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Cathodic overpotential of $La_{0.6}Sr_{0.4}CoO_3$ and its composite cathodes LSC–LSGM on $LaGaO_3$-based fuel cell

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Abstract

$La_{0.6}Sr_{0.4}CoO_3$ (LSC) and its composites with $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_3$ (LSGM) were tested as the possible cathode on LSGM electrolyte. The cathodic performance of LSC–LSGM composite electrodes did not improve from that of single-phase LSC electrode unlike $La_{0.9}Sr_{0.1}MnO_3$ (LSM)–LSGM system shown in a previous study. One reason is little reduction in particle size for the composite electrodes. The other reason is that the mixed (electronic and ionic) conductivity of composite cathodes is not increasing from that of single-phase LSC since LSC has high mixed conductivity.

Keywords: Cathodic overpotential; Electrical conductivity; Perovskites; Composites; Fuel cells

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1. Introduction

Solid oxide fuel cells (SOFCs) offer a low-pollution technology to generate electricity with high efficiency. Conventional SOFCs often use yttria-stabilized-zirconia (YSZ) which operates at 900–1000 °C, and the high operating temperature causes many problems. Current efforts are aimed at reducing the operating temperature to 800 °C or less. One approach is using a new electrolyte material that shows a higher oxygen-ion conductivity than YSZ at a low temperature, e.g., below 800 °C. It has been reported recently[1] that the doped lanthanum gallate, $La(Sr)Ga(Mg)O_{3-\alpha}$ possesses an oxygen-ion conductivity high enough to be used as an electrolyte at a reduced temperature in a broad range of oxygen partial pressure (P_{O_2}) in SOFC. Its conductivity at 800 °C is about the same as that of YSZ at 1000 °C. Therefore, LSGM is considered to be a serious candidate for the electrolyte of a reduced temperature SOFC. Since lowering the operation temperature increases not only ohmic loss but also polarization loss at the electrodes, it is necessary to develop highly active electrodes that show sufficiently a low polarization at the reduced temperature. Hence, developing highly active electrodes that are compatible with LSGM electrolyte is an important issue.

Many researchers examined perovskite materials for cathodes for LSGM electrolyte.[2–4] Especially LSC shows good electrode properties for fuel cells because of its high electronic and ionic conductivities as well as its high catalytic activities for oxygen reduction. LSC-based cathodes showed high performances with a ceria (CeO_2)-based electrolyte[5] or $LaGaO_3$-based electrolyte between 600 and 800 °C. Although the LSC materials have been utilized as cathodes in the $LaGaO_3$-based electrolyte, there still remain some problems due to the reaction with electrolyte material and thermal-expansion coefficient (TEC) mismatch between LSC cathode ($20.5 \times 10^{-6}\ K^{-1}$) and LSGM electrolyte ($11.6 \times 10^{-6}\ K^{-1}$).[6] LSM–LSGM composite cathode showed the lower overpotential than that for LSM due to the smaller particle size than LSM in addition to the higher mixed conductivity.[7] We also expect that TEC mismatch between composite cathode and electrolyte material would be smaller than that between single-phase cathode and electrolyte.

In this study, the cathodic properties of LSC and its composites with LSGM electrodes were studied for fuel cells employing LSGM electrolyte. We varied the ratio between LSC and LSGM content. Cathodic overpotential and polarization resistance were measured by current-interruption technique and impedance, respectively. The effect of microstructure and

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electrical conductivity on the cathode performance was studied to design a better electrode on LSGM electrolyte.

2. Experimental procedure

LSC and LSGM powders were prepared by a solid-state reaction method. All starting powders ($SrCO_3$, Ga_2O_3, MgO, and CoO) were purchased from the same company (99.9% purity, High Purity Chemicals, Japan) except La_2O_3 (99.99%, Strem Chemicals, USA). The mixed oxides for LSGM and LSC were ball-milled and then calcined at 1200 °C for 6 h and 1000 °C for 5 h for the phase formation, respectively. The xLSC–$(1-x)$LSGM composite powders were prepared by mixing the calcined LSC and the LSGM powder in various weight ratio ($x = 0.3$, 0.5, 0.7, 1). For the fabrication of LSGM bulk electrolyte, LSGM powder was die-pressed and then sintered at 1500 °C for 6 h for densification.

