

Synthesis of gadolinium-doped ceria nanoparticles by electrolysis of aqueous solutions

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Nanometre-sized Gd-doped ceria (GDC) particles were prepared by alternating and direct current electrolysis of mixed aqueous solutions containing Ce^{3+} ions (0.08 mol/l) and Gd^{3+} ions (0.02 mol/l) at 25°-80 °C for 24 h under an electric field strength of 3.3 V/cm. The GDC particles of the median sizes of 2.4-5.6 nm were produced under an AC field at 1 Hz of 3.3 V/cm, and the particle size and yield increased at a higher solution temperature. The increase of solution pH was also effective in increasing the particle yield. The addition of glycine to the $\text{Gd}(\text{NO}_3)_3$ - $\text{Ce}(\text{NO}_3)_3$ solution increased the particle yield at a low electrolysis temperature under a DC field of 3.3 V/cm. The Gd_2O_3 content of the GDC particles produced in the glycine-containing solution was close to the metal composition of the starting solution.

Key words: Organic compound, Gadolinium-doped ceria, Nanoparticles, Electrolysis.

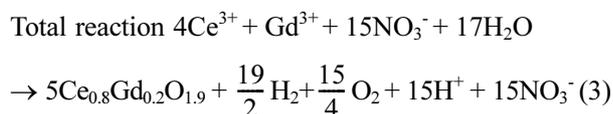
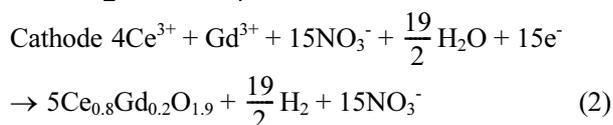
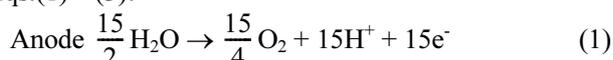
Introduction

Gadolinium-doped ceria (GDC) with a high oxide ion conductivity is used as an electrolyte for solid oxide fuel cells (SOFCs). The raw GDC powder is produced by the following methods: solid state reaction [1], combustion method [2, 3], high energy ball milling [4], metal cation complex [5], co-precipitation method [6], microwave heating [7, 8] and polymerized precursor method [9]. Chourashiya et al. [1] synthesized GDC powders by heating mixtures of commercial CeO_2 and Gd_2O_3 powders. The particle sizes of GDC powders produced were 0.4-0.75, 1.25-2, 1.8-2.5 and 2-3 μm upon heating at 1200°, 1300°, 1400° and 1500°C, respectively. However, a GDC single phase was not achieved by their solid state reaction. Singh et al. [2] prepared a $\text{Ce}_{0.85}\text{Gd}_{0.15}\text{O}_{1.925}$ single phase powder from ammonium cerium nitrate ($(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$), gadolinium nitrate and citric acid solution through an auto-combustion method. The mixed solution was heated at 200 °C and then the solid produced was calcined at 500 °C for 4 h. The particle size for the as-prepared powder (26 ± 5 nm) increased to 400 nm after heating at 1300 °C. Mahata et al. [3] also prepared GDC powders with 0-15 mol% Gd_2O_3 by a solution combustion method using cerium nitrate, gadolinium nitrate and citric acid. The sizes of the synthesized particles were in the range of 17-20 nm and increased to 26-35 nm after calcination at 600 °C.

