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## Desactivación de electrodos de oro modificados con hidróxido de níquel

### Deactivation of nickel hydroxide-gold modified electrodes

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#### Resumen

En este trabajo se estudió la modificación (desactivación) que sufre el proceso de transporte de carga en películas de hidróxido de níquel, sintetizadas electroquímicamente sobre electrodos de oro, cuando son almacenadas sin uso durante tiempo prolongado. Se encontró que las películas usadas después de ser almacenadas, se tornan menos conductoras que las películas usadas inmediatamente después de ser preparadas. En este estudio se empleó como técnica electroquímica, la Voltamperometría Estacionaria con Electrodo de Disco Rotante (VEEDR). Se analizó la variación de la corriente límite anódica en presencia del soluto electroactivo Deferasirox (ácido (4-(3,5-bis(2-hidroxifenil)-1,2,4-triazol-1-il) benzoico), a distintas velocidades de rotación del electrodo. En presencia de esta droga, el hidróxido de níquel actúa como mediador redox. Sobre la base de la teoría del "hopping" electrónico se obtuvo la dependencia de la velocidad de transporte de carga en función del tiempo de almacenamiento de las películas.

Palabras clave: Películas de hidróxido de níquel; Desactivación; Proceso de transporte de carga; Deferasirox; Mediación redox.

#### Abstract

The aim of the present work was to study how the charge-transport process of a nickel hydroxide film electrochemically synthesized on a gold substrate is modified when the electrode is stored for a long time. It was found that nickel hydroxide films are deactivated under storage, that is, films became less conductive than films immediately prepared (nondeactivated). This study was carried out in the context of the rotating disc electrode voltammetry when the modified electrode contacts an electroactive solution and a mediation reaction occurs at the Au-Ni(OH)<sub>2</sub> electrolyte interface. Variations of anodic limiting currents with the electrode rotation rate, for both nondeactivated and deactivated films in the presence of the electroactive solute deferasirox (4-(3,5-bis(2-hydroxyphenyl)-1,2,4-triazol-1-yl) benzoic acid) allowed the obtention of a charge transport rate across a nickel hydroxide film. This rate decreased with the increase of the storage time.

Keywords: Nickel hydroxide films; Deactivation; Charge transport process; Deferasirox; Mediation reaction.

#### Introduction

Nickel hydroxide is an important electroactive material for many applications of interest such as oxidation and determination of carbohydrates and alcohols [1,2], amino acids [3], hydrogen peroxide [4], methane [5], drugs [3] and some other organic and biologically important products [3,5-8]. Also, the material shows high electrocatalytic efficiency towards the oxidation of organic molecules via cyclic mediation electron-transfer processes in alkaline solutions [1,3-7,8].

The formation of nickel hydroxide on the electrode surface to construct Ni-hydroxide modified electrodes has been achieved, in principle, in several different ways: by

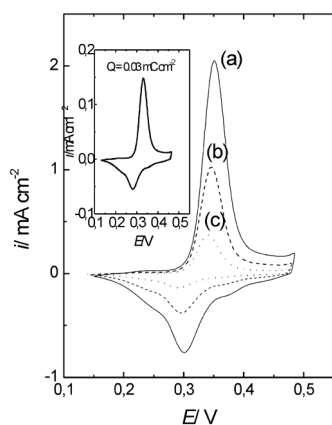
electrooxidation of nickel metal via different regimes of applied potential (e.g. potentiostatic, galvanostatic, anodic sweep), by cathodic deposition from a Ni(NO<sub>3</sub>)<sub>2</sub> solution on a conductive substrate and by placing a droplet of Ni(II) solution on the surface of the electrode and evaporating the solvent [3,5 and references cited therein].

Concerning practical applications, it is often indicated that nickel hydroxide films have good electrochemical properties in terms of conductivity and ion-permeability and also that they present good durability and long-term stability under storage during several weeks. In this regard, it is assumed that the reversible redox response and conducting properties of the modified electrode remain substantially unchanged before and after it have

been used. Considering the important applications of nickel hydroxide modified electrodes, not many efforts have been made to study in detail their true stability. The aim of the present work was study the limit of durability of a nickel hydroxide-gold modified electrode and how the electron-transport processes is modified when the electrode becomes stored without use during long time. This study was carried out by employing Rotating Disc Electrode Voltammetry (RDEV) for the interesting case where the modified electrode contacts an electrolyte solution containing an electroactive substrate and a mediation reaction occurs at the Ni-hydroxide|electrolyte interface. Deferasirox (4-(3,5-bis(2-hydroxyphenyl)-1,2,4-triazol-1-yl) benzoic acid) was selected as redox substrate in the present analysis. This drug is an oral iron chelator that is used clinically, mainly in patients with thalassemia [9-10]. The electrocatalytic oxidation and determination of this drug on a nickel hydroxide-modified electrode was studied in previous works [11].

