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

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Abstract

Ni–YSZ cermet anodes for solid oxide fuel cells (SOFCs) were fabricated at various sintering temperatures from NiO–YSZ composite particles made by spray pyrolysis (SP) technique. NiO particles covered with fine YSZ (Y_2O_3 stabilized ZrO_2) particles were used as the composite particles, and the initial ratio of Ni and YSZ was set at 75:25 (mol%). As a result, the cermet anode sintered at 1350 °C showed the morphology in which fine YSZ grains were uniformly dispersed on the surface of Ni grain network. Electrical performance such as electrochemical activity and internal resistance of a Ni–YSZ cermet anode changed with sintering temperature. The anode fabricated at 1350 °C showed the highest electrical performance. Especially, a single cell voltage with the Ni–YSZ cermet anode kept very stable for 8000 h at 1000 °C in the SOFC operation condition of H_2—3% H_2O and air. The cermet anode after a long-term test had its initial morphology. It indicates that the Ni–YSZ cermet anode fabricated from NiO–YSZ composite particles is a very promising material for its practical use as SOFCs. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Composite particle; Spray pyrolysis; SOFCs; Ni–YSZ cermet anode; Long-term stability

1. Introduction

Solid oxide fuel cell (SOFC) has attracted a great attention as a promising technique for electrical power generation. SOFCs can provide high efficiency when they are used in a gas turbine combined system because their high operation temperature, 1000 °C, gives the advantage of producing high temperature discharge gases [1]. They also promise little NO_x and SO_x emission [1]. It is essential to achieve not only higher performance but also longer-term stability at high temperature for their practical use, because SOFCs must be operated for long-term over 10,000 h in a practical use. The performances as electric efficiency and stability of SOFCs highly depend on the morphology and the chemical composition of a basic unit cell consisted of three layers of an anode, a cathode and an electrolyte. Especially, the sintering of Ni grains in Ni–YSZ (Y_2O_3 stabilized ZrO_2) cermet, which is a promising anode of SOFCs, is a serious problem in a long-term operation, because Ni grains in the cermet anode tend to sinter easily at high temperatures, which results in the degradation of SOFC performance [1,2].

In our previous study, we have proposed a new anode structure in which a few amount of fine YSZ grains are dispersed on the surface of Ni grains in order to improve the stability of a Ni–YSZ cermet anode. At the first step, we have demonstrated an excellent 5500 h stability of the anode [3]. The new anode structure was made by means of using the ceramic–ceramic composite particles, which consisted of NiO grains covered with fine YSZ grains, prepared by spray pyrolysis (SP) technique. However, longer-term operation as well as higher electrochemical activity of the Ni–YSZ cermet anode are crucial for its practical use. Especially the electrochemical activity of an anode strongly depends on a three-phase boundary (TPB) created among Ni grains, YSZ grains and pore, and it increases with increasing TPB length, because electrochemical reaction occurs on TPB in the anode [1,4,5]. The TPB structure of the anode changes with the morphology of composite particles as the starting powder and its fabrication conditions such as sintering temperature. Therefore, better control of the fabrication conditions will lead to improve an anode performance. The aim of this paper is to achieve higher performance and longer-term stability of the cermet anode made from the composite particles. In this paper, the relationships between anode performance and their morphology are discussed. At the first step, the morphology was changed with sintering

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temperature. Moreover, test results of a single cell operated for about a year are discussed.

