STUDY ON THE NETWORK-FORMATION PROCESS IN THE SINTERING OF THE NiO-SDC COMPOSITE POWDERS PREPARED BY SPRAY PYROLYSIS METHOD

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ABSTRACT

Microstructures of NiO and samaria-doped ceria (SDC) composite particles synthesized by spray pyrolysis method and porous cermets sintered at various temperatures were observed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). It was found that the particles had hollow structures, and the element mapping analysis showed that cerium was concentrated in the vicinity of the particle surface and nickel was distributed uniformly inside the particles. SEM images of the sintered cermets showed that the composite powder started connecting at around 1100°C. TEM measurement of the sintered cermet at 1150°C indicated that SDC on the surface of each particle was connected at the early stage of sintering. Aggregation of nickel can be prevented by the presence of SDC between particles at the early stage of sintering, and Ni-SDC anode gives very low polarization of less than 40 mV with a high current density of 0.9 A/cm² at 800°C.

INTRODUCTION

Solid oxide fuel cell (SOFC) is one of the most attractive energy conversion system because of its high efficiency, low pollution, and fuel flexibility. Reduced temperature SOFCs operating at 600-800°C have been investigated extensively in recent years. The electrolyte material generally used for SOFCs is yttia-stabilized zirconia (YSZ), a solid oxide that conducts oxygen ions at high temperature of around 1000°C. However, reducing operating temperature with the current YSZ-based cells extremely increases the resistance of electrolyte. Therefore, it is necessary to reduce the resistance of the electrolyte. Alternative electrolytes with higher ionic conductivity than YSZ have been investigated for reduced temperature SOFCs. La(Sr)Ga(Mg)O₃₋₅ (LSGM), recently, has been proposed as an electrolyte for reduced temperature SOFCs (1,2).

Polarization losses on anode and cathode as well as ohmic loss in electrolyte become
higher as operating temperature decreases. It is, therefore, necessary to develop electrodes having low polarization at reduced temperatures. Ceria-based anodes have been proposed as possible reduced temperature SOFC anode materials (3,4). Samaria-doped ceria (SDC) is considered to be the most attractive material among the ceria-based compounds because of the highest ionic and electronic conductivity in reducing atmosphere (5). Ni is more active for electrochemical reaction of H₂O generation and has higher electronic conductivity than that of SDC, therefore, SDC is usually composed with Ni. Ni-SDC cermet anode gives high performance due to synergistic effect of enlarging reaction area and increasing paths for ionic and electronic conduction. Ni-SDC cermet is usually prepared by mixing and sintering SDC and NiO powders, which are larger than tenths of micrometers. If anode is composed of smaller SDC and Ni particles, electrochemical reaction area can be larger and anodic polarization can be lower than that of conventional anode. In order to create such a structure, NiO-SDC composite was applied as a starting powder instead of a mixture of NiO and SDC. In this paper, spray pyrolysis method was used to prepare NiO-SDC composite powder.

The composite particles prepared by using spray pyrolysis method are considered to be suitable for the raw materials of SOFC anode, and Ni-SDC cermet anodes for reduced temperature SOFCs using the composite powder prepared by spray pyrolysis method have been developed (6,7). From scanning electron microscopy (SEM), it was observed that Ni particles formed a skeleton with well-connected SDC particles finely distributed over Ni particle surfaces on Ni-SDC anode (6,7). However, the relationship between the composite powders and the network structure of the anode has not investigated so far. In this paper, transmission electron microscopy (TEM) of the anode powders and the cell performance tests were carried out and the effect of internal structure of the composite powders on the microstructure of the resulting cermet anode is discussed.

EXPERIMENTAL PROCEDURE

Spray Pyrolysis Synthesis

Anode material was synthesized by spray pyrolysis method, the details of which were precisely described in a previous paper (6). This apparatus consisted of an aqueous solution chamber with ultrasonic vibrators for mist generation, a carrier gas supplier (air was used as a carrier in this study), reaction furnaces, and a filter to capture the powders. Reaction furnaces were divided into four parts and their temperatures were set at 200, 400, 800, and 1000°C, respectively.

