Oxygen-Response Ability of Hydrogen-Reduced Nanocrystalline Cerium Oxide

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Abstract The potential application of ultrafine cerium oxide (ceria, CeO_2) as an oxygen gas sensor has been investigated. Ceria was synthesized by a thermochemical process: first, a precursor powder was prepared by spray drying cerium-nitrate solution. Heat treatment in air was then performed to evaporate the volatile components in the precursor, thereby forming nanostructured CeO_2 having a size of approximately 20 nm and specific surface area of 100 m^2/g . After sintering with loosely compacted samples, hydrogen-reduction heat treatment was performed at 773K to increase the degree of non-stoichiometry, x , in CeO_{2-x} . In this manner, the electrical conductivity and oxygen-response ability could be enhanced by increasing the number of oxygen vacancies. After the hydrogen reduction at 773K, $\text{CeO}_{1.5}$ was obtained with nearly the same initial crystalline size and surface. The response time t_{90} measured at room temperature was extremely short at 4 s as compared to 14 s for normally sintered CeO_2 . We believe that this hydrogen-reduced ceria can perform capably as a high-performance oxygen sensor with good response abilities even at room temperature.

Keywords: Cerium oxide, Oxygen gas sensor, Nanoparticles, Thermochemical process

1. Introduction

Oxygen gas sensors have been actively developed for a wide variety of applications such as in medical incubators for infants and in various oxygen providers; exhaust gas sensors have also been employed in gasoline-powered automobiles [1]. Currently, the most widely used oxygen gas sensors are oxygen-ion-conductor cells made of yttrium-stabilized zirconia (YSZ); they are used for measuring the oxygen concentration in exhaust gases [2]. In this sensor, a cell-type structure is employed to detect the differences in the oxygen concentration between a reference electrode and a sensing electrode. This not only makes the device structure complicated, but it is also difficult to reduce the sensor size; moreover, the working temperature is also relatively high ($\sim 1123\text{K}$) [3].

On the other hand, a resistive type of oxygen sen-

sor made of single-phase oxides has exhibited some promising features such as high oxygen-sensing capabilities, short response times and accomplished by easy particle refinement to nanometer scale, relatively low working temperatures and easy miniaturization of sensor devices due to its simple sensing mechanism [3, 4]. Among the materials for resistive oxygen sensors, a good candidate is cerium oxide (ceria, CeO_2) [5, 6]. The high oxygen sensibility of ceria, with its wide range of oxygen non-stoichiometry ($\text{CeO}_{1.5-2.0}$), originates from its unique crystal structure in which significant amounts of oxygen vacancies provide good electrical mobility [7].

Furthermore, particle refinement causes many defects in surfaces, which leads to an increase of the x value in CeO_{2-x} ; this in turn increases electrical conductivity. Hence, the particle refinement is very important

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to increase electrical conductivity. In our previous work, nanostructured ceria powders having a size of 20 nm and specific surface area of 100 m²/g were synthesized by thermochemical processes and the oxygen response time (t_{90}) was studied [8]. Moreover, it was also reported that micron-sized ceria particles showed rapid increase in electrical conductivity with the degree of non-stoichiometry after hydrogen-reduction heat treatment [9]. In this study, we have attempted to understand the effects of hydrogen-reduction heat treatment on t_{90} and the powder properties of nano-sized ceria produced by thermochemical processes.

2. Experimental

The thermochemical processes consisted of two simple steps: (1) the preparation of the precursor by spray drying of cerium-nitrate solution and (2) the formation of ceria during heat treatment of the precursor in air. Subsequently, the spray-dried precursor was heat treated at 673K for 2 h in air to remove any volatile moisture content and NO₃ components. Simultaneously, the cerium component was oxidized to form nanostructured cerium oxide. The produced powders were compacted loosely at 1.5 Pa/cm² and sintered at 1273K for 1 h in air. The dimensions of the plate-type sintered specimens were approximately 0.5 mm × 5 mm × 12 mm. The sintered samples were then heat-treated from 473K to 1273K in hydrogen at a flow rate of 1 l/min.