2. Experimental

SP was used to prepare NiO–YSZ composite particles. 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 $Ni(CH_3COO)_2 \cdot 4H_2O$ solution. The concentration of the starting solution ($Ni(CH_3COO)_2$ and YSZ) was 0.25 mol/l and the initial ratio of Ni and YSZ was set at 75:25 (mol%) in this experiment. SP system employed in this study and the synthesis conditions of the composite particles are similar to those used previously by the authors, and described elsewhere [3,6]. The NiO–YSZ composite particles were mixed with organic binder. They were printed onto one side of YSZ (8 mol% Y_2O_3 stabilized ZrO_2) electrolyte pellet of 13 mm in diameter. Then, it was fired at 1200, 1300, 1350, 1400 and 1500 °C in air to produce the various NiO–YSZ anodes for SOFCs. 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 pellets, and they were fired at 1200 °C. Pt wire was used as the reference electrode. For measuring the anode polarization and the internal resistance (IR) between the anode and the reference electrode, the current interruption technique was applied. Various single cells obtained by this experiment were 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 anodes were reduced in H_2—3% H_2O to make Ni–YSZ cermet anodes. The morphology of the composite particles synthesized by SP and that of the resultant Ni–YSZ cermet anodes were analyzed by a scanning electron microscopy (SEM, Hitachi, S-800) with energy dispersire analysis of X-ray (EDAX, Philips, PV9900). Moreover, a single cell with Ni–YSZ cermet anode of 2 cm^2 electrode area was sintered at 1350 °C and fabricated by the earlier-mentioned method. In this test, 10YSZ (10 mol% Y_2O_3 stabilized ZrO_2) was used as an electrolyte because ionic conductivity of 8YSZ (8 mol% Y_2O_3 stabilized ZrO_2) decreased markedly with long-term operation [7,8]. 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, anode polarization and cathode polarization were measured during 1 year operation. After the cell test, the anode morphology was observed by SEM.

3. Results

3.1. Morphology of Ni–YSZ cermet anodes

Fig. 1 shows a SEM photograph of NiO–YSZ composite particles prepared by SP. The particles are relatively
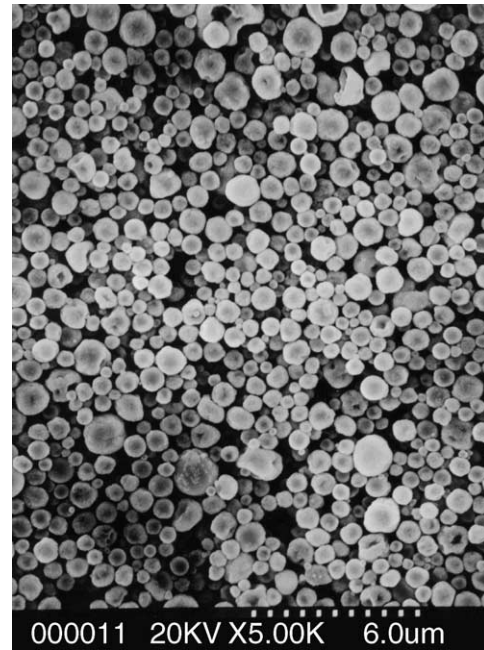

Fig. 1. SEM photograph of NiO–YSZ composite particles prepared by spray pyrolysis.

spherical, and the particle size distribution is fairly narrow with average particle size of about 1 μm. Fig. 2 shows the SEM photographs of Ni–YSZ cermet anodes fired at 1200, 1300, 1350 and 1400 °C and reduced in H_2—3% H_2O. It is clear from Fig. 2 that the morphology of Ni–YSZ cermet anode is changed with sintering temperature. Fig. 2(a) shows that a Ni–YSZ cermet anode fabricated at 1200 °C has morphology in which relatively spherical composite particles are partly and weakly connected. A new anode structure in which fine grains are dispersed on the surface of coarse grains is formed over 1300 °C of the sintering temperature (see Fig. 2(b) and (c)). Also, Ni and Zr elemental analysis in our previous paper [3] already revealed that spherical coarse grains and fine grains in these anodes are Ni and YSZ, respectively. Moreover, Ni grains and YSZ grains grow in a cermet anode fabricated at 1400 °C, and then the size of YSZ grains is almost the same as that of Ni grains (see Fig. 2(d)). Fig. 3 shows a SEM photograph of the cross-section of a Ni–YSZ cermet anode fabricated at 1350 °C. It is clear from Fig. 3 that the internal morphology of this anode consists of Ni grain network surrounded by fine YSZ grains. Such structure is almost similar to the surface morphology. It is also observed from this figure that the Ni–YSZ cermet anode connects sufficiently to an electrolyte.

