A NOx Sensor Based on Solid-Electrolyte Impedance Transducer
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Abstract A new solid-electrolyte impedance-metric NOx sensor device composed of a lithium ionic solid electrolyte: Li₁.₅Al₀.₅Ti₁.₅(PO₄)₃ (LATP) as a transducer and ceramic oxides (perovskite-type oxides, TiO₂, SnO₂, etc) as a receptor, respectively, have been systematically investigated for the detection of NOx (NO and NO₂) in the range 10 – 200 ppm at 400 - 500ºC. Responses of the sensors were able to divide component between resistance and capacitance, and it was found that the device was applicable to the selective detection of NO or NO₂ concentration in each ingredient. Especially, those using TiO₂ (n-type semiconductor) and perovskite-type oxides (LaCoO₃, LaNiO₃ and LaCrO₃) based receptors gave good responses to NO and NO₂. It was also found that the responses were different between n-type or p-type semiconductors, in which we tried to elucidate the sensing mechanism.

Introduction

It has been increasing the needs of reliable, inexpensive and compact nitrogen oxides (NOx: NO and NO₂) sensors for the protection of global environment. Therefore, compact NOx sensors which have high sensitivity, low cost and easily designed have been strongly required for improving combustion from engine and the regulation of exhaust NOx. Among the compact NOx sensors reported, the solid electrolyte type is of particular interest from the viewpoints of sensitivity, selectivity, and simple element structure. So far, potentiometric- (Nernst’s type) [1,2], amperometric- [3,4], mixed potentiometric- [5,6], impedance metric- [7] types of solid-electrolyte sensors were reported. The solid electrolyte type NOx sensors seem to bring about better sensing performance to NO and/or NO₂ as well as stability at higher temperatures. However, these sensor devices still have rather complicated structure, i.e., they still need the reference and/or the counter electrodes at the opposite side of the electrolyte. In this study, it was seen that a new type solid-state sensor combined with a solid electrolyte impedance transducer and an oxide receptor showed high sensing properties to NOx and it is applicable to a quite simple all-solid-state sensor. It turned out that the responses of the sensors were able to divide component between resistance and capacitance, and they are applicable to the selective detection of NO or NO₂ concentration in each ingredient. Here, we report the NOX sensing performance of the new solid-state device.

Experimental

Lithium ion conductor: Li₁.₅Al₀.₅Ti₁.₅(PO₄)₃ (LATP) disc was prepared by a sol-gel technique for a transducer. Aqueous solutions of TiO(OCCH₃CHCOCH₃), LiNO₃, NH₄H₂PO₄ and Al(NO₃)·9H₂O were mixed and evaporated with continuous stirring at 75 ºC. The obtained material was calcined at 500 ºC for 3 h. The obtained powder was pressed into a pellet at 300 MPa and sintered at 1000 ºC in air for 6 h. The lithium ion conductivity of the prepared LATP disk was as high as 7.0×10⁻⁴ and 5.3×10⁻² Scm⁻¹ at 30 ºC and 300 ºC, respectively. Commercial n-type (anatase-TiO₂, SnO₂, WO₃), p-type (NiO, Cr₂O₃) semiconductors, and perovskite-type oxide powders (LaBO₃; B = Cr, Mn, Fe, Co, Ni) which were prepared by a polymer precursor method [8] were used for a receptor. Metal nitrates of commercial origin (15 mmol each) were dissolved in an ethylene glycol solution with
acetylacetone. The obtained organic solution was mixed with PVA ([CH₂-CH(OH)]ₙ, n = 1500-1800) aqueous solution until a viscous sol was formed (7.5wt% PVA). The sol was dried at 150°C for 12h and finally heat-treated at 650 °C for 2h in air.

The LATP or all oxides examined were characterized by X-ray diffraction analysis (XRD) (JDX-3500, JEOL) using Cu-Kα radiation. The XRD patterns of the materials showed almost only the phases of LATP or oxides.

Figure 1 shows a schematic diagram of the all-solid state sensor device using the LATP disc and an oxide receptor with Ag electrodes at the opposite surface. A paste prepared with the prepared perovskite-type oxide powder and turpentine oil was painted onto the surface of the LATP disc, and dried and sintered at 500 °C. NOx sensing experiments were carried out in a conventional flow apparatus equipped with a heating facility at 300-500 °C. Sample gases containing NO, NO₂, and N₂O were prepared from each parent gas at the fixed O₂ pressure of 20-21 vol%. The sensor response, ΔZ, was measured with an impedance analyzer (3531, HIOKI) at 50Hz-5MHz at a total flow rate of ca. 100 cm³/min. Nyquist plots of this sensor were measured at various concentrations of each sample gases. The frequency was changed from 50 Hz to 5 MHz. The value of the relative sensitivity (S_R or S_C) was defined as S_R = (R_gas - R_air) / (gas concentration) or S_C = (C_gas - C_air) / (gas concentration) in which R_gas (C_gas) or R_air (C_air) is resistance (capacitance) in gas or air, respectively.

