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Low temperature preparation and characterization of LSGMC based IT-SOFC cell by aerosol deposition

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Abstract

A low temperature (≤650 °C) process for fabricating nano-structured (La, Sr) (Ga, Mg, Co)$O_{3-\delta}$ (LSGMC) electrolyte/(La, Sr) (Co, Fe)$O_{3-\delta}$–(Gd, Ce)$O_{2-\delta}$ (LSCF–GDC) cathode films, ∼7 and ∼25 μm in thickness, respectively, was developed using an aerosol deposition (AD) process for use in intermediate temperature solid oxide fuel cells (IT-SOFCs). NiO–GDC was used as an anode substrate in anode-supported type cells. The deposited LSGMC electrolyte and LSCF–GDC composite cathode film maintained good adhesion with the NiO–GDC anode, even though the coating processes were completed at the room temperature. The LSGMC electrolyte was composed of nano-sized grains smaller than 30 nm. The electrical conductivity of the LSGMC electrolyte fabricated at room-temperature was ∼30 mS/cm at 650 °C. The LSCF–GDC composite cathode showed ≥20% porosity with a grain size ≤100 nm. The peak power density of the LSGMC electrolyte-based, anode-supported-type cell with the nano-structured LSCF–GDC cathode produced at room-temperature by AD was 0.39 W/cm^2 at 650 °C.

Keywords: Aerosol deposition; IT-SOFC; LSGMC; Nano-structure; Low temperature process

1. Introduction

Solid oxide fuel cells (SOFCs) are the cleanest, most efficient and versatile chemical-to-electrical energy conversion systems. One of the critical challenges for the commercialization of SOFC is to develop cells that can operate at sufficiently low temperatures to reduce the cost and improve their reliability.[1,2] One of the main issues for reducing the SOFC operating temperature is to develop an electrolyte with sufficiently high ion conductivity, negligible electronic conductivity and high chemical stability.[3,4] Also, the cathode with high activity is required because most of the power losses arise from the cathode relevant to oxygen reduction, particularly at lower operation temperatures.[5] One promising electrolyte material is (La, Sr) (Ga, Mg)$O_{3-\delta}$ (LSGM) based perovskites, which have at least an order of magnitude higher ionic conductivity than conventional yttria stabilized zirconia.[4] The LSGM electrolyte shows almost pure ionic conductivity both in air and H_2 atmospheres, and the ionic conductivity can be improved by Co doping.[6] On the other hand, it is difficult to fabricate the LSGMC electrolyte directly on an anode substrate because the LSGM-based electrolyte has relatively high reactivity with the other components at high temperatures, particularly with NiO in the anode substrate.[7] Therefore, a low-temperature film deposition process is needed to minimize ion-blocking layer formation by a reaction between the electrolyte and anode, or cathode and electrolyte.

Recently, a low-temperature porous/dense ceramic thick film fabrication process using aerosol deposition (AD) was developed.[8,9] The AD process is a room-temperature operating powder consolidation method for the formation of thick and dense ceramic layers based on the impact adhesion of fine particles.[9] The porosity of the film can be controlled by the addition of a pore forming polymer into the starting powder composite.[8,10] The AD process has a strong potential for use in electrolyte/cathode fabrication owing to its high deposition rate (>5 μm/min), and low processing temperature because almost full densification (>95%) with a high adhesion strength (>30 MPa) can be achieved at room-temperature. In addition, the

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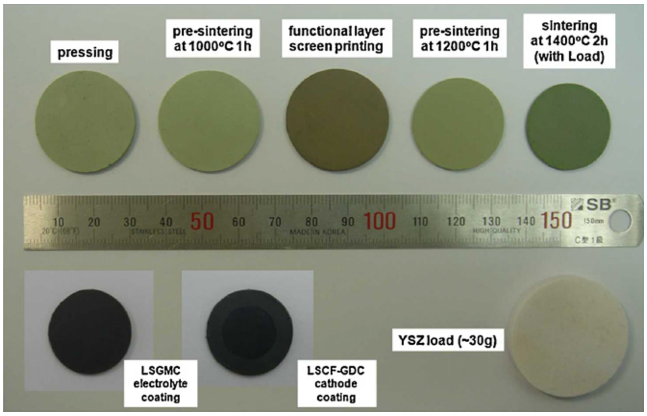


Fig. 1. Sample images of a NiO–GDC anode used as a substrate for the LSGMC electrolyte deposition at each preparation step.

process is suitable for the formation of nano-particulate interconnected microstructures because the film consolidated by the AD process has an extremely small crystalline size, generally ranging from 5 to 20 nm.[8–10]

In this study, LSGM-based SOFC cells were fabricated by an AD process using a Co-doped LSGM (LSGMC) film as an electrolyte and (La, Sr) (Co, Fe)$O_{3-\delta}$–(Gd, Ce)$O_{2-\delta}$(LSCF–GDC) film as cathode on the NiO–GDC anode substrate. The microstructure of each layer was optimized and observed, and related electrochemical analyses were performed.

