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Perovskite-Type Oxides as Ethanol Sensors*

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Some of the perovskite oxides such as $(Ln, M)BO_3$ (Ln = lanthanoid element, M = alkaline earth metal, and B = transition metal) are good oxidation catalysts. When the compounds are maintained at 150–400°C and a trace amount of reducing gas (such as ethanol or carbon monoxide) in air comes in contact with the oxides, the resistivity of the oxides increases in proportion to the gas concentration with a comparatively short response time, and it recovers to the initial value when the gas is removed. A new type of quantitative ethanol sensor making use of this property is described.

1. Introduction

Recently, there has been an increasing demand for reliable ethanol sensors to reduce traffic accidents caused by drunken driving. Existing direct-detecting type sensors utilize several methods including: (a) color change in certain metal ions due to reduction by ethanol (*1*), (b) acid electrolytic ethanol fuel cell (*2*), (c) conductivity change in n-type semiconductors with adsorption of ethanol (*3*), and so on. Besides the direct type, there are also indirect-type sensors, the details of which are summarized by Abernethy et al. (*4*). These methods are not entirely satisfactory from the standpoint of sensitivity, stability, and the useful life of the catalyst.

Some of the perovskite-type oxides show high electric conductivity and exhibit oxidation–reduction catalytic characteristics. We have found that when a trace amount of a reducing gas (such as ethanol) in air comes into contact with such oxides maintained at 150–400°C, the resistivity increases nearly proportionally to the gas concentration with a comparatively short response time, and the value returns to the initial one when the gas is removed. In this report we describe ethanol sensors employing perovskite-type oxide catalysts. This type of sensor overcomes some of the problems encountered with existing sensors.

2. Experimental

2.1. Sample Preparation

Most of the sample preparations are similar to those described in previous papers (*5*, *6*). The synthesized powder was pulverized to 325-mesh size and mixed with a small amount of turpentine to make a paste. Subsequently, the paste was printed on an alumina plate through a silk net and dried. The sample was then heated at 1000°C for 10 min and cooled in air. Electrical contacts were made using platinum/gold mixed paint at both ends of the painted oxide film. The film thickness was 15 to 20 μm.

2.2. Measurement of Resistance Change against Ethanol

Known concentrations of ethanol were obtained using a flow-type generator, as shown in Fig. 1. Air was used as a carrier gas. Pure ethanol was in a bubbler kept at 0°C. The ethanol-saturated gas was diluted with large amounts of air to provide a final ethanol concentration of 30 to 1000 ppm. Flowmeter F_2 compensated for changes in the amount of

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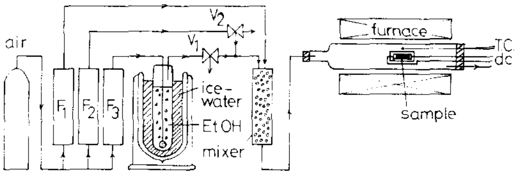

FIG. 1. Apparatus to generate a known concentration of ethanol vapor in air. Flowmeter F_2 compensates for the flow change caused by on–off switchings of valves V_1 and V_2, so that the total flow rate to the detection part may be kept constant. In the detecting part a small amount of dc current flows through the sample and its resistance change is recorded by a potentiometric recorder.

gas flow introduced into the detecting part. Two valves, V_1 and V_2, were used to introduce or stop the ethanol-containing gas at the detecting part. The final ethanol concentration was calibrated by gas chromatography using standard gas which was prepared by the method suggested by Oikawa (7), and the above generator also ensured that the ethanol vapor pressure reached equilibrium at 0°C. In the detecting part, the sensor element was kept between 100 and 400°C, and the resistance changes due to the presence of ethanol were recorded.

Several characteristics of the oxides are defined as follows: (i) Response ratio = $(R_{sat} - R_o)/R_o$; (ii) relative response ratio at time $t = (R_t - R_o)/R_{sat} - R_o$; and (iii) 90% response time (t_{90}), the time needed to reach 90% of ΔR_{sat}.

To ascertain the mechanism of the resistance change in the oxide, an oxide bed was used instead of the thin-film sample and the output gas was analyzed with a gas chromatograph (Hitachi, Type K53) using a column packed with 100-mesh size chromosorb 102. Weight changes of the sample on introduction to ethanol were recorded by a thermogravimetric balance (Shinku-riko, Type TGD-3000H).

3. Results and Discussion

A preliminary study showed that *B* ions in a (*Ln*, *M*)*B*O_3 perovskite-type oxide play an important role in determining whether or not the oxide changes its resistivity in the presence of ethanol. The *B* ions which showed this activity relative to ethanol include Fe, Co, Ni, but not Mn. In addition, the performance can be described in terms of two factors: response ratio and response time. The Fe-containing samples generally showed a higher response ratio, while Co- and Ni-containing samples showed shorter response time.

