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Electrosynthesis of Thin Films of Ni, Al Hydrotalcite Like Compounds

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Thin films of pure-nickel-based hydrotalcite-like compounds have been deposited on a Pt electrode by electrosynthesis. The best films have been obtained by cathodic reduction of a 0.03 M solution of Ni and Al nitrates in different molar ratios. The films, obtained in different experimental conditions, have been characterized by different techniques, such as SEM, AFM, and XRD. Particular attention has been devoted to understanding the mechanism of their growth. The electrochemical properties of the films obtained for different deposition times and Ni/Al ratios have been studied in basic solution (NaOH) by cyclic voltammetry and AC impedance spectroscopy.

1. Introduction

Layered double hydroxides (LDHs) or hydrotalcite like compounds (HTs) have the general formula $[M_a(II)_{1-x}M_b(III)_x(OH)_2]^{x+}(A^{n-}{}_{x/n})\cdot mH_2O$, shortly named $M_a/M_b{-}A$, where M_a and M_b are metals, A is an anion, and x ranges between 0.17 and 0.44 when M_a is nickel in order to have a pure HT phase.[1,2] Their structure consists of brucite-like layers positively charged and compensated by anions located in the interlayers. The HTs that contain a transition metal undergoing a reversible redox reaction between oxidized and reduced forms of the $M_a(II)/M_a(III)$ couple, like Ni or Co, have been proposed as materials with improved charge transport in the range of applied potential.[3−5]

Materials belonging to this family have many potential applications, such as precursors for coatings and catalysts,[6,7] hosts for photoactivation and photocatalysis,[8,9] and anion exchangers,[10] and are widely employed to modify electrode surfaces in order to obtain ion-selective electrodes or amperometric sensors.[11−13] For most of the cited applications, it is fundamental to prepare thin HT films. The most commonly employed procedure consists of depositing a fixed amount of a colloidal solution of the HT, previously synthesized in bulk by the coprecipitation method,[14] onto the electrode surface. The major drawback of this method is the short lifetime of the modified electrodes due to the poor adhesion of the HT to the support material (Pt, Au, or GC). Our research group has in the past investigated several ways of modifying electrode surfaces with chemically synthesized HTs, developing either membrane or composite electrodes, but in such cases, it was difficult to obtain thin films of controlled thickness.[15]

With this aim, we have performed an extensive study to find the best experimental conditions to modify different electrode materials by one-step electrosynthesis of the $Ni/Al{-}NO_3$ HT.[16] The great advantage of this method is the very short time employed to modify the electrode surface. The starting point of this research was two papers that reported the synthesis (in bulk) of HTs containing Co or Ni as bivalent and Al as trivalent metals by cathodic reduction of nitrate ions.[17,18]

When a cathodic potential is applied to a nitrate solution, several reactions, leading to the disappearance of H^+ and the generation of OH^-, take place and contribute to the precipitation of the HT close and on the electrode surface.[19]

Our previous study[16] was conducted using a 0.3 M deposition solution of Ni and Al nitrates; in such a condition,

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we were not able to record an XRD pattern of the electrosynthesized material directly on the electrode surface, but the precipitate was removed from the electrode and the powder analyzed. No study on the exact nature and composition of the material directly on the electrode surface was made.

In the present work, a detailed characterization of the films obtained using the 0.3 M solution of Ni and Al nitrates has revealed that they are disomogeneous and constituted by a mixed phase. Furthermore, their composition is that of a pure HT phase only for very high deposition times.

Extensive work aimed at finding the conditions to obtain thin films of a pure Ni/Al HT phase has been performed; using a deposition solution diluted by one order a magnitude, pure HT films can be obtained.

Particular attention has been devoted to the chemical nature of the material deposited on the electrode surface as a function of the electrosynthesis time and molar ratio of Ni and Al salts. Several techniques including cyclic voltammetry (CV), AC impedance spectroscopy, X-ray diffraction (XRD), FT-IR and optical microscopy, atomic force microscopy (AFM), and scanning electron microscopy (SEM) have been employed to characterize the HT films.

2. Experimental Section

2.1. Apparatus. All the electrochemical tests were carried out at room temperature using a single-compartment, three-electrode cell. Electrode potentials were measured with respect to an aqueous saturated calomel electrode (SCE). A Pt wire was used as counter electrode. The CV curves and the impedance spectra were recorded using a CHInstruments Mod. 660 A, controlled by a personal computer via CHInstruments software. All the electrochemical impedance spectroscopy dispersions were recorded between the frequencies of 1 mHz and 100 kHz. The temperature was controlled using a HAAKE D8 thermostat.

A Philips PW 1050/81−1710 diffractometer with Cu Kα radiation source ($\lambda = 1.5418$ Å) and a graphite monochromator in the path of the diffracted beam were used for XRD measurements; a 2θ range from 2 to 80° was explored at a scan rate of $0.05°\ s^{-1}$.

Surface roughness and morphology were evaluated by atomic force microscopy (AFM, scanning Probe Microscope Vista 100, Burleigh Instruments) operating in contact mode with a force of 32 nN and by optical microscopy (Reichert-Jung MeF3A additionated with a JVC-TK-C1381 color videocamera).

