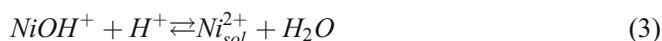
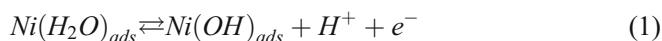


Joan Gregori · José J. García-Jareño ·
David Giménez-Romero · Francisco Vicente

Response to the “Comment on the paper ‘Kinetic calculations of Ni anodic dissolution from EIS’ (J Solid State Electrochem, 9:83, 2005) by G. G. Láng and G. Horányi”

Received: 15 February 2006 / Accepted: 14 March 2006 / Published online: 11 April 2006
© Springer-Verlag 2006

As indicated by G. G. Láng and G. Horányi in a recent “comment” [1] on our original paper published in the *Journal of Solid State Electrochemistry*, 9:83, 2005, several groups of researchers explain nickel electrodisso- lution kinetics by considering the formation of an “adsorbed” intermediate such as:



In such kind of mechanisms, the participation of some ions is explicitly considered, although many times, this participation is not clear and there is much disagreement, in general, about the ion role in hydrophilic (iron family metals such as nickel) metals electrodisso- lution [2]. It is also pointed out in [1] that the so-called catalytic mechanism is proposed to overcome a large number of experimental facts, which disagree with the expectations based on the above indicated consecutive mechanism [3].

It is noteworthy that there is much disagreement among the various groups of researchers regarding the kinetics of nickel dissolution. Several experimental causes can be the main reasons for this disagreement: relatively slow approach toward steady state, strong tendency for passivation in the vicinity of corrosion potential, strong interaction with hydrogen, etc [3, 4].

However, as indicated in such comment [1], an another possible assumption is to consider two single-electron charge transfers by means of the formation of two

intermediates in nickel electrodisso- lution process. This latter approach is considered by several workers in the literature [5–9]. And, for example, a similar mechanism is also considered by other researchers to interpret the kinetic of anodic dissolution of aluminum in a basic medium [10]. In this sense, the detailed and excellent work of Cachet and Wiart [11] and Wiart et al. [12] about zinc electrodisso- lution in acid sulfate and basic [13] media must be pointed out. A similar mechanism is even considered by Lorenz and Heusler [3] and Bech-Nielsen [14] to interpret the obtained kinetic information about iron electrodisso- lution in acid medium.

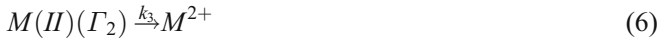
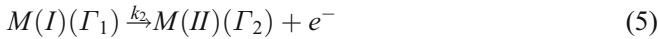
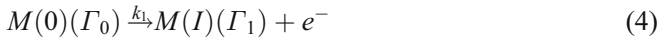
Based on these preliminary works about metals electro- dissolution in different media and also based on previous studies on the anodic dissolution of Zn by means of electrochemical impedance spectroscopy (EIS) and electrochemical quartz crystal microbalance (EQCM) [15], we assumed in our recent paper [16], which Láng and Horányi commented on [1], that nickel electrodisso- lution mechanism occurs across the formation of two reaction intermediates in certain experimental conditions. More- over, there are several experimental facts that cannot be disregarded concerning nickel electrodisso- lution in acid sulfate medium. First, ellipsometric measurements of Bockris et al. [17, 18] show that there is a prepassive film formation in the nickel electrodisso- lution potential range. Recent spectroscopic measurements of Nakamura et al. [19] are also consistent with these experimental findings. That way, the active to passive transition is produced by a progressive change in prepassive film conduction properties. Finally, according to Sato and Okamoto [5], under steady state conditions nickel electro- dissolution in acid sulfate medium is limited by the dissolution of the generated Ni(II) hydroxide species on the electrode surface. It is quite plausible to consider that there is a close relation between the prepassive film considered by Bockris and the Ni(II) hydroxide species considered by Sato.

