

Nanostructured LSM/YSZ cathode for intermediate temperature solid oxide fuel cells[†]

ABE Hiroya*, NAITO Makio**, SATO Kazuyoshi*** and KINOSHITA Toru****

Abstract

We have fabricated a nanostructured $(La_{0.85}Sr_{0.15})_{0.98}MnO_3$ (LSM)/Yttria-stabilized zirconia (YSZ) composite cathode consisting of homogeneously distributed and connected LSM and YSZ grains approximately 100 nm large. The detailed microstructural characterization by transmission electron microscopy with energy-dispersive X-ray spectroscopy revealed that many of the LSM/YSZ junctions in the cathode faced the homogeneously connected pore channels, indicating the formation of a considerable number of triple phase boundaries. The nanostructure exhibited low polarization resistance of 2.82, 1.18, 0.48 and 0.25 $\Omega\cdot cm^2$ at 650, 700, 750 and 800 °C, respectively under air atmosphere. Furthermore, no significant degradation of the cathode performance was observed during operation at 700 °C for 800 h under a constant current density of 0.2 A·cm⁻².

KEY WORDS: (Solid oxide fuel cells), (Cathode), (Co-precipitation), (Nanostructure)

1. Introduction

Solid oxide fuel cells (SOFCs) are efficient energy producers that emit smaller amount of CO₂ than most currently available hydrocarbon-fuel sources. In addition, SOFCs can operate on conventional fuels (e.g., natural gas, gasoline and diesel) and biofuels (biogas, ethanol and biodiesel), in contrast to polymer electrolyte membrane (PEM) fuel cells. With these advantages, SOFCs offer great promise as a clean and efficient process for directly converting chemical energy to electricity while providing significant environmental benefits [1].

Unfortunately, current SOFC technology must operate in the region of 800 C° or more to avoid unacceptably high polarization losses. Likewise, SOFCs require significant time and energy to heat up the units to operating temperature. Therefore, development of SOFCs to provide reasonable power output at lower temperature would make them more cost competitive in conventional technology. One of the biggest breakthroughs in lowering the SOFC operating temperature, while maintaining high power densities, is the development of anode-supported cells. With the advent of this technology, the major polarization loss moved from the electrolyte to the cathode [2].

A promising cathode material for solid oxide fuel cells (SOFCs) has been known to be a strontium-doped lanthanum manganite $(La_xSr_{1-x})_yMnO_3$ (LSM)/yttria-stabilized zirconia (YSZ) composite. Recently, Wang *et al.* reported that the performance of intermediate-temperature SOFC (IT-SOFC) can be significantly improved by reducing grains of the composite cathode from conventional micron size down to 100 nm [3]. However, no nanostructured cathodes have been reported in the literature after a report by Wang *et al.*, suggesting the difficulty of fabrication of homogeneous nanostructured cathodes. To date, most of LSM/YSZ composite cathodes can be described as a physical mixture of separately synthesized LSM and YSZ particles, in which grain size is typically on the order of one to several microns.

The present study aimed to fabricate the nanostructured LSM/YSZ cathode using newly developed LSM/YSZ nanocomposite particles. In our approach, a co-precipitation technique was applied in the perfect colloidal suspension of YSZ (~3 nm), and the co-precipitated precursor consisting of the YSZ nanoparticles and constituent metal carbonates for LSM

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* Associate Professor

** Professor

*** Department of Chemical & Environmental Engineering, Gunma University

**** New Technology Research Laboratory, Sumitomo Osaka Cement Co. Ltd.

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was calcined. Interestingly, the nanocomposite particles significantly suppressed both the grain growth and the pore closure during the sintering, and thereby the LSM/YSZ cathode had a smaller grain size (~100 nm). Herein, we report the detail of material processing and the effects of nanostructure on the performance and durability of SOFCs.

