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Electroless Deposition of $LaMnO_3$ Perovskite Film on Yttria Stabilized Zirconia Substrate

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Electroless deposition of $LaMnO_3$ precursors on YSZ substrate from a solution containing Mn^{2+}, La^{3+}, and an oxidizing agent was investigated. Peroxydisulfate was used as the oxidizing agent. Pretreatment of the substrate, sensitization in a solution of $SnCl_2$, and activation in a solution of $PdCl_2$ were necessary for deposition of the oxide film. The La/Mn atomic ratio in the oxide film increased with increases in the $[La^{3+}]/[Mn^{2+}]$ ratio and in the pH of the solution. The additives CH_3COONa and $AgNO_3$ in the solution improved the incorporation of La^{3+} ion into the oxide film during the electroless deposition and the adhesion of the as-deposited oxide film on YSZ. It was judged from the cyclic voltammetry of the as-deposited oxide film and from XPS, IR and XRD measurements that the as-deposited oxide film on YSZ was amorphous hydrous MnO_2 which contained La^{3+} ions by specific adsorption. La^{3+} ions existed in a state similar to that in La_2O_3, according to an XPS measurement. $La_{1-x}MnO_3$ perovskite film ($x = 0.85, 0.96$) was prepared by heat treatment of the deposited oxide film at 800°C for 5 hr. The mechanism of the electroless deposition of the $LaMnO_3$ precursor is discussed.

Introduction

Some complex oxide films can be prepared using electrochemical oxidation. We have electrochemically synthesized perovskite oxides, $LaMnO_3$ (*1–3*) and $LaCoO_3$ (*4*), where metal cations such as Mn^{2+} and Co^{2+} are electrochemically oxidized in solutions containing La^{3+}, followed by some chemical reactions with H_2O and La^{3+}.

The process using electrochemical oxidation will be very useful for the preparation of the complex oxide film, compared with other methods such as CVD and spattering, since the film can be prepared easily using a simple apparatus and under simple conditions. However, the substrate will be restricted to a conductor, because of a need for an external electrical current to the electrode substrate.

Some metal oxide films such as PbO_2 (*5*), MnO_2 (*6*), Tl_2O_3 (*6*), and NiO (*7*) have been electrolessly deposited on glass in solutions containing metal cations, where they are oxidized in heterogeneous reactions by an oxidizing agent, peroxydisulfate. In these cases, metal oxide films will also be formed by similar electrochemical reactions to those in anodic oxidation. Therefore a complex oxide film can be electrolessly deposited on a dielectric substrate, if the solution contains other metal cations and a suitable oxidizing agent.

$LaMnO_3$ is suitable as an air electrode material for high temperature solid oxide fuel cells (SOFC) because of its chemical

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stability at high temperature, electrocatalytic properties, high electron conductivity, and thermal expansion match with the solid oxide electrolyte yttria stabilized zirconia (YSZ) (*8*). Some preparation methods for $LaMnO_3$ on YSZ have been studied (*9*).

It is known that a manganese dioxide film can be electrolessly deposited in a solution containing Mn^{2+} and $S_2O_8^{2-}$ (*6*). Therefore, it may be also possible to deposit $LaMnO_3$ film on YSZ, if the solution containing both metal cations of Mn^{2+} and La^{3+} is oxidized by a oxidizing agent, peroxydisulfate. In this paper, electroless deposition of $LaMnO_3$ perovskite film on YSZ substrate is demonstrated and its mechanism is discussed.

