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Fabrication and characterization of thin film electrolytes deposited by RF magnetron sputtering for low temperature solid oxide fuel cells

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Abstract

Thin film solid electrolytes of $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ (LSGM), $Sm_{0.2}Ce_{0.8}O_{1.9}$ (SDC), and $Sc_{0.11}Zr_{0.89}O_{2-\delta}$ (ScSZ) were deposited by RF magnetron sputtering onto single crystal sapphire substrates as well as onto porous NiO–SDC anodes at deposition temperatures of RT $\leq T \leq$ 500 °C. The electrical conductivities, phase analyses as deposited and after annealing and microstructures of the deposited thin film electrolytes were examined. In addition, the electrochemical performance of single cells composed of $Sm_{0.5}Sr_{0.5}O_{3-\delta}$ (SSC) + SDC//SDC/ScSZ//NiO + SDC was demonstrated. Impervious and highly dense bilayer thin films of SDC and ScSZ have been successfully prepared on porous NiO–SDC anodes. Maximum power densities of 360 and 240 mW cm^{-2} from single cells of $Sm_{0.5}Sr_{0.5}O_{3-\delta}$ (SSC) + SDC//SDC/ScSZ//NiO + SDC were obtained at 600 and 550 °C, respectively, under humid 20% H_2 in Ar (3% H_2O) and air. RF magnetron sputtering can be applied for depositing high performance thin film electrolytes in low temperature SOFCs.

Keywords: RF magnetron sputtering; Thin film electrolyte; Bilayered; Low temperature solid oxide fuel cell

1. Introduction

Solid oxide fuel cells (SOFCs) have a variety of advantages such as highly efficient co-generation to produce heat and electricity, the utilization of hydrocarbon containing fuels, and a wide range of applications from small scale (1–10 kW) to large sized power systems (MW), in contrast to other type fuel cells. Conventional SOFCs require operating temperatures above 700 °C due to the low oxygen ionic conductivity of the yttria stabilized zirconia (YSZ) electrolyte. Lowering of the operating temperature of the solid oxide fuel cell from 700–800 °C to below 600 °C can provide higher thermodynamic efficiency, higher Nernstian voltages, enhanced durability of cell performance, and the usage of cheaper stainless steel interconnects and compliant high temperature gaskets.

The main problems encountered in lowering the operating temperature include an increase in the cell resistance and consequent losses in cell efficiency [1]. A decrease in the fuel cell operating temperature leads to rapid increases in the bulk resistance of the electrolyte and the interfacial resistance between the electrode and electrolyte. Alternative thin film electrolytes having a higher oxygen ionic conductivity and lower interfacial resistance than YSZ electrolyte can be used to overcome the above-mentioned problems. Potential candidates for intermediate temperature solid electrolytes are samarium or gadolinium-doped ceria (SDC or GDC), Sr- and Mg-doped lanthanum gallate (LSGM), and scandium doped zirconia (ScSZ). It has been demonstrated that SDC-based SOFCs can be operated at temperatures as low as 400 °C when using hydrogen as the fuel [2]. LSGM exhibits a slightly lower conductivity of 0.1 S cm^{-1} at 750 °C and higher stability under reducing atmospheres than doped ceria. LSGM can be considered as an attractive candidate to be used at temperatures around 600 °C, where the reduction of Ce^{4+} in doped ceria becomes significant [3]. ScSZ exhibits the highest ionic conductivity among acceptor-doped zirconia electrolytes. However, it reacts with low temperature cathodes such as $La_{1-x}Sr_xCoO_{3-\delta}$ (LSC) or $Sm_{1-x}Sr_xCoO_{3-\delta}$ (SSC) to form insulating compounds of Sr_2ZrO_4 and $La_2Zr_2O_7$. By introducing a doped ceria interlayer as a bilayered electrolyte, the interfacial resistance at the interface between SSC and ScSZ can be reduced [4].

