Contents lists available at ScienceDirect







journal homepage: www.elsevier.com/locate/electacta

Electrochemical studies of Zn underpotential/overpotential deposition on a nickel electrode from non-cyanide alkaline solution containing glycine

J.C. Ballesteros^{a,b}, E. Chaînet^b, P. Ozil^b, G. Trejo^{a,*}, Y. Meas^{a,*}

^a Centro de Investigación y Desarrollo Tecnológico en Electroquímica (CIDETEQ), Parque Tecnológico Sanfandila, Pedro Escobedo, Querétaro, C.P. 76703 Querétaro, Mexico ^b Laboratoire d'Electrochimie et de Physicochimie des Matériaux et des Interfaces, LEPMI, UMR 5631 CNRS-INPG-UJF, BP 75, 38402 Saint-Martin d'Heres Cedex, France

ARTICLE INFO

Article history: Received 15 November 2010 Received in revised form 24 February 2011 Accepted 25 February 2011 Available online 24 March 2011

Keywords: Electrodeposition Zinc Nickel Glycine UPD Nucleation

ABSTRACT

In this work we present an electrochemical study of the underpotential deposition (UPD) and overpotential deposition (OPD) of zinc onto nickel electrode (NE) from a non-cyanide alkaline solution containing glycine. The studied parameters were zinc concentration, glycine concentration and scanning rate. The analysis of the experimental data clearly showed the presence of UPD and OPD processes that started at -0.8 V vs. SCE and -1.4 V vs. SCE, respectively. The voltammetric studies also indicate diffusion control of the zinc UPD and OPD processes onto the NE. From the potentiostatic transients we found instantaneous nucleation (2D) mechanisms, which agree to that observed in the AFM study. In order to compare the effect of zinc/glycine concentration, we calculate thermodynamic parameters for the OPD process.

© 2011 Elsevier Ltd. All rights reserved.

1. Introduction

Zinc electroplating and its alloys have been widely used in the steel industry for the protection of steel products in corrosive environments [1]. Several factors such as zinc concentration [2], complexing agents [3], anions [4,5] and additives [6] play fundamental roles in zinc electrodeposition. These factors may modify the texture and morphology of zinc electrodeposited coating [7–10].

Alkaline non-cyanide zinc baths is the outcome of the efforts to produce a non-toxic cyanide free zinc electrolyte. Formerly, it was thought that these baths can produce only dark, spongy or powdery deposits and the addition of complexing agents like EDTA, gluconate, tartrate and triethanolamine in relatively large quantities can improve the zinc deposit quality [11].

The glycine has been used as a complexing agent in the electrodeposition of Zn–Ni [12], Cu–Co [13], Zn–Co [14], Zn–Co–Cu alloys [15] and more recently by our research group to obtain Zn–Co alloy [16]. These studies show that the deposits obtained from alkaline bath containing glycine are of high quality.

On the other hand, it is well known that during the electrocrystallization of metals on foreign substrates, very often an underpotential deposition occurs, prior to the formation of a bulk deposit [17]. When the work function of a metal being electrodeposited is lower than that of the substrate metal, the electrodeposition may occur at a potential more positive than the equilibrium potential, a phenomenon called underpotential deposition (UPD) [17]. The region where this process occurs on polycrystalline substrates is defined by the Kolb–Gerischer equation [18,19]:

$$\Delta E = 0.5 \ \Delta \varnothing \tag{1}$$

where (ΔE) is the underpotential shift in V and $(\Delta \emptyset)$ is the difference in the work function of the electron for both metals in eV.

On the basis of Eq. (1) and data published by Trasatti [18] on \emptyset for different metals, it is possible to calculate approximately the underpotential shift (ΔE) for the metal couple nickel substrate–zinc adsorbate, equal to (ΔE)=0.585 V. This, in turn, provides grounds for presuming that underpotential adsorption of zinc onto nickel electrode is possible.

Several investigators [20–37] have studied the effect of several factors on the zinc UPD process, such as: adanions, organic compounds, pH of the solution, hydrogen adsorption, and resulting morphology of the deposit have been investigated extensively at noble metal electrodes using electrochemical techniques coupled with other techniques.

Despite these many important contributions to the study of electrochemical reduction of zinc UPD, a study of this phenomenon

^{*} Corresponding authors. Tel.: +52 442 211 6070; fax: +52 442 211 6001. *E-mail addresses*: gtrejo@cideteq.mx (G. Trejo), yunnymeas@cideteq.mx (Y. Meas).

^{0013-4686/\$ -} see front matter © 2011 Elsevier Ltd. All rights reserved. doi:10.1016/j.electacta.2011.02.106

Chemical composition of solutions used in this work.								
Solution	$[Zn^{2+}] (mol L^{-1})$	$[Cl^{-}] (mol L^{-1})$						

Solution $[Zn^{2+}] (mol L^{-1})$ $[Cl^{-}] (mol L^{-1})$ $[G^{-}] (mol L^{-1})$ S00.20.41.6S10.40.82.2S20.61.22.8

on a nickel substrate and from zinc-glycine complexes in alkaline solution is still not done.

The aim of the present work is threefold. In a first part, we present a thermodynamic study on the zinc–glycine–water system by means of species distribution and potential–pH diagrams with the view to better understand the effect of the zinc/glycine concentration on the zinc electroreduction. In a second part, we present an electrochemical study in order to obtain information on the UPD and OPD processes from non-cyanide alkaline bath containing glycine. Finally, in a third part, we present an AFM morphological study of the zinc UPD processes.