Experimental

Substrates, 3 mol% Y_2O_3–ZrO_2 disks (14 mmϕ and 0.5 mm thick), were soaked in 46% HF for 5 min for cleaning and etching the surface. After rinsing in water, these were sensitized in 10 g/liter $SnCl_2$ + 40 ml/liter HCl solution for 5 min, followed by activation in 2 g/liter $PdCl_2$ + 20 ml/liter HCl solution for 3 min. The sensitization and the activation were necessary for the deposition of the oxide film on YSZ. After these pretreatments, the substrate was immersed with a vertical position in a mixed solution of $La(NO_3)_3$, $Mn(NO_3)_2$, and $(NH_4)_2S_2O_8$, in which the concentrations of $La(NO_3)_3$, and $(NH_4)_2S_2O_8$ were fixed at 0.5 and 0.167 *M* respectively and the $Mn(NO_3)_2$ concentration was changed from 0.0005 to 0.05 *M*. CH_3COONa and $AgNO_3$ were added to the solution as supporting electrolyte and catalyst for the persulfate oxidation, respectively. The $AgNO_3$ concentration was fixed at 5×10^{-6} *M* and the CH_3COONa concentration was changed from 0.05 to 1.5 *M*. The pH of the solution was adjusted to 4–6 by 0.01 *M* NaOH or 0.01 *M* HNO_3 titration. After an induction time of several hours, the solution gradually turned brown, and after 24 hr a compact and continuous oxide film was precipitated on the substrate. The induction time for the electroless deposition of oxide film was usually 24 hr. It should be noted that no precipitation of the oxide in the solution containing acetate ions was observed, and the color of the solution remained clear brown even after several days.

Pt plats (99.9%, 10 × 10 mm) were used as working and counter electrodes for the current/potential measurements, and a Ag/AgCl electrode was used as the reference. Electrode potential was referred to Ag/AgCl unless otherwise stated. Stationary current was measured after the electrode was polarized for a few decades of seconds. All experiments were carried out at room temperature.

The as-deposited oxide films prepared on YSZ were washed by immersion in distilled water for 1 min, followed by drying at room temperature. The as-deposited oxide films were examined by infrared absorption spectroscopy (IR) and X-ray photoelectron spectroscopy (XPS). All the samples were heated in air at 800°C for 5 hr for the purpose of crystallization, since the as-deposited oxide films were always amorphous. The structures of the oxide films after the heat-treatment were examined by X-ray diffraction analysis (XRD) using monochromatic Cu$K\alpha$ radiation. The oxide films were dissolved in HCl and then analyzed by inductively coupled plasma (ICP) spectroscopy to determine the La/Mn atomic ratios in the oxide films. Morphological observations of the oxide films were carried out with a scanning electron microscope (SEM).

Results and Discussion

Figure 1 shows typical stationary current/potential curves in the solutions, which demonstrate the mixed potential E_{MP} on the electroless deposition. Curve 1 was measured in the mixed solution of 0.5 *M* $La(NO_3)_3$–0.0005 *M* $Mn(NO_3)_2$ at pH 6. In this solution, anodic current is observed at the more positive potential than 0.6 V,

which is due to the formation of MnO_2. The anodic reaction is

$$Mn^{2+} + 2H_2O \rightarrow MnO_2 + 4H^+ + 2e^- + 2 \quad (1)$$

with the adsorption of La^{3+} ion onto the oxide, as stated in Ref. (*1*). Curve 2 was measured in 0.167 *M* $(NH_4)_2S_2O_8$ at pH 6. Cathodic current was observed at the more negative potential than 0.95 V, which result from the reduction of $S_2O_8^{2-}$, i.e.,

$$S_2O_8^{2-} + 2e^- \rightarrow 2SO_4^{2-}. \quad (2)$$

The mixed potential E_{MP} demonstrated by the current/potential curves was in the region 800 to 950 mV for all the solutions used for the experiments. The potential during the electroless deposition of the oxide films on Pt electrode was measured to be in this potential region, suggesting that the anodic and the cathodic partial reactions are based on reactions (1) and (2), respectively. The solution containing CH_3COONa changed color to clear brown without precipitation of the oxide in it during the electroless deposition, suggests that other anodic partial reactions to form the highly oxidized manganese complex ions maybe also exist during the electroless deposition. Perhaps ligands

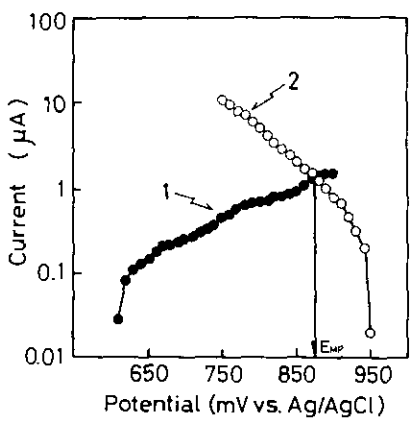

FIG. 1. Typical stationary current/potential curves of Pt electrode in solutions at pH = 6. Curves 1 and 2 were measured in solutions of 0.5 *M* $La(NO_3)_3$–0.0005 *M* $Mn(NO_3)_2$ and of 0.167 *M* $(NH_4)_2S_2O_8$, respectively. E_{MP} denotes the mixed potential on the electroless deposition of the oxide film.

