JOURNAL OF MATERIALS SCIENCE 20 (1985) 1207–1210

Physicochemical properties of rare earth perovskite oxides used as gas sensor material

TSUYOSHI ARAKAWA, HIROSHI KURACHI, JIRO SHIOKAWA
Department of Applied Chemistry, Faculty of Engineering, Osaka University, 2-1 Yamadaoka, Suita-shi, Osaka-fu, Japan

The change of the conductivity in the rare earth perovskite oxide took place after the chemisorption of flammable gases. The sensitivity for methanol was highest. From the conductivity change of these perovskite oxides after the injection of methanol, the energy needed to promote an electron from a conducting to a nonconducting state, $\Delta E = E_c - E_t$, could be derived from the equation $\sigma = A\sigma_0 \exp(-\Delta E/kT)$. $LnCoO_3$ had the smallest ΔE and ΔH (metal-O), which is the binding energy of oxygen coordinating to the metal ions, but exhibited the highest activity for gas sensing. The gas sensing mechanism was also considered.

1. Introduction

The detection of toxic and flammable gases is a matter of urgent public concern. The requirements to detect toxic and flammable gases have led to the development of gas detectable devices. A number of the most recent devices involving applications of surface chemistry and physics can be termed gas sensors, which include operating characteristics such as high sensitivity, fast response and a high degree of specificity. It is well known that the metal oxide semiconductors, ZnO or SnO_2, are used as gas sensor materials [1–3]. A decrease in electric resistance of an n-type oxide semiconductor is observed when a reducing gas is adsorbed onto the surface.

This paper describes in the main part the change in the conductivity of rare earth perovskite oxides in an attempt to obtain a new gas sensor material. Some of the perovskite type oxides show high electrical conductivity and exhibit oxidation–reduction catalytic characteristics. In particular, rare earth cobaltates have been suggested as substitutes for noble metals in electro-catalysis and in automotive-exhaust catalysis [4–6]. In the oxidation reaction of carbon monoxide or alcohols, the reactive gases cause a change in the oxygen balance of an oxide when the gases come into contact with the surface of the perovskite oxide at elevated temperatures. Thus, it is expected that a change in the electrical resistance of the perovskite is caused by the adsorption of reducing gases.

2. Experimental details

2.1. Materials

The samples were prepared by the solid-state reaction of dried Ln_2O_3 (Ln = La–Gd) and the transition metal oxides (Fe_2O_3, Cr_2O_3, Mn_2O_3 and CoO). The well-ground mixtures of the components were fired at 1300° C in air for 10 h. These compounds had perovskite structures, as determined by X-ray diffraction. Their BET surface was smaller than $2\,m^2\,g^{-1}$ in all cases.

2.2. Measurements

A thin film of perovskite oxide for electrical measurements was prepared using a procedure similar to that reported previously [7]. The thin film was placed in a Pyrex glass tube and a gaseous mixture ($40\,cm\,min^{-1}$) of $N_2(100 - x$ vol%) and $O_2(x$ vol%) was passed through. Methanol, hydrogen and carbon monoxide were introduced at an injection port. The conductivity changes due to the presence of the reducing gases were recorded

0022–2461/85 $03.00 + .12

as a source of direct current; a d.c. voltage generator (10 V) was used. For $LnFeO_3$ and $LnCrO_3$, the electric current flowing through the thin film was measured with an electric recorder as the potential drop across a fixed resistance (400 Ω) to be connected in series with the thin film. The conductivity changes in $LnMnO_3$ and $LnCoO_3$ thin films were measured by conventional methods over the range 25 to 500° C; the current, which depended upon the resistance of the film, was converted to voltage and recorded using an electric recorder.

3. Results and discussion

3.1. The selectivity of gases

When methanol was introduced into the system, a conductivity change in the thin oxide film was observed. An isolated example of conductivity change is shown in Fig. 1. For the $SmCoO_3$ thin film, the conductivity decreases immediately after the injection of methanol and then is restored to its initial value. Chemisorption of methanol on $LnMnO_3$, $LnCoO_3$ and $LnCrO_3$ led to a decrease in the conductivity of the oxide, whereas on $LnFeO_3$ the reverse was observed. Thus it is understood that the former acted as a p-type and the latter as an n-type semiconductor. When hydrogen or carbon monoxide was introduced into the system, a conductivity change was also observed. The temperature at which the change in the electrical resistance of a thin oxide film began was higher than that in the case of methanol. The temperature dependence of the response ratio of $SmCoO_3$ to the injection of reducing gases (2.5×10^{-2} mmol) is shown in Fig. 2. The response ratio is defined as follows; response ratio $= R - R_0 / R_0 \times 100(\%)$, where R is the maximum resistance after the adsorption of a reducing gas, and R_0 is the resistance in steady gas flow. The sequence of selectivity was $CH_3OH > H_2 > CO$.