2. Experimental procedure

For anode support fabrication, NiO (A grade, Novamet, USA), (Gd, Ce)$O_{2-\delta}$ (GDC, ULSA grade, Rhodia, USA), and polymethyl methacrylate (PMMA, S50, Sunjin Chem. South

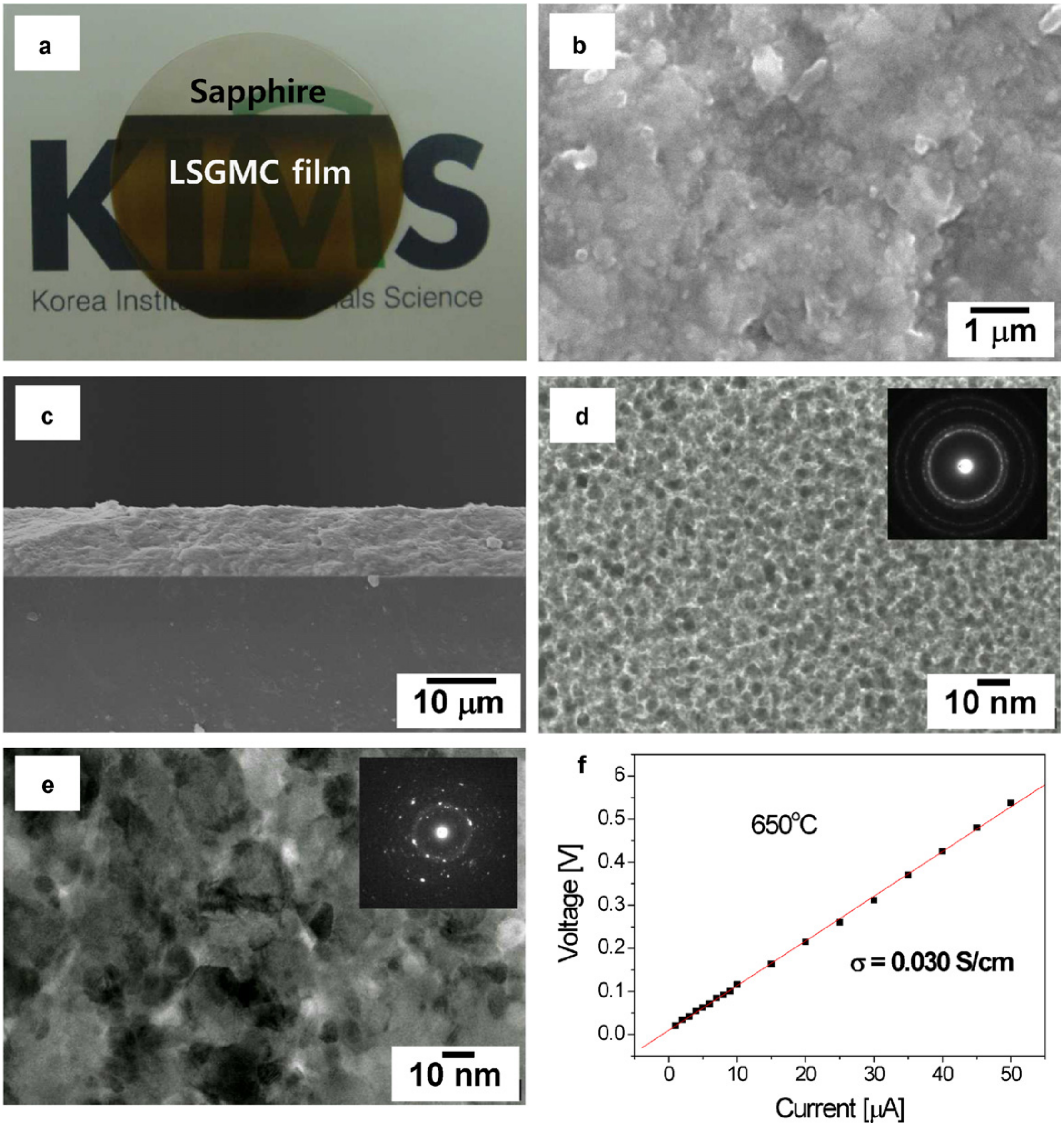


Fig. 2. (a) Sample image of the LSGMC film deposited on the sapphire substrate. (b and c) SEM images of the surface and cross-section of the as-deposited LSGMC film, respectively. (d and e) TEM images of the as deposited and 650 °C annealed LSGMC film, respectively. (f) electrical conductivity of the LSGMC film.

Korea) powder were mixed with 56.7:37.8:5.42 weight ratio by ball-milling for 24 h in a nylon jar using zirconia balls as the milling media and ethanol as the solvent. 8 wt% polyethylene glycol (PEG, M_n 400, 1500, 4600, 1:1:1 mixed, Aldrich Co., USA) was added as a binder/plasticizer. The powder was dry-pressed using a 30 mm diameter mold and pre-sintered at 1000 °C for 2 h at a heating rate of 0.5 °C/min. For anode functional layer screen printing, a paste was prepared using NiO (K Ceracell, nano grade, South Korea), GDC (10-M, Fuelcellmaterials, USA) and ink vehicle (VEH, Fuelcellmaterials, USA) mixed by planetary milling at a 6:4:15 weight ratio in a zirconia jar using zirconia balls as the milling media. The paste was screen-printed onto a pre-fired NiO–GDC pellet and sintered at 1450 °C for 2 h. A YSZ setter was used to avoid bending of the anode substrate during sintering.

An aerosol deposition process was used to deposit the electrolyte and cathode film on the anode substrate. For electrolyte layer deposition, commercially available (La, Sr) (Ga, Mg, Co)$O_{3-\delta}$ (LSGMC, K Ceracell, South Korea) powder was used. For cathode layer preparation, (La, Sr) (Co, Fe)$O_{3-\delta}$ (LSCF–P, Fuelcellmaterials, USA), (Gd, Ce)$O_{2-\delta}$ (GDC, ULSA grade, Rhodia, USA), and polyvinylidene fluoride (PVDF, Aldrich Co., USA) powders were mixed by ball-milling for 6 h. The prepared powders were mixed with the carrier gas to form an aerosol flow in the aerosol chamber. The aerosol flow was transported through a tube to a nozzle, accelerated and ejected into the deposition chamber through a $25 \times 0.8\,\text{mm}^2$ rectangular shaped nozzle, which was evacuated using a rotary pump with a mechanical booster. A schematic diagram of the AD equipment is shown elsewhere.