— Headline —

A Concept of Chemical Potential Pumping Effect of Nonstoichiometric Oxides and the NO_x Sensing Mechanism of the Perovskite-Type La_{0.5}Sr_{0.5}FeO₃

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A concept of chemical potential pumping effect was introduced to describe the NO_x sensing mechanism of oxide catalysts with high electronic conductivity and large carrier density. When NO_x gas in a gas-stream decomposed on the surface of the catalyst oxides continuously, the high oxygen potential released by the decomposition of NO_x stationarily covered the whole surface of the oxide. Then, the bulk oxide was equilibrated with the steady-state high oxygen potential of the surface, which was much larger than that determined by the oxygen pressure of the surrounding gas-phase. This effect was confirmed by the conductivity enhancement of La₂CuO₄ and La_{0.5}Sr_{0.5}FeO₃ with NO₂ as well as nonstoichiometry variation of La_{0.5}Sr_{0.5}CoO₃ and EMF of galvanic cell with La_{0.6}Sr_{0.4}CoO_{3-δ}. It was shown that the chemical potential pumping effect appears essentially on dense materials while the effect is hardly observed on porous material with large surface relative. On La_{0.5}Sr_{0.5}FeO₃ as well as on La₂CuO₄, NO₂ was found to decompose into NO and O₂, while NO was almost inactive on these oxides.

Key Words : Oxidation by NO_x Perovskite-type La_{0.5}Sr_{0.5}FeO₃, NO₂ Sensing Mechanism, Nonstoichiometry and Conductivity

1 Introduction

Semiconductor oxide gas sensors are known to detect the gaseous species adsorbed on its surface. The typical mechanism was proposed by Yamazoe and Seiyama.¹⁾ It is schematically shown in Fig. 1. In this model, the adsorbed species are expected to work either acceptor or donor to reduce or enhance the electronic carrier of the bulk, resulting in the conductivity variation of the semiconductor specimen. Typical example of this type is the series of SnO₂ gas sensors.

Since the sensitivity is affected by the ratio of [number of adsorbed species] / [number of bulk carriers], the sensing materials are desired to have large relative surface area. The bottle-neck structure in Fig. 1 is considered to work as a chemical switch when the adsorbed specimens show a strong affinity to the carriers: The carriers in the bottle-neck part are to be trapped by the

adsorbed species on the surface and the carriers in the bottle-neck become zero, resulting in the bottle-neck part insulating. Sensitivity as sensors is the higher for the materials with the more porous structures. This model holds for the sensing mechanism of the semiconductors with relatively small carrier concentration with a large band gap.

It is known that a similar gas sensing behavior is observed for the oxides with much larger carrier concentration. A typical example is the conductivity enhancement in La₂CuO₄ by a small amount of NO₂ in ambient atmosphere.²⁾ Since the carrier in these transition metal perovskite-type oxides is attributed to the mixed valence state of transition metal cations, the carrier concentration is of the order of the concentration of 3d metals, which is larger in several orders of magnitude than that of surface adsorbed species in the ordinary porous polycrystalline materials.

The authors have proposed a model to describe the NO_x sensing mechanism of La₂CuO₄,^{3,4)} and confirm this effect in the nonstoichiometry variation of La_{0.5}Sr_{0.5}CoO₃.⁵⁾ The direct observation of oxygen chemical potential enhancement by EMF was also demonstrated using the solid state electrochemical cell with a dense La_{0.6}Sr_{0.4}CoO₃ electrode.⁵⁾

In this article, the proposed model is summarized into a generalized concept of chemical potential pumping effect and the typical procedure to show the evidence of the effect is explained, displaying the data for dense and porous La_{0.5}Sr_{0.5}FeO₃ as a typical example. Also, discus-

Fig. 1 Sensing mechanism of typical semiconductor gas sensors.

sion is made on the surface reaction kinetics related to the chemical potential pumping effect.