The particle size depended on the gadolinium content and decreased at a higher Gd_2O_3 content. Khakpour et al. [4] synthesized a $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ powder by high energy milling of a mixture of CeO_2 and Gd_2O_3 powders. The X-ray diffraction peaks of Gd_2O_3 disappeared after 20 h of ball milling. Fluorite structure $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ solid solution nanoparticles with a specific surface area of 16.9 m^2/g and a particle size of 50 nm were produced after 30 h ball milling. Fuentes and Baker [5] synthesized a $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ powder using a complex of a metal cation citrate. The GDC powder calcined at 500 °C for 1 h provided a crystallite size of 10.5 nm and a specific surface area of 29.7 m^2/g . Gondolini et al. [7] produced a $\text{Ce}_{1-x}\text{Gd}_x\text{O}_{2-x/2}$ powder by microwave heating of a 0.1M diethylene glycol solution of cerium nitrate and gadolinium nitrate at 170 °C for 2 h. The as-prepared $\text{Ce}_{0.83}\text{Gd}_{0.17}\text{O}_{1.915}$ powder with a 4 nm crystallite size consisted of agglomerated secondary particles 300-900 nm in size. Wang and Maeda [9] synthesized a $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ powder by heating a polymeric precursor solution containing cerium nitrate, gadolinium nitrate, ethylene glycol and nitrate acid. After heating at 80 °C for 437 h, the precursor changed to cubic Gd-doped ceria particles with a specific surface area of 144 m^2/g . On the other hand, our group reported the formation of nanometre-sized CeO_2 particles (8-70 nm size) [10] and GDC particles (40-250 nm size) [11] by alternating current electrolysis of $\text{Ce}(\text{NO}_3)_3$ - $\text{Gd}(\text{NO}_3)_3$ mixed aqueous solutions at 10 V applied voltage using two platinum wire electrodes. In an AC field, the nucleation and growth rates of GDC particles are limited by the applied frequency. The electrochemical reactions for the formation of GDC particles are represented by

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Eqs.(1) - (3):



It was found that no particles were produced in the high frequency range above 100 Hz. However, the particle yield was low because of the consumption of the electrons supplied for the formation of H₂ gas at the cathode. In this paper, the effects of electrolysis temperature and solution pH during AC electrolysis on particle size, yield and composition of GDC powder were investigated. Furthermore, the steric influence of organic compounds interacting with Ce and Gd ions was studied to suppress the growth of GDC nuclei during the AC electrolysis.

Experimental Procedure

Aqueous solutions (0.1 mol/l, 70 ml) of cerium nitrate and gadolinium nitrate were mixed at a molar ratio of Ce³⁺/Gd³⁺ = 4/1. Acetylacetone (CH₃COCH₂COCH₃, molecular weight 100.13), glycine (H₂NCH₂COOH, molecular weight 75.07), glutamic acid (H₂NCH(CH₂CH₂COOH)COOH, molecular weight 147.13), leucine (H₂NCH(CH₂CH(CH₃)₂)COOH, molecular weight 131.17), phenylalanine (H₂NCH(CH₂C₆H₅)COOH, molecular weight 165.19) were mixed at a concentration of 0.3 mol/l. The pH values of aqueous solutions were adjusted by a 0.1M NH₄OH solution to be pH 3-5. Pt wire electrodes of 0.5 mm diameter were used in the DC and AC electrolysis. The distance between Pt electrodes was set to be 3 cm. The solutions

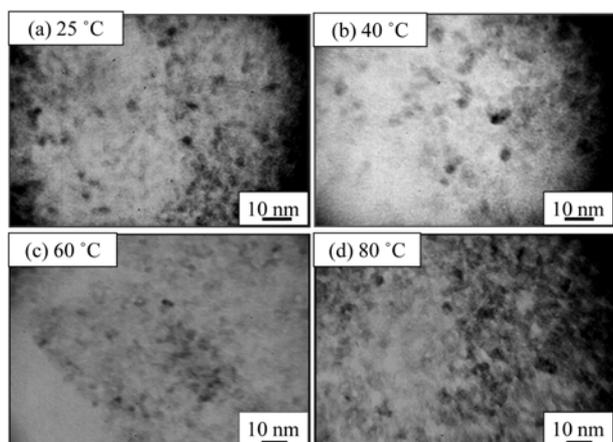


Fig. 1. Transmission electron micrographs of GDC particles, which were produced at 1 Hz and 3.3 V/cm for 24 h at (a) 25 °C, (b) 40 °C, (c) 60 °C and (d) 80 °C.

