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Effect of temperature on the porosity, microstructure, and properties of porous $La_{0.8}Sr_{0.2}MnO_3$ cathode materials

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Abstract

Porous $La_{0.8}Sr_{0.2}MnO_3$ cathode materials were prepared by the gelcasting technology. Carbon was employed to produce pores. It is shown that the open porosity decreases with increasing temperature. The proper sintering temperature is 1100 °C and the median pore size of the sample obtained at this temperature is about 460 nm. The microstructure indicates that the grain grows as the sintering temperature increases, which leads to the decrease of the number of open pores. Generally, the pores are located at multi-grain boundaries. Some closed pores appear in the sample prepared at 1100 °C and more. Both the conductivity and the interface bonding between $La_{0.8}Sr_{0.2}MnO_3$ and YSZ get better as the temperature increases. When the sintering temperature is more than 1250 °C, La and Mn ions begin to diffuse into YSZ, and therefore interface reactions happen. According to $\ln(\sigma T) \sim 1/T$ curves, E_a was calculated to be 10.18 kJ/mol.

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1. Introduction

Solid Oxide Fuel Cells (SOFCs) are promising efficient, energy-saving, and environment-friendly energy conversion devices that generate electricity and heat. The correlative materials become a focus of materials research [1]. As one of the key materials of SOFCs, the cathode materials are widely studied. Strontium-doped $LaMnO_3$, especially 20 mol% Sr-doped $LaMnO_3$ ($La_{0.8}Sr_{0.2}MnO_3$), is currently the preferred cathode material in SOFCs because of its high electronic conductivity [2], good compatibility with the solid electrolyte, 8 mol% yttria-stabilized zirconia (YSZ), in the oxidizing atmosphere [3] and similar coefficient of thermal expansion to that of YSZ for practical use [4]. The cathode material used for the cathode-supported SOFCs is porous and its open porosity is between 20 and 40%. Generally, the porous materials are prepared by dry-pressing process and adding the pore-producing materials (such as starch [5]). Even though dry-pressing process is simple, it is very difficult to obtain the material of uniform microstructure. Much attention has been paid to the gelcasting technology developed recently [6] due to its simplicity, low cost, and the resulting high strength and uniform microstructure of its products. The technology was originally used to prepare high-quality complex-shaped ceramics [7]. Subsequently, the technology was adopted to prepare the porous materials [8]. However, up to now, there are few reports on the preparation of the doped $LaMnO_3$ by the gelcasting technology. In the present paper, porous $La_{0.8}Sr_{0.2}MnO_3$ cathode material was prepared by the gelcasting technology and carbon was employed to produce pores. The effect of temperature on porosity, microstructure, and some other properties of porous $La_{0.8}Sr_{0.2}MnO_3$ was studied.

2. Experimental procedure

$La_{0.8}Sr_{0.2}MnO_3$ powder (the density is 6.73 g/cm^3 and the average grain size is 2.2 μm), dispersant (D3019, Romanhass Co. Limited, USA), carbon and the mixed solution of the monomer (acrylamide, AM), and crosslinker (N,N'-methylene bisacrylamide, MBAM) in the required amount were first ball-milling mixed in distilled water for 24 h with highly pure ZrO_2 balls. The solid loading 45 vol% suspension was obtained by adjusting pH to 8–9. And then, the suspension

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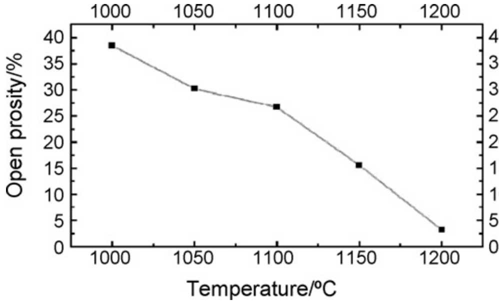

Fig. 1. Variation of the open porosity as a function of the sintering temperature.