2. Experimental

Zinc deposition onto NE was carried out in a conventional threeelectrode cell from the solutions shown in Table 1 at 25 °C. All solutions were prepared using analytic grade reagents (provided by Sigma-Aldrich Company) with ultra pure water (Millipore-Q system) and were deoxygenated by bubbling N₂ for 20 min before each experiment. The working electrode was a nickel electrode (NE) provided by Sigma-Aldrich, made of a nickel rod embedded in Teflon. The exposed surface area (0.726 cm^2) was polished to mirror finish with different grades of alumina down to 0.05 µm and ultrasonically cleaned before experiments. A graphite bar with an exposed area greater than the working electrode was used as counter electrode. A saturated calomel electrode (SCE) was used as reference, and all potentials refer to this scale. The electrochemical experiments were carried out with a potentiostat/galvanostat PAR273A (EG&G) connected to a personal computer running the general purpose electrochemical system software (GPES) (Eco Chemie B.V.) for control of experiments and data acquisition. The conditions for electrochemical experiments are chosen in where the ohmic drop is considered negligible. The solution temperature was controlled and made constant with a circulating water thermostat (Bioblock Scientific). AFM (Digital Instruments, Mod. Nanoscope E) in contact mode was used to obtain images of the UPD zinc deposit on the nickel electrode. Coating morphology was evaluated using a scanning electron microscope (Jeol Mod. DSM-5400LV).

3. Results and discussion

3.1. Zinc-glycine chemistry

Zinc ions in aqueous solutions have an octahedral coordination that allows for the accommodation of six ligands in its first hydration shell. For each of the solution compositions in this study, the speciation of zinc in glycine solution was examined by constructing the species repartition and potential–pH diagrams. Glycine, H_2NCH_2COOH , is the simplest amino acid, which exists under three different forms in aqueous solutions depending on the pH value: $^+H_3NCH_2COOH$ (cation), $^+H_3NCH_2COO^-$ (zwitterion), and $H_2NCH_2COO^-$ (anion). These species are denoted as: H_2G^+ , HG, and G^- , respectively, for brevity. The equilibria between these may be depicted as [38–40]:

which are characterized by the equilibrium constants:

$$K_{a1} = \frac{[\text{HG}][\text{H}^+]}{[\text{H}_2\text{G}^+]}$$
(3)

$$K_{a2} = \frac{[G^-][H^+]}{[HG]}$$
(4)

The pK's values of glycine are: $pK_{a1} = 2.07$ and $pK_{a2} = 9.97$ at 25 °C [38–40].

Depending on the zinc concentration, the glycine concentration and the pH, glycine molecules can successively replace water molecules in zinc's coordination octahedron, forming zinc–glycine complexes. An important point is to understand the deposition solution chemistry and specially the zinc species involved in the deposition process. In aqueous solutions, Zn(II) soluble species are Zn^{2+} , hydroxide complexes, chloride complexes and glycine complexes. The concentration of the latter are related to Zn^{2+} concentration by the equilibrium reaction:

$$Zn^{2+} + iL^{-} \leftrightarrow ZnL_{i}^{(2-i)}$$
(5)

each complex is characterized by its stability constant $\beta_i^{L^-}$.

$$\beta_{iZn}^{L^{-}} = \frac{[ZnL_{i}^{(2-i)}]}{[L^{-}][Zn^{2+}]}$$
(6)

where L⁻ represents a ligand, OH⁻, Cl⁻ or G⁻ in the present work, and *i* the coordination number. The values of $\beta_{iZn}^{L^-}$ were obtained from literature [38–40] and are reported in Table 2.

In addition, when the pH increases, there is an increasing tendency for the formation of metal hydroxide. With zinc cations, this equilibrium can be expressed by the following equilibriums:

$$Zn(OH)_{2(s)} \Leftrightarrow Zn^{2+} + 2OH^{-}$$
(7)

characterized by the solubility constant K_s.

$$K_{\rm s} = [{\rm Z}n^{2+}][{\rm O}{\rm H}^{-}]^2 \tag{8}$$

From the values of $\beta_{iZn}^{L^-}$ and K_s , it is possible to calculate the ratio between a soluble/insoluble zinc species and total zinc concentration in solution. The species repartition–pH diagrams were computed using the definition of complexation coefficient of Zn(II), $\alpha_{Zn(L=G^-,OH^-,CI^-)}$ [41]. It is defined as: the ratio $c_{Zn}/[Zn^{2+}]$, where c_{Zn} is the total concentration of zinc including all complexes, $[Zn^{2+}]$ and $[Zn(OH)_{2(s)}]$; and $[Zn^{2+}]$ is the concentration of free zinc cations Zn^{2+} .

$$\alpha_{Zn(L=G^-,OH^-,CI^-)} = \frac{c_{Zn}}{[Zn^{2+}]} = \frac{[Zn^{2+}] + \sum [ZnL_i^{(2-i)}] + [Zn(OH)_{2(s)}]}{[Zn^{2+}]}(9)$$

