CHARACTERIZATIONS OF SAMARIA DOPED CERIA ELECTROLYTE FOR SOFC PREPARED WITH FINE POWDER

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ABSTRACT

We have developed a SOFC with a low operating temperature of 800°C by using samaria doped ceria (SDC) as an electrolyte. SDC electrolyte has very high ionic conductivity (0.1 S/cm at 800°C) as compared with that of yttria stabilized zirconia (YSZ) electrolyte (<0.02 S/cm at 800°C). In this work, sintered SDC which has high mechanical strength was obtained by fine powdering process (<0.5 μm), and the microstructure of this electrolyte was observed by scanning electron microscopy (SEM). The ionic conductivity and the power density of cells were also evaluated.

INTRODUCTION

SDC electrolyte has very high ionic conductivity (0.1 S/cm at 800°C) as compared with that of YSZ electrolyte (<0.02 S/cm at 800°C), so that it is expected to be used at low temperatures as an electrolyte for the solid oxide fuel cell (SOFC), although some problems arise in the use of SDC as an electrolyte for the SOFC. For example, (I) a high sintering temperature to densify the SDC compact, (II) low mechanical strength compared with YSZ pellet, and (III) reduction at low oxygen partial pressures. In this paper, issues (I) and (II) were mainly investigated. The problem mentioned in (III) will be discussed in the near future.
Some research groups have reported that doped CeO$_2$ with high density was obtained at low sintering temperature using powders prepared by the oxalate coprecipitation method (1,2). The oxalate coprecipitation method is difficult to be commercialized because of its high cost. A new powder preparation process for SDC electrolyte is proposed in this report using CeO$_2$ and Sm$_2$O$_3$ as starting materials. It is known that the sintering of oxide materials for SDC is usually performed around 1650°C (3). However this sintering temperature is so high that oxide materials which can be easily sintered at low temperatures are required. Fine powders of CeO$_2$ and Sm$_2$O$_3$ were obtained by a new fine powdering process. As a result, SDC compacts were densified to the relative density (RD) of 97.5% at 1400°C and RD of 98.5% at 1500°C. The 3-point bending strengths were 184 MPa and 182 MPa, respectively.

In this study, the preparation of fine SDC powder (particle size < 0.5 μm) from CeO$_2$ and Sm$_2$O$_3$ is reported and its sinterability into SDC compacts is discussed. The mechanical strength of the SDC pellets and their electrical properties were also evaluated.

**EXPERIMENTAL**

**Sample preparation**

The powders of CeO$_2$ and SmO$_{1.3}$ with the molar ratio of 4:1 were mixed, and ground by a new grinding method for 1h. This new grinding method promotes the continuous dispersion of the powders by employing a horizontal grinding container with the agitator beads, and powders are ground into fine powders compared with that of conventional method employing a vertical grinding machine. Then these powders were calcined at 900°C or 1300°C for 10 hours. The calcined powder was ground again by the grinding machine and further ground in an autogrinding machine with an agate mortar and a pestle for 10 min.

The resulting powder was pressed into disks axially at 50 MPa and then isostatically at 200 MPa. Their pellet sizes were (a) 80 mm in diameter and 10 mm in thickness for samples for mechanical strength measurement, and (b) 25 mm in diameter and 2 mm in thickness for other measurements. Disks were sintered in the temperature range from 1400°C to 1650°C for 15 hours in air.

(a) The sintered bodies of 60 mm in diameter were cut into 10 disks (37 mm × 4 mm × 3 mm.)
The sintered bodies of 20 mm in diameter were polished to the thickness of 600 µm. Pt electrodes were deposited on both sides with the area of 0.2cm².

**Powder characteristics and sinterabilities of the compact**

Particle sizes of the CeO₂, Sm₂O₃ and SDC were measured by laser diffraction method. Grain sizes of the sintered SDC were observed by SEM.

**Mechanical strength of the sintered SDC**

The mechanical strengths of the sintered bodies were measured by the 3-point bending test at 25 °C.

**Electrical properties of SDC**

The ionic conductivities of various SDC electrolytes were measured in air between 600 and 800°C by an impedance analyzer. The I-V characteristics of various samples were measured at 800°C. Oxygen gas was fed to the cathode, and hydrogen gas with 3% steam was supplied to the anode as the fuel gas. The cells used in this measurement were as follows:

\[
\text{H}_2, \text{Pt} | \text{SDC} | \text{Pt}, \text{O}_2
\]

**RESULTS AND DISCUSSION**

**Powder characteristics**

Table 1 summarizes the characteristics of powders from the conventional and the new processes. Fig.1 and Fig.2 show particle size distribution of the powders from the conventional and the new processes, respectively.

In the case of the conventional process, the average particle size was 0.6 µm after grinding for 3h. On the other hand, by applying the new process, the average particle size was reduced to 0.34 µm. Furthermore, the particle size distribution range became narrow (0.14 µm ~ 0.58 µm).

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compared with that of the conventional process (0.24 ~ 1.94 μm).