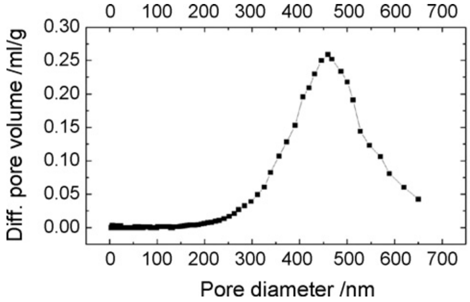

Fig. 2. Pore size distribution of the samples sintered at 1100 °C.

was deaired in vacuum, and an initiator (ammonium persulfate, $(NH_4)_2S_2O_4$) was added to the above suspension and mixed homogeneously by fiercely stirring. Finally, the above suspension was poured into a mold, gelled at 70–80 °C, removed from the mold, and naturally dried in air. The obtained green bodies were cut and sintered at 1000–1250 °C for 4 h in air. In order to study the interface properties of $La_{0.8}Sr_{0.2}MnO_3$/YSZ, the samples were prepared as the following process: $La_{0.8}Sr_{0.2}MnO_3$ materials sintered at 1100 °C were dipped in 50 vol% YSZ suspension, lifted at the same speed. As a result, the YSZ films were coated on the surface of $La_{0.8}Sr_{0.2}MnO_3$ materials. After drying, the obtained samples were treated at different temperatures for 4 h.

The open porosity was measured by the Archimedes method. Three-point flexural strength measurements were carried out with a span of 30 mm and a crosshead speed of 0.5 mm/min at room temperature by an Instron-1195 Universal Test machine. A minimum of six specimens was tested to obtain an average datum. The pore distribution was measured on Autopore IV Pressure Mercury Instrument (made in USA). The conductivity was measured by four-probe method. Scanning electron microscopy (SEM) coupled with energy-dispersive spectroscope (EDS) (JEOL-2000 Japan) was used to investigate the fracture images, grain size, pore distribution, and interface property.

