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Intermediate-Temperature NOx Sensor Based on an In^{3+}-Doped SnP_2O_7 Proton Conductor

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A potentiometric NOx sensor using a proton-conducting $Sn_{0.9}In_{0.1}P_2O_7$ electrolyte with a PtRh/C working electrode was fabricated to study sensing properties for NO and NO_2 at intermediate temperatures. The sensor showed electromotive force (emf) responses to changes in NO and NO_2 concentrations. Interestingly, the emf values for both NO and NO_2 increased in the positive direction with increasing gas concentration. The sensing mechanism was shown to be based on a mixed potential at the working electrode through measurements of the polarization curves of NO or NO_2 and water vapor.
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There has been considerable recent demand for the direct detection of NOx in combustion exhausts from automobiles to establish control systems for the reduction of the NOx emissions. At present, conventional NOx sensors signal a limiting current associated with electrochemical NO decomposition,[1,2] which requires using an expensive two-chamber cell structure connected in series. In addition, the limiting current of a few microamperes or lower is not sufficiently high to assure a high S/N ratio. Thus, the automobile industry needs alternate inexpensive and innovative NOx sensors. Potentiometric gas sensors inherently have low manufacturing costs because of their simple cell structure. Moreover, the voltage signal can be more easily amplified when compared to the current signal. Mixed-potential-type gas sensors are promising sensing devices for monitoring low concentrations of pollutants, such as H_2,[3-5] CO,[6,7] H_2S,[8] and hydrocarbons,[9-14] in exhausts. Miura et al. were the first to report this type of NOx sensor using yttria-stabilized zirconia (YSZ) as the electrolyte.[15] According to the sensing mechanism proposed by them,[16,17] the mixed potential is obtained by coupling the following electrochemical reactions at the working electrode

$$NO_2/O_2 \text{ mixture} \quad NO_2 + 2e^- \rightarrow NO + O^{2-} \qquad [1]$$

$$2O^{2-} \rightarrow O_2 + 4e^- \qquad [2]$$

$$NO/O_2 \text{ mixture} \quad NO + O^{2-} \rightarrow NO_2 + 2e^- \qquad [3]$$

$$O_2 + 4e^- \rightarrow 2O^{2-} \qquad [4]$$

As a result, the potential of the working electrode is shifted toward the positive direction with increasing NO_2 concentration and toward the negative direction with increasing NO concentration. Indeed, some research groups have reported opposite signals for the potential based on NO_2 and NO.[15-19] However, it should be noted that such signals complicate the interpretation of a mixed potential for NO/NO_2 mixtures in actual applications.

We recently reported that an anhydrous proton conductor, 10 mol % In^{3+}-doped SnP_2O_7 ($Sn_{0.9}In_{0.1}P_2O_7$), shows high proton conductivities $>10^{-1}$ S cm^{-1} between 150 and 350°C.[20] Attempts to apply this material as the electrolyte in some electrochemical devices were also described. A H_2-air fuel cell using 0.35 mm thick $Sn_{0.9}In_{0.1}P_2O_7$ electrolyte yielded a power density of 264 mW cm^{-2} at 250°C.[21] In addition, an electrochemical reactor using the $Sn_{0.9}In_{0.1}P_2O_7$ electrolyte with a PtBa/C cathode reduced NOx to N_2 with a current efficiency of 5.81% at 250°C in oxidizing atmospheres.[22] This material also has the potential to be used for NOx sensor applications because the following electrochemical reactions can be expected to occur at the working electrode

NO_2/O_2 mixture

$$NO_2 + 4 \text{ or } 2H^+ + 4 \text{ or } 2e^- \rightarrow 1/2N_2 \text{ or } NO + 2 \text{ or } 1H_2O \qquad [5]$$

$$NO/O_2 \text{ mixture} \quad NO + 2H^+ + 2e^- \rightarrow 1/2N_2 + H_2O \qquad [6]$$

$$\text{Both mixtures} \quad 2H_2O \rightarrow 4H^+ + O_2 + 4e^- \qquad [7]$$

These reactions suggest that both NO and NO_2 undergo cathodic reaction at the working electrode, thus providing a common shift of the mixed potential towards the positive direction.

