



# Solid oxide fuel cells with apatite-type lanthanum silicate-based electrolyte films deposited by radio frequency magnetron sputtering

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## HIGHLIGHTS

- Anode supported SOFC with  $\text{La}_{9.8}\text{Si}_{5.7}\text{Mg}_{0.3}\text{O}_{26.4}$  deposited by sputtering was built.
- A dense and c-axis oriented LSMO film with a thickness of  $\approx 2.8 \mu\text{m}$  was deposited.
- The SOFC reported an OCV of 0.982 V and a MPD of  $1.49 \text{ Wcm}^{-2}$  at  $850^\circ\text{C}$ .
- RF Sputtering is proved to be a feasible way to prepare fine LSMO films in SOFCs.

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## ABSTRACT

In this study, solid oxide fuel cells (SOFCs) containing high-quality apatite-type magnesium doped lanthanum silicate-based electrolyte films (LSMO) deposited by RF magnetron sputtering are successfully fabricated. The LSMO film deposited at an Ar:O<sub>2</sub> ratio of 6:4 on an anode supported NiO/Sm<sub>0.2</sub>Ce<sub>0.8</sub>O<sub>2.8</sub> (SDC) substrate followed by post-annealing at 1000 °C reveals a uniform and dense c-axis oriented polycrystalline structure, which is well adhered to the anode substrate. A composite SDC/La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.2</sub>Fe<sub>0.8</sub>O<sub>3.8</sub> cathode layer is subsequently screen-printed on the LSMO deposited anode substrate and fired. The SOFC fabricated with the LSMO film exhibits good mechanical integrity. The single cell with the LSMO layer of  $\approx 2.8 \mu\text{m}$  thickness reports a total cell resistance of 1.156 and 0.163  $\Omega\text{cm}^2$ , open circuit voltage of 1.051 and 0.982 V, and maximum power densities of 0.212 and 1.490  $\text{Wcm}^{-2}$  at measurement temperatures of 700 and 850 °C, respectively, which are comparable or superior to those of previously reported SOFCs with yttria stabilized zirconia electrolyte films. The results of the present study demonstrate the feasibility of deposition of high-quality LSMO films by RF magnetron sputtering on NiO-SDC anode substrates for the fabrication of SOFCs with good cell performance.

## 1. Introduction

Solid oxide fuel cells (SOFCs) have been regarded as highly efficient and environmentally friendly power sources [1]. Recently, intermediate temperature SOFCs (IT-SOFCs), operated at temperatures between 500 and 700 °C, have attracted considerable research interest owing to the use of inexpensive alloy interconnects, minimal interfacial reaction among cell components, stable sealing, and improved fuel durability [2,3]. The challenges related to IT-SOFCs include reduction of ohmic resistance of the electrolyte layer ( $R_o$ ) and polarization resistance ( $R_p$ ) of the electrodes [4]. The former can be achieved by exploiting other electrolytes with higher ionic conductivities at lower temperatures or by employing an electrolyte in the form of a thin film [5]. In addition to common oxide ion conductors, including fluorite-structured Zr<sub>0.84</sub>Y<sub>0.16</sub>O<sub>1.92</sub> (YSZ) and Sm<sub>0.2</sub>Ce<sub>0.8</sub>O<sub>2.8</sub> (SDC), and perovskite-

structured La<sub>0.9</sub>Sr<sub>0.41</sub>Ga<sub>0.8</sub>Mg<sub>0.2</sub>O<sub>3</sub> (LSGM) [6], apatite materials (general formula A<sub>10-x</sub>M<sub>6</sub>O<sub>26 ± 8</sub> where A = rare earth or alkaline earth and M = Si, Al, Ge, or P) have been explored as an alternative solid electrolyte for SOFCs [7]. The hexagonal structure of apatites with space group of P6<sub>3</sub>/m consists of isolated MO<sub>4</sub> tetrahedra forming channels that run parallel to the c-axis where loosely bound oxide-conducting anions are located. The oxide ions in the channels are considered mobile, leading to a high level of oxide ion conductivity [7]. Particular attention has been directed to the high oxide ion conductivity of La<sub>10-y</sub>Si<sub>6</sub>O<sub>26 ± 8</sub> reported initially by Nakayama et al. [8]. One of the methods to improve the electrical conductivity is doping that triggers nonstoichiometry in the form of either cation vacancy or oxygen excess [9]. For example, La<sub>9.8</sub>Si<sub>5.7</sub>Mg<sub>0.3</sub>O<sub>26.4</sub> and La<sub>10</sub>Si<sub>5.8</sub>Mg<sub>0.2</sub>O<sub>26.8</sub> have been reported to exhibit the highest ionic conductivity among apatite silicates [10]. However, fabrication of SOFCs based on lanthanum silicates

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for practical applications is still challenging because of their high sintering temperatures ( $> 1600\text{ }^{\circ}\text{C}$ ) [11].

