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Morphology control of Ni–YSZ cermet anode for lower temperature operation of SOFCs

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Abstract

A NiO–Y_2O_3 stabilized ZrO_2 (YSZ) composite particles for solid oxide fuel cell (SOFC) anode was fabricated by advanced mechanical method in dry process. The processed powder achieved better homogeneity of NiO and YSZ particles, where submicron NiO particles were covered with finer YSZ particles. A Ni–YSZ cermet anode fabricated from the NiO–YSZ composite particles showed the porous structure in which Ni and YSZ grains of less than several hundred nano-meter as well as micron-size pores were uniformly dispersed. The cermet anode achieved high electrical performance at low temperature operation (<800 °C). It was led by larger electrochemical area successfully obtained by the excellent structure of the anode.

Keywords: Composite particle; Morphology control; SOFCs; Ni–YSZ cermet anode; Electric performance

1. Introduction

The solid oxide fuel cell (SOFC) has attracted a great attention as promising system of electrical power generation because of a high conversion efficiency of chemical energy to electric power. Recent SOFC development has been focused on lower temperature operation less than 800 °C. Such operation enables us to use low-cost metallic interconnects, long-term cell materials stability, and decrease the materials corrosion for plant components. However, it also increases both the ohmic loss at the solid-state electrolyte and the polarization loss at both electrodes. To reduce the ohmic loss of the electrolyte, two approaches have been conducted. One is to use a thin film of Y_2O_3 stabilized ZrO_2 (YSZ), and another is to apply new materials such as La(Sr)Ga(Mg)O_3 or CeO_2 based oxides for electrolytes, which have higher conductivity than that of YSZ. Furthermore, the trial to increase the electrochemical activity at both electrodes has been conducted to achieve lower temperature operation less than 800 °C.

A Ni–YSZ cermet has been usually used as an anode material for SOFC. In this case, the electrochemical activity of the cermet anode strongly depends on a three-phase boundary (TPB) composed of Ni grains, YSZ grains and pores. It increases with the increase of TPB length, because the electrochemical reaction occurs on the TPB in the anode [1–3]. Therefore, it is crucial to obtain better morphology including larger TPB composed of Ni and YSZ grains for the achievement of high-performance anode. In this paper, high quality Ni and YSZ composite particles are fabricated by novel process called Mechanofusion method [4,5]. This method is defined as the technique of creating particulate materials with high qualities by mechanochemical surface fusion [6–8]. Composite particles created by this technique are used to make high performance anode, which has larger TPB than existing anode. The effect of such mechanical processing on the morphology and performance of a Ni–YSZ cermet anode will be discussed.

2. Experimental

Nickel oxide (NiO, Nicoh Rica Corp, F type) and 8 mol% Y_2O_3 stabilized ZrO_2 (YSZ, Tosoh Co., TZ-8Y) were used as starting materials. NiO and YSZ powder were mechanically processed by the advanced mechanical method to make composite particles (Mechanofusion system [4,5], Model AM-20F, Hosokawa Micron Corp., Japan). This equipment was designed to produce composite particles using high