The purpose of this study was to demonstrate the above suggestion by fabricating sensor elements using the $Sn_{0.9}In_{0.1}P_2O_7$ electrolyte. Pt/C and PtRh/C electrodes were chosen as the working electrodes due to high catalytic activities of Pt and Rh metals for the reduction of NOx.[23] The sensing properties of these sensors were tested at temperatures of 200°C or higher because Pt metal shows high CO tolerance under such conditions.[24] The dependences of sensing properties on the concentrations of other gases, including water vapor, O_2, and CO_2, were also evaluated to clarify the sensing mechanism of the present sensor.

Experimental

Figure 1 shows a sensor element used for NOx sensing tests in this study. $Sn_{0.9}In_{0.1}P_2O_7$ was prepared in the same manner as previously reported.[20-22] The corresponding oxides (SnO_2 and In_2O_3) were mixed with 85% H_3PO_4 and ion-exchanged water and then held with stirring at 300°C until a high viscosity paste was formed. The paste was calcined in an alumina pot at 650°C for 2.5 h and then ground in a mortar with a pestle. Finally, the compound powders were pressed into pellets (12 mm diam, 1.0–1.2 mm thick) under a pressure of 2×10^3 kg cm^{-2}.

Pt/C (10 wt % Pt/C) and PtRh/C (10 wt % PtRh/C, Pt:Rh = 4:1) electrodes were purchased from E-TEK Inc. A Pt reference electrode was attached on the side face of the electrolyte pellet. The working electrode was supplied with a mixture of 0–1000 ppm NO or 0–1000 ppm NO_2 and 0.6–11.1% water vapor, 2–8% O_2, and 0–10% CO_2 in Ar at a flow rate of 100 mL min^{-1}. The counter and reference electrodes were statically exposed to atmospheric air. The difference in potential (electromotive force, emf) between the working and counter electrodes was measured as a sensing signal with a digital electrometer (Hokuto Denko, HE-104). The polarization curves were measured in 200, 600, and 1000 ppm NO, or 200, 400, and 600 ppm NO_2 diluted with Ar and in 2.7% water vapor diluted with Ar by controlling the potential of the working electrode *vs* the reference electrode with a potentiostat (Hokuto Denko, HA-501).

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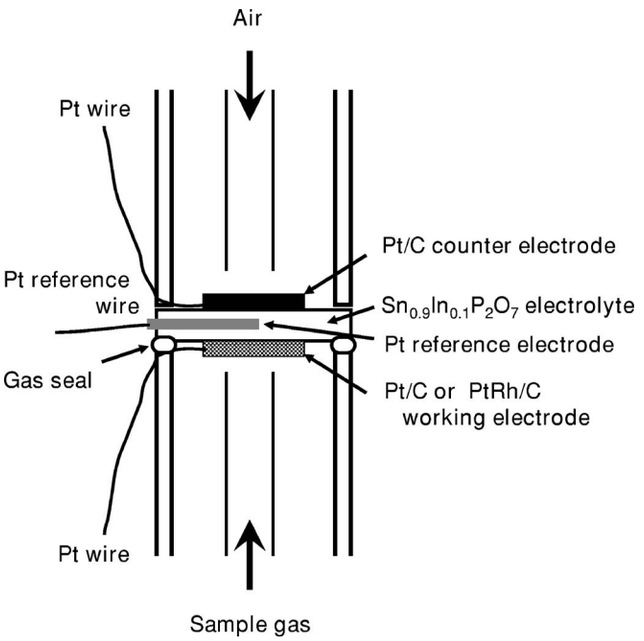

Figure 1. Schematic illustration of the electrochemical cell.

Results and Discussion

The response transients of the sensors with the Pt/C and PtRh/C working electrodes to NO and NO_2 were first measured at a temperature of 250°C. Figure 2 shows the results when mixtures of 200, 400, and 600 ppm NO or 200, 400, and 600 ppm NO_2 and 2.7% water vapor and 4% O_2 were fed into the working electrode. It was found that both the Pt/C and PtRh/C working electrodes yielded emf responses, depending on the NO and NO_2 concentrations. Characteristically, the extent of the emf response (defined as sensitivity) observed for these working electrodes was larger for NO_2 than for NO under the same conditions. Similar differences in the sensitivity between NO and NO_2 were reported for the YSZ-based NOx sensors.[15-19]It can also be seen from Fig. 2 that the PtRh/C working electrode showed higher sensitivities for NO and NO_2 than the Pt/C working electrode. Nanba et al. have indicated that the catalytic activity of a Pt catalyst for the selective reduction of NOx with H_2 was enhanced by the addition of a small amount of Rh.[25] It seems that Reactions 5 and 6 are similarly promoted for the PtRh/C working electrode, yielding higher sensitivities with the PtRh/C working electrode. However, it cannot be neglected that Reaction 7 is more

