

# Low temperature preparation and performance of Ni/YSZ anode with a multi-layered structure for SOFC

T. Hatae\*, N. Kakuda, T. Taniyama, Y. Yamazaki

*Department of Innovative and Engineered Materials, Graduate school of Science and Engineering, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama, Kanagawa-ken 226-8502, Japan*

Received 23 January 2004; received in revised form 19 March 2004; accepted 29 March 2004

Available online 17 June 2004

## Abstract

Ni/yttria-stabilized zirconia (YSZ) anodes with a multi-layered structure are prepared on YSZ substrates by a low temperature process using electron-beam evaporation method. The Ni/YSZ anode is obtained by reducing a NiO/YSZ anode, and both Ni and YSZ layers have no impurity phases. Scanning ion microscopy (SIM) observation of the cross-section of the anode shows a well-separated structure without Ni diffusion and agglomeration. Tight adhesion between the Ni and YSZ layers is realized by the low temperature process at 800 °C. The current–voltage and current–power characteristics for three separate single cell samples with the multi-layered anode are measured. The maximum power densities of the single cells using an YSZ as an electrolyte (0.5 mm thick) with a four-layered anode, a six-layered anode, and a 10-layered anode are obtained to be 0.14, 0.12, and 0.32 W/cm<sup>2</sup> at 800 °C, respectively. The improvement in the performance of the 10-layered anode compared with the four-layered and six-layered anodes is mainly due to an increase in the length of triple phase boundary in the structure and enhancement in the diffusivity of fuel gas.

© 2004 Elsevier B.V. All rights reserved.

*Keywords:* SOFC; Low temperature process; Multi-layered structure; Ni/YSZ anode

## 1. Introduction

Solid oxide fuel cells (SOFCs) provide high energy-conversion efficiency due to direct conversion of fuels into electric power at high temperature, in a cogeneration system, for example. Conventional SOFCs with an YSZ electrolyte are now being operated at 900 °C or higher temperature to attain power density sufficient to use in the system. However, the high temperature operation causes serious problems such as internal mechanical stress due to the difference in the thermal expansion coefficients of the materials and chemical reactions. Therefore, an operating temperature lower than 800 °C is desirable. The low operating temperature, on the other hand, leads to another difficulty in large voltage losses due to the ohmic resistance of the materials and the polarization at the electrodes. Since most of the voltage losses are generated from the ohmic resistance of the electrolyte, a number of approaches have been reported preparing a thinner electrolyte which reduces

the corresponding resistance [1–6], and high power density was obtained using YSZ thin film electrolytes [7,8].

In our previous study [9–11], we prepared an YSZ thin film electrolyte on a porous La<sub>0.7</sub>Sr<sub>0.3</sub>MnO<sub>3</sub> (LSM) cathode substrate using electron-beam evaporation method, and further deposited a Ni/YSZ anode on the electrolyte directly from Ni and YSZ sources. However, the adhesion of the Ni/YSZ anode to the YSZ thin film was not sufficient due to the different thermal expansion between YSZ and Ni. A heat treatment at about 1400 °C was needed to improve the adhesion, and the heat treatment caused chemical reaction of the YSZ with the LSM substrate [12], resulting in the low performance of generation of electricity. Therefore, a low temperature process is required for the preparation of an anode on a cathode-supported YSZ.

In this report, we propose a new approach preparing a Ni/YSZ anode on an YSZ electrolyte substrate at low temperature. The structure we propose is a Ni/YSZ multi-layered anode which can relax the mechanical stress and improve the adhesion to the electrolyte. In addition, we use NiO as an evaporation source instead of Ni metal in order to obtain tight adhesion. Muller et al. reported [13] that tight adhesion of a Ni/YSZ anode to an YSZ thin

\* Corresponding author. Tel.: +81 45 924 5412; fax: +81 45 924 5412.  
E-mail address: [hatae@iem.titech.ac.jp](mailto:hatae@iem.titech.ac.jp) (T. Hatae).

film was obtained by reducing a NiO/YSZ anode prepared at 1400 °C. We place emphasis on the preparation of the multi-layered anode at a low temperature of 800 °C. The low temperature process suppresses the exfoliation of the anode from the substrate and realizes tight adhesion. In fact, here we demonstrate excellent electrical performance of the anode with the multi-layered structure.