The morphology and chemical composition of HT films were investigated by SEM/EDS analysis, using an EVO 50 Series Instrument (LEO ZEISS) equipped with an INCAEnergy 350 EDS microanalysis system and INCASmartMap for imaging the spatial variation of elements in a sample (Oxford Instruments Analytical). The accelerating voltage was 25 kV, the beam current 1.5 nA, and the spectra collection time 100 s. After the electrodeposition, the films were rinsed gently with doubly distilled water, dried in a desiccator over silica gel, and then promptly submitted to the characterization analysis.

The Fourier transform infrared spectra (FT-IR) were recorded with a Nicolet Nexus 470 spectrometer, configured with a Nicolet Continuum microscope and a MCT/B liquid-nitrogen-cooled detector. Spectra were collected in ATR (attenuated total reflectance) mode through a Cassegrain objective (14×), reaching a spatial resolution of $\sim 100\ \mu m^2$. The spectra were recorded (as sum of 256 scans with a resolution of 4 cm^{-1}) in the spectral region of the medium infrared (800−4000 cm^{-1}).

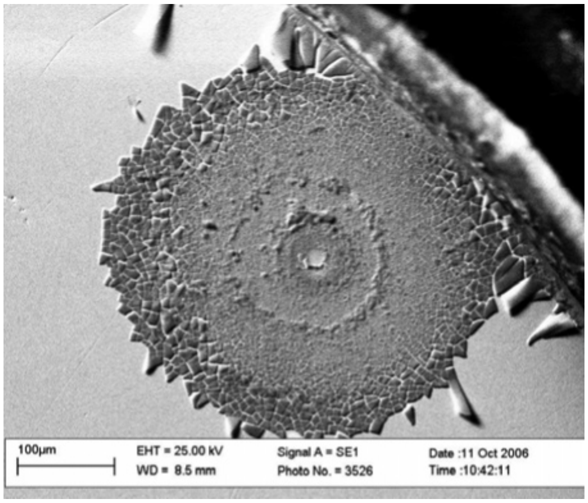

Figure 1. SEM micrograph of a Pt electrode modified with the film ($E_{app} = -0.9$ V, $t = 60$ s) obtained from a 0.3 M solution of Ni and Al nitrates (Ni/Al molar ratio = 3/1). A circular zone is shown. Magnification: 1000×.

2.2. Chemicals. All chemicals (Fluka) were of reagent grade purity and used as received. All solutions were prepared with doubly distilled water from glass apparatus. The Ni/Al−NO_3 HT was electrosynthesized starting from freshly prepared solutions of nickel and aluminum nitrates.

2.3. Preparation of Modified Electrodes. A Pt rod of 3 mm diameter was inserted inside a Teflon tube. The external surface was polished to a mirrorlike surface with an aqueous alumina (Logitech) slurry of three different granulometry (1, 0.3, and 0.05 μm) on a wet polishing cloth, rinsed with distilled water, and then sonically cleaned in a 1/1 ethanol/water mixture for 10 min to remove any trace of alumina. After the bare electrode was rinsed with carbon-dioxide-free water, it was dried at room temperature. A film of Ni/Al−NO_3 HT was deposited on the electrode surface by cathodic reduction of a solution containing $Ni(NO_3)_2$, $Al(NO_3)_3$, and 0.3 M KNO_3. Different concentrations and molar ratios of nickel and aluminum were employed.

Solution A: Total $Ni(NO_3)_2$ and $Al(NO_3)_3$ concentration, 0.3 M; Ni/Al molar ratio = 3/1.

Solution B: Total $Ni(NO_3)_2$ and $Al(NO_3)_3$ concentration, 0.03 M; Ni/Al molar ratios = 2/1, 3/1, 4/1, 5/1.

The electrochemical reaction was carried out in a single-compartment, three electrode cell by applying a potential of −0.9 V vs SCE.[16] Different deposition times (10, 30, 50, 60, 90, 120 s) were considered.

3. Results and Discussion

3.1. Electrosynthesis from Solution A. As stated in the introduction, we still performed the electrosynthesis starting from a 0.3 M solution of the Ni and Al salts (molar ratio 3/1) and with 0.3 M KNO_3. The natural pH of the solution is 2.8. The films obtained for different deposition times were submitted to SEM-EDS analysis.

The observation reveals well-covered surfaces with the presence of circular zones for all the deposition times, except 10 s. The number and dimension of these zones increases with the deposition time. Figure 1 shows a SEM image obtained for the film electrosynthesized for 60 s deposition time, showing a typical circular zone.