3.2. Performance of Ni–YSZ cermet anodes

Fig. 4 shows the anode polarization and the IR, which were measured by current interrupter method at 300 mA/cm^2 of current density. Anode polarization changes with
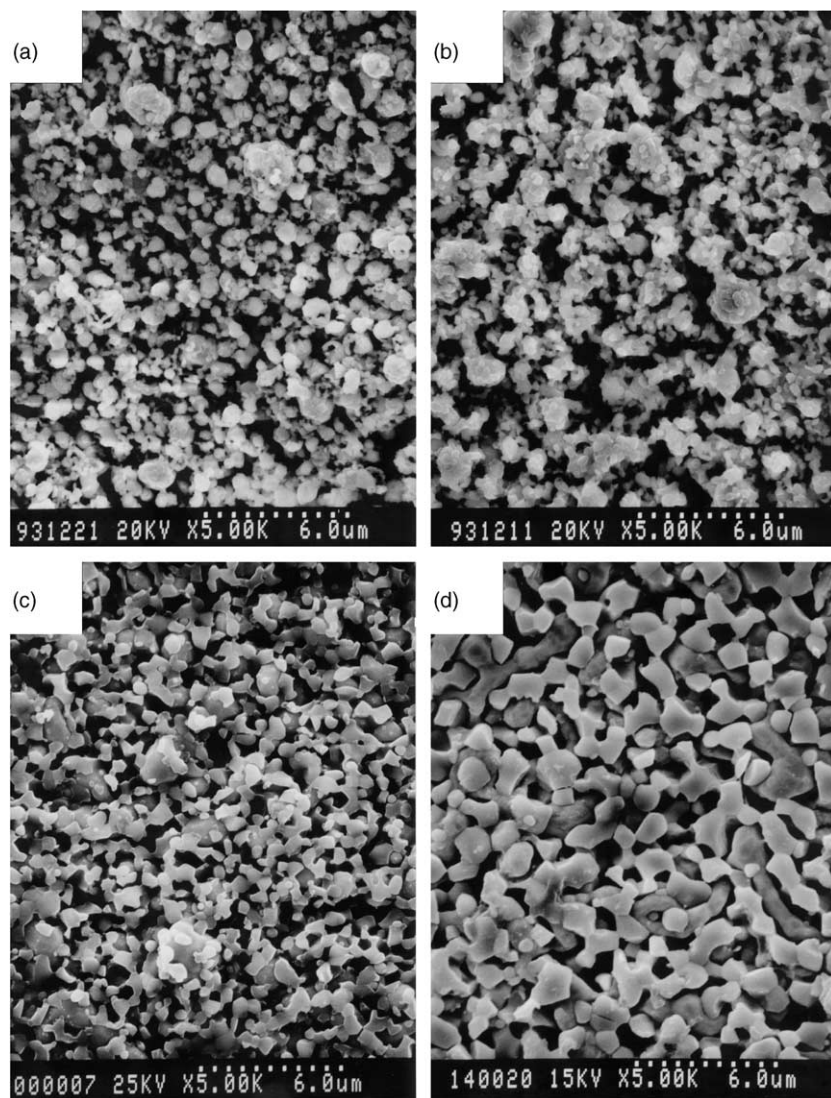
Fig. 2. SEM photographs of Ni–YSZ cermet anodes fabricated at various sintering temperature of (a) 1200 °C, (b) 1300 °C, (c) 1350 °C, and (d) 1400 °C from NiO–YSZ composite particles.

the sintering temperature of a NiO–YSZ anode. The minimum value exists at the sintering temperature of 1350 °C, and then the anode polarization slightly increases with sintering temperature (see Fig. 4(a)). In other words, the electrochemical activity of the cermet anode shows the maximum value at 1350 °C of the sintering temperature. Moreover, the electrochemical activity was better than that of conventional cermet anodes reported in previous studies [4,9–11]. On the other hand, IR of the cermet anodes decreases rapidly up to 1300 °C of sintering temperature, and indicates almost constant value from 1350 up to 1500 °C (see Fig. 4(b)).

