

# High-performance electrodes for reduced temperature solid oxide fuel cells with doped lanthanum gallate electrolyte

## II. La(Sr)CoO<sub>3</sub> cathode

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### Abstract

The reduced temperature solid oxide fuel cell (SOFC) with 0.5 mm thick La<sub>0.9</sub>Sr<sub>0.1</sub>Ga<sub>0.8</sub>Mg<sub>0.2</sub>O<sub>3-α</sub> (LSGM) electrolyte, La<sub>0.6</sub>Sr<sub>0.4</sub>CoO<sub>3-δ</sub> (LSCo) cathode, and Ni-(CeO<sub>2</sub>)<sub>0.8</sub>(SmO<sub>1.5</sub>)<sub>0.2</sub> (SDC) cermet anode showed an excellent initial performance, and high maximum power density, 0.47 W/cm<sup>2</sup>, at 800°C. The results were comparable to those for the conventional SOFC with yttria-stabilized zirconia (YSZ) electrolyte, La(Sr)MnO<sub>3</sub>-YSZ cathode and Ni-YSZ cermet anode at 1000°C. Using an LSCo powder prepared by spray pyrolysis, and selecting appropriate sintering temperatures, the lowest cathodic polarization of about 25 mV at 300 mA/cm<sup>2</sup> was measured for a cathode prepared by sintering at 1000°C. Life time cell test results, however, showed that the polarization of the LSCo cathode increased with operating time. From EPMA results, this behavior was considered to be related to the interdiffusion of the elements at the cathode/electrolyte interface. Calcination of LSCo powder could be a possible way to suppress this interdiffusion at the interface. © 2000 Elsevier Science S.A. All rights reserved.

**Keywords:** Solid oxide fuel cell; SOFC; Reduced temperature; La(Sr)CoO<sub>3-δ</sub> cathode; Spray pyrolysis; Life time

### 1. Introduction

The solid oxide fuel cell (SOFC) is one of the most attractive energy conversion systems because of its high efficiency, low pollution and fuel flexibility. Conventional SOFCs presently under development are operated at around 1000°C, because of the low oxide ion conductivity of YSZ at lower operating temperatures. However, the high operating temperature causes many serious problems such as: (i) severe restrictions on the choice of materials, (ii) electrode sintering, (iii) interfacial diffusion between electrode and electrolyte, and (iv) mechanical stress due to different thermal expansion coefficients. To overcome these problems, it is desirable to operate SOFCs at reduced temperatures ( $\leq 800^\circ\text{C}$ ).

To develop a practical reduced temperature SOFC, two approaches are under active consideration. One is to use an extremely thin YSZ membrane to make the ohmic loss due to electrolyte as small as possible. Another, is to use a new electrolyte material that shows an excellent oxide ion conductivity at the temperature of  $\leq 800^\circ\text{C}$ , comparable to that of YSZ at 1000°C. It has been reported recently [1–3] that doped lanthanum gallate, La(Sr)Ga(Mg)O<sub>3-α</sub> possesses oxide ion conductivity high enough to be used as an electrolyte at reduced temperature over a broad range of oxygen partial pressure 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 anode and the cathode, it is necessary to develop highly active electrodes that show sufficiently low polarization at the reduced temperature. Hence, developing highly active electrodes that are com-

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patible with  $\text{La}(\text{Sr})\text{Ga}(\text{Mg})\text{O}_{3-\alpha}$  electrolyte is an important issue.

Our previous study showed that the importance of microstructure control to obtain good electrode performance [4–6]. The results of further investigations on the performance of the anode were mentioned in a preceding paper [7]. Here the cathode performance of a single SOFC was investigated using  $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$  (LSCo), which has received a lot of attention as a cathode material, because it possesses mixed oxide ionic and electronic conductivity [8–12]. A mixed ionically/electronically conductive  $\text{Ni}(\text{CeO}_2)_{0.8}(\text{SmO}_{1.5})_{0.2}$  (SDC) cermet was used as an anode. Both electrode powders were prepared by a spray pyrolysis technique.  $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\alpha}$  (LSGM) electrolyte was prepared by a solid state reaction method. The polarization behavior of the cathode is discussed on the basis of our results obtained for a single cell, initial performance and life time test carried out at 800°C.

