

Short communication

# Preparation of LaGaO<sub>3</sub>-based perovskite oxide film by a pulsed-laser ablation method and application as a solid oxide fuel cell electrolyte

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## Abstract

LaGaO<sub>3</sub>-based perovskite oxide films are deposited on a dense substrate consisting of NiO, Fe<sub>3</sub>O<sub>4</sub>, and Sm-doped CeO<sub>2</sub> (SDC). After in situ reduction, NiO and Fe<sub>3</sub>O<sub>4</sub> are reduced to form an alloy and during reduction, the substrate becomes porous, and therefore can be used as a porous electrode substrate in a solid oxide fuel cell (SOFC). Since the reaction between NiO and LaGaO<sub>3</sub>-based oxide is known, an interlayer of SDC is introduced between the LaGaO<sub>3</sub> film and the substrate. The LaGaO<sub>3</sub>/SDC bilayer film exhibits electrical conductivity close to that of a bulk one. A single fuel cell using the LaGaO<sub>3</sub>/SDC bilayer film shows an open-circuit potential of 1.1 V, which is close to the theoretical value. A quite large power density of 0.6 W cm<sup>-2</sup> is achieved at 773 K with a LaGaO<sub>3</sub> film of 5 μm in thickness. The effects of LaGaO<sub>3</sub> film thickness on power generation are further studied. Although the open-circuit potential increases, the maximum power density decreases with increasing thickness. On the other hand, the open-circuit potential becomes lower with thicknesses below 5 μm. This suggests that the reaction between NiO and the LaGaO<sub>3</sub> film occurs with an excessively thin film. Therefore, the largest power density is obtained with a film thickness of 5 μm. The effects of interlayer compound are also examined. The application of La(Sr)Ga(Fe)O<sub>3</sub> (LSGF) is also effective in obtaining high power density, but the maximum value is less than that achieved with a SDC interlayer. A two-cell stack is successfully demonstrated.

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**Keywords:** LaGaO<sub>3</sub> thin film; Laser ablation method; Solid oxide fuel cell; Intermediate temperature operation

## 1. Introduction

Solid oxide fuel cells (SOFCs) can directly convert the chemical energy in fuels to electricity via electrochemical reactions. Because there is no mechanical conversion, the efficiency of an SOFC is not limited by the Carnot efficiency. Therefore, SOFCs offer high energy-conversion efficiency, namely greater than 50% for a normal single operation and over 70% for a combined system with turbine. In addition, including fuel flexibility, SOFCs offer many advantages over conventional power-generation technologies [1–5]. At present, the major obstacle to the commercialization of SOFCs is related to the high temperature of operation. At present, Y<sub>2</sub>O<sub>3</sub> stabilized ZrO<sub>2</sub> is the commonly used electrolyte for SOFCs. Due to the low oxide ionic conductivity, SOFCs are generally operated at around 1000 °C.

Such a high temperature requires the use of ceramic materials and restricts service life. Therefore, a decrease in operating temperature is an important issue in the development of SOFCs. With decrease in operating temperature, the output performance of an SOFC falls sharply because of an increase in internal resistance (IR drop). Therefore, a solid oxide electrolyte with a high conductivity and in the form of a thin film is essential in order to achieve a high power density at a decreased temperature [6–8]. Lanthanum gallate doped with Sr and Mg, i.e., La(Sr)Ga(Mg)O<sub>3</sub> denoted as LSGM in this study, is an alternative electrolyte [9]. Its conductivity is almost one order of magnitude higher than that of yttria stabilized zirconia over an intermediate temperature range (500–900 °C). Thus, it is considered to be a promising electrolyte for an intermediate temperature SOFC (IT-SOFC). It is however, rather difficult to fabricate LSGM thin films on anode substrates because of the high reactivity of LSGM and NiO [10,11]. In this study, a LSGM film was prepared on a Ni-based anode substrate and the power generation property of the SOFC was studied in details.

