Novel co-precipitation derived nanostructured LSM–YSZ cathode for intermediate temperature solid oxide fuel cells

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Strontium doped lanthanum manganite ((La$_{1-x}$Sr$_x$)$_{0.85}$MnO$_3$; LSM)/yttria-stabilized zirconia (YSZ) nanocomposite particles were synthesized through a novel co-precipitation method using YSZ nanoparticles with the average size of 3 nm as seed crystals. Phase evolution studies indicated that crystalline LSM/YSZ phases were obtained by calcining the co-precipitated precursor above 700°C. The nanocomposite particles calcined at 1000°C were screen printed on YSZ dense electrolytes and then sintered at 1100°C for cathode fabrication. The resulting cathode had a uniform porous structure consisting of fine grains ~100 nm in size, and exhibited low polarization resistance of 2.82, 1.18, 0.48 and 0.25 Ωcm$^2$ at 650, 700, 750 and 800°C, respectively under air atmosphere. These results indicated that the present nanostructured cathode may be applicable for intermediate temperature solid oxide fuel cells.

Key-words : Solid oxide fuel cells, Cathode, Co-precipitation, LSM, YSZ, Nanocomposites, Oxygen reduction, Electrochemical impedance spectroscopy

1. Introduction

Solid oxide fuel cell (SOFC) is one of the promising power sources of the 21st century because of its highly efficient and environmentally benign power generation. The cell configuration, yttria-stabilized zirconia (YSZ) for the electrolyte, Ni/YSZ for the anode and (La$_{1-x}$Sr$_x$)$_{0.85}$MnO$_3$ (LSM)/YSZ as the cathode have been most widely used. Recent research and development on SOFCs have been directing to reduce the operation temperature, aiming cost reduction and durability enhancement of the cells and the systems. However, reduced operation temperature often causes significant reduction of the power generation efficiency due to increased internal resistances related to ionic conduction in electrolyte and electrochemical oxidation/reduction reactions on both electrodes. Particularly, polarization resistance with respect to oxygen reduction reaction (ORR) in the LSM/YSZ cathode is the bottleneck of the performance in state-of-the-art SOFCs.

Previous studies indicated that the composite microstructure plays the key role to reduce the polarization resistance of the cathode because the ORR occurs in the vicinity of the triple phase boundary (TPB) where LSM, YSZ and pore phases meet. Thus, an increase of the TPB within the limited electrode volume is of primal importance in order to enhance the cathode performance. Theoretical calculations have shown that fine grains can lead to significant reduction of the polarization resistance thereby, a doubled current may be obtained by reducing the grain size from 1.0 to 0.25 μm when the porosity was assumed to be the same. Based on practical as well as theoretical studies, nanostructured cathode with sufficient porosity could drastically reduce the polarization resistance.

 Virtually all LSM/YSZ composite cathodes to date can be described as a physical mixture of separately synthesized LSM and YSZ particles. However achievable grain size of the cathode is typically above sub-microns. Fukui et al., demonstrated that the LSM/YSZ cathode with the grain size of about 100 nm can be fabricated using their nanocomposite particles synthesized by spray pyrolysis. Although chemical synthesis routes such as gel combustion and co-precipitation methods are better suited for large scale synthesis of the nanocomposite particles, resulting grain size was still a few hundred nanometers.

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 colloidal suspension of YSZ (~3 nm), and the co-precipitated precursor consisting of the YSZ nanoparticles and constituent metal carbonates for LSM 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 with smaller grain size (~100 nm). Herein, we report the detail of the material processing, microstructure of the present LSM/YSZ cathode and its electrochemical performance.

