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SHORT COMMUNICATION

A compact amperometric NO_2 sensor based on Na^+ conductive solid electrolyte

N. MIURA, M. ONO, K. SHIMANOE, 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

Recently, much attention has been paid to the development of compact, low-priced, solid-state sensors which can monitor directly the concentration of atmospheric NO_2. Several potentiometric solid-electrolyte NO_2 sensors have been proposed and examined [1–10]. Some sensors can detect a small amount of NO_2 in air, but the accuracy of concentration data obtained is not usually high because of the potentiometric signal, which varies logarithmically with gas concentration. Generally speaking, amperometric sensors, if properly fabricated, can give more precise concentration data than potentiometric sensors. However, there has been little work [11] on solid-state amperometric NO_2 sensors.

Lately, we have proposed and reported [12, 13] an amperometric NO_2 sensor using a NASICON (Na^+-super-ionic conductor) and sodium nitrite ($NaNO_2$). The current response of this sensor varied linearly with NO_2 concentration, but its lowest limit of NO_2 detection was several-hundred ppb. In addition, the original sensor needs a flow of air to a counter electrode side as a reference gas, so the simplification and miniaturization of sensor structure is not easy. To overcome these drawbacks we designed a relatively small and compact sensor which requires no reference-gas flow. This modified amperometric sensor was found to give excellent NO_2 sensing properties with a detection limit of 10 ppb, as described below. Here we report the preliminary sensing characteristics and sensing mechanism of this compact sensor.

2. Experimental details

A compact electrochemical sensing device was fabricated by using a small plate (5 mm × 8 mm × 0.7 mm) of NASICON ($Na_3Zr_2Si_2PO_{12}$), as shown in schematic form in Fig. 1. A commercial gold paste was applied on both sides of the plate, as a sensing counter and reference electrode, respectively, followed by annealing at 700 °C for 30 min. The counter gold electrode was then covered with a layer of $NaNO_2$. The thicknesses of the gold electrode and the $NaNO_2$ layer were about 10 μm and about 200 μm, respectively. The gold electrode was coated with an inorganic adhesive to avoid the direct contact with the sample gas. We confirmed that the potential of this reference electrode was quite stable even in the flow of the sample gas containing NO_2. Such a reference electrode has been successfully used in the other kinds of solid electrolyte gas sensors (e.g. [14]). The NO_2 sensing experiments were carried out in a conventional gas flow apparatus equipped with a heating facility. Sample gases containing various concentrations of NO_2 under a constant oxygen concentration of 21 vol % were allowed to flow over the whole sensor element at a rate of 100 $cm^3\,min^{-1}$. The sensing electrode was polarized at a constant value by means of a potentiostat (Hokuto Denko, HA-101), with reference to the gold electrode. On switching the gas flow between air and the sample gas, the electrolysis current flowing through the NASICON plate was measured as a sensor signal, mainly at 150 °C. The polarization curves for the device were also measured in air or in the sample gases.

3. Results and discussion

Figure 2 shows the polarization curves of the device measured in air and in the sample gases containing varying concentrations of NO_2 at 150 °C. It is seen that the cathodic current increases with increasing NO_2 concentration and a clear limiting current is observed in the sample gases when the sensing electrode is polarized at around $-130 \sim -280$ mV vs reference electrode. This indicates that the potential of the reference gold electrode coated with the inorganic adhesive layer remains constant even in the sample gas so that the electrode functions as a relatively stable reference electrode. Furthermore, the appearance of a limiting current suggests that the diffusion of NO_2 gas into the NASICON/sensing Au electrode interface is controlled by the gold layer which is porous.

The current response to NO_2 was then measured at a constant sensing-electrode potential of −150 mV at 150 °C. Figure 3 depicts the dependence of NO_2 sensitivity (absolute current value) on NO_2 concentration in air. An almost linear relationship between the sensitivity and NO_2 concentration is seen over a wide concentration range from 10 ppb to 1 ppm.

