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# Preparation, microstructures and electrical properties of a Ni/Sm-doped ceria cermet as an anode material of a solid oxide fuel cell

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This paper reports the preparation, microstructures and electrical properties of a Ni (55 vol%)/Sm-doped ceria cermet. A nickel powder of median size 14  $\mu$ m or a NiO powder of median size 2.5  $\mu$ m was mixed with Sm-doped ceria (SDC) powder (median size 0.87  $\mu$ m) with a composition of Ce<sub>0.8</sub>Sm<sub>0.2</sub>O<sub>1.9</sub>, which was produced by the calcination of an oxalate solid solution (Ce<sub>0.8</sub>Sm<sub>0.2</sub>)<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub> at 600°C. The mixtures of Ni/SDC (sample A) and NiO/SDC (sample B) were sintered at 1300°C in air to a relative density of 58.6% and 97.3%, respectively. During the sintering of the cermet, the Ni powder was oxidized to NiO in sample A. The NiO component in the as-sintered cermet was reduced to Ni in a H<sub>2</sub>-H<sub>2</sub>O atmosphere of an oxygen partial pressure ~10<sup>-20</sup> atm at 700°C. Both the cermets showed a high stability of high electronic conduction to 100 h of heating at 700°C in a low oxygen partial pressure atmosphere. Sample A with large Ni particles was too brittle to handle after the heating. Sintering of the fine Ni grains in sample B proceeded at 700°C.

Key words: Ni/Sm-doped ceria cermet, Anode material, Solid oxide fuel cell, Electronic conduction, Microstructure.

#### Introduction

It is reported that rare-earth-doped ceria has a higher oxide ion conductivity than Y<sub>2</sub>O<sub>3</sub>-stabilized ZrO<sub>2</sub> (YSZ) and is a candidate solid electrolyte for low temperature solid oxide fuel cells (SOFCs) [1-4]. The oxide ion conductivity of SDC is about 0.1 S cm<sup>-1</sup> at 800°C and this value is comparable to the ionic conductivity of YSZ at 1000°C. Reducing the operation temperature is effective in increasing the lifetime and expanding the choice of the constituent materials such as electrodes and metal gas separator of SOFCs. In addition, the lower operation temperature suppresses the undesirable electronic conduction of rare-earth-doped ceria which decreases the electromotive force of SOFC. The purpose of this research is to produce a high performance anode material for rare-earth-doped ceria ceramics. Some researchers have proposed the following candidate anode materials: Ni/Sm-doped ceria (SDC) cermet [5], Ni/ceria-gadolinia cermet [6], Ru/SDC cermet [7], and La<sub>0.9</sub>Sr<sub>0.1</sub>Ga<sub>0.8</sub>Mn<sub>0.2</sub>O<sub>3</sub> [8]. The anode of a SOFC contains a large amount of pores to enhance the reaction between oxide ions and H<sub>2</sub> gas at the triple phase boundary (electronic conductor-ionic conductor-H<sub>2</sub> gas). The sintering of Ni particles for the long-term operation of a SOFC at a high temperature should be prevented to keep the high reactivity at the triple phase boundary. In this experiment, a Ni/SDC cermet as anode material for a SDC electrolyte was prepared using Ni particles of 14  $\mu$ m size and NiO of 2.5  $\mu$ m size. The microstructures and electrical properties of the cermet were measured as a function of heating time at 700°C.

# **Experimental Procedure**

The detailed powder preparation method of SDC with a composition Ce<sub>0.8</sub>Sm<sub>0.2</sub>O<sub>1.9</sub> is reported in our previous papers [9, 10]. The oxalate solid solution  $(Ce_{0.8}Sm_{0.2})_2$ - $(C_2O_4)_3$  was produced at room temperature by adding the mixed nitrate solution (0.2 M) of Ce and Sm into 0.4 M oxalic acid solution. The co-precipitated oxalate powder decomposed to a polycrystalline oxide solid solution by heating to 600°C. Our previous observation of Y-doped ceria particles by transmission electron microscopy revealed that elongated secondary particles produced at 600°C consisted of spherical primary particles of about 10 nm diameter [10]. The platelike particles in the as-prepared powder were crushed to equiaxed fine particles. The Sm-doped ceria solid solution was milled with  $\alpha$ -alumina balls (0.3 cm diameter) at a rate of 85 rpm for 24 h. The specific surface area of the SDC powder after the milling was 20.8  $m^2/g$ , which corresponded to a 40 nm equivalent diameter spherical particle. Figure 1(a) shows the ballmilled equiaxed SDC particles. The particle size was measured by a particle size analyzer (CAPA-700, Horiba Ltd., Japan) using a centrifugal sedimentation method and the median size was 0.87 µm. This median size represents the secondary particle size. Figure 2 shows

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Fig. 1. Scanning electron micrographs of (a) Sm-doped ceria (SDC) powder, (b) Ni powder of  $14 \,\mu$ m of median size and (c) fine NiO powder preparated from oxlatate precursor.

