PREPARATION OF La(Sr)Ga(Mg)O$_3$ ELECTROLYTE FILM BY TAPE CASTING METHOD

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ABSTRACT

La$_{0.9}$Sr$_{0.1}$Ga$_{0.8}$Mg$_{0.2}$O$_{3.5}$ (LSGM) electrolyte film was prepared for the reduced temperature solid oxide fuel cells (SOFCs). The calcined LSGM powder was mixed in ethanol with organic additives. Then, a green sheet of LSGM was made by a tape casting method from the suspension (doctor blade method) and was fired in air. The resultant LSGM film was about 0.3 mm in thickness and its relative density was over 99%. A single cell including the LSGM film was fabricated with Ni-samaria doped ceria (Ni-SDC) cermet anode and La$_{0.6}$Sr$_{0.4}$Co$_3$O$_{7-δ}$ (LSCo) cathode, and its electrical performance at 700°C to 800°C was examined. The maximum power density of about 0.63 W/cm$^2$ was obtained at 800°C.

INTRODUCTION

Recently the reduced temperature SOFC has been attracting great attention, because it can use metallic separator. In order to realize a practical SOFC which operates at reduced temperature (800°C or less), it is essential to decrease the ohmic loss of the electrolyte. Two approaches for decreasing the ohmic loss are under active consideration. One is the reduction of the thickness of the yttria-stabilized zirconia (YSZ) electrolyte which is the conventional electrolyte used in SOFCs and the another is the application of another electrolyte having a high ionic conductivity below 800°C. LaGaO$_3$-based perovskite oxides have been proposed (1-6) as possible electrolyte materials. Among these oxides, La$_{0.9}$Sr$_{0.1}$Ga$_{0.8}$Mg$_{0.2}$O$_{3.5}$ (abbreviated as LSGM) demonstrates a high oxygen ion conductivity of about 0.10S cm$^{-1}$ at 800°C, i.e., four times higher than that of YSZ. We have

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adopted LSGM as the electrolyte, and developed high performance compatible electrodes (7-10).

It is also necessary to investigate the manufacturing process for the reduced temperature SOFCs. The tape casting method using a doctor blade is the most popular fabrication method for the electrolyte film for planar SOFCs, because it provides large size film with controlled thickness. Moreover, the tape casting method can be a low cost manufacturing process. In this study, we prepared LSGM electrolyte film by the tape casting method, and examined the electrical performance of a single cell with the LSGM film.

EXPERIMENTAL

LSGM Film Preparation

The starting materials for LSGM were La₂O₃, SrCO₃, Ga₂O₃, and MgO, all with purities higher than 99.9%. The ball-milled powder mixture of the starting materials was repeatedly calcined in air at 800°C and 1200°C. Then, the calcined powder was ball-milled for 48h to obtain LSGM powder, and the average particle size of it was 0.3 μm.

The LSGM powder was mixed in ethanol for 48h with a binder, plasticizer and a dispersing agent in the following fractions by weight:

- LSGM powder 100 parts
- binder 13 parts
- plasticizer 7.5 parts
- dispersing agent 2.2 parts
- ethanol 53.9 parts

The resultant suspension was de-gassed under vacuum in order to remove air trapped in it during mixing. The suspension was spread on a PET sheet. The viscosity of the suspension was set at about 15,000cps. The equipment of doctor blade is shown in Fig. 1. The thickness of the resultant green sheet was about 0.45mm. The green sheet was fired at 1460°C to obtain a LSGM film.

Cell Preparation and Power Generation Test

Using the LSGM film produced, a single cell for power generation test was prepared by the following method. NiO-SDC composite powder (SDC content 48 vol.%) synthesized by spray pyrolysis (11) was selected for the anode. The composite powder was screen-printed onto the LSGM film with an organic binder and the NiO-SDC layer was sintered at 1250°C in air for 2h. LSCo synthesized by spray pyrolysis (8) was selected for the cathode, and screen-printed onto the other side of the LSGM film. The LSCo layer was sintered at 1000°C in air for 4h. The area of the electrode was 0.282cm².
The cell was operated at 800°C and 700°C. 3% moisturized hydrogen gas (H2+3%H2O) and air were supplied to anode and cathode compartments, respectively. The flow rates in both compartments were set at 50cm³/min.

RESULTS AND DISCUSSION

LSGM Film Preparation

Figure 2 shows a LSGM green sheet prepared by the tape casting method. The LSGM green sheet was fired at 1460°C for 5h, and about 0.3mm thick LSGM films were obtained. During firing, the green sheet undergoes a volumetric shrinkage. This results from the decomposition of the binders, and sintering of LSGM. During this time, some cracks and warpage may occur in the LSGM films. One of the reasons for these is that the film experiences uneven shrinkage due to heterogeneity of the green sheet, and another reason is that the volumetric shrinkage progresses rapidly. Therefore, in order to avoid cracks and warpage, the green sheet must be homogenized. Moreover, degassing is required during firing and the heating rate must be slow to prevent rapid volumetric shrinkage. In this experiment, we conducted the degassing process at 500°C for 4h, and the heat up rate was about 0.7°C/min. In addition, to suppress the warpage, placing a setter on the sheet was effective. Fig. 3 shows the sheets before and after firing. Fig. 4 shows X-ray diffraction patterns of calcined LSGM powder and a film fired at 1460°C for 5h. It was confirmed from this figure that LSGM formed a single phase by firing at 1460°C for 5h. In addition, the relative density was above 99%. Fig. 5 shows SEM micrograph of the surface of the LSGM film. This figure shows that the grain size of LSGM was about 10 μm and no pore was observed.

Another problem is a heterogeneous phase, which is created in contact with the setter. In this study, we selected ZrO₂ as the setter. On the contact surface of LSGM film, there is a heterogeneous phase like SrLaGa₂O₇. In order to avoid contact of LSGM film with setter, we placed LSGM powder, after firing at 1500°C, between them. The reaction at the contact surface was prevented in this way.

A sintering temperature of 1460°C was adopted as the best condition because of above mentioned points. Namely, LSGM formed single phase, the relative density was high enough and LSGM film did not react with the setter and/or LSGM powder.

Cell Performance

Fig. 6 shows the i-V and i-P curves obtained with the LSGM film as an electrolyte at 800°C and 700°C. It was confirmed that there was no leakage between the anode and the cathode because the open circuit voltage almost agreed with the theoretical value. Maximum power density of the cell operating at 800°C was about 0.63W/cm² and at 700°C was about 0.32W/cm².
CONCLUSIONS

La_{0.1}Sr_{0.9}Ga_{0.4}Mg_{0.6}O_{3+δ} (LSGM) electrolyte film was prepared by a tape casting method. The resultant LSGM film was about 0.3mm in thickness and its relative density was over 99%. A single cell including the LSGM film was fabricated and its maximum power density was 0.63 W/cm² at 800°C.

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Fig. 1 Appearance of doctor blade.

Fig. 2 LSGM green sheet.
Fig. 3 LSGM film; left: green sheet, right: fired at 1460°C for 5h.

Fig. 4 X-ray diffraction patterns of LSGM;

- a: calcined powder,
- b: after firing at 1460°C for 5h in air.
Fig. 5 SEM micrograph of LSGM film surface fired at 1460°C for 5h.

Fig. 6 Single cell performance using LSGM film prepared by tape casting method.