Microstructure and electrical properties of nano-sized Ce$_{1-x}$Gd$_x$O$_2$ (0 ≤ x ≤ 0.2) particles prepared by spray pyrolysis

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Nano-sized Ce$_{1-x}$Gd$_x$O$_2$ (0 ≤ x ≤ 0.2) particles were prepared by spray pyrolysis process from the spray solution with ethylene glycol. The mean sizes of Ce$_x$Gd$_{1-x}$O$_2$ (x = 0, 0.05, 0.1, 0.2) particles were each 46, 33, 29, and 28 nm. The mean crystallite size of pure CeO$_2$ was 33 nm. However, the Gd-doped CeO$_2$ had the mean crystallite size of 28 nm irrespective of the molar ratio of Gd to Ce components. The mean grain size of the sintered CeO$_2$ pellet was about two or four times larger than those of the Gd-doped CeO$_2$ pellets. The mean grain sizes of Ce$_{0.9}$Gd$_{0.1}$O$_2$ and Ce$_{0.8}$Gd$_{0.2}$O$_2$ pellets are about 0.5–0.4 μm. The pure CeO$_2$ pellet had low relative density of 80%. However, Ce$_{0.9}$Gd$_{0.1}$O$_2$ and Ce$_{0.8}$Gd$_{0.2}$O$_2$ pellets had the high relative densities above 95%. The Ce$_{0.9}$Gd$_{0.1}$O$_2$ and Ce$_{0.8}$Gd$_{0.2}$O$_2$ pellets had similar conductivities at all measuring temperatures. The Ce$_{0.9}$Gd$_{0.1}$O$_2$ pellet had conductivities of 4.73 × 10$^{-2}$ and 1.16 × 10$^{-1}$ Scm$^{-1}$ at measuring temperatures of 800 and 900°C respectively.

Key-words : Spray pyrolysis, Ceria, Nano powder

1. Introduction

The trivalent rare-earth doped ceria has been extensively studied as electrolytes in low operating temperature solid oxide fuel cells (SOFCs) because of high ionic conductivity at low temperatures. It depends on the partial pressure of O$_2$ for the Ce$^{4+}$ to Ce$^{3+}$ transformation because the ionic conductivity of ceria resulting from oxygen vacancies depends on the dopants and their amount. Especially, gadolinium and samarium doped ceria have the highest electrical conductivity because of the close ionic radii of Gd$^{3+}$ and Sm$^{3+}$ compared to the radius of Ce$^{3+}$. The ceria is highly refractory oxide and difficult to sinter without sintering aids. However, the trivalent rare-earth doped ceria particles with nanometer size can be densified at much lower temperature because of high surface energy of the nanoparticles, and expected to make it possible to provide fast densification kinetics, finer microstructure and better properties of the sintered materials contrast to the bulk ones.

Many solution based techniques have been successfully employed for preparation of nanocrystalline Gd and Sm-doped CeO$_2$, such as hydrothermal, mimic alkoxide, micro emulsion, sol–gel, precipitation, glycine-nitrate combustion, hydrazine, and spray pyrolysis. It is well known that the morphology, mean size and electrical properties of the ceria particles are affected by the doping concentration of dopant as well as the preparation method. Castillo and Munz found that as the CeO$_2$ crystals start growing, the incorporation of dopant cations into the CeO$_2$ solid lattice retarded crystal growth. Mahata et al. found that specific surface area of ceria particles prepared by combustion method increased with increase in gadolinium content due to the lowering exothermicity.

In this work, nano-sized ceria particles with various doping concentrations of gadolinium were prepared by ultrasonic spray pyrolysis process. The effects of doping concentration of gadolinium on the mean size and morphology of the ceria particles obtained after calcination were investigated. The characteristics of sintered bodies of the prepared Gd-doped ceria particles were also investigated.

2. Experiments

The spray pyrolysis system consists of droplet generator, quartz reactor, and particle collector. A 1.7 MHz ultrasonic spray generator having six vibrators was used to generate a large amount of droplets, which are carried into the high-temperature tubular reactor by a carrier gas. Droplets and particles evaporated, decomposed, and/or crystallized in the quartz reactor. The length and diameter of the quartz reactor are 1200 and 50 mm, respectively. The details of the preparation procedure and analysis method of GDC particles are given in the schematic diagram as shown in Fig. 1. Cerium and gadolinium nitrates were used as the sources of Ce and Gd components. Ethylene glycol was used as additive to the spray solution to change the morphology of the as-prepared particles obtained by spray pyrolysis. The concentration of cerium and gadolinium nitrates was fixed at 0.3 M. The doping concentration of gadolinium was changed in the range from 0 to 20 mol% of cerium. The flow rate of air used as carrier gas was 40 l/min. The as-prepared particles obtained by spray pyrolysis at a temperature of 900°C were calcined in the box furnace maintained at 900°C for 2 h.

