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Performance of intermediate temperature solid oxide fuel cells with $La(Sr)Ga(Mg)O_3$ electrolyte film

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Abstract

A $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_3$ (LSGM) thin film was fabricated by the usual tape casting method using a doctor blade to reduce the operating temperature in solid oxide fuel cells (SOFCs). The resultant LSGM film was 130 ± 3 μm in thickness and its relative density was over 99%. Also, the thin LSGM film showed a single phase, and its conductivity was 0.113 S/cm at 800 °C and 0.054 S/cm at 700 °C, respectively. Therefore, it seemed that the thin LSGM film was suitable as an electrolyte for intermediate temperature operating SOFCs. Ni–SDC and $La(Sr)CoO_3$ synthesized by spray pyrolysis were used as an anode and a cathode, respectively, and a single cell was fabricated with the thin LSGM film as an electrolyte. This single cell with the thin LSGM electrolyte exhibited excellent electrical performance, of which power density was over 0.7 W/cm^2 at 800 °C and 0.4 W/cm^2 at 700 °C. These results suggested that the LSGM-based SOFCs with the thin LSGM film in this study would exhibit adequate performance at a temperature lower than 700 °C.

Keywords: Intermediate temperature; SOFCs; $La(Sr)Ga(Mg)O_3$; Electrical performance

1. Introduction

Solid oxide fuel cells (SOFCs) have been attracting a great attention as a promising technique for electrical power generation. SOFCs can provide high total efficiency when they are used in a cogeneration system and promise clean power sources with little production of NO_x and SO_x. In general, they must be operated at high temperature between 900 and 1000 °C because the Y_2O_3 stabilized ZrO_2 (YSZ) is used as the usual electrolyte material and has a low ionic conductivity at operating temperatures lower than 800 °C. Such high operating temperature leads to some serious problems, such as, physical and chemical degradation of SOFCs component materials. Therefore, it is desirable to develop SOFCs operating at intermediate temperatures below 800 °C. To reduce the operation temperature, two approaches are under active considerations as follows: one is the reduction of the thickness of the YSZ electrolyte as thin as a few tens of micrometers, and another is application of alternative electrolyte materials such as $La(Sr)Ga(Mg)O_{3-\alpha}$ (LSGM) [1–3] and Sm_2O_3 doped CeO_2 (SDC) [4], which have a higher ionic conductivity than YSZ.

We have developed some electrodes for the intermediate temperature operating SOFCs using LSGM electrolyte [5–8]. In our previous study, Ni–SDC was adapted as an anode and $La(Sr)CoO_{3-\alpha}$ (LSCo) as a cathode, and we have demonstrated high electrical performance at 800 °C by means of optimizing their morphology. In the practical use of LSGM-based SOFC, it is indispensable to develop large area and thin electrolyte films as well as highly active electrodes. Especially, a thin electrolyte film, of which thickness is under approximately 200 μm is needed to get enough power density at a temperature less than 700 °C in LSGM-based SOFCs.

Therefore, the aim of this paper is to fabricate the thin LSGM film for practical use of reduced temperature operating SOFCs. Some properties such as density, crystal structure and conductivity of the LSGM film were made clear. Moreover, the electrical performance of a single cell fabricated from the thin LSGM electrolyte, LSCo cathode and Ni–SDC anode was also investigated.

2. Experimental

2.1. Preparation of LSGM electrolyte film by tape casting method

LSGM powder was prepared by a solid-state reaction. La_2O_3, $SrCO_3$, Ga_2O_3 and MgO were used as the starting

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materials for the LSGM powder, and the composition $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\alpha}$ was chosen in this study. The ball-milled powder mixture of the starting materials was repeatedly calcined in air at 800 and 1200 °C. Then, the calcined powder was ball-milled for 48 h to obtain the LSGM powder. The LSGM powder was mixed in ethanol for 48 h with some organic additives. The suspension was spread on a PET sheet using doctor blade method. The resultant green sheet was fired at 1460 °C to obtain a LSGM film. The fabrication conditions and the doctor blade equipment in this study were similar to those used in our previous work, and described elsewhere [9]. The relative density, crystal structure and conductivity of the LSGM film were evaluated by Archimedes method, X-ray diffraction analysis and dc four-probes measurement [10], respectively.

