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Influence of Oxygen on Detection of Nitrogen Oxides with Solid Electrolyte Sensor Using $NaNO_3$

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The solid electrolyte sensor device using a sodium ionic conductor and $NaNO_3$ (auxiliary phase) was found to exhibit a remarkable feature that its EMF response to NO_2 is totally independent of the concentration of coexisting oxygen. The response to NO, however, was seriously affected by the presence and absence of O_2, suggesting the oxidation of NO to NO_2 prior to being sensed. In the absence of NOx, the sensor EMF changed with changing oxygen concentration following the Nernst's equation for a 2-electron reaction of O_2.

From the growing concern to the protection of global environments, there is an increasing need for compact, inexpensive solid-state sensors to detect nitrogen oxides (NO and NO_2) in combustion exhausts or in the atmosphere.[1,2] We have shown that electrochemical devices, which combine a sodium ionic conductor such as NASICON ($Na_3Zr_2Si_2PO_{12}$) and Na-β/β"-alumina with an auxiliary phase of $NaNO_3$[3,4] or $NaNO_2$,[5] show rather good sensing properties for detecting NO_2 and/or NO in air, following the Nernst equation for one-electron reduction of NO_2 or NO. The reaction mechanisms of NO_2 or NO detection by these sensors, however, remain to be elucidated. In this connection, We investigated the influence of oxygen concentration on the sensing behavior of the device attached with $NaNO_3$. As a result, the sensor response to NO_2 has been found to be totally independent of oxygen concentration in disagreement with what has so far been assumed. This paper deals with the influence of oxygen concentration on the EMF response to NO or NO_2 as well as on the EMF level in the absence of NO_2 or NO (base line EMF).

The sensor device fabricated is shown in Fig. 1. NASICON (Na-Super-Ionic-Conductor) was synthesized by calcining the mixture of $ZrSiO_4$ and Na_3PO_4 at 1200 °C. A disc of NASICON, 8 mm in diameter and 0.5 mm thick, was fixed at one end of a quartz glass tube with an inorganic adhesive. The outside surface of the disc was coated with a layer of $NaNO_3$ (ca. 0.1 mm thick) by a melting-quenching method, and on top of it a gold mesh (100 mesh) was placed as the sensing electrode. The counter electrode (platinum black) was applied on the inside surface of the disc and connected to an Au lead wire through a platinum mesh. The counter electrode was always

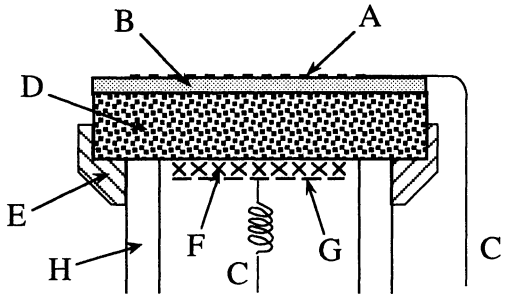

Fig. 1. Structure of NO_X sensor.
A: Au-mesh, B: $NaNO_3$ electrode, C: Au- wire, D: NASICON, E: Inorganic adhesive, F: Pt-black, G: Pt-mesh, H: Quartz glass tube.

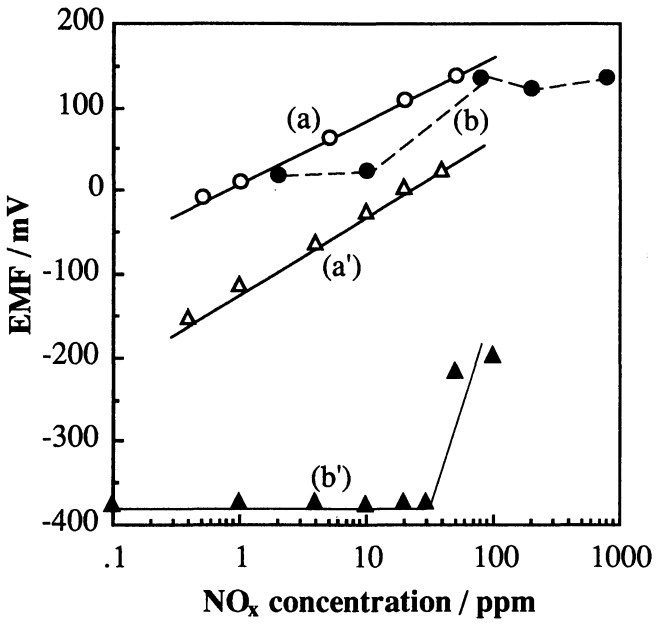

Fig. 2. Dependence of EMF on the concentration of NO or NO_2 in air or N_2.
(a) NO_2 in air at 150 °C; (a') NO_2 in N_2 at 190 °C;
(b) NO in air at 150 °C; (b') NO in N_2 at 190 °C.

