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OXYGEN PERMEATION THROUGH PEROVSKITE-TYPE OXIDES

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The rate of oxygen permeation through $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ was found to increase with an increase in Sr or Co content, showing that the permeability was mainly controlled by the amount of oxygen vacancies. The results obtained indicate that mixed conductive perovskite-type oxides are promising materials for oxygen permeation at elevated temperatures.

Some perovskite-type oxides which contain transition metals at B site show high electrical conductivity. The partial substitution of A site cations by other metal cations with lower valencies often brings about the formation of oxygen vacancies and appearance of ionic conduction. For example, $Nd_{0.8}Sr_{0.2}CoO_{3-\delta}$ was shown to have both good electronic conductivity and large ionic diffusion coefficient, i.e., $\approx 10^4$ $S\cdot cm^{-2}$ and $\approx 10^{-11}$ $cm^2\cdot s^{-1}$ at 25 °C, respectively.[1)] Perovskite-type oxides have been extensively studied for many technical applicaitons where mixed conduction by oxide ions and electrons (or holes) often seems to play an important role. We have reported[2,3)] that $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ can absorb or desorb a large amount of oxygen. This oxygen-sorptive properties plus the electronic conductive properties mentioned above suggest a possibility of using the defect perovskite-type oxides as an oxygen permeating membrane which can work without any need of electrodes and external electric circuit. In fact such a membrane using $La_{1-x}Sr_xCoO_{3-\delta}$ was claimed in a patent.[4)] In this paper, we have attemped to reveal the oxygen permeability of $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ in connection with its defect structure and oxygen-sorptive properties.

Eleven samples of $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ series oxides with varying x and y, as indicated by the circles in Fig. 3, were prepared by calcining the mixture of metal acetates (La, Sr, and Co) and nitrate (Fe) at 1123 K in air for 10 h. X-Ray diffraction analyses revealed that all the samples had perovskite-type structure, except $SrCoO_{2.5+\delta}$ which had brownmillerite-like structure with tetragonal unit cell.[5)] For measuring oxygen permeability, the powder of each sample thus prepared was compressed into a disc, 10 mm diameter and about 1 mm thick, under the hydrostatic pressure of ca. 260 MPa and sintered at 1473 K or 1523 K (for Fe containing samples) in air for 5 h. The apparent densities of the samples thus obtained were greater than 90% of theoretical. Both sides of the sintered disc were polished by emery paper before use. The oxygen permeability was measured with the apparatus shown in Fig. 1 in a temperature range 300-1150 K. Each sintered disc was welded to a mullite tube by using a silver ring as follows. A

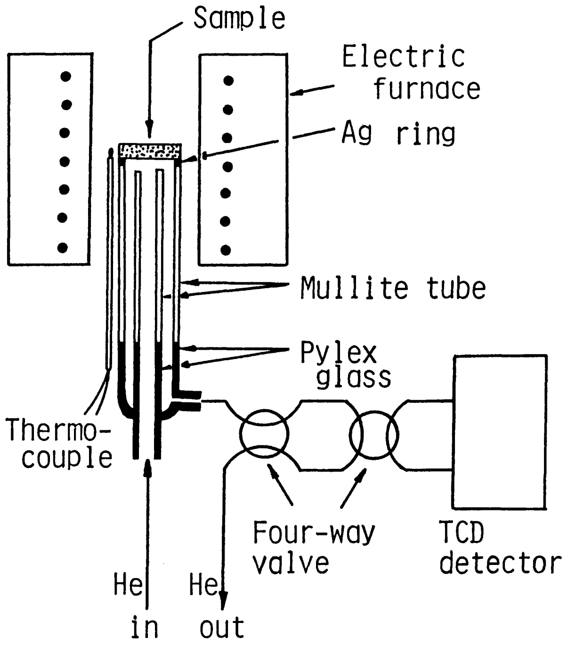

Fig. 1. The apparatus used for oxygen permeation measurements.

