# Development of Mass Production Process of Cerium Oxide Nanopowders

## Background

Cerium oxides are usually used as abrasives and ultraviolet absorbents, and in recent years, materials for decomposing suspended particulate matter (SPM), NOx and volatile organic compounds (VOC) have much gained attention as new uses of cerium oxides. Additionally, from the viewpoint of their high oxide-ion conduction, cerium oxides are considered to be the most promising materials for use as electrolytes in intermediate-temperature solid oxide fuel cells (IT-SOFCs) with an operating temperature of 500 - 600˚C. During SOFC fabrication, the electrolyte on a porous electrode is co-fired at rather high-temperatures over 1400˚C. Such high-temperature heat-treatment causes a degradation in the performance of the electrode, for example, the formation of poorly conductive compounds at an interface between the electrode and electrolyte, and the loss of porosity of electrodes. In order to prevent the degradation of the electrolyte and electrodes, it is desired to develop cerium oxide nanopowders with high-sintering characteristics.

## Objectives

CRIEPI has focused on a synthesis of cerium oxide nanopowder ($Ce_{0.9}Gd_{0.1}O_{1.95}$, CGO), which can attain fully-sintering temperatures <1200˚C [*1]. Electrolyte powders with dense sintering characteristics at the lower temperatures offer a large selection of conditions during the fabricating process and a significant economic advantage, in addition to an avoidance of the degradation by the chemical reaction and by the loss of porosity of electrode. The coprecipitation method is one of the most appropriate ways of synthesizing a nanopowder. In this study, the coprecipitation method was applied to the synthesis of nanopowder with high-sintering characteristics. Additionally, the mass production process of this nanopowder has been studied.

## Principal Results

### 1. Synthesis of cerium oxide nanopowders with high-sintering characteristics using nanoparticle growth technique

CRIEPI and Anan Kasei Co. Ltd. have devised the nanoparticle growth technique, which crystallizes the precipitate obtained by the coprecipitation method and grows the nanoparticles. Through this growth process, Ce and Gd elements on the surface of the primary particles are repeated dissolution and deposition processes. As it turned out, the secondary particle, which densely consists of the primary particles with particle size of 20 nm, are formed (Fig.1). Since these nanoparticles have high-sintering characteristics of the primary particles, they showed lower sintering temperature where the relative density of CGO samples was 94% (1050˚C, 2 h for CGO nanopowder vs. 1300˚C, 2 h for CGO conventional powder).

### 2. Development of mass production process of nanopowder and application to electrolytes in IT-SOFC [*2]

When the impurity of $NO^{3-}$ in the precipitate was removed by pure-water, it was noted that the oval particles grew into the branch-type tertiary particles (Fig.2). The tertiary particles broke easily into the oval secondary particles during the grinding process. In addition, it was found that two steps of low-temperature (300˚C for 10 h) and high-temperature (700˚C for 5 h) heat-treatments enlarge a surface area of nanopowder one and a half times. Using these techniques, the large scale bath with a capacity of 65 kg/batch has been developed. The sintering characteristics of this nanopowder are almost equivalent to that of the nanopowder synthesized by a small scale bath with a capacity of 0.1 kg/batch. This nanopowder was coated on the porous anode using the slurry coating technique, and was densely sintered (Fig.4). The results of these experiments clarify that the CGO nanopowder applies to the electrolyte in the IT-SOFCs. Because we realized the nanopowder with high-sintering characteristics and low material cost, Anan Kasei Co. Ltd. started to sale this nanopowder in FY2005.

## Future Developments

The NEDO project, “The Advanced Ceramic Reactor Project”, started in FY2005. The target of this project is the development of IT-SOFCs with scandia-stabilized zirconia and gadolia-doped ceria electrolytes. The CGO nanopowder, which is synthesized by a large scale bath with a capacity of 65 kg/batch, will be applied to the electrolyte in the project.

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***Reference***

E. Suda et.al., 2005, “Fabrication of oxides, oxides and sintered bodies of oxides”, JPN Patent 2005-079781 (in Japanese).

*1 : When the sintering temperature of CGO is over 1200˚C, the application of CGO to electrolytes in SOFC is limited.

*2 : This work is supported by the Regional New Consortium Projects / Regional New Industry Creative-Type Technology R&D Promotion Programs and collaborated by Anan Kasei Co. Ltd, The University of Tokushima and Tokushima Burin University.

