

Oxygen permeation and microstructure of intergrowth perovskite Sr–La–Fe–Co based mixed-conductive ceramics

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The partial oxidation reforming method is advantageous to develop highly effective and low-cost products of H₂ gas used for fuel cells. For the partial oxidation, however, large amount of pure O₂ gas are desirable for acceleration of the H₂ production. Electronic and oxygen ionic conductive (mixed-conductive) oxide ceramics can be used to obtain pure O₂ gas, because the mixed conductivity contributes to permeate pure O₂ gas from air at the elevated temperatures. However, high permeation temperature of above 900°C is a problem. Higher temperature for the permeation incurs deterioration of both the ceramics and the steel to support the ceramics. We intend to find out a new mixed-conductive oxide with high oxygen permeation at lower temperatures than 900°C. In this study, we focus the Sr–La–Fe–Co oxides characterized by the intergrowth structures. We have investigated an appropriate condition to prepare Sr_{3–x}La_xFeCoO_{7–δ} ceramics with intergrowth perovskite structure. Then we have investigated microstructures as well as oxygen permeation properties of a dense Sr_{2.45}La_{0.55}FeCoO_{7–δ} ceramics. The oxygen permeation flux of the Sr_{2.45}La_{0.55}FeCoO_{7–δ} ceramics was as high as that of cubic perovskite Sr_{0.8}La_{0.2}Fe_{0.8}Ga_{0.2}O_{3–δ} ceramics.

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Key-words : Mixed conductor, Oxygen permeation, Intergrowth structure, Sr–La–Fe–Co oxide, Microstructure

[Received May 13, 2009; Accepted August 20, 2009]

1. Introduction

The partial oxidation reforming method is advantageous to develop highly effective and low-cost products of H₂ gas used for fuel cells. For the partial oxidation, however, large amount of pure O₂ gas are desirable for acceleration of the H₂ production, resulting from reaction between CH₄ and the pure O₂.¹⁾

Electronic and oxygen ionic conductive (mixed-conductive) oxide ceramics can be used to easily obtain pure O₂ gas,^{2–4)} because the mixed conductivity contributes to permeate pure O₂ gas from air at the elevated temperatures according to the following equation.⁵⁾

$$j(\text{O}_2) = \frac{RT}{16F^2L} \int_{\ln P(\text{O}_2)'}^{\ln P(\text{O}_2)''} \frac{\sigma_{\text{el}}\sigma_{\text{ion}}}{\sigma_{\text{el}} + \sigma_{\text{ion}}} d \ln P(\text{O}_2) \quad (1)$$

Where $j(\text{O}_2)$ is oxygen permeation flux; σ_{el} and σ_{ion} are the electronic and ionic conductivity; $P(\text{O}_2)''$ and $P(\text{O}_2)'$ are the oxygen partial pressures at both the oxygen-rich and oxygen-lean sides of the permeating membrane; F is the Farady constant; and L is the thickness of the membrane. Equation (1) means that high electronic as well as high oxygen ionic conduction is desirable for high oxygen permeation. However, it has been an obstacle that the permeation temperature is too high to use as feasible oxygen separators, because oxygen ionic conductivity σ_{ion} abruptly reduces at lower temperatures. Higher oxygen permeation results in deterioration of both the mixed-conductive ceramics and the steel to support the ceramics. In addition, greater heat should be supplied from outside to increase temperature up to 900°C.

With the point of view, we try to find out a new mixed-

conductive oxide with higher oxygen permeation at lower temperatures than 900°C. In particular, we focus on the Sr–La–Fe–Co (SLFC) oxides characterized by the intergrowth based perovskite structures. The oxygen ionic conduction results from the ionic hopping throughout oxygen vacancies in oxides, suggesting that the crystal structure is an important factor for the oxygen ionic conductivity and oxygen permeation. Simple cubic perovskite SLFC oxide is a typical mixed-conductor with high oxygen permeation. Crystal structure of the intergrowth based perovskite SLFC oxides is slightly different from the cubic perovskite SLFC oxide. This study investigates an effect of the slight difference in crystal structure on the oxygen permeation, which is still rarely studied.^{6,7)} Based on the results, we discuss if the intergrowth perovskite structure is advantageous to achieve high oxygen permeation at lower temperatures.

