

Short communication

Ni-SDC cermet anode fabricated from NiO–SDC composite powder for intermediate temperature SOFC

Teruhiko Misono^a, Kenji Murata^a, Takehisa Fukui^{a,*}, Jintawat Chaichanawong^b, Kazuyoshi Sato^b, Hiroya Abe^b, Makio Naito^b

^a *Hosokawa Powder Technology Research Institute, 1-9 Tajika, Shoudai, Hirakata, Osaka 573-1132, Japan*

^b *Joining and Welding Research Institute, Osaka University, 11-1 Mihogaoka, Ibaraki, Osaka 567-0047, Japan*

Received 4 October 2005; received in revised form 12 January 2006; accepted 24 January 2006

Available online 2 March 2006

Abstract

We report a cost-effective processing method for fabricating intermediate temperature solid oxide fuel cells (SOFCs) with Ni-samarium doped ceria (SDC) anode. First, SDC and NiO powders were mechanically treated to make their composite powder. Then, the composite powder was applied into a ceramic tape casting method to form a thick layer for the anode supporting. Finally, an anode supported single cell with a configuration of Ni-SDC/SDC/La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} (LSCF) was prepared. Because of the usage of the composite powder, homogenous distribution and connection of each Ni and SDC were achieved. Peak power densities of 460, 750 and 910 mW cm⁻² were obtained on the single cell at 550, 600 and 650 °C, respectively.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Ni-SDC; Ceramic powder processing; Composite powder; Microstructural control

1. Introduction

Solid oxide fuel cells (SOFCs) offer a low-pollution technology to generate electricity electrochemically with high efficiency. Current efforts are aimed at decreasing the cost of SOFC by lowering the operating temperatures to 700 °C or less [1,2]. One of the critical challenges for operation of SOFCs at low temperature is how to reduce polarization losses at electrodes. For intermediate temperature operation of SOFC, Ni-samarium doped ceria (SDC) is a potential candidate as anode materials [3–5].

In Ni cermet anode, it has been recognized that controlled composite structures offer better performance due to the extension of triple phase boundary (TPB) [6–10].

To optimize the microstructure and distribution of each component, we have successfully developed a simple technique in a cost-effective manner. In our previous studies [9,10], Ni-YSZ cermet anode was fabricated by conventional ceramic processing

introducing NiO–YSZ composite powder. The composite powder was of YSZ coated on NiO particles, which was made by a mechanical method. The resultant Ni-YSZ cermet anode was consisting of fine YSZ connections, as the conducting pass of oxygen ions, on the surface of Ni network, as that of electrons, with continuous pore structure and as that of gaseous species indicating superior electrochemical performance at 700 °C.

In this study, an anode-supported cell with ceria-based materials was fabricated. Fig. 1 shows a schematic illustration of the present powder processing. First, SDC and NiO powders were mechanically treated to make their composite powder. Then, the composite powder was applied into a ceramic tape casting method to form thick layer for the anode supporting. The introduction of the composite powder is a possible way for achieving homogenous distribution and connection of each component in a cost-effective manner. The SOFCs with the anode showed good performance at intermediate temperatures.

2. Experimental

Two kinds of SDC powders were prepared by the coprecipitation method. One was calcined at 900 °C for electrolyte

* Corresponding author. Tel.: +81 72 855 2260; fax: +81 72 855 2260.

E-mail address: tfukui@hmc.hosokawa.com (T. Fukui).

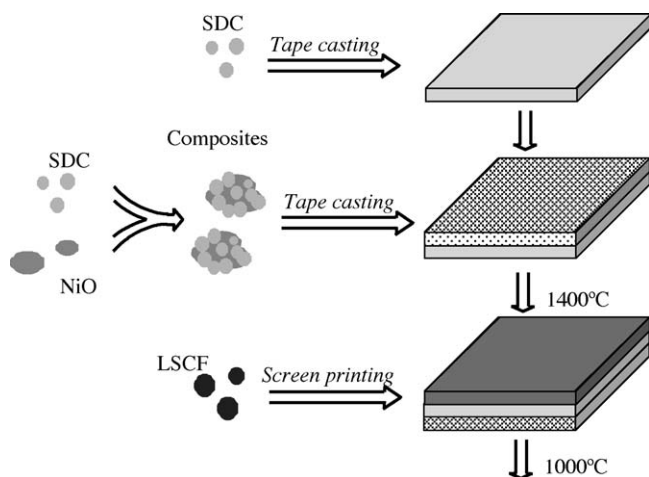


Fig. 1. Schematic illustration of the present powder processing for SOFC.

