High performance electrodes for reduced temperature solid oxide fuel cells with doped lanthanum gallate electrolyte
I. Ni–SDC cermet anode

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Abstract

A Ni–samaria-doped ceria (SDC) cermet was selected as the anode material for reduced temperature (800°C) solid oxide fuel cells. The NiO–SDC composite powder, synthesized by spray pyrolysis, was employed as the starting anode powder in this study. The influence of Ni content in Ni–SDC cermets on the electrode performance was investigated in order to create the most suitable microstructures. It was found that anodic polarization was strongly influenced by the Ni content in Ni–SDC cermets. The best results were obtained for anode cermets with Ni content of around 50 vol.%; anodic polarization was about 30 mV at a current density of 300 mA/cm^2. This high performance seems to be attributable to the microstructure, in which Ni grains form a skeleton with well-connected SDC grains finely distributed over the Ni grains surfaces; such microstructure was also conducive to high stability of the anode. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Ni–SDC anode; Microstructure; Reduced operation temperature; SOFCs

1. Introduction

Solid oxide fuel cells (SOFCs) are expected to be a new promising method for electrical power generation. SOFCs can provide high total efficiency when used in a cogeneration system and promise clean power sources with little NO$_x$. In general, they must operate at temperatures between 900°C and 1000°C because of the low ionic conductivity of an yttria-stabilized zirconia (YSZ) electrolyte at lower operating temperatures. Such high operating temperatures cause many serious problems such as physical and chemical degradation of the SOFCs component materials; therefore, it is desirable to develop SOFCs operating at temperatures of about 800°C or less.

Two approaches to operate SOFCs at reduced temperature are under active considerations. One is the reduction of the thickness of the YSZ electrolyte and the another is the application of another electrolyte having a high ionic conductivity at or below 800°C. Recently, La(Sr)Ga-(Mg)O$_{3-\alpha}$ (LSGM) [1,2] perovskite materials have been attracting great attention as an alternative electrolyte because they exhibit excellent oxide-ion conductivity over a broad range of oxygen partial pressures. The conductivity of LSGM based electrolytes is over 0.1 S/cm at 800°C and this value is the same as that of YSZ at 1000°C. Therefore, LSGM materials become strong candidates for the electrolyte for reduced temperature SOFCs.

Since operating at reduced temperature causes an increase in the polarization losses of both anode and cathode as well as ohmic loss in the electrolyte, it is necessary to develop high performance electrodes in order to operate SOFCs at reduced temperature. Our previous study reported the importance of microstructure control for obtaining good performance electrodes [3–5]. Here, a Ni–samaria-doped ceria (SDC) cermet was selected as the anode material for reduced temperature SOFCs; the goal of the study was to examined the influence of Ni contents in

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Table 1
Characteristics of NiO–SDC composite powder synthesized by spray pyrolysis

Composite powder	NiO content in powder (wt.%)	Ni content after reduction (vol.%)	Mean particle size (μm)
No. 1	40	30	0.6
No. 2	59	48	0.8
No. 3	65	56	0.8
No. 4	77	69	0.9
No. 5	92	89	0.9

Fig. 2. Anodic polarization vs. Ni content in Ni–SDC cermet.

Ni–SDC cermets with respect to electrode performance in order to identify the most suitable microstructures. In addition, the advantages of using NiO–SDC composite powders prepared by spray pyrolysis is underlined, since the characteris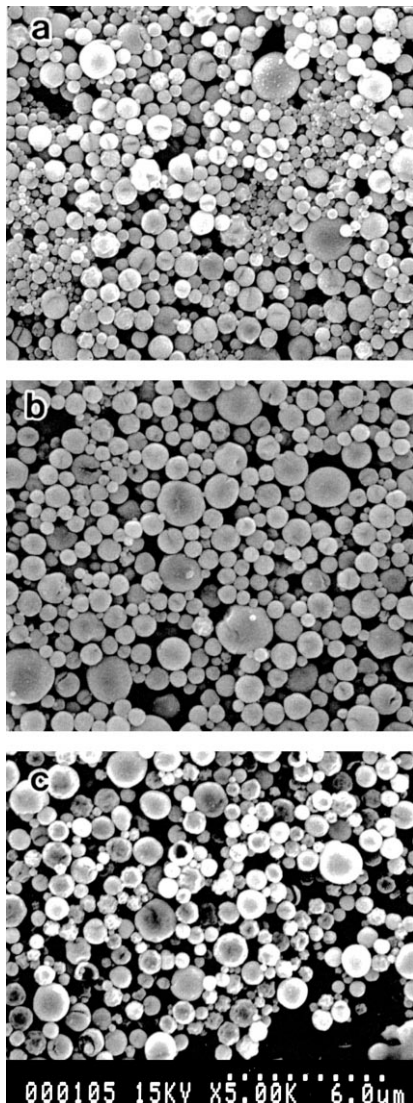tics of the starting electrode powder have a strong effect on the final electrode performance. The development of the cathode is reported in a following paper of this series [6].