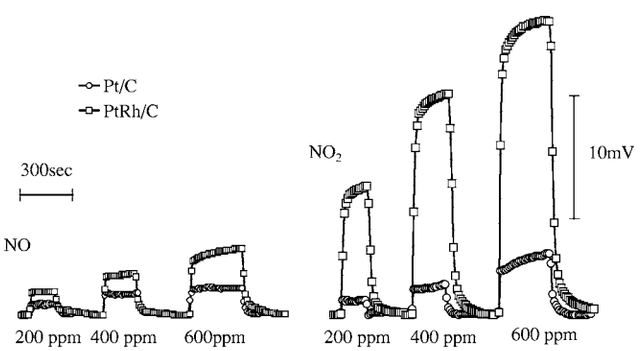

Figure 2. EMF responses of sensors with Pt/C and PtRh/C working electrodes to changes in NO and NO_2 concentrations at 250°C. The water-vapor and O_2 concentrations were maintained at constant values of 2.7 and 4%, respectively.

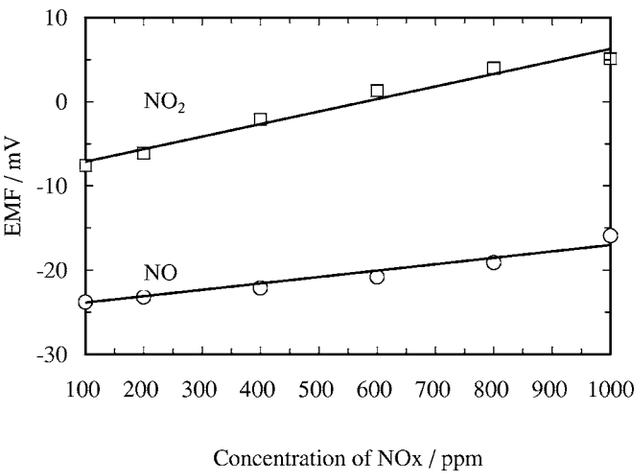

Figure 3. Dependences of emf values for NO and NO_2 on gas concentration at 250°C. The water-vapor and O_2 concentrations were maintained at constant values of 2.7 and 4%, respectively.

inhibited at the PtRh/C electrode as compared to the Pt/C electrode. This will also provide higher sensitivities for the PtRh/C working electrode. Another important result in Fig. 2 is that the direction of the emf response was positive for both NO and NO_2, indicating a distinguishable characteristic from the results reported for the YSZ-based NOx sensors.[15-19] Preliminary experiments showed that about 9% of the supplied NO was converted into NO_2 through the heterogeneous oxidation on the PtRh/C working electrode, suggesting that the contribution of the converted NO_2 to the emf response for NO is small. This also means the validity of Reactions 5-7. Based on the above results, the sensor with the PtRh/C working electrode was employed in subsequent experiments.

Plots of the emf values as a function of the NO or NO_2 concentration at 250°C are shown in Fig. 3, wherein the concentrations of water vapor and O_2 were maintained at constant values of 2.7 and 4%, respectively. At a NO or NO_2 concentration of 0 ppm, the sensor showed emf values of about −25 mV, which is almost in agreement with the theoretical value (Nernst potential) based on a steam concentration cell[26]

$$E = (RT/2F)\ln\{[P_{H_2O(WE)}/P_{H_2O(CE)}][P_{O_2(CE)}/P_{O_2(WE)}]^{1/2}\} \quad [8]$$

where the forward and reverse reactions of Reaction 7 take place at the working and counter electrodes, respectively. As can be seen in Fig. 3, the emf value increased in the positive direction with increasing NO or NO_2 concentration. There was an approximately linear relationship between the emf value and the NO or NO_2 concentration. These results suggest the possibility that the present sensor could be used to determine the total NOx (NO and NO_2) concentration, although the low sensitivity to NO must be improved.

