

Short communication

## Morphology control of $\text{La}(\text{Sr})\text{Fe}(\text{Co})\text{O}_{3-a}$ cathodes for IT-SOFCs

Kenji Murata<sup>a</sup>, Takehisa Fukui<sup>a,\*</sup>, Hiroya Abe<sup>b</sup>, Makio Naito<sup>b</sup>, Kiyoshi Nogi<sup>b</sup>

<sup>a</sup> *Hosokawa Powder Technology Research Institute, 1-9 Tajika, Shoudai, Hirakata, Osaka 573-1132, Japan*

<sup>b</sup> *Joining and Welding Research Institute, Osaka University, 11-1 Mihogaoka, Ibaraki, Osaka 567-0047, Japan*

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### Abstract

A  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-a}$  (LSCF) powder was prepared through a citric synthesis route and subsequent media agitating milling. The milling for 1.5 and 3 h reached the average particle sizes of 0.66 and 0.53  $\mu\text{m}$ , respectively. Then, the LSCF cathodes were formed using the two powders in a conventional manner. It was shown that the cathode performance was strongly influenced by the starting particle size as well as sintering temperature. The smallest cathode polarization for both 700 and 800 °C operations was obtained when using the finer powder (0.53  $\mu\text{m}$ ) and sintering at 850 °C, suggesting an excellent cathode morphology. An anode-supported single cell with this cathode structure was fabricated and demonstrated a good generation performance under intermediate temperature operation.

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### 1. Introduction

The solid oxide fuel cell (SOFC) has been promising for electrical power generation in terms of the high conversion efficiency of chemical energy to electric power. Recently, much attention is focused on lower temperature operation less than 800 °C, because such operation enables to use low-cost metallic interconnects, long-term cell materials stability, and decrease the materials corrosion for plant components. However, there are drawbacks that it increases the ohmic loss at the solid-state electrolyte as well as the polarization loss at both electrodes under the lower temperature operation.

To reduce the ohmic loss of the electrolyte, two approaches have been proposed. One is to use a thin film of  $\text{Y}_2\text{O}_3$  stabilized  $\text{ZrO}_2$  (YSZ), and the other is to develop new electrolytes with higher conductivity such as  $\text{La}(\text{Sr})\text{Ga}(\text{Mg})\text{O}_3$  or  $\text{CeO}_2$ . In reducing the polarization loss, trial has been conducted to increase the electrochemical activity at both electrodes.

Several perovskite compounds containing La and Sr on A-site and Co and/or Fe on B-site have been candidates as cathode materials for intermediate temperature operation SOFC because they exhibit high electric and ionic conductivity, and high catalytic activity for oxygen [1–6]. However, since the compounds with Co on B-site react very well with YSZ, insulating zirconate phases are often formed at interface of the cathode-electrolyte during sintering [6,7]. Therefore, a ceria based interlayer such as  $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_2$  is commonly used to depress that solid reaction [1–6]. The disadvantages of the introduction of the interlayer are the complexity of the cell structure, the manufacturing cost and instability in the stack due to the difference in the thermal expansion coefficient between ceria based oxide and YSZ.

In this study, the morphological control of  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-a}$  (LSCF) electrode was performed to improve the electrochemical activity for use in interlayer-free SOFC cells. Specific features focused on are the influences of the sintering temperature and the particle size on the morphology and electric performance of LSCF cathode. Also, the generation performance of an anode supported SOFC cell with the improved LSCF will be demonstrated.

\* Corresponding author. Tel.: +81 72 855 2260; fax: +81 72 855 4186.  
E-mail address: [tfukui@hmc.hosokawa.com](mailto:tfukui@hmc.hosokawa.com) (T. Fukui).

