**Microstructural Effect on Oxygen Permeability of Mixed Conducting Oxides**

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Dense oxide ionic conductors can transport oxygen ions under chemical potential gradients and, thus, separate oxygen from a gas mixture such as air [1]. Especially, perovskite-type mixed ionic-electronic conductors (MIEC) have been widely studied to apply as a cathode of SOFC and an oxygen separation membrane. To date, most of researches have been focused on the effect of cation substitution, electrical properties, oxygen transport and diffusion, nonstoichiometry and defect structure, and membrane synthesis and characterization. However, the microstructural effect on the oxygen permeability of polycrystalline mixed conductor has not been fully discussed. Furthermore, while most of studies for microstructural effects on ionic conductivity were devoted to solid electrolytes, such as doped zirconia [2], little attention has been given to perovskite-type mixed conductors. In this study, we intended to scrutinize the microstructural effects on the oxygen permeability of mixed conducting oxides, Sr- and Fe-doped $LaCoO_3$.

Composition of the powder synthesized by solid-state reaction was confirmed to coincide with theoretical values as shown in Table 1. Grain size could be controlled from 1.0 to 16.4 μm by varying sintering temperature and holding time (Fig. 1). Predominant contribution of electronic component on overall mixed conduction was revealed by electrical conductivity measurement, 4-probe method. We could find out that the activation energy for oxygen permeation of the conductor was changed with temperature range as shown in Fig. 2. The effect of surface modification with reactive composition, $LaSrCoO_3$, on the oxygen permeability of $LaSrCoFeO_3$ has been investigated. It was confirmed that the overall permeability of 1.7 mm-thick $LaSrCoFeO_3$ membrane is determined by bulk transport over all temperature range tested. Oxygen permeability increased for specimens sintered at higher temperature or for longer duration time, which indicated that grain boundaries have a negative effect on the oxygen permeability of $LaGaO_3$-based mixed conductors (Fig. 3). Consequently, grain boundary fraction and relative densities are assumed to be other factors in determining the oxygen permeability of Sr- and Fe-doped $LaGaO_3$ mixed conductor.

In the present study, an explicit oxygen permeability dependence on microstructure for mixed conducting membranes has been suggested. With these results, we could find out that the oxygen permeation flux of polycrystalline membrane can be predicted and controlled from readily controllable variables, such as sintering temperature and duration time.

References

[1] Y. Teraoka, H. M. Zhang, S. Furukawa, N. Yamazoe, *Chem. Lett.*, 1743 (1985).
[2] X. J. Chen, K. A. Khor, S. H. Chan, L. G. Yu, *Mat. Sci. & Eng. A*, **335** 246-252 (2002).

Table 1. Comparison between the theoretical value and measured value in weight ratio of compositional elements.

| Density (wt%) | La | Sr | Co | Fe |
|---|---|---|---|---|
| Theoretical value | 47.68 | 20.05 | 6.74 | 25.25 |
| Measured value | 48.77 | 20.13 | 6.06 | 25.03 |

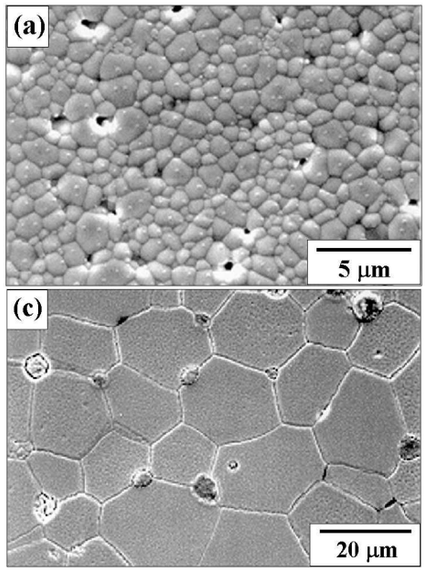


Fig. 1. SEM photographs of mixed conducting $LaSrCoFeO_3$ sintered at (a) 1200 °C and (c) 1400 °C for 5 h respectively.

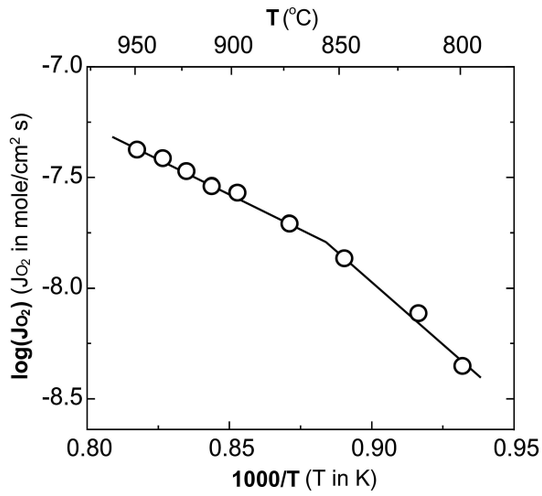


Fig. 2. Arrhenius plot for oxygen permeation flux of $LaSrCoFeO_3$ mixed conductor. The activation energy below 850 °C is 51.7 kJ/mol and that above 850 °C is 96.3 kJ/mol.

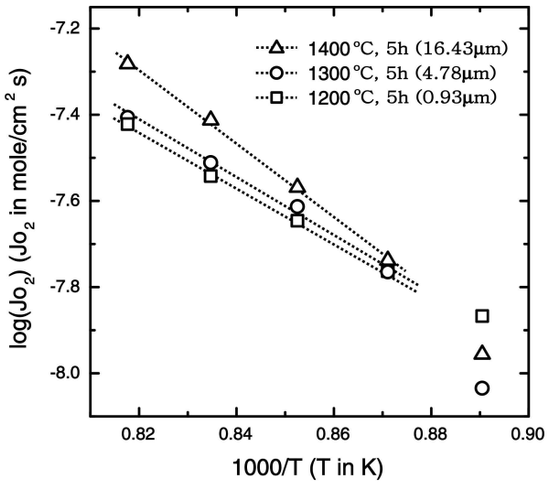


Fig. 3. Arrhenius plot for oxygen permeation flux of $LaSrCoFeO_3$ mixed conductor sintered at 1200, 1300, and 1400 °C for 5 h respectively.