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Spherical shaped pore structured cermet supports for solid oxide fuel cells

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Abstract

Anode-supported solid oxide fuel cells (SOFC) have been extensively investigated due to their ease of fabrication, robustness, and high electrochemical performance. In this study, anode supported SOFCs are fabricated and characterized as a function of the components in the anode supports. The addition of Fe_2O_3 to NiO–yttria stabilized zirconia (YSZ) anode support tape changes the morphology of the support. Nickel ferrite spinel from the reaction of Fe_2O_3 and NiO during co-firing produces spherical shaped macropores without a change in porosity. SOFCs fabricated by the addition of 0 wt%, 5 wt%, 10 wt%, and 20 wt% Fe_2O_3, exhibit maximum power densities of 2.24 W cm^{-2}, 2.45 W cm^{-2}, 2.38 W cm^{-2}, and 2.09 W cm^{-2}, respectively, at 800 °C with sufficient H_2 fuel. With a lower H_2 flow rate, SOFC fabricated without Fe_2O_3 shows fluctuating and lowered fuel cell performance. SOFC fabricated with 5 wt% Fe_2O_3 shows stable and improved performance. The dense percolation of spherical shaped macropores and a well-connected electrical conduction path, both of which are formed by adding Fe_2O_3, result in lowered charge and mass transfer polarization, which increase the fuel cell performance. However, as a result of the increased charge transfer polarization, the addition of 20 wt% Fe_2O_3 results in Fe diffusion into the anode functional layer and reduces the fuel cell performance. To obtain improved and stable fuel cell performance, the development of spherical shaped macropores is beneficial and the addition of other elements should be considered.

Keywords: Solid oxide fuel cell; Anode supported cell; Anode support; Porous electrode; Nickel iron

1. Introduction

SOFCs are considered to be the most promising energy generation system; they can directly convert various hydrocarbon containing fuels to electrical energy with high efficiency. The development of low cost materials and fabrication processes are the key technical challenges for increasing cell performance and improving the mechanical properties of SOFCs [1–4]. Anode-supported SOFCs, which consist of an Ni–YSZ anode support, Ni–YSZ anode functional layer (AFL), YSZ electrolyte, and cathode, are the most widely used types of SOFC in the current system [5,6]. The tape casting and co-firing method of anode support, AFL and electrolyte, is cost effective and is an easier process for fabricating planar anode supported SOFCs. In order to achieve excellent cell performance in the anode-supported SOFCs, a porous Ni–YSZ anode support has to fulfill the requirements of electronic conductivity, anodic properties, long-term functionality, and high permeability for the fuel gas and the reaction product (by a well-sized and connected porous structure). To improve fuel cell performances, the compositions and components of the Ni–YSZ anode support have been investigated in terms of conductivity and porosity [7–10]. The addition of iron has been reported to be beneficial for improving catalytic activity not only in AFL but also in the support [7]. NiFe has been developed as the reforming and oxidation catalyst in AFL due to the lower activity of iron for carbon formation and better performance in SOFCs with hydrocarbon fuel [9,10]. NiFe has a better matching of its thermal expansion coefficient (TEC), 12–17 × 10^{-6} K^{-1}, with the YSZ electrolyte than does Ni, which has a value of

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$15–18 \times 10^{-6}\ K^{-1}$. NiFe also forms extensive solid solutions and intermetallic phases [8]. In terms of processing and performance, Fe, as an additional material, could be a good candidate for anode support.

In this study, iron oxide is added and fabricated into an NiO–YSZ anode support layer tape in order to investigate the effects of iron oxide, which is co-fired with NiO–YSZ AFL and the YSZ electrolyte. The change of morphology of the anode support is characterized and the fuel cell performance is studied here in terms of the amount of iron oxide in the anode support tape.

