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Gadolinia-doped ceria barrier layer produced by sputtering and annealing for anode-supported solid oxide fuel cells

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ABSTRACT

We prepared gadolinia-doped ceria (GDC) barrier layers by sputtering and annealing at various temperatures. We then investigated the effects of the GDC barrier layers on the performance of anode-supported solid oxide fuel cells. Sputtering at 200 °C readily produced a uniform, thin layer of cubic GDC. Sputtering and annealing at 900–1100 °C formed uniform, thin, dense films, which effectively prevented the reaction between the yttria-stabilized zirconia electrolyte and the $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ cathode. The single cells assembled with the thin, dense GDC barrier layers sputtered at 200 °C and annealed at 900–1000 °C exhibited excellent electrochemical performance.

1. Introduction

For intermediate-temperature solid oxide fuel cells (IT-SOFCs) that use cobalt-containing perovskite cathodes, such as $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ (LSCF), $La_{1-x}Sr_xCoO_{3-\delta}$ (LSC), and $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF), it is essential to include a doped ceria barrier layer to prevent detrimental reactions between the cobalt-containing materials and the yttria-stabilized zirconia (YSZ) electrolyte [1–5]. Conventionally, this doped ceria barrier layer is prepared by wet-coating and sintering [5–9]. However, this process cannot produce an ideal doped barrier layer because of the severe reaction between ceria and YSZ, greatly increasing the ohmic resistance, as well as the increased porosity of the interface [5–7]. Better fabrication techniques for the doped ceria barrier layer are needed; one such candidate technique is sputtering [9–14].

A thin gadolinia-doped ceria (GDC) barrier layer should meet several requirements. First, it should be free of cracks and pinholes to suppress elemental diffusion and reaction between the cathode and YSZ electrolyte. Second, it should fully adhere to the YSZ electrolyte to reduce contact resistance. Third, it should be free of ceria-zirconia solid solution at ceria/YSZ interface to reduce ohmic resistance [5,6]. A thin, ceria-based electrolyte layer, fully adhered to YSZ electrolyte with no cracks or pin-holes, could be obtained by sputtering at deposition temperatures higher than 400 °C; however, performing this

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process in vacuum is quite complicated and inconvenient [10–12].

An alternative route for a thin and dense ceria barrier layer is a sputtering in combined with annealing process. Annealing can eliminate the defects in thin electrolyte film [15–17]. In this paper, the GDC barrier layers were prepared through sputtering and annealing, and the application of the GDC barrier layer for anode-supported SOFC was investigated. The elemental diffusion and interfacial reaction at the interfaces of GDC/YSZ and cathode/electrolyte, as well as the performance of Ni-YSZ/YSZ/GDC/BSCF-GDC single cells were studied.

2. Experimental

BSCF and GDC powders were prepared by a sol-gel process. BSCF powders were synthesized using citrate-EDTA as a complexing agent and calcined at 950 °C for 5 h. GDC powders were prepared using glycine as a complexing agent and calcined at 700 °C for 2 h. The cathode slurry was prepared from a mixture of the as-prepared BSCF and GDC powders (mass ratio 70:30), organic binder, and butanol solvent.

The NiO-YSZ (mass ratio 45:55) anode substrates were fabricated from mixed NiO and YSZ powders. The YSZ thin film was prepared on the NiO-YSZ substrate by tape-casting and co-firing at 1300 °C. The YSZ electrolyte film was ~20 μm thick. The NiO-YSZ/YSZ assemblies were ~20 mm in diameter and 0.6 mm in thickness. Before depositing the GDC layer, each NiO-YSZ/YSZ assembly was ultrasonically cleaned in acetone, ethanol, and deionized water successively for ~15 min and then dried. The GDC layer was deposited by radio frequency magnetron sputtering (JCP-200 instrument; Beijing Technical Company, Beijing, China) using an alloy target with a composition of 90 at% Ce and 10 at% Gd (99.9% pure, Huizhou Top Metal Material Co., Huizhou, China). The sputtering gas was a mixture of argon and oxygen at a 10:1 flow ratio. The NiO-YSZ/YSZ assembly was held at 200 °C during sputtering. The GDC interlayer was sputtered on the YSZ electrolyte film with a specific target power density of 9 W/cm^2 under 0.5 Pa for 50 min. The NiO-YSZ/YSZ/GDC assemblies were annealed at 800–1100 °C for 2 h. The BSCF-GDC cathode slurry was then coated on the GDC layer and sintered at 1000 °C for 3 h; the cathode area was ~0.5 cm^2.