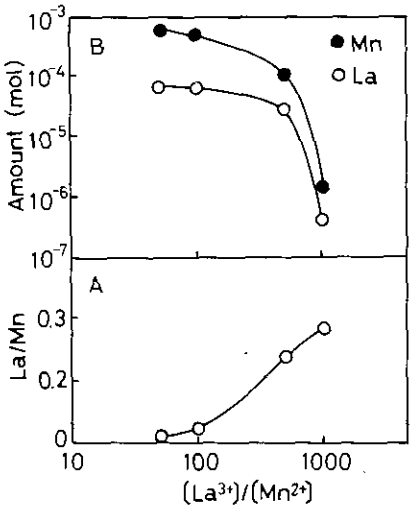

FIG. 2. La/Mn atomic ratio (A) and amounts of Mn and La (B) in the oxide film deposited on YSZ as a function of the $[La^{3+}]/[Mn^{2+}]$ ratio in the solution.

such as CH_3COOO^-, NO_3^-, $S_2O_8^{2-}$, and SO_4^{2-} in the solution contribute to the formation of the complex ions.

Figures 2A and B show the La/Mn atomic ratio and the amounts of Mn and La in the oxide film deposited on the YSZ as functions of the $[La^{3+}]/[Mn^{2+}]$ ratio in the solution without the additives such as CH_3COONa and $AgNO_3$, where the La^{3+} concentration was fixed at 0.5 *M*. The La/Mn atomic ratio in the oxide film increases, while the amounts of Mn and La in the oxide film decreases, with an increase in the $[La^{3+}]/[Mn^{2+}]$ ratio in the solution. This phenomenon is similar to the case of the oxide films prepared by electrochemical oxidation (*1*). Figure 3 shows the pH dependence of the La/Mn atomic ratio in the oxide film deposited in the solution with $[La^{3+}]/[Mn^{2+}]$ ratio of 0.5 *M*/0.0005 *M*, which did not contain CH_3COONa and $AgNO_3$. The La/Mn atomic ratio in the oxide film increases with an increase in the pH of the solution. Such a pH dependence of the La/Mn atomic ratio in the oxide film was not observed in the case of the oxide film prepared by electrochemical oxidation. These results suggest that the La is incorporated into the oxide

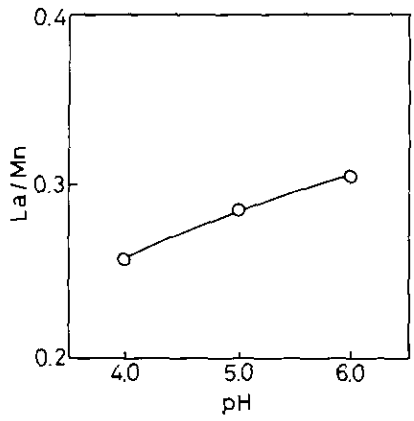

FIG. 3. pH dependence of the La/Mn atomic ratio in the oxide film deposited from the solution of 0.5 *M* $La(NO_3)_3$–0.0005 *M* $Mn(NO_3)_2$–0.167 *M* $(NH_4)_2S_2O_8$.

