



Fabrication of thin-film gadolinia-doped ceria (GDC) interdiffusion barrier layers for intermediate-temperature solid oxide fuel cells (IT-SOFCs) by chemical solution deposition (CSD)

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Abstract

A dense gadolinia-doped ceria (GDC) interdiffusion barrier layer as thin as 300 nm was successfully fabricated on a rigid anode/electrolyte bilayer substrate using the chemical solution deposition (CSD) process for intermediate temperature solid oxide fuel cells (SOFCs). Drying-related macro-defects were removed by employing drying control chemical additives (DCCA), which effectively relieved drying stresses. The major process flaws caused by the constraining effects of the rigid substrate were completely eliminated by the addition of GDC nanoparticles into the chemical solution, which suppressed the generation of microstructural anisotropy by mitigating the predominant bi-axial substrate constraints. As a consequence, a thin film GDC interlayer was successfully deposited with a high volumetric density, effectively preventing the chemical interaction between the electrolyte and cathode during the fabrication process and subsequent operation. The cell test and microstructural analysis confirmed excellent electrochemical performance and structural and chemical stability. The CSD process presented in this paper is considered to be a promising technology for the practical preparation of GDC thin film barrier layers for intermediate temperature SOFCs based on the film quality, processing costs and potential for large-scale production.

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1. Introduction

With the recent development of intermediate temperature solid oxide fuel cells (SOFCs) [1–3], ceria-based interdiffusion barrier layers have been extensively investigated [4–10] because they are an essential component of these applications to prevent unfavorable solid-state reactions between the yttria-stabilized zirconia (YSZ) electrolyte and high-performance cathode materials, such as iron- and/or cobalt-containing perovskites [11–13]. In general, the cell performance strongly depends on the fabrication process used to prepare the interdiffusion barrier layer, which dictates the microstructural development and heterogeneities [4,7,8,14]. A variety of vacuum deposition techniques, such as chemical vapor deposition

(CVD) and physical vapor deposition (PVD), have been used to produce a desirable gadolinia-doped ceria (GDC) or samaria-doped ceria (SDC) barrier layer with high density and reduced thickness, although the applicability of these methods for scale-up and mass production is questionable [4,6,10,15]. In contrast, GDC barrier layers fabricated by conventional ceramic processing techniques inevitably suffer from various microstructural heterogeneities including high residual porosity, anisotropic pores, and pore clusters originating from the constrained sintering due to the presence of the rigid substrate [4,16]. These microstructural heterogeneities facilitate cation migration from the cathode to the electrolyte via surface diffusion and/or gas phase transport, in the forms of SrO (g), Sr(OH)₂ (g) and LaO₂ (g) at the processing and operating temperatures [17–19], resulting in the formation of insulating phases such as La₂Zr₂O₇, SrZrO₃, and Sr₂ZrO₄ along the GDC/YSZ interface and in the continuous degradation of cell

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performance [11,20–22]. Therefore, it is highly desirable to develop a cost-efficient and scalable process to fabricate a thin and dense interdiffusion barrier layer free of microstructural heterogeneities. However, only limited studies have been reported thus far about the effects of constrained sintering on the generation of microstructural heterogeneities for such processes.

The microstructural heterogeneities observed in the previous investigations of GDC interdiffusion barrier layers can be classified into two groups: residual porosity and anisotropic process flaws. The high residual porosity, which results from insufficient densification, is the major heterogeneity in layers produced by conventional powder-based thick film techniques such as screen printing [4,23]. Although the residual pores can be reduced by elevating the sintering temperature, the temperature should not exceed 1200 °C to prevent the formation of an electrically resistive $(\text{GDC})_x(\text{YSZ})_{1-x}$ solid solution at the interface [12,24–27]. On the other hand, the chemical solution deposition (CSD) of the GDC barrier layer results in anisotropic process flaws, mainly in the through-thickness direction, due to severe substrate constraints as well as the extremely high sinterability and volume shrinkage of the precursor powders derived from the chemical solutions [5,28]. Such microstructural flaws usually result from transient stresses caused by differential densification [29–32], and should be eliminated to make the CSD technique a viable alternative to vacuum deposition techniques for the fabrication of a thin film GDC barrier layer, considering its exceptional advantages in processing costs and large scale production.