To better understand the nature of the circular zones, we performed EDS microanalysis inside and outside of them in order to evaluate the Ni/Al ratio, which gives us information

Table 1. Ni/Al Molar Ratios Obtained from EDS Microanalysis for Pt Electrodes Modified with the Films Obtained from a 0.3 M Solution of Ni and Al Nitrates (Ni/Al molar ratio = 3/1) at *E* = −0.9 V and Different Deposition Times

deposition time (s)	site of interest (inside or outside of the circular zones)	Ni/Al molar ratio
10	no evidence of circular zones	0.06/1
30	inside	0.39/1
	outside	0.05/1
50	inside	0.92/1
	outside	0.08/1
60	inside	0.98/1
	outside	0.08/1
90	inside	1.3/1
	outside	0.09/1
120	inside	1.9/1
	outside	0.1/1

on the nature of the electrosynthesized material. In fact, this parameter ranges from 1.3 to 4.9 for a pure HT like structure, containing nickel as bivalent metal.

Table 1 reports the data obtained for the investigated deposition times inside and outside of the circular zones.

Some important observations can be drawn from the reported data. For the shortest deposition time, the films do not show circular zones and are characterized by a very high Al percentage. Nickel content increases with the deposition time especially inside the circular zones, whereas outside of them, the Ni/Al molar ratio remains almost invariable. For the samples obtained after 90 s of electrosynthesis, the Ni/Al molar ratio inside the circular zones is compatible with that expected for a HT-like structure.

The results allow us to hypothesize a mechanism of the film growth on Pt electrodes similar to that occurring for bulk precipitation.[20] The first precipitate, which is essentially constituted by $Al(OH)_3$ because of its very low solubility, completely covers the electrode surface. The precipitation of $Al(OH)_3$ occurs very rapidly, because the initial concentration of Al^{3+} is high and the pH of precipitation is immediately established following the cathodic reduction of nitrate. The material deposited on Pt is amorphous[21] and does not lead to an uniform film but displays some circular zones, whose shape is probably due to the evolution of H_2 bubbles taking place during nitrate reduction. As long as the reduction goes on, the value of pH in the solution next to the electrode increases, causing $Al(OH)_3$ dissolution, and then a hydrotalcite-like structure precipitates on Pt surface, according to eq 1. This reaction takes place more effectively in the circular zones, probably because their thickness is lower and/or the local pH is more alkaline.

$$Al(OH)_3 + 2\,Ni^{2+} + 3OH^- + NO_3^- \rightarrow Al(III)[Ni(II)]_2(OH)_6NO_3 \quad (1)$$

XRD analysis, performed on the film electrosynthesized for 120 s, has shown no evidence of the typical reflections of a $Ni/Al{-}NO_3$ HT. One possible explanation is the poor crystallinity or low quantity of the HT material precipitated on the Pt surface. To obtain a characteristic XRD pattern, it is necessary to perform the electrosynthesis for much longer times and to analyze the product removed from the electrode surface, as reported in our previous study.[16]

3.2. Electrosynthesis from Solution B. Until now, we have demonstrated that it is possible to obtain a Ni/Al HT for high electrodeposition times, but the electrosynthesis from solution A does not allow us to obtain thin and homogeneous films of controlled thickness. For this reason, we performed the electrosynthesis starting from a less concentrated solution (diluted by 1 order of magnitude) of the Ni and Al salts, but with the same KNO_3 concentration. The natural pH of this solution is 3.8, i.e., one unit higher than the value of solution A. Different deposition times (10, 30, 60, 120 s) have also been tested in such a case.

The electrosynthesis lasted 120 s at the maximum, because for longer deposition times, the films were mechanically unstable and began to take off from the electrode surface.

The modified electrode surfaces, obtained for all the deposition times, were characterized by optical microscopy and scanning electron microscopy. Figure 2 reports the images obtained by the optical microscope for the bare substrate electrode and for the films electrosynthesized for 30 and 120 s. The films obtained in these conditions are uniform and homogeneous without any particular morphological feature and completely cover the electrode surface; they are very stable from a mechanical point of view for all the considered deposition times.

SEM was employed to investigate more in detail the morphology of the deposits. Figure 3 shows a typical SEM image obtained for the film derived from a 30 s electrodeposition, but similar images have been obtained for all the deposition times.

EDS analysis was again used to investigate the nature of the films; all the data reported in Table 2 are the mean of three measurements in different zones of the same sample. The Pt mass percentage has been reported because it gives us information about the local thickness of the film: the higher the Pt percentage, the lower the thickness of the deposit. From the results reported in Table 2, we can observe that for all the deposition times, even for the very short one, the Ni/Al ratio is in agreement with that of a hydrotalcite-like structure. Of particular interest is the comparison between Ni/Al ratio of the films obtained for 10 s deposition time using solutions A or B: in the former case, it was 0.06/1, whereas in the latter it is 1.5/1.

This different result, observed by submitting a less concentrated salt solution to electrolysis, can be explained by assuming a different mechanism for the HT formation. The nitrate concentration coming from KNO_3 is unchanged in respect to solution A. As soon as the cathodic potential is applied, the increase in OH^- concentration near the electrode surface is about the same for both solutions, but the spontaneous pH of solution B is 3.8. Therefore, we can hypothesize that, in such a case, the steep increase in local pH leads to the direct precipitation of the layered double hydroxide, without the involvement of the M(III) hydroxide.

