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Preparation of $LaGaO_3$ Based Oxide Thin Film on Porous Ni-Fe Metal Substrate and its SOFC Application

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ABSTRACT

$LaGaO_3$ thin film was prepared on Ni-Fe metal porous substrate by Pulsed Laser Deposition method. By the thermal reduction, the dense NiO-Fe_3O_4 substrate is changed to a porous Ni-Fe metal substrate. The volumetric shrinkage and porosity of the substrate are controlled by the reduction temperature. It was found that a thermal expansion property of the Ni-Fe porous metal substrate is almost the same with that of $LaGaO_3$ based oxide. $LaGaO_3$ based electrolyte films are prepared by the pulsed laser deposition (PLD) method. The film composition is sensitively affected by the deposition temperature. The obtained film is amorphous state after deposition. After post annealing at 1073 K in air, the single phase of $LaGaO_3$ perovskite was obtained. Since the thermal expansion coefficient of the film is almost the same with that of LSGM film, the obtained metal support LSGM film cell shows the high tolerance against a thermal shock and after 6 min startup from room temperature, the cell shows the almost theoretical open circuit potential.

Key words : Metal Support, $LaGaO_3$ electrolyte, Pulse Laser Ablation

1. Introduction

Solid oxide fuel cells (SOFCs) have been attracting much interest as the power generator for various fields because of a variety of fuel, long life, and highest energy efficiency in fuel cell.[1-4] Since the operations at the intermediate-temperature were important issues from short start-up time and variety of materials used, the SOFC using the lanthanum gallate doped with strontium and magnesium, La(Sr)Ga(Mg)$O_{3-\delta}$ (LSGM), is extensively studied because of the higher oxide-ion conductivity and high ionic transference number. In particular, in our previous study, $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ (LSGM) exhibited the high and stable oxide-ion conductivity over a wide range of oxygen partial pressure.[5-8] It has been reported already that the SOFC cell using the LSGM film shows high performance even at the intermediate-temperature like 773 K.[9-12]

In order to improve the cell performance, a porous anode and a thin and dense electrolyte film is essentially requested. The various methods such as spin coating,[13] colloidal deposition,[14] plasma spraying[15] and electrostatic assisted vapor deposition,[16] pulsed laser deposition (PLD)[7-10] and metal organic chemical vapor deposition[17] have been studied for deposition of the electrolyte on anode substrate. Recently, PLD method is attracting much interest among them because of simple technique, easy control of the film composition, and uniformity in film thickness.

Ni based cermet materials are generally used as anode material in conventional SOFCs. However, at the intermediate temperature, the performance of Ni based anode is not high enough. As well known, the catalytic activity was greatly improved by small amount of additives. In our previous work, the metal additives for anode were investigated, among the metal added Ni anodes, Fe added one exhibited the smallest over-potential in an intermediate temperature range.[12]

At present, usage of metal support for a thin film SOFC is important subject for improving reliability of SOFCs. However, because of a mismatch in thermal expansion property, preparation of SOFC on metal substrate is difficult up to now. In this work, we used the Ni-Fe bimetallic anode for a metal supporting SOFCs. In order to prepare the thin electrolyte film by PLD method, we used the dense composite oxide disk as the substrate. After the film deposition, the dense anode substrate was reduced to obtain the porous metal substrate in H_2 flow. Optimization of deposition condition of LSGM and also porous Ni-Fe metal substrate was investigated in this study.

2. Experiments

Fe_2O_3 coated NiO powder was prepared by a traditional impregnation method. $Fe(NO_3)_2 \cdot 6H_2O$ was dissolved in deionized water, and then NiO powder was added into the solution proportionately. After dryness, the obtained pow-

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der was calcined in a ventilated furnace at 673 K for 2 h to decompose nitrate acid and then fired at 1273 K for 6 h. The oxide mixture was pressed into disks (25 mm in diameter) under 20 MPa. After iso-statically pressing at 50 MPa, the obtained disks were sintered at 1723 K for 5 h.

