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Stabilized Zirconia-Based Potentiometric Sensor for Nitrogen Oxides

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An electrochemical device fabricated by combining an MgO-stabilized zirconia (MSZ) tube and a coating layer of $Ba(NO_3)_2$ (auxiliary phase) was found to exhibit fairly good Nernstian response to dilute NO_2 in air at elevated temperature (450 °C). The response to NO, which was far less satisfactory with the above device, could be much improved by the use of a binary system of $Ba(NO_3)_2$-$CaCO_3$ for the coating layer.

The detection of nitrogen oxides, NO_2 and NO (NO_x), has become increasingly important in resent years in relation with the global environmental issues. Among several NOx sensing devices so far investigated, those using solid electrolytes usually produce Nernst-type EMF responses and hence are in principle suited for detecting dilute NO_x. This type device was first fabricated by utilizing metal nitrate ($Ba(NO_3)_2$) as the base solid electrolyte.[1] Later, more practical devices for NO_x have been fabricated by combining a typical cation conductor such as Na-β- or β/β"-alumina[2,3] and NASICON ($Na_3Zr_2Si_2PO_{12}$)[4-8] with an auxiliary phase containing a metal nitrate or nitrite. We have reported that the sensing characteristics of these devices can be improved by the use of a mixed auxiliary phase such as $NaNO_3$-$Ba(NO_3)_2$,[5] $NaNO_2$-Li_2CO_3[7] and $NaNO_2$-Na_2CO_3,[8] and that the device using $NaNO_2$-Li_2CO_3 has an ability to detect as dilute as 5 ppb NO_2 in air at 150-250 °C. However, these devices are still far from being satisfactory as far as the NO_x sensing for combustion exhausts is concerned. That is, the device should operate at far higher temperature and the solid electrolyte used should be more resistant to chemical attack in the hostile atmospheres. This prompted us to investigate the possibility to utilize stabilized zirconia which is apparently more reliable than those solid electrolytes so far tested. Actually we have already proposed the use of stabilized zirconia for SO_x and CO_2 sensors.[9,10] In the present study, the devices combining an MgO-stabilized zirconia (MSZ) tube with a $Ba(NO_3)_2$ or $Sr(NO_3)_2$-based auxiliary phase were investigated for their sensing properties to NO_2 and NO at elevated temperature of 400 or 450 °C. The above nitrates were chosen

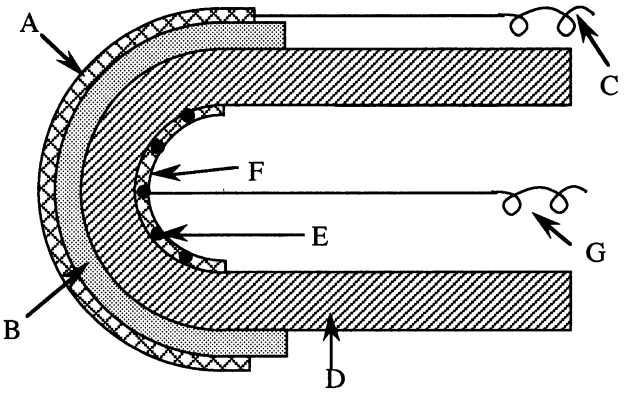

Fig. 1. Schematic diagram of NOx sensing device using a zirconia tube.
A: Au mesh (sensing electrode), B: auxiliary phase,
C: Au wire, D: Stabilized zirconia tube (MSZ),
E: Pt-black (counter electrode), F: Pt mesh, G: Pt wire.

because of their high melting points, i.e., 592 and 570 °C, respectively.

