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Effect of Cation Substitution on the Oxygen Semipermeability of Perovskite-type Oxides

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Oxygen semipermeability of $LnCoO_3$-based perovskite-type oxides changed drastically by the partial substitution of A site and B site cations, Ba and Cu being the most effective substituents, respectively. Host rare earth cations (Ln) also affected the oxygen semipermeability, which increased with a decrease in ionic radius of Ln.

Perovskite-type oxides in the Ln(rare earth metal)-Co family have been extensively studied as catalysts for complete oxidation of hydrocarbons[1)] and electrode processes,[2)] or materials for gas sensors.[3,4)] In these applications, partial substitution of A site as well as B site cations is said to be indispensable to improve the functional properties of the oxides. We recently reported[5)] that $La_{1-x}Sr_xCo_{1-y}Fe_yO_3$ showed oxygen semipermeability at temperatures above 500 °C and was potential to be used as an oxygen permeation (extraction) membrane at elevated temperatures. It was also revealed that the oxygen semipermeability was deeply correlated with the mixed (ionic and electronic) conductive property of the oxides and, with the electronic conductivities being always very high, the rate was controlled by the ionic conduction by oxide ions.[6)] This paper describes how the oxygen semipermeability is affected by the cation substitution. As the oxygen semipermeability is certainly affected by the oxide composition, $LnCoO_3$-based oxides with fixed compositions shown in Table 1 were selected in order to know the effects of A site substitution, B site substitution and host rare earth metal substitution in this study.

An aqueous solution dissolving acetates or nitrate (Fe) of constituent

Table 1. Sintering temperature applied to prepare perovskite-type oxide discs

Sample	$T_{\mathrm{sin.}}{}^{a)}$ / °C
$La_{0.6}Sr_{0.4}Co_{0.8}B'_{0.2}O_3$	
B' = Co	1200
B' = Mn, Fe, Ni, Cu	1250
B' = Cr	1300
$La_{0.6}A'_{0.4}Co_{0.8}Fe_{0.2}O_3$	
A' = Na	970
A' = Ba	1050
A' = La, Sr, Ca	1250
$Ln_{0.6}Sr_{0.4}CoO_3$	
Ln = La, Pr, Nd, Sm, Gd	1200

a) Sintering temperature.

metals of a desired perovskite-type oxide at a desired proportion was evaporated to dryness, followed by the calcination in air at 850 °C for 10 h. X-Ray diffraction analyses showed that all the oxides prepared had a perovskite-type structure. The powder of each sample was compressed into a disc, 20 mm in diameter and ca. 2 mm thick, under the hydrostatic pressure of 260 MPa and sintered in air for 5 h. Sintering temperature was found to be important to control not only the density but the oxygen semipermeability of the disc samples and the optimized temperatures were experimentally determined for the respective samples (Table 1). Both sides of the sintered disc thus obtained were polished by emery paper to obtain a ca. 1.5 mm thick disc. Oxygen semipermeation experiments were carried out in an apparatus very similar to that reported before.[5)] Under the condition that each side of the disc was exposed to air and a flow of He (30 cm^3min^{-1}), respectively, oxygen passing through the disc from the air side to the He side at temperatures below 870 °C was monitored with a TCD detector.

Figure 1 shows the temperature dependence of the rate of oxygen permeation (J) through $La_{0.6}Sr_{0.4}Co_{0.8}B'_{0.2}O_3$. The onset temperatures of oxygen semipermeation were almost the same for all the oxides (500 - 550 °C). However, J at fixed temperatures were different with B' cations. The oxygen semipermeability was improved by the substitution of Cu and Ni for Co of mother $La_{0.6}Sr_{0.4}CoO_3$ oxide while it was deteriorated by that of Fe, Cr, and Mn. We reported previously that J of $La_{1-x}Sr_xCo_{1-y}Fe_yO_3$ decreased with an increase in Fe content[5)] and that this

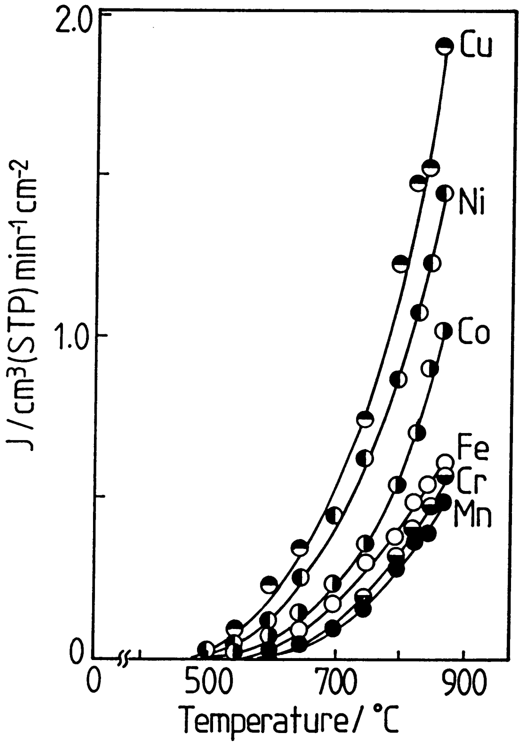

Fig. 1. Temperature dependence of the rate of oxygen permeation (J) through $La_{0.6}Sr_{0.4}Co_{0.8}B'_{0.2}O_3$ (B' = Cr, Mn, Fe, Co, Ni, Cu).

