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Electrosynthesis of $Ln(OH)_3$ (Ln = La, Nd) Coatings on Stainless Steel Substrates

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Micrometer thick coatings of the hydroxides of La and Nd can be electrodeposited on stainless steel substrates by cathodic reduction of aqueous solutions of the corresponding nitrates. The coatings are uniform, adherent, and stable to thermal treatment up to moderate temperatures. At high temperatures (>900 °C), the coatings react with the substrate to yield surface oxides having a perovskite-like structure. This technique can be adapted as a simple chemical alternative to conventional methods of fabricating hydroxide and oxide films and coatings.

Introduction

Most metal hydroxides crystallize in a number of polymorphic modifications, many of which are metastable in nature.[1] Metal hydroxides are widely employed as catalysts,[2] sensors,[3] ion exchangers,[4] and battery cathodes[5] and as protective coatings for metal substrates.[6] For many of these applications, the hydroxides have to be obtained in the form of thin/thick films or coatings. There are significant difficulties in achieving this objective.

Conventional methods of fabricating ceramic films such as pulsed laser deposition, sputtering, electron beam etching, and CVD cannot be used for hydroxide materials, as they are low temperature phases which rapidly decompose upon irradiation by high power electron, photon, or ion beams.

These problems can be overcome by using electrosynthetic techniques. Two different approaches have been developed for the synthesis of hydroxide films. Burke and co-workers[7] have evolved a technique of growing hydrous oxide films by potentiodynamic cycling of reactive metal electrodes in alkaline medium. In a typical reaction, the metal whose hydroxide is to be synthesized is taken as the anode in an alkaline electrolyte (pH > 14) and is potentiodynamically cycled at a very high scan rate, $0.5-1\ V\ s^{-1}$. After a large number of cycles, typically 10^3-10^4, a slow analytical cyclic voltammetric measurement is made. This usually reveals the growth of a hydrous oxide or in some systems the appropriate hydroxide. One of the best applications of this method has been the synthesis of mixed metal (Y, Ba, Cu) hydroxide films by cycling a Cu foil electrode in a barium hydroxide solution[8] containing dissolved salts of Y and Ba, with a view to obtaining a film of the superconducting 123 phase. However, this technique does not permit the solid-state characterization of the hydrous oxide or the investigation of its growth characteristics. As a result, it is not useful for the controlled growth of well-characterized hydroxide coatings of a desired thickness. It is also unsuitable for the growth of hydroxide coatings on inert electrode substrates.

The second approach is the synthesis of hydroxides by electrogeneration of base. Electrogeneration of base causes a rise in the pH of the solution close to the electrode surface. The bulk pH is not significantly affected, especially at low current densities. Therefore, hydroxide precipitation takes place close to the electrode and the precipitate deposits on the electrode in the form of an adherent coating. This technique has been used extensively in the alkaline battery industry for the manufacture of nickel hydroxide electrodes.[9] We have used this method to achieve the controlled growth of hydroxide coatings on conducting substrates. A number of hydroxides have been grown as coatings and in this paper we describe, as an illustration, the fabrication of adherent coatings of $Ln(OH)_3$ (Ln = La, Nd) on stainless steel substrates. Rare-earth-metal hydroxide coatings on conducting substrates are potential precursors for the synthesis of perovskite oxides with interesting electrical and magnetic properties.[10]

Experimental Section

All $Ln(OH)_3$ coatings were electodeposited on stainless steel (SS 316) flag electrodes (surface area, 6 cm^2) galvanostatically

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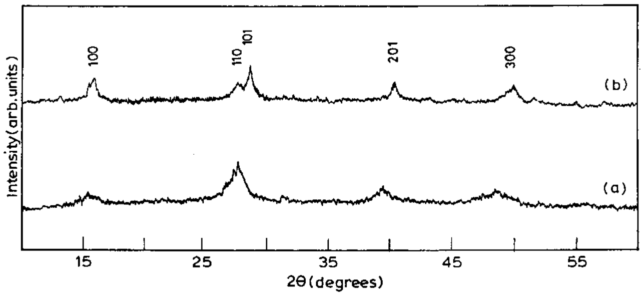

Figure 1. Powder X-ray diffraction patterns of $La(OH)_3$ (a) and $Nd(OH)_3$ (b) obtained after prolonged electrosynthesis.