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Recently many researchers have been attempting to reduce the thickness of the electrolyte using a variety of thin film techniques including chemical vapor deposition [5], electrochemical vapor deposition [6], sol–gel [7], spray pyrolysis [8], pulsed laser ablation [9], RF magnetron sputtering [10,11], dc reactive sputtering [1,12], and screen printing [13]. Magnetron sputtering (RF or dc) is an extremely reliable technique for thin film deposition and has the potential for large scale economic production of thin film solid electrolyte fuel cells. In this paper, thin film solid electrolytes of $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ (LSGM), $Sm_{0.2}Ce_{0.8}O_{1.9}$ (SDC), and $Sc_{0.11}Zr_{0.89}O_{2-\delta}$ (ScSZ) were deposited by RF magnetron sputtering onto single crystal sapphire substrates as well as onto porous NiO–SDC anodes at deposition temperatures of $RT \leq T \leq 500\,^{\circ}C$. The electrical conductivities, phase analyses as deposited and after annealing, and microstructures of deposited thin film electrolytes were examined. In addition, the electrochemical performance of single cells composed of $Sm_{0.5}Sr_{0.5}O_{3-\delta}$ (SSC) + SDC//SDC/ScSZ//NiO + SDC was demonstrated.

2. Experimental

2.1. RF magnetron sputtering

A custom-designed Sputter Deposition system with 2 in. Magnetron Sputter Guns (from Torr International, USA) was used for RF magnetron sputtering of dense SDC, LSGM, and ScSZ thin films using commercially available targets of $Sm_{0.2}Ce_{0.8}O_{1.9}$, $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$, and $Sc_{0.11}Zr_{0.89}O_{2-\delta}$ (99.9% purity, from Praxair Ceramics Inc.). The pressure of argon during deposition was 5 mTorr and thin films were deposited at an Ar:O_2 gas flow ratio of 80:20. Sputtering was performed at 3 W cm^{-2} RF power on the target and about 90 mm distance between substrate and target. The deposition rate was varied from 0.10 to 0.15 μm h^{-1} depending on the composition of targets. Substrates were heated from RT to 300–500 °C by halogen lamps. The samples were then post-annealed in air or oxygen at 800 °C for 2 h.

2.2. Characterization

The electrical conductivities of thin films on sapphire substrates were measured by 2-probe ac impedance method using an impedance/gain-phase analyzer Solartron SI 1260 and an electrochemical interface Solartron SI 1287 (Solartron Analytical, Farnborough, UK) over a frequency range 10^{-1} to 10^{6} Hz with an applied potential of 0.15 V and the temperature range 500–800 °C in air. The phase formation and lattice parameters of thin films deposited on sapphire substrates were examined by X-ray diffraction on a Bruker D8 Advanced X-ray diffractometer (Bruker AXS GmbH, Karlsruhe, Germany) using Cu Kα radiation. In situ high temperature X-ray diffraction was conducted with an Anton Parr HTK 1200 high temperature stage attached on D8 X-ray diffractometer at the temperature range RT to 1000 °C in air. The microstructure of thin films deposited on sapphire and NiO–SDC substrates was examined with field emission scanning electron microscope (Hitachi S-4800). The elemental determinations of the deposited thin films were performed with atomic absorption spectroscopy (AA) and field emission scanning electron microscope (SEM)/energy dispersive spectroscopy (EDS, Philips XL 30S) at 20 keV beam energy. A Dektak profilometer was used to determine the film thickness.