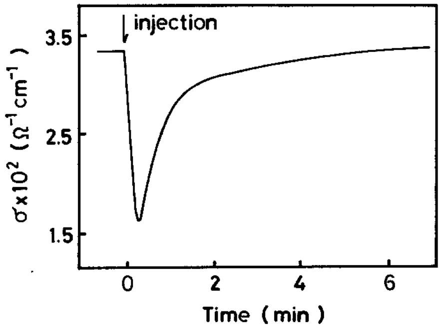

Figure 1 The variation of conductivity of $SmCoO_3$ with time after injection of CH_3OH at 240° C. Carrier gas: N_2 (40 cm^3 min^{-1}, contained $O_2 \simeq 50$ ppm).

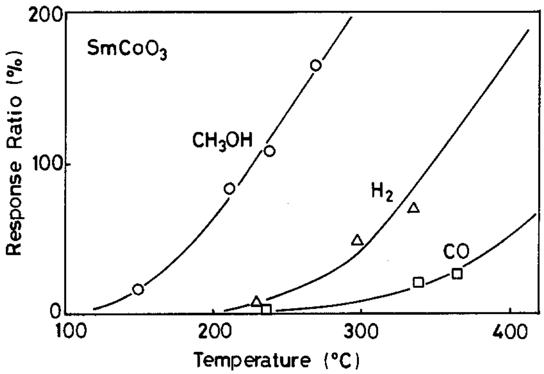

Figure 2 Response ratio as a function of temperature for CH_3OH, H_2 or CO adsorption.

3.2. The activity for gas sensing

The activity for methanol sensing, shown in Fig. 3, is given by the temperature at which for $LnMnO_3$ and $LnCoO_3$ a response ratio of 20% is attained, and for $LnCrO_3$ and $LnFeO_3$ the relative sensitivity attains 1. From the results it is clear that the activity of $SmCoO_3$ or $EuCoO_3$ is highest.

We may write for the conductivity;

$$\sigma = A\sigma_0 \exp\left(-(E_c - E_t)/kT\right), \qquad (1)$$

where σ is the minimum conductivity after the adsorption of a reducing gas, σ_0 is the conductivity in a steady gas flow, A is a constant, E_c is the

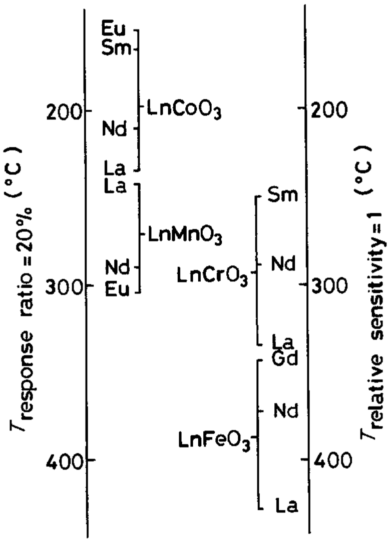

Figure 3 The sequence of the activity of various perovskite oxides for methanol sensing.

TABLE I ΔE^* for $LnMO_3$

Compound	ΔE (eV)	Compound	ΔE (eV)
$LaCoO_3$	0.14	$LaCrO_3$	0.28
$SmCoO_3$	0.13	$SmCrO_3$	0.22
$EuCoO_3$	0.09	$EuCrO_3$	0.14
$LaMnO_3$	0.25	$LaFeO_3$	0.98
$SmMnO_3$	0.25	$NdFeO_3$	0.74
$EuMnO_3$	0.27	$SmFeO_3$	0.55

*The absolute value.