2. Experimental procedure

2.1 Synthesis of LSM/YSZ nanocomposite particles

An aqueous colloidal suspension of YSZ (Y$_{0.15}$Zr$_{0.85}$O$_{1.925}$) nanoparticles (Sumitomo Osaka Cement Co., Ltd.) shown in Fig. 1 was employed as seed crystals. The dynamic light scattering method revealed that the nanoparticles have the average diameter of 3 nm and narrow size distribution, resulting in a highly transparent appearance due to their negligible visible light scattering. Figure 2 shows the schematic synthesis procedure of the LSM/YSZ nanocomposite particles. The mass ratio of LSM and YSZ was set to be 1:1 according to previous studies. Firstly, a solution containing La(NO$_3$)$_3$, Sr(NO$_3$)$_2$, Mn(NO$_3$)$_2$ and 6H$_2$O (Kanto Chemical Co., Inc.) with the molar ratio

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of 0.83:0.21:1.09 was prepared. The molar ratio was carefully controlled to provide a final composition of LSM as \((\text{La}_{0.85}\text{Sr}_{0.15})_0.98\text{MnO}_3\), with a considering residue of \(\text{Sr}^{2+}\) and \(\text{Mn}^{2+}\) 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 nitrate solution with the suspension, it maintained a high degree of transparency, indicating that the YSZ nanoparticles preserved their well dispersed state even under the high ionic concentration. The solution was added dropwise into 0.4 M of \(\text{NH}_4\text{HCO}_3\) (Kanto Chemical Co., Inc.) aqueous solution to nucleate the constituent metal carbonates for LSM onto the surface of dispersed YSZ nanoparticles, and to precipitate them simultaneously. The molar ratio of \(\text{NH}_4\text{HCO}_3\) and cations for LSM was set to be 1.5:1. During the co-precipitation processing, \(\text{NH}_3\) solution (Wako Pure Chemical Industries, Ltd.) was added simultaneously into the \(\text{NH}_4\text{HCO}_3\) solution to keep pH 8. The precursor was obtained through washing and subsequent drying of the precipitates. Finally, LSM/YSZ nanocomposite particles were obtained by calcining the precursor.

Thermal decomposition behavior of the precursor was examined by thermogravimetry - differential thermal analysis (TG–DTA, EXSTAR 6200, SII NanoTechnology Inc.) in the temperature range 25–1000°C with heating rate of 5°C/min under air flow of 100 ml·min\(^{-1}\). Phase identification of the precursor and the composite particles was carried out using powder X-ray diffraction (XRD, JDX–3530M, JEOL Ltd.) using Cu K\(\alpha\) radiation (\(\lambda = 0.1542 \text{ nm}\)) as the X-ray source. Morphology of the composite particles was characterized by scanning electron microscopy (SEM, ERA~8800FE, Elionix, Japan). Specific surface area of them was determined by nitrogen gas adsorption based on the Brunauer–Emmett–Teller (BET) method. Composition of the composite particles was determined by inductively coupled plasma-atomic emission spectroscopy (ICP–AES, SPS–5100, SII NanoTechnology Inc.).

2.2 Cell fabrication and electrochemical performance testing

An electrolyte-supported cell was employed for electrochemical performance testing. 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°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 Chemical Co., Inc.), followed by sintering at 1300°C for 2 h.\(^{10}\) LSM/YSZ nanocomposite particles calcined at 1000°C was 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°C for 2 h.

The setup for the electrochemical performance testing was the same as that in our previous studies.\(^{10,11}\) Polarity resistance for ORR on the LSM/YSZ cathode was examined by electrochemical impedance spectroscopy (EIS) in the temperature range 650–800°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 0.1–105 Hz, under open circuit voltage (OCV) with an applied amplitude of 50 mV. Microstructure of the LSM/YSZ cathode was observed by the SEM.

3. Results and discussion

It was confirmed that the composition of LSM was \((\text{La}_{0.85}\text{Sr}_{0.15})_0.98\text{MnO}_3\), and its mass fraction in the LSM/YSZ nanocomposite particles was 0.5 by ICP–AES analysis. These results evidenced that highly dispersed YSZ nanoparticles can be co-precipitated with the carbonates for LSM with quite high yield.