Several techniques have been used to deposit apatite silicate layers, including magnetron sputtering [12–17], spin coating [11,18], and thermal spraying [19]. Oliveira et al. [12,13,15] and Briois et al. [14] deposited La-Si-O thin films by reactive magnetron sputtering of La and Si metallic targets in an argon-oxygen atmosphere. Apatite-type lanthanum silicate thin films with c-axis perpendicular to the substrate were found to possess the highest conductivities among the La-Si-O films. Sakao et al. prepared apatite La-Si-O thin films by depositing  $\text{La}_2\text{SiO}_5$  and  $\text{La}_2\text{Si}_2\text{O}_5$  films by radio frequency (RF) magnetron sputtering of oxide targets in an Ar atmosphere. The formation of apatite lanthanum silicate films was achieved by bulk diffusion within the deposited films during post-annealing [16]. Even though apatite lanthanum silicate thin films have been deposited by DC reactive and RF magnetron sputtering techniques, SOFCs based on these films have not been fabricated and characterized. Thermal spray and spin-coating have also been used to deposit apatite-type magnesium doped lanthanum silicate (MDLS) films. Anode supported SOFCs based on MDLS films were subsequently built with a NiO-MDLS anode and a  $(\text{La}_{0.6}\text{Sr}_{0.4})(\text{Co}_{0.8}\text{Fe}_{0.2})\text{O}_{3.8}$  (LSCF) cathode; however, they showed low maximum power densities (MPDs) of 0.080 and  $0.150\text{ Wcm}^{-2}$ , respectively, at  $800\text{ }^{\circ}\text{C}$  [11,19].

In this study,  $\text{La}_{9.8}\text{Si}_{5.7}\text{Mg}_{0.3}\text{O}_{26.4}$  (LSMO) electrolyte films were deposited on NiO-SDC anode substrates by RF magnetron sputtering considering their high electrical conductivities [20,21]. The phase structure and the microstructure of the films were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). SOFCs were subsequently fabricated by screen printing an LSCF-SDC cathode on the anode-supported substrates with LSMO electrolyte films. The microstructure and the electrochemical performance of the SOFCs were then studied.

## 2. Experimental procedure

Commercially accessible materials, involving  $\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{2.8}$  (SDC;  $d_{50} = 0.53\text{ }\mu\text{m}$  and BET surface area =  $6.2\text{ m}^2\text{ g}^{-1}$ ; Fuel Cell Materials, USA), NiO (current collector layer:  $d_{50} = 10.1\text{ }\mu\text{m}$  and BET surface area =  $0.06\text{ m}^2\text{ g}^{-1}$ ; SHOWA, Japan; anode functional layer:  $d_{50} = 0.8\text{ }\mu\text{m}$  and BET surface area =  $3.4\text{ m}^2\text{ g}^{-1}$ ; Fuel Cell Materials, USA), and LSCF ( $d_{50} = 0.99\text{ }\mu\text{m}$  and BET surface area =  $5.4\text{ m}^2\text{ g}^{-1}$ ; Fuel Cell Materials, USA), were used to prepare the anode substrate and the cathode layer. The three-layer anode-supported substrates were composed of two functional layers of NiO-SDC composites with ratios of 60/40 wt.% and 50/50 wt.% and a current collector layer (outer layer) of pure NiO. The preparation process of the anode-supported substrates has been provided in a previous paper [22].

To prepare the LSMO target, high purity  $\text{La}_2\text{O}_3$  (SHOWA, Japan), MgO (SIGMA-ALDRICH, USA) powders, and  $\text{SiO}_2$  (Noah, USA) were used as raw materials, and the former two were heated at  $1100\text{ }^{\circ}\text{C}$  for 2 h to remove absorbed moisture and  $\text{CO}_2$  before weighing the formulation. According to the compositions of  $\text{La}_{9.4}\text{Si}_{5.7}\text{Mg}_{0.3}\text{O}_{25.8}$ , the powders were wet-mixed in methyl alcohol using  $\text{ZrO}_2$  media and polyethylene jars for 24 h and dried in an oven at  $80\text{ }^{\circ}\text{C}$  overnight. The mixed powders were then calcined at  $1300\text{ }^{\circ}\text{C}$  for 8 h, followed by re-milling for 24 h and drying in an oven at  $80\text{ }^{\circ}\text{C}$  overnight. The calcined powders were consequently mixed with 3.5 wt.% of a 15% polyvinyl alcohol solution and thereafter pelletized into a disc shape by applying a uniaxial pressure of 750 MPa. The green LSMO disc was binder burned-out at  $550\text{ }^{\circ}\text{C}$  for 4 h and then sintered at  $1550\text{ }^{\circ}\text{C}$  for 8 h.

