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Electrochemical Synthesis of $LaMnO_3$ Coatings on Conducting Substrates

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Cathodic reduction of a mixed metal nitrate solution containing La^{3+} and Mn^{2+} ions leads to the deposition of an X-ray amorphous mixed hydroxide coating, which on heat treatment (950 °C, 2 h) yields an adherent coating of $LaMnO_3$. This method can be adapted as a simple alternative to such conventional methods of fabricating ceramic films as laser ablation, rf sputtering, and chemical vapor deposition.

Introduction

The perovskite oxide $LaMnO_3$ has become a subject of widespread interest[1,2] on account of its GMR behavior. $LaMnO_3$ has also been used as an electrode material in solid oxide fuel cells, because its thermal expansivity matches with that of the solid oxide electrolyte PZT.[3] Further, on account of its chemical stability at high temperatures, it can be employed as a corrosion-resistant high-temperature protective coating for metal surfaces. For many of these and other applications (in the context of oxide electronics) it is of interest to obtain $LaMnO_3$ in the form of thin films and coatings. Oxide films are generally fabricated by techniques such as pulsed laser deposition,[4] sputtering,[5] or CVD.[6] Electrochemical deposition is fast emerging as a simple alternative for the fabrication of ceramic oxide films[7] and coatings.[8] In this paper we report the electrochemical synthesis of $LaMnO_3$ coatings on stainless steel (SS-310) substrates by the cathodic reduction of a mixed metal nitrate solution.

Experimental Section

A mixed metal nitrate solution (total concentration, 0.15 M) containing La^{3+} and Mn^{2+} ions ($[La^{3+}]/[Mn^{2+}] = 2/3$) was galvanostatically reduced (current density, 0.5 mA cm^{-2}) using a preweighed SS-310 flag electrode (surface area, 4.8 cm^2) in a divided cell. A KNO_3 solution (concentration, 0.15 M) was taken in the anodic chamber and a Pt flag was used as the counter electrode. The deposition time was varied from 0.5 to 2 h. At the end of the deposition, the working electrode was rinsed in distilled water, dried at 100 °C, and weighed. The pale brown coating which was adherent despite handling was inserted into a preheated furnace at 950 °C for 1 h. After heat treatment, a uniform black coating was obtained. It was weighed again to determine the weight loss during heat treatment.

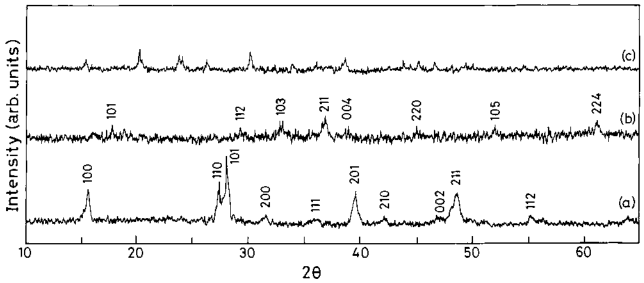

Figure 1. Powder X-ray diffraction patterns of hydroxide deposits obtained by the electroreduction of (a) lanthanum nitrate solution, (b) manganous nitrate solution, and (c) a mixed metal nitrate solution.

Gram quantities of the product could be obtained by prolonged electrodeposition (5 h) at higher current densities (66 mA cm^{-2}). Under these conditions, the electrodepositied film flakes off and collects in a heap at the bottom of the cathode chamber. It can be collected by filtration. Thermal decomposition of this powder also yields $LaMnO_3$. Prior to electrodeposition, the working electrode was cleaned with detergent and electrochemically polished as described elsewhere.[9] This pretreatment leads to a weight loss of 0.2 mg cm^{-2} of the electrode.

The as-prepared and heat-treated coatings and powders were characterized by X-ray diffractometry (JEOL model JDX-8P powder diffractometer, Cu Kα radiation), infrared spectroscopy (Nicolet Model Impact 400D FTIR spectrometer), scanning electron microscopy (JEOL JSM-840A scanning microscope), and thermogravimetry (homemade TG system, heating rate 2.5 °C min^{-1}). Direct current magnetic susceptibility measurements have been made in the range 300−100 K employing a Lewis Coil Force Magnetometer (George Associates, Model 2000).