2. Experimental

2.1. Synthesis of NiO–SDC composite powder by spray pyrolysis

Several NiO–SDC composite powders with different NiO contents were synthesized by spray pyrolysis; the method was similar to that used in a previously study [7]. It consisted of an ultrasonic vibrator, a reaction furnace, and an electrostatic precipitator. An aqueous solution was prepared by dissolving $Ni(CH_3COO)_2 \cdot 4H_2O$, $Ce(NO_3)_3 \cdot 7.5H_2O$, and Sm_2O_3 materials; the composition of SDC was $(CeO_2)_{0.8}(SmO_{1.5})_{0.2}$. This initial solution was atomized with an ultrasonic vibrator operating at 1.7 MHz. The droplets were transported to a reaction furnace using air as a carrier gas with a fixed flow rate of 3 l/min. The reaction furnace consisted of four independent heating zones. The temperatures of each heating zone, 1, 2, 3, and 4, were set at 200°C, 400°C, 800°C, and 1000°C, respectively. The powders from the furnace outlet were collected using an electrostatic precipitator.

2.2. Preparation of Ni–SDC anode and cell arrangements

NiO–SDC powders were calcined at 1000°C and, after calcination, screen printed onto dense LSGM ($La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\alpha}$) electrolyte disks with a thickness of 0.5 mm. An organic binder (polyethylene glycol) was used; the mixing ratio between the synthesized powder and the binder was 2.5 to 1 by weight. The NiO–SDC layer was sintered at below 1250°C in air for 2 h because the NiO reacted with LSGM electrolyte at higher sintering temperatures of above 1350°C [8]. A La(Sr)CoO₃ cathode was applied as the counter electrode. Both the working (anode) and counter electrode areas were 0.282 cm². In order to collect a current from the cell, Pt mesh was attached on the top of each electrode. The anode and cathode compartments were separated by the electrolyte

Fig. 1. SEM micrographs of NiO–SDC composite powders with different content of NiO: (a) 40, (b) 59, and (c) 77 wt.%.

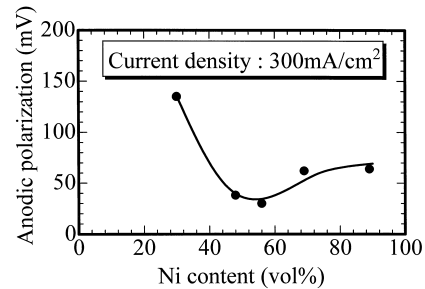disk and each compartment was sealed by a glass ring gasket. Platinum wire was wounded around the electrolyte disk as a reference electrode and it was fixed by platinum paste. The reference electrode was exposed to argon gas. The cell was operated at 800°C; 3% moisturized hydrogen gas ($H_2 + 3\%H_2O$) and air were supplied to the anode and cathode compartments, respectively. The flow rate in both compartments was 50 cm^3/min. For electrochemical characterization, the current interruption technique was used to measure anodic polarization.

2.3. Characterization

The composition of synthesized powders was evaluated by X-ray fluorescence analysis. Particle size distribution was measured by laser diffraction and scattering. The morphology of the powder and the microstructure of the
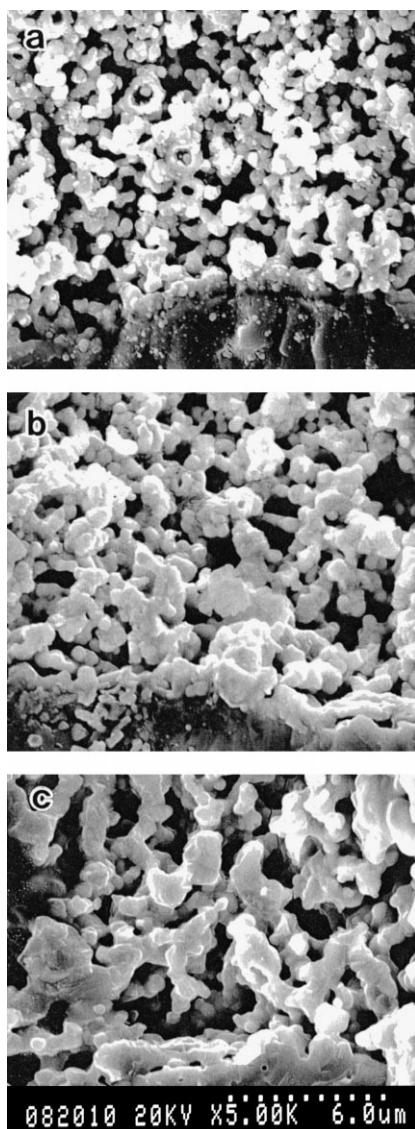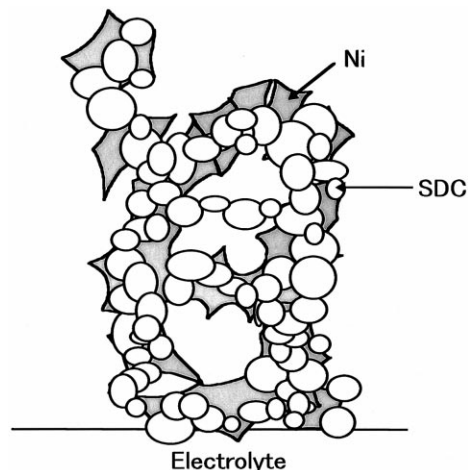

Fig. 4. Sketch of the possible microstructure of the anode with Ni content about 50 vol.%.