We have investigated an appropriate condition to prepare one of SLFC ceramics with intergrowth structure: Sr_{3–x}La_xFeCoO_{7–δ}, and then microstructures of the prepared sample. The chemical stability and density of the prepared ceramics sample was enough to use as an oxygen separator. Microstructures as well as oxygen permeation properties of the dense ceramic samples were investigated.

2. Experimentals

Ceramic samples of Sr_{3–x}La_xFeCoO_{7–δ} ($x = 0.3 - 0.7$) were prepared by a conventional solid state reaction process. Following to the chemical formula, the starting powders of SrCO₃ (99.5%), La₂O₃ (99.9%), Fe₂O₃ (99.99%) and Co₃O₄ (99.9%) were weighed and then ball-milled for 24 h in ethanol solution with ZrO₂ media with a diameter of 5 μm. The slurry was dried and calcined at 700–1000°C for 2 h in air. The obtained powders were formed into a pellet by uni-axially press. After then, the pellets were pressed under a hydrostatic pressure of 200 MPa. The pellet was sintered at 1400°C for 2 h in air.

The phase identification of the sintered sample was conducted

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by an ordinal X-ray powder diffraction method using Cu K α radiation. (XRPD; X'pert, PANalytical Inc.)

The oxygen permeation flux (OPF) of the sample was investigated under oxygen partial pressure difference between air (side I) and He gas with a flow rate of 20 sccm (side II). As shown in **Fig. 1**, a pellet sample with thickness of 1.2 mm were set between two quartz tubes, where a Pyrex glass ring was used for gas sealing. The sample was exposed to air when gas sealing was incomplete. After gas sealing, the He carrier gas was flowed with a rate of 20 sccm in side II. The gas composition was analyzed using a gas chromatograph (GC; GC323, GL Science Inc.). Leakage N₂ gas was negligible.

The microstructure of the sample surface was investigated by using an ordinal scanning electron microscopy (SEM; Tiny-SEM, Technex Inc.).

3. Results and discussion

XRPD patterns of the sintered Sr_{3-x}La_xFeCoO_{7- δ} ($x = 0.30 - 0.65$) are shown in **Fig. 2**. Sr₃Fe₂O_{7- δ} intergrowth type perovskite structure was observed as main phase. With increasing x , another phase of Sr₂FeO₄ became remarkable. As result, the solubility limit of Sr_{3-x}La_xFeCoO_{7- δ} was between $x = 0.55$ and 0.65 . The sample of the $x = 0.55$ was selected for OPF investigation. The sample of $x = 0.3$ was unstable at room temperature during keeping time owing to the reaction with CO₂ or moisture contained in ambient air. Thus the sample of $x = 0.3$ was not suitable for

the OPF investigation. It is same tendency to the case of the Sr₃Fe₂O₇ as reported in other literatures.^{6,7)} Reaction between Sr ions and moisture or CO₂ is active for the Sr₃Fe₂O_{7- δ} intergrowth type structure, thereby, further La substitution suppress the reaction.

OPF of the $x = 0.55$ sample at different temperatures between 800–900°C is shown in **Fig. 3**. The horizontal axis was the investigating duration time. The zero point of the investigating duration time signifies the point when the temperature reached 800°C. The duration investigating temperature rose from 800 to 900°C at first, and then returned to 800°C. Each investigating temperature was kept for 2 h.

As shown in **Fig. 3**, no time degeneration of OPF was observed at investigating temperatures less than 825°C. However the OPF investigated at further higher temperatures were found to be degenerated during keeping the temperature for 2 h. We suppose that the OPF degeneration is related to change of microstructure or crystal structure during rising temperature to 900°C. The SEM surface views of (a) the sample before the OPF investigation and (b) after the investigation are shown in **Fig. 4**. Anisotropic grain shape resulting from the intergrowth structure was observed in **Fig. 4(a)**. In contrast, the grain shape looks like more isotropic for **Fig. 4(b)**. In addition, smaller particles were observed in the vicinity of the grain boundaries. The difference in the microstructure implies that the intergrowth based structure is unstable over 825°C, thus other phase characterized by isotropic grains appeared. The XRPD pattern after investigating OPF showed that another phase of typical perovskite (Sr,L a)(Fe,Co)O₃ was present. (**Fig. 5**) The fact supposes that a part of the investigated sample decomposed from the intergrowth perovskite structure to the simple cubic perovskite one and other