## 2. Experimental

An anode with a multi-layered structure was prepared on a commercial YSZ disk substrate (Japan Fine Ceramics Co. Ltd.: 8 mol%  $Y_2O_3$ - $ZrO_2$ , diameter 30 mm, thickness 0.5 mm). One side of the substrate was covered with a Pt paste and Pt mesh for the use of a current collector and sintered at 900 °C for 2 h in air. A  $(NiO/YSZ)_n$  multi-layered anode was deposited on the other side of the substrate in a pressure of  $10^{-5}$  Torr and then the sample was heated at 800 °C using an ohmic heating method to realize tight adhesion of the NiO-YSZ anode to the YSZ substrate. YSZ and NiO evaporation sources were prepared in the following way. YSZ (Tohso: 8 mol%  $Y_2O_3$ - $ZrO_2$ ) or NiO powder was pressed uniaxially at 5 t/cm<sup>2</sup> and then pressed hydrostatically at 5 t/cm<sup>2</sup> into pellets. The pellets were sintered at 1400 °C for 10 h in air. Four-layered (NiO/YSZ/NiO/YSZ), six-layered, and 10-layered anodes were prepared. The thickness of each layer in the 10-layered anode is smaller than that in the four-layered anode and the total thickness of the anodes is the same. The NiO/YSZ anodes were reduced to Ni/YSZ anodes in Ar + 10% H<sub>2</sub> atmosphere at 800 °C for 5 h. The X-ray diffraction (XRD) patterns of as-deposited multi-layered anodes and those after reduction were obtained using a Rigaku Rint 2000 diffractometer system with Cu K $\alpha$  radiation. The cross-section of the multi-layered anodes was observed by scanning ion microscopy (SIM). The single cells with the multi-layered anode were operated in H<sub>2</sub>-3% H<sub>2</sub>O gas for the anode side and O<sub>2</sub> gas for the cathode side at 800 °C. The current-voltage (*I*-*V*) and current-power (*I*-*P*) characteristics of the cells were measured. The morphology of the multi-layered anodes was checked again after an 8 h performance test using SIM.

## 3. Results and discussion

Fig. 1 shows the XRD patterns of as-deposited multi-layered anodes and those after reduction. The diffraction peaks corresponding to YSZ and NiO are detected for the as-deposited anode without impurity phases, while no peak of NiO is seen for the reduced multi-layered anodes, indicating that NiO in the anodes was completely reduced to Ni metal. The color of the multi-layered anodes also changes from green to metallic one.

Fig. 2 shows the cross-sectional SIM images of the multi-layered anodes. The dark and bright contrast corre-

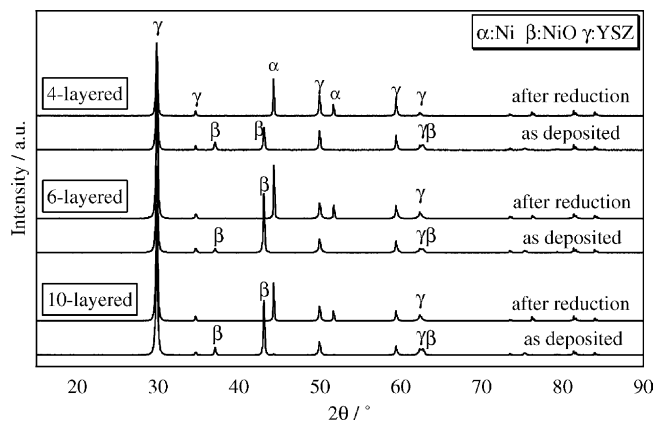


Fig. 1. XRD patterns of as-deposited multi-layered anodes and those after reduction.