3.1. $LaNiO_3$ and Its Derivatives

The response ratio of $LaNiO_3$ against ethanol concentrations is shown in Fig. 2. The compound begins to show activity at about 150°C, and the response ratio increases with temperature rise up to 270°C, and then decreases. The 90% response time decreases relatively rapidly as the temperature is elevated (Table I).

When Ni^{3+} in $LaNiO_3$ is partly replaced by Fe^{3+} ion, the response ratio is greatly improved. Figure 3 shows the response ratio of $LaNi_{1-y}Fe_yO_3$ at 350°C. The maximum response ratio is obtained at $0.4 \leq y \leq 0.6$.

3.2. $Ln_{0.5}Sr_{0.5}CoO_3$ (Ln: La, Pr, Sm, Gd) and Their Derivatives

Table II shows the response ratio of $Ln_{0.5}Sr_{0.5}CoO_3$ to 300 ppm ethanol at 330°C. The time needed to reach 90% of the saturation response ratio becomes longer as the atomic number of *Ln* increases. The response ratio increases as the *Ln* ionic radius decreases.

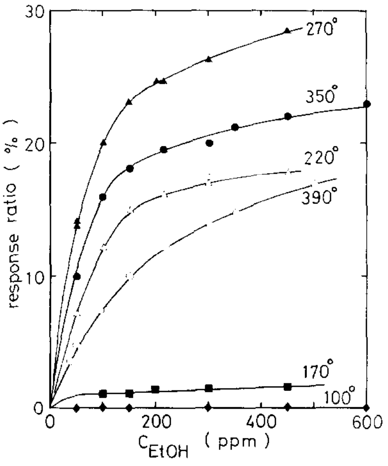

FIG. 2. Response ratio of $LaNiO_3$ against ethanol vapor at varied temperatures.

TABLE I

NINETY PERCENT RESPONSE TIME OF $LaNiO_3$ ELEMENTS FOR 150 ppm EtOH

T (°C)	t_{90} (sec)
100	Inactive (= ∞)
150	$>10^5$
170	$\sim 10^4$
220	$\sim 10^3$
270	120–150
330	40–60
350	5–10
390	<5

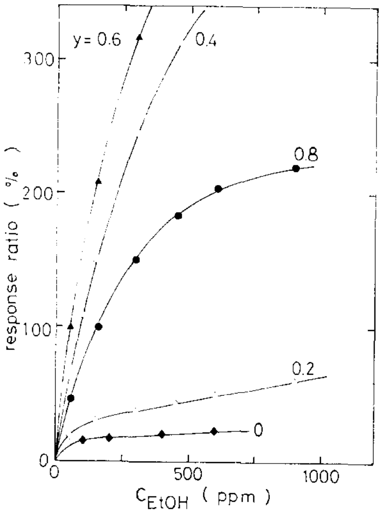

FIG. 3. Response ratio of $LaNi_{1-y}Fe_yO_3$ against ethanol vapor at 350°C.

However, it is possible that the spin states of B ions also may have a role in determining the catalytic activity of these oxides.

Considering both the response ratio and response time, $Sm_{0.5}Sr_{0.5}CoO_3$ shows the best trade-off characteristics. When Fe is doped in this compound, the resulting $Sm_{0.5}Sr_{0.5}Co_{1-y}Fe_yO_3$ has an almost cubic structure with a lattice constant increasing with y. There is a kink point at $y = 0.6$ suggesting that there is some kind of higher-order transformation around this composition. The response ratios for this system are summarized in Table II.

TABLE II

RESPONSE RATIO OF $Ln_{0.5}Sr_{0.5}CoO_3$ FOR 150 ppm EtOH AND RELATED COMPOUNDS AT 330°C

Compound	Response ratio (%)	t_{90} (sec)
$La_{0.5}Sr_{0.5}CoO_3$	25	50
$Nd_{0.5}Sr_{0.5}CoO_3$	40	150
$Sm_{0.5}Sr_{0.5}CoO_3$	50	100
$Gd_{0.5}Sr_{0.5}CoO_3$	90	250
$Sm_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_3$	130	—
$Sm_{0.5}Sr_{0.5}Co_{0.5}Fe_{0.5}O_3$	400	—
$Sm_{0.5}Sr_{0.5}FeO_3$	1200	—

3.3. *Resistance Change Mechanism*

In an attempt to understand the mechanism of resistance change of the oxides in the presence of ethanol, two possibilities were examined in the case of $LaNiO_3$. If the adsorption of ethanol on the oxide surface is the controlling factor, then the amount of the gas adsorbed should increase as the temperature is raised, because the response ratio increases with temperature, up to 270°C. The results of TGA measurements are summarized in Table III. As seen from this table, the weight increase is greater at lower temperatures where no net change in the resistance occurred (cf. Fig. 2). In addition, the time needed to reach saturation level is quite different from the time scale of resistance change. This implies that adsorption is not the cause of the resistance change.