## Experimental

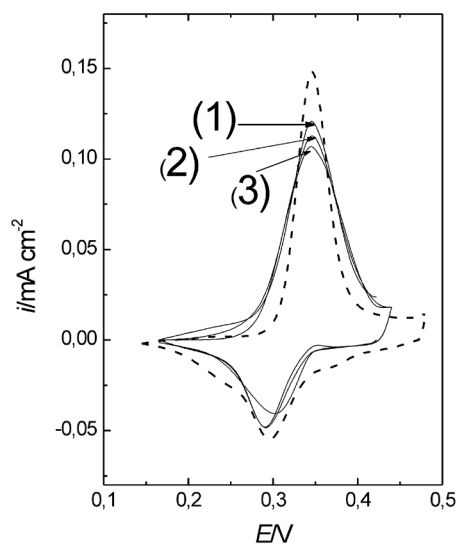
A conventional three electrodes cell was used for the experiments. A gold rotating disc electrode (RGDE) was employed as base electrode to deposit nickel hydroxide films. A platinum foil of large area was employed as counter electrode. All the potentials reported in this work are referred to the SCE. The RGDE consisted of a gold rod press-fitted with epoxy resin into a Teflon sleeve so as to leave a  $0.7 \text{ cm}^2$  disc area exposed.



**Figure 1:** Stable cyclic voltammograms at  $0.02 \text{ V s}^{-1}$  for nondeactivated Au/Ni-hydroxide modified electrodes in a  $0.1 \text{ M NaOH}$  solution. Voltammetric charge values of the nickel hydroxide films: (a)  $Q = 4 \text{ mC cm}^{-2}$ ; (b)  $Q = 2 \text{ mC cm}^{-2}$ ; (c)  $Q = 0.8 \text{ mC cm}^{-2}$ . Inset:  $Q = 0.03 \text{ mC cm}^{-2}$ .

Nickel hydroxide films were deposited on the RGDE employing the following procedure: firstly, the electrode was either cycled between  $0.0 \text{ V}$  and  $-0.5 \text{ V}$  ( $20 \text{ mV s}^{-1}$ ) or subjected to a constant potential of  $-0.5 \text{ V}$ , in a deaerated  $0.5 \text{ M Ni(NO}_3)_2$  solution. Then, the obtained modified elec-

trode was transferred to an electrochemical cell containing a  $0.1 \text{ M NaOH}$  solution and it was cycled between  $0.0 \text{ V}$  and  $0.6 \text{ V}$  (vs. SCE) until a stable voltammogram was achieved. These nickel hydroxide modified electrodes are called here, nondeactivated (or immediately prepared). Fig. 1 compares stabilized cyclic voltammograms at a scan rate  $0.02 \text{ V s}^{-1}$  in a  $0.1 \text{ M NaOH}$  solution for nondeactivated nickel hydroxide films of different voltammetric charge. When these immediately prepared nickel hydroxide films are stored (without use) in a deaerated  $0.1 \text{ M NaOH}$  solution at low temperature for different time periods, they suffer a deactivation, which is evident from the gradual change (slight reduction) of the voltammetric charge value as the storage time increases. These films are called deactivated. Fig. 2 shows the gradual change of the voltammetric response of an initially nondeactivated nickel hydroxide film ( $Q = 0.3 \text{ mC cm}^{-2}$ ) after to be subjected to different storage times in a deaerated  $0.1 \text{ M NaOH}$  solution at low temperature. Deactivated hydroxide nickel films do not recover the initial response corresponding to the immediately prepared (nondeactivated) film, even after prolonged potential cycling.



**Figure 2:** Stable cyclic voltammograms for a (----) nondeactivated Au/Ni-hydroxide modified electrode ( $Q = 0.3 \text{ mC cm}^{-2}$ ) and deactivated after storage in a deaerated  $0.1 \text{ M NaOH}$  solution at low temperature for different time periods: (1) 20 h; (2) 34 h; (3) 45 h. Electrolyte:  $0.1 \text{ M NaOH}$ . Scan rate:  $0.02 \text{ V s}^{-1}$ .

