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# Oxygen sensitivity of nanostructured cerium oxide prepared by a thermochemical process

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Ultra fine cerium oxide (ceria, CeO<sub>2</sub>) powder was synthesized by a thermochemical process and tested for its feasibility as an oxygen gas sensor. Procedures of the process consisted of the preparation of a precursor powder by spray drying a ceriumnitrate solution and the heat treatment in air to evaporate volatile components from the precursor, thereby forming nanostructured CeO<sub>2</sub>. The powder produced had a loose agglomerated structure with extremely fine CeO<sub>2</sub> particles about 15 nm in size, yielding a very high specific surface area (110 m<sup>2</sup>/g). The average grain size of a sample sintered from the ceria powder at 1000 °C was about 40 nm. At 600 °C, its oxygen sensitivity,  $n (\log \sigma \propto \log(P_{O_2}/P_0)^{-n})$  was about 0.25, which was considerably higher than that measured from the porous samples possessing micrometer- or 100~200 nanometer-size grains.

Key words: Ceria (CeO<sub>2</sub>), oxygen gas sensor, nanoparticles, thermochemical process.

## Introduction

Oxygen gas sensors have been actively developed for wide applications such as exhaust gas sensors in gasoline-powdered automobiles, medical incubators for infants, and various oxygen providers [1]. Currently, the most widely used oxygen gas sensors are oxygenion-conductor cells made of yttrium-stabilized zirconia (YZT) for measuring the oxygen concentration in exhaust gas [2]. However, since a cell-type structure is employed in these sensors to detect the difference in oxygen concentration between a reference electrode and a sensing electrode, their structure is relatively complicated and difficult to reduce in size. In addition, their working temperature is also significantly high (~850 °C) [3].

On the other hand, a resistive oxygen gas sensor that consists of a single phase oxide has exhibited some promising features such as high oxygen-sensing capability, short response time accomplished by a reduction of the powder size to the nanometer scale, relatively low working temperature, as well as easy miniaturization of the sensor due to its simple sensing mechanism [3, 4]. One of the good candidates for such high performance oxygen gas sensors is cerium oxide (ceria,  $CeO_2$ ) [5, 6]. The high oxygen sensitivity of ceria originates from its unique crystal structure that has a wide range of oxygen non-stoichiometry ( $CeO_{1.8-2.0}$ ) in which significant amounts of oxygen vacancies provide good electrical mobility. Accordingly, many studies have tried to obtain nanostructured ceria powder for fabrication of high performance resistive oxygen gas sensors [3, 4].

In this study, we attempted to synthesize nanostructured ceria by a thermochemical process. The synthesized powder and a subsequently sintered bulk sample were then characterized by various methods. In particular, the dependence of the electrical conductivity on the oxygen partial pressure and temperature was investigated to work out the oxygen sensitivity.

#### **Experimental**

The thermochemical process was performed in a simple sequence of 1) the preparation of a precursor by spray drying a cerium-nitrate solution and 2) the formation of cerium oxide (CeO<sub>2</sub>) during heat treatment of the precursor in air [7]. Cerium-nitrate ( $Ce(NO_3)_2 \cdot 6H_2O$ ) was dissolved in water with a nitrate concentration of 50% followed by spray drying of the solution by a centrifugal disk atomizer with a disk diameter of 66 mm and a rotation speed of 15,000 RPM. The spraydried precursor was then heat treated at 400 °C for 3 hours in air to remove volatile components and nitrate components and, at the same time, the cerium component was oxidized to form nanostructured cerium oxide. For the evaluation of electrical conductivity, the powder produced was compacted at 3 Pa/cm<sup>2</sup> and sintered at 1000 °C for 2 hours in air. The dimensions of the plate-type sintered specimens were approximately 0.5 mm×5 mm×12 mm.