TABLE III

WEIGHT CHANGE OF $LaNiO_3$ ON ADSORPTION OF C_2H_5OH

Temperature (°C)	Saturation amount[a] (μg)	Time for saturation (min)
145	>400	>120
205	260	≃60
250	100	≃20

[a] Initial weight of $LaNiO_3$ = 363.7 mg.

Analysis of the outlet gas from the oxide bed (3 mm diameter spheres) using gas chromatography showed a decrease in the ethanol concentration with increasing temperature. These experiments were carried out using pure oxygen as a carrier gas to make the interpretation easier. The results are shown in Fig. 4. Gas flow rate through the oxide bed is expressed by space velocity (Gas volume at NTP/hr · catalyst volume). The decrease in the ethanol concentration begins to take place when the temperature is higher than 150°C, and all the ethanol is consumed when the temperature is higher than 225°C. In air, the start of reaction is expected to shift slightly to the higher temperature side. The amounts of CO_2 and H_2O increased as the ethanol concentration became smaller; no other gases were detected.

Thus, we can give the overall reaction as,

$$C_2H_5OH + 3O_2 \xrightarrow{\text{cat.}} 2CO_2 + 3H_2O. \quad (1)$$

The data in Figs. 2 and 4 suggest the following mechanism for this reaction:

$$C_2H_5OH + 6O^{2-} \rightarrow 2CO_2 + 3H_2O + 6V^{\cdot\cdot} \quad (2)$$

$$6V^{\cdot\cdot} + 3O_2(\text{gas}) \rightleftarrows 6O^{2-} \quad (3)$$

where O^{2-} = oxygen ion in oxide lattice, $V^{\cdot\cdot}$ = oxygen ion vacancy of 2– charge. Assuming that the electrons of $V^{\cdot\cdot}$ are delocalized, we can formally express the M–O–M network as

$$\begin{aligned} M^{3+}\text{–}O^{2-}\text{–}M^{3+} &\rightarrow M^{3+}\text{–}V^{\cdot\cdot}\text{–}M^{3+} + \tfrac{1}{2}O_2, \\ M^{3+}\text{–}V^{\cdot\cdot}\text{–}M^{3+} &\rightleftarrows M^{2+}\text{–}V^{\circ}\text{–}M^{2+}. \\ \text{(I)} \qquad & \qquad \text{(II)} \end{aligned} \quad (4)$$

The actual state of electron distribution should be a linear combination of states (I) and (II).

The effects of oxygen vacancies of this type are: (a) breakdown of the metal anion ternary net through which collective electrons of M^{3+} move, (b) creation of scattering centers; and (c) change of spin state of M cations. A similar mechanism is proposed for CO oxidation by LnCoO$_3$ and related compounds by Parkash et al. (*8*) and for NO reduction by CO over Ru-containing perovskites by Voorhoeve et al. (*9*). Although they do not discuss the change of resistivity during the catalytic behaviors, it is likely that these compounds also will show similar resistivity changes.

If the above mechanism is correct, we would expect a change in resistivity with the oxygen partial pressure. This is indeed the case. As shown previously (*6*), the resistance is very sensitive to the oxygen partial pressure around $P_{O_2} = 0.2$ atm. If the reaction in Eq. (3) is correct, the weight change of $LaNiO_3$ against temperature under an appropriate oxygen pressure should be relatively large around 150–400°C. The result of a previous work showed that $LaNiO_3$ loses oxygen stepwise as the temperature is raised, and the first step takes place at temperatures between 150 and 400°C (*6*). The decrease in the response ratio of $LaNiO_3$ at $T > 270°C$ may be due to the increased rate of reverse reaction in Eq. (3), in which case the net change in the resistance becomes smaller.

The increase in response ratios in $LaNi_{1-y}Fe_yO_3$ and $Sm_{0.5}Sr_{0.5}Co_{1-y}Fe_yO_3$ when y is increased is probably related to the relative proportions of the transition metal ions in different spin states. When $y = 0.5$, the ratio of low-spin ions to high-spin ions would be nearly unity, as found by Mössbauer and other studies.

The resistivity changes against temperature for $LaNi_{1-y}Co_yO_3$, $LaCo_{1-x}Fe_yO_3$, and $LaNi_{1-y}Fe_yO_3$ are reported by Rao et al. (*10*).

