COMMENTS

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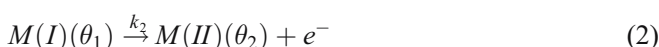# Comment on the paper "Kinetic calculations of Ni anodic dissolution from EIS" [J Solid State Electrochemistry (2005) 9:83]

In a recent publication [1], the anodic dissolution of Ni was investigated using electrochemical impedance spectroscopy (EIS), electrochemical quartz crystal microbalance technique (EQCM), and voltammetric methods, and a dissolution mechanism (based on the mechanism originally proposed in [2, 3]) was considered for the interpretation of the experimental data.

According to this complex reaction model, the dissolution occurs through adsorbed intermediates. It is claimed that the mechanism proposed for the interpretation of the anodic behavior of Ni is of general importance, i.e., similar mechanistic descriptions could be given for the anodic dissolution of other metals (M), e.g., Zn [4, 5].

In Gregori et al. [1], the following scheme was used for the interpretation of the data ("scheme A"):

$$M(\theta_0) \xrightarrow{k_1} M(I)(\theta_1) + e^- \tag{1}$$

$$M(I)(\theta_1) \xrightarrow{k_2} M(II)(\theta_2) + e^- \tag{2}$$

$$M(II)(\theta_2) \xrightarrow{k_3} M^{2+} \tag{3}$$

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where θ_0, θ_1, and θ_2 are the surface concentrations of $M(0)$, $M(I)$, and $M(II)$ species, respectively, while M^{2+} is the metal ion (e.g., Ni^{2+} or Zn^{2+}) in the solution. $M(I)(\theta_1)$ and $M(II)(\theta_2)$ are adsorbed intermediates.

According to the assumptions made in [1], the first and the second steps are two consecutive, irreversible single-electron transfers, and the third one is a physical process that consists of the solubilization of the $Me(II)$ species and transport of M^{2+} throughout the aqueous media. It was also assumed in [1] that the kinetic constants for the electrochemical steps follow a Butler–Volmer relationship and the elementary steps obey first-order kinetics. Then, the rates for each elemental step can be expressed as:

$$r_1 = k_{01}\theta_0 e^{b_1 E} \tag{4}$$

$$r_2 = k_{02}\theta_1 e^{b_2 E} \tag{5}$$

$$r_3 = k_{03}\theta_2 \tag{6}$$

The mass balance and the charge balance at the electrode surface were described by the following equations:

$$\frac{i_F}{F} = r_1 + r_2 \tag{7}$$

$$\frac{d\theta_0}{dt} = r_3 - r_1 \tag{8}$$

$$\frac{d\theta_1}{dt} = r_1 - r_2 = k_1\theta_0 - k_2\theta_1 \tag{9}$$

$$\frac{d\theta_2}{dt} = r_2 - r_3 = k_2\theta_1 - k_3\theta_2 \tag{10}$$

where r_i and k_i are the rates and their respective rate constants of the postulated steps. E is the applied potential, i_F is the faradaic current intensity, and F is the Faraday constant.

From Eqs. 7, 9, and 10, the theoretical faradaic impedance function corresponding to the above reaction mechanism could be deduced. (A method for the analysis and evaluation of impedance spectra deduced for a similar mechanism is also discussed in [5].)

However, in the electrochemical literature, other mechanisms suggested for nickel dissolution can be also found [6]. In earlier papers, some authors interpreted the observed kinetics in terms of a consecutive charge transfer mechanism ("scheme B") with the reaction

$$Ni(H_2O)_{ads} \underset{\rightarrow}{\leftarrow} Ni(OH)_{ads} + H^+ + e^- \tag{11}$$
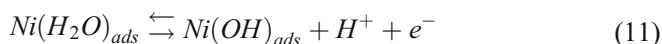
followed by the reaction