were electrolyzed at 1-10 Hz for 6-24 h at 25-80 °C in an AC field strength of 3.3 V/cm or for 24h at 25 °C in a DC field strength of 3.3 V/cm. The concentration of Ce³⁺ and Gd³⁺ ions remaining in the solution without organic compounds after the electrolysis was determined by chelatometric titration. Nanometre-sized GDC particles were collected by centrifugal separation at 4,000 rpm and freeze-dried. BET surface area measurement (Flow Sorb II 2300, Shimadzu, Japan), X-ray diffraction (RINT 2200PCH/KG, Rigaku Co., Tokyo, Japan), energy dispersive X-ray analysis (EDX, FEI XL30CP, Japan FEI, Tokyo, Japan) and a transmission electron microscope (TEM, JEM-3010, JEOL Ltd., Tokyo, Japan) were used to characterize the GDC particles formed.

Results and Discussion

Effects of pH and electrolysis temperature

Figure 1 shows the transmission electron micrographs of GDC particles (black regions) produced by AC electrolysis of Ce(NO₃)₃-Gd(NO₃)₃ solutions of pH 5 at (a) 25 °C, (b) 40 °C, (c) 60 °C, and (d) 80 °C. As seen in Fig. 1, fine particles smaller than 10 nm were produced. The particle size distributions were measured for 100-200 particles on TEM images and are plotted in Fig. 2. The solid lines represent a normal distribution function expressed by Eq.(4):

$$F(x) = \int_0^x \frac{1}{\sqrt{2\pi}\sigma} \exp\left(-\frac{(x-\mu)^2}{2\sigma^2}\right) dx \quad (4)$$

where F(x) is the cumulative percent, x the particle size, μ the average particle size and σ the standard deviation. The experimentally measured particle size distributions were well fitted by a normal distribution function with the correlation coefficients of 0.918-0.990. The median sizes of particles were 2.4 nm at 25 °C, 3.5 nm at 40 °C, 5.2 nm at 60 °C and 5.6 nm at 80 °C, respectively. Figure 3 shows a typical X-ray diffraction pattern of powder produced at 80 °C. All the diffraction peaks were indexed to be the diffraction planes of CeO₂. No

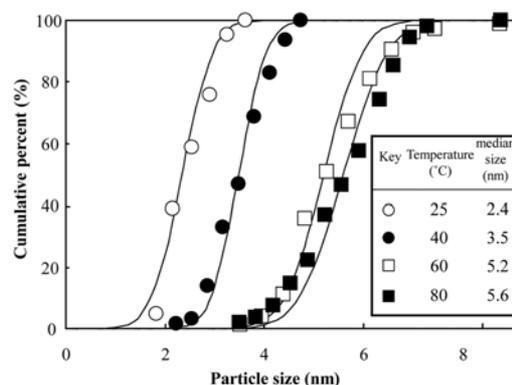


Fig. 2. Particle size distribution of GDC formed at 1 Hz and 10 V. The solid lines represent a normal distribution function, expressed by Eq. (4) in text.

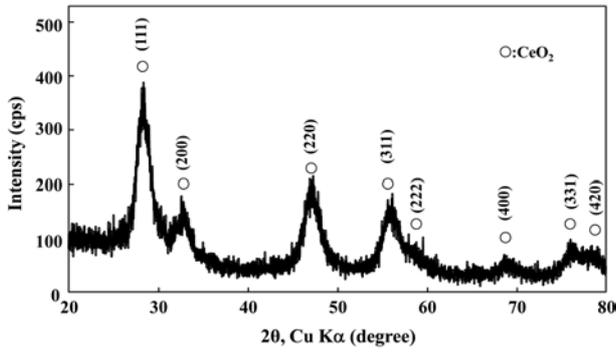


Fig. 3. X-ray diffraction pattern of GDC nanoparticles synthesized from $\text{Ce}(\text{NO}_3)_3$ - $\text{Gd}(\text{NO}_3)_3$ mixed solution at 80 °C in an AC field.