2. Experimental

2.1 Synthesis of LSM/YSZ nanocomposite particles

An aqueous colloidal suspension of YSZ ($\text{Y}_{0.15}\text{Zr}_{0.85}\text{O}_{1.925}$) nanoparticles (Sumitomo Osaka Cement Co. Ltd., Japan) shown in **Fig. 1** was employed as the seed crystals. The average diameter of YSZ was about 3 nm. Firstly, a solution containing $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Sr}(\text{NO}_3)_2$ and $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Kanto Chemicals Co., Japan) with the molar ratio of 0.83: 0.21: 1.09 was prepared. The molar ratio was carefully controlled to provide final composition of LSM as $(\text{La}_{0.85}\text{Sr}_{0.15})_{0.98}\text{MnO}_3$, by considering the residue of Sr^{2+} and Mn^{2+} in the solution. Then the colloidal YSZ suspension was mixed with the metal nitrate solution. Total concentrations of YSZ and the nitrates in the mixed solution were 0.2 M. Even mixing the metal nitrates solution with the suspension, it maintained a high degree of transparency, indicating that the YSZ nanoparticles preserved their well dispersed state even at the high ionic concentration. The solution was added dropwise into 0.4 M of NH_4HCO_3 (Kanto chemicals Co., Japan) aqueous solution to produce the constituent metal carbonates for LSM onto the surface of dispersed YSZ nanoparticles, and to precipitate them simultaneously. The precursor was obtained through washing and subsequent drying of the precipitates. Finally, LSM/YSZ nanocomposite particles were obtained by calcining the precursor.

Phase identification of the precursor and the composite particles was carried out using powder X-ray diffraction (XRD, JDX-3530M, JEOL, Japan) using Cu- α radiation ($\lambda=0.1542$ nm) as the X-ray source. Morphology of the composite particles was characterized by scanning electron microscopy (SEM, ERA-8800FE, Elionix, Japan). Specific surface area was determined by nitrogen gas adsorption based on Brunauer- Emmet- Teller (BET) method.

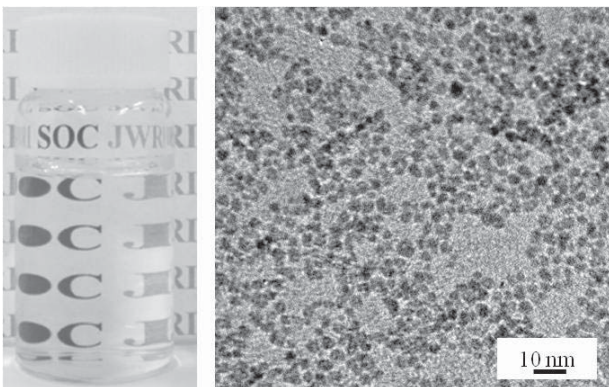


Fig. 1 Optical appearance of the aqueous suspension containing YSZ nanoparticles (left). A TEM image of the YSZ nanoparticles.

2.2 Cell fabrication and electrochemical performance testing

An electrolyte-supported cell was employed for electrochemical performance testing of the cathode. Firstly, fully dense YSZ electrolyte with the thickness of 300 μm and the diameter of 13 mm was fabricated by conventional tape casting, followed by sintering at 1350 $^\circ\text{C}$ for 2 h. Then the anode was fabricated on the electrolyte by screen printing a paste composed of NiO/YSZ nanocomposite particles and polyethylene glycol with the average molecular weight of 400 (Kanto Chemicals Co., Japan), followed by sintering at 1300 $^\circ\text{C}$ for 2 h [4]. LSM/YSZ nanocomposite particles calcined at 1000 $^\circ\text{C}$ were used for cathode fabrication. The paste was fabricated by mixing the ball milled nanocomposite particles and the PEG. Then the cathode was deposited on the electrolyte by screen printing the paste, followed by sintering at 1100 $^\circ\text{C}$ for 2 h.