## 2. Experimental

### 2.1. Powder preparation

$\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-a}$  (LSCF) precursor was prepared from carbonates of each element (99.9%, Wako pure chemical co.) by a citrate method. The LSCF powder was obtained after calcination of  $1000^\circ\text{C}$ , and subsequently crashed by media agitating milling (Model AQ-5, Hosokawa Micron Corp., Japan) for 1.5 h (LSCF-1) and 3 h (LSCF-2). NiO–YSZ composite powder for an anode [8,9] was prepared from NiO (NiO, Nicho Rica Corp, F type) and 8 mol%  $\text{Y}_2\text{O}_3$  stabilized  $\text{ZrO}_2$  (YSZ, Tosoh Co., TZ-8Y) powder by the advanced mechanical method (Mechanofusion system [10–12], Model AM-20F, Hosokawa Micron Corp., Japan). LSCF powders were observed by a scanning electron microscopy (SEM, Model S-3500N, Hitachi Ltd, Japan). The particle size distribution and specific surface area of the powders were measured by laser diffraction and scattering method (MICROTRAC, Model HRA9320-X100, NIKKISO Co. Ltd., Japan) and BET method (Macsorb, Model 1201, Mountech Ltd., USA), respectively.

### 2.2. Evaluation of the cathode performance

The electrolyte pellet was prepared by sintering at  $1450^\circ\text{C}$  from 8 mol%  $\text{Y}_2\text{O}_3$  stabilized  $\text{ZrO}_2$  powder (Tosoh, TZ-8Y). The NiO–YSZ composite powders were mixed with organic binder, and then printed onto one side of the YSZ electrolyte pellet (13 mm in diameter and 0.2 mm in thickness). After sintering it at  $1350^\circ\text{C}$  in air, LSCF powders were printed onto the other side of the pellet, and then sintered at 850, 900 or  $1000^\circ\text{C}$ . In the present study, no interlayer was employed.

The cathode polarization between the cathode and the reference electrode (Pt), and total internal resistance (IRt) were measured using the current interruption technique, up to  $0.5\text{ A cm}^{-2}$  of current density under operations of 700 and  $800^\circ\text{C}$  in supplying  $\text{H}_2$ –3% $\text{H}_2\text{O}$  for the anode and air for the cathode. The variation of the electrochemical measurements was roughly estimated to be 0.02 V. The morphology of the LSCF cathodes was observed by a SEM after the cell was tested.

### 2.3. Demonstration of an anode-supported single cell

To form an anode-supported single cell, the multi-layer of anode (NiO–YSZ) and electrolyte (YSZ) was first prepared by an organic tape casting method, and then it was sintered at  $1350^\circ\text{C}$ . After that, LSCF powder was printed onto YSZ electrolyte, and sintered at  $850^\circ\text{C}$ . Electric performance of this single cell was measured at  $700^\circ\text{C}$ .

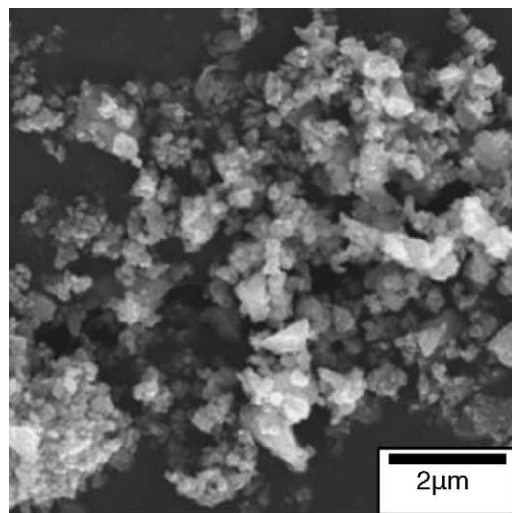


Fig. 1. SEM photographs of  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-a}$  (LSCF-2) powder.

## 3. Results and discussion

### 3.1. Morphology of LSCF powder

Fig. 1 shows a SEM photograph of LSCF-2 powder. It indicates that LSCF-2 powder was ground to finer particles. Table 1 shows the average particle size and specific surface area of LSCF-1 and LSCF-2. The particle size of the longer milled LSCF-2 powder ( $0.53\ \mu\text{m}$ ) is smaller than that of LSCF-1 ( $0.66\ \mu\text{m}$ ). It noted that only perovskite phase was detected on X-ray diffraction patterns of these LSCF powders.

