Preparation of $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ 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

(Received August 10, 2015; Revised October 1, 2015; Accepted October 4, 2015)

ABSTRACT

$\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ (GDC20) powder was prepared from a mixture of submicron-sized CeO_2 powder and Gd precipitates using ammonium carbonate $((\text{NH}_4)_2\text{CO}_3)$ 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

1. 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 ($>1500^\circ\text{C}$) for a long time since densification is very difficult.¹⁾ Therefore, powder synthesis methods such as oxalate coprecipitation method,^{2,3)} hydrate precipitation method,⁴⁾ ammonium carbonate coprecipitation method,⁵⁻⁷⁾ 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.⁶⁾

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.¹⁰⁻¹³⁾ Among these oxides, Co oxides are known to lower the sintering temperatures most effectively and to enable sintering at 850°C ~ 1000°C. How-

ever, 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 ($\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$) powder from the slurry of a mixture of submicron-sized CeO_2 powder and Gd precipitates precipitated by ammonium carbonate $((\text{NH}_4)_2\text{CO}_3)$; 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 ($\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 99.9%, Sigma-Aldrich) solution, and 1M ammonium carbonate $((\text{NH}_4)_2\text{CO}_3)$, 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 ($\Phi 3\text{ mm}$) 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 ($\Phi 10\text{ mm}$) and then allowed to dry naturally with continuous stirring. For CoO doping, the powder was mixed with Co nitrate

[†]Corresponding author : Soo-Man Sim

E-mail : smsim@hongik.ac.kr

Tel : +82-44-860-2518 Fax : +82-44-862-2774

($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, >98%, Aldrich), a sintering aid, in ethanol. Then the mixture was ball milled for 2 h with ZrO_2 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 ($\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$).

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 (CuK_α , 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.

$$D_{\text{BET}} = \frac{6 \times 10^3}{d_{\text{th}} \times S_{\text{BET}}} \quad (1)$$

where d_{th} represents the theoretical density of GDC20, and S_{BET} the specific surface area (m^2/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/cm^3)³⁾ 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 $\text{Gd}(\text{Gd}(\text{OH})\text{CO}_3 \cdot 2.5\text{H}_2\text{O})$ which is known to form at 2.5 molar ratio of $(\text{NH}_4)_2\text{CO}_3$ to Gd^{3+} ions.⁶⁾ 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 CeO_2 powder and Gd precipitates; only thermal decomposition behavior of the Gd precipitates was observed because CeO_2 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 CeO_2 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 Gd_2O_3 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 CeO_2

Fig. 1. TG/DTA curves of as-prepared powders at a heating rate of 5°C/min in air: (a) Gd precipitate and (b) GDC precipitate.

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 CeO_2 diffraction peaks were observed at all calcination temperatures because main Gd_2O_3 peaks overlapped with CeO_2 peaks and a small amount of Gd_2O_3 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 CeO_2 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. CeO_2 solid solution can form during the calcination process because of high reactivity of decomposed nano-crystalline Gd_2O_3 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.¹⁴⁾

Table 1 shows specific surface areas and particle diameters (D_{BET}) of the GDC powder calcined at various tempera-

Fig. 2. XRD patterns of as-prepared GDC powders calcined at various temperatures.

Fig. 3. XRD patterns of GDC samples doped with 0 and 5 mol% CoO sintered at 1400°C for 4 h.

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

Temperature (°C)	Time (h)	Specific surface area (m^2/g)	Calculated D_{BET} (nm)
400	2	97.6	8.5
600	2	76.6	10.8
	4	76.3	10.9
700	2	38.1	21.8
	4	37.0	22.5
800	2	19.4	42.9
1000	2	7.5	110.6

Fig. 4. SEM micrographs of (a) as-received CeO_2 and (b) calcined GDC powders.

tures. The specific surface area of the powder was drastically decreased from $97.6 \text{ m}^2/\text{g}$ to $7.5 \text{ m}^2/\text{g}$ 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 $0.46 \mu\text{m}$ 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 $0.47 \mu\text{m}$ with a distribution from $0.3 \mu\text{m}$ to $1 \mu\text{m}$ in particle sizes, showing a

Fig. 5. Particle size distributions of calcined and milled GDC powders.

Fig. 6. Relative densities and open porosities of GDC samples doped with 0 and 5 mol% CoO sintered at various temperatures for 4 h.

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 CeO_2 and Gd_2O_3 powders of 0.5 μm in particle size by Ma et al.¹⁴ 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.¹⁵ 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 CeO_2 powder. Kleinogel and Gauckler¹⁰ obtained a density higher than 99% at 900°C by doping GDC20 nano-powder with 5 mol% CoO, while Nicholas and De Jonghe¹² also reported the density of 93.3% at 800°C by doping GDC10 ($\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$) nano-powder with 5 mol% CoO. Recently, Hari Prasad et al.¹³ 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.¹⁰⁻¹³ 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.¹⁴

Fig. 7. SEM micrographs of undoped GDC samples sintered at (a) 1100°C, (b) 1300°C, and (c) 1500°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 ($\sim 0.5 \mu\text{m}$ in size at 1100°C) were grown to $\sim 20 \mu\text{m}$ at 1500°C due to the enhanced grain growth by CoO doping, whereas the grains of pure GDC grew to only $\sim 5 \mu\text{m}$ at 1500°C.

