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Journal of the European Ceramic Society 23 (2003) 2963–2967

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Performance and stability of SOFC anode fabricated from NiO/YSZ composite particles

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Abstract

NiO/YSZ composite particles with 20–35 mol% Y_2O_3 stabilized ZrO_2 (YSZ) were synthesized by the spray pyrolysis (SP) method. The NiO/YSZ composite particles showed morphology of NiO grains partially or fully covered with fine YSZ grains. The composite particles also had good interface connection between nickel oxide and yttria stabilized zirconia (YSZ). The morphology of the Ni/YSZ cermet anode fabricated from composite particles is noticeably influenced by the YSZ content of the composite particles. Ni/YSZ cermet anodes with 25 mol% YSZ show the highest electrochemical activity and lowest internal resistance (IR). The electrochemical activity and IR of the anode in solid oxide fuel cells (SOFCs) highly depend on the three-phase boundary structure based on the metal (Ni) and ceramic (YSZ) interface as well as the network structure of each Ni grains. Moreover, the cell voltage of a single cell with the Ni/YSZ cermet anode kept almost constant value during 7200 h of operation. Consequently, it is concluded that the performance and stability of the Ni/YSZ cermet anode is improved by controlling the morphology of the NiO/YSZ composite particles.

Keywords: Composite particle; Electrical properties; Fuel cells; Ni-YSZ; Spray pyrolysis

1. Introduction

Solid oxide fuel cells (SOFCs) have been attracting great attention as a promising new technology for electrical power generation.[1] In the SOFCs, Nickel (Ni) and Y_2O_3 stabilized ZrO_2 (YSZ) cermet is widely used as an anode material because of its high catalytic property and low cost.[1] The Ni/YSZ cermet anode has two important functions. One of the features is to suppress sintering of Ni grains during high temperature operation of SOFCs (stability of its structure is needed at high temperature of 1000 °C). Electrochemical activity is the second important feature of the Ni/YSZ cermet anode. In general, fuel gas is electrochemically oxidized at the nickel/electrolyte/fuel gas interface, at what is called a three-phase boundary (TPB) region, and the electrochemical activity of the cermet anode highly depends on the length of TPB region.[2–4] Therefore, both the stability and activity of Ni/YSZ cermet anodes are strongly influenced by the morphology formed from metal (Ni) and ceramic (YSZ) interface. For practical use of SOFCs, it is essential to improve the stability, reliability and activity of the Ni/YSZ cermet anode.

The authors have already reported that the stability of a Ni/YSZ cermet anode is improved at high temperature (1000 °C) operation of SOFCs by means of controlling its morphology using NiO/YSZ composite particles.[5] These particles are composed of NiO grains covered with fine YSZ grains and are prepared by spray pyrolysis (SP). The morphology of the anode fabricated from the composite particles, which was consisted of a Ni grain network surrounded with fine YSZ grains, achieved stable long-term SOFC operation, because the YSZ grains on the Ni network successfully prevented the grain growth of Ni at high temperature. However, it is not enough to examine the electrochemical activity of the Ni/YSZ cermet anode.

In general, the electrochemical activity increases with increasing the length of TPB region. The TPB region of the cermet anode is essentially influenced by the Ni and YSZ ratio, and the resultant morphology such as the grain size, connection of each grains, and the porosity.

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0955-2219/03/$ - see front matter
doi:10.1016/S0955-2219(03)00311-X

Therefore, the ratio of Ni and YSZ as well as the morphology of the starting powders are important factors to control the morphology of anode resulting in a high-activity anode for SOFCs.

The aim of this paper is to produce a high-activity and stable cermet anode by making use of NiO/YSZ composite particles. The morphology of the anodes fabricated from the composite particles is analyzed, and the electrical performance and stability of the anodes is examined. Then, both relationships will be discussed based on these results.

