

Preparation of porous M_2O_3 -doped ceria particles by controlled co-precipitation

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A controlled co-precipitation technique was used to synthesize porous M_2O_3 -doped ($M = \text{Gd}, \text{Sm}$) CeO_2 submicrometer particles with a narrow size distribution. Various precipitates in spherical or oval shape were obtained. The particles were made from a nitrate/urea solution by consideration of three aspects: the addition sequence of M-nitrate into Ce-nitrate/urea solution, the concentration ratio of M/Ce in the nitrate solutions, and the effect of seeding. Heterogeneous and secondary precipitations of fine particles and the cross-section of the particles were analyzed by electron microscopes (SEM and TEM) equipped with energy dispersive X-ray spectroscopy (EDS). The differential precipitation rate of Ce- and M-nitrates in the urea solution, and the specific surface area of the synthesized powder calcined at temperatures up to 750 °C are also reported.

Key words: Ceria, Precipitation, Microstructure, Powder.

Introduction

Porous ceria (CeO_2) and its oxide compounds, such as gadolinia doped ceria (GDC) or samaria doped ceria (SDC) are useful as catalytic materials of fuel reformers for solid oxide fuel cells (SOFCs) [1-7]. But dense doped ceria is currently used as an electrolyte of SOFCs because its ionic conductivity is higher than that of 8 mol% yttria-doped zirconia (8YSZ) at intermediate temperature [8-10].

A ceria-based electrolyte should be dense and homogeneous for a SOFC application, to prevent fuel leakage and maximize power output. Submicrometer mono-sized spherical particles are therefore favored for the ease of densification of the oxide electrolyte made by tape-casting, spin coating, or screen printing [11]. However, the particles before densification are porous and useful for surface controlled catalytic reactions.

Several synthesis methods have been reported on how to prepare GDC or SDC particles. These methods include a glycine-nitrate process [12], a hydrothermal process [13, 14], co-precipitation [15-17], or a forced precipitation method with various additives, such as citric acid [18], for preparation of fibrous particles. Usually, the required quantities of starting precursors are separately dissolved in water, then co-precipitated with additives [17, 18] at 70 °C or higher temperatures. However, none of the reports have considered the stoichiometry of the Gd/Ce or Sm/Ce ratio and porosity in synthesized GDC or SDC particles which are produced by the above-mentioned precipitation methods. The chemical composition of the products might differ

from the composition of the precursor mixture.

Based on our previous studies [18-21], a homogeneous precipitation process was proposed to obtain single phase, high quality, monodispersive In_2O_3 or Y_2O_3 particles. The process was modified and adapted to prepare GDC or SDC particles in this study in order to control the precipitation rate and particle size. However, the dopant, either Gd or Sm, was added and apparently changed the shape of the precipitates and reaction kinetics. The formation mechanism of various particle morphologies is important and needs an in-depth investigation.

Shaw and Bordeaux reported that urea undergoes hydrolysis in an aqueous solution, yielding ammonium NH_4^+ ions, OH^- and CO_2 [22]. The other reactant, Ce nitrate underwent hydration in water and to form hydrated precipitates with the composition, for instance, $(\text{Ce}, \text{Sm})_2(\text{OH})_2(\text{CO}_3)_2 \cdot \text{H}_2\text{O}$ [17]. The precipitates appeared with different shapes [23], which were formed due to the ratio of Sm/Ce in the precursor solution.

The reaction kinetics of these ions, Ce, Gd and Sm, in a urea solution are different with the same processing conditions, for instance, the concentration of added species and the solution temperature. The control of the shapes and the compositional content of the precipitates for any multiple cation system should be more complex than those of single-component system. Therefore, several issues are concerned in this study. The composition variation and the morphological evolution, mainly the size and shape, of the precipitates are carefully investigated and discussed concerning the sequence of doping and differential precipitation rate of Gd and Ce-species.

Experimental Procedure

Pure, Gd-doped, and Sm-doped CeO_2 powders were

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synthesized by a controlled precipitation method conducted in aqueous solutions. The starting materials were cerium (III) nitrate hexahydrate ($Ce(NO_3)_3 \cdot 6H_2O$, 99.5%, ACROS, USA), gadolinium (III) nitrate hexahydrate ($Gd(NO_3)_3 \cdot 6H_2O$, 99.5%, ACROS, USA), and samarium (III) nitrate hexahydrate ($Sm(NO_3)_3 \cdot 6H_2O$, 99.5%, ACROS, USA). Urea (CH_4N_2O , 99.5%, ACROS, USA) was used to adjust the pH to a basic condition when the mixture was heated to the temperatures higher than 65 °C. A solid precipitate was found after aging for no more than 24 h. The suspension was mixed until the end of the synthesis. The residual concentration of metallic ions (Ce^{3+} , Gd^{3+}) in the supernatant of the synthesis solution was analyzed by inductive coupled plasma spectroscopy (ICP-OES, JOBIN YVON, Ultima 2000, France).