the flow chart for the preparation of anode material from large Ni powder. The milled SDC powder was mixed with Ni powder (99.9 mass%, specific surface area 0.34 m<sup>2</sup>/g) at a 55 vol% Ni fraction by dry ball-milling with alumina balls (0.3 cm diameter) for 24 h [11]. Figure 1(b) shows the as-received Ni powder. The Ni powder consisted of spherical particles of a median size 14  $\mu$ m. The milled powder mixture was compacted uniaxially under a pressure of 49 MPa to a pellet of 10 mm diameter and 2 mm thickness, and sintered at 1300°C for 4 h in air (sample A). On the other hand, a fine NiO powder was produced from nickel oxalate NiC<sub>2</sub>O<sub>4</sub>. 0.2 M Ni (NO<sub>3</sub>)<sub>2</sub> solution was added into 0.4 M oxalic acid solution and aged for 120 h at room



Fig. 2. Flow chart for the preparation of anode material from SDC and large Ni particles.

temperature [12]. The  $NiC_2O_4$  produced was vacuumfiltrated, washed with distilled water and dried at 40°C overnight and then calcined in a platinum crucible at 600°C in air. Figure 1(c) shows the as-calcined NiO powder with a specific surface area of 2.23  $m^2/g$ . The particle size of the NiO powder was measured by a particle size analyzer (CAPA-700, Horiba Ltd., Japan) and the median size was 2.5 µm. Figure 3 shows the flow chart for the preparation of the anode cermet from fine NiO powder. The milled SDC and calcined NiO powders were mixed at 63.7 vol% NiO fraction (corresponding to 45 vol% SDC and 55 vol% Ni) and milled with  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> balls (0.3 cm diameter) in a NH<sub>4</sub>OH solution at pH 10.5 for 24 h. After the ball-milling, the mixed powder suspension was filtered through a net of 30 µm mesh size and degassed to remove air bubbles in



Fig. 3. Flow chart for the preparation of SDC/Ni cermet with fine NiO powder.

a bell-jar under a reduced pressure. This suspension was consolidated by filtration through a gypsum mold to a cylindrical pellet of 10 mm diameter and 40 mm height. The green compacts were heated to 1300°C at a rate of 200 Kh<sup>-1</sup>, and sintered for 4 h in air (sample B). The density of the sintered sample was measured by the Archimedes method using distilled water. The complex impedance of sintered samples A and B using a self-inductance-capacitance-impedance LCZ meter (model 4276A, 4277A and 4193A, Yokogawa Hewlett-Packard Co., Tokyo, Japan) in the frequency range from 100 Hz to 110 MHz was measured in an atmosphere of H<sub>2</sub>-H<sub>2</sub>O with an oxygen partial pressure in the range of  $1.0 \times 10^{-20}$ -9.0 × 10<sup>-20</sup> atm. Similarly, the direct current output of the sintered cermet was measured by a potentiostat (HA-501G, Hokuto Denko Co., Tokyo, Japan) at 700 °C under a low oxygen partial pressure. The oxygen partial pressure of the H<sub>2</sub>-H<sub>2</sub>O system was monitored with a YSZ oxygen sensor (KOA-200, Kaken Inc., Ibaraki, Japan). Electrical contact was made via Pt plates with Pt lead wires.

#### **Results and Discussion**

#### **Electrical properties**

Table 1 shows the relative densities of samples A and B after sintering at 1300°C in air. Sample A with 14 µm Ni resulted in a low relative density (58.6%). Sample B with fine NiO showed a high sinterability (97.3% relative density). Figure 4 shows (a) the complex impedance plot and (b) the direct current output with applied voltage for the short-circuited Pt plates (diameter 10 mm, thickness 3 mm) with Pt lead wires (diameter 0.5 mm, length 2.7 m) in an oxygen partial pressure range from  $2.95 \times 10^{-20}$  to  $5.26 \times 10^{-20}$  atm at 700-703°C. The straight line in the complex impedance plot corresponds to the series circuit of a resistance and coil. The resistance of the Pt electrodes was determined to be 2.582  $\Omega$  from the real part at lower frequency. This value was very close to the resistance measured in Fig. 4(b) (2.333  $\Omega$ ). Figure 5 shows (a) the complex impedance plot and (b) direct current output with applied voltage for sample B heated at 702°C for 1-100 h under an oxygen partial pressure of  $5.12 \times 10^{-20}$  atm. Both the data in Figs. 5(a) and (b) showed no significant

 
 Table 1. Relative density, porosity and crystalline phases of NiO/ Sm-doped ceria cermet sintered at 1300°C in air

	Sample A	Sample B
Starting Ni (µm)	14.2	-
Starting NiO (µm)	-	2.5
Relative density (%)	58.6	97.3
Open pores (%)	38.4	0.6
Closed pores (%)	3.0	2.1
Crystalline phases	NiO	NiO
	$Ce_{0.8}Sm_{0.2}O_{1.9}$	$Ce_{0.8}Sm_{0.2}O_{1.9}$



**Fig. 4.** Complex impedance plot (a) and direct current output with applied voltage (b) for the short-circuited Pt plates (10 mm diameter, 3 mm thickness) with Pt wires (0.5 mm diameter, 2.7 m length) under an oxygen partial pressure of  $\sim 10^{-20}$  atm at 700-703°C.



