Mechanism of NO₂ Sensing by the Variation of Conductivity of La₂CuO₄

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Summary

In order to make clear the mechanism of the variation in the conductivity of La₂CuO₄ with a small amount of NO₂ (x=1.2) in oxygen atmosphere, measurements were made on the conductivity of La₂CuO₄ in the stream of NO₂ - O₂ - N₂ gas mixtures at temperatures 773-1023K and the outlet gas was analyzed by a zirconia sensor. The conductivity and the EMF of the zirconia sensor were analyzed in relation to P(NO₂), P(O₂) and T. When NO₂ was applied to La₂CuO₄, catalytic reaction of NO₂ → NO + (1/2)O₂ was found to take place. In the catalytic reaction process, excess oxygen was considered to be incorporated into La₂CuO₄. Under the steady state, the oxygen potential in La₂CuO₄ was kept much higher than that in the gas phase, resulting in the increase in the p-type conduction of La₂CuO₄. Numerical calculations were made for the oxygen potential enhanced in La₂CuO₄ as a function of P(NO₂) and T to make clear the detection limits of La₂CuO₄-type NO₂ sensors in relation to the gas phase P(O₂) and T. Under the condition studied, NO affects very little to reduce the conductivity of La₂CuO₄. The reason was discussed based on the catalytic reaction kinetics to show the direction to enhance the NO effect in La₂CuO₄.

Key Words: NO₂, sensor, Perovskite type oxide, La₂CuO₄, conductivity, Nonstoichiometry

1. Introduction

Recently, requirements for the development of high temperature NO₂ sensors have been increased for the application to controlling exhaust gas of combustion engines. Many reports have been published from the researches in this area. Most of the sensors reported were categorized into two types, solid electrolyte cell-types and surface adsorption-types. A general sensing mechanism of the latter sensors is well known. The adsorbed species on the surface of semiconductors may be more or less ionized to work as acceptors or donors to capture or release electrons, resulting in the increase or decrease in the conductivity due to electrons and vise-versa in the conductivity due to electron holes. To obtain good sensitivity with these semiconductor gas-sensors, the number of the adsorbed species is desired to be comparable to that of the bulk carriers. That is, it is desirable for the carrier concentration to be very low, such as wide-gap semiconductors, or for the surface/bulk ratio in the oxide of the sensing element to be very large. The oxide is desired to be thin films or porous materials with very thin bottle necks to connect grains. In the latter case, the adsorbed species on the bottle-neck area controls the number of carriers at the bottleneck and works as a non-mechanical switch or a chemical gate.

In these years, several oxides of the perovskite- or perovskite-related structure with transition metals in their B-site elements, such as Ln₂CuO₄(Ln=La, Nd),(1-3) doped LaMO₃(M=Cr, Mn, Fe, Co) and titinate series,(4) have been reported as NO₂ sensing material. The conductivity of these oxides varies with the change in NO₂ concentration in the gas phase, the behavior of which is very similar to that of usual wide-gap semi-conductors, typically SnO₂. However, these perovskite-type oxides (except for titanates) are known as hopping conductor, or metals or semimetals both with degenerated d-band, in which the carrier density is extraordinarily high. Percents to half of the transition metal ions in the oxide are considered to work as hopping sites or release carriers. The density of carriers exceeds 10²¹ cm⁻³. It is not likely for the concept of usual adsorption-type semiconductor sensors to be valid in these materials. As to Ln₂CuO₄, Miyayama et al.(5) found that the enhancement of conductivity by NO₂ and depressing by NO are observed on rather dense samples. Their finding may indicate that the general mechanism for semiconductor gas sensors is not applicable to this material. The author and co-investigators have been studying the electronic properties of La₃₋xSrₓCuO₄ as functions of P(O₂) and temperature(6) to elucidate the relationship to the nonstoichiometric variation of oxygen content. Based on these preceding works, the present research aims to make clear the mechanism of conductivity variation with NO₂ gas by the measurements of the electronic conductivity of bulk La₂CuO₄ as functions of P(NO₂), P(NO) and temperature.