In order to achieve a uniform and nano size-controlled pore in metal, the successive reduction of NiO-Fe_2O_3 nano composite was adopted. In according to the phase diagram,[19] metal oxide composite of Ni:Fe (9:1 by the weight ratio) consists of two phase mixture of $(Ni_{0.95}Fe_{0.05})O$ and $(Fe_{0.7}Ni_{0.3})_3O_4$. Since Ni rich phase of $(Ni_{0.95}Fe_{0.05})O$ is readily reduced comparing with that of Fe rich one, $(Fe_{0.7}Ni_{0.3})_3O_4$, reduction of two phase mixture leads to micro pore by a preferential reduction of $(Ni_{0.95}Fe_{0.05})O$ but $(Fe_{0.7}Ni_{0.3})_3O_4$ is reduced slowly resulting in suppression of shrinkage and form pore. The substrates were reduced at various temperature ranged from 573 to 973 K and the porosity and volume shrinkage were measured after reduction at various temperature.

LSGM and SDC bilayer films were deposited on the dense NiO-Fe_2O_3 substrate by laser ablation method with commercial equipment (PLD-7, PASCAL). Before deposition, the chamber was evacuated to a pressure lower than 10^{-7} torr and then adjusted to a designated pressure, 0.005 torr, by introducing oxygen. The laser power and frequency were controlled at 180 mJ/pulse and 10 Hz, respectively. The substrate was heated to 773, 973 and 1073 K before deposition. The heating and cooling rate was 200 K/h. Sm-doped CeO_2 ($Sm_{0.2}Ce_{0.8}O_2$, Daiichi Kigenso) was deposited between LSGM and NiO-Fe_2O_3 substrate with same conditions for preventing reaction between LSGM and NiO. Morphology and composition of films prepared at different temperature was determined by SEM-EDAX.

3. Results and Discussion

3.1. Preparation of Ni-Fe porous metal substrate

For the preparation of porous metal substrate, several methods, mainly mechanical drilling, were used. However, considering the cost, mass production, and uniformity in pore size, chemical reduction method is more preferable. However, detail study on the preparation of porous metal by a chemical reduction method is not reported up to now. Fig. 1 shows the SEM image of the substrate after sintering of NiO-Fe_3O_4 mixed oxide. After sintering at 1723 K, the color of disk was changed from green to black suggesting that the reduction of NiO or Fe_3O_4 is occurred. Evidently, highly dense substrate without crack and hole was obtained as shown in Fig. 1. These dense disks are suitable for depositing the electrolyte film with a few ìm scales by PLD method.

As mentioned above, in order to get the good cell performance, both the thin electrolyte film and the porous substrates are requested. So, we investigated the effects of reduction temperature in H_2 for obtaining the optimal porous substrate. The reductions were carried out in H_2 stream (100 ml/min). Fig. 2 show the SEM images of reduced NiO-Fe_2O_3 disks at various temperatures. The shape of big grains can still be observed, however, it is seen that each grains are consisted of small and uniform pores and turned to be porous. At temperature lower than 773 K, the size of pores is large and seems like a crack. This may be occurred by the slow reduction rate and the large shrinkage of NiO particle. Although, when the reduction temperature was higher than 773 K, the uniform and randomly distributed porous structures were obtained.

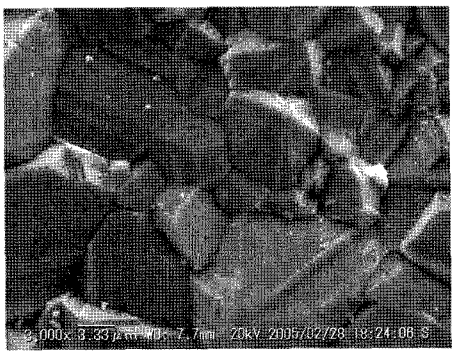

Fig. 1. SEM image of NiO-Fe_2O_3 substrate prepared in this study.

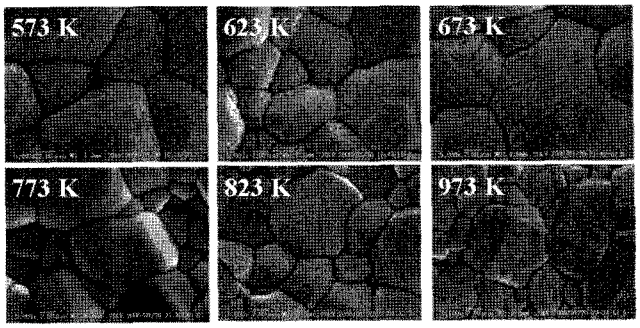

Fig. 2. SEM image of the NiO-Fe_3O_4 substrate after reduction at different temperature.

