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Performance of a carbon monoxide sensor based on zirconia-doped ceria

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ABSTRACT

Resistive-type carbon monoxide sensors were fabricated using zirconia-doped ceria, and their sensing properties were evaluated and compared with equivalent devices based on non-doped ceria. The response of both sensor types was found to increase with decreasing temperature, while the response at 450 °C of a sensor fired at 950 °C was greater than that of a sensor fired at 1100 °C. When fired at 950 °C, however, the response at 450 °C of a sensor created using zirconia-doped ceria was slightly less than that of a sensor constructed from non-doped ceria. Multivariate analysis confirmed that the response of both sensor types is proportional to the resistance raised to the power of about 0.5, and inversely proportional to the particle size raised to a power of about 0.8. The sensor response time can be considered almost the same regardless of whether zirconia doping is used or not.

1. Introduction

Although there have been various reports of resistive-type oxygen gas sensors [1–5] and carbon monoxide sensors [6–8] being fabricated from cerium oxide (ceria), their mechanism is very different to that of more conventional gas sensors based on tin dioxide [9]. Specifically, it is the resistance of the total bulk that changes when ceria comes into contact with CO, whereas the resistance of tin dioxide only changes at the surface. As a result of this, ceria-based gas sensors are considered to have an advantage in terms of stability and reliability [9].

It has been reported that resistive-type oxygen gas [10] sensors based on ceria have a fast response. The use of zirconia-doped ceria can improve the response time even further to about ~10 ms at 800 °C, as doping helps to reduce the resistance of ceria [11]. Similarly, the fast response of ceria-based carbon monoxide sensors [12] can be improved by adding gold nanoparticles and/or clustering ceria nanoparticles [6]. However, there have been no reports of resistive-type carbon monoxide sensors using zirconia-doped ceria, just a single report [13] outlining the electrical conductivity of zirconia-doped ceria films in air and/or CO + CO_2 for the detection of oxygen levels. To address this shortcoming, resistive-type carbon monoxide sensors were fabricated using zirconia-doped ceria, the sensing properties of which are herein discussed through comparison with the performance of sensors based on non-doped ceria.

2. Experimental

2.1. Sensor fabrication

$Ce(NO_3)_3 \cdot xH_2O$ and $ZrO(NO_3)_2 \cdot xH_2O$ were first dissolved in distilled water to give a Zr:Ce molar ratio of 1:9 or 0:10 and a total cation concentration of 0.10 mol/L. After stirring for several minutes, this solution was mixed with 25% aqueous ammonia and the resulting precipitate was filtered to obtain a white gel. This white gel was mixed with commercial carbon powder using a hybrid mixer, dried in air at 70 °C for several hours, and then calcined in air at 900 °C for 4 h to obtain fine zirconia-doped ceria ($Ce_{0.9}Zr_{0.1}O_2$) and non-doped ceria (CeO_2) powders.

In oxygen sensors using cerium oxide, there are large differences in the sensing properties between any zirconia-doped ceria and completely non-doped ceria [14]. On the other hand, the sensing properties change only slightly as a function of zirconia concentration in the range from 5 to 40 mol% [14]. With this in mind, the present study, as a first trial, focuses on $Ce_{0.9}Zr_{0.1}O_2$ to facilitate a basic comparison between zirconia-doped and non-doped ceria.

The fine zirconia-doped ceria and non-doped ceria powders were mixed with an organic binder containing terpineol and ethyl cellulose to produce pastes that were then screen printed onto

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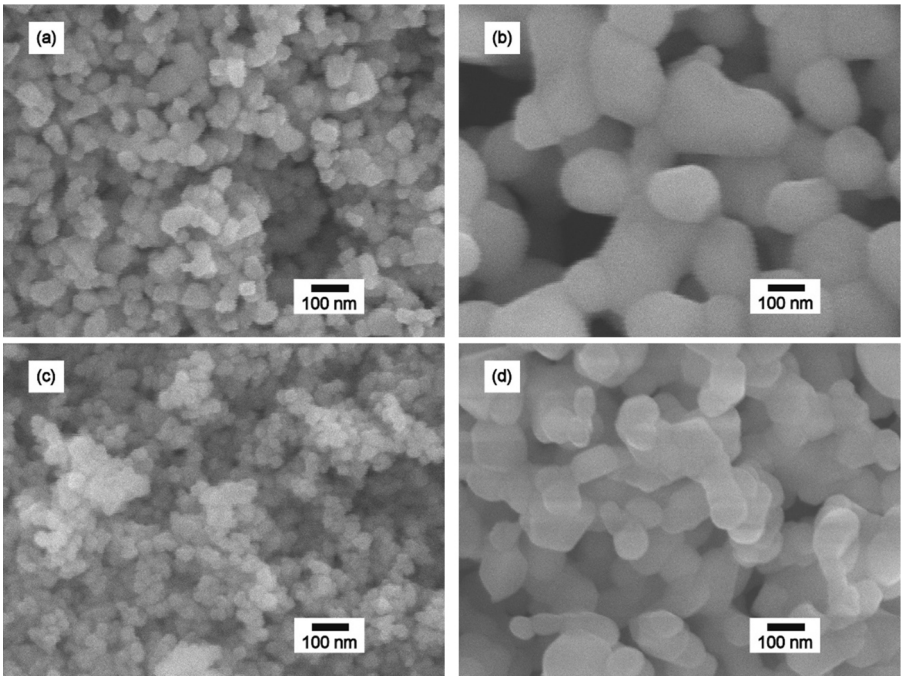