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Pulsed-laser deposition can be utilized to prepare a dense oxide film with a crystalline phase at relative low temperature [12–14]. There is however, a limitation to thickness if the film is directly deposited on a porous substrate. Therefore, in this study, the electrolyte films were first deposited on dense NiO(FeO)–SDC substrates, and then by in-situ reduction, porous cermet anode substrates were obtained and the resulting LSGM film on a porous cermet anode was used in SOFC single cells. In this way, thin electrolyte films of a few micrometer are easily fabricated and a high power density is achieved at reduced temperature.

## 2. Experimental

NiO–Fe<sub>3</sub>O<sub>4</sub> mixed oxide powder (9:1 in metallic weight ratio) was prepared by an impregnation method. First, Fe(NO<sub>3</sub>)<sub>2</sub>·H<sub>2</sub>O was dissolved in de-ionized water and then NiO powder was added to the solution. After the suspension was dried while stirring, it was decomposed in a ventilated furnace at 673 K for 4 h. The resulting powder was calcined in a muffle furnace at 1073 K for 4 h. NiO(Fe<sub>3</sub>O<sub>4</sub>) was thoroughly mixed with SDC at a NiO:SDC = 6:4 weight ratio using a mortar and pestle. The resulting powder was die-pressed at 10 MPa into discs with a diameter of 20 mm and a weight of 2 g, and then isostatically pressed at 40 MPa. The green discs were sintered at 1723 K for 5 h. Before depositing the electrolyte films, the surfaces of the substrates were ground with a diamond polisher.

The SDC (Sm<sub>0.2</sub>Ce<sub>0.8</sub>O<sub>2</sub>) interlayer and LSGM (La<sub>0.9</sub>Sr<sub>0.1</sub>Ga<sub>0.8</sub>Mg<sub>0.2</sub>O<sub>3</sub>) films were deposited by means of commercial PLD equipment (Pascal PLD-7). The composition of the resulting film was determined by X-ray fluorescence measurement (XRF). The deposition chamber was evacuated to 10<sup>-7</sup>–10<sup>-8</sup> Pa and then filled with O<sub>2</sub> to 5 × 10<sup>-3</sup> Pa. The substrate was heated to 1073 K by a IR heater before the deposition was performed. The heating and cooling rate were controlled at 200 K h<sup>-1</sup>. After deposition, the films were post-annealed in air at 1073 K for 2 h.

A cathode oxide of Sm<sub>0.5</sub>Sr<sub>0.5</sub>CoO<sub>3</sub>, was synthesized by the modified citric acid method. The cathode was prepared by slurry-coating and then fired at 1073 K for 30 min. Silver paste was used for the reference electrode, which was set close to the cathode. Power-generating curves were measured by the 4-probe method and the corresponding polarization was measured by the current interruption technique. The electrical conductivity of the films was determined with the Van der Pauw method and an Al<sub>2</sub>O<sub>3</sub> dense substrate was used.

## 3. Results and discussion

The effects of oxygen partial pressure in deposition chamber on the quality and composition of the film was studied in detail. This is because the background oxygen partial pressure is one of the most important parameters for obtaining a high quality film. The compositions of the resulting LSGM films as a function of the oxygen partial pressure are given in Fig. 1. It is obvious that the composition of the LSGM film is nearly independent of the oxygen pressure at low  $P_{O_2}$  pressure. When the oxygen partial

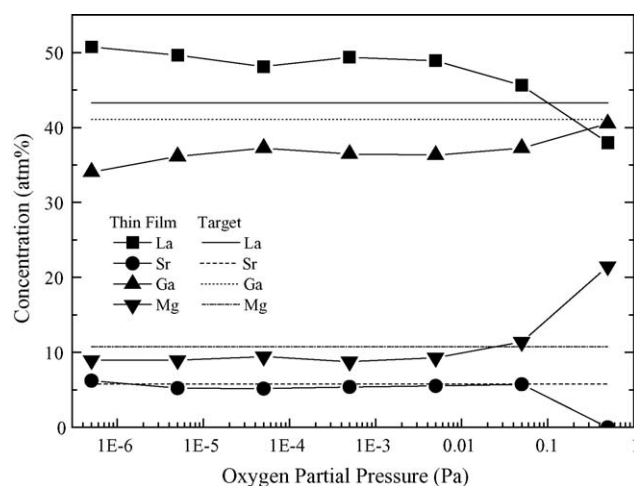


Fig. 1. Dependence of composition of LSGM films on oxygen pressure in deposition chamber.