The LSMO thin films were deposited by RF magnetron sputtering on the anode substrates using an LSMO target in a sputtering system equipped with a turbomolecular pump which was used to obtain a base pressure  $< 2 \times 10^{-7}$  Torr. Argon ( $> 99.995\%$  pure) was used as the working gas for sputtering. The target was sputter-cleaned prior to the deposition. The films were deposited at a working pressure of

**Table 1**

Components of the anode-supported SOFC with the LSMO electrolyte layer.

Function	Material	Thickness
Bi-layer cathode	LSCF	9 $\mu\text{m}$
	LSCF/SDC	8 $\mu\text{m}$
Electrolyte layer	LSMO	2.8 $\mu\text{m}$
Tri-layer anode	NiO/SDC (50 wt%/50 wt%)	6 $\mu\text{m}$
	NiO/SDC (60 wt%/40 wt%)	636 $\mu\text{m}$
	NiO	20 $\mu\text{m}$

$1 \times 10^{-2}$  Torr, RF power of 50–150 W, and various Ar: $\text{O}_2$  ratios. The as-deposited films were post-annealed at  $1000\text{ }^{\circ}\text{C}$  in air for 4 h. XRD (Bruker AXS, D2Phaser A26-X1-A2B0B2), SEM (JOEL JLSM-6510LV), electron probe microanalyzer (EPMA; JEOL JXA-8200), and high resolution X-ray photoelectron spectroscopy (XPS, VG Scientific ESCALAB 250) were performed on both the sintered target surfaces and the as-deposited films to confirm the formation of phases, characterize the microstructures, determine the composition, and examine the bonding structure.

To fabricate the SOFC cells, a bi-layer cathode comprising a composite layer of 50 wt.% SDC and 50 wt.% LSCF powder and a LSCF layer was deposited on the anode-supported substrates with the LSMO film by screen printing. The cathode pastes were prepared by mixing the functional powder with appropriate amounts of terpineol (solvent) and ethyl cellulose (binder). The cathode was then fired at  $1000\text{ }^{\circ}\text{C}$  for 4 h. The dimensions of the components of the anode-supported SOFC single cell are listed in Table 1. The electrochemical performance of the single cell was measured using the set-up of a commercially available ProboStat (NorECs, Norway). During the experiment, the flow rates of hydrogen and air were kept at 40 and 160 sccm respectively, by electronic mass flow controllers. Current density as a function of cell voltage (I-V curves) was evaluated under different applied loads across the cell, and measurements were carried out from  $700$  to  $900\text{ }^{\circ}\text{C}$  at intervals of  $50\text{ }^{\circ}\text{C}$ . Electrochemical impedance spectra (EIS) were measured after holding the cells under OCV for 15 min at the temperatures ranging from  $700$  to  $900\text{ }^{\circ}\text{C}$ . The EIS measurements were performed using a four-lead two-electrode configuration using a multi-channel Potentiostat/Galvanostat (Solartron 1470E) connected with a 1260 frequency response analyzer with a computer interface and Corr-view software. The frequency range was from  $10^5$  Hz to 0.015 Hz, and the signal amplitude read 10 mV. I-V curves and power curves were obtained using linear sweep from OCV to 0.2 V at a sweep rate of  $5\text{ mVs}^{-1}$ . After testing, the microstructure of the cells was examined by SEM.

## 3. Results and discussion

To compensate for the dissimilar sputtering yields of La, Si, and Mg during the deposition of LSMO ( $\text{La}_{9.8}\text{Si}_{5.7}\text{Mg}_{0.3}\text{O}_{26.4}$ ) films, the composition of the target was adjusted to  $\text{La}_{9.4}\text{Si}_{5.7}\text{Mg}_{0.3}\text{O}_{25.8}$  throughout this study. This was achieved by performing several experiments with different target compositions and analyzing the EPMA results of the deposited films. Fig. 1 shows the XRD pattern of the  $\text{La}_{9.4}\text{Si}_{5.7}\text{Mg}_{0.3}\text{O}_{25.8}$  target sintered at  $1500\text{ }^{\circ}\text{C}$  for 8 h. The XRD pattern of the apatite ceramic target was indexed based on the peaks corresponding to the hexagonal  $\text{La}_{10}\text{Si}_6\text{O}_{27}$  phase (JCPDS 53-0291), although the diffraction peaks of the former slightly shifted to lower angles as compared to those of the latter because of the difference in the ionic sizes of  $\text{Mg}^{2+}$  ( $0.57\text{ \AA}$ ) and  $\text{Si}^{4+}$  ( $0.26\text{ \AA}$ ) [23]. The XRD pattern revealed a pure hexagonal phase with predominant (211) and (112) peaks; peaks corresponding to a second phase were not observed.

Fig. 2(a) shows the XRD pattern of the electrolyte-side surface of the NiO-SDC anode substrate, which shows the presence of cubic NiO (JCPDS 65-7545) and cubic SDC (75-0158) phases. The absence of a peak-shift in either phase indicates that there was no inter-doping. The origin of the tiny peak at approximately  $32^{\circ}$  is not understood at

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