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Composite cathode $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$–$Sm_{0.1}Ce_{0.9}O_{1.95}$–Ag for intermediate-temperature solid oxide fuel cells

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Abstract

$Sm_{0.1}Ce_{0.9}O_{1.95}$ (SDC) and $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ (LSCF) were synthesized by a glycine–nitrate process. A composite LSCF–SDC–Ag cathode was prepared and its structure was analyzed by X-ray diffraction. No chemical reactions among LSCF, SDC, and Ag in the composite cathode were found. The composite cathode was applied onto SDC electrolyte and the microstructure of the electrolyte–electrode interface was examined by SEM. The overpotential of the interface was measured. A single SOFC was prepared by using LSCF–SDC–Ag as cathode, SDC as electrolyte, and Ni–SDC as anode and its performance was measured. Compared to a similar SOFC with LSCF–SDC cathode, it is found that adding Ag in the cathode improved the SOFC performance significantly.

Keywords: Solid oxide fuel cells; Composite cathode; LSCF; SDC

1. Introduction

Strontium doped lanthanum manganate ($La_{1-x}Sr_xMnO_3$, LSM) is commonly used as cathode material in traditional high temperature solid oxide fuel cells [1]. Nowadays, the operating temperature of SOFCs might hopefully be reduced to 600–800 °C due to improvement of the techniques in making a thin electrolyte and the use of some intermediate temperature electrolytes [2,3]. LSM is not suitable as cathode of SOFCs operating in this temperature range under which its conductivity is not high enough and its electrochemical activity is too low. Much work has been done in searching new cathode materials for SOFCs operating at such intermediate temperatures. Lai et al. reported that the conductivity of the electron-ion mixed conductor $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ (LSCF) was larger than 300 S/cm in the temperature range of 600–800 °C [4]. Murray et al. [5] made a composite cathode LSCF–GDC by mixing LSCF with gadolinium-doped ceria (GDC). While the polarization of the cathode–electrolyte was reduced by using the composite cathode, the electronic conductivity of the cathode decreased.

In this paper, we describe the performance improvement of LSCF by mixing it with samarium doped ceria (SDC) and silver Ag. Here the function of SDC is similar to GDC in the work of Murray et al. [5]. Ag was added based on the following considerations: (1) Silver is a fine electronic conductor and it should improve the electronic conduction of the cathode; (2) the melting point of Ag is 961 °C and it can work at temperatures between 600 and 800 °C; (3) as its melting point is low, it might aid the sintering behavior of the cathode at lower temperatures.

2. Experiment

SDC and LSCF were synthesized by a glycine–nitrate process [6]. Weighing $Ce(NO_3)_3{\cdot}6H_2O$ (AP, Shanghai Chemicals) and Sm_2O_3 (99.9%, Shanghai XinXing Chemicals) according to the mole ratio of Ce^{3+} to Sm^{3+} as 9:1. Sm_2O_3 was dissolved in nitric acid to obtain the corresponding nitrate. The Ce and Sm nitrates were dissolved in pure water together

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with a proper amount of glycine. The solution of the mixture was heated until it dried and combusted seriously producing ultra-fine SDC powder. The SDC powder was pre-fired at 600 °C and then pressed into pellets with a diameter of 13 mm and thickness of ∼0.5 mm. The pellets were sintered at 1400 °C for 4 h, then, the electrolyte pellets were ready.

A proper amount of glycine was dissolved in $Ni(NO_3)_2·6H_2O$ (AP, Shanghai Shanpu Chemical Inc.) solution and the solution was heated until it combusted producing fine NiO powder. The NiO powder was mixed with 35 wt.% SDC powder by grinding them with some ethanol in an agate mortar. Then some organic binder was added and mixed with the powder to obtain the anode paste. The NiO–SDC anode paste was applied on one side of the SDC electrolyte pellet and sintered at 1200 °C in air for 2 h. Similarly, LSCF was synthesized. The original materials for making LSCF were: $La(NO_3)_3·6H_2O$ (AP, Beijing Chemical Plant), $Sr(NO_3)_2$ (Beijing Xinhua Chemical Plant), $Co(NO_3)_3·6H_2O$ (AP, Beijing Yili Chemical Inc.) and $Fe(NO_3)_3·6H_2O$ (AP, Beijing Chemical Plant). The LSCF powder was mixed with 30 wt.% SDC by grinding. Some organic binder was added to make the cathode LSCF–SDC paste. Then, some LSCF–SDC paste was mixed with Ag paste (DAD-87, Shanghai Institute of Synthesized Risen) with Ag content of 30 wt.% to make LSCF–SDC–Ag composite cathode paste. LSCF–SDC paste was applied on the other side of some of the SDC electrolyte pellets already with the anode on one side mentioned above, while LSCF–SDC–Ag paste was applied on the other pellets in the same way. The pellets with LSCF–SDC cathode was sintered at 950 °C for 3 h and those with LSCF–SDC–Ag were sintered at 850 °C for 3 h.