pressure is higher than 0.1 Pa, the composition of the LSGM film deviates drastically. From the viewpoint of composition, lower  $P_{O_2}$  is preferable, but the deposition rate increases with increasing  $P_{O_2}$  while the crystallinity of the film becomes lower with decreasing  $P_{O_2}$ . In terms of the quality and composition of the film, the optimized  $P_{O_2}$  seems to be 0.05 Pa. Therefore, the oxygen partial pressure during deposition is always kept at 0.05 Pa in this study.

The XRD patterns of the prepared LSGM/SDC bilayer film before reduction and after reduction are shown in Fig. 2. The perovskite phase of LSGM and the fluorite phase of SDC are already formed in the as-deposited condition. On comparison with the diffraction pattern of LSGM in JCPDS files, the relative intensity of the main peak of which index is (1 1 2) is found to be strong. Therefore, the obtained LSGM film may be oriented in the (1 1 2) direction. Except for the change in relative peak intensity, no diffraction peaks from a secondary phase nor a shift in diffraction angle of the LSGM as well as the SDC film are observed. Therefore, the reaction between LSGM, SDC and Ni-based cermet substrate is negligible.

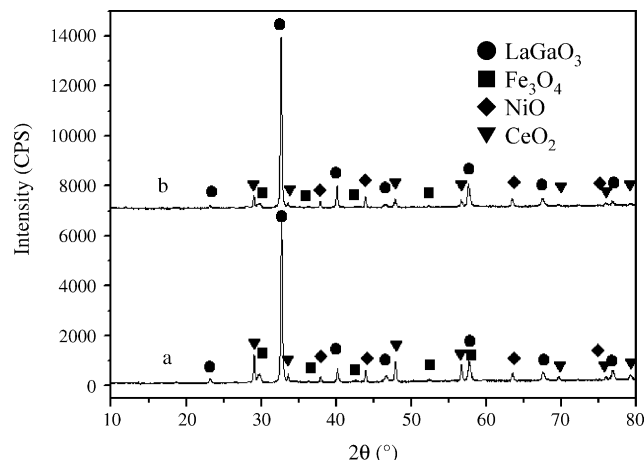


Fig. 2. XRD patterns of prepared LSGM/SDC bilayer film before reduction and after reduction.

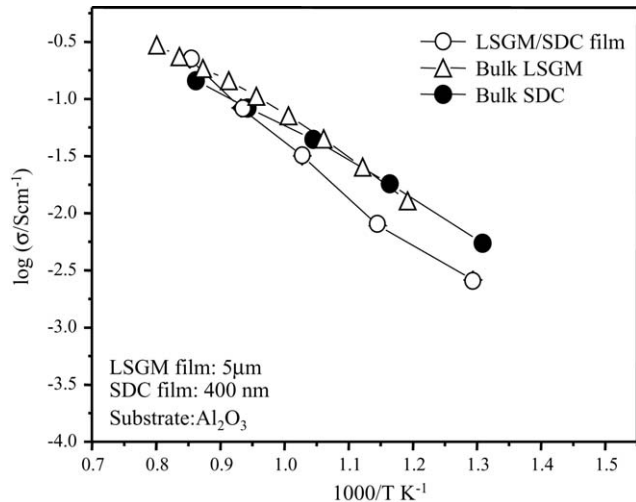


Fig. 3. Temperature dependence of electrical conductivity of LSC-SDC bilayer film, bulk LSGM and bulk SDC.

