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**Solid Electrolyte NOx Sensor Using Pyrochlore -Type Oxide Electrode**

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Solid Electrolyte NOx Sensor Using Pyrochlore-Type Oxide Electrode

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Abstract

Solid electrolyte electrochemical devices based on sodium super-ionic conductor (NASICON: Na$_{1+x}$Zr$_2$Si$_x$P$_{3-x}$O$_{12}$) and pyrochlore-type oxide (Pb$_2$M$_2$O$_{7-y}$ : M= Ir, Ru$_{1-x}$Pbx; x=0 - 0.75) electrodes were found to exhibit good performance for the potentiometric sensing of NO as well as NO$_2$ at 400°C. The EMF responses were almost linear to the logarithm of NO or NO$_2$ concentration. Among the elements tested, the device attached with Pb$_2$Ru$_{1.5}$Pb$_{0.5}$O$_{7-y}$ electrode gave excellent NO sensing properties, and the EMF changed with changing gas concentration of NO diluted in N$_2$ or NO diluted in an O$_2$ and N$_2$ mixture with negative or positive slope, respectively, while it kept almost constant to the concentration change of NO$_2$ and CO$_2$ diluted in air.

Keywords: Pyrochlore-type oxide, NOx sensor, NASICON, Solid electrolyte

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1. Introduction

Monitoring of nitrogen oxides (NOx: NO and NO2) as serious gas pollutants is becoming very important for the protection of global environments. Among compact NOx sensors, the electrochemical cell type based on solid electrolytes [1-5] is of particular interest from the view points of sensitivity, selectivity, and simple element structure. Most of the solid electrolyte NOx sensors so far investigated have generally used nitrate-based 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. Recently, solid electrolyte sensor elements using sodium nitrite [6, 7] or nitrate-based binary systems [8] were reported to show high sensitivity to NO as well as NO2. However they still have problems for chemical and/or thermal stability of the materials. Solid-state electrochemical elements, which combine solid electrolytes with oxide-based electrode, seem to bring about high chemical and thermal stability, and the devices for CO [9], CO2 [10], and H2S [11] have been proposed. It was also reported that the use of metal oxide electrodes, such as CdMn2O4 [12] and Cr2O3 [13], instead of conventional metal salts for the auxiliary phase of solid electrolyte NOx sensor seems to bring about better sensing performance to NO and/or NO2 as well as stability at higher temperatures. It has been reported that the oxide electrode used at an auxiliary phase acts as an electrode catalyst and the response is based on the change of mixed potential at the electrode reactions. In our previous study [13], it was seen that some NOx sensor elements attached with metal oxide thin-film electrodes have high sensitivities to NO and/or NO2, however most of which lack stability in the atmosphere including NOx gases. It is well known that pyrochlore-type oxides such as Pb-Ru-O and Pb-Ir-O systems have high chemical stability even in an acidic solution as well as high catalytic activities to oxygen reduction and/or oxygen evolution [14-16]. In this study, we have tried to use pyrochlore-type oxide electrodes for solid electrolyte-based NO and/or NO2
sensors. It has turned out that the devices using pyrochlore-type oxide have high sensitivities and stability to NO as well as NO2 at 400 °C. It was further found that the device attached with Pb2[RU1.5Pb0.5]O7-y showed higher sensitivity to NO than that to NO2 at 400°C.

2. Experimental

2.1 Pyrochlore-type oxide preparation

Pyrochlore-type oxides (Pb2Ru2-xPbxO7-y: x= 0 - 0.75, Pb2Ir2O7-y) were prepared by a precipitation method [15, 16]. An aqueous solution was obtained by dissolving starting materials, Ru- and Ir- chlorides and Pb nitride of special grade reagents (Kishida Chemical Co., Ltd.), in a proportion of desired pyrochlore-type oxides. Then, an excess amount of 2 mol·dm⁻³ NaOH was added slowly to the solution and co-precipitation was carried out at 75°C under constant stirring and purging with oxygen for 24h. The filtered products were dried at 120°C for 12h and calcined at 500 - 780 °C for 2h in atmospheric air. The obtained materials were washed with distilled water for removing a by-product, NaCl, and then finally dried at 120°C for 12h. The products were characterized with X-ray diffraction analysis (XRD) (JDX-3500K, JEOL Ltd.) using Cu-Kα radiation. Figure 1 shows XRD patterns of Pb2Ir2O7-y and Pb2Ru2O7-y powders after calcined at 780 and 500 °C, respectively. Although a slight impurity phase of RuO2 was seen only for the Pb2Ru2O7-y, most of the powders obtained with this method showed well crystallized and almost single-phase oxides.