All the powders and sintered specimens were examined by using a scanning electron microscope (HITACHI S4200) and Cu $K\alpha$ X-ray diffraction (RIKAKU R2000). The electrical resistance was measured using a multimeter (KEITHLEY 2000); here, four-probe-type platinum electrodes (5 mm × 5 mm) were contacted on both sides of a sintered plate. Finally, the oxygen response times, t_{90} were obtained from the resistance profiles that varied with sudden changes in the oxygen partial pressure from 0.2 to 0 at room temperature.

3. Results and Discussion

During the spray drying, helically generated droplets were dried inside the chamber, leading to the formation of amorphous particles comprising Ce-O-NO₃ components and small amounts of moisture. The particles were fully transformed into the cerium oxide phase after the removal of volatile components by heat treatment in air at 673K. The formation of the amorphous phase by spray drying and the nanosized oxide particles by the de-binding heat treatment has been studied previously [9, 10].

Fig. 1 shows the morphology of the ceria particles after the de-binding treatment. The ceria particles were extremely fine and nearly spherical with a diameter of approximately 15 nm. Further, they were loosely agglomerated with a specific surface area of 110 m²/g. Moreover, the phase was revealed to be pure cerium oxide (JCPDS file No. 34-0394) [8].

In the next step, to prepare the sample for electrical resistivity measurements, the de-binding powders were loosely compressed and sintered at 1273K for 2 h; its SEM microstructure is shown in Fig. 2. The low-magnification figure (Fig. 2a) shows a flat surface well formed by die compaction, while the size of internal particles still remained approximately 40 nm with a good porous structure (Fig. 2b).

It is interesting that gradual weight loss occurred

Fig. 1. SEM microstructure of cerium oxide particles obtained after debinding heat treatment in air at 673K for 2 h.

Fig. 2. SEM microstructures at (a) low and (b) high magnifications for ceria sample sintered at 1273K for 1 h.

Fig. 3. Thermogravimetric (TG) profile during heating of sintered sample at heating rate of 5 °C/min in hydrogen atmosphere.

during the continuous heating at 5°C/min in hydrogen atmosphere as result of the reduction effect of the reaction $\text{CeO}_2 + x\text{H}_2 \rightarrow \text{CeO}_{2-x} + x\text{H}_2\text{O}$. In the

Fig. 4. X-ray diffraction patterns measured in samples sintered and further H_2 -reduced at 773K for 1 h (a) normal and (b) magnified patterns reflected at (111) crystal plane.

thermogravimetric profile shown in Fig. 3, it was found that the stoichiometry decreased to $\text{CeO}_{1.5}$ by the reduction effect at 773K, and it further decreases at elevated temperatures.

The X-ray diffraction patterns in Fig. 4 show that at 873K, the samples were sintered and further hydrogen-reduced. Both the normal and magnified images shown the ceria phase; moreover, the magnified profile showed left-shift for the reflection at the (111) plane by hydrogen heat treatment. Such peak shifting obviously resulted from an increase in the lattice parameter caused by the formation of oxygen deficiencies [11].

Sample characterizations were obtained after hydrogen-reduction heat treatment at various temperatures (Fig. 5). Fig. 5 indicates that the particle coarsening

Fig. 5. Changes in crystal sizes, surface areas, and lattice parameters of ceria samples obtained after hydrogen-reduction heat treatments at various temperatures for 1 h.

was inhibited until 773K, and the specific area was maintained at around $100 \text{ m}^2/\text{g}$. It can be theorized that the hydrogen reduction occurs particularly on the particle surface. The lattice parameter reached maximum value around 773K but decreased with higher temperatures due to the core-bulk effect of particle coarsening.

SEM microstructures of the ceria samples that were hydrogen-reduced for 1 h at 573K, 973K, and 1273K are shown in Fig. 6. Slight coarsening of the particles occurred at 973K, while at the elevated temperature of 1273K, the particle growth was considerable, which is probably a result of crystal insta-

Fig. 6. SEM microstructures of ceria samples hydrogen-reduced for 1 h at (a) 673 K, (b) 973K, and (c) 1273K after sintering.

bility due to the oxygen deficiencies. Finally, from Fig. 3, Fig. 4 and Fig. 5, it can be decided that the optimum temperature for H₂-reduction heat treatment was 773K; the maximum values of the lattice parameter and surface areas were obtained at this

temperature.