FT-IR analysis (spectra not shown) was carried out to characterize the nature of the interlayer anions. The analysis was performed on the film obtained after 120 s because it is the thickest one and, consequently, provides higher absorp-

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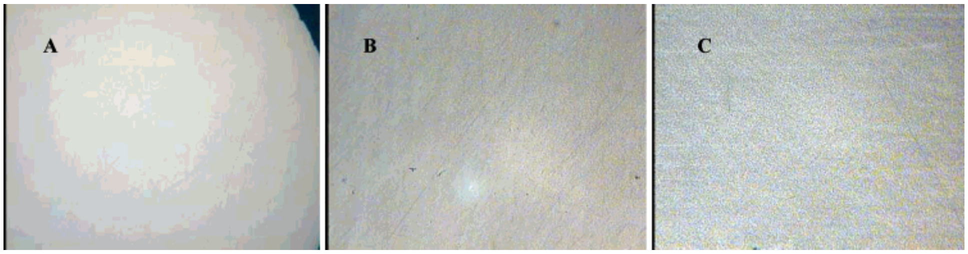

Figure 2. Optical microscope photographs of (A) the bare Pt electrode, and of the films obtained on Pt from a 0.03 M solution of Ni and Al nitrates (Ni/Al molar ratio = 3/1) at (B) $E = -0.9$ V, $t = 30$ s and (C) $E = -0.9$ V, $t = 120$ s. Magnification = 10×.

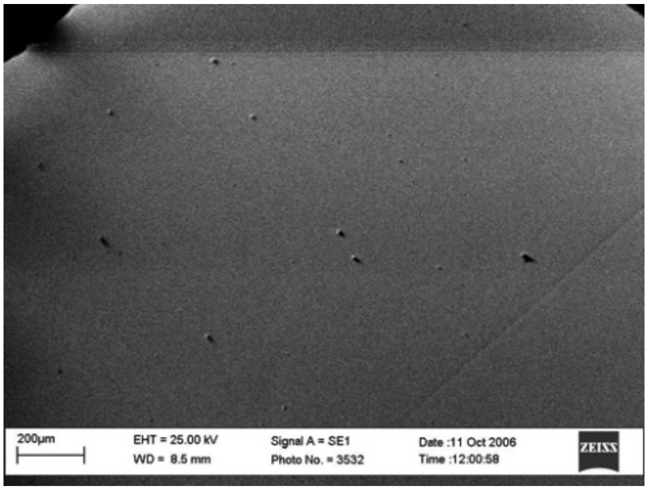

Figure 3. SEM micrograph of a Pt electrode modified with the film ($E_{app}= -0.9$ V, $t = 30$ s) obtained from a 0.03 M solution of Ni and Al nitrates (Ni/Al molar ratio = 3/1). Magnification: 400×.

Table 2. Ni, Al, Pt Mass Percentages Obtained from EDS Microanalysis (mean values ± SD) and the Corresponding Calculated Ni/Al Molar Ratios for Pt Electrodes Modified with the Films Obtained from a 0.03 M Solution of Ni and Al Nitrates (Ni/Al molar ratio = 3/1) at $E = -0.9$ V and Different Deposition Times

	10 s	30 s	60 s	120 s
Al mass %	0.49 (0.02)	0.62 (0.03)	0.72 (0.02)	0.84 (0.03)
Ni mass %	1.61 (0.10)	2.23 (0.09)	2.93 (0.21)	3.21 (0.08)
Pt mass %	76.34 (0.23)	71.44 (0.31)	55.57 (0.20)	43.49 (0.13)
Ni/Al molar ratio	1.5/1	1.7/1	1.9/1	1.9/1

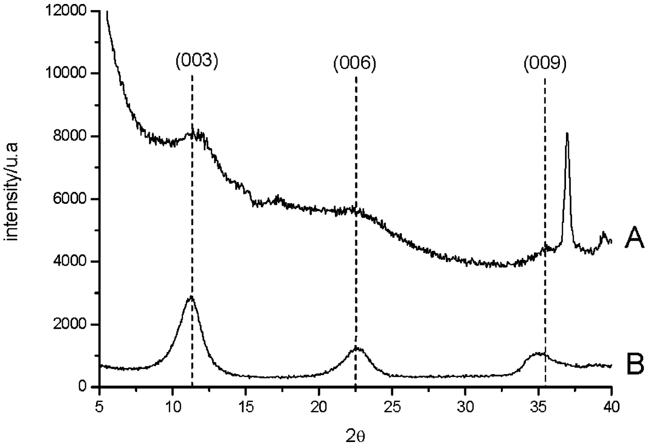

Figure 4. XRD patterns of (A) Ni/Al−NO_3 HT electrosynthesized on a Pt electrode ($E_{app} = -0.9$ V, $t = 120$ s) from a 0.03 M solution of Ni and Al nitrates (Ni/Al molar ratio = 3/1), and (B) chemically synthesized Ni/Al−NO_3 HT.