2.2 Sensor measurements

Figure 2 shows a schematic diagram of NOx sensor element using pyrochlore-type oxide electrodes. A NASICON (Na3Zr2Si2PO12) disc, 11 mm in diameter and 0.8 mm thick, prepared by a sol-gel method using aqueous solution [17, 18], was fixed on an alumina tube with a ceramic adhesive. Oxide
electrodes were fabricated by a painting method [19], i.e., powders of the prepared pyrochlore-type oxides or RuO₂ (Mitsuwa Chemical Co. Ltd.) were kneaded with a small portion of turpentine oil (Kishida Chemical Co. Ltd.), and a paste thus obtained was painted onto the surface of the NASICON disc, and dried and finally sintered at 500 °C for 1 h to form a layer of oxide as a sensing electrode. An Au mesh was attached on the top of the oxide layer to connect a Pt-wire lead. 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 100-500 °C. Sample gases containing NO or NO₂ were prepared from each parent gas, i.e., NO diluted with nitrogen or NO₂ diluted with a dry synthetic air (N₂+O₂ gas mixture), by mixing it with N₂ (99.999 vol%) or the air. The sensor response, EMF, was measured with a digital electrometer (R8240; Advantest Corp.) at a total flow rate of 100 cm³/min.

3. Results and Discussion

3.1 Pb₂M₂O₇₋y (M= Ir, Ru) electrodes

First, NO₂ sensing performance of NASICON-based sensor elements combined with Pb₂Ir₂O₇₋y or Pb₂Ru₂O₇₋y was investigated. As shown in Fig. 3, both devices responded rather well to NO₂. The EMF responses were linear to the logarithm of NO₂ concentration (logPNO₂) between 20 and 200 ppm with both positive slopes of +50 mV/decade or +30 mV/decade for the elements using Pb₂Ir₂O₇₋y or Pb₂Ru₂O₇₋y, respectively. The Pb₂Ir₂O₇₋y based element showed rather quick response to NO₂, i.e., the 90% response time for the concentration change from 110 ppm to 220 ppm NO₂ in air was as short as 30s at 400°C. Pb₂Ru₂O₇₋y based element, on the other hand, showed a unique transient curve and the EMF value at each concentration gave a steady value within about 5-20 min.
It was further found that these devices could also respond to NO diluted in N₂ at the examined concentration range between 50 and 1000 ppm at 400 °C, with the 90% response time of about 1-10 min., as shown in Fig. 4. Both EMF changes (ΔE) were linear to the logarithm of NO concentration (logPNO), with negative slopes of -29 mV/decade or -86 mV/decade for the elements using Pb₂Ir₂O₇-y or Pb₂Ru₂O₇-y, respectively.

Dependence of the sensing performance to NOₓ on operation temperatures was further investigated by using the Pb₂Ir₂O₇-y based element. For NO₂ sensing, the element showed EMF responses at the examined temperatures between 100 and 400°C. EMF responses increased with increasing NO₂ concentration at each temperature, being linear to logPNO₂, with all positive slopes. The magnitude of the slopes decreased with increasing operation temperature, as shown in Fig. 5 (a). At temperatures below 300°C, it was hard to recover the initial EMF value when switching back to air. For NO sensing, the element also showed EMF responses at the examined temperatures between 200 and 500°C. The EMF values decreased with increasing NO concentration, and showed linear relationship between EMF and logPNO with all negative slopes at the all temperatures examined. As shown in Fig. 5 (b), the slope for EMF vs. logPNO, the sensitivity to NO, decreased with increasing operation temperature. On the other hand, the reversibility of the responses became poor with decreasing operation temperature. The quickest response rate and the complete reversibility of EMF response were obtained at the operation temperature of 400°C for NO as well as NO₂. It still has high sensitivities of -29 mV/decade and +50 mV/decade for NO and NO₂, respectively at 400°C. Thus, the best operation temperature should be 400°C for NO₂ as well as NO sensing.

The reason for the dependence of the sensor responses on operation temperature was not clear yet, but it seems to come from the catalytic activity and/or sorption-desorption properties of the pyrochlore-type oxide electrodes to the
reaction gases. Further investigation is now in progress. Hereafter, operation temperature has been fixed at 400°C.

