ABSTRACT

Reaction and cation diffusion for calcium substituted lanthanum cobaltite / rare earth substituted ceria are investigated by using diffusion couples of dense polycrystalline bodies annealed at temperatures $T = 1300 \sim 1500$ K. The interface of $\text{Ce}_{0.8}\text{Y}_{0.2}\text{O}_{1.9}/\text{La}_{0.8}\text{Ca}_{0.2}\text{Co}_3\text{O}_5$ was not stable when it is annealed at $T = 1150^\circ\text{C}$ for 14 hours, and the precipitation of secondary phase was observed on both surfaces. This secondary phase contains mainly cerium, yttrium, and lanthanum, and a small amount of calcium. Similar reaction is also observed at the interface of $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}/\text{La}_{0.8}\text{Ca}_{0.2}\text{Co}_3\text{O}_5$, and a thick layer of $(\text{Ce, Gd, Ca, La})_\text{O}_2$ is precipitated at the interface.

INTRODUCTION

Alkaline-earth substituted lanthanum cobaltites, $(\text{La, A})\text{Co}_3$, $(A = \text{Ca or Sr})$, have both high electrical conductivity and high catalytic activity for oxygen reduction, and are regarded as very promising cathode materials for cathodes in solid oxide fuel cells (SOFCs). However, a high reactivity with yttria stabilized zirconia (YSZ) electrolyte forming $\text{La}_2\text{Zr}_2\text{O}_7$ or alkaline earth zirconate $(\text{AZrO}_3)$ always causes the degradation of cell performance. Sase et al. reported that the interface of YSZ single crystal and $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_3\text{O}_5$ dense thin film prepared by pulsed laser deposition technique (PLD) at $T = 973$ K was not stable, and significant interdiffusion of cations and SrZrO$_3$ formation was possible during annealing in oxygen flow $T = 973$ K for 180 days (1). Rare earth
substituted ceria is often used as an interlayer to avoid the reaction, for example, Uchida et al. reported that the insertion of \((\text{CeO}_2)_{0.8}(\text{SmO}_1.5)_{0.2}\) interlayer (SDC) between YSZ and \(La_0.6Sr_0.4\text{CoO}_3\) resulted in a high performance (2).

Although there are very few papers about the reactivity of lanthanum cobaltite and ceria, the effect of diffusion of cations at the interface will not be negligible in the preparation or during the long term operation at high temperatures. The interdiffusion of cations may cause changes in electrical conductivity or catalytic activity of lanthanum cobaltites, and furthermore, chemical stabilities of both materials. In this paper, the reaction and cation diffusion are investigated at the interface of \((\text{La, Ca})\text{CoO}_3\) and \((\text{Ce, R})\text{O}_2\) \((\text{R} = \text{Y, Gd})\) by using diffusion couples of dense polycrystalline bodies. The elemental distribution in the vicinity of the surface was analyzed by secondary ion mass spectrometry (SIMS). The effect of alkaline earths and temperature was investigated.

**EXPERIMENTAL**

**Sample Preparation**

The sample compositions adopted in this investigation were \(La_{0.8}Ca_{0.2}\text{CoO}_3\) (abbreviated to LCC), \(Ce_{0.8}Y_{0.2}\text{O}_1.9\) (CYO) and \(Ce_{0.8}Gd_{0.2}\text{O}_1.9\) (CGO). The LCC was synthesized by ceramic method, and the dense polycrystalline body was prepared by sintering in air at \(T = 1523\) K \((1250^\circ\text{C})\). The dense polycrystalline bodies of CYO and CGO were prepared by sintering the commercial powders (Seimi Chemical Co. Ltd.) at \(T = 1673\) K. The surface of each sample was thoroughly polished by using diamond paste (Marumoto Struers K. K. Japan). A diffusion couple was prepared by putting the polished surfaces of two samples together, and tightly fixed with platinum wire. The couples of LCC+CYO, LCC+CGO were placed in platinum crucibles. The annealing conditions were, \(1060^\circ\text{C}\) for 5h or \(1150^\circ\text{C}\) for 14 h in air. The samples were rapidly cooled to room temperature.

**Analyses**

After annealing procedures, the diffusion couples were detached. The elemental distribution in the vicinity of the sample surface was analyzed by secondary ion mass spectrometry (SIMS, CAMECA ims5f) depth profiling. Prior to SIMS analyses, a thin gold layer was made on each sample surface to prevent undesirable charge-up effects. The sample surface was etched by a focused Cs\(^+\) ion beam (acceleration voltage = 10 kV), and emitted substances from the sample were accelerated and detected as secondary ions (acceleration voltage = -4.5 kV). The intensities of secondary ions \(^{16}\text{O}^+, ^{40}\text{Ca}^{16}\text{O}^+, ^{59}\text{Co}^{16}\text{O}^+, ^{89}\text{Y}^{16}\text{O}^+, ^{139}\text{La}^{16}\text{O}^+, ^{140}\text{Ce}^{16}\text{O}^+\) were collected as a function of etching time. After the measurements, the depth of etched area was measured by a surface profiler (Dektak\(^3\), Veeco/Sloan Co. Ltd). The depth profile of secondary ion intensity was drawn by assuming a constant sputtering rate. The surfaces of some samples after annealing were investigated by scanning electron microscope (SEM, VE-7000 Keyence Co.) / energy...
RESULTS AND DISCUSSION

