Electrical properties of $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}$ ceramic synthesized by solid-state reaction method

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$La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}$ ceramics was prepared by means of the solid-state reaction method under the sintering condition of 1100°C for 5 h. The X-ray diffraction and Raman spectroscopy results indicated that the sample possessed a pseudo-cubic structure. The temperature-dependent electrical conductivity was measured by the *dc* four-electrode technique, and the calculated activation energy was 9.64 kJ/mol based on the Arrhenius relationship. The electrical conductivity relaxation data of the sample under different oxygen partial pressures (0.1−0.2 kPa) were analyzed and the surface emission coefficients at 600°C, 700°C and 800°C were obtained.

Keywords: ceramics, solid-state reaction method, electrical properties, XRD, Raman, electrical conductivity relaxation.

Електричні властивості кераміки $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}$, синтезованої методом твердофазної реакції. *Yandong Wang, Xinlong Li*

Кераміку $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}$ отримано методом твердофазної реакції в умовах спікання при температурі 1100°C протягом 5 ч. Результати рентгенівської дифракції і рамановської спектроскопії показали, що зразок має псевдокубічну структуру. Температурну залежність електропровідності вимірювали чотириелектродним методом постійного струму. Розрахована енергія активації склала 9,64 кДж/моль на основі співвідношення Арреніуса. Проаналізовано дані релаксації електропровідності зразка при різному парціальному тиску кисню (0,1− 0,2 кПа), і приведено коефіцієнти поверхневої емісії при 600°C, 700°C і 800°C.

Керамика $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}$ получена методом твердофазной реакции в условиях спекания при температуре 1100°C в течение 5 ч. Результаты рентгеновской дифракции и рамановской спектроскопии показали, что образец имеет псевдокубическую структуру. Температурную зависимость электропроводности измеряли четырехэлектродным методом постоянного тока, рассчитанная энергия активации составила 9,64 кДж/моль на основе соотношения Аррениуса. Проанализированы данные релаксации электропроводности образца при различном парциальном давлении кислорода (0,1−0,2 кПа), и приведены коэффициенты поверхностной эмиссии при 600°C, 700°C и 800°C.

1. Introduction

Energy crisis and environmental problems have become challenges for our society. Solid oxide fuel cells (SOFC) convert the chemical energy directly to electricity and play an important role in the energy conversation and emission reduction [1, 2].

When fuel gases such as hydrogen (H_2) and methane (CH_4) are continuously intro-duced to the anode side of SOFC, they are adsorbed on the surface of the catalytic anode and diffused through the porous structure of the anode to the interface between the anode and the electrolyte. When oxygen or air is continuously injected into the cathode side, oxygen is adsorbed on the surface of the cathode. Owing to the catalytic behavior of the cathode, O_2 are converted to O^{2-}. Due to a concentration gradient, O^{2-} eventually diffuses

to the interface between the anode and the electrolyte, where O^{2-} reacts with the fuel gas, and the lost electrons return to the cathode through the external circuit.
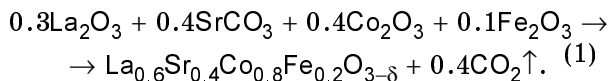
Materials with mixed electron-ion conducting (MIEC) with a perovskite structure are widely used as cathode materials of SOFC, oxygen separation membranes and oxygen sensors due to their high oxygen permeability rate and high oxygen ion conductivity. Most of these materials are transition-metal oxides with rare-earth elements; and materials based on $LaCoO_3$ have attracted much attention for their stable and fast transportation capacity of oxygen ions. J.Castro-Robles et al. and W.Wang et al. carried out important studies on the electrical properties such as the hopping conductivity of small polarons and the surface oxygen emission coefficient [3–5]. However, the mechanisms for electrical conductivity, relaxation and other properties are still not well understood and more detailed study should be conducted.

In this paper, we study the preparation condition, structure and electrical properties of $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}$ ceramics.