The setup for the electrochemical performance testing was the same as that in our previous studies [4-5]. Polarization resistance in the LSM/YSZ cathode was examined by electrochemical impedance spectroscopy (EIS) in the temperature range 650 - 800 $^\circ\text{C}$ under dry air atmosphere (oxygen partial pressure of 0.21 atm). The EIS spectra were recorded using a frequency response analyzer with a potentiostat (Parstat 2263, Princeton Applied Research, TN) in the frequency range 0.1 - 10^5 Hz, under open circuit voltage (OCV) with an applied amplitude of 50 mV. Microstructure of the LSM/YSZ cathode was observed by the SEM.

Symmetric cells were fabricated for the durability test of the cathode in the following manner. An LSM/YSZ layer 6 mm in diameter was deposited symmetrically on both sides of the YSZ disk. Platinum paste 2 mm in diameter was applied onto the counter-electrode side of the YSZ disk and sintered at 900 $^\circ\text{C}$ to create a reference electrode. The reference electrode was placed 3 mm away from the counter electrode. The durability of the cathodes was tested at 700 $^\circ\text{C}$ under air flow of 30 l/h. The tests were conducted for up to 800 h with a constant current density of 0.2 $\text{A}\cdot\text{cm}^{-2}$ using a three electrodes-four leads geometry.

3. Results and discussion

Figure 2 shows XRD patterns of the composite particles calcined between 700 and 1200 $^\circ\text{C}$. Only the broad peaks correspond to YSZ phase were observed in the precursor. The constituent carbonates for LSM were presented as noncrystalline phase (not shown here). The small peaks correspond to LSM appeared at 700 $^\circ\text{C}$. When calcined at 1000 $^\circ\text{C}$, the crystalline size of LSM and YSZ was estimated to be only 23 and 24 nm, respectively from full width of half maxima (FWHM) on LSM (220) ($2\theta=46.68^\circ$) and YSZ (111) ($2\theta=30.10^\circ$) peaks using Scherrer's formula. Any peaks correspond to undesirable resistive by-products such as $\text{La}_2\text{Zr}_2\text{O}_7$ (LZO) were not observed even in the composite calcined at 1200 $^\circ\text{C}$. The results indicated that the constituent elements of LSM were uniformly distributed in the precursor and the composite particles. If not uniformly distributed, LZO phase will be formed at the interface between the lanthanum rich region

and YSZ [6]. It was found that the very fine and homogeneous LSM/YSZ nanocomposite particles were successfully fabricated by the simple co-precipitation method using the colloidal suspensions of very fine YSZ nanoparticles (3 nm).

Figure 3 (a) shows cross sectional view of the LSM/YSZ cathode. The cathode layer had uniform microstructure consisting of three dimensionally connecting solid stems and pore channels. Good adhesion of the interfaces even at the relatively low sintering temperature can be due to high sinterability of the nano-sized particles, while the sintering temperature of about 1200 °C is needed for the conventional LSM/YSZ particles. Suppressed pore closure even at the high sinterability of the nanocomposites can be ascribed to the smaller grains than pores [7,8]. As shown in Fig.3 (b), the solid stems consisted of grains with the size of approximately 100 nm. Obviously, the formation of the nanostructured LSM/YSZ cathode can be attributed to the homogeneous LSM/YSZ nanocomposite particles made by the present co-precipitation method. The nanostructured cathode was expected to be broadened TPB.

Figure 4 shows EIS spectra of the cathode measured in the range 650- 800 °C under air atmosphere. The polarization resistance (R_p) with respect to ORR, represented as the difference between high and low frequency intercepts of the arc with the real axis was 2.82, 1.18, 0.48 and 0.25 $\Omega \cdot \text{cm}^2$ at 650, 700, 750 and 800 °C, respectively. The present nanostructured LSM/YSZ cathode had a clear advantage in performance at the intermediate temperature range compared with the coarser cathodes reported in the previous studies [9-12].