For screen-printing of cathode, the powders were mixed with an organic solution of α-terpineol and ethylene cellulose in weight ratio of 10:1. The resulting slurry was screen-printed on dense LSGM electrolyte and heat treated (or sintered) either at 1100 or 900 °C in air for 2 h. Three-electrode configuration cells were fabricated for current-interruption technique; the working electrode is a cathode under investigation and the counter and the reference electrodes are platinum. Two-electrode configuration cells were fabricated for impedance measurement. Platinum paste (Engelhard no. 6082, USA) was heated for 1 h at 800 °C after painting. Pt mesh (Aldrich 52 mesh, USA), as a current collector, was bonded at 800 °C for 1 h to electrodes. The electrolyte diameter was 1.8 cm. The thickness of electrode was ∼18 μm after sintering, and the electrode area was 0.78 cm^2. In order to measure the electrical conductivity of electrode material, the rectangular-shaped thick films (thickness: 20 μm, width: 1cm, and length: 3cm) were screen printed on the alumina substrate and sintered at 1100 °C in air for 2 h.

For the electrochemical characterization, the current-interruption technique was used to measure ohmic loss (IR-drop) and cathodic overpotential (η_c) value of the cells. Impedance analyzer (Solartron, model SI-1260 & 1287, UK) was used to obtain the pattern and four-probe d.c. method was used to measure the electrical conductivity of electrode materials on alumina substrates. The measurements were performed from 600 to 800 °C with 50 °C step in oxygen atmosphere. Microstructure observation was performed by using a field-emission scanning-electron-microscope (JEOL, model 6330F, Japan).

3. Results and discussion

The cathodic overpotential of LSC–LSGM electrodes, measured at 800 °C in oxygen atmosphere, was shown (Fig. 1). The cathodic overpotential values of LSM–LSGM electrodes were shown for comparison (∼100 mV at 40 mA/cm^2).[7] The reaction between LSM and LSGM was declared as a possible reason of the high cathodic overpotential of LSM cathode.[7] The overpotential markedly decreased and showed value of ∼40 mV at 100 mA/cm^2 for the LSM–LSGM composite electrode due to the smaller particle size and increased mixed conduction from that of LSM.[7] However, the overpotential of cell employing the LSM–LSGM composite cathode was still too high. The overpotential of LSC (7 mV at 100 mA/cm^2) was much reduced from that of LSM (197 mV at 100 mA/cm^2). The observation implies that the reaction layer formed between LSC and LSGM is not highly insulating. Cobalt addition into LSGM electrolyte is shown to increase both p-type electronic and ionic conductivity rather than forming insulating layer.[8]

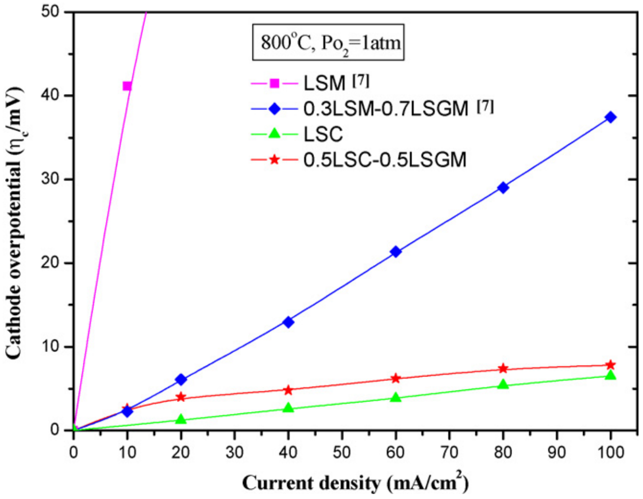

Fig. 1. The cathodic overpotential values of various electrode materials were measured at 800 °C in oxygen atmosphere. Only one data point of LSM was shown due to the scale of graph. LSM and 0.3LSM–0.7LSGM were heat treated at 1200 °C.[7] LSC and 0.5LSC–0.5LSGM, in this study, were heat treated at 1100 °C.