Figure 4 depicts the response transients to NO_2 of various concentrations under the operating conditions mentioned above. It is seen that the response of the device is relatively quick even for very diluted NO_2 gas, that is, the 90% response time in 20 ppb NO_2 was as short as ~60 s. Furthermore, it was confirmed that the cross sensitivities to other gases, such as 100 ppb NO, 100 ppm H_2, 100 ppm CO,

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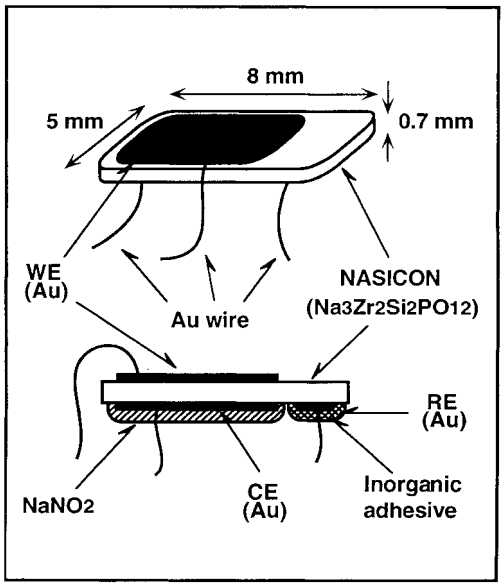

Fig. 1. Configuration of the compact amperometric NO_2 sensing device.

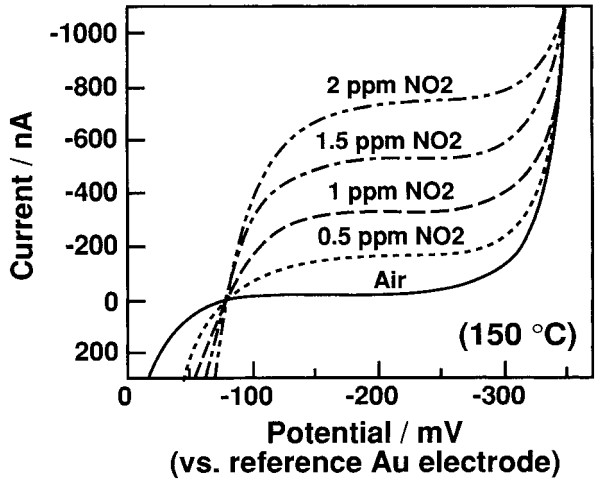

Fig. 2. Polarization curves of the device in air and in sample gases (NO_2 + air) at 150 °C.

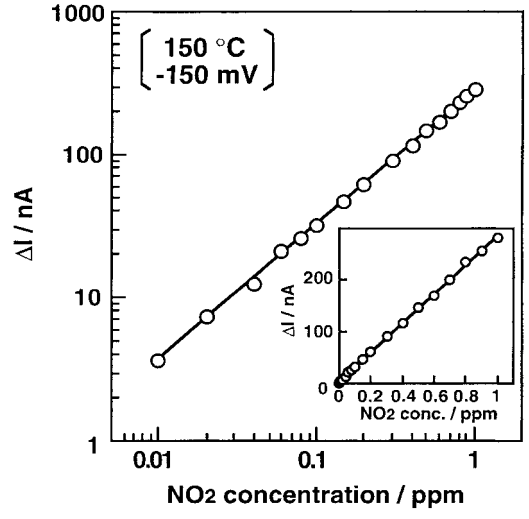

Fig. 3. Dependence of sensitivity (ΔI) on NO_2 concentration at 150 °C. Working electrode potential : −150 mV vs reference Au electrode.

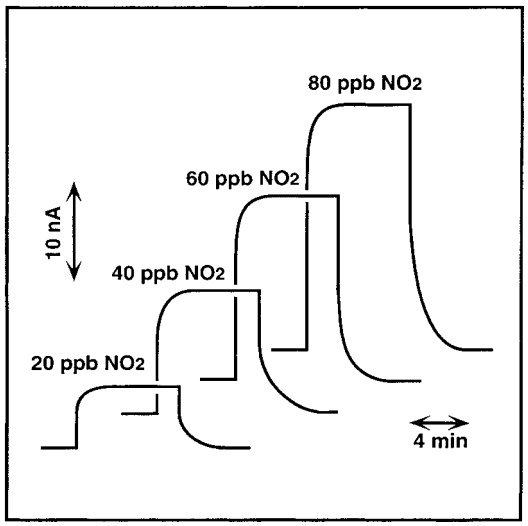

Fig. 4. Response transients to NO_2 at 150 °C. Working electrode potential: −150 mV vs reference Au electrode.