Before microscopic analysis, the precipitates after washing (3 times by de-ionized water) were dried at 105 °C for 30 minutes (min), then dispersed in de-ionized water to form a stable suspension. A drop of the suspension was dried on a carbon film or silicon wafer for morphological observation to measure the particle size (field emission scanning electron microscopy, FESEM-1530, LEO Instrument, Cambridge, UK). A transmission electron microscope (TEM 200, Tecnai G², Philips) equipped with EDS was also used to investigate the morphologies of the particles on a carbon film. A dual-beam focused ion beam (DB-FIB, FEI Noviq-200 NanoLab, USA) was used to prepare cross-sectional samples for TEM-EDS analysis. The particles (~320 nm in diameter) were sliced to a uniform thickness from core to shell. The spot size of the electron beam for TEM/EDS was ~10 nm and the pitch between two analyzed points was ~25 nm. Normally, as-synthesized particles will be damaged by the electron beam of a TEM or DB-FIB. The calcination temperature of the particles was set at 350 °C, which is high enough to dehydrate and limit the effect on the composition of Gd/Ce in the particle.

Average particle size was statistically measured from at least 150 particles from SEM micrographs. The Gd and Sm contents in calcined particles were measured by EDS (EDAX Corp., USA). All EDS measurement conditions in the SEM and TEM were kept constant.*¹ The SEM/EDS analysis was also calibrated by a standard sample (prepared from a commercial 20 mol% Gd doped CeO_2 (20GDC) powder purchased from

Table 1. Formulation and synthesis conditions of the particles with specified Gd (or Sm) and Ce contents

Sample No.	Concentration*			Aging time (h)	Abbreviation
	$Ce(NO_3)_3$	$Gd(NO_3)_3$	$Sm(NO_3)_3$		
1-1	25.00	X	X	1-24	100 Ce
1-2	X	25.00	X	1-10	100 Gd
1-3	X	X	25.00	1-10	100 Sm
2-1 (1-1)	25.00	X	X	7-24	0 GDC
2-2	23.75	1.25	X	7-24	5 GDC
2-3	22.50	2.50	X	7-24	10 GDC
2-4	21.25	3.75	X	7-24	15 GDC
2-5	20.00	5.00	X	7-24	20 GDC
2-6	18.75	6.25	X	7-24	25 GDC
3	20.00	X	5.00	7-24	20 SDC

*The unit of the nitrate concentration is 10^{-3} mol/kg

#In all cases a urea solution of 150 ± 10^{-3} mol/kg was added and aged at 80 °C.

NEXTECH materials (Lewis Center, OH, USA).

Table 1 lists the symbols of the formulation and synthesis conditions of pure Ce, GDC, or SDC samples. In order to investigate the formation behavior of the precipitates, controlled precipitation with seeding was conducted. Pure Ce-, Gd-, and Sm-nitrate solutions with urea (the samples 100 Ce, 100 Gd and 100 Sm) were first aged at 80 °C in a bath for 60 min, then a second freshly-prepared nitrate/urea solution was added into the previous one. A total of 4 series of samples, abbreviated as Ce_Gd, Ce_Sm, Gd_Ce and Sm_Ce were prepared.

Results

Three preliminary experiments were first carried out to depict the precipitation results of pure Ce-, Gd-, and Sm-nitrates with urea (samples 100 Ce, 100 Gd and 100 Sm, respectively). Figs. 1(a)-1(c) show the morphology of the precipitates aged at 80 °C for 7 h. Oval-shape precipitates in lengths of submicrometer to several micrometers were obtained from the pure Ce-solution. However, uniform submicrometer spheres were seen from the precipitates of Gd- and Sm-solutions. The size of both Gd- or Sm-particles was ~250 nm.

Effects of Gd-dopant

Cases 2-3~2-6 in Table 1 show that 10~25 GDC (10~25 mol% Gd-doped CeO_2) form spherical particles, but not for case 2-2, as shown in Fig. 2. The particle morphology changed from an oval-shape to spherical when the Gd-nitrate content was higher than 5 mol% (see case 2-3 in Fig. 2(c)). As a result, the processing boundary to obtain a spherical precipitate was between 5 GDC and 10 GDC. Similar results were observed in Sm-doped CeO_2 series.

