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Synthesis of samaria doped CeO_2 nanosize powders by a hydrothermal process

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Nanosized Sm_2O_3-CeO_2 powders were prepared under high temperature and pressure conditions by precipitation from metal nitrates with aqueous potassium hydroxide. Spherical shape Sm_2O_3-CeO_2 powders were obtained in the temperature range of 175 °C~185 °C after 6 hours. TEM and X-ray diffraction patterns showed that the synthesized particles were crystalline. The average size and size distribution of the synthesized particles were below 8 nm and narrow, respectively.

Key words: Sm_2O_3-CeO_2, Nano powder, Hydrothermal process, SOFC, Solid electrolyte.

Introduction

Recently, there has been an increasing interest in the synthesis of the cerium oxide because it is used as an oxygen conductor in solid oxide fuel cells (SOFC). Cerium oxide has found applications such as catalysis, optical additive, ionic conduction, etc. Samaria-doped ceria has a high ion conductivity at a low temperature near the region of 800 °C. Samaria -doped ceria is expected to be used as a solid electrolyte material in order to be applied in solid oxide fuel cells (SOFC) which may be operated at low temperature [1]. As the ionic conductivity of the samaria-doped ceria electrolyte is higher than that of yttria-stabilized zirconia electrolyte, an SOFC with the samaria-doped ceria electrolyte can be operated at lower temperatures owing to its lower internal resistance. The grain boundary resistivity changes with the grain size. When the grain size decreases from a few micrometers to the nano level, the grain boundaries show unusually high conductivity [2-4].

Hydrothermal processes have the potential for the direct preparation of crystalline ceramic powders and offer a low-temperature alternative to conventional powder synthesis techniques in the production of oxide powders [3]. This process can produce fine, high-purity, stoichiometric particles of single and multi-component metal oxides. Furthermore, if process conditions such as solute concentration, reaction temperature, reaction time and the type of solvent are carefully controlled, the desired shape and size of the particles can be produced [4, 5]. A uniform distribution of the particles is key for optimal control of grain size and microstructure to maintain high reliability. It has been demonstrated that such powders are composed of much softer agglomerates and sinter much better than those prepared by calcination decomposition of the same oxides [6]. These powders could be sintered at low temperature without calcination and milling steps [7, 8].

The objective of this study is to prepare nano size samaria-doped cerium oxide powders by a hydrothermal process and to determine the influence of the processing conditions on the formation and phase of the powders.

Experimental Procedure

The starting materials used were a $Ce(NO_3)_3\ 6H_2O$ (Aldrich Chemical Co.) and $Sm(NO_3)_3\ 6H_2O$ (Aldrich Chemical Co.). Samarium oxide was selected as a cationic dopant for forming oxygen ion vacancies within the CeO_2 matrix. The process for preparing cerium oxide powders by this hydrothermal process in aqueous solution is schematically illustrated in Fig. 1.

The precursor was precipitated from 0.1 M $Sm(NO_3)_3 \cdot 6H_2O$ and 0.1 M $Ce(NO_3)_3 \cdot 6H_2O$ mixed solution by slowly adding 1 M KOH solution with rapid stirring. The precipitation of the mixed $Sm(NO_3)_3 \cdot 6H_2O$ and $Ce(NO_3)_3 \cdot 6H_2O$ was studied with 1 M KOH solution as a function of the pH of starting solutions. Among the starting solutions, the pH of one of them was 10. The reaction products were washed five times by repeated cycles of centrifugation and re-dispersion in deionized water. Excess solution was decanted after the final washing and the wet precursor was re-dispersed in 250 ml water under vigorous stirring. The resulting suspension was placed in a 1000 ml stainless steel pressure vessel. The vessel was then heated to the desired temperature at a rate of 10 Kminute^{-1}. The pressure of the reactor gradually increased to about 8.9×10^4 Pa

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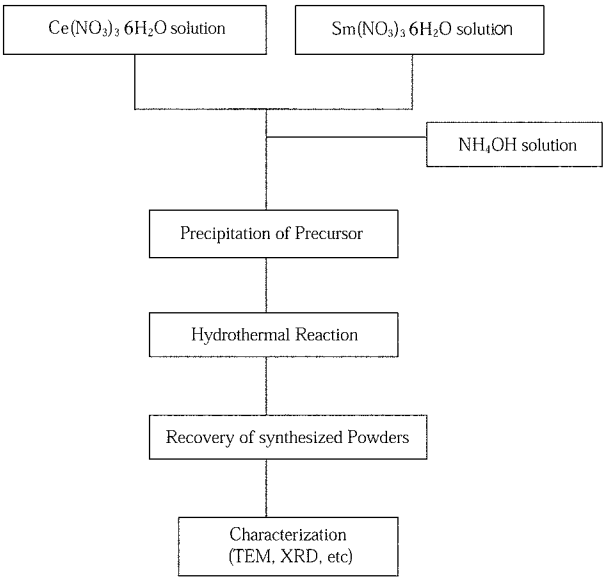

