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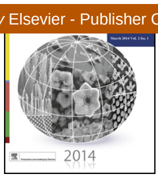

Performance of a carbon monoxide sensor based on zirconia-doped ceria

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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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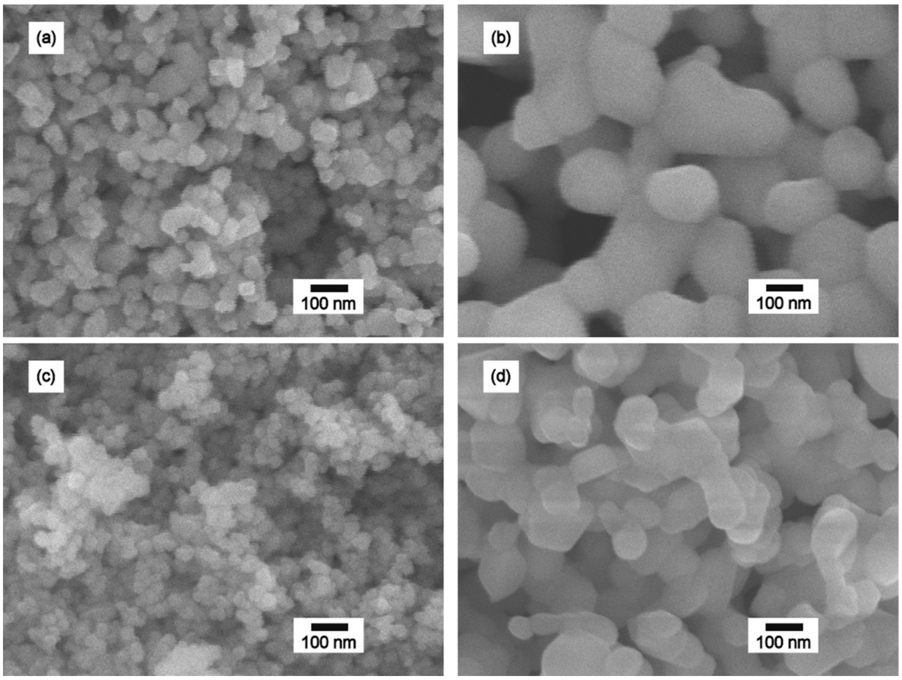

Fig. 1. SEM images of (a) Ce100-950, (b) Ce100-1100, (c) CeZr10-950 and (d) CeZr10-1100 thick films.

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.

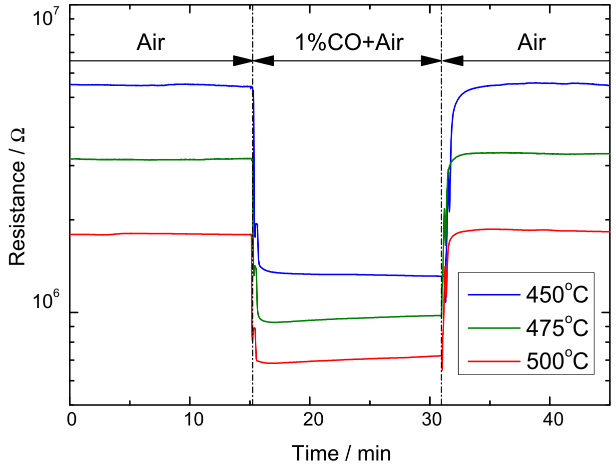

Fig. 2. Response curves of a CeZr10-950 sensor toward 1%CO + air at various operating temperatures.

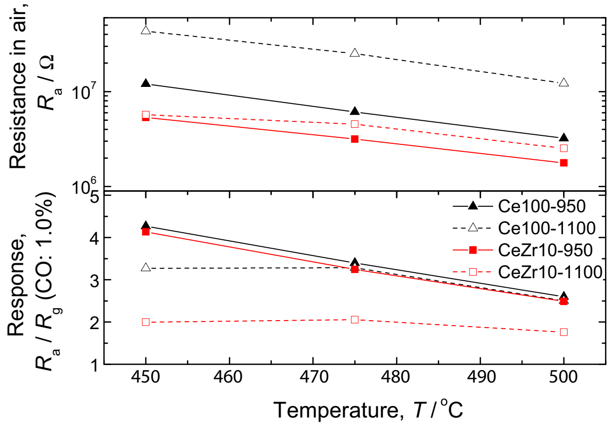

Fig. 3. Resistance and response values obtained from the response curves of CeZr10-950 (Fig. 2) and other sensors.