## 2. Experimental

### 2.1. Preparations of LSGM electrolyte

LSGM was prepared by a solid state reaction method [13]. The starting materials were  $\text{La}_2\text{O}_3$ ,  $\text{SrCO}_3$ ,  $\text{Ga}_2\text{O}_3$ , and  $\text{MgO}$ . The ball-milled powder mixtures of the starting materials were calcined in air at 1150°C for 10 h. The calcined powder, uniaxially pressed into pellets at a pressure of 49 MPa, followed by isostatic pressing at 294 MPa, was sintered in air at 1500°C for 10 h. The densities of the sintered materials were measured using the Archimedes method. The relative density, the ratio of the absolute density to the theoretical density was about 98%. Powder X-ray diffraction was measured with pulverized sintered materials to confirm their Perovskite structure. The sintered materials were then cut and polished to a size of 13 mm in diameter and 0.5 mm thick.

### 2.2. Preparation of LSCo powder and NiO-SDC composite powder

LSCo starting powder for the cathode was synthesized by spray pyrolysis, as described previously [4,5]. An aqueous nitric acid solution containing  $\text{La}_2\text{O}_3$ ,  $\text{SrCO}_3$ , and  $\text{Co}_3\text{O}_4$ , with a concentration of 0.1 mol/l as the composition of LSCo, was atomized with an ultrasonic vibrator operating at 1.7 MHz. The droplets were transported into a reaction furnace using air as a carrier gas with a fixed flow rate of 3 l/min. The reaction furnace consisted of four independent heating zones, of which temperatures were set at 200, 400, 800, and 1000°C, respectively. The particles were collected using an electrostatic precipitator. The morphology of the powder was analyzed by scanning electron microscopy (SEM, Hitachi, S-800). Similarly, NiO-SDC

composite starting powder for Ni-SDC cermet anodes was synthesized as described in Ref. [7].

### 2.3. Single SOFC tests

The construction of single cells is described in detail elsewhere [4,5]. LSCo cathodes were deposited by the screen printing technique onto LSGM pellets. Once the green cathode layers were applied to a fuel cell, the cell was sintered to generate an adherent and electrically conducting electrode. The cells were sintered at different temperatures of 950, 1000, 1050, and 1200°C for 4 h with heating and cooling rates of 3.3°C/min. NiO-SDC powder was sintered on the opposite side of the LSGM pellet at 1300°C for 2 h before cathode sintering, then NiO was reduced to Ni under a fuel atmosphere. The effective electrode area was 0.282 cm<sup>2</sup>. Pt wires, wound around the LSGM pellet and fixed with platinum paste, were used as a reference. The single cell tests were carried out at 800°C. Air was used as an oxidant, and 3% moisturized hydrogen gas ( $\text{H}_2 + 3\% \text{H}_2\text{O}$ ) was used as fuel. For the electrochemical characterization, the current-interruption technique was used to measure cathodic polarization loss ( $\eta_c$ ). After the cell tests, the microstructure and the elemental distribution near the LSCo/LSGM interface were observed by using an electron probe microanalyzer (EPMA) (Model JEOL JXA-8699 superprobe).

## 3. Results and discussion

Fig. 1 shows the cathodic polarization  $\eta_c$  measured for 800°C at 300 mA/cm<sup>2</sup>, as a function of sintering temperature. Clearly the cathodic performance is dependent on the sintering temperature in the range of 950 to 1200°C. The lowest cathodic polarization of about 25 mV at 300 mA/cm<sup>2</sup> was obtained for the cathode sintered at 1000°C (Fig. 2). This result is better than the results obtained with LSGM electrolyte-cells [14,15,18]. The cathode sintered at 1000°C consisted of well-bonded particles. Each agglomerated particle is an aggregate of small particles. Well-con-

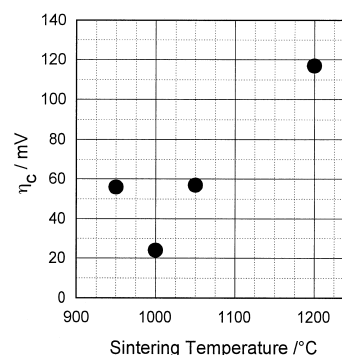


Fig. 1. Cathodic polarization at 300 mA/cm<sup>2</sup> vs. sintering temperature of LSCo cathode.

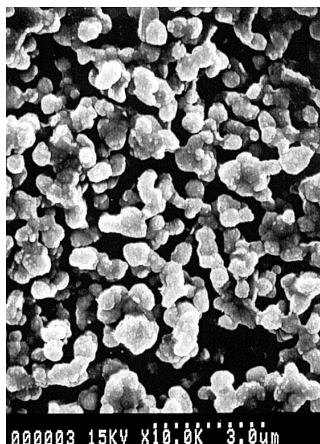


Fig. 2. SEM image of LSCo cathode sintered at 1000°C.

nected agglomerates allow utilization of a large surface area of the porous electrode for reduction of  $O_2$  to  $O^{2-}$ , and therefore measured cathodic polarization was very low.