Fig. 1. SEM images of (a) Ce100-950, (b) Ce100-1100, (c) CeZr10-950 and (d) CeZr10-1100 thick films.

interdigital structured Pt electrodes with Al_2O_3 substrates. These screen-printed thick films were calcined in air at 500 °C for 5 h, and then fired at 950 °C or 1100 °C for 2 h in air. The zirconia-doped ceria ($Ce_{0.9}Zr_{0.1}O_2$) and non-doped ceria (CeO_2) samples were labeled as CeZr10-*X* and Ce100-*X*, respectively, where, *X* represents the firing temperature (e.g., CeZr10-1100 is a zirconia-doped ceria ($Ce_{0.9}Zr_{0.1}O_2$) sensor obtained by firing at 1100 °C).

Each of the thick films was characterized by X-ray diffraction (XRD) using Cu Kα radiation (RINT2100V/PC, Rigaku Corporation), as well as by scanning electron microscopy (SEM: JSM-6335F, JEOL).

2.2. Evaluation of sensing properties

Each sensor element was set in a quartz glass tube in a furnace, which was then heated to a predetermined temperature. Air, followed by air containing CO, was then introduced into the quartz tube and the resistance of the thick film was measured as a function of time at various CO concentrations. The resistance ratio was defined as R_a/R_g, where R_a and R_g represent the resistances of the thick film in air and air/CO mixtures of various concentrations.

The response time of the sensor to CO was measured using a previously described [12] method. For this, the sensor was first set in a small container and sealed inside by placing a thin rubber film over the opening. This small container was then placed inside a larger container, into which CO was introduced. The thin rubber film was then torn to create a sudden change in the CO concentration inside the small container and the change in resistance of the sensor was recorded.

3. Results and discussion

The XRD patterns of the ceria and zirconia-doped ceria thick films prepared in this study revealed them to be a single phase with a fluorite structure. The SEM images in Fig. 1 show the thick films fired at 950 and 1100 °C, while Table 1 provides a summary of the particle size calculated from these SEM images. Note that for a given firing temperature the particle size of CeZr10 is smaller than that of Ce100, which is consistent with previously reported results [11,15] and confirms that zirconia prevents an increase in particle size during firing. The thickness of all films was 4–6 μm.

Table 1
Particle size of thick films, as obtained from SEM images.

	Particle size (nm)	
	Firing temperature 950 °C	Firing temperature 1100 °C
Ce100	64	170
CeZr10	34	126

Fig. 2 shows the response curves of a CeZr10 sensor when exposed to 1%CO + air at various operating temperatures. We see from this that although the resistance is stable when in air, there is a dramatic decrease in resistance when the atmosphere changed to 1%CO + air, but becomes stable within a few minutes. When the atmosphere is changed back, the resistance increases dramatically to the initial value.

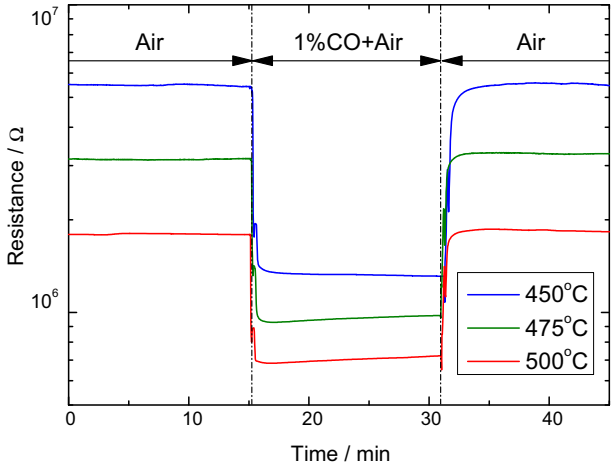

Fig. 2. Response curves of a CeZr10-950 sensor toward 1%CO + air at various operating temperatures.