Combining Eqs. (6), (8) and (9), $\alpha_{\rm Zn(L=G^-,OH^-,CI^-)}$ can be expressed as:

$$\alpha_{Zn(L=G^{-},OH^{-},CI^{-})} = 1 + \beta_{1Zn}^{L}[G^{-}] + \beta_{2Zn}^{L}[G^{-}]^{2} + \beta_{3Zn}^{L}[G^{-}]^{3} + \beta_{1Zn}^{CI}[CI^{-}] + \beta_{2Zn}^{CI}[CI^{-}]^{2} + \beta_{3Zn}^{CI}[CI^{-}]^{3} + \beta_{4Zn}^{CI}[CI^{-}]^{4} + \beta_{4Zn}^{OH}[OH^{-}]^{4} + K_{s}\frac{(K_{w})^{2}}{[H^{+}]^{2}}$$
(10)

Using this last equation, one can easily calculate the distribution of different species:

$$%Zn^{2+} = \frac{100}{\alpha_{Zn(L=G^-,OH^-,CI^-)}}$$
(11)

$$%ZnL_{i}^{(2-i)} = \beta_{iZn}^{L^{-}}[L^{-}] %Zn^{2+}$$
(12)

$$%Zn(OH)_{2(s)} = %Zn^{2+} \frac{K_s(K_w)^2}{[H^+]^2}$$
(13)

Table 2

Equilibrium constants for the overall formation of complexes in the zinc–glycine–OH⁻ system and the hydroxide solubility product obtained from the literature [38–40], $\beta_i^L = [ML_i^{(2-i)}]/[M^{2+}][L^-]^i$.

L=OH ⁻			L = C1 ⁻				L=G ⁻		p <i>K</i> s			
i	1	2	3	4	1	2	3	4	1	2	3	
	4.4	11.3	13.7	16.6	0.43	0.61	0.53	0.20	4.88	9.06	11.56	16.92

As a result, the key point of the calculation is the determination of [G⁻]. In a first step, we can establish the glycine protonation coefficient α_{G^-} , defined as:

$$\alpha_{G^{-}} = \frac{[G^{-}] + [HG] + [H_2G^{+}]}{[G^{-}]} = 1 + \frac{[H^{+}]}{K_{a1}} + \frac{[H^{+}]^2}{K_{a1}K_{a2}}$$
(14)

It must be pointed out that under our experimental conditions α_{G^-} differs from the $c_{G^-}/[G^-]$ ratio, where c_{G^-} is the overall-glycine concentration, assuming that a significant part of glycine ions is involved in the formation of complexes. Then, this ratio can be expressed as:

$$\frac{c_{\rm G^-}}{[{\rm G}^-]} = \alpha_{\rm G^-} + \frac{[{\rm ZnG}^+ + 2[{\rm ZnG}_2]] + 3[{\rm ZnG}_3^-]}{[{\rm G}^-]}$$
(15)

leading to a third degree equation:

$$3\beta_{3Zn}^{G^{-}} \frac{c_{Zn}}{\alpha_{Zn(L=G^{-},OH^{-},CI^{-})}} [G^{-}]^{3} + 2\beta_{2Zn}^{G^{-}} \frac{c_{Zn}}{\alpha_{Zn(L=G^{-},OH^{-},CI^{-})}} [G^{-}]^{2} + \left(\alpha_{G^{-}} + \beta_{1Zn}^{G^{-}} \frac{c_{Cu}}{\alpha_{Zn(L=G^{-},OH^{-},CI^{-})}}\right) [G^{-}] - c_{G^{-}} = 0$$
(16)

The determination of $[G^-]$ can be achieved by an iterative method involving Eqs. (10), (14) and (16). Then, using Relations (11)–(13), one can easily obtain the distribution diagram for the zinc/glycine system in aqueous solution. Three such diagrams are presented in Fig. 1(a)–(c).

Fig. 1 shows the species repartition diagrams obtained from Relations (11)–(13) and considering the conditions displayed in Table 1. In these diagrams it is possible to observe four characteristic pH regions. The first region is characterized by the free zinc ion and zinc–chloride complexes as the most stable species (pH region 0–4). In the second region, between pH 4 and pH 8, the predominant zinc species are ZnG^+ and ZnG_2 complexes. In the third region, from pH 8 to pH 12, the predominant zinc species are ZnG^- complexes. The fourth region, above pH 12, is characterized by two zinc hydroxides; between pH 12 and pH 14, the predominant zinc hydroxide is the insoluble species $Zn(OH)_{2(s)}$ and for pH > 14 the predominant zinc species is the soluble hydroxide $Zn(OH)_4^{2-}$.

These results clearly indicate that under our experimental conditions the anionic 1:3 ZnG_3^- complex predominates in three solutions mentioned in Table 1 for pH ranging from 8 to 12.

Based on the information provided by the species repartition diagrams, we have constructed the E-pH diagram for values of pH above 7. Fig. 2 shows the E-pH diagram for the system with 0.2 M Zn^{2+} + 0.4 M Cl⁻ + 1.6 M G⁻.

On the basis of these results, we therefore assume that under our experimental conditions the overall reaction of zinc electrodeposition process at pH 10 will be the following:

$$ZnG_3^- + 2e^- \Leftrightarrow Zn^0 + 3G$$

The conditional (formal) potential for the reaction (17) is given by:

$$E_{eq}^{o'}(ZnG_3^-/Zn(0)) = -1.346 - 0.089 \log[G'] + 0.0296 \log[Zn']$$

where $E_{eq}^{o}(ZnG_3^-/Zn(0))$ represents the conditional (formal) potential, in volts vs. SCE, for the system $ZnG_3^-/Zn(0)$. The notation generalized Zn' represents the free zinc ions solution, the soluble zinc–glycine complexes, or the metal hydroxide in either the soluble or insoluble form; in this diagram G' corresponds to the free concentration of glycine.

