Solid Electrolyte-Based NO_X Sensor Using Auxiliary Phase of Metal Oxide

Youichi Shimizu* and Koji Maeda
Department of Chemistry, Faculty of Engineering, Kyushu Institute of Technology, Tobata, Kitakyushu 804

(Received October 23, 1995)

Solid electrolyte-based electrochemical elements fabricated with sodium super-ionic conductor (NASICON) and auxiliary phases of metal oxides were tested for the detection of NO and NO_2 in the range between 10 and 200 ppm. The elements having Cr_2O_3/NASICON and CuO/NASICON combinations exhibited rather good performance for potentiometric sensing of NO as well as NO_2 at 250 °C.

Nitrogen oxides (NOx: NO and NO_2) released from automobiles and combustion facilities are serious pollutants and their monitoring is becoming important for the protection of global environments. Among various types of compact NOx sensors, the electrochemical cell type using solid electrolytes[1,2] is of particular interest from the view points of sensitivity, selectivity, and simple element structure. Most of these NOx sensors so far reported are based on metal salts as an auxiliary phase, and they are not intrinsically suited for detection of NO, which is the major component of NOx in combustion exhausts, except the element using $NaNO_2$ auxiliary phase.[3,4] For practical applications, the use of metal oxides instead of conventional metal salts for the auxiliary phase seems to bring about better sensing performance to NO as well as stability at higher temperatures. Solid-state electrochemical elements, which combine solid electrolytes with oxide containing electrodes, have been reported for CO or H_2S sensors.[5,6] It is known that the oxide of these sensors acts as an electrode catalyst and the response is based on the change of mixed potential at the electrode reactions. Weppner et al. reported that the sensor element which was consisted of solid ionic conductor and SnO_2-based electrode could detect CO_2 at room temperature, although the EMF (electromotive force) response was decreased above 100 °C.[7] In this study, we have tested the use of metal oxides for the auxiliary phase as an approach to new solid electrolyte-based NO and/or NO_2 sensors. It has turned out that the devices are sensitive to NO as well as NO_2 at 250 °C.

The sensor devices fabricated here were almost similar to those already reported.[3] A disc of NASICON ($Na_3Zr_2Si_2PO_{12}$) prepared by a sol-gel method[8] was fixed on a glass tube with an adhesive. A mixed solution, prepared from organo-metal compound (Mn-,Cu-,V- naphthenates; Pb-,Fe-, Co-, Ni-, Zn- octates; Cr-, Mo- actylacetonates), toluene, and n-butanol, was spin-coated onto the surface of the NASICON disc, and dried and finally sintered at 600 °C for 2 h to form a thin layer of oxide as an auxiliary phase.[9,10] An Au mesh (sensing electrode) was attached on the top of the oxide layer. A reference Pt electrode attached on the inside surface of the NASICON disc was always exposed to static atmospheric air. NOx sensing experiments were carried out in a conventional flow apparatus equipped with a heating facility at 250 °C. 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 (N_2+O_2 gas mixture), by mixing it with N_2 or air. The sensor response, EMF, was measured with a digital electrometer at a total flow rate of 100 cm^3/min.

X-ray diffraction analysis revealed that well-crystallized single-phase oxides could be easily prepared from the solution with organo-metal compounds. First, the NO-sensing performance of a NASICON-based sensor element combined

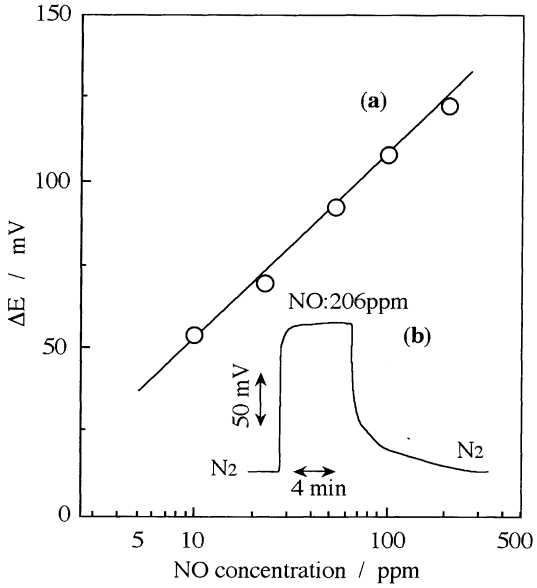

Figure 1. Sensing performance to NO of the device having Cr_2O_3/NASICON combination at 250 °C: (a) ΔE vs. NO concentration; (b) response transient to 206 ppm NO.

