

# Oxygen ionic conductivity of a composite electrolyte SDC-LSGM prepared via glycine-nitrate process

Wu Liwei<sup>1</sup> Zheng Yingping<sup>1</sup> Wang Shaorong<sup>2</sup> Wang Zhenrong<sup>2</sup> Jing Yao<sup>1</sup> Sun Yueming<sup>1</sup>

(<sup>1</sup>School of Chemistry and Chemical Engineering, Southeast University, Nanjing 211189, China)

(<sup>2</sup>Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China)

**Abstract:**  $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9-8}\text{-La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-8}$  (SDC-LSGM) is prepared by the glycine-nitrate process (GNP). SDC-LSGM composite electrolyte samples with different weight ratios are prepared by the co-combustion method so as to obtain homogeneous nano-sized precursor powders. The X-ray diffraction (XRD) and the scan electron microscope (SEM) are used to investigate the phases and microstructures. The measurements and analyses of oxygen ionic conductivity of SDC-LSGM are carried out through the four-terminal direct current (DC) method and the electrochemical impedance spectroscopy, respectively. The optimum weight ratio of SDC-LSGM is 8 : 2, of which the ionic conductivity is 0.113 S/cm at 800 °C and the conductivity activation energy is 0.620 eV. The impedance spectra shows that the grain boundary resistance becomes the main barrier for the ionic conductivity of electrolyte at lower temperatures. The appropriate introduction of LSGM to the electrolyte SDC can not only decrease the electronic conductivity but also improve the conditions of the grain and grain boundary, which is advantageous to cause an increase in oxygen ionic conductivity.

**Key words:**  $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9-8}$ ;  $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-8}$ ; composite electrolyte; oxygen ionic conductivity

The solid oxide fuel cell (SOFC) is notable for its high efficiency and environmental friendliness. Decreasing the operating temperature of the SOFC from 800 to 600 °C has attracted worldwide interest for the reasons of long-term stability and cost; however, the decreased operating temperature will reduce the oxygen ionic conductivity of the electrolyte in parallel with the electrode reaction activity. Two approaches, reducing the electrolyte thickness and searching for available materials with high ionic conductivity, are widely adopted to alleviate the problem of ohmic loss.

Enormous efforts can be found in the literature on the improvements of electrolyte ionic conductivity, including ceria-based oxides and lanthanum gallate-based oxides<sup>[1-3]</sup>. Samaria doped ceria (SDC) is reckoned as a prominent electrolyte candidate for its good oxygen ion conductor in an intermediate temperature. A major shortage of SDC exists in its instability in reducing atmosphere; i. e., under anode conditions  $\text{Ce}^{4+}$  can be reduced to  $\text{Ce}^{3+}$  which results in the

increase in electronic conduction and can eventually be harmful to the performance of cells. The doping of the perovskite  $\text{LaGaO}_3$  with Sr and Mg (LSGM) introduces a quantity of oxygen vacancies that results in high conductivity ( $> 0.10$  S/cm at 800 °C). Moreover, this compound has negligible electronic conduction at temperatures  $T < 1\,000$  °C over a broad range of oxygen partial pressure from  $P_{\text{O}_2} = 1$  to  $10^{-22}$  atm<sup>[4]</sup>. However, LSGM is known to have higher chemical reactivity with Ni-based cermet anodes, and the reaction between LSGM and Ni results in the formation of high-resistivity compounds such as  $\text{LaNiO}_3$  and  $\text{LaSrGa}_3\text{O}_7$ <sup>[5]</sup>. These reaction products can also lead to the degradation of cell performance due to an anomalous increase in ohmic loss. To fully take advantage of SDC and LSGM, the composite electrolyte SDC-LSGM is a feasible material that can be applied in the electrolyte materials of SOFC. Xu et al.<sup>[6]</sup> reported that the SDC and LSGM powders were mixed by mechanical means, and found that the optimal mixed weight ratio is 9 : 1, in which to a certain extent LSGM can block off the electronic current in the electrolyte and result in an increase in ionic conductivity.