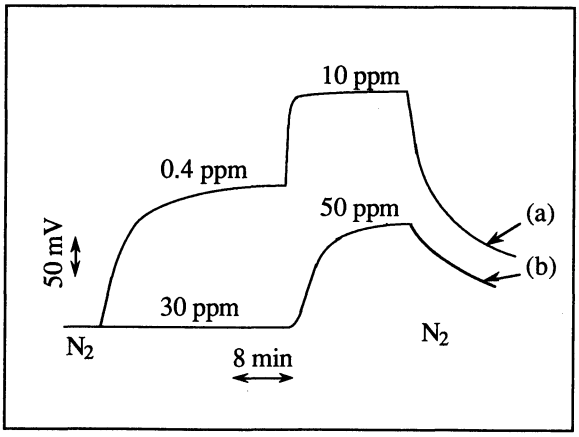

Fig. 3. Response transients to NO_2 (a) and NO (b) in N_2 at 190 °C.

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 or NO_2 diluted with nitrogen, by mixing it with pure oxygen and/or pure nitrogen. EMF of the device was measured with a digital electrometer (Advantest, TR 8552) at a total flow rate of 100 cm^3/min.

We have already reported that the present sensor can detect NO_2 in air rather well. At 150 °C, for example, it responds to NO_2 in air with 90% response time of about 2 min to produce NO_2 concentration-dependent EMF as presented by (a) in Fig. 2. The Nernst's slope, 84 mV/decade, indicates an one electron reduction of NO_2 (n = 1), and is consistent with the following sensing electrode reaction assumed so far. If this

$$Na^+ + NO_2 + (1/2)O_2 + e^- = NaNO_3 \quad (1)$$

reaction is correct, the sensor would not be able to operate in the absence of oxygen. Surprisingly the sensor turned out to operate as an NO_2 sensor in the absence of oxygen as described below.

Transient (a) in Fig. 3 shows the behavior of the device on turning-on or -off NO_2 in the flow of nitrogen at 190 °C. It is seen that EMF changes with a change of NO_2 concentration as it does in the air flow. The rates of response and recovery were also similar to those in the air flow. EMF values to various concentrations of NO_2 in the N_2 flow are plotted in Fig. 2 (a'). Again the data fit the Nernst's equation for n = 1. The difference in EMF between (a) and (a') is due to the difference in the operation temperature. This indicates that the NO_2 sensing characteristics are not influenced by oxygen.

To confirm the O_2-independent nature of the sensor response to NO_2, further experiments were carried out as shown by transients (a) and (b) in Fig. 4. Here, the sensor was first exposed to NO_2 at 40 ppm (a) or 4

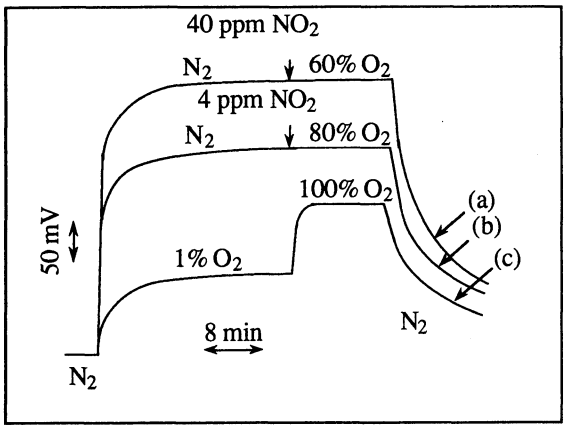

Fig. 4. Response transients to NO_2 and/or O_2 (N_2 balance, 190 °C).
(a) and (b): Exposure to NO_2 (40 or 4 ppm) in N_2, followed by the addition of oxygen at the points of arrows,
(c): Successive exposure to 1% and 100 % O_2 (without NOx).