3.3. Long-term operation test

Fig. 5 shows the cell voltage of a single cell with a Ni–YSZ cermet anode fabricated at 1350 °C for about a year. It is clear from this figure that this cell voltage keeps almost constant value for 8000 h. It just shows that the single cell has a superior long-term stability in the conditions of H_2—3% H_2O and air at 1000 °C. We also confirmed that both anode and cathode polarization were constant by the current interruption measurement. The anode performance was a bit low in comparison with that showed in Fig. 4 because the conductivity of 10YSZ electrolyte used in this long-term experiment was lower than that of 8YSZ electrolyte. Watanabe et al. [12] reported the anode polarization decreased with increasing ionic conductivity of the zirconia electrolyte. The morphology of the Ni–YSZ cermet anode after operation of 8000 h about 1 year is shown in Fig. 6. It is obvious from this figure and Fig. 2(c) that the cermet anode completely keeps its initial morphology in which fine YSZ grains are uniformly dispersed on the surface of Ni grain network.
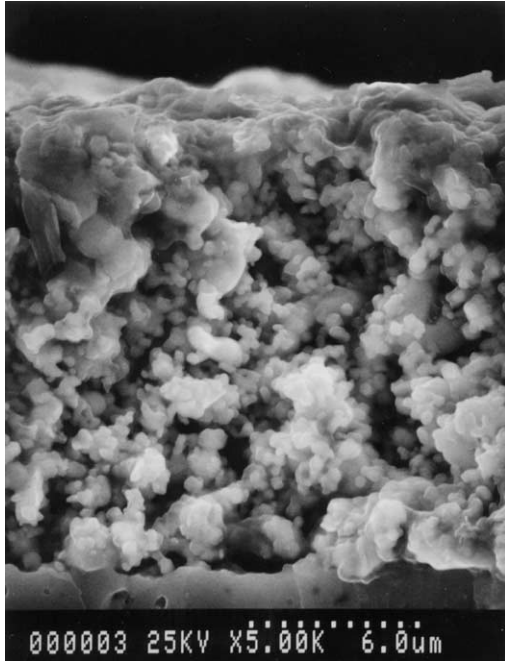
Fig. 3. SEM photograph of the cross-section of Ni–YSZ cermet anode fabricated at 1350 °C.

4. Discussion

Electrical performance of a Ni–YSZ cermet anode is highly influenced by its morphology such as TPB length and Ni grain connection [1,4,5]. Increasing the TPB length and creating good Ni connection in the cermet anode are
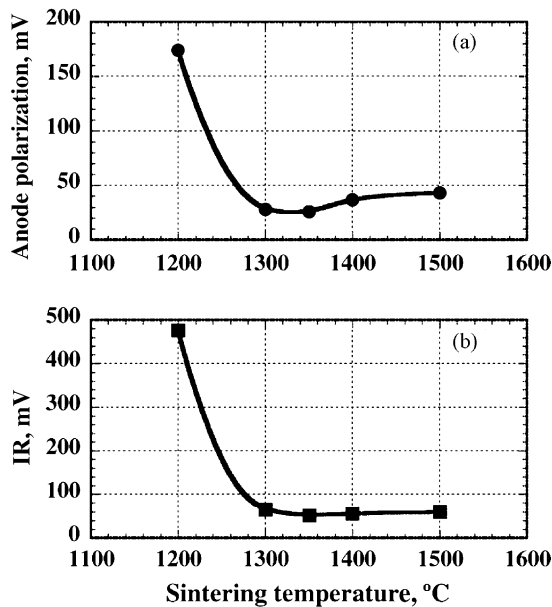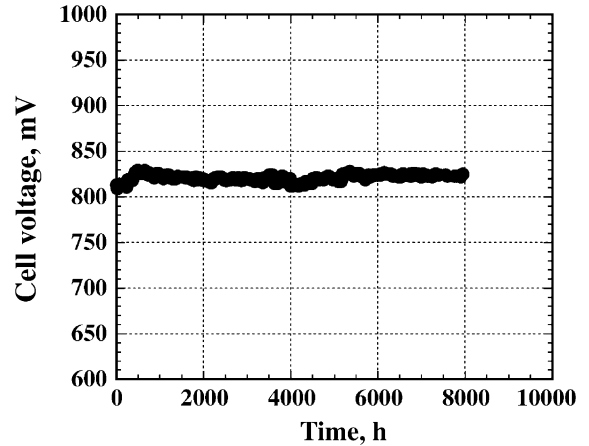

Fig. 5. Electrical performance of a single SOFC with Ni–YSZ cermet anode fabricated at 1350 °C.