$$Ni(OH)_{ads} \rightarrow NiOH^+ + e^- \tag{12}$$

Fig. 1 Schematic picture representing the movement of ions and electrons at the surface, in the adjacent bulk phases, and in the "outer circuit" during a charge transfer step. *1* Ammeter, *2* potentiostat, *3* electrochemical cell, *I* current in the outer circuit and in the cell. **a** Initial state with adsorbed ions (open circuit or equilibrium case). No net current is flowing through the electrode and no current is flowing in the outer circuit (*I*=0). **b** The oxidation of the metal (e.g., Ni) atoms in the surface layer to adsorbed metal ions (Ni$^+_{ads}$) is connected with the simultaneous displacement (and adsorption) of the anions in the solution phase. **c** The formation of adsorbed metal ions (Ni$^+_{ads}$) is followed by the desorption of positively charged ions from the surface. The resulting electrons are moving through the bulk metal phase, and the positive ions are moving from the interphase into the bulk solution phase
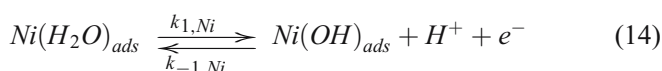

○ : metal atom on the surface ⊕ : adsorbed metal ion

⊕ : cation ⊖ : anion
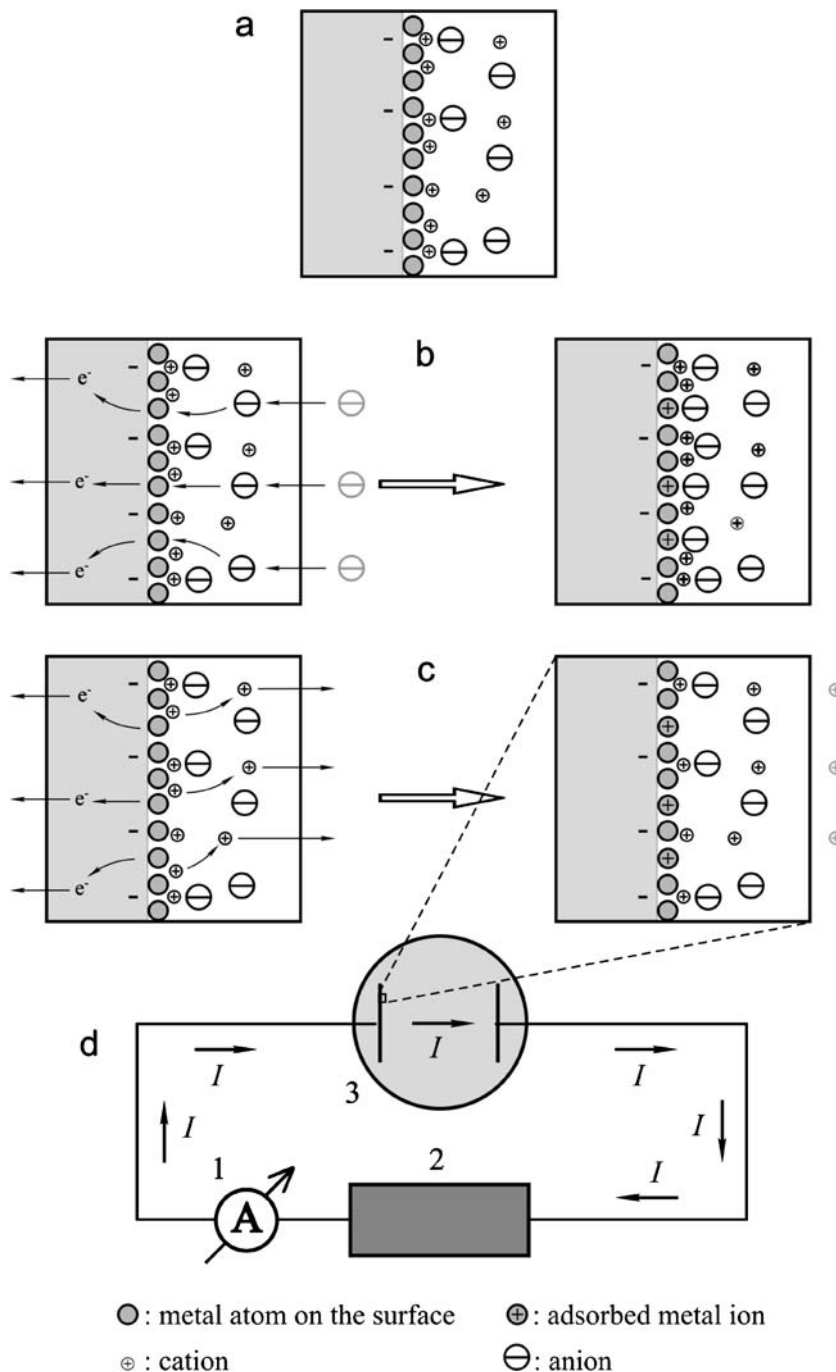
as the rate-determining step, and subsequent establishment of the homogeneous equilibrium