films deposited on YSZ in a slightly different manner from that of the oxide film prepared by electrochemical oxidation, where La^{3+} ions were incorporated into the oxide film by adsorption with the weak chemical bond (1). The La/Mn atomic ratios of the oxide films deposited in the solution without CH_3COONa and $AgNO_3$ never went over 0.35. Consequently, the effect of the additives such as CH_3COONa and $AgNO_3$ on the incorporation of La into the oxide films was determined for the solution with the $[La^{3+}]/[Mn^{2+}]$ ratio of 0.5 *M*/0.0005 *M* at pH = 6. Figures 4A and B show the La/Mn atomic ratio and the amounts of Mn and La in the oxide film as a function of the CH_3COONa concentration in the solution. The La/Mn atomic ratio in the oxide film increases, while the amounts of Mn and La in the oxide film decrease with an increase in the concentration of CH_3COONa. Perhaps the formation of the complex ions by reaction with CH_3COO^- may suppress the deposition of the oxide, resulting in the slow deposition of MnO_2. This may contribute to the improvement of the incorporation of La^{3+} ion into the oxide film. In the case of the oxide films electrolessly deposited in the solution containing $AgNO_3$, the La/Mn atomic ratio in the oxide film became progressively greater as shown in Fig. 4A. It is well known that Ag^+ is the catalyst for the persulfate oxidation, where Ag^+ is oxidized by $S_2O_8^{2-}$ and the generated Ag^{3+} acts as an oxidizing agent. The pH of the solution containing $AgNO_3$ before the pH adjustment was always higher than 6.0. The rise in pH of the solution may also contribute to the improvement of the incorporation of La^{3+} ion into the oxide film. These results indicate that additives such as CH_3COONa and $AgNO_3$ improve the incorporation of La^{3+} ion into the oxide film. These additives have also improved the adhesion of the as-deposited oxide film onto the substrate. However, the details of these mechanisms have not been clear. As can be seen from Fig. 4A, the oxide films with La/Mn atomic ratio of 0.8 to 1.0 are electrolessly deposited, which are expressed as $La_{1-x}MnO_3$ precursor because of the nonstoichiometry of the $LaMnO_3$ perovskite (*10*).

Figure 5 shows a typical cyclic voltammogram of the $La_{1-x}MnO_3$ precursor film elec-

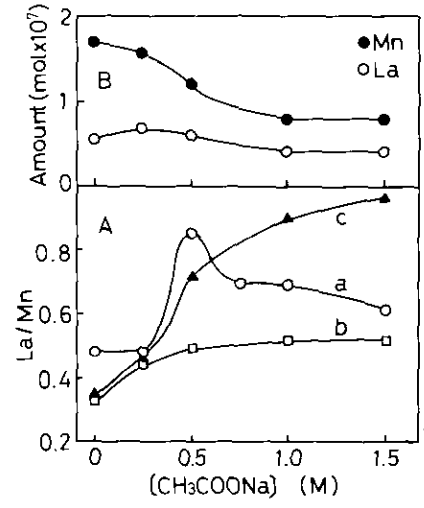

FIG. 4. La/Mn atomic ratio (A) and amounts of Mn and La (B) in the oxide film deposited in the various solutions, in which the concentrations of $Mn(NO_3)_2$, $La(NO_3)_3$, and $(NH_4)_2S_2O_8$ were 0.0005, 0.5, and 0.167 *M*, respectively, as a function of CH_3COONa concentration in the solution. a and b denote solutions with 5×10^{-6} *M* $AgNO_3$ at pH = 6 and with no $AgNO_3$ at pH = 6, respectively. c denotes the solution containing 5×10^{-6} *M* $AgNO_3$ whose pH was not adjusted. Amounts of Mn and La were illustrated only for the oxide film in solution a.

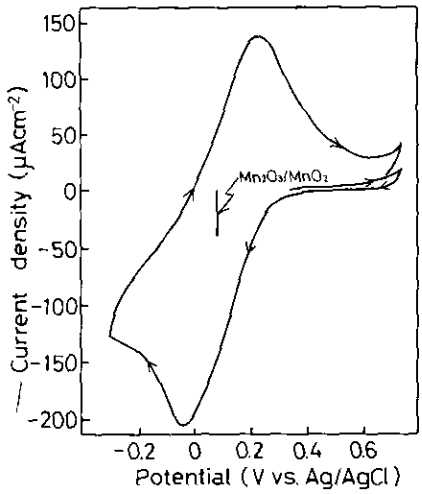

FIG. 5. Voltammogram of the $La_{0.85}MnO_3$ precursor film on the Pt electrode in 0.05 *M* NaOH, which was prepared in a solution of 0.5 *M* $La(NO_3)_3$–0.0005 *M* $Mn(NO_3)_2$–0.167 *M* $(NH_4)_2S_2O_8$–0.5 *M* CH_3COONa–5 × 10^{-6} *M* $AgNO_3$ at pH = 6.