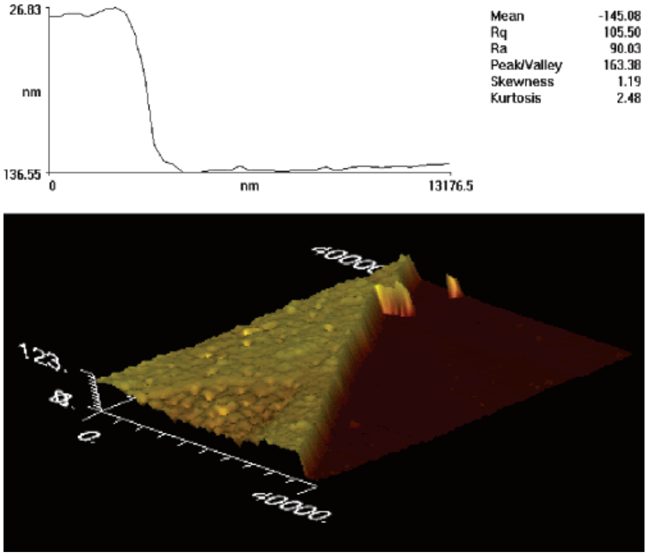

Figure 5. Three-dimensional AFM images, collected by working in contact mode, of the HT film ($E_{app}= -0.9$ V, $t = 10$ s) obtained from a 0.03 M solution of Ni and Al nitrates (Ni/Al molar ratio = 3/1), after etching with 0.1 M HCl.

tions. Even if the spectra are characterized by a very high noise due to the low quantity of the material, the presence of NO_3^- anion was confirmed by the absorption peak at about 1380 cm^{-1} (asymmetric stretching).[22]

XRD analysis was carried out on the same film. The choice was again due to the coating thickness, which was sufficient to make the spectrum recordable. The analysis was performed in a limited 2θ range because, at 2θ values higher than 40°, sharp peaks ascribable to the Pt electrode avoid pointing out any reflection due to the HT material. The diffraction maxima are quite broad, probably because of the fast kinetics of the HT precipitation, which hinders an ordered stacking of the brucite layer. They are located at the angles typical of a hydrotalcite-like phase. In particular, the reflections at 7.83, 3.90, and 2.61 Å, which are typical of pure hydrotalcite compounds containing nickel,[22] correspond to diffraction by basal planes (003), (006), and (009), respectively. The sharp reflection centered at $2\theta = 35.5°$ is ascribable to the Pt electrode, as the analysis was performed directly on the electrode surface.

AFM was employed to get information on the roughness and thickness of the films. Figure 5 shows the AFM images obtained for a portion (40 μm × 40 μm) of the film electrosynthesized for 10 s; the film appears continuous and its roughness is low, about 5 nm. The roughness slightly increases for longer deposition times, to about 25 nm for a

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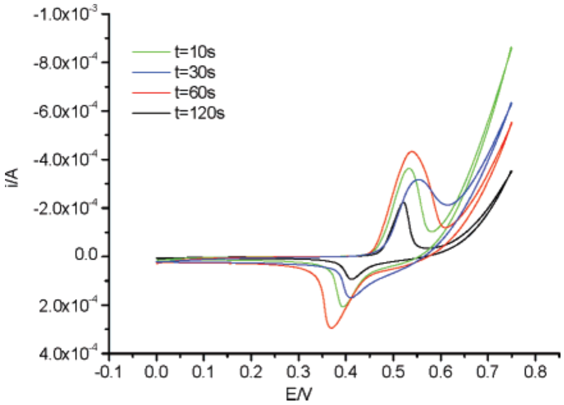

Figure 6. Cyclic voltammogramms recorded in 0.1 M NaOH at a Pt electrode modified with the films ($E_{app}= -0.9$ V; $t = 10, 30, 60, 120$ s) electrosynthesized from a 0.03 M solution of Ni and Al nitrates (Ni/Al molar ratio = 3/1); potential scan rate = 0.02 V s^{-1}.

Table 3. Thickness and Roughness Values Obtained by AFM for Depositions of Solution B at Different Times

seposition time (s)	thickness (nm)	roughness (nm)
10	100	5
30	195	10
60	390	15
120	750	25

120 s deposition time. AFM was also employed to estimate the film thickness, after etching a portion with a 0.1 M HCl solution; as expected, the thickness increases as the deposition time increases. The mean value ranges from about 100 nm for the shortest deposition time to about 750 nm for a 120 s deposition time. The details relevant to the film thickness are reported in Table 3.

All the electrosynthesized films have been characterized by CV in a 0.1 M NaOH aqueous solution (pH 12.8) in a potential range from 0 to 0.75 V vs SCE.

For a Ni/Al HT, the redox process in basic medium can be represented by the following reaction[11]

$$\mathrm{HT{-}Ni(II)} + \mathrm{OH^{-}}_{sol} \leftrightarrow \mathrm{HT(OH^{-}){-}Ni(III)} + e^{-} \qquad (2)$$

The charge transport inside the material is due to a mixed mechanism involving an "electron hopping" along the HT layers, and a migration of anions from the solution into the interlayers to compensate the positive extra-charge when an anodic potential is applied.

