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SYNTHESIS AND CHARACTERIZATION HOLLOW SPHERICAL $La_{0,7}Sr_{0,2}Ca_{0,1}Co_{0,9}Fe_{0,1}O_{3-\delta}$ (LSCCT) FOR CATHODE OF SOLID OXIDE FUEL CELL (SOFC)

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Preliminary Note – Prethodno priopćenje

Hollow spheres structures of $La_{0,7}Sr_{0,2}Ca_{0,1}Co_{0,9}Fe_{0,1}O_{3-\delta}$ (LSCCT) have been synthesized via hydrothermal method using carbon spheres as template. The structure and electrical conductivity of obtained samples are characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), transmission electron microscope (TEM) and direct current (DC) four-probe method respectively. The results show that hollow spheres structures of LSCCT with the mean particle size of 0,9 - 1,2 μm is single perovskite. The electrical conductivity of the samples is higher than 100 S/cm from 600 to 800 ℃ and can meet the demand of the electrical properties for the cathode materials.

Key words: synthesis, $La_{0,7}Sr_{0,2}Ca_{0,1}Co_{0,9}Fe_{0,1}O_{3-\delta}$, hollow spheres, structures, electrical conductivity

INTRODUCTION

Intermediate temperature solid oxide fuel cell (IT-SOFC) is attracting a wide range of interest because of their potential application to automobile power and/or compact size co-generation units for home or office use [1]. The performance of ITSOFC is strongly dependent on the electrode performance as the temperature (600 – 800 °C) [2]. The develop- ment of new cathode materials for these temperatures is thus an active field of research. Materials with the perovskite structure (ABO_3) are the most widely studied as ITSOFC cathodes [3].

In recent years, special attention has been mainly paid to the following two aspects. On one hand, investigations of shape-controllable synthesis for the perovskite structure are of great interest. So far, ABO_3 has been prepared in various morphologies, such as nanowires, nanocubes, hollow fibres and spheres [4-6].On the other hand, the preparation process and functional of the cathode also influenced its industrialization [7,8]. To lower the thermal expansion, $La_{0,7}Sr_{0,2}Ca_{0,1}Co_{0,9}Fe_{0,1}O_{3-\delta}$ (LSCCT) as the new cathode for ITSOFC exhibits good electrical performance and chemical compatibility [1,8]. However, to the best of our knowledge, LSCCT hollow micro- spheres have rarely been reported in the literature. This structure are likely to have a great specific area and have recently been suggested as cathodes.

In the present contribution, we report the facile synthesis of LSCCT hollow microspheres through hydrothermal and followed heat treatment.

EXPERIMENTAL

The chemicals reagents including glucose monohydrate, Lanthanum nitrate hexahydrate, Strontium nitrate, Calcium nitrate, Cobalt carbonate hydroxide and Iron nitrate nonahydrate provided by Sinopharm Chemical Reagent Shenyang Co., Ltd, China (Chemical grade).

A mixture of glucose monohydrate (40,0 mmol), $La(NO_3)_3 \cdot 6H_2O$ (3,5 mmol), $Sr(NO_3)_2$ (1,0 mmol), $Ca(NO_3)_2$ (0,5 mmol), $Co(NO_3)_2 \cdot 6H_2O$ (4,5 mmol), $Fe(NO_3)_3 \cdot 9H_2O$ (0,5 mmol), and 60 mL distilled water were heated at 180 ℃ for 15 h in a 100 mL autoclave. Then it was cooled to room temperature. The resulting precursors were isolated by centrifugation at 5 000 rpm. Next, the mixtures were dried at 80 °C for more than 4 h. LSCCT were obtained by heating the precursor in air at 600 ℃ for 3 h and 1 000 °C for 2 h.

Phase characterization of the samples was determined by XRD (Rigaku D/max- RB). Morphology of the samples was analyzed by using SEM (Hitachi S-3400N) and TEM (FEI F20).

The prepared powders of LSCCT were pressed at 200 MPa of 10 mm in diameter, and subsequently sintered at 1 200 °C for 3 h. The sintered pellets were cooled and attached silver electrode on both side by screen printing technique. The electrical conductivity was measured in air of temperature from 100 to 800 °C using the conventional DC four-probe method.