2.3. Fabrication of substrates and single cells

The porous NiO–SDC substrates were fabricated by conventional powder pressing and sintering methods. Mixtures of NiO (J.T. Baker) and $Sm_{0.2}Ce_{0.8}O_{1.9}$ (Praxair) were ball milled and pressed into 20 mm disks, and sintered in air at 1200 °C for 2 h. The porosity was 26 ± 2%, as measured by the Archimedes method. In order to prevent the formation of defects such as uncovered pores, cracks and pinholes on the deposited films, the functional layer having controlled open pores smaller than 0.5 μm was screen printed on the surface of the porous NiO–SDC substrates (a diameter of 16–17 mm and thickness of 0.6 mm) using the paste composed of fine grade NiO–SDC powders and commercially available ink vehicle (Nextech), and sintered at 1150 °C for 2 h in air. The electrochemical performance of single cells composed of $Sm_{0.5}Sr_{0.5}O_{3-\delta}$ (SSC) + SDC//SDC/ScSZ//NiO + SDC was evaluated at the temperature range 500–600 °C under humid 8–20% H_2 in Ar (3% H_2O) as the fuel gas and air as the oxidant gas.

3. Results and discussion

3.1. Characterization of thin films

LSGM and SDC thin films were individually deposited on sapphire substrates at 300 °C by RF magnetron sputtering. The X-ray diffraction patterns of RF magnetron sputtered LSGM and SDC thin films annealed at 800–1000 °C in air are shown in Figs. 1 and 2, respectively. As shown in Fig. 1, it was quite difficult to deposit single phase LSGM even with high temperature post-annealing. The content of a secondary phase, $La_4Ga_2O_9$,

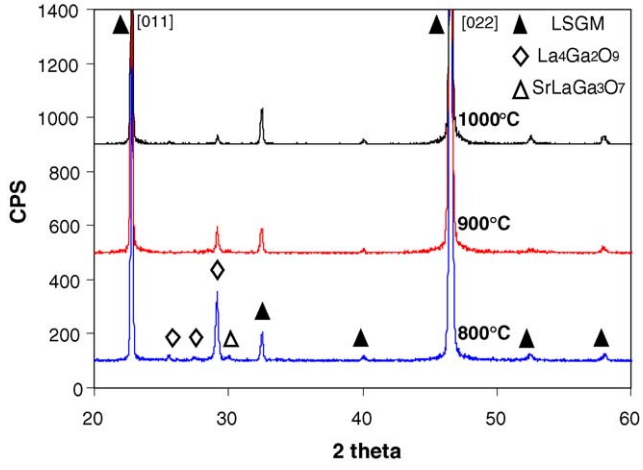

Fig. 1. XRD patterns of LSGM thin films annealed at 800–1000 °C in air.

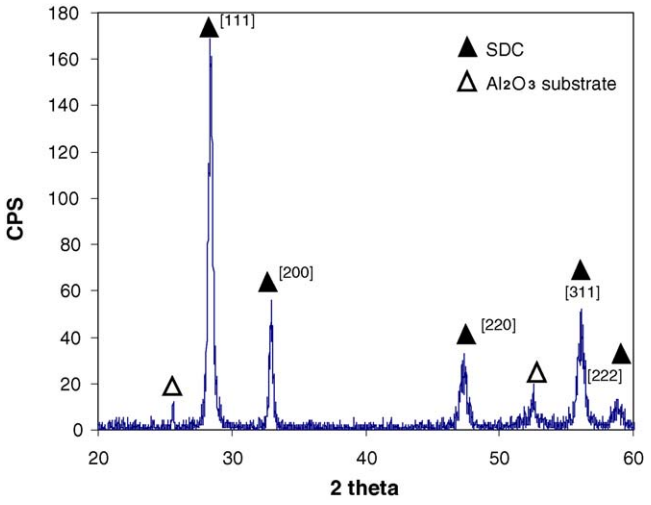

Fig. 2. XRD patterns of SDC thin film annealed at 800 °C in air.

