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Magnetron sputtered LSC thin films for solid oxide fuel cell application

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Abstract. In this study, $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ (LSC) thin films were deposited by pulsed DC magnetron sputtering at oblique angle of the LSC target. The effect of post-annealing temperature in the range of 600-1000°C on the film crystalline structure was investigated. The phase composition, crystalline structure and surface morphology of the films were determined using X-ray diffraction, scanning electron microscopy and atomic force microscopy, respectively. Anode-supported solid oxide fuel cells (SOFCs) with bi-layered thin-film yttria-stabilized zirconia (YSZ) / gadolinium-doped ceria (GDC) electrolyte and an LSC thin film interlayer were fabricated. Polarization curves were measured in the temperature range from 700 to 800°C. It was shown that the LSC interlayer improves SOFC power density. Our results demonstrate that magnetron sputtering provides a low-temperature synthesis route for realizing thin LSC films for intermediate-temperature SOFCs.

1. Introduction

Solid oxide fuel cells (SOFC) are promising generators of electricity due to high efficiency, low pollution, noiseless operation and adaptability to a wide range of fuel. Recently, the studies have been actively conducted to decrease the SOFC operating temperature in order to increase the service life and to reduce the cost of materials for manufacturing [1]. However, decreased temperature leads to increased resistance in all layers of the fuel cell, and the largest losses caused by polarization resistance occur in the cathode layer. Therefore, it is necessary to search for new materials with suitable properties or to change approaches to the formation of the cathode material studied before. One of the most promising cathode materials for medium-temperature SOFC is $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ (LSC) with mixed electron and ionic conductivity [2-5]. However, LSC (20-23 x 10 -6 K -1) has a high thermal expansion coefficient, in contrast to typical YSZ and CGO electrolytes (11-12 x 10 -6 K -1) [6, 7]. This can cause delamination of electrolyte and cathode, especially during thermal cycling. This problem can be solved through the formation of an intermediate thin LSC matching layer [3]. Park [8] uses thin LSC-CGO films. A number of methods used for depositing a thin layer have been described. In most of the studies, LSC films in the form of a paste are deposited on cells and brought to the desired thickness by spin-coating [9, 10]. Vacuum methods for formation of coatings through physical

techniques of vapor deposition, such as pulsed laser deposition [4, 8], RF magnetron sputtering [11, 12], and pulsed DC magnetron sputtering are used as well [13].

This paper investigates dense thin cathode films produced by magnetron sputtering of the LSC target.

The paper aims to demonstrate an increase in the fuel cell power by depositing an LSC interlayer between electrolyte and cathode.

2. Experimental

NiO/YSZ anode supports (Ningbo SOFCMAN Energy Technology Co. Ltd, China) with magnetron sputtered bi-layered YSZ (4 μm)/GDC (2 μm) electrolyte [14] were used as substrates for LSC films deposition. The films were fabricated by pulsed DC magnetron sputtering at oblique angle of the $La_{0.6}Sr_{0.4}CoO_3$ target (Nova Fabrica Ltd., Lithuania) with a diameter of 72 mm and a thickness of 3 mm. A vacuum chamber was evacuated to the base pressure of 0.01 Pa. Prior to film deposition, the substrate surface was subjected to ion beam pre-cleaning. The sputtering discharge power was fixed at 200 W at a frequency of 80 kHz. The distance between the target and the substrate was 50 mm. The operating pressure was stabilized at 0.8 Pa. The film deposition rate was 33 nm/min.

An LSC cathode contact layer was applied to the fuel cells by screen-printing the $La_{0.6}Sr_{0.4}CoO_3$ paste (CERA-FC Co, Korea). The layer was sintered *in-situ* during the start up of the fuel cell at a temperature of 800ºC for 1 h. Current-voltage (I-V) and current-power (I-P) characteristics of the fuel cells were measured in the temperature range from 700 to 800ºC using a four-electrode potentiostat P150 (Elins Ltd., Russia). Ag meshes were used as current collectors for both anode and cathode. 180 sccm of H_2 was fed to the anode chamber, and air was supplied to the cathode chamber at a flow rate of 400 sccm. A test rig is described in detail in [15].

Grazing incidence X-ray diffraction analysis of the LSC films was performed with a XRD-6000 diffractometer using CuKα radiation. Some films were annealed in the Nabertherm RHTH 120/600/18 tube furnace at 600-1000ºC in air for 2 h. The structure of the LSC films was investigated by NT-MDT NTEGRA Prima atomic force microscopy (AFM) and Quanta 200D scanning electron microscopy (SEM).

3. Results and discussion

Diffraction patterns of the nanoscaled LSC cathode produced by magnetron sputtering on the anode substrate with bilayer YSZ/GDC electrolyte and then annealed at different temperatures are presented in figure 1.