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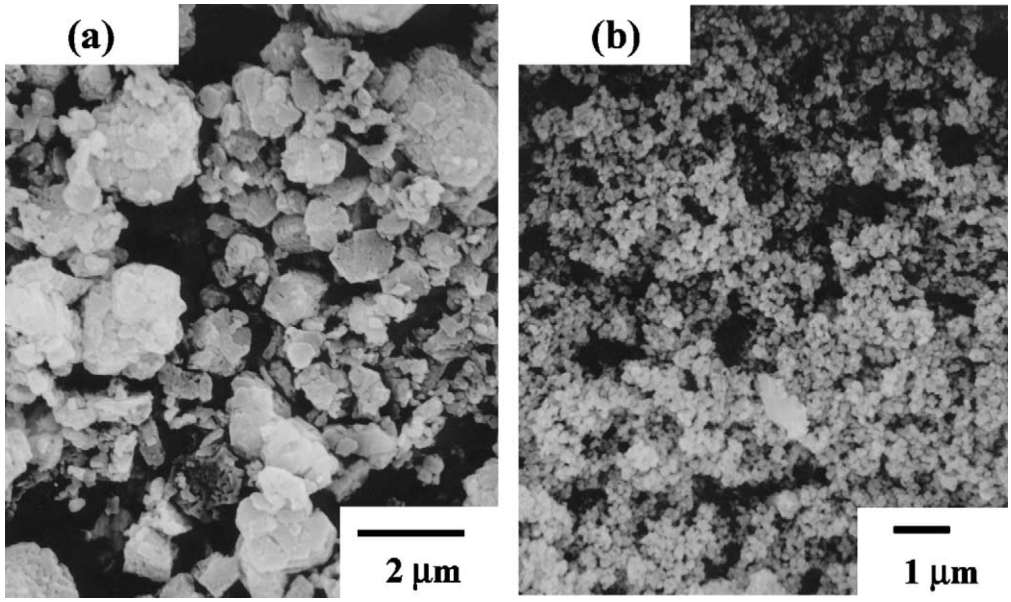

Fig. 1. SEM photographs of NiO (a) and YSZ (b) starting powders.

shear and compression force in dry process. It is originally composed of a rotating vessel, arm head and scraper. NiO and YSZ powders were put into the vessel, and processed in the gap between the vessel and the arm-head. Then, the processed powder bed was dispersed by the scraper, and the same operation was repeated with the rotation of the vessel. Rotation speed of the vessel was set at 2800 rpm, and operation time was set at 40 min. In this experiment, NiO and YSZ mass ratio was 65.2:34.8. Composite particles prepared by this operation were observed by a scanning electron microscopy (SEM, Model S-3500N, Hitachi Ltd., Japan) with an energy dispersive analysis of X-ray (EDAX, Model EX-200, HORIBA Ltd., Japan). Particle size distribution was measured by laser diffraction and scattering method (MICROTRAC, Model HRA9320-X100, NIKKISO Co. Ltd., Japan). The powder sample was dispersed in distilled water before particle size measurement.

Then, NiO–YSZ composite particles were mixed with organic binder. They were printed onto one side of YSZ electrolyte pellet of 13 mm in diameter and 0.2 mm in thickness. The printed body was fired at 1350 °C in air to produce the NiO–YSZ anode. After that, (La,Sr)MnO_3(LSM)–YSZ powder selected as a cathode material [9] was printed onto the other side of the YSZ electrolyte pellet, and the pellet was fired at 1200 °C. Pt wire was used as the reference electrode. The anode polarization and the internal resistance (IR) between the anode and the reference electrode were measured by the current interruption technique up to 1 A/cm^2 of current density. The single cell obtained by this experiment was operated in the conditions of H_2—3% H_2O for the anode and air for the cathode. The operation temperature was selected 800 and 700 °C, respectively. A NiO–YSZ anode was reduced in H_2—3% H_2O to make a Ni–YSZ cermet anode. The morphology of the Ni–YSZ cermet anode was observed by a SEM with EDAX after the cell test was finished.

3. Results

3.1. Morphology of NiO–YSZ composite particles

Fig. 1 shows SEM photographs of starting powders. Fig. 1(a) shows NiO, and Fig. 1(b) shows YSZ, respectively. Fig. 2 shows the particle size distribution of starting NiO powder measured by laser diffraction and scattering method. It shows that NiO powder has a broad and bimodal particle size distribution. On the other hand, YSZ powder is composed of fine particles of less than 1 μm as shown in Fig. 1(b). The BET surface area of YSZ

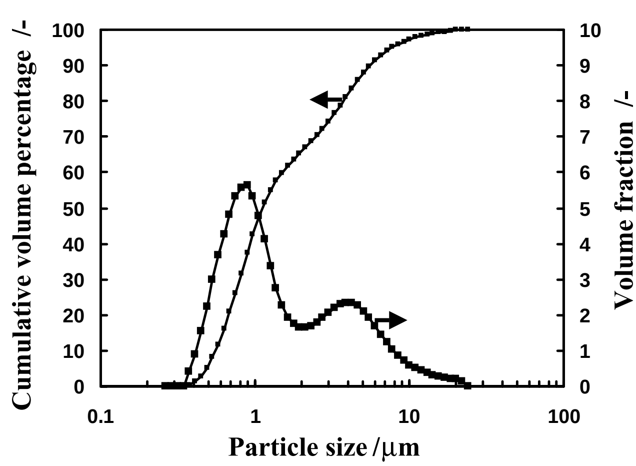

Fig. 2. Particles size distribution of NiO starting powder.