Fig. 3 show the XRD patterns of the NiO-Fe_2O_3 bimetal substrate before and after reduction. Before reduction, the substrate is just composite oxide of NiO and Fe_2O_3. However, after reduction, only diffraction peaks from Ni is observed and so Ni-Fe alloy seems to be form. It is also noted that lattice parameter increased suggesting solid solution of Fe with larger atomic radii. From phase diagrams, Ni and Fe form an alloy in all composition range and so Ni-Fe bimetal with FCC structure is formed after reduction of NiO-Fe_3O_4 precursor after H_2 reduction.

Fig. 4 shows the volumetric shrinkage and the porosity of the disk as a function of reduction temperature. The porosity was measured with the Archimedes method and the shrinkage was estimated by comparing the size of the disk before and after reduction. In order to achieve a high power generation, the randomly distributed and uniform pores should be obtained because of three phase boundary (TPB) as large as possible. The largest porosity was achieved by

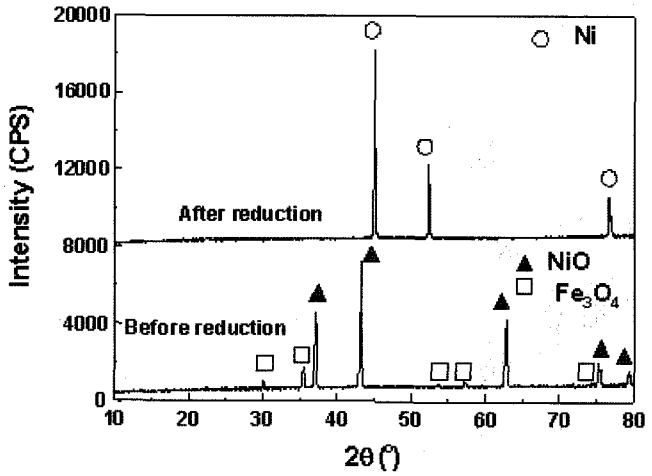

Fig. 3. XRD patterns of the anode substrate before and after reduction.

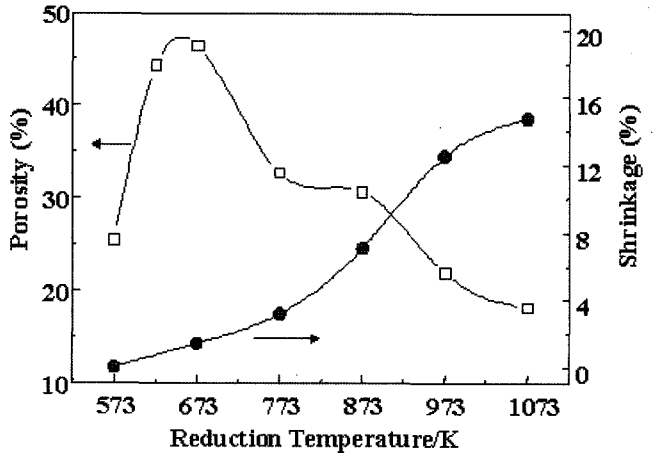

Fig. 4. The porosity and the volumetric shrinkage of anode substrate as a function of reduction temperature.

the reduction at around 673 K. However, the big pore like a crack was formed when the substrate was reduced at 673 K. These big pores may create the fuel leakage during the power generation and cannot form large TPB. Although the porosities of substrate reduced above 773 K were comparatively small, it is considered that this substrate were sufficient for the porous substrate of SOFCs. In order to obtain the thin electrolyte without cracking after the reduction of substrate, the shrinkage of substrate should be as small as possible. Shrinkage of the substrate increased as the reduction temperature increases. However, shrinkage is not significant up to 873 K and so, if electrolyte film deposited on the surface of NiO-Fe_2O_3 dense substrate followed by reducing, the mechanical stress caused by shrinkage of disk seems not to be large.

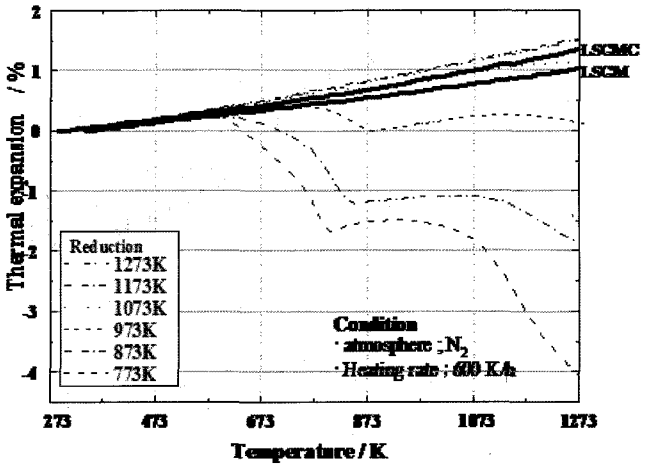

Fig. 5. Thermal expansion property of the Ni-Fe bimetal substrate after reduction at various temperatures.

