-Communication-

Electrochemical Synthesis of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ Perovskite Films

Takeshi SASAKI*, Tomoaki MORIKAWA, Jukichi HOMBO and Yasumichi MATSUMOTO

Received January 12, 1990 ; Accepted April 26, 1990

$\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ perovskite is one of the suitable electrode materials for oxygen reduction in solid oxide fuel cells (SOFC), because of its thermal stability, good electrocatalysis and thermal expansion compatibility with the solid oxide electrolyte, such as yttria stabilized zirconia (YSZ).¹⁾ Some methods for the preparation of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ perovskite films have been reported.²⁾ It has been found that the complex oxide films such as $\text{Fe}_{3-x}\text{Li}_x\text{O}_4$ spinel³⁾ and LaMnO_3 perovskite⁴⁾ can be electrochemically synthesized, if the electrolytes contain Li^+ and La^{3+} ions for the former and latter oxides, respectively.

$\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ is more preferable to LaMnO_3 as an oxygen electrode material, because the conductivities of the former oxides are higher than that of the latter oxide. In this paper, the electrochemical synthesis of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ film and the effects of Sr^{2+} ion on this synthesis are demonstrated.

EXPERIMENTAL

Pt plates were used as the working and the counter electrodes. The electrolytes were the mixtures of aqueous solutions of metal nitrates such as $\text{Mn}(\text{NO}_3)_2$, $\text{La}(\text{NO}_3)_3$ and $\text{Sr}(\text{NO}_3)_2$, where the total concentration of the metal ions was 1M. The $([\text{La}^{3+}]/[\text{Sr}^{2+}])/[\text{Mn}^{2+}]$ ratio in the solution was held 1000/1, since LaMnO_3 single phase was obtained only when a large excess of La^{3+} ion (A site ion) compared with Mn^{2+} ion (B site ion) exist in the electrolyte.⁴⁾ The electrolysis was carried out under a constant current density of 0.5 mA/cm² for 3 hours at room temperature. The current efficiencies for the present oxide depositions were less than about 10%. The oxide films deposited on the electrode were washed with distilled water, followed by drying at room temperature. The deposited oxide films were dissolved into HCl and then analyzed with an ICP spectrometry. All the samples were heated at 1000 °C in O_2 for 4 hours in order to crystallize their oxide films.

RESULTS AND DISCUSSION

All the as-deposited oxide films were amorphous and porous, and their thickness were about 3-4 μm. Figure 1 shows the typical diffraction peaks for the oxide films after the heat-treatment, which were prepared in the solutions with the $[\text{La}^{3+}]/[\text{Sr}^{2+}]$ ratios of 1000/0(A), 999/1(B) and 900/100(C). The heat-treated oxide films, which were prepared in the solutions with the $[\text{La}^{3+}]/[\text{Sr}^{2+}]$ ratios of 1000/0 and 999/1, consist of the perovskite single phase, but that in the case of the $[\text{La}^{3+}]/[\text{Sr}^{2+}]$ ratio of 900/100 consists of the mixed phase containing Mn_3O_4 . The oxide films prepared in the solutions where the $[\text{La}^{3+}]/[\text{Sr}^{2+}]$ ratio is less than about 990/10, always consisted of the mixed phase of the perovskite and Mn_3O_4 , as described below. In the case of the $[\text{La}^{3+}]/[\text{Sr}^{2+}]$ ratio of 0/1000 in the solution, where the ratio of $[\text{Sr}^{2+}]/[\text{Mn}^{2+}]$ is 1000/1, the oxide film consisted of $\text{SrMn}_{3-2x}\text{O}_{6-x}$ and Mn_3O_4 .

The following equation using the diffraction peak intensities of the perovskite and Mn_3O_4 was used for the qualitative evaluation of the degree of the perovskite formation in the heat-treated oxide film,

$$I_{\text{pero}} = I_{\text{pero}}(100) / [I_{\text{pero}}(100) + I_{\text{Mn3O4}}(121)] \quad (1)$$

where $I_{\text{pero}}(100)$ and $I_{\text{Mn3O4}}(121)$ are the intensities of (100) diffraction peak of the perovskite and of (121) diffraction peak of Mn_3O_4 , respectively, as shown in Fig. 1(C). Therefore, the heat-treated oxide film consists of the perovskite single phase, if I_{pero} equals one. Figure 2 shows the I_{pero} (A), the atomic ratios of Sr/La(B) and of (La+Sr)/Mn(C) in the oxide films as a function of the $[\text{La}^{3+}]/[\text{Sr}^{2+}]$ ratio in the solution.