2 Concept of the Chemical Potential Pumping Effect

2.1 Concept

It is known that NO_x gas in ordinary or reduced atmospheres is unstable. However, it does not decompose unless it hits some appropriate catalytic surface. Once it hits the catalytic surface, it decomposes to release highly active oxygen, which may oxidize the substrate catalysts or other adsorbed species on the surface. Thus, NO_x is a well-known oxidant.

When the catalyst oxide is placed in the gas stream containing NO_x , the decomposition of NO_x gas continuously takes place on the surface, as shown in Fig. 2. Due to the high activity oxygen released from NO_x , the surface oxygen chemical potential is kept much higher than that of the gas phase determined by the partial pressure of oxygen gas.

Since the bulk of the oxide is surrounded by the surface with enhanced oxygen chemical potential, the situation of the bulk is considered thermodynamically equivalent to the condition being kept under a very high oxygen pressure. Then, the bulk is considered eventually equilibrated to the high oxygen chemical potential of the surface. That is, the high oxygen potential in the gas phase NO_x is pumped up into the catalyst oxide, as shown in Fig. 3. The variation of oxygen chemical potential in the oxide accompanies the variation of the nonstoichiometric composition and the variation of the related properties such as electrical conductivity.

2.2 Characteristic appearance of chemical potential

Fig. 2 Schematic mechanism of the oxygen chemical potential pumping effect.

Fig. 3 Schematic diagram of the chemical potential pumping effect.

pumping effect

When the conductivity of an oxide is affected by gaseous species by means of the chemical potential pumping effect, the way of the conductivity variation is expected much different from that for the conventional semiconductor sensors with materials such as SnO_2 . The typical characteristics are schematically shown in Fig. 4.

In the SnO_2 sensors, sensitivity is larger when the surface area / bulk volume ratio is larger, and thinner films or porous materials with narrower bottle neck give higher sensitivity. On the other hand, when the conductivity variation is caused by the chemical potential pumping effect, dense materials are considered more sensitive. The catalytic reaction takes place when the reactant hits the surface. Gaseous species introduced into micro pores are considered experienced the catalytic reaction near the entrance of the pore. Then, inside of the pore is expected filled with the equilibrated species. That is, although the chemical potential enhancement takes place on the outer surface, the effect is suppressed by the relaxation from the inner surface of the pores. The high effective oxygen potential produced on the outer surface by NO_x will be relaxed to the equilibrated lower oxygen potential of the $\text{N}_2\text{-O}_2$ gas-mixtures of the inner surface.

This infers that chemical pumping effect may appear most strongly for the single crystals or dense materials without pores or cracks. For these materials, the chemical potential of the bulk is determined only by the surface catalytic reaction. That is, the magnitude of the chemical potential enhancement is independent of the thickness or volume of the crystals. In the following, experimental evidence of the chemical potential pumping effect³⁻⁵⁾ is summarized with a particular focus on $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_3$ ⁴⁾ to show the difference between the dense

Fig. 4 Characteristics of the appearance of the chemical potential pumping effect.

Fig. 5 Conductivity of dense and porous $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_3$ at 750-850 °C. Solid curves indicate the reported conductivity data.⁶⁾

and porous materials in the appearance of chemical potential pumping effect.

3 Conductivity of $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_3$ in O_2 - N_2 atmospheres without NO_x

In Fig. 5, three sets of the data are compared for the conductivity in O_2 - N_2 atmospheres at 750-850 °C as a function of $P(\text{O}_2)$ measured by the present authors, expressed by symbols, and by Patrakeeve *et al.*⁶⁾ expressed by solid lines. Here, the authors prepared the $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_3$ powders by means of a co-precipitation method followed by calcinations at 950 °C.⁷⁾ Dense sample (92% of X-ray density) was prepared by sintering the pressed powder at 1305 °C, while the porous sample (71%) was obtained by sintering at 1200 °C.⁴⁾

