Influence of Thickness of Cr_2O_3 Sensing-electrode on Sensing Characteristics of Mixed-potential-type NO_2 Sensor Based on Stabilized Zirconia

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A planar NO_2 sensor was fabricated by using a yttria-stabilized zirconia (YSZ) plate and Cr_2O_3 sensing-electrode (SE). The NO_2 sensing performances were evaluated at 700°C in the presence of 5 vol.% water vapor for the sensor attached with each of Cr_2O_3 -SE having different thicknesses. It was found that the NO_2 sensitivity of the sensor was highest when the thinnest Cr_2O_3 -SE was used and decreased with increasing thickness of SE. A linear correlation between the sensitivity and the NO_2 concentration was observed at 700°C in the range of 50 – 400 ppm for each sensor. Based on the results of the measurements for the NO_2 conversion to NO on each of Cr_2O_3 layers having different thicknesses, it was confirmed that the catalytic activity to the gas-phase NO_2 decomposition on the Cr_2O_3 -SE matrix played an important role in deciding the NO_2 sensitivity of the present sensor.

Key Words : NOx Sensor, YSZ, Cr_2O_3 , Solid Electrolyte, Mixed Potential

1 Introduction

There has been a strong global demand for the development of high-performance NOx sensors that can control and monitor gaseous air pollutants (typically NO and NO_2) mostly exhausted from automotive vehicles. The air pollutants cause adverse effects on environment and a eco-system, leading to smog, acid rain and respiratory diseases. It is fact that the emission standard around the world is becoming very severe for detecting and monitoring exhaust gases. Such a sever standard has led to the introduction of a lean-burn (or direct-injection type) gasoline-engine system, into the market to improve fuel efficiency and to reduce CO_2 emission from an engine system.¹⁾ Due to the fact that NOx emitted from these vehicles can not be easily converted to nitrogen under lean-burn (air-rich) condition by a conventional three-way catalyst (TWC), it is necessary to use a new NOx-storage catalyst. In this regard, it is important to develop an excellent NOx sensor that can monitor and control NOx concentration in automotive exhausts.

Among several types of solid-state NOx sensors so far examined, mixed-potential-type zirconia-based sensors have attracted much attention because of their excellent features, such as high sensitivity, fast response, compactness, low cost of drive-control circuit and high-temperature operation. We have been working on development of the solid-state NOx sensors based on YSZ and oxide-SEs for last ten years.^{2–12)} Quite recently, we have reported that the sensor using NiO-SE can detect NO_2 even at high temperature of 900°C under wet condition.^{13–15)} Several papers regarding the mixed-potential-type NOx sensors using oxide SE have been also reported by other research groups^{16–25)} since our first reports in 1996.^{2, 3)} The NO_2 sensitivity was reportedly varied

with the kind of SE material^{3, 5, 10, 12, 13)} and the sintering temperature of SE used.^{14, 19)} However, to the best of our knowledge, there are no reports on the effect of thickness of SE on the sensing performances of mixed-potential-type NO_2 sensors. The thickness of SE also seems to be an important factor in deciding the NO_2 sensitivity of this type sensor.

Here, we examined the sensing performances of NO_2 sensor based on an YSZ plate as well as Cr_2O_3 -SE having different thicknesses to understand the sensing mechanism of the mixed-potential-type NOx sensor. The use of Cr_2O_3 -SE was reported for the laminated-type YSZ-based sensor for monitoring total NOx in car exhausts.²⁶⁾ It was shown that the NO_2 sensitivity of the sensor increased with decreasing thickness of Cr_2O_3 -SE.

2 Experimental

2.1 Fabrication of sensing device

An yttria-stabilized (8 wt.%) zirconia plate (10×10 mm, 0.2 mm in thickness) was utilized for fabrication of the planar sensor-device. Platinum paste was printed on both sides of the YSZ plate by means of a screen-printing method and was dried at 1000°C for 2 h in air. On the one side of the YSZ plate, two rectangular Pt-stripes were formed as a reference electrode (RE) of the sensor, and on the other side, six narrow Pt-stripes were formed as a current collector for the SE layer. Chromium oxide (Cr_2O_3) powder was thoroughly mixed with an organic solvent, α -terpineol. The resulting paste was printed on a transfer paper by means of the screen-printing technique. The oxide-printed transfer paper was dried at 130°C for 1 h. Then, a cover spray was applied on the oxide-printed layer and the whole paper was again dried at 130°C for 1 h. The fabrication process of the oxide

