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SHORT COMMUNICATION

A high temperature amperometric NO sensor based on stabilized zirconia and $CdCr_2O_4$ electrode

G. LU, N. MIURA, N. YAMAZOE

Department of Materials Science and Technology, Graduate School of Engineering Sciences, Kyushu University, Kasuga-shi, Fukuoka 816, Japan

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1. Introduction

The emission of nitrogen oxides (NO and NO_2 abbreviated as NO_x) from automobiles and boilers is one of the main sources of atmospheric pollution. Generally speaking, combustion exhausts, as emitted, usually contain ten times as much NO as NO_2, so that, for emission control, the sensitive and selective detection of NO in high-temperature combustion exhausts is more important than that of NO_2. Several solid-state sensors to detect NO_2 and/or NO have been reported [1–8], but these have problems in applications to emission control. For example, potentiometric or amperometric sensors using NASICON (Na^+-superionic conductor) and nitrite auxiliary phase [2–5] cannot be operated at temperatures above ~250 °C because of the low melting point of the nitrites used (e.g., $NaNO_2$: 271 °C).

We recently proposed a new type of potentiometric sensor using a stabilized zirconia and oxide electrode (typically $CdCr_2O_4$). The devices are based on a sensing mechanism involving mixed potential at the oxide sensing electrode, and detect NO or NO_2 in oxygen containing atmospheres at higher temperature, for example, 500–600 °C [6–8]. Unfortunately, however, one problem is that the sensitivity to NO is far smaller than that to NO_2, a problem often encountered with potentiometric devices. A solution was suggested by recent reports that zirconia oxygen pumps may be used for the amperometric detection of NO in oxygen containing atmospheres at high temperature [9–12]. The sensor developed consisted of two serial oxygen pumps, which pumped out gaseous oxygen (first) and measured the limiting current due to the electrochemical decomposition of NO (second), respectively. This stimulated us to test the possibility of extending our device containing stabilized zirconia and the $CdCr_2O_4$ electrode to an amperometric NO sensor. As a result, this extension has been found to be possible by polarizing the oxide electrode appropriately. The amperometric sensor obtained can detect NO selectively in the presence of oxygen at 500 °C. For this sensor, it is not necessary to pump out the coexisting oxygen beforehand, as described below.

2. Experimental details

Figure 1 shows schematically a cross-sectional view of the amperometric sensor examined. It was fabricated on a half-open yttria–stabilized zirconia tube (YSZ, 8 mol % Y_2O_3 doped, NKT), 30 cm long, and 5 and 8 mm in inner and outer diameter, respectively. A commercial Pt paste was applied on the inside of the closed bottom of the tube as a counter (or reference) electrode, followed by calcining at 1200 °C for 30 min. A belt-shaped working (or sensing) electrode electrode consisting of Pt and oxide layers was formed on the outer surface of the YSZ tube as follows. The Pt paste was first applied on the designated area (width: 10 mm, total area: 2.5 cm^2) of the tube and calcined at 1200 °C for 30 min. The Pt layer thus formed was porous and about 30 μm thick. Then a $CdCr_2O_4$ paste was applied on top and sintered at 700 °C for 5 h. The porous oxide layer was also about 30 μm thick. The $CdCr_2O_4$ paste was prepared by mixing the oxide powder with α-terpineol and ethyl cellulose. A device unattached to the oxide layer was also fabricated for comparison.

Polarization curves and sensing characteristics were measured in a conventional gas flow apparatus. Sample gases containing NO (or NO_2) were prepared by diluting the parent gases, that is, 1000 ppm NO in N_2 or 200 ppm NO_2 in air, with a synthetic dry air (and/or oxygen). The gas flow (100 $cm^3\,min^{-1}$) over the sensing electrode was switched between synthetic air and the sample gases, while the counter (reference) Pt electrode was always exposed to atmospheric air. The sensing electrode potential was polarized by a potentiostat (Hokuto Denko, HA 101), referred to the counter (reference) electrode. The electric current flowing through the stabilized zirconia was measured as a sensing signal mainly at 500 °C.