In this paper, SDC-LSGM composite electrolyte samples with different weight ratios are prepared by the co-combustion method so as to obtain homogeneous nano-sized precursor powders. The ionic conductivity of the electrolyte is composed of grain and grain boundary conductivity, and the grain resistance is influenced by its microstructure, while the properties of grain boundary are determined by the mismatch of the lattice, second phase segregation, space charge and microcracks. Therefore, the more homogenous the precursor powders are, the higher the ionic conductivity of the composite electrolyte will be.

## 1 Experimental

$\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (99.9%),  $\text{Sm}_2\text{O}_3$  (99.9%),  $\text{La}_2\text{O}_3$  (99.9%),  $\text{SrCO}_3$  (99.9%),  $\text{Ga}_2\text{O}_3$  (99.9%),  $\text{MgO}$  (99.9%) and other chemicals are purchased from Sinopharm Chemical Reagent Co., Ltd., Shanghai.  $\text{La}_2\text{O}_3$  and  $\text{MgO}$  powders are calcined at 1 000 °C for 2 h to eliminate the impurities.

Varied SDC-LSGM composite electrolyte samples with different weight ratios from 9 : 1 to 5 : 5 (hereafter named as SL91, SL82, SL73, SL64, SL55) and SDC are synthesized by the GNP method; stoichiometric amounts of  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{Sm}_2\text{O}_3$ ,  $\text{La}_2\text{O}_3$ ,  $\text{SrCO}_3$ ,  $\text{Ga}_2\text{O}_3$  and  $\text{MgO}$  are dissolved in dilute nitric acid according to the weight ratios of SDC-LSGM. The mole ratio of glycine to metal is 1.5. The solution is heated on a hotplate and stirred until a sticky gel appears, resulting in rapid and self-sustaining combustion. The resultant ash is calcined at 1 400 °C for 4 h in air to re-

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**Biographies:** Wu Liwei (1986—), male, graduate; Sun Yueming (corresponding author), male, doctor, professor, ypz\_99@yahoo.com.cn.

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move possible carbon residues and form the SDC and LSGM phase of the fluorite and perovskite structure respectively. The resulting powders are pulverized and isostatically pressed into disks (30 mm in diameter and 0.4 mm in thickness) at 30 MPa. Then the disks are finally sintered at 1400 °C for 6 h. The Pt slurry is painted on both the sides of the disks for the measurement of electrochemical impedance spectroscopy (EIS).

The crystal phase structures of SDC-LSGM and pure SDC powders are identified with Cu K $\alpha$  radiation using an XD-3A diffractometer. The conductivity of all the specimens is measured by the standard four-terminal DC method in the temperature range from 900 to 500 °C. Cross-section morphologies are examined in a Sirion scanning electron microscope (SEM). EIS measurements are carried out using a Zahner IM6ex analyzer.

## 2 Results and Discussion

### 2.1 XRD patterns of composite materials

Fig. 1(a) shows the XRD patterns of the different composite electrolyte and pure SDC powders after being calcined at 1400 °C for 4 h. It can be seen that the spectra of SL91 and SL82 are almost the same as the pure SDC in that all reveal a cubic fluorite structure, and no impurity peaks are found. It can be extrapolated that there is a possibility of the entrance of the La<sup>3+</sup> ion into the lattice site of the SDC. The main peaks of SL91 and SL82 shown in Fig. 1(b) shift to low angle for 0.2° and 0.3°, respectively, compared with the SDC. This minute variation can confirm the introduction of the La<sup>3+</sup> ion into the SDC lattice. The ionic radius of the La<sup>3+</sup> (0.106 nm) is larger than that of the Ce<sup>4+</sup> (0.092 nm). Hence introducing the La<sup>3+</sup> ion into the SDC lattice will lead to expansion of the lattice. Tab. 1 shows the lattice