Results and Discussion

Within a few minutes of electrolysis of a mixed metal nitrate solution containing La^{3+} and Mn^{2+} ions, the

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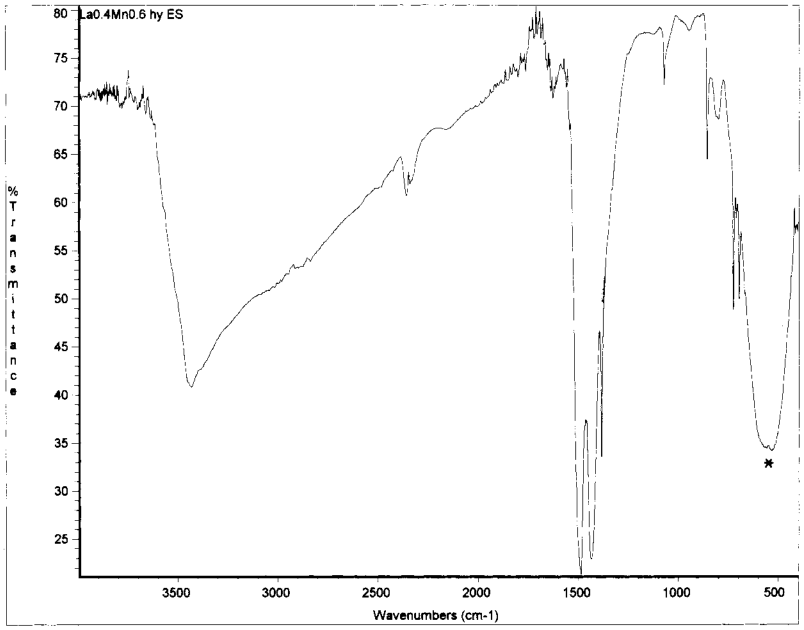

Figure 2. Infrared spectrum of the hydroxide deposit obtained by the electroreduction of a mixed metal nitrate solution. The peak marked by an asterisk is due to the MnO(OH) phase.

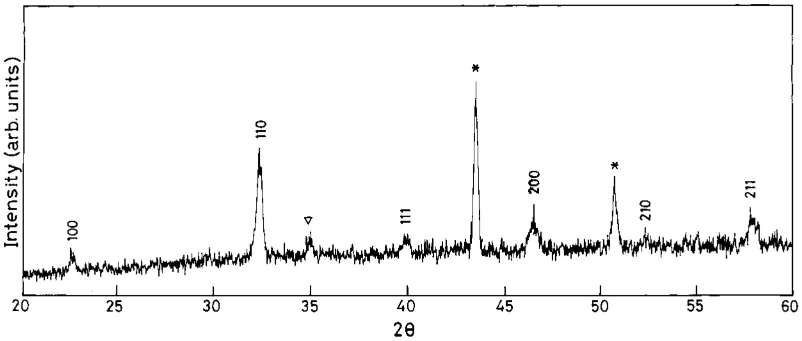

Figure 3. X-ray diffraction pattern of a $LaMnO_3$ coating obtained by the heat treatment of a mixed metal hydroxide coating. Peaks marked by an asterisk are due to the substrate and that marked by ▽ is due to an impurity.

growth of an uniform white deposit on the cathode could be visually observed. The deposition was carried out for different durations (0.5–2 h). The coating turns a pale brown on drying in air, due to the oxidation of Mn^{2+} to Mn^{3+}. The X-ray diffraction pattern of this coating is shown in Figure 1, together with those of the deposits obtained by the electroreduction of pure $La(NO_3)_3$ and $Mn(NO_3)_2$ solutions. Electroreduction of a $La(NO_3)_3$ solution leads to the formation of $La(OH)_3$, while the latter leads to the formation of poorly crystalline MnO(OH) phase. The deposit obtained from the mixed metal nitrate solution is X-ray amorphous with weak reflections which could not be assigned to any of the known binary and ternary hydroxides of La or Mn. However, it is clear that no stable crystalline oxide/hydroxides of either Mn or La are formed in this process. The IR spectrum of the deposit (see Figure 2) shows vibrations due to both $La(OH)_3$ and MnO(OH), showing that both of these phases have been codeposited in an X-ray amorphous form. This composite decomposes on heating and TG data exhibit a total 14% weight loss consistent with the reaction (calculated 12.9%)

$$La(OH)_3{\cdot}MnO(OH) \rightarrow LaMnO_3$$

The product of decomposition was found to be single phase pseudocubic ($a = 3.89$ Å) $LaMnO_3$ (see Figure 3),

