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Low Temperature Operation of Ceria-based Oxygen Sensors Using Perovskite-type Oxide Electrodes

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The lowest limit of operation temperature for ceria-based solid electrolyte oxygen sensor was significantly reduced with a use of perovskite-type oxide electrodes. In particular, the sensor with $La_{0.6}Sr_{0.4}Co_{0.98}Ni_{0.02}O_3$ exhibited theoretical emf even at 200 °C. The cathodic overpotential, which was measured by current interruption method, was low for an electrode operative at low temperatures.

Oxide ionic conductors have been widely employed in solid electrolyte oxygen sensors, especially for controlling the air/fuel ratio in automotive exhaust and detection of oxygen in molten iron. General construction of the oxygen concentration cell is described as O_2,Pt/stabilized zirconia/Pt,O_2. However, the oxygen sensor of such a construction is normally operative only above 600 °C using a Pt paste electrode. The lowest limit of operation temperature and the response rate of the sensor are strongly affected by electrode materials.$^{1)}$ The response of oxygen sensors with perovskite-type oxide electrodes are maintained to be Nernstian at lower temperature than those with Pt and noble metal electrodes. In this paper, we investigated the effect of cation composition of perovskite-type oxides on the response of oxygen sensor. The lowest operation temperature and response rate were strongly affected by doping of a small amount of additives in the perovskite lattice.

Calcia-doped ceria, being used as a solid electrolyte, was prepared by calcination of the powder mixture of CeO_2 and $CaCO_3$ at 1300 °C for 10 h. The calcined powder was then pressed into a disk (20 mm in diameter and 1.5 mm thick) by cold isostatic press at 2.7 t/cm^2 and was subsequently sintered at 1450 °C for 15 h. The electrode performances of various perovskite-type oxides were compared with that of a Pt paste electrode (Tanaka Matthey, KT-5). Perovskite-type oxides were prepared by pyrolysis of the mixture of corresponding metal acetates and subsequent solid state reaction at 900 °C. The oxide powders were mixed with turpentine oil and the slurry thus obtained was applied on to the flat surfaces of a solid electrolyte disk. The electrode was 6 mm in diameter and average thickness was 2 µm. Electromotive forces of following gas concentration cell were measured by the previous method.$^{2)}$

$$O_2\ (P_{O_2}'=1\ \text{atm}),\ M/(CeO_2)_{0.9}(CaO)_{0.1}/M,\ O_2\ (P_{O_2}), \qquad (1)$$

where M is an electrode material. The polarization curves for the Pt and oxide cathodes were measured by the current interruption method. The voltage drop after current interruption was separated into an I-R drop, which is simultaneously observed with current interruption, and overpotential, which decays with time.

Electromotive forces of the oxygen sensors with several kinds of electrodes are plotted in Fig. 1 as a function of temperature. The emf values were taken after 15 min from the change of P_{O_2} from 1 atm to 0.1 atm or to 0.01 atm. The broken lines in the figure are theoretical emf from the Nernst equation. Above 600 °C, the response of the sensor with a Pt electrode agreed with theoretical emf, but below, it was smaller than the expected one. This means that the electrode reaction is too slow to attain the equilibrium state at low temperatures. The use of some perovskite-type oxides electrode enables us to detect oxygen partial pressure at lower temperature than the Pt electrode.[3)] Especially, Sr-substituted perovskite-type oxide, $La_{0.6}Sr_{0.4}CoO_3$, was operative even at 300 °C.

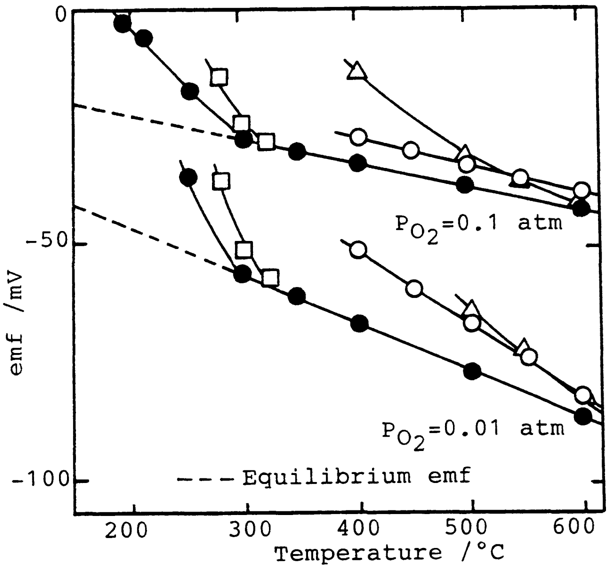

Fig. 1. Electromotive force of the oxygen concentration cell.
○ $LaCoO_3$, ● $La_{0.6}Sr_{0.4}CoO_3$
△ Pt paste, □ $La_{0.6}Sr_{0.4}MnO_3$

