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The effect of sintering temperature on the performance of IT-SOFC $SrFe_{0.9}Sb_{0.1}O_{3-\delta}$ perovskite oxide

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Abstract. The perovskite cathode material of $SrFe_{0.9}Sb_{0.1}O_{3-\delta}$ (SFS) was prepared by glycine-nitrate process (GNP). The SFS oxides sintered at 1150， 1200 and 1250 ºC for 10 h were crystallized into a single phase perovskite structure, respectively. The effect of sintering temperature on crystal structure, conductivity and polarization resistance was also discussed in detail. The X-ray diffraction and SEM results show that the density increases with the increase of sintering temperature. The results of electrical properties show that the conductivity of SFS samples is dominated by p-type conductivity, and the conduction behavior is in accordance with the mechanism of small polaron jumping. With the rising sintering temperature, the conductivity of prepared samples increases gradually. In the temperature 650−800 ºC, the conductivity values are 57.8−32.5, 63.6−35.8 and 74.5−40.3 S cm^{-1} for the SFS samples of sintering at 1150, 1200 and 1250 ºC, respectively. The SFS cathode has a good chemical compatibility with the SDC electrolyte at temperatures below 950 °C. The polarization resistances of SFS cathode were 0.064, 0.052 and 0.047 Ω cm^2 at 800 ºC, respectively. The results show that the SFS material of sintering at 1250 °C has promising prospects for the application of IT-SOFCs.

Introduction

Nonstoichiometric ferrites with the perovskite structure, $ABO_{3-\delta}$, has a high mixed oxygen-ionic/electronic conductivity and has a potential attraction as a catalytic membrane reactors for controlled partial oxidation of hydrocarbons, materials for oxygen separation membranes, and electrodes of solid oxide fuel cells [1].

Strontium ferrite, $SrFeO_{3-\delta}$, is known to become a new type of cathode materials for intermediate-temperature SOFCs (IT-SOFCs) with good electrochemical performanc. At the same time, it has the drawback that, with the temperature rise, δ close to 0.5. As a result, the oxygen vacancies in $SrFeO_{2.5}$ undergo ordering at temperatures below 870 °C, leading to the formation of the brownmillerite structure [2]. The perovskite-brownmillerite phase transition is accompanied by a significant volume change. In addition, the phase transition sharply reduces both the oxygen ionic and electronic conductivities owing to the localization of the oxygen vacancies and the change from metallic to semiconducting behavior of conductivity[3]. Thus, an important practical problem is to suppress the orthorhombic brownmillerite structural phase transition so that $SrFeO_{3-\delta}$ will retain high conductivity of the cubic structure at low temperature.

This possibility has been successfully demonstrated in works[4–6] where substitutions were used of Mo, Nb and Ti for Fe. It has been shown that moderate doping has no significant effect on the ionic conductivity of dopant derivatives. In the early work, $SrFeO_{3-\delta}$ based cubic perovskite oxide, $SrFe_{1-x}Mo_xO_{3-\delta}$, and $SrFe_{0.9}Nb_{0.1}O_{3-\delta}$ have confirmed the positive electrode material with good potential for the electrochemical performance of medium temperature solid oxide fuel cells[7,8]. In particular, Ling et al.[9] have studied a cobalt-free $SrFe_{0.9}Sb_{0.1}O_{3-\delta}$ cathode material for proton-conducting SOFCs with stable $BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3-\delta}$ electrolyte, and confirmed the applicability of mixed conductive cathode materials. Therefore, it is necessary to develop $SrFeO_{3-\delta}$-based perovskite cathode materials in order to examine the effects of practical application of SOFCs.

The $SrFe_{0.9}Sb_{0.1}O_{3-\delta}$ material can be considered to be better cathodic candidate. The purpose of

this work was to synthesize $SrFe_{0.9}Sb_{0.1}O_{3-\delta}$ perovskites and to explore the effects of sintering temperature on the crystal structure, electrical conductivity and the polarization resistances were also discussed in detail.