Figure 3 shows TG–DTA curves of the precursor. Thermal decomposition (weight loss) of the precursor was almost finished below 700°C. The weight loss below 200°C with a broad endothermic peak corresponds to the evaporation of adsorbed water.\(^{25}\) Although subsequent multiple events appeared at 215°C and 330°C with exothermic peaks and at 510°C with distinctive weight loss involving dehydration and decarbonation,\(^{25}\) the sample weight continuously decreased with the increasing tempera-
ture. The weight loss behavior suggested that these thermal events occurred simultaneously over the temperature range.

Figure 4 shows XRD patterns of the precursor and the composite particles calcined between 700 and 1200°C. Only the broad peaks which correspond to the YSZ phase were observed in the precursor. The result indicated that the constituent carbonates for LSM were presented as a noncrystalline phase. The small peaks which correspond to LSM appeared at 700°C. When calcined at 1000°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 (2θ = 46.68°) and YSZ (111) (2θ = 30.10°) peaks using Sherrer’s formula. The tiny crystalline sizes suggested that LSM and YSZ phases were uniformly distributed in the composite and the co-existing phases significantly suppressed each other’s grain growth. Any peaks which correspond to undesirable resistive by-products such as La2Zr2O7 (LZO) were not observed even in the composite calcined at 1200°C. The results evidenced that the constituent elements of LSM was uniformly distributed in the precursor and the composite particles. If not uniformly distributed, LZO phase will surely formed at the interface between the lanthanum rich region and YSZ. Thus, it was demonstrated that the very fine and homogeneous LSM/YSZ nanocomposite particles were successfully fabricated by the present co-precipitation method using the colloidal suspensions of YSZ nanoparticles (3 nm).

Figure 5 shows morphological evolution of the composite particles as a function of calcination temperature. Although the particle sizes gradually increased with increasing the calcination temperature, it did not exceed 100 nm even in the composite calcined at 1000°C. The fine grain size could be attributed to the suppressed grain growth by the uniformly distributed LSM and YSZ phases as mentioned above. Also, pore coarsening with an increasing calcination temperature was clearly observed. The mass fraction of both LSM (m_{LSM}) and YSZ (m_{YSZ}) was 0.5 in the present composites as mentioned above. Thus \( \rho \) can be calculated as 6.13 kg·m⁻³. The equivalent diameter was calculated to be 11, 17, 34 and 148 nm for the composite particles calcined at 700, 800, 900 and 1000°C, respectively. Good agreement of the equivalent diameter with the apparent size in the SEM images indicated that the particles well dispersed without significant densification in the range 700–900°C. The larger estimated size than the apparent one in the composite calcined at 1000°C could be attributed to significant neck growth between the particles as seen in Fig. 5(d).

Figure 6(a) shows the cross-sectional view of the LSM/YSZ cathode. The cathode layer had uniform microstructure consist-
ing of three dimensionally connecting solid stems and pore channels. Fig. 6(b) shows magnified image of the cathode/electrolyte interface. 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.17) A suppressed pore closure even though the high sinterability of the nanocomposites can be ascribed to the smaller grains than pores.18),19) As shown in Fig. 6(c), the solid stems consisted of grains with the size of approximately 100 nm. To our knowledge, LSM/YSZ composite cathodes with such small grain sizes have not been fabricated through the chemical route. 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 and consequently have good ORR properties.

Figure 7 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 real axis was 2.82, 1.18, 0.48 and 0.25 $\Omega$·cm$^2$ at 650, 700, 750 and 800°C, respectively. The present nanostructured LSM/YSZ cathode had clear advantage in the performance at the intermediate temperature range compared with the coarser cathodes reported in the previous studies.3,9),20),21) The similar $E_a$ suggested that the high performance of the present cathode can be attributed to the formation of broad TPB. A more detailed investigation on the rare limiting steps for ORR in the cathode are needed for further performance enhancement. It will be reported in future work.

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 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 temperatures. The nanostructured cathode exhibited high catalytic activity for ORR even at the intermediate temperature range due to the formation of broad TPB.

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