Oxygen evolution at ultrathin nanostructured Ni(OH)$_2$ layers deposited on conducting glass

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**Abstract**

Ultrathin and transparent nanostructured Ni(OH)$_2$ films were deposited on conducting glass (F:SnO$_2$) by a urea-based chemical bath deposition method. By controlling the deposition time, the amount of deposited Ni(OH)$_2$ was varied over 7 orders of magnitude. The turnover number for O$_2$ generation, defined as the number of O$_2$ molecules generated per catalytic site (Ni atom) and per second, increases drastically as the electrocatalyst amount decreases. The electrocatalytic activity of the studied samples (measured as the current density at a certain potential) increases with the amount of deposited Ni(OH)$_2$ until a saturation value is already obtained for a thin film of around 1 nm in thickness, composed of Ni(OH)$_2$ nanoplatelets lying flat on the conductive support. The deposition of additional amounts of catalyst generates a porous honeycomb structure that does not improve (only maintains) the electrocatalytic activity. The optimized ultrathin electrodes show a remarkable stability, which indicates that the preparation of highly transparent electrodes, efficient for oxygen evolution, with a minimum amount of nickel is possible.

**1. Introduction**

Ni(OH)$_2$ thin films are of current interest for electrochromic applications [1–3], as positive electrodes for secondary batteries [4–7] and in electrocatalysis. All the aforementioned applications require a complete, quick and reversible Ni(OH)$_2$/NiOOH transformation.

The interest in the NiOOH/Ni(OH)$_2$ redox pair for electrocatalysis is due to the fact that Ni$^{3+}$ [8] is particularly catalytic for a wide range of redox processes. The electrocatalytic properties of NiOOH have been studied and confirmed for many different types of reactions: oxidation of alcohols to yield carbonyl compounds [9–12], direct electrooxidation of carbohydrates [13] and urea [14], green route oxidation of sulfide ions [15], and oxygen evolution reaction (OER) in alkaline media. The electrocatalytic effect arises from the lower degree of occupancy of d orbitals associated with the oxidized form (NiOOH). The metal ion in its high valence state has more activity for bond formation with adsorbed species, thus facilitating electrocatalysis in general [16–18].

The importance of studying the OER over NiO/Ni(OH)$_2$ in alkaline media derives from the fact that the best electrode choices in acid, RuO$_2$ or IrO$_2$, suffer from poor chemical stability in alkaline media [19]. NiO/Ni(OH)$_2$ offers a compromise solution: although it possesses inferior electrocatalytic activity, it displays excellent long term corrosion resistance in alkaline media and it has the added advantage of being relatively inexpensive.

Water (photo)electrolysis in alkaline media is an environmentally friendly procedure for the production of hydrogen, offering an attractive alternative for energy storage. This process is limited by the large anodic overpotential of the OER. The energy consumption at the anode in the (photo)electrolysis decreases with the decrease in the onset potential for O$_2$ generation. Considerable research effort is devoted to the...
design, synthesis and characterization of anode materials with the purpose of achieving useful rates of the OER at the lowest possible overpotential to optimize the overall (photo) electrocatalytic process [20].

It is well known that by moving from bulk materials to nanosized structures, the catalytic activity for the OER can be significantly increased [21]. Thus, decreasing the particle size and/or optimizing the surface morphology could be a good strategy for achieving efficient electrocatalysis.

In this work, ultrathin nanostructured Ni(OH)$_2$ films were deposited on F:SnO$_2$ (FTO) conducting glass substrates by a chemical bath deposition (CBD) method. This method, apart from inexpensive, practical for large area deposition, and straightforward, offers the possibility of tuning the Ni(OH)$_2$ morphology by controlling only the deposition time. In this way, we have synthesized thin films with different amounts of deposited Ni(OH)$_2$ and studied their catalytic ability toward the OER. It is worth noting that only minute amounts of nickel are employed in the optimum case and that the resulting electrodes are highly transparent, which is important for their potential application in photoelectrochemical devices (i.e. water photosplitting cells).