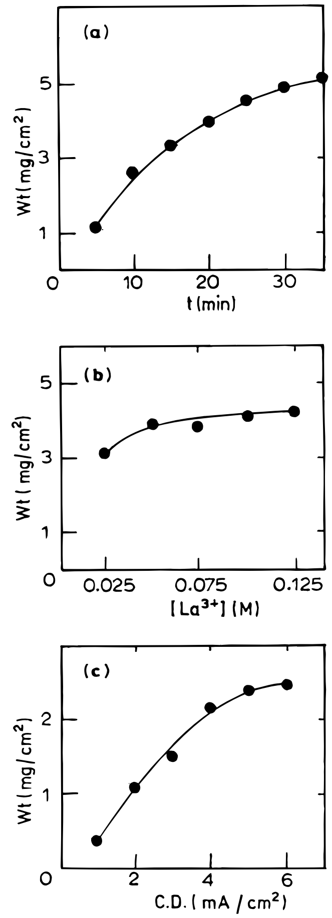

Figure 2. Growth characteristics of a $La(OH)_3$ coating as a function of time (current density 5 mA cm^{-2}; 0.05 M [La^{3+}]) (a), as a function of bath concentration (current density 5 mA cm^{-2}; $t = 30$ min) (b), and as a function of current density (0.1 M [La^{3+}]; $t = 10$ min) (c).

(current density, 1−6 mA cm^{-2}) in an undivided cell (volume, 50 cm^3) containing the appropriate aqueous $Ln(NO_3)_3$ solution (concentration, 0.01−0.15 mol dm^{-3}; pH, 2.8 for Ln = La and 2.3 for Ln = Nd). A cylindrical platinum mesh (geometric area, 28 cm^2) was employed as the anode. The potential of the working electrode during deposition was measured with respect to a SCE using a high impedance Meco, multimeter. Prior to deposition, the working electrode was cleaned in detergent and electrochemically treated as described elsewhere.[11] This treatment led to a weight loss of ∼0.2 mg cm^{-2}. The preweighed electrode was used for electrodeposition.

Within a few minutes of electrolysis, a deposit could be visually seen on the working electrode. At the end of the deposition ($t = 0.5-2$ h), the working electrode was rinsed in distilled water and dried to constant weight at 100 °C and weighed again to determine the coating weight. The coating weight was measured in a series of experiments, by systematically varying the deposition conditions. All coatings reported here were uniform in appearance, adherent to the substrate and stable to washing, drying and thermal treatment. The hydroxide coatings were heat treated for 1 h at 750 °C and for 12 h at 950 °C.

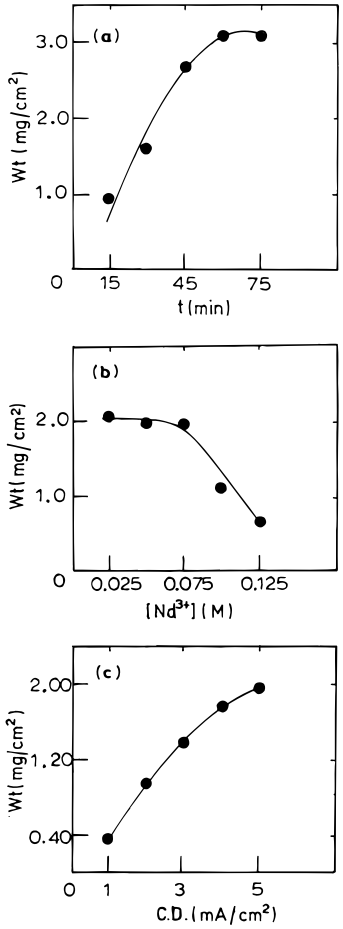

Figure 3. Growth characteristics of a $Nd(OH)_3$ coating as a function of time (current density 2 mA cm^{-2}; 0.05 M [Nd^{3+}]) (a), as a function of bath concentration (current density 5 mA cm^{-2}; $t = 15$ min) (b), and as a function of current density (0.05 M [Nd^{3+}]; $t = 15$ min) (c).