Fig. 8. SEM micrographs of GDC samples doped with 5 mol% CoO sintered at (a) 1100°C, (b) 1300°C, and (c) 1500°C.

REFERENCES

1. H. Inaba and H. Tagawa, "Review Ceria-Based Solid Electrolytes," *Solid State Ionics*, **83** 1-16 (1996).
2. K. Higashi, K. Sonoda, H. Ono, S. Sameshima, and Y. Horata, "Synthesis and Sintering of Rare-Earth-Doped Ceria Powder by Oxalate Coprecipitation Method," *J. Mater. Res.*, **14** [3] 957-67 (1999).
3. I.-D. Han, K.-Y. Lim, and S.-M. Sim, "Preparation and Sintering Characteristics of Gd-doped CeO_2 Powder by Oxalate Co-Precipitation," *J. Korean Ceram. Soc.*, **43** [10] 666-72 (2006).
4. D. Hair Prasad, H.-R. Kim, J.-S. Park, J.-W. Son, B.-K. Kim, H.-W. Lee, and J.-H. Lee, "Superior Sinterability of Nono-Crystalline Gadolinium Doped Ceria Powders Synthesized by Co-Precipitation Method," *J. Alloys Compd.*, **495** 238-41 (2010).
5. J.-G. Li, T. Ikegami, Y. Wang, and T. Mori, "10 mol%

- Gd₂O₃-Doped CeO₂ Solid Solutions via Carbonate Coprecipitation: A Comparative Study," *J. Am. Ceram. Soc.*, **86** [6] 915-21 (2003).
6. A. I. Y. Tok, L. H. Luo, and F. Y. C. Boey, "Carbonate Coprecipitation of Gd₂O₃-doped CeO₂ Solid Solution Nanoparticles," *Mat. Sci. & Eng.*, **A383** 229-34 (2004).
 7. Y.-C. Yoo, B.-J. Chung, and S.-M. Sim, "Preparation and Sintering Characteristics of Ce_{0.8}Gd_{0.2}O_{1.9} Powder by Ammonium Carbonate Co-Precipitation," *J. Korean Ceram. Soc.*, **49** [1] 118-23 (2012).
 8. R. O. Fuentes and R. T. Baker, "Structural, Morphological and Electrical Properties of Gd_{0.1}Ce_{0.9}O_{1.95} Prepared by a Citrate Complexation Method," *J. Power Sources*, **186** 268-77 (2009).
 9. L. D. Jadhav, M. G. Chourashiya, K. M. Subhedar, A. K. Tyagi, and J. Y. Patil, "Synthesis of Nanocrystalline Gd Doped Ceria by Combustion Technique," *J. Alloys Compd.*, **470** 383-86 (2009).
 10. C. M. Kleinlogel and L. J. Gauckler, "Sintering and Properties of Nanosized Ceria Solid Solutions," *Solid State Ionics*, **135** 567-73 (2000).
 11. G. S. Lewis, A. Atkinson, B. C. H. Steele, and J. Drennan, "Effect of Co Addition on the Lattice Parameter, Electrical Conductivity and Sintering of Gadolinia-doped Ceria," *Solid State Ionics*, **152-153** 567-73 (2002).
 12. J. D. Nicholas and L. C. De Jonghe, "Prediction and Evaluation of Sintering Aids for Cerium Gadolinium Oxide," *Solid State Ionics*, **178** 1187-94 (2007).
 13. D. Hari Prasad, S. Y. Park, H. Ji, H.-R. Kim, J.-W. Son, B.-K. Kim, H.-W. Lee, and J.-H. Lee, "Cobalt Oxide Co-doping Effect on the Sinterability and Electrical Conductivity of Nano-Crystalline Gd-Doped Ceria," *Ceram. Int.*, **38S** S497-S500 (2012).
 14. J. Ma, T. S. Zhang, L. B. Kong, P. Hing, and S. H. Chan, "Ce_{0.8}Gd_{0.2}O_{2.5} Ceramics Derived from Commercial Submicron-Sized CeO₂ and Gd₂O₃ Powders for Use as Electrolytes in Solid Oxide Fuel Cells," *J. Power Sources*, **132** 71-76 (2004).
 15. R. S. Torrens, N. M. Sammes, and G. A. Tomsett, "Characterisation of (CeO₂)_{0.8}(GdO_{1.5})_{0.2} Synthesised Using Various Techniques," *Solid State Ionics*, **111** 9-15 (1998).