[11] Compressed air dried through a dehumidifying filter was used as the carrier gas at a flow rate of 30 l/min. The accelerated LSGMC and LSCF–GDC–PVDF mixture particles collided with the NiO–YSZ and LSGMC-coated NiO–YSZ, respectively, which were located 5 mm away from the nozzle. The LSGMC was also coated on a sapphire substrate for the electrical conductivity measurements.

Fig. 1 summarized the sample images of the each preparation step for the fabrication of a NiO–GDC anode used as a substrate for the LSGMC electrolyte deposition. The NiO–GDC support was fabricated using PMMA as a pore former and PEG as a forming agent. The NiO–GDC support was dry-pressed and pre-sintered at 1000 °C for 2 h. An AFL of the same composition with the support was screen-printed on the pre-sintered support and sintered again at 1200 °C for 2 h. Finally, the AFL-printed support was sintered at 1450 °C for 2 h with YSZ load to avoid bending of the anode caused by the shrinkage difference between the support and AFL. The LSGMC electrolyte/LSCF–GDC cathode was prepared sequentially on the anode substrate by AD. The area of the LSCF–GDC cathode was ~1.7 cm^2.

The crystalline phases of the LSGMC and LSCF–GDC powders and film coated on silicon were examined by X-ray diffraction (XRD, D-MAX 2200, Rigaku, Japan). The film microstructures of the surface and the fractured cross section were examined by scanning electron microscopy (SEM, JSM-5800, JEOL, Japan) and scanning transmission electron microscopy (STEM, JEM-2100F, JEOL, Japan) equipped with an energy dispersion X-ray (EDX) spectrometer. The porosity of the LSCF–GDC cathode film was measured from the SEM micrograph using image analysis software (Image-Pro Plus, version 3.0, Media Cybernetics, USA).

