Influence of Size Distribution of LSM/YSZ Composite Powder on Microstructure and Performance of SOFC Cathode

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Abstract

$La_{0.8}Sr_{0.2}MnO_3$(LSM)/Y_2O_3 stabilized ZrO_2(YSZ) composite powders were mechanically prepared. By changing the mechanical conditions, three composite powders with different size distributions were obtained. Then, they were applied into cathodes of solid oxide fuel cells (SOFCs). Microstructures of the cathodes were carefully characterized by scanning electron microscope (SEM). Losses of internal resistance (IR) and polarization between the electrolyte and the cathode were measured with a current interruption technique. The significant change associated with the particle size distribution was observed in the microstructures and the losses.

KEY WORDS: SOFC, LSM/YSZ composites, Particle size distribution, Microstructure

1. Introduction

Solid oxide fuel cells (SOFCs) offer a low-pollution technology to generate electricity electrochemically with high efficiency. Over the last two decades, SOFCs based on Y_2O_3 stabilized ZrO_2 (YSZ) have been developed for operation in the temperature range of 900-1000ºC,[1), 2)] YSZ for the electrolyte, Ni-YSZ cermet for the anode, and $La_{0.8}Sr_{0.2}MnO_3$ (LSM) for the cathode.

Current efforts are aimed at decreasing the cost of SOFC by lowering the operating temperatures to 800 °C or less. There are two major efforts to do so.[3)- 5)] One is to minimize the ohmic loss from the electrolyte, and the other is to decrease the polarization losses at both electrodes. To date, the change of cell design and the improvement of powder processing have resulted in decreases of these losses for laboratory planner SOFCs. The polarization losses at both electrodes can be decreased by increasing their electrochemical activity.[6)] Since their electrochemical reaction occurs at the area where gaseous species, ions and electrons meet, triple phase boundaries (TPB), a microstructure with large TPB leads to the decrease of polarization loss and therefore the microstructural control of anode or cathode electrode has been studied.

Recently, the authors have demonstrated that the Ni/YSZ composites made from NiO-YSZ composite particles provided large TPB, and thereby substantially decreased the polarization loss of the anode electrode.[7)] For the cathode electrode, the LSM/YSZ composites have been attempted as well.[8)] As widely accepted, not only the processing conditions but also the powder properties such as particle distributions are important factors to obtain well-controlled microstructures. However, the discussion of the latter has been rather limited.

In this study, the microstructure control of LSM/YSZ cathode was attempted using LSM/YSZ composite particles for lowering the temperature to operate SOFCs. The specific feature focused on was to investigate the influence of the size distribution of LSM/YSZ composite particles on the electrical performance of the cathode.

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Transactions of JWRI is published by Joining and Welding Research Institute, Osaka University, Ibaraki, Osaka 567-0047, Japan

2. Experimental

Figure 1 shows the processing flow for the LSM/YSZ composite particles used in this study. La_2O_3 (KCM Corp., Japan), $SrCO_3$ (KCM Corp., Japan) and Mn_3O_4 (KCM Corp., Japan) powders were milled for 60 min, followed by heated at 800 °C for 2 h. The synthesized LSM powders were ground by ball milling in ethanol for 12 h. After drying, LSM powder was mixed with YSZ (TZ-8Y, Tosoh Inc., Japan) by an advanced mechanical method to make composite particles (Mechanofusion system,[7] Model AMS-LAB, Hosokawa Micron Corp., Japan). The weight ratio of LSM to YSZ was 7:3. The processed powders for 10 min and 30min are referred to as LSM/YSZ-1 and LSM/YSZ-2 in the description below. In addition, the powder for 30 min was ball-milled in ethanol for 12 h (referred as LSM/YSZ-3).

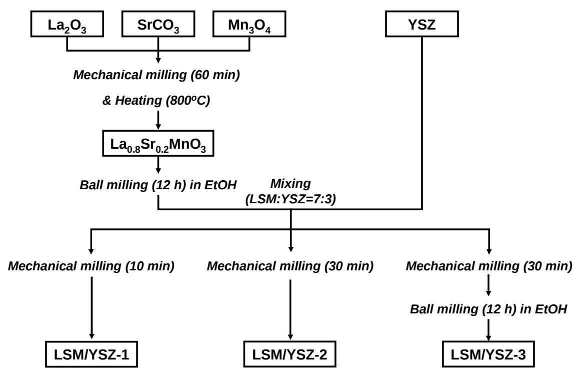


Fig. 1 Processing flow of LSM/YSZ composite particles.