and the other was calcined at 400 °C for anode, and their specific surface areas (SSA) were 10 and 39 m² g⁻¹, respectively. The SDC powder calcined at 900 °C was dispersed in ethanol solvent with organic binders, and then tape-casted to form 20 μm thick green sheet. After drying, the second green sheet of NiO–SDC composite (750 μm thick) was formed on the SDC sheet. Before the tape casting, NiO (Nikko-Rika Corp) and the SDC powder calcined at 400 °C mixture (mass ratio NiO:SDC = 61.3:38.7) were processed using an attrition type milling device (Nobilta NOB-130, Hosokawamicon Corp. Japan) in dry ambience. The mechanical treatment can present NiO–SDC composite powder. The NiO–SDC/SDC bilayer was co-sintered at 1400 °C for 2 h in air. La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} (LSCF) powder was prepared by a citrate method for cathode material [11]. The LSCF powder was mixed with polyethylene glycol to form paste, screen-printed onto the SDC/NiO–SDC bilayer, and sintered at 1000 °C for 4 h in air. NiO–SDC composite layer was converted into a Ni–SDC cermet anode, when hydrogen fuel was supplied to the cell for the first time. Finally, we made the Ni–SDC anode supported SOFC single cell with diameter of 80 mm.

The microstructural analysis of Ni–SDC cermet anode was conducted with SEM (ERA-8800FE, Elionix, Japan), and EDX (EMAX-7021H, HORIBA). The anode-supported SOFC fabricated was operated in the conditions of H₂-3%H₂O for the anode and air for the cathode at 500–650 °C. Pt mesh was used as the current collector for both the Ni–SDC cermet anode and the LSCF cathode.

3. Results and discussion

3.1. NiO–SDC composite powder

Figs. 2 and 3 show the SEM image of the milled powder and its size distribution measured by laser diffraction and scattering method. From the distribution, the average size was estimated to be 441 nm. On the other hand, those of NiO and SDC estimated from their specific surface areas were 113 and 21 nm, respectively. Therefore, aggregated particles were made by the present mechanical treatment. Since Ni and Ce signals were homo-

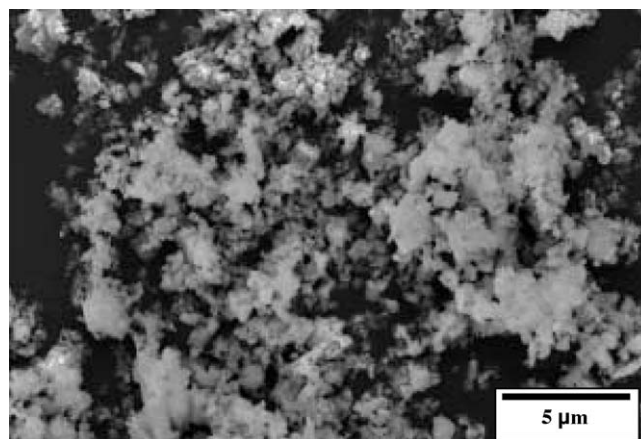


Fig. 2. SEM image of the prepared NiO–SDC composite powder.

geneously detected for the aggregated particles in SEM–EDX analysis, the aggregated particles formed in this study consisted of NiO and SDC particles, i.e., were NiO–SDC composite particles. In our previous studies, NiO–YSZ composite particles have been made in the similar manner [9,10]. Although the detail nature of the mechanically induced particle bonding in metal oxides is still under investigation, this method can be applicable to design particles or powders for advanced materials [12,13].

3.2. Structure of the fabricated SOFC

Fig. 4 shows the cross-sectional SEM image of the SOFC. Thickness of the dense SDC layer is about 20 μm. Thickness of the porous anode and cathode electrodes were about 570 and 20 μm, respectively. The present anode exhibited enough strength to support the SOFC. Fig. 5(a) shows the magnified SEM image of the Ni–SDC cermet anode. Micron-sized porous structure was homogeneously formed, and porosity of the anode layer was estimated to be about 35% from their volume and weight. Fig. 5(b) and (c) shows the EDX mapping of Ni and Ce in the region of Fig. 5(a). It reflected network structures of SDC and Ni grains. These results indicated that Ni–SDC composite anode was consisting of SDC connections, as the conducting

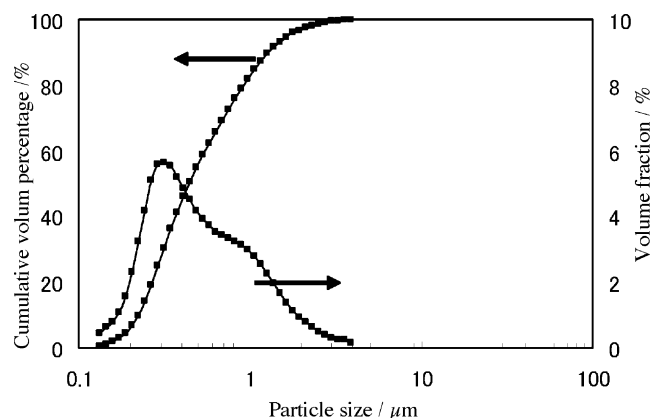


Fig. 3. Particle size distribution of the NiO–SDC composite powder.

