Advanced Powder Technology 26 (2015) 1245–1249

Contents lists available at ScienceDirect

Advanced Powder Technology

journal homepage: www.elsevier.com/locate/apt

Original Research Paper

Low-temperature synthesis of lanthanum strontium cobalt ferrite by the citrate complex method adding oleic acid

Shin Mimuro [a,b,*], Yuki Makinose [a], Nobuhiro Matsushita [a]

[a] Materials and Structures Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan
[b] EV System Laboratory, Nissan Research Center, Nissan Motor Co., Ltd., 1, Natsushima-cho, Yokosuka 237-8523, Japan

ARTICLE INFO

Article history:
Received 15 September 2014
Received in revised form 8 June 2015
Accepted 19 June 2015
Available online 29 June 2015

Keywords:
Lanthanum strontium cobalt ferrite
Low-temperature synthesis
Citrate complex method
Oleic acid
Surfactant

ABSTRACT

Crystalline lanthanum strontium cobalt ferrite (LSCF) was obtained by calcination at a low temperature of 500 °C from precursor nanoparticles. The precursor nanoparticles were synthesized by the citrate complex method adding oleic acid as a surfactant, and dynamic laser scattering measurements suggested that they exhibited high dispersibility in the solution with an average diameter less than around 20 nm. The crystallite size decreased and the total specific area increased as the calcination temperature was decreased from 800 to 500 °C. It was found that the oleic acid functioned as a surfactant to form homogeneous fine precursor, and then assisted in the crystallization of LSCF even at a low calcination temperature of 500 °C. Such a low temperature synthesis suppressed the agglomeration and growth of LSCF particles so that fine powders with particle size less than 20 nm were obtained.

1. Introduction

Lanthanum strontium cobalt ferrite (LSCF, $La_{1-x}Sr_xCo_{1-y}Fe_yO_3$, $0 < x < 1$, $0 < y < 1$) is one of the main cathode materials for solid oxide fuel cells because of its relatively high electronic and oxygen ion mixed conductivities [1,2] and high catalytic activity for the oxygen reduction reaction [3]. For decades, the solid-state reaction method has been used to synthesize single-phase materials because of its simplicity. However, it requires a high process temperature greater than 1000 °C to diffuse and to react the raw materials and to form the single-phase crystal [4]. Because such high temperature calcination increases production costs, the development of a low-temperature process that enables the crystallization of LSCF has long been anticipated [4]. In recent years, several wet chemical syntheses have been investigated to solve this issue [5]. Fan and Liu [6] and Ghouse et al. [7] prepared single-phase LSCF at 700 °C by citric acid combustion and polymerized complex methods, respectively. Baqué et al. [8] reported that single-phase LSCF was obtained by calcination at 750 °C using citric acid and hexamethylenetetramine as combustion fuels.

To further decrease the calcination temperature, we propose a new type of calcination process using oleic acid in addition to citric acid. Taniguchi et al. reported that uniform-sized nano CeO_2 was successfully synthesized by the hydrothermal method using oleic acid as a surfactant [9]. From the result, we selected the oleic acid to synthesize nano-sized LSCF in this study. In our new process, oleic acid functions as a surfactant to improve the dispersibility of the precursor complex in the solution and to promote the formation of a fine and highly homogeneous precipitate. Such a fine precipitate improves the surface energy and reactivity so that the crystallization at a low temperature can be expected. The objective of this study is to prepare single-phase LSCF at a low calcination temperature and to investigate its formation mechanism.

2. Experimental

2.1. Sample preparation

We selected the composition of La:Sr:Co:Fe = 0.6:0.4:0.2:0.8 because the composition is widely selected in terms of the consistency of the thermal expansion coefficient with the electrolyte(YSZ) and higher electron and oxide ion mixed conductivities. The precursor powders with composition $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ were prepared by a citrate complex method using $La(NO_3)_3{\cdot}6H2O$ (99.9%), $Sr(NO_3)_2$ (98%), $Fe(NO_3)_3{\cdot}9H_2O$ (99.9%), $Co(NO_3)_3{\cdot}6H_2O$ (99.5%) and citric acid ($C_6H_8O_7$) purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan).

---

[*] Corresponding author at: EV System Laboratory, Nissan Research Center, Nissan Motor Co., Ltd., 1, Natsushima-cho, Yokosuka 226-8523, Japan. Tel.: +81 50 3751 6810.

E-mail address: mimuro@mail.nissan.co.jp (S. Mimuro).

http://dx.doi.org/10.1016/j.apt.2015.06.006

Stoichiometric amounts of the nitrates were dissolved in diluted water at 60 °C on the hotplate and mixed at 200 rpm using a magnetic stirrer, and then citric acid in equal molar amount to total metal ions was added to the solution. The sample prepared with the above process is called LS-cit, and the sample with an equal molar amount of oleic acid ($C_{18}H_{34}O_2$, Wako Pure Chemical Industries, Ltd.) also added to LS-cit is called LS-ol.

The pH of the solution was adjusted between 7 and 9 using dilute nitric acid and aqueous ammonia. The solution was gradually dried to form the precursor gel. The precursor gel was heated at 130 °C for 1 h and then at 400 °C for 1 h, and finally it was calcined in the range from 400 to 900 °C for 2 h in air.

The composition ratio of some of the resulting powders was checked by inductively coupled plasma (ICP) spectroscopy and it was almost consistent with that of the fed raw materials.