2.2. Synthesis of electrode powders by spray pyrolysis

Spray pyrolysis (SP) was used to prepare NiO–SDC composite powder and LSCo powder. The NiO–SDC composite powder was synthesized from an aqueous solution, which was prepared from $Ni(CH_3COO)_2{\cdot}4H_2O$, Sm_2O_3 and $Ce(NO_3)_3{\cdot}7.5H_2O$. The composition of SDC was set to be $(CeO_2)_{0.8}(SmO_{1.5})_{0.2}$, and the initial ratios of Ni and SDC was 52:48 (mol%). LSCo powder was also prepared from an aqueous nitric acid solution, which was containing La_2O_3, $SrCO_3$ and Co_3O_4. The composition of the LSCo was set to be $La_{0.6}Sr_{0.4}CoO_{3-\alpha}$. The SP system employed in this study and the synthesis conditions of the electrode powders are similar to those used previously by the authors, and those described elsewhere [7,8].

2.3. Fabrication of a single cell and evaluation of its electrical performance

The NiO–SDC composite powder was mixed with organic binder. They were printed onto one side of an LSGM electrolyte pellet of 13 mm in diameter. Then, it was fired at 1250 °C in air to produce the NiO–SDC anode. After that, LSCo powder was printed onto the other side of the LSGM electrolyte pellets, and it was fired at 1000 °C to produce a single cell. This single cell was operated in the conditions of H_2–3% H_2O for an anode and air for a cathode at 700–800 °C. In the first stage of the cell test, the NiO–SDC anode was reduced in H_2–3% H_2O to make a Ni–SDC cermet anode. Then the electrical performance such as the *I–V*, *I–P* characteristics was measured. Moreover, the morphology of the electrodes and the electrolyte of the single cell after test were analyzed by scanning electron microscopy (SEM, Hitachi, S-800).

3. Results and discussions

3.1. Characterization of LSGM film

The tape casting method using a doctor blade is suitable to fabricate large area thin sheets for SOFC thin electrolyte. Figs. 1 and 2 show a LSGM green sheet prepared by tape casting method and a LSGM film fired at 1460 °C for 5 h. It is clear from Fig. 1 that a flat green sheet was obtained in this study. The thickness of the green sheet was 170 ± 3 μm. Also, a LSGM electrolyte film (Fig. 2) fired at 1460 °C showed a relative density of about 99% and its thickness was 130 ± 3 μm. As a result of X-ray diffraction analysis, the LSGM film showed single phase, and an impurity phase like $SrLaGa_3O_7$ was not detected. Moreover, the LSGM film exhibited almost the same conductivity as bulk LSGM samples prepared by pressing and sintering of the LSGM powder [11], and the conductivity measured by dc four-probes measurement was 0.113 S/cm at 800 °C and 0.054 S/cm at 700 °C, respectively. Therefore, it seems that the

Fig. 1. Photograph of a LSGM sheet prepared by tape casting method.

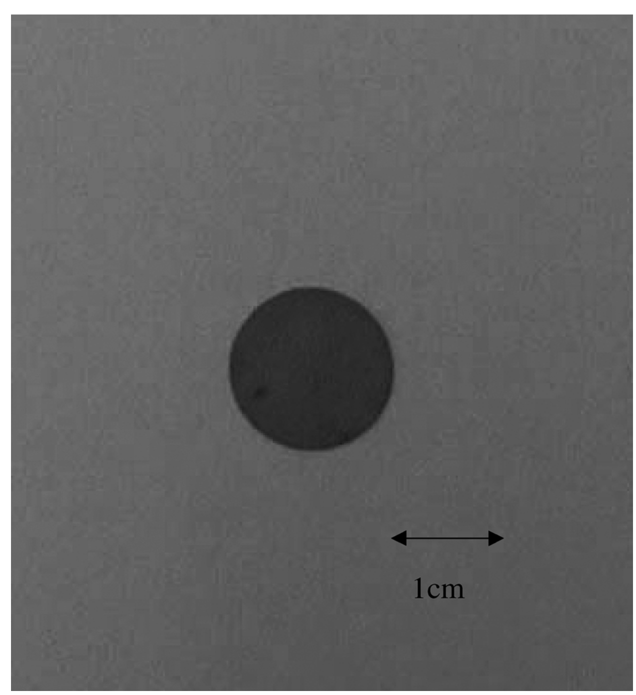

Fig. 2. Photograph of a thin LSGM film fired at 1460 °C.