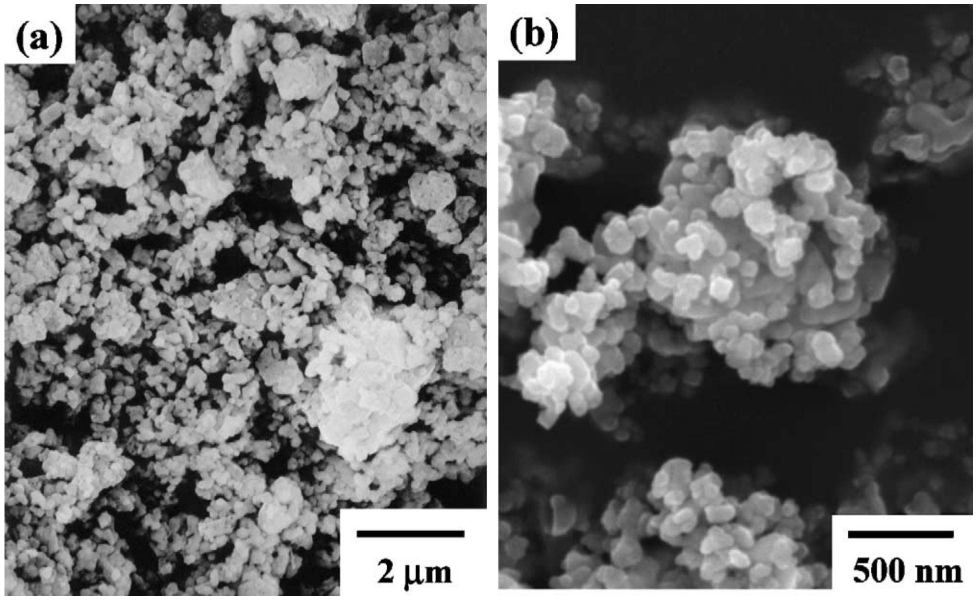

Fig. 3. SEM photographs of NiO–YSZ composite particles: (a) low magnification, (b) high magnification.

powder was measured 12 m^2/g. It corresponds to 0.1 μm when the BET surface area was calculated into the particle diameter.

Fig. 3 shows the SEM photographs of NiO–YSZ composite particles prepared by the mechanofusion system. Fig. 4 shows the size distribution of the composite particles. It is clear from Figs. 2 and 4 that NiO powder is ground to finer NiO particles. It is also obvious from Figs. 1(a) and 3(a) that NiO powder was ground finer particles. As a result of SEM–EDAX analysis in high magnification, it was observed that the ground NiO particles are partially covered with YSZ fine particles. Average sizes of the ground NiO particles and YSZ particles are about 600 and 100 nm in this figure, respectively. It shows that composite particles less than 1 μm are successfully fabricated by the advanced mechanical method using Mechanofusion system.

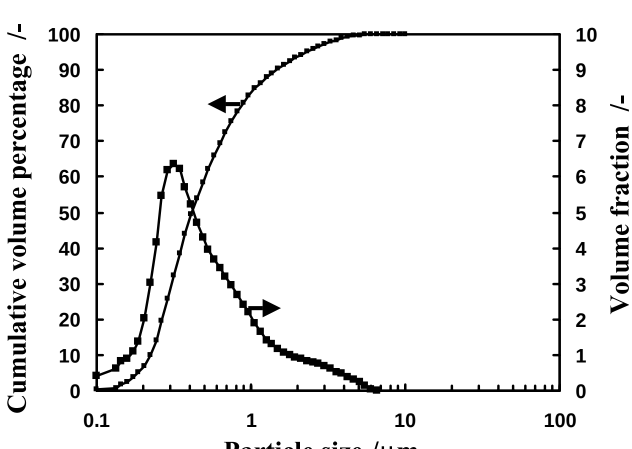

Fig. 4. Particles size distribution of NiO–YSZ composite particles.