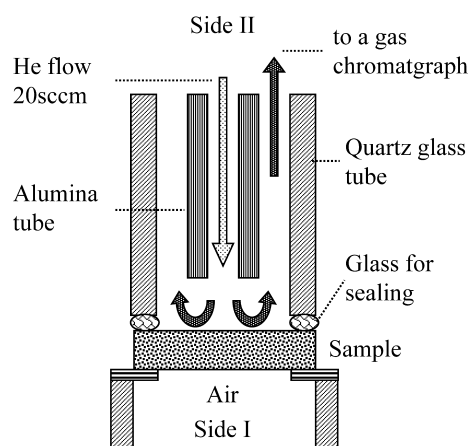


Fig. 1. Scheme of OPF investigating system.

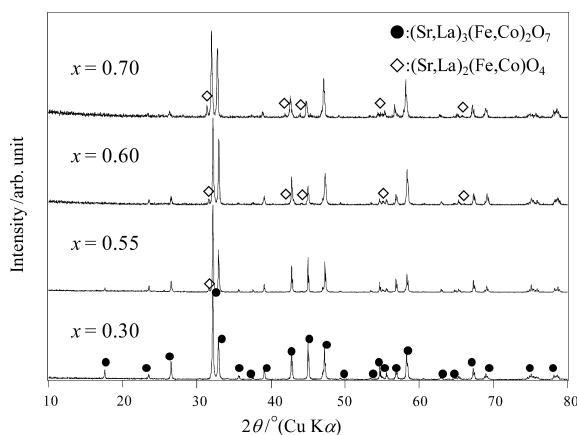


Fig. 2. XRPD patterns of the prepared Sr_{3-x}La_xFeCoO_{7- δ} ($x = 0.30 - 0.65$).

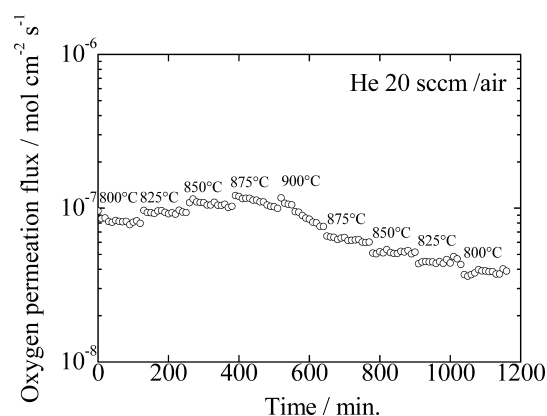


Fig. 3. OPF of the $x = 0.55$ sample investigated at different temperatures.

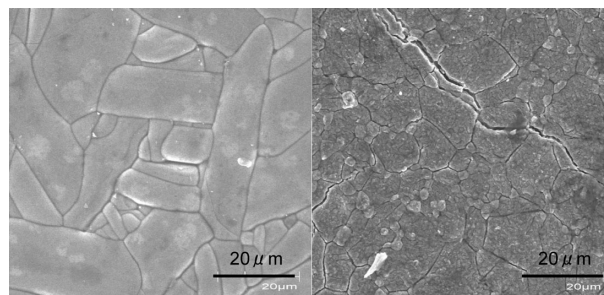


Fig. 4. SEM view of the $x = 0.55$ sample surface (a) before and (b) after OPF investigation.