### 3.2. Performance and morphology of LSCF cathode

Fig. 2 shows the electrochemical polarization curve at 700 and  $800^\circ\text{C}$  of LSCF-1 cathode formed with different sintering temperature. As can be seen, the electrochemical polarization of LSCF-1 cathodes strongly depends on the sintering temperature. The cathode sintered at  $1000^\circ\text{C}$  had the worst performance, whereas those sintered at 850 and  $900^\circ\text{C}$  show good electrochemical performances. Fig. 3 shows SEM photographs of the LSCF-1 cathodes sintered at 850, 900 and  $1000^\circ\text{C}$ . The coarse grains are clearly seen for the cathode sintered at  $1000^\circ\text{C}$ .

The resistivity of the cell with LSCF-1 cathodes sintered at 850, 900 and  $1000^\circ\text{C}$  was 0.83, 0.84 and  $1.36\ \Omega\text{ cm}^2$  at  $800^\circ\text{C}$  operation, respectively. The increased resistivity can

Table 1  
Average particle size and specific surface area of LSCF powder

	Average particle size ( $\mu\text{m}$ )	BET specific surface area ( $\text{m}^2\text{ g}^{-1}$ )
LSCF-1	0.66	5.5
LSCF-2	0.53	8.9

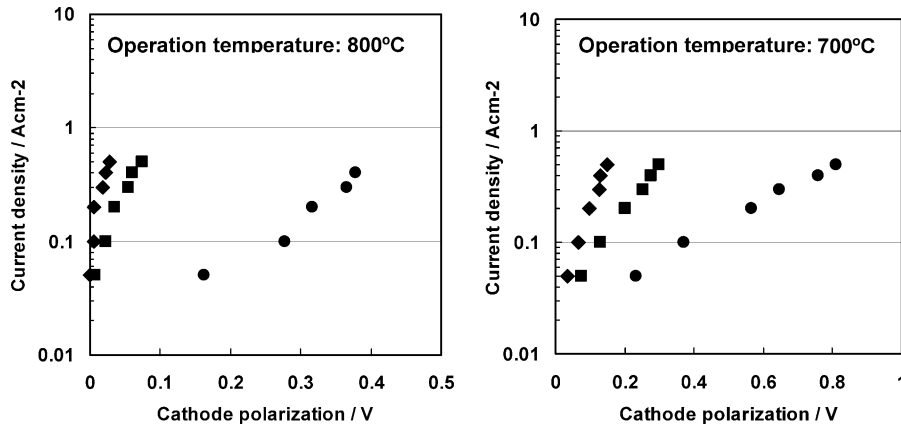


Fig. 2. Cathode polarization of LSCF-1 sintered at (◆) 850 °C, (■) 900 °C and (●) 1000 °C and operation temperature of 700 and 800 °C.

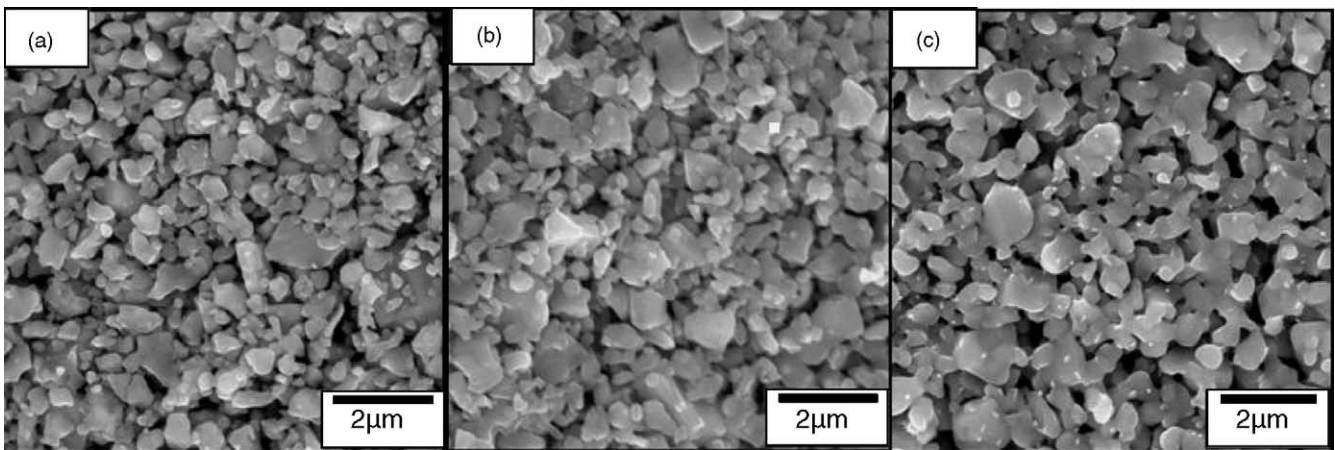


Fig. 3. SEM photographs of the surface of LSCF-1 cathode sintered at (a) 850 °C, (b) 900 °C and (c) 1000 °C.