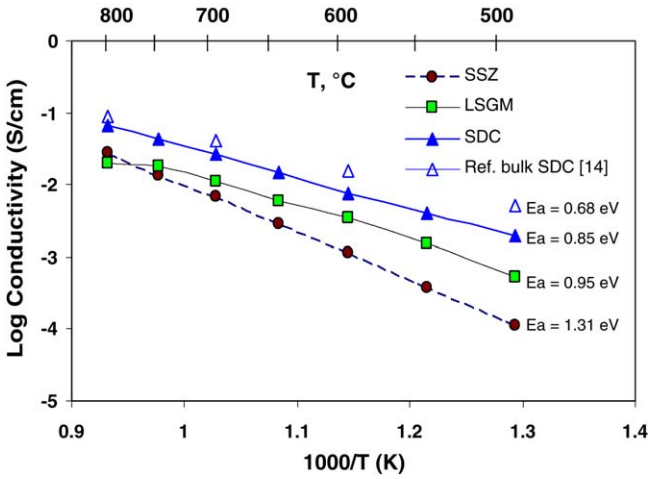

Fig. 4. Electrical conductivities of thin films deposited by RF magnetron sputtering as a function of temperature in air.

in the LSGM thin film annealed at 1000 °C was about 1.2 wt.% as determined by the Rietveld method using a preferential orientation correction. In the case of SDC, a single phase thin film on a sapphire substrate was prepared successfully as shown in Fig. 2. Scanning electron micrographs of LSGM as deposited at RT and 500 °C on sapphire substrate, porous anode w/o functional layer, and LSGM electrolyte deposited on porous anode are shown in Fig. 3. LSGM deposited at 500 °C on sapphire substrate exhibits much larger grain size in comparison to that of LSGM deposited at RT. All open pores on the surface of anode without functional layer were covered by LSGM thin film to provide gas tight sealing.

The electrical conductivities of thin films on sapphire substrates were measured by a 2-probe ac impedance method and are shown in Fig. 4. SDC thin film deposited by RF magnetron sputtering exhibited higher activation energy and approximately two and half times lower conductivity in comparison to bulk SDC at 500 °C [14]. This is likely due to the deviation of the deposited film composition from the target composition as well as contamination by unknown trace elements such as silicon, etc. in the chamber during deposition. The chemical compositions of thin films were in good agreement with those of the targets within the error limits of the experiment. It was determined that the LSGM film has a composition of $La_{0.84}Sr_{0.09}Ga_{0.84}Mg_{0.16}O_{3-\delta}$