Fig. 5 shows the comparison of thermal expansion property of the prepared Ni-Fe bimetallic porous substrate and that of LSGM. In general, thermal expansion of metal is much larger than that of oxide. However, it is expected that thermal expansion coefficient (TEC) can be controlled by a porosity and additives. As shown in Fig. 5, when the reduction temperature is low, sintering of porous substrate occurred resulting in the shrinkage of disk in spite of increasing temperature. However, in low temperature range, TEC is almost the same with that of LSGM or $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.15}Co_{0.05}O_3$ (LSGMC). On the other hand, when the NiO-Fe_3O_4 substrate is reduced at temperature higher than 973 K, it is evident that the thermal expansion of Ni-Fe substrate is almost the same with that of LSGM or LSGMC. Also, there is no shrinkage of disk by sintering.

Table 1. Thermal Expansion of Ni-Fe Metal Substrates Reduced at Different Temperature

Sample		100°C→400°C		600°C→800°C	
		Expansion(ΔL/L)/%	CTE×10^{-5}/K^{-1}	Expansion(ΔL/L)/%	CTE×10^{-5}/K^{-1}
NiFe	1000°Cred.	0.409	1.36	0.339	1.70
	900°Cred.	0.428	1.43	0.342	1.71
	800°Cred.	0.415	1.38	0.267	1.34
	700°Cred.	0.349	1.16	0.217	1.09
	600°Cred.	0.040	0.14	0.089	0.45
	500°Cred.	−0.501	−1.67	−0.618	−3.09
LSGM-9182		0.414	1.04	0.233	1.16
LSGMC-5		0.474	1.18	0.324	1.62

Therefore, in spite of metal, Ni-Fe bimetallic porous substrate shows almost the same TEC with that of LSGM as shown Table 1. Therefore, the metal supporting SOFC can be easily prepared by deposition of electrolyte film on NiO-Fe_3O_4 dense substrate followed by reduction. Considering the shrinkage, porosity, and thermal expansion property, the optimum reduction temperature for NiO-Fe_3O_4 substrate after LSGM electrolyte deposited seems to exist around 1073~1173 K.

3.2. Optimization of LSGM/SDC bilayer film preparation by PLD method

Since LSGM consists of 4 elements, control of the film composition is rather difficult but highly important for the deposition of LSGM film for electrolyte. It is well-known that PLD method has an advantage of small deviation in composition from that of the target. However, in our previous study, it is seen that the composition of the deposited film tends to change with increasing the number of component elements. In this study, adjustment of the film composition for LSGM electrolyte by substrate temperature and deposition parameter was studied.

The composition of LSGM film was changed sensitively by the substrate temperatures as shown in Fig. 6. By elevating substrate temperature, the concentration of strontium and magnesium decreased although that of gallium increased. These changes are related with the vapor pressure of the elements. For example, temperature of vapor pressure at 1 Pa for La, Sr, Ga and Mg are 2005, 796, 1310 and 701 K, respectively. This suggests that strontium and magnesium is evaporated easily and also the composition of the film may be changed by the successive evaporation from the deposited film. Therefore, it is expected that deposition temperature is an important factor for controlling the film composition. As shown in Fig.6, in case of La, the amount of La in film is hardly dependent on substrate temperature, however, it is seen that Ga content monotonically increased with elevating substrate temperature. In contrast, in case of Sr and Mg, almost opposite dependency on substrate temperature is observed. This could be explained by an evaporation pressure of each element. In any case, it is seen that almost the same composition to $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_3$ was obtained at substrate temperature of 1073 K. Therefore, the optimum substrate temperature for LSGM film deposition seems to be 1073 K.

