Preparation of Ce$_{0.8}$Gd$_{0.2}$O$_{1.9}$ Powder Using CeO$_2$ Powder and Gd Precipitation and Effect of CoO doping on Sintering

Soo-Man Sim$^{†}$
School of Materials Science and Engineering, Hongik University, Sejong 30016, Korea
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ABSTRACT

Ce$_{0.8}$Gd$_{0.2}$O$_{1.9}$(GDC20) powder was prepared from a mixture of submicron-sized CeO$_2$ powder and Gd precipitates using ammonium carbonate ((NH$_4$)$_2$CO$_3$) as a precipitant. The mixture was calcined at 700°C for 4 h followed by ball-milling that resulted in the GDC powder with an average particle size of 0.46 µm. The powder had a very uniform particle size distribution with particle sizes ranging from 0.3 µm to 1 µm. Sintering of undoped GDC samples did not show a relative density of 99.2% until the temperature was increased to 1500°C, whereas GDC samples doped with 5 mol% CoO exhibited a significant densification at lower temperature reaching a relative density of 97.6% at 1100°C and of 98.8% at 1200°C.

Key words : SOFC electrolyte, GDC, CeO$_2$ powder, CoO doping, Sintering

I. Introduction

Gd-doped CeO$_2$(GDC) has received much attention as an intermediate-temperature solid oxide fuel cell electrolyte due to its higher ionic conductivity than that of YSZ. However, the synthesis of GDC by using Ce and Gd oxide powders requires sintering at high temperatures (>1500°C) for a long time since densification is very difficult.$^{3}$ Therefore, powder synthesis methods such as oxalate coprecipitation method,$^{4,5}$ hydrate precipitation method,$^{6}$ ammonium carbonate coprecipitation method,$^{7}$ citrate method,$^{8}$ glycine-nitrate method,$^{9}$ etc. have been employed to prepare a dense GDC at low temperatures. Metal carbonate precipitates obtained from ammonium carbonate coprecipitation method undergo less agglomeration during the drying process than that derived from hydrate method. So the ammonium carbonate precipitation method allows us to minimize particle agglomeration in the calcined powders. Also, the precipitates have the advantages of excellent sinterability in that they have a relatively low decomposition temperature and leave no decomposition products, allowing low-temperature calcination and high reactivity for the final oxides.$^{10}$

To obtain high-density GDC at low temperatures, there is a method of using transition metal oxides of Co, Mn, Fe, etc. as a sintering aid, in addition to the synthesis of powders with excellent sinterability.$^{10,11}$ Among these oxides, Co oxides are known to lower the sintering temperatures most effectively and to enable sintering at 850°C ~ 1000°C. However, no studies have been attempted on preparation of GDC by the addition of sintering aids to submicron-size commercial powders, while most results of the studies on preparation of GDC by using sintering aids were obtained from nano-powders and powders synthesized by the solution method. In the present study, we have synthesized GDC20 (Ce$_{0.8}$Gd$_{0.2}$O$_{1.9}$) powder from the slurry of a mixture of submicron-sized CeO$_2$ powder and Gd precipitates precipitated by ammonium carbonate ((NH$_4$)$_2$CO$_3$); and investigated its thermal decomposition and phase-forming behavior, calcination behavior and the effect of 5 mol% CoO doping on sintering.

2. Experimental Procedure

CeO$_2$ powder (99.99%, Kojundo Chem.), 0.5M Gd nitrate (Gd(NO$_3$)$_3$·6H$_2$O, 99.9%, Sigma-Aldrich) solution, and 1M ammonium carbonate ((NH$_4$)$_2$CO$_3$, Sigma-Aldrich) solution as a precipitant were used for the synthesis of GDC20 powder.

