Co-firing of LSM-GDC/GDC/NiO-GDC with addition of nano-GDC powder

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Co-firing of a La0.8Sr2.3MnO3-δ (LSM)-gadolinium doped ceria(GDC)/GDC/NiO-GDC cell is investigated by the application of a mixed GDC powder. A fine starting GDC powder is synthesized by the homogeneous precipitation process, using hexamethylenetetramine (HMT), and mixed with a commercially available GDC powder. Shrinkage behavior of the chemically prepared, the commercial, and the mixed GDC powders is examined by thermo-mechanical analysis (TMA), which suggests that the mixed powder has good sinterability and compatible shrinkage with electrodes. A LSM-GDC/GDC/NiO-GDC cell prepared by lamination of electrode and electrolyte green sheets is co-fired at 1300°C for 4 h. The prepared fuel cell gives an output power density of 0.35 W/cm² at 600°C.

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1. Introduction

Solid oxide fuel cells (SOFCs) have attracted considerable research interest, because they offer many advantages as energy conversion devices. Yttria-stabilized zirconia (YSZ) is a traditional electrolyte material of SOFCs operated at around 1000°C. However, such high operating temperature leads to some disadvantages, e.g., reactions between the components, poor thermal stability, high manufacturing cost, and lack of appropriate interconnecting and sealing materials. Recently, intermediate temperature SOFCs (IT-SOFCs) operating below 650°C have been investigated intensively. Cerium oxide (CeO₂) doped with Gd or Sm (GDC, SDC) has attracted much attention as an electrolyte for IT-SOFCs, because it has a higher oxygen-ion conductivity than yttria stabilized zirconia (YSZ) at lower temperatures.

The co-firing process is suitable for fabricating high-performance cells at low cost, because it is a simple process capable of producing a thin electrolyte. In this process, such cells are fabricated by lamination of cathode, electrolyte, and anode green sheets with subsequent co-sintering. However, fabrication of SOFC cells by the co-firing process is usually difficult, because the optimum sintering temperature of each component is different. The electrodes of SOFCs should be porous for the diffusion of fuel or oxygen gases, while the electrolyte must be dense enough to avoid direct reaction of fuel and oxygen. So, the shrinkage behavior of each material should be adjusted to avoid bending and/or peeling of the stacked cell.

Ohru et al. fabricated three-layered cells of LSM-YSZ/YSZ/NiO-YSZ by co-firing at 1300°C. They mixed carbon powder with cathode material to obtain optimum porosity at the sintering temperature and observed a high power density of 0.8 W at 1000°C for the co-fired cell.

As stated above, much interest has been focused on ceria based electrolytes to obtain good performance at relatively lower temperatures. However, it is difficult to make a dense doped ceria electrolyte below 1300°C because the melting point of pure CeO₂ is very high (> 2400°C).

In order to lower the sintering temperature of doped ceria, ultra-fine powders with nanometer size have been prepared by various precipitation methods using ammonia, urea, hydrazine hydrate, oxalate, and hexamethylenetetramine (HMT). It is, however, difficult to apply these powders as a starting material for co-firing process, because these powders are very fine and shows extremely large shrinkage compared to the electrode materials.

Liu et al. already reported that the co-firing of SOFCs with GDC electrolyte and LSCF cathode can be done using fine GDC powders prepared by chemical processes. They also pointed out that the co-firing process caused the diffusion of cobalt into the electrolyte which degraded the electric properties, such as the open circuit voltage. On the other hand, LaₓSrₓMnO₃₋δ cathode was commonly used for high temperature SOFC system with zirconia based electrolyte, although it has lower conductivity. While LSM has not been considered as a cathode material for IT-SOFC, it was better cathode than LSCF in terms of reactivity with GDC electrolyte.

