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Synthesis of Homogeneous $La_{0.8}Sr_{0.2}CrO_3$ Powders Using an Ultrasonic Spray Pyrolysis Method

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ABSTRACT

A process to synthesize $La_{0.8}Sr_{0.2}CrO_3$ (LSC), which is a promising material for use as a separator in a soild oxide fuel cell, is investigated in this study. LSC powders without secondary phases could be synthesized with ultrasonic spray pyrolysis and a heat treatment at 1200°C for 20 h; however, it showed an average diameter of 0.6 μm with a wide particle size distribution. On the other hand, LSC powders synthesized with spray pyrolysis at 800°C, heat-treated at 900°C for 5 h, ball-milled and finally heat-treated again at 1200°C for 20 h showed a smaller average diameter of 0.3 μm and narrower size distribution. Very few particles above 0.5 μm were found. Thus, a proper combination of the heat treatment and milling process after spray pyrolysis it determined to be very important in synthesizing fine and uniform LSC perovskite powders.

Key words*: *Solid oxide fuel cell, $La_{0.8}Sr_{0.2}CrO_3$, Separator, Ultrasonic spray pyrolysis

1. Introduction

An important issue in manufacturing solid oxide fuel cells (SOFCs) which operate at high temperatures is to find a suitable material for use as a separator. It must maintain excellent chemical stability and gas impermeability as well as high electronic conductivity under oxidizing and reducing conditions, as it is to be located between the anode and cathode in a SOFC. Lanthanum strontium chromite is known as a promising ceramic material that satisfies these requirements; however, this material has problems related to sintering densification due to the high sintering temperatures above 1800°C and the evaporation of the Cr component.[1-4] Generally, it is very effective for reducing the sintering temperature and for obtaining the outstanding mechanical properties to use the ceramic powders of a very fine size and narrow size distribution in sintering. Ultrasonic spray pyrolysis is one method that is able to synthesize fine, spherical and uniform powders with an average diameter of ~0.5 μm.[5-8] In addition, it has the advantage of creating powders with a stoichiometric homogeneous composition easily due to the use of different chemical solutions as the starting materials. Therefore, in this study, a process of synthesizing $La_{0.8}Sr_{0.2}CrO_3$ (LSC) powders with submicron sizes and a narrow size distribution is investigated using an ultrasonic spray pyrolysis method following a combination of milling and different stages of heat treatments.

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2. Experimental Procedure

The apparatus for the ultrasonic spray pyrolysis used in this study for powder preparation consists of an ultrasonicator that generates liquid droplets, a vertical furnace and a powder collector. The starting materials, lanthanum acetate ($La(CH_3CO_2)_3 \cdot H_2O$), strontium nitrate ($Sr(NO_3)_2$), and chromium nitrate ($Cr(NO_3)_3 \cdot 9H_2O$) were dissolved in an aqueous solution to a concentration of 0.25 mol/L. This solution was sprayed with the ultrasonicator at a frequency of 1.67 MHz to make droplets, and these droplets were carried into the furnace with an air flow at 5 L/min. The diameter and length of the reaction tube in the furnace were 40 and 900 mm, respectively. Reaction temperatures of 700, 800 and 900°C were used in this experiment. The synthesized powders were successively calcined at 900°C for 5 h and then at 1200°C for 20 h in air. A phase analysis of the powders was conducted using XRD (Model D/Max-3A, Rigaku) with a scanning rate of 2°/min and the microstructures were observed with SEM (Model L-240, Hitachi).

3. Results and Discussion

The liquid droplets sprayed by the ultrasonicator were spherical. They became a powder when passing through the reaction the tube after 15 seconds. Fig. 1 shows SEM micrographs of the resulting particles produced at reaction temperatures of 700, 800 and 900°C. The diameters of most particles, which were hollow and agglomerated with smaller primary particles of 20~50 nm, were 1~2 μm; there were no significant differences between the reaction temperatures. Fig. 2 shows the XRD results of these particles. The

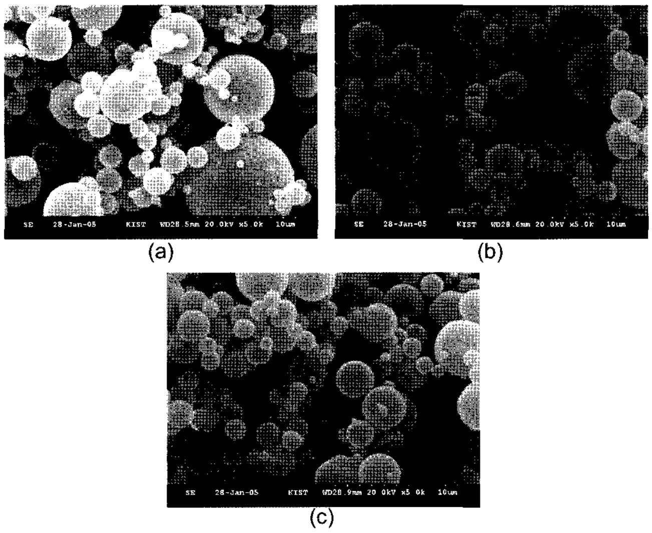

Fig. 1. SEM micrographs of particles synthesized via spray pyrolysis at (a) 700, (b) 800, and (c) 900°C.