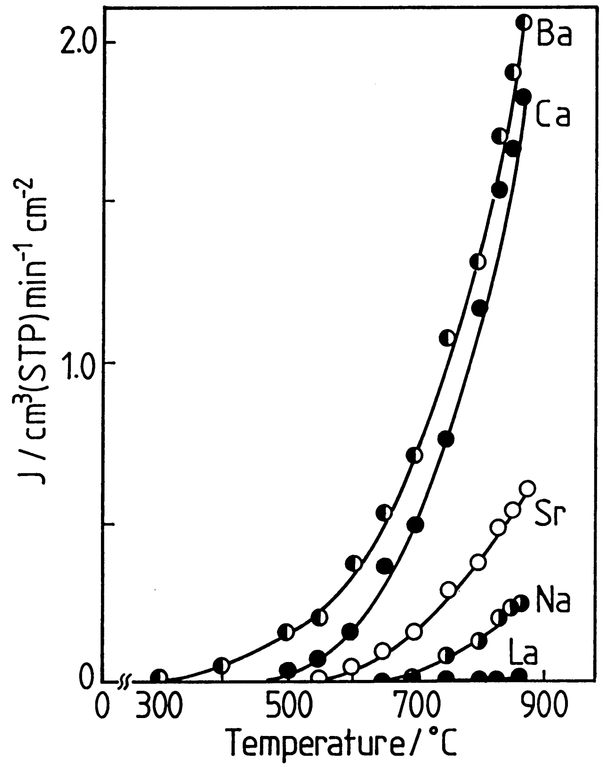

Fig. 2. Temperature dependence of the rate of oxygen permeation (J) through $La_{0.6}A'_{0.4}Co_{.8}Fe_{0.2}O_3$ (A' = Na, Ba, Ca, Sr).

was responsible to the decreasing oxide ion conductivity with Fe substitution.[6]) The same explanation may also be applicable to the deteriorative effect of Cr and Mn substitution. On the other hand, Cu and Ni ions naturally take the divalent oxidation state which is lower than the normal oxidation state of Co ion (trivalent) in a perovskite-type oxide. Accordingly, the substitution of Cu or Ni for Co may bring about the formation of oxide ion vacancies and therefore improve the oxygen semipermeability.

In Fig. 2, **J** of $La_{0.6}A'_{0.4}Co_{0.8}Fe_{0.2}O_3$ are depicted as a function of temperature. $LaCo_{0.8}Fe_{0.2}O_3$ scarcely permeated oxygen in the temperature range examined, while the A site-substituted samples showed oxygen semipermeating properties at higher temperature region. This appearance of the oxygen semipermeability is no doubt accomplished by the formation of oxide ion vacancies. **J** at fixed temperatures increased as Na < Sr < Ca < Ba. In marked contrast to the B site substitution, the onset temperature was largely lowered with A' cations, the effects being in the order of Na < Sr < Ca < Ba. It is worthy of note that the Ba substitution not only improve the rate of oxygen permeation but also lowers the onset temperature as low as 300 °C.

Oxygen semipermeability was found to be affected by host rare earth cations as well. In Fig. 3, **J** of $Ln_{0.6}Sr_{0.4}CoO_3$ at 750, 800, and 820 °C are plotted against ionic radii of rare earth cations. At each temperature **J** increased with a decrease in ionic radius, that is, La < Pr < Nd < Sm < Gd. The onset temperature of oxygen semipermeation was identical through a series of oxides (500 °C). From a geometric calculation on $A^{3+}B^{3+}O_3$ compounds, Kilner and Brook showed that the migration of oxide ions in the crystal lattice became easier with decreasing the size of A cation when B cation was fixed.[7]) It seems that the potential energy barrier for the oxide ion migration decreases with decreasing the ionic radius of rare earth cation.