Eq. (18) allows us to predict a displacement in the value of equilibrium potential when there is a change in glycine and/or zinc ions concentration. Table 3 contains $E_{eq}^{o}(ZnG_3^-/Zn(0))$ values obtained from Eq. (18), which correspond to the conditions used in the solutions S₀ (-1.384 V vs. SCE), S₁ (-1.388 V vs. SCE), S₂ (-1.392 V vs. SCE).

3.2. Voltammetric study

Cyclic voltammetry study was performed in the potential range 0 to -1.65 V vs. SCE onto NE from solutions S₀, S₁ and S₂. The potential scan was initiated in the negative direction from the open circuit potential (E_{OCP}) at scan rate (υ) of 10 mV s⁻¹.

It is possible to define the region of the UPD process from previous thermodynamic study. The potential of the $ZnG_3^{-}/Zn(0)$ couple under our experimental conditions was previously determined as -1.388 V vs. SCE (average value). Therefore, the deposition of zinc that takes place at potentials more positive than -1.388 V vs. SCE will be defined as occurring by the UPD process, and zinc deposition that occurs at more negative potential values is defined as the OPD process.

Typical cyclic voltammograms obtained for zinc are presented in Fig. 3. During the direct scan it is possible to note that all voltammograms present the following characteristics: a negligible cathodic current from the E_{OCP} to -0.8 V vs. SCE that indicates none reaction occurring in this potential range; the formation of two cathodic peaks, A and B, at the peak potentials -1.30 V vs. SCE and -1.55 V vs. SCE, respectively (this potential value depends on the composition of the solution). The peak A appears at more positive potential values than the equilibrium potential predicted from Eq. (18) and this start at -0.8 V vs. SCE. which is a value 0.6 V before that the predicted from Eq. (18). Is important to note that this value is very close to the calculated ($\Delta E = 0.585 \text{ V}$) from Eq. (1) for the underpotential shift. The peak B is located at more negative potential values than the equilibrium potential of the $ZnG_3^{-}/Zn(0)$ couple and this start at $E_0 = -1.4$ V vs. SCE. On the basis of these results, we associate the peak A to the zinc UPD deposition onto the NE and the peak B to the zinc OPD deposition of the chemical species ZnG₃⁻ to Zn(0), as is proposed in Eq. (17).

Table 3	
---------	--

Voltammetric parameters of zinc deposition on NE from solutions S_0 , S_1 and S_2 .

Solution	$E_{eq}^{o'}(ZnG_3^-/Zn(0))(Vvs.SCE)$	$E_{\rm PB}$ (V vs. SCE)	$E_{\rm PB'}$ (V vs. SCE)	$E_{\rm PB/2}$ (V vs. SCE)	$(E_{\rm PB} + E_{\rm PB'})/2 (V \rm vs. SCE)$	$i_{\rm PB}~({ m mAcm^2})$
S0	-1.384	-1.537	-1.215	-1.451	-1.376	-23.541
S1	-1.388	-1.564	-1.251	-1.479	-1.389	-30.601
S2	-1.392	-1.574	-1.259	-1.480	-1.417	-41.939

(17)



Fig. 1. Species distribution diagrams as a function of the solution pH for the zinc(II)-glycine-water system. These diagrams were constructed under the conditions mentioned in Table 1: (a) solution S₀, (b) solution S₁ and (c) solution S₂.

When the scan direction was reversed in the switching potential $E_{\lambda} = -1.65$ V vs. SCE, three anodic current density peaks appeared at potentials of -1.45, -1.26 and -0.41 V vs. SCE. The peaks at -1.45 V vs. SCE (which appears as a shoulder) and B' could be due to the oxidation of different zinc phases. At potentials more positive than peak B' region, an anodic peak A' is observed; this peak could be



Fig. 2. Potential–pH diagram for the reduction of Zn(II)' species. The conditions considered in the computation of this diagram correspond with the given for the solution S_0 .

associated with the dissolution of the zinc UPD deposition. Similar behavior has been reported by Ortiz-Aparicio [16] for zinc-glycine complexes reduction at pH 11.

In our experiments, the difference between the anodic B' and cathodic B peak potentials ($\Delta E_{\rm P} = E_{\rm PB} - E_{\rm PB'}$), for cyclic voltammograms in Fig. 3, are 0.322, 0.349 and 0.315 V vs. SCE for S₀, S₁ and S₂ solutions, respectively. The obtained values for $\Delta E_{\rm P}$ significantly exceed the quantity characteristic of a reversible process, $\Delta E_{\rm P} = 0.059/n$ at 25 °C and n = 2 [42]. Therefore, we could assume that a totally irreversible reaction might be the case, from the cyclic voltammograms recorded (Fig. 3) and then from Fig. 3(a) one can determine the magnitude of the product $\alpha_c n_{\alpha}$, where α_c is the cathodic transfer coefficient and n_{α} is the number of electrons transferred up to, and including, the rate determining steps. With this purpose, such a parameter of the mentioned cyclic voltammograms as the shape factor $|E_{\rm PB} - E_{\rm PB/2}|$ can be applied [42]:

$$|E_{\rm PB} - E_{\rm PB/2}| = \frac{48}{\alpha_c n_\alpha} \, \text{mV} \quad \text{at} \quad 25 \,^{\circ}\text{C} \tag{19}$$

where $E_{\rm PB/2}$ is the potential of a half-peak. It was found that $\alpha_{\rm c} n_{\alpha} \approx 0.558$, if the reaction (17) is considered as totally irreversible.