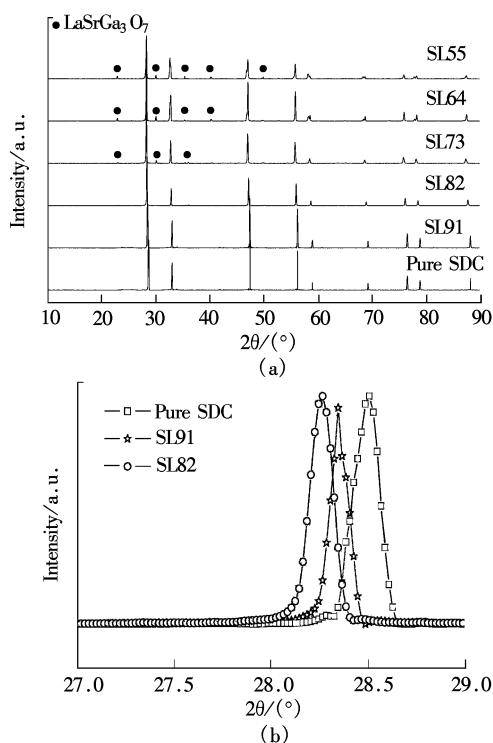
parameters and the crystal size of pure SDC, SL91 and SL82. Cell parameters are calculated by fitting the observed reflections with an MDI JADE5 program and the crystallite size of the calcined powders is estimated using the Scherrer formula. The lattice parameters continuously enlarge with the increase of La<sup>3+</sup> ion concentration, which is consistent with the results of Fig. 1(b). For SL73, SL64 and SL55, a trace of impurity phase of LaSrGa<sub>3</sub>O<sub>7</sub> is observed and becomes much more evident with the incremental LSGM.

**Tab. 1** Lattice parameter and crystal size

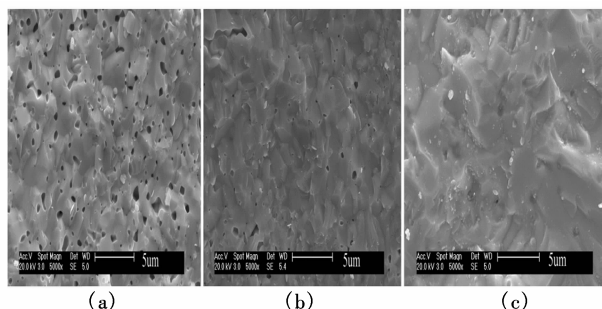
| Sample   | Lattice parameter/nm | Volume of crystal cell/nm <sup>3</sup> | Crystal size/nm |
|----------|----------------------|--|-----------------|
| Pure SDC | 0.541 3              | 0.158 6                                | 39.1            |
| SL91     | 0.542 8              | 0.159 9                                | 40.3            |
| SL82     | 0.545 0              | 0.161 9                                | 41.2            |

### 2.2 SEM analysis

Fig. 2 shows the SEM images of the cross-sections of the sintered SDC, SL91 and SL82. In the pure SDC, the boundaries between grains are clear to see and the porosity is great; however, the amount of pores diminishes with the increase in the LSGM. As for SL91, the grain boundaries tend to merge and blur accompanied with the decrease in pores. In the case of SL82, no significant porosity is observed in the image. It seems that the introduction of LSGM enables it to enhance the grain growth as well as to prompt the atoms at the edge of grains to arrange in an ordered way. The adjacent grains adjust the arranged way of their atoms at the boundary site to make the thickness of the boundary as small as possible<sup>[7]</sup>, and eventually they merge with each other. The remarkable improvement of the porosity and the grain boundaries of SL91 and SL82 must influence the whole conductivity in some way.



**Fig. 1** XRD patterns of composite electrolyte. (a) SL55, SL64, SL73, SL82, SL91 and pure SDC; (b) Partial enlarged view of pure SDC, SL91 and SL82 from 27° to 29°

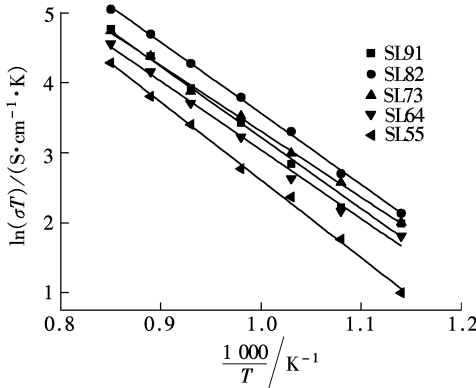


**Fig. 2** Cross-section SEM images of different composite electrolytes. (a) Pure SDC; (b) SL91; (c) SL82

### 2.3 Electrical conductivity

The electrical conductivity of the sintered composite electrolytes is summarized and plotted in an Arrhenius diagram (see Fig. 3). According to the Arrhenius equation, the activation energy can be gained from the slope of each line. For SL82, the activation energy (0.620 eV) is the lowest and the conductivity (0.113 S/cm at 800 °C and 0.059 S/cm at 700 °C) is the highest among the five samples. The reason for the high conductivity of SL82 is that it is possible that a certain amount of La<sup>3+</sup> ion dissolves into the ceria phase. This behavior not only stabilizes the cubic phase but also increases the oxygen vacancy concentration in the ceria, and LSGM also plays an important role in blocking the reduction of quadrivalent cerium ionic to becoming trivalent. SL82 seems to be