**Fig. 5.** Complex impedance plot (a) and direct current output with applied voltage (b) for sample B heated at 702°C for 1-100 h under an oxygen partial pressure of  $5.12 \times 10^{-20}$  atm. See Table 1 for sample B.

change with heating time, indicating no electrical degradation of anode performance. In addition, the measured resistance of sample B was close to the resistance of the Pt electrodes, indicating a high electronic conduction of sample B. In this experiment, it was difficult to measure the resistance of the SDC/Ni cermet accurately because it was too small. A similar result was also measured for sample A.

Figure 6 shows the comparison of resistance of samples A and B with Pt electrodes, determined from the complex impedance plots at 700°-707°C as a function of heating time. Both the samples showed a high stability of electronic conduction to 100 h. No difference in the resistance of samples A and B suggests a small influence of the Ni grain size on the electrical properties of the anode in the reduced atmosphere. Figure 7 shows the influence of the length of the Pt lead wire on the measurement of resistance of samples A and B. The



Fig. 6. Resistance of samples A and B with Pt electrodes, determined from the complex impedance plots at  $700^{\circ}$ - $707^{\circ}$ C as a function of heating time. See Table 1 for sample A.



Fig. 7. Influence of the length of Pt lead wire on the measurement of resistance of samples A and B.

high linearity of the mixed resistance of the Pt electrodes+SDC/Ni cermet with the Pt wires indicates that the resistance of the lead wires dominates the resistance of the anode because of the high electronic conduction of the SDC/Ni cermet. This information should be reflected in the design of SOFC electrodes to reduce the anode-related resistance.

#### Microstructures

Figure 8 shows the microstructures of samples A and B heated in the H<sub>2</sub>-H<sub>2</sub>O atmosphere at 700°C. The assintered sample A (a) had 58.6% of theoretical density, 38.4% of open pores and 3.0% of closed pores. The large NiO grains (~8.8  $\mu$ m) were surrounded by fine SDC grains (~2.5  $\mu$ m). After the reduction of NiO to Ni metal by heating for 1 h (b) and 10 h (c), fine pores below 1  $\mu$ m in size were produced in the Ni grains. Sample A heated for 10 h at 700°C was too brittle to handle. Figure 8(d) shows a scanning electron micrograph of the as-sintered sample B with 97.2% of theoretical density. The SDC grains appear brighter than the NiO grains due to the effective reflection of secondary electrons by heavy atoms (Ce and Sm). The grain area ratio of NiO to SDC, which was measured



**Fig. 8.** Microstructures of (a) as-sintered sample A, (b) sample A heated at 700°C for 1 h in the H<sub>2</sub>-H<sub>2</sub>O atmosphere, (c) sample A heated at 700°C for 10 h in the H<sub>2</sub>-H<sub>2</sub>O atmosphere, (d) as-sintered sample B, (e) sample B heated at 700°C for 1 h in the H<sub>2</sub>-H<sub>2</sub>O atmosphere and (f) sample B heated at 700°C for 100 h in the H<sub>2</sub>-H<sub>2</sub>O atmosphere.

by an image analyzer with a computer, was 56.7/43.3. This ratio was close to the mixing raito of the starting powders, NiO/SDC=59.7/40.3. Reduction of NiO to Ni in the H<sub>2</sub>-H<sub>2</sub>O atmosphere for 1 h (e) and 100 h (f) at 700°C gave homogeneous pores in the cermet. The change in the domain structures from (e) to (f) is due to the sintering of the fine Ni grains. In the microstructure (f), it was difficult to distinguish SDC and Ni grains.

## Conclusions

(1) The sinterability of the Ni/SDC cermet (Ni/SDC=55/45, in volume ratio) in air at 1300°C was greatly influenced by the size of the Ni particles. The addition of fine NiO to SDC particles increased the sinterability of the cermet.

(2) The NiO component in the as-sintered cermet was reduced to Ni in a H<sub>2</sub>-H<sub>2</sub>O atmosphere ( $\sim 10^{-20}$  atm of oxygen partial pressure) at 700°C. The cermet showed a high stability of electronic conduction to 100 h of heating at 700°C in the reduced atmosphere.

(3) The grain size of Ni in the cermet gave no significant influence on the electrical properties. The resistance of Pt lead wires dominated the resistance of the anode for the Ni/SDC cermet.

(4) The reduction of NiO to Ni produced continuous fine pores in the cermet. The larger Ni grains (~14  $\mu$ m) decreased the mechanical strength after the reduction in

the  $H_2$ - $H_2O$  atmosphere. Sintering of the fine Ni grains proceeded at 700°C in the  $H_2$ - $H_2O$  atmosphere.

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