Challenge for lowering concentration polarization in solid oxide fuel cells

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HIGHLIGHTS

- Porous microstructure control technique using extrusion process was developed.
- A Ni-YSZ anode shows 53.6 vol.% porosity with a median pore diameter of 0.911 μm.
- Lowing concentration polarization is essential to achieve high power density.
- Reduced concentration polarization in SOFC resulted in 3.09 W cm^{-2} at 800 °C.
- Estimated concentration overpotential was less than 0.1 V at 10 A cm^{-2}.

GRAPHICAL ABSTRACT
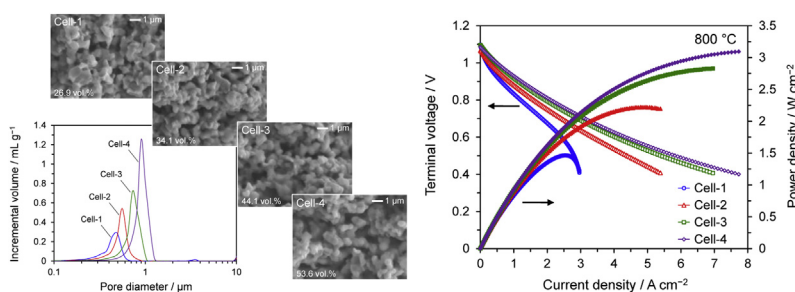
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ABSTRACT

In the scope of electrochemical phenomena, concentration polarization at electrodes is theoretically inevitable, and lowering the concentration overpotential to improve the performance of electrochemical cells has been a continuing challenge. Electrodes with highly controlled microstructure, i.e., high porosity and uniform large pores are therefore essential to achieve high performance electrochemical cells. In this study, state-of-the-art technology for controlling the microstructure of electrodes has been developed for realizing high performance support electrodes of solid oxide fuel cells (SOFCs). The key is controlling the porosity and pore size distribution to improve gas diffusion, while maintaining the integrity of the electrolyte and the structural strength of actual sized electrode supports needed for the target application. Planar anode-supported SOFCs developed in this study realize 5 μm thick dense electrolyte (yttria-stabilized zirconia: YSZ) and the anode substrate (Ni-YSZ) of 53.6 vol.% porosity with a large median pore diameter of 0.911 μm. Electrochemical measurements reveal that the performance of the anode-supported SOFCs improves with increasing anode porosity. This Ni-YSZ anode minimizes the concentration polarization, resulting in a maximum power density of 3.09 W cm^{-2} at 800 °C using humidified hydrogen fuel without any electrode functional layers.

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1. Introduction

Electrochemical ceramic cells such as solid oxide fuel cells (SOFCs) are expected to apply to next generation power devices due

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to their high energy conversion efficiency and fuel flexibility. For system minimization and cost reduction, high power density operation of SOFCs is needed, and thus improvement in single cell performance is essential. Planar anode-supported SOFCs are the most promising candidate type to achieve high power density because their ohmic resistance is very low due to thin electrolyte and short current pass in the electrodes [1–5]. Although the performance of planar anode-supported SOFCs is dominated by electrode polarization resistance with decreasing ohmic resistance, electrode performance is improved by using materials having high intrinsic catalytic activity [6–9] and also by using nano-size materials [10–15] to extend the electrochemically active area such as the triple-phase boundary (TPB), where electronic, ionic, and gas phases are in contact.

Electrode polarization resistance is mainly attributed to two processes, namely, interfacial reaction and gas diffusion. The resistances due to these processes are respectively called activation polarization resistance and the concentration polarization resistance. Although the dominant resistance in electrodes is generally due to activation polarization, concentration polarization often notably affects electrode performance when the electrode is relatively thick, such as in anode-supported SOFCs [2,16–20]. In particular, the concentration polarization resistance is crucial to maximize cell performance at high temperature operation (≥ 700 °C), in which the ohmic resistance of the electrolyte and the activation polarization resistance of the electrodes are significantly lowered although the concentration polarization resistance remains relatively constant or is slightly increased [2,16–23]. Concentration polarization, defined as the electrode polarization due to the difference in partial pressure of oxygen, p_{O_2}, between the anode surface and the anode/electrolyte interface, of porous electrodes is a theoretically inevitable phenomenon. Therefore, achieving high power density in planar anode-supported SOFCs requires developing an anode substrate that has good gas diffusion properties such as high porosity and large pore size and can enhance catalytic activity.

