Amperometric NO\textsubscript{x} sensor based on oxygen pumping current by using LaGaO\textsubscript{3}-based solid electrolyte for monitoring exhaust gas

Atanu Dutta, Tatsumi Ishihara*  
Department of Applied Chemistry, Faculty of Engineering, Kyushu University, Hakozaki 6-10-1, Higashi-Ku, Fukuoka 812-8581, Japan

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Abstract
An amperometric NO sensor using a LaGaO\textsubscript{3} base solid electrolyte was investigated based on the difference of catalytic activity of the electrode. It was found that oxygen pumping current increased upon exposure to NO when Sr\textsubscript{0.6}La\textsubscript{0.4}Mn\textsubscript{0.8}Ni\textsubscript{0.2}O\textsubscript{3} and La\textsubscript{0.5}Sr\textsubscript{0.5}MnO\textsubscript{3} (LSM 55) were used as active and inactive electrodes for NO oxidation, respectively. Effects of electrolyte on the sensitivity were investigated and the sensitivity to NO becomes higher with increasing oxide ion conductivity for electrolyte. By applying LaGaO\textsubscript{3} doped with Ni or Co, the sensitivity of the sensor becomes $1842 \mu A$ per decade of NO concentration at 823 K. The oxygen pumping current linearly increased with increasing NO concentration and the sensor responded NO and recovered to the original level within 1 min. The appearance of mixed potential in potentiometric study suggests that oxidation of NO to NO\textsubscript{2} mainly occurs on Sr\textsubscript{0.6}La\textsubscript{0.4}Mn\textsubscript{0.8}Ni\textsubscript{0.2}O\textsubscript{3} electrode. Although oxygen pumping current of this sensor was slightly affected by change in oxygen partial pressure ($P_{O_2}$), influence by $P_{O_2}$ change is negligibly small. Cross-sensitivity study revealed that NO in exhaust gas can be selectively detected in presence of coexisting gases.  
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1. Introduction
It is well known that NO\textsubscript{x} is one of the most hazardous gases, which causes many health problems, acid rains and destroy the protective ozone layer. The emission of NO and NO\textsubscript{2} mostly occurs from automobile exhaust, distributed power plants, and various boiler industries. Therefore, removal of NO from exhaust gas is an important subject. One of the useful methods is to directly convert NO into N\textsubscript{2} and O\textsubscript{2} catalytically and many reports have been published on the selective reduction catalysts [1–3]. But deactivation of catalyst by the formed oxygen is one major issue to solve for the NO direct decomposition catalyst. Therefore, at present, selective reduction of NO with NH\textsubscript{3}, or three-way catalyst is used for NO\textsubscript{x} removal. Recently, in these systems, detection of NO and to adjust the amount of reductant or to tune the combustion system for lowering the pollution are demanded. For this purpose, a NO\textsubscript{x} sensor with high sensitivity, selectivity, and stability is essentially required and a NO\textsubscript{x} sensor has been studied extensively. Several reports are available on detection of NO\textsubscript{x} using either the resistive [4,5], the potentiometric [6–9] or the amperometric mode [10,11]. The reliability of the sensors for selective detection while operating at high temperature (>773 K) is a lingering issue. In the present article, we reported the NO sensing property of the solid-state amperometric sensor consisting of the perovskite oxides as electrodes. Investigation was made to optimize the suitable electrolyte and electrode materials for NO detection. The selectivity of the sensor was also addressed.