At last, the SOFC units (single cell) were assembled with Ag paste as sealing material [7]. The SOFCs were tested using H_2 as fuel and air as oxidant.

The performance of the SOFCs was measured by a Solartron SI1287 Electrochemical Interface. The measuring temperature range was 250–750 °C. The X-ray spectra of the specimen were obtained by a Rigaku D/Max-rA X-ray diffractometer. A SHIMADZU SSX-550 Scanning Electron Microscope was used to examine the microstructures of the electrode, the electrolyte and the electrode–electrolyte interface.

3. Results and discussions

3.1. XRD analysis

Fig. 1 shows the X-ray spectra of LSCF and SDC powders. The spectra of the sintered composite cathodes LSCF–GDC and LSCF–GDC–Ag are also shown in the same figure. It can be seen that the main phase of the LSCF powder made by the glycine–nitrate process is the rhombohedral perovskite [8]. The structure of SDC is cubic. After the LSCF–SDC mixture was sintered at 950 °C, LSCF and SDC retained their own structures, respectively and there was no chemical reaction between the two components. As Ag was added and the composite cathode was sintered at 850 °C for 3 h, there was no chemical reaction between other components, either. This makes it possible for each component in the composite cathode to function with its own advantages, i.e., the mixed conduction of LSCF promoting the cathode reactions, SDC reducing the electrode–electrolyte interface polarization, Ag enhancing the electronic conductivity of the cathode. A high performance cathode should be obtained by combining all these merits.

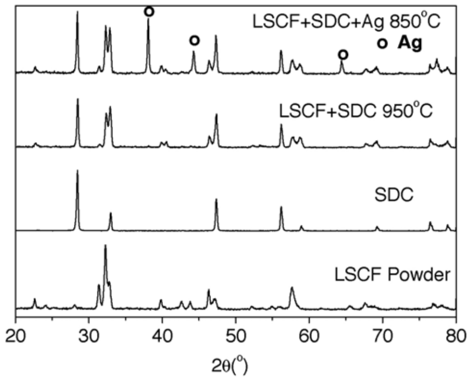

Fig. 1. The X-ray diffraction patterns of the SDC, LSCF powders and the sintered composite cathodes.

3.2. SEM

SEM images were obtained for the electrolyte and the interfaces of electrode–electrolyte for the tested SOFCs and they are shown in Fig. 2. Fig. 2(a) shows the SEM images of the SDC electrolyte sintered at 1400 °C with a magnification of 20,000. It can be seen that the SDC electrolyte is relatively dense with some scattered closed pores. This means that the SDC will not cause any gas leakage as SOFC electrolytes because of its porosity. The interface sections of LSCF–SDC/SDC (electrolyte) and LSCF–SDC–Ag/SDC are shown in Fig. 2(b) and (c), respectively with a magnification of 1000×. There is an obvious line at the LSCF–SDC–electrolyte interface and the adhesion of the cathode on the electrolyte is poor as the cathode and the electrolyte separate at many parts around the interface area. This will raise the polarization loss at the interface. While, the adhesion of the cathode with Ag on the electrolyte is much better with no gap between the cathode and the electrolyte. Note that the sintering temperature of the cathode with Ag was lower than that without Ag. This was done considering the low melting point of Ag as well as the possible improvement of adhesion for the cathode without Ag with higher sintering temperature. In addition, the microstructure of the cathode with Ag is more uniform than that without Ag. This may partly have contributed to the ability of enhancing sintering behavior of Ag, i.e., Ag functioned as a sintering aid in this case.