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Both the powder and the sintered specimens were examined by means of a scanning electron microscope (HITACHI S4200) and Cu  $K\alpha$  X-ray diffraction (RIGAKU R2000). In order to measure the electrical conductivity, four-probe type platinum electrodes (5 mm×5 mm) were contacted onto both sides of a sintered plate. Then resistance outputs were read using a multimeter (KEITHLEY 2000) under various oxygen partial pressures (0.0-0.25) and temperatures (550-700 °C). The resistance values were finally converted to electrical conductivities by adding the size factor of the sintered specimen.

### **Results and Discussion**

During spray drying, the helically generated droplets from the rotating disk were dried inside the chamber, leading to the formation of a uniformly distributed precursor powder. The powder was confirmed to be amorphous by X-ray diffraction, which was obviously a mixture of Ce atoms and NO<sub>3</sub> molecules. The NO<sub>3</sub> in the precursor powder should be removed immediately because it can easily absorb moisture again. It is necessary then to find an optimum temperature of heat treatment for removal of the NO<sub>3</sub> and other volatile components. To do this, the weight change in the precursor powder by evaporation of the volatile components was examined by thermogravimetric analysis as shown in Fig. 1. It can be seen in the figure that  $NO_3$ was fully removed upon heating above 300 °C after the removal of moisture at about 220 °C. Therefore, the heat treatment for the removal of volatile components in the precursor was done at 400 °C.

Figure 2 shows the morphology of the ceria powder after heat treatment. The shape of the particles in a wide range from 1 to 30  $\mu$ m was fairly irregular. However, it was found that, as shown in Fig. 3, each irregular particle was in fact a cluster of extremely fine spherical particles about 15 nm in diameter which were



Fig. 1. TGA profile of precursor powder. (Heating rate: 10  $\text{Kminute}^{-1}$ )

 Λοον
 Spot Magn
 Det. WD
 10 μm

 Λοον
 Spot Magn
 Det. WD
 10 μm

Fig. 2. SEM microstructure of cerium oxide powder.



Fig. 3. Closer look at the cerium oxide powder in Fig. 2.

loosely agglomerated. Such loosely bound clusters yielded a very high specific surface area ( $110 \text{ m}^2/\text{g}$ ). As shown in Fig. 4, the heat-treated powder was confirmed to be pure cerium oxide (JCPDS file No. 34-0394). The particle size calculated by the well-known Scherrer formula was about 8 nm, much smaller than that



Fig. 4. X-ray diffraction pattern measured from the cerium oxide powder.

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Fig. 5. SEM microstructure of a specimen sintered at  $1000\,^{\circ}$ C for 2 hours.

measured from the visible microstructure in Fig. 3. This indicates that individual spherical nanoparticles in Fig. 3 may also consist of two or more cerium oxide subparticles.

The density of the CeO<sub>2</sub> green compact compressed at 3 Pa/cm<sup>2</sup> was 0.19 g/cm<sup>3</sup>. However, it increased to  $4.10 \text{ g/cm}^3$  (relative density; 57%) after sintering at 1000 °C for 2 hours. Moreover, grains in the sintered specimen still remained in the nanometer range as shown in Fig. 5, resulting in the average grain size of about 40 nm.

In gernal, the elecrical conductivity  $\sigma$  is proportional to  $(P_{O_2}/P_o)^{-n}$  where  $P_{O_2}/P_o$  is the oxygen partial pressure and *n* is the  $P_{O_2}$  dependence, representing the sensitivity of a sensor. It is necessary therefore to get the relationship between log  $\sigma$  and log  $(P_{O_2}/P_o)$  to determine the behavior of a sensor. As shown in Fig. 6, the relationships between log  $\sigma$  and log  $(P_{O_2}/P_o)$  were relatively linear and similar to each other regardless of the temperature. As a result, *n* values, measured from the slope of each curve, were also almost the same, indicating that *n* is independent of temperature. A



Fig. 6. Relationship between logarithmic electrical conductivities and oxygen partial pressures measured at various temperatures.



Fig. 7. Relationship between logarithmic electrical conductivities and oxygen partial pressures measured at 600 °C.

typical value of n obtained from the curve at 600 °C was 0.245 as revealed in Fig. 7.