2. Experimental
Nickel or cobalt-doped lanthanum gallate solid electrolyte of composition La\textsubscript{1-x}Sr\textsubscript{x}Ga\textsubscript{2}Mg\textsubscript{1-x}O\textsubscript{3} (X = Ni or Co) were prepared by the solid-state reaction route using the appropriate molar weight ratio of La\textsubscript{2}O\textsubscript{3} and Ga\textsubscript{2}O\textsubscript{3} (High Pu-
Nitric oxide (NO) concentration was measured in every 10 s interval both in base gas (1% O\textsubscript{2} in N\textsubscript{2}) and sample gas (N\textsubscript{2} + 1% O\textsubscript{2} + NO). NO sensitivity was measured in base gas and active electrode was always positive. Normal operation was achieved by applying 1 V DC bias (Sr\textsubscript{0.6}La\textsubscript{0.4}Mn\textsubscript{0.8}Ni\textsubscript{0.2}O\textsubscript{3} for electrolyte). The sensor element was tested in a measurement system consisting of a conventional gas flow line and an electronic furnace for keeping sensor element at temperature in the range of 773–973 K. The sensor was tested in the amperometric mode by applying 1 V DC bias (Sr\textsubscript{0.6}La\textsubscript{0.4}Mn\textsubscript{0.8}Ni\textsubscript{0.2}O\textsubscript{3} electrode was always positive) and the oxygen pumping current was measured in every 10 s interval both in base gas (N\textsubscript{2} + 1% O\textsubscript{2}) and sample gas (N\textsubscript{2} + 1% O\textsubscript{2} + NO). NO concentration was adjusted from 500 to 2000 ppm by mixing commercial 1% O\textsubscript{2} in N\textsubscript{2} with diluted NO (1%) in He. DC potential was applied by using constant DC source (Ken-wood, model PA-18–3A) and the resultant current was monitored with a digital multimeter (Advantest, model R6451A). Sensitivity of the sensor was defined as the current change stored with a digital multimeter (Advantest, model R6451A). Selectivity is defined as a ratio of the sensor sensitivity to each individual gas.

3. Results and discussion

3.1. Effects of electrolyte on NO sensitivity

It is well known that strontium-doped LaMnO\textsubscript{3} (LSM) is very stable and chemically active for the oxygen reduction reaction at the cathode electrode for solid oxide fuel cells at high temperature [12]. The interface analysis of La\textsubscript{0.8}Sr\textsubscript{0.2}Ga\textsubscript{0.8}Mg\textsubscript{0.1}Ni\textsubscript{0.1}O\textsubscript{3} revealed no chemical compound formed at the interface [13]. In our previous work on the hydrocarbon sensor, it was demonstrated that La\textsubscript{0.8}Sr\textsubscript{0.2}Ga\textsubscript{0.8}Mg\textsubscript{0.1}Ni\textsubscript{0.1}O\textsubscript{3} (LSGMN) showed the best performance for oxygen reduction in the temperature range 473–723 K [14]. In the present investigation, LSM 55 was also chosen as the inactive electrode for NO detection. On the other hand, perovskite oxides ABO\textsubscript{3} have been widely studied as NO\textsubscript{2} decomposition catalysts with high activity in the exhaust gas environment [2]. These mixed conducting oxide electrodes could be good replacement for metals (Pt, Rh or Ag) or their alloy electrode. Normally, it has been observed that the substitution of the A site of the perovskite oxide (for example, Sr\textsuperscript{2+} at La site) causes an increase in the amount of oxygen vacancy and varied valence state, and as a result, there is an enhancement of catalytic activity to NO decomposition. In fact, Sr\textsubscript{0.7}La\textsubscript{0.3}Mn\textsubscript{0.9}Ni\textsubscript{0.1}O\textsubscript{3} [15] is such material proposed for NO direct decomposition. Hence, for development of amperometric NO sensor, we fixed these perovskite oxides for an active electrode.