3. Results and discussion

The polarization curves of the devices attached and unattached to the $CdCr_2O_4$ layer were measured in air and the sample gas containing 200 ppm NO or 200 ppm NO_2 at 500 °C. As shown in Fig. 2(a), the oxide–unattached device exhibited a typical polarization curve in which anodic or cathodic current increase exponentially with increase in anodic or

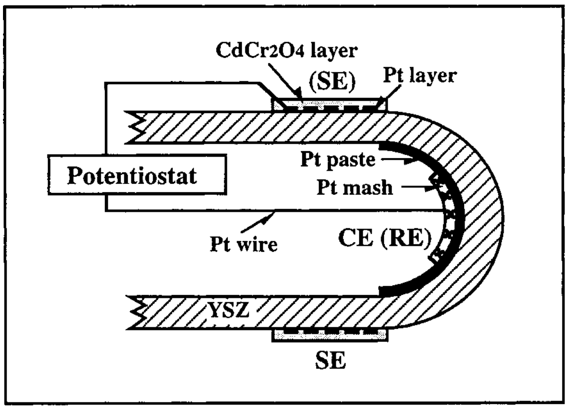

Fig. 1. Cross-sectional view of amperometric sensor device using YSZ and $CdCr_2O_4$ electrode. (SE: sensing electrode, CE: counter electrode, RE: reference electrode.)

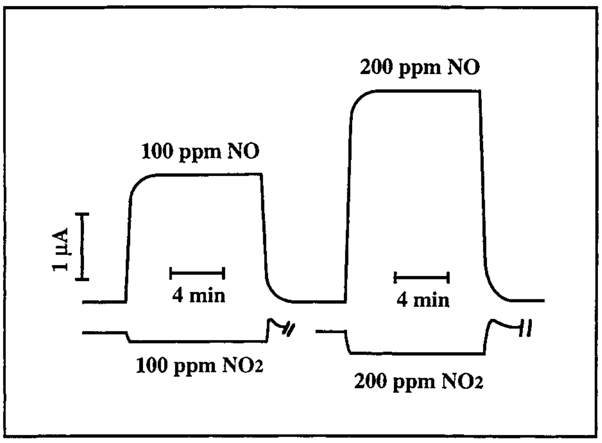

Fig. 3. Response and recovery transients of oxide-attached YSZ device to switching-on and-off NO and NO_2 (100 and 200 ppm in air) at 500 °C. (The sensing electrode potential: polarized at +100 mV with respect to the reference Pt electrode.)

cathodic polarization, respectively. Upon exposure to NO or NO_2, the polarization curve tended to shift upward or downward from that in air in the anodic or cathodic potential range, respectively. This tendency was similar, but more intense, with the oxide-attached device (Fig 2(b)). This suggests that the oxide layer plays an important role in promoting the electrochemical reaction of NO (or NO_2) at the sensing electrode. A more important difference between the two devices is noted in the anodic region. That is, the increase in anodic current is seen to be larger than that due to NO_2 in the potential range 0–300 mV for the oxide-attached device, whereas such behavior is scarcely seen for the other device. In the cathodic region, NO_2 is always more effective in increasing the cathodic current than NO. These observations indicate that the selective detection of NO over NO_2 is possible with the oxide-attached device if the sensing electrode is polarized, preferably at about 100 mV with respect to the reference Pt electrode. Thus the gas-sensing properties of this device under polarization at 100 mV were examined in more detail.

Figure 3 shows typical response transients to NO and NO_2, 100 and 200 ppm, at 500 °C for the oxide-attached device polarized at 100 mV. At this particular potential, NO sharply increased the anodic current from the air level, while NO_2 lead to a slight decrease. This device is thus far more sensitive to NO than NO_2 under these conditions. The response to NO was speedy and stable, that is, the 90% response and recovery times to 100 ppm NO were about 20 s and 30 s, respectively. Figure 4 depicts the depen-

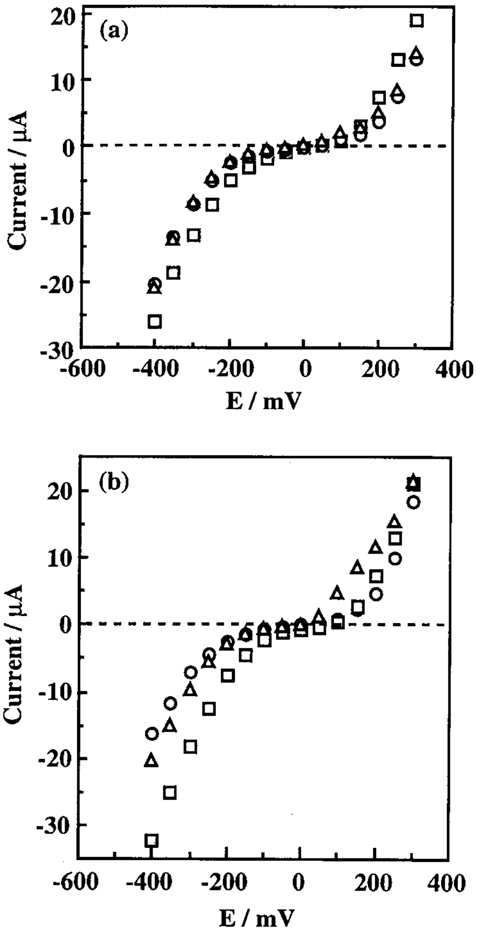

Fig. 2. Polarization curves in air, 200 ppm NO(+air), and 200 ppm NO_2(+air) at 500 °C. (a) Device attached with Pt layer only (oxide-unattached device), (b) Device attached with Pt layer and $CdCr_2O_4$ layer (oxide-attached device). Key: (○) air, (□) NO_2 and (△) NO.