A schematic view of the sensor device is shown in Fig. 1. A tubular-type device was fabricated by using a half-open, MgO (15 mol%)-stabilized zirconia (MSZ) tube (ZR-15M, NKT Co. Ltd) with 5 and 8 mm inner and outer diameter, respectively. A Pt electrode (counter electrode) was attached on the inside bottom of the tube by applying Pt black powder, followed by annealing it at about 600 °C. This electrode was connected to a Pt lead through a mechanically pressed Pt mesh, and was always exposed to atmospheric air. The metal nitrate-containing auxiliary phases was coated on the outside bottom of the tube by dipping that part in the molten nitrate, followed by cooling it rapidly in atmospheric air. Then it was covered with an Au mesh (sensing electrode) connected to an Au lead.

Gas sensing experiments were carried out in a conventional gas flow apparatus equipped with a heating facility. Sample gases containing various concentrations of NO_2 or NO under a constant oxygen concentration of 21 vol% were prepared by diluting each parent gases (200 ppm NO_2 in air or 1000 ppm NO in N_2) with dry synthetic air and/or pure oxygen. In the flow (100 cm^3/min) of air or the sample gases containing NO_x, EMF of each device was monitored with a digital electrometer (Advantest, TR8652).

NO_2 or NO sensing experiments were first carried out for the device coated with $Ba(NO_3)_2$ or $Sr(NO_3)_2$. Figure 2 shows the resulting EMF responses as a function of the concentration of NO_2 or NO at 450 °C. The device coated with $Ba(NO_3)_2$ exhibited EMF values varying in proportion to the logarithm of NO_2 concentration as indicated. The slope of the Nernst's correlation , 147 mV/decade, was well coincident with n=1 where n stands for the number of electrons involved in the electrochemical reaction of one NO_2 molecule. These results assure that the MSZ-based device works as an NO_2 sensor, similar to the cases of NASICON-based devices reported previously. The device coated with $Sr(NO_3)_2$, on the other hand, hardly gave such satisfactory Nernst-type responses to NO_2, indicating that $Sr(NO_3)_2$ is inferior to $Ba(NO_3)_2$ as an auxiliary phase. Even the device using $Ba(NO_3)_2$, however, was not satisfactory for detecting NO. The responses to NO showed apparent Nernst-type behavior, but its slope, 43 mV/decade (or n=3.3), was far smaller than that expected (n=1). As is well known, combustion exhausts usually contain NO much more than NO_2, and NO sensing is thus more important than NO_2 sensing. In an attempt to improve the NO sensing properties of the device, $Ba(NO_3)_2$ was mixed with other oxysalts, i.e., carbonates, phosphates, and sulphates (10 or 20 mol% each) and the resulting binary systems were used for the auxiliary phase. The sensitivity of each device to 100 ppm NO_2 or 500 ppm NO in air at 450 °C, ΔE, defined as an increment of EMF on switching from air

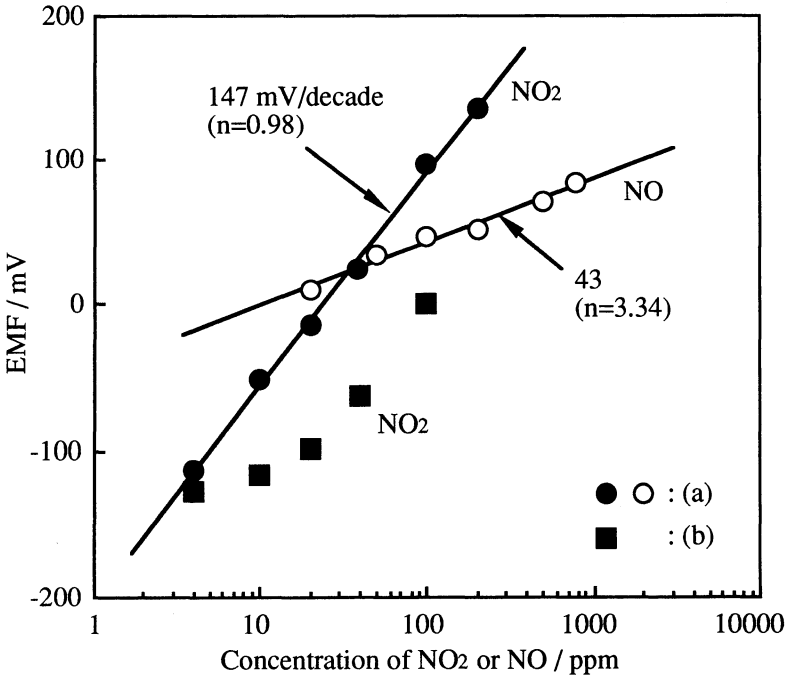

Fig. 2. EMF vs. NO2 or NO concentration for the device fitted with Ba(NO3)2 (a) or Sr(NO3)2 (b) at 450 °C.