A slurry was prepared by slowly injecting Gd nitrate solution into an attrition jar containing CeO$_2$ powder and ZrO$_2$ balls (Φ3 mm) while being stirred at a low speed. The ammonium nitrate solution (2.5 times of the moles of Gd) was slowly added into the jar. The jar was rotated at 500 rpm and the milling was continued until complete precipitation. The resulting slurry, a mixture of CeO$_2$ powder and Gd precipitates, was filtered with a filter press (YT30 142HW, Millipore), and subjected to repeated washing with deionized water and ethanol, followed by drying at 80°C for 12 h. Then the dried powder was calcined at 700°C for 4 h followed by ball-milling for 2 h using ZrO$_2$ balls (Φ10 mm) and then allowed to dry naturally with continuous stirring. For CoO doping, the powder was mixed with Co nitrate...
(Co(NO₃)₂·6H₂O, >98%, Aldrich), a sintering aid, in ethanol. Then the mixture was ball milled for 2 h with ZrO₂ ball (Φ 10 mm), dried at room temperature, and calcined at 300°C in air for 4 h. The amount of CoO corresponded to 5 mol% of GDC20 (Ce₀.₈Gd₀.₂O₁.₉). The powder was mixed with a binder (0.5 wt%, PVB, Aldrich), uniaxially pressed into pellets (Φ 15 mm) at 50 MPa and subsequently isostatically pressed at 200 MPa. The pellets were held at 600°C for 2 h to remove the binder and sintered at 1100°C ~ 1500°C in air for 4 h.

Thermal decomposition behavior of GDC powder was investigated at a heating rate of 5°C/min in air up to 1000°C by TG/DTA (TG-DTA 2000, MAC Science). For phase analysis, the powders were heated at 400°C ~ 1000°C in air for 2 h and examined by XRD (CuKα, M03XHF, MAC Science). The sintered samples were also analyzed. Specific surface area of the calcined powder was measured by the multi-point BET method (BELSORP-mini II, BEL Japan Inc.). The average equivalent particle size (D_{BET}, nm) was calculated using the following equation.

\[
\frac{D_{BET}}{d_{th}} = \frac{6 \times 10^3}{S_{BET}}
\]

where \(d_{th}\) represents the theoretical density of GDC20, and \(S_{BET}\) the specific surface area (m²/g). Bulk density of the sintered sample was determined according to the Archimedes principle. Relative density was calculated from the theoretical density of GDC (7.22 g/cm³) and the bulk density. Particle size distribution was measured with a laser diffraction particle size analyzer (SALD-2001, Shimadzu). The morphology of the powder and microstructures of the sintered samples were observed with a SEM (FE-SEM, FEI).

3. Results and Discussion

Figure 1(a) shows a TG/DTA curve of Gd precipitates obtained under the same conditions of GDC powder synthesis. The Gd precipitate is presumably a basic carbonate of Gd(OH)CO₃·2.5H₂O which is known to form at 2.5 molar ratio of (NH₄)₂CO₃ to Gd³⁺ ions. The endothermic peak at ~100°C accompanied by a weight loss was due to evaporation of the adsorbed water, while the weight loss up to ~650°C was caused by removal of the crystal water and decomposition of the carbonate. The total weight loss was found to be 39.7%. Fig. 1(b) shows a TG/DTA curve of the mixture of CeO₂ powder and Gd precipitates; only thermal decomposition behavior of the Gd precipitates was observed because CeO₂ powder was present along with the precipitates. The precipitates showed a gradual weight loss up to ~650°C without any endothermic peak unlike in Fig. 1(a). Since CeO₂ is mostly present in the precipitate, the weight loss due to decomposition of Gd precipitates was only 15.6%, and all of the precipitates were changed to Gd₂O₃ at ~650°C with almost no weight change.