Fig. 3. Cyclic voltammetry of zinc as a function of zinc chloride and glycine concentration at pH 10 and $25 \,^{\circ}$ C. (a) Solution S₀, (b) solution S₁ and (c) solution S₂. Scanning rate: $10 \,\text{mV} \,\text{s}^{-1}$.

It has also been known that on the basis of diffusion-controlled cyclic voltammograms a formal standard redox potential can be approximated by the mid-point potential of the anodic and cathodic peak potentials [42]. Regarding ZnG₃⁻/Zn(0) equilibrium, it should be noted that the theoretical value of this equilibrium is known of the thermodynamic study. From the cyclic voltammograms recorded, the $(E_{PB} + E_{PB'})/2$ value of the average peak potential for the $ZnG_3^{-}/Zn(0)$ couple were found to be ca. -1.376, -1.389 and -1.417 V vs. SCE for S₀, S₁ and S₂ solutions, respectively. Differences of approximately 8, 1 and 21 mV, between experimental and theoretical potentials $E_{eq}^{o'}(ZnG_3^-/Zn(0))$, were found for S₀, S₁ and S₂ solutions, respectively. These differences can be associated to adsorption process or formation of chemical species in the interphase. On the basis of these results, it is possible to propose that $E_{eq}^{o'}(ZnG_3^-/Zn(0))$ corresponds to the equilibrium potential of $ZnG_3^{-}/Zn(0)$ couple.

In Fig. 3, it is clearly seen that the peak B potential (E_P) and the peak B current maximum density (i_P) depend on the composition of the solution, see Table 3. Note that the magnitude of the cathodic peak B diminished proportionally to the decrease of Zn(II) concentration in solution, as expected. The concentration of chloride and glycine in solution affect the position of the cathodic peak B mentioned, which is negatively shifted with the increase of glycine and chloride concentration.

The effect of scanning rate on cyclic voltammograms from solutions S_0 , S_1 and S_2 is given in Fig. 4(a)–(c), respectively. The voltammograms, all initiated from the E_{OCP} , were scanned in the negative direction at rates ranging from 10 to 100 mV s⁻¹.

According to Fig. 4(a)–(c), the voltammograms are characterized by two cathodic (A and B) and anodic (A' and B') peaks. The cathodic peak maximum currents (i_c) were found to increase and the cathodic peak potentials (E_P) shifted negatively when v was increased during the scan.

In either case, the maximum current value of the peak B were found to be proportional to the square root of the sweep rate within the range of sweep rates applied (Fig. 5(a)), indicating a diffusioncontrolled process [42].

The cathodic peak potentials E_P shift in the negative direction, as mentioned above, and are nearly linear with respect to the decimal logarithm of the sweep rate (Fig. 5b), suggesting that the reaction (16) is not reversible and tentatively may be considered as irreversible. Then, from the variation of E_P with log v given by the following equation [42]:

$$E_{\rm P} = K - \left(\frac{2.3RT}{2\alpha_{\rm c} nF}\right) \log \upsilon \tag{20}$$

where

$$K = E^{o} - \left(\frac{RT}{\alpha_{c}n_{\alpha}F}\right) \left[-0.78 - \left(\frac{2.3}{2}\right)\log\left(\frac{\alpha_{c}n_{\alpha}FD}{K_{s}^{2}RT}\right)\right]$$
(21)

 $K_{\rm S}$ is the standard rate constant, and the other terms have their usual significance, it should be expected that $E_{\rm P}$ shifts by $30/\alpha_c n_\alpha$ mV for each decade increase in υ . However, as is evident from Fig. 5b, the experimental shift of $E_{\rm P}$ for the S₀, S₁ and S₂ solutions with increasing υ from 10 to 100 mV s⁻¹ is equal to 122, 154 and 166 mV, respectively. Quite apparently, such values of the negative shift of $E_{\rm P}$ for each decade increase in υ are in a considerable excess of that expected for the totally irreversible reaction [42]. These features of cyclic voltammograms recorded in this work clearly show that the diagnostic criteria for a totally irreversible system reported in the literature [42] are not wholly satisfied. Consequently, the reaction (16) could not be considered as a simple irreversible reaction.



Fig. 4. Voltammetric curves obtained onto NE at different scan rates from solutions: (a) S_0 , (b) S_1 and (c) S_2 .

3.3. Study of zinc UPD process onto nickel electrode

Fig. 6 shows the cyclic voltammograms displaying the effects of scan rate on zinc electrodeposition in UPD deposition region in solution S_1 . Note that the Fig. 6 shows the dependences of the peak



Fig. 5. Variation of current density maxima i_P and potentials E_P for peaks B and B' in the cyclic voltammograms as a function of the scan rate. (a) j_{PB} vs. $v^{1/2}$ and (b) E_P vs. log v.



Fig. 6. Voltammetric curves obtained from the solution S_1 at different scan rates in the zinc UPD region.



Fig. 7. Current density maxima j_P and potentials E_P for peaks A and A' in the cyclic voltammograms as a function of the square root of scan rate. (a) E_P vs. $v^{1/2}$ and (b) j_P vs. $v^{-1/2}$.

A and the peak A' on scan rate. However, the potential values associated with these peaks do not change significantly as expected for UPD processes, which occurs trough adsorption, in sum a linear relationship is found between E_P vs. $v^{1/2}$ (see Fig. 7(a)).