2. Experimental procedures

Anode supported SOFC was fabricated by a co-firing process in three thin layers; anode support, AFL, and electrolyte. The slurry for the porous support tape consisted of NiO (0.4 μm, High Purity Chemicals), Fe_2O_3 (0.15 μm, High Purity Chemicals), graphite (~5 μm, Carbonix) and an organic binder of polyvinyl butyral (PVB). Each support is coded with the Fe_2O_3 weight ratio to NiO, such as 0 wt% Fe_2O_3 (NiO 65 wt% and YSZ 35 wt%), 5 wt% Fe_2O_3 (NiO 61.75 wt%, Fe_2O_3 3.25%, and YSZ 35 wt%), 10 wt% Fe_2O_3 (NiO 58.5 wt%, Fe_2O_3 6.5%, and YSZ 35 wt%), and 20 wt% Fe_2O_3 (NiO 52 wt%, Fe_2O_3 13%, and YSZ 35 wt%). The starting materials were mixed and ball-milled with zirconia balls (diameter = 10 mm and 5 mm) for 48 h. In order to prepare the AFL tape, NiO (0.1 μm, J.T. Baker Chemical Co) powder and 8 mol% Y_2O_3–stabilized ZrO_2 (YSZ, TZ8Y, Tosoh) powder at a 6:4 weight ratio were mixed and ball-milled with polyvinyl butyral (PVB) binder solution. The YSZ electrolyte tape was prepared with YSZ powder and PVB binder solution. The support, AFL, and electrolyte tapes were laminated under conditions of 40 MPa at 80 °C for 10 min. The laminated tapes with dimensions of 25 cm × 25 cm were fired at 700 °C for 2 h to burn out the graphite, binder, and organic additives. Subsequently, the laminated tapes were sintered at 1370 °C for 3 h in an air atmosphere. A gadonillium doped ceria (GDC) interlayer of ~1 μm was formed on the YSZ electrolyte via aerosol deposition method after the co-firing process. The anode supported cells (ASCs) with NiO–Fe_2O_3–YSZ support (~900 μm)/NiO–YSZ AFL (~15 μm)/YSZ(~10 μm)/GDC (~1 μm) were cut into circles with diameters of 2.6 cm from the co-fired cell. A composite paste with a composition of $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF, Seimi Chemicals) and GDC (Anan Kasei) in a 5:5 weight ratio as a cathode was screen-printed on the GDC interlayer of ASC. Subsequently, a paste with pure LSCF was screen-printed on the LSCF and GDC composite cathode in order to improve the current collection. The cathode active area was 1 cm^2. The fabricated cell was assembled and sealed with Cerama bond TM 571 from AREMCO in an alumina jig to measure the current–voltage characteristics and impedances. Pt paste and mesh were used for current collection. The cell was heated to 800 °C over a period of 9 h and anode reduction was performed with 300 cc min^{-1} of 97% H_2–3% H_2O for 3 h. To study the current–voltage characteristics, SOFCs were tested with 300 cc min^{-1} of 97% H_2–3% H_2O and 1000 cc min^{-1} of air at 800 °C and 750 °C with a KIKUSUI PLZ-30F. To characterize the effects of fuel flow rate, SOFCs with an anode support of 0 wt% Fe_2O_3 and 5 wt% Fe_2O_3 were characterized at 700 °C as a function of H_2 flow rates of 500, 250, and 100 cc min^{-1}. Impedance measurements with biases of 0–0.45 V were carried out with a Biologic SP300 in the frequency range of 100 kHz–0.1 Hz with an applied AC voltage amplitude of 100 mV. The anode support layers were characterized using the X-ray diffraction method to investigate the phase formation after co-firing. The pore size distribution and porosity of the anode support after reduction were measured using a mercury porosimeter (Autopore IV, Micromeritics, USA). The microstructures of the SOFCs were characterized via scanning electron microscopy (SEM) using a JSM-6480LV before and after anode support reduction. After the electrochemical performance measurement, the microstructures of the SOFCs were also characterized via SEM.

3. Results and discussion

The starting materials for the anode support consist of NiO, Fe_2O_3 and YSZ. The composition of YSZ is 35 wt% and the sum of NiO and Fe_2O_3 is 65 wt%. Fe_2O_3 is added at ratios of 5 wt%, 10 wt%, and 20 wt% of the sum of the weight ratio of NiO and Fe_2O_3. After co-firing of the anode supported SOFC at 1370 °C for 3 h in an air atmosphere, the XRD patterns of the anode support were determined and are shown in Fig. 1. Peaks of NiO and YSZ can be observed in the anode support with 0 wt% Fe_2O_3. With the addition of Fe_2O_3, the peaks for Fe_2O_3 are not observed, and the peaks for the $NiFe_2O_4$ phase are observed and strengthened with increasing amounts of Fe_2O_3. YSZ and NiO can be seen clearly as shown in Fig. 1. The XRD patterns show that the addition of Fe_2O_3 forms $NiFe_2O_4$ spinels via the reaction with NiO. The single-phase XRD patterns of YSZ indicate the full dissolution of Fe_2O_3 into YSZ grains and/or grain boundaries [11]. The addition of

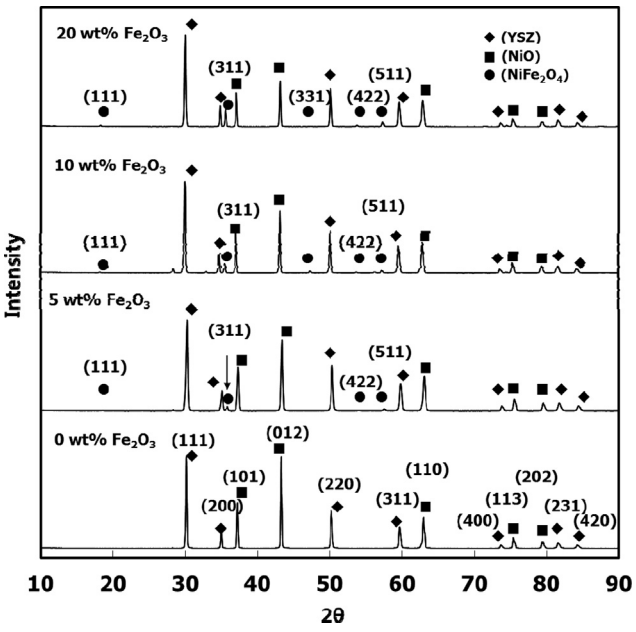

Fig. 1. XRD patterns of support layer.