Although high porosity leads to lower concentration polarization, fabricating highly porous structured anodes with sufficient mechanical strength for use as actual sized substrate in SOFCs is difficult. Furthermore, to obtain the dense electrolyte and porous anode structure, the anode substrates must have the same sintering and shrinkage behaviors as the electrolyte because they undergo co-sintering with the electrolyte. Thus, the development of an electrode substrate fabrication process that can finely control porous microstructure is required. Extrusion is a conventionally used process to fabricate ceramic substrates for tubular [5,9,24], flat-tube [25], and honeycomb SOFCs [26]. Porous ceramic substrates that possess high porosity and mechanical strength can be obtained by the addition of pore former and the optimization of the extrusion process. Also, this process is attractive for industrial manufacturing because it can yield ceramic substrates even without organic solvent and with only a relatively small amount of binder compared with the other wet ceramic processes such as tape casting.

In the present study, we focus on the effect of the gas diffusion properties at nickel (Ni) and yttria-stabilized zirconia (YSZ) composite porous anodes on electrochemical performance in SOFCs, and report challenges to realize highly microstructure-controlled Ni-YSZ anodes with high porosity and uniform large pores. To achieve high porosity in the anodes while maintaining the mechanical strength that allows their use for actual size planar anode-supported SOFCs, we developed a microstructure control technique using the extrusion process. The porosity and pore size of extruded nickel oxide (NiO)-YSZ anode substrates were controlled by adding pore former and by adjusting the sintering temperature. The electrochemical performance of fabricated anode-supported SOFCs was

evaluated in the temperature range of 650–800 °C, and then the impact of the concentration polarization on cell performance in high power density operation was discussed.

2. Experimental

2.1. Fabrication of planar anode substrates by extrusion process

NiO powder (0.7 μm in median diameter, Sumitomo Metal Mining Co.) and YSZ powder (8 mol% Y_2O_3–ZrO_2, TZ-8YS, Tosoh) at a weight ratio of 60:40 were mixed with pore former and binder. The pore former was a mixture of graphite carbon (UF-G10, Showa Denko) and cellulose (TG-101, Asahi Kasei Chemicals) at a weight ratio of 2:1, and was added to the NiO-YSZ at three different composition ratios, namely, 11.3, 22.6, and 33.8 wt.% of the NiO and YSZ powders. These materials were stirred for 30 min in a vacuum chamber, and then after the addition of a proper amount of distilled water, the mixture was stirred again for 1 h. The mixture was then aged in ambient atmosphere for 15 h, yielding clay for extrusion. To produce NiO-YSZ green sheets (Fig. 1a), the clay was then extruded through a metal mold (0.7 mm thick, 65 mm wide) using a screw type extruder (Miyazaki Iron Works Co.). NiO-YSZ anode substrates were finally fabricated by cutting the green sheets into a desired size and then sintering them at 1250 °C for 1 h in air.

2.2. Fabrication of anode-supported SOFCs

A YSZ paste was prepared by mixing YSZ powder (TZ-8Y, Tosoh) in α-terpineol solvent (Kanto Chemical Co.) with ethyl cellulose 45 cp (Kishida Chemical Co.), a dispersant, and a plasticizer. The YSZ paste was screen-printed onto the prefabricated NiO-YSZ anode substrates. Then the anode substrates with YSZ were co-sintered at either 1350 or 1400 °C for 3 h in air. The $Ce_{0.9}Gd_{0.1}O_{1.95}$ (GDC) interlayer was prepared by screen-printing a GDC paste, made from GDC powder (40 m^2 g^{-1} in specific surface area, Anan Kasei Co.) and the same admixtures as in the YSZ paste, onto the YSZ electrolyte and sintering at 1300 °C for 1 h in air. Note that 0.3 mol% Mn was added to the GDC paste to improve the sinterability of GDC. The detailed fabrication procedure has been presented elsewhere [27]. Also, an $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF)-GDC paste for the cathode was prepared using LSCF powder (0.7 μm in median diameter, AGC Seimi Chemical Co.) and the same GDC powder as the interlayer material at a weight ratio of 70:30 with the same admixtures as in the YSZ paste, and then screen-printed on the GDC interlayer and sintered at 950 °C for 1 h in air. In electrochemical measurements, button cells with an effective cathode area of 0.283 cm^2 were used (Fig. 1b). Four different anode-supported SOFC samples were fabricated with different pore former content and sintering temperature of the anode substrates, namely, 11.3 wt.% pore former and sintered at 1400 °C (denoted as Cell-1), 11.3 wt.% pore former and sintered at 1350 °C (Cell-2), 22.6 wt.% pore former and sintered at 1350 °C (Cell-3), and 33.8 wt.% pore former and sintered at 1350 °C (Cell-4).

2.3. Characterization and electrochemical measurements

The microstructure of the fabricated samples was observed using scanning electron microscopy (SEM, JSM-5600, JEOL) and field emission scanning electron microscopy (FE-SEM, JSM-6330F, JEOL) after the electrochemical measurements. To estimate the relative density of the YSZ electrolyte and the GDC interlayer, SEM images were first converted into binary images where pore and material phases were separated, and then the discernible material phase area was numerically integrated. To prepare the Ni-YSZ substrate samples for the porosity and pore size distribution measurements,