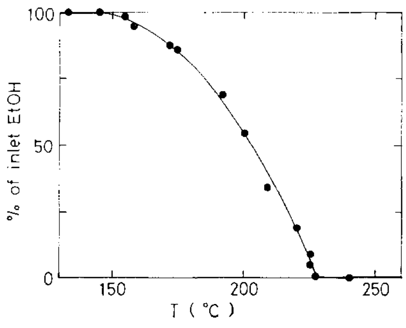

FIG. 4. Oxidation of ethanol vapor in O_2 by $LaNiO_3$. Experimental conditions: space velocity, 4000 hr^{-1}; column, chromosorb 102, 1 m long kept at 150°C; GC detector, thermal conductivity-type detector, detector temperature, 100°C; GC carrier gas, He 60 ml/min.

They found a shift from metallic to semiconductive behavior in the last two systems as the Fe content increased and explained the electron transport and magnetic properties in terms of the localized versus collective behavior of the $3d$ electrons. According to them, the $3d$ electrons in the low-spin Ni^{3+} ions are collective while they are localized in the high-spin Fe^{3+} ions. They also report that in $La_{1-x}Sr_xCoO_3$, the oxidation activity is enhanced when $Sr \gtrsim 0.3$ due to the presence of time-averaged electronic configurations of B ions in such a system. This line of argument is useful in explaining the enhancement of the response ratio with an Fe content in $LaNi_{1-x}Fe_yO_3$. It is likely that the high-spin state acts as the active adsorption site and the low-spin state reduces the activation energy for the oxygen-transfer reaction; this line of study should be carried out further to clarify the mechanism.

Direct evidence for the participation of oxide ions in the crystal lattice in oxidizing ethanol could be obtained by ^{18}O isotope exchange experiments. Such studies are presently in progress in this laboratory. Measurements of oxygen diffusion constants in $Nd_{1-x}Sr_xCoO_3$ at room temperature by Kudo et al. gave the value $D \simeq 10^{-11}$ to 10^{-14} cm^2/sec (*11*). With these magnitudes at room temperature, it is very likely that the oxygen ions in the lattice are more mobile at elevated temperatures in the oxidation reaction of ethanol.

3.4. Application to Ethanol Sensor and Other Gas Sensors

The breath ethanol level of intoxicated persons is almost proportional to the blood ethanol level and it is usually less than 500 ppm. It is exactly in this range that the perovskite-type oxides studied here show nearly linear response with relatively quick response time.

We feel that these oxides could be employed effectively for quantitative detection of ethanol. The stability of a prototype sensor has proved to be good; some of the characteristics are summarized in Table IV. These oxides did not show any resistivity change against 5 vol% H_2O and/or 1 vol% CO_2, which are considered as sources for erroneous operations of sensors under ambient atmosphere.

TABLE IV

SOME CHARACTERISTICS OF PROTOTYPE ETHANOL SENSOR

Compound	$LaNiO_3$
Response ratio	20% against 200 ppm EtOH
Sensitivity	30 ppm
t_{90}	$\simeq 5$ sec
Ethanol on–off cycle	$>1.2 \times 10^4$ ~
Heat cycle (r.t. ~ 400°C)	$>5 \times 10^3$ ~
400°C keep	>2000 hr

As the oxidation of ethanol is the cause of the resistivity change, similar behavior would be expected to occur with other gases as well. Preliminary examination has shown that CO and certain organic molecules do exhibit the same phenomena although at temperatures different from ethanol. Detailed results of studies on these compounds will be published at a later date.

References

1. T. KITAGAWA, *Japan Analyst* **12**, 1074 (1963).
2. H. W. BAY, K. F. BLUTON, H. C. LIEB, AND H. G. OSWIN, *Nature (London)* **240** (3), 52 (1972).
3. D. P. MCARTHUR, H. BLISS, AND J. B. BUTT, *J. Catal.* **28**, 183 (1973).
4. C. N. ABERNETHY III AND E. D. SUSSMAN, "Laboratory Evaluation of Alcohol Safety Interlock Systems," Vol. 1, Department of Transportations, National Highway Traffic Safety Administration Research Institute (1974).
5. H. OBAYASHI, T. KUDO, AND T. GEJO, *Japan. J. Appl. Phys.* **13**, 1 (1974).
6. H. OBAYASHI AND T. KUDO, *Japan. J. Appl. Phys.* **14**, 330 (1975).
7. T. OIKAWA, *J. Hygienic Chem. (Japan)* **13**, 116 (1967).
8. O. PRAKASH, P. GAUGULY, G. R. RAO, AND C. N. R. RAO, *Mat. Res. Bull.* **9**, 1173 (1974).
9. R. J. H. VOORHOEVE, J. P. REMEIKA, AND L. E. TRIMBLE, *Mat. Res. Bull.* **9**, 1393 (1974).
10. C. N. R. RAO, O. PRAKASH, AND P. G. ANGULY, *J. Solid State Chem.*, in press.
11. T. KUDO, H. OBAYASHI, AND T. GEJO, *J. Electrochem. Soc.* **122**, 159 (1975).