In this work, we first prepared a fine GDC powder by the co-precipitation method using HMT and applied it as a starting material for electrolyte by mixing with commercially available GDC powder. As a cathode material, we selected LSM according to the report of Murray et al. (1)

2. Experimental

2.1 Synthesis and characterization of Ce₀.₉Gd₀.₁O₂₋₉.₅ powder

The fine powder of Ce₀.₉Gd₀.₁O₂₋₉.₅ (10 GDC) ceramics was prepared by a homogeneous precipitation method using hexamethylenetetramine as a precipitant as reported by Zhang et al. Ce(NO₃)₃-6H₂O (> 98.0% pure, Kishida Chemical Co., Ltd.), Gd(NO₃)₃-5.2H₂O (> 99.9% pure, Kojundo Chemical Lab Co., Ltd.) and hexamethylenetetramine ((C₂H₆)₂N₄, HMT, > 99.5% pure, Kishida Chemical Co., Ltd.) were used as starting mater-
A 250 ml solution of 0.08 M cerium and gadolinium nitrate solution was prepared with an atomic ratio of Ce/Gd = 9/1 and was added into 250 ml of 0.5 M hexamethylenetetramine solution. Then, the mixed solution was continuously stirred and aged at 40°C overnight and finally heated to 70°C for 1 h to induce precipitation. The resultant suspension was ultrafiltrated, and the recovered powder was washed five times with distilled water and twice with ethanol. After drying at 100°C overnight in air, the precursor powders were calcined at 300-700°C for 1-4 h. The thermal behaviors of the precursor powders were analyzed by differential thermal analysis/thermogravimetry (DTA/TG; THERMOFLEX TAS3300, Rigaku). Phase identification was studied by using X-ray diffractometry (XRD; RINT2000, Rigaku), and chemical composition analysis was performed using inductively coupled plasma (ICP; IRIS Intrepid II, Thermo electron). The morphologies of as-prepared and calcined 10 GDC nanoparticles were observed by transmission electron microscopy (TEM; H-800, Hitachi). The specific surface area of 10 GDC powder was evaluated by the Brunauer-Emmet-Teller method (BET; ChemBET-3000 Quantachrome) using nitrogen as the absorption gas.

2.2 Preparation of SOFC cell

The synthesized 10 GDC powder was mixed with commercially available 10 GDC powder (CGO 90/10 SY LSA, specific surface area: 11 m²/g, Anan Kasei Co., Ltd.) by using planetary ball milling with ethanol. The commercial, the mixed, and the pure synthesized nano-GDC powders were pressed by cold isostatic pressing (CIP) under 200 MPa into pellets with a diameter of 10 mm. These pellets were sintered in a temperature range of 1100-1300°C for 6 h in air. Sintering behaviors were studied in air using dilatometry (Thermo Plus TMA8310, Rigaku) with a heating rate of 5°C/min. The bulk density of sintered bodies was measured by Archimedes method in water. The relative density of the 10 GDC ceramics was calculated based on 7.28 g/cm³.

The mixed 10 GDC was used for the electrolyte material. A mixture of 65 mass% NiO (Kishida Chemical Co., Ltd.) and 35 mass% commercial GDC was used for the anode material. A mixture of La₀.₆Sr₀.₄MnO₃₋δ (LSM) and 50 mass% commercial GDC was used as cathode material. La₀.₆Sr₀.₄MnO₃₋δ powder was prepared by solid state reaction using lanthanum, strontium and manganese carbonate, followed by planetary ball milling with ethanol.

All cells were fabricated from green sheets prepared by the doctor blade method as illustrated in Fig. 1. Tape casting slurries were prepared by mixing ceramics powder, dispersant, binder, plasticizer, defomer, and solvent, and then ball milling. The slurry was treated using a hybrid mixer (HM-500, KEYENCE) to remove entrapped air bubbles, and was cast on polymer tape by the doctor blade method. The casting gap was adjusted to 100-200 μm. After casting, the prepared sheets were dried under well-controlled temperature and humidity conditions using a LH21-11P (Nagano Science Co., Ltd.).

Circular sheets with a diameter of 16 mm were sprayed with the 20% water-EtOH solution and were then laminated and co-pressed at 45 MPa. In order to obtain the final thickness of each layer, one cathode sheet, one electrolyte sheet, and three anode sheets were stacked. The thickness of cathode, electrolyte, and anode was 70 μm, 50 μm, and 300 μm, respectively. The binder was burned out by slow heating up to 500°C with a heating rate of 2°C/min. After holding at 500°C for 2 h, the three layered cell was sintered at 1300°C for 4 h with a heating rate of 5°C/min.

2.3 Characterization

A silver paste (TR–6182, Tanaka Precious Metal) was painted on the cathode of the specimens as a current collector and dried at 100°C. Fuel-cell performances were measured using a Solartron 1255B and SI1287 system. Hydrogen gas humidified with water at 30°C and air were used as the fuel and oxidant, respectively, with a flow rate of 50 ml/min. The microstructure of the cell after the measurement of cell performance was examined by scanning electron microscopy (SEM; JSM 5600, JEOL).