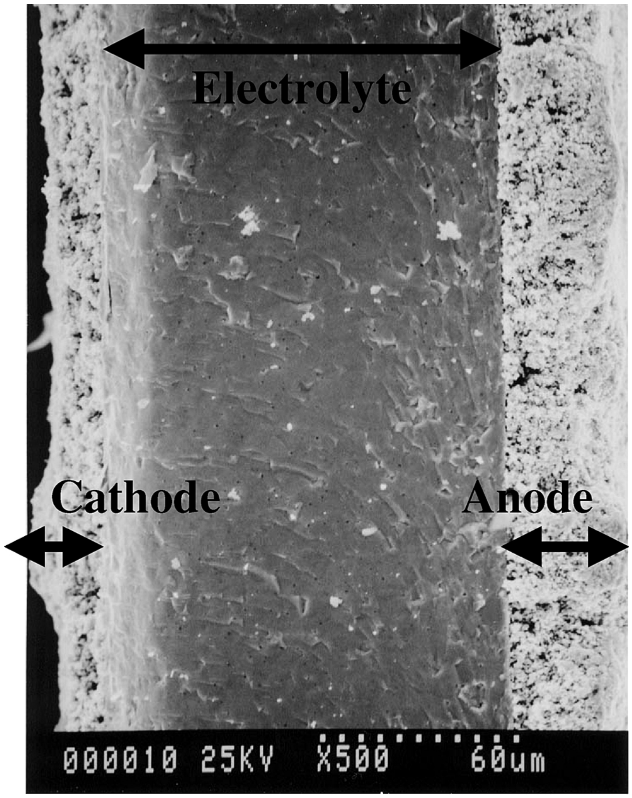

Fig. 3. SEM photograph of the cross section of a single cell fabricated with thin LSGM film as an electrolyte.

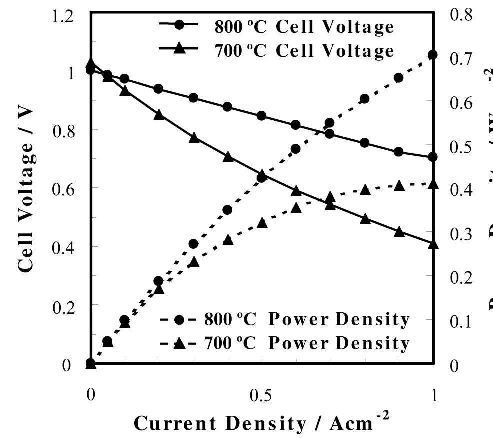

Fig. 4. Electrical performance of a single cell using thin LSGM film.

LSGM film obtained in this study can be adapted as an electrolyte for SOFCs.

3.2. Cell performance

Fig. 3 shows a SEM photograph of the cross section of a single cell using the thin LSGM electrolyte film after performance test. It is evident from Fig. 3 that the LSGM electrolyte is almost dense and no open pore is observed in the electrolyte. A Ni–SDC anode exhibited relatively homogeneous porous structure and its thickness was about 30 μm. A LSCo cathode also exhibited porous structure and its thickness was about 20 μm. It was confirmed from high magnification SEM observation that both electrodes were strongly adhered to the surface of the LSGM electrolyte. Moreover, the morphology of both electrodes was the almost same as that in our previous studies [5–8].

Fig. 4 shows the *I–V* and *I–P* curves obtained with the thin LSGM film as an electrolyte at 800 and 700 °C. Power density of the single cell operating at 800 °C is 0.7 W/cm^2 at the current density of 1 A/cm^2, and its maximum value will be expected to achieve about 0.9 W/cm^2. Maximum power density of the cell at 700 °C is about 0.41 W/cm^2. These maximum power densities showed the highest values among our studies [6,8]. Therefore, it seems that the thin LSGM film fabricated in this study can be used as an electrolyte for practical SOFCs. However, it is clear from Fig. 4 that the open circuit voltage in this test is a little lower than the theoretical value. It was thought that a little leakage occurred unfortunately through the melt glass sealing or between the anode and the cathode. We expect that a LSGM-based SOFC using the thin electrolyte film will exhibit higher power density if there is no leakage. It suggests that this thin LSGM electrolyte is useful for reduced temperature operating SOFCs. Further experiments are needed to make the electrical performance and stability of the thin LSGM-based SOFC clearer. This will be reported in another paper in the future.

4. Conclusions

A LSGM thin film was fabricated by a conventional tape casting method using a doctor blade to reduce the operating temperature in SOFCs. The LSGM thin film exhibited a dense structure, of which the relative density was about 99%, and its thickness was 130 ± 3 μm. Also, the thin film showed a single phase containing no impurity phase like $SrLaGa_3O_7$, and its conductivity was 0.113 S/cm at 800 °C and 0.054 S/cm at 700 °C, respectively. Moreover, a single cell containing this thin film had excellent electrical performance, of which the power density was over 0.7 W/cm^2 at 800 °C and 0.4 W/cm^2 at 700 °C. This suggests that the thin LSGM film obtained in this study can be adopted as an electrolyte for the intermediate temperature operating SOFCs.

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