The temperature dependence of the electrical conductivity of the LSC/SDC bilayer film and that of bulk LSGM and SDC are presented in Fig. 3. The electrical conductivity of the deposited LSGM/SDC film is slightly lower than that of bulk LSGM and SDC. In addition, the apparent activation energy for the conductivity is slightly larger than that of LSGM or SDC. Compared with the bulk sample, the decrease in conductivity of the film is small and also considering the potential barrier at the interface between the LSGM and the SDC film, it is concluded that the LSGM/SDC film has almost the same conductivity as that of bulk LSGM and SDC. Therefore, in accordance with the XRD results, the reaction between LSGM and NiO can be prevented by a SDC buffer layer.

Application of the LSGM/SDC bilayer electrolyte film in a SOFC was studied. The open-circuit voltage (OCV) and the maximum power density (MPD) as a function of the thickness of the LSGM film at 873 K is presented in Fig. 4. The IR loss, and the anodic and cathodic overpotentials are given as a function of LSGM film thickness at  $0.5 \text{ A cm}^{-2}$ . Here, it is noted that the thickness of the SDC layer was kept to a thickness of

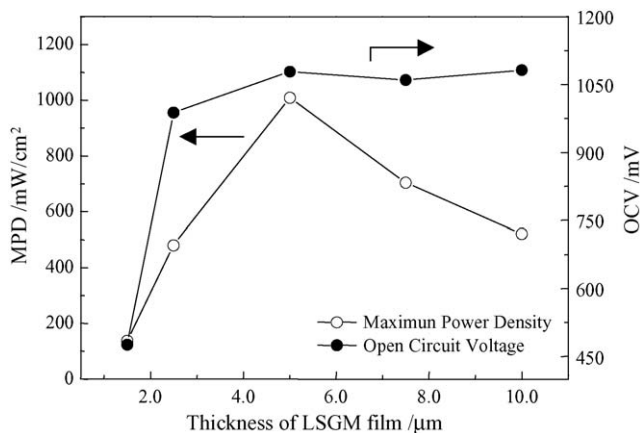


Fig. 4. Maximum power density (MPD) and open-circuit voltage (OCV) of SOFC single cells based on LSGM films with various thicknesses (with SDC interlayer of 200 nm thickness) at 873 K.

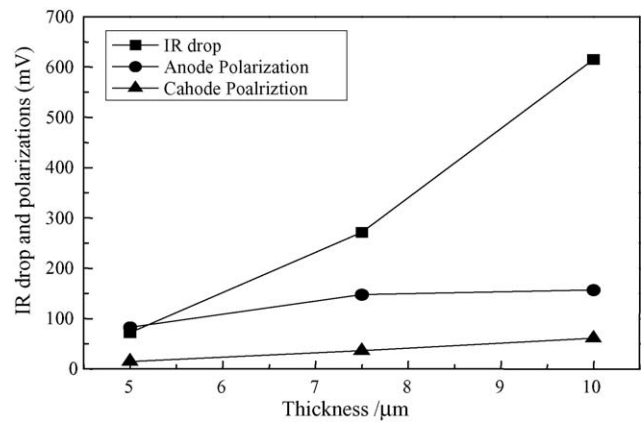


Fig. 5. Internal resistance of cell as function of thickness of LSGM/SDC bilayer film at  $0.5 \text{ A cm}^{-2}$ .

200 nm. Since the short-circuit current becomes too small to be measured, the internal resistance, IR drop and overpotential cannot be measured at thicknesses of less than  $3 \mu\text{m}$ . The detailed internal resistance of cell using a LSGM film thicker than  $5 \mu\text{m}$  is shown in Fig. 5. With decrease in the thickness of the LSGM film from 10 to  $5 \mu\text{m}$ , the OCV remains nearly constant, but the maximum power density increases linearly. This is explained by decrease in the electrical resistance of the electrolyte, which can be seen from the decreased IR loss, as shown in Fig. 5. Increase in power density with decreasing electrolyte thickness is reasonable. With further decrease in the thickness of the LSGM film, the OCV deviates from the theoretical value. In particular, when the film thickness is thinner than  $2 \mu\text{m}$ , the OCV drops sharply. In accordance with the decrease in OCV, the MPD of the cell also decreases. At present, the exact reason for the decreased OCV is not clear, but, three causes are possible: (i) gas leakage from the LSGM film due to pinholes formed in LSGM film; (ii) partial electronic conduction resulting in a short-circuited condition of the cell; (iii) a physical short-circuit during application of the  $\text{Sm}(\text{Sr})\text{CoO}_3$  oxide cathode. Scanning electron microscope observations suggest that the film is still dense even at  $2 \mu\text{m}$  in thickness. Therefore, physical gas leakage from the LSGM film can be excluded as a cause of decreased OCV. Although it is reported that the partial electrical conductivity in bulk LSGM is negligibly small, it becomes significant with decreasing thickness due to an increased oxygen gradient. At present, this seems to be the most reasonable explanation for the decreased OCV. In any event, due to the decrease in OCV at excessively thin film thicknesses, the LSGM film has an optimum thickness, of around  $5 \mu\text{m}$  according to the results in Fig. 4. At this thickness, a MPD of  $1 \text{ W cm}^{-2}$  is achieved at 873 K.