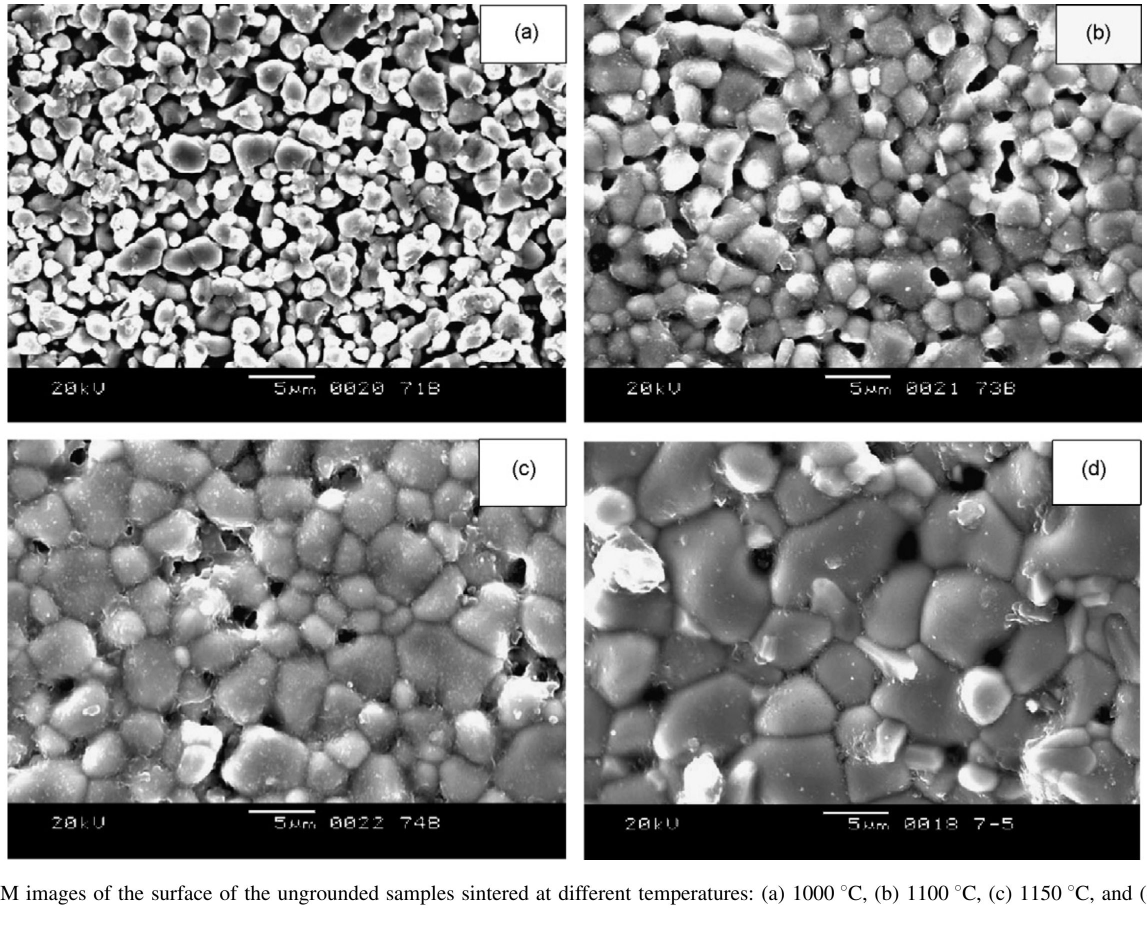

Fig. 3. SEM images of the surface of the ungrounded samples sintered at different temperatures: (a) 1000 °C, (b) 1100 °C, (c) 1150 °C, and (d) 1200°C.

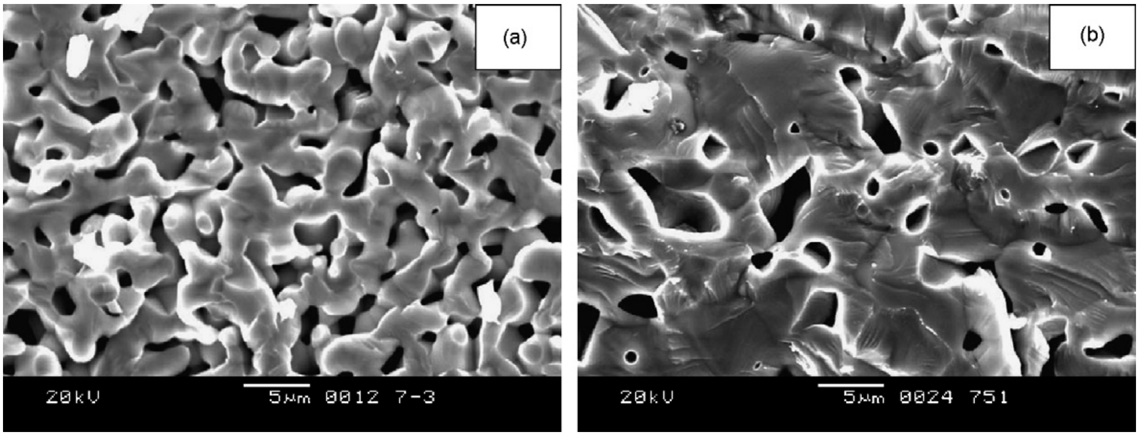

Fig. 4. SEM micrographs of fracture surface of the samples sintered at: (a) 1100 °C and (b) 1200 °C.

3. Results and discussions

3.1. Porosity of materials

The variation of open porosity of the samples as the function of the sintering temperature is shown in Fig. 1. It can be clearly seen from Fig. 1 that the open porosity of the samples decreases with increasing the sintering temperature. Especially, in the range of 1100–1200 °C, the open porosity decreases rapidly, which reduces from 26.7% to 3.2%. The open porosity of the samples obtained at 1050–1100 °C meets the requirements for the needed porosity, but the fracture strength of ca. 70 MPa of the sample sintering at 1100 °C is much bigger than that of ca. 48 MPa of the samples at 1050 °C. Considering the comprehensive properties, it is suggested that the proper sintering temperature is 1100 °C. As shown in Fig. 2, the median pore size is about 460 nm.

3.2. Microstructure of materials

Fig. 3 gives the SEM images of the surface of the ungrounded samples sintered at different temperatures. Evidently, with increasing the sintering temperature, the grains agglomerate and grow, the number of the open pores reduces, and the open pores are located at multi-grain boundaries. As observed from the SEM images of the fracture surfaces (Fig. 4), some closed pores appear on the bulk. The higher temperature is, the larger the number of the closed pores is. Especially the sample sintered at 1200 °C, the pores in the bulk of the sample are much more than those of the ungrounded surface. Thus, the porous materials are composed of the open and closed pores.