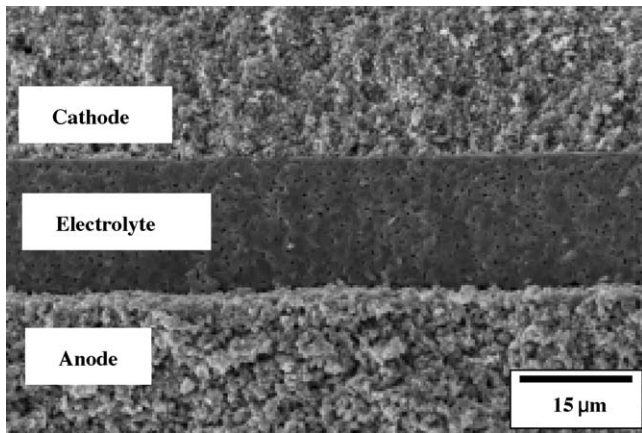


Fig. 4. SEM image of the cross-sectional SOFC fabricated in this study.

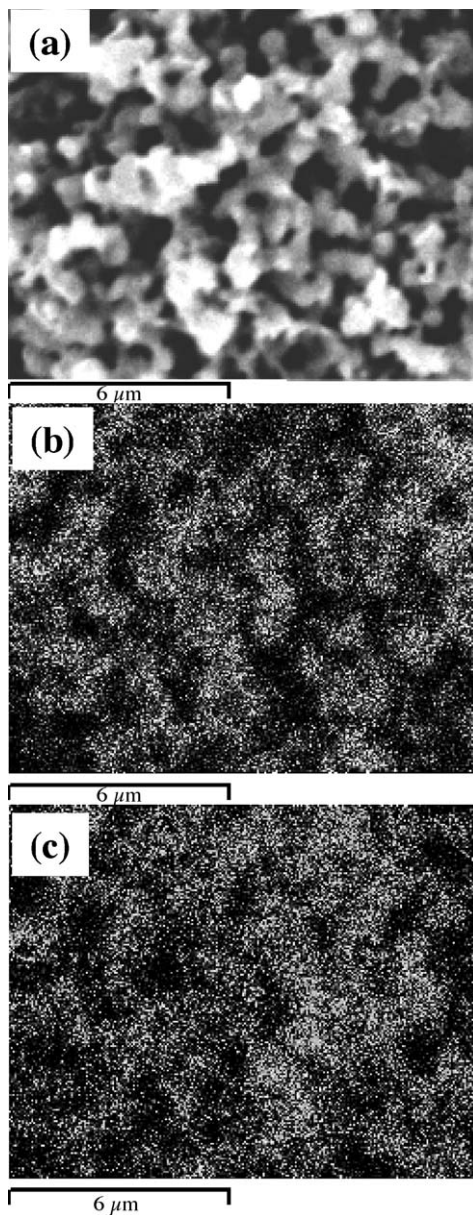


Fig. 5. SEM-EDX analysis of Ni-SDC cermet anode, (a) magnified SEM image, (b) mapping of Ni element, (c) mapping of Ce element (the mapped element is white).

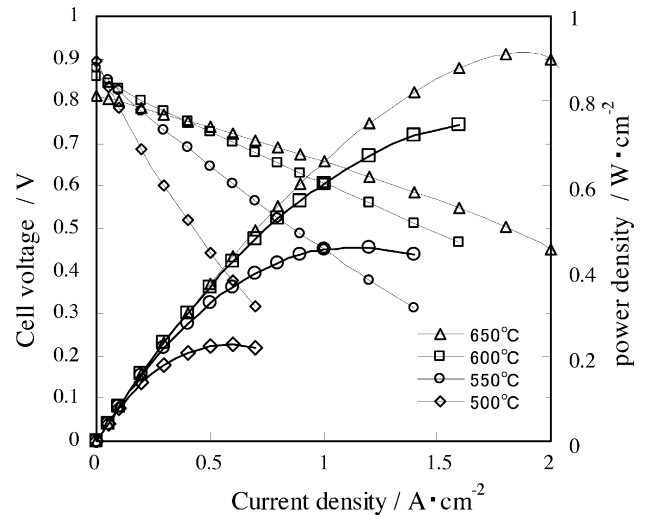


Fig. 6. I - V and power density curves of the anode-supported cell.

pass of oxygen ions, on the surface of Ni connections, as that of electrons, with continuous pore structure and as that of gaseous species.