2. Experimental

$La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}$ ceramics (LSCF) is synthesized by many methods such as hydrothermal, so-gel and solid-state reaction [4–5]. The hydrothermal reaction is performed in a pressure vessel, in which water is used as a solvent, and the original powders are dissolved in water and then recrystallized. This method has the advantages such as high crystallinity, perfectly fine grains, good distribution, low cost and low reaction temperature, but also has disadvantages such as long reaction period, equipment dependence. The reaction mechanisms of the hydrothermal method are still unclear now. The so-gel method is common in preparation of functional ceramic powders, and has the merits of fine grains, high purity, good uniformity, low reaction temperature. The disadvantages of this method are long reaction period, high cost and so on. The solid-state reaction method has the advantages of simple process, high production efficiency, batch production and controllable process.

In this work, we adopted the solid-state reaction method to prepare LSCF ceramics. The chemical reaction equation is as follows:

$$0.3La_2O_3 + 0.4SrCO_3 + 0.4Co_2O_3 + 0.1Fe_2O_3 \rightarrow$$
$$\rightarrow La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta} + 0.4CO_2\uparrow. \quad (1)$$

The reagents were first weighted according to the formula, and then were thoroughly grounded in an agate mortar for 1 h. The mixed powder was calcined at 500°C for 5 h and was grounded again. Then, the calcined powder was pressed into rectangle green samples (20 mm×15 mm×1 mm in dimension) under 50 MPa. Finally, these green samples were sintered at 1100°C for 5 h in air and naturally cooled.

To determine the crystal structure, powder XRD measurements at room temperature were carried out on a diffractometer DX-2700 (Dandong, China) with Cu–Kα radiation. The measurement step and the counting time were 0.02 deg and 3 s, respectively. Raman spectrum was recorded on an XploRa spectrometer (Horiba Jobin Yvon, France) with the 532 nm line of a Nd:YAG laser. The surface morphology of the samples was characterized by scanning electron microscopy (SEM, EVO MA10, Zeiss, Germany).

Before the electrical measurement, the sample was cut into pieces 3 mm wide. The Ag paste was used as an electrode, and the distance between two adjacent electrodes was 7 mm. The sample was placed in a muffle furnace with a controlled measured temperature. The temperature range was 30–650°C, and the heating rate was 3°C/min. The resistance data were collected by a Keithley 2400 source meter, and conductivity was calculated from the geometric dimensions of the sample.

The principle of measuring the relaxation of electrical conductivity

For a stripy sample, the transport of oxygen ions obeys Fick's second law [5]

$$\frac{\partial C}{\partial t} = D\left(\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2}\right). \quad (2)$$

When the thickness of the sample is close to the characteristic depth of oxygen diffusion, the above equation can be rewritten as [6]

$$f(t) = \frac{\sigma(t) - \sigma(0)}{\sigma(\infty) - \sigma(0)} = \quad (3)$$

$$= 1 - \sum_{n=1}^{\infty} \frac{2C^2 \exp\left(-\alpha D_O t/l^2\right)}{\alpha_n^2\left(\alpha_n^2 + C^2 + C\right)} \approx 1 - \exp\left(-\frac{t}{\tau}\right).$$

Here we define a new function $g(t)$

$$g(t) = 1 - f(t) = \frac{\sigma(\infty) - \sigma(t)}{\sigma(\infty) - \sigma(0)} = \exp(-t/\tau), \quad (4)$$
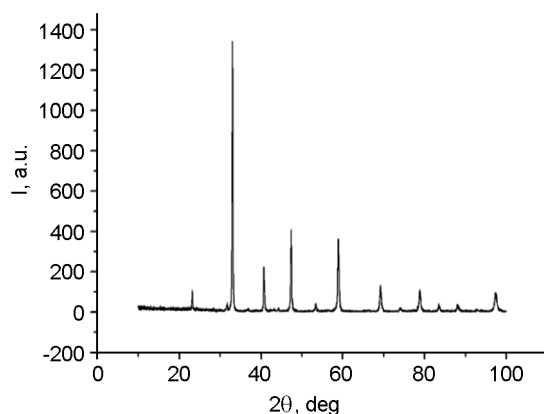
Fig. 1. XRD pattern of an LSCF sample at room temperature.