In the analysis made by Láng and Horányi [1], the kinetic mechanism defined above by Eqs. 1, 2 and 3 does not consider the formation of such a prepassive film. This

J. Gregori · J. J. García-Jareño ·
D. Giménez-Romero · F. Vicente (✉)
Department of Physical Chemistry, University of Valencia,
C/ Dr. Moliner 50,
Burjassot 46100, Spain
e-mail: Francisco.Vicente@uv.es

could be one of the main causes for the many disagreements encountered in the different analysis of the experimental findings related with nickel electrodisolution. The formation of such prepassive film is in agreement with the rather general theoretical scheme developed by Sato et al. to explain the anion effect in the metal corrosion processes [20–22]. In such context, prepassive layer properties are highly dependent on the electrolyte composition because of the great importance of the anions in the anodic dissolution of nickel [23, 24]. It is evident that the nature, properties, and dissolution of the prepassive film depend to a great extent on the anion present in the electrolyte.

In our paper about the anodic dissolution of nickel [16], the following simplified and schematic mechanism is considered to interpret a series of electrochemical impedance spectra measured in nickel electrodisolution potential range under certain experimental conditions:



where Γ_0 , Γ_1 , and Γ_2 are the surface concentrations of M(0), M(I), and M(II) species, respectively, and M^{2+} is the solvated metal ion (e.g., Ni^{2+}) in the solution. In the mechanism defined by Eqs. 4, 5 and 6, M(II) should represent the above-mentioned prepassive film. Obviously, the oxidation states M(I) and M(II) are stabilized by the formation of stable compounds at the electrode surface by means of anion participation [22]. Anion role is not explicitly considered in the notation of Eqs. 4, 5 and 6 but

they are implicitly considered in the functional form of each reaction rate r_i associated to the elemental reaction steps. In the above mechanism, Eq. 6 represents the solubilization and transport of Ni^{2+} from the surface to the solution phase. It is evident, in agreement with the discussion made in p. 4 of [1], that ions play a key role during charge balance at the electrode surface when an electroodic process takes place.

Theoretical assumptions made in our work [16] and also in the critical comments of Láng and Horányi [1] are actually simplifications because there are many factors involved in the overall anodic dissolution process. For example, it is well known that nickel dissolution occurs simultaneously by almost two different ways in acid media depending on the electrode surface history and experimental conditions [6, 25–28]. For this reason, it is obvious that the mechanism defined by Eqs. 4, 5 and 6 allows us to obtain quantitative magnitudes from EIS, which are only useful for a comparative perspective. Unfortunately, our assumed scheme does not include all the variables that can occur in all the experimental circumstances of the anodic dissolution of nickel. From our point of view, the assumed mechanism in [16] is only a possible accurate approximation to the reality of this complex scientific problem. But the comments made by Láng and Horányi are not a theoretical or a new experimental contribution to the general culture about this subject. However, from the theoretical impedance function calculated for our assumed kinetic model, a quantitative physical meaning to the experimental impedance spectra is done. By means of this procedure, a clear relation between kinetics and equivalent circuits allows us to interpret the shape of EIS, i.e., the detection of an inductive loop in the presence of chloride ions or a capacitive loop in a sulfate acid medium.

The following theoretical impedance function was obtained by means of the procedure previously described in [16]:

$$FZ_F = \frac{\frac{\partial r_1}{\partial \Gamma_0} \frac{\partial r_2}{\partial \Gamma_1} + \left(\frac{\partial r_1}{\partial \Gamma_0} + \frac{\partial r_2}{\partial \Gamma_1} \right) \frac{\partial r_3}{\partial \Gamma_2} + \left(\frac{\partial r_1}{\partial \Gamma_0} + \frac{\partial r_2}{\partial \Gamma_1} + \frac{\partial r_3}{\partial \Gamma_2} \right) j\omega - \omega^2}{2 \frac{\partial r_2}{\partial E} \frac{\partial r_1}{\partial \Gamma_0} \frac{\partial r_3}{\partial \Gamma_2} + 2 \frac{\partial r_1}{\partial E} \frac{\partial r_2}{\partial \Gamma_1} \frac{\partial r_3}{\partial \Gamma_2} + \left(\frac{\partial r_2}{\partial E} \frac{\partial r_1}{\partial \Gamma_0} + 2 \frac{\partial r_1}{\partial E} \frac{\partial r_2}{\partial \Gamma_1} + \frac{\partial r_1}{\partial E} \frac{\partial r_3}{\partial \Gamma_2} + \frac{\partial r_2}{\partial E} \frac{\partial r_3}{\partial \Gamma_2} \right) j\omega - \left(\frac{\partial r_1}{\partial E} + \frac{\partial r_2}{\partial E} \right) \omega^2} \quad (7)$$