2. Experimental

2.1 Samples
La₂CuO₄ was prepared from the powder mixtures of commercial La₂O₃ (99.9%) and CuO (99.9%). Prior to weighing, the La₂O₃ powder was baked at 1273K in air for 3h to avoid contamination of carbonate and hydrate. The CuO powder was baked at 1075K under 1 atm pure oxygen for 2h to avoid nonstoichiometric deviation in composition and possible contamination of Cu₂O. After these heat treatments, the powders were weight and mixed together in the proper metallic ratio for La₂CuO₄ with ethanol using alumina mortar and pestle. The mixtures were calcined at 1273K in air for 12h, crashed into powders, and the structure was analyzed by XRD. Then, re-mixing and re-calcination process was repeated until the powder XRD pattern showed no other peak than the single series of La₂CuO₄. Finally, the powders were pressed into disks of 10 mm in diameter and 3 mm in thickness and sintered at 1520K for 4 h in air. The density of the specimen after sintering was more than 93%. The pellets were cut into rectangular bars of about 1.5×1.5×9 mm³.
2.2 Gas system

Figure 1 shows the schematic diagram of the measuring system. Gas mixtures of \( \text{O}_2 \) (10^{-2}-1atm), \( \text{NO} \) or \( \text{NO}_2 \) (0-10^{-3}atm) and \( \text{N}_2 \) in appropriate ratios were prepared controlling the flow rate of standard gases of 1% \( \text{O}_2 \)-\( \text{N}_2 \), 0.01%\( \text{O}_2 \)-\( \text{N}_2 \), 0.01%\( \text{NO} \)-\( \text{N}_2 \), 0.01%\( \text{NO}_2 \)-\( \text{N}_2 \), \( \text{N}_2 \) (99.999%) and pure \( \text{O}_2 \), respectively, by the use of needle-valves and gas flowmeters. The total flow rate of the gas mixtures was kept at 200ml/min at room temperature. The gas mixtures were let flow through a sample chamber in a furnace to a zirconia cell in another furnace. To avoid the reaction of \( \text{NO} \) or \( \text{NO}_2 \) before reaching the surface of the sample and in the path between the sample chamber and the zirconia cell, glass tubes were used for the walls of high temperature chambers and the exposure of materials with high catalytic activity was avoided through the system except for the samples and the electrodes of zirconia sensors.

2.3 Conductivity measurements

A standard d.c. four probes method was employed using Au wires (0.3mmφ) winding around the rectangular samples by 2.5-3.0mm intervals. The conductivity at the steady-state was determined from the relationship of the potential difference, \( \Delta E \), between the potential electrodes and the current, \( i \), let flow between the current electrodes. The current of ±2 and ±3mA was applied for respective conditions and, after \( \Delta E \) reached a stationary value, \( \Delta E \) was recorded. The conductivity was calculated from the slope of \( \Delta E \) vs. \( i \) so as to avoid the effect of thermoelectric power. Au was selected for electrodes because preliminary studies revealed that Au is almost inactive against the gas atmosphere employed in this study while Pt, a standard electrode materials for high temperature conductivity measurements, is active to \( \text{NO}_2 \). Measurements were made as a function of \( P(\text{O}_2) \), \( P(\text{NO}) \) and \( P(\text{NO}_2) \) at temperatures of 773-1023K.

2.4 Monitoring of the outlet gas

The outlet gas from the sample chamber was analyzed by a zirconia sensor composed of an electrochemical cell with stabilized zirconia (8 mole % \( \text{Y}_2\text{O}_3 \)-doped \( \text{ZrO}_2 \)) as a solid electrolyte and porous Pt electrodes: Platinum paste (non-flux-type, Tanaka Kikinzoku Co., TR7905) was mounted to the inside and outside of the end of a zirconia tube (8 mole % \( \text{Y}_2\text{O}_3 \)-doped \( \text{ZrO}_2 \), 8mm in outer diameter, 30mm in length, Nippon Kagaku Togyo Co.) as electrodes and baked at 1173K for 1h. On the electrodes, Pt mesh was applied as current collector and Pt wires were attached as leads. Inside of the tube was exposed to air and outside was exposed to the outlet gas. The cell was placed in a temperature regulated furnace and the EMF was measured by an electrometer.