Figure 3 shows the Gd content of the xGDC samples

1. The operation conditions for SEM were kept as the following, working distance (the distance between the top surface of the sample to the lower surface of the pole piece of the magnetic lens) was fixed at 8.5 mm, the tilt angle at 15 °, X-ray count rate within 2500 ± 150 cps, collection time 100 s, and ~5 nm electron beam size. The conditions for TEM, working distance ~2.3 mm, sample tilt at 10 °, signal collection at the rate of ~1200 cps, collection time lasting for 60 s and beam size of ~2 nm.

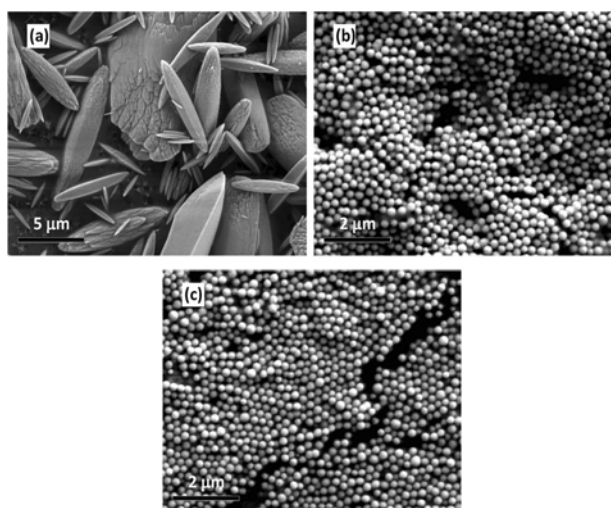


Fig. 1. SEM micrographs of as-synthesized particles from (a) Ce-, (b) Gd-, and (c) Sm-solutions aged at 80 °C for 7 h.

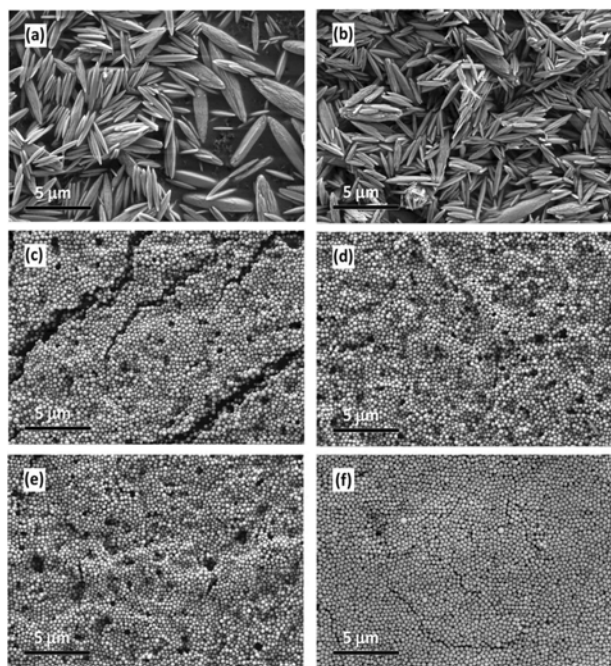


Fig. 2. SEM images of the particles prepared from (a) 0 GDC (pure Ce-ppt), (b) 5 GDC, (c) 10 GDC, (d) 15 GDC, (e) 20 GDC, and (f) 25 GDC solutions aged at 80 °C for 7 h.

measured by quantitative SEM-EDS. Two data of 20 SDC either prepared by the urea decomposition process in this study or “20 GDC by a solid state reaction” are also plotted in the diagram. The results reveal that the average Gd content of all xGDC-precipitates was higher than the initial Gd/Ce ratio in the precursor solutions. The EDS analysis results of 20 SDC-precipitates were similar to these of 20 GDC-precipitates as well.

In order to reveal the co-precipitation behavior of xGDC by urea, the residual Gd and Ce contents in the supernatant of a 15 GDC solution by ICP-OES are shown in Fig. 4. The original content of Ce and Gd was

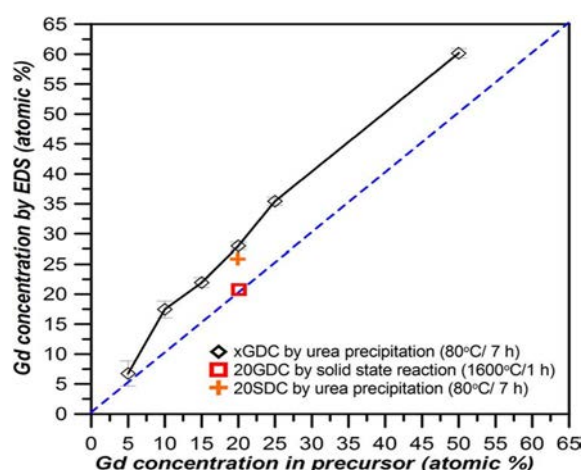


Fig. 3. EDS analysis of xGDC ($x = 5-50$) precipitates. All the precipitates were obtained from the specific solution aged at 80 °C for 7 h. The results of 20 SDC prepared by precipitation or by a solid state reaction are also plotted in the diagram. The error bar represents standard deviation of the EDS results.

