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Journal of the European Ceramic Society 24 (2004) 1359–1363

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Cathodic properties of $La_{0.9}Sr_{0.1}MnO_3$ electrode for fuel cells based on $LaGaO_3$ solid electrolyte

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Abstract

Since $LaMnO_3$ cathode shows good electrode properties for fuel cells employing YSZ (Yttria Stabilized Zirconia) electrolyte, it is interesting to see if $LaMnO_3$ can also be used as an electrode material for $LaGaO_3$- based fuel cells. In this study, the cathodic properties of $La_{0.9}Sr_{0.1}MnO_3$ (LSM) and LSM mixed with $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_3$ (LSGM) were studied. When LSM was mixed with LSGM for electrode, the resulting mixture cathode showed the lower overpotential than that for LSM. It also showed the smaller particle size than LSM in addition to the expected mixed conductivity. The cathodic overpotential of LSM was much higher on LSGM electrolyte than that on YSZ electrolyte due possibly to the insulating phase produced by the reaction between LSM and LSGM. With varying cell preparation condition, it was shown that the thickness of reaction layer can be controlled, and the electrode overpotential can be reduced.

Keywords: Fuel cell cathode; LSGM; LSM; Mixed conductor; Overpotential

1. Introduction

Solid Oxide Fuel Cells (SOFCs) are promising for the generation of electricity with little environmental pollution. Commercially available SOFCs employ YSZ as an electrolyte and require operating temperature ~1000 °C to minimize ohmic loss.[1] Since lowering the operating temperature has many advantages, such as broad choice of cheap interconnect materials and long term stability of cell components, etc., much effort has thus been concentrated on finding electrolyte material with higher ion conductivity than YSZ. LSGM is a promising material that serves such need.[2]

Many researchers examined perovskite materials[3–5] for cathodes for LSGM electrolyte. LSM[3], LSC ($La_{0.6}Sr_{0.4}CoO_3$)[4], and LSGN ($La_{0.9}Sr_{0.1}Ga_{0.5}Ni_{0.5}O_3$)[5] cathodes were tested on LSGM electrolyte. Although LSM cathode shows good electrode properties for fuel cells employing YSZ electrolyte,[6] it was not promising for LSGM electrolyte.[3] However, the electrode properties of LSM on LSGM electrolyte have not been intensively investigated, and it is not yet clear why LSM cathode has high overpotential on LSGM electrolyte. Since mixed electronic and ionic conduction and optimum microstructure are needed for good electrode performance, we previously studied[7] the phase formation in $(1-x)$LSGM$-x$LSM (or $La_{0.9}Sr_{0.1}(Ga_{0.8}Mg_{0.2})_{1-x}Mn_xO_3$) system. It was found that the two-phase mixture was formed in most composition ranges and the mixed conductivity was predicted.

In this study, the cathodic properties of LSM and the $(1-x)$LSGM$-x$LSM mixture electrodes for fuel cells employing LSGM electrolyte were studied. The effect of microstructure, in addition to the composition, on the overpotential was studied to find a possible method to use LSM electrode on LSGM electrolyte.

2. Experimental

Stoichiometric amount of La_2O_3 (99.99%, Strem Chemicals, USA), $SrCO_3$ (99.9%, High Purity Chemicals, Japan), Ga_2O_3 (99.9%, High Purity Chemicals), MgO (99.9%, High Purity Chemicals), and Mn_2O_3

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0955-2219/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/S0955-2219(03)00569-7

(99.9%, High Purity Chemicals) powders were mixed to prepare $(1-x)$LSGM-xLSM compositions with x varying between 0.2 and 1. With this notation, B-site $Ga_{0.8}Mg_{0.2}$ is progressively replaced with Mn as x increases. We may also write it as $La_{0.9}Sr_{0.1}(Ga_{0.8}Mg_{0.2})_{1-x}Mn_xO_3$ (LSGMM). The powder mixtures were ball-milled with zirconia balls in distilled water for 12 h and dried in air at 80 °C for few hours. To control particle size, the powder mixtures were calcined at 900 °C for 3 h or 1200 °C for 6 h.