It was observed that $\frac{\partial r_1}{\partial \Gamma_0} \gg \frac{\partial r_2}{\partial \Gamma_1}, \frac{\partial r_3}{\partial \Gamma_2}$. Then, from a mathematical point of view, the following limit can be considered:

$$\lim_{\frac{\partial r_1}{\partial \Gamma_0} \rightarrow \infty} FZ_F = \frac{\frac{\partial r_2}{\partial \Gamma_1} + \frac{\partial r_3}{\partial \Gamma_2} + j\omega}{2 \frac{\partial r_2}{\partial E} \frac{\partial r_3}{\partial \Gamma_2} + \frac{\partial r_2}{\partial E} j\omega} = \frac{1}{\frac{\partial r_2}{\partial E}} + \frac{1}{\frac{\partial r_2}{\partial E} 2 \frac{\partial r_3}{\partial \Gamma_2} + j\omega} \quad (8)$$

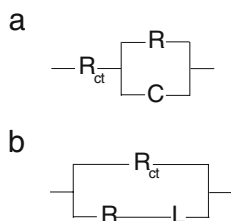
The impedance function represented in Eq. 8 is mathematically equivalent to the impedance functions for the equivalent circuits of Fig. 1, defined by Eqs. 9 and 10, which

correspond to capacitive/inductive loops, respectively, at low frequencies:

$$Z_a = R_{ct} + \frac{1}{\frac{1}{R} + Cj\omega} \quad (9)$$

$$Z_b = R_{ct} - \frac{R_{ct}}{R + R_{ct} + Lj\omega} \quad (10)$$

Fig. 1 Equivalent circuits of **a** capacitive and **b** inductive loops for a faradaic impedance



Then, it becomes evident that when $\frac{\partial r_2}{\partial \Gamma_1} > \frac{\partial r_3}{\partial \Gamma_2}$, a capacitive loop will be defined at low frequencies in the Nyquist representation, whereas when $\frac{\partial r_2}{\partial \Gamma_1} < \frac{\partial r_3}{\partial \Gamma_2}$, then an inductive loop will be observed. In our paper [16], the fitting of experimental impedance data to the proposed equivalent circuit was carried out by means of a nonlinear least squares procedure based on the Marquardt algorithm for function optimization [29, 30]. In all cases, the obtained error for the elements of the considered equivalent circuits was less than 5%, which allows us to determine with considerable accuracy, the above partial derivatives values.

With respect to the interpretation of the quartz crystal microbalance results in combination with the voltammetry made in [16], the calculated values for the instantaneous mass/charge ratio (Fdm/dQ function) show a value close to $-30 \text{ g}\cdot\text{mol}^{-1}$ at the potential range of the anodic peak, which corresponds to nickel electrodisolution (see Fig. 2) in aqueous sulfate acid medium and in the absence of chloride at room temperature. This anodic peak is interpreted to be associated to nickel electrodisolution because there is a clear mass decrease in this potential interval as explained in [16]. This is also the common interpretation in the literature [31, 32]. The obtained Fdm/dQ = $-30 \text{ g}\cdot\text{mol}^{-1}$ in the absence of chloride is very close to the theoretical value [(Fdm/dQ)_{diss} = $-29 \text{ g}\cdot\text{mol}^{-1}$] expected for an overall nickel electrodisolution process such as:



although there are several possibilities for explaining the obtained instantaneous mass/charge ratio (Fdm/dQ) values