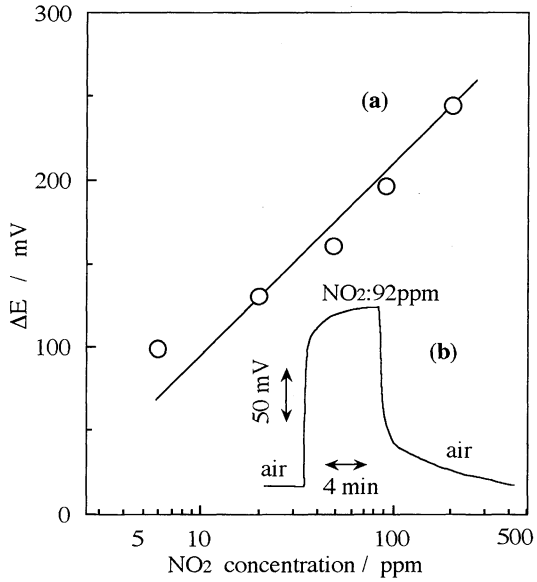

Figure 2. Sensing performance to NO_2 of the device having Cr_2O_3/NASICON combination at 250 °C: (a) ΔE vs. NO_2 concentration; (b) response transient to 92 ppm NO_2.

Table 1. Sensing performance of the sensor devices using NASICON and various oxides as an auxiliary phase

Auxiliary phase	n[a]		90% response time (min)[b]		Stability[c]
	NO	NO_2	NO	NO_2	
V_2O_5	1.9	1.0	5.2	6.0	Δ
Cr_2O_3	2.0	1.1	2.2	2.8	○
Mn_2O_3	1.3	2.0	6.8	2.0	Δ
Fe_2O_3	-	-	-	-	×
Co_3O_4	1.1	1.1	5.6	0.8	×
NiO	4.8	2.4	4.0	3.2	×
CuO	2.2	1.2	5.2	3.6	○
ZnO	1.8	1.1	10.6	1.0	×
MoO_3	2.0	1.5	4.0	1.6	Δ
PbO	2.0	0.9	2.0	0.4	Δ

[a]The number of electrons involved in the electrode reaction per NO (NO_2) molecule. [b]NOx concentration (100ppm). [c]○: good, Δ :unstable to NO_2, × :poor .

with Cr_2O_3 was investigated. As shown in Figure 1, the device responded rather well to switching between nitrogen and nitrogen containing 206 ppm NO at 250 °C, with the 90% response time of ca. 2 min. The EMF change (ΔE) was linear to the logarithm of NO concentration, with a Nernst slope of 53 mV/decade, or n=2.0, where n is the number of electrons involved in the electrode reaction. It was further found that this device could also respond to NO_2 as well as NO, as shown in Figure 2. The EMF response also followed the Nernst equation in the NO_2 concentration range 10-200 ppm, while ΔE to NO_2 was larger than that to NO. The Nernst slope of 94 mV/decade for NO_2 was in good agreement with n=1.1, differing from the case for NO. The 90% response time on exposure to NO_2 was ca. 1-3 min when the NO_2 concentration was 100 ppm and below, and it became more slow at higher NO_2 concentrations.

Sensing performance to NOx of the various sensor elements having some oxides as the auxiliary phases was further investigated. Table 1 summarizes the response characteristics of various sensor devices fabricated. All devices except Fe_2O_3/NASICON combination showed EMF responses to the sample gases containing NO or NO_2, while the stability, response rate, and the electrode reactions were largely dependent on the oxide used. Among the oxides tested, Cr_2O_3- and CuO-based elements showed rather good sensing properties to NO and NO_2. V_2O_5-, PbO-, and MoO_3-based elements responded rather well to NO, however they were unstable in the sample gas containing NO_2.