Experimental

Sample of $SrFe_{0.9}Sb_{0.1}O_{3-\delta}$ (SFS) was synthesized via the glycine-nitrate process (GNP), a self-combustion method using glycine as fuel and nitrates of the metal components as oxidant. Sb_2O_3 (99%), $Fe(NO_3)_3 \cdot 9H_2O$ (98.5%), $Sr(NO_3)_2$(99.5%) were used as raw materials. In the course of GNP, glycine was added in the aqueous nitrate solutions containing metal cations in the stoichiometric proportions; the glycine/nitrate molar ratio was 1.2 of the stoichiometric one, assuming the only gaseous reaction products to be N_2, CO_2 and H_2O. The solutions were dried and heated on a hot plate until autoignition occurred, leaving a foam-like reaction product; then the powders were annealed at 900 °C for 6 h to remove the residual organic matter. The SFS powders were pressed into pellets (13 mm in diameter and 1 mm thickness) and cylinders (6 mm in diameter, 5 mm to 6 mm thickness) at 200 MPa and subsequently sintered at 1150, 1200, and 1250 °C for 10 h.

$Ce_{0.8}Sm_{0.2}O_{1.9}$ (SDC) powders were synthesized via the glycine–nitrate process. The SDC powders were pressed into pellets (13 mm in diameter), that were sintered at 1400 °C for 10 h in air to obtain dense SDC pellets. The thickness of the final SDC pellets was fixed at 0.3 mm by grinding the two sides of the samples.

Phase purity and structural analyses of the synthesized samples were carried out by powder using an X-ray diffractometer (Rigaku–D–Max γA, $\lambda = 0.15418$ nm) by step scanning in the range of $20° \leq 2\theta \leq 80°$ at an increment of 0.02°. The chemical compatibility of the SFS sample with the SDC electrolyte was investigated by calcining the mixture of the two material powders in air at 950 °C for 10 h. Microstructure and morphology of the samples were examined with a scanning electron microscope (SEM, JEOL JSM- 6480LV). The bulk densities of the sintered samples were measured by the Archimedes method, using deionized water as a medium. The conductivities of the samples were measured by the four-probe DC technique at 300–850 °C in air. Symmetrical SFS/SDC/SFS cells were prepared by screen printing, after drying, and calcining at 950 °C for 2 h in air. The symmetrical cells were analyzed via impedance spectroscopy using an electrochemical analyzer (CHI 604D, Chenhua, China). Measurements were performed frequency range from 0.1 Hz to 100 kHz and at an AC amplitude of 10 mV under open-circuit conditions. The impedance data were fitted using Z-View 3.1 software.

Results and discussion

The XRD patterns of at different sintering temperature are shown in Fig. 1. The XRD patterns reveal that the samples are single-phase. All the diffraction peaks can be indexed in the cubic Pm3m space group. No any impurity peaks are observed in the XRD patterns. In addition, the XRD diffraction peaks shift to a higher angle with the increase of sintering temperature, and gradually increase the intensity of the diffraction peak, peak shape become more acute, further suggesting that the grain size increases.

The SEM micrographs of SFS samples processed at different sintering temperature for 10 h in air are shown in Fig. 2. These micrographs clearly show that the sample sintered at 1150 °C for 10 h has a lot of stomata. The stomatas reduce and grain sizes gradually increase with the rise of sintering temperature, suggesting that SFS sample of sintering at 1250 °C for 10 h is relatively dense. The sintering densities of SFS samples reach 86.4， 88.5 and 92.6 % of the theoretical density.

Fig. 3 shows the temperature dependence of electrical conductivity of the SFS samples at different sintering temperature for 10 h in air. It is clear form Fig. 3 that the total electrical conductivities of SFS samples increase with the rise of sintering temperature. The sample at low sintering temperature has a large number of stomatas, and the relative density is low, lead to increase of oxygen vacancy

migration resistance, therefore electrical conductivity is low. The increase of sintering temperature is helpful for grain growth and the improvement of the contact area between grain, at the same time, porosity reduce or disappear and the relative density increases. The oxygen ion migration channel is more unobstructed, and the migration path is shortened, which leads to the increase of conductivity. In the temperature 650−800 °C, the electrical conductivity values are 57.8−32.5, 63.6−35.8 and 74.5−40.3 S cm^{-1} for the SFS samples of sintering at 1150, 1200 and 1250 °C, respectively.