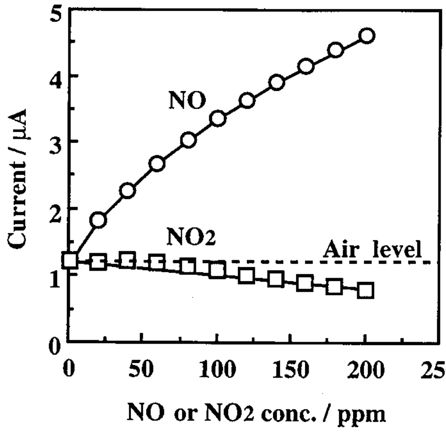

Fig. 4. Anodic current as function of NO or NO_2 concentration in air at 500 °C for the oxide-attached device. (The sensing electrode potential: +100 mV.)

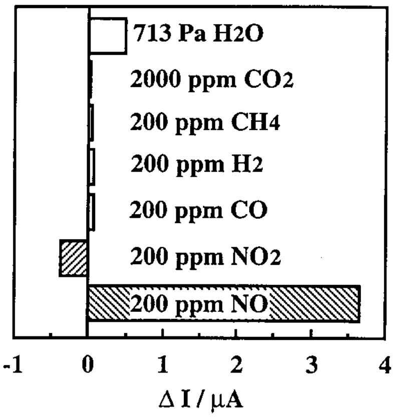

Fig. 5. Sensitivity to various gases at 500 °C for the oxide-attached device. (The sensing electrode potential: +100 mV.)

dence of the current values on the NO or NO_2 concentration at 500 °C for the present device. A good correlation was observed between the current value and the NO concentration in the range 0–200 ppm, whereas the current was far less affected by the variation of NO_2 concentration as expected. The cross-sensitivity of the device to 200 ppm CO, 200 ppm H_2, 200 ppm CH_4, 2000 ppm CO_2, and 713 Pa water vapour, all diluted in dry synthetic air, has been confirmed to be far less than that to 200 ppm NO, as shown in Fig. 5. With such good sensing properties, the amperometric device attached with $CdCr_2O_4$ shows promise as a new amperometric sensor to monitor NO in combustion exhausts at high-temperature.

The present sensor device comprises a kind of oxygen pump. When the sensing electrode potential is polarized at 100 mV in air with respect to the counter electrode, the following anodic and cathodic reactions take place at the sensing electrode and the counter electrode, respectively:

$$2\,O^{2-} \rightarrow O_2 + 4\,e^- \qquad (1)$$

$$O_2 + 4\,e^- \rightarrow 2\,O^{2-} \qquad (2)$$

Oxygen can be pumped from the counter electrode side to the sensing electrode side, giving rise to an anodic current. Under the coexistence of NO, NO can also participate in the anodic process as follows, for example:

$$NO + O^{2-} \rightarrow NO_2 + 2\,e^- \qquad (3)$$

If the anodic process is rate determining, this reaction will increase the anodic current as observed for the oxide-attached device. In the same way, the cathodic process will be facilitated under the coexistence of NO_2 as also observed with both the oxide-attached devices.

A remarkable fact is that the NO-selective increase in the anodic process at 100 mV takes place only in the oxide-attached device. Since the oxide ($CdCr_2O_4$) was applied on the porous Pt layer, part of it can contact with the YSZ surface directly, forming three-phase contacts involving YSZ/the oxide interface. If it is assumed that these three-phase contacts are more efficient for the anodic reaction (3) than the conventional three-phase contacts involving YSZ/Pt interface, the above fact can be accounted for. However, this assumption remains to be clarified. There is a further aspect of device behaviour which cannot be explained well on the basis of the electrode processes and assumptions outlined above. For example, the partial equilibration of the NO or NO_2 gas into a mixture of NO or NO_2 over the electrode materials, to account for why NO or NO_2 increases the cathodic or anodic current, respectively, must be considered. Further investigations are under way.

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