It has been found that the electrical conductivity of ceria, which is known to an n-type semiconductor, is dominated by the mobility of the electrons trapped by cerium and oxygen vacancies [8]. By the formation of one oxygen vacancy, 2 electrons can contribute to the conductivity as [9]:

$$2Ce^{x}_{Ce}+O^{x}_{o}=2Ce^{2}_{Ce}+V^{**}_{o}+1/2O_{2}$$

where Ce<sup>x</sup><sub>Ce</sub> and O<sup>x</sup><sub>o</sub> are regular lattice ions whereas Ce'<sub>Ce</sub> and V<sup>\*\*</sup><sub>o</sub> are charged defects. Here, Ce'<sub>Ce</sub> represents the electron trapped by  $Ce_{Ce}^{x}$  and  $V_{o}^{**}$  represents the doubly ionized oxygen vacancies, respectively. Accordingly, the concentration of mobile electrons can be determined by the oxygen partial pressure. In ceria, it is known that the conductivity is proportional to  $(P_{O_2}/P_o)^{-1/6}$  in the intrinsic state whereas to  $(P_{O_2}/P_o)^{-1/4}$ in the extrinsic state [8]. This means that the concentration of oxygen vacancies in ceria is mainly determined by impurities and not by the equilibrium oxygen pressure. It should be noted that the concentration of vacancies can be controlled by doping trivalent impurity cations (M<sup>+3</sup>) into the original tetravalent cation (M<sup>+4</sup>) sites, as with yttrium-stabilized zirconium oxide  $(Zr(Y)O_2)$ . Recently, it has been reported that an undoped porous ceria possessing micrometer-sized grains exhibits a  $P_{02}$  dependence of 1/6 that is a typical intrinsic property [10, 11]. By contrast, as shown in Fig. 7, a specimen that has an average grain size of 40 nm exhibits a  $P_{O_2}$  dependence of 1/4.

Assuming that the  $P_{O_2}$  dependence *n* of a sensor is simply an intrinsic property of a material, not influenced by testing modes, the *n* values obtained from this study were compared with the values reported in other investigations. As shown in Fig. 8, a porous bulk ceria with an average grain size of 100 or 200 nm exhibited 1/6 dependencies [12, 13]. However, a bulk, with an average grain size of ~40 nm, made from the nano-



Fig. 8. Comparison of oxygen sensitivities with other reported results.

structured powder synthesized in this study exhibited 1/4 dependencies, similarly to those of thin film ceria possessing approximately 20 nm-size grains [8]. Such high  $P_{\Omega_2}$  dependencies are obviously attributed to the enlargement of grain boundary area due to grain refinement [14]. It has been reported that cerium oxide can behave both intrinsically and extrinsically in theory because Ce<sup>4+</sup> and Ce<sup>3+</sup> ions can coexist in the compound, creating the doping effect by Ce<sup>3+</sup> which leads to the formation of  $Ce^{4+}(xCe^{3+})O_{2-x}$  [15]. Therefore, as demonstrated in this study, pure ceria is able to have a  $P_{\Omega_2}$  dependency of 1/4 without doping when its grain size decreases below 50 nm because the enlarged grain boundary area promotes the formation of a sufficient quantity of defects and oxygen vacancies that possibly give the extrinsic behavior of the material and increase the concentration of mobile electrons.

#### Conclusions

Nanostructured ceria particles of about 15 nm in size were successfully synthesized by a thermochemical process. The precursor powder was prepared by spray drying a cerium-nitrate solution and then the precursor was heat treated at 400 °C in air to evaporate volatile components, thereby forming nanostructured CeO<sub>2</sub>. The average grain size of a specimen sintered from the synthesized ceria powder at 1000 °C was about 40 nm. The oxygen sensitivity *n* of the sintered specimen was about 1/4 in the temperature range 550-700 °C, which was considerably higher than that measured from porous specimens possessing micrometer- or 100~200 nanometer-size grains.

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