3. Results and discussion

3.1 Characterization of GDC powder

The XRD profile in Fig. 2(a) shows that the as-prepared powder clearly has the major diffraction lines of a fluorite structure, indicating that the powder is crystalline even immediately after precipitation. The diffractions of the powder became sharper depending on the calcination temperatures, and a highly crystalline powder was obtained at 700°C as seen in Fig. 2(d).

Figure 3 is the DTA/TG curves observed for the as-prepared GDC powder. A broad endothermic reaction up to 200°C accompanying weight loss could be due to the evaporation of water. The major weight losses and exothermic peak occurred up to 400°C, indicating that the burning of an organic component derived from hexamethylenetetramine. As stated above, nanocrystalline 10 GDC powder could be directly formed without heat treatment during the HMT-based homogeneous precipitation process. The chemistry of the formation of ceria in solution is quite complicated, involving a three-step chemical reaction: the oxidation of Ce⁴⁺ to Ce⁶⁺, the hydration of Ce⁶⁺, and the release of H²⁺ ions from the cerium hydroxide complex. The precipitation rate can be controlled by adjusting the hydrolysis rate of HMT into formaldehyde and ammonia. In this way, very fine powders with a narrow size distribution could be obtained. However, the ammonia introduced from the HMT possesses a reducing character; it causes the reduction of Ce⁶⁺ to lower valance states and metal cerium before the oxidation of Ce⁴⁺, indicating that the composition of the prepared powder may be different from the starting one. In order to suppress these effects,
a high cation concentration and controlled hydrolysis of HMT were used to promote \( \text{Ce(OH)}_4 \) formation and suppress the reduction of \( \text{Ce}^{3+} \). ICP analysis revealed that the powder has a \( \text{Ce}:\text{Gd} \) ratio of 89:11 when the starting composition was \( \text{Ce}:\text{Gd} = 90:10 \).

The effect of calcined temperature on the specific surface area of the GDC powder is shown in Table 1. The specific surface area decreased with increasing calcination temperatures. This behavior could be derived from the growth of fine crystallites and hard aggregate formation during calcination. The GDC powder calcined at 300°C has the highest specific surface area of 150 m²/g. This powder also shows small weight loss based on DTA/TG analysis, indicating that the burning of organic materials occurred in the temperature range of 250 to 400°C. Residual organics led to very poor sinterability of the GDC powder due to the release of gas from the organics and subsequent cracking during sintering. The GDC powder suitable for sintering was prepared by calcinations at 500°C based on the results of XRD, DTA/TG, ICP, and BET analysis. Figure 4 shows a TEM micrograph of the chemically prepared powders and the powder calcined at 500°C for 1 h. The primary particle size was confirmed to be about 5 nm in diameter. Electron diffraction data revealed that the powder was crystalline in the as-precipitated stage, which is compatible with the XRD data.

3.2 Sintering behavior of GDC

The chemically synthesized nano-10 GDC powder was mixed with commercial 10 GDC powder. Figure 5 shows the TEM micrograph of the mixed powder. The agglomerates of nanoparticles shown in white circles can be observed around the sub-micron GDC particles. Figure 6 shows the sintering behavior of the pressed compacts of nanopowders, mixed powders, and commercially available powders as observed by TMA. Shrinkage of the pure synthesized nano-GDC started below 500°C and continued up to 1100°C, although those of the other two samples started around 850°C and continue up to 1300°C. Table 2 shows the relative density of the samples sintered at 1100°C for 6 h.

| Table 1. Specific Surface Area of Chemically Prepared GDC Powder as a Function of Heat Treatment Temperature |
|----------------------|----------------|----------------|----------------|
| Calcination temperature (°C) | 300 | 500 | 700 |
| Specific surface area (m²/g) | 150 | 130 | 63 |

Fig. 2. XRD profiles of the 10 GDC powder prepared by homogeneous precipitation method. (a) As-prepared GDC nano-powder, (b) GDC powder calcined at 300°C for 1 h, (c) GDC powder calcined at 500°C for 1 h, (d) GDC powder calcined at 700°C for 4 h.

Fig. 3. DTA/TG curves for the as-dried GDC powder prepared by homogeneous precipitation method.

