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Characteristics of nano-sized La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O₃ powders prepared by spray pyrolysis

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Nano-sized $La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_3$ (LSCM) powders were prepared by calcination of precursor powders obtained by spray pyrolysis. The precursor powders prepared from the spray solutions with citric acid or ethylene glycol had a spherical shape and a hollow morphology. The precursor powders were converted to nano-sized LSCM powders after calcination at high temperatures. The mean sizes of the LSCM powders calcined at temperatures of 700 and 800 °C were 70 and 90 nm. However, the mean sizes of the LSCM powders calcined at temperatures of 1000 and 1100 °C were 0.38 and 0.78 μ m. The sintered pellets formed from the LSCM powders obtained from the spray solution without an organic additive had high porosities. The hollow structure of the LSCM powders produced the sintered pellets with high porosities. The sintered pellets obtained from the nanosized LSCM powders had dense structures and low porosities. However, the sintered pellets obtained from the submicrometresized LSCM powders had regular pore structures and high porosities.

Key Words: spray pyrolysis; nano powder; lanthanum manganate

Introduction

It is well known that traditional Ni-YSZ cermet anodes of solid oxide fuel cells (SOFCs) have excellent catalytic properties and stability at SOFC operation conditions [1-2]. However, Ni-based anodes have the drawback of carbon deposition because of the high reactivity of Ni for hydrocarbon cracking reactions [3-7]. To overcome the disadvantage of the traditional Ni-based anode, alternative oxides such as ceria, titanate and lanthanum chromite-based oxides are being investigated as potential anodes for SOFCs. Doped LaMnO₃ is a promising material, which allows interesting modifications of their electronic as well as their catalytic properties [8-11].

The microstructure of electrodes sintered at high temperature strongly affects the electrocatalytic activity of electrodes for SOFCs. The microstructure of the sintered electrodes is affected by the morphologies and means sizes of the powders. Therefore, powder synthesis processes play an important role in the preparation of anode powders. Various synthesis processes have been adapted for the preparation of the anode materials for SOFCs such as a solid-state reaction, co-precipitation, combustion, and a sol-gel method [12-16].

A spray pyrolysis process has been used to prepare

multicomponent oxide powders with various morphologies and mean sizes. The microstructures of powders prepared by spray pyrolysis are affected by the preparation conditions such as flow rates of the carrier gas, preparation temperatures, concentrations of the spray solution and types of organic additives [17-19].

In this study, the morphologies and mean sizes of the $La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_3$ (LSCM) powders prepared by spray pyrolysis were controlled by changing the types of spray solutions. The effects of mean sizes and morphologies of LSCM powders prepared by spray pyrolysis on the sintering characteristics of the pellets were investigated.

Experimental Procedure

The spray pyrolysis system consists of a droplet generator, a quartz reactor, and a powder collector. A 1.7 MHz ultrasonic spray generator having six vibrators was used to generate a large amount of droplets, which were carried into the high-temperature tubular reactor by a carrier gas. Droplets and powders were evaporated, decomposed, and/or crystallized in the quartz reactor. The length and diameter of the quartz reactor are 600 and 50 mm, respectively. The details of the preparation procedure of La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O₃ (LSCM) powders are given in the schematic diagram shown in Fig. 1. Lanthanum nitrate, strontium nitrate, chromium nitrate, and manganese acetate were used as the precursors of the La, Sr, Cr and Mn components. Citric acid monohydrate(CA) and ethylene glycol(EG) were used as organic additives. The total concentration

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Fig. 1. Synthesis flowchart of the LSCM powders by spray pyrolysis.

of La, Sr, Cr and Mn components was fixed at 0.2 M. The flow rate of air used as carrier gas was 40 L·minute⁻¹. The precursor powders obtained by spray pyrolysis at a temperature of 900 °C were calcined in a box furnace maintained from 700 °C to 1000 °C for 3 h.

The crystal structures of the calcined LSCM powders were studied by X-ray diffraction (XRD, RIGAKU, D/ MAX-RB) with Cu K α radiation ($\lambda = 1.5418 \times 10^{-10}$ m). The mean crystallite size of the LSCM powders was estimated from Scherrer's equation. The morphological characteristics of the powders were investigated using scanning electron microscopy (SEM, JEOL, JSM 6060) and a transmission electron microscope (TEM, FEI, TECHNAI 300 K). The calcined powders were pressed into pellets with a uniaxial hydraulic press at 150 MPa. The sintering temperature of the pellets was 1200 °C and the pellets were cooled naturally to room temperature with the furnace power was off. The grain sizes and microstructures of the pellets were observed by SEM.

Results and Discussion

The morphologies of the precursor powders prepared by spray pyrolysis are shown in Fig. 2. The precursor powders prepared from the aqueous spray solution without an organic additive had a spherical shape and hollow morphology because of the high drying and decomposition rates of the droplet or powders. A high flow rate of the carrier gas at 40 L·minute⁻¹ was applied to improve the hollowness of the precursor powders. The hollowness of the precursor powders was also improved by adding organic additives to the spray solutions. Figs. 2(b) and (c) show the morphologies of the precursor powders prepared from the spray solutions with citric acid and ethylene glycol added. The addition of organic additives increased the mean size of the precursor powders. The hollow



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Fig. 2. SEM images of the precursor powders prepared by spray pyrolysis. (a) No additive; (b) 0.4 M CA; (c) 0.4 M EG.

structure increased the mean size of the precursor powders prepared from the spray solutions with organic additives.