2. Experimental

Ni(OH)$_2$ was synthesized by CBD on F:SnO$_2$-coated transparent conducting glass plates (15 Ω/□, Pilkington TEC 15) with an approximate surface area of 3–4 cm$^2$. The deposition solution contained 25 ml of 0.5 M NiSO$_4$ (for nickel plating, Riedel-de Hae¨ n), 12.5 ml of 1 M urea (p.a, Sigma–Aldrich) and 12.5 ml of H$_2$O (ultra pure, Millipore Elix 3) [22]. The glass plates were vertically supported with the conducting side against the beaker wall and the solution was heated up to 100 °C. The chemistry of the deposition process is based on the fact that urea decomposes to CO$_2$ and NH$_3$ by heating at sufficiently high temperatures (90–100 °C). The Ni$^{2+}$ cations and the hydroxide ions released by the protolytic reaction of ammonia react creating Ni(OH)$_2$ thin films.

Different deposition times (from 5 min to 3.5 h) were employed as to control the Ni(OH)$_2$ layer thickness. After the deposition, the samples were annealed at 200 °C in air for 1 h.

Electrochemical measurements were performed at room temperature in a standard three-electrode cell. All potentials were measured against and are referred to a Ag/AgCl/KCl(sat) reference electrode, whereas a Pt wire was used as a counter electrode. Measurements were performed with a computer controlled Autolab PGSTAT30 potentiostat. In all the experiments, a N$_2$-purged 1 M NaOH (pellets, extra pure, Scharlau) solution prepared with ultrapure water was used as working electrolyte.

The identification of the deposition as Ni(OH)$_2$ was confirmed by X-ray Photoelectron Spectroscopy (XPS) carried out using a K-Alfa Thermoscientific spectrometer. The morphological characterization of the Ni(OH)$_2$ thin films was performed by means of Atomic Force Microscopy (AFM) using a Nanoscope III (Digital instruments) operated at room temperature in air. Images were obtained in tapping mode using silicon tips at a driving frequency of ~270 kHz. The Ni(OH)$_2$ film thickness was measured by means of an Alpha Step D-100 profilometer.

3. Results and discussion

Fig. 1 shows the AFM images for FTO substrates before (Fig. 1a) and after chemical bath deposition (and subsequent thermal annealing) of Ni(OH)$_2$ for 80 min (Fig. 1b) and 2 h (Fig. 1c). As observed in Fig. 1a, the FTO substrate is relatively rough. As AFM provides a reliable picture of the actual topography of the sample, we have estimated the roughness factor as the ratio of the real surface area evaluated from the AFM image and the corresponding plane-projected area. The resulting substrate roughness factor attains a value of 4.5, which should be considered as a good estimate because of both the high resolution of the AFM and the non-porous character of the sample. Fig. 1b shows the formation of a clear overstructure on the relatively rough surface of the FTO substrate. It is composed of ultrathin and elongated nanoplatelets (average dimension: 175 × 50 nm). The surface topography does not vary in an important way after 80 min of deposition. That is, the Ni(OH)$_2$ deposit follows to a large extent, the substrate morphology, even after a deposition time of 80 min. AFM images obtained for deposition times up to 40 min and lower did not show any discernible feature revealing the presence of Ni(OH)$_2$. For a deposition time of 2 h, there is a visible loss of the nanoplatelet structure due to the vertical growth and interconnection of the nanoobjects. This structure, apparently formed by flakes, is porous with large open voids, which facilitates its interaction with the electrolyte (Fig. 1c).

Fig. 1d–e contains XPS spectra of the sample obtained for a deposition time of 80 min. The XPS spectrum of Ni (Fig. 1d) shows peaks with binding energies (BE) of 856.3 eV and 874.2 eV, corresponding, respectively, to the Ni 2p$_{3/2}$ and 2p$_{1/2}$ transitions. The O 1s transition (Fig. 1e) with a BE of 531.7 eV is also observed. Both the Ni 2p$_{3/2}$ and O 1s peaks are shifted to higher BE values with respect to those for NiO, providing evidence that the as-prepared samples are entirely composed of Ni(OH)$_2$ [23–25]. Although Fig. 1d–e refers to the 80 min deposit, it should be conveyed that similar spectra were also obtained in the cases of shorter (40 min) or longer (2 h) deposition times.