The thickness of the SDC interlayer was also examined. The output performances of SOFC single cells with SDC interlayers of different thickness are shown in Fig. 6. It is expected that the internal resistance of the cell will increase with increasing interlayer thickness and result in decreased power density. On the other hand, if the thickness of SDC interlayer is too thin, then the reaction between LSGM and NiO or even SDC cannot be prevented and will result in the formation of impurities with high resistance. Therefore, it is reasonably considered

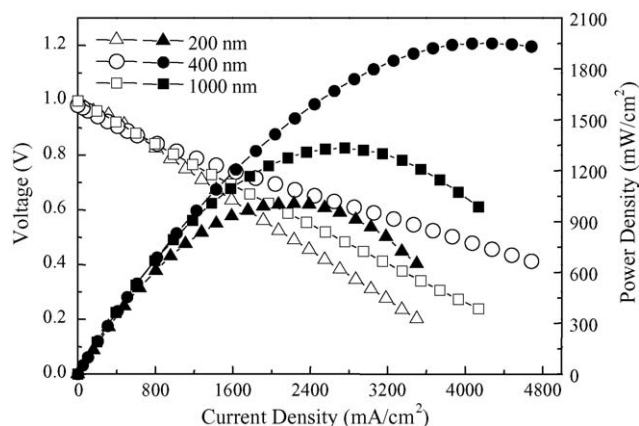


Fig. 6. Effect of SDC interlayer thickness on power density of SOFC using LSGM film of 5 μm thickness at 873 K.

that a suitable thickness of the SDC interlayer should exist. In accordance with this expectation, the power density of the cell decreases when the SDC thickness is increased to 1 μm. By contrast, it also decreases when a SDC of thickness of 200 nm is used for interlayer. Accordingly, the highest power density of the cell is obtained with a SDC interlayer of 400 nm. Thus, in the following studies, a 5-μm LSGM and a 400-nm SDC is employed in the bilayer electrolyte.

The effects of the interlayer compound have been further studied. The power generation property of a single-cell SOFC using a 5 μm thick LSGM electrolyte is presented in Fig. 7. It is obvious that the OCV becomes much smaller than that of the LSGM–SDC bilayer film. This can be explained by a reaction between LSGM and NiO in the substrate. Although the OCV is as small as 0.7 V, an extremely large power density of 2 W cm<sup>-2</sup> is achieved at 973 K and even at 673 K some power can be obtained. Therefore, although no protection layer is inserted, the LSGM film works as an oxide ion conductor. A higher power density can be anticipated by preventing reaction between the LSGM film and the NiO-based substrate. Up to now, SDC has been used for the interlayer compound in order to prevent reaction. Nevertheless, since SDC has some reactivity with LSGM and La easily diffuses into the SDC layer, better protection-layer