3.2. Performance and morphology of Ni–YSZ cermet anode

Fig. 5 shows the anode polarization of a Ni–YSZ cermet anode at 700 and 800 °C of operation temperature, respectively. The electrochemical polarization of the cermet anode shows less than 0.2 V at high current density of 1 A/cm^2 and at operation of 800 °C. The IR drop obtained by the current interruption measurement was in almost agreement with the estimated IR drop by taking account of YSZ electrolyte thickness and its conductivity. This result shows that the electrical path of Ni grains works well in the anode. Excellent performance compared to other papers was obtained by the cermet anode. Table 1 summarized some anode

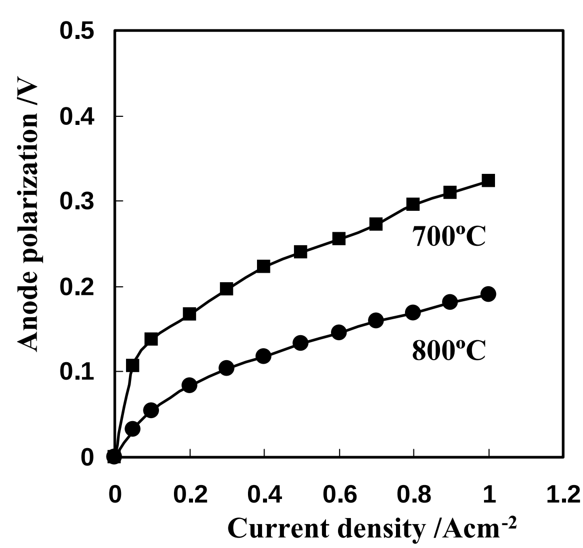

Fig. 5. Change of electrochemical polarization of Ni–YSZ cermet anodes with current density.

Table 1
Electrochemical polarization (V) of some cermet anodes

Current density (A/cm^2)	Ni–YSZ cermet anode			Ni–SDC cermet anode	
	This study (at 800 °C)	[10] (at 1000 °C)	[11] (at 1000 °C)	[13] (at 800 °C)	[14] (at 800 °C)
0.5	0.12	0.10	0.15	0.10	0.06
1.0	0.19	0.20	0.18	–	–

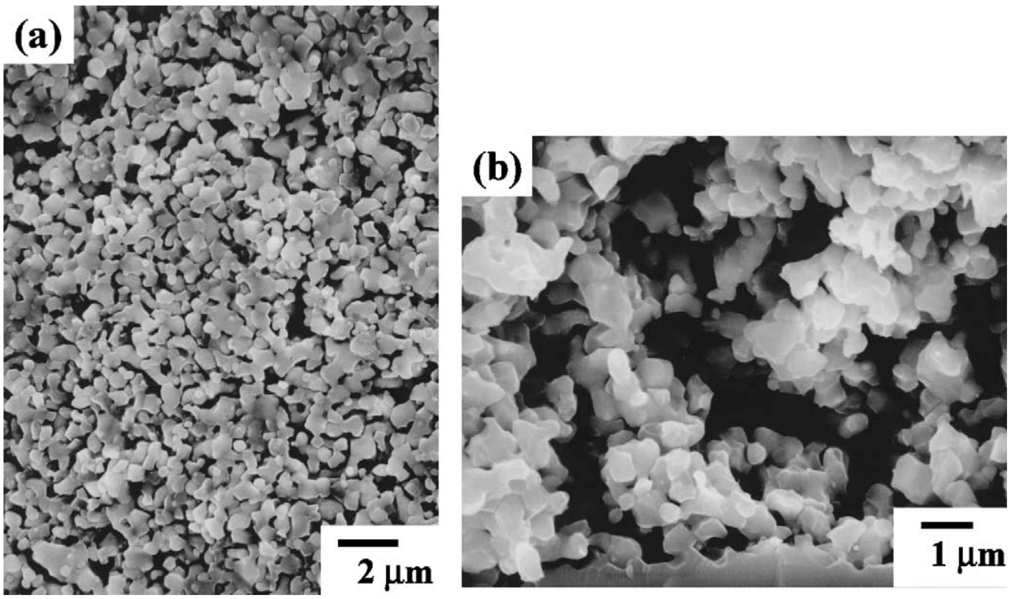

Fig. 6. SEM photographs of the surface and cross section of Ni–YSZ cermet anode.

