EXPANSION BEHAVIOR OF Mn$_3$O$_4$+$\delta$ SPINEL AND SHRINKAGE BEHAVIOR OF La$_{0.6}$Sr$_{0.4}$MnO$_3$ COMPOSITES WITH THE SPINEL DURING THERMAL CYCLING IN O$_2$ ATMOSPHERE

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ABSTRACT

The thermal expansion behaviors of the porous and dense Mn$_3$O$_4$+$\delta$ spinel bodies, and the La$_{0.6}$Sr$_{0.4}$MnO$_3$ composite with the spinel during a thermal cycle measurement have been investigated in an O$_2$ atmosphere. The porous Mn$_3$O$_4$+$\delta$ body with relative density of 81% showed a large expansion at temperatures between 1018 and 1064°C during the heating cycle and its expansion irreversibly continued between 1018 and 1064°C every heating cycle. On the other hand, the dense Mn$_3$O$_4$+$\delta$ specimen with relative density of 98% showed no anomalous expansion. From the results of thermogravimetry and high-temperature X-ray diffractometry, the phase change from $\alpha$-Mn$_2$O$_3$ with the C-type rare earth structure into Mn$_3$O$_4$+$\delta$ spinel, which is caused by the oxygen release, relates to the expansion behavior of the porous specimen. Although the La$_{0.6}$Sr$_{0.4}$MnO$_3$ perovskite showed no shrinkage behavior during a thermal cycle measurement, the La$_{0.6}$Sr$_{0.4}$MnO$_3$ composite with 20 vol% Mn$_3$O$_4$+$\delta$ spinel shrank.

INTRODUCTION

High-temperature solid oxide fuel cell (SOFC) generators undergo many thermal cycles between an operating temperature and room temperature. The SOFC is principally composed of the ceramic cell components: the Y$_2$O$_3$ stabilized ZrO$_2$ (YSZ) electrolyte, the LaMnO$_3$-based cathode, the Ni-YSZ cermet anode and the LaCrO$_3$-based separator. Thus, the most significant limitation for SOFC configurations is imposed by their weak and brittle mechanical properties. To reduce thermal stresses in the SOFC generators, a detailed understanding of thermal expansion behavior of the cell components under each atmosphere is necessary (1-3).

Alkaline earth metal (AE = Ca and Sr)-doped lanthanum manganese perovskites, (La$_{1-x}$AE$_x$)MnO$_3+$\delta, have been considered to be the most promising candidates for the cathode of the SOFC. Quite recently, the shrinkage behavior was observed in the thermal expansion curves for the La$_{1-x}$AE$_x$MnO$_3$ samples with an AE-content of 0 ≤ x ≤ 0.3, and for the La$_{1.3}$MnO$_3$ samples with A-site deficiency of 0 ≤ x ≤ 0.1 for the thermal cycle measurement made in air and the O$_2$ atmosphere (4). On the other hand, the La$_{0.6}$Sr$_{0.4}$MnO$_3$ perovskite showed no shrinkage. Therefore, it has been thought that the phase change, and the release and absorption of oxygen in the perovskites, which was observed during thermal cycling between 600 and 1100°C under the oxidizing...
The LaMnO₃-based cathodes include manganese oxide such as Mn₂O₃ and Mn₃O₄ in order to prevent a solid-state reaction between the cathode and YSZ electrolyte during the SOFC fabrication and operation (5,6). In the case of planar-type cell configurations, the lanthanum manganites are used as electric current collectors between the cathode and the LaCrO₃-based separator, and manganese oxides in the LaMnO₃-based cathode can decrease their average linear thermal expansion coefficients (TEC) and enhance their sintering characteristics (7). Therefore, thermal expansion behaviors of manganese oxides and LaMnO₃-based cathodes including manganese oxide during thermal cycling under oxidizing atmospheres are quite important.

Since sintering at a rather high temperature (≥ 1200°C) is required in the SOFC fabrication processes, Mn₂O₃ with the C-type rare earth structure changes into Mn₃O₄ with the spinel structure at approximately 940°C in air and at approximately 1020°C in the O₂ atmosphere (8,9). It is well known that Mn₃O₄ shows oxygen excess and oxygen deficiency depending on temperature and partial oxygen pressure (10), and stably exists at room temperature when it is quenched (11). This paper focuses on unique thermal expansion behaviors of the dense and porous Mn₃O₄ spinel specimens during thermal cycling in an O₂ atmosphere and describes problems when the doped LaMnO₃ cathode with manganese oxide is used as the cathode and the electric current collector.