2. Experimental

Spray pyrolysis (SP) was used to prepare NiO/YSZ composite particles because it is one of the promising techniques to control the morphology and composition of particles.[6,7] The composite particles were prepared from YSZ sol (8 mol% Y_2O_3 stabilized ZrO_2 sol, average particle size: 60 nm, Nissan Chemical Product Ltd.) and $Ni(CH_3COO)_2.4H_2O$ solution by SP method. SP system employed in this study was similar to that used previously by the authors.[7] The synthesis conditions of the composite particles are also described elsewhere.[7] $Ni(CH_3COO)_2.4H_2O$ was dissolved in a dilute water and YSZ sol was added to the solution. The concentration of starting solution ($Ni(CH_3COO)_2$ and YSZ) was 0.25 mol/l and the initial ratios of Ni and YSZ was set at 80:20, 75:25, 70:30 and 65:35 (mol%).

The NiO/YSZ composite particles were mixed with organic binder. They were printed onto one side of a 8 mol% Y_2O_3 stabilized ZrO_2 (8YSZ) electrolyte pellet of 13 mm in diameter, and then, it was fired at 1350 °C in air to produce the NiO/YSZ anode for SOFCs. The electrode area was 0.282 cm^2. After that, (La,Sr)-MnO_3(LSM)–YSZ powder, which was selected as a cathode material, was printed onto the other side of the YSZ electrolyte pellet, and it was fired at 1200 °C. Pt wire was used as the reference electrode. For measuring the anode polarization as the electrochemical activity, and the internal resistance (IR) between the anode and the reference electrode of the Ni/YSZ cermet anode, the current interruption technique was applied. The SOFC operated in the conditions of H_2–3%H_2O for the anode and air for the cathode at 1000 °C. In the first stage of the cell test, NiO/YSZ anode sintered at 1350 °C was reduced in H_2–3%H_2O to make Ni/YSZ cermet anode. The morphology of the composite particles synthesized by SP and that of the resultant Ni/YSZ cermet anode were analyzed by a scanning electron microscopy (SEM, Hitachi, S-800) with an energy dispersive analysis of X-ray (EDAX, Philips, PV9900). Moreover, the composite particles were embedded into the epoxy resin and then cut ultra sections (thickness: about 70–80 nm) by Microtome (LKB, LKB-4800). Internal microstructure of the composite particles was analyzed by a transmission electron microscopy (TEM, Jeol, JEM2000EX) using the ultra sections.

Moreover, a single cell with Ni–YSZ cermet anode of 2 cm^2 electrode area was sintered at 1350 °C and fabricated by the above-mentioned method. In this test, 10 mol% Y_2O_3 stabilized ZrO_2 (10YSZ) was used as an electrolyte because ionic conductivity of 8YSZ decreased markedly with long-term operation.[8,9] The cell was operated at 1000 °C and a current density of 300 mA/cm^2 in the conditions of H_2–3%H_2O and air. The cell voltage and anode polarization were measured during 7200 h.

3. Results and discussion

3.1. NiO/YSZ composite particle

Fig. 1 shows SEM photographs of NiO/YSZ composite particles synthesized by SP. The powder synthesized by SP is relatively spherical and, its average particle size is observed about 1 μm in each case. It was also confirmed from SEM–EDAX observation that a composite particle