The Specific surface area and particle size distribution of the composite powders were measured by a nitrogen gas adsorption instrument (Micromeritics ASAP 2010, Shimadzu, Japan) based on the BET method and laser diffraction and scattering method (MICROTRAC, Model HRA9320-X100, NIKKISO Co. Ltd., Japan), respectively. The morphology of LSM/YSZ powders was observed by a scanning electron microscopy (SEM, Model S-3500N, Hitachi Ltd., Japan). Phase identification of the composite powders was determined with X-ray diffraction method (XRD: JDX-3530M, JEOL, Japan) using CuKα radiation as X-ray source. The XRD patterns were collected in the range of 10- 70º with a step size of 0.02º.

The electrolyte sheet was prepared using YSZ powder (TZ-8Y, Tosoh Inc., Japan). The NiO (Nicoh Rita Corp, F-Type)-YSZ composite powders[7), 9)] were mixed with organic binder, and then print onto one size of the YSZ electrolyte pellet. The pellet was sintered at 1350 °C. The LSM/YSZ composite particles were printed on the other side of electrolyte sheet, and then sintered at 1150 °C. The losses of IR and polarization were measured between the electrolyte YSZ layer and the cathode using the current interruption technique, up to 0.5 A cm^{-2} of current density under operation of 700 °C in supplying H_2-3%H_2O for anode and air for cathode. The microstructure of the cathode was observed by SEM (Model S-3500N, Hitachi Ltd., Japan).

3. Results and discussion

3.1 Powders characterization

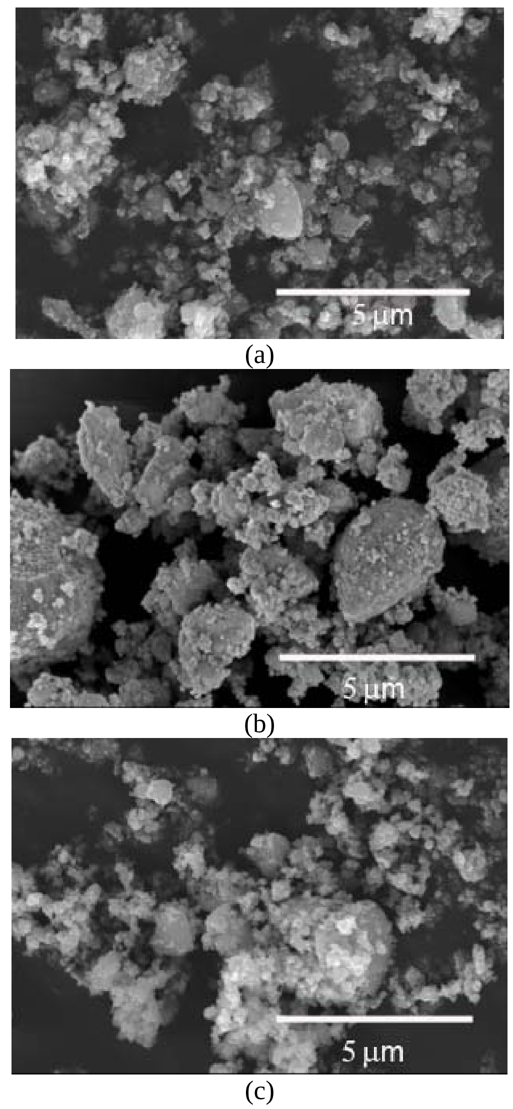


Fig. 2 SEM micrographs of LSM/YSZ composite particles: (a) LSM/YSZ-1; (b) LSM/YSZ-2; (c) LSM/YSZ-3.

Figure 2 shows the SEM micrographs of the three LSM/YSZ composite particles. Their particle size distributions are shown in Fig. 3. The sizes of LSM/YSZ-1 (D_{50}=0.45μm) and LSM/YSZ-3 (D_{50}=0.37μm) powders distributed from 0.1 μm to a few microns. Those of LSM/YSZ-2 (D_{50}=6.49μm) was much broader, ranging from 0.1 to 100 μm. There was no large difference in their specific surface area. Those of LSM/YSZ-1, LSM/YSZ-2 and LSM/YSZ-3 were 8.7, 8.1 and 10.9m^2/g, respectively.

Figure 4 shows the XRD patterns of the three composites particles. Only LSM and YSZ phases were identified. Any zirconate phases were not observed.

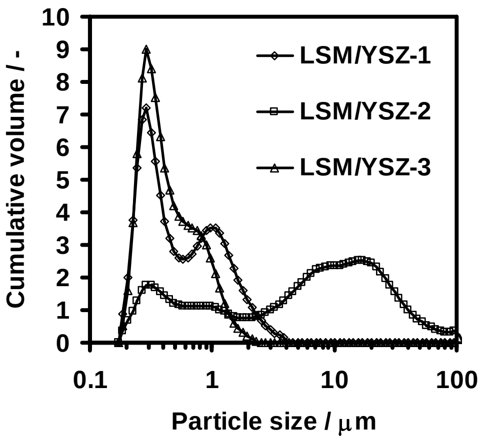


Fig. 3 Particle size distributions of LSM/YSZ composite particles.

