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Degradation of nickel–yttria-stabilized zirconia anode in solid oxide fuel cells under changing temperature and humidity conditions

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HIGHLIGHTS

- Long-term stability was investigated at 1000–1200 °C under the OCV condition.
- The microstructural change in the Ni–YSZ anode was quantitatively analyzed.
- A mechanism of Ni aggregation under high humidity atmosphere was suggested.

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ABSTRACT

The performance degradation of Ni–yttria-stabilized zirconia (Ni–YSZ) cermet anode was measured by impedance spectroscopy at 1000–1200 °C and humidity atmospheres under the open circuit condition in SOFCs. More significant crack formation can be observed at 1200 °C under 40% H_2O–60% H_2 atmosphere. This crack formation gave rise to interruption of the ionic and electronic conduction path in the in-plane direction of anode layer, resulting in performance deterioration of anode. Focused ion beam-scanning electron microscopy (FIB–SEM) analyses were conducted for the anode layers, and then the 3D microstructures of Ni–YSZ anode were reconstructed. According to analysis of these data, the particle size of Ni was grown to the larger under higher temperature and humidity condition, accompanying with increase of isolated Ni-phase and the reduction of triple phase boundary (TPB) length.

1. Introduction

Solid oxide fuel cells (SOFCs) are one of the attractive power generation systems due to the low emission, high efficiency, and fuel flexibility at high temperatures [1,2]. The Ni–yttria-stabilized zirconia (Ni–YSZ) cermet is the most common material of anode. The electrochemical reaction between oxide ion, hydrogen, and electron only takes place at triple-phase boundaries (TPB) in Ni–YSZ anode [3–5]. Therefore, the anode is porous to allow the hydrogen to flow towards the electrolyte, and transport electron and oxide ions in the Ni and YSZ, respectively. The YSZ component serves to inhibit the sintering of the Ni particles and to provide a close thermal expansion coefficient for Ni–YSZ cermet to that of the YSZ electrolyte. Moreover, with mixing Ni and YSZ, the TPB length can extend efficiently to improve cell performance. However, the performance of the Ni–YSZ anode cermet sometimes degraded after long-term operation by supplying humid hydrogen [6–10].

Many studies have been devoted to clarify the degradation factors for Ni–YSZ anode during long-term operation. Simwonis et al. reported that the electrical conductivity of Ni–YSZ cermet decreased at 1000 °C during supply of 4% H_2–3% H_2O–93% Ar for 4000 h [9]. The size of YSZ particles shows no changes before and after treatments. On the other hand, the sintering behavior of Ni particles has been observed. Tanasini et al. have shown that the polarization resistance increased after operation at a constant current density of 0.6 A cm^{-2} at 850 °C for 1000 h with a supply of 97% H_2–3% H_2O, resulting from Ni coarsening [10]. One possible reason for the performance degradation was growth of Ni-particles size in association with a reduction of TPB length [10].

In addition, the sintering of Ni particles became apparent with increasing temperature and humidity [11–13]. The migration mechanism of Ni particles has been considered to proceed via (1) surface diffusion and/or (2) transportation in the gas phase. The

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surface diffusion is affected by temperature primarily. In the case of transportation in the gas phase especially under humidity atmospheres, according to thermodynamic data, Ni species i.e. $Ni(OH)_{2(g)}$ is more volatile than $Ni_{(g)}$ at 950 °C over *ca.* 20% H_2O concentration [12]. Additionally, it was shown that the equilibrium pressure of Ni-hydroxide complexes is more sensitive to the H_2O concentration [13]. Therefore, the coarsening of Ni particles due to increase of humidity may be associated with the partial pressure of Ni-hydroxide complexes. However, the quantitative relationship between the sintering of Ni particles and performance deterioration has not been elucidated sufficiently.

Recently, the quantitative measurements of SOFC electrode microstructure have been conducted with focused ion beam–scanning electron microscopy (FIB–SEM) [14–18]. In this study, the Ni–YSZ anode of cells were treated at 1100 °C and 1200 °C at open circuit condition for 50 h under highly humidified hydrogen atmospheres to accelerate the microstructural changes of cermet anode. After the heat treatments, samples were analyzed by FIB–SEM, and their microstructural change was quantified to clarify the degradation factors.

2. Experimental

The NiO–YSZ powder with a volumetric ratio of Ni:YSZ = 50:50 and a perovskite-type oxide of $(La_{0.8}Sr_{0.2})_{0.97}MnO_3$ (LSM) powder were used for the anode and cathode, respectively. The Ni–YSZ cermet was prepared from NiO (Wako Pure Chemical Industries) and YSZ powders (8 mol% Y_2O_3–ZrO_2, Tosoh). The mixture of NiO and YSZ was heat-treated at 1200 °C for 5 h. An LSM power was prepared from corresponding metal acetates, and calcined at 900 °C for 5 h. The resulting powder of each electrode material was mixed with polyethylene glycol (Wako Pure Chemical Industries) to form slurry. The NiO–YSZ cermet slurry was screen-printed on one face of the YSZ disk (Tosoh, thickness: 500 μm, diameter: 24 mm) at the center, followed by the calcination at 1400 °C for 5 h (anode thickness: *ca.* 40 μm). The cathode slurry was coated in the same way on the other face of the disk and subsequently heated at 1150 °C for 5 h. The fabricated cell was sandwiched by alumina tubes with Pyrex glass seals, as is shown in previous paper [19].