be attributed to the formation of zirconate phases such as  $\text{SrZrO}_3$ , because it is well known that LSCF reacts with YSZ at temperature as low as 800 °C [6,7]. The coarse grains and considerable zirconate phases as seen in LSCF-1 cathode sintered at 1000 °C lead to the direct decrease of the cathode reaction zone, resulting in large cathode polarization. As a result, sintering at 850 and 900 °C can be applicable for cathode formation.

Fig. 4 shows the cathode polarization of LSCF-1 and LSCF-2 cathodes sintered at 850 and 900 °C when the current density was  $0.5 \text{ A cm}^{-2}$ . The cathode polarization of 850 °C sintered LSCF-2 is the lowest at both 700 and 800 °C operation. This performance is almost similar to those reported in previous studies [1,5,6] which employed ceria-based interlayer. The morphology of LSCF-2 cathodes sintered at 850 and 900 °C is shown in Fig. 5. The finer and

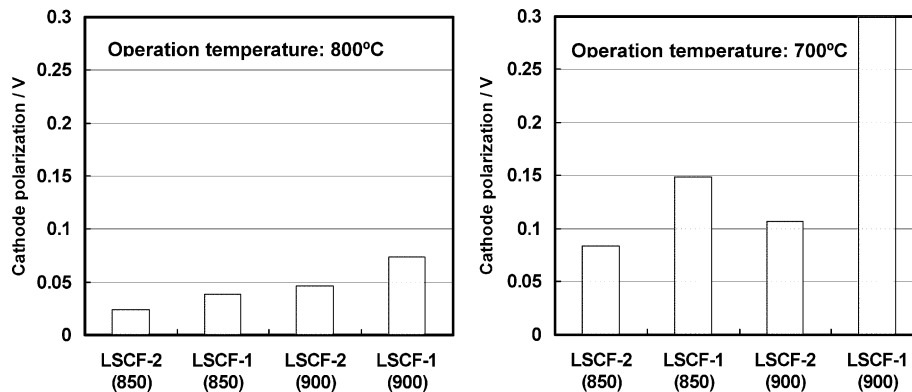


Fig. 4. Cathode polarization at the current density of  $0.5 \text{ A cm}^{-2}$  of LSCF-1 and LSCF-2 sintered at 850 and 900 °C.

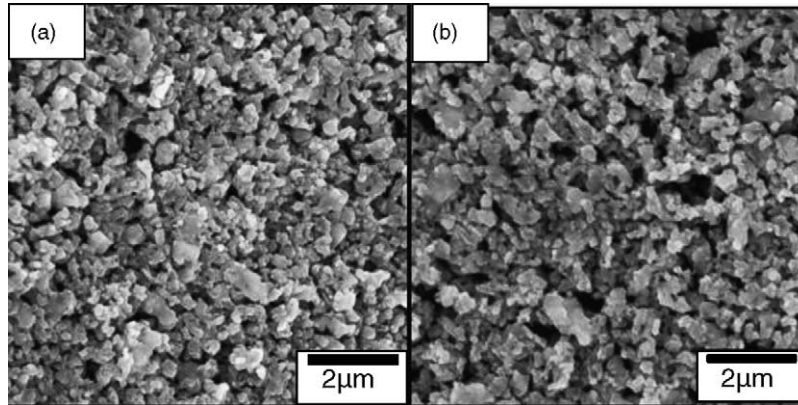


Fig. 5. SEM photographs of the surface of LSCF-2 cathode sintered at (a) 850 °C and (b) 900 °C.

more homogeneous morphology with grain size of about 0.5  $\mu\text{m}$  is seen. The improvement of LSCF cathode performance observed in LSCF-2 might be caused by this structure which presents a higher surface area for  $\text{O}_2$  reduction reaction.