Fig. 1 shows the temperature dependence of the sensitivity to NO on various sensors in which four different oxide ion conductors were used for electrolyte. It is obvious that sensitivity is strongly dependent on the oxide ion conductor used for electrolyte and it increases in the following order, La\textsubscript{0.8}Sr\textsubscript{0.2}Ga\textsubscript{0.8}Mg\textsubscript{0.1}Ni\textsubscript{0.1}O\textsubscript{3} (LSGMN) > La\textsubscript{0.5}Sr\textsubscript{0.5}Mn\textsubscript{0.9}Ni\textsubscript{0.1}O\textsubscript{3} (LSGM) > Y\textsubscript{1.0}Zr\textsubscript{0.16}O\textsubscript{2} (YSZ) > Sm\textsubscript{0.15}Ce\textsubscript{0.85}O\textsubscript{2} (SDC). Since oxide ion conductivity increases in almost the same order [16], higher sensitivity can be achieved on higher oxide ion conductor used for the electrolyte of sensor. However, in case of SDC, almost no sensitivity was observed in the measured temperature range. This may result from a large contribution of electron conductivity in SDC under reducing atmosphere. Although oxygen partial pressure (P\textsubscript{O\textsubscript{2}}) in gas phase is not so reducing, oxygen pumping under 1 V application, which corresponds to P\textsubscript{O\textsubscript{2}} = 10^{-20} atm, is highly reducing atmosphere and so partial electronic conduction is significant in case of CeO\textsubscript{2}. Therefore, it is seen that the application of high oxide ion conductor is effective for achieving high sensitivity to NO. Although the NO sensitivity became slightly higher at 873 K on the sensor using LSGMC for electrolyte, the sensor using LSGMN for electrolyte was studied in detail in this study because the highest sensitivity at 823 K is almost the same between these two oxides for electrolyte. It is also noted that the highest sensitivity of this sensor using LSGMN elec-

Current as a function of NO concentration on the sensor using four different oxide ion conductors at 823 K (500–5000 ppm NO, 1% O2, and N2 balance). Although similar high sensitivity is achieved on the sensor using LSGMC electrolyte, the base current in the reference atmosphere, 1% O2 in He, was higher on the sensor using LSGMN electrolyte than that using LSGMC. Therefore, in the following study, we used LSGMN for the electrolyte for amperometric NO sensor.

Fig. 2 shows the current as a function of NO concentration on the sensor using four different oxide ion conductors at 823 K. It is evident that oxygen pumping current of each sensor linearly increased with increasing logarithms of NO concentration. Therefore, NO concentration can be estimated from oxygen pumping current in this sensor. On the other hand, as already discussed, slope in NO dependence in Fig. 2 is strongly dependent on the oxide ion conductors using for electrolyte. When LSGMN or LSGMC is used for electrolyte, not only base current but also current change on exposure to NO is reasonably large. Small electrical resistance of the electrolyte assigning to high oxide ion conductivity leads to high oxygen pumping current resulting in high sensitivity to NO.

Temperature dependence for the 90% response time on the sensor using LSGMN electrolyte to 1000 ppm NO is shown in Fig. 3. It is seen that 90% response time of the sensor drastically decreased with elevating operating temperature and 90% response can be achieved within 1 min at temperature higher than 823 K. Therefore, considering only response time, a higher operating temperature is desirable. In contrast, sensitivity to NO decreased with increasing operating temperature higher than 823 K. As a result, it can be said that the optimum operating temperature for this sensor exists around 823 K. Decreased sensitivity with elevating temperature higher than 823 K may be explained by following two reasons: one is that simple electrochemical oxygen pumping becomes dominant at excessively high temperature and the other is that chemical equilibrium favors NO and oxidation of NO, which seems to be important electrode reaction in this sensor, cannot proceed by limitation of chemical equilibrium at high temperature. At present, oxidation of NO into NO2 on the active and the formation of oxide ion in the inactive electrode from O2 or NO seems to be important for changing in current in this sensor upon exposure to NO. In any case, it is evident that oxygen pumping current of the sensor using LSGMN for electrolyte is highly sensitive for NO detection.