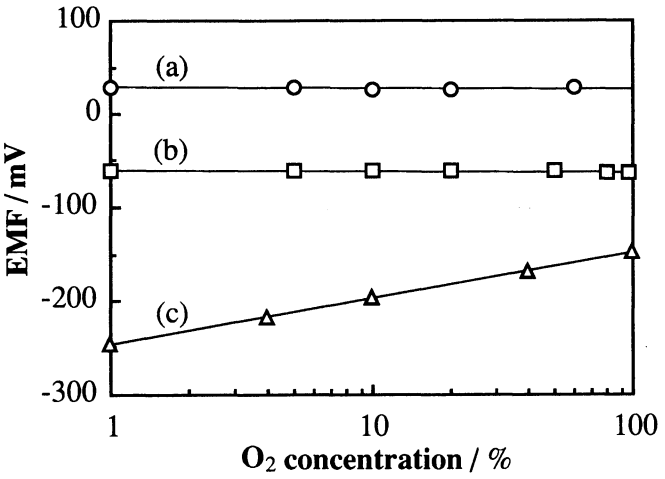

Fig. 5. Influence of oxygen concentration on EMF (190 °C).
(a) 40 ppm NO_2; (b) 4 ppm NO_2;
(c) In the absence of NO_2.

ppm (b) in the N_2 flow. Then, at the position indicated by an arrow, the flow was switched to one which was added with 60% O_2 (a) or 80% O_2 (b). Nothing happened about EMF confirming the irrelevance of oxygen. It would be of interest to know the interaction of the sensor with oxygen in the absence of NO_2. As shown by transient (c) in Fig. 4, EMF changed with changing the O_2 concentration, indicating that the sensor interacts with oxygen when NO_2 is absent.

Oxygen concentration was varied in the presence or absence of NO_2. Resulting EMF data are shown in Fig. 5. In the presence of 40 or 4 ppm NO_2 (a or b), the EMF values were totally independent of oxygen concentration over the whole range tested from 0% to almost 100%. In the absence of NO_2(c), however, EMF changed linearly with an increase in the logarithm of oxygen concentration. The Nernst's slope, 46 mV/decade, coincided perfectly with the 2-electron reaction of O_2 (n = 2). This clearly shows that the sensor works as an oxygen sensor in the absence of NO_2.

As mentioned above, the NO_2 sensing mechanism can not be accounted for by the reaction (1). The electrode reaction of NO_2 does not involve gaseous oxygen, while the same electrode can interact with oxygen in the absence of NO_2. The following mechanisms, though still highly speculative, may be suggested for the sensor responses to NO_2 and O_2. To explain the electrode reaction of O_2 invclving 2 electrons, one has to assume the presence of excess oxygen of the state of O_2^{2-} or O^- in the auxiliary phase. If one assumes the presence of Na_2O_2, the electrode reaction may be written as

$$2Na^+ + O_2 + 2e^- = Na_2O_2, \quad (2)$$

in agreement with the observed results. The excess oxygen possibly takes part in the NO_2 sensing reaction, as follows for example:

$$Na^+ + NO_2 + Na_2O_2 + e^- = NaNO_3 + Na_2O. \quad (3)$$

This explains the observed one-electron reaction of NO_2, independent of gaseous oxygen, if Na_2O_2 is assumed

to exist as a solid component.

The influence of oxygen on the response to NO is briefly described below. As reported previously, the sensor responds to NO in air but EMF is not a simple function of NO concentration, as shown by (b) in Fig. 2. The response transients to NO in the absence of oxygen are shown by (b) in Fig. 3. 30 ppm NO was inert but 50 ppm NO caused EMF to change. When plotted as a function of NO concentration in N_2, EMF was unchanged up to about 30 ppm NO, above which EMF increased rather abruptly, as shown by (b') in Fig. 2. Such EMF behavior suggests that NO is responded indirectly. NO can be oxidized into NO_2 in air or it may undergo a disproportionation reaction $3NO \rightarrow N_2O + NO_2$ when NO concentration increases. It is plausible that the NO_2 thus produced from NO is responsible for the EMF response to NO in air as well as in N_2.

In conclusion, detection of NO_2 by the present sensor is independent of gaseous oxygen, though oxygen actively interacts with the sensor in the absence of NO_2. The response to NO appears to be generated indirectly after it is converted into NO_2.

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