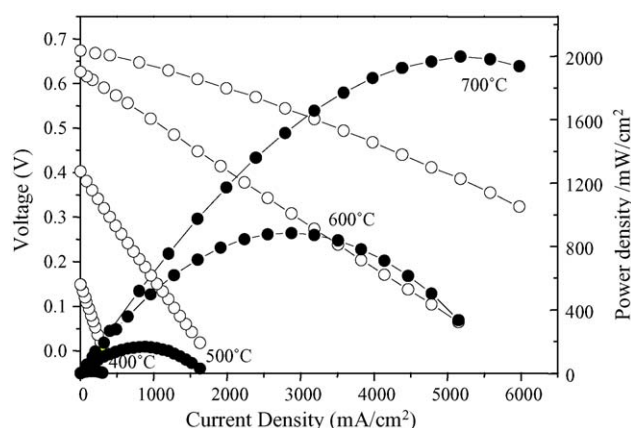


Fig. 7. Power generation property of single SOFC using 5 μm thick LSGM electrolyte.

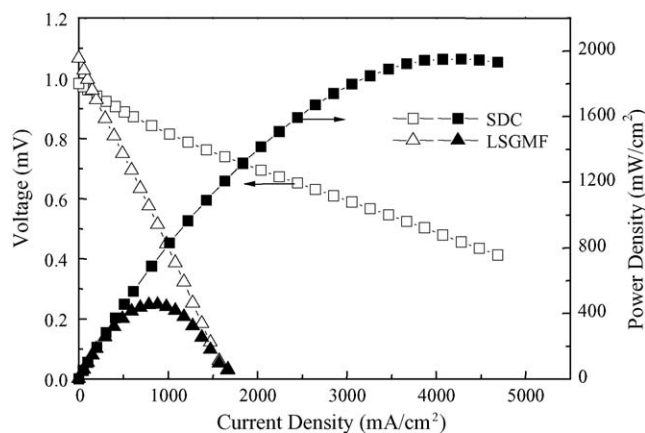


Fig. 8. Comparison of power-generating property of SOFC using SDC or LSGMF interlayer compound at 873 K. LSGM film with 5 μm always used.

compound is necessary to achieve further improvement in power density. Recently, it has been found [15] that Fe doped LaGaO<sub>3</sub>, i.e., La<sub>0.7</sub>Sr<sub>0.3</sub>Ga<sub>0.7</sub>Fe<sub>0.2</sub>Mg<sub>0.1</sub>O<sub>3</sub>, (LSGMF) is another interesting oxide ion conductor. Therefore, application of LSGMF has been evaluated for the interlayer.

A comparison of the power generating property of SOFCs using SDC or a LSGMF interlayer compound at 873 K is given in Fig. 8. The interlayer compound has a great influence on the power-generating property despite the fact that the same thickness of LSGM electrolyte film is used. It is obvious that a much higher power density is achieved by using SDC for the interlayer compound. The OCV, however, becomes lower than the theoretical value. By contrast, when LSGMF is used for the interlayer compound, the OCV is close to 1.0 V, which is much higher than that of a SDC interlayer. At present, the mechanism by which OCV depends on the interlayer compound is not clear; it might be related to the partial electronic conductivity of the interlayer compound. The internal resistance was also measured in detail and the comparison is summarized in Table 1. Since the interlayer compound is inserted in the anodic side, the overpotential of the cathode is almost independent of the composition of the interlayer compound. On the other hand, it is seen that the interlayer compound significantly affects not only the IR loss but also the anodic overpotential. Since LSGMF is a p-type semiconductor and its electrical conductivity becomes lower with decreasing  $P_{O_2}$ , the large electrical resistance appears to originate from the low electrical conductivity of LSGMF under H<sub>2</sub> atmosphere. The electronic conductivity is dominant with a SDC under a hydrogen atmosphere. The total electrical conductivity becomes much higher in a reducing atmosphere case of

Table 1  
Internal resistance, anodic and cathodic polarization (under a current density of 1000 mA cm<sup>-2</sup>) of SOFC single cells with different interlayers between LSGM films and the anode substrates at 873 K

Interlayer material	IR (mV)	$\eta_a$ (mV)	$\eta_c$ (mV)
Non	53.26	79.66	27.53
SDC	49.08	84.22	28.00
LSGMF	155.96	440.26	31.54