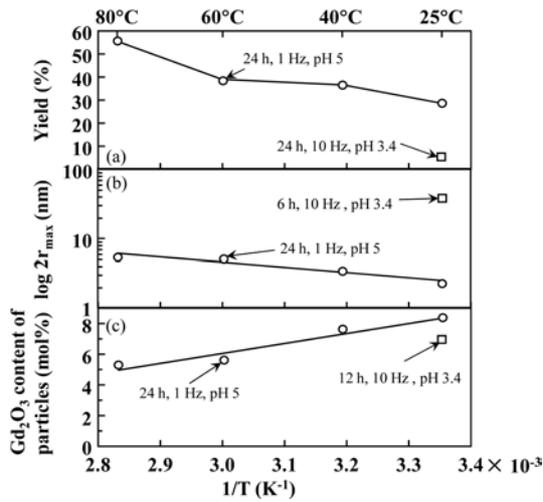


Fig. 4. (a) Yield based on concentration of Ce^{3+} and Gd^{3+} ions, (b) size, and (c) Gd_2O_3 content of nanometre-sized GDC particles formed in an AC field.

diffraction peaks of Gd_2O_3 were observed.

According to our previous work [10], the Arrhenius plot of the measured particle size ($2r_{\text{max}}$, r : radius) is given by Eq.(5):

$$\ln 2r_{\text{max}} = \frac{1}{3} \ln \left[\frac{3(C_i - C_r)D_0}{\pi^2 \delta (n/A)(C_p - C_0)f} \right] - \frac{E}{3RT} \quad (5)$$

where C_i is the concentration of metal ions, C_r the surface concentration of diffusing metal ions on a Pt electrode, D_0 the pre-exponential factor of the diffusion coefficient of metal ions, δ the effective diffusion layer thickness, n the number of CeO_2 nuclei on a Pt electrode, A the surface area of a Pt electrode, C_p the concentration of metal ions in particles, C_0 the equilibrium solubility of particles, f the applied frequency, E the activation energy for diffusion of metal ions, R the gas constant and T the solution temperature.

Figure 4 summarizes the particle yield based on metal ion concentration (chelometric titration), particle size and Gd_2O_3 content of GDC particles formed under an AC field of $\text{Gd}(\text{NO}_3)_3$ - $\text{Ce}(\text{NO}_3)_3$ mixed solutions as a function of electrolysis temperature. When one

particle was analyzed using TEM with EDX, both Ce and Gd elements were detected, indicating that the particles produced were a solid solution of the CeO_2 - Gd_2O_3 system. The yield of GDC particles increased at a higher pH of the electrolysis solution. The solubility (C_0) of CeO_2 is 6.918×10^{-21} , 6.918×10^{-29} and 6.918×10^{-37} mol/l at pH 3, 5 and 7, respectively, and decreases at a high pH [10]. That is, the difference of the Ce^{3+} ion concentrations between a starting solution (C_i) and the solubility of CeO_2 ($C_0 \approx C_r$) increases at a higher pH of the electrolysis solution, leading to the increased yield. The particle yield became higher at a higher electrolysis temperature. This result is explained by the larger diffusion coefficients of Gd^{3+} and Ce^{3+} ions with increasing temperature. The particle sizes measured on TEM images increased at higher temperatures because of the increased flux of Gd^{3+} and Ce^{3+} ions on a Pt electrode. As seen in Fig. 4, the increased pH causes a decrease in the particle size and the increases in particle yield. This result suggests that the number of GDC nuclei per unit surface area of a Pt electrode (n/A value in Eq.(5)) increases greatly at a high solution pH because of the low solubility of CeO_2 . As a result, the subsequent grain growth rate of GDC becomes small in a high pH solution. The Gd content of GDC particles decreased at a higher temperature. The ratio of fluxes (J) of Gd^{3+} and Ce^{3+} ions is expressed by Eq.(6) [11].