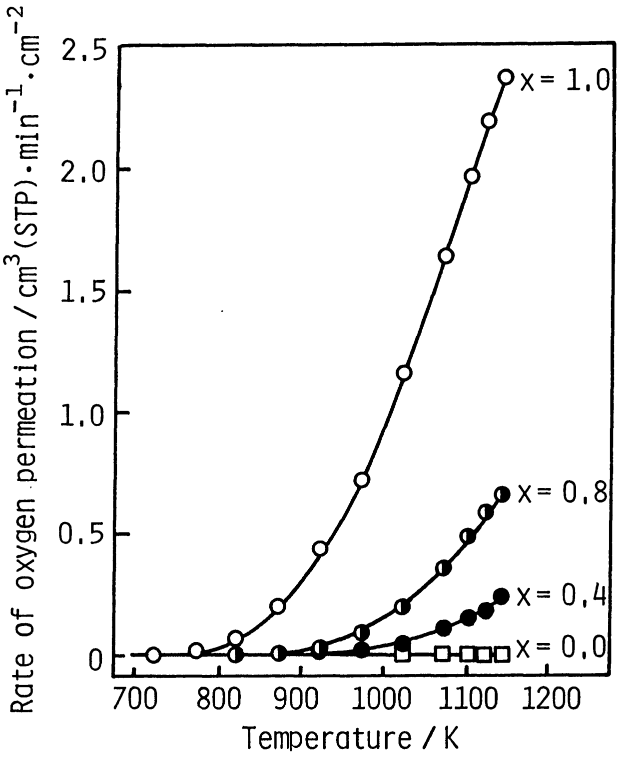

Fig. 2. Temperature dependence of the rate of oxygen permeation through $La_{1-x}Sr_xCo_{0.4}Fe_{0.6}O_{3-\delta}$ (x = 0.0, 0.4, 0.8, and 1.0).

silver ring was placed between the disc and the mullite tube and heated up to the melting point of silver (1234 K) in a vertical-type electric furnace. After holding for a few seconds at that temperature, they were cooled down to room temperature. This method was found to ensure the gas tightness of the cell. With one side of the disc being exposing to air, the other side was exposed to a flow of hellium (flow rate 30 cm^3/min) as shown in Fig. 1. Under this condition, the cell was heated stepwise from 300 K to 1150 K and the oxygen passing through the disc from the air side to the hellium side at respective temperatures was monitored with a thermal conductivity detector connected to the gas outlet line. Gas leakage through cracks of the disc, if present, could be detected by monitoring nitrogen concentration in the hellium gas stream.

Figure 2 shows the temperature dependence of the rate of oxygen permeation through $La_{1-x}Sr_xCo_{0.4}Fe_{0.6}O_{3-\delta}$ (x=0.0, 0.4, 0.8, and 1.0). It is seen that, while the sample with x=0 scarcely permeates oxygen in the temperature range examined, all the Sr-substituted samples show oxygen permeating properties at the higher temperature region; the onset temperature of oxygen permeation lowered with an increase in x and the rate of oxgen permeation at fixed temperature increased with x. The partial substitution of Sr^{2+} for La^{3+} creates oxygen vacancies, which, as we have reported,[3)] are intimately correlated with the oxygen sorptive properties of the perovskite-type oxide. The above results allow us to attribute the enhancement of oxygen permeability by Sr substitution also to the increase of oxygen vacancies. Ishigaki et al.[6)] reported that oxygen vacancies were responsible for the diffusion of oxide ions in $LaCoO_3$ single crystal. Accordingly, the determination of the amount of oxygen vacancies, δ, in the future study seems to be vary important for more quantitative discussion of the oxygen permeability.

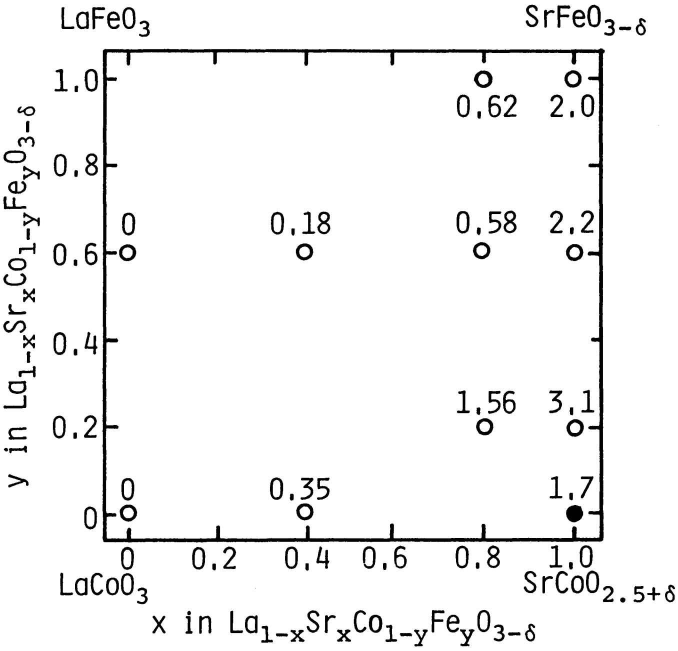

Fig. 3. Distribution of the rate of oxygen permeation at 1123 K. (in unit of $cm^3(STP)\cdot min^{-1}\cdot cm^{-2}$) sample thickness ; 0.1 cm

