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Use of Sodium Nitrite Auxiliary Electrode for Solid Electrolyte Sensor to Detect Nitrogen Oxides

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An Na^+-conductor (NASICON)-based solid electrolyte device fitted with an $NaNO_2$ auxiliary electrode showed excellent sensing characteristics to NO and NO_2 in air. The electromotive force, EMF, followed the Nernst's equation for 1 - 800 ppm NO and 0.1-200 ppm NO_2 at temperatures of 150 - 240 °C, the Nernst's slopes indicating one-electron reduction for both gases.

The nitrogen oxides (NO_x: NO and NO_2) generated from automobiles and combustion facilities are serious air pollutants, and their monitoring is urgently needed for the protection of global environments. Many kinds of NOx sensors have already been reported, such as conductivity type sensors using oxide semiconductors[1-4] or metal phthalocyanines,[5] electrochemical sensors using solid electrolytes[6-9] and SAW sensors using phthalocyanines.[10] Most of these sensors have aimed at detecting NO_2 out of NO_x, since NO_2 is generally more reactive and easier to detect than NO. For the practical control of combustion exhausts which usually contain far more NO than NO_2, it is more desirable to detect NO. In this respect, only a few sensors such as those based on TiO_2[1] and WO_3[4] have so far been reported to detect NO. The detection of NO_2, on the other hand, is very important for the environmental monitoring, because NO_2 dominates in the environmental NO_x. For this purpose, sensors should be sensitive enough to detect as dilute as a few tens ppb NO_2. Among various types of NO_x sensors, those using solid electrolytes are of particular interest from the viewpoints of selectivity and simple element structure. We have reported that an electrochemical device using a sodium ion conductor, such as NASICON ($Na_3Zr_2Si_2PO_{12}$) and β''-alumina, shows rather good sensing characteristics to NO_2 in air when fitted with an auxiliary electrode of metal nitrates.[8,9] However, this sensor can not work as an NO sensor as will be shown later. As an approach to a solid electrolyte NO sensor, we have tested the use of $NaNO_2$ instead of metal nitrates for the auxiliary electrode. It has turned out that the new device not only makes it possible to detect NO but also provide far better sensing characteristics to NO_2 than the previous one, as described below.

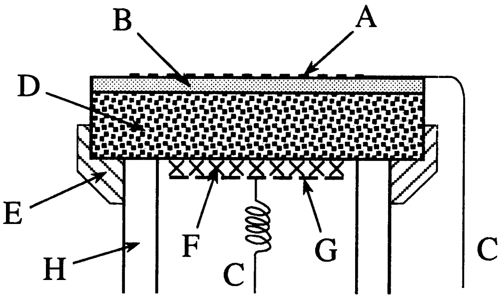

Fig. 1. Structure of NO_x sensor device.
A : Au-mesh, B : $NaNO_3$ or $NaNO_2$ electrode,
C : Au-wire, D : NASICON,
E : Inorganic adhesive, F : Pt-black,
G : Pt-mesh, H: Quartz glass tube.

The sensor device fabricated is shown in Fig.1. A disc of NASICON, 8 mm in diameter and 0.5 mm thick, was fixed on the end of a quartz glass tube with an inorganic adhesive. The sensing electrode was fabricated by covering the outside surface of the disc with $NaNO_2$ or $NaNO_3$ by a melting-quenching method, followed by fixing a gold mesh (100 mesh) on the top of it. The counter electrode (platium black) was applied on the inside surface of the disc and mechanically contacted to a platium mesh attached with an Au lead. The counter electrode was always exposed to static atmospheric air. Sensing experiments were conducted in a conventional flow apparatus equipped with heating facilities under atmospheric pressure. Sample gases containing NO or NO_2 were prepared from each parent gas, i.e., NO diluted with nitrogen or NO_2 diluted with air, by mixing it with synthetic air and/or pure oxygen. The oxygen concentration of the sample gases was maintained at a constant of 21 vol%. The sensor response, EMF, was measured with a digital electrometer (Advantest, TR 8552) at a total flow rate of 100 cm^3/min.