Potentiodynamic and steady-state experiments were performed with deactivated and nondeactivated the nickel hydroxide gold-modified electrodes in contact with a  $0.1 \text{ M NaOH} + 2 \times 10^{-3} \text{ M deferasirox}$  solution. In steady-state experiments the current-potential ( $I-E$ ) curves were recorded at different electrode rotation rates ( $\Omega$ ). Potentiodynamic and steady-state experiments were performed using a measurement system comprising a PAR model 175 universal programmer and a PAR model 173 potentiostat-galvanostat. A Philips model 8134 x-y1-y2 recorded was

used to record the stationary current-potential curves. The electrode rotation rate  $\Omega$  was controlled with home-made equipment that allowed one to select a constant  $\Omega$  value in the range  $50 \text{ rev min}^{-1} < \Omega < 8000 \text{ rev min}^{-1}$ . In some cases higher electrode rotation speed values ( $> 10000 \text{ rev min}^{-1}$ ) were employed. This was controlled with a digital phototachometer (Power Instruments model 891).

AR grade chemicals were employed throughout.  $\text{Ni}(\text{NO}_3)_2$  Fluka was employed.  $\text{NaOH}$  (Merck) was used without purification. The solution were prepared with water purified using a Millipore Milli-Q system. Deferasirox was synthesized as described in [10].

## Results and discussion

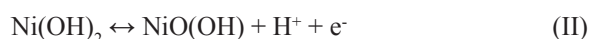
### Cyclic voltammetry experiments

The surface coverage ( $\Gamma_{\text{Au-Ni}}$ ) of the different Au/Ni modified electrodes shown in Fig. 1 can be estimated from the voltammetric oxidation (or reduction) charge ( $Q$ ) evaluated in the supporting electrolyte solution (0.1 M  $\text{NaOH}$ ) by using the equation  $\Gamma_{\text{Au-Ni}} = Q/nFA$ , where  $Q$ , is anodic (or cathodic) voltammetric charge corresponding to the oxidation (or reduction) process, assuming that all the nickel redox sites are electroactive on the voltammetric time scale,  $F$  is the Faraday's constant,  $A$  is the geometric surface area of the gold electrode and  $n$ , is the number of electrons transferred in  $\text{Ni}(\text{II}) \rightarrow \text{Ni}(\text{III})$  oxidation reaction.

The redox system corresponding to the peaks shown in Fig. 1 was attributed to the redox process  $\text{Ni}(\text{II})/\text{Ni}(\text{III})$ . The process can be represented by the following electrochemical reaction [12]



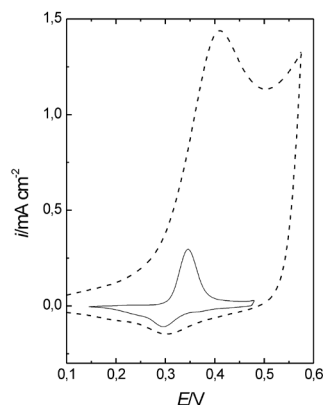
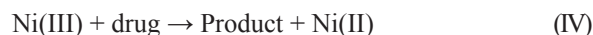
or as done in [13,14], by:



Although the voltammetric response of an immediately prepared nickel hydroxide film undergoes profound changes during the first cycles, a stable voltammogram is obtained after about 150 cycles.  $\text{Ni}(\text{OH})_2$  and  $\text{NiOOH}$  are considered good electronic conductors with a structure of poor or not barrier character.

Stabilized voltammograms of a nickel hydroxide film whose charge value is  $0.3 \text{ mC cm}^{-2}$  (surface coverage,  $\Gamma = 4.4 \cdot 10^{-9} \text{ moles/cm}^2$ ), in the absence and in the presence of deferasirox, are compared in Fig. 3. It can be seen that in the presence of deferasirox, the anodic current increased dramatically, whereas the cathodic one remains almost the

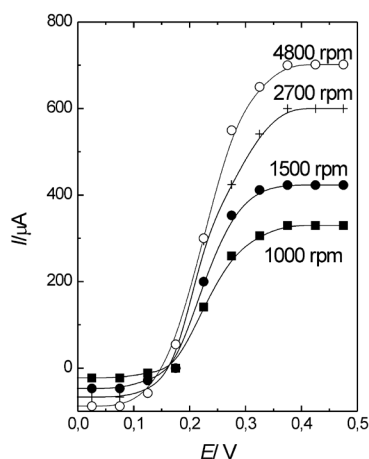
same. A simplified reaction scheme was proposed in [11] for the mediated oxidation of deferasirox on the nickel hydroxide surface:



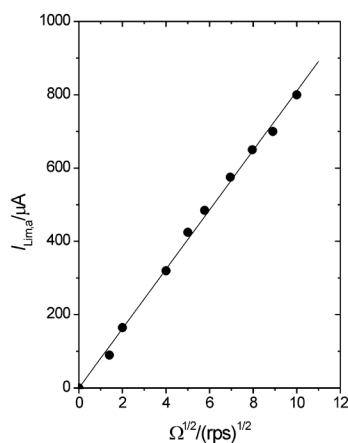
**Figure 3:** Cyclic voltammograms of a Au/Ni-hydroxide modified electrode  $Q = 0.3 \text{ mC cm}^{-2}$  ( $\Gamma = 4.44 \times 10^{-9} \text{ moles cm}^{-2}$ ) in a 0.1 M  $\text{NaOH}$  solution: (—) in the absence and (---) in the presence of 2 mM deferasirox.