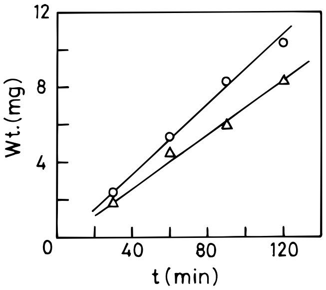

Figure 4. Coating growth as a function of the deposition time for as-prepared (a) and heat-treated (b) coatings.

when the bath composition was $[La^{3+}]/[Mn^{2+}] = 2/3$. A single-phase product was obtained only when the deposit was heat treated by insertion into a preheated (950 °C) furnace. Impurity peaks, possibly arising from undecomposed $La(OH)_3$, and some unidentified impurity were observed when the deposit was heated in the furnace from room temperature upward.

In Figure 4 is shown the coating weight as a function of the deposition time, before and after heat treatment. The growth is linear in time. On prolonged deposition ($t > 2$ h) the coating was found to crack and flake off due to the effect of evolved gases (H_2 evolution takes place simultaneously with the deposition). The thick-

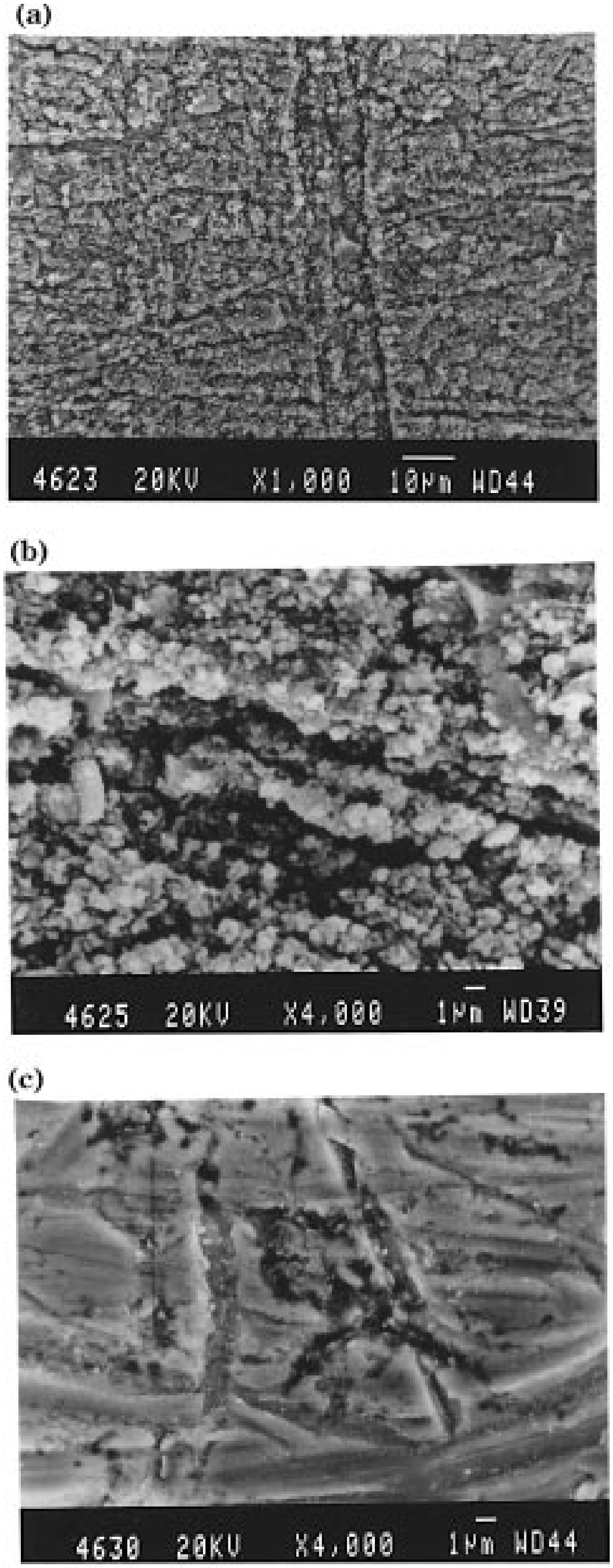

Figure 5. Scanning electron micrographs of a $LaMnO_3$ coating (a, b) compared with that of the substrate (c).

