



Electrodeposition of Layered Double Hydroxides on platinum: Insights into the reactions sequence



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ABSTRACT

The electrodeposition of four Layered Double Hydroxides (LDHs) has been attempted by applying different cathodic potentials to electrochemically pre-treated Pt surfaces soaked into solutions containing Al and four divalent cations (Co, Ni, Zn, Mg) in the form of nitrates. The syntheses have been performed in the presence (C1 condition) or in the absence (C2 condition) of KNO₃ which acts both as supporting electrolyte and as additional source of nitrates necessary for the generation of the hydroxide anions. A systematic characterization of all the materials obtained in C1 condition has been performed to investigate the reactions sequence during precipitation. Two pathways for the LDHs electrodeposition have been demonstrated which are related to the OH⁻ production rate. If it is slow the electrodeposition involves two steps: the first is the precipitation of Al(OH)₃ and the second is the formation of LDH from the reaction between Al(OH)₃ and M(II). On the other hand, the LDH is directly formed starting from M(II) and Al(III) when a high amount of OH⁻ is generated at the electrode surface.

In C2 condition only the most cathodic potential has been investigated. The obtained results indicate that in such a case both M(II) and Al precipitate simultaneously.

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1. Introduction

Layered Double Hydroxides (LDHs), which have the general formula $[M(II)_{1-x}M(III)_x(OH)_2]^{x+}[X_q^{x/q-}.nH_2O]$, abbreviated as M(II)/M(III), are inorganic solids showing 2D structural arrangement which are also called anionic clays or hydroxalite like compounds. LDHs can be easily prepared in laboratory with several synthetic methods [1–3], such as, for instance, coprecipitation at constant pH [1], coprecipitation using a retardant base such as urea [4] or hydrolysis of metal salt precursors in polyol medium [5]. LDHs have extensive applications in many fields such as electrochemical devices, catalysis, medicine or environment [6]. Some of these applications like sensors, biosensors, supercapacitors or electrochromic devices require the formation of LDH thin films [7–11]. Recent research works concern the preparation of LDHs delaminated nanosheets to be used as building blocks for the preparation of thin films via the layer by layer method [9]. Electrosynthesis techniques exploiting the base electrogeneration provide a simple and

inexpensive alternative route to the synthesis of hydroxides and LDHs thin films [12–15].

In particular, in the last few years our group has optimized the one-step electrodeposition, mainly on Pt electrodes, of LDHs based on Ni or Co and Al [9,16,17]. This method is based on the electrochemical generation of hydroxide anions by cathodic reduction of nitrates [18] and has the advantage to synthesize the LDHs on the electrode surface in a very short time; a complete electrode coverage can be achieved in 60 s. LDHs electrodeposition can be also performed on other conductive materials, e.g. ITO [19], glassy carbon [20], gold [12], FeCrAlloy [21], and Ni [22]. The film thickness can be easily controlled by changing the value of the applied potential (potentiostatic synthesis) or the current density (galvanostatic synthesis) and the length of the application time. Macroporous thin films can be obtained by the LDHs electrogeneration through colloidal crystals of polystyrene beads self-assembled on Pt which are used as sacrificial template [16]. Such electrogenerated thin films have been also prepared in the presence of enzymes leading to direct enzyme immobilization [23,24].

In using such a synthetic approach, LDH decorated graphene nanosheets-modified electrodes have been prepared [25,26], as well as Au nanoparticles@LDHs [19,27]. Growing interest for this

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synthesis process justifies, therefore, a detailed study of the reactions sequence occurring during the electrodeposition.

The LDHs electrosyntheses are usually performed in a KNO_3 electrolyte solution as an additional source of nitrate ions. However, an adequate Pt pretreatment increases the rate of hydroxyl ions production [17], thus allowing the deposition of the LDHs only in the presence of the M(II) and M(III) salts as source of nitrates, i.e. without the supporting electrolyte. Such electro-synthesis conditions have been demonstrated to produce Ni/Al LDH films displaying a very high adhesion on the electrode surface [28].

Here, we present a study aimed at elucidating the reactions sequence of the electrodeposition of different LDH materials on electrochemically treated Pt surfaces starting from solutions containing Al(III) and four divalent cations (Co, Ni, Zn, and Mg). Two electrolytic solutions for the electro-synthesis (with and without KNO_3) have been investigated. A systematic characterization of all the films resulting from the depositions at different cathodic potentials has been performed.

2. Experimental

2.1. Chemicals

Magnesium nitrate (99%), nickel nitrate (>99%), zinc nitrate (>99%), cobalt nitrate (98%), aluminum nitrate (98%), and sodium hydroxide were purchased from Sigma–Aldrich. Potassium nitrate (>99%), and sulfuric acid were obtained from Fluka. All solutions were prepared with doubly distilled (DD) water.