3. Results and discussion

3.1 Effect of small amount of \( \text{NO}_2 \) and \( \text{NO} \) on the conductivity vs. \( P(\text{O}_2) \) relationship of \( \text{La}_2\text{CuO}_4 \)

Fig. 2 shows the conductivity, \( \sigma \), of \( \text{La}_2\text{CuO}_4 \) at 773-1023K in \( \log \sigma \) vs. \( \log P(\text{O}_2) \) plot. The conductivity at different temperatures happens to fall on a straight line. That is, \( \sigma \) under given \( P(\text{O}_2) \) is independent of temperature. From Fig. 2, the \( P(\text{O}_2) \) dependence of \( \sigma \) is expressed by

\[
\sigma = 12.6P(\text{O}_2)^{1.6}
\]

This relationship is essentially in accord with the results by Hashimoto et al.\(^{(8)}\) and Nishiyama et al.\(^{(9)}\) Since \( \text{La}_2\text{CuO}_4 \) shows oxygen excess nonstoichiometry with doubly charged interstitial oxygen ions, \( \text{O}^{2-} \), and the electronic conduction is p-type, the defect equilibrium in \( \text{La}_2\text{CuO}_4 \) can be expressed as follows.

\[(1/2)\text{O}_2(g) \leftrightarrow \text{O}^{2-} + 2h_+ \quad K_{\text{eq}} = [\text{O}^{2-}][h]^2P(\text{O}_2)^{-1/2} \] (2)

where \( h \) indicates electron holes, \( K_{\text{eq}} \) is an equilibrium constant and \( [ \ ] \) indicates the concentration of the species in the brackets. The electric neutrality maintained in bulk is given by

\[2[\text{O}^{2-}] = [h] \] (3)

From Eqs. (2) and (3), we have

\[ [h] = 2([\text{O}^{2-}]) = (2K_{\text{eq}})^{-1/2}P(\text{O}_2)^{1/2} \] (4)

This equation indicates that the carrier concentration is proportional to \( P(\text{O}_2)^{1/2} \), in accord with the \( P(\text{O}_2) \) dependence of \( \sigma \). That is, the variation of conductivity at given temperature directly reflects that of the carrier concentration and the mobility of carriers at given temperature is expected constant independent of the carrier concentration. The mobility may change with temperature because \( \text{O}^{2-} \) at given \( P(\text{O}_2) \) may vary with temperature. Further details on the defect chemistry is given in Kanai et al.\(^{(9)}\).
3.1.2 Effect of NO₂

Typical examples of the variation of $\alpha$ with $P(\text{NO}_2)$ in the $\text{O}_2$-$\text{NO}_2$ gas mixtures at constant $P(\text{O}_2)$ is shown in Fig. 3. The increase in $\alpha$ with $P(\text{NO}_2)$ is more remarkable with decreasing temperature. Since NO₂ may decompose into N₂ and O₂ by the equation

$$\text{NO}_2 \rightarrow (1/2)\text{N}_2 + \text{O}_2 \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots
3.1.3 Effect of NO

Fig. 6 shows the variation of \( \sigma \) with \( P(\text{NO}) \) in the gas mixtures with the gas phase oxygen of \( P(\text{O}_2) = 10^{-5} \text{atm} \) and \( 10^{-3} \text{atm} \). A small decrease in \( \sigma \) was observed for the conditions of \( P(\text{O}_2) = 10^{-5} \text{atm} \) at 773-873K. However, no other obvious variation was observed under the conditions at which the present work was made. Since the effect of NO on \( \sigma \) differs with the gas phase \( P(\text{O}_2) \), the NO effect may not be due to the adsorption of NO.

So far found in this work, NO effect is very small on \( \sigma \) of La\(_2\)CuO\(_4\). It seems this result is contradictory to the one reported by Morita et al.\(^{(3)}\) although their measurements were made at lower temperatures and higher \( P(\text{NO}) \) than the present work. The reason will be discussed briefly in 3.3.2.

3.2 EMF of zirconia sensor vs. \( P(\text{O}_2) \), \( P(\text{NO}_2) \) and \( P(\text{NO}) \) with and without La\(_2\)CuO\(_4\).

