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Flexible solid oxide fuel cells supported on thin and porous metal

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ABSTRACT

A thin metal (NiFe)-supported SOFC is fabricated by tape casting and co-sintering, and its mechanical flexibility is tested. A single cell, composed of ~120 μm-thick NiFe-support, ~30 μm-thick Ni-YSZ (yttria-stabilized zirconia) anode, and ~15 μm-thick YSZ electrolyte, shows a good mechanical flexibility. With the use of a thin metal (NiFe) support, the degree of bending for the metal-supported cell is much larger than that for the anode- or electrolyte-supported SOFCs as the displacement shows under the mechanical load. The rupture of the cell is also largely prevented due to its flexibility. A thin NiFe-supported cell that operated at 800 °C with a LSCF ($La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$) cathode shows a power density of ~430 mW cm^{-2}. This type of cell is promising as a mobile or portable power generator because it is light weight and highly resistant to mechanical shocks.

Introduction

Solid oxide fuel cells (SOFCs) are a promising energy-conversion system with high electrical efficiency and environmentally friendly nature. Electrolyte-supported and anode-supported SOFCs are popular world-wide and recent developments in electrode and electrolyte materials have lowered their operating temperatures, making it possible to fabricate SOFCs with a metal support. The metal-supported SOFCs are attractive for their high mechanical strength, high thermal conductivity, and low material cost. The good mechanical and thermal properties of metal help ceramic cells to overcome their weakness to mechanical and thermal shocks [1]. To date, thermal-shock resistance has been tested and shown only for very thin electrolyte-supported cells [2] or small tubular cells [3]. As the cells have become more resistive to external impacts and thermal cycles, SOFCs become suitable for mobile as well as stationary applications.

Because of the advantages of metal-supported SOFCs, efforts are underway to fabricate metal-supported SOFCs. In most studies, stainless steels (STSs) have been used for metallic supports because of their thermal-expansion coefficient (TEC) match with that of other cell components [4–10]. With the use of stainless steel (STS), the performance of SOFCs is maintained after rapid heating and cooling [11].

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Furthermore, STS-supported SOFCs are found to be more stable than anode-supported SOFCs in redox cycling conditions because the STSs show a high oxidation resistance [7]. However, STS-supported cells are difficult to fabricate due to the reaction between Fe, Cr in STS and Ni in anode and thus the poisoning of anode [5,12]. The use of diffusion barrier layer between STS and anode is suggested and tested [13,14] to prevent the reaction. Metal-supported SOFCs often use thick (t > 1 mm) STSs for the supporting metal [15]. This type of cell is very rigid and massive, which limits its usage in portable devices. However, thin-metal supports (e.g., thickness < ~200 μm) can solve these problems and provide enough strength to support a single cell. The use of thin supports has further advantages such as low material cost and light weight. In addition, the thin supports make the cells flexible. In this study, we define the flexibility as the cell's ability to bend under a load and return to its original shape after removal of the load. In other words, the cell is elastic under a limited load. During cell stacking, a high external load is often required in order to improve the electrical contact between cells and the current collector. The resultant cracking of cells, due to the brittle nature of ceramics, often leads to the failure of an entire stack. This is one of the major problems that limit the scale-up of SOFCs. However, if cells have mechanical flexibility, the cells can be more easily stacked without destruction.

In our previous study [16], a thin Ni-supported SOFC was successfully fabricated and characterized. A thin and porous Ni layer of ~150 μm thickness was used as a supporting metal. As a result, the single cell showed enough strength and good electrochemical performance. However, Ni metal has a large TEC (thermal-expansion coefficient) value mismatch with YSZ electrolyte. Thus the NiFe alloy can be more resilient than the Ni as a support because the TEC of NiFe approaches that of YSZ when the composition is 5:5 (wt. ratio) of Ni:Fe [17]. Reports were found that use different compositions of NiFe alloys and very thick supports [18,19]. In contrast to STS-supported cell, NiFe-supported cell can be fabricated by co-firing of Ni–Fe-oxide with electrolyte and anode in air followed by reduction in wet H_2 gas. The fabrication of thin NiFe-supported cell can also be found elsewhere [20].

