism of small polaron jumps and temperature is [7]

$$\ln\sigma T = \ln A - \frac{E_a}{k_B} \cdot \frac{1}{T}.$$

Among them,  $\sigma$  is the conductivity of the sample,  $T$  is the thermodynamic temperature,  $k_B$  is the Boltzmann constant,  $E_a$  is the activation energy needed for small polaron jumps, and  $A$  is the coefficient related to the specific material.

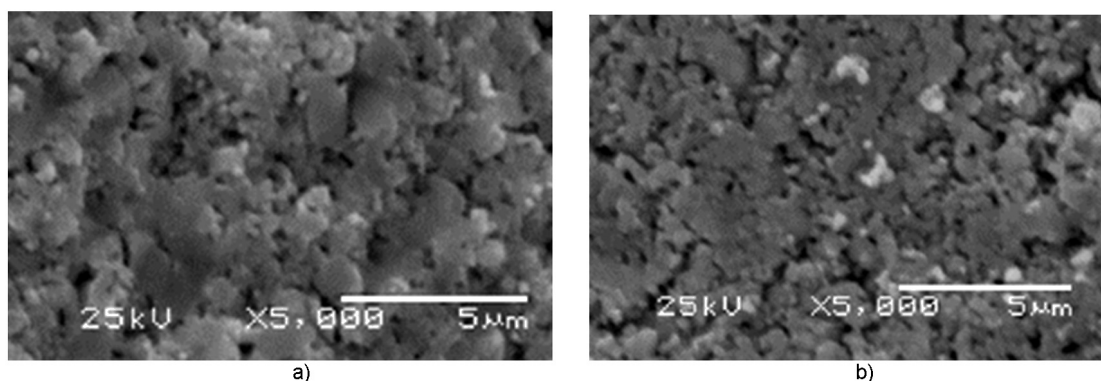


Fig. 2. Scanning microscopic images of LSCF and LSCF-SDC samples.

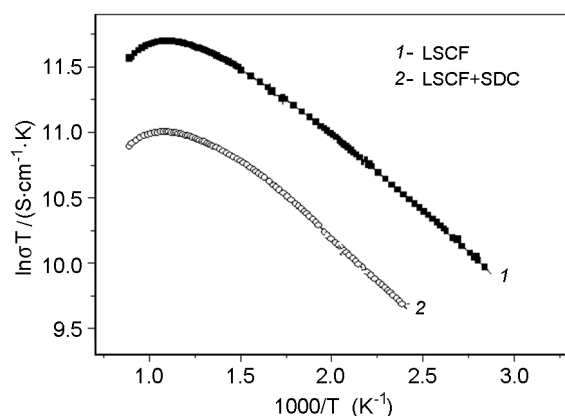


Fig. 3. Arrhenius plots for the conductivity of LSCF and LSCF-SDC samples.

The natural logarithm of the product of conductivity  $\sigma$  and temperature  $T$  is part of a linear relationship with  $1/T$ , as shown in Fig. 3. The product of the linear slope of the curve at low temperature and the Boltzmann constant  $k_B$  is the activation energy of small polaron jump conduction for the two samples. The conductivity activation energy  $E_{a1} = 9.92 \pm 0.03$  kJ/mol of single-phase LSCF can be obtained by measuring the straight-line part of the plot. The activation energy of the samples is similar to those prepared by the GNP method. The conductivity activation energy  $E_{a2} = 12.34 \pm 0.03$  kJ/mol was measured for LSCF-SDC. When SDC is added, the resistivity of the sample increases, and the activation energy of conductivity of the composite slightly increases. In the high temperature region, the ionic compensation is caused by the distorted charge of  $\text{Co}^{3+}$  ions excited by high temperature and the formation of oxygen defect vacancies, so the conductivity reaches the maximum and then decreases.

The conductivity of  $\text{Co}^{3+}$  ions is considered as metal conductivity [8].

#### 4. Conclusions

In this paper, the electrical properties of single-phase LSCF and LSCF-GDC composites were studied by the temperature-varying method. The electrical conductivities and conductivity activation energies of the two materials at high temperature were obtained. The results show that electronic conductivity still prevails in LSCF-SDC composites, but lower than in single-phase LSCF, and the activation energy of conduction is close to the activation energy of small polaron jumps. These results indicate that the performance of compounds is excellent and suitable for solid oxide fuel cells.

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