The results of X-ray diffraction analysis showed that the as-deposited LSC film is represented by the $La_{0.6}\ Sr_{1.4}CoO_4$ phase, which is undesirable since its electronic conductivity is several times less than the $La_{0.6}Sr_{0.4}CoO_3$ phase conductivity (1600 S/cm) [7, 16], and also by phase $Ce_{0.9}Gd_{0.1}O_{1.95}$ which refers to the electrolyte material. The required phase of $La_{0.6}Sr_{0.4}CoO_3$ is formed as a result of subsequent annealing of LSC films at 600, 800 and 1000°C. Its volume content in the films annealed at 800 and 1000°C is greater than the content of this phase in the film annealed at 600°C by 30%. The crystallite sizes of the $La_{0.6}Sr_{0.4}CoO_3$ phase were 32, 23 and 39 nm for the annealing temperatures of 600, 800 and 1000°C, respectively. In addition to the main phase, the $Ce_{0.9}Gd_{0.1}O_{1.95}$ phase and a certain amount of the $La_{0.6}Sr_{1.4}CoO_4$ phase were detected in all annealed films. The results obtained showed that the annealing temperature of 800°C is optimal, since the structure of the LSC films annealed at 600°C is incomplete, and the annealing temperature increased to 1000°C did not lead to a significant improvement in the structural parameters. Therefore, a separate technological stage such as sintering of the cathode layer was eliminated in this study. The cathode was sintered *in-situ* during the first start-up of the cell at 800°C for 1 h.

Figure 2 presents the results of the study of the electrolyte surface morphology (a) used as a substrate, and the magnetron sputtered nanoscaled LSC thin film cathode before (b) and after (c) testing. It can be seen that the morphology of the as-deposited LSC thin film follows the morphology of the substrate, which is expected for a nanoscaled (600 nm) thin films. The grain size of the substrate

and the LSC coating varies in the range of 177–516 nm. The reduction of the grain size to 96–355 nm was observed for LSC coating after its electrochemical testing.

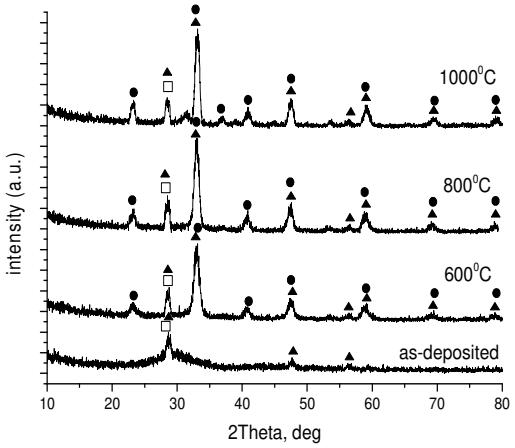

Figure 1. XRD patterns of magnetron sputtered LSC cathode interlayers on the anode supports with the YSZ/GDC bilayer electrolyte annealed at different temperatures: ● - $La_{0.6}Sr_{0.4}CoO_3$; ▲ - $Ce_{0.9}Gd_{0.1}O_{1.95}$; □ - $La_{0.6}Sr_{1.4}CoO_4$.

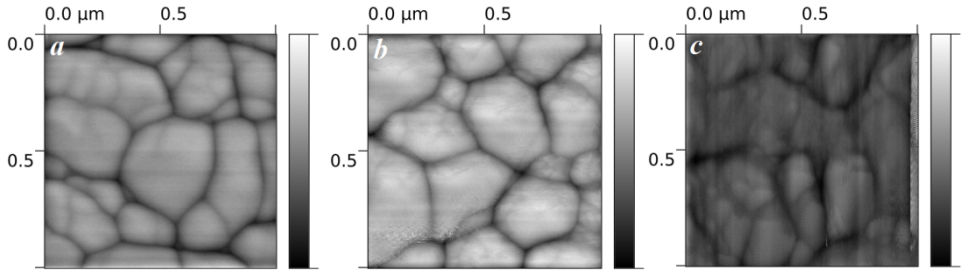

Figure 2. AFM images of the GDC electrolyte (a) and magnetron sputtered LSC thin films.

The fuel cell microstructure was also studied using a scanning electron microscope. The SEM image of the cross-section of the single cell including anode support, YSZ/GDC bilayer electrolyte and magnetron sputtered 1-µm-thick LSC film are shown on figure 3.

Good adhesion between the coating and the substrate without cracks and delamination is distinctly visible. The border between them is virtually indistinguishable. However, the microstructure of the cathode layer slightly differs from that of the electrolyte. It is seen to be more granular. Thus, the deposited LSC film, the so-called functional layer, acts as a transition region between the dense electrolyte and the porous cathode contact layer. This will provide developed triple-phase boundary, which is essential for a high rate of the oxygen transport to solid electrolyte.

To study the effect of magnetron sputtered LSC cathode interlayer on the SOFC operation efficiency, a series of samples with a LSC thin film 400, 600 and 1000 nm thick was obtained. A single SOFC cell with a contact LSC cathode only formed by the screen method was also fabricated. The comparison of the voltage–current and power–current characteristics of the single fuel cells showed the following. The maximum power density of the cell with the 400-nm-thick LSC interlayer was about 1610 mW/cm^2 at 800°C. An increase in the thickness of the LSC cathode interlayer up to 600 nm significantly increased the maximum power density of the cell, which amounted to 2150 mW/cm^2. This is about 38% higher than that of the cell without LSC interlayer. Its maximum power density at 800°C was 1340 mW/cm^2. A further increase in the thickness of the LSC interlayer

resulted in a slight decrease in power density. Thus, the value of the maximum power density of the cell with an LSC interlayer 1000 nm thick was 1930 mW/cm^2. A similar behavior of the power characteristics was observed at 750 and 700°C. the voltage-current and power-current characteristics of the cells with magnetron sputtered LSC cathode interlayer with the thickness in the range of 400–1000 nm and without interlayer at 750°C are presented in figure 4.