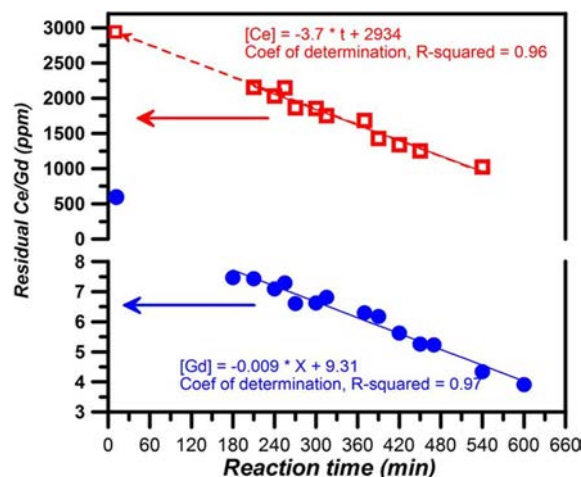


Fig. 4. Residual Ce and Gd concentrations in the 15 GDC solution aged at 80 °C. The original concentration of Ce and Gd is 2980 ppm and 590 ppm, respectively.

2980 ppm and 590 ppm in the solution, respectively. The co-precipitation behavior of the Ce in the solution follows a zero-order reaction with a reaction rate of -220 ppm/h at 80 °C. The Gd content precipitated at a rate of -0.5 ppm/h after aging for 3 h. Gd precipitated at a relatively low rate compared to that of Ce-species.

Growth of spheres with seeds

Controlled precipitation tests with various seeds were carried out. The samples 1-1, 1-2 and 1-3, aged at 80 °C for 1 h were used as the seeds. Figures 5(a) and 6(b) show the precipitates of pure Ce-nitrate/urea mixture aged at 80 °C for 2 h similar to Fig. 1(a) aged for 8 h. Oval-shape precipitates were obtained and the length and width of the Ce-precipitates are around 10 μm and 3.0 μm, respectively. For the Ce_Gd sample aged for another 2 h (Figs. 5(c) and 5(d)), a bimodal size distribution of the precipitates was obvious. SEM-

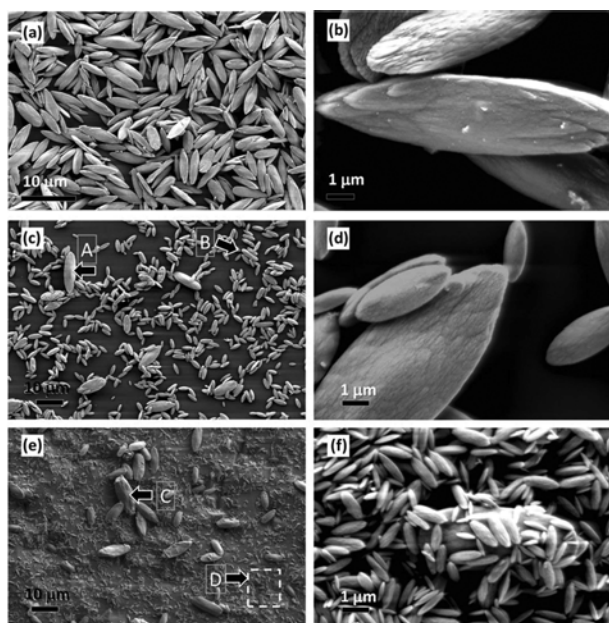


Fig. 5. SEM images of the precipitates sampled from (a) and (b) Ce-nitrate/urea solution aged at 80 °C for 2 h (100 Ce/2 h), (c) and (d) Ce-nitrate/urea solution aged at 80 °C for 1 h, then added Gd-nitrate/urea solution with further aging for 1 h (Ce_Gd/2 h), (e) and (f) Ce-nitrate/urea solution aged at 80 °C for 1 h, then added Sm-nitrate/urea solution with further aging for another 1 h (Ce_Sm/2 h).

EDS analysis revealed that the Ce/Gd ratio of the larger ones (larger than 10 μm in length, marked “A”) and smaller ones (smaller than 5 μm in length, marked “B”) was 95.1/4.9 and 62.1/37.9, as well as with a standard deviation of 7% and 5%, respectively. But, the SEM-EDS result of the same sample (Ce_Gd) from the large and small particles in a 500 $\mu\text{m} \times 500 \mu\text{m}$ region was 71.9/28.1 (Ce/Gd).