$$\frac{J(\text{Gd}^{3+})}{J(\text{Ce}^{3+})} = \frac{D(\text{Gd}^{3+})C_i(\text{Gd}^{3+}) - C_r(\text{Gd}^{3+})}{D(\text{Ce}^{3+})C_i(\text{Ce}^{3+}) - C_r(\text{Ce}^{3+})} \quad (6)$$

That is, the Gd_2O_3 content of the GDC powder is controlled by the diffusion coefficients (D) and concentrations of Gd^{3+} and Ce^{3+} ions. The $J(\text{Gd}^{3+})/J(\text{Ce}^{3+})$ ratio is close to the $C_i(\text{Gd}^{3+})/C_i(\text{Ce}^{3+})$ ratio under the conditions of $D(\text{Gd}^{3+}) \approx D(\text{Ce}^{3+})$ and $C_i \gg C_r$. However, the experimental result in Fig. 4 (c) indicates the relation of $J(\text{Gd}^{3+})/J(\text{Ce}^{3+}) < C_i(\text{Gd}^{3+})/C_i(\text{Ce}^{3+}) = 0.25$. Therefore, the $D(\text{Gd}^{3+})/D(\text{Ce}^{3+})$ ratio is smaller than unity. This conclusion is supported by the following discussion.

It is well known that the electrical conductivities of aqueous solutions containing alkali metal ions increases in the following order of $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Rb}^+ < \text{Cs}^+$ [12]. This order is associated with the ionic radius of alkali metal ions (Li^+ : 0.060 nm, Na^+ : 0.095 nm, K^+ : 0.133 nm, Rb^+ : 0.148 nm, Cs^+ : 0.169 nm). Since the size of an hydrated metal ion becomes larger for a smaller ion, the migration rate becomes lower for a smaller ion. A similar relation may occur between Gd^{3+} and Ce^{3+} ions. The radii of Gd^{3+} and Ce^{3+} ions are reported to be 0.094 and 0.102 nm, respectively. That is, the size of an hydrated ion may become larger for a Gd^{3+} ion than for a Ce^{3+} ion, resulting in the decreased diffusion coefficient for hydrated Gd^{3+} ions. Figure 5 shows the Arrhenius plots of particle sizes of CeO_2 and Gd_2O_3 formed by AC electrolysis (1 Hz) for 24 h. The

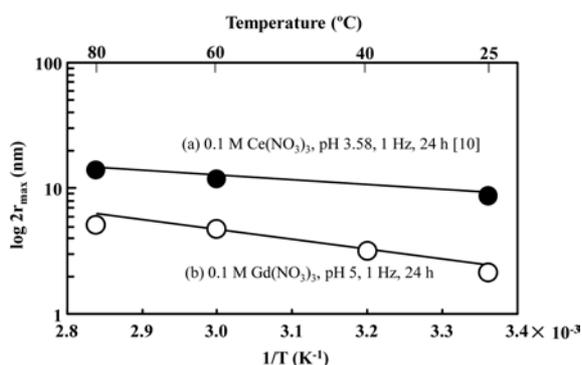


Fig. 5. Arrhenius plots of particles sizes of CeO_2 and Gd_2O_3 formed by AC electrolysis at 1 Hz.

particle size became larger for CeO_2 than for Gd_2O_3 , supporting the relation of diffusion coefficients of $D(\text{Ce}^{3+}) > D(\text{Gd}^{3+})$ as mentioned above. The temperature dependence of the particle size in Fig. 5 provides activation energies of 22.3 and 42.6 kJ/mol for the formation of CeO_2 and Gd_2O_3 particles, respectively. This result leads to a prediction of an increased Gd_2O_3 content of GDC particles at a higher AC electrolysis temperature. However, the Gd_2O_3 content of GDC particles in Fig. 4 (c) decreased at a higher temperature. The reason for the above result is not clear at this moment.