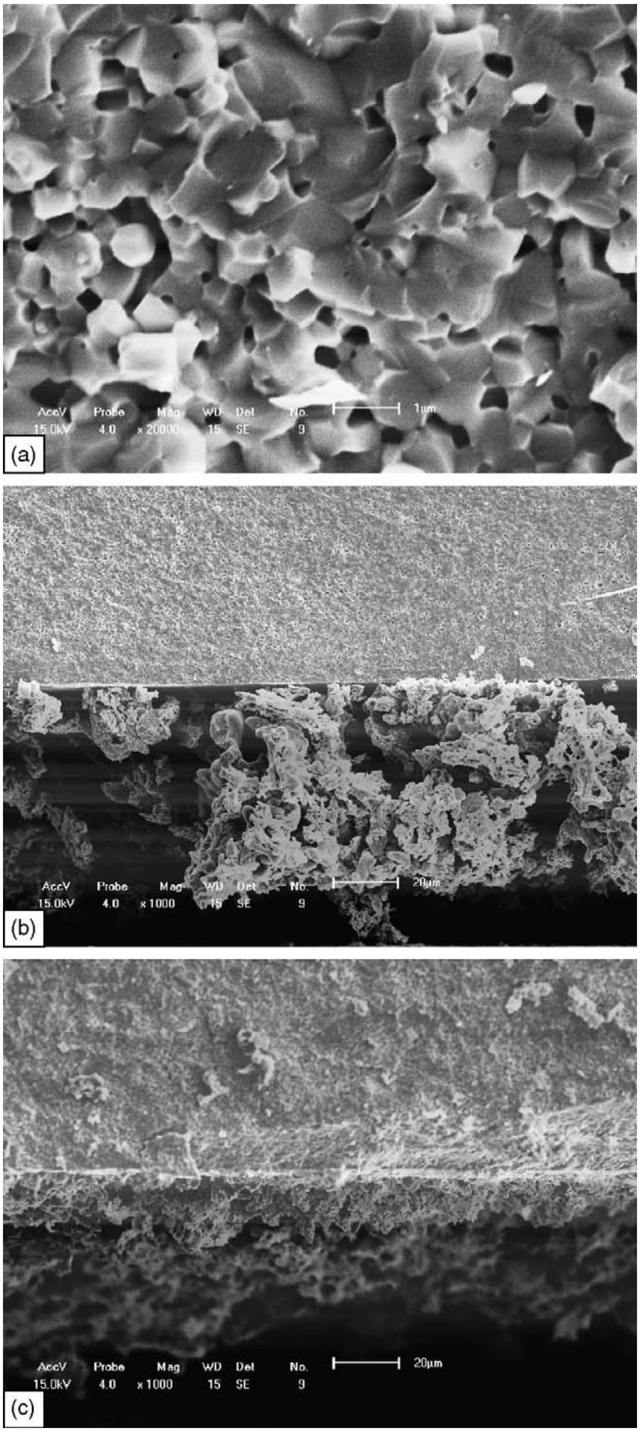

Fig. 2. SEM images of the SDC electrolyte (a), the cathode–electrolyte interfaces of LSCF–SDC/SDC (b) and LSCF–SDC–Ag/SDC (c).

3.3. *Overpotential*

The overpotential is an important factor representing the electrode performance, and the value of the overpotential affects the performance of the corresponding SOFCs directly. Overpotential is also called polarization with respect to the electrode performance of SOFCs. The overpotential or polarization is mainly caused by activation losses because of the slowness of the reactions taking place on the surface of the electrodes, fuel crossover and internal currents through the electrolyte, Ohmic losses and mass transport or concentration losses result from the change in concentration of the reactants at the surface of the electrodes as the fuel is used [9]. The potential of the electrode will deviate from its ideal value when polarization occurs. Fig. 3 shows the relations of the overpotential and current density for the composite cathodes LSCF–SDC and LSCF–SDC–Ag on SDC electrolytes. The measuring temperatures were 650 and 750 °C. It can be seen that the overpotential increases with temperature for the same cathode. At the same temperature, the overpotential of LSCF–SDC–Ag is much lower than the cathode without Ag. This is consistent with the SEM images in Fig. 2 showing the cathode with Ag has better microstructure and adhesion.