layer on the YSZ plate was done by means of a slide-off-printing technique, as described elsewhere.²⁷⁾ The oxide-printed layer containing the cover spray was put into large quantity of water and was kept for about 10 min as it is. Then, the oxide-printed layer was separated from the transfer paper by using tweezers. The oxide layer (film) thus obtained was attached on the front side of the YSZ plate attached with the narrow Pt-strips. In order to increase the thickness of the SE layer, the required number of the oxide film was attached on YSZ plates, sequentially. To make a good electrical contact with a measuring equipment, Pt wires (0.1 mm in diameter) were spot-welded onto Pt connecting-spots of both SE and RE using Pt paste. Finally, the YSZ plates containing the oxide layer and the Pt-strips were sintered at 1400 °C for 2 h in N₂ atmosphere (including about 50 ppm O₂) to form SE and RE. The surface morphology as well as the thickness of SE was observed by means of a field-emission scanning-electron microscope (FE-SEM, JEOL, JSM-340F) operating at 15 kV.

2.2 Measurements of sensing characteristics

Sensing characteristics were evaluated by using a conventional gas-flow apparatus equipped with a furnace operating at 700 °C. The sample gases containing various concentrations of NO₂ (+ 5 vol.% O₂ + N₂ balance) were prepared by diluting a standard NO₂ gas with dry N₂. The base gas was composed of 5 vol.% O₂, 5 vol.% water vapor and N₂ balance. The base gas and the sample gas were humidified with 5 vol.% (50,000 ppm) water vapor by using a water-vapor generator coupled with a small evaporator and a micro-flow pump (Hitachi, L-2100). The total flow-rate of the sample gas (or the base gas) was fixed at 100 cm³ min⁻¹. The NO₂ concentration was changed from 50 ppm to 400 ppm. The ppm refers to the volume concentration of NO₂. SE and RE were exposed simultaneously to the sample gas or the base gas. The difference in potential between SE and RE was monitored as a sensing signal with a digital electrometer (Advantest R8240) at 700 °C. The potential of the SE was always positive with respect to RE. The complex impedance of the sensor was measured in the frequency range from 0.001 Hz to 1 MHz with exciting voltage of 5 mV by means of an impedance analyzer (Solartron, 1255 WB) at 700 °C.

2.3 Measurements of NO₂ conversion to NO

The catalytic activity to the gas-phase decomposition of NO₂ to NO was evaluated for each of Cr₂O₃ layers having different thicknesses. For this measurement, each of Cr₂O₃ layers having different thicknesses was newly formed on one side of the YSZ plate used for fabricating the sensor, by means of the same slide-off-printing technique mentioned above. Then, the resulting YSZ plates were sintered at 1400 °C for 2 h in N₂ atmosphere (including about 50 ppm O₂). Each whole-piece (*ca.* 0.12 g) of the obtained YSZ-plates attached with each of the Cr₂O₃ layers was used as the sample for the measurement. The sample gas (100 ppm NO₂ + 5 vol.% O₂ + N₂ balance) was let to flow over each sample at the flow rate of 100 cm³ min⁻¹. The NO₂ conversion to NO was measured in the temperature range of 200 – 700 °C by using a con-

ventional gas-flow apparatus and a chemiluminescence NO_x analyzer (Yanaco, ECL-88A).

3 Results and Discussion

3.1 Morphology of Cr₂O₃-SE layers

Figure 1 shows the SEM micrographs of the cross-sections of Cr₂O₃-SEs. It is seen that SEs have different thicknesses (4, 7 and 11 μm) and the thickness is almost uniform throughout each SE matrix. The SEM micrographs of the surfaces of each Cr₂O₃-SEs were also taken (not shown here). It was observed that each SE matrix consisted uniform size of Cr₂O₃ grains and pores. An average Cr₂O₃ grain-size and the average pore-size were evaluated in large areas and were about 2 μm and about 0.5 μm, respectively, for each SE.

3.2 Evaluation of sensing characteristics

The response transients to different concentrations of NO₂ were measured at 700 °C for the planar sensor using each of Cr₂O₃-SEs having various thicknesses in the presence of 5 vol.% water vapor. Figure 2 shows the representative response transients to 200 ppm NO₂ for each

Fig. 1 SEM micrographs of cross-sections of Cr₂O₃-SEs on an YSZ plate. SE thickness: (a) 4 μm, (b) 7 μm, (c) 11 μm.