2.2. Apparatus

All the electrochemical tests were carried out in a single compartment three-electrode cell, without removing oxygen. Electrode potentials were measured with respect to an aqueous saturated calomel electrode (SCE). The working electrode was a Pt disk (3 mm diameter) or a Pt foil (1 cm² area). A Pt gauze was used as the counter electrode. The electrochemical tests were made with an Autolab PGSTAT 20 (Ecochemie, Utrecht, The Netherlands) potentiostat/galvanostat interfaced with a personal computer. Cyclic voltammograms were recorded in 0.1 M NaOH ($\nu = 10 \text{ mV s}^{-1}$) for Co/Al LDH thin films prepared in C1 and C2 conditions. The electrochemical quartz microbalance (EQCM) experiments were performed with a MAXTEK PM-710 device, equipped with a 5 MHz-AT cut quartz crystal coated with sputtered Pt (surface area 1.37 cm²). The morphology of LDH films was investigated by SEM analysis, using an EVO 50 Series Instrument (LEO ZEISS). The

accelerating voltage was 25 kV, the beam current 1.5 nA and the spectra collection time 60 s.

The PXRD patterns of the powder samples and of thin films were recorded using a Philips X'Pert Pro diffractometer with a Cu K α radiation ($\lambda = 0.15415 \text{ nm}$) in the 6°–70° 2 θ range, in steps of 0.0167° with a counting time per step of 400 s. In order to directly record the XRD patterns the electrodeposition step was repeated 10 times at the same electrode (total deposition time of 600 s). In the case of the LDH based on Co and Al, deposited at -0.60 V , the diffractogram was recorded using the powder that had been scratched from the Pt foil, since the signal coming from 10 electrodeposited layers was not high enough for the PXRD analysis. FTIR spectra were recorded by a Nicolet 5700 (Thermo Electron Corporation) spectrometer.

2.3. LDH electrodeposition

The surface of the Pt disks was polished to a mirror-like surface, first with sand-paper and then with aqueous alumina (0.05 μm) slurry on a wet polishing cloth. After rinsing with DD water the electrodes were soaked into a 1:1 ethanol/water mixture, under sonication for 10 min, in order to remove any trace of alumina. The electrodes for EQCM experiments were used as received. In order to investigate the reproducibility of the electrodeposition, the electrodes were kept in 0.5 M H_2SO_4 aqueous solution, to remove the LDH film, until the starting frequency was restored.

Two experimental conditions were employed to perform the electrochemical syntheses: in the first one (C1), prior to proceed with the LDH deposition, the Pt electrodes were submitted to a potentiodynamic electrochemical pretreatment consisting of 250CV cycles between -0.20 and $+1.30 \text{ V}$, in 0.1 M H_2SO_4 , at a scan rate of 1 V s^{-1} (Pt-CVT). The LDHs films were further deposited on the electrode surface by electrochemical reduction at different applied potentials (-0.60 , -0.75 , -0.90 V vs SCE) of a solution containing the divalent metal (M(II) = Co, Ni, Zn, Mg) as nitrate salt at a concentration of 0.0225 M, 0.0075 M $\text{Al}(\text{NO}_3)_3$ and 0.3 M KNO_3 as the supporting electrolyte.

In the second condition (C2), the Pt electrodes were submitted to a more complex electrochemical pretreatment. After performing the Pt-CVT treatment, a cathodic potential of -0.90 V was applied to the electrode for 300 s while it was soaked in 1 M H_2SO_4 , keeping the solution under stirring to eliminate H_2 bubbles that were formed on Pt surface. Finally, the electrode was submitted to three CV cycles between -0.20 and $+1.30 \text{ V}$, in 0.1 M H_2SO_4 (Pt-CT). The LDHs films were deposited on the electrode surface by electrochemical reduction ($E_{\text{app}} = -0.90 \text{ V vs SCE}$) of a

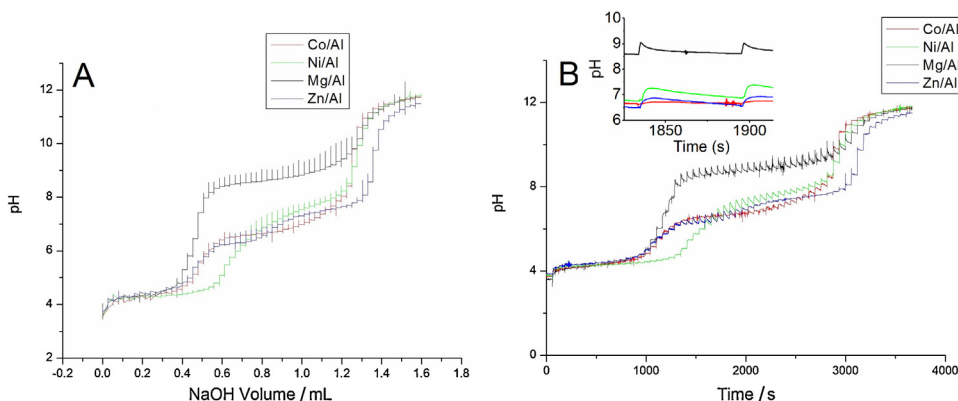


Fig. 1. Titration curves obtained by adding fixed aliquots (26.6 μL) of the titrant (1.000 M NaOH), every 61 s, to a mixed salts solution (0.0075 M $\text{Al}(\text{NO}_3)_3$ + 0.0225 M $\text{M}(\text{NO}_3)_2$, with M(II) = Co, Ni, Mg, Zn). The curves are reported vs the added volume (A) and vs time (B). The inset shows a magnification of the central part of the second plateau to highlight the rate of pH decrease after each NaOH addition.

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