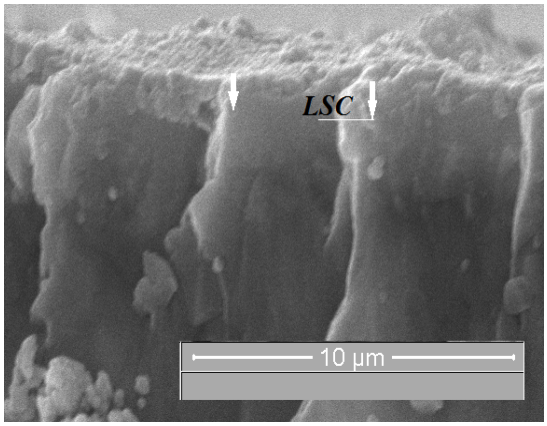

Figure 3. SEM image of the YSZ/GDC electrolyte and magnetron sputtered LSC thin films.

It can be seen that the characteristics of the cells with LSC cathode interlayer 400 nm thick and without it differ insignificantly. Their maximum power density values were 1200 and 1150 mW/cm^2, respectively. Significantly better results were demonstrated by cells with LSC cathode interlayers 600 and 1000 nm thick, for which the maximum power density values were 1612 and 1483 mW/cm^2, respectively. The results obtained in this work uniquely show that the formation of a nanoscaled LSC cathode interlayer significantly improves the SOFC efficiency, other things being equal, which evidently affects the power characteristics of the fuel cells tested.

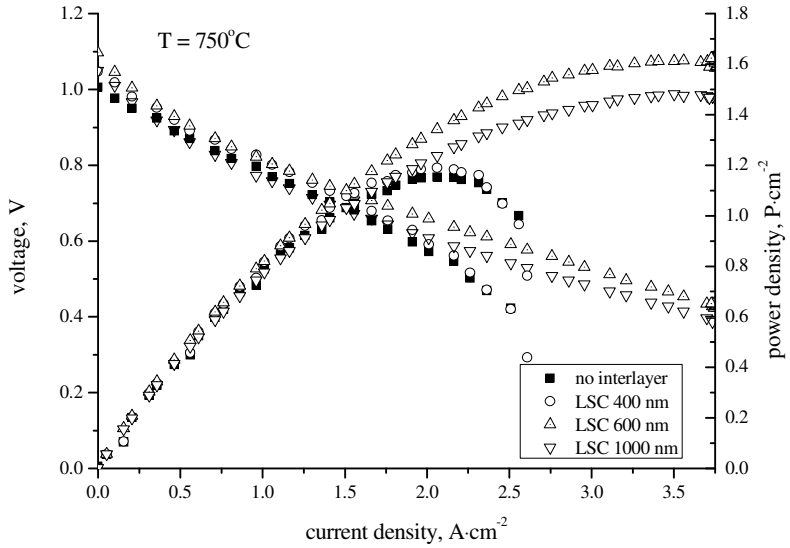

Figure 4. Voltage-current and power-current characteristics of the cells with magnetron sputtered LSC cathode interlayer (400, 600, 1000 nm) and without it at 750°C.

This behavior can be explained, first of all, by the larger contact area between the electrolyte and the magnetron sputtered thin LSC cathode interlayer, which implies a larger electrochemical reaction area as compared with the cathode layer formed by the screen printing method. The latter has only point contacts with the electrolyte in those regions, where the granules of the composite LSC cathode are in contact with the CGO electrolyte. The experimental results showed that the LSC films deposited by pulsed magnetron sputtering have sufficient electrochemical activity and can be used as an intermediate layer between the cathode and the electrolyte of the solid oxide fuel cell to increase the power density and to improve adhesion between the cathode and the electrolyte.

4. Conclusion

This work showed that the formation of a nanoscaled LSC cathode interlayer is a promising way to improve the efficiency of thin-film SOFC. We have demonstrated that pulsed DC magnetron sputtering can be successfully applied for the specified purposes. This method can be used as a low-temperature synthesis method to deposit $La0.6Sr0.4CoO_3$ thin films. It was determined that the thickness of the nanoscaled LSC cathode interlayer 600 nm thick is optimal. This thickness of the LSC cathode interlayer provided the maximum power density value, which attained 2150 mW/cm^2 at 800°C, that is, it is 38% higher than that of the cell without LSC interlayer. This effect is achieved primarily due to the formation of a developed area of the interphase contact between the electrolyte and the cathode, which improves the efficiency of the electrochemical reaction at the cathode side.

Acknowledgements

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