RESULTS AND DISCUSSION

The XRD patterns of the LSCCT samples have presented in Figure 1. Notably, no charac- teristic peaks of perovskite structure can be founded in Figure 1(a), it implies that the precursor is composed of amorphous

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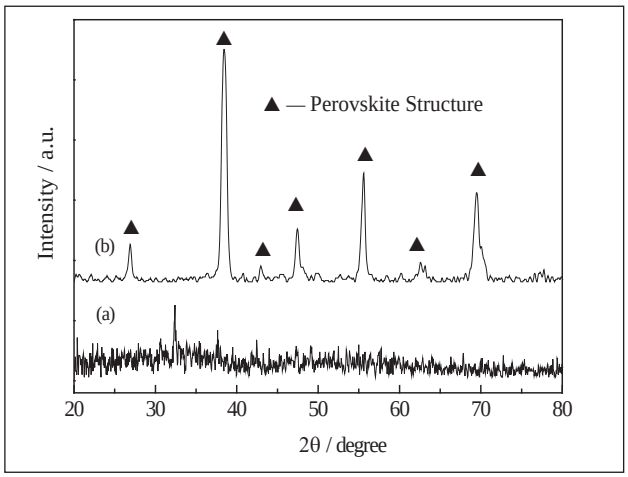

Figure 1 XRD pattern of LSCCT (a): precursors, (b): the precursor heated at 600 °C and 1 000 °C for 2 h

molecular. In Figure 1(b), all diffraction peaks can be indexed well to pure phase of perovskite structure according to the reported literature [1]. No peaks of any other phase was detected implies that the sample has single perovskite phase.

The SEM patterns of the LSCCT samples have presented in Figure 2. The SEM of precursors indicated that the samples consist of uniform separated spheres with diameter of about ca. 1,2 - 1,5 μm in Figure 2(a).

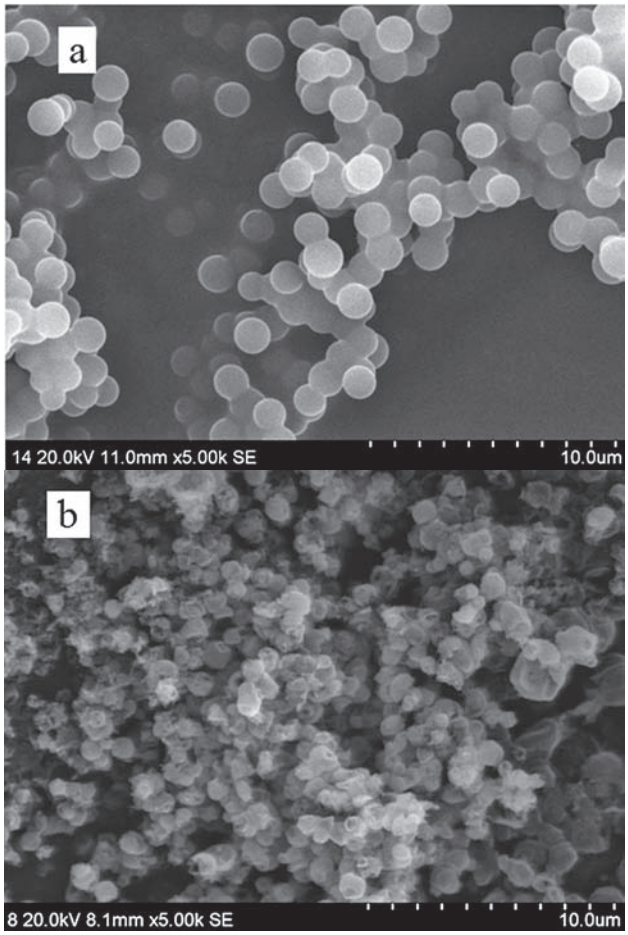

Figure 2 SEM pattern of LSCCT (a): precursors, (b): the precursor heated at 600 °C and 1 000 °C for 2 h.

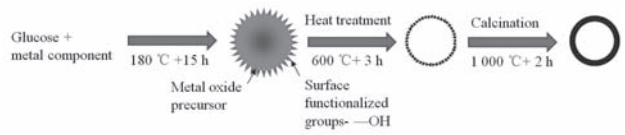

Figure 3 Schematic illustration for the formation of LSCCT hollow spheres

The SEM of samples by heat treatment indicated that the samples also consist of uniform separated spheres with diameter of about ca. 0,9 - 1,2 μm in Figure 2(b). The diameter of as-prepared samples is smaller than that of precursor for the shrink and densification during heating. The SEM micrographs reveal that the presence of metal ions have little influence on the morphology of the products (Figures 2(a, b)).

A possible forming process of LSCCT hollow spheres is shown schematically in Figure 3. The carbon spheres template could be synthesized from carbonification of glucose via hydrothermal treatment at 180 ℃. It has been reported that glucose went to aromatize and carbonize when the temperature is higher than that needed for normal glycosidation [9]. Then the metal ingredient can be absorbed into the surface layer of the carbon spheres due to chelation between the hydroxyl, carboxyl and metal component. Carbon was removed and metal oxide gradually formed after heat treatment at 600 ℃ for 3 h. A further increase of annealing temperature to 1 000 ℃ completely trans- formed the amorphous microspheres to the spinel phase with hollow spherical structures.