In this study, we have chosen a thin Ni–Fe (5:5 wt. ratio) as a model support material for the fabrication of flexible SOFCs. A thin metal-supported SOFC (total thickness ~165 μm) was fabricated using a NiFe alloy as a support. The aim of this study is to demonstrate flexibility of thin metal-supported cell by means of 3-point bending test, and compare it with that of conventional electrolyte- or anode-supported SOFCs.

Experimental procedure

The fabrication process of a metal-supported SOFC is illustrated in Fig. 1. Commercial NiO (1 μm, 99.97%, Kojundo Chemical, Japan) and Fe_2O_3 (5 μm, Aldrich, USA) powders were chosen as the starting materials for the fabrication of the metal support, and they were mixed together to attain a composition of NiFe (5:5 wt. ratio, hereafter NiFe or NiFe alloy) after reduction. As a pore former, 10 wt.% of starch powders (D.C. Chemicals, Korea) were added into the NiO–Fe_2O_3 powders.

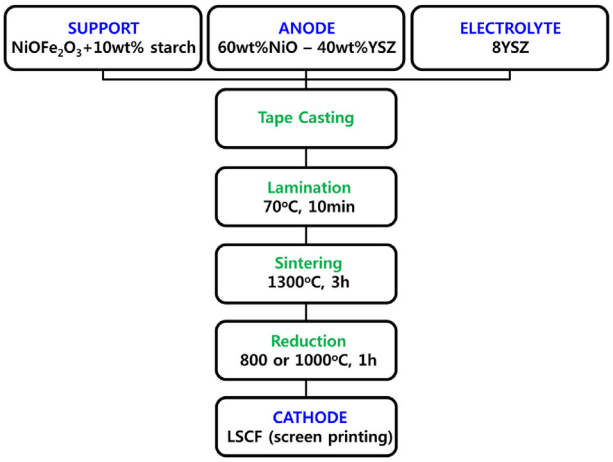

Fig. 1 – Fabrication procedure of metal-supported SOFCs using tape casting, lamination, and a two-step firing process.

A green sheet was fabricated by using the tape casting method (STC-14C, Hansung System, Korea). The binder solution, used for tape casting, was composed of toluene, ethanol, polyvinyl butyral (PVB, B-74), and dioctyl phthalate. Slurries were prepared by ball milling the mixture of powders and the binder solution for 24 h. A NiO (1 μm, 99.97%, Kojundo Chemical, Japan) – YSZ (Y_2O_3-stabilized ZrO_2, TZ-8Y, Tosoh, Japan) anode in a 6:4 weight ratio and YSZ electrolyte were also prepared as green sheets by tape casting.

The support, the anode, and the electrolyte tapes were laminated (HMM-04A, Hansung System, Korea) with 30 kg cm^{-2} of pressure at 70 °C for 10 min. Then the tapes were punched out to have a diameter of 25 mm. The three-layered cell was co-fired using two-step firing process [21]. The green cells were fired at or below 400 °C in air for 5 h to burn binder (heating rate: 2 °C/min) and further fired at 1300 °C in air for 3 h (3 °C/min) in the first step. In the following step, the cell was cooled to 800 °C (cooling rate: 2 °C/min) and reduced for 1 h in wet H_2 atmosphere to transform Ni–Fe oxide to metallic Ni–Fe alloy. The cell was further cooled to room temperature (3 °C/min). During entire firing process, a porous zirconia plate (20 g) was positioned on top of the cell in order to prevent the warping of the cell. For the electrochemical test of cell, $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF, AGC Seimi Chemical Co., Japan) paste was screen-printed as a cathode (Area: 0.502 cm^2) on YSZ electrolyte and the cell was mounted on alumina tube with sealing cement (Model 571, Aremco, USA). The cell was fired at 900 °C for 2 h while maintaining the reducing atmosphere in the anode side to avoid oxidation of Ni–Fe support, and open air in the cathode side. After pre-firing of the cell with LSCF cathode, the cell was cooled to room temperature. After attachment of Pt mesh with paste as a current collector, the cell was heated to 800 °C for electrochemical measurement. Cathode and anode, respectively, were exposed to open air and wet H_2 gas (97% H_2 + 3% H_2O) flow (~100 cm^3 min^{-1}). After 2-step firing, a 3-point bending test was carried out using a micro-load system (RB302, RnB, Korea) to confirm the mechanical property of the thin metal-supported cell as shown in Fig. 2a. The circular cells with 20 mm diameter were