If the sensing mechanism of the present sensor is based on the mixed potential resulting from Reactions 5-7, it can be assumed that Reaction 5 or 6 and Reaction 7 simultaneously proceed at the working electrode. These reaction rates are equal to each other due to the formation of a local cell at the working electrode, resulting in the appearance of a mixed potential. To clarify this mechanism, we measured the cathodic polarization curves of 200, 600, and 1000 ppm NO or 200, 400, and 600 ppm NO_2 under dry conditions, and the anodic polarization curve of 2.7% water vapor in the absence of NO and NO_2 at 250°C. The results are summarized in Fig. 4, wherein the direction of the cathodic current is reversed. The cathodic polarization curves for both NO and NO_2 were shifted toward the positive direction with increasing gas concentration. This tendency was especially remarkable for NO_2. As a result, the intersection points of the anodic and cathodic polarization curves,

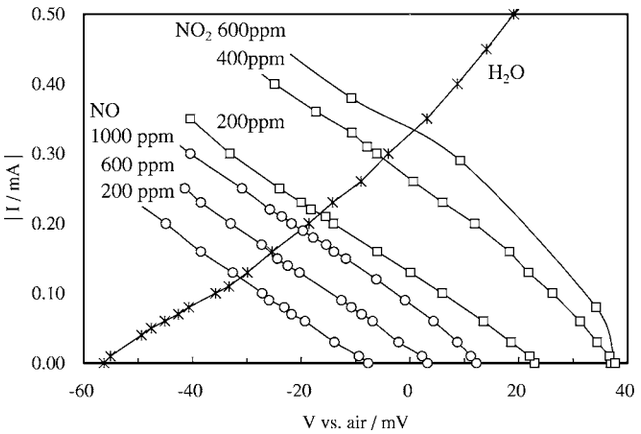

Figure 4. Cathodic polarization curves for 200–1000 ppm NO and 200–600 ppm NO_2, and anodic polarization curve for 2.7% water vapor at 250°C. The direction of the cathodic current is reversed.

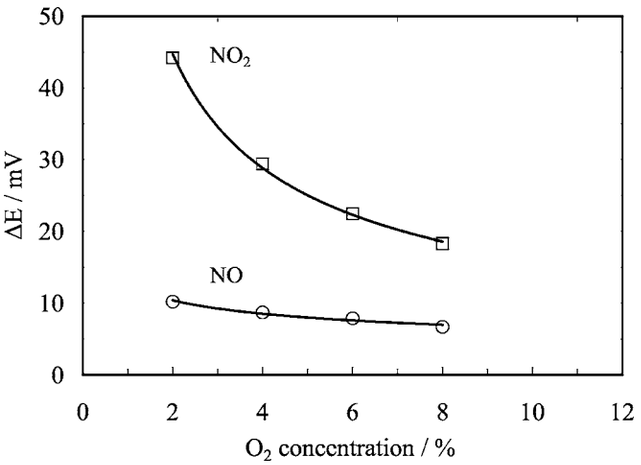

Figure 6. Dependences of sensitivities to 1000 ppm NO and 1000 ppm NO_2 on O_2 concentration at 250°C. The water-vapor concentration was maintained at a constant value of 2.7%.

which correspond to the mixed potentials, were at −31, − 25, and −19 mV for 200, 600, and 1000 ppm NO, respectively, and −16, − 4, and 0 mV for 200, 400, and 600 ppm NO_2, respectively. Although these mixed potentials qualitatively explain the results shown in Fig. 2 and 3, they are somewhat less positive than the observed emf values of −23, − 20, and −15 mV for 200, 600, and 1000 ppm NO, respectively, and −6, − 2, 1 mV for 200, 400, and 600 ppm NO_2, respectively. One possible explanation for this discrepancy is that the following cathodic reaction also contributes to the emf value when NOx coexists with O_2

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad [9]$$

Because this reaction participates in the cathodic reaction together with Reactions 5 and 6, the emf values measured in the presence of O_2 can be considered to be more positive than the mixed potential measured in the absence of O_2.