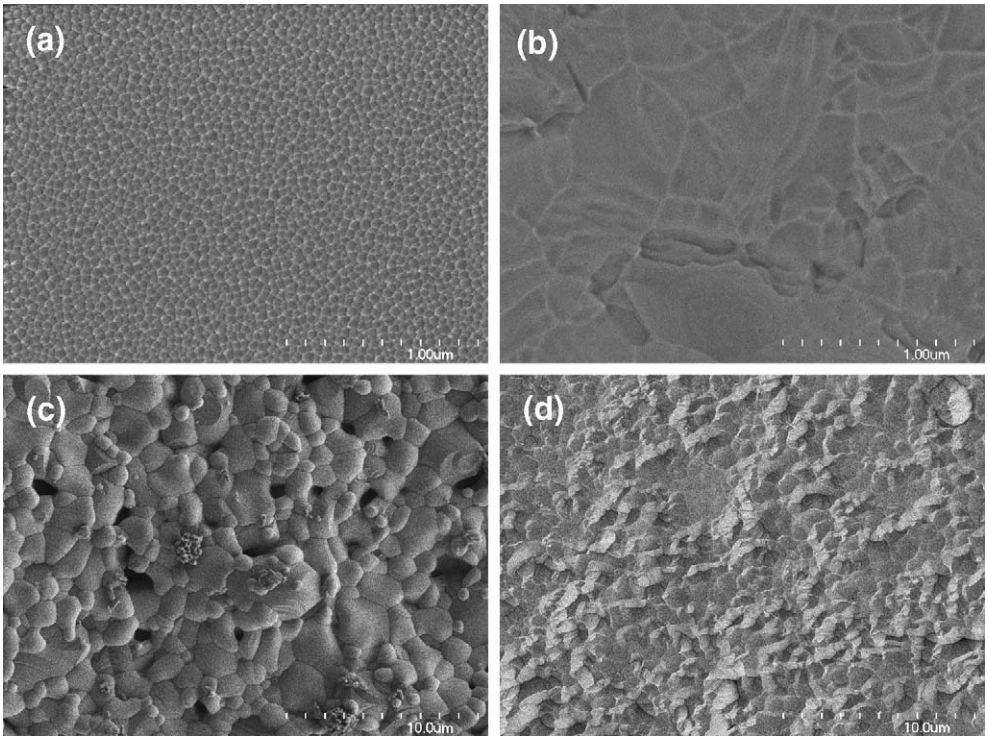

Fig. 3. Scanning electron micrograph of (a) LSGM as deposited at RT, (b) LSGM as deposited at 500 °C on a sapphire substrate, (c) porous anode w/o functional layer, and (d) LSGM electrolyte deposited on a porous anode.

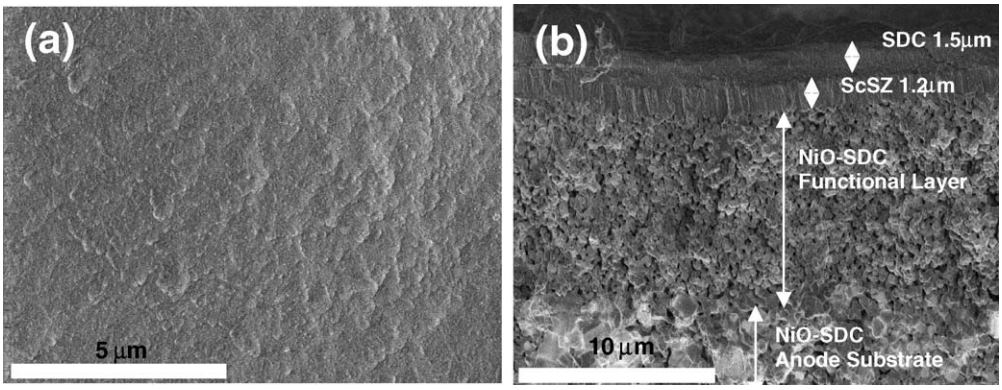

Fig. 5. Scanning electron micrograph of (a) the surface morphology and (b) the fracture cross-section of the bilayered SDC and ScSZ thin film electrolyte on a porous NiO–YSZ support.

using AA analysis. The compositions of the ScSZ and SDC thin films as determined by EDS analysis were $Sc_{0.11}Zr_{0.89}O_{2-\delta}$ and $Sm_{0.22}Ce_{0.78}O_{2-\delta}$, respectively.

Single cells having only a 1–2 μm-thick SDC thin film electrolyte, exhibited a low open circuit potential of 0.85 V at 700 °C and poor mechanical strength during reduction and oxidation cycling which would result in fast degradation of cell performance. Therefore a bilayer electrolyte of SDC and ScSZ was deposited on NiO–SDC anode substrates to enhance the power density and durability of the thin film electrolyte single cells. In addition, the interfacial resistance between the ScSZ electrolyte and the low temperature composite cathode of $Sm_{0.5}Sr_{0.5}O_{3-\delta}$ (Praxair) and 10 wt.% SDC can be reduced by using the dense SDC interlayer. Fig. 5 shows scanning electron micrographs of the surface morphology and the fracture cross-section of the bilayered SDC and ScSZ thin film electrolyte deposited by RF magnetron sputtering on a porous NiO–YSZ support. Continuous 1.5 μm thick SDC and 1.2 μm thick ScSZ thin films having a dense columnar structure covered successfully all of the open pores on the surface of the NiO–SDC functional layer additionally prepared on the porous NiO–SDC anode support. Large size open pores in the NiO–SDC substrate can cause a defect formation of small pin-holes that decrease the OCV and cell performance. Therefore the NiO–SDC functional layer having small open pores (≥0.5 μm) was very effective in preventing any serious defect formation in the SDC/ScSZ bilayered thin films.