The crystal structure of deposited films on the NiO-Fe_2O_3 substrate was measured by X-ray diffraction (XRD) and the results are shown in Fig. 7. Since the composition of film is rich in La, no diffraction peaks from $LaGaO_3$ structure was observed when the substrate temperature was lower than 973 K, as shown Fig. 7(a). On the other hand, in case of the film deposited at 1073 K, evidently, strong X-ray diffraction peaks from $LaGaO_3$ phase is observed, which is in good agreement with the chemical analysis results as shown in Fig. 6. Since no diffraction peaks from secondary phase and also no shift in diffraction angle was observed, single phase of LSGM seems to be successfully obtained by PLD method on NiO-Fe_3O_4 substrate, which was coated with SDC. Com-

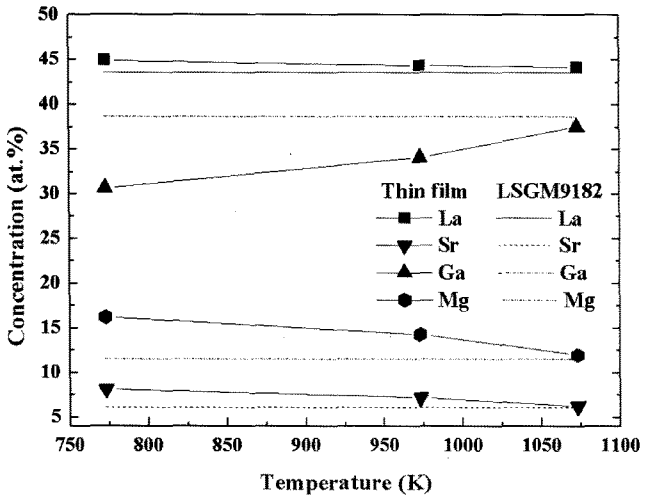

Fig. 6. EDX analysis results of the LSGM film as a function of the substrate temperature. Target composition is $La_{0.7282}Sr_{0.1}Ga_{0.6380}Mg_{0.4255}O_3$.

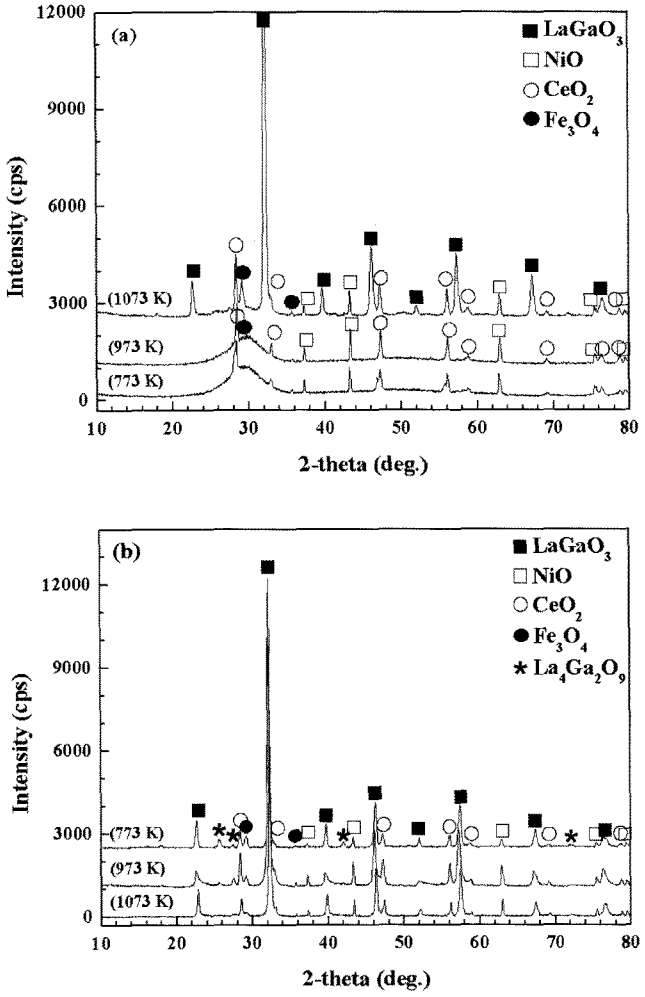

Fig. 7. XRD patterns of the LSGM film obtained at different substrate temperature.
(a) As-deposited film (b) After post anneal at 1073 K.