To better understand the above mechanism, the dependences of the sensitivities to NO and NO_2 on water vapor, O_2, and CO_2 concentrations were measured at 250°C. As shown in Fig. 5, the sensitivities to NO and NO_2 increased with decreasing water-vapor concentration. This can be explained by an increase in the polarization resistance of Reaction 7 with decreasing water-vapor concentration. Namely, as the polarization resistance of Reaction 7 increases, the intersection of the anodic and cathodic polarization curves becomes more positive. This dependence is similar to the dependence of the sensitivities to NO and NO_2 in the YSZ-based NOx sensors on the O_2 concentration.[15-19] As shown in Fig. 6, the sensitivities to NO and NO_2 also increased with decreasing O_2 concentration. As described earlier, Reactions 5 and 6 compete with Reaction 9 at the working electrode. Because the reaction kinetics of these reactions naturally depend on their gas concentrations, Reaction 5 or 6 contributes to the mixed potential more than Reaction 9 at low O_2 concentrations. On the other hand, in contrast to the results shown in Fig. 5 and 6, the NO and NO_2 sensitivities were seen to be independent of the CO_2 concentration in Fig. 7. This is strong evidence that CO_2 functions as an inert gas for the mixed potential at the working electrode. Similarly, a small amount of CO and hydrocarbons were found to be inert gases. In any case, it should be emphasized that the results shown in Fig. 5-7 can be interpreted by the proposed mixed-potential-mechanism.

Finally, we describe the dependence of the sensitivities to NO and NO_2 on the temperature. Our preliminary experiments revealed that the sensitivities to NO and NO_2 increased with decreasing temperature. This is likely due to more selective adsorption of NO or NO_2 than O_2 on the surface of the PtRh/C catalyst at lower tem-

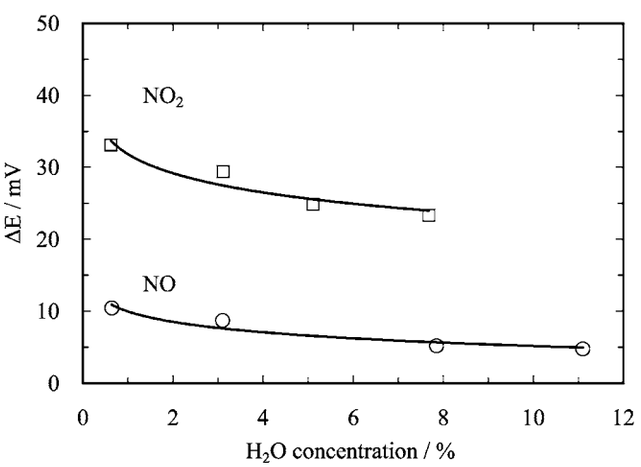

Figure 5. Dependences of sensitivities to 1000 ppm NO and 1000 ppm NO_2 on water-vapor concentration at 250°C. The O_2 concentration was maintained at a constant value of 4%.

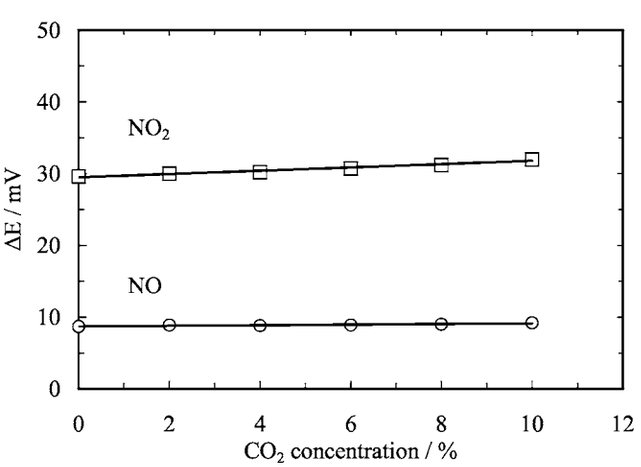

Figure 7. Dependences of sensitivities to 1000 ppm NO and 1000 ppm NO_2 on CO_2 concentration at 250°C. The water-vapor and O_2 concentration were maintained at constant values of 2.7 and 4%, respectively.

peratures. This not only supports the mixed-potential-mechanism proposed above, but also suggests that the sensitivities to NO and NO_2 would be further improved by the addition of a basic material such as alkaline earth carbonates to the PtRh/C, since NOx are acid molecules.[27]

Conclusions

A sensor using a proton-conducting $Sn_{0.9}In_{0.1}P_2O_7$ as the electrolyte exhibited largely positive emf values to both NO and NO_2, which is a distinguishable characteristic from the results reported for the YSZ-based sensors. This was due to the mixed potential at the working electrode, wherein a cathodic reaction of NO or NO_2 and an anodic reaction of water vapor simultaneously proceeded. The dependences of the sensitivities to NO and NO_2 on the water-vapor and O_2 concentrations could be explained by using a mixed-potential-mechanism. The present sensor is shown to be a promising NOx sensor at intermediate temperatures. Additional experiments must be performed to establish the long-term reliability for actual applications.

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