

Materials science communication

Factors affecting formation of ceria nanoparticles by alternating current electrolysis of aqueous solutions

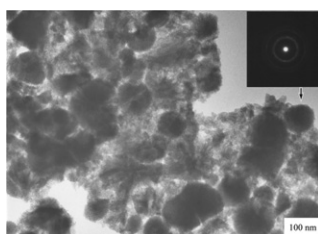
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HIGHLIGHTS

- ▶ Factors affecting formation of ceria nanoparticles by AC electrolysis were studied.
- ▶ The increase of the surface area of Pt electrode formed smaller particles.
- ▶ The electric field strength gave little influence on the size and yield.
- ▶ The increased pH and volume of solution enhanced the quantity of particles.

GRAPHICAL ABSTRACT



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ABSTRACT

Nanometer-sized ceria particles (primary particle size 6–70 nm) were prepared in 0.1 M $\text{Ce}(\text{NO}_3)_3$ aqueous solutions by alternating current electrolysis of 1 Hz at 10 V for 24 h. The influence of the surface area of Pt electrode, electric field strength, solution pH and volume of $\text{Ce}(\text{NO}_3)_3$ aqueous solution on the size and yield of CeO_2 nanoparticles were studied at 25 °C and 60 °C. The increase of the surface area of Pt electrode caused the decrease of current density and contributed to the formation of smaller particles. The electric field strength gave little influence on the size and yield of CeO_2 nanoparticles. The increased pH and increased volume of electrolysis solution were effective to increase the quantity of CeO_2 particles formed.

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1. Introduction

Nanometer-sized ceria particles are useful as a glass polishing powder [1], a raw material of oxide ion conductor [2], an automobile exhaust catalyst [3] and a UV filter [4], and may be used in biomedical applications [5–10]. Following chemical methods have been proposed to synthesize nanometer-sized CeO_2 particles: precipitation method [11,12], sol–gel process [13–15], microemulsion method [16–18], spray pyrolysis technique [19], hydrothermal synthesis [20], supercritical synthesis [21] and sonochemical synthesis [22]. Xu [11] prepared 30 nm ceria particles by calcination of the precipitate of $\text{Ce}(\text{NO}_3)_3$ in NH_4OH solution at

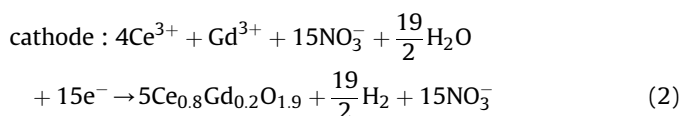
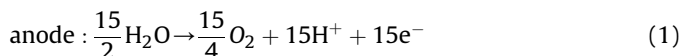
400 °C for 6 h. Pinjari and Pandit [22] report the formation of non-agglomerated CeO_2 nanoparticles from the $\text{Ce}(\text{NO}_3)_3$ -NaOH system by applying an ultrasonic pulse with 5 s interval at 22 kHz. In microemulsion method, non-agglomerated ceria nanoparticles with 5 nm diameter were formed in toluene using surfactant, aqueous cerium nitrate solution and ammonium hydroxide solution [16]. Kang et al. [19] synthesized ceria nanoparticles of 8 nm crystallite size by spray pyrolysis technique of the aqueous solution of $\text{Ce}(\text{NO}_3)_3$ -citric acid-ethylene glycol system at 600–1000 °C.

As compared with the above preparation methods of nanoparticles, electrolysis method has the following characteristics: (1) particle size is easily controlled by the combination of solution conditions (pH, temperature, concentration of precursor compound) and electrolysis conditions (applied voltage, AC or DC, current density). In microemulsion method, a toxic solvent such as toluene or a toxic complex surfactant such as sodium

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bis(2-ethylhexyl) sulphosuccinate is frequently used [16–18]. In sol–gel processing, starting alkoxides are sensitive to the moisture in air and the handling of alkoxides needs a specific dried atmosphere [13–15]. On the other hand, electrolysis method of an aqueous solution of metal precursor is quite safety and the operation of the equipment is easy. Recently our group reported the formation of nanometer-sized Gd-doped CeO₂ particles (GDC) of 40–250 nm in size by alternating current electrolysis of an acidic aqueous solution containing Ce³⁺ and Gd³⁺ ions at the frequency below 20 Hz at 10 V of applied voltage between two platinum wire electrodes [23]. The electrochemical reactions for the formation of GDC particles are expressed as follows.