The electrical conductivity of the LSMGC electrolyte was measured using a conventional DC 4 probe measurements technique. The 4-point probe technique with 4 Pt aligned electrodes was used. Four Pt wires were connected to the sample using Pt paste. The two outer probes were the current-carrying electrodes (I_1, I_2) and the two inner ones (placed 10 mm apart) were used to measure the voltage (E_1, E_2).[12] The gas permeability of the LSGMC electrolyte and Ni–GDC anode was detected using a bubble flow meter (ADM2000, Agilent Technologies, USA). For the cell test, a Pt mesh with a small amount of Pt paste was attached as a current collector in both the cathode and anode sides. The cell test temperature range was 650 °C, but the temperature was increased before the test up to 750 °C for gas sealing using a Pyrex ring. Air and H_2 were employed as the oxidant and fuel, respectively, at a flow rate of 600 and 200 sccm, respectively.

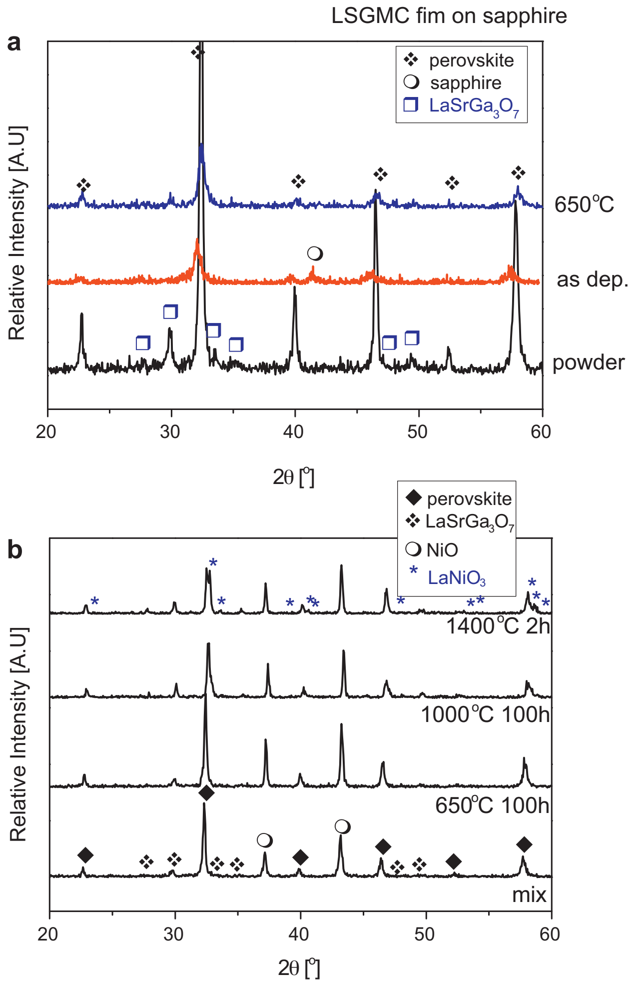


Fig. 3. XRD phase analysis. (a) LSGMC powder and film before and after annealing at 650 °C, (b) LSGMC–NiO mixed powder at a 1:1 weight ratio and annealed at 650 °C for 100 h, 1000 °C for 2 h and 1400 °C for 2 h.