Fig. 1. Experimental flow chart of synthesis of the Sm_2O_3-CeO_2 powders.

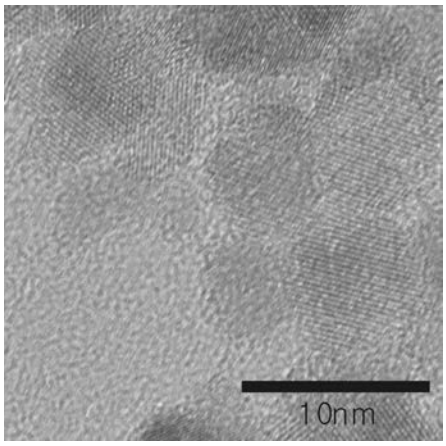

Fig. 2. HRTEM micrographs of the synthesized Sm_2O_3-CeO_2 powders by hyrothermal treatment at 175 °C for 6 h.

and maintained 8.9×10^4 Pa during the holding period. The reaction products were washed five times by repeated cycles of centrifugation and re-dispersion in ethanol. The recovered powders were analyzed for phase composition using X-ray diffraction (Philips, PW 1825/00) over the 2 theta range from 10-70° at the rate of 2.5° minute^{-1}. The morphology of the synthesized particles was observed using transmission electron microscopy (TEM, JEOL, JEM-200CX). The particle size of the iron oxide powder was observed by a light scattering method (Malvern Instruments Ltd.).

Results and Discussion

Figure 2 shows a high-resolution transmission electron micrograph (HRTEM) of the Sm_2O_3-CeO_2 crystalline particles. The average size and size distribution of the synthesized particles were below 7 nm and uniform, respectively. The shape of the synthesized particles was nearly spherical. For most of the particles their lattice images could be revealed by HRTEM. These results clearly mean that the synthesized particles were crystallized.

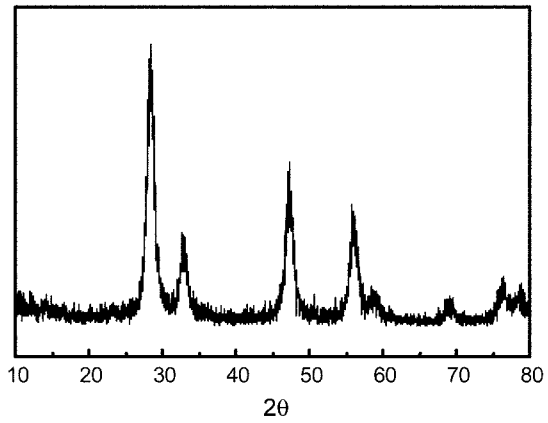

Fig. 3. X-ray diffraction pattern of the synthesized Sm_2O_3-CeO_2 powders by hydrothermal treatment at 175 °C for 6 h.

Figure 3 shows an X-ray diffraction pattern of the synthesized particles. From the X-ray analysis, the crystalline phase of the synthesized particles was found to be cubic CeO_2.

The crystalline size of the synthesized sample were determined from the X-ray line broadening using Scherrer's equation:

$$D = 0.9\lambda/(\beta \cos\theta)$$

where D is the average diameter of crystallites, λ is the wavelength of the X-rays, θ is the diffraction angle, and β is the full width at half maximum of the peak. The average crystalline size of the Sm_2O_3-CeO_2 particles was found to be about 8 nm.

Conclusions

The nanosized Sm_2O_3-CeO_2 particles were prepared under high temperature and pressure conditions by precipitation from metal nitrates with aqueous potassium hydroxide. Spherical shape Sm_2O_3-CeO_2 powders were obtained in the temperature range of 175 °C-185 °C after 6 hours. From HRTEM and X-ray analysis, the synthesized particles were crystalline. The average size and size distribution of the synthesized particles were below 7nm and narrow, respectively.

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