Effect of organic compounds

Table 1 shows the characteristics of GDC powders produced by AC and DC electrolysis. In the AC electrolysis of a $\text{Gd}(\text{NO}_3)_3$ - $\text{Ce}(\text{NO}_3)_3$ aqueous solution, the powder produced consisted of GDC particles. The

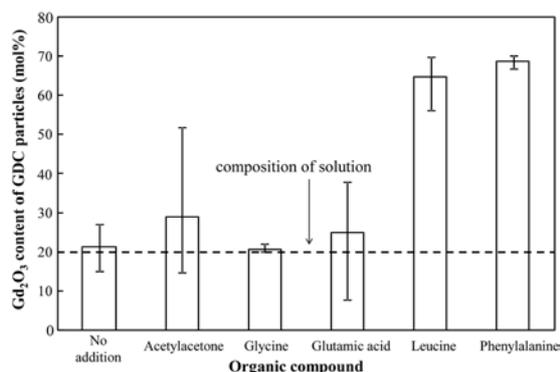


Fig. 6. Gd_2O_3 content of GDC powders produced by DC electrolysis of a $\text{Ce}(\text{NO}_3)_3$ - $\text{Gd}(\text{NO}_3)_3$ solution.

addition of the organic compounds in Table 1 provided the mixtures of GDC particles and black carbon-based compounds. The organic compound produced in the solution with acetylacetone was identified to be umbelliferone ($\text{C}_9\text{H}_6\text{O}_3$) from its X-ray diffraction pattern. In the other samples, it was difficult to identify the organic compounds produced, which were oxidized by heating in air. The yield of particles collected by centrifugal separation was less than 2% in the AC electrolysis. This result indicates that Gd^{3+} and Ce^{3+} ions were covered with the organic compounds and were stable in the AC electrolysis conditions. On the other hand, DC electrolysis of the aqueous solutions in Table 1 provided nanometre-sized GDC particles at a yield of 1.5-44.9%. The particle sizes calculated from the surface areas of powders calcined at 400 °C in air were in the range of 11-63 nm. The crystallite sizes were 2-9 nm as seen in Table 1.

Table 1. Influence of organic compound on size, phase and yield of powders produced by AC and DC electrolysis of $\text{Gd}(\text{NO}_3)_3$ - $\text{Ce}(\text{NO}_3)_3$ solution at 25 °C.

Organic compound ^{a)}	AC (3.3 V/cm, 1 Hz, 24 h)				DC (3.3 V/cm, 24 h)						
	Maximum current density (mA/cm ²)	Particle Yield ^{b)} (%)	Product	TG weight loss at 800 °C	Particle yield (%)	Product calcined at 400 °C	TG weight loss at 800 °C	Specific surface area (m ² /g)	Particle size for BET surface area (nm)	Crystallite size (nm)	
										(220)	(311)
No addition (pH 5)	38	0.47	GDC	16.3	1.45	GDC	20.5	26.2	31.7	8.74	7.95
Acetylacetone (pH5)	134	1.11	Organic ^{c)} plus CeO_2	90.8	10.74	GDC	51.6	21.9	37.9	5.30	5.00
Glycine (pH5)	126	Very few			44.86	GDC	16.7	36.0	23.0	4.48	4.37
Glutamic acid (pH3)	113	1.59	Organic plus CeO_2	82.8	1.97	GDC	85.4	77.0	10.8	3.50	3.36
Leucine (pH5)	94	0.34		37.7	3.13	GDC	36.3	28.7	28.9	2.13	1.88
Phenylalanine (pH5)	79	0.34	Organic plus CeO_2	63.6	3.14	GDC	53.5	13.2	62.7	3.02	2.96