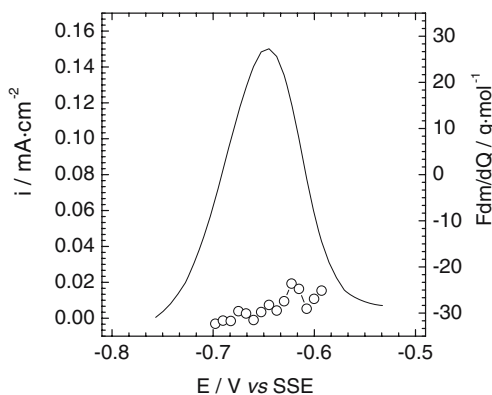


Fig. 2 Anodic peak (solid line) and instantaneous mass/charge ratio values (open circles) corresponding to the voltammogram in the potential window [200–1,500 mV]. Scan rate = 20 mV/s . 10^{-3} M NiSO_4 , $0.245 \text{ M K}_2\text{SO}_4$, $5 \times 10^{-3} \text{ M H}_2\text{SO}_4$, pH = 2.7 and $T = 298 \text{ K}$

and the observed mass decrease in the potential range, which corresponds to the observed anodic voltammetric peak. Each possibility can consider different combinations of adsorption/desorption of anions to explain that Fdm/dQ = $-30 \text{ g}\cdot\text{mol}^{-1}$. However, our point of view is that Eq. 11 is the most simple and most probable possibility for explaining the obtained results. Moreover, it must be reminded that no mass increase is observed at any potential during anodic peak [16]. This implies that if anion adsorption/desorption takes place in nickel electrodisolution, this process is so fast that it does not have any influence on the overall mass balance. This interpretation and the obtained experimental results are in agreement with the work of Itagaki et al. [33] about EQCM studies of nickel electrodisolution in aqueous acid sulfate media.

In Appendix I in our original paper [16], there is a rather general deduction of the theoretical impedance function, which corresponds to the reaction mechanism defined by Eqs. 4, 5 and 6. This deduction was based on the formalism developed by Armstrong et al. [34] several years ago. However, several hypotheses and approximations were made in [16] to obtain an analytical expression for checking with the obtained experimental results. The hypotheses were as follows: (1) It was considered that r_1 only depends on applied potential E and Γ_0 , (2) r_2 only depends on applied potential E and Γ_1 , and (3) r_3 only depends on Γ_2 values. These are quite plausible and common hypotheses from a kinetic point of view [35]. If it is considered that r_i is a function of anion concentration c_j , then:

$$r_i = r_i(E, \Gamma_k, c_j) \rightarrow \delta r_i = \frac{\partial r_i}{\partial E} \delta E + \frac{\partial r_i}{\partial \Gamma_k} \delta \Gamma_k + \frac{\partial r_i}{\partial c_j} \delta c_j \quad (12)$$

However, it can be considered that in the presence of an excess of supporting electrolyte, as a first approximation, c_j values remain constant during impedance experiments, then $\delta c_j = 0$, and therefore mass transport limitations due to anions in the charge transfer processes were apparently not considered in [16]. As a consequence of this approximation, c_j values are included within the expressions of the kinetic rate constants. Moreover, the obtained experimental results in the form of electrochemical impedance spectra were consistent with such approximation. It is true that a more detailed study should require more accurate considerations about the anion concentration effect on nickel electrodisolution process. But the simplified approach to the problem made in [16] allows us to obtain, as a first approximation, valuable kinetic information such as surface concentrations of the different reaction Ni-intermediates. It is expected that the anion present in the electrolyte has a considerable influence on the Γ_i values.

It is true that according to the results reported in [16], the rate coefficient k_3 were dependent on the potential, although according to the reaction scheme, it should be potential-independent. There was no explicit k_3 potential-dependence consideration in the derivation of the theoret-

ical impedance function because the analysis in [16] pretended to be a first approximation to the problem of nickel electrodisolution in acid sulfate medium, if passive layer formation is not considered. However, it must be pointed out that the consideration $r_3=r_3(E,\Gamma_2)$ is not the only possibility for explaining such k_3 potential dependence. It is also possible that k_3 depends on a nontrivial manner on Γ_2 if an interaction is established between Ni(II) species [36]. It is interesting to observe that this latter approximation is sometimes considered for explaining the active anodic dissolution/passive transition and the instable dynamical behavior observed many times in such a potential range [36, 37].

Acknowledgements This work was supported by the Spanish Ministry of Science and Technology (Project CICyT-CTQ2004-08026/BQU) and the Spanish Ministry of Environmental (Project 6.1-210/2005). J. Gregori acknowledges a Fellowship from the Spanish Education Ministry (FPU program). J. J. García-Jareño acknowledges the Spanish Ministry of Science and Technology for their position ("Ramón y Cajal" Program). D. Giménez-Romero acknowledges a Fellowship from the Regional Government (Post-doctoral Program).

