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Short communication

$Y_{0.08}Sr_{0.88}TiO_3$–CeO_2 composite as a diffusion barrier layer for stainless-steel supported solid oxide fuel cell

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HIGHLIGHTS

- STS-supported SOFC with YSZ and Ni-YSZ is tape-casted and co-fired at 1350 °C.
- $Y_{0.08}Sr_{0.88}TiO_3$–CeO_2 composite is tested as a new diffusion barrier layer (DBL).
- The cell with DBL shows peak power density ~220 mW cm^{-2} and maintains it at 700 °C.

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ABSTRACT

A new diffusion barrier layer (DBL) is proposed for solid oxide fuel cells (SOFCs) supported on stainless-steel where DBL prevents inter-diffusion of atoms between anode and stainless steel (STS) support during fabrication and operation of STS-supported SOFCs. Half cells consisting of dense yttria-stabilized zirconia (YSZ) electrolyte, porous Ni-YSZ anode layer, and ferritic STS support, with or without $Y_{0.08}Sr_{0.88}TiO_3$–CeO_2 (YST-CeO_2) composite DBL, are prepared by tape casting and co-firing at 1250 and 1350 °C, respectively, in reducing (H_2) atmosphere. The porous YST-CeO_2 layer (t ~ 60 μm) blocks inter-diffusion of Fe and Ni, and captures the evaporated Cr during cell fabrication (1350 °C). The cell with DBL and $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) cathode achieved a maximum power density of ~220 mW cm^{-2} which is stable at 700 °C. In order to further improve the power performance, Ni coarsening in anode during co-firing must be prevented or alternative anode which is resistive to coarsening is suggested. This study demonstrates that the new YST-CeO_2 layer is a promising as a DBL for stainless-steel-supported SOFCs fabricated with co-firing process.

1. Introduction

Solid oxide fuel cells (SOFCs) have possible applications as energy conversion devices due to their high energy conversion efficiency and the diversity of fuels [1]. Recent developments in the electrodes and electrolytes have decreased the operating temperature to ~600 °C, so metal (e.g., Ni)-ceramic supports can be replaced by metal supports such as stainless steel (STS) [2]. The metal can provide high mechanical strength and thermal-shock resistance for the brittle ceramics and thus strengthen the cell [3]. Thus, STS-supported SOFCs (STS-SOFCs) may possibly be used for mobile application that requires both low temperature operation and fast cycling speed. Appropriate selection of a supporting metal is essential to achieve high power density and durability. In addition to mechanical strength and electrical conductivity, other requirements such as reactivity with other components and matching of thermal expansion coefficients (TECs) also must be considered because these are directly related to power density and durability of the cell. STS is a popular supporting metal for metal-supported SOFCs (MS-SOFCs); it shows good TEC-compatibility (10–12 ppm K^{-1}) with electrolyte materials and ferritic STS without Ni is cheaper than many special metals. STS-supported SOFCs are often fabricated by co-firing of layers at high-temperature in a reducing atmosphere to avoid metal oxidation. However, inter-diffusion between Fe, Cr in ferritic-STS support and Ni from the anode can occur during fabrication and during cell operation [4–6]. When Ni from the anode diffuses into the STS support, it changes STS from ferrite to austenite, and this

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transformation causes undesirable TEC change [7]. In addition, diffusion of Cr into the anode may cause oxide scales to form on the Ni particles; this passivated part would increase anodic polarization, leading to the poor power density and fast degradation of the cell [8].

Several attempts have been made to overcome these problems. Fabrication of cells at relatively low temperature has been studied using methods such as electrophoretic deposition (EPD) [9], pulsed laser deposition (PLD) [10] and plasma spray. These cells have shown relatively high power density without Ni contamination. However, fabrication at low temperature requires high-cost equipment and entails a complicated procedure. Furthermore, cells with a large area and various shapes cannot be easily fabricated by these methods. Other approach to address the problems is the infiltration techniques to prepare the anode [11]. However, Ni coarsening during operation degrades power density [11]. Lastly, insertion of a diffusion barrier layer (DBL) has been explored extensively as a solution to avoid reaction of Ni and Fe/Cr [12–16]. The barrier layer must prevent inter-diffusion while allowing electron and gas transport. The layer should also have similar TECs with the other cell components, and be stable and compatible with the relevant operating and processing conditions. Applying a DBL is one of the most promising methods in terms of stability and practical use. Compositions based on $LaCrO_3$ and $LaMnO_3$ [8,13,14]; Cr_2O_3/Cr_2MnO_4, CeO_2, and $Ce_{0.8}Gd_{0.2}O_2$ (GDC) [15] have been evaluated as diffusion barriers. $LaMnO_3$-based composition is expected to be decomposed in the fuel atmosphere [16], and Cr_2O_3 based has shown Cr diffusion into the Ni-based anode [15]. CeO_2 and GDC form an effective diffusion barrier. However, the cation of CeO_2 or GDC is partially reduced from Ce^{4+} to Ce^{3+} in low oxygen partial-pressure (Po_2) leading to lattice expansion that may result in the mechanical failure [17], particularly during firing at high temperature.

To compensate for the mechanical stability of CeO_2, an additional composition should be considered. Donor (Y or La)-doped $SrTiO_3$, evaluated as an alternative anode material, could be a good additive material to remedy the shortcomings of CeO_2. (Y, Sr) TiO_3 (YST) or (La, Sr)TiO_3 (LST) are chemically stable in a reducing atmosphere. The electrical conductivity of donor-doped $SrTiO_3$ sintered in reducing atmosphere is 1–2 orders of magnitude higher than that sintered in air or CeO_2 [18,19]. In addition, the donor-doped $SrTiO_3$ based materials have TEC (12 ppm K^{-1}) similar to those of the typical electrolyte materials. Thus, the addition of donor-doped $SrTiO_3$ to CeO_2 could yield a stable diffusion barrier.