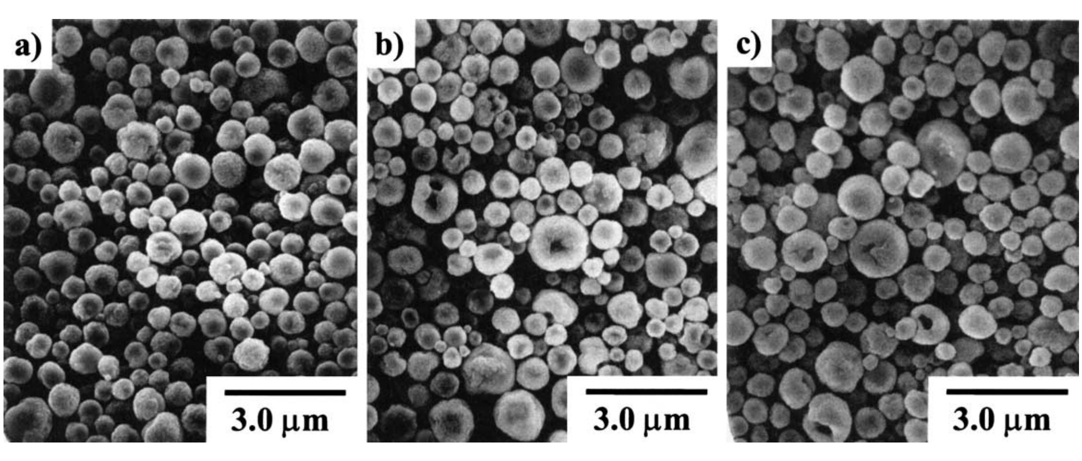

Fig. 1. SEM photographs of NiO–YSZ composite particles with (a) 20 mol%, (b) 25 mol%, (c) 30 mol% of YSZ content prepared by spray pyrolysis.

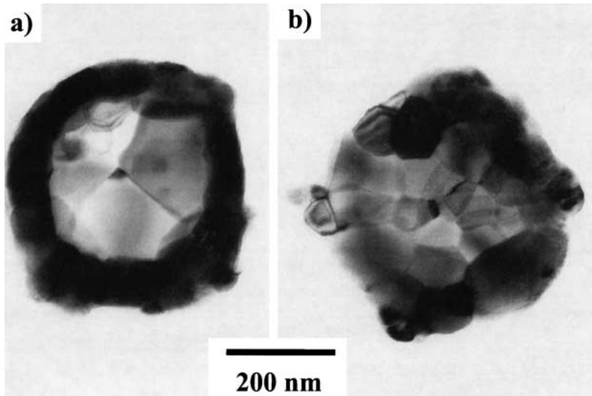

Fig. 2. TEM photographs of ultra cross section of NiO–YSZ composite particles with 25 mol%.

was formed by Ni, Y and Zr elements. Surface of the NiO/YSZ composite particle with 20 mol% of YSZ content is partially covered with fine particles [Fig. 1(a)]. Fine particles on the surface of composite particles increases with YSZ content and, the surface of the particles is fully and uniformly covered with fine particles in 30 mol% of YSZ content. Fig. 2 shows TEM photographs of ultra cross section of the composite particles with 25 mol% YSZ content. Internal structure of the composite particles can be observed in this figure. It is confirmed from Fig. 2 that the NiO/YSZ composite particle is composed of two kinds of grains (dark and black parts). TEM–EDAX analysis also showed that the black part was YSZ grains and the dark part was NiO grains. Therefore, a composite particle in Fig. 2(a) consists of NiO grains fully covered with fine YSZ grains. A particle in Fig. 2(b) consists of NiO grains partially covered with fine YSZ grains. It is thought that the composite particles have good interfacial connection between ceramic NiO and YSZ.

3.2. Morphology of Ni/YSZ cermet anodes

Fig. 3 shows SEM photographs of Ni/YSZ cermet anodes fabricated from NiO/YSZ composite particles with 20, 25 and 30 mol% of YSZ content and reduced in H_2–3%H_2O, respectively. It is clear from Fig. 3 that the morphology of Ni/YSZ cermet anodes changes with increasing YSZ content. In Fig. 3(a) (20 mol% YSZ content), it is confirmed by SEM–EDAX that YSZ grains are observed as fine ones and Ni grains as coarse ones, and fine YSZ grains surround the coarse Ni grains. In Fig. 3(b), relatively spherical grains are observed as Ni and fine grains as YSZ and, the size of Ni grains decreases with increasing YSZ content. The morphology of Ni/YSZ cermet anodes with 25 mol% YSZ also consists of Ni grains surrounded by fine YSZ grains. On the other hand, Fig. 3(c) shows that YSZ grains grow in the cermet, and that the size of them is almost the same as that of Ni grains.

