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Preparation of a porous ceria coating for a resistive oxygen sensor

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ABSTRACT

Oxygen sensors play important roles in areas such as determining the oxygen content in exhaust gas and optimizing combustion. Resistive oxygen sensors made of an *n*-type semiconductor, doped ceria (CeO$_2$), have recently received much attention due to their relatively compact and simple structures. In the present study, alumina substrate was first coated with electrodes by screen printing. Porous ceria films were then coated on the electrodes using different mixtures of two undoped ceria powders synthesized by spray-pyrolysis and precipitation, respectively. The ratios of the two powders were varied to produce differences in the heat-treated porosity of the ceria films. The resistive oxygen sensors exhibited a 3-D interconnected pore structure that could be optimized by varying the powder ratio for sensing properties. The dynamic response to the change in oxygen partial pressure of the optimized porous structure at 1073 and 1123 K was >1.8 times faster than those of non-optimized structures. Details on the processing, optimization of compositions, and responses to variation in oxygen partial pressure are provided. The mechanisms for the formations of the powders and the porous coatings are also described.

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1. Introduction

Advances in industrial technology and economic development accelerate the need for automatic production, and due to increases in exhaust gas emissions, it is important to reduce industrial and automotive emissions. The oxygen gas sensor, one of the most widely used types of sensors, can be applied to control the air/fuel combustion ratio in exhaust gas emitted from industrial plants and vehicles so that fuel efficiency and engine performance can meet demanding environmental criteria [1–3]. Therefore, in recent years, it has been the aim of numerous researchers to develop oxygen sensors with high performance and low cost.

Among the several types of gas sensor, the resistive sensor has recently received much attention. It is relatively compact, has a simple structure, and may be relatively inexpensive to produce [2,4]. Undoped ceria (cerium dioxide, CeO$_2$) with a non-stoichiometric structure (CeO$_{2-x}$) can be used as the sensing material in resistive-type oxygen sensors because its *n*-type semiconductor behavior operates under various oxygen partial pressures at intermediate temperatures (above 973 K) [2,5–8]. This prevents any surface

contamination of the sensor, which could occur during operation at low temperatures [4]. Moreover, in addition to having high oxygen-ion conductivity under an oxygen partial pressure (P_{O_2}) of 10^5 Pa or lower, ceria also exhibits good structural stability and high oxygen mobility. Our previous study has demonstrated that a resistive oxygen sensor with good temperature independence can be fabricated from precipitated ceria–zirconia solid solution powders [9]. In that study, ceria powders with different amounts of zirconia doping were respectively coated onto a platinum electrode printed substrate as the oxygen partial pressure measurement material (OMM) and temperature compensating material (TCM). However, the microstructure of the ceria sensor coating was not adjusted or investigated to optimize the sensing performance. This optimization may be crucial to the performance of a ceria gas sensor. Several studies have demonstrated that porous ceramic coatings can be used in gas sensors [10], catalyst supports [11], and other applications. Porous and/or mesoporous ceria have shown great potential for optical, magnetic [12], and catalytic applications [13,14] due to their high surface area and the increased dispersion of active secondary additions. However, the structural collapse of porous ceria during surfactant removal may cause poor thermal stability at elevated temperatures [15]. This commonly limits the use of porous ceria as a coating in gas sensors.

A sensor coating with a porous structure can be expected to produce better sensing performance due to its high surface area for reacting with the sensed gas [16–19]. However, because it is

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difficult to quantify a specific surface area of a film on the substrate, it is more practical and easier to directly measure the characteristics that are influenced by the surface area of the film, such as sensing properties and electrochemical reactivity. In the literature, porous ceramics have been produced by numerous processing routes, such as partial sintering, replica technique, sacrificial template, and direct foaming methods [11]. Based on similar concepts, these approaches have been adopted for the preparation of porous sensor coatings. Moreover, although the nanostructured CeO_2 has been known to be an advantageous oxygen sensor for a decade [6], the high operation temperature may cause the nanostructured CeO_2 coating to coalesce, resulting in a decline in the sensing performance. For application in gas sensors, however, to the best of our knowledge, the porous microstructure of the ceria coating has not yet been adjusted directly and systematically by powder synthesis to optimize the sensing performance.

In this study, two undoped ceria powders prepared respectively by spray pyrolysis (sp) and precipitation (p) methods were mixed to various (sp/p) ratios; subsequently, the powder mixtures were screen-printed onto a Pt-electrode coated alumina substrate for the fabrication of an oxygen gas sensor. Post heat treatments were carried out to improve the thermal stability and promote the formation of the porous ceria coating before the sensing properties were measured. The particulate morphology of the resulting powders was observed by transmission electron microscopy (TEM). The phase and microstructure of the porous films were identified by X-ray diffractometry (XRD) and scanning electron microscopy (SEM), respectively. The electrical resistive behavior of the ceria coatings was measured under various oxygen partial pressures as a function of operation temperature. The sensing behavior, including the response times of the powder coatings to changes in oxygen partial pressure, was investigated as a function of sp/p ratio. We propose a reasonable mechanism for adjusting the performance of a resistive oxygen sensor by adjusting systematically the microstructure of the ceria coating.