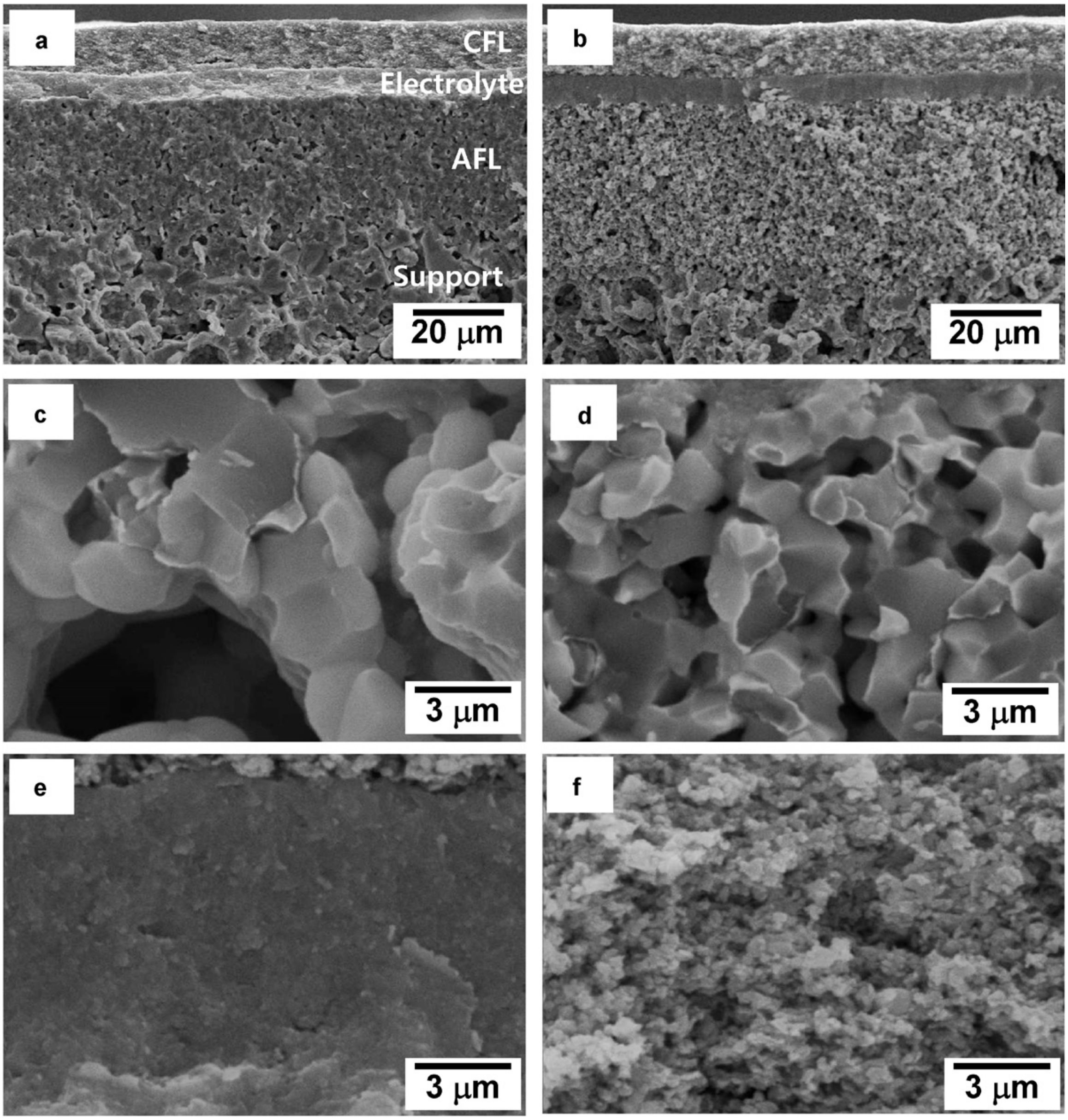


Fig. 4. SEM images of the cell. (a) Low-magnification view of the cell before reduction. (b) Low-magnification view of the cell after cell-test (anode reduction). (c–f) High-magnification image of each layer; anode support, anode functional layer, electrolyte and cathode, respectively.

3. Results and discussion

Fig. 2 shows the LSGMC film deposited on the sapphire substrate and the electrical conductivity. Fig. 2(a) shows the sample image of the LSGMC/sapphire, and Fig. 2(b) and (c) shows SEM images of the surface and fractured film, respectively. The film was fairly dense and translucent, as shown in Fig. 2(a)–(c). Fig. 2(d) and (e) shows STEM images and diffraction patterns of the as deposited and 650 °C post-annealed LSGMC films, respectively. The TEM image in Fig. 2(d) showed that the as-deposited film consisted of small crystallites, 5–15 nm in size, but it conserved its crystalline nature.[13] The diffraction pattern also indicated that the as-deposited film remained as a crystalline phase with very small crystallites formed by the collision of the accelerated particles with high kinetic energy during deposition.[9,13] On the other hand, the film annealed at 650 °C showed enhanced crystallinity with a grain size of ~30 nm, as shown in Fig. 2(e). Fig. 2(f) shows the electrical conductivity of the film measured using the DC 4 probe technique. The conductivity calculated from the slope of the line fitting of all data points was ~0.030 S/cm at 650 °C, which agrees well with the previously reported value.[14]