Fig. 3 shows that the morphology of the Ni/YSZ cermet anode is influenced by the morphology and NiO/YSZ ratio of the composite particles in the starting material. When the composite particles are partially covered with fine YSZ particles [Fig. 1(a)], Ni grains in a cermet anode grow three-times bigger than size of initial composite particle and, the resultant cermet anode shows an inhomogeneous structure. On the other hand, when the YSZ ratio in a composite particle increases (NiO/YSZ = 75/25 mol%) and the particles are almost uniformly covered with fine YSZ particles [Fig. 1(b)], the resultant cermet anode shows a homogenous morphology which forms fine YSZ grains uniformly dispersed on Ni grains [Fig. 3(b)]. In the Ni/YSZ cermet anode, the Ni and YSZ volume ratio is almost 50:50. Therefore, it is thought that the morphology of an anode fabricated from the composite particles partially covered with fine YSZ particles is relatively inhomogeneous in comparison with the anode fabricated

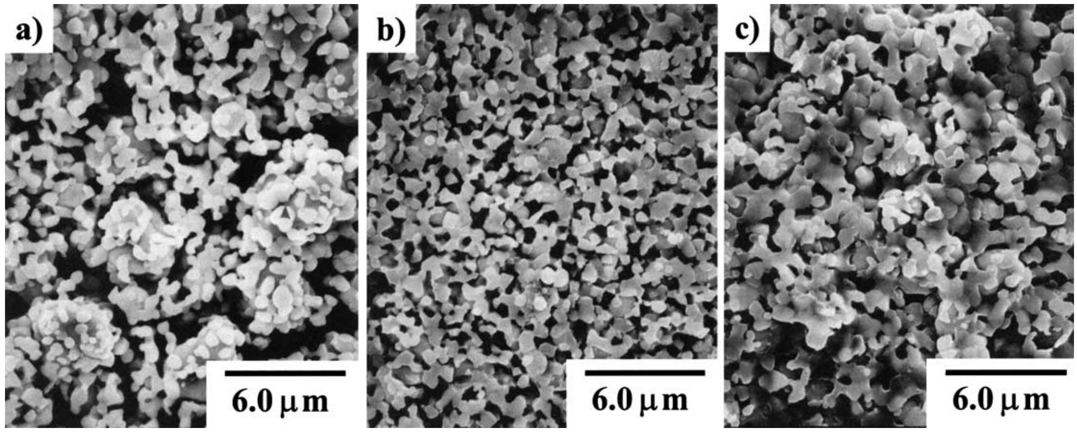

Fig. 3. SEM photographs of Ni/YSZ cermet anodes with (a) 20 mol%, (b) 25 mol%, (c) 30 mol% of YSZ content fabricated from the NiO–YSZ composite particles.

from the composite particles uniformly covered with fine YSZ particles. Moreover, a cermet anode fabricated from composite particles with excessive YSZ particle content develops an inhomogeneous morphology by means of YSZ grain-growth.

3.3. Performance of Ni/YSZ cermet anodes

Fig. 4 shows the anode polarization and IR which were measured by the current interrupter method at a current density of 500 mA/cm^2. The anode polarization changes with YSZ content in the cermet anode. It shows a minimum value at 25 mol% YSZ content, and then the anode polarization increases with increasing YSZ content. In other words, the electrochemical activity of the cermet anode shows the maximum value at 25 mol% of YSZ content. In this case, the electrochemical activity of the Ni/YSZ cermet anode was higher than that of conventional cermet anodes.[2,4,10,11] On the other hand, the IR of the cermet anode indicates an almost constant value between 25 and 30 mol% YSZ content, and then increases over 30 mol% and less than 25 mol%.

Generally, the electrochemical activity of an anode in SOFCs strongly depends on the length of three-phase boundary created among Ni grains, YSZ grains and pores.[2–4] In this study, Ni/YSZ cermet anodes with 25 mol% YSZ show the highest electrochemical activity. This is probably caused by the homogeneous morphology of Ni/YSZ cermet anode, which composes of fine YSZ grains uniformly dispersed on the Ni grains, which may increase the length of three-phase boundary based on metal (Ni) and ceramic (YSZ) interface. On the other hand, the IR of an anode in SOFCs also depends on the network structure of Ni grains in the anode, because current flows through Ni grains network. In this case, it is thought that increase of IR on the cermet anodes less than 25 and over 30 mol% of YSZ content is caused by