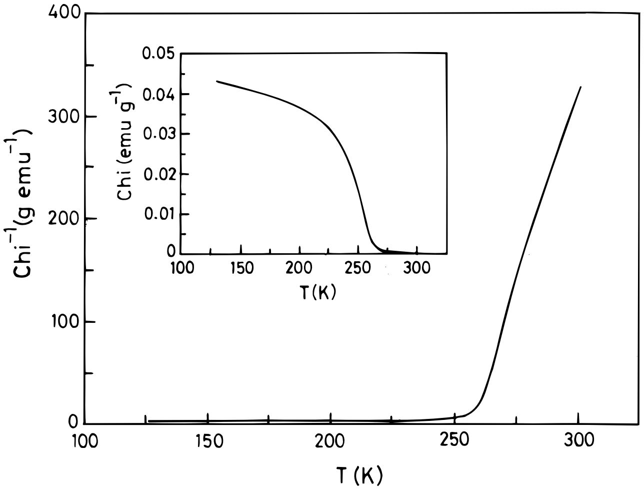

Figure 6. Variation of the dc magnetic susceptibility of electrosynthesized $LaMnO_3$ as a function of temperature.

ness of the heat-treated $LaMnO_3$ coatings, as estimated from the coating weight (density of $LaMnO_3$, 6.55 g cm^{-3}),[10] range from 0.5 to 2.6 μm. The heat-treated $LaMnO_3$ coatings could be reimmersed in the electrolyte for the electrodeposition of a fresh hydroxide film, and in this way, alternative deposition and heat treatment up to 4 cycles yielded thick coatings.

In Figure 5 are shown scanning electron micrographs of a $LaMnO_3$ coating. While the substrate exhibits deep pits (see Figure 5c), the $LaMnO_3$ coating has a fine granular morphology (Figure 5a). The coating is criss-crossed by a few scratches, and one of these has been examined at a higher magnification in Figure 5b. However, it is evident that fine grains exist even inside these scratches and the substrate surface is not exposed.

In Figure 6 is shown the variation of the dc magnetic susceptibility of an electrosynthesized $LaMnO_3$ sample as a function of temperature. The sample undergoes a clear ferromagnetic transition at 265 K, typical of oxygen excess $LaMnO_{3+\delta}$ phases, with δ being approximately 0.18.[11] This magnetic behavior is indicative of the existence of the GMR property of this sample.[12]

Electroreduction of an aqueous nitrate solution results in two classes of reactions, which have been described by Switzer[13] and Matsumoto et al.[14] One class pertains to nitrate reduction and the other to hydrogen evolution. Representative reactions of these two classes are given below

$$NO_3^- + H_2O + 2e^- \rightarrow NO_2^- + 2OH^- \quad E° = 0.01\ V \tag{1}$$

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2 \quad E° = -0.83\ V \tag{2}$$

Both classes of reactions release OH^- ions and lead to an increase in pH close to the electrode. Consequently, metal ions get electrodeposited on the cathode as hydroxide/oxide coatings

$$M^{n+} + nOH^- \rightarrow M(OH)_n \tag{3}$$

whose thickness can be varied from nanometers to

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microns. In the present instance, La^{3+} and Mn^{2+} codeposit as X-ray amorphous composite coatings. Sasaki et al.[15] have also succeeded in electrochemically fabricating LaMnO$_3$ coatings, but they employed the anodic oxidation route. In this, Mn^{2+} was oxidized and deposited in the form of γ-MnO$_2$ and Mn$_3$O$_4$, both of which yield stable crystalline phases. As La^{3+} has no anodic reaction of its own, incorporation of La^{3+} into the manganese oxide layers could be achieved by enriching the electrolyte with La by 10^2−10^3 times, which causes the La^{3+} ions to adsorb on the Mn oxide coatings. Cathodic reduction is an inherently superior technique as (i) both La^{3+} and Mn^{2+} participate in the reaction (3) leading to facile codeposition and (ii) the resultant deposit is X-ray amorphous and is therefore likely to undergo facile decomposition.

In conclusion, we report here the electrochemical synthesis of LaMnO$_3$ coatings on metal substrates. This method can be adapted as a simple and inexpensive alternative to the conventional techniques of fabricating oxide films.

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