3.2.1 EMF in \( \text{O}_2-\text{N}_2 \) atmosphere with no \( \text{NO}_x \) component

The EMF of the zirconia sensor observed against the \( P(\text{O}_2) \) of the \( \text{N}_2-\text{O}_2 \) gas mixtures without \( \text{NO}_x \) is shown in Fig. 7. The data fall on one line irrespective of whether \( \text{La}_2\text{CuO}_4 \) is place in the chamber or not, and whatever the temperature of \( \text{La}_2\text{CuO}_4 \) is. The line corresponds to the Nernst relationship.

\[
\text{EMF} = \frac{2.303 \cdot R \cdot T}{4F} \log \left( \frac{P(\text{O}_2, \text{test gas})}{P(\text{O}_2, \text{air})} \right)
\]

\( T = 973K \)

\( P(\text{O}_2, \text{air}) = 0.21 \text{atm} \) .......... (6)

Here \( R \) is the gas constant and \( F \) is the Faraday constant. As expected, \( \text{La}_2\text{CuO}_4 \) in equilibrium with the \( \text{N}_2-\text{O}_2 \) gas mixtures does not affect the \( P(\text{O}_2) \) of the gas phase. In this section, we use \( \Delta P(\text{O}_2) \):

\[
\Delta P(\text{O}_2) = P(\text{O}_2) \text{ calculated from EMF}
- P(\text{O}_2) \text{ in the prepared composition of gas-mixtures} ............. (7)
\]

to discuss the effects of \( \text{NO}_x \) observed by the zirconia sensor.

3.2.2 Effect of \( \text{NO}_2 \) directly attacking the zirconia sensor

When the sample chamber is empty of sample and the \( \text{N}_2-\text{NO}_2 \) gas is directly supplied to the zirconia cell, EMF shows an anomalously large oxygen potential. Among several data sets in Fig. 8, here we focus our interest on the lines \(<\text{Nernst Eq.}>\) and \(<\text{without sample in NO}_2>\).

The line \(<\text{Nernst Eq.}>\) is calculated for the case all \( \text{NO}_2 \) gas was decomposed by Eq. (5) and the \( \text{O}_3 \) thus formed is added to the \( \text{O}_2 \) in the prepared gas mixtures. That is, \( \Delta P(\text{O}_2) = P(\text{NO}_2) \). The curve \(<\text{without sample in NO}_2>\) is the one calculated from the observed EMF in the gas mixture of \( P(\text{O}_2) + P(\text{NO}_2) \) with \( P(\text{O}_2) = 0.001 \text{atm} \).

Since \( \text{NO}_2 \) is thermodynamically unstable at the experimental condition, it releases an oxygen potential twice as large as the same amount of \( \text{O}_3 \) gas at the Pt electrode of the zirconia sensor due to the catalytic effect of Pt.

3.2.3 Effect of \( \text{NO} \) directly attacking the zirconia sensor

In Fig. 8, the \( \Delta P(\text{O}_2) \) caused by the \( \text{NO} \) gas in the \( \text{N}_2-\text{O}_2(0.001 \text{atm}) \) gas mixtures is also shown. Contrary to the effect of \( \text{NO}_2 \), \( \text{NO} \) does not affect the EMF and \( \Delta P(\text{O}_2) \) due to the variation of \( P(\text{NO}) \) is zero. Although the \( \text{NO} \) gas in the present gas mixtures is thermodynamically unstable as well as \( \text{NO}_2 \), the Pt electrode on the zirconia cell was not active as a catalyst for the reaction of NO.

3.2.4 Catalytic effect of \( \text{La}_2\text{CuO}_4 \) appeared on EMF of oxygen sensors

When the sample is placed in the chamber, \( \Delta P(\text{O}_2) \) with \( \text{NO}_2 \) becomes much different from that without \( \text{La}_2\text{CuO}_4 \). As shown in Fig. 8, \( \Delta P(\text{O}_2) \) calculated from EMF is close to a half of the \(<\text{Nernst Eq.}>\) irrespective of the temperature of the sample between 773 and 1023K. That is,

\[
\Delta P(\text{O}_2) = P(\text{NO}_2)/2 ......................... (8)
\]

Fig. 9 shows the similar relationship obtained under different oxygen content in the prepared gas mixtures of \( P(\text{O}_2) = 10^{-5} \) and \( 10^{-3} \text{atm} \). \( \Delta P(\text{O}_2) \) is similar irrespective of the oxygen content.