**Results and Discussion**

The NOx response characteristic of the element using perovskite-type oxide and LATP receptor was firstly examined. It has been understood that the impedance change into the NOx concentration change is seen in the interfacial impedance area of the element as a result of Nyquist’s plots. Figure 2 shows the response curve of the LaCoO₃/LATP element in 10 kHz at 500 °C. A good response was found being comparatively obtained as the capacity of the element (C) although the a little drift was seen, while the response with the change of NO concentration was not seen as the resistance of the element (R) at 500 °C. The sensor hardly responded to NO₂ at 500 °C, while the element of which the response was seen to NO as shown in Fig. 3. In addition, it has been understood that LaCoO₃/LATP element shows a high NO selective detection as not showing the response to O₂ and CO₂ at 500 °C. When the other LaBO₃ (B = Cr, Mn, Fe, Ni)
systems were examined, it was found that most of the devices show an excellent response to both NO and NO\(_2\) at 400 °C as well as the LaCoO\(_3\)-based element. It was further found that the only LaNiO\(_3\)-based element showed the high response characteristics to NO\(_2\) at 500 °C, and the response was not shown in other elements at 500 °C at all. In addition, the response with an excellent resistance or capacitance change was observed to NO at 500 °C for the LaCrO\(_3\)- and the LaFeO\(_3\)-based elements. The NO\(_x\) response characteristics of the TiO\(_2\)/LATP device were shown in Fig. 4. The impedance responses of the sensor with the TiO\(_2\) receptor were able to divide component between the resistance (R) and the capacitance (C). Although the a little drift was seen which seems come from the state of Ag electrodes, a good NO\(_2\) response was found being comparatively obtained as the resistance (R) and capacitance (C) of the element at 400 °C. Nyquist plots of the TiO\(_2\)/LATP device to various concentrations of NO\(_2\) at 400°C revealed that the impedance change at various concentrations of NO\(_x\) was caused at the interface impedance area. For most of the case, we could investigate the response from 1 kHz.

The most of the other n-type semiconductor oxides examined exhibited higher sensitivity to NO\(_x\) than that of the p-type semiconductor oxides. The use of n-type receptor, TiO\(_2\) or SnO\(_2\) showed good responses to NO and NO\(_2\) at 400°C. The sensor with WO\(_3\) slightly responded as the resistance change, while it hardly responded for the capacitance change at 400°C. At the temperature of 500°C, the sensors with the receptors of n-type and p-type semiconductor oxides showed no responses at all. While, the sensors attached with LaCrO\(_3\) and LaMnO\(_3\) showed high sensitivity to

![Fig. 3 Sensing performance to NOx gases of the LaCoO\(_3\)/LATP system at 400 or 500°C.](image1)

![Fig. 4 Resistance and capacitance responses of the TiO\(_2\)/LATP device to different concentrations of NO\(_2\) at 400°C. (1 kHz)](image2)
NO and NO$_2$ at 500°C. Furthermore, all the sensor elements did not show the response in N$_2$O at all. The sensor attached with TiO$_2$ (n-type) (a) or NiO (p-type) (b) receptors responded to NO and NO$_2$ indicated the same direction, while those to O$_2$ indicated the opposite in sign for both sensors. For the capacitance change, it was found that the sensing responses to NO gave higher sensitivity than that of NO$_2$, and the sensing responses to O$_2$ gave small and opposite direction from those of NOx for TiO$_2$- and NiO-based devices. For the resistance ingredients ($\Delta R$) of the sensor responses, the resistances of the sensors with both n-type and p-type oxides receptors were increased with increasing NOx concentrations. On the other hand, for the capacitance ingredients ($\Delta C$) of those devices, the capacitances of the sensors with n-type oxides receptor were decreased with increasing NOx concentrations. The capacitances of sensors with p-type oxides were increased with increasing NOx concentrations.

The sensitivities to NOx of the typical sensors were summarized in Fig. 5. The sensor responses with all receptors to CO$_2$ were similar to responses to NOx on both the resistance and capacitance ingredients. However, the all sensor responses to O$_2$ showed opposite in sign to those of NOx and CO$_2$ gases on the resistance and capacitance ingredients. It was also found that the sensitivities of the sensors hardly related to the surface areas of the receptors used. Thus, the difference in sensitivity seems to be come from the electrochemical reactivity of the receptors used.

A large difference was seen in the sensor response to NO and NO$_2$ at 400 °C and 500 °C as stated above. A large amount of NO desorption was seen at the temperatures less than 500 °C by the temperature programmed desorption (TPD) measurement. It is thought that it is because the gas adsorption characteristic on the surface of the oxide receptor is greatly different at 400 °C and 500 °C.

As these responses were all the one under the oxygen coexistence in NOx gases, the charge transfer in the oxide layer by the surface adsorption with NO, NO$_2$, and O$_2$ might bring the impedance change in the solid electrolyte. However, the sensing mechanisms of the present electrochemical device still need further investigations.

![Fig. 5 NO and NO$_2$ sensitivity of the various Oxide / LATP devices at 400°C.](image)

**References**