Similar controlled precipitation was obtained in the sample Ce_Sm (Figs. 5(e) and 5(f)). But the size dissimilarity between larger Ce_Sm particles and smaller ones was more obvious than that of Ce_Gd. The EDS result (Ce/Sm ratio) of the bigger ones (larger than 10 μm in length in Fig. 6(e), marked “C”) was 88.4/11.6 and smaller ones (smaller than 1 μm in length, marked “D”) was 46.8/53.2, as well as a composition deviation of 12% and 11%, respectively. The EDS (Ce/Sm) result of the case Ce_Sm in a general region (500 $\mu\text{m} \times 500 \mu\text{m}$, including large and small particles) was 49.5/50.5.

Figure 6(a) shows an SEM image of the precipitates of 100 Gd solution aged for 2 h at 80 °C. Only uniform submicrometer spheres were obtained. Spheres were also observed in the Gd_Ce solution aged for a total of 2 h (Fig. 6(b)). EDS analysis of the particles in the “E” rectangular region in Fig. 6(b) revealed the ratio of Ce/Gd to be 29.7/70.3. The outer shell of the Gd_Ce particles was Ce-species, which was not thick enough to limit the X-ray intensity from its Gd-core. This is why the EDS result is rich in the Gd ingredient. By

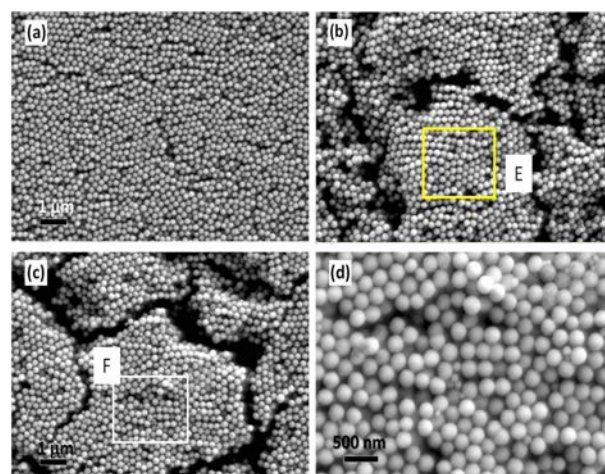


Fig. 6. SEM images of the precipitates sampled from (a) Gd-nitrate/urea solution aged at 80 °C for 2 h (100 Gd/2 h), (b) Gd-nitrate/urea solution aged at 80 °C for 1 h, then added Ce-nitrate/urea solution with further aging for another 1 h (Gd_Ce/2 h), (c) and (d) Gd_Gd/2 h.

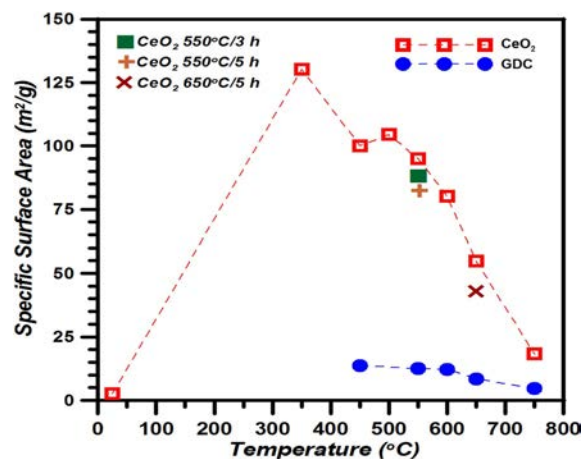


Fig. 7. Specific surface area of two calcined particles, 100 Ce and 15 GDC, plotted against the calcination temperature.

replacing the added Ce-solution with a Gd-solution aged at 80 °C for an additional 1 h (Gd_Gd aged for 2 h, Fig. 6(c)), submicrometer precipitates and tiny spherical precipitates (80 nm in size) were observed. Secondary precipitation of the tiny spheres from the Gd-solution was evident to grow new Gd particles if the Gd content in the solution becomes over-saturated again.

In the Sm-system, the samples 100 Sm, Sm_Ce, and Sm_Sm all aged for 2 h showed similar morphological results (not shown here) as those reported previously (Fig. 6). The EDS analysis of Sm_Ce aged for 2 h (all spheres) showed that the Ce/Sm ratio equaled to 24.8/75.2.

Two powders, 100 Ce and 15 GDC, were analyzed to reveal the specific surface area (Fig. 7) as a function of calcination temperature and porous morphologies (Figs. 8 and 9). The 100 Ce sample calcined at 350 °C showed the highest surface area of 130 m²/g, which was significantly higher than that of the 15 GDC powder.