Figure 5 shows the polarization of a nanostructured LSM/YSZ cathode as a function of operation time measured using the symmetric cell at 700 °C under a current load of 0.2 $\text{A} \cdot \text{cm}^{-2}$. The cathode exhibited good long-term performance stability under the test condition. The polarization after 800 h was almost the same as at the beginning, even though the presence of some minor perturbations which probably due to some changes in the experimental conditions such as local temperature and humidity of supplied air. Liu *et al.* suggest that the formation of zirconates at the cathode/electrolyte interface was responsible for the performance degradation of the cathode, and their formation can be related to the chemical instability of LSM under a current load [13]. They estimate the risk of zirconate formation as a function of oxygen partial pressure at the interface ($p(\text{O}_2, \text{Interface})$) based on a thermodynamic model. The value of $p(\text{O}_2, \text{Interface})$ during operation can be estimated by the Nernst equation as a function of cathodic polarization and temperature [13]. Polarization of the present nanostructured LSM/YSZ cathode extracted from the total polarization of the symmetric cell using the current interruption technique [14, 15] was 0.17 V at the initial stage of testing. The calculated $p(\text{O}_2, \text{Interface})$ was 6.30×10^{-5} atm, and is high enough to avoid the formation of zirconates at 700 °C [13].

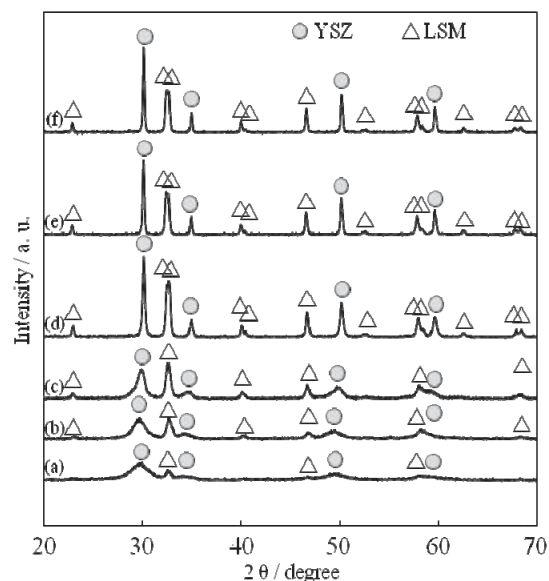


Fig. 2 XRD patterns of the composite particles calcined at (a)700, (b)800, (c)900, (d) 1000, (e) 1100 and (f) 1200 °C.

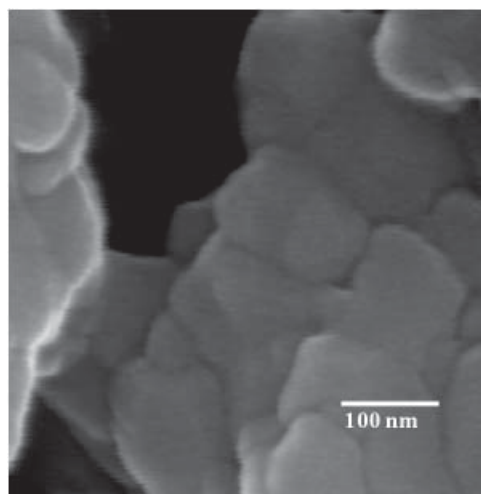
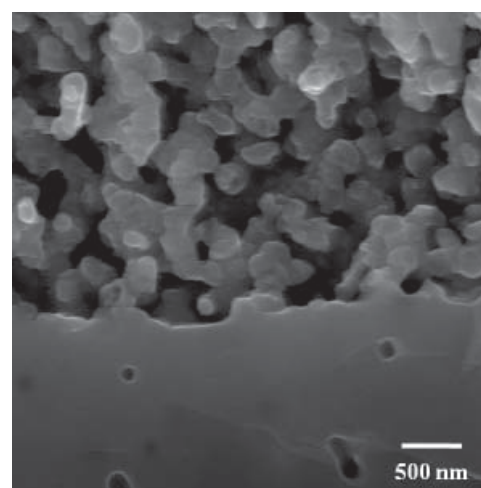


Fig. 3 SEM micrographs of (a) the cathode/electrolyte interface and (b) the magnified image of a solid stem.