**EXPERIMENTAL**

As starting materials, Mn₂O₃ (99.9 %, Mitsuwa, Japan) powders without being preheated and with a preheat of 1300°C for 5 h were used. La₀.₆Sr₀.₄MnO₃ perovskite sample powders were synthesized by the co-precipitation method (12). Using the Mn₂O₃ and La₀.₆Sr₀.₄MnO₃ powders, the composites were mixed and sintered at 1200°C for 5 h. The powders were compacted into tablets at 40 MPa and were then sintered at 1300°C for 5 h and 1500°C for 5 h in air. All the samples were confirmed by powder X-ray diffractometry (XRD) (18 kW, Mac Science, M18XHF) using monochromated CuKa radiation and a scintillation detector. High-temperature XRD measurement was carried out in the temperature range from room temperature to 1100°C in the O₂ atmosphere (≥ 99.9999 %). Stepwise heating and cooling were employed, where the sample temperature was raised or lowered by 5°C/min and maintained for 15 min at that temperature. A scanning rate of 0.02 °C/s was used.

TECs and thermal expansion behavior during thermal cycling were measured using a Mac Science TD5000S system (1). Specimens were cut into rectangular shapes of 5 mm × 5 mm × 20 mm length. A sapphire reference was used in the present TEC and thermal cycle measurements. The TECs and thermal cycle measurements were carried out at a heating/cooling rate of 5°C/min in the temperature range between 50 and 1100°C with a flow rate of 50 mL/min O₂ gas (≥ 99.9999 %), and the specimen temperatures were maintained for 30 min at 600 and 1100°C. Although not strictly accurate from the academic viewpoint, the TECs of the materials in this study are calculated by the following equation (1):

\[
\alpha = \frac{1}{L_1} \frac{(L_2 - L_1)}{(T_2 - T_1)}
\]
where $\alpha$ is the TEC, $T_1$ is the starting temperature, $T_2$ is the terminal temperature of an experiment, $L_1$ and $L_2$ are initial and final gauge lengths, respectively. We have confirmed that this dilatometer has an experimental error within $±0.1 \times 10^{-6}/°C$ for the measurement.

Thermogravimetry (TG) and differential thermal analysis (DTA) were examined using a Mac Science TG-DTA5000S system in the temperature range from room temperature to 1100°C in the $O_2$ atmosphere at a heating/cooling rate of 20°C/min. Reference used for the present measurements was $\alpha$-Al$_2$O$_3$ powder.

RESULTS AND DISCUSSION

Sample Condition of Mn$_3$O$_4$+S Spinel

When a theoretical density of Mn$_3$O$_4$ used was 4.718 g/cm$^3$, the relative density of the sintered Mn$_3$O$_4$+S specimens obtained was 81% after heating at 1300°C for 5 h and 98% after heating at 1500°C for 5 h. The powdered XRD patterns of the dense and porous Mn$_3$O$_4$+S specimens showed no second phases, and no remarkable difference in the XRD patterns between the dense and porous samples was observed. The Mn$_3$O$_4$+S specimens crystallized in tetragonal unit cell (Space group: I4$_1$/amd), and their lattice parameters were $a = 5.7630 \AA$, $c = 9.4688 \AA$, and $z = 8$ for the porous sample and $a = 5.7633 \AA$, $c = 9.4720 \AA$, and $z = 8$ for the dense one. These values were in good agreement with the previous work (13).

Figures 1(a) and (b) show the scanning electron microscopy (SEM) micrographs of the porous and dense Mn$_3$O$_4$+S specimens before the thermal cycle measurement. The porous specimen with small remaining pores shows the obscure grain-boundaries (Fig. 1(a)). On the other hand, the grain-boundaries of the dense specimen were quite clear and its microstructure consists of quite large grain size of 10 - 100 μm (Fig. 1(b)).