Fig. 3(a) shows XRD patterns of the LSGMC powder and films deposited on a sapphire substrate before and after heat-treatment at 650 °C in air. The commercial LSMGC powder contained a small amount of $LaSrGa_3O_7$ second phase. The as-deposited films showed broad peaks due to the nano-crystalline structure formed during the collision of the powders with the substrate, as confirmed by TEM (Fig. 2(e)). In addition, the peaks were shifted toward a low angle due to the compressive stress induced during deposition, which is a typical characteristic of aerosol-deposited films.[13] After annealing at 650 °C, the peaks reverted to the position of the bulk material due to crystal growth and stress recovery, and the peaks of LSGMC and $LaSrGa_3O_7$ second phase became shaper.

Fig. 3(b) shows the XRD phase analysis of the LSGMC and NiO powder mixture with a 1:1 ratio annealed at various temperatures and holding times to observe the reactivity and second phase formation temperature between the LSGMC electrolyte and Ni-containing anode. As shown in the figure, no severe reaction phase formation was observed after annealing at 650 °C for 100 h, which highlights its potential for using this low temperature deposition process to suppress the interfacial low-conductivity phase formation. On the other hand, the mixed powder annealed at 1000 °C and 1400 °C show $LaNiO_3$ phase formation, which is known to block oxygen ion conduction due to its low ionic conductivity.[15]

A SOFC cell consisting of NiO–GDC (support)/NiO–GDC (anode functional layer, AFL), LSGMC (electrolyte) and LSCF–GDC (cathode functional layer, CFL) was fabricated to characterize the cell performance. The microstructure of the cell was observed and is summarized in Fig. 4. Fig. 4(a) and (b) shows the overall cell structure before and after reduction of the anode/decomposition of the PVDF pore former in the cathode by cell *I–V* test at 650 °C, respectively. The micrographs show dense LSGMC electrolyte/porous Ni–GDC anode and LSCF–GDC cathode microstructure clearly. The thickness of the support, AFL, electrolyte and CFL was 1500, 20, 7 and 10 μm, respectively. The support, AFL, electrolyte and CFL layers were observed with higher magnification and the microstructures of each layer were shown in Fig. 4(c)–(f), respectively. The porosity of the Ni–GDC anode support and LSCF–GDC cathode was ~33 and 24%, respectively.