In Fig. 6 is possible to observe that during the anodic scan a second cathodic peak is observed. We expected that the cathodic peak A occurs only at the fraction of active sites that are not blocked by chloride ions and/or glycine molecules and/or HER. Thus, during the anodic scan occurs the desorption of chloride ions from the nickel surface, allowing the reduction of Zn(II) ions to take place at the active sites vacated by the chloride ions. However, additional studies should be realized to support this hypothesis.

In order to determine the type of nucleation that occurs during the zinc UPD deposition, the maximum current density value (i_P) associated with the peak A was plotted as a function of $v^{-1/2}$ (Fig. 7b) and both E_P vs. i_P (not shown). A linear relationship was found for both cases indicating an instantaneous nucleation process [42].

The former of the peak A could be associated with incipient hydrogen reduction followed by zinc UPD deposition [36],

$$2H_2O + 2e^- \Leftrightarrow H_2 + 2OH^- E^0 = -1.069 \text{ Vvs.SCE}$$
 (22)

and

$$Zn^{2+} + OH^{-} + 2e^{-} \Leftrightarrow Zn(OH)_{ads}^{-} E^{o} = -1.131 Vvs.SCE$$
(23)

Previous studies reported that the inhibition of HER (hydrogen evolution reaction) in presence of zinc ions in alkaline [43–46] and acid [47] solutions is due to the formation of sub-monolayer of Zn on the substrate. It is proposed that zinc UPD competes with hydrogen evolution reaction [16,33].

The cathodic charges associated with the peak A and A' were obtained by integration from the voltammetric curves (Fig. 6). The magnitude of the integrated charges was found to be approximately 195 μ C cm⁻² and 165 μ C cm⁻² for peak A and A', respectively. The difference between both values can be attributed to the hydrogen evolution reaction, which occurs simultaneously with the zinc UPD process. The theoretical charge for a zinc monolayer corresponds to 367 μ C cm⁻², which was determined from the exposed surface area (0.726 cm²) of the NE. This value is very close to predicted by Kolb [17] for polycrystalline surfaces, 200(*n*) μ C cm⁻², where *n* is the electron number involved in the electrochemical reaction. The degree of coverage by zinc $\theta_{Zn-UPD} = 0.45$, which was determinate of the ratio: $Q_{A'}/367$. This result indicates that the zinc UPD corresponds to the formation of sub-monolayer of zinc and that this occurs simultaneously with HER onto the NE.

When the scan direction was reversed in the switching potential $E_{\lambda} = -1.41$ V vs. SCE, an anodic peak (peak A') is observed; this peak was previously associated with the dissolution of zinc UPD deposition (peak A). Fig. 7(a) shows the peak potentials (E_P) as a function of $\upsilon^{1/2}$ associated with the peak A'. Fig. 7(b) shows the maximum current density value (i_P) associated with the peak A', which was plotted as a function of $\upsilon^{-1/2}$.

Fig. 7(a) and (b) shows the linear dependence of the peak potentials and current maxima for peaks A and A' on $v^{1/2}$ and $v^{-1/2}$, respectively. In the literature [48,49] has been shown that this behavior is characteristic of an instantaneous nucleation process, as was mentioned above. It is important to mention that this test is valid for small sweep rate.

3.3.1. Potentiostatic study

Chronoamperometry was used as a supporting experimental technique to further elucidate the nucleation mechanisms of zinc onto NE. Current transients in Fig. 8 were measured by the double-potential step technique from solution S₁. The experiments consisted in application of an initial potential of -0.62 V vs. SCE, where zinc deposition had not started yet. After application of this initial potential, a second potential step was applied to the electrode surface for 80 s. The second potential values correspond with the zinc UPD region (peak A in Fig. 6).

Fig. 8 shows a set of current transients recorded at different potentials from solution S₁. The shape of these transients is independent of the final potential. In sum, the shape of these transients is quite similar to those reported by Holzle et al. [49] and Mendoza-Huizar [50]. Linearization of the transients by either the Cotrell equation $(j \approx 1/\sqrt{t})$ or an exponential law $(j \approx e^{-kt})$ has been realized and was found failed; this indicates that there is no pure diffusion control.

The previous results obtained from voltammetry cyclic indicated two features of the zinc UPD process on NE; the first feature is that it involves an instantaneous two-dimensional nucleation



Fig. 8. Set of experimental current transients recorded during the zinc UPD process in the solution S₁. In all cases, the starting potential of -0.62 V vs. SCE was applied to the NE surface and t = 80 s.

mechanism and the second is that diffusion is the rate controlling step of the zinc UPD process, however an additional process is involved. The theoretical description of similar potentiostatic current transients as shown in Fig. 8 has been predicted adequately by Mendoza-Huizar [50]:

$$j_{\text{total}}(t) = j_{\text{ads}}(t) + j_{\text{2Di-dc}}(t)$$
(24)

where

$$j_{ads}(t) = k_1 \exp(-k_2 t) \tag{25}$$

and

$$j_{\text{2Di-dc}}(t) = k_3 \exp(-k_4 t) \tag{26}$$

 $j_{ads}(t)$ is the current density for a Lagmuir type adsorption–desorption process and j_{2Di-dc} is the current density associated to an instantaneous two-dimensional nucleation mechanism. $k_1 = k_2 Q_{ads}$ and Q_{ads} is the charge density due to the adsorption process. The potential dependence of k_2 is assumed to obey the Butler–Volmer relation. $k_3 = q_{mon}\pi S^2 D$, $k_4 = \pi S^2 D N_0$. In these equations, q_{mon} is the charge density associated with formation of the monolayer, *S* is a constant controlled by the potential, *D* is the diffusion coefficient of the metal ion, and N_0 is the density number of active sites. Note that $k_3 = k_4 Q_{nucl}$ and Q_{nucl} is the charge density due to the 2D nucleation process.