Fig. 2 Typical response transients to 200 ppm NO₂ at 700 °C in the presence of 5 vol.% water vapor for the planar sensors using each of Cr₂O₃-SEs having different thicknesses.

Fig. 3 Dependence of *emf* on the logarithm of NO₂ concentration at 700 °C in the presence of 5 vol.% water vapor for the planar sensors using each of Cr₂O₃-SEs having different thicknesses.

sensor. It is seen that the *emf* value is zero in the base gas because of the planar structure of sensor and quickly increases from the base level upon exposure to NO₂. Then, the steady-state *emf* value is attained in due time for each sensor. The response and recovery rates of the sensor are almost same, irrespective of the thickness of Cr₂O₃-SE used. In the case of the 7 μm-thick SE, the 80% response and the 80% recovery rates are typically about 50 s and 95 s, respectively. Figure 3 displays the dependence of *emf* (NO₂ sensitivity) on the logarithm of NO₂ concentration for each Cr₂O₃-SE at 700 °C in the presence

of 5 vol.% water vapor. It is clear that in each case the *emf* value increases linearly with increasing NO₂ concentration on a logarithmic scale. Such a linear variation is typical for a mixed-potential-type sensor. It is also observed that the slope of the linear plot decreases as the thickness of SE is increased. This change in slope seems to be attributable to the degree of the gas-phase NO₂ decomposition, as discussed later. It is worthy to note that the sensitivity to NO₂ varies with the thickness of Cr₂O₃-SE. The NO₂ sensitivity increases significantly with decreasing thickness of Cr₂O₃-SE and the highest sensitivity is observed for the sensor attached with the 4 μm-thick SE. The *emf* value to 200 ppm NO₂ is about 10, 23 and 60 mV for the sensors using each of Cr₂O₃-SEs having different thicknesses of 11, 7 and 4 μm, respectively. It is also noted that the sensor using the 4 μm-thick Cr₂O₃-SE exhibits such a high NO₂ sensitivity even at 700 °C. There is still high possibility to obtain higher sensitivity when the thickness of SE is further reduced.

3. 3 Explanation of effect of SE thickness on sensing property

In order to rationalize the above-mentioned sensing characteristics of the present sensor, we have carried out complex-impedance measurements at 700 °C by using the same YSZ-based planar sensor attached with each of Cr₂O₃-SEs having various thicknesses. Figure 4 shows the complex-impedance plots (Nyquist plots) obtained in the base gas and in the sample gas containing 400 ppm NO₂ (+ 5 vol.% O₂ + N₂ balance) in the presence of 5 vol.% water vapor. Each plot gave a shape of compressed semicircle. The diameter of each semicircle seems to indicate the resistance of the electrode reaction occurring at the interface of YSZ/Cr₂O₃-SE, as reported before.¹⁴⁾ It is worthy to note that the diameter of semicircle in the base gas as well as in the sample gas is hardly varying with increasing thickness of Cr₂O₃-SE. This means that the catalytic activity to the electrode reaction at the interface is almost same irrespective of the thickness of SE. This seems to happen because each SE has been formed by using the identical mesh (screen) size for the screen-printing and has been sintered at the same temperature (1400 °C). Consequently, it is expected that each of the YSZ/oxide interfaces has a similar state irrespective of the SE thickness. Thus, from the results obtained above, we can infer that the catalytic activity of electrode reactions (1), especially the electrochemical reaction of oxygen (1), is almost equal in each case. As a result, the sensor gave almost equal recovery rate, as given in Fig. 2.

The sensing mechanism of this type potentiometric YSZ-based NO₂ sensor can be basically explained by mixed-potential which is generated at the interface of YSZ/SE.^{6, 8-12)} This mixed potential appears when the anodic reaction of oxygen (2) and the cathodic reaction of NO₂ (3) proceed simultaneously at an equal rate.

Fig. 4 Nyquist plots in the base gas (5 vol.% O₂) and in 400 ppm NO₂ (+ 5 vol.% O₂ + N₂ balance) at 700 °C in the presence of 5 vol.% water vapor for the planar sensors using each of Cr₂O₃-SEs having different thicknesses. SE thickness: (a) 4 μm, (b) 7 μm, (c) 11 μm.