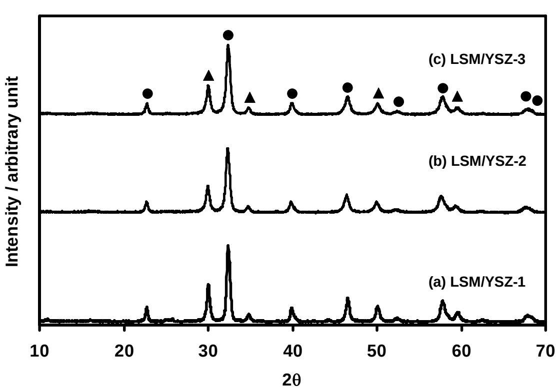


Fig. 4 XRD patterns of LSM/YSZ powders. (LSM, ●; YSZ, ▲)

3.2 Microstructure and performance of LSM/YSZ composite cathode

Figure 5 shows the SEM micrographs of the surface of the LSM/YSZ composite cathodes. Figure 6 shows the cross-sectional SEM micrographs of the electrolyte/cathode interface. The microstructure of LSM/YSZ composite cathode made from LSM/YSZ-2 powders consisted of coarse grains and non-uniform porosity, suggesting low effective area for electrochemical reaction. The coarse grains and large pores were also seen in near interfaces between cathode and electrolyte, suggesting low contact area, i.e., increasing IR loss at interfaces. On the other hands, the microstructures of the cathodes made from LSM/YSZ-1 and LSM/YSZ-3 powders consisted of the smaller particles and more uniform porous structure. The good contacts between the electrolyte and the cathode were also seen.

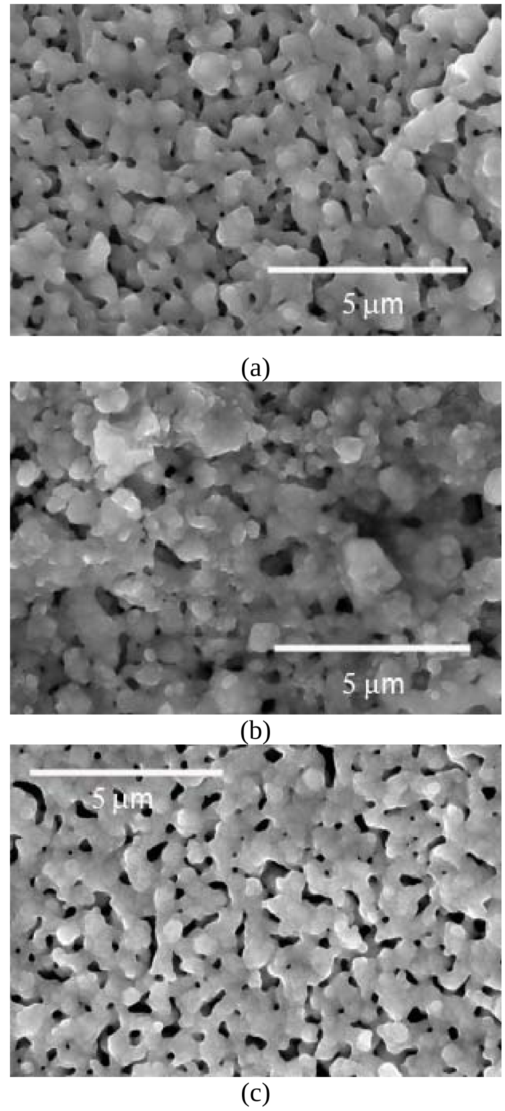
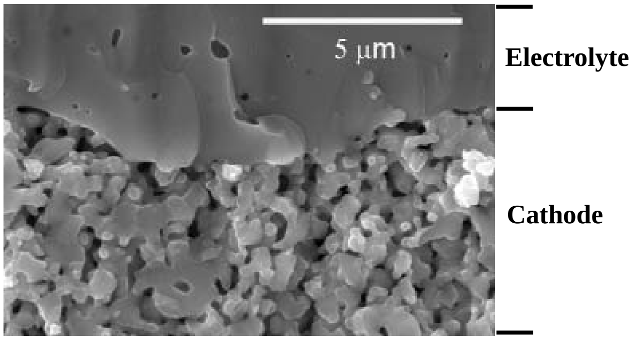
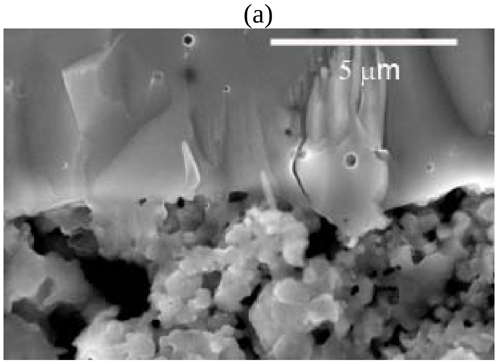


Fig. 5 SEM micrographs of the surface of LSM/YSZ cathodes: (a) LSM/YSZ-1; (b) LSM/YSZ-2; (c) LSM/YSZ-3. The sintering temperature was 1150 ^{o}C, 2 h.