3.3. Performance of the SOFC

Fig. 6 shows the I - V and power density curves of the anode-supported SOFC tested at 500–650 °C. The maximum powder densities were 230, 460, 750 and 910 mW cm⁻² at 500, 550 600 and 650 °C, respectively. A possible cause of the obtained high performance can be considered to be the well-controlled Ni-SDC cermet anode as shown in Fig. 5. It is remarkable that the present SOFC exhibited higher performance than those of recently fabricated Ni-SDC anode supported SOFCs [14,15]. Ai et al. have ball milled a mixture of NiO and SDC powders and finally fabricated Ni-SDC/SDC(15 μm)/Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O₃(BSCF)-SDC layers which showed a maximum power density of 648 mW cm⁻² at 600 °C [14]. Yin et al. prepared NiO-SDC composite particles using gel-casting technique and finally fabricated Ni-SDC/SDC(25 μm)/Sm_{0.5}Sr_{0.5}CoO₃-SDC layers which showed a maximum power density of 491 mW cm⁻² at 600 °C [15].

In case of Ni-YSZ based SOFCs, a variety of preparation methods have been tried to make NiO-YSZ composite particles such as co-precipitation reaction [16], spray pyrolysis [4,17] and citrate/nitrate combustion [18]. The anode polarization were lowered and showed superior stability at high temperature [17]. Recently, the authors have mechanochemically prepared NiO-YSZ composite particles using an attrition milling device and demonstrated the higher electrochemical activity [9,10]. In this study, it was also demonstrated that the NiO-SDC composite particles made through the mechanical method can improve performance of IT-SOFC. A recently discovered high performance cathode material, BSCF [2], will be applied into our processing method in a future. It is also noted that the present mechanical method is one of promising methods to present mass production of composite particles.

4. Conclusion

The Ni-SDC cermet anode has been fabricated by conventional ceramic processing using NiO–SDC composite particles. The resultant Ni-SDC anode provided good connections of SDC grains, Ni grains, and pores, and substantially decreased the polarization loss. For a single cell with a configuration of Ni-SDC/SDC/LSCF, peak densities of 460, 750 and 910 mW cm⁻² were achieved at 550, 600 and 650 °C, respectively. It can be concluded that the present processing is one of promising approaches for achieving homogenous distribution and connection of each component and pores in a cost-effective manner.

Acknowledgment

Part of the work had been supported by NEDO, as part of the Advanced Ceramic Reactor Project.

References

- [1] Y. Liu, S. Zha, M. Liu, *Chem. Mater.* 16 (2004) 3502.
- [2] Z.P. Shao, S.M. Haile, *Nature* 431 (2004) 170.
- [3] R. Maric, S. Ohara, T. Fukui, T. Inagaki, J. Fujita, *Electrochem. Solid-State Lett.* 1 (1998) 201.
- [4] S. Ohara, R. Maric, X. Zhang, K. Mukai, T. Fukui, H. Yoshida, T. Inagaki, K. Miura, *J. Power Sources* 86 (2000) 455.
- [5] M.M. Cruz, E.P. Hong, P. Jacobson, S.J. Visco, L.C. Dejonghe, *Electrochem. Soc. Proc.* 7 (2003) 253.
- [6] T. Ioroi, Y. Uchimoto, Z. Ogumi, Z. Takehara, *Denki Kagaku* 64 (1996) 562.
- [7] N. Nakagawa, K. Nakajima, M. Sato, K. Kato, *J. Electrochem. Soc.* 146 (1999) 1290.
- [8] T. Fukui, S. Ohara, M. Naito, K. Nogi, *J. Eur. Ceram. Soc.* 23 (2003) 2963.
- [9] T. Fukui, K. Murata, S. Ohara, H. Abe, M. Naito, K. Nogi, *J. Power Sources* 125 (2004) 17.
- [10] K. Murata, T. Fukui, H. Abe, M. Naito, K. Nogi, *JCEJ* 37 (2004) 568.
- [11] K. Murata, T. Fukui, H. Abe, M. Naito, K. Nogi, *J. Power Sources* 145 (2005) 257.
- [12] H. Abe, I. Abe, K. Sato, M. Naito, *J. Am. Ceram. Soc.* 88 (2005) 1359.
- [13] M. Naito, H. Abe, *Ceram. Trans.* 157 (2004) 69.
- [14] N. Ai, Z. Lu, K. Chen, X. Huang, B. Wei, Y. Zhang, S. Li, X. Xin, X. Sha, W. Su, *J. Power Sources*, in press.
- [15] Y. Yin, W. Zhu, C. Xia, G. Meng, *J. Power Sources* 132 (2005) 36.
- [16] S. Wang, T. Kato, S. Nagata, *J. Electrochem. Soc.* 149 (2002) A927.
- [17] T. Fukui, S. Ohara, M. Naito, K. Nogi, *J. Power Sources* 110 (2002) 91.
- [18] M. Marinsek, K. Zupan, J. Maecck, *J. Power Sources* 106 (2002) 178.