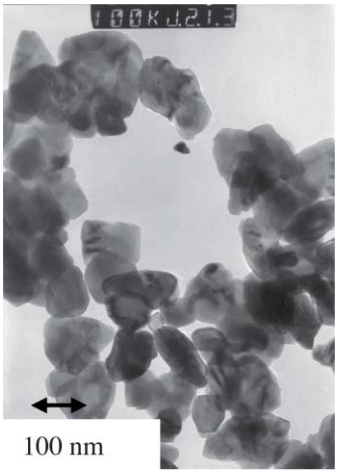


**Fig.1** Transmission Electron Microscopy (TEM) micrograph of CGO by a small scale bath with a capacity of 0.1 kg/batch

Although the primary particle size in Fig.1 was approximately 100 nm, the primary particle size was calculated to be approximately 20 nm from the results of X-ray diffraction analysis. This discrepancy indicated that the particles in Fig. 1 should be the secondary particles densely consisted of the primary particles[*3] with 20 nm.

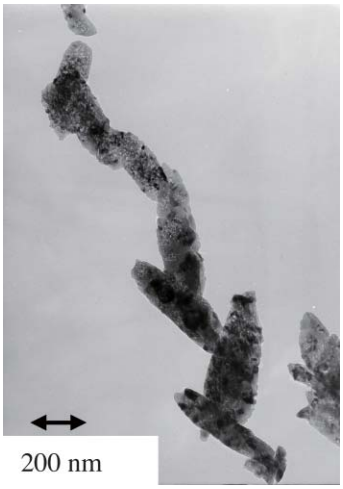


**Fig.2** TEM micrograph of CGO by a large scale bath with a capacity of 65 kg/batch

Because the grain growth proceeds like branches, the tertiary particles were formed by the oval secondary particles. The secondary particles might consist of the primary particles with 20 nm. The branch-type tertiary particles are easy to breake into oval shape secondary particles during the grinding process.

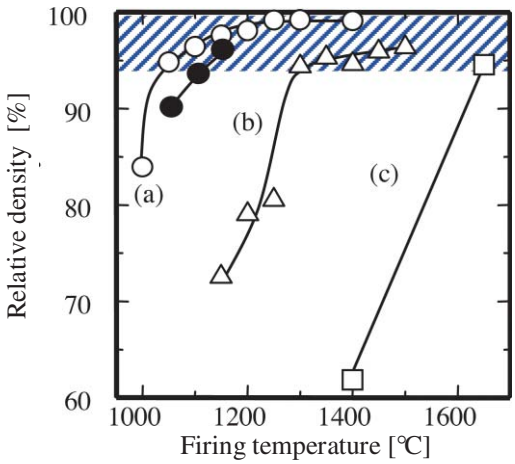


**Fig.3** Relative densities of CGO synthesized by various methods, as a function of firing temperature

●: A large scale bath with a capacity of 65 kg/batch, (a)A small scale bath with a capacity of 0.1 kg/batch, (b)Coprecipitation method, (c) Solid-state technique. The shaded region in Fig.3 represents relative densities more than 94% and shows the area of an acceptable relative density of electrolyte in IT-SOFCs.

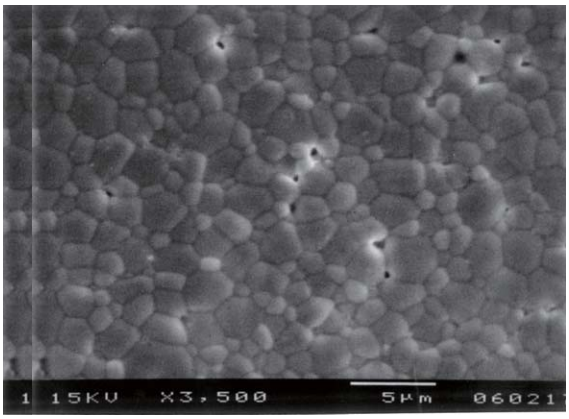


**Fig.4** Scanning electron microscopy (SEM) micrograph of CGO electrolyte on the porous anode in IT- SOFCs

SEM micrograph shows the surface of CGO electrolyte on the porous anode using the slurry coating technique. The particles on the surface are densely packed without pores. This indicates that the electrolyte layer would be impervious.

＊3：The smallest particles are called as the primary particles and the secondary particles are aggregated by the primary particles.