Fig. 9 shows a comparison between the experimental results for the transient obtained at -1.15 V vs. SCE during zinc UPD and the nonlinear fit of Eq. (24). It is clear from this figure that the nucleation of zinc UPD conforms to the 2Di-dc model. Table 4 lists the values of the parameters pertaining to Eq. (24) that best fitted the experimental data. From these parameters it is possible to estimate the charge density due to both nucleation (Q_{nucl}) and adsorption (Q_{ads}) processes. From Table 4, $Q_{nucl} = 20.6 \,\mu\text{C}\,\text{cm}^{-2}$ indicating that the degree of coverage by zinc $\theta_{Zn-UPD} = 0.06$. It is interesting to observe that the contribution due to the nucleation process is 76% indicating

Table 4

Best fit parameters obtained from non-linear adjustment of Eq. (22) to the experimental current density transient recorded during zinc UPD on NE.

E vs. SCE (V)	$\dot{J}_{ m ads}$		j _{nucl}		Q _{ads} (%)	$Q_{ m nucl}$ (%)
	$k_1 (\mu A \mathrm{cm}^{-2})$	$k_2 (s^{-1})$	$k_3 (\mu A \mathrm{cm}^{-2})$	$k_4 (s^{-1})$		
-1.15	7.98 ± 0.02	1.11 ± 0.01	1.65 ± 0.03	0.08 ± 0.02	24	76



Fig. 9. Comparison of an experimental current density transient recorded during zinc electrodeposition at -1.15 V vs. SCE onto a polycrystalline nickel electrode from the solution S₁ and a theoretical transient obtained by non-linear fit of Eq. (21).



Fig. 10. AFM image of zinc electrodeposited onto NE in solution S_1 at -1.15 V vs. SCE, t = 80 s.

that under our experimental conditions the 2D nucleation process is favored.

3.3.2. AFM study

In order to analyze the initial stages of the zinc electrodeposition process in greater detail, an AFM study was realized. The AFM image was taken in the ex situ mode. Fig. 10 shows an AFM image of the deposit of Zn at -1.15 V, t = 80 s. This image shows crystals of similar size and that these grow faster laterally than vertically (nucleation 2D). It is also is clearly observed that the surface of the NE is not completely covered. This behavior confirms that the zinc UPD process is associated with a sub-monolayer.

4. Conclusions

A thermodynamic, electrochemical and morphological study on the zinc electrodeposition onto polycrystalline nickel electrode from non-cyanide alkaline solutions at pH 10.0 containing glycine was carried out through speciation and *E*–pH diagrams, electrochemical techniques and microscopic techniques, respectively.

Our thermodynamic calculations of zinc–glycine–water system indicate that the ZnG₃⁻ complexes are the predominant species in

solution for the conditions used in this work and that from these complexes the electrodeposition of zinc occurs.

Analysis of the experimental data clearly shows that a zinc adlayer is formed during application of potential in the UPD region and which corresponds to the formation of a submonolayer. In sum, also was founded that this zinc submonolayer involves the simultaneous presence of both adsorption and 2D nucleation under a mass-transfer controlled process. The morphology of zinc UPD obtained by AFM confirmed the formation of a submonolayer onto the nickel electrode.

The experimental data obtained by cyclic voltammetry confirms unambiguously that the electrodeposition of zinc onto nickel electrode occurs simultaneously with the HER, but that this last is diminished by effect of the formation of the zinc submonolayer.

Acknowledgments

This work was supported by the Consejo Nacional de Ciencia y Tecnología (CONACyT-PCP, México-France). J.C. Ballesteros thanks CONACyT-PCP-México-France for scholarship support.