The composite cathode (0.5LSC–0.5LSGM) on LSGM electrolyte exhibited similar performance with single-phase LSC cathode. The overpotential values of both electrodes were less than 10 mV at 100 mA/cm^2 (800 °C). The single-phase LSC or composite LSC–LSGM cathode showed much reduced cathodic overpotential from single-phase LSM or composite LSM–LSGM cathodes. Since LSC ($\log \sigma_e = 3.2$ S/cm, $\log \sigma_i = -0.66$ S/cm at 800 °C)[6] is known to show higher mixed ionic and electronic conducting than LSM ($\log \sigma_e = 2.01$ S/cm, $\log \sigma_i = -3.77$ S/cm at 800 °C),[6] no marked decrease in cathodic overpotential from single-phase LSC cathode was observed in LSC–LSGM system unlike LSM–LSGM composite electrode.

Microstructures of the LSC-based electrodes are shown in Fig. 2. The interface revealed the good adhesion of LSC electrode on the LSGM electrolyte. Although we expected the decreased particle size in composite cathode, no appreciable difference in microstructure was shown between LSC and LSC–LSGM cathode as shown in Fig. 2.

Fig. 3 shows XRD patterns of LSC, LSGM and 0.7LSC–0.3LSGM composite. In a composite phase, the distinct peaks of LSC and LSGM are shown. Thus, there are no significant reactions between LSC and LSGM, or solid solution formation. Heat-treatment at 1100 °C for 2 h does not induce the reaction between two phases. The LSC and LSGM phases are mixed together and thus there is no change in particle size.

The cathodic overpotential of various electrode compositions was measured from 600 to 800 °C in oxygen atmosphere. In

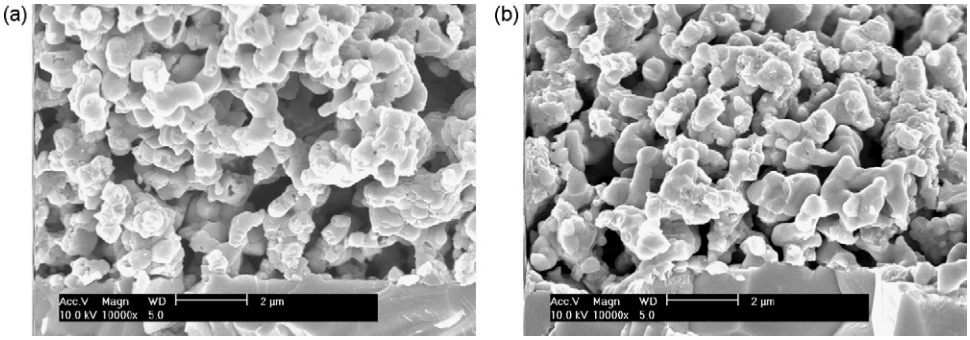

Fig. 2. Microstructure of two electrodes sintered at 1100 °C for 2 h for (a) LSC and (b) 0.5LSC–0.5LSGM after electrochemical measurement. The LSC powder and the LSGM powder were calcined at 1000 °C for 5 h, and 1200 °C for 6 h, respectively, for phase formation.

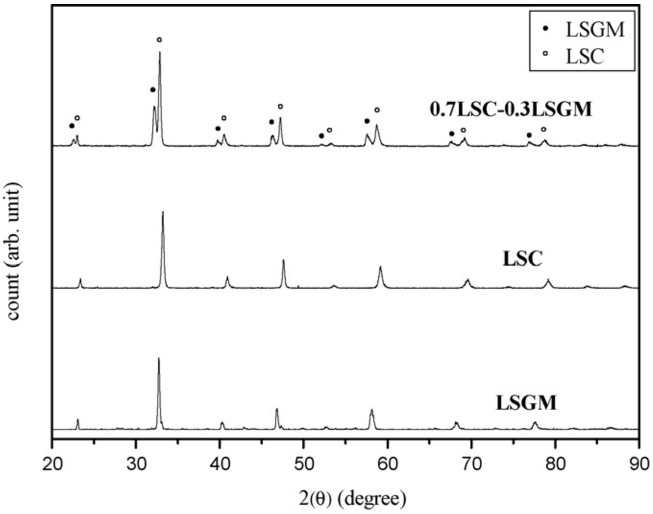

Fig. 3. The XRD patterns of LSC, LSGM and 0.7LSC–0.3LSGM phases were shown.