Ni–SDC anode were examined by scanning electron microscopy (SEM) with energy dispersive analysis of X-ray (EDAX).

3. Results and discussion

3.1. Characteristics of NiO–SDC composite powder

Table 1 shows the composition and mean particle size for five kinds of NiO–SDC composite powders with different NiO content prepared via spray pyrolysis. The Ni content in the Ni–SDC anode after reduction was calculated by using the density for the NiO, Ni, and SDC. The SEM photographs of several powders are shown in Fig. 1. All powders were spherical and the particle size distribution was narrow. It was confirmed by SEM-EDS that the spherical powder consisted of fine NiO and SDC particles smaller than 0.1 μm. These powders were used as the anode starting powders.

3.2. Performance of Ni–SDC anode

Fig. 2 shows the anodic polarization as a function of Ni content in Ni–SDC cermet sintered at 1250°C, for a current density of 300 mA/cm^2. The thickness of anodes was about 15 μm for all cells tested. These results clearly show that the anodic polarization strongly depends on the Ni content in the cermet. The best results were obtained for the anode cermet with an Ni content of around 50 vol.%; anodic polarization was about 30 mV at a current density of 300 mA/cm^2 for these specimens. An SEM image of the fracture surface of several Ni–SDC anodes is given in Fig. 3. It was observed that all Ni–SDC anodes have a homogenous porous microstructures, although the grain size was slightly increased with increasing the Ni content. These results indicate that good connections between Ni–

Fig. 3. SEM micrographs of Ni–SDC anodes with different content of Ni: (a) 30, (b) 48, and (c) 69 vol.%.
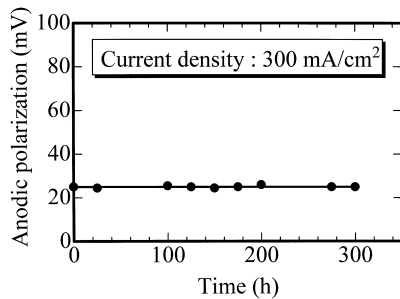
Fig. 5. Time dependence of anodic polarization for Ni–SDC cermet with Ni content of 56 vol.%.

Ni, SDC–SDC, and Ni–SDC grains is important in fabricating a high performance Ni–SDC anode cermet. Thus, the high performance of this anode seems to be attributable to the increase in the number of active sites at the boundary between Ni, SDC and H_2 gas. The possible microstructure of Ni–SDC anodes with Ni content of around 50 vol.% is sketched in Fig. 4. As shown schematically, the Ni grains form a skeleton with well-connected SDC grains finely distributed over the Ni grains surfaces. This microstructures seems to result from using the NiO–SDC composite powder because the microstructure is strongly influenced by the starting powder characteristics. In addition, such Ni–SDC anode cermets are expected to have good long-term stability, because a few small SDC grains are dispersed on the surface of the Ni grains; thus, the distributed SDC grains are expected to suppress sintering of the Ni grains as well as to isolate many Ni grains from direct contact with LSGM electrolyte. For the most part, SDC was firmly distributed on the surface of LSGM. Fig. 5 shows the time dependence of anodic polarization for a Ni–SDC cermet with Ni content of 56 vol.%. The anodic polarization of the cermet, sintered at 1300°C was about 30 mV at a current density of 300 mA/cm^2 and was very stable during 300 h at 800°C. It was observed that the microstructure of the Ni–SDC anode after 300 h of operation was substantially changed. As is evident from Fig. 5,

the microstructure which was proposed in the present study has a good stability as well as high performance.

4. Conclusion

A Ni–SDC cermet prepared from NiO–SDC composite powder was selected as the anode material for reduced temperature SOFCs; the influence of Ni contents in Ni–SDC on the anodic polarization was examined. The anodic polarization was strongly influenced by the Ni content in Ni–SDC cermet; the lowest anodic polarization of the cermet with Ni content of around 50 vol.% was about 30 mV at a current density of 300 mA/cm^2. This Ni–SDC anode had good stability as well as high performance. These results appear to be due to the microstructure in which Ni grains form a skeleton with well-connected SDC grains finely distributed over the Ni grains surfaces; there is little contact between Ni and LSGM electrolyte, therefore the stability of this type of anode has been demonstrated to be high.

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