Prolonged deposition ($t > 4$ h) led to thickening of the deposit and consequent loss of adherence. The thick film cracks and collects at the bottom of the cell and gram quantities of the product could be recovered. The samples were subjected to wet chemical analysis. To determine the Ln^{3+} content, an accurately weighed amount of the hydroxide was dissolved in dilute HCl and added to a solution of standardized oxalic acid and the excess oxalic acid was estimated by titrating it with a standard $KMnO_4$ solution. The hydroxyl content of the sample was estimated by dissolving an accurately weighed amount of the hydroxide in excess acid and back-titrating the excess with a standard solution of NaOH using a pH meter. The unaccounted weight was attributed to the presence of water, which was also determined by thermogravimetry.

All coatings and polycrystalline products were analyzed by powder X-ray diffraction (JEOL model JDX-8P powder diffractometer, Cu Kα, $\lambda = 1.541$ Å), IR spectroscopy (Nicolet model Impact 400D FTIR spectrometer, KBr pellets, 4 cm^{-1} resolution), thermogravimetry (lab-built system, heating rate, 5 °C min^{-1}) and scanning electron microscopy (JEOL JSM-840A scanning electron microscope).

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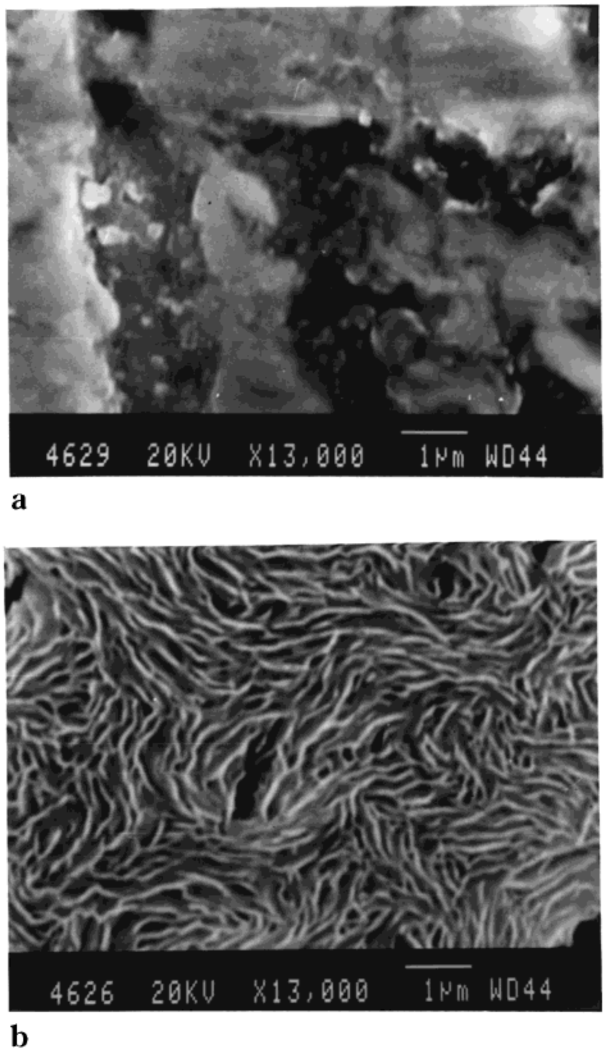

Figure 4. Scanning electron micrograph of a stainless steel surface before (a) and after (b) electrodeposition of a La(OH)$_3$ coating.