Anode material, as prepared, was composed of NiO and SDC. Atomic ratio of Ce:Sm was set for 80:20 to give the highest ionic conductivity (5). Volume ratios of Ni:SDC were set for 50:50 and 60:40 to give the highest electrode performance. The anode powders were prepared from an aqueous nitric acid solution of cerium nitrate hexahydrate, samarium nitrate hexahydrate, and nickel acetate tetrahydrate.

Microstructure analysis

The lattice structures of the powder were measured by X-ray diffraction (XRD, XRD-6000, Shimadzu), and the powder was confirmed to be composed of NiO and SDC. The microstructure variation from powders to cermet after fuel cell test was observed by SEM.
The composite powders were molded in polymer resin, followed by slicing at a thickness of 70-80 nm, which was then put on a Cu grid before TEM observation. The distributions of Ce and Ni in composite powders were analyzed by TEM with energy-dispersive X-ray spectroscopy (EDS, Noran Vantage System). The composite powder (Ni:SDC = 60:40 by volume) was sintered at temperatures in the range between 800 and 1280°C for 3 h after screen printing on lanthanum gallate based substrate (La0.9Sr0.1Ga0.8Mg0.2O2.85, LSGM). The morphology of the NiO-SDC sintered at 1150°C was observed by TEM-EDS (KEVEX SIGMA LEVEL2) after Ar ion etching for obtaining a thin sample.

**Single Cell Test**

LSGM was used as the electrolyte material. It was synthesized by common solid state reaction method from La2O3, SrCO3, Ga2O3, and MgO, followed by uniaxial and isostatic pressing at 49 and 294 MPa, respectively, and then sintered at 1500°C for 10 h. La6Sr14Co3 (LSCo) was used as the cathode, which is one of the most attractive materials for cathode (8,9). LSCo was also prepared by spray pyrolysis method from a solution composed of the stoichiometric amounts of La2O3, SrCO3, and Co2O3 dissolved in an aqueous nitric acid.

NiO-SDC composite powder (Ni:SDC = 50:50 by volume) was calcined at 1000°C for 24 h, followed by screen printing onto the electrolyte disks with 32 mm in diameter and 0.5 mm in thickness. After screen printing, it was sintered at 1250°C for 3 h. Then, LSCo calcined at 1000°C for 18 h was printed onto the other side of the electrolyte and sintered at 1100°C for 2 h. For the measurement of the anodic polarization, platinum wire of 0.3 mm φ as a reference electrode was wound around the cells, and was fixed with platinum paste, followed by calcination at 1000°C.

A glass ring was used as a sealing gasket at each compartment to avoid leakage of gases. The assembled cell was placed in the electric furnace. Hydrogen containing 3% steam and dry air were supplied to the anode and cathode compartment, respectively, at sufficiently high flow rates of 200 ml/min. The Ni-SDC/LSGM/LSCo cell (the electrode area: 2 cm²) was operated at 800°C. For the electrochemical characterization, the current-interruption method was used to separate the polarization of electrochemical reaction and IR drop from the total cell resistance.

**RESULTS AND DISCUSSION**

**Microstructures of NiO-SDC Composite Powders**

At first, the microstructures of the NiO-SDC composite powders synthesized by spray pyrolysis method were investigated by SEM and TEM. The powders were found to consist of spherical particles around 1 μm from the SEM images, which has been shown in a previous paper (7). Then, the internal structure of the composite particle was investigated to determine the relation between the microstructures of the prepared powder and the resulting anode. Figure 1 shows the TEM images and the distributions of Ce and Ni inside the composite particles before calcination.
It was found that the particles had hollow structures (Figure 1a). Oxygen was distributed all over the particles (Figure 1b), because all the compounds in the particles were oxides. Cerium was concentrated in the vicinity of the particle surface (Figure 1c). However, part of cerium seemed to be located inside the large particle at the left-hand side. It is considered to have open structure toward the outside of the particle. On the other hand, nickel was distributed uniformly inside the particles (Figure 1d). Therefore, the prepared particles were found to be core-shell type composite. A part of nickel also existed at the surface, which is expected to work as a catalyst for adsorption and dissociation of H$_2$.