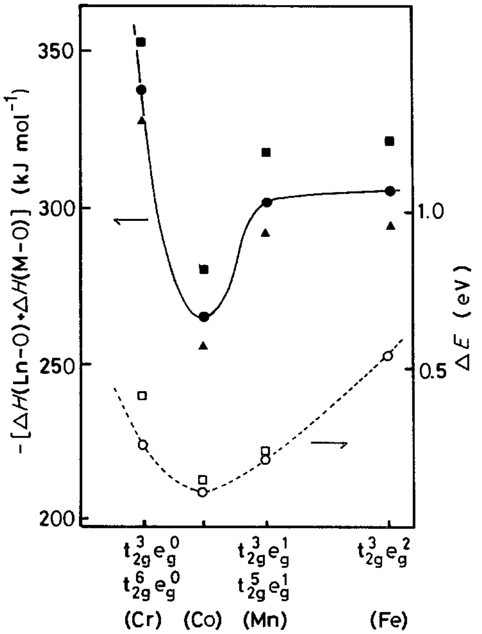

Figure 4 — $[\Delta H(\text{Ln–O}) + \Delta H(\text{M–O})]$ and ΔE as a function of the electronic configuration of the M ion for $LnMO_3$. ■, □: La, ●, ○: Sm, ▲: Eu.

energy of the conduction band, and E_t is the energy of the surface state [8, 9]. $E_c - E_t$ is taken as ΔE. In the derivation of Equation 1, there are several assumptions, i.e. the mobility of electrons and the ratio of the density of occupied and unoccupied states is insensitive to temperature. At constant surface coverage or constant density of states, ΔE is derived from a plot of $\ln(\sigma/\sigma_0)$ against $1/T$. From the conductivity changes of $LnMO_3$ after the injection of methanol, we estimated ΔE as summarized in Table I. ΔE for $SmCoO_3$ is smaller than that for other perovskite oxides. It is noteworthy that $LnCoO_3$, which has the highest sensitivity, has the smallest ΔE.

From studies of the electrical conductivity of the p-type rare earth perovskites, the most probable mechanism for the transport of charge carriers is by the hopping of positive holes*. That is, M^{4+} ions present as a result of native defects give rise to p-type extrinsic conduction. The activation energy (E_a) of the electrical transport for these oxides was low, i.e. the value of E_a for $LaCrO_3$ was 0.22 eV, for $LaMnO_3$ 0.13 eV. The value of ΔE for $LaCrO_3$ is close to that of E_a. When the reducing gases were adsorbed on $LnMO_3$ (M = Mn, Cr, Co), the conductivity decreased. Thus the chemisorption of the reducing gases led to a decrease in the number of positive holes as the charge carriers.

The reaction products in the outlet gas were CO_2 and H_2O in all cases. X-ray powder diffraction patterns of the thin oxide films measured before and after the reaction confirmed that there was no detectable loss in crystallinity. Therefore, it seems that the catalytic oxidation of methanol occurs on the surface of the thin solid. For $LnFeO_3$ (Ln = La–Gd), it has been pointed out that the sequence of the activity for methanol sensing is consistent with that of the activity for methanol oxidation [7]. The catalytic activity of $SmCoO_3$ for the methanol–O_2 reaction was tested over a wide range of temperature. Although the conditions for the catalytic reaction differed from those for gas sensing, the conversion of methanol to reaction products (CO_2 and H_2O) reached 50% at 260° C and 100% at 300° C.

The binding energy of oxygen which coordinates to metal ions in various perovskite oxides is estimated from the following equation [10],

$$\Delta H(\text{metal–O}) = \frac{1}{C_n m}\left(H_f - H_s m - \frac{n}{2} D_0\right), \qquad (2)$$

where H_f, H_s, D_0 and C_n are enthalpy of formation on one mole of oxide M_mO_n, the sublimation energy of metal, the dissociation energy of O_2 and the coordination number of metal ions, respectively. The values of $\Delta H(\text{Ln–O}) + \Delta H(\text{M–O})$ for the various perovskite oxides were calculated from Equation 2. The pattern between $\Delta H(\text{Ln–O}) + \Delta H(\text{M–O})$ and the electric configuration of the M ion according to Goodenough's classification method [11] is shown in Fig. 4, compared with that for ΔE. ΔE is evaluated by the absolute value, as ΔE is represented by the energy needed to promote the conductivity change

---

*A hopping polaron model has been employed to explain conduction in $LaCoO_3$. Small-polaron Cr^{4+} ions exist in $LaCrO_3$. For $LaMnO_3$ the charge carriers are localized at Mn^{4+} sites.

after the injection of methanol. A similar pattern has been observed in the catalytic oxidation of CO on various perovskite oxides [12]. From Fig. 4, it is obvious that the decrease in the binding energy corresponds well to the decrease in ΔE. ΔE for $LnCoO_3$ shows a minimum value at the minimum binding energy. These results indicate that the strength of the metal–oxygen bond in various perovskites is an important factor in methanol sensing, because the catalytic reaction occurs on the surface of the thin oxide film as described above. Thus, $LnMO_3$ materials conform to the interaction which relates the semiconductor conductivity to the surface chemical catalytic reactivity.