Results and Discussion

In Figure 1 are shown the powder X-ray diffraction patterns (pXRD) of the products obtained from a prolonged electrolysis of the rare-earth-metal nitrate solutions. The broad reflections and their low intensities indicate a small domain size. The pattern of the sample obtained by the reduction of the La(NO$_3$)$_3$ solution matches with that assigned to La(OH)$_3$ (PDF: 36-1481). The pattern of the sample obtained by the reduction of the Nd(NO$_3$)$_3$ solution matches with that reported for Nd(OH)$_3$ (PDF: 45-0085). Two other patterns (PDF: 13-0085, 6-0601) have also been ascribed to Nd(OH)$_3$. Both of these correspond to samples obtained by high-pressure preparations and are unsuitable for comparison with our sample. Unfortunately the PDF: 45-0085 pattern has not been indexed. Since it is very similar to the pattern of La(OH)$_3$, we have indexed both patterns using La(OH)$_3$ as the model. Wet chemical analyses of our samples also exhibit a Ln:OH mole ratio of 1:3 for both La and Nd indicating that the products of electrosynthesis are hydroxides of the type Ln(OH)$_3$.

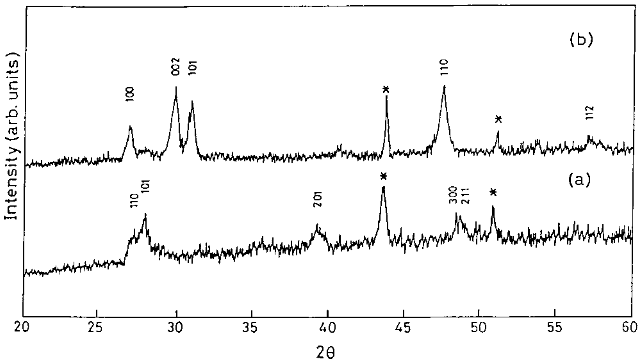

Figure 5. Powder X-ray diffraction patterns of La(OH)$_3$ (a) and Nd(OH)$_3$ (b) coatings after heat treatment at 750 °C. Peaks marked by asterisks are due to substrate.

Cathodic reduction of metal nitrate solutions results[12] in the generation of hydroxyl ions leading to a steep increase in the pH close to the electrode. This leads to the precipitation of the rare-earth-metal ion as

$$\mathrm{Ln}^{3+} + 3\mathrm{OH}^- \rightarrow \mathrm{Ln(OH)}_3\downarrow$$

The precipitate deposits in the form of a coating on the cathode. The coating growth characteristics are shown in Figures 2 and 3. The coating grows as a function of time initially and then levels off to a limiting thickness (Figures 2a and 3a). The limiting thicknesses estimated from density data (4.45 g cm^{-3})[13] are 11.2 and 6.9 μm for La(OH)$_3$ and Nd(OH)$_3$, respectively.

In Figures 2b and 3b are shown the variations in the coating weight as a function of the electrolyte concentration. While the La(OH)$_3$ coating weight increases with increase in electrolyte concentration and reaches the limiting thickness, the Nd(OH)$_3$ coating weight decreases with increase in electrolyte concentration. There are two possible explanations:

(1) The existence of parasitic reactions in the Nd(NO$_3$)$_3$ bath at higher concentrations that consume charge without generating hydroxyl ions.

(2) The formation of partially hydrolyzed soluble complex species of the type $[\mathrm{Ln}_x(\mathrm{OH})_y]^{(3x-y)+}$.

The formation constants of the LnOH^{2+} species are nearly an order of magnitude higher in the case of Nd compared to the La system,[14] indicating that the latter explanation is responsible for the decreased yield of Nd(OH)$_3$.

The effect of current density on coating growth is shown in Figures 2c and 3c. At a fixed deposition time, the coating weight increases with increase in current density and the coating thickness reaches a limiting value (5.4 and 4.4 μm, respectively, for Ln = La, Nd at ~6 mA cm^{-2}). At higher current densities the coating weight suddenly increases (not shown in the figures) even at low deposition times. Gel formation was observed in the bath. The coating, on examination was found to be uneven and the Coulombic efficiency, estimated as a ratio of the moles of hydroxide produced to the coulombs of charge passed was in excess of 100%. This is due to chemical precipitation as high rates of base generation increase the bulk pH. In the case of the Nd system, the Coulombic efficiencies do not exceed 65%