spond to YSZ and NiO or Ni, respectively. The anodes have a multi-layered structure and there is no exfoliation of the anodes from the substrate. The tight adhesion of the Ni/YSZ anode to the YSZ substrate was obtained using a low temperature process at 800 °C. A clear morphological difference between the as-deposited anodes and those after reduction is observed; the dense NiO layers change to porous Ni layers and the NiO layers are well reduced to Ni even in the layers close to the substrate. The pores appeared in the Ni layers, which can promote the diffusion of fuel gas, may result from a decrease in the volume due to dissociation of oxygen in the NiO layers during the reduction process. Muller et al. also reported [13] that sufficient porosity was achieved after reduction of a NiO/YSZ anode, which is consistent with our results. In contrast, no morphological difference is seen in the YSZ layers. The YSZ layers prevent Ni diffusion and agglomeration across the layers, suggesting that the multi-layered structure relaxes different thermal expansion between layers and prevents the anode exfoliating from the substrate. It should be noted that the morphological difference between the four-layered or six-layered anode and the 10-layered anode is significant in the region close to the top layers. In particular, the morphology of the 10-layered anode close to the surface is similar to that of a cermet anode in contrast to the four-layered and six-layered anodes.

Fig. 3 shows the cross-sectional SIM images of the multi-layered anodes after a performance test. Although a large Ni agglomeration is seen in the four-layered and six-layered anodes after the performance test, the agglomeration is suppressed as the number of layers increases, indicating that Ni agglomeration can be avoided using YSZ layers effectively. In the 10-layered anodes, the morphology of the layers close to the surface is homogeneous and the borders are indistinguishable.

Fig. 4 shows the *I*-*V* and *I*-*P* characteristics of test single cells with the multi-layered anodes at 800 °C. The cells configuration is as follows:

H<sub>2</sub> + 3% H<sub>2</sub>O, (Ni/YSZ)<sub>n</sub>|YSZ(0.5 mm)|Pt, O<sub>2</sub>,

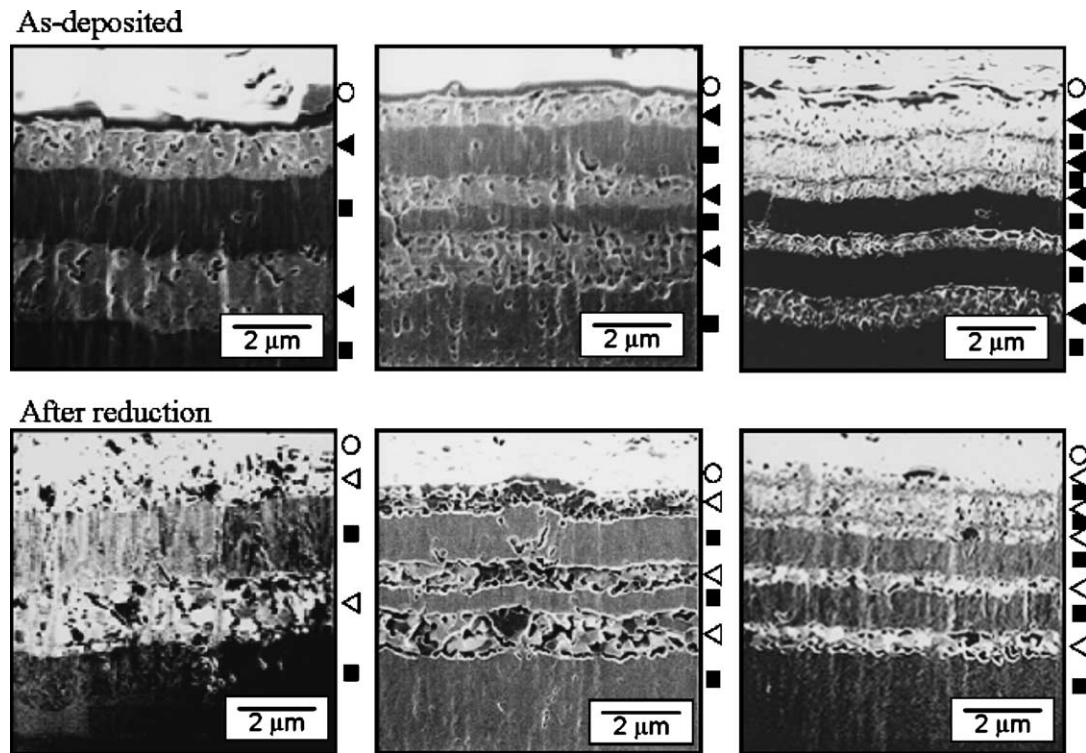


Fig. 2. Cross-sectional SIM images of as-deposited multi-layered anode and those after reduction. (○) Surface; (◁) Ni; (◄) NiO; (■) YSZ.