The lowest limit of temperature at which a sensor exhibits a Nernstian response, T_L, is evaluated for various perovskite-type oxide electrodes as summarized in Table 1. Cobalt-based oxides had lower T_L than manganese-based oxides. The lowest operation temperature of the sensor was reduced by Sr-substitution. The optimum composition of Sr-substitution was $La_{0.6}Sr_{0.4}CoO_3$, at which T_L of 300 °C was attained. In the perovskite-type oxides of $LaCoO_3$, $LaMnO_3$ and $LaFeO_3$, substitution of Sr for La is known to lead to the formation of oxygen vacancies due to charge compensation. The number of adsorption site for oxygen increases

Table 1. The lowest operation temperature of sensors with perovskite-type oxide electrodes

Electrode	T_L a) /°C	Electrode	T_L /°C
$LaCoO_3$	650	$LaMnO_3$	650
$La_{0.8}Sr_{0.2}CoO_3$	360	$La_{0.6}Sr_{0.4}MnO_3$	330
$La_{0.6}Sr_{0.4}CoO_3$	300	$La_{0.6}Sr_{0.4}MnO_3+CeO_2$	300
$La_{0.4}Sr_{0.6}CoO_3$	330	$La_{0.6}Sr_{0.4}FeO_3$	400
$La_{0.6}Sr_{0.4}CoO_3+CeO_2$	280	$La_{0.97}Sr_{0.03}NiO_3$	350
$La_{0.6}Sr_{0.4}Co_{0.98}Ni_{0.02}O_3$	200	$La_{0.6}Sr_{0.4}Co_{0.98}Fe_{0.02}O_3$	250
$La_{0.6}Sr_{0.4}Co_{0.95}Ni_{0.05}O_3$	210	$La_{0.6}Sr_{0.4}Co_{0.98}Mn_{0.02}O_3$	280
$La_{0.6}Sr_{0.4}Co_{0.9}Ni_{0.1}O_3$	220	$La_{0.6}Sr_{0.4}Co_{0.98}Cu_{0.02}O_3$	250
Pt paste	600		

a) T_L: The lowest temperature at which an Nernstian response is obtained for detection of P_{O_2}=1 atm-0.01 atm.

and activation of oxygen is promoted with Sr substitution. An addition of CeO_2 was also effective in lowering the operation temperature of $La_{0.6}Sr_{0.4}CoO_3$ and $La_{0.6}Sr_{0.4}MnO_3$. Since the sticking of electrodes to the electrolyte disk was significantly improved by the addition of CeO_2, the low operation temperature is attributed to a good electric contact between the electrode and electrolyte. It is noted that a very small amount of Ni or Fe substitution for Co significantly lowered T_L. Since sticking of the electrode was not improved with this substitution, the effect of Ni or Fe is obviously different from that of CeO_2. Of the sensors with various electrodes, the lowest operation temperature attained in the present study was 200 °C by use of the $La_{0.6}Sr_{0.4}Co_{0.98}Ni_{0.02}O_3$ electrode.

The response curves of the sensors with an abrupt change in P_{O_2} from 1 atm to 0.1 atm at 300 °C are shown in Fig. 2. As mentioned, the response of the sensor with a Pt electrode scarcely approached to theoretical emf at this temperature. The $La_{0.6}Sr_{0.4}Co_{0.98}Ni_{0.02}O_3$ electrode exhibited the most rapid response to reach theoretical emf within 1 min.

Cathodic polarization is expected to be related with the electrode performance as has been reported for metal electrodes.[1,3] The cathodic polarization curves of the sensors were measured at 600 °C by the current-interruption method (Fig. 3). It is evident that the $La_{0.6}Sr_{0.4}Co_{0.98}Ni_{0.02}O_3$ electrode has the lowest overpotential among various electrodes. Low overpotential for $La_{0.6}Sr_{0.4}Co_{0.98}Ni_{0.02}O_3$ is desirable not only as an oxygen electrode for an oxygen sensor, but also as one for a solid oxide fuel cell in deriving a large output

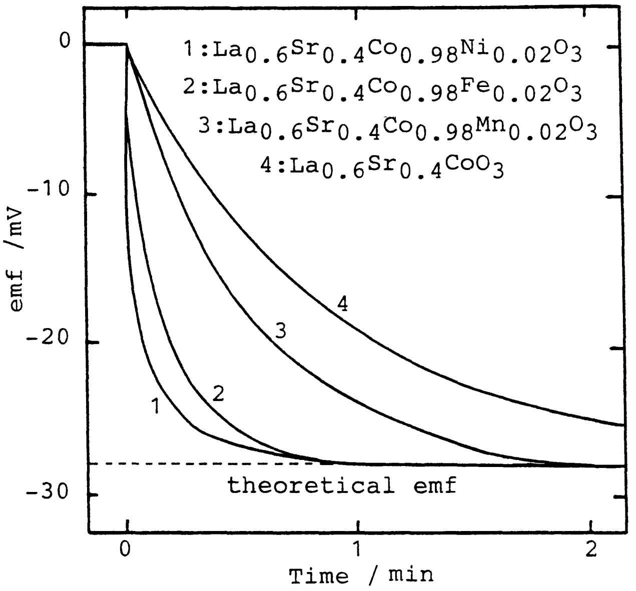

Fig. 2. Time course of the emf of oxygen concentration cell with various electrodes at 300 °C. (P'_{O_2}=1 atm, P_{O_2}=1 → 0.1 atm)