3.3. The mechanism for gas sensing

The conductivity change after the injection of CH_3OH, H_2 or CO has been closely related to the surface chemical reactivity as mentioned before. We may picture an adsorption or surface reaction occurring as

$$CO(g) + O^{2-}(s) \rightarrow CO_2(s) + 2e^- \qquad (3)$$

$$H_2(g) + O^{2-}(s) \rightarrow H_2O(s) + 2e^- \qquad (4)$$

$$CH_3OH(g) + 3O^{2-}(s) \rightarrow CO_2(s) + 2H_2O(s) + 6e^-. \qquad (5)$$

As an electron is liberated upon adsorption, where (s) denotes a surface species and (g) a gaseous species, because the magnitude of ΔE for $LnMO_3$ is correlated with that of the binding energy of metal–oxygen in $LnMO_3$, it appears that $O^{2-}(s)$ and lattice oxygen in $LnMO_3$ attains equilibrium fairly rapidly at the reaction temperature as follows:

$$O^{2-}(s) \rightleftarrows O_L^{2-} \ (O_L^{2-}\text{: lattice oxygen in } LnMO_3). \qquad (6)$$

Equations 3, 4 and 5 can result in the loss of a conductivity hole by interaction with the free electron. Hence the conductivity would decrease under the chemisorption of the reducing gases, as is observed. Recently, for the adsorption of CO on $LaCoO_3$, it has been proposed that CO is adsorbed onto surface O^{2-} ions and oxygen onto surface metallic ions (Co^{3+} or La^{3+}) of $LaCoO_3$ [13]. It has also been reported that the heat of adsorption of CO on $LaCoO_3$ was 0.15 to 0.05 eV in the temperature range, 113 to 273 K. ΔE, the energy needed to promote an electron from a conducting to a nonconducting state, for the adsorption of CO on $LaCoO_3$ was about 0.05 eV. This value was close to the heat of adsorption of CO on $LaCoO_3$.

The catalytic decomposition of methanol on $LnMO_3$ takes place at first as follows:

$$CH_3OH \rightarrow CH_3O + H. \qquad (7)$$

Moreover, (CH_3O) is decomposed to such adsorbed species as (CH_2O), (CHO) or CO [14]. CO and H_2, however, could not be detected in the outlet gases under the experimental conditions. Therefore, it appears that the reaction between these species and adsorbed oxygen is extremely fast. However, in Equation 5 the reaction path to final products H_2O and CO_2 seems to be very complex.

References

1. T. SEIYAMA, A. KATO, F. FUJIISHI and M. NAGTANI, *Anal. Chem.* **34** (1962) 1502.
2. T. SEIYAMA and S. KAGAWA, *ibid.* **38** (1966) 1069.
3. N. TAGUCHI, US Patent 3 695 848, 3 October (1972).
4. H. OBAYASHI, Y. SAKURAI and T. GOJO, *J. Solid State Chem.* **17** (1976) 299.
5. E. M. VOGEL, D. W. JOHNSON Jr and P. K. GALLAGHER, *J. Amer. Ceram. Soc.* **60** (1977) 31.
6. R. J. H. VOORHOEVE, D. W. JOHNSON Jr, J. P. REMEIKA and P. K. GALLAGHER, *Science* **195** (1977) 827.
7. T. ARAKAWA, S. TSUCHI-YA and J. SHIOKAWA, *J. Catal.* **74** (1982) 317.
8. S. R. MORRISON, *Surf. Sci.* **45** (1974) 20.
9. J. R. STETTER, *J. Colloid Interface Sci.* **65** (1978) 432.
10. R. J. H. VOORHOEVE, J. P. REMEIKA and L. E. TRIMBLE, "The Catalytic Chemistry of Nitrogen Oxides" (Plenum Press, New York, 1975) p. 145.
11. J. B. GOODENOUGH, "Progress in Solid State Chemistry" (Pergamon Press, Oxford, 1971) p. 145.
12. R. J. H. VOORHOEVE, "Advanced Materials in Catalysts" (Academic Press, Oxford, 1971) p. 129.
13. J. M. D. TASCÓN and L. GONZÁLEZ TEJUCA, *Z. Phys. Chem. Neue Folge, Bd.* **121** (1980) 63.
14. F. STEINBACH, H. J. SPENGLER, H. J. BOHLMANN and J. HYNDING, Proceedings 7th International Congress on Catalysis (Kodansha-Elsevier, Tokyo, 1981) p. 122.

*Received 18 April
and accepted 23 May 1984*