### RDEV experiments with nondeactivated and deactivated nickel hydroxide-gold modified electrodes in the presence of deferasirox

It is often indicated that nickel hydroxide films retain their electroactivity, after storage without use in an alkaline solution, for several weeks [1-5]. This is very important for electroactive materials employed in analytical applications. Development of analytical sensors with long-term stability will remain a mainstay to meet needs for routine clinical, environmental and industrial applications. However, we find that although nondeactivated films maintain unaltered their electroactivity for more than 200 potential cycles under continuous use, if they are stored in an alkaline solution without use for different time periods, suffer an irreversible deactivation. Although this deactivation process becomes not so evident from the slight distortion of the voltammetric response (the whole voltammetric charge of a nondeactivated film is reduced less than 18% after storage for 80 h, see Fig. 2), it is more noticeable from the steady state current-potential experiments in the presence of an electroactive solute (see below).



**Figura 4:** Steady-state current-potential ( $I$ - $E$ ) curves for a nondeactivated nickel hydroxide gold modified electrode,  $Q = 0.3 \text{ mC cm}^{-2}$  ( $\Gamma = 4.44 \times 10^{-9} \text{ moles cm}^{-2}$ ) in contact with a  $0.1 \text{ M Na(OH)} + 2 \times 10^{-3} \text{ M}$  deferasirox solution. Different rotation rates indicated on the figure.

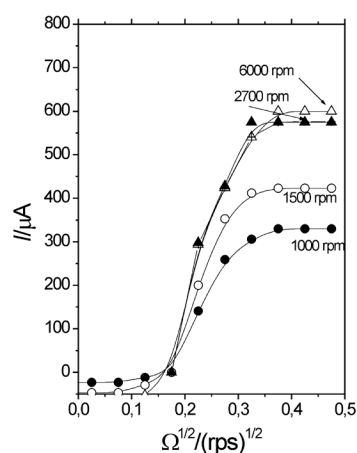


**Figura 5:** Levich representation ( $I_{\text{lim,a}}$  vs.  $W^{1/2}$ ) for a nondeactivated nickel hydroxide gold modified electrode in contact with a  $0.1 \text{ M Na(OH)} + 2 \times 10^{-3} \text{ M}$  deferasirox solution.

Three series of nickel hydroxide gold-modified electrodes were prepared in this work to quantitatively study their deactivation by employing RDEV. Each series was conformed by 6 hydroxide films. The voltammetric charge of the 6 films of each series was 0.3; 2 and 4  $\text{mC cm}^{-2}$ , ( $\Gamma = 0.44$ ; 2.96 and 5.92  $\times 10^{-8} \text{ moles/cm}^2$ ), respectively. That is, each series was constituted by 6 films all of the same voltammetric charge. Then, each one of the 6 nickel hydroxide films corresponding to each series, after being equilibrated within the potential region  $0.0 \text{ V} < E < 0.6 \text{ V}$  in the  $0.1 \text{ M NaOH}$  solution, was stored (without use) in a deaerated  $0.1 \text{ M NaOH}$  solution at low temperature for different time periods. That is, each one of the 6 films of each series was subjected to the same storage time sequence (first column in Table 1). RDEV experiments were performed with both, nondeactivated and deactivated films, in the presence of the electroactive substrate deferasirox.

Fig. 4 show steady-state current-potential ( $I$ - $E$ ) curves, at different electrode rotation rates,  $\Omega$ , for the nondeacti-

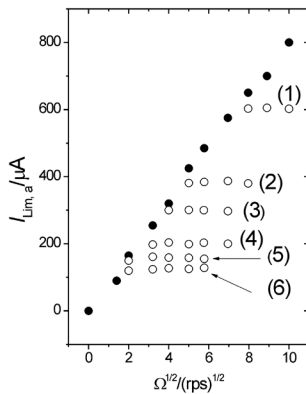
vated nickel hydroxide film of  $0.3 \text{ mC cm}^{-2}$ . As can be seen from this figure, diffusion-limited currents are observed at  $E > 0.45 \text{ V}$  (vs. SCE) for the deferasirox oxidation. The anodic limiting currents, at each electrode rotation rate, are independent on the nickel hydroxide charge value and follow the Levich equation (Fig. 5). The behavior observed in Fig. 5, for nondeactivated films of different voltammetric charges would be related to a rapid electron-transfer mediation at the nickel hydroxide/deferasirox solution interface.