The nucleation and growth of GDC particles are dominated by the frequency of alternating current. Increased frequency (short electrolysis time) leads to a low growth rate of GDC particles. In our previous paper [24], a theoretical equation of maximum particle size (r_{max}) as functions of metal concentration, electrolysis temperature and applied frequency was derived (Eq. (3)).

$$\frac{4}{3}\pi r_{\text{max}}^3 = \frac{(C_i - C_r)D_0 \exp(-E/RT)}{2\pi\delta(n/A)(C_p - C_0)f} \quad (3)$$

In Eq. (3), C_i is the concentration of metal ions in a bulk solution, C_r the concentration of metal ions at the surface of Pt electrode, D_0 the pre-exponential factor of diffusion coefficient of metal ions, E the activation energy for diffusion of metal ions in a solution, R the gas constant, T the solution temperature, δ the effective diffusion layer thickness, n the number of nuclei formed on Pt electrode, A the surface area of electrode, C_p the concentration of metal ions in oxide particles, C_0 the equilibrium concentration of metal ions for a rapid surface reaction and f the applied frequency. As seen in Eq. (3), direct current electrolysis ($f \rightarrow 0$) results in the increased particle size but alternating current electrolysis at a higher frequency provides smaller particles. The measured sizes of CeO₂ particles in previous paper [24] were in accordance with the prediction from Eq. (3). However, the following factors affecting the size and yield of GDC particles or CeO₂ particles have not been studied in previous papers: (1) surface area of Pt electrode, (2) electric field strength, (3) pH of electrolysis solution and (4) volume

of Ce(NO₃)₃ electrolysis solution. This paper reports the experimental results of the above four factors during AC electrolysis of Ce(NO₃)₃ solution.

2. Experimental procedure

A 0.1 M Ce(NO₃)₃ solution and Pt wire electrodes of 0.5 mm diameter and 40–80 mm length were used in the electrolysis experiments at 25 and 60 °C. An alternating current of 1 Hz at 10 V was flowed between the Pt electrodes for 24 h (function synthesizer 1915, NF Co., Yokohama, Japan). The yield of ceria particles formed was determined from the difference in Ce³⁺ ion concentrations in the solutions before and after the AC electrolysis. The Ce³⁺ ion concentration was analyzed by chelatometric titration. Nanometer-sized ceria particles were collected by centrifugal separation method at 4000 rpm and freeze-dried. X-ray diffraction (RINT 2200 PCH/KG, Rigaku Co., Tokyo, Japan) and transmission electron microscope (JEM-3010 and JEM-2010F, JEOL Ltd., Tokyo, Japan) were used to evaluate the ceria particles formed. Particle size distributions for 50–150 particles on TEM images were measured by image analyzer assuming spherical particles. Crystallite sizes of ceria particles were measured with diffraction peaks of (220) and (311) using the Scherrer's equation, $B = K\lambda/\beta\cos\theta$, where B is the crystallite size, K the constant (0.9), λ the wave length of Cu K α line (0.154178 nm), β the full width of half maximum intensity and θ the Bragg's angle.

3. Results and discussion

Table 1 shows the experimental AC electrolysis conditions and characteristics of produced ceria particles. Fig. 1 shows a typical TEM image of ceria particles of sample No.1 in Table 1. Equiaxial particles in the range of 44–288 nm (secondary particles) were agglomerated by more fine irregular shape primary nanoparticles. The selected area diffraction pattern for the arrowed spherical particle showed a ring pattern of polycrystalline. Fig. 2(a) shows the XRD pattern of ceria particles of sample No.1. All the diffraction peaks were identified by the diffraction planes of CeO₂. The crystallite sizes for (220) and (311) of CeO₂ particles were 3.5 and 3.3 nm, respectively. The measured primary particle sizes were 6–20 nm and larger than the crystallite sizes, suggesting the formation of polycrystalline particles. This electrolysis method provides very fine crystalline CeO₂ nanoparticles.

The increased surface area of Pt electrode (samples Nos.1–3) caused (1) decrease in the current density, (2) increase in the particle yield and (3) no change of primary particle size. However, no particles were formed in the condition of sample No.3 and thin

Table 1
AC electrolysis conditions and characteristics of produced ceria particles.

No.	Volume of Ce(NO ₃) ₃ solution (ml)	Temp. (°C)	pH		Surface area of electrode (cm ²)	Electric field strength (V/cm)	Current density (mA/cm ²)	CeO ₂ particles					
			before	after				Yield (%)	Quantity (g)	Size distribution (nm)		Crystallite size (nm)	
										Primary particles	Secondary particles	(220)	(311)
1	70	25	3.2	0.9	0.47	3.3	228	7.2	0.09	6.0–21	44–288	3.5	3.3
2	70	25	3.2	0.9	0.94	3.3	130	17.8	0.21	6.4–20			
3	70	25	3.2	2.6	2.83	3.3	63			film			
4	70	25	3.2	1.0	0.47	10.0	218	7.4	0.09	7.1–60			
5	70	25	3.2	2.3	0.47	2.5	222	5.7	0.07	11–34	47–328	3.5	3.4
6	70	25	5.0	0.8	0.47	3.3	245	27.2	0.33	8.9–47	51–376	3.8	3.8
7	70	25	6.3	1.0	0.47	3.3	241	40.8	0.49	7.8–70			
8	200	25	3.2	1.9	0.47	3.3	277	4.8	0.16	7.9–34			
9	500	25	3.2	2.7	0.47	3.3	296	3.0	0.26	12–57			
10	70	60	5.5	1.0	2.83	10.0	51	61.7	0.74	4.0–17			

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