Selecting 1000°C as a sintering temperature for the cathode and that for the anode being 1300°C [4], we constructed a single SOFC. The electrode area was 0.785  $cm^2$  in this case. Fig. 3 shows the  $i$ - $V$  and  $i$ - $P$  curves obtained with LSCo cathode sintered at 1000°C with LSGM as an electrolyte and Ni-SDC cermet as an anode at 800°C. The maximum power density was about 0.47  $W/cm^2$ , which was an excellent initial performance for a 0.5 mm thick electrolyte at 800°C. This compares favorably with results for the YSZ electrolyte, whose performance was reported to be 0.37  $W/cm^2$  at 1000°C with microstructure-optimized electrodes [16].

After we obtained this excellent initial property of a reduced temperature SOFC with microstructure-optimized electrodes for LSGM electrolyte, life time cell tests were performed to evaluate the compatibility of the electrodes with respect to the LSGM electrolyte. Fig. 4 shows the time dependence of the cathodic polarization for a LSCo/LSGM/Ni-SDC single cell test at 800°C with 300  $mA/cm^2$ . The cathodic polarization ( $\eta_c$ ) rapidly increased

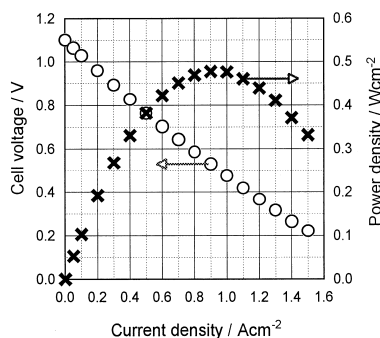


Fig. 3. Initial single SOFC performance at reduced temperature of 800°C.

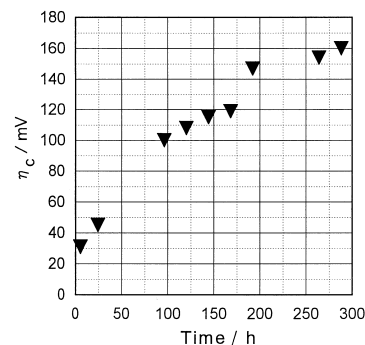


Fig. 4. Time dependence of the cathodic polarization,  $\eta_c$ , at 800°C with 300  $mA/cm^2$ .

with time. After about 300 h of operation, the cathodic polarization was more than five times higher than for the initial performance. In contrast, the anodic polarization appeared to be stable [7].

To investigate the reason for the cathodic polarization increase, the cathode/electrolyte interaction on the cathodes was investigated by EPMA. An EPMA image of LSCo/LSGM interface after 1 h of operation is shown in Fig. 5. There are two distinct regions, which correspond to LSGM and LSCo, respectively. These materials were confirmed by line analysis. Line analysis was also performed for impurities such as Cr, Si, and Al, and none of these were detected. Significant interdiffusion of Co into LSGM and Ga into LSCo during firing at 1050°C for 2 h reported by Huang et al. [17] was not observed in our experiments (at a firing temperature of 1000°C).

The EPMA micrograph in Fig. 6a shows a representative part of the cathode/electrolyte interface layer after 300 h of operation. It suggests that there is some reaction zone formed at the interface. Elemental distribution analysis showed that the reaction zone was rich in La and Ga (Fig. 6b,c), and that the adjacent part of the electrolyte to the reaction zone was lean in La and Ga. More detailed investigation of its phenomena needs to be carried out including consideration of the mechanism of interdiffusion.

The calcined LSCo powder, which was obtained by heating of LSCo powder at 1000°C for 4 h, was used in

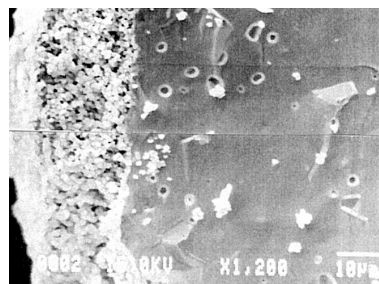


Fig. 5. EPMA image of the fracture surface near LSCo/LSGM interface after 1 h operation.