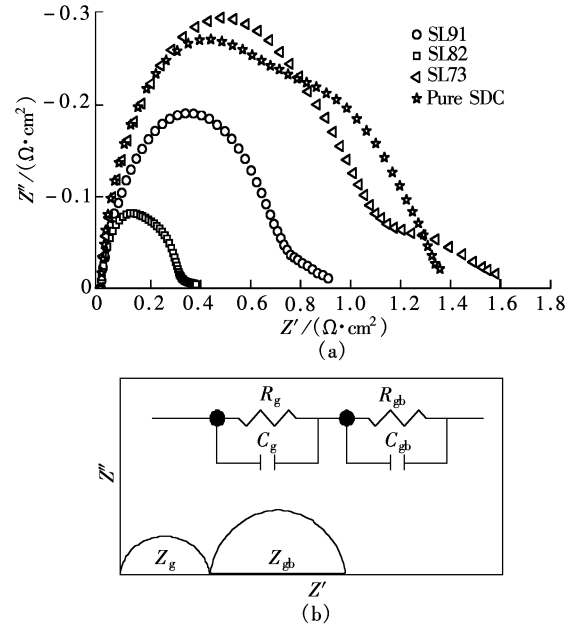
the optimum composition in terms of electrical conductivity which is in good agreement with SEM analysis; however, the conductivity of the composite electrolytes decreases with the increase in LSGM in the cases of SL73, SL64 and SL55. This can explain why the increase of LSGM as a secondary phase in the composite electrolytes is due to saturated dissolution of lanthanum ions into the ceria phase. Besides, the new impurity phase of  $\text{LaSrGa}_3\text{O}_7$ , which can be found in SL73, SL64 and SL55 functions as a nonconductor, will dwindle the conductivity dramatically<sup>[8-9]</sup>.



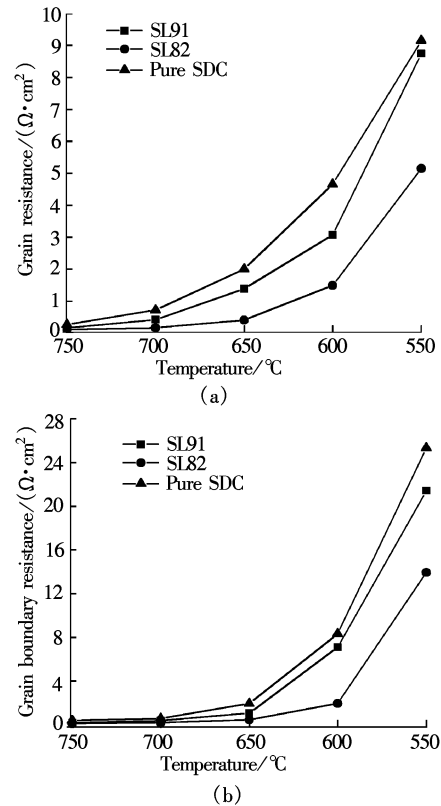
**Fig. 3** Arrhenius plot of conductivity for sintered SDC-LSGM composites with different LSGM weight ratios