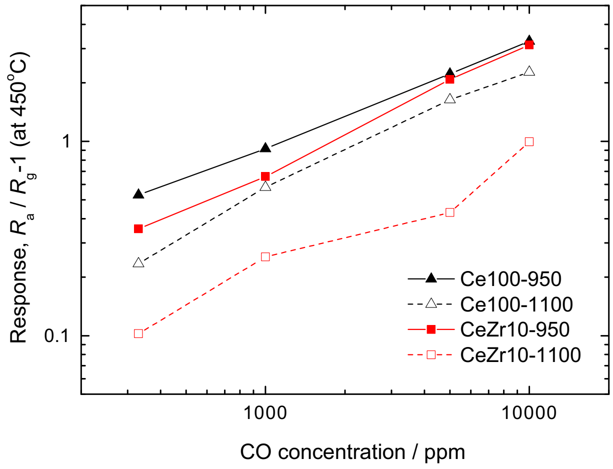

Fig. 4. Relationship between sensor response and CO concentration at an operating temperature of 450 °C.

Fig. 3 provides a summary of the data obtained from the response curves of CeZr10-950 (Fig. 2) and other sensors. Note that when the firing temperature is the same, the resistance of CeZr10 in air is lower than that of Ce100, which is consistent with a reported decrease in resistance by doping with 20–30 mol% zirconia [16]. That study found that the resistance decreased with increasing zirconia concentration, up to 30 mol% zirconia. However, the resistance then increased with increasing zirconia concentration in the range from 30 mol% to 50 mol%. In ceria, the following defect reaction has been reported [16–21]:

$$2\mathrm{Ce}_{\mathrm{Ce}}^{X} + \mathrm{O}_{\mathrm{O}}^{X} = 2\mathrm{Ce}'_{\mathrm{Ce}} + \mathrm{V}_{\mathrm{O}}^{\cdot\cdot} + 1/2\mathrm{O}_2 \qquad (1)$$

Here, $\mathrm{Ce}'_{\mathrm{Ce}}$ represents a quasi-free electron localized on a cerium ion, because conduction in ceria is known to proceed via a hopping type mechanism [17]. Since the Zr ion is tetravalent, point defects do not form in ceria as a direct result of Zr ion doping. However, it has been reported that doping zirconium causes the equilibrium of the defect reaction (1) to shift to the right [22]. This may be the reason for the decreasing resistance that occurs at moderate levels of zirconia doping.

For a given zirconia concentration, the resistance of the sensor obtained by firing at 950 °C is smaller than that of the sensor obtained by firing at 1100 °C. This means that the resistance of a sensor is reduced by having a smaller particle size, which is also consistent with the results of a previous study [23] in which the equilibrium of the defect reaction (1) shifted to the right, and the bulk resistance decreased when the particle size decreased. When the particle size is decreased, the surface area and the volume occupied by grain boundaries both increase as a percentage of the bulk volume. These features (including surface area, grain boundaries and bulk properties) may all be affected by the rightward equilibrium shift of the defect reaction (1). The resistances of the sensors produced in this study therefore follow an order (CeZr10-950 < CeZr10-1100 < Ce100-950 ≪ Ce100-1100) that can be attributed to the effects of both particle size and zirconia-doping levels.

The response of Ce100-950 and CeZr10-950 can be seen in Fig. 3 to largely increase with decreasing operating temperature, although Ce100-1100 and CeZr10-1100 both show a smaller dependence on operating temperature with regards to their response.

Table 2 presents a summary of the response time of the various sensors, in which we see that zirconia doping has very little effect. A previous report [12] has suggested that the rate-limiting step could be the permeation of gas into the thick film, meaning that the pore size (which would be the same for CeZr10-950 and Ce100-950) determines the response time. However, it is also possible that a response time of less than 2 s may not be evaluated precisely by the apparatus used in this instance given the time (~2 s) taken to change atmospheres, which may explain why the response times of CeZr10-950 and Ce100-950 are almost the same. Consequently, more detailed experiments and analysis are needed to fully explain the reason for the similarity between these two sensor types.

Fig. 4 shows the relationship between the sensor response and CO concentration at an operating temperature of 450 °C, which gave the maximum response value. Note that the response of Ce100-1100 at this temperature is much greater than that of CeZr10-1100, while the response of Ce100-950 is slightly larger than that of CeZr10-950. The order of response at 450 °C can therefore be written as follows: CeZr10-1100 < Ce100-1100 < CeZr10-950 ~ Ce100-950 (for CO concentrations on the order of 5000 ppm).

Having qualitatively established that the response of non-doped and zirconia-doped ceria sensors increases with decreasing particle size and/or increasing resistance, a multivariate analysis was carried to quantitatively determine the effect of particle size and

Table 2
Response time (t_{90}) of sensors when changing from air to air with CO.