The typical CV recorded at a Pt electrode modified with a Ni/Al HT obtained by chemical methods shows, from the first cycles, two redox peaks. Their position is dependent on the potential scan rate and the electrolyte concentration:[11] in 0.1 M NaOH, at a potential scan rate of 0.05 V s^{-1}, E_{pa} = 0.57 V and E_p = 0.40 V vs SCE.

In Figure 6 are reported the cyclic voltammetric curves recorded in 0.1 M NaOH at the electrodes modified with the electrosynthesized films. The CVs show two redox peaks whose position depends on the film deposition time; the anodic peak potentials range from a value of 0.52 V for the thinnest film (10 s) to a value of 0.55 V for the thickest one (120 s), and the cathodic ones from 0.38 to 0.40 V. These values are in good agreement with those obtained with electrodes modified with the chemically synthesized HT. From the CV responses, we observe that the current increases with film deposition time until 60 s and then decreases for the film obtained at 120 s. This behavior can be easily explained by taking into account the number of Ni centers, which is dependent on the film thickness. The increment of current recorded when the electrosynthesis is prolonged from 10 to 60 s is due to the increase in the Ni centers involved in reaction 2; when the thickness is too high, the film exhibits a decreased capacity to charge transport, which prevails over the increase of Ni centers.

Table 4. Ni, Al, Pt Mass Percentages Obtained from EDS Microanalysis (mean values ± SD) and the Corresponding Calculated Ni/Al Molar Ratios for a Pt Electrode Modified with the Film Obtained from a 0.03 M Solution of Ni and Al Nitrates (Ni/Al molar ratio = 3/1) at E = −0.9 V, t = 60 s

	before cycling	after 100 cycles
Al mass %	0.72 (0.02)	0.58 (0.06)
Ni mass %	2.93 (0.21)	2.92 (0.10)
Pt mass %	55.57 (0.20)	55.62 (0.19)
Ni/Al molar ratio	1.9/1	2.2/1

The CVs relevant to all the electrodes are quite stable, being the current practically unchanged during the first 100 voltammetric cycles. After the electrochemical tests are performed, the observation of the electrodes reveals a change in color from white to black, which is a well-known phenomenon that occurs both at $Ni(OH)_2$ and Ni−HT modified electrodes.[23,24] The persistence of the black color is due to an imcomplete reversibility of the Ni redox reaction, which leaves Ni at a partial oxidized state; the reduction of Ni(III) is, in fact, much slower than its reoxidation so that the complete reduction of Ni sites does not occur.[25]

The film electrosynthesized for 60 s was analyzed by SEM after 100 potential cycles, and no change in its morphology was observed. As to the chemical composition, the EDS analysis revealed a decrease in Al content with a consequent increase in Ni/Al ratio, as reported in Table 4. This result is similar to what was observed by Roto et al.[25] and suggests a partial dissolution of Al when the film is cycled in basic solution; these authors have recently demonstrated that Ni-based HTs are quite stable during voltammetric experiments in basic media and that some structural changes take place cycling Ni/Al−Cl HT in NaOH 0.1 M, but they are almost negligible in the case of the more stable Ni/Al−CO_3.[25] The electrochemical behavior of Ni/Al−NO_3 HT is similar to that of the HT containing chloride, the two anions being very similar for in charge and dimension.

AC impedance spectroscopy was employed to further characterize the modified electrodes and to quantify the electron and charge-transfer resistances of the films. The Nyquist plots obtained in 0.1 M NaOH aqueous solution at a potential of 0.58 V for all the electrosynthesized films are reported in Figure 7.

The Nyquist plots can be simulated using the equivalent circuit (EC) we have previously proposed to simulate the redox behavior of Ni/Al HT films, when the material was obtained by a bulk coprecipitation method.[26]

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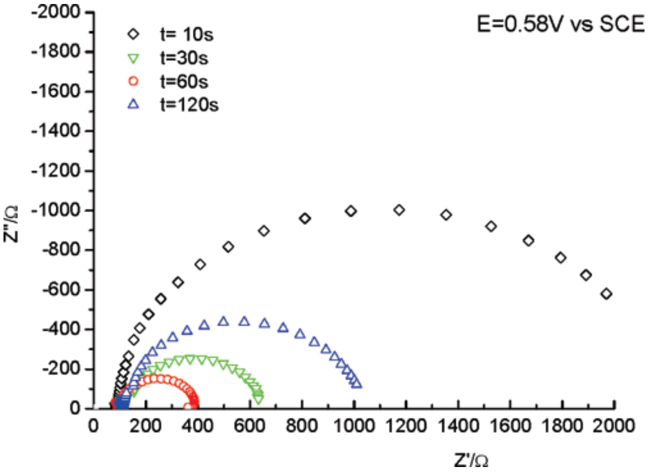

Figure 7. Nyquist plots obtained for modified electrodes in 0.1 M NaOH ($T = 22$ °C) for the films ($E_{app} = -0.9$ V; $t = 10$, 30, 60, 120 s) electrosynthesized from a 0.03 M solution of Ni and Al nitrates (Ni/Al molar ratio = 3/1).