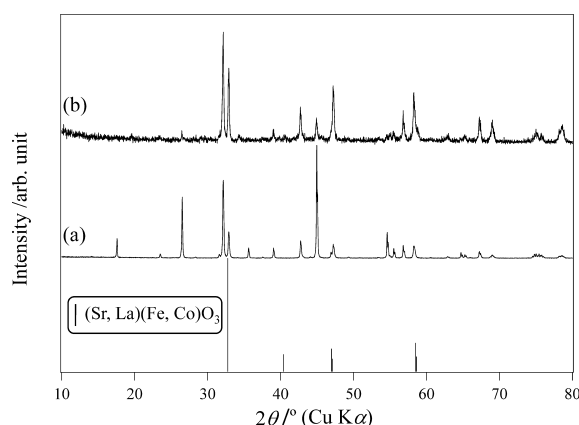


Fig. 5. XRPD patterns of the $x = 0.55$ sample (a) before and (b) after OPF investigation. The solid lines represent the XRPD pattern of cubic perovskite $(\text{Sr, La})(\text{Fe, Co})\text{O}_3$.

phases, accompanied with appearance of the isotropic particles between the grains. We suppose that the oxygen partial pressure difference between air and He with a flow rate of 20sccm at high temperature results in decomposition of the intergrowth structure as well as the microstructure change. It is considerable that the decomposition is closely related to the OPF deterioration investigated over 825°C. When investigating temperature was again decreased from 900 to 800°C, no OPF deterioration was observed during keeping the temperature, because lower temperature prevents the phase decomposition.

The OPF of the intergrowth based $\text{Sr}_{3-x}\text{La}_x\text{FeCoO}_{7-\delta}$ ($x = 0.55$) are compared to those of other typical cubic perovskite oxides characterized by high oxygen permeation. (Fig. 6) The OPF at 800°C before rising temperature up to 900°C was approximately $0.8 (\mu\text{mol cm}^{-1} \text{s}^{-1})$, which was slightly higher compared to $\text{Sr}_{0.7}\text{La}_{0.3}\text{Fe}_{0.8}\text{Ga}_{0.2}\text{O}_{3-\delta}$, which is a typical oxygen permeable oxide.⁸⁾ Thus the intergrowth based perovskite SLFC sample possesses a potential for oxygen permeable ceramics with high performance. The OPF investigated during cooling process was comparable or slightly lower than them because of the deterioration as described above.

4. Conclusion

We prepared the dense mixed-conductive $\text{Sr}_{2.45}\text{La}_{0.55}\text{FeCoO}_{7-\delta}$ ceramics by a conventional solid state reaction process. We investigated an appropriate condition to prepare the dense SLFC ceramics with intergrowth structure. The OPF and microstructure of dense $\text{Sr}_{2.45}\text{La}_{0.55}\text{FeCoO}_{7-\delta}$ ceramics were investigated.

No time degeneration of OPF was observed at investigating temperatures below 825°C. However the OPF was found to be

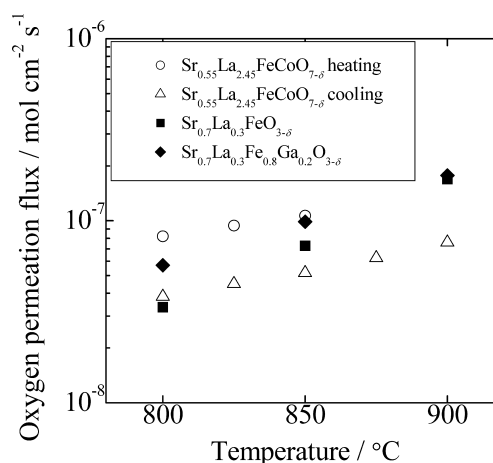


Fig. 6. Comparison of the OPF of the $x = 0.55$ sample with $\text{Sr}_{0.7}\text{La}_{0.3}\text{FeO}_{3-\delta}$ or $\text{Sr}_{0.7}\text{La}_{0.3}\text{Fe}_{0.8}\text{Ga}_{0.2}\text{O}_{3-\delta}$.⁸⁾

decreased during keeping time at further higher temperatures, suggesting that the intergrowth based perovskite structure was unstable over 825°C, where the typical cubic perovskite phase characterized by isotropic grains appeared. The OPF at 800°C was as high as that of $\text{Sr}_{0.7}\text{La}_{0.3}\text{FeO}_{3-\delta}$ or $\text{Sr}_{0.7}\text{La}_{0.3}\text{Fe}_{0.8}\text{Ga}_{0.2}\text{O}_{3-\delta}$.

Acknowledgments A part of this study was supported by a Grant-in Aid for Young Scientists (B) No.19760490 from the JSPS, Mukai Science and Technology Foundation and Iketani Science and Technology Foundation.

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