3.2. NO sensing property of the sensor using LSGMN for electrolyte

Since the application area of the proposed sensor is for monitoring of exhaust gas, in which various gases are contained, one of the most serious problems for NO sensors for such purpose is oxygen partial pressure changing always with operation mode of engines. Fig. 4 shows the oxygen pumping current in 1000 ppm NO as a function of coexisting oxygen partial pressure at 823 K (500–5000 ppm NO, 0.5–5% O2, and N2 balance).
and without $O_2$ is not so large. As a result, it is expected that interference by $P_{O_2}$ change is not serious. Since both electrodes are exposed to the same atmosphere, influence of $P_{O_2}$ change may not be serious in this sensor. This is because the influence caused by $P_{O_2}$ change is almost the same on the both electrode.

Fig. 5 shows the oxygen pumping current on the solid-state amperometric sensor using the LSGMN electrolyte as a function of concentration of the typical coexisting gases in exhaust gas. Table 1 also summarized the cross-sensitivity and selectivity of the present sensor for CO, $C_3H_6$ (typical hydrocarbon present in exhaust gas), $H_2$, NO$_2$, and CO$_2$ at 823 K. Since the exhaust gas contains much higher concentration of CO$_2$ (% level) due to fuel combustion, the present sensor was checked to CO$_2$ sensitivity in few % variation (1–20%). Obviously, the sensor shows quite high selectivity to NO and almost no sensitivity or slightly small negative sensitivity to these typical coexisting gases in flue gas. Therefore, comparing with the sensitivity in amperometric mode, that in potentiometric mode is much smaller, and so, it can be said that this sensor is more suitable for amperometric mode than potentiometric mode. On the other hand, origin of the current change in this sensor seems to be changed in mixed potential. This is because the mixed potential is also similar dependence on NO with that of sensitivity. Therefore, change in mixed potential leads to change in applied potential and change in current signal in the amperometric mode. The sensitivity to NO became much smaller by applying DC current at opposite direction and the current always increased upon exposure to NO. Therefore, it seems likely that the electrode of La$_{0.5}$Sr$_{0.5}$MnO$_3$ works as an oxygen activation electrode. There are two oxygen sources considered, i.e. gaseous oxygen or NO and at present, it is not clear which oxygen source is used for the present sensor. On the other hand, it is considered that NO oxidation ($NO + (1/2)O_2 = NO_2$) occurs on the Sr$_{0.6}$La$_{0.4}$Mn$_{0.8}$Ni$_{0.2}$O$_3$ electrode. Since oxidation of NO$_2$ does not exist, sensitivity to NO$_2$ became smaller on this sensor. Further details on electrode reaction are now under investigation. Consequently, this study revealed that the amperometric NO sensor using oxygen pumping current through La$_{0.8}$Sr$_{0.2}$Ga$_{0.8}$Mg$_{0.1}$Ni$_{0.1}$O$_3$ is highly sensitive and selective for NO.

4. Conclusion

The present investigation revealed that Ni-doped LaGaO$_3$-based electrolyte with superior ionic conductivity is effective.

![Fig. 5. Oxygen pumping current on the solid-state amperometric sensor using LSGMN electrolyte as a function of concentration of the typical coexisting gases in exhaust gas at 823 K (500–5000 ppm sensing gas, 0.5–5% $O_2$, and $N_2$ balance).](image1)

![Fig. 6. Open circuit potential of the sensor using LSGMN electrolyte as a function of NO concentration (1000–5000 ppm NO, 1%$O_2$, and $N_2$ balance).](image2)

### Table 1

<table>
<thead>
<tr>
<th>Gas</th>
<th>Sensitivity (μA per decade)</th>
<th>Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO</td>
<td>1840</td>
<td>1.00</td>
</tr>
<tr>
<td>NO$_2$</td>
<td>71</td>
<td>0.04</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>-10</td>
<td>0.01</td>
</tr>
<tr>
<td>$C_3H_6$</td>
<td>11</td>
<td>0.01</td>
</tr>
<tr>
<td>$H_2$</td>
<td>-43</td>
<td>0.02</td>
</tr>
<tr>
<td>CO</td>
<td>-106</td>
<td>0.06</td>
</tr>
<tr>
<td>NO in 2.8% H$_2$O</td>
<td>1850</td>
<td>1.01</td>
</tr>
</tbody>
</table>

Selectivity = absolute value of sensitivity ratio $S_{NO}/S_{NO}$. 