The sensing characteristics of the device fitted with an $NaNO_3$ electrode are shown in Figs. 2 and 3. As reported previously, the device responded rather well to switching between synthetic air (0 ppm NO_2) and 1 or 20 ppm NO_2 at 150 °C (Fig. 2(a)), the times for 90% response and 90% recovery being ca. 2 min and 14 min, respectively . The EMF responses were linear to the logarithm of the NO_2 concentration (Fig. 3(a)), with a Nernst's slope of 84 mV/decade, or n=1.0, where n is the number of electrons involved in the electrode reaction per NO_2 molecule. The device also responded to NO as shown in Fig. 2(b), but the EMF responses were not well correlated with the NO concentration as shown in Fig. 3(b). Possibly NO was partly oxidized to NO_2 on the electrode and the produced NO_2 was responsible for the EMF response. Anyway this device could not be used as an NO sensor.

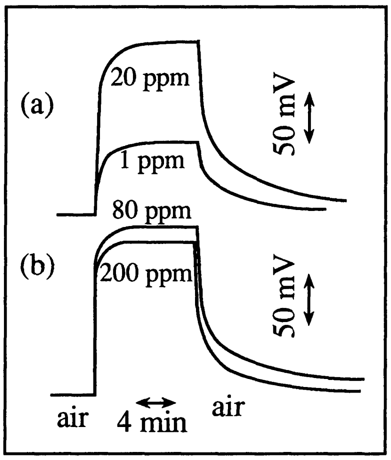

Fig. 2. Response transients of the device fitted with $NaNO_3$ electrode at 150 °C. (a), NO_2; (b), NO.

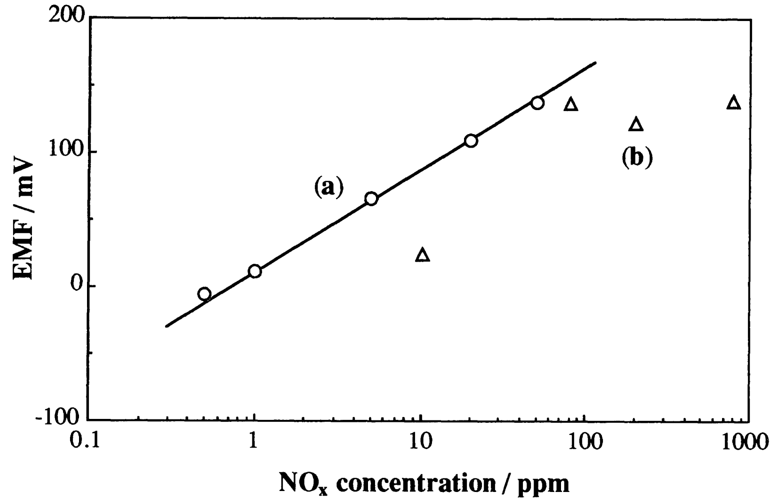

Fig. 3. EMF vs. NO_2 or NO concentration at 150 °C for the device fitted with $NaNO_3$ electrode. (a): NO_2; (b): NO.

The sensing properties of the new device using $NaNO_2$ are shown in Figs. 4 and 5. It could respond to both NO_2 and NO (Fig. 4). The EMF response followed the Nernst's equation for both gases (Fig. 5). The Nernst's slope of 84 mV/decade for NO was in agreement with $n = 1$. Although the slope for NO_2 gave $n = 1.1$ in this particular experiment, the n values for NO_2 were very close to 1.0 in most cases. These results indicate that the use of the $NaNO_2$ auxiliary electrode enables one to fabricate an NO sensor unlike the case of the $NaNO_3$ electrode. In addition, the same device can also work as an excellent NO_2 sensor.