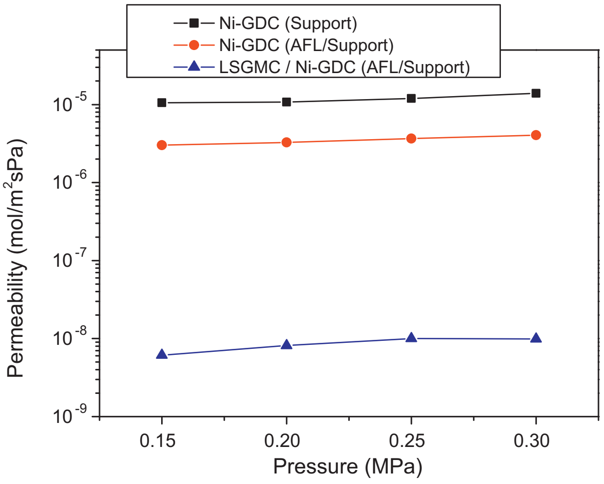
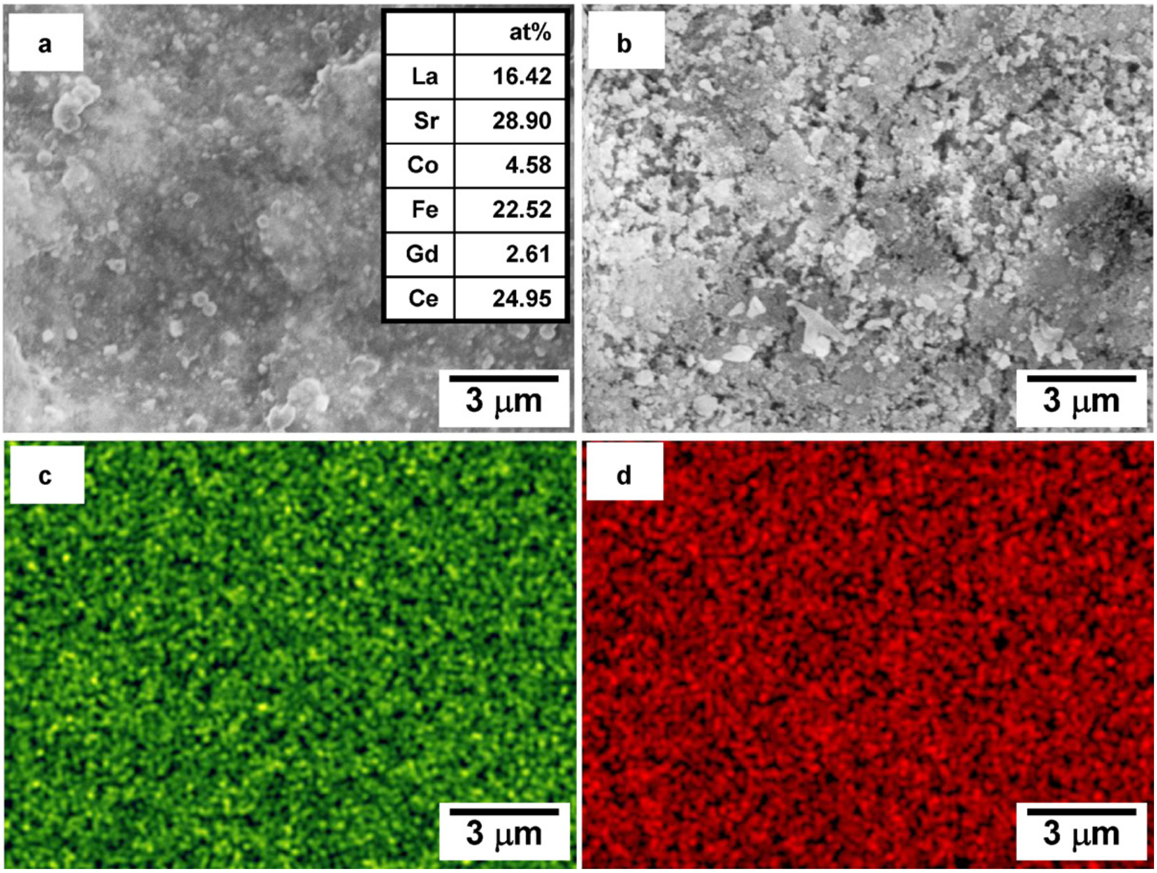


Fig. 5. Gas permeability of the Ni–GDC anode and LSGMC electrolyte.

The gas permeability of the Ni–GDC anode/LSGMC electrolyte at room temperature was measured using a gas flow meter (Fig. 5). The Ni–GDC anode support sintered at 1450 °C



	at%
La	16.42
Sr	28.90
Co	4.58
Fe	22.52
Gd	2.61
Ce	24.95

Fig. 6. SEM images of the LSGF–GDC cathode surface; (a) as deposited, (b) after annealing at 650 °C. (c and d) EDX map of La and Ce, respectively.