Fig. 3 shows the morphologies of the calcined LSCM powders. The precursor powders obtained by spray pyrolysis were calcined at a temperature of 900 °C. The calcined



324





(c)

Fig. 3. SEM images of the LSCM powders calcined at 900 $^{\rm o}C$ for 3 h. (a) No additive; (b) 0.4 M CA; (c) 0.4 M EG.

powders had aggregated structures of the primary powders with a nanometre size. The LSCM powders obtained from the spray solution without an organic additive had a hard aggregated structure of the primary powders. On the other hand, the LSCM powders obtained from the spray



Fig. 4. TEM images of the LSCM powders calcined at 900 °C for 3 h. (a) No additive; (b) 0.4 M CA.



Fig. 5. X-ray diffraction patterns of the LSCM powders calcined at 1000 $^{\circ}\mathrm{C}$ for 3 h.

solutions with organic additives had slightly aggregated structures of the primary powders with nanometre sizes. Fig. 4 shows the TEM images of the calcined LSCM powders. The calcined powders were milled by hand using an agate mortar to prepare the TEM samples. The LSCM powders obtained from the spray solution without an organic additive had spherical shape and a hollow structure. However, the LSCM powders had a non-spherical shape and a slightly aggregated morphology of the primary powders. The necked structure of the nano-sized LSCM powders may facilitate the formation of a network with an intimate contact between the particles after sintering to obtain an LSCM electrode. A micro-scale network with intimate contact between the LSCM particles could be important for the electrocatalytic activity of the LSCM electrode [15]. The mean size of the primary particles as shown in Fig. 4(b) was 20 nm. Fig. 5 shows the XRD patterns of the powders calcined at a temperature of 1000 °C. The calcined powders had a pure perovskite phase structure irrespective of the addition of organic additives into the spray solutions. The mean crystallite sizes of the LSCM powders obtained from the spray solutions without and with citric acid were 26 and 20 nm.



Fig. 6. X-ray diffraction patterns of the LSCM powders calcined at different temperatures.

Fig. 6 shows the XRD patterns of the powders calcined at different temperatures. The precursor powders obtained from the spray solution with citric acid were calcined at temperatures between 700 and 1100 °C. The powders calcined at temperatures below 900 °C had impurity peaks as shown in Fig. 6. Single phase LSCM powders with the perovskite crystal structure were prepared at temperatures above 1000 °C. Fig. 7 shows the SEM images of the powders calcined at different temperatures. The calcined powders were milled by hand using an agate mortar. The mean sizes of the calcined powders increased with an increase in the post-treatment temperature. The mean sizes of the LSCM powders calcined at temperatures of 700 and 800 °C were 70 and 90 nm. However, the mean sizes of the LSCM powders calcined at temperatures of 1000 and 1100 °C were 0.38 and 0.78 μ m.

The pore structures in the sintered thick films obtained from the powders are important to improve the electrocatalytic activities of LSCM electrodes. Therefore, the sintering characteristics of the LSCM powders prepared from the spray solutions with and without organic additives were investigated as shown in Fig. 8. The pellets formed from the LSCM powders calcined at a temperature of 900 °C were sintered at a temperature of 1200 °C for 3 h. The pellet formed from the powders obtained from the spray solution without an organic additive had a high porosity. The hollow structure of the LSCM powders produced sintered pellets with a high porosity. On the other hand, the pellets formed from the powders obtained from the spray solution with organic additives had low porosities. Sintering of the nano-sized LSCM powders occurred well at a sintering temperature of 1200 °C. Therefore, the hollow structure of LSCM powders will remove the necessity of the pore formers added into the anode in order to increase the porosities of anode thick films [16].



Fig. 7. SEM images of the LSCM powders calcined at different temperatures. (a) 700 °C; (b) 800 °C; (c) 900 °C; 1000 °C.



Fig. 8. SEM images of the LSCM ceramics sintered at a temperature of 1200°C for 3 h. (a) No additive; (b) 0.4 M CA; (c) 0.4 M EG

The effects of the size of powders on the LSCM electrode structure are investigated in Fig. 9. The pellets obtained from the LSCM powders as shown in Fig. 7 were sintered at a temperature of 1200 °C. The mean sizes of the LSCM powders were controlled by changing the calcination temperature. The sintered pellets obtained from the nanosized LSCM powders had a dense structure and low porosities. However, the sintered pellet obtained from the LSCM powders as shown in Fig. 7 (d) had a regular pore structure and a high porosity.

Conclusions

The effects of mean sizes and morphologies of LSCM powders prepared by spray pyrolysis on the sintering characteristics of the powders were investigated. The precursor and calcined LSCM powders obtained from the spray solution without an organic additive had micrometre sizes, spherical shapes and hollow morphologies. However, the precursor powders obtained from the spray solutions with citric acid or ethylene glycol were turned into finesized LSCM powders after calcination at high temper-



(a)





Fig. 9. SEM images of the LSCM ceramics obtained from the LSCM powders calcined at different temperatures and then sintered at a temperature of 1200 °C for 3 h. (a) 900 °C; (b) 1000 °C; (c) 1100 °C

atures. The pellet formed from the powders obtained from the spray solution without an organic additive had a high porosity. The hollow structure of the LSCM powders produced a sintered pellet with a high porosity. On the other hand, the pellets formed from the nano-sized powders obtained from the spray solution with organic additives had low porosities. The porosities of the sintered pellets increased with an increase in the mean size of the LSCM powders.

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