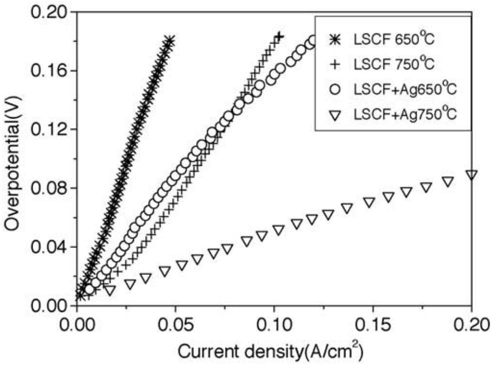

Fig. 3. Relations of overpotential and current density for different cathodes on the SDC electrolytes measured at 650 and 750 °C.

3.4. *Performance of the SOFCs*

Fig. 4 shows the plots of cell voltage and power density versus current density for the SOFC with LSCF–SDC–Ag cathode at different temperatures. It can be seen from the figure that the voltage and the output power density change with temperature. At the same voltage, the current density, thus the power density increases with temperature. The maximum current density and power density at 750 °C are 605.3 and 173.8 mW/cm^2, respectively. While, the open circuit

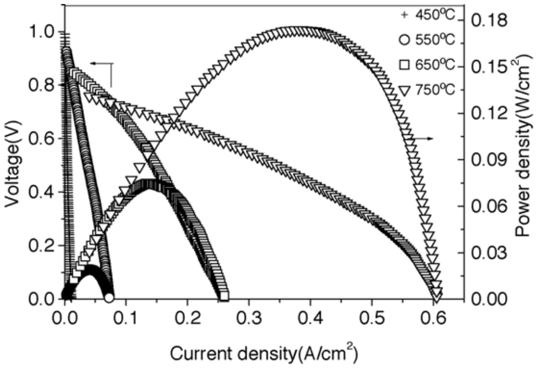

Fig. 4. The single SOFC performance with LSCF + SDC + Ag composite cathode at different temperatures.

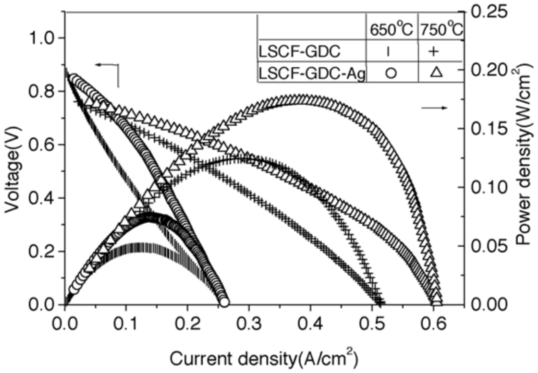

Fig. 5. The performance comparison of the SOFCs with LSCF–SDC and LSCF–SDC–Ag cathodes tested at 650 and 750 °C.

voltage decreases with temperature, from 0.99 V at 450 °C drops to 0.76 V at 750 °C. This is because at higher temperatures, some Ce^{4+} ions in the electrolyte are reduced to Ce^{3+} ions in reducing atmosphere causing some electronic conduction in the electrolyte and results in the OCV drop. A comparison of the performance of SOFCs with LSCF–SDC and LSCF–SDC–Ag cathodes at 650 and 750 °C (Fig. 5) shows that the maximum power density of the SOFC with LSCF–SDC cathode is 124.6 mW/cm^2. This value is higher than that in our previous work [10], but lower than the SOFC with LSCF–SDC–Ag which gives a value of 173.8 mW/cm^2. This fact indicates the important role of Ag in improving the cathode performance of SOFCs. The improvement may be realized through several ways: (1) the electronic conductivity of Ag is very high and it will enhance the cathode conductivity. Xia et al. [11] have reported that they added Ag into their low temperature SOFC Bi_2O_3-based composite cathode. While the Ag in their experiment was added as Ag oxide, we added Ag as metal powder directly and Ag is more conductive than Ag oxide. (2) As the melting point of Ag is relatively low, it may serve as some sintering aid in cathode sintering and an improved microstructure and better adhesion on the electrolyte could be obtained. Thus, the cathode–electrolyte interfacial resistance loss (polarization) could be reduced further.

4. Conclusions

A composite LSCF–SDC–Ag cathode can be used as the cathode of intermediate-temperature SOFCs. Silver in this composite cathode plays an important role in improving the cathode performance compared to the LSCF–SDC cathode. Each component in the cathode retains its own phase and properties after sintering. Ag can enhance the electronic conductivity of cathode as a fine conductor and improve the microstructure of the cathode as a sintering aid.

Acknowledgements

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