References

- M. Schlesinger, M. Paunovic, Modern Electroplating, fourth ed., John Wiley & Sons, Inc., New York, 2000.
- 2] G. Trejo, R. Ortega-Borges, Y. Meas, E. Chainet, B. Nguyen, P. Ozil, J. Electrochem. Soc. 145 (1998) 4090.
- [3] D.D.N. Singh, M. Dey, V. Singh, Corrosion 58 (2002) 971.
- [4] M. Sanchez-Cruz, F. Alonso, J.M. Palacios, J. Appl. Electrochem. 23 (1993) 364.
- [5] J. Yu, H. Yang, X. Ai, Y. Chen, Russ. J. Electrochem. 38 (2002) 321.
- [6] D.S. Baik, D.J. Fray, J. Appl. Electrochem. 31 (2001) 1141.
- [7] K. Deblauw, A. Deboeck, J. Bollen, W. Timmermans, Proceedings of the ICOTOM 12, Montreal, Quebec, Canada, 1999, p. 1293.
- [8] X. Ye, J.P. Celis, M. de Bonte, J.R. Roos, J. Electrochem. Soc. 141 (1994) 2698.
- [9] H. Park, J.A. Szpunar, Proceedings of the ICOTOM 12, Montreal, Quebec, Canada, 1999, p. 1421.
- [10] I. Tomov, C.H.R. Cvetkova, V. Velinov, J. Appl. Electrochem. 19 (1989) 377.
- [11] H. Geduld, Zinc Plating, ASM International Metals Park, Ohio, 1988.
- [12] I. Rodriguez-Torres, G. Valentin, S. Chanel, F. Lapicque, Electrochim. Acta 46 (2000) 279.
- [13] A.E. Mohamed, S.M. Rashwan, S.M. Abdel-Wahaab, M.M. Kamel, J. Appl. Electrochem. 33 (2003) 1085.
- [14] S.M. Rashwan, A.E. Mohamed, S.M. Abdel-Wahaab, M.M. Kamel, J. Appl. Electrochem. 33 (2003) 1035.
- [15] S.M. Rashwan, Mater. Chem. Phys. 89 (2005) 192.
- [16] J.L. Ortiz-Aparicio, Y. Meas, G. Trejo, R. Ortega, T.W. Chapman, E. Chainet, P. Ozil, Electrochim. Acta 52 (2007) 4742.
- [17] D. Kolb, in: H. Gerischer, C.W. Tobias (Eds.), Advances in Electrochemistry and Electrochemical Engineering, vol. 11, Wiley-Interscience, New York, 1978, p. 125.
- [18] S. Trasatti, J. Electroanal. Chem. Interfacial Electrochem. 33 (1971) 351.
- [19] D. Kolb, M. Przasnyski, H. Gerischer, J. Electroanal. Chem. Interfacial Electrochem. 54 (1974) 25.
- [20] S. Takahashi, K. Hasebe, A. Aramata, Electrochem. Commun. 1 (1999) 301.
- [21] A. Aramata, S. Taguchi, T. Fukuda, M. Nakamura, G. Horanyi, Electrochim. Acta 44 (1998) 999.
- [22] S. Taguchi, A. Aramata, J. Electroanal. Chem. 457 (1998) 73.
- [23] S. Taguchi, A. Aramata, M.A. Auaiyyum, M. Enyo, J. Electroanal. Chem. 374 (1994) 275.
- [24] S. Taguchi, A. Aramata, J. Electroanal. Chem. 396 (1995) 131.
- [25] M.A. Quaiyyum, A. Aramata, S. Moniwa, S. Taguchi, M. Enyo, J. Electroanal. Chem. 373 (1994) 61.
- [26] S. Moniwa, A. Aramata, J. Electroanal. Chem. 376 (1994) 203.
- [27] S. Taguchi, T. Fukuda, A. Aramata, J. Electroanal. Chem. 435 (1997) 55.
- [28] M. Nakamura, A. Aramata, A. Yamagishi, M. Taniguchi, J. Electroanal. Chem. 446 (1996) 227.
- [29] A.A. El-Shafei, J. Electroanal. Chem. 380 (1995) 269.
- [30] S. Rashkov, C. Bozhkov, V. Kudryavtsev, K. Pedan, S. Bagaev, J. Electroanal. Chem. 248 (1988) 421.
- [31] B.N. Popov, G. Zheng, R.E. White, Corros. Sci. 36 (1994) 2139.
- [32] A.R. Despic, M.G. Pavlovic, Electrochim. Acta 27 (1982) 1539.
- [33] J. Lee, J.W. Kim, M.K. Lee, H.J. Shin, H.T. Kim, S.M. Park, J. Electrochem. Soc. 151 (2004) C25.
- [34] J.W. Kim, J.Y. Lee, S.M. Park, Langmuir 20 (2004) 459.
- [35] S.J. Kim, H.T. Kim, S.M. Park, J. Electrochem. Soc. 151 (2004) C850.
- [36] S. Shanmugasigamani, M. Pushpavanam, J. Appl. Electrochem. 36 (2006) 315.
- [37] S. Shanmugasigamani, M. Pushpavanam, Port. Electrochim. Acta 27 (2009) 725.
- [38] R.M. Smith, A.E. Martell, Critical Stability Constants, Plenum, New York, 1989.

- [39] D.D. Perrin, Stability Constants of Metal-ion Complexes, Pergamon, Oxford, 1979.
- [40] E.P. Serjeant, B. Dempsey, Ionization Constants of Organic Acids in Aqueous Solution, Pergamon, Oxford, 1972.
 [41] B. Tremillon, Electrochimie Analytique et Reactions en Solution, Masson, Paris,
- [41] B. Tremillon, Electrochimie Analytique et Reactions en Solution, Masson, Paris, 1993.
- [42] Southampton Electrochemistry Group, Instrumental Methods in Electrochemistry, Ellis Horwood Ltd., Chichester, 1985.
- [43] V.N. Titova, A.A. Javich, N.V. Petrova, V.A. Kazakov, S. Biallozor, Bull. Electrochem. 16 (1995) 425.
- [44] J.H.O.J. Wijenberg, J.T. Stevels, J.H.W. de Wit, Electrochim. Acta 43 (1995) 649.
- [45] J. McBreen Abd, E.J. Cairns, Adv. Electrochem. Eng. 11 (1978) 273.
- [46] H.J. Bard, Encyclopedia of Electrochemistry of the Elements, 5, Marcel Decker Inc., New York, 1982.
- [47] T.S. Lee, J. Electrochem. Soc. 18 (1971) 1278.
- [48] E. Bosco, S.K. Rangarajan, J. Electroanal. Chem. 129 (1981) 25.
- [49] M.H. Holzle, U. Retter, D.M. Kolb, J. Electroanal. Chem. 371 (1994) 101.
- [50] L.H. Mendoza-Huizar, J. Robles, M. Palomar-Pardave, J. Electroanal. Chem. 51 (2002) 95.