Fig. 4, it is shown that cathodic overpotential value changed with temperature and the mixing ratio of composite. The composition dependence of the cathodic overpotential was compared at 100 mA/cm^2. All screen-printed LSC–LSGM electrodes were heat treated or sintered at 1100 °C in air for 2 h. LSC sintered at 900 °C has a higher overpotential value than that sintered at 1100 °C due to the bad adherence to electrolyte. For LSC, 900 °C is not high enough for good attachment of LSC to LSGM. As the content of ion-conducting LSGM increase (or decreasing the content of LSC), the overpotential increased. The reason for the higher overpotential of composite cathode than that of single-phase LSC can be explained by considering the mixed conductivity. LSC ($\log \sigma_i = -0.66$ S/cm at 800 °C) already has the partial ionic conductivity higher than that of LSGM ($\log \sigma_i = -1$ S/cm at 800 °C), in addition to the high electronic conductivity. Therefore, LSC–LSGM system has no advantage from single-phase LSC. The system is expected to show the different effect from LSM–LSGM system. However, the composite electrode has an advantage unless the overpotential is much larger than that of single phase. The TEC value of composite electrode should be smaller than that of single-phase electrode.

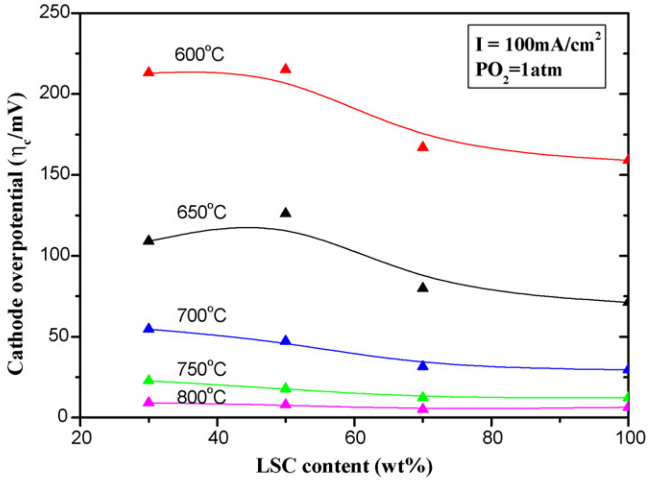

Fig. 4. The cathodic overpotential values of xLSC–$(1-x)$LSGM cathodes ($x = 0.3, 0.5, 0.7, 1$) were compared at 600–800 °C.

Fig. 5 shows the impedance spectra of xLSC–$(1-x)$LSGM at 700 °C in oxygen atmosphere ($x = 0.3, 0.5, 0.7, 1$). The thickness of LSGM substrates was similar, ~450 µm, and the electrode area was the same, ~0.78 cm^2. Nearly the same impedance values for LSGM electrolytes were shown. The polarization resistance (R_p) value of 0.7LSC–0.3LSGM was nearly the same with that of LSC, ~0.24 cm^2. However, R_p increased with decreasing LSC content from 0.39 to 0.46 cm^2 for $x = 0.5$ and 0.3, respectively.

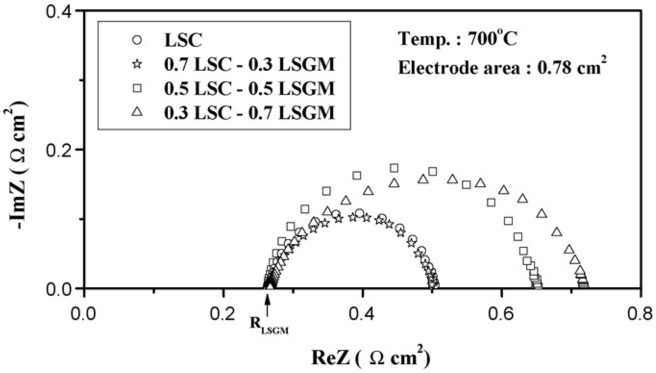

Fig. 5. The impedance spectra of xLSC–$(1-x)$LSGM ($x = 0.3, 0.5, 0.7, 1$) were compared on LSGM electrolyte at 700 °C in oxygen atmosphere. Electrolyte thicknesses were similar: ~450 µm, electrode areas were the same for all samples: ~0.78 cm^2.