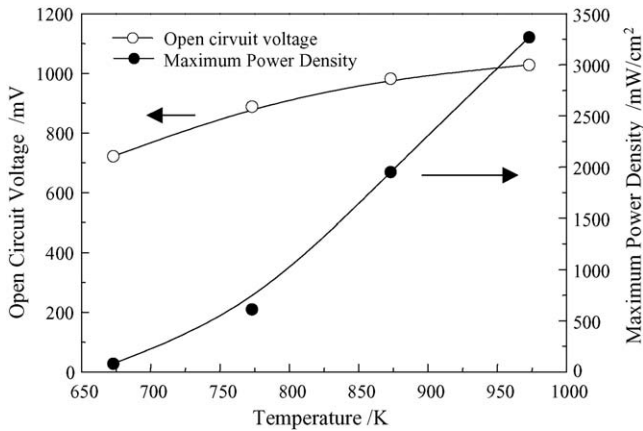


Fig. 9. Temperature dependence of OCV and MPD of the cell using LSGM (5 μm)–SDC (400 nm) bilayer film for electrolyte.

SDC, which leads to the observed small interlayer resistance. In any case, given that the OCV, LSGFM are optimum, the SDC appears to be a better interlayer compound due to its high power density.

The temperature dependence of the OCV and the MPD of a cell using a LSGM (5 μm)/SDC (400 nm) bilayer film for electrolyte are shown in Fig. 9. It is obvious that an extremely high power density can be achieved with this cell and the maximum value at 673 K is as high as 80 mW cm<sup>-2</sup>. These data suggests that the operating temperature of the SOFC can be lowered to 773 K. On the other hand, the OCV of this cell also decreases with decreasing temperature. This may be due to partial electronic conduction and physical gas leakage. Therefore, in order to enhance the power density at reduced temperature, further improvement of the LSGM composition as well as the interlayer compound is required. This is now under investigation and the results will be reported elsewhere.

Since high power density is achieved with the single cell, the power generation properties of a two-cell stack was investigated. A schematic view of the set-up of the stack is shown in Fig. 10. Circular-shaped planer type cells with a seal-less structure [16] were adopted. The single cell had a diameter of 20 mm and the fuel and oxidant were fed into the cell at the centre of each bipolar plate. The flow rate of H<sub>2</sub> with 3 vol% H<sub>2</sub>O and that of air were set at 300 and 200 ml min<sup>-1</sup>, respectively.

The power-generating characteristics of cell stacks consisting of two single cells with a LSGM (5 μm)/SDC (400 nm) bilayer

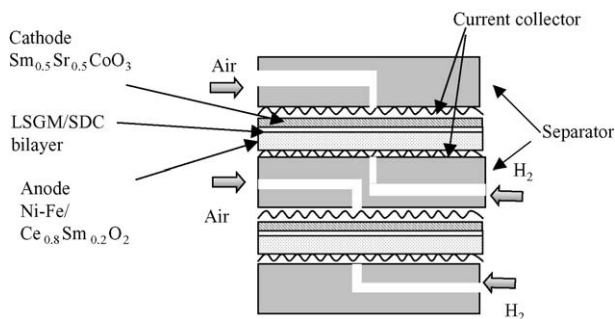


Fig. 10. Schematic view of set-up for cell stack.

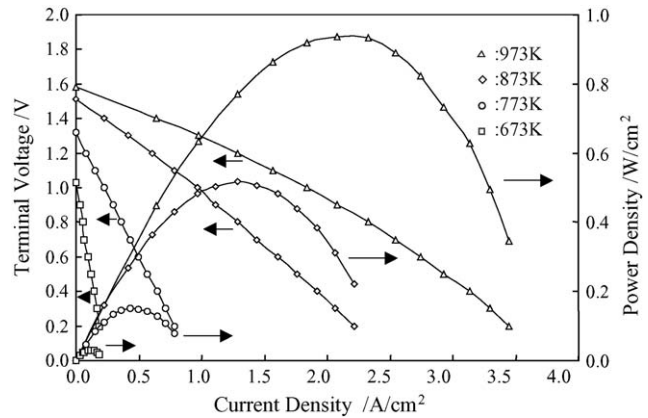


Fig. 11. Power-generating property of cell stacks consisting of two single cells with LSGM (5 μm)–SDC (400 nm) bilayer electrolyte.