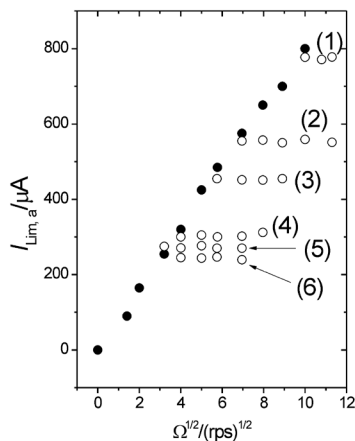
**Figura 6:** Steady-state current-potential ( $I$ - $E$ ) curves for a deactivated nickel hydroxide gold modified electrode  $Q = 0.3 \text{ mC cm}^{-2}$  ( $\Gamma = 4.44 \times 10^{-9} \text{ moles cm}^{-2}$ ) in contact with a  $0.1 \text{ M Na(OH)} + 2 \times 10^{-3} \text{ M}$  deferasirox solution. Different rotation rates indicated on the figure. Storage time 10 h.

Fig. 6 shows steady-state current-potential curves ( $I$  vs.  $E$ ) at different  $\Omega$  values for the nickel hydroxide film ( $Q = 0.3 \text{ mC cm}^{-2}$ ) after to be stored in the alkaline solution for 10 h without use. As can be seen by comparing Fig. 6 with Fig. 4, the anodic limiting current for the deactivated film increases with the rotation rate increase until a given value, from which it becomes  $\Omega$  independent. Fig. 7 shows the  $I_{\text{Lim,a}}$  vs.  $\Omega^{1/2}$  dependences for the nondeactivated film of  $Q = 0.3 \text{ mC cm}^{-2}$  and the same film deactivated after storage in an alkaline solution for different time periods. While the nondeactivated film gives a Levich dependence, a constant current value is obtained after a given  $\Omega$  value for the deactivated films. This constant current is indicative of a deactivation process. As can be seen from Fig. 7, as the higher is the storage time the lower is the electrode rotation rate at which a constant current value is reached and then, more deactivated is the film. The constant current value achieved for different deactivated nickel hydroxide films by employing a fixed storage time, depends on their voltammetric charge value. Fig. 8 shows the  $I_{\text{Lim,a}}$  vs.  $\Omega^{1/2}$  dependences for a nondeactivated film of  $Q = 2 \text{ mC cm}^{-2}$  and the same film after to be deactivated by employing the same sequence of storage times as for a film of  $Q = 0.3 \text{ mC cm}^{-2}$ . As can be seen by comparing Fig. 7 and Fig. 8, the  $I_{\text{const}}$  for the same storage time is observed at higher electrode rotation rate as the higher is the voltammetric

charge value of the film. In this regard, nickel hydroxide films of high voltammetric charge become less deactivated than thin ones for a fixed storage time. The rows of Table 1 allows one comparing the  $I_{const}$  values for nickel hydroxide films of different  $Q$  values, which were deactivated by employing the same storage time in an alkaline solution.



**Figure 7:** Levich representations ( $I_{lim,a}$  vs.  $W^{1/2}$ ) for a nondeactivated nickel hydroxide film (●) in contact with a 0.1 M Na(OH) +  $2 \times 10^{-3}$  M deferasirox solution and the same film deactivated after storage in an alkaline solution for different time periods (1) 10 h; (2) 20 h; (3) 25 h; (4) 45 h; (5) 65 h; (6) 85 h.  $Q = 0.3 \text{ mC cm}^{-2}$  ( $\Gamma = 4.44 \times 10^{-9}$  moles  $\text{cm}^{-2}$ ).



**Figure 8:** Levich representations ( $I_{lim,a}$  vs.  $W^{1/2}$ ) for a nondeactivated nickel hydroxide film (●) in contact with a 0.1 M Na(OH) +  $2 \times 10^{-3}$  M deferasirox solution and the same film deactivated after storage in an alkaline solution for different time periods (1) 10 h; (2) 20 h; (3) 25 h; (4) 45 h; (5) 65 h; (6) 85 h.  $Q = 2 \text{ mC cm}^{-2}$  ( $\Gamma = 2.96 \times 10^{-8}$  moles  $\text{cm}^{-2}$ ).