Figure 2 shows XRD patterns of the GDC powders calcined for 2 h. The as-prepared powder exhibited only CeO₂ diffraction peaks of the fluorite structure since the Gd precipitates were in the form of amorphous carbonate. The intensities of diffraction peaks were greatly increased at 1000°C as the crystal growth was accelerated with increasing the calcination temperature. Also, only CeO₂ diffraction peaks were observed at all calcination temperatures because main Gd₂O₃ peaks overlapped with CeO₂ peaks and a small amount of Gd₂O₃ contained in the sample. Figure 3 shows XRD patterns of the samples doped with 0 and 5 mol% of CoO and sintered at 1400°C for 4 h. Both samples revealed CeO₂ diffraction peaks of higher intensity than those calcined at 1000°C. In the doped sample, there was no diffraction peaks due to Co oxide observed. The diffraction peaks of the sintered samples are considered to correspond to GDC. CeO₂ solid solution can form during the calcination process because of high reactivity of decomposed nano-crystalline Gd₂O₃ particles. It has been reported that a mixture of Ce and Gd oxides forms a solid solution at temperature above 1500°C, while co-precipitate of Ce and Gd forms a solid solution at relatively low calcination temperature.

Table 1 shows specific surface areas and particle diameters (D_{BET}) of the GDC powder calcined at various tempera-
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The specific surface area of the powder was drastically decreased from 97.6 m$^2$/g to 7.5 m$^2$/g due to particle growth as the calcination temperature was increased from 400°C to 1000°C. Since the particle growth was slow at 600°C and 700°C even after calcination up to 4 h the specific surface areas of the powders calcined for 4 h showed little difference from those calcined for 2 h. The calculated BET particle size based on spherical and nonporous particles represents primary particle size. The primary particle size increased from 8.5 nm to 21.8 nm when the temperature was changed from 400°C to 700°C, and the particle size increased greatly to 110.6 nm at 1000°C because of the acceleration in particle growth above 800°C. Such particle growth can also be seen from the large increase in the intensity of diffraction peaks at temperatures above 700°C as shown in Fig. 2.

Figures 4 (a) and (b) are SEM photographs of CeO$_2$ powder and calcined GDC powder, respectively, showing almost similar particle sizes and shapes. CeO$_2$ powder of Fig. 4(a) consists of spherical particles with an average particle size of 0.46 μm where nano-sized primary particles are agglomerated. In GDC powder of Fig. 4(b), the primary particles were grown to the size similar to the BET particle size (22.5 nm) in the calcination process, and severely agglomerated. According to the particle size distribution in Fig. 5, the calcined powder had an average particle size of 0.47 μm with a distribution from 0.3 μm to 1 μm in particle sizes, showing a

Table 1. Surface Areas and Particle Sizes of GDC Powders Calcined at Various Temperatures

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Time (h)</th>
<th>Specific surface area (m$^2$/g)</th>
<th>Calculated $D_{BET}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>2</td>
<td>97.6</td>
<td>8.5</td>
</tr>
<tr>
<td>600</td>
<td>2</td>
<td>76.6</td>
<td>10.8</td>
</tr>
<tr>
<td>700</td>
<td>2</td>
<td>76.3</td>
<td>19.9</td>
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<td>4</td>
<td>38.1</td>
<td>21.8</td>
</tr>
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<td>2</td>
<td>19.4</td>
<td>42.9</td>
</tr>
<tr>
<td>1000</td>
<td>2</td>
<td>7.5</td>
<td>110.6</td>
</tr>
</tbody>
</table>
partial sintering occurred in the pure GDC samples at the present study (94.8%), only 86%, which was considerably lower than that found in powder of 0.3 μm in particle size, the density at 1400°C was to be excellent as compared with that from the mixed oxide of the GDC powder prepared in the present study was found to have a very uniform distribution. When the calcined powder was ball-milled for 2 h, the powder showed a slight reduction in average particle size to 0.46 μm but the same particle size distribution as that of the calcined powder.

Figure 6 shows relative densities and open porosities of the GDC samples sintered at 1100°C ~ 1500°C for 4 h. Since partial sintering occurred in the pure GDC samples at 1100°C, the density was only 62.0%. After a gradual increase due to slow densification between 1100°C and 1400°C, the density became 99.2% at 1500°C. Sinterability of the GDC powder prepared in the present study was found to be excellent as compared with that from the mixed oxide method. The density of GDC20 prepared from CeO₂ and Gd₂O₃ powders of 0.5 μm in particle size by Ma et al. was 73% at 1300°C, which was lower than 80.3% in the present study, and became 97% at 1600°C. Although Torrens et al. also reported the density of 98% at 1650°C with the GDC20 powder of 0.3 μm in particle size, the density at 1400°C was only 86%, which was considerably lower than that found in the present study (94.8%).