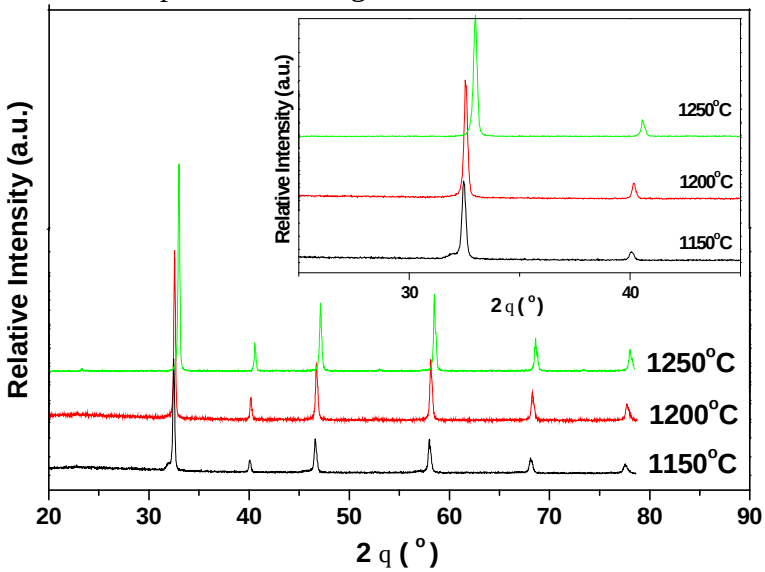

Fig. 1. XRD patterns of the SFS samples.

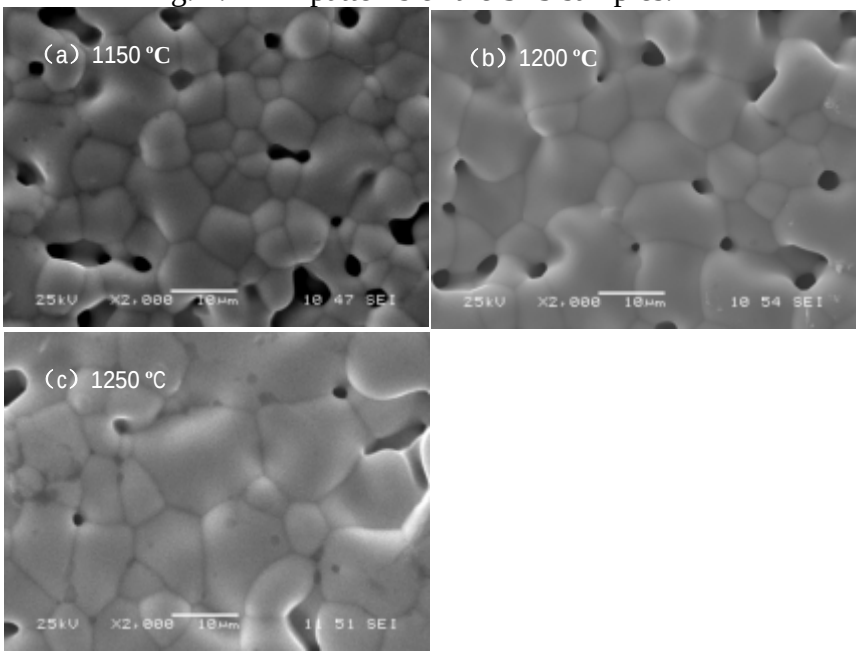

Fig. 2. SEM micrographs of the SFS samples at different sintering temperature.

The conductivity of all samples increases with increasing temperature, reaching a maximum at about 450 °C , and then decreases with further increasing temperature, exhibiting semiconductor-type behavior in the low-temperature range until an apparent transition to metallic-like conduction. The inflections on the conductivity curves at 450 °C are attributed to the oxygen loss and the thermal reduction of Fe^{4+} cations on heating. The maximum conductivity values are 100, 109 and 118 S cm^{-1} at sintering temperature for 1150 °C, 1200 °C and 1250 °C, respectively.