## 2.4 EIS analysis

The EIS is applied to fully understand the impact on the grain and grain boundary resistance resulting from the doping of LSGM. Basically, the impedance spectra of the electrolyte exhibits two circular arcs which belong to  $R_g-C_g$  corresponding to the grain resistance at higher frequency and  $R_{gb}-C_{gb}$  corresponding to the grain boundary resistance at lower frequency as indicated in Fig. 4(b). The impedance spectra of pure SDC, SL91, SL82 and SL73 measured at 700 °C in air are shown in Fig. 4 (a). The wire resistance is ignored for reasons of comparison. The resistance of SL82, which is equivalent to the intercept of the arc with the  $Z'$  axis, is  $0.4 \Omega \cdot \text{cm}^2$  and is smaller than  $0.9 \Omega \cdot \text{cm}^2$  and  $1.4 \Omega \cdot \text{cm}^2$  for SL91 and the pure SDC, respectively at 700 °C. However, in Fig. 4(a), the two arcs of the grain and grain boundary resistance merge together and become indistinguishable since the time constants ( $\tau = RC$ ) of the grain and grain boundary are close to each other; hence, the resistance of the electrolyte  $R_{el}$  is not equal to the summation of  $R_g$  and  $R_{gb}$ <sup>[10-11]</sup>. The grain and grain boundary resistances of pure SDC, SL91 and SL82 are calculated from the fitting of impedance arcs, which are plotted in the Fig. 5. It is obvious that the grain and grain boundary resistances both decrease with the increase in LSGM. These decreases can possibly be attributed to the improvement in grain and grain boundary conditions, which is consistent with SEM analysis. Besides, it needs to be noticed that the grain boundary resistance increases much more dramatically than the grain resistance. For example, in the case of SL82, the increments of the grain and grain boundary are  $5.0$  and  $13.8 \Omega \cdot \text{cm}^2$ , respectively as the temperature drops from 750 to 550 °C, indicating that the grain boundary conduction is the major barrier for the ionic conductivity of the electrolyte at low temperature.



**Fig. 4** Impedance spectra measured at 700 °C in air. (a) Pure SDC, SL91, SL82 and SL73; (b) Equivalent circuit of a typical electrolyte material



**Fig. 5** Grain and grain boundary resistance of pure SDC, SL91 and SL82 at different temperatures. (a) Grain resistance; (b) Grain boundary resistance

## 3 Conclusion

Ionic conductivity and sinter behavior can be significantly improved by introducing LSGM into SDC. Among all the specimens measured in the experiment, SL82 is the optimum mix ratio with the ionic conductivity of  $0.113 \text{ S/cm}$  at 800 °C and  $0.059 \text{ S/cm}$  at 700 °C. It is believed that the properties of the grain and grain boundaries in the electro-

lyte, such as grain size, impurity segregation and space charge, play an important role in the ionic conductivity, especially at low temperatures. Besides, certain additives can be used to scavenge the grain boundary to enhance the ionic conductivity in the future work.

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# SDC-LSGM 复合电解质的 GNP 法合成与氧离子电导性能

郭理伟<sup>1</sup> 郑颖平<sup>1</sup> 王绍荣<sup>2</sup> 王振荣<sup>2</sup> 景尧<sup>1</sup> 孙岳明<sup>1</sup>

(<sup>1</sup> 东南大学化学化工学院, 南京 211189)

(<sup>2</sup> 中国科学院上海硅酸盐研究所, 上海 200050)

**摘要:** 通过甘氨酸-硝酸盐(GNP)法合成了 Ce<sub>0.8</sub>Sm<sub>0.2</sub>O<sub>1.9-δ</sub>-La<sub>0.9</sub>Sr<sub>0.1</sub>Ga<sub>0.8</sub>Mg<sub>0.2</sub>O<sub>3-δ</sub> (SDC-LSGM) 复合电解质。采取共燃烧法制备了一系列不同质量百分比的复合粉体以提高这 2 种粉体的混和均匀度。通过 XRD 和 SEM 分析了复合电解质的物相和结构, 并且采用直流四端子法和交流阻抗谱研究分析了复合电解质的氧离子电导率。SDC 与 LSGM 的最佳混合质量比为 8:2, 其电导率在 800 °C 时为 0.113 S/cm, 而电导活化能仅为 0.620 eV。交流阻抗谱显示, 随着温度的降低, 晶界电阻是复合电解质氧离子传输的主要障碍, 在 SDC 中掺入一定量的 LSGM 不仅可以减少电解质的电子传导, 还能改善电解质中晶粒与晶界微观结构, 有助于氧离子传导性能的提高。

**关键词:** Ce<sub>0.8</sub>Sm<sub>0.2</sub>O<sub>1.9-δ</sub>; La<sub>0.9</sub>Sr<sub>0.1</sub>Ga<sub>0.8</sub>Mg<sub>0.2</sub>O<sub>3-δ</sub>; 复合电解质; 氧离子电导率

**中图分类号:** TM911.47