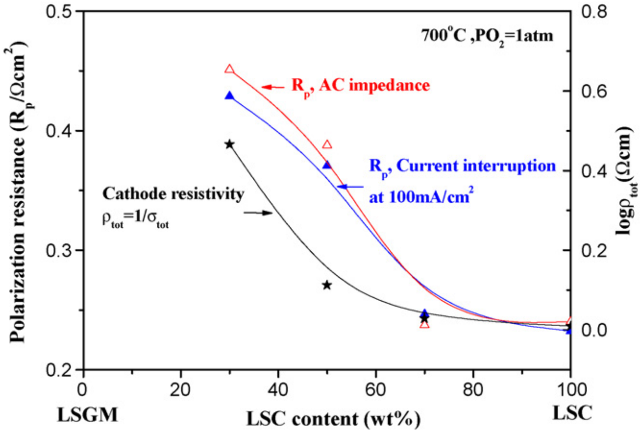

Fig. 6. The polarization resistance values, obtained from current-interruption technique and impedance pattern, were compared with the total resistivity values for xLSC–$(1-x)$LSGM cathodes (x = 0.3, 0.5, 0.7, 1). All data were obtained at 700 °C in oxygen atmosphere.

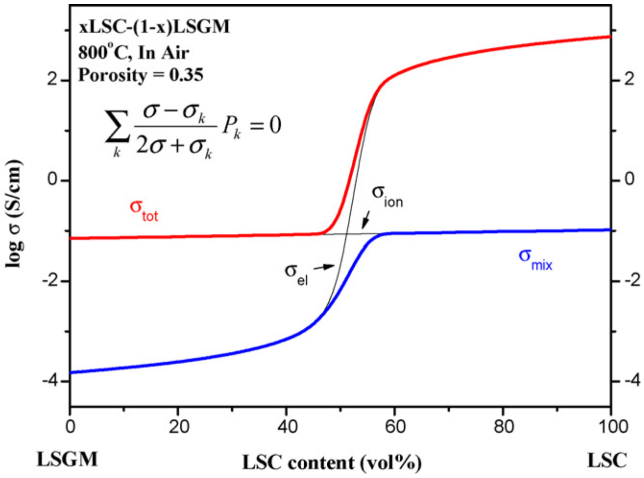

Fig. 7. The σ_{mix} values of composites were estimated by using the known values of σ_{ion}, σ_{el} values of end members and an effective medium equation[10] for LSC–$(1-x)$LSGM cathodes. The σ_{ion}, σ_{el} and σ_{mix} denote the ionic, the electronic and the mixed conductivity, respectively. An effective medium equation was shown in the figure where σ_k is the conductivity of end members, and P_k is volume fraction, respectively.

The R_p values were compared with the electrical resistivity of cathode material coated on alumina substrate (Fig. 6). The R_p values were measured by two different methods, one from the current-interruption method ($R_p = \eta_c/i$ (100 mA/cm^2)), the other from impedance. The R_p was roughly proportional to the resistivity of composite. Assuming R_p is due to the charge-transfer resistance, the proportionality between R_p and the mixed conductivity is expected.[9]

The observed proportionality between R_p and the total resistivity can be explained if the total resistivity is inversely proportional to the mixed conductivity. The total and mixed electrical conductivity as a function of LSC content were estimated as shown in Fig. 7. Based on effective medium model,[10] the ionic, the electronic and the total conductivity of composite phases can be calculated using the known value of ionic and electronic conductivity of two end members (LSC, LSGM). Assuming the porosity of electrode is ∼35%, the conductivity of composite at 800 °C as a function of LSC content was calculated. The total and the mixed conductivity rapidly increased above ∼50% of LSC content. The trend shown in Fig. 7 explains the rough proportionality between R_p and the total conductivity.

4. Conclusions

Although LSM–LSGM composite showed better cathodic performance than single-phase LSM as shown in the previous study, no such effects were shown for LSC–LSGM composite system. The cathodic performance of LSC–LSGM composite electrodes was not any better than that of single-phase LSC electrode. The observation was possibly due to the higher partial ionic conductivity of LSC than the ionic conductivity of LSGM. However, the composite electrode, 0.7LSC–0.3LSGM, may be useful due to the smaller thermal-expansion coefficient expected for the composite phase than for the single-phase LSC.

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