where  $n = 2, 3,$  and  $5$  correspond to the four-layered, six-layered, and 10-layered anodes, respectively. The  $I$ - $P$  curves in Fig. 4 show that the maximum power densities of the test cells with the four-layered anode, six-layered anode, and 10-layered anode are  $0.14, 0.12,$  and  $0.32 \text{ W/cm}^2$  at  $800^\circ\text{C}$ , respectively. The performance of the cell with the 10-layered anode is considerably improved. Since the same materials of an YSZ electrolyte and a Pt cathode are used in the three test cells, the voltage loss is most likely to be associated with different polarization at the anode. In the present case, the reduction in the polarization at the 10-layered anode is associated with the micro-structure of the anode. The electronic conducting path among the Ni layers is formed at the edge of the anodes since deposited Ni layers spread out-

side the edge of the anodes, which is confirmed using scanning electron microscopy (SEM), and are connected through a Pt mesh used as a current collector.

We note that the four-layered and six-layered anodes have less porous Ni layers than the corresponding as-deposited anodes as shown in Fig. 3. In contrast, the porosity in the 10-layered anode remains after the performance test, which may be attributed to the thinner Ni layers than those of the four-layered and six-layered anodes. The high porosity of the 10-layered anode enhances the gas diffusivity. This could be one of the reasons for the high performance of the 10-layered anode. Also, since the thickness of the YSZ layer has a significant effect on the gas diffusivity, the YSZ thin layers in the 10-layered anode which are thin enough not to

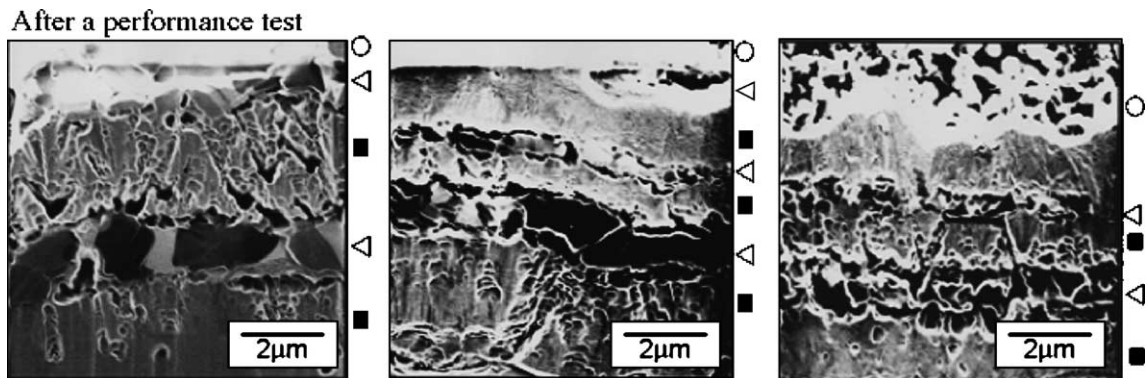


Fig. 3. Cross-sectional SIM images of the multi-layered anodes after a performance test. (○) Surface; (◁) Ni; (■) YSZ.

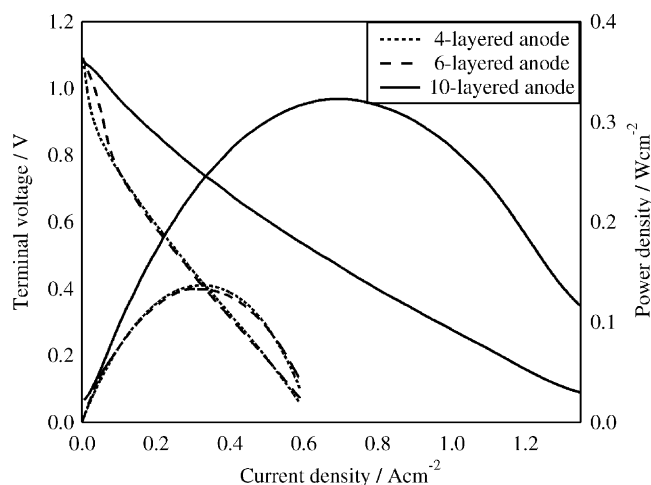


Fig. 4. The  $I$ - $V$  and  $I$ - $P$  characteristics of single cells with the multi-layered anodes at 800 °C. The thickness of the electrolyte is 0.5 mm, the area of the electrodes is 0.196 cm<sup>2</sup>, and the flow rates of H<sub>2</sub> and O<sub>2</sub> are 30 ml/min.

suppress gas diffusion result in the great performance in the anode. The high porosity also increases an area where an electrolyte contacts the first Ni layer, resulting in the increase in the length of triple phase boundary which consists of the first Ni layer and the electrolyte.