trolessly deposited on the Pt electrode in 0.05 *M* NaOH (pH = 12.5), where the equilibrium potential of Mn_2O_3/MnO_2 (0.09 V) is also shown. The $La_{0.85}MnO_3$ precursor was prepared in a mixed solution of 0.5 *M* $La(NO_3)_3$–0.0005 *M* $Mn(NO_3)_2$–0.167 *M* $(NH_4)_2S_2O_8$–0.5 *M* CH_3COONa–5 × 10^{-6} *M* $AgNO_3$ at pH = 6, whose La/Mn atomic ratio was 0.85, as shown in Fig. 4A. In the first potential sweep from the rest potential (0.35 V) to 0.75 V, no other anodic current is observed except for the current caused by the evolution of O_2. In the subsequent potential sweep, both anodic and cathodic currents are observed and its redox potential agrees with the equilibrium potential of Mn_2O_3/MnO_2, indicating that Mn in the $La_{1-x}MnO_3$ precursor exists as MnO_2. This result is supported by XPS measurement of the $La_{0.85}MnO_3$ precursor, whose binding energy of $Mn2p_{3/2}$ level of 641.9 eV reflects that of Mn^{4+}. In the infrared absorption measurement of the $La_{0.85}MnO_3$ precursor on YSZ, a small absorption band based on the O–H bending vibration in the adsorbed water was observed at 1600 cm^{-1}, suggesting that the $La_{0.85}MnO_3$ precursor consists of hydrous MnO_2 containing La^{3+} ions.

The amorphous $LaMnO_3$ precursor on the Pt electrode prepared using electrochemical oxidation at room temperature was determined to be an amorphous $MnO_{2-\delta}$ containing $La(OH)_3$ and water (*1*). However, it is judged from the following result that the state of La in the $La_{1-x}MnO_3$ precursor deposited on YSZ is different from that in the above $MnO_{2-\delta}$. La in the $La_{1-x}MnO_3$ precursor deposited on YSZ is hardly released into water by immersion in water for 30 min, while that in the $LaMnO_3$ precursor electrochemically prepared on the Pt electrode is easily released by this immersion (*1*), suggesting that the La^{3+} ions in the electrolessly deposited oxide film strongly combine with hydrous MnO_2. The XPS spectra of $La3d_{5/2}$ in the $La_{0.85}MnO_3$ precursor and La_2O_3 are shown in Fig. 6. The binding energies in the $La_{0.85}MnO_3$ precursor on YSZ of 838.2 eV and 834.6 eV were close to those in La_2O_3 of 838.0 eV and 834.9 eV, suggesting that La in the $La_{0.85}MnO_3$ precursor on the YSZ exist in a state similar to that in La_2O_3.

Figures 7A and B show the La/Mn atomic ratio and the amounts of La and Mn in the oxide film deposited on YSZ as functions of the induction time for the electroless deposition of the oxide film, where the oxide films were deposited in the mixed solution of 0.5

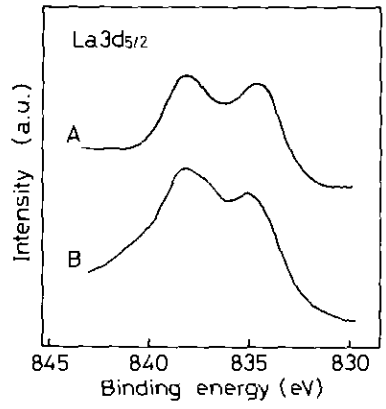

FIG. 6. XPS spectra of $La3d_{5/2}$ in the $La_{0.85}MnO_3$ precursor (A) and La_2O_3 (B). The $La_{0.85}MnO_3$ precursor was prepared in a solution of 0.5 *M* $La(NO_3)_3$–0.0005 *M* $Mn(NO_3)_2$–0.167 *M* $(NH_4)_2S_2O_8$–0.5 *M* CH_3COONa–5 × 10^{-6} *M* $AgNO_3$ at pH = 6.