**Interpretation of RDEV experiments**

The steady state experiments above described seem to indicate that deactivation of nickel hydroxide films could be associated to a restriction in the charge transport process across the film. Then, interpretation of nickel hydroxide films deactivation was made in this work on the basis of the Eq. (1) [15]:

$$I_{const} = n F A D_{ct} (c_o / \phi_{film}) \tag{1}$$

Eq. (1) was previously employed to describe the charge

transport processes in other materials such as electroactive redox polymers that also contain active redox sites and then, these polymers are able to act as mediators in redox reactions [16-21]. In Eq. (1),  $c_o$  is the total volumetric concentration of redox sites into the electroactive film and  $\phi_{film}$  the film thickness. The parameter  $c_o$  is equal to  $c_{Red} + c_{Ox}$ , where  $c_{Red}$  and  $c_{Ox}$  are the volumetric concentration of reduced and oxidized redox sites, respectively (Ni(II)/Ni(III) redox sites).  $D_{ct}$  represents a measure of the charge transport rate within the film. Then, in the case of nickel hydroxide films  $D_{ct}$  should represent the rate of electron transport across the Ni(II)/Ni(III) redox sites. The number  $n$  expresses the number of transferred electrons in the redox process of the electroactive material,  $A$  is the electrode area and  $F$  the Faraday's constant. The limiting current value at which  $I_{Lim,a}$  ( $= I_{const}$ ) becomes constant (see Fig. 7 and Fig. 8) can be considered as a representation of the maximum flux of charge transported across the electroactive film.

**Table 1:**  $I_{const}$  values for deactivated nickel hydroxide films of different thickness

*t/h	<sup>b</sup> $10^3 I_{const}/\mu A$ ( $Q = 0.3 \text{ mC cm}^{-2}$ )	<sup>b</sup> $10^6 I_{const}/\mu A$ ( $Q = 2 \text{ mC cm}^{-2}$ )	<sup>b</sup> $10^6 I_{const}/\mu A$ ( $Q = 4 \text{ mC cm}^{-2}$ )
10	607	775	850
20	375	550	712
25	300	455	600
45	200	320	452
65	160	290	400
80	157	270	407

Electrode area: 0.7  $\text{cm}^2$

\*Storage time in a 0.1M NaOH solution (a different film was employed for each storage time)

<sup>b</sup> $I_{const}$  was obtained in a 0.1M NaOH + 2 mM Deferasirox solution. Q is the voltammetric charge value for the oxidation process Ni(II)/Ni(III) in the 0.1M NaOH solution.

On the assumption that nickel hydroxide films are uniform and homogeneous, the film thickness can be expressed as  $\phi_{film} = \Gamma/c_o$ . Then, Eq. (1) can be written as:

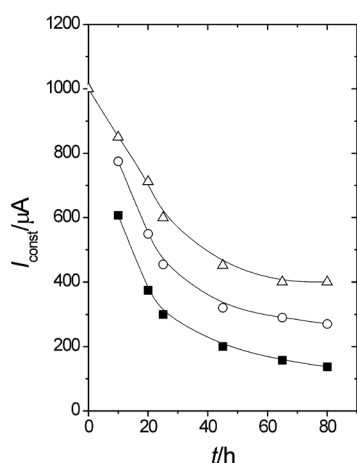
$$I_{const} = n F A D_{ct} (c_o^2 / \Gamma) \tag{2}$$

While  $I_{const}$  (Fig. 7 and Fig. 8) and  $\Gamma$  are experimental parameters, the interpretation of diffusion coefficients ( $D_{ct}$ ) in solid materials depends on the model employed to describe the charge propagation and sometimes on the technique used in its measurement. In this regard the rate of charge transport in solid materials can vary over several orders of magnitude ( $10^{-7}$ - $10^{-14}$   $\text{cm}^2 \text{ s}^{-1}$ ). On the assumption that  $c_o$  remains constant the deactivation effect could only be attributed to a reduction of the charge propagation rate,  $D_{ct}$ .

The existence of a constant current  $I_{const}$  in a deactivated film can be explained in the following way. As one increases the flux of electroactive species ( $\Omega$  increase) from the bulk solution, then if the flux exceeds the supply of charge from the gold electrode through the nickel hydroxide film to the electrolyte interface, the rate-limiting step will shift from the limiting transport of the electroactive species to the limiting transport of the charge through the nickel hydroxide film. This consideration seems to be verified by the fact that  $I_{const}$  is observed at a lower electrode rotation



rate as more deactivated is the nickel hydroxide film for a given voltammetric charge (or film thickness). However,  $I_{\text{const}}$  also depends on the nickel hydroxide voltammetric charge for a given storage time. These findings seem to indicate a charge transport process limited by both the degree of deactivation and film thickness. Fig. 9 shows the  $I_{\text{const}}$  vs. storage time dependence for each one of the 3 series of nickel hydroxide films employed in this work (each series conformed by 6 films) whose voltammetric charge values are 0.3, 2 and 4 mC cm<sup>-2</sup>, respectively. This representation shows again that for a constant storage time a thin nickel hydroxide film deactivates more than a thick one.