The change in anodic performance was investigated by holding under the open-circuit condition at 1000 °C, 1100 °C, and 1200 °C for 50 h. A gaseous mixture of 10% H_2O–90% H_2 or 40% H_2O–60% H_2 was supplied to the anode with a flow rate of 100 ml min^{-1}. During these operations, pure oxygen was fed to the cathode as an oxidant with a flow rate of 100 ml min^{-1}. The Cell Test system (Solarton Analytical, potentiostat/galvanostat 1470E and frequency response analyzer 1455A) was used for the electrochemical impedance measurement.

After the evaluation of cell performance, the structural change in Ni–YSZ anode was observed by a dual-beam focused ion beam-scanning electron microscope (FIB–SEM, Nvision 40, Carl Zeiss–SIINT) equipped with an energy dispersive X-ray spectrometer (EDX, Oxford). The sample was infiltrated with epoxy resin, and then the anode cross-section of SEM images (*x*–*y* plane as Fig. 1) was observed. Two dimensional SEM pictures were collected along the *z*-direction by milling-and-see operation [20]. The 3D microstructure of anode was reconstructed in a computational field (Fig. 1). The more detailed description of analysis using a FIB–SEM is reported by Iwai et al. [20]. In this study, the microstructural parameters were quantitatively analyzed; volume fraction, size distribution of particles, ratio of isolated-Ni phase, and triple phase boundary (TPB) length. The particle size distribution of each phase was evaluated by the line intercept method. The TPB length was calculated by the volume expansion method [20].

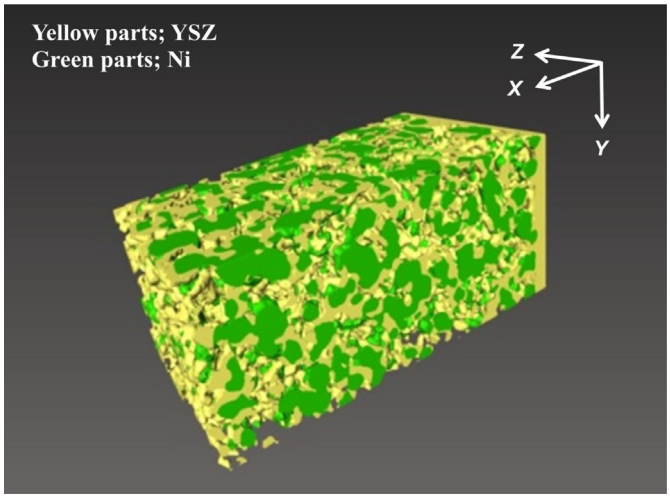

Fig. 1. 3D reconstructed Ni (green) and YSZ (yellow) phase in anode. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

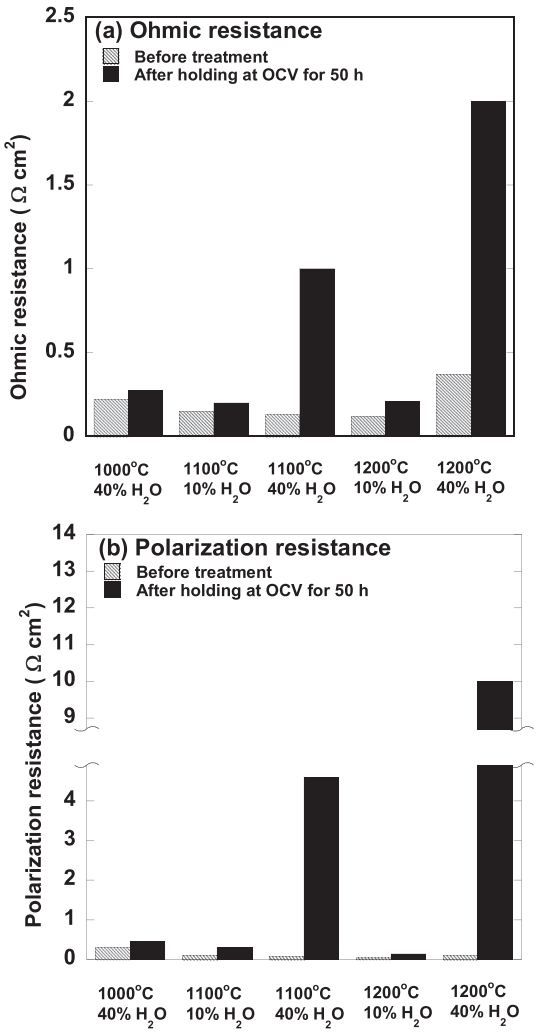

Fig. 2. (a) Ohmic and (b) polarization resistances of anode before and after holding under the OCV for 50 h at 1000 °C–1200 °C with a supply of 10% H_2O–90% H_2 and 40% H_2O–60% H_2.