—Communication—

High Performance Solid Electrolyte NO₂ Sensor Using Auxiliary Phase of Nitrite—Carbonate Mixture

Sheng YAO, Youichi SHIMIZU, Norio MIURA and Noboru YAMAZOE

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1. INTRODUCTION

Emission of nitrogen oxides (NO and NO₂, abbreviated as NO_x) from automobiles and stationary combustion facilities is one of the main causes for air pollution problems. Compact solid state sensors for NO and NO₂ are strongly needed in order to facilitate the development of new technology to solve current environmental problems. Among various types of NO_x sensors so far investigated, solid electrolyte sensors of type III have appeared to be very promising. This type sensor device is attached with an auxiliary phase (gas-sensitive layer) to cover the surface of the solid electrolyte used together with the sensing metal electrode. An NO₂ sensor of this type was first fabricated by covering a Na-β/β"-alumina-based electrochemical cell with a layer of NaNO₃ (auxiliary phase). We have been investigating NASICON (Na₃Zr₂Si₂PO₁₂, Na⁺-conducting solid electrolyte)-based sensors for NO and NO₂. It has been found that the use of NaNO₂ as an auxiliary phase brings about far better sensing characteristics to NO₂ than that of NaNO₃, in addition to making the device to be sensitive to NO. It seems that the choice and design of the auxiliary materials are decisively important for this type sensors. Recently we found that the NO₂ sensing properties of the NASICON-based device could be further improved significantly by using a binary system of NaNO₂-M₂CO₃ (M = Na or Li) for the auxiliary phase. This device could detect as dilute as 5 ppb NO₂, without being disturbed by CO₂ up to 40 vol % CO₂, as described below.

2. EXPERIMENTAL

Sensor devices were fabricated in the same structure as those already reported⁴). A disc of NASICON (8 mm in diameter, 0.5 mm thick) was fixed on one end of a quartz glass tube with an inorganic adhesive. The outside surface of the disc

was covered with a layer of either pure NaNO₂ or a nitrite-carbonate mixture of NaNO₂-M₂CO₃ (9:1 in molar ratio, M = Li, Na) by a melting-quenching method, on top of which the sensing electrode (Au mesh) was attached. The counter electrode (Pt black and Pt mesh) was attached onto the inside surface of the disc. NO_x sensing experiments were conducted in a flow apparatus equipped with a heating facility under an atmospheric pressure. Sample gases containing various partial pressures of NO_x (PNO_x) at a fixed P_{O2} (0.21 atm) or in N₂ balance were allowed to flow over the sensing electrode at a rate of 100 cm³/min, while the counter electrode was always exposed to the static atmospheric air. The electromotive force (EMF) of the device was measured with a digital electrometer (Advantest, TR 8552) at 150 °C.

3. RESULTS AND DISCUSSION

As reported previously, the NASICON-based electrochemical cell fitted with NaNO₂ (Device I) could detect more dilute NO₂ in air than one fitted with NaNO₃⁴). In the present study, the sensing characteristic to dilute NO₂ could be further improved significantly with one fitted with NaNO₂-Li₂CO₃ (Device II). Figure 1 shows the response transients of Device I and II to NO₂ in air at 150 °C. Both devices showed sharp transients to extremely small concentrations of NO₂. However, Device II could still show reasonable transients even at 5 ppb NO₂, although the times for 90% response and 90%

Fig. 1 Response transients to NO₂ at 150 °C.
a: Device I, fitted with NaNO₂;
b: Device II, fitted with NaNO₂-Li₂CO₃ (9:1).

Department of Materials Science and Technology,
Graduate School of Engineering Sciences, Kyushu
University, Kasuga-shi, Fukuoka 816
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Fig. 2 Dependence of EMF on the concentration of NO₂ (a and b) or CO₂ (c) as well as the air levels (a' and b') at 150 °C. a and a' for Device I; b, b' and c for Device II.

recovery under this condition were prolonged to be approximately 3 and 10 min, respectively.

Figure 2 shows the correlation between EMF and NO₂ concentration at 150 °C for the two devices. In the higher concentration range of NO₂ (0.3 ppm and above), EMF of Device I was linear to the logarithm of NO₂ concentration, with the Nernst's slope corresponding to $n = 1$, where n is the number of electrons involved in the electrode reaction per NO₂ molecule. In the lower concentration range (< 0.3 ppm), EMF deviated from the correlation line for $n = 1$. On the other hand, Device II was found to hold a linear correlation ($n=1$) between EMF and NO₂ concentration down to the lowest NO₂ concentration examined (5 ppb). Both devices exhibited EMF under exposure to synthetic air (air level), the respective air levels (a', b') being indicated in Fig. 2. It is considered that the EMF vs. NO₂ concentration correlation follows a theoretical line as far as the EMF value involved is sufficiently high above the air level, whereas it deviates otherwise. Thus the lower concentration limit of detection is deeply related with the location of the correlation line relative to the air level. As seen from Fig. 2, Device II has lower air level than Device I, while it exhibits higher EMF than Device I to a given concentration of NO₂. These two effects apparently have contributed to lowering the concentration limit of detection for Device II.

It is known that CO₂ sensors are obtained when NASICON-based devices are attached with carbonates. Therefore the cross sensitivity to CO₂ seems to be a matter of practical importance for the present device using NaNO₂-Li₂CO₃. It was found that the device was hardly sensitive to CO₂ in air up to 40 vol.%, as shown in Fig. 2. The cross sensitivity to CO₂ was in fact dependent on the

composition of the auxiliary phase and the device using NaNO₂-Li₂CO₃ (3 : 1) was significantly sensitive to CO₂.

Almost the same improvement as above could also be obtained when NaNO₂-Na₂CO₃ (9 : 1) was used as an auxiliary phase. These results indicate that the mixing of NaNO₂ with a carbonate is advantageous for improving the sensitivity to very dilute NO₂. It seems possible to apply the resulting solid electrolyte devices for monitoring NO₂ in an urban environmental atmosphere.

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