The conductivity of dense sample is essentially the same to those reported by Patrakeeve *et al.*⁶⁾ except for the region of $\log \{P(\text{O}_2)/\text{bar}\} < -3$, at which the slope of $\log \sigma$ vs. $\log P(\text{O}_2)$ of our data is a little steeper than that of the data by Patrakeeve *et al.* The $P(\text{O}_2)$ dependence of the conductivity of porous sample is essentially the same to the other sets of the data. However, the absolute value of the conductivity of porous sample is nearly 1/5 of the dense sample. The authors proposed a model to describe the relationship between the porosity and the conductivity in the course of ceramic sintering process.^{8, 9)} According to the model, the ratio, nearly 1/5, of the conductivity of porous materials vs. dense ones indicates that the grains in the porous material are connected only by narrow bottle-necks.⁹⁾ That is, the geometrical structure of the porous materials is basically similar to that in the upper drawing of Fig. 4.

The conduction mechanism is known to be a small polaron hopping conduction between $\text{Fe}_{\text{Fe}}^{\text{X}}$ and $\text{Fe}_{\text{Fe}}^{\bullet}$. Here, we employed Kroeger-Vink notation for defects.¹⁰⁾ The $P(\text{O}_2)$ dependence of conductivity is known to be described by the defect equilibrium and the variation of oxygen nonstoichiometry.^{7, 11)} Roughly, the conductivity is essentially proportional to $P(\text{O}_2)^{1/6}$. That is, the conduc-

tivity is nearly doubled by the increase of $P(\text{O}_2)$ in two orders of magnitude.

4 Chemical Potential Pumping Effect Appeared with $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_3$ from NO_x Containing Atmospheres

4.1 Conductivity of dense $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_3$ in NO_x containing atmospheres

A schematic diagram for the measuring system of the chemical pumping effect by conductivity in NO_2 containing atmospheres are shown in Fig. 6. Four probe conductivity measurements were employed with Au as electrodes and lead wires as shown in Fig. 6.^{3, 5)} The use of Pt was avoided at any part except for the zirconia sensor electrode because Pt was found active to NO_2 .³⁾ The outlet gas was introduced into a potentiometric zirconia sensor of the type

$$\text{sample gas, Pt / YSZ / Pt, air} \quad (1)$$

to analyze the degree of the catalytic NO_x decomposition on the sample.

The conductivity of dense $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_3$ in the NO_2 - O_2 - N_2 gas mixtures is shown in Fig. 7 as a function of $P(\text{NO}_2)$ under the condition of fixed $P(\text{O}_2)$. In this article, unless noted by additional suffix, the partial pressures of the gaseous components are given in the as-mixed non-equilibrium state.

Fig. 6 Diagram of gas-mixtures controlling -system for the measurements of NO_x effects on the conductivity of $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_3$.

Fig. 7 Variation of the conductivity of dense $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_3$ by NO_2 .

The conductivity increases with $P(\text{NO}_2)$ irrespective of temperature and $P(\text{O}_2)$. However, the increasing tendency with $P(\text{NO}_2)$ becomes weaker with the increase in temperature and $P(\text{O}_2)$. At 750 °C, the conductivity at $P(\text{O}_2) = 0.1$ bar increases very weakly with $P(\text{NO}_2)$ while the conductivities at $P(\text{O}_2) = 10^{-3}$ and 10^{-5} bar are similar in absolute value and obviously increase with $P(\text{NO}_2)$ as shown in the figure. At 800 °C, the conductivity at $P(\text{O}_2) = 0.1$ bar is almost independent of $P(\text{NO}_2)$ and the dependence on $P(\text{NO}_2)$ of the conductivity at $P(\text{O}_2) = 10^{-3}$ bar becomes weaker. At 850 °C, the conductivity at $P(\text{O}_2) = 10^{-3}$ bar becomes almost independent of $P(\text{NO}_2)$.