1000 ppm CO_2, and 1.84 vol % H_2O, were very low compared to that to 100 ppb NO, as shown in Fig. 5. With such excellent sensing performances, the present device appears promising for NO_2 monitoring in atmospheric air.

Figure 6 shows the schematic NO_2 sensing model for the present device. At the sensing electrode, whose potential is polarized cathodically in the NO_2 gas flow, the following cathodic reduction (Equation 1) of NO_2 takes place to produce $NaNO_2$:

$$Na^+ + NO_2 + e^- \rightarrow NaNO_2 \qquad (1)$$

At the counter electrode, on the other hand, the anodic reaction (Equation 2) of $NaNO_2$ (decomposition reaction) occurs giving Na^+ and NO_2:

$$NaNO_2 \rightarrow Na^+ + NO_2 + e^- \qquad (2)$$

Thus the sodium ions migrate through the NASICON plate from the counter electrode side to the sensing electrode side. This is accompanied by current flow in the external electric circuit as a sensing

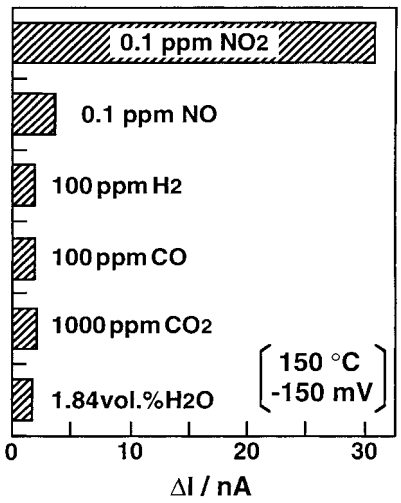

Fig. 5. Sensitivities (ΔI) to various gases at 150 °C. Working electrode potential: −150 mV vs the reference Au electrode.

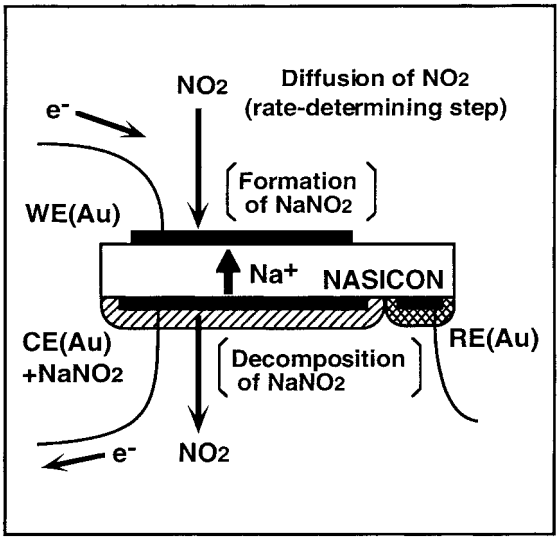

Fig. 6. Schematic model for NO_2 sensing.

response. Since the sensing gold electrode is porous and may work as a diffusion barrier to NO_2 gas, the limiting-current response is observed in the polarization curves. In addition, the above electrochemical reactions (1 and 2) involving NO_2 proceed very selectively under the present operating condition, so that the NO_2 sensitivity is hardly affected by other gases.

It is concluded that excellent amperometric detection of NO_2 (10 ppb–1 ppm) in air can be attained by the use of the NASICON–based compact device without a reference gas. It is proposed that the NO_2 sensing mechanism of the device involves the formation and decomposition of $NaNO_2$ at the sensing- and counter-electrode, respectively. However, further investigations on the sensing properties, as well as the sensing mechanism, remain to be carried out.

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