In order to examine the NOx sensing mechanism, the effect of coexistent oxygen concentration on NO or NO_2 detection was tested for Cr_2O_3/NASICON device. As shown in Figure 3, the EMF of the sensor device was hardly dependent on the coexistent O_2 concentration if the concentration of NO_2 was fixed, while it was dependent on the logarithm of coexistent O_2 concentration in the presence of a fixed concentration of NO, following Nernst's equation (n=4). From these EMF response behaviors, the following electrochemical reactions have been assumed to take

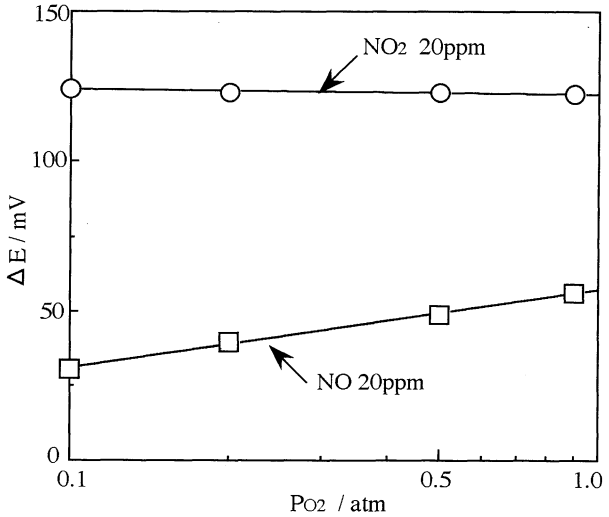

Figure 3. Effect of oxygen concentration on EMF responses of the device having Cr_2O_3/NASICON combination under the conditions of fixed (20ppm) NO or NO_2 at 250 °C.

place on the sensing electrodes for NO and NO_2, respectively.

$$2Na^+ + NO + (1/2)O_2 + 2e^- + CrO_X(\text{in } Cr_2O_3) = NaNO_2 + NaCrO_X \quad (1)$$

$$Na^+ + NO_2 + e^- = NaNO_2 \quad (2)$$

In the reaction (1), the surface of Cr_2O_3 is to be reduced by NO to form CrO_X (x<1.5), and oxygen is an impurity of N_2 gas used. In the reaction (2), Cr_2O_3 should be acted as an electrode catalyst. However, the sensing mechanism of the present electrochemical device still needs further investigations.

This study was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports, and Culture of Japan, and the Okura Kazuchika Foundation's Research Grant.

References

1 M. Gauthier and A. Chamberland, *J. Electrochem. Soc.*, **124**, 1579 (1977).
2 G. Hötzel and W. Weppner, *Solid State Ionics*, **18/19**, 1223 (1986).
3 S. Yao, Y. Shimizu, N. Miura, and N. Yamazoe, *Chem. Lett.*, **1992**, 587.
4 N. Miura, S. Yao, Y. Shimizu, and N. Yamazoe, *Sensors & Actuators B*, **13/14**, 387 (1993).
5 H. Okamoto, H. Obayashi, and T. Kudo, *Solid State Ionics*, **1**, 319 (1980).
6 Y. Yan, N. Miura, and N. Yamazoe, *Chem. Lett.*, **1994**, 1753.
7 S. Brediklin, J. Liu, and W. Weppner, *Appl. Phys. A*, **57**, 37 (1993).
8 Y. Shimizu, S. Michishita, and T. Murata, *Jpn. J. Appl. Phys.*, **34**, L833 (1995).
9 T. Kumagai, H. Yokota, K. Kawaguchi, W. Kondo, and S. Mizuta, *Chem. Lett.*, **1987**, 1645.
10 M. Ando, T. Kobayashi, and M. Haruta, *Chemical Sensors*, **7**, Sup. B, 165 (1991).