τ is the time constant for electrical-conduction-relaxation process and could be calculated through the electrical conductivity data. In general case, the theoretical expression of τ could be written as [6]

$$\tau = \frac{1 - V_V}{S_V k_{chem}} , \qquad (5)$$

where k_{chem} is the oxygen surface emission coefficient of the measured sample, S_V is the ratio between the surface area and volume, and V_V is the volume fraction. By fitting the electrical conductivity data at different oxygen partial pressures, we can obtain the time constant, and then get the value of k_{chem}.

The sample with four electrodes is placed in a quartz tube furnace, and the temperatures of the furnace are maintained at 600°C, 700°C and 800°C, respectively. A high purity O_2/N_2 gas mixture was used and the pressure in the tube was maintained at 1 kPa. When the furnace temperature stabilizes, the O_2/N_2 ratio is adjusted from 0.1:0.9 to 0.2:0.8, and the change in conductivity over time is recorded until the values become almost constant.

3. Results and discussion

XRD measurements were carried out to determine the crystal structure of LSCF; the XRD pattern of an as-sintered LSCF sample is shown in Fig. 1. Compared with the standard PDF card and the measurement of Amjad Aman [5], the diffraction peaks show a well-defined crystalline phase and can be indexed by a single pseudo-cubic perovskite structure without impurity phases.
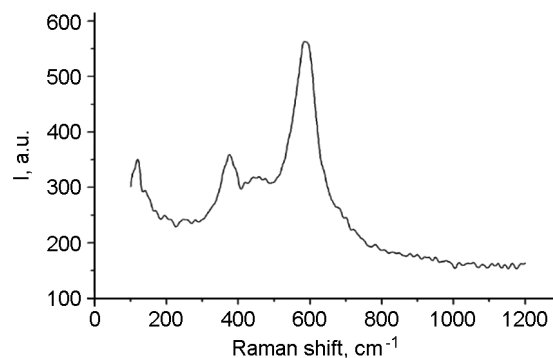

Fig. 2. Raman spectrum of an LSCF sample at room temperature.

Raman spectroscopy is a sensitive tool for detecting local symmetries and was used to further analyze the structure of LSCF in a wavenumber range of 100–1200 cm−1; the results are presented in Fig. 2. For the LSCF sample, two characteristic bands around 400 cm^{-1} and 620 cm^{-1} were reported [7, 8]. The Raman spectrum of the LSCF sample is consistent with the XRD results and literature results confirming the cubic structure of the LSCF perovskite.

The SEM image of an LSCF sample is shown in Fig. 3. The sample has a good crystallinity, and no second phase segregation is observed at grain boundaries. The calculated values of S_V and V_V are $1.06 \cdot 10^4$ cm^{-1} and 0.74, respectively, and the value of V_V is equal to that obtained by the Archimedean method.

The temperature-dependent conductivity of an LSCF sample is shown in Fig. 4. It is known that the conduction mechanism for LSCF is the hopping conductivity of small polarons; and the relation between the conductivity σ and temperature T can be written as [9, 10]

$$\sigma = \frac{A}{T} \exp\left(\frac{E_a}{k_b T}\right), \qquad (6)$$

where k_b is the Boltzmann constant, E_a is the activation energy of hopping of a small polaron, and A is the pre-exponential factor. This equation can be rewritten as:

$$\ln \sigma T = \ln A - \frac{E_a}{k_b} \frac{1}{T}. \qquad (7)$$

The plot of $\ln(\sigma T)$ vs T^{-1} is a straight line, and E_a can be derived from the slope of the line. From Fig. 3a straight line is obtained in the low-temperature range, confirming the mechanism of hopping conduc-
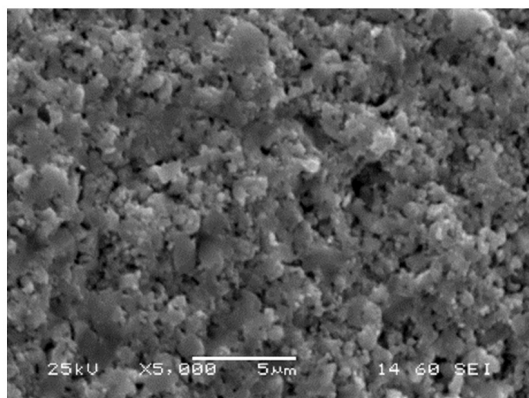
Fig. 3. SEM image of an LSCF sample.