Fig. 4 shows XRD patterns of SFS-SDC mixed calcined at 950 °C for 10 h, SEM micrograph of the cross section of the SFS/SDC/SFS symmetrical cell, and EDS spectrum near the interface between electrolyte and cathode. XRD results indicate that no reaction products or peak shifts can be detected for SFS-SDC mixture after calcining at 950 °C for 10 h (Fig. 4(b)). SEM/EDS analysis was performed at the interface between SFS cathode and SDC electrolyte (Fig. 4(a),(c)). The results show good

contact between SFS cathode and SDC electrolyte. Meawhile, no diffusion was observed, and no other elements were observed in the respective figure. The fact that the SFS cathode has a good chemical compatibility with SDC electrolyte at 950 °C for 10 h, thus ensuring that the SFS materials did not react with the SDC electrolyte under the conditions employed in the fabrication and test for the cathode of SOFCs.

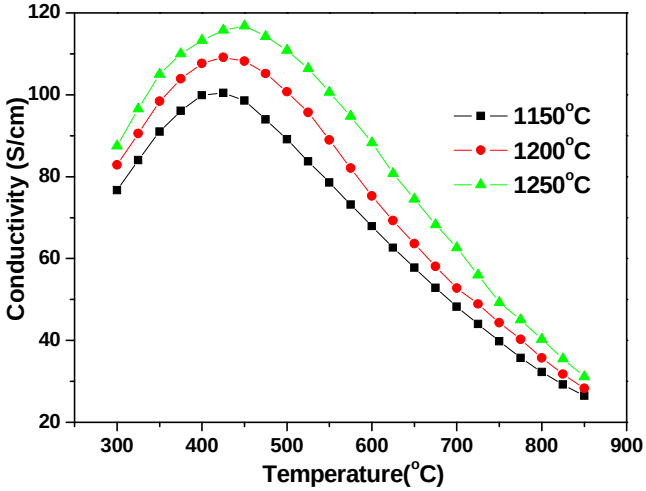

Fig. 3. The electrical conductivity of the SFS samples at different sintering temperature.

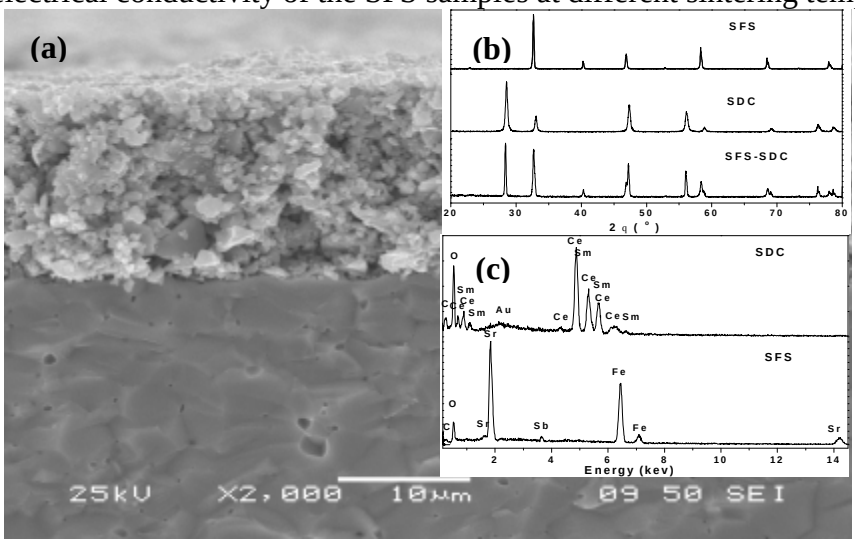

Fig. 4. (a) SEM micrograph of the cross section of the SFS/SDC/SFS symmetrical cell after calcining at 950 ºC for 2 h; (b)XRD patterns of SFS–SDC mixture calcined at 950 ºC for 10 h; (c) EDS spectrum near the interface between electrolyte and cathode.