The use of the $NaNO_2$ electrode was found to also bring about other advantageous effects. First, the rates of response to NO and NO_2 were far higher than those observed with the $NaNO_3$ electrode. The 90% response times on exposure to NO and NO_2 at 150 °C were as short as 8 s when the gas concentrations were 10 ppm and above, while the recovery rates on turning-off the gases were rather slow at the same temperature. The recovery rates increased drastically with increasing operation temperature, to give the 90% recovery times of ca. 2 min for

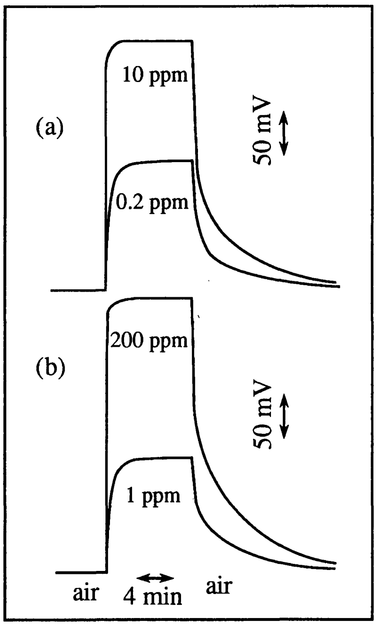

Fig. 4. Response transients of the device fitted with $NaNO_2$ electrode at 150 °C. (a), NO_2; (b), NO.

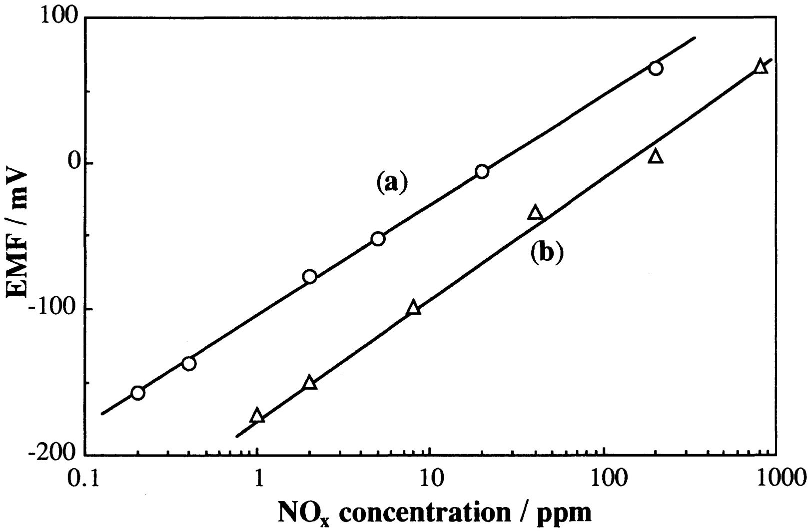

Fig. 5. EMF vs. NO_2 or NO concentration at 150 °C for the device fitted with $NaNO_2$ electrode. (a): NO_2; (b): NO.

1 - 200 ppm NO and 1 - 100 ppm NO_2 at 180 °C (Fig. 6(a)). The rates increased further at higher temperature, as seen from the response transients at 225 °C (Fig. 6(b)). No such quick response and recovery could be observed with the $NaNO_3$ electrode even when temperature was raised.

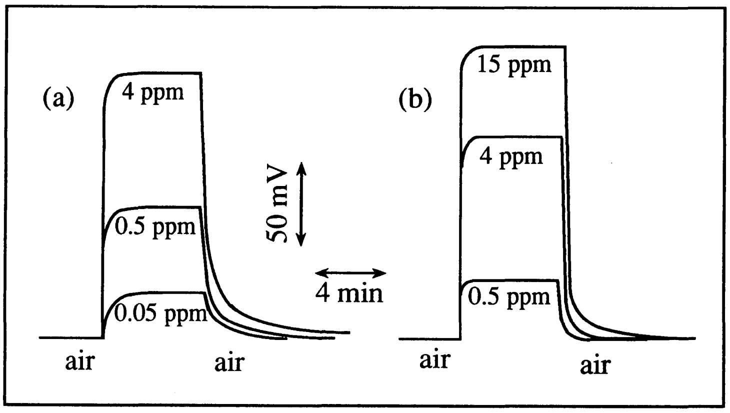

Fig. 6. NO_2 response transients of the device fitted with $NaNO_2$ electrode at 180 °C (a) and 225 °C (b).