These results indicate that the gas mixtures after passing the
Fig. 8. The deviation of EMF from the Nernst equation in the gas phase $P(O_2)$ by the influence of NO, transformed into the deviation of $P(NO_2)$ using Nernst equation, $\Delta P(O_2)$, as a function of $P(NO_2)$. The line <Nernst Eq.> indicates the $\Delta P(O_2)$ expected when the gas phase $P(O_2)$ is increased by the decomposition of NO, into N, and O,

$P(O_2) = 10^{-3}$ atm

As shown in Fig. 8 and 9, we could not observe $\Delta P(O_2)$ with the change in NO, even when La$_2$CuO$_4$ is placed and heated in the sample chamber. It leads that NO is essentially inactive on the La$_2$CuO$_4$ sample as well as on the Pt electrode of the zirconia sensor.

3.3 Mechanism of conductivity change by NO,

3.3.1 Enhancement by NO$_2$

From the discussion above, the variation of $\sigma$ with NO, in La$_2$CuO$_4$ is attributed to the change in the oxygen potential change in La$_2$CuO$_4$ and the variation associates the decomposition of NO, by Eq. (9). Here, we consider the mechanism to enhance the oxygen potential in La$_2$CuO$_4$.

A possible reaction mechanism is shown in Fig. 10. When NO$_2$ decomposes on some surface sites of La$_2$CuO$_4$, it release there oxygen of much higher activity than the gas phase and in the bulk of La$_2$CuO$_4$ which has been kept in equilibrium with the gas phase. Then, a part of the released oxygen may diffuse into La$_2$CuO$_4$. When NO$_2$ comes continuously to the reaction sites, the oxygen may be enriched and the oxygen potential increases in La$_2$CuO$_4$. Of course, oxygen transport takes place between gas phase and bulk of La$_2$CuO$_4$ and when the oxygen potential in the bulk is higher than the gas phase, oxygen is released from La$_2$CuO$_4$ at some other sites of the surface. Under a steady-state, the oxygen potential in the La$_2$CuO$_4$ is kept at certain value between the maximum possible oxygen potential NO, can produce and the value of the gas phase $P(O_2)$. The relationship is schematically shown in Fig. 11. In the figure, $\Delta P(O_2)_{eff}$ is the oxygen potential enhanced in La$_2$CuO$_4$.

From the experimental data, $\Delta P(O_2)_{eff}$ can be calculated as follows. Let us consider the observed conductivity at the condition of $(P(O_2)_A, P(NO_2)_A)$, the value of which we assign as $(\sigma_A)$. If we want to attain the conductivity $\sigma_A$ under the oxygen atmosphere without NO, we must fix the oxygen pressure in the gas phase as $P(\sigma_A)$ determined by Eq. (1). That is,

$$ (\sigma_A) = 12.6 P(O_2)^{1/6} \quad (10) $$

This means that the combination of $(P(O_2)_A, P(NO_2)_A)$ gives the effective oxygen potential of $P(O_2)_A$ to the bulk of La$_2$CuO$_4$. Then, $\Delta P(O_2)_A$, the oxygen potential enhanced by $P(NO_2)_A$, is given by
Fig. 12. Oxygen potential enhanced in La$_2$CuO$_4$ by NO$_2$, expressed in terms of the oxygen pressure. $\Delta P(O_2)_{\text{eff}}$ as a function of $P(\text{NO}_2)$.

$\Delta P(O_2)_{\text{eff}} = P(O_2)_\text{atm} - P(O_2)_\text{ph}$ ........................................ (11)

Fig. 12 shows $\Delta P(O_2)_{\text{eff}}$ calculated from the respective data points of $(\sigma, P(O_2), P(\text{NO}_2))$ using Eqs. (10) and (11).

Comparing the open (log $P(O_2)/\text{atm} = -3$) and the closed (log $P(O_2)/\text{atm} = -5$) symbols at respective temperatures, two typical features are found. First, in spite of the large difference in the gas phase $P(O_2)$, $\Delta P(O_2)_{\text{eff}}$ is close. That is, the $\Delta P(O_2)_{\text{eff}}$ is essentially the function of $P(\text{NO}_2)$ and independent of the gas phase $P(O_2)$. Second, the relationship between $\Delta P(O_2)_{\text{eff}}$ and $P(\text{NO}_2)$ can be empirically expressed by

$\Delta P(O_2)_{\text{eff}} = kP(\text{NO}_2)^2$ ........................................ (12)

where $k$ is a function of temperature which increases with decreasing $T$.