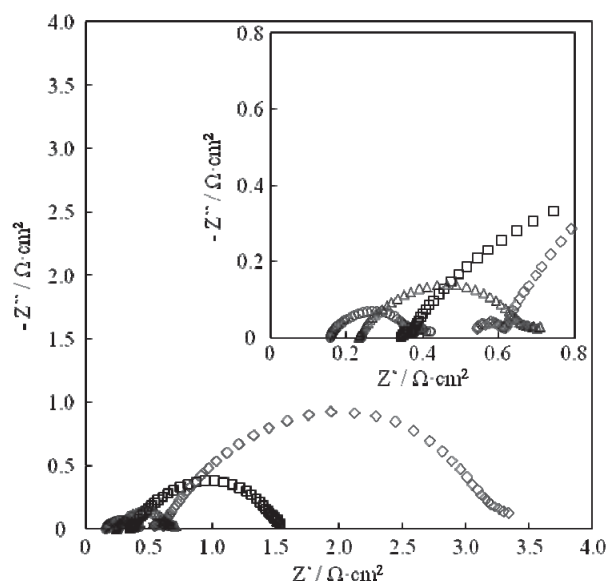


Fig. 4 EIS spectra for ORR measured at (\diamond) 650, (\square) 700, (\triangle) 750 and (\circ) 800 °C at OCV under air atmosphere. Inset shows the magnified view of the spectra.

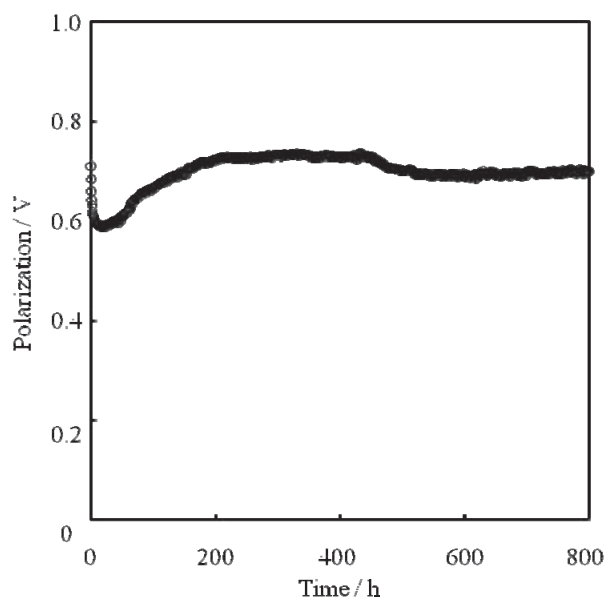


Fig. 5 Polarization of the cathode vs time under a constant current density of $0.2 \text{ A}\cdot\text{cm}^{-2}$ at 700 °C.

4. Conclusions

We demonstrated that the homogeneous nanostructured LSM/YSZ cathode can be fabricated through the synthesis of their nanocomposite particles by a newly developed co-precipitation method using a colloidal suspension of YSZ nanoparticles. Uniformly distributed nano-sized LSM and YSZ phases in the composite particles significantly retarded each other's grain growth and pore closure during the sintering. In addition, uniform elemental distributions

in the precursor and the composite particles suppressed the formation of undesirable insulating by-products such as LZO at high temperature. The nanostructured cathode exhibited high catalytic activity even at the intermediate temperature range due to the formation of broad TPB. Such a high-performance nanostructured cathode can enhance the long-term performance stability by suppressing zirconate formation, crack extension and grain growth during operation. The present nanostructured LSM/YSZ is a promising cathode material for IT-SOFCs.

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