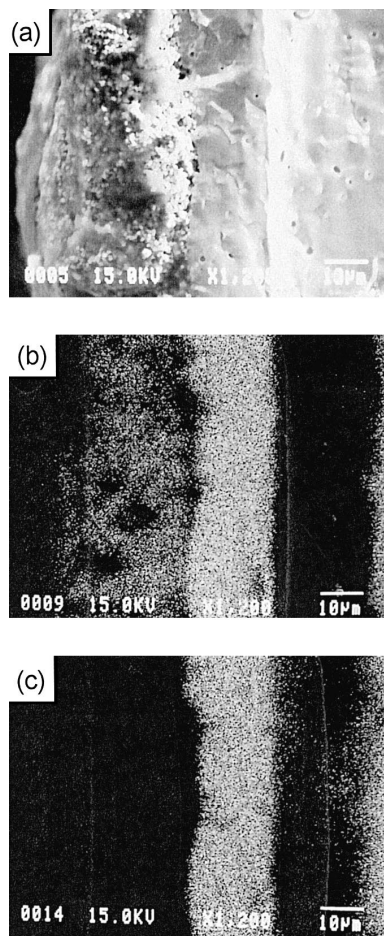


Fig. 6. EPMA analysis results; (a) image of the fracture surface near LSCo/LSGM interface after 300 h operation, and (b) La and (c) Ga distribution.

order to suppress diffusion at the cathode/electrolyte interface. Both of the morphologies of uncalcined and calcined LSCo powders are shown in Fig. 7a and b. The spherical shape of the LSCo powder changed to a rather rugged shape, which indicated sintering and crystal growth

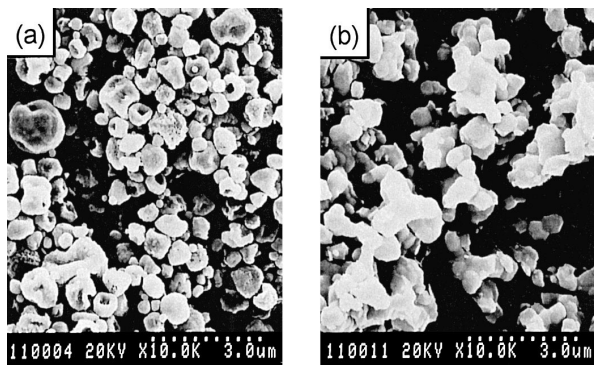


Fig. 7. SEM images of LSCo powder; (a) before and (b) after calcination at 1000°C

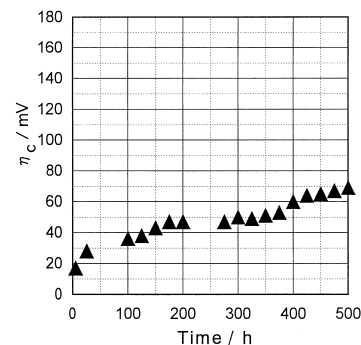


Fig. 8. Time dependence of the cathodic polarization,  $\eta_c$ , at 300 mA/cm<sup>2</sup> current,  $T_{\text{operation}} = 800^\circ\text{C}$ , using the cathode prepared with LSCo calcined at 1000°C.

in progress. For the cathode prepared using the calcined LSCo powder, lifetime cell testing was performed at 800°C and a current density of 300 mA/cm<sup>2</sup>. Fig. 8 shows that the time dependence of cathodic polarization for a LSCo/LSGM/Ni-SDC single cell. Compared with the results shown in Fig. 4, it is clear that the increase of  $\eta_c$  with the calcined LSCo-cell is much slower. The cathodic polarization  $\eta_c$  at about 300 h operation with calcined LSCo was 50 mV, which was 110 mV lower than in the case of uncalcined LSCo-cell. The results obtained so far indicate that the calcination of cathode powder could be one way to suppress diffusion during current flow for both the cathode and the electrolyte. We are now investigating the effect of calcination of LSCo on cell stability, together with optimization of the composition of LSCo and introduction of some intermediate layer between the cathode and the electrolyte to prevent interdiffusion.

#### 4. Conclusions

The single SOFC with 0.5 mm thick LSGM electrolyte, LSCo cathode, and Ni-SDC cermet anode showed an excellent initial performance with maximum power density of 0.47 W/cm<sup>2</sup> at reduced temperature of 800°C. The results are comparable to those for the conventional SOFC with yttria-stabilized zirconia (YSZ) electrolyte, La(Sr)-MnO<sub>3</sub>-YSZ cathode and Ni-YSZ cermet anode at 1000°C. By optimizing the sintering temperature of the submicron LSCo powder, synthesized with a spray pyrolysis technique, the lowest cathodic polarization of about 25 mV at 300 mA/cm<sup>2</sup> was obtained. Life time cell test results, however, showed that the polarization of the LSCo cathode increased with operating time. From EPMA results, this behaviour was considered to be related to the interdiffusion of the elements at the cathode/electrolyte interface. Calcination of LSCo powder could be a possible way to suppress interdiffusion at the interface. More detailed investigations into the effect of the calcination of LSCo on the cell stability are underway.

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