Second, for a fixed concentration of NO or NO_2, the increment of EMF on switching from air to the sample gas, i.e., the difference in EMF between the air level and the stationary gas level, was much larger with the $NaNO_2$ electrode than with $NaNO_3$. This is apparent when one compares the response transients in Fig. 4 ($NaNO_2$) with those in Fig. 2 ($NaNO_3$). At 150 °C the air levels were ca. -300 mV and ca. -60 mV, while the stationary gas levels to 1 ppm NO_2, for example, were -95 mV and 11 mV, for the $NaNO_2$ and $NaNO_3$ electrodes, respectively. With such a large increment of EMF, the device using $NaNO_2$ has a potential capability of sensing very dilute NO and NO_2. In fact, the increment of EMF was as large as ca. 120 mV to 100 ppb NO_2 at 150 °C. Combined with the rapidly responding nature just mentioned, the device could respond to as dilute as 50 ppb NO_2 at 180 °C (Fig. 6(a)). It seems possible to measure directly the environmental NO_2 with this device.

A problem about the $NaNO_2$ electrode seems to be its chemical stability to oxidation to $NaNO_3$. It was found that a small amount of $NaNO_3$ phase was formed when $NaNO_2$ was heated above its melting point (270 °C) for 30 min in air. Probably because of such oxidation, the sensing performances of the device for NO and NO_2 began to be unstable at higher temperatures than 240 °C.

The sensing mechanisms of the present electrochemical device are still under investigation. The device is expressed as follows,

air, Pt / NASICON / $NaNO_2$, Au, NO_x + air.
(counter electrode) (Na^+ conductor) (sensing electrode)

We have previously postulated the NO_2 sensing mechanism of the $NaNO_3$-fitted device.[8,9] It is possible to postulate a similar mechanism for NO sensing by the present device. The following electrochemical reactions are assumed to take place on the sensing and counter electrodes.

$$\text{(Sensing electrode)}\quad Na^+ + NO + \frac{1}{2}O_2 + e^- = NaNO_2. \tag{1}$$

$$\text{(Counter electrode)}\quad Na^+ + \frac{1}{4}O_2 + e^- = \frac{1}{2}Na_2O\ \text{(in NASICON)}. \tag{2}$$

The overall chemical reaction is then reduced to

$$\frac{1}{2}Na_2O + NO + \frac{1}{4}O_2 = NaNO_2. \tag{3}$$

Under the conditions of constant activities of $NaNO_2$ and Na_2O and a constant oxygen partial pressure, EMF is expressed as

$$E = E^\circ + (RT/F)\ln P(NO), \tag{4}$$

where P(NO) is the partial pressure of NO, E° is a constant, and RT and F have their conventional meanings. This mechanism accounts for the observed Nernst's slope for NO (n = 1).

There are two possibilities for the NO_2 sensing mechanism. The first one is to assume that NO_2 undergoes the sensing electrode reaction,

$$Na^+ + NO_2 + e^- = NaNO_2. \tag{5}$$

Combining Eq. 5 with Eq. 2, one obtains an expression of EMF similar to Eq. 4. The second one is to assume that the partial formation of $NaNO_3$ from $NaNO_2$ allows the same NO_2 sensing mechanism to operate as postulated for the $NaNO_3$ electrode. It is not clear at present which mechanism dominates.

In conclusion, the NASICON-based solid electrolyte device fitted with an $NaNO_2$ auxiliary electrode exhibits fascinating characteristics for sensing NO and NO_2. Elucidation of the sensing mechanisms as well as the method to stabilize the nitrite electrode appear to be important subjects of further investigations.

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