3.3. Detection mechanism in the present sensor

In our previous study on the amperometric hydrocarbon sensor with the similar structure, reduction of oxygen and oxidation of hydrocarbon occurs on each electrode to achieve high selectivity. In a similar manner with the hydrocarbon sensor, it is expected that the similar reduction and oxidation reactions occur on this sensor. Fig. 6 shows the open circuit potential of the sensor using the LSGMN electrolyte as a function of NO concentration. It is also observed that the open circuit potential monotonically increased with increasing NO concentration and the estimated sensitivity was a value of 150 μV per decade. Therefore, comparing with the sensitivity in amperometric mode, that in potentiometric mode is much smaller, and so, it can be said that this sensor is more suitable for amperometric mode than potentiometric mode. On the other hand, origin of the current change in this sensor seems to be changed in mixed potential. This is because the mixed potential is also similar dependence on NO with that of sensitivity. Therefore, change in mixed potential leads to change in applied potential and change in current signal in the amperometric mode. The sensitivity to NO became much smaller by applying DC current at opposite direction and the current always increased upon exposure to NO. Therefore, it seems likely that the electrode of La$_{0.5}$Sr$_{0.5}$MnO$_3$ works as an oxygen activation electrode. There are two oxygen sources considered, i.e. gaseous oxygen or NO and at present, it is not clear which oxygen source is used for the present sensor. On the other hand, it is considered that NO oxidation ($NO + (1/2)O_2 = NO_2$) occurs on the Sr$_{0.6}$La$_{0.4}$Mn$_{0.8}$Ni$_{0.2}$O$_3$ electrode. Since oxidation of NO$_2$ does not exist, sensitivity to NO$_2$ became smaller on this sensor. Further details on electrode reaction are now under investigation. Consequently, this study revealed that the amperometric NO sensor using oxygen pumping current through La$_{0.8}$Sr$_{0.2}$Ga$_{0.8}$Mg$_{0.1}$Ni$_{0.1}$O$_3$ is highly sensitive and selective for NO.
to detect NO. Using various common electrolytes such as YSZ or Sm-doped CeO₂, it was clearly demonstrated that much higher sensitivity in amperometric mode is achieved by using LaGaO₃-based fast oxide ion conductors. Among the examined electrolytes, Ni-doped LaGaO₃ had the highest sensitivity to NO. The sensitivity of the proposed sensor was high in the whole temperature range (773–973 K). The sensing mechanism was briefly identified from the potentiometric measurements. Since the base current was sufficiently high and the change in current in presence of different concentrations of NO was around a few mA range, the developed sensor is highly selective to NO and even for NO₂, almost no sensitivity is observed. Therefore, this study reveals that the proposed solid-state amperometric sensor is highly sensitive and selective to NO and it is promising sensor for monitoring NO in exhaust gas from internal combustion engines.

References


Biographies

Atanu Dutta received his Ph.D degree in Materials Science from Indian Institute of Technology, Kharagpur, India. He joined University of Roma, Italy under ICTP scholarship in 2000. His postdoctoral research work there was on YSZ based electrochemical sensors for environmental monitoring. Then he joined Osaka University, Japan for research investigation on hydrocarbon sensors based on lanthanum gallate. Presently, he is working in Kyushu University on NO₂ sensor for exhaust gas monitoring. His research interests include semiconductor and electrochemical sensors, electro-catalysts for fuel cell applications.

Tatsumi Ishihara received the B.E. degree in applied chemistry in 1984 and the Dr. Eng. degree in 1989 from Kyushu University. He joined the Graduate School of Engineering Science in Kyushu University in 1986 and in 1988 he joined the Faculty of Engineering in Osaka University. In 2003, he moved to Faculty of Engineering in Kyushu University. He has worked on catalytic chemistry and oxide ion conducting electrolytes.