Fig. 4. Arrhenius plot of electrical conductivity of an LSCF sample.

tivity of small polarons [8] in LSCF. The value of E_a is found to be 9.64 kJ/mol.

The plots of $g(t)$ vs time at different temperatures are presented in Fig. 5. The dependence of $g(t)$ satisfies the equation (4), and the time constant can be fitted. The values of τ for 600°C, 700°C and 800°C are 7.4, 6.4 and 5.7, respectively. The time constant decreases with increasing temperature, which is attributed to the higher diffusion rate at a higher temperature. By substitution of the values of S_V and V_V into equation (5), the oxygen surface emission coefficient k was calculated. The values of k for 600°C, 700°C and 800°C are $3.31 \cdot 10^{-6}$ cm·s^{-1}, $3.83 \cdot 10^{-6}$ cm·s^{-1} and $4.30 \cdot 10^{-6}$ cm·s^{-1}, respectively, which are close to the results of secondary ion mass spectroscopy by Kostogloudis et al.

4. Conclusions

The XRD pattern confirmed a pseudo-cubic perovskite structure of LSCF;

Characteristic Raman bands at 400 cm^{-1} and 620 cm^{-1} were consistent with the XRD result.

The plot of $\ln(\sigma T)$ vs T^{-1} showed a straight line, confirming the hopping conductivity of small polarons. The activation energy calculated from the slope of the Arrhenius relation was 9.64 kJ/mol.

The time constants for the process of electrical conductivity relaxation were obtained by means of conductivity measurements. The values of the surface oxygen emission coefficient are $3.31 \cdot 10^{-6}$ cm·s^{-1}, $3.83 \cdot 10^{-6}$ cm·s^{-1} and $4.30 \cdot 10^{-6}$ cm·s^{-1} for 600°C, 700°C and 800°C, respectively.

The properties indicate that the $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}$ ceramics (LSCF) is suitable for solid oxide fuel cells (SOFC).

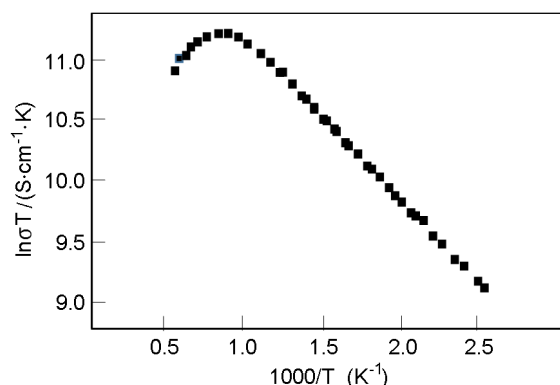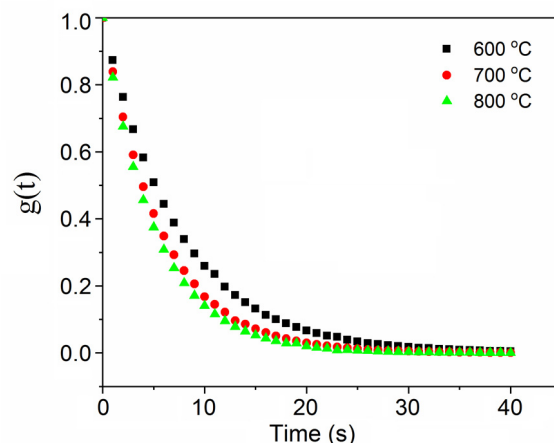Fig. 5. Plots of relaxation of electrical conductivity of an LSCF sample at various temperatures.

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