Sample	Operating temperature (°C)	CO concentration (ppm)	Response time, t_{90} (s)
Ce100-950	450	1000	2.5 ± 0.3
Ce100-950	450	5000	2.0 ± 0.7
Ce100-950	500	1000	2.6 ± 0.7
Ce100-950	500	5000	3.0 ± 1.8
CeZr10-950	450	1000	2.5 ± 0.5
CeZr10-950	450	5000	3.4 ± 0.5
CeZr10-950	500	1000	4.0 ± 1.7
CeZr10-950	500	5000	3.4 ± 0.7

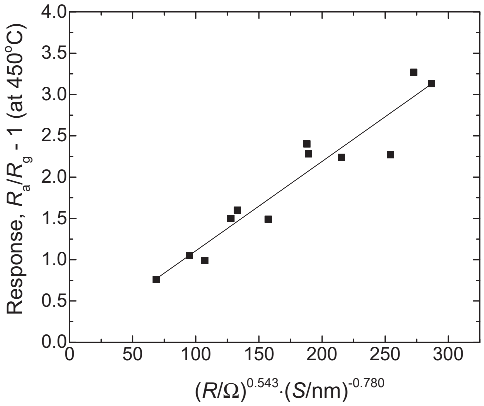

Fig. 5. Relationship between particle size, resistance and response for Ce100-950, Ce100-1100, CeZr10-950, and CeZr10-1100.

resistance. Here, it was assumed that the response value of the sensors is only dependent on particle size and resistance, and that:

$$(\alpha - 1) = \frac{AR_a^n}{S^m} \quad (2)$$

where, $\alpha = R_a/R_g$; A, n, and m are constants; and S is the particle size. Thus, when either n or m is 0, the resistance or the particle size, respectively, cannot influence the response. However, when n is greater than 0, the response will be dependent on the resistance; and when m is greater than 0, the response will be dependent on the particle size. Eq. (2) can therefore be changed to:

$$\log(\alpha - 1) = \log A + n \log R_a - m \log S \quad (3)$$

Through multivariate analysis using Eq. (3), the following equation was obtained:

$$(\alpha - 1) \propto \frac{R_a^n}{S^m}, \quad n = 0.543 \pm 0.05, \quad m = 0.780 \pm 0.08 \quad (4)$$

Fig. 5 shows the linear relationship between particle size, resistance and response when vertical and horizontal axes of $(\alpha - 1)$ and ${R_a}^{0.543}/S^{0.780}$ are used. This reveals that response is proportional to the resistance raised to the power of ~0.5 and inversely proportional to the particle size raised to the power of ~0.8. In other words, the effect of particle size is greater than that of resistance in the case of the sensors obtained in this study. It is believed that the number of points on the surface of the particles where CO molecules can react chemically increases when the particle size is decreased; this would be due to the increase of surface area. Moreover, as mentioned above, the number of point defects such as oxygen vacancies and trivalent cerium ions also increase due to the rightward equilibrium shift of the defect reaction (1) that results from decreasing particle size. These increases in the number of reaction points and point defects may activate the adsorption and/or oxidation reactions involving CO. On the other hand, the ratio of resistances with and without CO will increase in the case of a device with a high resistance in air even if the change of carrier concentration ($\mathrm{Ce}'_{\mathrm{Ce}}$) is small, because the carrier concentration of a high-resistance device in air is closer to zero compared with that of a low-resistance device in air. Thus, the relative response value increases. However, the increase of resistance in air must cause a leftward equilibrium shift in the defect reaction (1), which causes a decrease in the number of point defects, and negatively influences the adsorption and/or oxidation reactions of CO. This causes a partial cancelation—or offset—of the effects of high resistance. This partial offset may be attributed to the smaller resistance effect ($n \approx 0.5$) compared with the particle size effect ($m \approx 0.8$). It is the doping with 10 mol% zirconia that is responsible for the decrease in particle size and subsequent increase in response, but this also has the effect of reducing the resistance and therefore also the response.

Considering the practical uses of CO sensors, a low resistance is just as important as a good response. This is because the electrical circuitry needed for high-resistance sensors is very complicated and expensive. The results obtained in this study indicated that Ce100-950 is most suitable for practical use considering response sensitivity, resistance and response time.

4. Conclusions

The response of four different kinds of ceria-based CO sensor has been shown to increase with decreasing temperature. At the lowest operating temperature tested (450 °C), the response of a sensor fired at 950 °C was greater than that of the sensor fired at 1100 °C, but a sensor using zirconia-doped ceria fired at 950 °C had a slightly smaller response at this temperature than a sensor using non-doped ceria. This is attributed to the fact that zirconia doping not only reduces the particle size, thereby increasing the response, but also reduces the response through a decrease in resistance. Consequently, the response times of sensors with and without zirconia doping are almost the same; however, multivariate analysis has revealed that response is proportional to the resistance raised to the power of ~0.5, and inversely proportional to the particle size raised to the power of ~0.8.

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