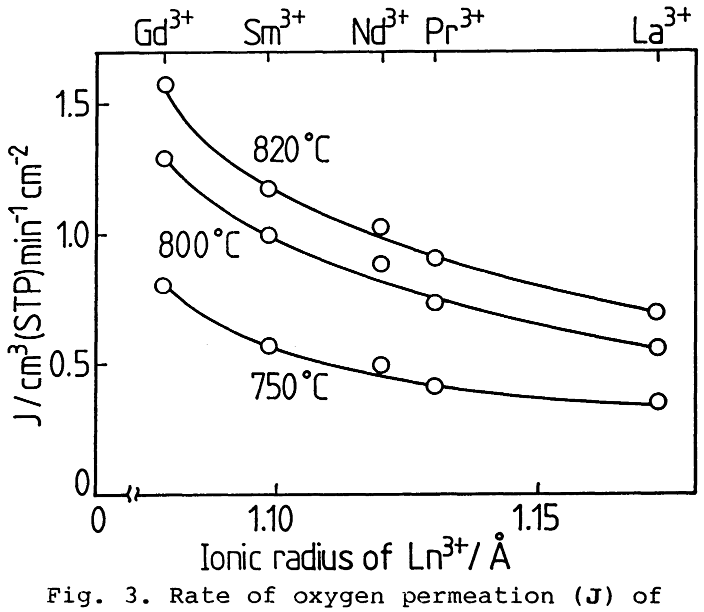

Fig. 3. Rate of oxygen permeation (**J**) of $Ln_{0.6}Sr_{0.4}CoO_3$ as a function of ionic radius of rare earth cations (Ln^{3+}).

The effects of cation substitution mentioned above can be summarized as follows.

B site substitution ;
Cu > Ni > Co > Fe > Cr > Mn
A site substitution ;
Ba > Ca > Sr > Na
Host rare earth cation ;
Gd > Sm > Nd > Pr > La

These results immediately lead us to an idea that perovskite-type oxides containing Cu, Ba, and Gd may be excellent in oxygen semipermeability. Figure 4 shows an example tested with $Gd_{0.2}Ba_{0.8}Co_{0.7}Cu_{0.2}Fe_{0.1}O_3$, in which Fe was incorporated so as to preserve perovskite-type structure at this high alkaline earth metal content.[8]) It is seen that J abruptly increased above 700 °C and reached a value as large as 5.5 $cm^3(STP)min^{-1}cm^{-2}$ at 870 °C, the highest value in our experiments, whereas J remained at an unexpected low level below 700 °C. This example seems to suggest a possibility of further improvements of oxygen permeation membrane by proper material design.

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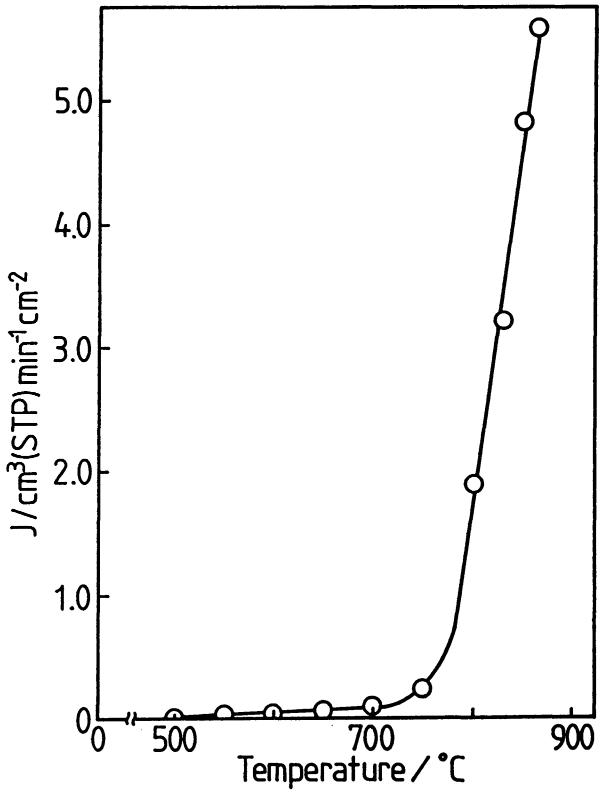

Fig. 4. Rate of oxygen permeation (J) of $Gd_{0.2}Ba_{0.8}Co_{0.7}Cu_{0.2}Fe_{0.1}O_3$.

References

1) R.J.H. Voorhoeve, "Advanced Materials in Catalysis," Academic Press, New York (1977), p. 134.
2) N. Miura, Y. Shimizu, and N. Yamazoe, Nippon Kagaku Kaishi, 1986, 751.
3) H. Obayashi and T. Kudo, Nippon Kagaku Kaishi, 1980, 1568.
4) Y. Yamamura, Y. Ninomiya, and S. Sekido, "Proceedings of the International Meeting on Chemical Sensors," Kodansha and Elsevier, Tokyo and Amsterdam (1983), p. 187.
5) Y. Teraoka, H.M. Zhang, S. Furukawa, and N. Yamazoe, Chem. Lett., 1985, 1743.
6) Y. Teraoka, H.M. Zhang, K. Okamoto, and N. Yamazoe, Mater. Res. Bull., 23(1), in press.
7) J.A. Kilner and R.J. Brook, Solid State Ionics, 6, 237 (1982).
8) Y. Teraoka, H.M. Zhang, and N. Yamazoe, Chem. Lett., 1985, 1367.

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