3.2 Pb2[Ru2-xPbx]O7-y electrodes

As Pb2Ru2O7-y based element showed higher sensitivity to NO than that to NO2, i.e., the slope for NO was three times as high as that for NO2, the Pb-Ru-O family has been further studied as the electrode materials.

NOx sensing performance of the various sensor elements based on Pb2[Ru2-xPbx]O7-y as well as Pb2Ir2O7-y electrodes at 400°C was summarized in Fig. 6 (a, b). All devices based on the Pb-(Ru/Pb)-O system showed higher EMF responses to the sample gases containing NO than that on Pb2Ir2O7-y. It was further found that the sensor elements using the Pb-(Ru/Pb)-O system except Pb2Ru1.25Pb0.75O7-y (x= 0.75) showed high sensitivity to NO than that to NO2. NO sensitivity, the slope of EMF vs. logPNO, decreased with increasing x in Pb2[Ru2-xPbx]O7-y, although it still has high sensitivity of -35mV/decade even at x= 0.75. Surprisingly, it was found that the Pb2Ru1.5Pb0.5O7-y (x= 0.5) / NASICON combination showed only a little NO2 sensitivity at the concentration range between 20 and 220 ppm at 400°C, although it had good NO sensitivity. Figure 7 shows response transients to NO or NO2 for the device using Pb2Ru1.5Pb0.5O7-y. Although the transient in NO2 showed overshoot at switching NO2 concentration, the each EMF at the different NO2 concentration became a steady value of about +10 mV from the initial EMF value in air within about 20min. The device showed poor NO2 sensitivity, while it had good EMF response to NO diluted in N2, with a 90% response time of about 2-10 min.

Figure 8 shows dependence of EMF of the sensor device using the Pb2Ru1.5Pb0.5O7-y / NASICON combination on gas concentration. The sensor hardly responded to NO2 and CO2 diluted in air, while it showed high EMF
response to NO diluted in N2, being linear to logPNOx with a negative slope of -40 mV/decade.

In order to discuss the sensing properties of the Pb2Ru2-\(x\)Pb\(x\)O7-\(y\) system from the crystal structure, the lattice parameter of the pyrochlore-type oxides (cubic) was calculated. As shown in Fig. 9, the lattice parameter (a) of the Pb2Ru2-\(x\)Pb\(x\)O7-\(y\) system increased with increasing \(x\) up to 0.50 and was saturated at around \(x=0.75\). It was reported that Pb2Ru2O7-\(y\) is represented by the general formula, Pb\(^{2+}\)\(2[Ru^{4+}Ru^{5+}]O_{6.5}\) [15]. The present Pb-(Ru/Pb)-O system should be written as Pb\(^{2+}\)\(2[Ru^{4+1-x}Ru^{5+1-x}]Pb^{4+x}\)O7-\(y\) (\(x=x'+x''\)). The expansion of the unit cell is consistent with the difference in the ionic radii of Ru\(^{4+}\) (0.62Å, and further small for Ru\(^{5+}\)) and Pb\(^{4+}\) (0.775Å) [15]. RuO\(_2\) (Ru\(^{4+}\))-based element showed higher sensitivity to NO\(_2\) than that to NO, as shown in Fig. 6 (c). PbO(Pb\(^{2+}\))-based element also showed higher NO\(_2\) sensitivity than NO in our previous study. High NO sensitivity of Pb-Ru-O family seems to come from the effect of Ru\(^{5+}\) in the lattice. The decrease in NO\(_2\) sensitivity with increasing \(x\) up to 0.50 should be related to Pb\(^{4+}\) and/or oxygen vacancy in the systems. Further studies should be necessary to clarify the electrode systems more quantitatively.

In order to examine the NO\(_x\) sensing mechanism, the effect of co-existent oxygen on the measurement of NO concentration was tested for the Pb2Ru1.5Pb0.5O7-\(y\) based device. As shown in Fig. 10, the element showed rather well EMF response to NO co-existed 10% oxygen with linear relationship between EMF vs. logPNO. However, the slope of +43 mV/decade was completely different in sign from that for NO in N\(_2\) (Fig. 8 (a)).