to the sample gas, is listed in Table 1. ΔE was found to depend strikingly on the oxysalts introduced, though its reason is utterly unclear at present. Interestingly, the system $Ba(NO_3)_2$-$CaCO_3$ (10 mol%) was found to exhibit the highest sensitivity to 500 ppm NO (290 mV) among all the auxiliary systems tested, while its sensitivity to 100 ppm NO_2 (254 mV) was a little lower than that of the pure $Ba(NO_3)_2$ (287 mV). These results suggest that the NO sensing properties of this type device can be improved by introducing such a multi-component auxiliary phase.

Figure 3 shows the correlations between EMF and the logarithm of NO_2 or NO concentration for the device using $Ba(NO_3)_2$-$CaCO_3$ (10 mol%) at 400 °C and 450 °C. The EMF responses to NO_2 followed the Nernst equation for the 1-electron reduction of NO_2 in the concentration range of 4-200 ppm at both temperatures. The EMF responses to NO at 450 °C also fell on a linear Nernst-type correlation, the slope of which was far closer to that corresponding to n=1 than that observed with $Ba(NO_3)_2$-coated device (Fig. 2). As a result, this device could produce roughly comparable EMF responses to both NO_2 and NO in a rather wide range of NO_x concentration (ca 10-200 ppm) at this temperature. At 400 °C, however, the NO sensing properties deviated too seriously from the reasonable Nernst-type behavior, making the device hardly feasible for monitoring NO_x.

Table 1. Sensitivities to NO_2 (100 ppm) and NO (500 ppm) at 450 °C for the devices fitted with various $Ba(NO_3)_2$-based auxiliary phases.

Oxysalt added	Content / mol%	ΔE* / mV NO_2	ΔE* / mV NO
none	-	287	113
Li_3PO_4	20	80	-
$Ba_3(PO_4)_2$	10	150	-
Li_2CO_3	10	145	37
$BaCO_3$	10	288	127
$CaCO_3$	10	254	290
$BaSO_4$	20	211	172
$SrSO_4$	10	196	123

* EMF relative to the air level (base).

Figure 4 depicts the response transients of the device coated with $Ba(NO_3)_2$-$CaCO_3$ (10 mol%) to 100 ppm NO_2 or 500 ppm NO in air at 450 °C. Both transients were quite sharp and stable, with 90% response and recovery times of about 30 s and about 1 min, respectively.

As mentioned above, stabilized zirconia could be utilized as a base solid electrolyte for an electrochemical NO_x sensor. Combining it with an auxiliary phase containing $Ba(NO_3)_2$ gave satisfactory NO_2 sensing properties at elevated temperature of 400 or 450 °C. The NO sensing properties, on the other hand, were far more subject to change