The crystal structures of the calcined GDC particles were studied by X-ray diffraction (XRD, RIGAKU, D/MAX-RB) with Cu Kα radiation (λ = 1.5418 × 10$^{-10}$ m). The mean crystallite size of the GDC particles was estimated from Scherrer’s equation. The morphological characteristics of the particles were investigated using scanning electron microscopy (SEM, JEOL, JSM 6060) and transmission electron microscope (TEM, FEI, TECHNAI 300K). The density and electrical conductivity mea-
measurements are conducted on sintered GDC pellets. The calcined particles were pressed into pellets with a uniaxial hydraulic, followed by a cold-isostatic press at 250 MPa. The sintering temperature of the pellet was 1400°C and the pellets were cooled naturally to room temperature while furnace power was off. The density was measured by the Archimedes principle. The grain size and microstructure of the pellets were observed by SEM. The ionic conductivity was determined via electrochemical impedance spectroscopy at temperature ranges between 600 and 900°C in air atmosphere.

3. Results and discussion

The key idea to prepare the nano-sized Ce$_{1-x}$Gd$_x$O$_2$ particles is to make precursor particles with hollow and thin wall structures. Ethylene glycol added to the spray solution produced the particles with hollow and thin wall structure. Figure 2 shows the SEM photographs of the Ce$_{1-x}$Gd$_x$O$_2$ precursor particles with Ce:Gd molar ratios of 1:0, 0.95:0.05, 0.9:0.1, 0.8:0.2 obtained by spray pyrolysis from the spray solution with ethylene glycol. The precursor particles had large size, hollow and thin wall structures irrespective of the mole ratios of Ce to Gd components. Gas evolution generated by the decomposition of the ethylene glycol caused the particles with hollow and thin wall structures.

Figure 3 shows the SEM and TEM photographs of the Ce$_{1-x}$Gd$_x$O$_2$ particles calcined at a temperature of 900°C. The calcined powders were milled by hand using agate mortar for the preparation of TEM sample. The spherical shape and several micron sizes of the precursor particles were maintained after post-treatment. The micron-sized Ce$_{1-x}$Gd$_x$O$_2$ particles had slightly aggregated morphology of primary particles with nanometer size irrespective of the molar ratios of Gd to Ce components. In the TEM photograph as shown in Fig. 3(a), the pure...
Fig. 3. SEM and TEM photographs of calcined Ce$_{1-x}$Gd$_x$O$_2$ particles: (a) CeO$_2$, (b) Ce$_{0.95}$Gd$_{0.05}$O$_2$, (c) Ce$_{0.9}$Gd$_{0.1}$O$_2$, (d) Ce$_{0.8}$Gd$_{0.2}$O$_2$. 
CeO$_2$ particles had a hardly aggregated morphology with fine primary particle size. However, in the TEM photographs, the Gd-doped CeO$_2$ particles had a more loosely aggregated and regular morphology than the pure CeO$_2$ particles. Moreover, the degree of aggregation between the primary particles decreased with increasing the mole ratio of Gd to Ce components. The unique morphologies of the particles prepared by spray pyrolysis affected the aggregation characteristics of the Gd-doped ceria particles. The precursor particles with hollow and thin wall structure turned to the aggregated or slightly aggregated particles after post-treatment. The morphologies of the precursor particles with and without Gd dopant had the same morphologies. Therefore, the morphological characteristics of the post-treated particles are affected by the crystal growth characteristics of the ceria particles with and without Gd dopant. The incorporation of Gd-dopant into the CeO$_2$ solid lattice retarded crystal growth, as the CeO$_2$ crystals starts growing. Therefore, it is easy to dis-integrate the nano-structured Ce$_{1-x}$Gd$_x$O$_2$ particles into non-aggregated particles with nanometer size by a simple milling process. The mean size of the primary particles decreased with increasing the molar ratio of Gd. The mean sizes of Ce$_{1-x}$Gd$_x$O$_2$ ($x = 0, 0.05, 0.1, 0.2$) particles measured from the TEM images were each 46, 33, 29, and 28 nm. The calcined Ce$_{1-x}$Gd$_x$O$_2$ particles had yellowish-white color, which indicates the high crystallinity of prepared ceria particles.