To study the interfacial reactions occurred at the cathode/electrolyte and YSZ/GDC interfaces, X-ray diffraction (XRD; Rigaku D/max-2500PC) was performed from the cathode side after scraping off the cathode. SEM (FEI QUANTA 200F) was also performed for the GDC interlayer.

The single cells were sealed at the ends of two alumina tubes in a resistance furnace. The cathode surface was coated with silver paste to improve current collection. The cathode and anode were spring-pressed with silver and nickel mesh current collectors, respectively. The electrochemical performance was measured by the four-probe method. Hydrogen humidified at room temperature was fed to the anode at 100 ml/min, while air was fed to the cathode at 200 ml/min. The NiO-YSZ anode was reduced *in situ* at 800 °C using hydrogen. Polarization curves were measured after the cells were discharged at 0.9 V for 3 h. Impedance was typically measured from 1 MHz to 0.08 Hz with signal amplitude of 10 mV under open-circuit conditions on a Solartron 1287 potentiostat and a 1260 frequency response analyzer.

3. Results and discussion

3.1. XRD results

Figure 1 shows XRD patterns of the GDC barrier layers fabricated by sputtering and annealing at different temperatures. All samples exhibited diffraction peaks corresponding to the cubic fluorite phases of GDC (JCPDS 75-0161) and YSZ (JCPDS 30-1468) electrolyte. The cubic fluorite phase of GDC was formed during sputtering at 200 °C, first by oxidation of metallic Ce and Gd, followed by crystallization into the cubic fluorite structure oxide. The YSZ diffraction peaks came from the YSZ electrolyte substrate. The appearance of very strong diffraction peaks from the YSZ demonstrates that the GDC layer was very thin. The peak intensity and width of the GDC barrier layer varied with annealing temperature. As the annealing temperature increased, the peaks become sharper and stronger, indicating that the GDC crystals grew as the temperature increased. Using the Scherrer equation, we calculated the average GDC crystal size to be ~18 nm in the as-sputtered film and ~26 nm in the film annealed at 900 °C. These results are similar to those of combustion-synthesized GDC powders, whose crystal size increased from 5–12.5 nm in the primary powders to 27.9 nm in the powders calcined at 900 °C [18]. As the annealing temperature increased, the GDC diffraction peaks gradually shifted to higher angles, reflecting decreases in its lattice parameters. The diffusion of Zr^{4+} and/or Y^{3+} from the YSZ electrolyte into the GDC layer can reduce the unit cell volume of ceria-based oxides [5,6,19]. This reduction in lattice parameters indicates that the GDC layer and YSZ film reacted to form a solid solution during annealing at high temperatures.

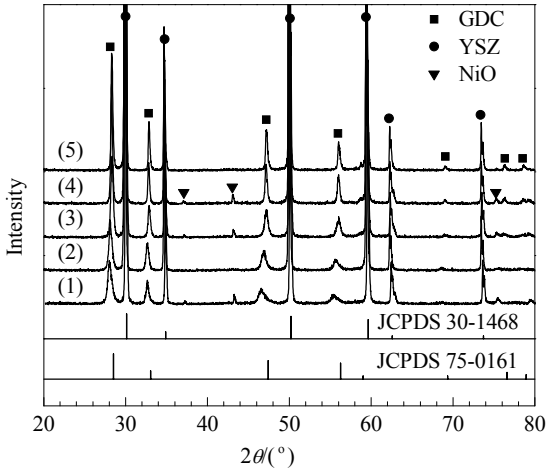

Fig. 1. XRD patterns of the GDC barrier layers as-sputtered (1) and annealed at 800 °C (2), 900 °C (3), 1000 °C (4), and 1100 °C (5). The patterns were taken from the side of the GDC barrier layer. The two patterns at the bottom are the standard XRD patterns of YSZ (JCPDS 30-1468) and GDC (JCPDS 75-0161).