Fig. 5 shows the typical impedance spectra of the SFS cathode on the SDC electrolyte at different sintering temperature. The impedance spectra for oxygen reduction on the SFS cathode includes a high-frequency arc and a low-frequency arc, which indicate the occurrence of at least two electrode processes. The high-frequency arc reflects the charge transport process between cathode and electrolyte interface, and the low-frequency arc reflects the charge transfer in the cathode reaction process, oxygen adsorption and release, the gas phase diffusion process of the electrode surface and body[10,11]. The intercept at high-frequency represents the ohmic resistance of the cell, whereas the intercept at low-frequency corresponds to the total resistance of the cell. The difference between the two intercepts on the real axis is taken as the area-specific resistance (ASR) of the two interfaces[12]. The overall ASR divided by two will be the polarization resistance of one cathode on electrolyte. As shown in Fig. 5, the ASRs decrease significantly with the increase in the operation temperatures. Because the conductivity of the cathode material increases with the rise of the temperature, and the ability of adsorption and dissociation of oxygen is enhanced. For example, the ASR values of the cathode at 1250 °C sintering on SDC electrolyte are 0.46, 0.19, 0.089 and 0.047 Ω cm^2 at 650, 700,

750, and 800 °C, respectively. The results show that the SFS cathode has higher electrocatalytic activity for oxygen reduction reaction.