Table 1  Powder characteristics of the SDC from the conventional and the new processes

|                         | Conventional process | New process |
|-------------------------|----------------------|-------------|
| Grinding method         | batch                | continuous  |
| Grinding time           | 3 h                  | 1 h         |
| Average particle size   | 0.6 μm               | 0.34 μm     |

Sinterabilities of the SDC

The sinterabilities of the resulting powder were examined by dilatometry, the densimetry and the grain size. Table 2 summarizes the heat-treatment conditions of the SDC pellets.

Figure 3 shows the relative densities of the various pellets by the conventional and the new processes as a function of the sintering temperature. In this research, the calcination at 900 °C was preferable to that at 1300 °C. The calcination at 1300 °C was so high that the surface energy of the SDC powder became low. The shrinkage rate of the SDC compacts was extremely small compared with the optimized condition in pellet 3.

As shown in Fig. 3, the compacts of the SDC powder prepared by the conventional process attained the density of ca. 95 % at 1650°C, but they were not densified more than 95 % at temperatures lower than 1650°C. On the other hand, compacts of the SDC powder prepared by the new process (calcined at 900 °C) were sintered to density of ca. 97.5 % at 1400°C. After sintering at 1500 °C or higher temperatures, although their relative densities were kept at 98.5 %, grain growth was observed. The sintering temperature of the compacts could be reduced as the starting powders became finer.

Figure 4 shows SEM photographs of the samples after heating at various sintering temperatures. After sintering at 1650°C for 15h (Fig. 4(a)), some pores were observed in and between the grains throughout the sample. The average grain size was about 33 μm.
In the case of the sintered bodies obtained by the new process (Fig.4(b)~(d)), pores were hardly observed throughout the sample. The average grain sizes were 15.9 μm (Fig.4(b)), 0.97 μm (Fig.4(c)) and 2.98 μm (Fig.4(d)), respectively.

Table 2  Heat-treatment conditions of the various SDC pellets

| Powder preparation method | Calcination condition | Sintering condition | Sample notation |
|--------------------------|-----------------------|--------------------|----------------|
| pellet 1                 | conventional process  | 1300°C, 10h        | 1650°C, 15h    | C 1300-1650   |
| pellet 2                 | new process           | 1300°C, 10h        | 1650°C, 15h    | N 1300-1650   |
| pellet 3                 | new process           | 900°C, 10h         | 1400°C, 15h    | N 900-1400    |
| pellet 4                 | new process           | 900°C, 10h         | 1500°C, 15h    | N 900-1500    |

**Mechanical strength of the SDC**

In Fig.4, 3-point bending strength of the pellets is also shown. The 3-point bending strength of the pellet 1 was 101 MPa. On the other hand the strength of the pellet 3 was 184 MPa. The bending strength of these SDC pellets increased with decreasing average grain size. Some researches have reported the relationship between the grain size and strength (4,5). In these literatures, mechanical strength increased with decreasing grain size because of the dispersion of stress and suppression of crack propagation.

**Ionic conductivity**

The conductivities in air of various SDC pellets were measured from 600°C to 800°C as expressed in an Arrhenius plot in Fig.5. Only small differences can be seen among four samples. Their ionic conductivities in air were about 0.11 S/cm at 800°C.

**I-V characteristics**

The results from single cell measurements with SDC electrolytes (600 μm) are shown in Fig.6. The maximum power densities were 187 mW/cm², 211 mW/cm², 291 mW/cm² and 221 mW/cm² for pellets 1 to 4, respectively. The open circuit voltages of these pellets were around 0.8 V.
In future, the cell performance will be improved by using passivation materials, making electrolyte thinner, and applying suitable electrodes.

CONCLUSIONS

SDC powder was prepared by using CeO₂ and Sm₂O₃ as starting powders. The average particle size of SDC powders was 0.34 μm, their particle size distribution became narrow as compared with that of the conventional process. The SDC compacts were densified to 97.5 % and 98.5 % at the sintering temperature of 1400°C and 1500°C, respectively. Their maximum 3-point bending strength was 184 MPa, and maximum power density was 291 mW / cm² for the 600 μm thick samples after sintering at 1400°C for 15 h.

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Particle size / $\mu$m

Fig. 1 Particle size distribution of the SDC powder prepared by conventional process.

Particle size / $\mu$m

Fig. 2 Particle size distribution of the SDC powders prepared by new process.

Fig. 3 Relationship between sintering temperatures and relative densities of sintered bodies.

N: new process, C: conventional process

( ) is the average particle size of SDC powders.
| Sample name | Microstructure | Average grain size | 3-point bending strength |
|-------------|----------------|--------------------|-------------------------|
| (a) Pellet 1 | C 1300 1650   | 33 μm              | 101MPa                  |
| (b) Pellet 2 | N 1300 1650   | 15.9 μm            | 139MPa                  |
| (c) Pellet 3 | N 900 1400    | 0.97 μm            | 184MPa                  |
| (d) Pellet 4 | N 900 1500    | 2.98 μm            | 182MPa                  |

Fig.4 SEM photographs, average grain sizes and 3-point bending strength of the various pellets.
Fig. 5 Arrhenius plots of the conductivities for SDC samples

Fig. 6 I-V and I-P characteristics of cells (at 800°C) with 600 μm thick electrolytes