Fig. 1 shows the depth profiles of secondary ion intensity ratios of \( \frac{I(M^{16}O^\text{+})}{I(16O^-)} \) (M = Ca, Co, Y, Ce) of CYO and LCC annealed at \( T = 1066^\circ\text{C} \) for 5h. In each analysis, the intensity ratio \( M^{16}O^\text{+}/16O^- \) has a linear dependence on the concentration of each cation \( C(M) \) in the samples. However, it should be noted that the comparison of intensity ratios among different \( M^{16}O^\text{+}/16O^- \) is not possible because each secondary ion has a different correlation factor. In the CYO sample, a small amount of diffusion of lanthanum component is observed in the range of depth < 0.5 \( \mu \text{m} \). The intensities of other components were almost flat; however, the intensities of \( ^{40}\text{Ca}^{16}O^\text{+}/16O^- \) and \( ^{59}\text{Co}^{16}O^\text{+}/16O^- \) are definitely higher than those of untreated CYO. On the other hand, some yttrium diffusion is observed for LCC (Fig. 1(b)). For the case of CGO+LCC annealed at the same temperature, the diffusions of calcium and cobalt components in CGO were more clearly observed as shown in Fig. 2(a). However, the diffusion behavior of calcium and cobalt varied from place to place on the CGO sample, which indicated that the calcium and cobalt distribution is quite inhomogeneous on the surface.

After the annealing at \( T = 1150^\circ\text{C} \) for 14 h, a remarkable change was observed at the interface with LCC. Both diffusion couples, CYO+LCC and CGO+LCC could be detached; however, both surfaces were covered by some precipitates. Fig. 3 shows the depth profiles of CYO and LCC, in which a thick layer mainly containing yttrium, cerium, lanthanum and calcium is found on both surfaces. In this precipitate, the intensity of \( ^{59}\text{Co}^{16}O^\text{+}/16O^- \) was suppressed as shown in the Fig. 3(b). Similar behavior was also observed for the case of CGO+LCC, i.e., a layer containing cerium, gadolinium, lanthanum and calcium is found on the surfaces (Fig. 4). It should be noted that in such layers, the cobalt intensity was low or exhibited somewhat irregular changes.

The SEM images of LCC after the annealing with GDC is shown as Fig. 5, in which the original surface of LCC was completely covered by a thick rugged layer of \( (\text{Ce, Gd, La, Ca})\text{O}_x \) precipitates. By using a standard less EDX quantification, the calcium content in this layer is determined to be about 0.4 atomic per cent. It was hard to estimate the lanthanum content because of the overlapping of \( \text{Ce(La)} \) and \( \text{(LaLa)} \) lines.

The present experimental results indicate that the diffusion and reaction mechanisms at ceria/lanthanum cobaltite are greatly influenced by the type of alkaline earths substituted in lanthanum cobaltite. The precipitation of \( (\text{Ce, R, La, Ca})\text{O}_x \) layer at the interface was observed only when the diffusion couples were prepared with LCC. Hence, some instability of LCC may enhance the formation of the \( (\text{Ce, R, La, Ca})\text{O}_x \) layer. This layer is considered to have a fluorite structure, so that it is hard to detect as a secondary phase in XRD analyses.

At the present time, the effect of \( (\text{Ce, R, La, Ca})\text{O}_x \) formation on the electrochemical
property is not clear. However, if this layer grows in a long term operation, it would result in the depletion of lanthanum and calcium component in LCC which may lead to the segregation of cobalt-rich phase. On the other hand, the calcium component in (Ce, R, La, Ca)Oₓ layer may be segregated again as CaO, because the calcium ion (Ca²⁺) is considered to be unstable in the fluorite structure.

REFERENCES

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Figure 1. SIMS depth profile of normalized intensity ratio \( \frac{I(M^{16}O)}{I(16O)} \) of CYO (a) and LCC (b) annealed at \( T = 1066 \, ^{\circ}C \) for 5h.

Figure 2. SIMS depth profile of normalized intensity ratio \( \frac{I(M^{16}O)}{I(16O)} \) of CGO (a) and LCC (b) annealed at \( T = 1066 \, ^{\circ}C \) for 5h.
Figure 3. SIMS depth profile of normalized intensity ratio \((I(M^{16}O)/I(16O))\) of CYO (a) and LCC (b) annealed at \(T = 1150^\circ C\) for 14 h.

Figure 4. SIMS depth profile of normalized intensity ratio \((I(M^{16}O)/I(16O))\) of CGO (a) and LCC (b) annealed at \(T = 1150^\circ C\) for 14h.

Figure 5. SEM image of the LCC surface annealed with CGO at \(T = 1150^\circ C\) for 14 h.