The calcined powders were mixed with an organic solution of α-terpineol and ethylene cellulose in weight ratio of 10:1. The viscosity of the solution was controlled by adding di-ethylene glycol butyl ether. The mixing ratio between the calcined powder and the organic solution was 1:1 by volume for all electrodes. The resulting slurry was screen-printed on LSGM electrolyte and heat treated or sintered at 1000–1300 °C in air for 2 h. Three-electrode configuration cells were fabricated; the working electrode is a cathode under investigation and the counter and the reference electrodes are platinum. Platinum paste (Engelhard No 6926, USA) was heated for 1 h at 1000 °C after painting. Pt mesh (Aldrich 52 mesh, USA), as a current collector, was bonded at 1000 °C for 1 h to three electrodes.

The ohmic- and the over-potential values were measured by using a current interruption device (Doosung Induction, model DSI-10, Korea), a current source (Solartron, model SI 1287, UK) and digitizing oscilloscope (Tektronix, model TDS 3032, USA). The electrochemical measurement was performed between 800 and 900 °C in oxygen atmosphere. Microstructure observation and EDS analysis were performed by a field-emission scanning electron microscope (JEOL, model 6330F, Japan).

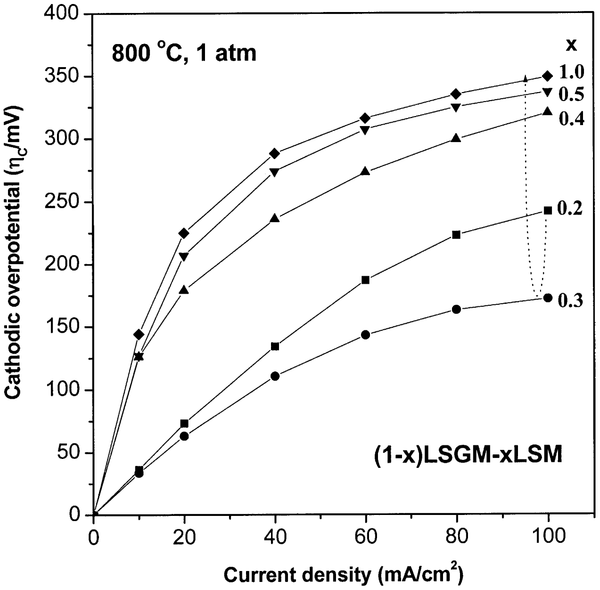

Fig. 1. The cathodic overpotential values of various electrode compositions measured at 800 °C in oxygen atmosphere. Electrode powders were calcined at 1200 °C for 6 h and the screen-printed electrodes were sintered at 1300 °C for 2 h.

3. Results and discussion

The cathodic overpotential of various electrode compositions was measured at 800 °C in oxygen atmosphere (Fig. 1). The powders were calcined at 1200 °C in air for 6 h and the screen-printed electrodes were heat-treated or sintered at 1300 °C in air for 2 h. The cathodic overpotential value of LSM ($x=1.0$) electrode is ~350 mV at 100 mA/cm^2, coinciding with literature data.[3] As the content of ion conducting LSGM increases (or decreasing x), the overpotential markedly decreases and shows a minimum value of 172 mV at $x=0.3$. The dashed arrow indicates the direction of cathodic overpotential change. In our previous study[7], the mixture of hexagonal and orthorhombic perovskite phases was identified for $x=0.3$ and the mixed ionic and electronic conduction was also predicted. Since the particle size for $x=0.3$ composition was much smaller than that for LSM ($x=1.0$), both the mixed ionic and electronic conduction and the small particle size were two important factors in reducing cathodic overpotential.

Fig. 2 shows cathodic overpotential values of LSM ($x=1.0$) electrodes with different cell preparation conditions. As the sintering temperature decreases from 1300 to 1000 °C, the overpotential markedly decreases, however, the decrease was small for 1000 °C-sintered sample. The observed temperature dependence of the cathodic overpotential is due to both the compositional and the microstructural effects as explained in the following paragraphs.