The geometrically anisotropic pores in the vertical direction in GDC films indicate that the constraining stress generated by the rigid substrate is in tension in the lateral direction [5,29–31]. The bi-axial tensile stress field allows the consolidated precursor powders in the film to shrink only in the direction normal to the substrate with negligible shrinkage in the parallel direction, resulting in microstructural anisotropy, e.g., preferential densification and grain growth along with pore elongation in the direction normal to the substrate. Therefore, it is critical to reduce the predominant effect of the substrate constraints on the densification of the precursor powders to suppress the differential densification and the formation of major process flaws. In the present study, local constraints were introduced in the precursor powder matrix by dispersing slow-sintering GDC nanoparticles to disrupt and counteract the substrate constraints in a predominant bi-axial stress state. The effect of GDC nanoparticle addition on the constrained sintering behavior was investigated in terms of microstructural heterogeneities. The thin film GDC barrier layer was successfully deposited onto a rigid anode/electrolyte bi-layer substrate by multiple spin coating depositions of the chemical solution and low temperature sintering. The cell, fabricated with a thin film GDC barrier layer and a $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF) cathode, was tested, and its electrochemical performance and structural stability were investigated in detail.

2. Experimental procedures

Gadolinium nitrate hexahydrate $[\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}]$, Aldrich, USA] and cerium nitrate hexahydrate $[\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}]$,

Aldrich, USA] were used as precursors for the GDC chemical solution. Premixed solvent was prepared by mixing dimethylformamide [DMF, Aldrich, USA], ethanol [EtOH, Aldrich, USA], water, acetylacetone [Acac, Aldrich, USA] and acetic acid [Ac, Aldrich, USA] at a molar ratio of DMF:EtOH:H₂O:Acac:Ac=1.072:0.627:1:0.443:0.363. DMF is a solvent as well as a drying control chemical additive (DCCA). EtOH and water are co-solvents, and Acac and Ac are complexing agents. Ac also increases the solubility of the precursors. The precursors of Gd and Ce were added to the pre-mixed solvent at a molar ratio of Ce:Gd=8:2 and stirred for 1 h at room temperature. The total concentration was 0.1 M, and the pH value of the solution was adjusted to ~4. Then, the solution was aged on a hot plate at 90 °C for 3 h to adjust the viscosity.

A solution containing GDC nanopowder was prepared by adding 5 vol% nanopowder based on total GDC yield. The GDC nanopowder was prepared by a co-precipitation method as described in our previous report [33]. The primary particle size and surface area of the powder were approximately 10 nm and 97 m²/g, respectively. Dispersion stability of GDC nanoparticles was achieved by adding 10 wt% PVP [$M_n=10,000$, Aldrich, USA] based on the dry weight of the powder. Additionally, glycerol $[\text{C}_3\text{H}_5(\text{OH})_3]$, Aldrich, USA] was used as a DCCA to prevent drying defects caused by differential drying.

The prepared solution was applied on top of the YSZ electrolyte layer of the conventionally processed anode-electrolyte bi-layer substrate as previously described [34] by spin coating at a rotation speed of 2000 rpm for 60 s using a spin-coater [JSP4D, JD Tech, Korea]. After spin coating, the film was dried in air at 300 °C by a rapid thermal processing (RTP) generator [RTP system, SNTTEK, Korea]. This process was repeated 4 times to increase the coating thickness to approximately 400 nm. The film was finally sintered at 1000–1050 °C with a heating rate of 0.25–1 °C/min.

Then, the LSCF/GDC adhesion promotion layer and the LSCF cathode layer were subsequently deposited on top of the GDC layer by spin coating depositions. The LSCF solution was prepared using lanthanum nitrate hexahydrate $[\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}]$, Aldrich, USA], strontium nitrate $[\text{Sr}(\text{NO}_3)_3]$, Aldrich, USA], cobalt nitrate hexahydrate $[\text{Co}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}]$, Aldrich, USA] and iron nitrate nonahydrate $[\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}]$, Aldrich, USA] as the precursors, and 1,3-propanediol $[\text{C}_3\text{H}_8\text{O}_2]$, Aldrich, USA] and 2-methoxyethanol $[\text{C}_3\text{H}_8\text{O}_2]$, Aldrich, USA] as co-solvents. A 0.2 M LSCF solution (with molar ratio La:Sr:Co:Fe=6:4:2:8) was prepared by mixing the precursors and solvents at the molar ratio of propanediol:2-methoxyethanol:H₂O:Acac:Ac=2.3:0.98:0.34:0.32:0.53 and stirred at room temperature for 6 h. To prepare the adhesion promotion layer, the GDC/LSCF solution containing 45 vol% of GDC nanoparticles based on final solid yield was prepared by dispersing the GDC nanoparticles in the LSCF solution containing 10 wt% PVP as a dispersant. For the cathode, the LSCF nanopowder was synthesized using a combined EDTA-citrate complexing sol-gel process [35,36] and calcined at 700 °C for 3 h. The primary particle size and surface area of the calcined LSCF nanopowder were 54 nm and 17 m²/g, respectively. Then, the LSCF nanopowder was added to the LSCF solution with

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