As a matter of course, I_{pero} significantly relates to the ratio of (La+Sr)/Mn in the deposited oxide film, as shown in Fig. 2. The heat-treated oxide films consist of the mixed phase of the perovskite and Mn_3O_4 if their (La+Sr)/Mn ratios are much less than one, while those consist of the perovskite single phase if their (La+Sr)/Mn ratios are about one. The (La+Sr)/Mn ratio in the deposited

Department of Applied chemistry, Faculty of Engineering, Kumamoto University
(2-39-1, Kurokami, Kumamoto 860).

Key words: Mn-oxide, Perovskite, Oxide Film, Electrochemical Synthesis

oxide film decreases with a decrease in the $[\text{La}^{3+}]/[\text{Sr}^{2+}]$ ratio in the solution, leading to the mixed phase by the heat-treatment. It should be noted that the ratios of $(\text{La}+\text{Sr})/\text{Mn}$ in the oxide films are about 0.8, even if their oxide films consist of the perovskite single phase, while this ratio is about one, when the $[\text{La}^{3+}]/[\text{Sr}^{2+}]$ ratio is 1000/0, as denoted by the triangle symbol in Fig. 2. In conclusion, Sr^{2+} ion suppresses the incorporation of La^{3+} and itself into the oxide in the electrochemical deposition. Therefore, the compositions of the perovskites prepared by the present electrochemical synthesis using the solutions containing Sr^{2+} ion can be represented as follows.

(2)

The composition of the perovskite in the ratio of La/Sr can be estimated from Fig. 2(B), even in the case of the mixed phase, because other phase is always Mn_2O_3 which will contain no La and Sr in its lattice.

Fig. 1 X-ray diffraction patterns of the oxide films after heat-treatment, which were prepared in the solutions with the $[\text{La}^{3+}]/[\text{Sr}^{2+}]$ ratios of 1000/0(A), 999/1(B) and 900/100(C).

Fig. 3 SEM micrograph of the oxide film which were prepared in the solution with the $[\text{La}^{3+}]/[\text{Sr}^{2+}]$ ratio of 999/1.

of Sr exist in the oxide, because the $(n00)$ diffraction peak intensities of the perovskite are very high as shown in Fig. 1(B). The SEM micrograph of this oxide film is shown in Fig. 3. The particle size of the perovskite is uniform and is about $0.2\text{--}0.5\mu\text{m}$ for this oxide film, while the particle sizes were $0.5\text{--}1.0\mu\text{m}$ and $0.1\text{--}0.2\mu\text{m}$ for the cases of $\text{La}_0.8\text{MnO}_3$ and of $(\text{La}_{0.6}\text{Sr}_{0.4})_{0.8}\text{MnO}_3$, respectively. Thus, the particle size decreased with an increase in amount of Sr in the oxide film. These phenomena are also the effects of Sr on the crystallization in the heat-treatment.

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Fig. 2 I_{pero} calculated from the x-ray diffraction peak intensities (A), the atomic ratios of Sr/La (B) and $(\text{La}+\text{Sr})/\text{Mn}$ (C) in the oxide films as a function of the $[\text{La}^{3+}]/[\text{Sr}^{2+}]$ ratio in the solution. The triangle symbol denotes the case of the $[\text{La}^{3+}]/[\text{Sr}^{2+}]$ ratio of 1000/0 in the solution.

For example, it may be concluded that the composition is $(\text{La}_{0.6}\text{Sr}_{0.4})_{0.8}\text{MnO}_3$ for the case of the oxide prepared in the $[\text{La}^{3+}]/[\text{Sr}^{2+}]=500/500$ solution. The lattice parameters of this perovskite (rhombohedral, $a=3.875\text{ \AA}$, $\alpha=90^\circ 12'$) almost agrees with that of the perovskite with the same composition in the Sr/La ratio (rhombohedral, $a=3.878\text{ \AA}$, $\alpha=90^\circ 14'$) which is prepared by a ceramic technique.⁵⁾

It should be also noted that the crystallization together with $(n00)$ orientation is promoted in the heat-treatment when trace amounts