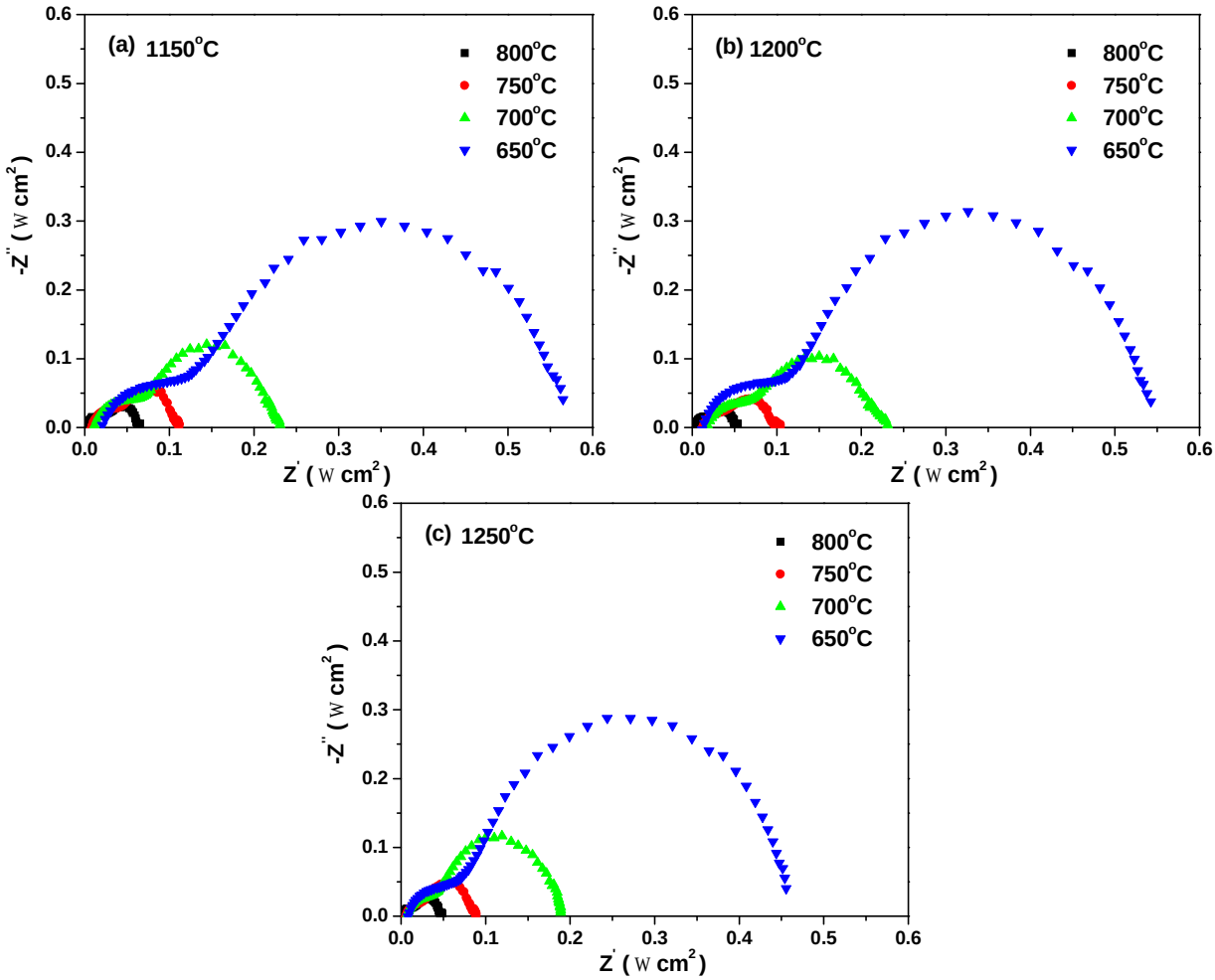

Fig. 5. Typical impedance spectra of the SFS: (a)1150 °C; (b)1200 °C; (c)1250 °C.

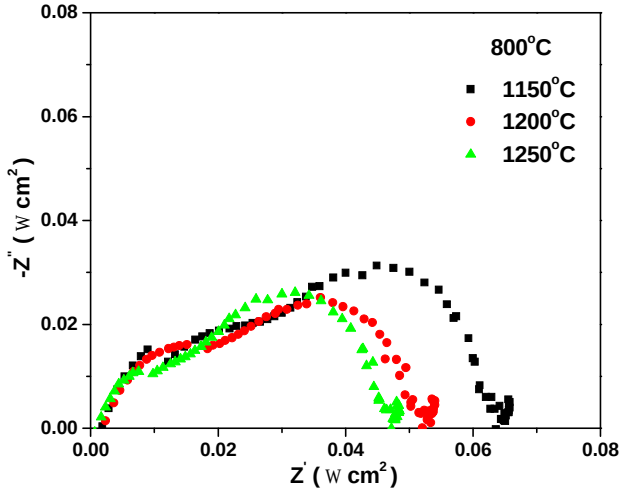

Fig. 6. Typical impedance spectra of the SFS at different sintering temperature measured at 800 °C.

Fig. 6 shows the typical impedance spectra of the SFS cathodes at different sintering temperature on the SDC electrolytes measured at 800 °C in air. In order to compare the polarization resistance of the electrode sintered at different temperatures, the spectrum of the electrolyte is deducted from the high frequency. The polarization resistance of the electrode can be obtained from the span of the spectrum. At 800 ºC, the ASR values of the SFS cathodes at 1150, 1200 and 1250 °C sintering are 0.064, 0.052, and 0.047 Ω cm^2, respectively. The cathode at 1250 °C sintering exhibits the best electrochemical performance. The ascension of the cathodic performances can be attributed to the grain grow and the conductivity increase with the increase of sintering temperature. Therefore, the

sample at 1250 °C sintering has higher electronic and ionic conductivity, it can provide a large number of oxygen atoms adsorption and desorption of the effective reaction area. At the same time, it provides the way of the diffusion of oxygen ions to the three phase boundaries(TPB) and SFS/SDC interface, thereby reduces the interfacial polarization resistance].

Conclusions

Perovskite cathode materials of $SrFe_{0.9}Sb_{0.1}O_{3-\delta}$ (SFS) were prepared via the glycine-nitrate process (GNP). The SFS oxide of sintering at 1150, 1200 and 1250 °C for 10 h crystallized in a single phase perovskite structure, respectively. The effect of sintering conditions on the microstructure and conductivity of SFS showed the same rule. The X-ray diffraction and SEM results show that the density increases with an increase sintering temperature. The measurement results of electrical properties reveal that the conductivities of SFS samples are dominated by p-type conduction, and the conduction behavior conforms to the small polaron hopping transport mechanism. With the rising sintering temperature, the conductivities of prepared samples gradually increase. In the temperature 650−800 °C, the electrical conductivity values are 57.8−32.5, 63.6−35.8 and 74.5−40.3 S cm^{-1} for the SFS samples of sintering at 1150, 1200 and 1250 ºC, respectively. The SFS cathodes have a good chemical compatibility with the SDC electrolyte at temperatures below 950 °C. The polarization resistances of SFS cathodes were 0.064, 0.052 and 0.047 Ω cm^2 at 800 °C, respectively. The results indicated that the SFS material of sintering at 1250 °C is promising for application IT-SOFCs.

Acknowledgments

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