Fig. 2a shows cyclic voltammograms for FTO/Ni(OH)$_2$ electrodes prepared for different deposition times (20, 80 and 120 min) together with a blank voltammogram for the FTO electrode. A quasi-reversible couple of peaks appear between 0.2 and 0.5 V. It is associated with the redox process:

$$\text{Ni(OH)}_2 + \text{OH}^- \rightleftharpoons \text{NiOOH} + \text{H}_2\text{O} + e$$

(1)

If we compare the shape of the voltammetric profiles corresponding to the NiOOH/Ni(OH)$_2$ couple with those obtained for thicker films (Fig. 2b), we realize that incipient deposits show a more reversible electrochemical behavior. Fig. 3 gives the separation of the anodic and cathodic voltammetric peaks ($\Delta E_p$) and the Full Width at Half Maximum (FWHM) for the cathodic peak as a function of the deposition time. As observed the value of $\Delta E_p$ increases as the Ni(OH)$_2$ deposit becomes thicker, indicating a progressive deviation from the reversible behavior for surface confined redox couples ($\Delta E_p = 0$). It is also remarkable that for low coverages rather sharp peaks are observed with a FWHM as low as 25 mV, significantly smaller than those typical of other Ni(OH)$_2$ nanoparticulate electrodes [20,26,27]. Such a high degree of
definition in the response suggests that the Ni sites in the sample are equivalent and that there exist attractive interactions between the participating redox centers [28]. The well-defined voltammetric profiles obtained for low Ni(OH)₂ coverages allow us to identify the structure of the hydroxide, taking advantage of the seminal study performed by Kim and Kim [29] in which the voltammetric curves for α-Ni(OH)₂ and β-Ni(OH)₂ were obtained. By comparing the potentials of the cathodic and anodic peaks observed in that work with those obtained here (Fig. 2a), we can conclude that CBD (together with the annealing treatment that could lead to a partial dehydration) gives rise to a β-Ni(OH)₂ deposit, as expected [30]. Although the electrochemical reversibility of β-Ni(OH)₂ is poorer than that of α-Ni(OH)₂, the former is a better electrocatalyst for oxygen evolution [29]. It is worth noting that for low coverages, the electrochemical behavior of β-Ni(OH)₂ shows good reversibility. This is not surprising as the structural and chemical changes linked to Ni(OH)₂ oxidation can be more easily accommodated in incipient deposits. Therefore, in order to maximize the rate of the NiOOH/Ni(OH)₂ electrochemical process, one should decrease the thickness of the deposit. In this way, most of the Ni species would be close to the conducting substrate, which is the source and sink of electrons.

As already reported, at potentials immediately above the peak for Ni(OH)₂ oxidation, appreciable currents due to oxygen evolution are observed [20,31,32]. The evolution of O₂ on the bare substrate is negligible with respect to the FTO/Ni(OH)₂ electrodes (Fig. 2a). In the case of deposition times of 20 and 80 min, the anodic peak of the Ni(OH)₂/NiOOH couple is well separated from the wave of O₂ generation. Thus, it is apparent that NiOOH once formed is not able to immediately oxidize water. This result suggests that at sufficiently high potentials, NiOOH transforms into a highly reactive species that mediates the generation of O₂. This assumption is consistent with several recent reports for the OER at various Ni-based electrodes in which the formation of NiO₂ as an intermediate species is proposed [20,33]. Recently [34,35], two mechanisms have been proposed for the evolution of oxygen in alkaline solutions on Ni-based electrodes, entailing the formation of adsorbed superoxy and peroxide intermediates. Based on these ideas, the following pathway could be envisaged for the OER at NiOOH in alkaline media:

\[
\begin{align*}
\text{NiOOH} + \text{OH}^- & \rightarrow \text{NiO(OH)}_2 + e^- \quad E = 1.434 \text{ V} \quad (2) \\
\text{NiO(OH)}_2 + \text{OH}^- & \rightarrow \text{NiO(OOH)} + \text{H}_2\text{O} + e \quad (3) \\
\text{NiO(OOH)} + \text{OH}^- & \rightarrow \text{NiOO}_2 + \text{H}_2\text{O} + e \quad (4) \\
\text{NiOO}_2 + \text{OH}^- & \rightarrow \text{NiOOH} + \text{O}_2 + e \quad (5)
\end{align*}
\]

Our experimental results are compatible with this mechanism. In fact, the onset potential for the development of the OER-associated current is 1.45 V vs. SHE, which coincides with the standard potential for the first step (Eq. (2)). In addition, the Tafel slope of around 40 mV dec⁻¹ (Fig. 4) observed at low overpotentials for 5-min deposits is compatible with the first step (Eq. (2)) being in pseudo-equilibrium and the second one (Eq. (3)) being the rate determining step (rds). As observed in Fig. 4, at higher overpotentials the Tafel slope increases to values of 120–180 mV dec⁻¹, which suggests that under these conditions, the first step becomes the rds. In any case, it is clear that the electrocatalytic properties of NiOOH will depend on the ability of NiOOH to transfer electrons to the conducting substrate.