The polarization is believed to be reduced by increasing activation sites (triple phase boundary) at which an electrochemical reaction occurs. It is likely that the 10-layered anode has more conducting paths of electrons and oxygen ions and diffusion path of fuel gas across the multi-layers, compared with the four-layered and six-layered anodes as shown in Fig. 3. The increase in the conducting and diffusion paths enhances triple phase boundary length in the anode, leading to a high performance of the 10-layered anode. A generation of these paths is attributed to the thickness of the Ni and YSZ layers in the 10-layered anode. Therefore, we conclude that higher performance can be achieved in a laminate with Ni and YSZ thin layers.

#### 4. Conclusion

The Ni/YSZ anodes with a multi-layered structure were obtained by a low temperature process at 800 °C using electron-beam evaporation method. The Ni and YSZ layers

have a single phase without impurity. Cross-sectional SIM observation of the multi-layered anodes shows that the YSZ layers suppress Ni diffusion and agglomeration effectively, and that the multi-layered structure relaxes the different thermal expansion between the Ni/YSZ anode and the YSZ substrate, resulting in no exfoliation of the anodes from the substrate at 800 °C. Therefore, we expect that this process can avoid chemical reactions which occur in the preparation process of cathode-supported SOFCs and be useful for the preparation of thin film SOFC. A single cell using a thick YSZ electrolyte (0.5 mm thick) with a 10-layered anode showed excellent electrical performance with a maximum power density of 0.32 W/cm<sup>2</sup> at 800 °C, which is mainly due to an increase in the triple phase boundary length in the structure and an enhancement in the diffusivity of fuel gas, resulting in an enhancement in the performance of the anode. A SIM observation after a performance test suggests that the porosity in the Ni layers remains in the 10-layered anode due to the thin Ni layers compared with those of four-layered and six-layered anodes. We believe that higher performance is achievable by laminating Ni and YSZ thin layers.

#### References

- [1] N.Q. Nihh, *J. Am. Ceram. Soc.* 76 (1993) 563.
- [2] A. Negishi, K. Nozaki, T. Ozawa, *Solid State Ionics* 3–4 (1981) 443.
- [3] A.O. Isenberg, *Solid State Ionics* 3–4 (1981) 431.
- [4] T. Setogushi, T. Inou, H. Takebe, K. Eguchi, K. Morinaga, H. Arai, *J. Electrochem. Soc.* 139 (1992) 2875.
- [5] L.A. Chick, L.R. Pederson, G.D. Mauipin, J.L. Bates, L.E. Thomas, G.I. Exartos, *Mater. Lett.* 10 (1990) 6.
- [6] C.C. Chen, M.M. Nasrallah, H.U. Anderson, *Solid State Ionics* 70–71 (1994) 101.
- [7] S. de Souza, S.J. Visco, L.C. De Jonghe, *Solid State Ionics* 98 (1997) 57.
- [8] J.-W. Kim, A.V. Virkar, K.-Z. Fung, K. Mehta, S.C. Singhal, *J. Electrochem. Soc.* 146 (1) (1999) 69.
- [9] K. Tomida, T. Namikawa, Y. Yamazaki, *Denki Kagaku* 61 (1993) 251.
- [10] K. Tomida, T. Namikawa, Y. Yamazaki, *Denki Kagaku* 62 (1994) 1043.
- [11] M. Suzuki, Y. Yamazaki, in: *The Eighth Symposium on Solid Oxide Fuel Cells in Japan Extended Abstracts*, 1999, p. 155.
- [12] H.Y. Lee, S.M. Oh, *Solid State Ionics* 90 (1996) 133.
- [13] A.C. Muller, D. Herbstritt, E. Ivers-Tiffée, *Solid State Ionics* 152–153 (2002) 537.