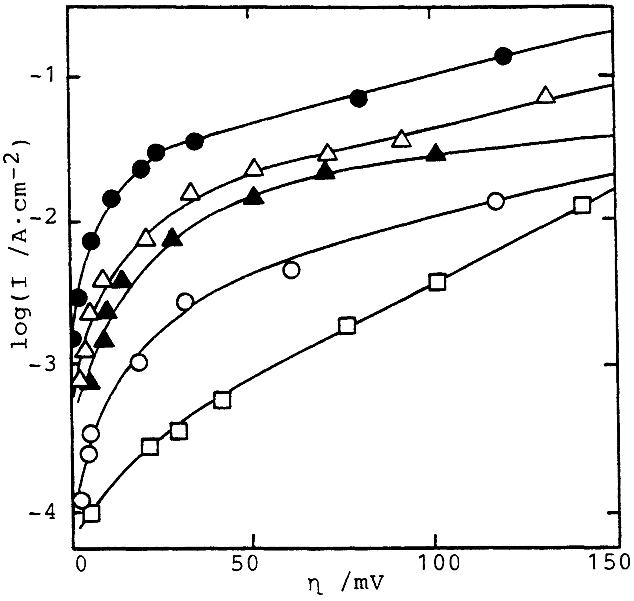

Fig. 3. Cathodic polarization curves for various electrodes at 600 °C. (P_{O_2}=1 atm)

● $La_{0.6}Sr_{0.4}Co_{0.98}Ni_{0.02}O_3$
△ $La_{0.6}Sr_{0.4}Co_{0.98}Fe_{0.02}O_3$
▲ $La_{0.6}Sr_{0.4}Co_{0.98}Mn_{0.02}O_3$
○ $La_{0.6}Sr_{0.4}CoO_3$ □ Pt paste

current. The current increased linearly with η in low η region, where the electrode reaction is controlled by the rate of charge transfer. From the slope of the plots in low η region, an exchange current density, I_0, is estimated from[4)]

$$I_0=IRT/(a_a+a_c)\eta F \qquad (2)$$

where a_a and a_c are the anodic and cathodic transfer coeffients, respectively; F is Faraday constant. The electrode which was effective for low temperature detection of P_{O_2} possessed a large exchange current. Thus, the charge transfer process is suggested to be important in determining the overall electrode reaction rate.

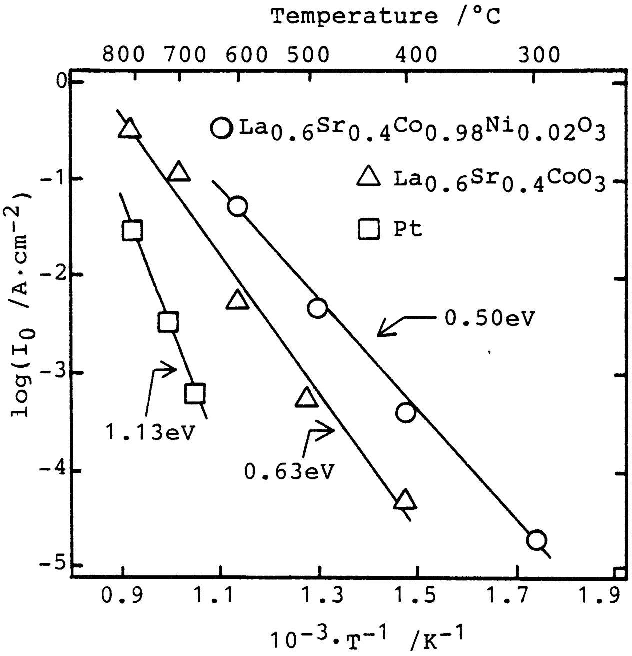

Fig. 4. Arrhenius plots of exchange current density, I_0.

The Arrhenius plots of the exchange current for the electrodes were linear as shown in Fig. 4. The apparent activation energies which are estimated from the slopes are shown in Fig. 4. The slopes for the perovskite-type oxide electrodes were more gradual than that for the Pt electrode. Thus, the perovskite-type oxide electrode exhibits large exchange current density, and hence large reaction rate, at relatively low temperatures. Pt electrode is more active than the perovskite system only above 1000 °C as can be expected from the slopes of the Arrhenius plots.

According to the sequence of reducibility reported by Nakamura et al.[5)] ($LaNiO_3$ > $LaMnO_3$ > $LaFeO_3$), the oxygen ions in $LaNiO_3$, being weakly bonded to metal cations, are expected to be active at low temperatures. But Ni-based perovskite easily decomposed into the component oxides. Thus, relatively high T_L for $La_{0.97}Sr_{0.03}NiO_3$ is likely due to partial decomposition of the perovskite structure. The $La_{0.6}Sr_{0.4}CoO_3$ crystal likely serves as host lattice to stabilize Ni ions in the perovskite structure. The small amount of Ni ions doped in this lattice significantly improved the electrode performance.

References

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