Similar sets of measurements were also made using NO instead of NO_2 . However, so far, no clear effect was observed with NO for $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_3$ ⁽⁴⁾ as well as for La_2CuO_4 ^(3,4) and $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ ^(4,5)

4.2 Catalytic NO_2 decomposition on dense

$\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_3$ surface

Since $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_3$ works as a catalyst for NO_2 decomposition, the real oxygen partial pressure on the surface of $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_3$ is considered higher than the nominal $P(\text{O}_2)$ of the gas mixtures. Figure 8 shows the oxygen partial pressure of the downstream gas from the sample chamber, $P(\text{O}_2)_{\text{ds}}$, being monitored by a zirconia oxygen sensor. Here, $P(\text{O}_2)_{\text{ds}}$ is calculated from the observed EMF, E , of the cell (1) by the equation.

$$P(\text{O}_2)_{\text{dw}} = 0.21 \exp(-EF/4RT) \quad (2)$$

The catalytic decomposition of NO_2 on $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_3$ may take place by either of the following equations,

or

Fig. 8 NO_2 decomposition on high density $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_3$ analyzed by the zirconia sensor placed downstream side of the sample. Symbols: observed value for the outlet gas. Nominal upstream oxygen concentration: $P(\text{O}_2) = 0.00125$ bar.

When the decomposition takes place by Eq. (3), $P(\text{O}_2)_{\text{ds}}$ is expressed by

$$P(\text{O}_2)_{\text{ds}} = P(\text{O}_2) + (1/2)P(\text{NO}_2) \quad (5)$$

while Eq. (4) holds for the decomposition, we have

$$P(\text{O}_2)_{\text{ds}} = P(\text{O}_2) + P(\text{NO}_2) \quad (6)$$

In Fig. 8, the solid line indicates Eq. (6) while the dotted line is calculated by Eq. (5), where we put $P(\text{O}_2) = 1.26 \times 10^{-3}$ bar. The nominal oxygen concentration of the premixed gas in this case was 0.1% while the EMF of zirconia sensor rather indicated the $P(\text{O}_2)$ around 0.12 ~ 0.13%. The difference may be attributed to the sum of the errors in the composition of supplied gas-mixtures, in the accuracy of zirconia sensor and in a slightly pressurized gas-stream due to a bubbler for the NO_x trap being placed at the outlet of the gas-stream from the system.

As can be seen from Fig. 8, the observed $P(\text{O}_2)_{\text{ds}}$ is in between the calculated ones by Eqs. (5) and (6), and is rather close to the calculated value by Eq. (5). When NO_2 decomposes on the sample surface, the $P(\text{O}_2)$ in the gas phase increases. The oxygen partial pressure of the sample chamber is considered nearly the same to that of the outlet or downstream gas, $P(\text{O}_2)_{\text{ds}}$. Assuming that NO_2 decomposes by Eq. (3) on the surface of $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_3$, the conductivity of $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_3$ in NO_2 containing atmospheres are replotted as a function of $P(\text{O}_2)_{\text{ds}} = P(\text{O}_2) + (1/2)P(\text{NO}_2)$ and is shown in Fig. 9. In the figure, σ in the $\text{O}_2 - \text{N}_2$ atmospheres without NO_2 (open symbols in Fig. 5) is also plotted.

Since the predominant decomposition reaction is Eq. (3) and NO remains stably in the gas phase, it is natural that NO shows no effect on conductivity as experimentally observed, which was mentioned in 4.1.

4.3 Chemical potential pumping effect

Although the increase in oxygen concentration by the decomposition of NO_2 is already accounted in Fig. 9, there still remain large positive deviation in the conduc-

Fig. 9 Conductivity in NO_2 containing atmospheres compared with that without NO_2 as a function of $P(\text{O}_2)_{\text{ds}}$.

tivity in NO_2 containing atmosphere compared with that in the atmosphere without NO_2 , indicating the existence of conductivity enhancement effect by NO_2 besides the effect of simple decomposition of NO_2 . The effect is explained by the chemical potential pumping effect described in section 2. Fig. 10 schematically shows the quantitative evaluation of the effect.