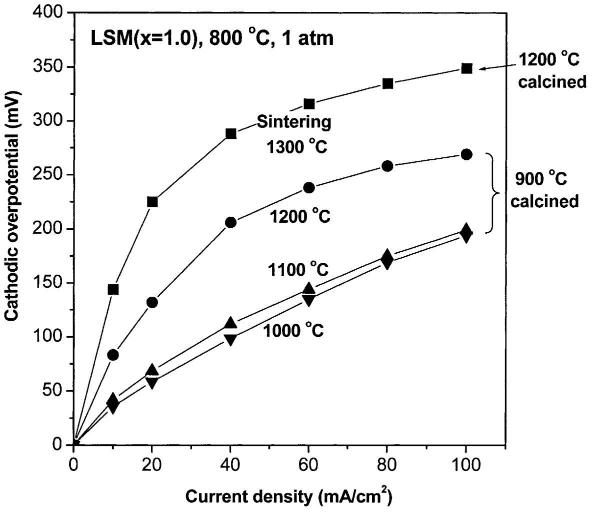

Fig. 2. Cathodic overpotential values of LSM electrodes with different cell preparation conditions that were measured at 800 °C in oxygen atmosphere.

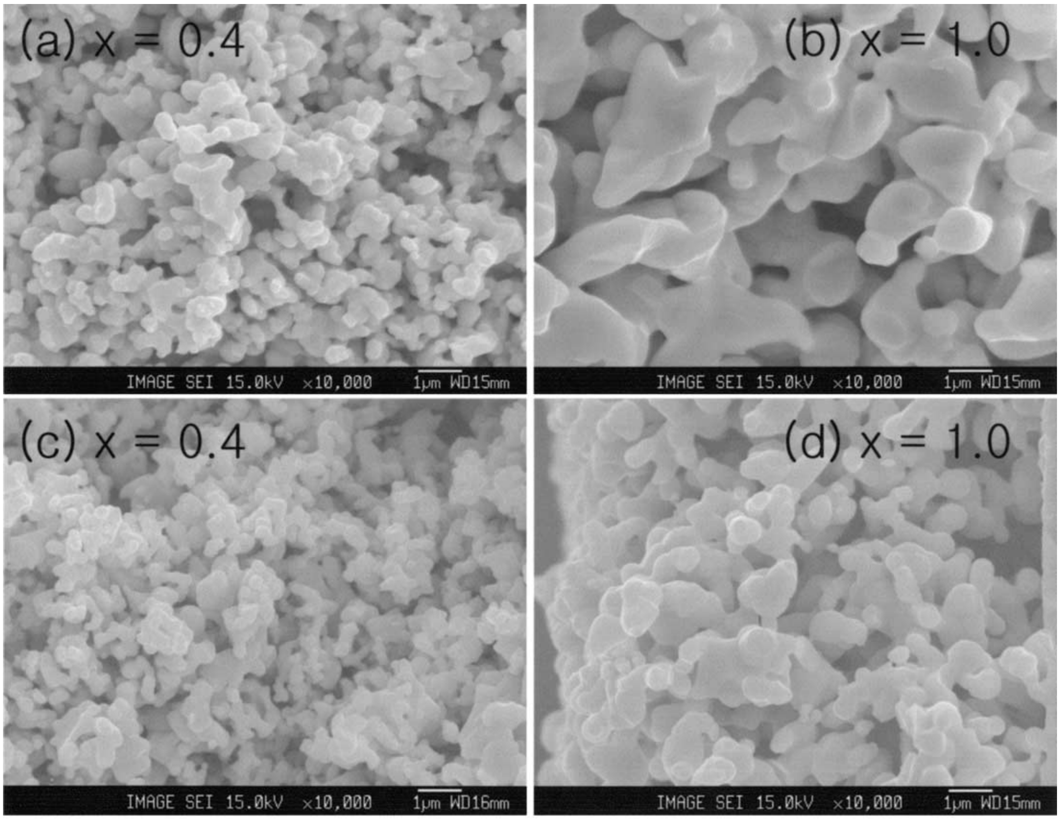

Fig. 3. Microstructures of electrode compositions for (a) $x = 0.4$ and (b) $x = 1.0$ sintered at 1300 °C (calcined at 1200 °C) and for (c) $x = 0.4$ and (d) $x = 1.0$ sintered at 1200 °C (calcined at 900 °C). All four figures have the same scales. (bar = 1 μm).

