Solid electrolyte type nitrogen monoxide gas sensor operating at intermediate temperature region

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Abstract

A new solid electrolyte type nitrogen monoxide (NO) gas sensor which can operate in the intermediate temperature region was fabricated by the combination of trivalent aluminum cation conducting \((Al_{0.2}Zr_{0.8})_{20/19}Nb(PO_4)_3\) and divalent oxide anion conducting yttria stabilized zirconia (YSZ) with LiNO₃-doped \((Gd_{0.9}La_{0.1})_2O_3\) as the sensing auxiliary electrode. The present sensor shows such a practical performance of a rapid, stable, continuous, and reproducible response as low as at 523 K, and the linear relationship, which obeys the Nernst theoretical relationship, was clearly observed between the sensor EMF output and the logarithm of the NO concentration. Since the present sensor using the LiNO₃-doped \((Gd_{0.9}La_{0.1})_2O_3\) auxiliary electrode shows such a high sensing performance, it is greatly expected to be a new type of the NO gas sensing device applicable in the intermediate temperature range of around 523 K.

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1. Introduction

Nitrogen oxides (NOₓ) exhausted from automobile engines, boilers, and so on, are one of air pollutant gas species. Recently, the emission of NOₓ gas steadily increases and the suppression of the NOₓ gas emission has been requested from the environmental conservation point of view. To achieve this purpose, it is essential to develop a rapid and exact NOₓ gas sensing apparatus and to monitor the NOₓ gas concentration at every emitting site. Some instrumental apparatuses based on IR absorption and chemical luminescence have been widely utilized for the measurement of NOₓ gas concentration. Although these instruments can exactly detect the NOₓ gas concentration, they are generally too expensive and large sized, and some pre-treatments are inevitable. For the reasons described above, they are not suitable for the in situ monitoring gas sensing tool. Such disadvantages make clear the importance of developing NOₓ gas sensors which can realize in situ monitoring. Up till now, various types of compact and solid-state NOₓ gas sensors have been proposed to overcome these disadvantages, such as semiconductor types, [1–4] and potentiometric, and amperometric solid electrolyte types [5–7]. Among these solid-state sensors, the solid electrolyte type sensor has an advanced merit of high selectivity, because the gas sensing mechanism is based on the characteristic that only single ion species can migrate in solid electrolytes. Therefore, the solid electrolyte type sensor is expected to be the most practical candidate for the NOₓ gas sensing tool.

Recently, we have proposed a solid electrolyte type NOₓ gas sensor [8] which combines two kinds of solid electrolytes of the \(Al_{13}Zr_{68}Nb(PO_4)_3\) [9] and the \(O_2^-\) ion conducting yttria stabilized zirconia (YSZ) with the \(K^+\) ion conducting \(0.35Gd_2O_3-0.3KNO_3\) solid solution [10] as the sensing auxiliary electrode. This sensor was developed to detect NOₓ gas in the high temperature region, and could detect not only the individual NOₓ (NO or NO₂) gas...
but also the total concentration of NO\textsubscript{x} (NO and NO\textsubscript{2}) gas at the high temperature of 723 K as intended. Besides such a sensor applicable at high temperatures, there is a brisk demand for sensors operating in the intermediate temperature region (473–573 K) to realize development of portable type NO\textsubscript{x} gas sensors. Since the sensor previously reported cannot operate at the temperatures lower than 723 K, it is necessary to develop a new type of NO\textsubscript{x} gas sensor which can operate between 473 K and 573 K. In order to improve the conductivity of the sensing auxiliary electrode, we developed the high Li\textsuperscript{+} ion conducting (1−\(x\))(Gd\textsubscript{0.9}La\textsubscript{0.1})\textsubscript{2}O\textsubscript{3}−\(x\)LiNO\textsubscript{3} [11] and utilized as the sensing auxiliary electrode with Al\textsuperscript{3+} ion and O\textsuperscript{2−} ion conductors, and the preliminary NO gas sensing characteristics are measured at 523–573 K [12,13].

In this study, the optimization of the sensing auxiliary electrode was achieved, and the optimized electrode was combined with two types of solid electrolytes, (Al\textsubscript{0.2}Zr\textsubscript{0.8})\textsubscript{20}/19 Nb(PO\textsubscript{4})\textsubscript{3} and YSZ. The sensing characteristics of the proposed new type of NO gas sensing were investigated in detail.