**Figura 9:**  $I_{\text{const}}$  vs. storage time dependence for different voltammetric charge values: (■)  $Q = 0.3 \text{ mC cm}^{-2}$ ; (○)  $Q = 2 \text{ mC cm}^{-2}$ ; (Δ)  $Q = 4 \text{ mC cm}^{-2}$ . Solution:  $0.1 \text{ M Na(OH)} + 2 \times 10^{-3} \text{ M deferasirox}$ .

With regard to transport properties, experimental  $I_{\text{const}}$  values for different deactivated films were employed in Eq. (2) to extract the transport parameter  $D_{\text{ct}}c_0^2$  as a function of the storage time (Table 2). As can be seen from Table 2,  $D_{\text{ct}}c_0^2$  decreases as the storage time increases for each film thickness and also, at a constant storage time a thick film exhibits a higher charge transport parameter as compared with a thin one. As was indicated, on the assumption that  $c_0$  remains nearly constant, the deactivation effect could only be attributed to a reduction of the charge propagation rate,  $D_{\text{ct}}$ . One can not obtain absolute values of the diffusion coefficient for the charge transport from experimental  $I_{\text{const}}$  values due to the lack of data about  $c_0$  for electrochemically synthesized nickel hydroxide films. Thus, from experimental  $I_{\text{const}}$  values, only the parameter ( $D_{\text{ct}}c_0^2$ ) was estimated.  $D_{\text{ct}}c_0^2$  values for each  $Q$  value and different storage times are also collected in Table 2.

With regard to  $D_{\text{ct}}$ , as was indicated, it should represent the rate of electron transport across the Ni(II)/Ni(III) redox sites. The conduction mechanism of some materials containing redox sites [22], is considered in terms of the electron hopping model with the participation of the redox sites as acceptor or donor sites. The  $D_{\text{ct}}c_0^2$  decrease for a nickel hydroxide film stored in an alkaline solution could

be strictly attributed to either a  $D_{\text{ct}}$  decrease or  $c_0$  decrease or both of them. On the assumption that  $c_0$  (total redox sites volumetric concentration) remains constant, the  $D_{\text{ct}}$  decrease could be explained in terms of the increase of the hopping distance between active redox active sites (Ni(II)/Ni(III)) because after deactivation some redox sites becomes inactive. In this connection, the electron diffusion coefficient,  $D_{\text{ct}}$ , has been expressed in terms of the mean distance between adjacent active redox sites [23], according to  $D_{\text{ct}} = (a^2k_0)$ , where  $k_0$  is the intermolecular electron-transfer rate constant and  $a$  is the mean distance between two adjacent redox sites. The hopping rate,  $k_0$ , exhibits an exponential dependence on  $a$ , through the energy  $-U(x+a)$  of a state with an electron in the position  $x$  along the current direction (see Eq. (23) in Ref. [23]). Thus, the  $D_{\text{ct}}$  decrease could explain the electron current  $I_{\text{const}}$  decrease with the increase of the storage time. As was indicated, the interpretation of diffusion coefficients in solid materials depends on the model employed to describe the charge propagation and sometimes on the technique used in its measurement.

**Table 2:**  $D_{\text{ct}}c_0^2$  values for different deactivated nickel hydroxide films

$t/h$	${}^b10^{16}D_{\text{ct}}c_0^2 / \text{moles}^2\text{cm}^{-4} \text{ s}^{-1}$ ( $Q = 0.3 \text{ mC cm}^{-2}$ )	${}^b10^{16}D_{\text{ct}}c_0^2 / \text{moles}^2\text{cm}^{-4} \text{ s}^{-1}$ ( $Q = 2 \text{ mC cm}^{-2}$ )	${}^b10^{16}D_{\text{ct}}c_0^2 / \text{moles}^2\text{cm}^{-4} \text{ s}^{-1}$ ( $Q = 4 \text{ mC cm}^{-2}$ )
10	0.39	3.39	7.45
20	0.24	2.41	6.24
25	0.19	1.99	5.26
45	0.17	1.40	3.96
65	0.10	1.27	3.50
80	0.09	1.18	3.52

Electrode area:  $0.7 \text{ cm}^2$

a Storage time in a  $0.1 \text{ M NaOH}$  solution (a different film was employed for each storage time)

b  $D_{\text{ct}}c_0^2$  was obtained in a  $0.1 \text{ M NaOH} + 2 \text{ mM Deferasirox}$  solution.  $Q$  is the voltammetric charge value for the oxidation process Ni(II)/Ni(III) in the  $0.1 \text{ M NaOH}$  solution.

