High Oxygen Sensitivity of Nanocrystalline Ceria Prepared by a Thermochemical Process

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Abstract

Nanostructured ceria powder was synthesized by a thermochemical process and investigated its applicability for an oxygen gas sensor. An amorphous precursor powders prepared by spray drying a cerium-nitrate solution were transformed successfully into nanostructured ceria by heat-treatment in air atmosphere. The powders were a loose agglomerated structure with extremely fine CeO_2 particles about 15 nm in size, resulting in a very high specific surface area (110 m^2/g). The oxygen sensitivity and the response time t_{90} measured at sintered sample at 1000°C was about -0.25 and very short, i.e., 3 ~ 5 seconds, respectively.

Keywords : Cerium Oxide, Oxygen sensor, Nanoparticles, Thermochemical Process

1. Introduction

Many studies have been devoted to develop oxygen gas sensors for wide applications such as exhaust gas sensors in gasoline-powdered automobiles, medical incubators for infants, and various oxygen providers [1]. Unlike the most widely used oxygen gas sensors made of yttrium-stabilized zirconia (YSZ), a resistive oxygen gas sensor that consists of 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, and easy miniaturization of the sensor due to its simple sensing mechanism [2,3]. One of good candidates for such high performance oxygen gas sensors is cerium oxide (ceria, CeO_2) [4,5]. The high oxygen sensitivity of the cerium oxide originates from its unique crystal structure that has wide range of oxygen non-stoichiometry ($CeO_{1.8\sim2.0}$) in which significant amounts of oxygen vacancies provide good electrical mobility. For that reason, many works have been attempted to obtain nanostructured cerium oxide for fabrication of high performance resistive oxygen gas sensors [2,3].

We tried a fabrication of nanostructured ceria powder by a thermochemical process in this study with the investigation of their feasibility as oxygen gas sensors.

2. Experimental and Results

The thermochemical process was accomplished in a simple sequence of the preparation of a precursor by spray drying a cerium-nitrate solution and the formation of cerium oxide (CeO_2) during heat treatment of the precursor in air [6]. The spray-dried precursor powder 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 sensor properties the powder synthesized was compacted at 3 Pa/cm^2 and sintered at 800~1100°C for 2 hours in air.

Both the powder and the sintered specimens were examined by scanning electron microscopy and X-ray diffraction. In the sintered samples at 800~1100°C, the sensor sensitivities and dynamic response times were measured in the resistance analizer with four-probe platinum.

Fig. 1 shows the morphology of the cerium-oxide powder after heat treatment for the removal of volatile components. The extremely fine spherical particles about 15 nm in diameter were loosely agglomerated. Such loosely bound clusters yielded a very high specific surface area (110 m^2/g). By X-ray diffraction, the heat-treated powder was confirmed to be pure cerium oxide (JCPDS file No. 34-0394.

The density of the ceria green compact compressed at 3 Pa/cm^2 was only 0.19 g/cm^3. But it increased to 4.10 g/cm^3 (relative density; 57%) after sintering at 1000°C for 2 hours. Moreover, we found that the grains in the sintered specimen still remained in the nanometer range, resulting in the average grain size of about 40nm.

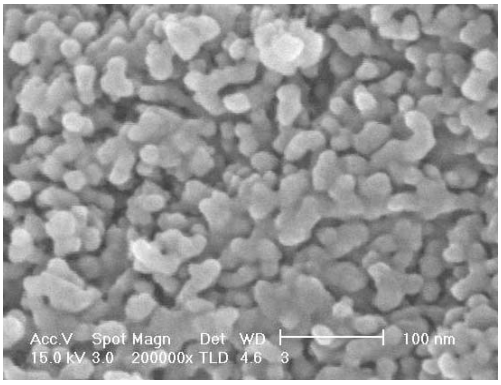

Fig. 1. SEM structure of produced ceria nano-particles

The electrical conductivity σ is generally 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. We found that the relationships between log σ and log (P_{O_2}/P_o) were relatively linear and similar to each other in the temperature range from 500°C to 700°C [7]. A typical value of n obtained at 600°C was 0.245, i.e., about 1/4 [8], which was considerably higher than the value 1/6 measured from an undoped porous ceria possessing micrometer-size grains [8,9].

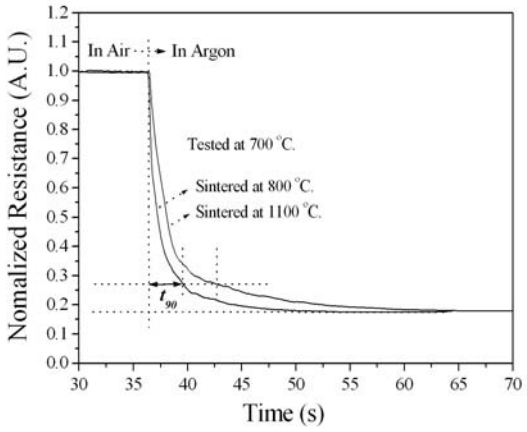

Fig. 2. The response time t_{90} of the specimens sintered from the nanostructured ceria powder.

As shown in Fig. 2, the response time t_{90}, time for replying to a sudden change of oxygen partial pressure, of the bulk specimens sintered from the nanostructured powder synthesized in this study was measured at 700°C.

The response time for the specimen sintered at 1100°C was 5 seconds and for the one sintered at 800°C was even shorter, 3 seconds. Such rapid responses to the oxygen pressure change are obviously due to the faster reaction of the oxygen on the nanostructured grain surface. Furthermore, the response time would become shorter as the grain surface area increases. In fact, the relative density of the specimen sintered at 800°C was 53%, yielding a specific surface area of 76 m^2/g whereas that of the specimen sintered at 1100°C was 78%, with a specific surface area of 42 m^2/g. The response times measured from a porous bulk ceria with an average grain size of 100 or 200 nm were 5~8 seconds [2], which are approximately two times longer than those measured from the sintered specimens prepared in this study.

3. Summary

We have successfully synthesized nanostructured ceria particles of about 15 nm in size by a thermochemical process. The average grain size of a specimen sintered from the synthesized ceria powder at 1000°C was about 40 nm. The response time t_{90} of the specimens sintered at 800~1100°C was 3 to 5 seconds, which was quite faster than those measured from porous bulk specimens possessing micrometer- or 100 ~ 200 nanometer-size grains

4. References

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