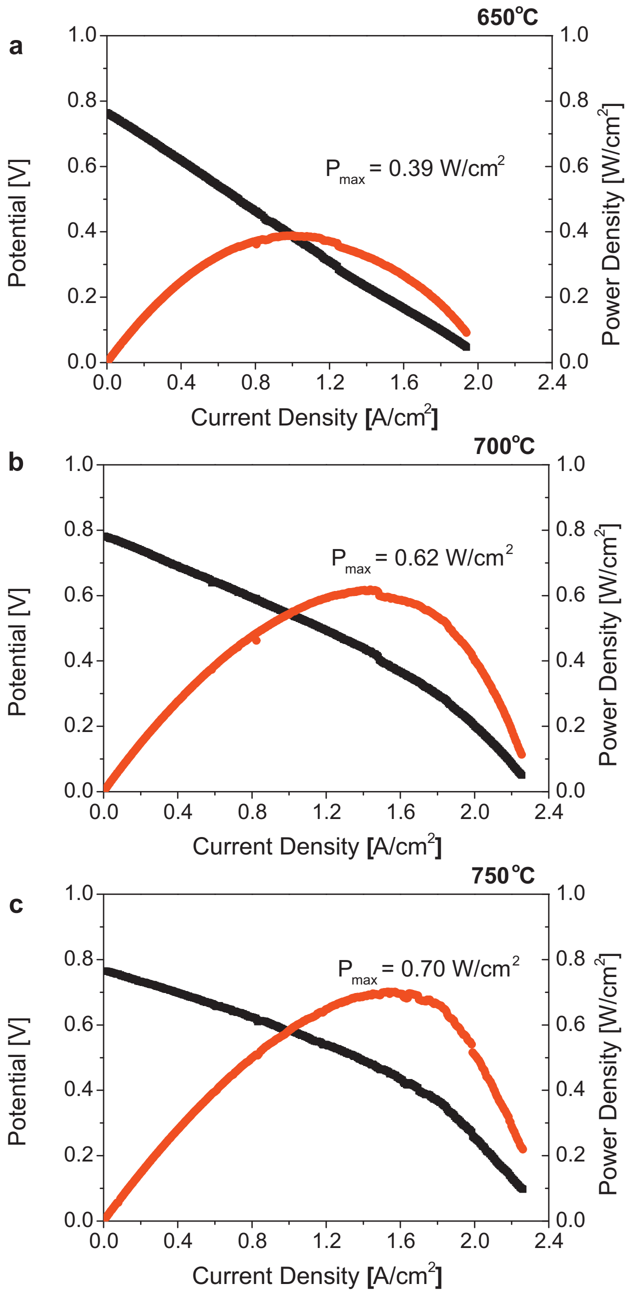


Fig. 7. *I–V* and power density characteristics of the cell tested at (a) 650 °C, (b) 700 °C and (c) 750 °C.

and reduced at 650 °C in a 10% H_2–N_2 atmosphere showed a permeability of ~1.1 × 10^{-5} mol/m^2 s Pa. This value decreased to ~3.0 × 10^{-6} when the anode functional layer was screen-printed, which is still high enough to minimize the concentration polarization.[16] On the other hand, the LSGMC electrolyte coated anode support showed a permeability ≤1.0 × 10^{-8}, which is low enough to use as an electrolyte.[17]

The microstructure observation and composition analysis of the LSCF–GDC cathode were performed by SEM with attached EDX equipment. Fig. 6 provides a summary of the results. Fig. 6(a) and (b) show the surface microstructure of the LSCF–GDC–PVDF composite cathode before and after annealing at 500 °C, respectively. The film was dense before annealing whereas nano-sized pores were generated after annealing by thermal decomposition of PVDF. Fig. 6(c) and (d) shows the EDX mapping of La and Ce atoms, which represent the LSCF and GDC, respectively. The LSCF–GDC composite appears to be mixed homogeneously according to EDX mapping, and the volume ratio of LSCF/(LSCF + GDC) in the film calculated based on the EDX quantification results was 63%.

The *I–V* characteristics and power densities of the cell consisted of LSCF–GDC cathode/LSGMC electrolyte/Ni–GDC anode was characterized at 650, 700 and 750 °C, as shown in Fig. 7(a)–(c), respectively. The open-circuit voltages (OCV) at 650, 700 and 750 °C were 0.764, 0.781 and 0.765 V, respectively. Because OCV is lower than the reported value[6] and independent from temperature, there seems to be a leakage in the electrolyte film probably due to the poor AFL density/homogeneity and LSGMC film uniformity. The peak power densities of the cell at 650, 700 and 750 °C were 0.39, 0.62 and 0.70 W/cm^2, respectively. The relatively low power densities compared to the LSGMC electrolyte based cell of the anode supported type fabricated by pulsed laser deposition (PLD)[18] appears to be related to the poor phase purity, as shown in Fig. 3 and an absence of a diffusion barrier layer between electrolyte and anode. The lower OCV value also appears to be originated from the electronic conductivity of the LSGMC electrolyte caused by second phase formation. Further studies will be focused on optimizing the thickness, composition and microstructure to further enhance the performance including long-term stability test.

4. Summary and conclusions

A nano-structured anode-supported type SOFC cell with a LSGMC electrolyte/LSCF–GDC cathode was fabricated using an AD process on a NiO–GDC anode substrate at low temperature (≤650 °C). The thickness and particle size of the LSGMC electrolyte and composite cathode was ~7 μm and 30 nm, respectively, and those of the LSCF–GDC composite cathode was ~25 μm and <100 nm. The electrical conductivity of the LSGMC electrolyte fabricated at room-temperature was ≥30 mS/cm at 650 °C. The peak power density of the LSGMC electrolyte-based, anode-supported-type cell with the nano-structured LSCF–GDC cathode produced at room-temperature by AD was 0.39 W/cm^2 at 650 °C.

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