Fig. 2a reveals explicitly that, although the quantity of deposited Ni(OH)₂ increases with deposition time, the rate of O₂
generation is not following this trend. At a given potential value, the current density observed for the 80-min deposit is slightly higher than that of the 2-h deposit. Otherwise, we could estimate the overpotential for the OER process at which the current density equals 0.5 mA cm\(^{-2}\) for each electrode. The minimum overpotential (0.30 V) is obtained for the 80-min deposit (see inset in Fig. 2a).

These results clearly demonstrate that the \(\text{O}_2\) generation rate is not simply proportional to the quantity of deposited Ni(OH)\(_2\), but rather depends on physical and morphological characteristics of the Ni(OH)\(_2\) deposit (particle size\([36]\), crystal structure\([37]\), dispersion of the deposited particles, etc.). For deposition times longer than 2 h, it is difficult to voltammetrically separate the \(\text{O}_2\) generation current (Fig. 2b) from that linked to the oxidation of Ni(OH)\(_2\). For these samples, chronoamperometric measurements were performed upon stepping the potential from 0 to 0.7 V (Fig. 5). These measurements confirm the initial idea that a larger amount of electrocatalyst does not lead to a higher \(\text{O}_2\) generation rate. For instance, for the Ni(OH)\(_2\) films resulting from a 3.5 h deposition, OER currents (Fig. 5a) are virtually equal to those obtained for the optimal deposition time (80 min) (Fig. 5b), suggesting that there exists a limiting value for the Ni(OH)\(_2\) electrocatalytic activity.

On the other hand, in both chronoamperometric curves, the current is constant, which indicates that the deposits are stable within the time scale of the experiment. For the 3.5-h deposit electrode, the initial decay in current, as well as the cathodic current observed upon stepping the potential back to 0 V are due to the NiOOH/Ni(OH)\(_2\) redox process. These contributions are not discernible in the case of the 80-min deposit.

In this work, the electrocatalytic activity is defined as the current density for \(\text{O}_2\) evolution (\(j(\text{O}_2)\)) at 0.7 V vs. Ag/AgCl. Fig. 6a shows a plot of the electrocatalytic activity with respect to the charge density corresponding to the reduction of NiOOH, which is obtained by integration of the corresponding voltammetric cathodic peak because it is free of interference from the OER current. Obviously, such a plot is representing how the electrocatalytic activity varies as a function of the amount of Ni, which, in turn, is dependent on the deposition time.

As the charge density corresponding to the NiOOH reduction peak (proportional to the amount of deposited Ni(OH)\(_3\))
increases up to 1.8 mC cm\(^{-2}\), the electrocatalytic activity monotonously grows until a plateau is reached. Chronoamperometric measurements indicate that for larger amounts of deposited Ni(OH)\(_2\), no further improvement of the electrocatalytic activity is observed. However, it is worth noting that the electrocatalytic activity defined above is not a measure of the specific electrocatalytic ability of the system under scope, because it is expected to be proportional to the amount of catalyst. The specific electrocatalytic ability of the system can be given in terms of the turnover number (TON), defined here as the number of oxygen molecules generated at 0.7 V per second and per catalytic site (Nickel atom). Accordingly, the TON will be calculated as (see Appendix A):

\[
\text{TON} = \frac{1}{N_{\text{Ni}}} \frac{dN_{\text{O}_2}}{dt} = \frac{j_{0.7\,\text{V}}}{4q_{\text{Ni}}} \tag{6}
\]

where \(q_{\text{Ni}}\) is the charge density corresponding to the reduction of NiOOH. Obviously, all the electroactive Ni atoms are considered in the TON calculation.