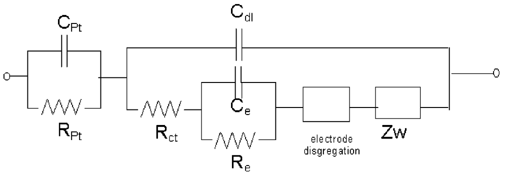

Figure 8. Equivalent circuit describing the EIS spectra.

The EC reported in Figure 8 contains the following elements: the first (RC) parallel element describes the phenomena occurring at the interface of the Pt collector; the R_{ct} and C_{dl} describe, respectively, the charge-transfer resistance and the associated capacitance at the interface electrode/solution; C_e and R_e describe the electronic transfer resistance inside the material and a related capacitance, probably due to a nanosize accumulation of charges inside the active grain of the material[27] or the rough nature of the modified electrode.[28] The element related to the electrode disgregation has been described with a parallel of a negative resistance and a negative capacitance, whereas the Z_w element represents a Warburg impedance associated with diffusion. All the C elements were substituted with a constant phase element (CPE)[29] with n close to 1, to take into account the local nonhomogeneous nature of the electrode.

We interpolated all the experimental data using the EC program by Boukamp[30] with the equivalent circuit just described, which was able to fit all the spectra, giving χ^2 values on the order of 1×10^{-4} to 1×10^{-3}.

The main parameter that affects the intrinsic behavior of the electrosynthesized films is R_e value, which is strongly dependent on the electrodeposition time. On the contrary, R_{ct} and R_{Pt} remain almost constant in any case.

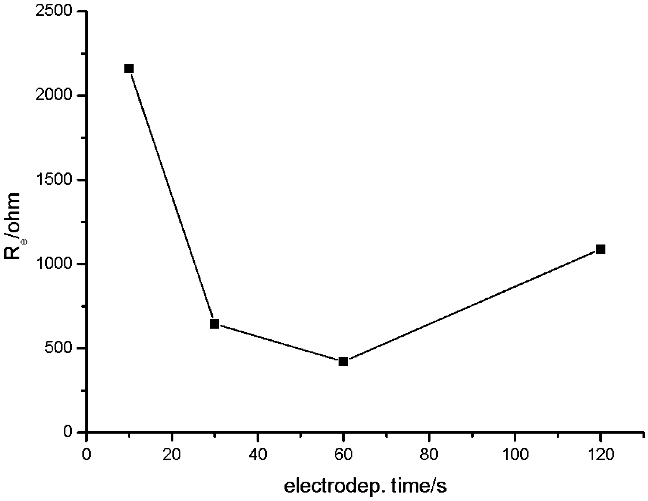

Figure 9. Plot of R_e, obtained from the simulations of the spectra recorded at 0.58 V vs SCE, as a function of the film electrodeposition time.

Table 5. Ni, Al, Pt Mass Percentages Obtained from EDS Microanalysis (mean values ± SD) and the Corresponding Calculated Ni/Al Molar Ratios for a Pt Electrode Modified with the Film Obtained from a 0.03 M Solution of Ni and Al Nitrates (molar ratios from 2/1 to 5/1) at $E = -0.9$ V, $t = 60$ s

	Ni/Al = 2/1	Ni/Al = 3/1	Ni/Al = 4/1	Ni/Al = 5/1
Al mass %	1.44 (0.10)	0.72 (0.02)	0.58 (0.08)	0.41 (0.05)
Ni mass %	3.40 (0.23)	2.93 (0.21)	3.07 (0.12)	3.16 (0.19)
Pt mass %	56.78 (0.22)	55.57 (0.20)	54.98 (0.21)	57.65 (0.17)
Ni/Al molar ratio	1.1/1	1.9/1	2.4/1	3.5/1

From the data shown in Figure 9, we can conclude that the most conductive HT film is obtained for a deposition time of 60 s; this time allows an optimal compromise between number of electroactive Ni centers and thickness. In fact, for higher deposition times, the deposits are too thick and create a major resistance to electron transport, whereas for lower deposition times, few Ni centers are involved in the electron hopping mechanism and, consequently, the film conductivity is worse.

3.2.1. Effect of Ni/Al Ratio on the HT Composition. Solutions containing Ni and Al nitrates (0.03 M) in molar ratios different from 3/1 (Ni/Al = 2/1, 4/1, 5/1) were investigated to evaluate if this parameter affects the metal content in the resulting HT film. The electrosynthesis was performed for 60 s and the resulting films were investigated with SEM/EDS. All the films are homogeneous, and the electrode surfaces are completely covered in any cases. Table 5 reports the results obtained from EDS analysis.

From the data reported in Table 5, we can see that it is possible to modulate the Ni/Al molar ratio of the electrosynthesized material starting from deposition solutions containing different Ni/Al molar ratios. In any case, the Ni/Al ratio of the electrosynthesized film is lower than the corresponding value in the deposition solutions. Up to now, no explanation of this evidence can be given.