It was found that oxygen permeating properties were also influenced by the composition of B site cations. Figure 3 summarizes the rates of oxygen permeation at 1123 K for all the oxides investigated in a series of $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$. As stated above, the value of x is most influential to the oxygen permeation: the rate was zero for samples with x=0 irrespective of the B site composition (y) and increased with an increase in x for the samples with a fixed y. For a fixed x, on the other hand, the rate tended to increase significantly with decrease in y, i.e., with an increase in Co content, except for $SrCoO_{2.5+\delta}$ (x=1 and y=1). It is suspected that higher Co content is of advantage for the diffusion of oxide ions because Co^{3+} has a smaller ionic radius as well as smaller bonding energy to oxide ions than Fe^{3+}. Accordingly it is concluded that the permeability of this oxide system to oxygen can be improved as the contents of both Sr and Co increased as much as possible. A comment may be necessary on the unexpected low oxygen permeability of $SrCoO_{2.5+\delta}$. As previously reported,[5)] among the oxides tested in the present study, only this oxide has a structure somewhat different from perovskite and the absorption and desorption of oxygen result in the change of cell dimension and the reordering of oxygen vacancies. Such a structural difference may be a reason for the deviation of this oxide in the oxygen permeating properties. It is conceived that perovskite-type structure is important for the high permeability to oxygen. In this connection, an additional comment is stated on the role of Fe substitution for Co. Although as B site cations Co provides better oxygen permeating properties than Fe as stated, a small amount of Fe is nonetheless necessary to preserve perovskite-type structure at high Sr contents.[3)] The highest rate and the lowest onset temperature of oxygen permeation were observed with $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ in this study.

The dependence of the rate of oxygen permeation on the thickness of sample disc showed that the oxygen permeation follows the Fick's law at high temperatures (above 1073 K), while deviation from the law become significant as temperature lowered. This indicates that not only the gradient of oxygen chemical potential but also the oxygen sorption and desorption processes are important for the oxygen permeation.

Finally we compare the oxygen permeability of this oxide system with that of stabilized zirconia (Fig. 4). The rates of oxygen permeation (J) through stabilized zirconia under the short-circuited conditions were evaluated from the ionic conductivities (σ) obtained by Johansen and Cleary$^{7)}$ and Kingery et al.$^{8)}$ by using the following equation.

$$J\ [\mathrm{cm^3(STP)\cdot min^{-1}\cdot cm^{-2}}] = 1.72 \times 10^{-4}\ \frac{T\cdot\sigma}{d}\ \log\frac{P'_{O_2}}{P''_{O_2}}$$

where d is the thickness of disc and P'_{O_2} and P''_{O_2} are oxygen partial pressures: values of d, P'_{O_2}, and P''_{O_2} were taken as 0.1 cm, 0.21 atm, and 1×10^{-3} atm. As seen from Fig. 4, the permeation rates of perovskite-type oxides were one or two orders of magnitude greater than those of stabilized zirconia. Thus $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ appears to be a promising oxygen permeating material which works under the driving force of the difference in oxygen partial pressure without any need of external applied voltage. Although this oxide system need relatively high temperature for oxygen permeation, it is superior to oxygen permeable polymer membranes in the points of selectivity and thermal stability.

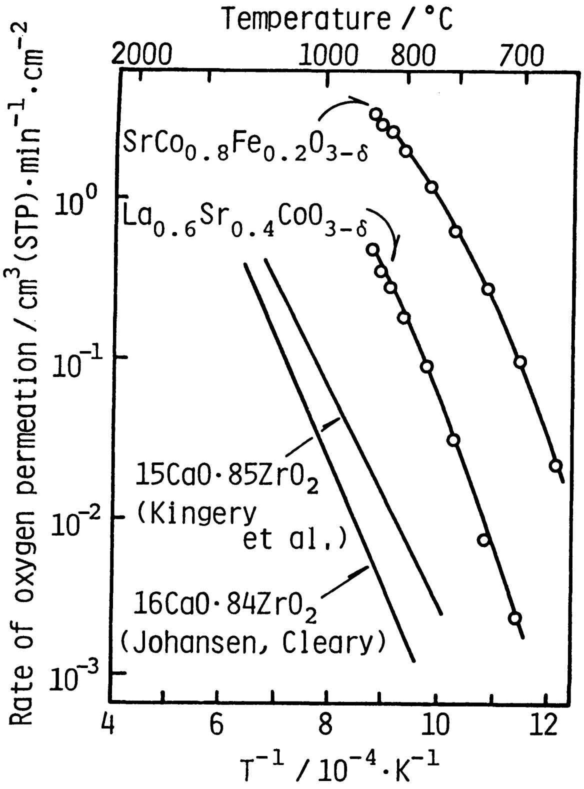

Fig. 4. Rate of oxygen permeation through $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$, $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ and stabilized zirconia.

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