important to improve its electrical performance. It is obvious from Figs. 2 and 4 that electrical performance such as the anode polarization and IR of Ni–YSZ cermet anode also depends on the morphology change. The Ni–YSZ cermet anode fabricated at 1200 °C has the morphology in which composite particles are weakly connected (see Fig. 2(a)), and its electrical performance shows high IR and high anode polarization. It means that the connection of grains in the anode is not quite enough. Increasing the sintering temperature leads to better connection of grains in the cermet anode (see Figs. 2b, c and 3), and then its IR rapidly decreases with its morphology change. Moreover, when the sintering temperature reaches 1350 °C, the good morphology in which

Fig. 4. (a) The anode polarization, and (b) internal resistance (IR) of the Ni–YSZ cermet anodes as a function of the sintering temperature measured at the current density of 300 mA/cm^2 and at 1000 °C in the condition of H$_2$—3% H$_2$O.
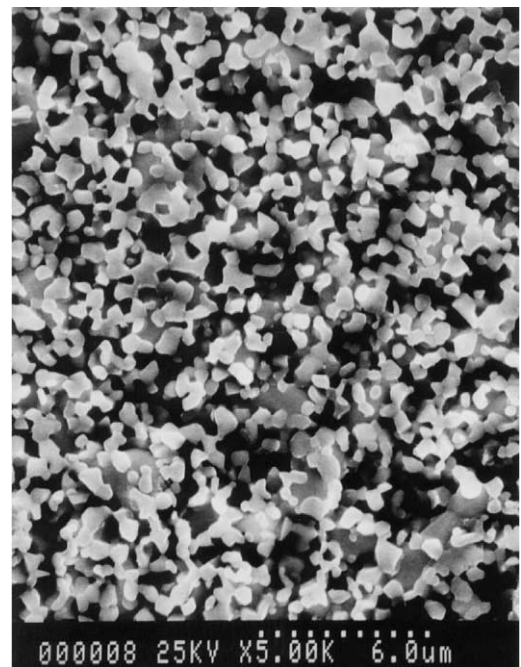

Fig. 6. SEM photograph of a Ni–YSZ cermet anode fabricated at 1350 °C after 8000 h operation.

fine YSZ grains are uniformly dispersed on the surface of Ni grain network is fabricated (Fig. 3). The anode morphology is very similar to that prepared by the vapor-deposition method [13,14]. The vapor-deposited Ni–YSZ anode had lager number of TPB than conventional anode, and achieved good performance [14]. Therefore, this unique morphology also leads to longer TPB length, and the minimum value of its anode polarization. It seems that such morphology causes the best electrical performance in Ni–YSZ cermet anodes in this experiment. The polarization of the cermet anode also increases slightly when the sintering temperature is over 1400 °C. It is caused by the decrease of TPB length due to the growth of YSZ grains and Ni grains in the cermet anode (see Fig. 2(d)).

As shown in Fig. 5, a Ni–YSZ cermet anode fabricated at 1350 °C shows the superior stability at high temperature SOFC operation. It is thought that this superior stability also depends on the morphology in which fine YSZ grains were uniformly dispersed on the surface of Ni grain network. 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 in this temperature region. Therefore, it seems that such effect kept the initial morphology even after 8000 h operation. It suggests that this Ni–YSZ cermet anode has a possibility to keep initial structure even over 10,000 h. Further experiments are needed to make clear the relations between the electrical performance and morphology of a cermet anode in more details. It will be reported by another paper in future.

5. Conclusions

Ni–YSZ cermet anodes were fabricated at various sintering temperatures from NiO–YSZ composite particles. Morphology and electrical performance of the cermet anode were highly influenced by the sintering temperature. A Ni–YSZ cermet anode fabricated at 1350 °C of the sintering temperature showed the highest electrochemical activity as well as the lowest IR, because this morphology led longer TPB and better Ni connection. Moreover, the cell voltage of a single cell with the Ni–YSZ cermet anode kept very stable for 8000 h in the SOFC operation condition of H_2— 3% H_2O and air at 1000 °C. The Ni–YSZ cermet anode fabricated at 1350 °C of the sintering temperature also had the superior stability of electrical performance. Therefore, it shows that the Ni–YSZ cermet anode fabricated from the composite particles is very promising for practical use of SOFCs.

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