Cyclic voltammetric curves and EIS spectra have been recorded in order to evaluate how the Ni/Al ratio affects the electrochemical behavior of the electrosynthesized material. As can be seen from Figure 10, the increase in Ni/Al ratio leads to an increase in the peak currents and a shift of the peak potentials toward less anodic values. These effects are more evident when the Ni/Al ratio in the electrosynthesized film changes from 1/1 to 2.4/1, whereas it is almost negligible when the Ni/Al ratio further increases to 3.5/1. This evidence can be explained on the basis of the electron hopping mechanism, which is the parameter mostly affecting the

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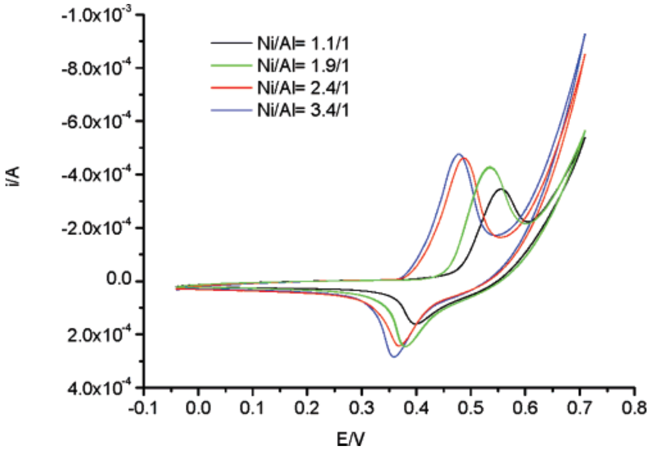

Figure 10. Cyclic voltammogramms recorded in 0.1 M NaOH at a Pt electrode modified with the films containing different Ni/Al ratios, potentiostatically electrosynthesized from a 0.03 M solution of Ni and Al nitrates at $E = -0.9$ V for 60 s; potential scan rate = 0.02 V s^{-1}.

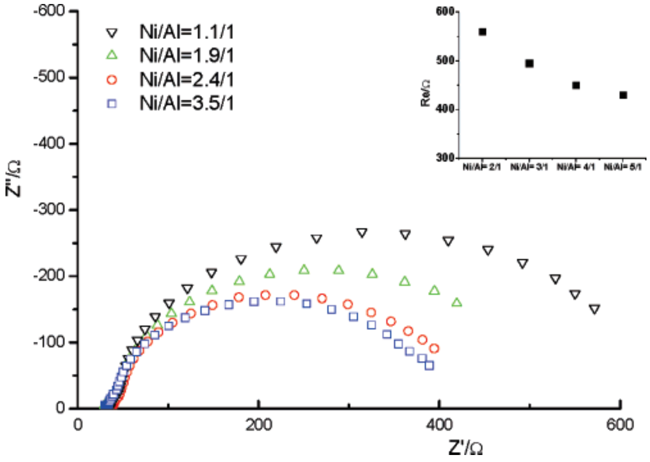

Figure 11. Nyquist plots obtained for Pt electrodes modified with the films containing different Ni/Al ratios, electrosynthesized potentiostatically from a 0.03 M solution of Ni and Al nitrates at $E = -0.9$ V for 60 s in 0.1 M NaOH ($T = 22$ °C).

conductivity of the material. Looking at the mass percentages reported in Table 5, we can observe that a marked decrease of Al % occurs. On the contrary, Ni % changes slightly. The key parameter affecting the peak height and its position is the number of electroactive Ni centers involved in the electron-hopping process. If the Al % decreases, it is more probable that more Ni centers are close to each other, and this condition makes the electron hopping easier. This effect is no longer evident when the Al% is even lower, maybe because the electron-hopping rate cannot further increase.

The same conclusions can be drawn from EIS spectra, reported in Figure 11. The Re value decreases as the Ni/Al ratio increases and is almost constant when the ratio goes from 2.4 to 3.5, as shown in the inset.

4. Conclusions

A study has been performed to find the best conditions to electrosynthesize thin and homogeneous films of a Ni/Al−NO_3 HT. The starting point of the present study was the electrosynthesis conducted using a 0.3 M solution of Ni and Al nitrates; the films electrodeposited on the Pt electrode are not uniform and display circular zones whose number increases with electrosynthesis time. The chemical composition of the deposit is not constant and depends on the electrosynthesis duration. The first precipitate is constituted by $Al(OH)_3$, which converts to a HT phase as long as the electrosynthesis goes on.

Using a nitrate solution more diluted by 1 order of magnitude, we can obtain thin films of pure HT that are homogeneous and continuous. The Ni/Al ratio is compatible with that of a pure HT phase and can be changed by using deposition solutions with different Ni/Al ratios, e.g., the resulting ratio is 2/1 when we start from a solution where Ni/Al is 3/1. A hypothesis has been made on the mechanism of film growth: as soon as the cathodic potential is applied to the electrode, the direct precipitation of the layered double hydroxide occurs. All the modified electrodes have been characterized in basic solution by cyclic voltammetry and AC impedance spectroscopy. Our findings demonstrate that the electronic transfer resistance is the parameter mostly affected by the electrodeposition time, i.e., by the film thickness and the Ni/Al ratio.

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