The bulk electronic conductivity of transient metal oxides is determined by the carrier concentration and the mobility. The former is determined by the oxygen nonstoichiometry or the chemical potential of oxygen in the bulk. The latter is determined essentially by the electronic structure of the oxide. When the oxygen potential in the chamber or $P(\text{O}_2)_{\text{ds}}$ is determined by $\text{O}_2(\text{g})$ only, the conductivity of bulk $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_3$ is σ^0 indicated in Fig. 10. When NO_2 is introduced, the conductivity becomes σ^* . On the other hand, $P(\text{O}_2)_{\text{ds}}$ becomes the sum of $P(\text{O}_2)$ and the oxygen gas due to the

Fig. 10 Chemical potential pumping effect appeared in the conductivity enhancement by the surface decomposition of NO_2 on $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_3$.

Fig. 11 Pumped up oxygen potential $\Delta P(\text{O}_2)_{\text{eff}}$ from the gas mixtures of $\text{NO}_2\text{-O}_2\text{-N}_2$.

partial decomposition of NO_2 on the $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_3$ surface as described by Eq. (5). As shown in the figure, σ^* is much larger than the conductivity expected from $P(\text{O}_2)_{\text{ds}}$. It is because the effective oxygen potential on the surface is enhanced due to the continuous catalytic decomposition of NO_2 , as shown in Fig. 2 and 3.

The effective oxygen potential, $P(\text{O}_2)_{\text{eff}}$ is given by the $P(\text{O}_2)$ at which the conductivity in oxygen atmosphere without NO_2 becomes σ^* . The difference between the $P(\text{O}_2)_{\text{eff}}$ and $P(\text{O}_2)_{\text{dw}}$, $\Delta P(\text{O}_2)_{\text{eff}}$, is the oxygen potential pumped up from the NO_2 containing gas phase to the bulk of $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_3$. The value of $\log \Delta P(\text{O}_2)_{\text{eff}}$ is calculated from the data in Fig. 9 and is plotted in Fig. 11 as a function of $\log P(\text{NO}_2)$.

We can find characteristic features of the chemical potential pumping effect from the plot. At respective temperatures, $\Delta P(\text{O}_2)_{\text{eff}}$ is determined by $P(\text{NO}_2)$ irrespective of $P(\text{O}_2)$. At 750°C, $\Delta P(\text{O}_2)_{\text{eff}}$ is almost proportional to $P(\text{NO}_2)^2$. At 800-850°C, the dependence can be seen weaker, rather close to the first order of $P(\text{NO}_2)$. However, at the higher temperatures above 800°C, due to very small $\Delta P(\text{O}_2)_{\text{eff}}$, it is not easy to conclude the relationship between $\Delta P(\text{O}_2)_{\text{eff}}$ and $P(\text{NO}_2)$.

5 Chemical Potential Pumping Effect on porous $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_3$

The catalytic NO_2 decomposition on porous $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_3$ is examined by the measurements of $P(\text{O}_2)_{\text{ds}}$ and is shown in Fig. 12. Similar to the case in Fig. 8, the decomposition proceeds to the degree in between Eqs. (5) and (6), suggesting that the NO_2 decomposition on the surface of porous $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_3$ is essentially the same with the dense $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_3$. However, contrary to the case of dense material, the conductivity of porous materials in the NO_2 containing atmosphere is exactly the same to the O_2 atmosphere as shown in Fig. 13, and no chemical potential pumping effect due to NO_2 is

Fig. 12 NO_2 decomposition on low density $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_3$ analyzed by the zirconia sensor placed downstream side of the sample. Symbols: observed value for the outlet gas. Nominal upstream oxygen concentration: $P(\text{O}_2) = 0.00125$ bar.

Fig. 13 Chemical potential pumping effect of porous $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_3$ with NO_2 in the plot of conductivity vs. $P(\text{O}_2)_{\text{ds}}$. No effect was observed.

observed. This is exactly the phenomena predicted in 2.2 and Fig. 4.

