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Preparation and characterization of nanometer-scale powders ceria by electrochemical deposition method

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Abstract

Ceria (CeO_2) nanoparticles of 10–30 nm in average particle size have been synthesized via electrochemical deposition method in cerium(III) chloride solution with an undivided cell as electrochemical cell and ethanol–acetylacetone as additives. X-ray diffraction (XRD), transmission electron microscopy (TEM), Fourier transformation infrared spectroscopy (FT-IR) and thermal analysis (TG–DTA) are introduced to characterize the samples. The results indicate that the as-prepared powders after being treated at 650 °C are nanocrystalline with the cubic fluorite structure and the sphericity in shape. It is revealed that the size of ceria nanoparticles can be decreased effectively by adding the ethanol–acetylacetone solution. In addition, the possible formed mechanism of CeO_2 nanometer-scale powder. The role of additive is also investigated in this paper.

Keywords: A. Oxides; B. Chemical synthesis

1. Introduction

In recent years, many researches have devoted to the preparation of cerium oxide (CeO_2) because of its effective and potential technological applications in several fields. Nanometer-scale CeO_2 particles are widely used as automobile exhaust catalysts [1], polishing materials [2], fuel-cells [3], phosphors [4], UV filters [5] and so on. Furthermore, numerous techniques have been proposed to make nano-sized CeO_2 particles, such as homogeneous precipitation [6], a reverse micelles route [7], hydrothermal method [8], microwave-assisted heating hydrolysis method [9], pyrolysis [10], sonochemical [11] and combustion synthesis [12], to name just a few.

Electrochemical synthesis of composition in aqueous solution has been recognized as an attractive method because it offers the advantages of low cost and high purity [13,14]. In addition, the speed of the synthesis can be easily controlled by adjusting the electrochemical parameters. Both anodic and cathodic methods can be employed to synthesize CeO_2. Cathodic deposition used to produce the oxide and hydroxide has also been coined as the base generation deposition, which was first proposed by Switzer to make ceramic oxide films and powders [15–17]. It is well known that the formed mechanism of oxide or hydroxide is that a metal ion is oxidized by oxidant at the electrode surface. Meanwhile, base is produced at the vicinity of the working electrode. The pH of the solution is increased so that the initial oxidation state or higher oxidation state is hydrolyzed and the metal hydroxide or oxide is formed.

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Despite the high interest in the development of new methods to prepare nanometer-scale CeO_2, to the best of our knowledge, less information is reported on the methods of electrochemical synthesis of nanometer-scale CeO_2 powder by undivided cell electrolysis. Therefore, in the present work, the method of electrochemical deposition is used to electrolyze the cerium(III) chloride solution in an undivided cell. On the anode, chlorine (Cl_2) is produced by electrolysis of the cerium(III) chloride. The Cl_2-rich ambient would benefit the oxidation of Ce(III) to Ce(IV), and results in the formation of CeO_2 quickly. On the cathode, hydroxide ion and hydrogen gas are produced by the reduction of water. The cathode surface as a template releases OH^- and then Ce(III) hydrolyses to $Ce(OH)_3$ or $CeO_2{\cdot}xH_2O$ deposition. It is emphasized that the synthesis of nanometer-scale CeO_2 powder in an undivided cell has the advantages of lower electrolytic potential, simple process, easy scale-up and low cost. In addition, it is found that the presence of the additive of mixed alcohol–acetylacetone solution in the electrolyte could decrease the size of CeO_2.

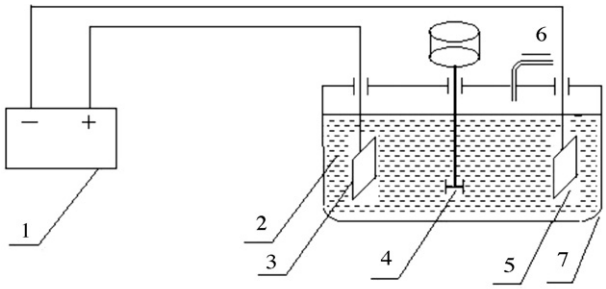
2. Experimental details

All chemicals are reagent grade and used without further purification. A 150 ml of aqueous cerium chloride solution (1 M) is used as the cerium precursor. The anode is a platinum wire with the length of 60 mm. The cathode, which acts as the working electrode, is a Ru–Ti mesh. $CeCl_3$ solution (pH 3.6) is put into the cell (Fig. 1) under vigorous stirring. The experiment is performed in the galvanostatic mode at current densities of 100 A/m^2 and at room temperature (RT). At the beginning of the reaction, the color of the solution becomes yellow green immediately, after that the color turns into turbid, and then purple suspension, finally pale yellow. At the end of the predetermined reaction time the precipitate is centrifuged and followed by washing with de-ionized water, and with DI-water several times to ensure the removal of chloride. After drying 2 h in an oven at 80 °C, the precursor of $CeO_2{\cdot}xH_2O$ is obtained, and then the precursor is calcined at 650 °C for 2 h, the nanometer-scale CeO_2 powder which is named sample (I) is obtained. During the same process as above, the additive of mixed alcohol–acetylacetone solution is added in the cell. Finally, CeO_2 particle is prepared, which is named the sample (II). The crystalline structure is studied with a M18XHF22-SRA diffractometer using Cu Kα radiation (A = 0.15406 nm). The tube source is operated at 18 kV and 400 mA. The morphology and particle size of the samples are observed with a Hitachi H-600 transmission electron microscope. For the TEM observation, an appropriate amount of particle suspension is dropped onto the carbon-coated copper grids. The average particle size and size distribution are determined from TEM images by counting more than 100 particles. Fourier transform infrared (FT-IR) spectrum is collected using a BRUKER EQUINOX55 spectrometer. TG–DTA thermal analysis is employed a NETZSCH STA 449C TG–DTA instrument. The temperature for scanning ranges from 20 °C to 800 °C and the scanning speed is 10 °C/min in air.

3. Results and discussion

3.1. XRD analysis

The as-prepared CeO_2 powder calcined at different temperatures is characterized by X-ray diffraction (XRD) (Fig. 2). The X-ray diffraction of fresh powder treated at 100 °C exhibits a broad peak at ca. 28° (Fig. 2a). It is revealed



1. potentiostat/galvanostat 2. electrolyte 3. Pt electrode 4. agitator
5. Ru-Ti electrode 6. vent-pipe 7. the electrochemical cell

Fig. 1. Setup of electrochemical deposition of CeO_2.