However, the non-electrochemical gas-phase reaction (4) occurring in a SE matrix also plays a very important role in deciding the NO₂ sensitivity of this type sensor.^{9, 12, 14)}

Since the state of the YSZ/Cr₂O₃ interface has been confirmed to be almost same in each SE having different thicknesses, it is highly possible that the NO₂ sensitivity in the present case is determined by the degree of the gas-phase NO₂ decomposition to NO (4) occurring in the oxide-SE matrix. Figure 5 illustrates schematically the influence of thickness of oxide-SE on the actual concentration of NO_x at the YSZ/oxide interface at high temperature (*e.g.*, 700 °C). When a thin SE is used, NO₂ can reach the YSZ/oxide interface by diffusion through the thin layer without serious decomposition of NO₂ into NO. Thus, when the NO₂ sample gas (not including NO) is introduced to the surface of SE, the actual concentration of NO₂ at the interface is predominantly high compare to that of NO; the NO_x composition at the interface is far from the equilibrium (*e.g.*, NO : NO₂ = 95 : 5 in volume ratio at 700 °C). Such a high NO₂ concentration at the interface results in high NO₂ sensitivity of the sensor. On the other hand, when the SE is rather thick, in the course of diffusion of NO₂ through the thick oxide-layer, NO₂ can be easily decomposed into NO due to the pro-

Fig. 5 Graphical explanation of the influence of Cr₂O₃-SE thickness on the actual concentration of NO₂ at the YSZ/Cr₂O₃ interface in the cases of small SE-thickness (a) and large SE-thickness (b).

nounced gas-phase reaction (4). The surface of Cr₂O₃ grains may act as a catalyst for the NO₂ decomposition. Although Cr₂O₃ is generally used as a catalyst for oxidation, the gas-phase NO₂ decomposition to NO is also catalyzed by Cr₂O₃, as reported similarly before.²⁴⁾ Thus, it is rather difficult for NO₂ to arrive at the YSZ/oxide interface. In such a case, the NO_x composition may come closer to the equilibrium at the interface. As a result, the NO₂ sensitivity is low for the device using the thick SE. In this case, there is little driving force for the electrochemical reaction getting involved with the occurrence of mixed potential when the NO₂ composition comes closer to the equilibrium. When the thickness of SE is middle, a moderate NO₂ sensitivity can be obtained.

In order to substantiate the above explanation, the catalytic activity of the gas-phase decomposition of NO₂ (4) was evaluated in the temperature range of 200 – 700 °C for each of the Cr₂O₃-SE layers having different thicknesses. The NO₂ concentration was set to 100 ppm in the carrier gas containing 5 vol.% O₂ and N₂ balance. The obtained results are shown in Fig. 6. It is seen that the percentage of NO₂ conversion tends to increase as the thickness of Cr₂O₃ layer is increased and the thickest Cr₂O₃-layer exhibits the highest NO₂ conversion. This result clearly indicates that larger SE thickness leads to higher catalytic activity to the gas-phase decomposition of NO₂ (4), as expected, although these are still qualitative results. Thus, in the present case, it can be said that the catalytic activity to the gas-phase reaction (4) on the SE matrix plays a quite important role in deciding the NO₂ sensitivity of the sensor, as also reported for the hydrocarbon and CO sensors.^{20, 28, 29)}

Fig. 6 Temperature dependence of the NO_2 conversion to NO for the gas-phase decomposition reaction (4) on the thickness of Cr_2O_3 layer.

4 Conclusions

The correlation between the thickness of oxide-SE and the sensing performance was examined at 700°C for the planar NO_2 sensors based on YSZ. The sensor attached with Cr_2O_3 -SE exhibited the highest NO_2 sensitivity when the thickness of SE was as small as 4 μm . It was confirmed that the NO_2 sensitivity was dependent on the degree of the gas-phase decomposition reaction of NO_2 to NO (4) in the Cr_2O_3 -SE matrix. When a thin SE is employed, the composition of NO_x at the YSZ/ Cr_2O_3 interface is far from the equilibrium and then the high NO_2 sensitivity can be obtained. On the other hand, when a thick Cr_2O_3 -layer is utilized, due to high rate of the gas-phase reaction in the oxide layer, the NO_x composition reaches the equilibrium at the interface, leading to low sensitivity. Thus, it is concluded that the sensitivity of the present sensor can be controlled by varying the thickness of oxide-SE layer.

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