In this study, 8 mol% Y-doped $SrTiO_3$ ($Y_{0.08}Sr_{0.88}TiO_3$) was selected due to its highest conductivity among YSTs [20] to composite with 50 wt.% CeO_2 and the $Y_{0.08}Sr_{0.88}TiO_3$–CeO_2 composite was tested as a DBL. After co-firing of STS-supported SOFCs with and without DBL at elevated temperature (1250–1350 °C) in the reducing atmosphere, compositional changes across Ni-YSZ anode, DBL, and STS layers were examined. The effect of DBL on the electrochemical performance and stability was monitored at 700 °C.

2. Experiment

Button-type SOFCs with and without $Y_{0.08}Sr_{0.88}TiO_3$–CeO_2 (YST-CeO_2) composite as a DBL were fabricated by the tape-casting method (Fig. 1). The cell without DBL, (a) Pt/YSZ/Ni-YSZ/STS, was fired at 1250 °C and the cell with DBL, (b) $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF)/YSZ/Ni-YSZ/YST-CeO_2/STS, was fired at 1350 °C. The firing temperatures were selected for the proper densification of YSZ layer. For the DBL, YST was prepared from Y_2O_3, $SrCO_3$ and TiO_2 (99.9%, High Purity Chemicals, Japan). The mixed powders were milled with zirconia balls in ethanol (99.9%, SAMCHEN Chemicals, Korea) for 12 h then the ethanol was removed by evaporation. The dried powder was calcined at 1200 °C for 5 h in air. X-ray diffraction (XRD) measurement confirmed that the resultant powder is a single-phase YST. The synthesized YST and an equal weight of CeO_2 (99.9%, High Purity Chemicals, Japan) with 15 wt.% of corn starch (D.C. Chemicals, Korea) as a pore former consist of DBL powder. To prepare the slurry for tape casting, powders were mixed with binder solution composed of toluene and ethanol as solvents, polyvinyl butyral (PVB, B-76) as a binder (10% of raw powders) and dioctyl phthalate (DOP) as a plasticizer (50% of binder contents). Then, the mixture of powders and binder solution was milled with zirconia balls (diameter; 10 mm and 5 mm) for 72 h. Green sheets of DBL were cast to a thickness of 40–50 μm after drying. Commercial stainless-steel powder (STS-434L, 400–500 mesh, Daekwang Industry, Korea) was chosen as a material for metal support. Planetary-milled (Pulverisette 6, Netzsch, Germany) NiO (1 μm, 99.97%, Kojundo chemical, Japan) powder and 8 mol% Y_2O_3-stabilized ZrO_2 (YSZ, 0.3 μm, TZ-8YS, Tosoh, Japan) powder were mixed in 60:40 wt.% for anode slurries. YSZ slurries for electrolyte were prepared in a similar method to form green sheets. As-cast green sheets of support, DBL, anode, and electrolyte were used for the cells with or without DBL. Both green cells with and without DBL layer were laminated at 30 MPa and 60 °C for 20 min to achieve the desired thickness, then punched out to yield a circular green-cell of 24-mm diameter. The green cells were heated to burn binder at or below 400 °C for 12 h and co-fired at 1350 °C for the cell with DBL and 1250 °C for the cell without DBL, respectively, for 3 h in dry hydrogen atmosphere. To avoid deformation of the sample during the firing process, a porous ZrO_2 plate was used to apply a vertical load (1.5 g cm^{-2}) to the cell. The shrinkage curves of YSZ, STS434L, Ni-YSZ and YST-CeO_2 tapes (50×5 mm^2 size) were determined simultaneously by positioning and firing all the tapes along the temperature gradient of a tube furnace (754–1277 °C) in dry H_2. The temperature of each position was measured using an R-type thermocouple. The heating rate was 2 °C/min and the cooling rate was 5 °C/min.

For the electrochemical measurement of cells, ceramic bond (Model 571, Aremco, USA) was used to mount the sintered cell on an alumina tube. Platinum (#6082, Heraeus, Germany) and $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF, AGC Seimi Chemical Co., Japan) pastes, respectively, were screen-printed as a cathode (0.502 cm^2) for the cell with and without DBL, respectively. Although Pt cathode is stable and easy to prepare, it is expected to show high polarization resistance. A mixed ionic and electronic conductor (MIEC) cathode (LSCF) was selected for the cell with DBL to obtain a better performance. For firing of the LSCF cathode, the cell was pre-fired at 900 °C for 2 h while maintaining the reducing atmosphere in the anode and open air in the cathode. Pt was used as a cathode for the cell without DBL and was not pre-fired. After pre-firing of the cell with LSCF cathode, the cell was cooled to room temperature, then Pt paste and mesh were attached on the cathode as a current collector. The electrochemical performances of both cells were evaluated using wet H_2 gas as a fuel gas and open air as an oxidant gas. The expected (or calculated) Po_2 in the anode gas was ~10^{-22} atm at 800 °C.

The microstructure of cross-section of the cell was examined using a field emission scanning electron microscope (FE-SEM, Model XL30S FEG, Philips Electron Optics B.V., Netherlands). Atomic (Ni, Fe, Cr) distributions across anode, DBL, and STS support layers were examined using an energy dispersive spectroscopy (EDS) line profile to examine the possible reaction between the layers. The current-voltage-power (I–V–P) curve and the impedance were measured using an AC impedance analyzer (VSP, Bio Logic Science instruments, France) using wet H_2 (97% H_2 + 3% H_2O) as a fuel gas and open air as an oxidant gas. Current-voltage-power measurements were conducted at 700 °C for 40 h.