electrolyte is shown in Fig. 11. Compared with the performance of a single cell (Fig. 9), a two-cell stack shows a smaller OCV and a maximum power density. The lower OCV can be assigned to the seal-less structure. The maximum power density of the cell reaches a value of 0.95 W cm<sup>-2</sup> at 973 K. Considering the power density of the single cell, the power density of the two-cells stuck is much smaller, and this can be assigned to the problem of gas distribution. Nevertheless, considering the operation temperature, it can be said that the maximum power density of this short stack is reasonably high. In addition, current can be drawn even at 673 K and the MPD at 773 K is higher than 100 mW cm<sup>-2</sup>. Therefore, as shown in Fig. 11 this study successfully demonstrated good short-cell stack performance. In order to identify the decrease in power density, the power-generating property of each cell is shown in Fig. 12 at 973 K. The OCVs of cells 1 and 2 are 0.75 and 0.9 V, respectively. In addition, the maximum power density of the cell 1 is 0.54 W cm<sup>-2</sup>, which is almost half of that cell 2. Therefore, if the performance of this cell could be improved, the power density of the stack could be elevated appreciably. Nevertheless, this study reveals that a SOFC using a LSGM/SDC bilayer film exhibits high power density at a reduced temperature in both a single cell and a short stack.

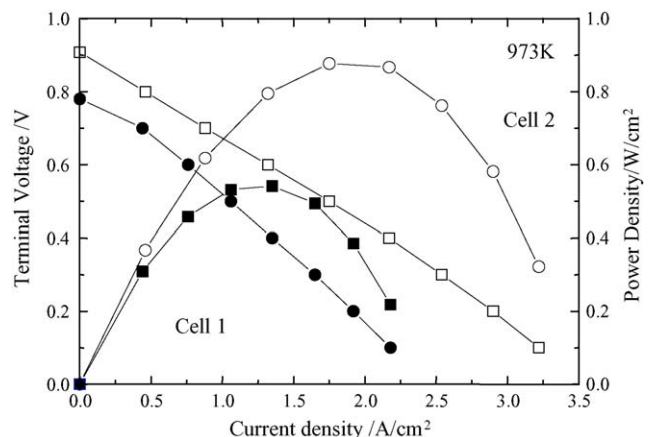


Fig. 12. Power-generating property of each cell in stack at 973 K.

#### 4. Conclusions

Dense LSGM thin films of 5  $\mu\text{m}$  in thickness have been fabricated on dense  $\text{NiO}(\text{Fe}_3\text{O}_4)$ –SDC substrates by pulsed-laser deposition and using SDC (400 nm) for the interlayer. The composition of the films is nearly independent of the background pressure of oxygen in the deposition chamber when the pressure is low. After in situ reducing  $\text{NiO}$  and  $\text{Fe}_3\text{O}_4$ , porous cermet substrates are formed, and exhibit high electrochemical activity for hydrogen oxidation. The output performance of SOFC single cells using LSGM/SDC bilayer films as electrolyte increases with decreasing thickness of the LSGM film (when the film thickness is larger than 5  $\mu\text{m}$ ) because of a decrease of IR drop. Further decrease in the thickness of the LSGM film leads to a fall in OCV due to a short-circuit between the two electrodes and gas leakage through the film. The thickness of the SDC interlayer also affects cell performance and the optimum thickness of SDC interlayer is about 400 nm. High power density can be achieved, not only with a single cell but also with a two-cell stack. Since the power density of cell 1 is much lower than that of cell 2, the power density of stack is lower than that of single cell. Nevertheless, a reasonably high power density can be achieved with the stack; the maximum power density at 773 K is as high as  $100 \text{ mW cm}^{-2}$ . Consequently, this study reveals that the operating temperature of SOFC can be lowered to less than 773 K by using LSGM film.

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