$$NiOH^+ + H^+ \rightleftarrows Ni^{2+}_{sol} + H_2O, \qquad (13)$$
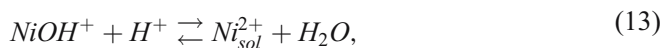
where subscript "ads" denotes that the species is adsorbed, while the subscript "sol" refers to components in the solution phase.

On the other hand, similar to iron dissolution, a so-called catalytic mechanism is also proposed in several publications, since a number of experimental facts disagree with the expectations based on a consecutive mechanism [6, p. 69].

Using the consecutive mechanism for iron dissolution as a reference, Itagaki et al. [7] proposed the following mechanism for nickel dissolution, which is very similar to the "traditional" scheme (scheme B):

$$Ni(H_2O)_{ads} \underset{k_{-1,Ni}}{\overset{k_{1,Ni}}{\rightleftarrows}} Ni(OH)_{ads} + H^+ + e^- \qquad (14)$$

$$NiOH_{ads} \overset{k_2}{\rightarrow} NiOH^+ + e^- \qquad (15)$$

$$NiOH^+ \rightarrow Ni^{2+} + OH^- \qquad (16)$$

By comparing schemes A and B, it is easy to demonstrate that the two mechanisms are hardly reconcilable.

At least two main differences are obvious. The first one is quite evident: in scheme B only one adsorbed intermediate is considered, while in scheme A two are considered. The second difference is connected with the formulation of the charge transfer processes. In the case of scheme B in the reaction equations (Eqs. 11, 12, 14, and 15), both adsorbed and dissolved species are involved. In contrast to this, Eqs. 1 and 2 in scheme A are formulated as charge transfer processes between adsorbed species.

In light of the above facts, it is rather surprising that Gregori et al. [1] introduce their mechanism without any critical remarks concerning the traditional scheme B. Even the reader of [1] can easily get the impression that scheme A is an equivalent, "improved" version of scheme B. However, contrary to the statement made in [1], the existence of two adsorbed intermediates does not unambiguously follow from the results and conclusions of the cited literature, especially not from Itagaki et al. [7], who fundamentally treated their data in terms of scheme B with only one adsorbed intermediate.

It is true that the existence of two adsorbed intermediates is a possible assumption; however, if we consider the physical meaning of the notion of "charge transfer," the validity of the formulation of a charge transfer process between two adsorbed species without participation of any dissolved component is rather problematic.

The problem of charge and mass balance

Neither the steps 1 and 2 in scheme A can be considered as a real charge transfer step, since a charged particle does not move from the adsorbed layer into the solution and/or vice versa. (see IUPAC definition in [8]). On the other hand, Eqs. 11, 12, 14, and 15) correspond to the IUPAC definition of a charge transfer step.