3.2. Cell performance of single cells

Figs. 6 and 7 show the electrochemical performance of single cells composed of $Sm_{0.5}Sr_{0.5}O_{3-\delta}$ (SSC) + SDC//SDC/ScSZ//NiO + SDC at the temperature range 500–600 °C under humid 8 and 20% H_2 in Ar (3% H_2O), respectively, as the fuel gas and air as the oxidant gas at a flow rate of 100 mL min^{-1}. The open circuit voltages were around 1.02–1.04 V at 500–600 °C indicating negligible gas leakage through the electrolyte. Maximum power densities of 270, 180 and 110 mW cm^{-2} were obtained at 600, 550 and 500 °C, respectively, under 8% H_2 in Ar (3% H_2O). In the case of 20% H_2 in Ar (3% H_2O), maximum power densities of 360 and 240 mW cm^{-2} were obtained at 600 and 550 °C, respectively. The cell performance was stable during the period of the test (up to 130 h).

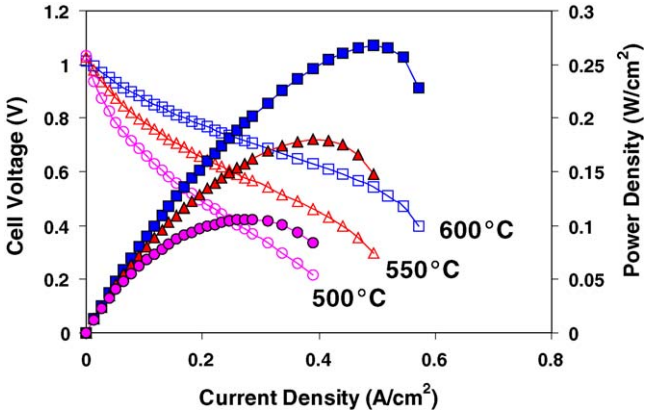

Fig. 6. *I–V* characteristics of $Sm_{0.5}Sr_{0.5}O_{3-\delta}$ (SSC) + SDC//SDC/ScSZ//NiO + SDC at the temperature range 500–600 °C under humid 8% H_2 in Ar (3% H_2O) and air.

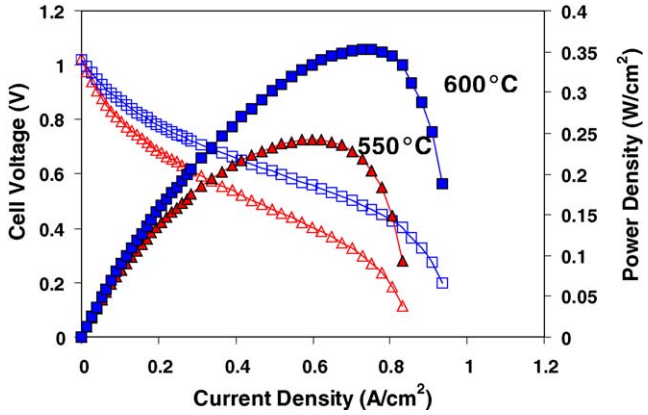

Fig. 7. *I–V* characteristics of $Sm_{0.5}Sr_{0.5}O_{3-\delta}$ (SSC) + SDC//SDC/ScSZ//NiO + SDC at the temperature range 550–600 °C under humid 20% H_2 in Ar (3% H_2O) and air.

4. Conclusions

Impervious and highly dense bilayer thin films of SDC and ScSZ have been successfully prepared on porous NiO–SDC anodes. Maximum power densities of 360 and 240 mW cm^{-2} from single cells of $Sm_{0.5}Sr_{0.5}O_{3-\delta}$ (SSC) + SDC//SDC/ScSZ//NiO + SDC were obtained at 600 and 550 °C, respectively, under humid 20% H_2 in Ar (3% H_2O) and air. RF magnetron sputtering can be applied for depositing high performance thin film electrolytes for low temperature SOFCs.

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