References

- Láng GG, Horányi G (2006) *J Solid State Electrochem*
- Lazorenko-Manevich RM, Podobaev AN (2001) *Prot Met* 37:440
- Lorenz WJ, Heusler KE (1987) Anodic dissolution of iron group metals. In: Mansfeld F (ed) *Corrosion mechanisms*. Marcel Dekker, New York, p 1
- Keddám M (2002) Anodic dissolution. In: Marcus P, Oudar J (eds) *Corrosion mechanism in theory and practice*. Marcel Dekker, New York, p 97
- Sato N, Okamoto G (1964) *J Electrochem Soc* 111:897
- Barbosa MR, Real SG, Vilche JR, Arvía AJ (1988) *J Electrochem Soc* 135:1077
- Zinola CF, Castro-Luna AM (1995) *Corros Sci* 37:1919
- Sanchez S, Picard GS (1996) *Electrochim Acta* 41:2035
- Schrebler R, Gardiazabal JJ, Cordova R, Gomez H (1990) *Bol Soc Chil Quim* 35:177
- Shao HB, Wang JM, Zhang Z, Zhang JQ, Cao CN (2003) *J Electroanal Chem* 549:145
- Cachet C, Wiart R (1981) *J Electroanal Chem* 129:103
- Cachet C, Ganne F, Maurin G, Petitjean J, Vivier V, Wiart R (2001) *Electrochim Acta* 47:509
- Cachet C, Saidani B, Wiart R (1992) *J Electrochem Soc* 139:644
- Bech-Nielsen G (1974) *Electrochim Acta* 19:821
- Giménez-Romero D, García-Jareño JJ, Vicente F (2003) *J Electroanal Chem* 558:25
- Gregori J, García-Jareño JJ, Gimenez-Romero D, Vicente F (2005) *J Solid State Electrochem* 9:83
- Reddy AKN, Rao B, Bockris JO'M (1965) *J Chem Phys* 42:2246
- Bockris JO'M, Reddy AKN, Rao B (1966) *J Electrochem Soc* 113:1133
- Nakamura M, Ikemiya N, Iwasaki A, Suzuki Y, Ito M (2004) *J Electroanal Chem* 566:385
- Sakashita M, Sato N (1979) *Corrosion* 35:351
- Sato N (1989) *Corrosion* 45:354
- Sato N (1996) *Electrochim Acta* 41:1525
- Gregori J, García-Jareño JJ, Gimenez-Romero D, Vicente F (2005) *J Solid State Electrochem* (in press). DOI:1007/s10008-004-0643-5
- Vicente F, Gregori J, García-Jareño JJ, Giménez-Romero D (2005) *J Solid State Electrochem* 9:684
- Vilche JR, Arvía AJ (1976) *J Electrochem Soc* 123:1061
- Vilche JR, Arvía AJ (1978) *Corros Sci* 18:441
- Vilche JR, Arvía AJ (1975) *Corros Sci* 15:419
- Barbosa MR, Bastos JA, Gacia-Jareño JJ, Vicente F (1998) *Electrochim Acta* 44:957
- Macdonald JR (1992) *Solid State Ion* 58:97
- García-Jareño JJ, Navarro J, Roig AF, Scholl H, Vicente F (1995) *Electrochim Acta* 40:1113
- Lachenwitzer A, Magnussen OM (2000) *J Phys Chem B* 104:7424
- Lachenwitzer A, Morin S, Magnussen OM, Behm RJ (2001) *Phys Chem Chem Phys* 3:3351
- Itagaki M, Nakazawa H, Watanabe K, Noda K (1997) *Corros Sci* 39:901
- Armstrong RD, Firman RE, Thirsk HR (1973) *Faraday Discuss* 56:44
- Gabrielli C, Keddám M (1996) *Electrochim Acta* 41:957
- Griffin GL (1984) *J Electrochem Soc* 131:18
- Brynn-Hibbert D, Murphy SV (1991) *J Electrochem Soc* 138:L30