Fig. 5 shows a log–log plot of the TON as a function of the Ni(OH)\(_2\) deposited mass calculated from the charge density exchanged in the NiOOH reduction. The resulting slope of around \(-0.95\) indicates that the TON is almost inversely proportional to the mass of Ni(OH)\(_2\) deposited. This is valid for as many as 7 orders of magnitude of deposited mass. In any case, the TON drastically increases with decreasing amounts of deposited Ni(OH)\(_2\), which suggests that the morphology of the film (average size of the incipient nanoplatelets as well as their dispersion on the substrate) is an important factor governing its electrocatalytic activity. It is estimated (see Appendix B) that about 2 monolayers of Ni(OH)\(_2\) (or around 1 nm of film thickness), already lead to the optimal electrocatalytic activity. Beyond this point, additional amounts of Ni(OH)\(_2\) do not trigger further improvement. For a 3-h deposit, the calculated thickness is of 45 nm on the basis of the charge density exchanged in the NiOOH/Ni(OH)\(_2\) process by both assuming a compact layer deposition and taking into account the estimated FTO roughness factor. This value is much smaller than the measured one of 1.2 \(\mu\)m, indicating a high degree of porosity and/or the existence of electrochemically inactive Ni(OH)\(_2\) far away from the conducting substrate. As the conductivity of Ni(OH)\(_2\) is rather low, only the bottom-most part of the film would be converted into NiOOH, which is the actual electrocatalyst for the OER. It was also estimated that all the Ni(OH)\(_2\) films with a TON number higher than 1 s\(^{-1}\) are submonolayer deposits. The maximum value of TON measured corresponds to a coverage of \(3.5 \times 10^{-5}\) monolayers.
More studies are needed to clarify the reasons for the TON behavior. However, one could speculate that, for very low submonolayer coverages, most of the nickel atoms are in islands one monolayer in height. These isolated and flat Ni(OH)2 islands would be able to quickly exchange electrons with the conducting substrate, facilitating their role as electrocatalysts. As coverage grows, an increasing fraction of the Ni atoms would be in second and successive monolayers depending on their functioning as catalytic centers on charge transport processes through the nickel hydroxide layer. It is also apparent that the fraction of nickel atoms exposed to the electrolyte (those active in electrocatalysis) will be maximum as the amount of deposited catalyst is minimized. Finally, it is worth mentioning that the boundary sites F:SnO2—Ni(OH)2 do not seem to be particularly catalytic, as the electrocatalytic activity of the sample reaches its maximum value at a coverage of around 2 monolayers (rectangular framed point, Fig. 6) when no bare FTO seems to be left (Fig. 1b).

4. Conclusions

Ultrathin films of Ni(OH)2 were deposited on FTO by means of chemical bath deposition. By controlling the deposition time, samples with Ni(OH)2 masses varying over 7 orders of magnitude have been prepared. The electrocatalytic activity of the samples was studied as a function of the amount of electroactive Ni(OH)2. The turnover number for O2 evolution increases drastically as the amount of deposited Ni(OH)2 decreases. A maximum value close to 104 s−1 has been calculated for an overpotential for the OER process of 0.47 V (potential of 0.7 V vs. Ag/AgCl/KCl(sat)), corresponding to a fractional coverage of 3.5·10−3, which is thought to correspond to a submonolayer structure formed by isolated islands. It seems that the proximity of the Ni sites to the conducting substrate is critical to achieve a maximum TON. The fact that the oxidation of Ni(III) to Ni(IV) could be involved in the OER mechanism and the low electrical conductivity of Ni(OH)2 would explain that Ni atoms far from the conducting substrate (as in thick films) are less effective for promoting the OER. In fact, the Ni sites far away from the conducting substrate could remain in a low oxidation state (II), being inactive in the OER process.

The maximum electrocatalytic activity was obtained for a film with an average thickness of only 1 nm (around 2 monolayers). Such a film is composed of Ni(OH)2 nanoplatelets lying flat on the conductive support. These thin film electrodes are characterized by a well-defined voltammogram with sharp peaks corresponding to the NiOOH/Ni(OH)2 redox process. Thicker films do not show improved electrocatalytic properties, although they retain the electrocatalytic activity because of their porous structure.

This study shows that through a fine control of the layer thickness and nanostructure, ultrathin films of Ni(OH)2 (1 nm in thickness) can yield an electrocatalytic activity equal to that of much thicker films. In such a way, not only the amount of electrocatalyst is minimized but also anodes highly transparent and virtually colorless under operating conditions can be prepared. This could be important in the design of photo-electrochemical devices including anodes efficient for promoting oxygen evolution (for instance, water photo-splitting ones).

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Appendix A. Calculation of the turnover number (TON)

According to the Faraday law, the charge corresponding to the NiOOH reduction process is:

$$Q_{NiOOH} = \frac{N_{NiOOH}}{N_0}$$

where $Q_{NiOOH}$ is the total charge exchanged during NiOOH reduction, $N_{NiOOH}$ is the number of Ni species participating in the electrochemical process, $F$ is the Faraday constant and $N_0$ is the Avogadro’s number.