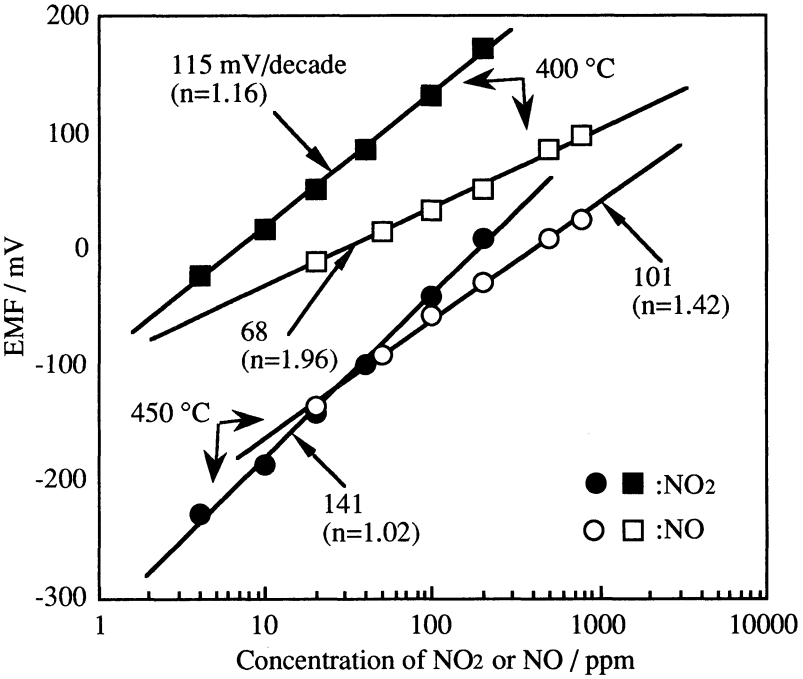

Fig. 3. EMF as correlated with a function of NO_2 or NO concentration for the device fitted with $Ba(NO_3)_2$-$CaCO_3$ (10 mol%) at 400 °C and 450 °C.

with the auxiliary phases used, and fairly good NO sensing properties were obtained with a device using $Ba(NO_3)_2$-$CaCO_3$ (10 mol%) at 450 °C. These results suggest that such an approach may be promising for developing a practical NO_x sensor for combustion exhausts. It should be beared in mind that introduction of too much carbonate in the auxiliary phase can induce the sensitivity to CO_2. Therefore optimization of the auxiliary materials would also be important.

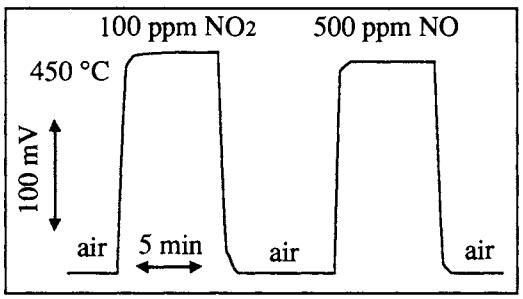

Fig. 4. Response transients of the device fitted with $Ba(NO_3)_2$-$CaCO_3$ (10 mol%) at 450 °C.

The working mechanism of the present sensor device is considered to be essentially similar to what has been proposed for the stabilized zirconia-based SO_x or CO_2 sensors.[9,10] The present device conforms the following electrochemical cell:

air, Pt | MgO-ZrO_2 (MSZ) || $Ba(NO_3)_2$ -based phase | Au, NO_x+air

(counter electrode) (O^{2-} conductor) (Ba^{2+} conductor) (sensing electrode)

The electrochemical junction between $Ba(NO_3)_2$ and MSZ is achieved if one assumes the formation of an interfacial compound containing Ba^{2+} and O^{2-}; On assuming $BaZrO_3$, for example, the junction can be achieved with the following reaction.

$$Ba^{2+} + O^{2-} + ZrO_2 = BaZrO_3 \quad (1)$$

In the case of NO_2 sensing, the sensing and counter electrode reactions will be given as follows, respectively.

$$(1/2)Ba^{2+} + NO_2 + (1/2)O_2 + e^- = (1/2)Ba(NO_3)_2 \quad (2)$$

$$O_2 + 4e^- = 2O^{2-} \quad (3)$$

Under the fixed partial pressure of oxygen, the EMF response to NO_2 would thus follow the Nernst equation for n=1, as observed experimentally.

The sensing mechanism for NO, however, remains ambiguous; NO may be responded directly as it is or indirectly after being oxidized to NO_2. Further investigations are necessary to elucidate the sensing mechanism as well as the amazing effects exerted by the binary auxiliary phase $Ba(NO_3)_2$-$CaCO_3$.

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