With regard to  $c_0$ , we have attempted to estimate this parameter for our nickel hydroxide films from data reported in other papers. An ellipsometric study of nickel hydroxide electrodes formed by *ex situ* chemical precipitation is reported in [24]. Different ellipsometric parameters of nickel hydroxide films, including the ellipsometric thickness, as a function of the voltammetric charge are presented in [24]. These parameters approach to limiting values as electrode charge is increased. The dependency of the nickel hydroxide film thickness on the voltammetric charge extracted from table 1 of Ref. [24], allows one estimating a  $c_0$  value. Although is likely that the proper characteristics of nickel hydroxide layers obtained by chemical precipitation used in [24] are not exactly the same for layers cathodically produced, a  $c_0$  value was extracted from data presented in [24]. By employing the ellipsometric thickness value ( $d_{\text{ellip}} = 95 \text{ nm}$ ) given in [24] for a charge value around  $4 \text{ mC cm}^{-2}$ , and considering  $c_0 = \Gamma/d_{\text{ellip}} = Q/nFA d_{\text{ellip}}$ , a  $c_0$  value

around  $3.86 \times 10^{-3} \text{ mol cm}^{-3}$  is obtained.

At this point it is interesting to compare  $D_{ct}c_o^2$  values obtained in this work for nickel hydroxide films with those obtained for other materials such as electroactive redox polymers that also are able to act as mediators in redox reactions [16-21]. In this regard, the electroactive polymer poly(*o*-aminophenol) immediately synthesized, that acts as mediator in the presence of different electroactive solutes ( $\text{Fe}(\text{CN})_6^{4-/3-}$  and hydroquinone-benzoquinone) exhibits a  $D_{ct}c_o^2$  value around  $7.32 \times 10^{-14} \text{ mol}^2 \text{ s}^{-1} \text{ cm}^{-4}$  [18]. This  $D_{ct}c_o^2$  value for poly(*o*-aminophenol) arises from well-known diffusion coefficient ( $D_{ct}$ ) and total redox sites concentration ( $c_o$ ) values of  $2.93 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$  and  $5 \times 10^{-3} \text{ mol cm}^{-3}$ , respectively [19]. As can be seen from Table 2,  $D_{ct}c_o^2$  values for deactivated nickel hydroxide films are lower than the value reported for immediately prepared poly(*o*-aminophenol) film electrodes. However, the deactivation of the electroactive polymer poly(*o*-aminophenol) by ferric cations was also studied by rotating disc electrode voltammetry and impedance spectroscopy in previous works [20,21]. It was found that the diffusion coefficient values of poly(*o*-aminophenol) decreases about two orders of magnitude, that is, from  $2.93 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$  to  $2.4 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$  [20] as the degree of deactivation increases from 0.1 to 0.6. Thus, a  $D_{ct}c_o^2$  value around  $6 \times 10^{-16} \text{ mol}^2 \text{ s}^{-1} \text{ cm}^{-4}$  arises for a deactivated poly(*o*-aminophenol) film, which is comparable to the value corresponding to a deactivated nickel hydroxide film.

## Conclusions

Nickel hydroxide films electrochemically synthesized on a gold base electrode suffer an irreversible deactivation under storage in an alkaline solution. Although the phenomenon is visible on the voltammetric response in the sole presence of the supporting electrolyte solution (0.1 M NaOH), it is more clearly detected by employing rotating disc electrode voltammetry when a mediation reaction occurs at the Au-Ni(OH)<sub>2</sub>/electrolyte interface. The comparison of steady state current-potential curves at different electrode rotation rates for both nondeactivated and deactivated films in the presence of the electroactive solute deferasirox, allowed one obtaining a charge propagation rate which decrease with the increase of the storage time. The degree of deactivation seems to depend on the nickel hydroxide film voltammetric charge. Thick films ( $Q > 4 \text{ mC cm}^{-2}$ ) are less deactivated (remain more conductive) than thin ones for a fixed storage time. From the practical viewpoint, as nickel hydroxide is often employed as electroactive material in the determination of different organic and biologically important products, an immediately synthesized film should be used in each analysis. The results of this work allowed us not only to obtain some information about the durability and long-term stability with potential cycling and storage of a nickel hydroxide-

modified electrode but also to gain further insights into the charge-propagation process at this modified electrode.

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