Figure 4 shows the electrical conduc- tivity of LSCCF sintered at 1 200 ℃ for 3 h. Figure 5 shows the arrhenius plots of its electrical conductivity. Figures 4 and 5 indicate that the electrical conduc- tivity of the sample increases with temperature increasing, then decreases gradually.

At temperature below 600 ℃, with substituting the lower-valence ion of Sr^{2+} and Ca^{2+} on A site for La^{3+}, the charge compensate is achieved by part of Co^{3+} converting to Co^{4+} mainly, thus, the electrical conductivity of the materials can be enhanced and the conducting mechanism is p-type small polar on hopping process due to the formation of cation vacancies and plots of ln σT vs 1/T being almost a straight. The transition of

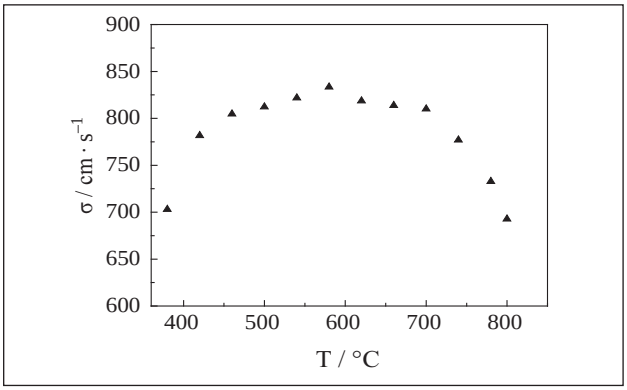

Figure 4 Electrical conductivity (σ) of LSCCF at 380-800 °C

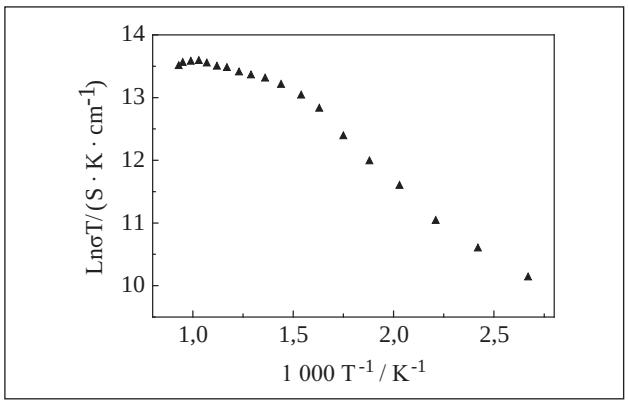

Figure 5 Arrhenius relation plots of electrical conductivity of LSCCF

$Co^{3+} \rightarrow Co^{4+}$ can happen more easily because 3d electron energy of Co^{3+} rise with the temperature increasing, which can excite more and more carrier. And the mobility of carrier also increases with the temperature, so the electrical conductivity increase gradually.

At temperature above 600 °C, the carrier achieves saturation with the temperature increasing, following with the increasing of energy and amount of phonon brought by Co^{3+} transition, and scattering of the phonon causes decrease of the electrical conductivity. At the same time, the disengaging amount of crystal lattice oxygen increases obviously at high temperature, thus oxygen vacancy content increases. When one oxygen vacancy occurs, the two Co^{3+} transitions are countervailed, which causes the charge compensate changes from electron conducting to oxygen ion compensate, the carrier concentration decreases. Moreover, the high oxygen vacancy content can make oxygen vacancy become the scattering center or capturing trap of electron, which leads mobility of the carrier decrease synchronously, and subsequently causes the electrical conductivity down. Therefore, the electrical conductivity decreases with the temperature increasing in high temperature phase, the electric conduction mechanism changes from semiconductor type to metal type, which leads the curve according to ln σT and 1/T departure the Arrhenius formula.

CONCLUSION

LSCCT hollow spheres have been syn- thesized via carbon spheres with metal component embedded precursors hydro- thermal method.

The synthesized LSCCT hollow spheres with the diameter of about ca. 0,9 - 1,2 μm has single perovskite phase. At low tem- perature below 600℃, the conducting mechanism of LSCCF is p-type small polaron hopping process. At high temperature above 600 °C, the conducting mechanism of LSCCF is metal type. The electrical conductivity of the samples is higher than 100 S/cm from 600 to 800 °C , which can not only meet the electrical properties demand for cathode materials in ITSOFC, but also reduce the cost of the cathode materials.

Acknowledgments

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Note: The responsible translator for English language is K. Bei, Hangzhou Qihang translation Co.LTD, China