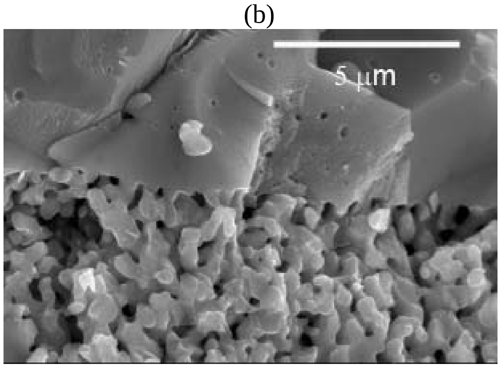
Figure 7 shows the losses of IR between the electrolyte



(a)



(b)



(c)

Fig. 6 SEM micrographs of the cross section of LSM/YSZ cathodes: (a) LSM/YSZ-1; (b) LSM/YSZ-2; (c) LSM/YSZ-3. The sintering temperature was 1150 ^{o}C, 2 h.

layer and the cathode and the cathode polarization. Both losses were the largest, when LSM/YSZ-2 composite particles were used. The cathodes made from LSM/YSZ-1 and LSM/YSZ-3 showed lower values.

The wide size distribution containing large amount of coarse particles (LSM/YSZ-2) resulted in non-uniform microstructure and less contacts on electrolyte layer. The polarization loss of the cathode was increased with increasing the content of coarse particle. The IR loss also showed the similar tendency. The optimization of the size distribution of the composite particles is being progressed.

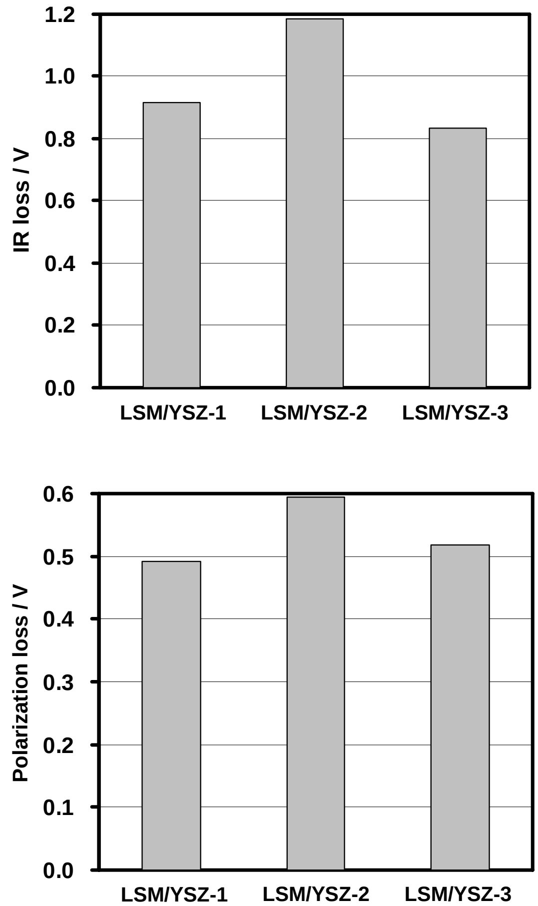


Fig. 7 Losses of internal resistance (IR) and polarization of the LSM/YSZ composite cathodes at 0.5 A cm^{-2}, 700 ^{o}C.

4. Conclusions

The influence of particle size distribution of the LSM/YSZ composite particles on the microstructure, internal resistance (IR) and polarization loss of cathode of solid oxide fuel cell (SOFC) was investigated. In this study, LSM/YSZ composite particles with three different particle size distributions were prepared. The cathode fabricated by using the narrowest particle size distribution showed the fine grains, uniform porous structure, and good contact onto electrolyte layer, and thereby it showed the low IR and polarization losses. In contrast, the cathode fabricated from the wide particle size distribution containing large amount of coarse particles resulted in the non-uniform structure in grains and pores, and the high IR and polarization losses were observed. The controlling the size distribution of the LSM/YSZ composite particles was quite important to obtain higher performance of the cathodes.

Acknowledgement

This work was supported financially by Japan Science and Technology Agency (JST). Jintawat Chaichanawong and Wiwut Tanthapanichakoon also received research grant from Thailand Research Fund (TRF) [Grant No. PHD/0135/2546 of Royal Golden Jubilee Ph.D. Program (TRF-RGJ)]

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