3.3. Conductivity of materials

$LaMnO_3$ has intrinsic p-type conductivity due to the formation of cation vacancies and the electrical conductivity of the material can be enhanced by substituting a lower-valence ion, such as Sr^{2+}, Ca^{2+}, etc., on La^{3+} sites. Thus, Sr-doped $LaMnO_3$ enhances the electronic conductivity of the materials by increasing the Mn^{4+} content by the substitution of La^{3+} by Sr^{2+}[9]:

$$\tfrac{1}{2}O_2 + 2SrO \xrightarrow{LaMnO_3} 2Sr'_{La} + 2h^{\bullet} + 3O^{\times} \tag{1}$$

$$2Mn_{Mn}{}^{\bullet} + O_O \rightarrow 2Mn_{Mn}^{\times} + V_O{}^{\bullet\bullet} + \tfrac{1}{2}O_2 \tag{2}$$

The produced $h^{\bullet}$ is bonded around Mn^{3+} to form Mn^{4+}, and the electronic conductivity even polaron, namely $Mn^{3+} \rightarrow Mn^{4+}$ is built. In the electric field, $h^{\bullet}$ that is weakly bonded around Mn^{3+} produces electronic transition conduction, and at the same time, the produced oxygen vacancies can produce O^{2-} conduction.

Fig. 5 shows the conductivities of the sample obtained at 1100 °C as a function of temperature. It can be seen that conductivities increase with the increase of temperature. At temperatures below 800 °C, plots of $\ln(\sigma T)$ versus $1/T$ are linear, as predicated by the following equation [10]:

$$\ln(\sigma T) = -\frac{E_a}{RT} + \ln A \tag{3}$$

where σ, A, T, R, and E_a are conductivity of material, constant associated with crystalline structure and chemical composition, absolute temperature, gas constant, and activation energy of conductance, respectively. According to $\ln(\sigma T) \sim 1/T$ curves, E_a was calculated to be 10.18 kJ/mol. At temperatures

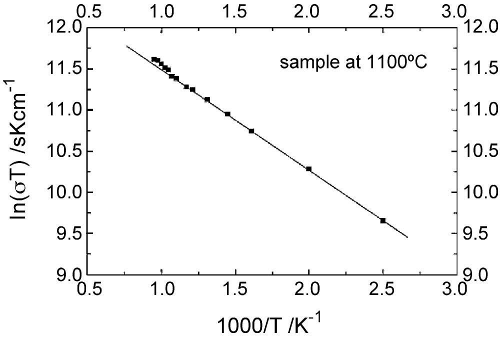

Fig. 5. Conductivities vs. temperatures curve.

