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Short Communication

Ceria-based electrolyte reinforced by sol–gel technique for intermediate-temperature solid oxide fuel cells

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ABSTRACT

High performance solid oxide fuel cells (SOFCs) based on gadolinia-doped ceria (GDC) electrolyte are demonstrated for intermediate temperature operation. The inherent technical limitations of the GDC electrolyte in sinterability and mechanical properties are overcome by applying sol–gel coating technique to the screen-printed film. When the quality of the electrolyte film is enhanced by the additional sol–gel coating, the OCV and maximum power density increase from 0.73 to 0.90 V and from 0.55 to 0.95 W cm^{-2}, respectively, at 650 °C with humidified hydrogen (3% H_2O) as fuel and air as oxidant. The impedance analysis reveals that the reinforcement of the thin electrolyte with sol–gel coating significantly reduces the polarization resistance. Elementary reaction steps for the anode and cathode are analyzed based on the systematic impedance study, and the relation between the structural integrity of the electrolyte and the electrode polarization is discussed in detail.

1. Introduction

Solid oxide fuel cells (SOFCs) represent one of the most efficient ways to generate electricity from a variety of fuels with low levels of pollutant emissions. Currently, the key issues for the successful development and deployment of SOFC technology on a commercial scale are costs and reliability, which are closely related to its high operating temperature. Therefore, over the past decade, considerable efforts have been made to reduce the operating temperature to the intermediate range (~650 °C), which would lower materials and manufacturing costs, improve reliability, simplify the balance-of-plant (BOP) components, and enable thermal cycling. Gadolinia-doped ceria (GDC) is considered to be one of the most promising electrolyte materials for intermediate temperature SOFCs due to its outstanding ionic conductivity and chemical compatibility with highly active cobalt-containing cathode materials [1]. In addition, Ni–GDC cermet is considered to be the ideal anode material to match with GDC electrolyte due to its excellent catalytic activity, carbon tolerance, and sulfur resistance [2]. Therefore, anode-supported SOFCs with Ni–GDC anode, GDC electrolyte, and

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Co-containing cathode would be one of the most promising propositions for high performance intermediate-temperature SOFCs.

For fabrication of GDC-based anode-supported SOFCs, thin electrolyte is generally co-sintered with the anode support, and various coating techniques have been explored for deposition of gas-tight electrolyte film on the anode support, such as screen printing [3], tape casting [4], spin coating [2,5], spray coating [6,7] and dry co-pressing [8]. In these processes, it is known to be extremely difficult to obtain fully dense GDC electrolyte at the practical co-sintering temperatures because of its inferior sintering behavior [9,10]. In addition, since GDC exhibits lower mechanical strength than YSZ, GDC electrolyte is prone to processing defects such as micro-cracks after co-sintering due to the internal stress caused by the sintering shrinkage mismatch [11]. Consequently, open circuit voltage (OCV) values for ceria-based SOFCs are inconsistent in the literature [12,13], which could possibly be explained by the variation in the quality of the electrolyte film. Since the cross-leakage of the gases through the electrolyte reduces the overall efficiency of the SOFC system, dense and gas-tight GDC electrolyte film is highly desirable for successful development of intermediate-temperature SOFC technology.

In this study, high performance SOFCs based on GDC electrolyte were fabricated for intermediate temperature operation. Thin film GDC electrolyte was deposited by screen printing, and sol–gel coating was additionally applied to remove open pores and processing flaws such as micro-cracks. The fabricated cells were electrochemically characterized, and the effect of the sol–gel coating process on the performance of the GDC-based SOFCs was discussed in detail.

2. Experimental

Chemical solution for GDC sol–gel coating was prepared by mixing stoichiometric amount of $Gd(NO_3)_3 \cdot 6H_2O$ and $Ce(NO_3)_3 \cdot 6H_2O$ in a solvent composed of dimethylformamide (DMF), ethanol (EtOH), water, acetylacetone (Acac), and acetic acid (Ac). For sol infiltration, glycerin was added to the chemical solution as a drying control chemical agent (DCCA), while glycerin along with polyvinylpyrrolidone (PVP) binder was added for thin film deposition.