2. Experimental procedures

In the present study, the oxygen sensing properties of a porous ceria coating were investigated by screen printing two ceria powders onto alumina substrate. Two undoped ceria powders were synthesized respectively by spray-pyrolysis (sp) and precipitation (p) methods to produce different particulate morphologies. Then powders with various sp/p ratios were mixed with organics to produce a paste for screen printing onto a Pt-electrode-printed alumina substrate. The powder coatings were subsequently calcined and heat-treated to remove organics, sinter the particles, and adhere the coating on the substrate. Subsequently, the oxygen sensing properties of the powder coatings were characterized.

In the spray pyrolysis process, the precursor used to synthesize the CeO_2 powder was cerium nitrate hydrate (CeNH). The chemical formula is $Ce(NO_3)_3 \cdot 6H_2O$ (Alfa Aesar, A Johnson Matthey Co.), at reagent grade. The molecular weight of CeNH reported by the manufacturers is 434.23. The powder was synthesized using a bench-scale precursor-droplet nebulizer, tubular furnace, and electrostatic deposition system [20,21]. The nebulizer first atomized 5.0 wt.% CeNH aqueous solution into droplets with a resonant frequency of 1.65 MHz (King Ultrasonics Co., Ltd., Taipei, Taiwan). The precursor droplets were then carried into the tubular furnace, which consisted of a three-zone heated furnace and a tubular quartz reactor (length of 90 cm and inner diameter of ~6.8 cm). The precursor droplets passed through solvent evaporation, solute precipitation, and decomposition, and were finally sintered into particles. Subsequently, the resulting particles were collected by a homemade cylindrical electrostatic collector, which consisted of
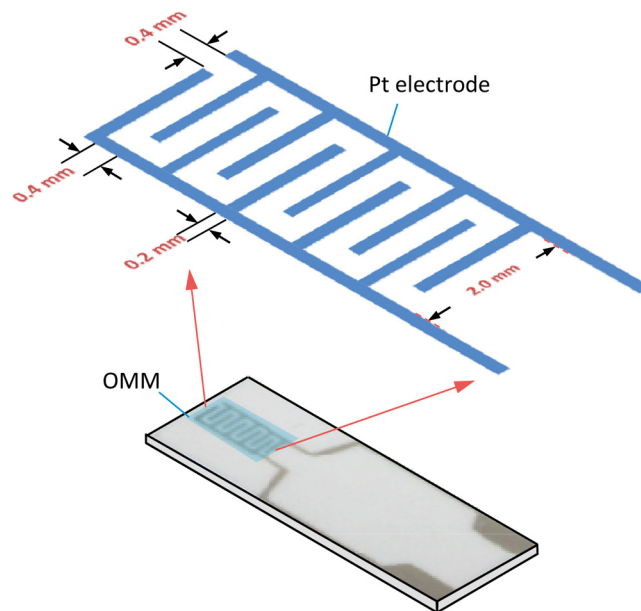

Fig. 1. Interdigital structure electrode and its configurational details used for sensor characterizations of OMM in the present study.

an outer stainless-steel cylinder insulated with Teflon and a central discharge electrode wire. A power supply was used to apply a negative voltage of 16 kV to the central electrode, and the collection cylinder was grounded. The pyrolysis temperature in the middle zone was set at 923 K. In the precipitation process, the same precursor (CeNH) was used. The concentration of the precursor solution, CeNH in de-ionized water, was 5.0 wt.% for precipitation. The pH value of the aqueous solution was maintained at 10 by adding aqueous ammonia under stirring at 343 K for 1 h. Then the precipitate was rinsed several times and dried at 353 K for 24 h. After cooling to room temperature, the resulting precipitate was collected. Subsequently, powders synthesized by spray pyrolysis (sp) and precipitation (p) with various sp/p ratios were mixed with terpineol (J.T. Baker Co., USA) and ethyl cellulose (48%, Aldrich Co., USA) to create a paste. The sp/p powder ratios of 10/0, 7/3, 5/5, 3/7, and 0/10 are denoted as sp10p0, sp7p3, sp5p5, sp3p7, and sp0p10, respectively. Then the powder paste was screen-printed onto Pt-electrode coated Al_2O_3 substrates (4 mm × 8 mm × 0.6 mm). The weight ratios of the terpineol to ethyl cellulose and the organics to powder were set at 93.5:6.5 and 60:40, respectively. Single interdigital structures of Pt electrode were designed for sensing measurements. The details of the interdigital electrode configuration are presented in Fig. 1. To remove the residual organics and confirm the formation of the oxide coating, the screen-printed thick films were calcined at 773 K for 5 h in air (TF55035A, Lindberg/Blue M, USA). The heating and cooling rates were 5 K/min. Subsequently, the films were heat treated at 1473 K for 2 h in air (BF51314 C, Lindberg/Blue M, USA). The heating and cooling rates were both 5 K/min.

The microstructures of as-mixed and heat-treated thick films were observed using high resolution transmission electron microscopy (TEM, 1200EX, JEOL II, Japan) and field emission scanning electronic microscopy (FE-SEM, Hitachi S-4800, Japan), respectively. The phases were identified by X-ray diffractometry using CuKα radiation (XRD, SRA M18XHF, MacScience Co., Ltd, Japan). The electrical resistance of the thick films was recorded in a 2.5 in. tubular furnace (HTF 55322C, Lindberg/Blue M with a quartz tube of 5.3 cm inner diameter and 100 cm length) as a function of temperature under various oxygen partial pressures by a data acquisition apparatus (Agilent 34970A, USA). In the