It is important to conduct detailed measurements of the lattice parameters from the results of X-ray diffraction patterns obtained in the ceria samples before and after the hydrogen heat treatment at 773K. The extrapolation technique was used to define it [12].

a_i is each lattice parameter measured by each peak reflected at each (h_p, k_p, l_i) plane; it is given by the following equation:

$$a_i = (h_i^2 + k_i^2 + l_i^2)^{1/2} \times \lambda / 2 \sin \theta \quad (1)$$

Further, $f(\theta)$ is a function obtained using the following equation, wherein the theta-value corresponds to the (h_p, k_p, l_i) peak.

$$f(\theta) = \cos^2 \theta / \sin \theta_i + \cos^2 \theta_i / \theta_i \quad (2)$$

In other words, the real lattice parameter can be defined as $f(\theta)$ approaches zero. Fig. 7 shows the results of applying the above concept; the lattice parameter measured in the samples sintered and hydrogen treated were 5.416 Å and 5.442 Å, respectively. This clearly demonstrates the considerable increase in the lattice parameter by hydrogen reduction [11]. The slight difference in the lattice parameter values between the sintered sample and the JCPDS standard can be explained by the different particle sizes or sample structures of the used ceria materials.

Finally, the oxygen response-abilities of the sin-

Fig. 7. Determination of lattice parameters of sintered and hydrogen-reduced ceria.

tered and post H₂-reduced samples are compared. Ceria is known to a n-type semiconductor, and its electrical conductivity is dominated by the mobility of the electrons trapped by cerium and oxygen vacancies [7]. From the formation of one oxygen vacancy, 2 electrons can contribute to the conductivity as follows:

Here $\text{Ce}_{\text{Ce}}^{\times}$ and $\text{O}_{\text{O}}^{\times}$ are regular lattice ions whereas $\text{Ce}_{\text{Ce}}^{\prime}$ and V_{O}^{**} are charged defects; $\text{Ce}_{\text{Ce}}^{\prime}$ represents the electron trapped by $\text{Ce}_{\text{Ce}}^{\times}$ while V_{O}^{**} represents the doubly ionized oxygen vacancies. Accordingly, the high density of mobile electrons, $\text{Ce}_{\text{Ce}}^{\times}$ may help to increase the response ability against any sudden changes in the oxygen partial pressure. It has also been considered that the electron density as well as the vacancy density is higher in the H₂-reduced sample due to the oxygen reduction effect. The normalized resistance profiles measured at room temperature - with the sudden changes from air to argon atmosphere - are compared in Fig. 8. Actually, the resistance signal could not be detected at room temperature in normal micron-sized ceria sample by our multi-meter because it was nearly non-conducting material.

The response time t_{90} was obtained after normalizing the actual resistance profiles. It is considerably

Fig. 8. Comparison of the response times t_{90} of sintered and hydrogen-reduced ceria.

shorter (4 s) than that in the sintered sample (14 s). In our previous work, t_{90} in sintered nano-ceria was 3~5 s at 973K [8]. Moreover, it has been reported that t_{90} is 8~35 s at 1080~1275K in 1 mm ceria [13], 8 s at 1080 K in 200 nm ceria [14], and 10~11 s at 888~936K in 100 nm ceria [15]. Therefore, it must be emphasized that t_{90} obtained in this study is very short even at room temperature. Therefore, it is believed that the developed H₂-reduced ceria can perform as a high-performance O₂-sensor with good response abilities even at room temperature.

4. Conclusions

Nanostructured ceria particles having a size of approximately 15 nm were successfully synthesized by thermochemical processes. Precursor powder was prepared by spray drying cerium-nitrate solution and then heat-treating at 673K in air to evaporate volatile components, thereby forming nanostructured ceria. The average grain size of sintered ceria at 1273K was approximately 40 nm. By hydrogen reduction of the sintered sample, the lattice parameter and non-stoichiometric degree were increased. The response time t_{90} of the hydrogen-reduced specimen was 4 s, which is considerably shorter than that of normal sintered nano-ceria, 14 s. This H₂-reduced ceria can capably perform as a high-performance O₂-sensor even at room temperature. We are now investigating

sensor reliability as well as device miniaturization techniques to maximize the resistance signal.

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