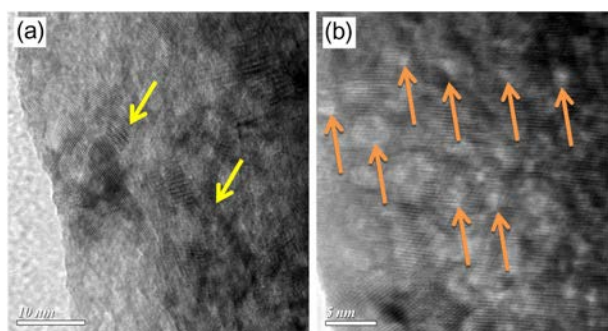


Fig. 8. High resolution TEM images of CeO_2 oval particles (100 Ce) calcined at 450°C for 1 h, showing (a) nano-crystals and (b) nano-pores pointed-out by arrows.

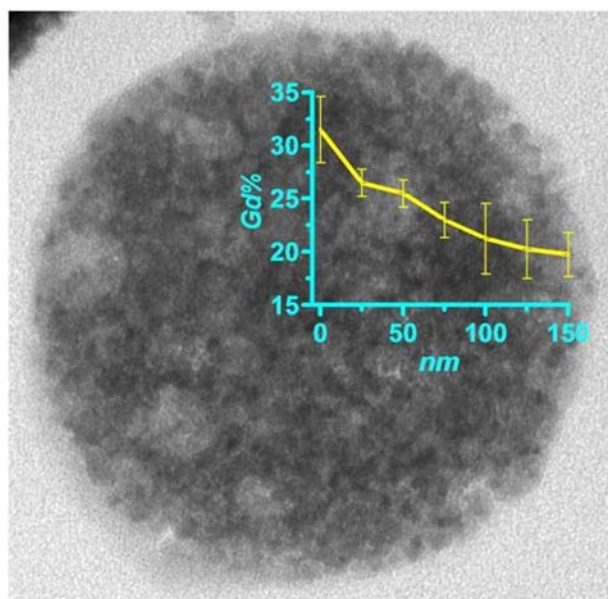


Fig. 9. High resolution TEM image illustrating the cross section of one 15 GDC particle and the Gd content distribution along the radius. The particle was synthesized from the 2-4 solution aging at 80°C for 7 h, then calcined at 350°C for 15 min.

Besides, the surface areas decrease dramatically when the calcination temperature was greater than 600°C .

High resolution images (Fig. 8) of the 100 Ce powder revealed partial crystallized and porous characters. The morphologies were formed due to dehydration and the threshold of surface diffusion of Ce species. But the 15 GDC particle (Fig. 9) was denser and showed a dilution of the Gd content from the center to the surface.

Discussion

Differential precipitation rate

This study has shown that the particle morphology of pure Gd- or Sm-ppt is spherical, but Ce-ppt is not (Fig. 2). A spherical Ce-ppt is also possibly made from a $\text{Ce}(\text{SO}_4)_2\text{-H}_2\text{SO}_4$ aqueous solution by forced hydrolysis at 90°C [23], or from a $\text{Ce}(\text{NO}_3)_3\text{-H}_2\text{O}$ solution via a simple polymer-assisted hydrothermal method at 140°C

[24]. However, the literature does not report the detailed composition change of these co-precipitated CeO_2 particles.

Spherical particles can be obtained when the amount of Gd-nitrate dopant is higher than 5 mol% in a xGDC solution, as shown in Fig. 2. This implies that the existence of enough Gd ions would change the co-precipitation behavior of the xGDC solution. By using SEM-EDS to analyze the Gd content of the dried precipitate from the xGDC solution aged at 80°C for 7 h, the Gd/Ce content is always higher than the ratio of Gd/Ce in the corresponding precursor solution. A possible reason is the precipitation rate of Gd in the nitrate/urea solution, especially in an early stage of the precipitation, if this is higher than that of Ce in its nitrate/urea solution aged at 80°C . As a result, spherical Gd seeds grow first, followed by the precipitation of the species with the ratio of Gd/Ce reducing to 0.5 : 220 when the aging process is more than 3 h (Fig. 4).

Evidence of a differential precipitation rate is provided by monitoring the residual Ce^{4+} and Gd^{3+} in the 15GDC solution at 80°C (Fig. 4). The result shows that almost all Gd^{3+} ions in the solution are consumed to a low level (< 8 ppm) in 3 h. On the other hand, the precipitation of Ce^{3+} and Gd^{3+} follows zero-order reaction kinetics with a precipitation rate of 220 ppm/h. The zero-order reaction is possibly controlled by the urea decomposition rate [19, 20]. The composition analysis results (Fig. 3) revealed that the average Gd content of as-calcined 15 GDC-spheres (aged for 7 h) is consistent to that by the ICP test, i.e. 26 mol%.