LSM electrode shows superior electrode property (i.e., low overpotential) on YSZ electrolyte to that on LSGM electrolyte. Large overpotential of LSM on LSGM is possibly due to the insulating phase formed by the reaction between LSM and LSGM. As shown in the previous report,[7] the Mn added in LSGM decreases the conductivity of LSGM and thus the resistive LSGM-LSM composite phases are formed. However, it was shown in Fig. 2 that the overpotential value of LSM can be reduced by controlling the cell preparation condition. If we apply this strategy for $x = 0.3$ composition, the overpotential values shown in Fig. 1 can be further reduced.

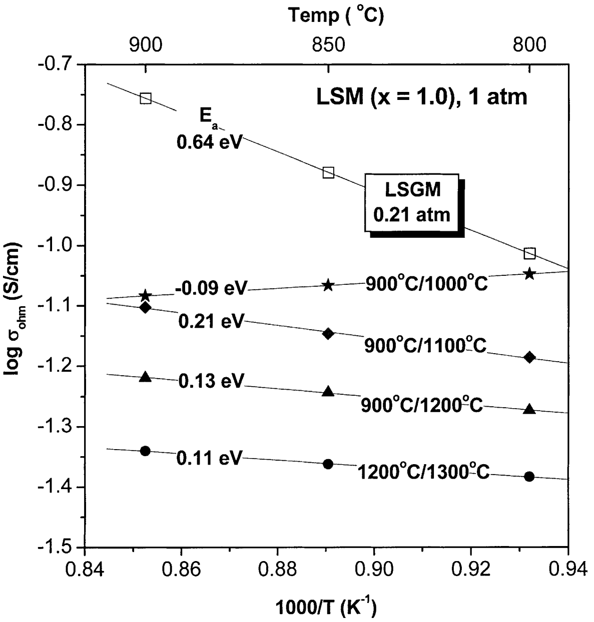

Fig. 4. The temperature dependence of ohmic conductivities in oxygen atmosphere for $x = 1.0$ samples prepared at different temperatures.

Microstructures of the electrodes for (a) $x = 0.4$ and (b) $x = 1.0$ sintered at 1300 °C (calcined at 900 °C) are shown in Fig. 3 and those sintered at 1200 °C (calcined at 900 °C) are shown in Fig. 3(c) and (d). $x = 0.4$ shows the smaller particle size than $x = 1.0$ whether it is sintered at 1300 or 1200 °C. The particle size is about 0.3–0.5 μm for $x = 0.4$ (Fig. 3a) and 1–3 μm for $x = 1.0$ (Fig. 3b). Although the particle size decreases only slightly with decreasing sintering temperature for $x = 0.4$ (Fig. 3c), that for $x = 1.0$ (Fig. 3d) decreases markedly. This large decrease in particle size for LSM electrode is an important reason for the rapid decrease in cathodic overpotential with decreasing temperature shown in Fig. 2.

Fig. 4 shows the temperature dependence of the ohmic conductivity (σ_{ohm}) of half-cell. The ohmic conductivity is defined as:

$$\sigma_{\text{ohm}} = \frac{1}{R_{\text{ohm}}} \cdot \frac{t}{A} \qquad (1)$$

where R_{ohm} is the ohmic resistance of cell determined from current-interruption measurement, t is the electrolyte thickness, and A is the electrode area.