2.2. Characterization

The samples were analyzed by X-ray diffraction (XRD) for phase identification with Cu Kα radiation of 40 kV/40 mA at room temperature. The lattice parameters were refined by the Rietveld method [10]. The compositions of the samples were confirmed by ICP at room temperature. Raman spectroscopy analysis was performed at room temperature. The particle size distribution and zeta potential of the precursor solution were examined using a dynamic laser scattering (DLS) system. Thermogravimetry–differential thermal analysis (TG/DTA) measurements of the precursor powder were performed with temperature in the range from room temperature to 900 °C in air. The crystallite sizes of the LSCF sample powders were observed by transmission electron microscopy (TEM).

3. Results and discussion

3.1. Phase purity

Figs. 1 and 2 show the XRD profiles of the LS-ol and LS-cit samples calcined at various temperatures. The simulated profile of single-phase LSCF with rhombohedral symmetry of the space group $R3c$ was calculated using the reported data [11] and is shown at the bottom in Figs. 1 and 2. No secondary phases were observed for the LS-ol sample calcined in the range 500–800 °C, and the XRD pattern is in good agreement with the simulated profile, as shown in Fig. 1.

While the sample calcined at 400 °C was not a single phase, the impurity phase was not assigned. The desired composition of $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ was confirmed for the samples calcined at 500–800 °C by ICP. As one of representatives, the results of LS-ol calcined at 800 °C are shown in Table 1. Conversely, a single phase was not obtained for the LS-cit samples even at a high calcination temperature of 900 °C, as shown in Fig. 2.

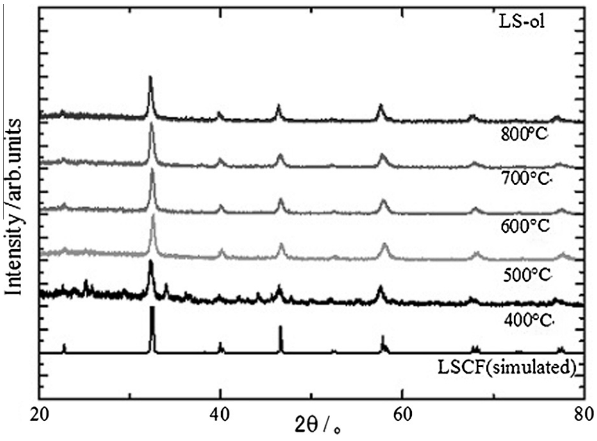

Fig. 1. XRD profiles of LS-ol samples calcined at various temperatures.

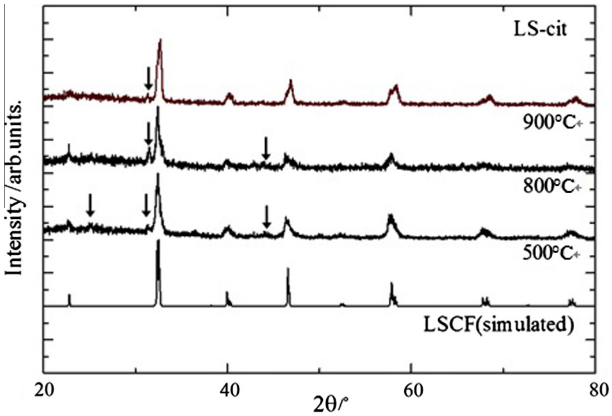

Fig. 2. XRD profiles of LS-cit samples calcined at various temperatures. The impurity phase peaks are indicated by arrows.

The calculated lattice parameters of the LS-ol samples by the Rietveld method are shown in Fig. 3. They agreed well with the reported values [12,13,18]. In the case of LS-ol calcined at 700 °C, for example, the reliable factors R_{wp}, R_p and S were 17.765, 13.187 and 1.4169, respectively. Although those values were relatively high to investigate precise crystal parameters, it was enough low for our main objective to judge whether LSCF was successfully synthesized or not by comparing the obtained lattice parameters to the reported ones.

From these results, the calcination of precursors prepared by the citrate complex method adding oleic acid enabled the formation of LSCF powders in a single phase even at a low temperature of 500 °C. However, a single phase was not obtained for LS-cit precursors even after calcination at a high temperature of 900 °C, as shown in Fig. 2. We examined the particle size distribution of LS-ol and LS-cit precursors in the solution to explain these results (Fig. 4).

The profile of the LS-ol precursor in Fig. 4 shows a single sharp peak, suggesting a small particle size of several tens of nanometers and a narrow size distribution. Conversely, the profile of the LS-cit sample was split into two peaks, suggesting a much larger particle size than LS-ol.

These results indicate that oleic acid on the particle surface functioned as a surfactant in the case of LS-ol to promote the dispersibility of the precursor in the solution and helped to attain high homogeneity. We believe that the high dispersibility and homogeneity enabled the formation of single-phase LSCF even at a low calcination temperature of 500 °C. Another possibility is that LSCF crystallization was also assisted by combustion heat from oleic acid during the calcination, as shown in Fig. 5.

Table 1
ICP results of LS-ol calcined at 800 °C. A11 data were averaged values for 10 times measurements. Sample weight 10.34 mg.

	Fe	Co	Sr	La
Concentration (mg l^{-1})	40.26	9.70	31.36	72.65
R	0.65	0.17	0.53	1.13
S	0.20	0.06	0.17	0.46
C_v	0.49	0.57	0.54	0.63
Molar ratio	4.38	1.00	2.18	3.18

R – resolution of the each element.
S – standard delation of measurements.
C_v – coefficient of the variation.