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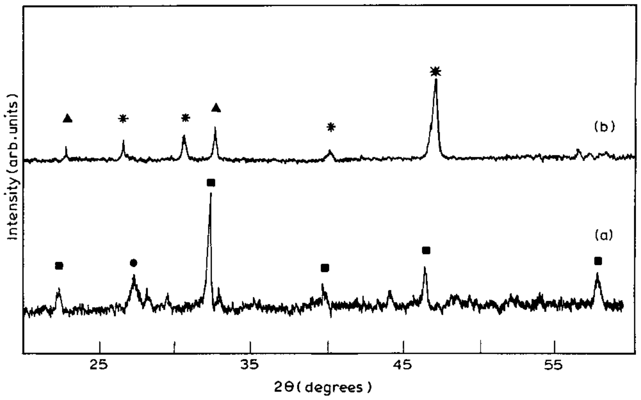

Figure 6. Powder X-ray diffraction patterns of $La(OH)_3$ (a) and $Nd(OH)_3$ (b) coating after heat treatment at 950 °C. Peaks marked by ■, ●, ▲, and ∗ correspond to $LaCrO_3$, $La(OH)_3$, $NdCrO_3$, and Nd_2O_3 phases, respectively.

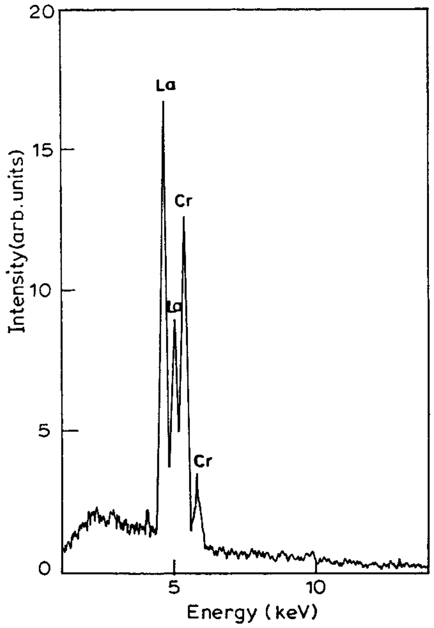

Figure 7. EDXA data for the $La(OH)_3$ coating heat treated at 950 °C showing the presence of 40 atom % of Cr.

under any conditions, showing the possible formation of soluble hydrolyzed species.

In Figure 4, we show the scanning electron micrographs of a $La(OH)_3$ coating obtained on a stainless steel substrate. While the substrate was rough and full of scratches, the as-deposited hydroxide film provides an even coat having a fibrous morphology.

The coatings are adherent and upon thermal treatment (750 °C, 1 h) the $La(OH)_3$ coating is unchanged while the $Nd(OH)_3$ coating has decomposed to yield Nd_2O_3 (Figure 5). On further heating (950 °C, 12 h) the reflections corresponding to the perovskite oxide, $LnMO_3$, were also found to appear in the pXRD patterns of the coatings (Figure 6). To understand the nature of the perovskite coat, the coatings were scraped and subjected to EDX analysis. The oxide coat in both cases showed the presence of Cr in addition to the rare-earth metal (Figure 7) showing that the hydroxide coating reacts with the Cr of the substrate. The *d* spacings observed for the heat treated $La(OH)_3$ coating at 3.90, 2.755, 2.254, 1.949, and 1.590 Å, respectively, match with those reported for $LaCrO_3$ (PDF: 33-0702) and the *d* spacings observed for the heat treated $Nd(OH)_3$ at 3.85 and 2.72 Å correspond to the two main reflections reported for $NdCrO_3$ (PDF: 39-1429). However the reaction is incomplete (Ln:Cr = 60:40 atom %) even after prolonged treatment. This is borne out by the pXRD patterns in Figure 6 which show the presence of unreacted $La(OH)_3$ (Nd_2O_3).

Conclusions

In conclusion, we have shown that unary transition-metal hydroxide coatings of micrometer thickness can be prepared in a single step by electrogeneration of base. The $Ln(OH)_3$ (Ln = La, Nd) system was chosen as a model. This can be extended to the preparation of any other hydroxide coating. Controlled growth of these coatings can be realized by suitable choice of deposition parameters such as current density, concentration, pH, and duration of deposition. Heat treatment of these coatings results in the formation of perovskite oxides.

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