The open square symbol (□) represents the conductivity measured by 4-probe d.c. method of LSGM.[7] The solid symbols represent those measured from current-interruption method. The thickness of electrolyte was measured from SEM image. The numbers on the lines denote calcination and sintering temperatures. For example, 1200/1300 °C denotes that the LSM electrode powder was calcined at 1200 °C and the screen-printed electrode was sintered at 1300 °C. All ohmic conductivities determined from current-interruption measurement (solid symbols) are lower than that of dense LSGM electrolyte (open symbol) and the activation energies are much smaller. The difference in magnitude of conductivity increases as the sintering temperature increases. This observation is explained by the formation of insulation phase after the reaction between LSM electrode and LSGM electrolyte. The thickness of reaction layer increases with sintering temperature explaining the increasing cathodic overpotential of the unit-cell shown in Fig. 2. The increase in the thickness of the reaction layer not only decreases the ohmic conductivity but also degrades the electrode performance. The low activation energy for the ohmic conductivity is due mostly to the lower activation energy of the reaction layer than that for LSGM[7]. In other words, the contribution of the reaction layer to the ohmic resistance is large enough to change the ohmic conductivity.

In all cells except the cell sintered at 1000 °C, the ohmic conductivity increases as the measurement temperature increases, however, the activation energy decreases with increasing sintering temperature. This means that the contribution of reaction layer becomes larger in the decrease of ohmic conductivity. On the other hand, for the cells sintered at 1000 °C, the ohmic