2. Experimental

Gd\textsubscript{2}O\textsubscript{3} and La\textsubscript{2}O\textsubscript{3} powder was mixed by a ball mill method in a stoichiometric ratio and the mixed powder was heated at 1273 K for 12 h in air. The obtained (Gd\textsubscript{0.9}La\textsubscript{0.1})\textsubscript{2}O\textsubscript{3} solid solution was mixed with LiNO\textsubscript{3}, pelletized, and heated at 773 K for 12 h in air. The synthesized (1−\(x\))(Gd\textsubscript{0.9}La\textsubscript{0.1})\textsubscript{2}O\textsubscript{3}−\(x\)LiNO\textsubscript{3} was made into pellets after pulverizing and sintered at 773 K for 12 h in air. The Al\textsuperscript{3+} ion conductor (Al\textsubscript{0.2}Zr\textsubscript{0.8})\textsubscript{20}/19 Nb(PO\textsubscript{4})\textsubscript{3} was prepared by mixing the starting materials of Al(OH)\textsubscript{3}, ZrO\textsubscript{2}, Nb\textsubscript{2}O\textsubscript{5}, and (NH\textsubscript{4})\textsubscript{2}H(PO\textsubscript{4})\textsubscript{3} in a molar ratio of 8:32:19:114. The mixed powder was successively heated at 1273 K for 12 h, at 1473 K for 12 h, and then, at 1573 K for 12 h in air. The obtained (Al\textsubscript{0.2}Zr\textsubscript{0.8})\textsubscript{20}/19 Nb(PO\textsubscript{4})\textsubscript{3} was pelletized and sintered at 1573 K for 12 h in air. The O\textsuperscript{2−} ion conductor (ZrO\textsubscript{2})\textsubscript{0.92}(Y\textsubscript{2}O\textsubscript{3})\textsubscript{0.08} (YSZ) was prepared by mixing ZrO\textsubscript{2} and Y\textsubscript{2}O\textsubscript{3} in a molar ratio of 92:8, and the mixed powder was heated at 1873 K for 6 h. The obtained YSZ was pelletized and sintered at 1873 K for 12 h. The sample characterization was carried out by X-ray powder diffraction with Cu K\alpha radiation (Rigaku, Multiflex 2 kW). The ac conductivity measurement was carried out using two gold electrodes as an ion-blocking electrode by a complex impedance method in the frequency range between 5 Hz and 13 MHz (Precision LCR meter 4192A, Hewlett Packard). The thermal analysis was performed using a thermal gravimetric/differential thermal analysis (TG-DTA) apparatus (Shimadzu DTG-50).

After two solid electrolyte pellets of (Al\textsubscript{0.2}Zr\textsubscript{0.8})\textsubscript{20}/19 Nb(PO\textsubscript{4})\textsubscript{3} and (ZrO\textsubscript{2})\textsubscript{0.92}(Y\textsubscript{2}O\textsubscript{3})\textsubscript{0.08} were tightly fixed by inorganic adhesive agent (Asahi, Sumiceram 17-D), the (1−\(x\))(Gd\textsubscript{0.9}La\textsubscript{0.1})\textsubscript{2}O\textsubscript{3}−\(x\)LiNO\textsubscript{3} solid solution electrode was put on the Al\textsuperscript{3+} ion conducting solid electrolyte surface (Fig. 1) and heated to the operating temperature of 523 K.

3. Results and discussion

Fig. 2 shows the X-ray powder diffraction patterns of (1−\(x\))(Gd\textsubscript{0.9}La\textsubscript{0.1})\textsubscript{2}O\textsubscript{3}−\(x\)LiNO\textsubscript{3} (\(x\)= 0–0.4). In the region of \(x\leq 0.35\), the samples are in a single phase of the cubic
C-type rare earth oxide, but LiNO$_3$ appeared as a secondary phase for the sample of $x=0.4$. The lattice constant estimated from the XRD pattern increases monotonously with the LiNO$_3$ content (see inset in Fig. 2), and maintains a constant value at $z=0.35$. From these results, it is clear that the (1−$x$)/(2(Gd$_{0.9}$La$_{0.1}$)$_2$O$_3$)−LiNO$_3$ forms the solid solution in the range of 0 < $x$ < 0.35.