Thermal Expansion Behaviors of Mn$_3$O$_4$+S During Thermal Cycling

Figure 2 shows the thermal expansion curves of the porous and dense Mn$_3$O$_4$+S specimens during thermal cycling in the $O_2$ atmosphere. The TEC in the temperature range from 50 to 1000°C was $8.9 \times 10^{-6}/°C$ for the porous specimen and $8.8 \times 10^{-6}/°C$ for the dense specimen. The porous specimen gradually expanded with increasing temperature, and then showed an unexpected and large expansion between approximately 1018 and 1064°C (Fig. 2(a)). The expansion of the porous specimen irreversibly continued between 1018 and 1064°C every heating cycle, and its coefficients have a tendency to decrease with thermal cycles. In addition, the anomalous large expansion of this specimen increased with increasing difference between the highest and lowest temperatures during the thermal cycle measurement. On the other hand, a shrinkage of the dense specimen during the thermal cycling was observed (Fig. 2(b)). The shrinkage of the specimen gradually disappeared with thermal cycling and the specimen showed no shrinkage behavior after 12th thermal cycling. Note that when the specimens with and without porosity were held at 1100°C, a decrease of their length with time was observed. However, when the specimens were held at 600°C, no change of these specimens was observed. Therefore, it suggests that the shrinkage of the dense sample during thermal cycle is related to its microstructure.

Figure 3 shows the differential coefficient of thermal expansion-temperature
curve of the porous and dense Mn₃O₄⁺⁶ specimens in the O₂ atmosphere. The open and closed circles represent the results for the porous and dense Mn₃O₄⁺⁶ specimens, respectively. In Fig. 3(a), the TEC curve of the porous specimen shows two significant decreases at approximately 375°C and 616°C. To make the comparison easier, the differential coefficient of thermal expansion-temperature curve of the porous Mn₃O₄⁺⁶ specimen in the O₂ atmosphere is plotted in Fig. 3(b). Each data point of the porous specimens in this figure corresponds to those in Fig. 3(a). It is clear that the anomalous expansion of the porous specimen occurred at approximately 1020°C. It is seen in Fig. 3(a) that the TEC value of the dense specimen was constant regardless of temperature ≤ approximately 800°C. The TEC of the dense specimen started to decrease at approximately 800°C. A very small peak for the expansion in the TEC curve was observed at approximately 1020°C. It is quite interesting to note why there is a difference in the TEC results from the porous and dense specimens.

**Microstructure of Mn₃O₄⁺⁶ Specimen After Thermal Cycle Measurement**

Figures 4(a) and (b) show the SEM micrographs of the porous and dense specimens after the thermal cycling measurement, which should be compared to Figure 1(a) and (b). The increase of the large radiated pores is seen in Fig. 4(a). On the other hand, the surface of the dense specimen shows obscure grain-boundary and grain relief after 48 thermal cycles. These results suggest that the reaction between oxygen and Mn₃O₄⁺⁶ specimen relates to the expansion and shrinkage behaviors during thermal cycling in the O₂ atmosphere.

**Oxygen Releases and Absorbs of Mn₃O₄⁺⁶ in the O₂ Atmosphere**

Figure 5 shows the TG-DTA curves of the Mn₃O₄⁺⁶ powder in the O₂ atmosphere when the oxygen content of Mn₃O₄⁺⁶ powder heated at 1300°C for 10 h in air is assumed to be 4. The broken line shows the oxygen content of Mn₂O₃. During the heating cycle, the weight increase, which is oxygen absorption, started at approximately 638°C, and then the oxygen of the sample reached to that of Mn₂O₃. At approximately 1020°C, the oxygen in the sample was dramatically released. During the cooling cycle, absorption of oxygen in Mn₃O₄⁺⁶ started at approximately 793°C, and then its oxygen content was quite constant at temperatures ≤ 683°C. In the DTA curve during the heating cycle, an exothermic peak at approximately 624°C and an endothermic peak at approximately 1016°C were observed.

**Phase Change between Mn₃O₄ and Mn₂O₃ During Thermal Cycling**

Figures 6 and 7 show the high-temperature XRD patterns of the Mn₃O₄⁺⁶ powder during the heating cycle in the O₂ atmosphere. The symbols s, c and u stand for the spinel structure, the C-type rare earth structure and uncertain structure, respectively. In Fig. 6(a), the XRD pattern shows the Mn₃O₄⁺⁶ with spinel structure, and no peak was observed for other phases. It is seen in Fig. 6(b) that α-Mn₂O₃ phase appeared in the Mn₃O₄⁺⁶ spinel phase. With increasing temperature, the peaks of the Mn₃O₄⁺⁶ spinel phase gradually disappeared, and the XRD pattern of the powders showed almost the single α-Mn₂O₃ phase after heating at temperatures ≥ 600 °C. It is seen in Fig. 7(b) that the peaks for spinel phase appeared again in one of the α-Mn₂O₃ phase. After the oxygen release, the XRD pattern exhibited the spinel structure in Fig. 7(c).