**Microstructures of NiO-SDC Sintered on Substrate**

Figure 2 shows SEM images of NiO-SDC sintered on LSGM at various temperatures. Particles were merely deposited on the substrate and any connections of the particles were not observed by sintering at 1000°C (Figure 2a) or lower temperatures. The sintering at 1100°C caused the particles to start connecting to the neighboring particles (Figure 2b), and the sintering at 1200°C brought about the formation of the network structures (Figure 2c). The sample sintered at 1280°C showed wide channels and the shape of the original powder disappeared.
Figure 2. SEM images of NiO-SDC sintered on LSGM at (a): 1000°C, (b): 1100°C, (c): 1200°C, (d): 1280°C for 3 h.

The network-formation process on sintering is considered to affect the performance of the anode. Therefore, direct observation of the network-formation process is very important, and the microstructure and the distribution of NiO-SDC sintered at 1150°C were analyzed by TEM-EDS.

Figure 3 shows a high angle annular dark field (HAADF)-scanning transmission electron microscope (STEM) image. This measurement is sensitive to atomic mass and an element having larger atomic mass should be brighter than that having lower one. It was found that connecting domains between particles were brighter than internal particles, which indicated that SDC on the surface of each particle connected at the early stage of sintering.

Figure 3 also shows EDS images of oxygen, nickel, and cerium. Distribution of oxygen was confirmed to be equal to HAADF-STEM image. Nickel was distributed inside particles and connections between particles were not observed. On the other hand, cerium was distributed between particles, which corresponded to HAADF-STEM image. This result indicates that the aggregation of nickel can be controlled by SDC between particles at the early stages of sintering.
Performance of the Ni-SDC/LSGM/LSCo Cell

The performance of the Ni-SDC/LSGM/LSCo cell is shown in Figure 4. Though the maximum power density was slightly higher than 0.5 W/cm², it can be higher by using thinner electrolyte because the main part of the voltage loss was the ohmic loss of the electrolyte. The whole ohmic loss of the cell composed of the electrolyte, the anode, and the cathode was almost the same as the IR drop of LSGM speculated from the conductivity measured in a previous study (10). Figure 4b shows the variation of anodic polarization with current (IR free) measured at 800°C. Anodic polarization was lower than 40 mV even with a high current density of 0.9 A/cm². This performance was due to the network structure of Ni and SDC particles (10).

Figure 5 shows the SEM image of the anode after the cell performance tests. Brighter and darker particles were assigned as SDC and Ni, respectively. Creation of many interfaces...
between Ni and SDC particles leads to the higher activity of the anode. Some of Ni parts were observed behind SDC parts. When most of Ni parts come out to the surface of the particles, Ni particles may sinter with each other during cell operation. On the contrary, when all Ni parts stay inside of the particles, the activity of electrochemical reaction becomes lower. Therefore, the optimum amount of Ni on the surface of the anode should give low polarization. The volume ratio of Ni and SDC between 50:50 and 60:40, therefore, was considered to be the optimum ratio for both initial and long-term performances.

![Figure 4](image1.png)

**Figure 4.** The Ni-SDC/LSGM/LSCo cell performance at 800°C; (a) I-V and I-P curves, (b) anodic polarization (IR free).

![Figure 5](image2.png)

**Figure 5.** SEM image of Ni-SDC anode after cell test.

**CONCLUSIONS**

NiO-SDC composite powders were synthesized by spray pyrolysis method. TEM observations of the powders were carried out to show that cerium was concentrated at
around the surface of the particles, and nickel was distributed all over inside the particles. HAADF-STEM image and EDS images of the sintered cermet at 1150°C indicated that SDC on the surface of each particle connected at the early stage of sintering. Single fuel cell test with Ni-SDC anode, LSGM electrolyte, and LSCo cathode was carried out at 800°C, and the anodic polarization was lower than 40 mV at 800°C even with 0.9 A/cm². From the SEM image of Ni-SDC anode after cell test, the optimum amount of nickel was considered to appear on the surface of the anode to give an ideal microstructure.

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