### 3.3. Performance of an anode-supported single cell

Fig. 6 shows the generation performance of the anode-supported single cell with LSCF-2 cathode. The plot indicates the cell voltage-current density and the power density-current density operated at 700 °C. The maximum power density is about  $0.7 \text{ W cm}^{-2}$  at  $1.5 \text{ A cm}^{-2}$  and the power density at 0.7 V is about  $0.5 \text{ W cm}^{-2}$ , of which performances are comparable in other studies [4,6]. Fig. 7 shows the cross sectional image of the single cell. The dense and thin (about 10  $\mu\text{m}$ ) electrolyte is formed in the cell. The good performance observed in this study may be resulted from not only the improvement of cathode performance but also the dense and thin electrolyte layer. The anode performance has

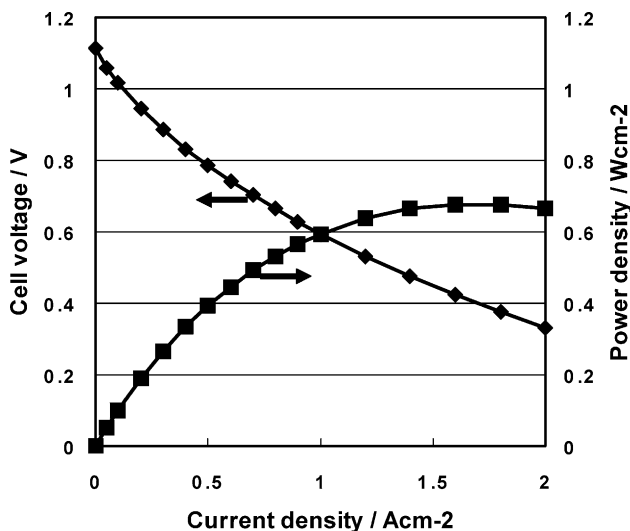


Fig. 6. Cell performance data at 700 °C for anode-supported single cell with LSCF-2 cathode sintered at 850 °C.

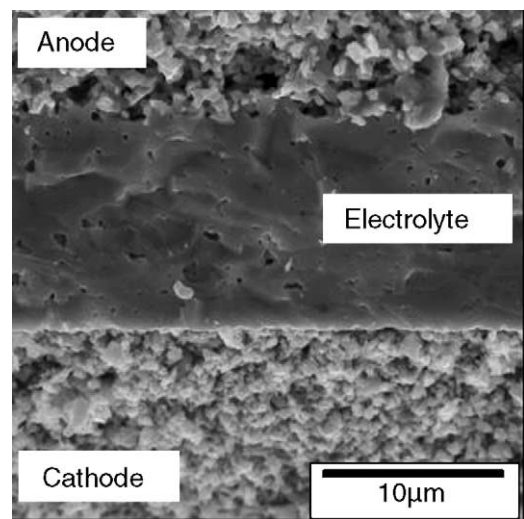


Fig. 7. SEM photograph of the cross section of an anode-supported single cell with LSCF-2 cathode sintered at 850 °C.

been already improved by the morphological control using NiO–YSZ composite powder [8,9].

This study indicates that LSCF-2 cathode is useful for intermediate temperature SOFC, because the LSCF-2 cathode realize a good electrochemical performance and does not need the interlayer. The interlayer-free design can lead to simplifying the cell structure and manufacturing process for IT-SOFC.

## 4. Conclusions

- (1)  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-a}$  (LSCF) powder was prepared by a citrate method. Fine ( $\sim 0.5 \mu\text{m}$ ) LSCF powder was obtained by subsequent milling for 3 h.
- (2) The electrochemical polarization of LSCF cathode depended on its sintering temperature, and LSCF cathode sintered at 850 and 900 °C showed a good cathode performance. Moreover, significantly fine and homogeneous LSCF cathode was prepared by 850 °C sintering of the

finer powder (0.53  $\mu\text{m}$ ), resulting in an excellent cathode performance without interlayer.

- (3) An anode-supported single cell with the improved LSCF cathode and dense-thin electrolyte layer was fabricated. This single cell demonstrated comparatively good generation performance (the power density, about  $0.5 \text{ W cm}^{-2}$  at 0.7 V, 700 °C) for intermediate temperature SOFC.

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