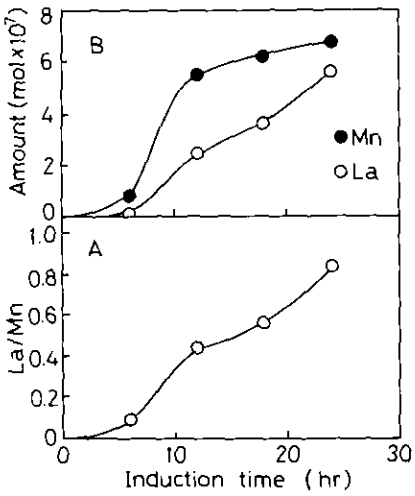

FIG. 7. La/Mn atomic ratio (A) and amounts of Mn and La (B) in the oxide film deposited in the solution of 0.5 *M* $La(NO_3)_3$–0.0005 *M* $Mn(NO_3)_2$–0.167 *M* $(NH_4)_2S_2O_8$–0.5 *M* CH_3COONa–5 × 10^{-6} *M* $AgNO_3$ at pH = 6 as a function of the induction time for the electroless deposition of the oxide film.

M $La(NO_3)_3$–0.0005 *M* $Mn(NO_3)_2$–0.167 *M* $(NH_4)_2S_2O_8$–0.5 *M* CH_3COONa–5 × 10^{-6} *M* $AgNO_3$ at pH = 6. The La/Mn atomic ratio in the oxide film increases with the induction time. However, the amount of Mn in the oxide film is saturated after 12 hr, while the amount of La in the oxide film increases even after 12 hr. In order to evaluate the contribution of simple adsorption of La^{3+} ion to the incorporation, MnO_2 films prepared on the YSZ in the mixed solution of 0.005 *M* $Mn(NO_3)_2$–0.167 *M* $(NH_4)_2S_2O_8$ at pH = 6 were immersed in 0.5 *M* $La(NO_3)_3$ at pH = 6 for 1–24 hr. La/Mn atomic ratios of the above oxide films were always 0.12 ± 0.02. These results suggest that the incorporation of La^{3+} ion into the oxide films is mainly based on specific adsorption, while the contribution of the simple adsorption of La^{3+} on the oxide films to the incorporation is very small. It should be noted that the incorporation of La^{3+} ion into the oxide film depends on the pH in the solution, as shown in Fig. 3. This phenomenon was also observed in the case of the oxide film deposited on YSZ in the solution containing CH_3COONa and $AgNO_3$. It is known that manganese dioxide has an ion-exchange property, where the some metal cations were exchanged for H^+ ions on the MnO_2 (*11, 12*). The amount of adsorbed metal cations on MnO_2 depends on the pH of the solution, as well as our case as shown in Fig. 3. Thus, the incorporation of La^{3+} ions into the oxide film may be based on ion exchange, where La^{3+} ions in the solution were exchanged for H^+ ions on the deposited MnO_2. Consequently, the formation of $La_{1-x}MnO_3$ precursor on YSZ occurs through two steps as follows. The first step is the formation of MnO_2 resulting from the oxidation of Mn^{2+} by peroxydisulfate; i.e, reactions (1) and (2) proceed, where the bonding water in the MnO_2 is neglected, but the MnO_2 in the oxide film must have some water. The second step is the incorporation of La^{3+} ion into the amorphous and hydrous MnO_2 by an ion-exchange reaction,

$$Mn_2O_4nH_2O + 2(1 - x)La^{3+} \rightarrow Mn_2O_4(2n - 3 + 3x)H_2O\ (3 - 3x)O\ (2 - 2x)La + 3(1 - x)H^+, \quad (3)$$

where x must be 0.15 and the value of n is not apparent as for the $La_{0.85}MnO_3$ precursor deposited in the mixed solution of 0.5 *M* $La(NO_3)_3$–0.0005 *M* $Mn(NO_3)_2$–0.167 *M* $(NH_4)_2S_2O_8$–0.5 *M* CH_3COONa–5 × 10^{-6} *M* $AgNO_3$ at pH = 6.