6 Comparison with Other Oxides and Further Remarks

As shown in Fig. 11, $\Delta P(\text{O}_2)_{\text{eff}}$ for dense $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_3$ is proportional to $P(\text{NO}_2)^2$. Similar relationship has been found for the conductivity enhancement in La_2CuO_4 by NO_2 .³⁾ In these cases, the $P(\text{O}_2)_{\text{ds}}$ observed by the zirconia oxygen sensor is given essentially by

$$P(\text{O}_2)_{\text{ds}} = P(\text{O}_2) + (1/2)P(\text{NO}_2) \quad (5)$$

On the other hand, for $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ and $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$, thermogravimetric and potentiometric studies⁵⁾ revealed that $\Delta P(\text{O}_2)_{\text{eff}}$ is proportional to the first order of $P(\text{NO}_2)$. The difference of the $P(\text{NO}_2)$ dependence of $\Delta P(\text{O}_2)_{\text{eff}}$ is considered to be attributed to the difference in the decomposition process of NO_2 on the surface or in the oxygen activity enhanced zone in Fig. 2.

Let us consider more precisely the overall reaction expressed by Eqs. (3) and (4). As mentioned in section 2.1, NO_2 is unstable and highly oxidizing. It decomposes on appropriate catalytic surface to release highly active oxygen on the surface, which can be expressed by means of high effective oxygen partial pressure as shown in 4.3. When we consider the adsorbed oxygen, O_{ad} , on the catalytic surface, it stationarily stays on the surface as far as the decomposition reaction continuously takes place to give the high effective oxygen activity, $a_{\text{O eff}}$. The catalytic decomposition is expressed by

or

Assuming the NO_2 decomposition as the rate deter-

mining reaction, the activity of O_{ad} stationarily enhanced during the continuous catalytic decomposition may be expressed by

$$\Delta a_{\text{O eff}} = kP(\text{NO}_2) \quad (9)$$

or

$$\Delta a_{\text{O eff}} = k'P(\text{NO}_2)^{1/2} \quad (10)$$

Since we have

$$\Delta P(\text{O}_2)_{\text{eff}} = \Delta a_{\text{O eff}}^2, \quad (11)$$

we obtain the relationship exactly in accordance to our experimental data. That is, for $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_3$ and La_2CuO_4 ,

$$\text{NO}_2 \rightarrow \text{NO} + 1/2\text{O}_2; \Delta P(\text{O}_2)_{\text{eff}} \propto P(\text{NO}_2)^2 \quad (12)$$

For $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$ and $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$,

$$\text{NO}_2 \rightarrow 1/2\text{N}_2 + \text{O}_2; \Delta P(\text{O}_2)_{\text{eff}} \propto P(\text{NO}_2) \quad (13)$$

As shown above, the chemical potential pumping effect becomes weaker as the temperature increases. At high temperatures, O_{ad} produced by the decomposition of NO_2 may not strongly stick to the surface compared with the strong adsorption at the lower temperatures. Then, the high chemical potential of the produced O_{ad} may not be effectively transferred to the bulk of the oxide at high temperatures.

However, when the temperature decreased, the chemical diffusion in the oxide becomes slower and the relaxation time becomes longer, as demonstrated for the case of $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$.⁵⁾ That is, the accurate observation of chemical potential pumping effect becomes difficult at low temperatures.

When we apply the oxygen chemical potential pumping effect in chemical sensors, temperature control to the best condition would be important. Also, the oxides as sensing materials should be dense but the diffusion length should be short. That is, a dense thin plate type oxide would be the most sensitive structure of the sensing element.

7 Conclusion

The high effective oxygen potential of dilute NO_2 gas can be pumped up by the catalyst oxide. NO_2 releases oxygen of very high effective activity on the surface of oxide to give the oxide bulk the oxygen potential much higher than that of the gas phase. This phenomenon is clearly observed for dense materials, while for the oxides with porous and sufficient inner surface area, the chemical potential pumping effect is hardly observed. The effective oxygen potential, $\Delta P(\text{O}_2)_{\text{eff}}$ pumped up from the NO_2 containing atmosphere is determined by $P(\text{NO}_2)$ and T , independent of $P(\text{O}_2)$. In this paper, the phenomena is confirmed for $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_3$,

For La_2CuO_4 and $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_3$, the decomposition

reaction and pumped up chemical potential are given by

However, detailed surface reaction kinetics still remains to be clarified, especially why these different kinetics appear on the similar perovskite-type oxides.

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