The other evidence is reported from the TEM/EDS result of one cross sectional image of a 15 GDC particle shown in Fig. 9. The composition distribution reveals that the average Gd content in 15 GDC particles (averaged from four particles with a similar diameter) decreases gradually from the core to the shell. The evidence supports the idea that the Gd in the nitrate/urea solution is precipitating faster than the Ce in the early stage of the synthesis.

Heterogeneous precipitation

Controlled precipitation tests with various seeds were carried out to clarify the influence of the seeding and the co-precipitation of Ce with Gd-species. The formation of the Ce_Gd and Gd_Ce precipitates was taken as the case and summarized in Fig. 10, which shows three possible morphological evolutions.

The first case is shown in the top of Fig. 10 that a Ce-nitrate/urea solution aged at 80°C for 1 h was prepared as the seeds, then fresh Gd-nitrate/urea solution was added into the suspension (i.e. aqueous solution with Ce-seeds), aged for another 1 h, as the samples Ce_Gd/2 h and Ce_Sm/2 h were prepared. No spherical precipitates, but oval-shape precipitate in a bimodal size are observed, as shown in Figs. 5(c) to 5(f).

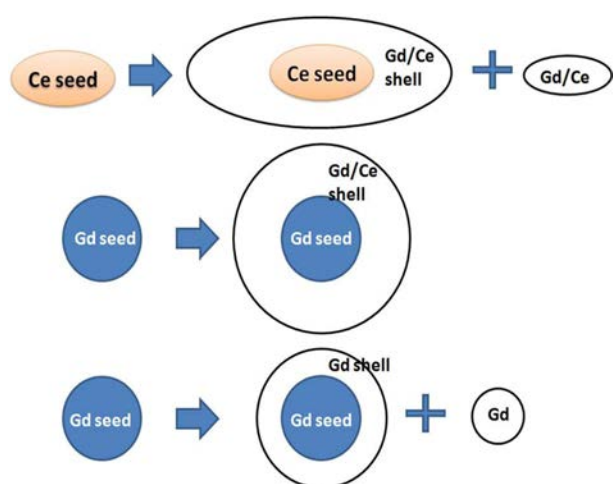


Fig. 10. Schematic diagram illustrating three possible reaction products of oval and spherical particles growing in a xGDC (or xSDC) solution. (top) Ce_{Gd}, (med) Gd_{Ce}, and (bottom) Gd_{Gd}.

The composition disparity of smaller and larger particles in Fig. 5 has implied the precipitation of the two species is controlled by the relative reaction rate. For Ce_{Gd}/2 h particles, about 5 mol% Gd content was detected in large oval particles (larger than 10 μm in length) and 38 mol% Gd in small ones (smaller than 5 μm in length). Similar conditions of size and composition disparity were also noted in the Ce_{Sm}/2 h particles. Presumably, the smaller particles were generated from secondary precipitation. When Ce (of > 90%) and Gd (of < 10%) concentrations were co-precipitated without any pre-existent spherical seeds and the concentration of Gd was less than 10 mol%, Ce-precipitation dominated the growth behavior of the precipitates.

Gd_{Ce} and Sm_{Ce} were shown as the apogee of the previous case. Gd or Sm-precipitates (as the seeds) were first prepared as the seeds for the 100 Ce solution. Heterogeneous growth on the spherical Gd- or Sm-seeds dominated and demonstrated a constant spherical growth, as for the case shown in Fig. 6(b). A comparable case (100 Gd/2 h in Fig. 6(a)) shows spherical precipitates from the Gd-nitrate/urea mixture aged at 80 $^{\circ}\text{C}$ for 2 h. All particles were spherical, and no secondary precipitation (i.e. small particles) was found, indicating that the Ce-precipitate is only formed on the spherical Gd seeds.

Two SEM-EDS results of the Gd_{Ce}/2 h, (1) about 30 mol% Ce was detected (as “E” in Fig. 6(b)), supporting the precipitation of Ce-species in the second-hour of aging; (2) the difference of average particle size of the precipitates, 230 nm for 100 Gd/2 h and 270 nm for Gd_{Ce}/2 h, implying the latter case having more Ce precipitation in the second-hour of aging. When the aging period of the Gd_{Ce} solution was extended to 12 h, the content of Ce in Gd_{Ce}/12 h increases to 47 mol% and the shape of Ce/Gd-precipitates

remained spherical. The evidence strongly indicates heterogeneous growth and the important role of pre-existent seeds.

Furthermore, smaller spheres in the Gd_{Gd} solution can be observed due to secondary precipitation. The addition of a Gd-nitrate/urea mixture into the aged Gd-nitrate/urea solution resulted in not only large particles growing from 230 nm to 250 nm in average size, but some smaller particles are also found in Fig. 6(d). Those tiny particles can be the result of the freshly prepared Gd/urea solution. Similar precipitation behavior was seen also in the cases of Sm_{Ce}/2 h and Sm_{Sm}/2 h.