To show that the proposed reaction equations and the concept of a "pure surface reaction" cannot be correct, reaction Eq. 1 can be used as an illustrative example.

The main problem with the use of this equation together with Eq. 7 is that the current flow in the system is ascribed to a charge transfer process considered as a surface reaction. Faraday law states that simultaneous charge and material transfer takes place between the phases and the origin of this charge during a current flow, and material transfer should be ascribed to one or more components present in the bulk liquid phase.

If a current I can be measured in the system with an ammeter, electrons are flowing from one electrode to the other through wires (and other electrical elements) in the "outer circuit." The current can be measured outside of a galvanic cell only in the outer circuit, where the leads connected to the electrodes are purely electronic conductors. The electrochemical cell and the outer circuit elements form a series circuit (see Fig. 1d). The current in all parts of a series circuit has the same magnitude. In electrolyte solutions, the electrical current is carried by ions. It means that the circuit can be closed, and current can be measured only if ions are moving in the cell from one electrode to the other, i.e., in the bulk phase of the solution in the cell.

Taking into account the charge balances, a very schematic picture of the possible processes at the working electrode is given in Fig. 1.

Figure 1a shows the open-circuit case or the case at a certain electrode potential: no net current is flowing trough the electrode, and no current is flowing in the outer circuit and in the electrolyte solution.
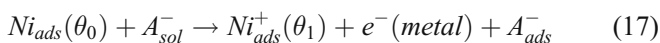
Two possibilities for the formation of a net current are shown in Fig. 1b,c, e.g., after the application of an appropriate electrode potential.

As shown in Fig 1b, the oxidation of the metal atoms in the surface layer to adsorbed metal ions is connected with the simultaneous displacement (and adsorption) of the anions in the solution phase. This step is evidently a real charge transfer step, since the resulting electrons are moving through the bulk metal phase and the outer circuit to the other electrode. Of course, a simultaneous charge transfer reaction at the other (counter)electrode is also necessary.
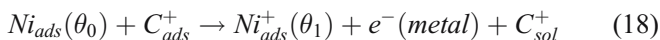
A different case is shown in Fig. 1c: the formation of adsorbed metal ions is followed by the desorption of positively charged ions from the surface. The resulting electrons are moving through the bulk metal phase, and the positive ions are moving from the interphase into the bulk solution phase. It means that this step can be also considered as a real charge transfer step.

Anyway, it is common in such type of processes that ions move from the interphase into the solution, or conversely, charged species enter the interphase. Nevertheless, a reaction between adsorbed species without participation of charged components from the solution phase could not be a charge transfer process corresponding to a current flow in the external circuit [9].
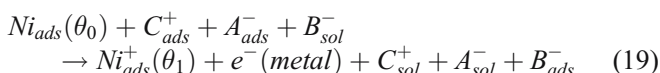
According to the above considerations, the complete form of Eq. 1 should be:

$$Ni_{ads}(\theta_0) + A_{sol}^- \rightarrow Ni_{ads}^+(\theta_1) + e^-(metal) + A_{ads}^- \qquad (17)$$

or

$$Ni_{ads}(\theta_0) + C_{ads}^+ \rightarrow Ni_{ads}^+(\theta_1) + e^-(metal) + C_{sol}^+ \qquad (18)$$

or

$$Ni_{ads}(\theta_0) + C_{ads}^+ + A_{ads}^- + B_{sol}^- \\ \rightarrow Ni_{ads}^+(\theta_1) + e^-(metal) + C_{sol}^+ + A_{sol}^- + B_{ads}^- \qquad (19)$$

etc. (C^+ is some kind of positively charged species, A^- and B^- are negatively charged ions.) A similar statement holds for step 2 (Eq. 2) in scheme A, as well. On the other hand, it can be clearly seen that the reaction equations in scheme B are in agreement with the requirements discussed above.