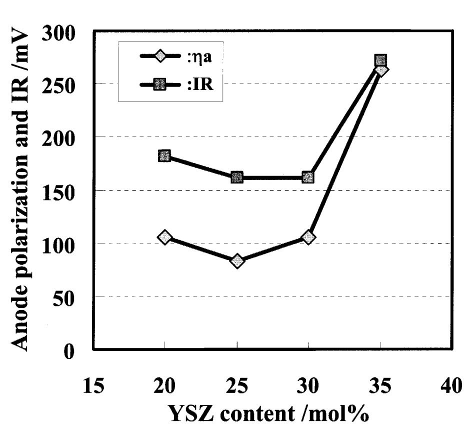

Fig. 4. Anode polarization (η_a) and IR of Ni/YSZ cermet anodes as a function of YSZ content at 1000 °C of SOFC operation temperature and 500 mA/cm^2 of the current density.

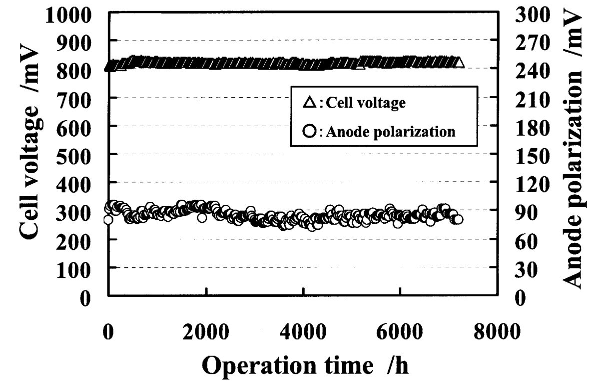

Fig. 5. Cell voltage and anode polarization of a single SOFC with Ni–YSZ cermet anode as a function of operation time.

partially cut of the Ni grain network path by means of Ni and YSZ grain-growth, respectively.

3.4. Long-term stability of the Ni/YSZ cermet anode

Fig. 5 shows a cell voltage of a single cell with Ni/YSZ cermet anode of 25 mol% YSZ content during 7200 h of high temperature (1000 °C) operation. Time dependence of anode polarization for the Ni/YSZ cermet anode is also shown in Fig. 5. It is clear from this figure that the cell voltage as well as the anode polarization is almost constant for 7200 h. The Ni–YSZ cermet anode with 25 mol% YSZ shows superior stability at high temperature SOFC operation. It is thought that this superior stability also depends on the morphology in which fine YSZ grains are uniformly dispersed on the surface of Ni grain network [see Fig. 3(b)]. Generally, Ni grains easily tend to sinter at high temperature such as 1000 °C. In this case, fine YSZ grains on the surface of Ni grains in the cermet anode prevented the sintering of Ni grains during this high temperature operation.

We have demonstrated improvement of anode polarization and stability for SOFC cermet anodes by controlling the interface structure between metal and ceramic. This also suggests that the use of composite particles is an excellent way to control the morphology of ceramic and cermet materials.

4. Conclusion

NiO/YSZ composite particles with various YSZ content were synthesized by spray pyrolysis and, Ni/YSZ cermet anodes were fabricated from the composite particles. The NiO/YSZ composite particles showed a morphology in which NiO grains are partially or fully covered with fine YSZ grains. The composite particles also had good interface connection between ceramic NiO and YSZ. Morphology and electrical performance of the Ni/YSZ cermet anode were highly influenced by the NiO/YSZ ratio of the composite particles. A Ni/YSZ cermet anode with 25 mol% YSZ content showed the highest electrochemical activity as well as the lowest IR. Moreover, the cell voltage as well as anode polarization of a single cell with the Ni–YSZ cermet anode kept very stable during 7200 h of high temperature (1000 °C) operation. The Ni–YSZ cermet anode also had the superior stability of electrical performance at high temperature condition. Therefore, it is found that the Ni–YSZ cermet anode fabricated from the composite particles is very promising for practical use of SOFCs.

Acknowledgements

This work has been carried out as a part of NEDO International Joint Research Grant supervised by the Ministry of Economy, Trade and Industry of Japan.

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