Fig. 3 presents the compositional dependencies of the conductivity for the (1−$x$)/(2(Gd$_{0.9}$La$_{0.1}$)$_2$O$_3$)−LiNO$_3$ solid solution. From the results obtained in Figs. 2–4, it is concluded that the solid solution would be a promising candidate for the NO gas detecting electrode.

The reactions were expected to occur at the detecting electrode, the interface between the sensing auxiliary electrode and the Al$^{3+}$ ion conducting electrolyte, the interface between the two solid electrolytes, and the reference electrode. The reactions are shown below.

\[
\begin{align*}
\text{LiNO}_3(\text{in Gd$_{0.9}$La$_{0.1}$O$_2$}) & \rightleftharpoons \text{Li}^{+} + \text{NO} + \text{O}_2^+ + e^- \\
\text{Al}^{3+} + \text{Li}^{+} + \frac{1}{2} \text{O}_2^+ & \leftrightarrow \frac{1}{2} \text{Al}_2\text{O}_3
\end{align*}
\]
(O^I and O^II represent the oxygen gas appearing on the surface of the sensing auxiliary electrode and the reference electrode side, respectively.) From Eqs. (1)–(4), overall reaction is described as follows.

\[
\text{LiNO}_3 + \frac{1}{12}(\text{Al}_{0.2}\text{Zr}_{0.8})_{20/19}\text{Nb(PO}_4)_3 + \frac{1}{2}\text{O}_2^\text{II} \\
\leftrightarrow \frac{1}{6}\text{Al}_2\text{O}_3 + \frac{1}{12}(\text{Li}_{0.6}\text{Zr}_{0.8})_{20/19}\text{Nb(PO}_4)_3 + \text{NO} + \text{O}_2^\text{I}
\] (5)

Therefore, the Nernst equation derived from the Eq. (5) is described as the next equation:

\[
E = E_0 - \frac{RT}{nF} \ln\left(\frac{a(\text{LiNO}_3)^{-1/2}}{a(\text{Al}_{0.2}\text{Zr}_{0.8})_{20/19}\text{Nb(PO}_4)_3} \times (a\text{PO}_2)^{-1/4}\right) \quad (6)
\]

\[
E_0 \text{ is a constant value, } n = 1.00 \text{ in this case, and } R, T, \text{ and } F \text{ are the gas constant, absolute temperature, and the Faraday's constant, respectively. The activity of solids is constant at a fixed temperature and oxygen partial pressure is always constant at 0.21 atm. Therefore, the Eq. (6) is simplified as follows:}
\]

\[
E = C(\text{constant}) - \frac{RT}{nF} \ln(\text{PNO}) \quad (n = 1.00) \quad (7)
\]

Fig. 6 depicts a typical sensor response curve of the present sensor with the \((1-x)\text{Gd}_2\text{O}_3-x\text{LiNO}_3 (x = 0.35)\) solid solution as the sensing auxiliary electrode when the NO gas concentration was changed from 200 to 2000 ppm and vice versa at 523 K. The sensor EMF outputs at the same NO gas concentration were almost equal in both increase and decrease processes. The response time defined as the time to attain a 90% of total response was within 2 min, demonstrating that the present sensor shows a rapid and reversible response for the NO gas detection. Furthermore, the response rate of the present sensor operating at 523 K is more than three times faster that of the previous sensor with \text{Gd}_2\text{O}_3-K\text{NO}_3 (x = 0.35) solid solution as the sensing auxiliary electrode operating at 723 K. It is expected that the present sensor can respond faster by enhancing the ion conductivity of the sensing electrode.

4. Conclusions

A new type of nitrogen monoxide gas sensor operating at 523 K was fabricated by the combination of the Al^{3+} ion conducting and the O^{2-} ion conducting solid electrolytes with Li^{+} ion conducting \((1-x)\text{Gd}_2\text{O}_3-x\text{LiNO}_3 (x = 0.35)\) solid solution as the sensing auxiliary electrode operating at 723 K. It is expected that the present sensor can respond faster by enhancing the ion conductivity of the sensing electrode.

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References


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