Conclusions

In this study, the precipitation behavior and morphological evolution of porous CeO₂ particles with different dopants have been investigated. A Gd- or Sm-nitrate/urea solution formed spherical particles, which can be used as the seeds to grow either Gd_{Ce} or Sm_{Ce} particles in mono-sized conditions. This heterogeneous growing mechanism not only produced particles with a core-shell structure, but also formed secondary precipitation (for instance, Gd_{Gd}/2 h and Ce_{Gd}/2 h), which is controlled by the relative concentration of Gd vs. Ce in the precursory solution.

TEM-EDS analysis of the cross section of Gd-doped (15 GDC) particles revealed porous characteristics, and a higher Gd content (~32%) at the core region than that of the shell. The EDS result supports the idea that the precipitation reaction of Gd in the nitrate/urea solution is much faster than that of Ce in the early stage of the reaction (3 h at 80 $^{\circ}\text{C}$).

Other than spherical precipitates, oval-precipitates of CeO₂ and GDC particles with little Gd-content in a nitrate/urea solution (i.e., ≤ 5 GDC cases) and without spherical seeds can be prepared from the 100 Ce solution and co-precipitation of the Ce/Gd nitrate solution. The relative concentration of Gd/Ce, the presence of seeds, and the sequence of doping greatly dominate the growth behavior and morphologies of GDC and SDC precipitations.

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References

1. G.J. Offer, J. Mermelstein, E. Brightman, N.P. Brandon, J. Am. Ceram. Soc., 92 (2009) 763-780.
2. S. Lee, J.M. Vohs, R.J. Gorte, J. Electrochem. Soc. 151 (2004) A1319-13-23.
3. T.J. Huang, J.F. Li, J. Power Source, 173 (2007) 959-964.
4. T.J. Huang, J.F. Li, J. Power Source, 181 (2008) 62-68.

5. L. Blum, W.A. Meulenberg, H. Nabielek, R.S. Wilckens, *Int. J. Appl. Ceram. Technol.*, 2 [6] (2005) 482-492.
6. M. Mogensen, K. Kammer, *Annu. Rev. Mater. Res.*, 33 (2003) 321-331.
7. X. Zhang, S. Ohara, H. Chen, T. Fukui, *Fuel*, 81 (2002) 989-996.
8. V. Esposito, E. Traversa, *J. Am. Ceram. Soc.*, 91 (2008) 1037-1051.
9. S. Omar, E.D. Wachsman, J.L. Jones, J.C. Nino, *J. Am. Ceram. Soc.*, 92 (2008) 2674-2681.
10. V.V. Kharton, F.M.B. Marques, A. Atkinson, *Solid State Ionics*, 174 (2004) 135-149.
11. L.H. Luo, A.I.Y. Tok, F.Y.C. Boey, *Mat. Sci. Eng. A*, 429 (2006) 266-271.
12. R. Peng, C. Xia, Q. Fu, G. Meng, D. Peng, *Mat. Lett.*, 56 (2002) 1043-1047.
13. Y. Wang, T. Mori, J.G. Li, Y. Yajima, *Sci. Technol. Adv. Mater.*, 4 (2003) 229-238.
14. S. Zha, C. Xia, G. Meng, *J. Power Sources*, 115 (2003) 44-48.
15. J. Li, T. Ikegami, T. Mori, T. Wada, *Chem. Mater.*, 13 (2001) 2913-2920.
16. J. Li, T. Ikegami, Y. Wang, T. Mori, *J. Am. Ceram. Soc.*, 86 (2003) 915-921.
17. A.I.Y. Tok, L.H. Luo, F.Y.C. Boey, *Mat. Sci. Eng. A*, 383 (2004) 229-234.
18. J.Y. Yu, W.C.J. Wei, S.E. Lin, J.M. Sung, *Mater. Chem. Phys.*, 118 (2009) 410-416.
19. J.M. Sung, S.E. Lin, W.C.J. Wei, *J. Euro. Ceram. Soc.*, 27 (2007) 2605-2611.
20. S.E. Lin, W.C.J. Wei, *J. Am. Ceram. Soc.*, 89 (2006) 527-533.
21. S.E. Lin, W.C.J. Wei, *J. Am. Ceram. Soc.*, 91 (2008) 1121-1128.
22. W.H.R. Shaw, J.J. Bordeaux, *J. Chem. Soc.*, 77 (1955) 4729-4733.
23. W.P. Hsu, L. Ronnquist, E. Matijevic, *Langmir*, 4 (1988) 31-37.
24. F. Zhou, X. Ni, Y. Zhang, H. Zheng, *J. Colloid Interf. Sci.*, 307 (2007) 135-138.