SEM micrographs of the $La_{0.85}MnO_3$ precursor on YSZ (A) and film after heat treatment at 800°C for 5 hr (B, C) are shown in Fig. 8. The $La_{0.85}MnO_3$ precursor consists of 0.5–1.0 μm grains, but was determined to be amorphous by X-ray analysis. The grain size and the thickness of the heat-treated film were about 0.2–0.5 μm and 1.0 μm, respectively. The x-ray diffraction pattern of the oxide film on YSZ heat-treated at 800°C for 5 hr is shown in Fig. 9. The oxide film consists of a perovskite single phase, which was prepared by heat treatment of the precursor at a lower temperature than the preparation temperature (ca. 1200°C) in the ceramic technique. $La_{0.96}MnO_3$ perovskite film was also prepared by heat treat-

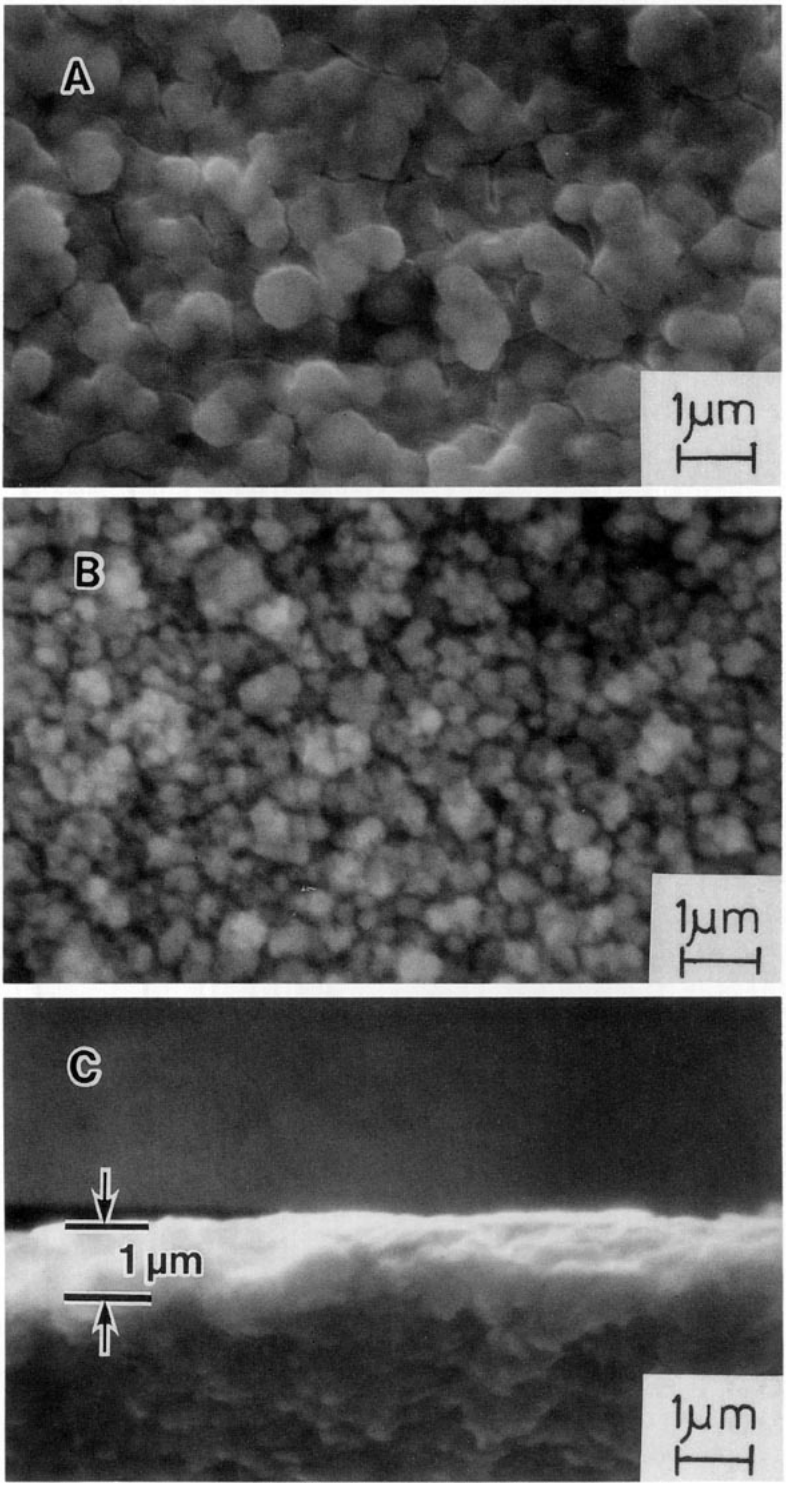

FIG. 8. SEM micrographs of $La_{0.85}MnO_3$ precursor (A) and $La_{0.85}MnO_3$ perovskite (B, C) prepared by heat treatment of the $La_{0.85}MnO_3$ precursor at 800°C for 5 hr. The $La_{0.85}MnO_3$ precursor was prepared in a solution of 0.5 *M* $La(NO_3)_3$–0.0005 *M* $Mn(NO_3)_2$–0.167 *M* $(NH_4)_2S_2O_8$–0.5 *M* CH_3COONa–5 × 10^{-6} *M* $AgNO_3$ at pH = 6.

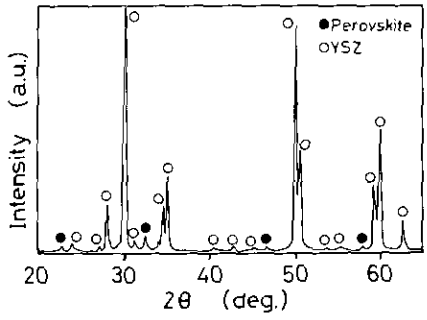

FIG. 9. X-ray diffraction pattern of the $La_{0.85}MnO_3$ perovskite film on YSZ which was prepared in a solution of 0.5 *M* $La(NO_3)_3$–0.0005 *M* $Mn(NO_3)_2$–0.167 *M* $(NH_4)_2S_2O_8$–0.5 *M* CH_3COONa–5 × 10^{-6} *M* $AgNO_3$ at pH = 6 and then heated at 800°C for 5 hr.

ment of $La_{0.96}MnO_3$ precursor, which was deposited from the mixed solution of 0.5 *M* $La(NO_3)_3$–0.0005 *M* $Mn(NO_3)_2$–0.167 *M* $(NH_4)_2S_2O_8$–1.5 *M* CH_3COONa–5 × 10^{-6} *M* $AgNO_3$ at pH = 6.9. The thickness of $La_{0.96}MnO_3$ perovskite film was very thin compared with that of $La_{0.85}MnO_3$ perovskite film, since the deposited amount of the $La_{0.96}MnO_3$ precursor was less than that of $La_{0.85}MnO_3$ precursor. Thus, a thin film of $La_{1-x}MnO_3$ perovskite on YSZ was easily prepared by the present method, and its composition could be controlled by the composition of the solution and/or some additives. Therefore the present method will be very useful for the preparation of $La_{1-x}MnO_3$ electrodes in SOFC. A study of the capabilities of the oxide film prepared by the present method as an air electrode in SOFC is in progress.

Summary

The oxidation of the mixed solution of $Mn(NO_3)_2$–$La(NO_3)_3$ with peroxydisulfate resulted in the formation of the oxide. The oxide film was deposited only on the YSZ substrate sensitized in a solution of $SnCl_2$ and activated in a solution of $PdCl_2$. The atomic ratio of La/Mn in the oxide film increased with increases in the $[La^{3+}]/[Mn^{2+}]$ ratio and in the pH of the solution. The oxide film with an La/Mn atomic ratio of 0.8–1.0 ($La_{1-x}MnO_3$ precursor) was electrolessly deposited in a solution containing both CH_3COONa and $AgNO_3$. These additives improved the incorporation of La^{3+} ion into the oxide film and the adhesion of the as-deposited oxide film on YSZ. From cyclic voltammetry of the as-deposited oxide film, XPS, IR, and XRD measurements indicated that the $La_{1-x}MnO_3$ precursor was amorphous hydrous MnO_2 which contained La^{3+} ions by specific adsorption. It can be presumed that the La^{3+} ion was incorporated into amorphous hydrous MnO_2 by an ion-exchange reaction, where La^{3+} ion in the solution is exchanged for H^+ ions on the electrolessly deposited MnO_2. $La_{0.85}MnO_3$ perovskite film (1.0 μm thick) was prepared by heat treatment of the electrolessly deposited oxide film with La/Mn = 0.85 at 800°C for 5 hr. The grain size of its film was 0.2–0.5 μm. $La_{0.96}MnO_3$ perovskite film was also prepared by the same method.

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