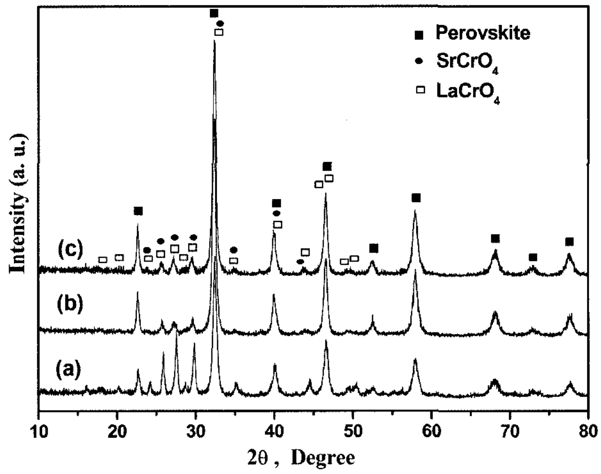

Fig. 2. XRD patterns of particles synthesized via spray pyrolysis at (a) 700, (b) 800, and (c) 900°C.

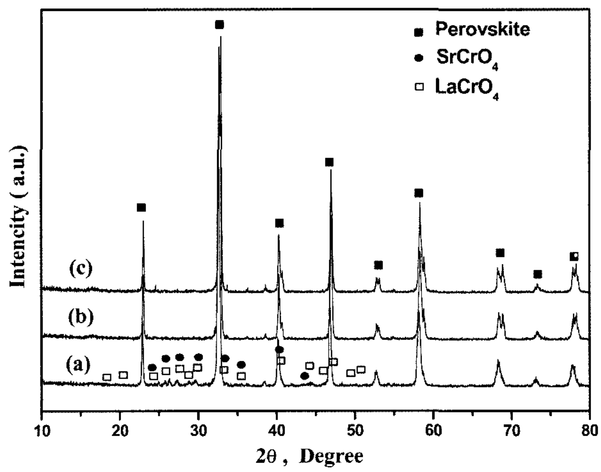

Fig. 3. XRD patterns of particles heat-treated at (a) 1100, (b) 1200, and (c) 1300°C for 20 h after spray pyrolysis at 800°C.

particles at 700°C have secondary phases of $LaCrO_4$ and $SrCrO_4$ as well as a LSC perovskite phase while those at 800 and 900°C have only one secondary phase, $SrCrO_4$. This result indicates that various chemical reactions occurred, even when the synthesizing time was very short during the spray pyrolysis procedure.

Fig. 3 shows the XRD results of particles that were heat-treated at 1100, 1200 and 1300°C for 20 h in air after spray pyrolysis at 800°C. The secondary phase, $SrCrO_4$, which formed during the spray pyrolysis procedure remained after a heat treatment of 1100°C but disappeared at 1200 and 1300°C. Therefore LSC powders without secondary phases could be synthesized with ultrasonic spray pyrolysis and a heat treatment of 1200 or 1300°C. Fig. 4 shows a SEM micrograph and the size distribution of these particles. The average diameter of the particles is 0.55 μm, but the size distribution is relatively wide (the standard deviation is 0.20).

Fig. 5 shows a SEM micrograph and the size distribution of particles obtained only with the conventional drying of a starting solution and a heat treatment at 1200°C for 20 h without using spray pyrolysis. The average diameter and size distribution of these particles are very similar to those of the particles formulated by the spray pyrolysis procedure above. On the other hand, the XRD patterns in Fig. 6 show that the secondary phase, $SrCrO_4$, remains after a heat treatment at 1200°C for 20 h but disappears at 1300°C via this process. This result indicates that the synthesizing temperature of single-phase LSC powders during the ultrasonic spray pyrolysis method was 100°C lower than it was in the conventional process.