performance data reported in other paper [10–14]. For example, this anode polarization obtained at 800 °C is almost similar to those of another studies [10–12] at higher temperature operation of 1000 °C. On the other hand, a Ni–SDC (Sm_2O_3 doped CeO_2) cermet anode has been developed as a promising anode for lower temperature operation. Various papers [13,14] reported that the electrochemical polarization of Ni–SDC cermet anodes ranges from 0.06 to 0.1 V at 0.5 A/cm^2 of the current density and at the operation of 800 °C. The performance of Ni–YSZ cermet anode in this paper almost reaches that of the Ni–SDC cermet anode as shown in Fig. 5.

Fig. 6 shows SEM photographs of the Ni–YSZ cermet anode after the cell test was finished. Fig. 6(a) shows a SEM photograph of its surface and Fig. 6(b) shows a photograph of its cross section. It is obvious from these SEM photographs that the cermet anode achieved successfully homogeneous porous structure, and consists of fine and highly-dispersed Ni and YSZ grains. It is confirmed from Fig. 6(b) that the size of grains in the cermet anode keeps less than 1 μm.

4. Discussion

To produce Ni–YSZ cermet anode, NiO–YSZ powder mixture has been generally used as starting material by conventional process including slurry method. In this case, the morphology of the resultant Ni–YSZ cermet anode strongly depends on the particle size and its shape of powder mixture. Therefore, finer NiO and YSZ particles are crucial to get higher performance anode. However, finer NiO particles in NiO–YSZ green body easily tend to grow into lager grain size during sintering process, because densification temperature of NiO is apparently lower than that of YSZ. Therefore, it is very difficult to achieve the anode morphology which has smaller size of grains.

In this study, the anode morphology consists of fine size of Ni and YSZ grains. The well-dispersed Ni and YSZ grains (Fig. 6) were fabricated by using novel NiO–YSZ composite particles as shown in Fig. 3. In this case, NiO was partially covered with fine YSZ particles (Fig. 3). Therefore, the grain-growth of NiO was prevented during its sintering process. As a result, very fine Ni and YSZ grains were successfully created. Moreover, grains in the cermet anode less than 1 μm are observed from Fig. 6. To achieve such structure, NiO and YSZ have to form composite particles which satisfy nano-size scale of dispersion. As a result, the resultant Ni–YSZ cermet anode increases the TPB length drastically in the anode. The drastic increase of TPB length may be attributed to the nano-scale structure of Ni and YSZ. It leads to the excellent performance at lower temperature operation ($<$800 °C) of a Ni–YSZ cermet anode. It is difficult to observe such nano-scale structure fabricated by this experiment. More detail observation of the composite particles and anode in nano-scale size should be needed in future.

5. Conclusions

A NiO–YSZ composite particle for SOFC anode was fabricated from commercialized NiO and YSZ powder by advanced mechanical method called Mechanofusion. The composite particles achieved better homogeneity of NiO and YSZ particles, where submicron NiO particles were covered with fine YSZ particles.

A Ni–YSZ cermet anode was fabricated from the NiO–YSZ composite particles. At lower temperature operation ($<800\,^{\circ}C$), the Ni–YSZ cermet anode achieved lower values of the electrochemical polarization than those reported other papers.

The Ni–YSZ cermet anode showed more homogeneous porous structure which had fine YSZ grains, fine Ni grains and micron-size pores. Highly-dispersed fine grains in the cermet anode contributed to the increase of TPB length (electrochemical reaction area), thus led to the excellent performance of the anode.

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