During the cooling cycle in the high-temperature XRD measurement, the phase changes for the Mn₃O₄⁺⁶ spinel phase and α-Mn₂O₃ phase were almost similar to that
during heating cycle. The stable α-Mn$_2$O$_3$ phase existed until room temperature. Fig. 8(a) and (b) shows the XRD patterns of the dense and porous specimens after the TEC measurement. Although the XRD patterns of the dense specimen showed the Mn$_3$O$_4$ spinel structure, the porous one showed the α-Mn$_2$O$_3$ structure.

Expansion Behavior of Phase Change Between Mn$_3$O$_4$ and α-Mn$_2$O$_3$.

During the thermal cycle measurement of the porous specimen, the phase change between α-Mn$_2$O$_3$ and Mn$_3$O$_4$ takes place. Therefore the phase change might be related to the anomalous expansion behavior. The C-type rare earth structure is similar to that of fluorite-type (13). In the fluorite structure, the cation is surrounded by eight anions. The C-type rare earth structure has six anions, and there are two kinds of coordinations for six anions. Even so, we should note that this structure shows a cubic closed packing of cations. Mn$_3$O$_4$ spinel shows a cubic closed packing of anions. Therefore, the phase change between Mn$_3$O$_4$ and α-Mn$_2$O$_3$ by the oxygen release has a rearrangement of these atoms. In the ABO$_3$ perovskite structure, six oxygen atoms are coordinated around the B-site metal, and the resulting octahedrons make the corner-shared network. In addition, oxygen and A-site metals show a cubic close packing. From the viewpoint of this close packed structure, non-doped and AE-doped lanthanum manganites have been said to form cation deficiency, such as the formula of La$_{1-x}$Mn$_{1+x}$O$_3$. By the O$_2$ release, the perovskite has a rearrangement of these atoms. The oxygen release in the spinel causes the extraordinary expansion of the sample, whereas in the perovskite causes the shrinkage of the sample.

Effect of Anomalous Expansion of Mn$_3$O$_4$ on LaMnO$_3$ Cathode

As reported previously [5,6], the degradation in the performance of the SOFC cathode is due to the formation of poorly conductive compounds such as La$_2$Zr$_2$O$_7$ and SrZrO$_3$ at the interface between the cathode and the electrolyte by solid-state reaction with the YSZ electrolyte. It is, therefore, desirable to retard the reaction by the addition of manganese oxide. Yokokawa et al. [5] reported that the reaction of LaMn$_3$O$_7$ cathode and YSZ electrolyte originates from the thermodynamic nature of LaMn$_3$O$_7$ having A-site deficiency. It was experimentally confirmed by the solid-state technique that excess manganese oxide in the LaMn$_3$O$_7$ cathode is quite useful to prevent the reaction [6]. From the viewpoint of thermal cycling characteristics, since no shrinkage was observed during the thermal cycle measurement, the La$_{0.6}$Sr$_{0.4}$Mn$_3$O$_7$ perovskites are considered to be the best candidates for practical use as cathode and electric current collector in the SOFC. There remains the TEC mismatch between La$_{0.6}$Sr$_{0.4}$Mn$_3$O$_7$ cathode and YSZ electrolyte.

Figure 9 shows the XRD patterns of La$_{0.6}$Sr$_{0.4}$Mn$_3$O$_7$ and 80 vol%La$_{0.6}$Sr$_{0.4}$Mn$_3$O$_7$–Mn$_3$O$_4$ composite after the reaction with YSZ electrolyte at 1200°C for 5 h in air. The La$_{0.6}$Sr$_{0.4}$Mn$_3$O$_7$ reacted with YSZ electrolyte and the reactant of SrZrO$_3$ was observed (Fig. 9(a)). However, the 80 vol%La$_{0.6}$Sr$_{0.4}$Mn$_3$O$_7$ composite did not react with YSZ (Fig. 9(b)). From the viewpoint of the reaction between the cathode and YSZ electrolyte, the composites of La$_{0.6}$Sr$_{0.4}$Mn$_3$O$_7$ and Mn$_3$O$_4$ are quite useful as cathode.