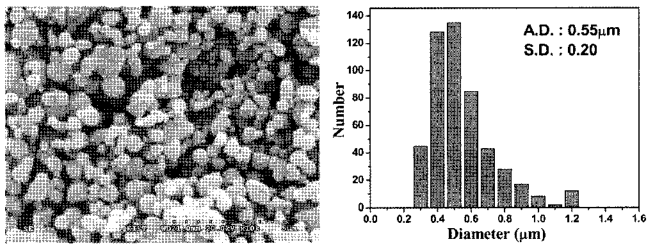

Fig. 4. SEM micrograph and size distribution of particles synthesized via spray pyrolysis at 800°C and a heat treatment of 1200°C for 20 h. (A.D.: average diameter, S.D.: standard deviation)

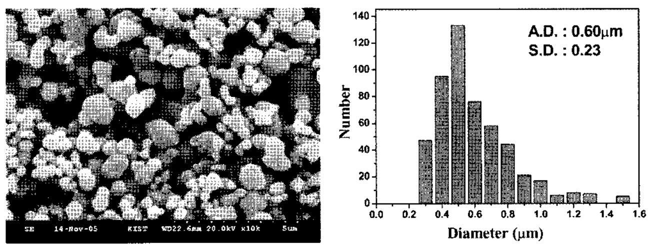

Fig. 5. SEM micrograph and size distribution of particles synthesized only with the conventional drying of a starting solution and a heat treatment of 1200°C for 20 h. (A.D.: average diameter, S.D.: standard deviation)

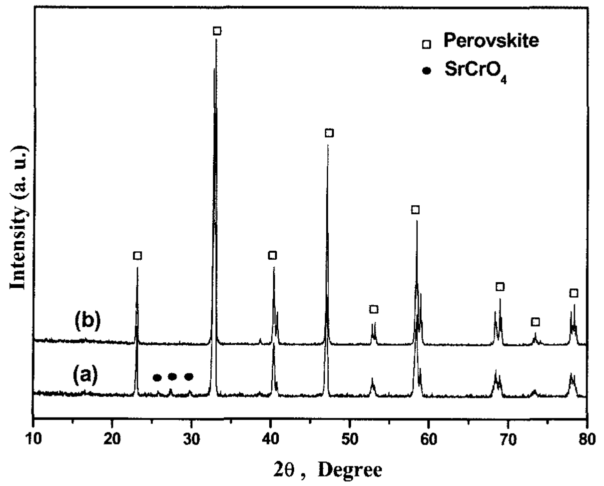

Fig. 6. XRD patterns of particles synthesized only with the conventional drying of a starting solution and a heat treatment of (a) 1200 and (b) 1300°C for 20 h.

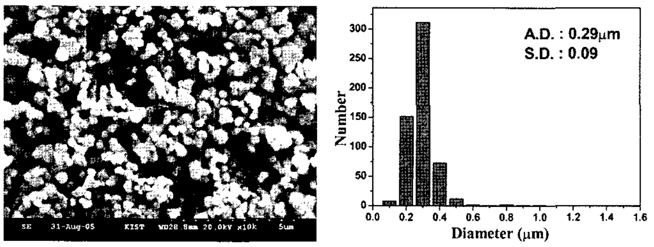

Fig. 7. SEM micrograph and size distribution of particles synthesized via spray pyrolysis at 800°C, heat-treated at 900°C for 5 h, ball-milled and finally heat-treated again at 1200°C for 20 h. (A.D.: average diameter, S.D.: standard deviation)

Fig. 7 shows a SEM micrograph and the size distribution of particles that were synthesized with spray pyrolysis at 800°C heat-treated at 900°C for 5 h, ball-milled, and finally heat-treated again at 1200°C for 20 h. The average diameter of these particles, which consist of only the LSC perovskite phase, is 0.29 μm. The particle size distribution is narrow enough to make finding particles larger than 0.5 μm rare. Therefore, the proper combination of the heat treatment and milling process after spray pyrolysis is thought to be very important in synthesizing fine and uniform LSC powders.

4. Conclusions

A process to synthesize $La_{0.8}Sr_{0.2}CrO_3$ powders of a submicron size and a narrow size distribution for use as separator materials in a solid oxide fuel cell is investigated in this study. LSC powders with very few secondary phases could be synthesized via ultrasonic spray pyrolysis and a heat treatment of 1200°C for 20 h, but showed the average diameter of 0.55 μm and a wide particle size distribution, which was similar to the result using the conventional drying of a starting solution and a heat treatment of 1200°C. In contrast, LSC powders synthesized via spray pyrolysis at 800°C, and successively heat-treated at 900°C for 5 h, ball-milled, and heat-treated again at 1200°C for 20 h showed a smaller average diameter of 0.29 μm and a narrow particle size distribution. It was rare with this process to find particles larger than 0.5 μm. Therefore, a proper combination of the heat treatment and milling process after spray pyrolysis was found to be very important in synthesizing fine and uniform LSC perovskite powders.

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