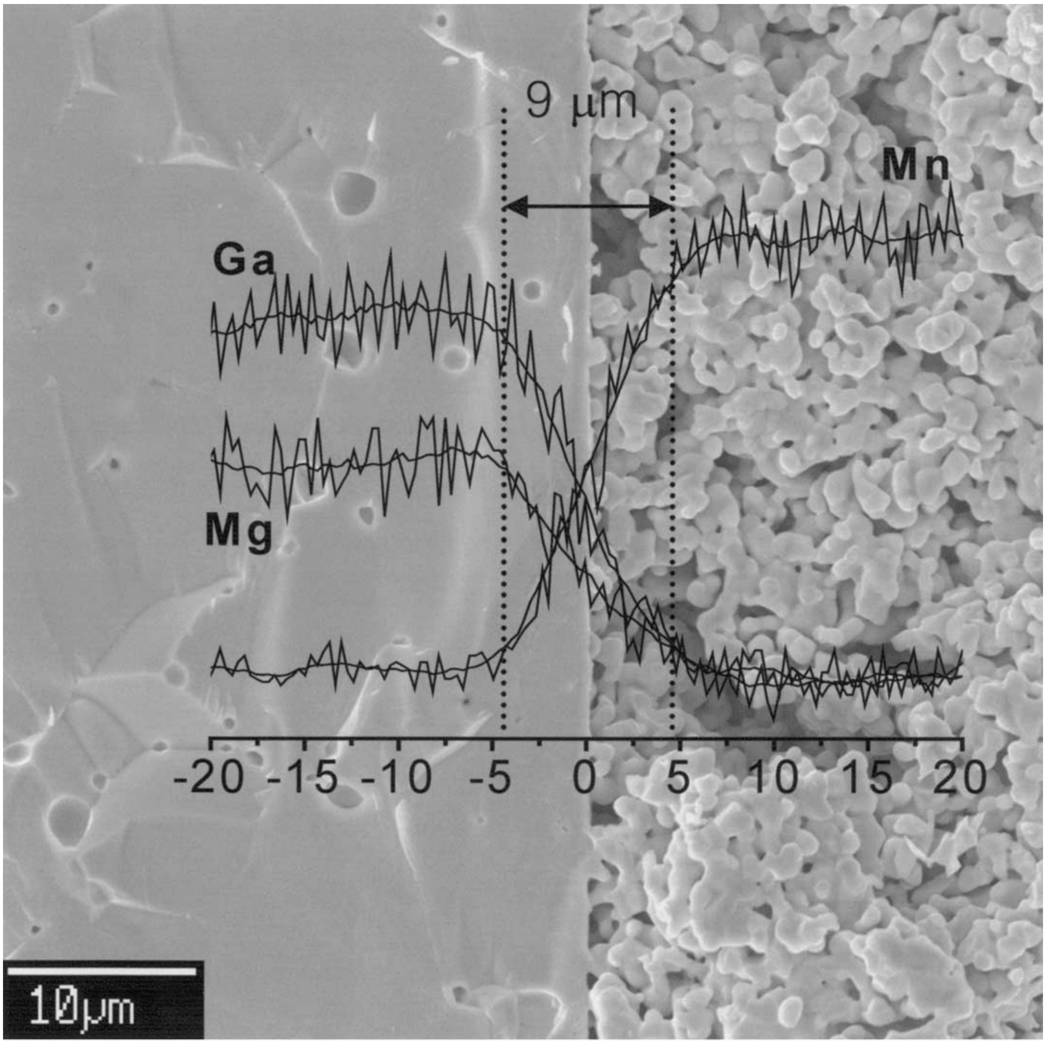

Fig. 5. EDS line profiles of Mn, Ga, and Mg of cells as a function of distance from the interface between LSM and LSGM. The powder was calcined at 1200 °C for 6 h and the screen-printed electrode was sintered at 1300 °C for 2 h.

conductivity decreases as the measurement temperature increases. Since the activation energy closer to that of LSGM is expected for 1000 °C sintered sample due to the low temperature sintering, this observation was not expected. This is better explained by assuming that the phase formed between electrode and electrolyte continues to form during the measurement. Since the sintering temperature was not much higher than measurement temperature, the thickness of the reaction layer continues to increase as the measurement temperature increases from 800 to 900 °C. For samples sintered at higher temperature, the reaction layer mostly formed during sintering after screen-printing.

To prove the formation of the reaction layer, we obtained the EDS (Energy Dispersive Spectroscopy) line profiles from the SEM images. The EDS line profiles of the cell sintered at 1300 °C are shown in Fig. 5. Since the content of La and Sr is the same in both electrode and electrolyte, the signals of Mn, Ga, and Mg are only demonstrated. To minimize the fluctuation due to the porous electrode morphology, five different line profiles were averaged. While the thickness of the transition region of B-site elements in the cell sintered at 1200 °C is about 6 μm (not shown), that in the cell sintered at 1300 °C is about 9 μm (Fig. 5). This difference in the thickness of transition region explains the difference in the ohmic conductivity shown in Fig. 4. Similar experimental report[8] showed that the thickness of the reaction layer formed between LSM and LSGM was 20 μm when it was sintered at 1470 °C for 36 h. The thickness of transition region due to the Ni diffusion from LSGN electrode to LSGM electrolyte, sintered at 1400 °C for 2 h, was reported[5] as 5 μm, while that of Co from LSC electrode, sintered at 1050 °C for 2 h, to LSGM electrolyte[8] was 25 μm. The conductivity of the transition region can be estimated from the conductivity[7] and the thickness of LSGM and the thickness of transition region. Although the conductivity of transition region changes with distance, assuming the conductivity of transition region is uniform, for simplicity, the conductivity is 2.5×10^{-3} S/cm at 800 °C for the cell sintered at 1300 °C. The lowest conductivity[7] at 800 °C in dense $(1-x)$LSGM$-x$LSM system is about 4.2×10^{-3} S/cm at $x=0.16$. The lower conductivity of transition region than the reported conductivity is due to the porous morphology of electrode.

4. Conclusions

When LSM was mixed with LSGM, the electrode shows better performance than single-phase LSM as a cathode for LSGM electrolyte. This is due to the decreased particle size in addition to the expected mixed electronic and ionic conduction of composite electrode. The reduction of sintering temperature decreases the thickness of the reaction layer formed between LSM and LSGM. The further enhancement of electrode performance can be expected with the controlled calcination and sintering condition for the composite electrode, for example, for $x=0.3$.

Acknowledgements

This work was supported by the BK21 Project. The authors thank to Doosung Induction Co., Korea for the support of electronic switch for the electrochemical measurement.

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