Figure 10 shows the thermal expansion behaviors of La$_{0.6}$Sr$_{0.4}$Mn$_3$O$_7$ and 80 vol%La$_{0.6}$Sr$_{0.4}$Mn$_3$O$_7$–Mn$_3$O$_4$ composite during thermal cycling in the O$_2$ atmosphere. The relative densities of the La$_{0.6}$Sr$_{0.4}$Mn$_3$O$_7$ and 80 vol%La$_{0.6}$Sr$_{0.4}$Mn$_3$O$_7$–Mn$_3$O$_4$ composite were 62 % and 73 %, respectively. No shrinkage of La$_{0.6}$Sr$_{0.4}$Mn$_3$O$_7$ perovskite specimen was observed in thermal expansion curve. However, 80
vol\%Lao.6Sr0.4MnO3–Mn3O4 composite showed a shrinkage behavior during thermal cycling. This is the reverse result when compared to that of the porous Mn3O4. The present anomalous expansion of the LaMnO3 cathode with Mn3O4 is quite important from the viewpoint of these problems being associated with the thermal cycling under the oxidizing atmosphere. Further investigations on the shrinkage behaviors of the LaMnO3 cathode with Mn3O4 are in progress.

CONCLUSIONS

It was found that, during thermal cycling, the oxygen release remarkably affects the thermal expansion behavior of Mn3O4+δ specimens, and their relative densities are related to the anomalous expansion and shrinkage behavior. Since Mn3O4+δ material is used in the LaMnO3-based cathode and electric current collector between cathode and separator in high-temperature SOFCs, the thermal expansion behaviors of Mn3O4+δ in the LaMnO3-based cathode are of technological importance. Therefore, it is necessary to clarify the thermal expansion mechanism of Mn3O4+δ under oxidizing atmosphere.

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Fig. 1 SEM micrographs of the specimens before thermal cycle measurement.

(a) Porous specimen
(b) Dense specimen

Fig. 2 Thermal expansion curves of the porous and dense Mn$_3$O$_4$ spinels in an O$_2$ atmosphere during thermal cycling.
(a) Porous specimen (20.25 mm)
(b) Dense specimen (19.65 mm)

Fig. 3 Differential coefficient of thermal expansion—temperature curve of the porous and dense Mn$_3$O$_4$ spinels in an O$_2$ atmosphere.
(a) Porous specimen
(b) Porous and dense specimen
Fig. 4 SEM micrographs of the specimens after thermal cycle measurement.

Fig. 5 TG-DTA measurement curves for Mn$_3$O$_{4+δ}$ spinel in an O$_2$ atmosphere.
(a) TG curve  
(b) DTA curve

Fig. 6 High-temperature XRD patterns of Mn$_3$O$_{4+δ}$ in an O$_2$ atmosphere.
(a) 820°C, (b) 1000°C, (c) 1100°C.
Fig. 7 High-temperature XRD patterns of Mn$_3$O$_4$ in an O$_2$ atmosphere during the cooling cycle. (a) 800°C, (b) 600°C.

Fig. 8 XRD patterns of the porous and dense specimens after a thermal cycle measurement in an O$_2$ atmosphere.

Fig. 9 XRD patterns of the perovskite and the composite with YSZ electrolyte after heating at 1200°C for 5 h in air. (a) La$_{0.6}$Sr$_{0.4}$MnO$_3$ (b) 80 vol% La$_{0.6}$Sr$_{0.4}$MnO$_3$-Mn$_3$O$_4$ composite

Fig. 10 Thermal expansion behaviors of the perovskite and 80 vol% La$_{0.6}$Sr$_{0.4}$MnO$_3$-Mn$_3$O$_4$ composite with YSZ electrolyte during the thermal cycling in an O$_2$ atmosphere. (a) La$_{0.6}$Sr$_{0.4}$MnO$_3$ (b) 80 vol% La$_{0.6}$Sr$_{0.4}$MnO$_3$-Mn$_3$O$_4$ composite