**Figure 4** shows the X-ray diffraction patterns of Ce$_{1-x}$Gd$_x$O$_2$.
particles calcined at a temperature of 900°C. The peaks of all Ce_{1-x}Gd_xO_2 particles closely overlapped with CeO_2 peaks, which are cubic fluorite structure. However, the Gd dopant affected the crystallite sizes of the Ce_{1-x}Gd_xO_2 particles. The mean crystallite size of pure CeO_2 was 33 nm. However, the Gd-doped CeO_2 had the mean crystallite size of 28 nm irrespective of the molar ratio of Gd to Ce components. Especially, the mean crystallite size and primary particle size of the Gd-doped CeO_2 were similar. This indicates that the prepared Gd-doped CeO_2 particles with nanometer size are single crystal. High magnification TEM photograph and electron beam diffraction as shown in Fig. 5 reveal the single crystal of the Ce_{0.9}Gd_{0.1}O_2 particle.

The SEM photographs of the sintered Ce_{1-x}Gd_xO_2 pellets are shown in Fig. 6. Apparently, an increasing doping amount of Gd decreased the mean grain size of Ce_{1-x}Gd_xO_2 pellets. The mean grain size of the pure CeO_2 is about two or four times larger than those of the Gd-doped CeO_2 pellets. The mean grain sizes of Ce_{0.8}Gd_{0.2}O_2 and Ce_{0.9}Gd_{0.1}O_2 pellets are about 0.5–0.4 μm, which are very small size. The incorporation of Gd-dopant into the CeO_2 solid lattice retarded grain growth of Ce_{1-x}Gd_xO_2 pellets.

The ionic conductivity of GDC electrolyte is strongly affected by the density of the sintered body. For the use of sintered sample as an impermeable electrolyte membrane in an SOFC, the high density (> 95%) is generally considered to be an acceptable level of density. Figure 7 shows the relative densities of the sintered Ce_{1-x}Gd_xO_2 pellets measured by Archimedes principle using real and theoretical densities. The theoretical density of the Ce_{1-x}Gd_xO_2 pellets can be calculated using the following equation:

\[ D_b = 4/3\pi \rho [1+(1-x)M_{Ce}+xM_{Gd}+2(0.5422M_{Ce})] \]  

Where \( a \) is the lattice constant of the solid solution at room temperature, which is equal to 0.5422 nm, \( N \) is the Avogadro number and \( M \) refers to the atomic weight.\(^{26}\) The pure CeO_2 pellet had low relative density of 80%. However, Ce_{0.9}Gd_{0.1}O_2 and Ce_{0.8}Gd_{0.2}O_2 pellets had high relative densities above 95%. The high surface energy of the nano-sized Ce_{1-x}Gd_xO_2 particles produced the sintered pellets with high relative densities at a sintering temperature of 1400°C.

Figure 8 shows the Arrhenius plots of the conductivities of the sintered Ce_{1-x}Gd_xO_2 pellets in air atmosphere. The conductivities of Ce_{1-x}Gd_xO_2 pellets are strongly affected by the molar ratio of Gd to Ce components and the measuring temperature. The Ce_{0.9}Gd_{0.1}O_2 and Ce_{0.8}Gd_{0.2}O_2 pellets had similar conductivities at all measuring temperatures. The Ce_{0.9}Gd_{0.1}O_2 pellets has conductivities of 4.73 × 10^{-2} and 1.16 × 10^{-2} Scm^{-1} at measuring temperatures of 800 and 900°C respectively. The Ce_{0.9}Gd_{0.1}O_2 and Ce_{0.8}Gd_{0.2}O_2 pellets had high conductivities at temperatures of 800 and 900°C because of high densities resulted from the Gd-doped ceramic particles with nanometer size and regular morphology. Gadolinia doping in ceria introduces vacancies in the oxygen sub-lattice as charge compensating defects. Therefore, the conductivities of the Ce_{1-x}Gd_xO_2 (5 ≤ x ≤ 20) pellets were higher than that of the CeO_2 pellet.\(^{5-8}\)

4. Conclusion

The effects of doping concentration of gadolinium on the mean size and morphology of the nano-sized ceria particles prepared by spray pyrolysis were investigated. The Ce_{1-x}Gd_xO_2 particles obtained by spray pyrolysis had slightly aggregated morphology of primary particles with nanometer size irrespective of the mole ratios of Gd to Ce components. However, the degree of aggregation between the primary particles decreased with increasing the mole ratio of Gd to Ce components. The incorporation of Gd-dopant into the CeO_2 solid lattice retarded crystal growth. The concentrations of Gd-dopant also affected the characteristics of the sintered Ce_{1-x}Gd_xO_2 pellets, such as mean grain size, density, and conductivity. Ce_{0.9}Gd_{0.1}O_2 and Ce_{0.8}Gd_{0.2}O_2 pellets had fine grain sizes, high densities and high conductivities.

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References