a) acetyl acetone: $\text{C}_5\text{H}_8\text{O}_2$, glycine: $\text{C}_2\text{H}_5\text{NO}_2$, glutamic acid: $\text{C}_5\text{H}_9\text{NO}_4$, leucine: $\text{C}_6\text{H}_{13}\text{NO}_2$, phenylalanine: $\text{C}_9\text{H}_{11}\text{NO}_2$

b) collected by centrifugal separation at 4,000 rpm

c) umbelliferone: $\text{C}_9\text{H}_6\text{O}_3$

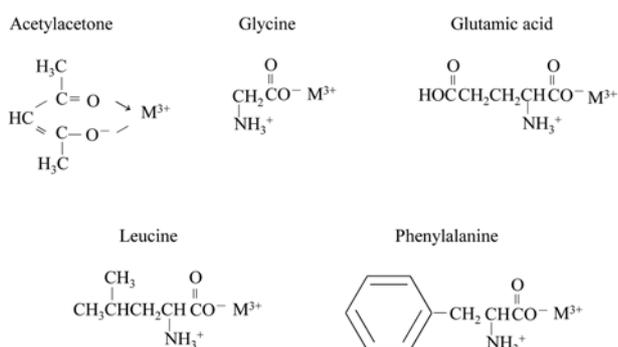


Fig. 7. Possible interactions between M^{3+} ($\text{M} = \text{Gd}, \text{Ce}$) ion and organic compounds in aqueous solutions at pH 3-5.

Figure 6 shows the Gd_2O_3 content of the GDC particles produced by DC electrolysis. No significant difference of the Gd_2O_3 content was measured between the starting solution and the powders produced in the solution without an organic compound or with glycine. However, more Gd_2O_3 -enriched particles were produced in the other solutions as seen in Fig. 6. The above result is different from the Gd_2O_3 content of GDC powder produced in the AC field in Fig. 4. Under the DC field, the $D(\text{Gd}^{3+})/D(\text{Ce}^{3+})$ ratio of Eq.(7) is close to unity in the aqueous solutions with glycine and without organic compound. In the other solutions, the $D(\text{Gd}^{3+})/D(\text{Ce}^{3+})$ ratio becomes larger than unity.

Figure 7 shows the possible interaction between M^{3+} ($\text{M} = \text{Gd}, \text{Ce}$) ions and organic compounds in aqueous solutions at pH 3-5. The sizes of Gd^{3+} and Ce^{3+} ions with the organic compounds in Fig. 7 become larger than those of the metal ions in vacuum. In addition to the interaction between M^{3+} ions and the organic compounds, the electrostatic interaction between the COO^- group and NH_3^+ group of adjacent organic molecules increases more the size of M^{3+} ions coordinated by the organic compound, resulting in a decreased diffusion coefficient. The above size effect by adsorbed leucine and phenylalanine may be larger in Ce^{3+} ions than in Gd^{3+} ions because the Gd_2O_3 content was higher in GDC particles than the starting solution. Although the detailed mechanisms of powder formation in Table 1 with organic compounds are not clear at this moment, the addition of glycine is recommended to produce nanometre-sized GDC particles from the view points of high particle yield and little change of Gd_2O_3 content as compared with the metal composition of the solution.

Conclusions

Nanometre-sized GDC particles were produced under an AC field of a $\text{Gd}(\text{NO}_3)_3$ - $\text{Ce}(\text{NO}_3)_3$ mixed solution and also produced under a DC field of the mixed solution containing an organic compound. The

yield and size of GDC nanoparticles produced in the AC field increased at a higher solution temperature and at a higher solution pH. The Gd_2O_3 content of GDC particles was lower than the composition of the starting solution. The addition of glycine under a DC field at room temperature was effective in increasing the particle yield of nanometre-sized GDC particles. The Gd_2O_3 content of GDC particles produced in the glycine-containing solution was close to the metal composition of the starting solution.

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