As mentioned above, the sensor signal was largely influenced by the coexisted oxygen. The mixed potential mechanism [12] should proceed on the sensing electrode. Therefore, the each EMF value could be determined by the potential at which cathodic and anodic reactions proceed at an equal rate. For
NO₂ sensing, the following electrochemical reactions (1) and (2) are assumed for the cathodic and anodic reactions, respectively.

\[
\begin{align*}
\text{NO}_2 + 2e^- &= \text{NO} + \text{O}^{2-} \quad (1) \\
\text{O}^{2-} &= (1/2)\text{O}_2 + 2e^- \quad (2)
\end{align*}
\]

For NO sensing, the reactions changed drastically by the coexisted oxygen. When the co-existed oxygen is rare (NO sensing in N₂), reactions (3) and (4) are assumed for the cathodic and anodic reactions, respectively. When an enough amount of oxygen is co-existed, reactions (5) and (2) are assumed for the cathodic and anodic reactions, respectively.

\[
\begin{align*}
\text{NO} + \text{O}^{2-} &= \text{NO}_2 + 2e^- \quad (3) \\
(1/2)\text{O}_2 + 2e^- &= \text{O}^{2-} \quad (4) \\
\text{NO} + \text{O}_2 + 2e^- &= \text{NO}_2 + \text{O}^{2-} \quad (5)
\end{align*}
\]

Oxygen in reaction (4) should be considered as an impurity (10ppm O₂) of N₂ gas used. However, the sensing mechanisms of the present electrochemical device still need further investigations.

4. Conclusion

Solid electrolyte NOx sensor using NASICON and pyrochlore-type oxide (Pb₂M₂O₇₋y; M=Ir, Ru₁₋ₓPbx; x = 0 - 0.75) electrodes were found to exhibit good performance for the potentiometric sensing of NO as well as NO₂ at 400°C. EMF responses were linear to the logarithm of NO or NO₂ concentration. The device attached with Pb₂Ru₁.₅Pb₀.₅O₇₋y electrode gave excellent NO sensing properties. The mixed potential should be considered for the sensing mechanism.

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References


Biographies

Youichi Shimizu has been an associate professor at Kyushu Institute of Technology since 1993. He received the B. Eng. degree in applied chemistry in 1983 and the Dr. Eng. degree in 1992 from Kyushu University. His current research interests include the solid-state gas sensors and ion sensors.

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Figure captions

Fig. 1  XRD patterns of Pb$_2$Ir$_2$O$_{7-y}$ (a) or Pb$_2$Ru$_2$O$_{7-y}$ (b) powders after calcined at 780°C or 500°C, respectively.

Fig. 2  Schematic diagram of NOx sensor device using NASICON and pyrochlore-type oxide electrode.

Fig. 3  Sensing performance to NO$_2$ of the devices using Pb$_2$Ir$_2$O$_{7-y}$ (a) or Pb$_2$Ru$_2$O$_{7-y}$ (b) electrodes at 400°C.

Fig. 4  Sensing performance to NO of the devices using Pb$_2$Ir$_2$O$_{7-y}$ (a) or Pb$_2$Ru$_2$O$_{7-y}$ (b) at 400°C.

Fig. 5  Effect of operation temperature on the sensing properties to NO$_2$ (a) or NO (b) of Pb$_2$Ir$_2$O$_{7-y}$ based element.

Fig. 6  Sensing performance to NO$_2$ or NO of the various sensor devices using Pb$_2$Ru$_{2-x}$Pb$_x$O$_{7-y}$ (x=0~0.75) (a), Pb$_2$Ir$_2$O$_{7-y}$ (b), and RuO$_2$ (c) electrodes at 400°C.

Fig. 7  Response transients to NO$_2$ (a) or NO (b) of the device using Pb$_2$Ru$_{1.5}$Pb$_{0.5}$O$_{7-y}$ at 400°C.

Fig. 8  Sensing performance of the device using Pb$_2$Ru$_{1.5}$Pb$_{0.5}$O$_{7-y}$ electrode to NO in N$_2$ (a), NO$_2$ in air (b), and CO$_2$ in air (c) at 400°C.

Fig. 9  Effect of partial substitution of Pb for Ru site on the lattice parameter (a) for Pb$_2$Ru$_{2-x}$Pb$_x$O$_{7-y}$ (x=0~0.75) system.

Fig. 10  NO sensing performance of the device using Pb$_2$Ru$_{1.5}$Pb$_{0.5}$O$_{7-y}$ electrode under coexisted oxygen (10%) at 400°C.
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