Analogously, for the OER we can write:

$$Q_{OER} = z_{OER}F = 4O^2^- \rightarrow O_2 + 2H_2O + 4e^{-}$$

The derivative of the Eq. (A2) with respect to time, leads to the current intensity corresponding to the oxidation of water.

$$I_{O2} = 4F \frac{d(N_{O2})/N_0}{dt} = 4F \frac{dN_{O2}}{dt}$$

The turnover number is defined and calculated as:

$$TON = \frac{1}{N_{Ni}} \frac{dN_{O2}}{dt} = \frac{F}{Q_{NiOOH}} \frac{I_{O2} \cdot t}{N_0} - \frac{1}{4} \frac{I_{O2} \cdot V}{Q_{Ni}} \frac{1}{4} \frac{I_{O2} \cdot V}{Q_{Ni}}$$

where $j_{O2}$ is the current density at 0.7 V and $Q_{NiOOH}$ is the charge density exchanged during the reduction of NiOOH.

Appendix B. Estimate of the number of Ni(OH)2 monolayers.

The crystal structure of Ni(OH)2 is similar to that of CdI2. The unit cell is hexagonal with the Ni atoms situated at the corners of the unit cell and two O atoms (actually OH groups) inside. This means that there is one Ni atom per unit cell in a layered structure where the distance between Ni neighboring layers equals the height (c) of the unit cell.

The cell parameters in the case of Ni(OH)2 [38] are: $a = b = 3.126 \text{ Å}$, $c = 4.605 \text{ Å}$.

The number of hexagonal unit cells that can be accommodated (with the c-axis perpendicular to the substrate) in the unit surface area of the electrode (i.e. 1 cm2) equals the number of Ni atoms in one layer. The area of the base of the unit cell ($A_{base}$) is that of a rhombus with two angles of 120° and
two of 60°. Thus, the area corresponding to a unit cell can be calculated as:

\[ A_{uc} = a^2 \sin 60° = \left( 3.126 \ A \right)^2 \sin 60° = 8.462 \ A^2 \]
\[ = 8.462 \times 10^{-16} \ \text{cm}^2 \]

The number of Ni atoms in a monolayer (ML) per unit of real surface area \( (N_{Ni,ML}/A_{uc}) \) can be calculated as:

\[ \frac{N_{Ni,ML}}{A_{uc}} = 1 \frac{q_{Ni}}{A_{uc}} \]  \hspace{1cm} (B1)

and results to be equal to \( 1.18 \times 10^{15} \ \text{cm}^{-2} \).

Taking into account that the real area is the geometric one (A) multiplied by the roughness factor \( (f) \), we may write:

\[ \frac{N_{Ni,ML}}{A} = f \frac{q_{Ni}}{A_{uc}} \]  \hspace{1cm} (B2)

On the other hand, from Eq. (A1), the total number of Ni atoms per unit of geometric electrode surface area can be calculated as:

\[ \frac{N_{Ni}}{A} = q_{Ni} \frac{N_{uc}}{F} \]  \hspace{1cm} (B3)

Finally, the number of Ni(OH)\textsubscript{2} MLs (coverage, \( \theta \)) would be evaluated as:

\[ \theta = \frac{N_{Ni}}{N_{Ni,ML}} \frac{q_{Ni} N_{uc} A_{uc}}{f F} \]  \hspace{1cm} (B4)

Taking into account that both the charge density for the NiOOH reduction process corresponding to the optimum electrode is 1.82 mC cm\textsuperscript{-2} and the roughness factor of the FTO substrate is ca. 4.5, the number of equivalent monolayers would be of 2. It should be noted that for a deposition time of 3 h, the estimated number of monolayers is 100 and the estimated film thickness for a layer-by-layer deposition giving a compact film would be of 45 nm. In fact, due to the porous structure of the deposit (and probably to the existence of electrochemically inactive Ni(II) species), the real thickness is much larger. Actually, the thickness of a 3-h deposit is of 1.2 \( \mu \)m. These data are in line with the surface morphology of Ni(OH)\textsubscript{2} revealed by means of AFM (Fig. 1c).

Fig. B1 — Sketch of the Ni(OH)\textsubscript{2} unit cell.

**REFERENCES**