It should be noted that in the electrochemical literature, authors very often neglect the effect of movement of anions and use "simplified" equations in reaction schemes like Eqs. 1, 2, and 3. The usual answer to the criticism on such a formulation is that it does not cause any problem in the interpretation of the experimental data providing that the concentration of a "supporting electrolyte" is enough high. However, such a simplification is very questionable and may be misleading if one is studying the mass and charge balance at the electrode surface, because the ions originating from the supporting electrolyte are also charged species with a finite mass.

Thus, the evaluation of the results of EQCM studies in conjunction with other electrochemical measurements requires a very cautious approach. In addition, there are ample evidences reported in the literature [10–26] that the specific adsorption of anions on metal surfaces becomes very pronounced in the course of dissolution in wide potential range. This possibility should be taken into account in the case of the analysis of EQCM results obtained from transient studies (e.g., cyclic voltammetry). It is very surprising that in [1], the possible adsorption of the solution components is completely left out of consideration (see the explanations to the superficial mass vs potential curve). Without a detailed analysis of the sorption phenomena occurring in the system, no realistic picture on the metal dissolution can be created.

Remarks to the impedance results

There are some additional remarks specific to the derivation of the impedance function and analysis of the results:

(1) For the derivation of the impedance function, it is not necessary to formulate Eqs. A8, A9, and A10 (in [1]; Eqs. 4, 5, and 6 in this article) corresponding to the assumption that the individual steps obey first-order kinetics. The impedance expression could be obtained by using a general formulation of the rate equations like $r_i = r_i(E, \theta_i, \ldots)$, etc. [27], indicating that each step in the reaction scheme may follow a complex mechanism. In this case, there is no direct contradiction between the formulation of the reaction steps and the notion of "charge transfer process."

(2) Unfortunately, no statistical analysis of the estimated parameters are given in [1]. This makes the estimation of the reliability of the derived values (calculated from the fitting results) very difficult.

Nevertheless, according to the results reported in [1], the rate coefficient k_3 depends strongly on the potential, although according to the reaction scheme, it should be potential-independent.

The explanation of the authors ("… as seen in Table 2, the k_3 value is smaller than k_1 and k_2 in all the potential range studied. The dependence of k_3 on the potential could be explained if the transport of Ni^{2+} to the solution is a migration; however, this point requires further studies since neither the solubilization and transport of Ni^{2+} from the surface to the solution nor the other paths of the assumed mechanism (Eqs. (1), (2) and (3)) are really elementary steps." [1, p. 87]) is clearly in contradiction with the assumptions made with respect to scheme A ("… r_1, r_2 and r_3 are the reaction rates for each elementary step … If each elementary step obeys kinetics of first order, it can be expressed as:

$$r_1 = k_1\theta_0 \qquad (A8)$$

$$r_2 = k_2\theta_1 \qquad (A9)$$

$$r_3 = k_3\theta_2 \qquad (A10)$$

[1, p.88], or "If it is considered that the kinetic constants for the electrochemical steps follow a Butler–Volmer relationship and the elementary steps obey first-order kinetics, then the rates for each elemental step can be expressed as:

$$r_1 = k_{01}\theta_0 e^{b_1 E} \qquad (4)$$

$$r_2 = k_{02}\theta_1 e^{b_2 E} \tag{5}$$

$$r_3 = k_{03}\theta_2 \tag{6}$$

[1, p.83].), indicating the internal inconsistency of the model.

Conclusions

The main points discussed in this paper can be summarized as follows:

(1) Comparing the mechanism scheme A, suggested for Ni dissolution in [1] with those "traditional" ones mostly accepted in the literature, it should be stated that the former one cannot be reconciled with the latter ones. In addition, it can be easily demonstrated that the formulation of reaction equations, describing the charge transfer steps and consequently the corresponding kinetic equations, could lead to mechanistic misinterpretations.

(2) For the interpretation of the EIS measurements and EQCM data (especially those obtained under transient conditions), the possible role of the adsorption of all components present in the system should be taken into account.

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