For cell fabrication, GDC, NiO, and poly(methyl methacrylate) (PMMA) were ball-milled for 24 h in ethanol with dispersant (0.2 wt%), binder (1.5 wt%), and plasticizer (1.5 wt %), and the granules were obtained by spray drying. Volume ratio of GDC, NiO, and PMMA was 0.37:0.33:0.3. Anode substrates (2 cm × 2 cm) were fabricated by uni-axially pressing the granules at 60 MPa. The slurries for anode functional layer, electrolyte, cathode functional layer, and cathode current collecting layer were prepared by mixing ceramic powders with dispersant (0.5 wt%), binder (2.5 wt%), and plasticizer (2.5 wt%) in α-terpineol using planetary mill for screen printing. The anode functional layer (NiO/GDC) and electrolyte (GDC) were screen printed sequentially, followed by co-sintering at 1430 °C. On top of the co-sintered GDC electrolyte, the chemical solutions for GDC infiltration and thin film deposition were spin-coated subsequently, followed by thermal treatment at 600 °C for 5 min. Then, the cathode functional layer ($La_{0.8}Sr_{0.2}CoO_3$ (LSC) + GDC) and cathode current collecting layer (LSC) were screen printed and sintered at 950 °C in air. The effective electrode area was 1 cm × 1 cm. The fabricated cells were tested with humidified hydrogen (3% H_2O) as fuel and air as oxidant at 650 °C. Electrochemical measurements were performed using Solartron 1260/1287 frequency response analyzer and potentiostat. After testing, the cells were sectioned and impregnated with epoxy in vacuum. After epoxy was hardened, they were polished down to 0.25 μm, and the cross-sections were examined using scanning electron microscopy (SEM) analysis (Philips FEI XL-30 FEG). The microstructural features such as thickness and porosity were measured using the image analysis software program ImageJ.

3. Results and discussion

Sol-gel coating process was developed to enhance the quality of the GDC electrolyte fabricated by screen printing. Fig. 1(a) shows the SEM image of the surface of the GDC film prepared by conventional sol–gel process using the chemical solution composed of nitrate precursors and solvent. The film was

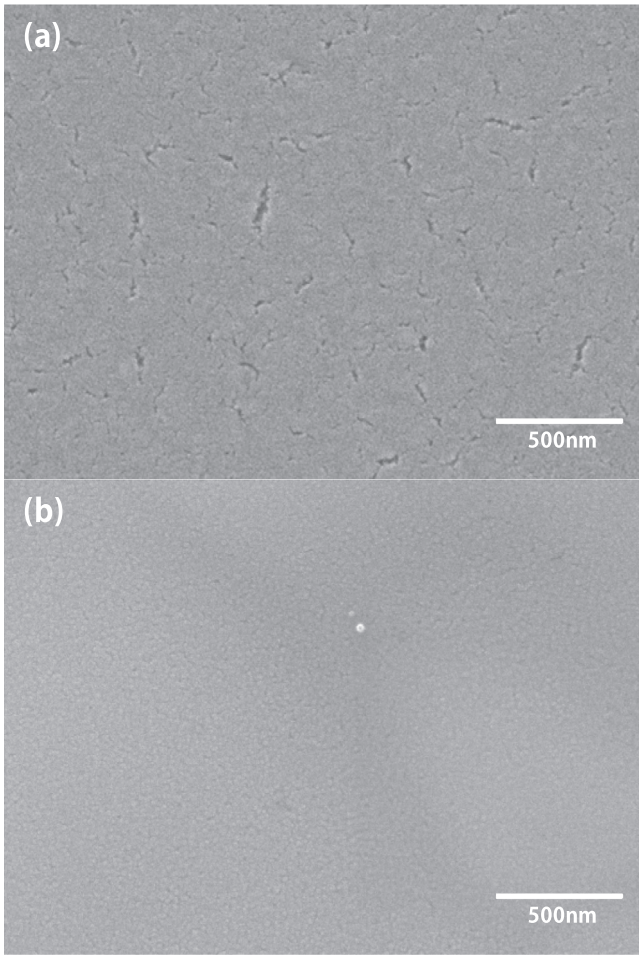

Fig. 1 – SEM images of the surface of GDC film prepared by spin coating of chemical solution (a) without and (b) with DCCA. Images were taken after drying at 300 °C in air.