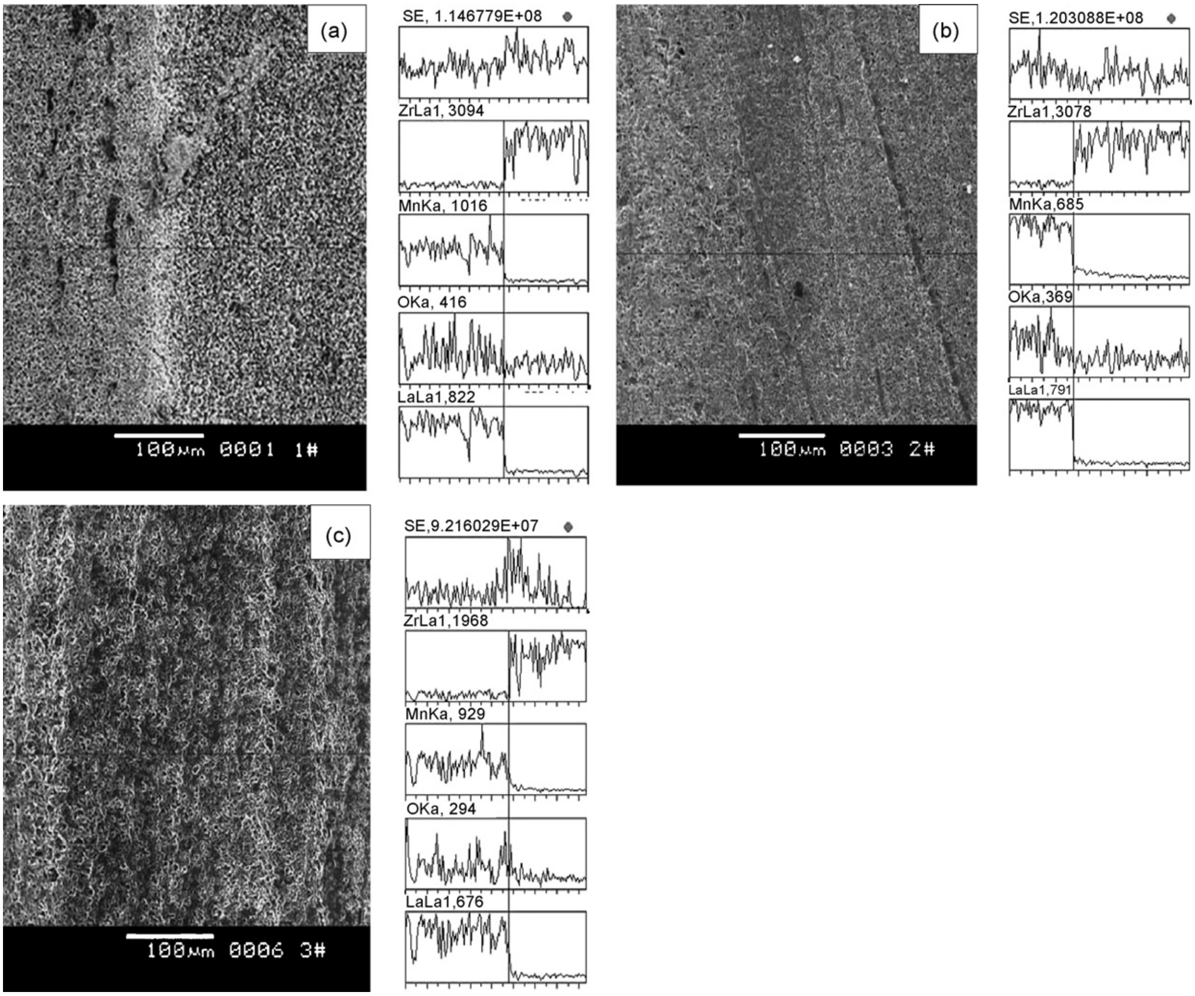

Fig. 6. Micrographs and corresponding line EDS spectra of cross-section of $La_{0.8}Sr_{0.2}MnO_3$/YSZ materials obtained at different temperatures: (a) 1100 °C, (b) 1200 °C, and (c) 1250 °C.

above 800 °C, the differential increment of conductivity (σ) reduces, the conductivities shows negative temperature dependence, which indicates a semiconducting-to-metallic transition.

3.4. Interface property of $La_{0.8}Sr_{0.2}MnO_3$/YSZ

In the process of SOFCs operation at high temperature, the chemical stability of $La_{0.8}Sr_{0.2}MnO_3$ cathode and the YSZ electrolyte (YSZ is commonly used for the electrolyte of SOFCs) is a key problem that is related to whether SOFCs can work efficiently and stably. Thus, it is necessary to study the interface property of $La_{0.8}Sr_{0.2}MnO_3$/YSZ.

Fig. 6 is the micrographs and the corresponding line EDS spectra of the cross-section of $La_{0.8}Sr_{0.2}MnO_3$/YSZ materials obtained at different temperatures. It can be seen that the bonding of the $La_{0.8}Sr_{0.2}MnO_3$/YSZ interface gets closer with increasing temperature. It can be observed from the corresponding EDS spectra that when the temperature is below 1200 °C (Fig. 6a and b), ionic inter-diffusion is not observed. When the temperature is 1250 °C (Fig. 6c), La and Mn ions begin to diffuse to YSZ and Zr ions do not diffuse to $La_{0.8}Sr_{0.2}MnO_3$, which indicates interface reaction has happened.

4. Conclusions

The porous $La_{0.8}Sr_{0.2}MnO_3$ cathode materials were prepared by the gelcasting technology. Carbon was employed to produce pores. The open porosities decrease and grains grow as sintering temperature increases. The proper sintering temperature of the porous materials is 1100 °C. At this temperature, the median size of the obtained sample is about 460 nm. The pores are located at multi-grain boundary. There are some closed pores in the sample prepared at 1100 °C and more. The conductivities increase and the interface bonding of $La_{0.8}Sr_{0.2}MnO_3$/YSZ get better with increasing temperature. The interface reaction of $La_{0.8}Sr_{0.2}MnO_3$/YSZ has taken place at 1250 °C.

Acknowledgements

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