Fig. 4. TEM micrograph of the GDC powder prepared by homogeneous precipitation method. (a) As-prepared GDC nano-powder, (b) GDC nano-powder calcined at 500°C for 1 h.

Fig. 5. TEM micrograph of the mixed GDC powder.
densities of synthesized and mixed GDC are greater than 90%. This result suggested that the chemically synthesized nano-powder has good sinterability with extremely large shrinkage, while the mixed GDC powder shows moderate shrinkage and improved sinterability compared to the commercial powder.

In order to co-fire an anode-electrolyte-cathode three layer structure, the sinterability of the electrolyte components should be better than that of the electrodes. Extremely large shrinkage of the pure nano-powder, however, cannot match the other electrode components and causes cracks or peeling. Figure 7 shows the shrinkage behavior of the mixed GDC electrolyte and the cathode and anode materials. The mixed GDC powder could be a good material for co-firing with electrodes because of its smaller shrinkage and improved sinterability.

3.3 Fabrication of SOFCs by Co-firing

Based on the results, the mixed 10 GDC powder was selected as a starting material for electrolyte green sheets. All the green sheets were flexible, defect-free, and easy to handle. The sheet thickness was controlled in a range of 50–300 μm. LSM powder for the cathode was mixed and milled with GDC by planetary ball milling to control the sintering behavior. The lamination of these sheets was carried out by the spraying of 20% water-EtOH and pressing with a pressure of 45 MPa. A flat and crack free three layered cell was successfully formed and then co-fired at 1300°C for 4 h.

3.4 Performance of Co-fired cell

Figure 8 shows the power densities and voltage as functions of the current densities and temperature for the co-fired cell. The peak power density was 79, 154, 248, 350 mW/cm² at 450, 500, 550, 600°C, respectively. This power density is rather high compared to that reported for cells with the YSZ electrolyte system, although the other SOFCs with GDC electrolyte usually show a much higher power when other cathodes such as LSCF were applied. It is, however, interesting that the cell prepared in this work demonstrates the usefulness of

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**Table 2. Relative Density of GDC Ceramics Sintered at 1100°C for 6 h**

<table>
<thead>
<tr>
<th>GDC Powder</th>
<th>Synthesized nano-powder</th>
<th>Commercial powder</th>
<th>Mixed* powder</th>
</tr>
</thead>
<tbody>
<tr>
<td>Green Body (%)**</td>
<td>41</td>
<td>58</td>
<td>58</td>
</tr>
<tr>
<td>Sintered Body (%)**</td>
<td>93</td>
<td>87</td>
<td>94</td>
</tr>
</tbody>
</table>

* mixed powder; A mixture of 10% nano-powder and 90% commercial powder.

** The relative density of the 10 GDC ceramics was calculated based on 7.28 g/cm³.

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![Fig. 6. Shrinkage behavior of the GDC powders at a heating rate of 5°C/min. (a) Mixed GDC powder; 90% commercial powder + 10% synthesized nano-powder calcined at 500°C, (b) Commercial GDC powder, (c) Chemically prepared GDC nano-powder calcined at 500°C.](image6)

![Fig. 7. Shrinkage behavior of the ceramic green sheets. (a) LSM-GDC cathode, (b) NiO-GDC anode, (c) Mixed GDC electrolyte; 90% commercial powder + 10% synthesized nano-powder.](image7)

![Fig. 8. Performance of the three layered cell co-fired at 1300°C. Cell voltage and power density as functions of current density and operating temperature.](image8)

![Fig. 9. SEM micrograph of the co-fired cell after cell performance measurement.](image9)
the LSM electrode even at 600°C. Figure 9 shows a SEM micrograph of the co-fired cell after measurement of cell performance. It can be observed that the cathode and anode were porous and that the electrolyte was dense. Furthermore, no cracks or evidence of degraded structure could be observed.

4. Conclusions

Preparation of a LSM-GDC/GDC/NiO-GDC cell was carried out by the co-firing process using chemically prepared nano-GDC powder. The prepared cell demonstrates a rather good power density of 0.35 W/cm² at a current density of 1 A/cm². Although the cell performance was not as large as that of LSCF-GDC/GDC/NiO-GDC prepared by a step-by-step process, this study affords a new and simple fabrication method for making designed structures through a one-firing process. Further improvement on the selection of cathode electrode is in progress.

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