For the GDC powder doped with 5 mol% CoO, densification was completed at 1100°C because of the excellent sinterability, a density of 97.6% was already achieved, and a density of 98.8%, which was similar to the density of the pure GDC at 1500°C (99.2%), was obtained only at 1200°C. However, at temperatures above 1300°C, a tendency of gradual decrease in density was exhibited. Open pores in the doped samples completely disappeared at 1100°C, whereas the open pores in the pure GDC samples disappeared at 1400°C. This indicates that CoO doping enhances densification. Even though the present study did not reach the results for doping nano-powder with CoO, the study suggests that preparation of dense GDC at low temperatures is possible by using submicron-sized CeO₂ powder. Kleinlogel and Gauckler obtained a density higher than 99% at 900°C by doping GDC20 nano-powder with 5 mol% CoO, while Nicholas and De Jonghe also reported the density of 93.3% at 800°C by doping GDC10 (Ce₀.₉₋ₓGdₓO₁.₉₅) nano-powder with 5 mol% CoO. Recently, Hari Prasad et al. have obtained the density of 97% at 850°C through doping GDC10 powder prepared by hydrate precipitation method with 3 mol% Co.

Figures 7 (a), (b), and (c) are SEM photographs of the pure GDC samples sintered at 1100°C, 1300°C and 1500°C, respectively. In the pure GDC, no sintering occurred at 1100°C (Fig. 7(a)), and grains began to form by particle coalescence and many pores of irregular forms were present between particles at 1300°C (Fig. 7(b)). At 1500°C, however, densification was completed, resulting in pore-free microstructure as shown in Fig. 7(c). Large pores of irregular forms disappeared completely and grains were grown up to ~5 μm in size.

Figures 8 (a), (b), and (c) are SEM photographs of the samples doped with 5 mol% CoO and sintered at 1100°C, 1300°C and 1500°C, respectively, illustrating the effect of CoO doping on GDC sintering. In the doped samples, densification was nearly completed at 1100°C, reaching the density of 97.6% with well-developed grains of ~0.5 μm in size, and the density reached 98.5% at 1300°C with grains grown to a size of ~3 μm. Although the density was rather decreased when the sintering temperature was raised to 1500°C, grain growth was accelerated so much that the grains were significantly increased to ~20 μm in size.

Many reports have shown that the addition of cobalt oxides enhances sintering of GDC due to liquid phase formed with impurities or increased grain boundary mobility by dissolution of Co in GDC. However, it could not be ascertained by the present results. The reduction of densities with increasing the sintering temperatures can be attributed to the pores at 1500°C which were not visible at 1100°C as shown in Fig. 8(a)). These were presumably produced by volatilization of CoO, which is known to have a very high volatility above 1400°C.
4. Conclusions

Mixtures of submicron-sized CeO$_2$ powder and Gd precipitates were calcined at 700°C for 4 h followed by ball-milling that resulted in GDC20 powder with an average particle size of 0.46 μm. The powder consisting of spherical particles had a very uniform particle size distribution with particle sizes ranging from 0.3 μm to 1 μm. GDC sample doped with 5 mol% CoO exhibited an excellent sinterability allowing a density as high as 97.6% at 1100°C. The density of 98.8% was obtained only at 1200°C, which was lower by as much as 300°C from 1500°C at which pure GDC has the density of 99.2%. The doped GDC grains (~ 0.5 μm in size at 1100°C) were grown to ~ 20 μm at 1500°C due to the enhanced grain growth by CoO doping, whereas the grains of pure GDC grew to only ~ 5 μm at 1500°C.

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