Since $\sigma$ of La$_2$CuO$_4$ in the gas-mixtures of $(P(O_2), P(\text{NO}_2))$ is determined by $P(O_2) + \Delta P(O_2)_{\text{eff}}$. when $\Delta P(O_2)_{\text{eff}} \ll P(O_2)$, no clear enhancement of $\sigma$ would be observed. This would be the reason why $\sigma$ at $P(O_2) = 0.1$ atm was not enhanced at 1023K, because $\Delta P(O_2)_{\text{eff}} < 10^{-3}$ atm at 1023K as shown in Fig. 4. At $T < 800K$, $\Delta P(O_2)_{\text{eff}}$ at $P(\text{NO}_2) > 10^3$ atm may exceed 0.1 atm. Under such conditions, enhancement of $\sigma$ is expected even when NO$_2$ is in air and $P(\text{NO}_2)$ is of the order of $10^4$ - $10^5$ atm. This is consistent with the reported data by Morita et al. (2)

Investigation on the detailed chemical meaning of Eq. (12) is left for future studies.

3.3.2 Depression by NO

As mentioned in 3.1.3, the decrease in $\sigma$ with $P(\text{NO})$ in Fig. 6 can not be interpreted by the adsorption model of semiconductor gas sensors. On the other hand, when the catalytic reaction of

NO $+ (1/2)O_2(g) \rightarrow NO_2$ ........................................ (13)

or

$2NO \rightarrow N_2 + O_2$ ........................................ (14)

takes place on La$_2$CuO$_4$, the gas phase $(P(O_2))$ and/or $P(\text{NO}_2)$ would change resulting in the EMF variation of the zirconia sensor. However, such variation was not detected as shown in Fig. 8.

As a possible interpretation, it is considered that the catalytic reaction takes place but only a small amount which could not be detected by the EMF change of the zirconia sensors. Since $\sigma$ is depressed by NO, NO works as a reductant of La$_2$CuO$_4$. The reaction can be expressed by

NO + O(La$_2$CuO$_4$) $\rightarrow NO_2$ ........................................ (15)

The oxygen taken out from La$_2$CuO$_4$ would be compensated from gas phase $O_2$ or even from the produced NO$_2$.

Chemical reactions proceed to the direction to attain the chemical equilibrium. Among $O_2$, NO and NO$_2$, the equilibrium can be written by

NO $+ (1/2)O_2(g) \rightarrow NO_2$ : $P(O_2)^{1/2}K_P = P(\text{NO}_2)/P(NO)$ ........................................ (16)

where $K_P$ is the equilibrium constant. As shown above, NO$_2$ is considered to decompose almost completely on La$_2$CuO$_4$. That is, in equilibrium, the ratio of $P(\text{NO}_2)/P(\text{NO})$ is very small. However, Eq. (16) also indicates that very small but certain amount of NO$_2$ should be produced by the oxidation of NO when NO free NO is exposed to catalysts, such as La$_2$CuO$_4$. This is what happened on NO in the present study.

Since the decrease in $\sigma$ is observed only for the condition of $P(O_2) = 10^{-3}$ atm, $\Delta P(O_2)_{\text{eff}}$ by Eq. (15) and the following oxidation process is of the order of $10^{-3}$ atm. At the $P(O_2)$ higher than $10^{-3}$ atm, such a small $\Delta P(O_2)_{\text{eff}}$ can not be observed.

In order to exaggerate the decrease in $\sigma$ by NO, it is necessary to enhance the reaction in Eq. (15). From thermodynamic calculations, $K_P$ increases with decreasing $T$ under constant $P(\text{O}_2)$. The conversion of NO into NO$_2$ becomes easier with decreasing $T$. Then, to decrease the temperature may enhance Eq. (15) and, consequently, enhance the decrease in $\sigma$ by NO gas.

4. Conclusion

The variation of the conductivity of La$_2$CuO$_4$ by a small amount of NO$_2$ and NO in oxygen containing atmospheres are found to be interpreted by considering the mechanism of the catalytic redox reaction of NO$_2$ and NO on La$_2$CuO$_4$. The reaction process involves the oxygen in La$_2$CuO$_4$ and, under the steady state, the oxygen potential La$_2$CuO$_4$ deviates from that of the gas phase. This deviation is observed as a variation of the conductivity.

This work was supported by a Grant-in-Aid for Scientific Research, No. 06453113 and 08555212 from Ministry of Education, Science, Sports and Culture, Japan

(Manuscript received Aug. 28, 1997, revised Nov. 4, 1997)

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