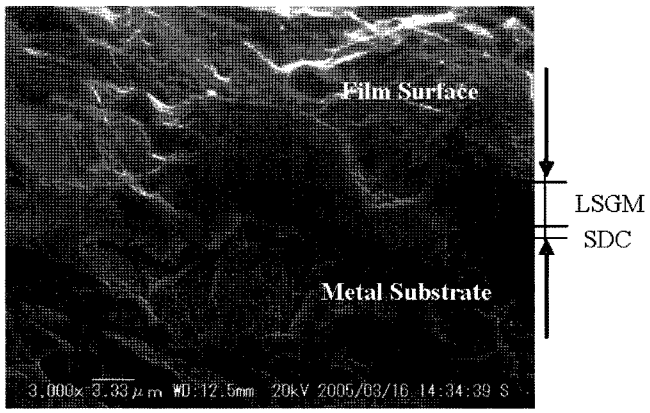

Fig. 8. SEM image of LSGM/SDC bi-layer film deposited on the substrate by pulsed laser deposition after reduction at 1073 K.

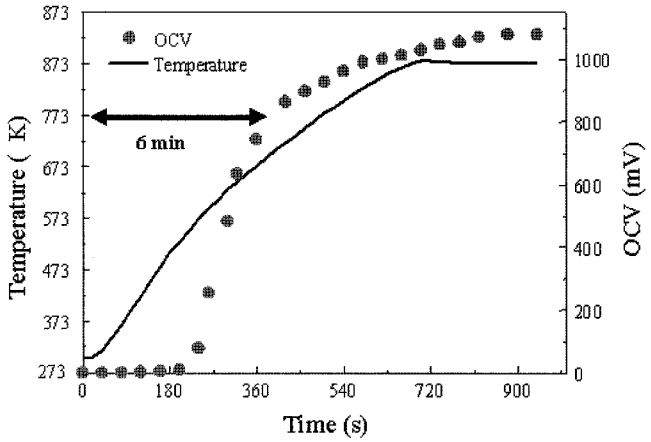

Fig. 9. Programmed temperature, actual furnace temperature, and open circuit potential of the cell as a function of time after heating started.

paring with the relative intensity of the diffraction peaks from polycrystalline $LaGaO_3$, the relative intensity of diffraction peaks from (110) plane was strong on LSGM film suggesting that the film orientated to (110) direction.

Fig. 8 shows LSGM and SDC bi-layer film on the bimetallic porous support of Ni-Fe substrate, which is reduced at 1073 K in H_2. It is seen that the thickness of the deposited LSGM film is around 5 μm and that of SDC is not clearly observed but considering the deposition period, thickness of SDC layer is estimated to be 400 nm. We can confirm the formation of pores in the substrate. On the other hand, it is seen that the deposited film is highly dense and no cracks or pin holes are observed after reduction.

One of the great advantages of the metal supporting SOFCs is the high mechanical strength and the tolerance against the thermal shock. Fig. 9 shows the heating program, the actual temperature for heating SOFCs, and the observed open circuit potential of SOFCs. We adopted the heating rate of 100 K/min and it is seen that the actual temperature of the cell can be elevated to 873 K within 720 s However, the OCV drastically increased from 573 K and it became higher than 0.9 V after 360 s after heating starts. Since the OCV is elevated to a value higher than 1.0 V, which is close to the theoretical OCV, during a quick heat-up, there is no fracture formed and the cell is highly tolerant against the thermal shock.

Consequently, we can successfully deposited LSGM/SDC bilayer electrolyte film on porous Ni-Fe bimetallic substrate, which shows almost theoretical EMF after 6 min heating starts.

4. Conclusion

In this study, the effect of substrate temperature was investigated in the pulse laser deposition method. The thin LSGM film was prepared on the dense NiO-Fe_3O_4 substrate heated to 1073 K. The film has similar composition with that of LSGM9182 and highly dense without holes and cracks. After in-situ reduction of NiO and Fe_3O_4, the porous alloy substrates were successfully obtained and by optimizing the reduction temperature, the shrinkage of the disk could be suppressed within 15% but the reasonably high porosity of 20% was achieved. It is also observed that the thermal expansion property of Ni-Fe alloy porous substrate shows good compatibility with that of LSGM electrolyte. So it is expected that the prepared SOFC using LSGM electrolyte shows superior tolerance against the thermal shock. In fact, theoretical open circuit potential was observed after 6 min heating from room temperature. The prepared LSGM cell supporting on metal substrate shows a high mechanical strength and highly reliable from mechanical property.

Acknowledgments

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