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# The effects of temperature on current–potential profiles from electrochemical film production: A theoretical approach

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#### Abstract

In this paper we improve an equation that describes the current–potential curves obtained during electrochemical deposition of metals on *n*-silicon. The equation give us the theoretical description of the voltammograms and was previously introduced in terms of the ion concentration and the potential, however it still requires the inclusion of factors that describe the influence of the temperature. Temperature controls the diffusion constant *D*, the electrical resistivity of the electrolytic solution  $\rho$ , and the conduction electron density on the electrode surface *N*. In this paper we take explicitly into account the dependence of *D*,  $\rho$  and *N* on the temperature and succeeded to relate them to a defined reaction rate *k*. To complete the description, we considered that the influence of the temperature could be accounted by renormalizing the magnitude of the potential that triggers the deposition. Thus, a final expression for the current *I*, as a function of voltage *V*, ion concentration  $c_b$  and temperature affects the magnitude of the stationary currents, the amplitude of the nucleation loops and the intensity of diffusion-limited growth peak, producing a shift of the current–voltage curves toward less negative values of *V*. The same description allowed us to observe similar effects in the current transients. © 2007 Elsevier Ltd. All rights reserved.

Keywords: Voltammograms; Current transients; Diffusion; Reaction; Electrochemical deposition

# 1. Introduction

Electrochemistry has been studied, tested and explored over the last 200 years without loosing interest by the academic community. In fact its appeal grows renewed every day because the claim for new technologies, related to microelectronic applications [1–4]. Moreover many biological processes, from biological sensors to ion transport through membranes [5], seem to require for a deep understanding on electrochemical deposition. However the application of electrochemical techniques to other fields demands for theoretical descriptions that made explicit a relation between the transients and the many physical variables that renders singular every system, that is, temperature, potential, ion concentration, electrical resistivity of the electrolytic bath, and time.

From the beautiful review given by Hyde and Compton [6] we realize that notwithstanding the many models [7–25] proposed

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to describe the current transients and despite the high quality of all these models, it still lacks current expressions put forward as a function of those parameters, currently used to control the deposition processes.

As a consequence, in this article the main purpose is to improve a former theoretical description of the transients and voltammograms [26,27], putting them as functions of these parameters, namely: temperature, potential, ion concentration, electrical resistivity of the electrolytic bath, and time.

In the first article [26], we derived and expression for the current transients assuming that there are two fundamental mechanisms to be considered, namely the diffusion of ions near the electrode and the reactions on the electrode surface. Fick's second law,

$$\frac{\partial}{\partial t}c(x,t) = D\frac{\partial}{\partial x^2}c(x,t),\tag{1}$$

was solved assuming a finite system regulated by a time-dependent boundary condition,

$$c(0, t) = (c_{\rm b} - c_{\rm s}) \exp(-kt) + c_{\rm s},$$
 (2a)

that takes into account the reaction rate k, i.e. rate at which the ions are reduced at the surface and two boundary conditions:

$$c(x,0) = c_{\mathsf{b}}, \quad 0 < x < \delta \tag{2b}$$

$$c(\delta, t) = c_{\mathbf{b}}, \quad \forall t. \tag{2c}$$

In Eqs. (1) and (2) c(x, t) is the ion's concentration, *D* the diffusion constant,  $c_b$  and  $c_s$  the ion's concentration in the bulk and on the electrode surface, respectively.  $\delta$  is a length that defines the thickness of the stationary diffusion layer, in which the ion concentration decay.

Under conditions (2) we solve Eq. (1) to obtain the current density expression, given by [26]:

$$I(t) = -\frac{zFD(c_{\rm b} - c_{\rm s})}{\delta} \times \left[1 - \exp(-kt) + 2k\sum_{i=1}^{\infty} \frac{\exp(-kt) - \exp(-\lambda_i^2 t)}{\lambda_i^2 - k}\right],$$
(3)

In Eq. (3) z is the charge number, F the Faraday constant and  $\lambda_i = (i\pi/\delta)^2 D$  is a parameter that appears during the solution of Fick's second equation, an eigenvalue.

Once the current density, Eq. (3), is given, any additional physical information must be included in the reaction rate *k*. As a consequence in a second article [27], we made explicit the connection between the reaction rate *k* and the potential, through the formula,

$$k = [1 + \exp\{b(V - V_k)\}]^{-1} \left[1 + \exp\left(\frac{zF\alpha(V - V_l)}{RT}\right)\right]^{-1}.$$
(4)

This expression was derived on the assumption that an ion on the electrode surface must choose one of two possible outcomes: to receive or not an electron charge from the electrode, that is, even when there are afforded advantage for a charge transfer there is a finite probability for the non-occurrence of a reduction reaction.

In Eq. (4) R is the gas constant and  $\alpha$  is a non-dimensional factor that must contain the contributions that came from another physical condition, other than those related to a potential difference. Also in Eq. (4),  $V_1$  is the characteristic reduction potential for the ion, that is, the potential that defines the minimum energy necessary for a charge transfer between electrode and ion.

Because the reaction rate make sense if, and only if, the electrolytic cell is on a potential equal or greater that  $V_1$ , we multiply the reaction rate by a conditional probability that appears inside the first bracket in Eq. (4). This first bracket works like a switch for the current (reduction process). This function mimics the step function without loosing the continuous behavior.  $V_k$  is a potential that localizes the half value of the function (a sigmoid function) and is chosen because the trigger mechanism departs from zero when  $V = V_1$ . The positive constant *b* that appears in the formula is used to quantify the changes produced by the sigmoid function.

In a voltammogram,  $V_k$  demarks the onset potential for ion reduction or the potential at which the reaction stop, when the applied potential retraces back to the initial value.

Because V evolves in time through a constant rate  $\omega$  (the scan rate), it is written through the linear equation  $V = V_0 + \omega t$ , where  $V_0$  is the starting applied potential. As a consequence, t and V are connected variables and Eq. (3) could be used to depict the current transient curves  $I(c_b, V, T, t)$ , when concentration, potential and temperature were fixed or, yet, to reproduce the voltammograms  $I(c_b, \omega, T, V)$  at fixed concentration, scan rate and temperature.

In order to make a complete description, we will open the current dependency on temperature introducing it into the parameter  $\alpha$  of Eq. (4), which has a dependency on the diffusion constant *D*, the electrical resistivity  $\rho$  and conduction electron density at the surface of the electrode *N*. To conclude the article we perform a qualitative comparison between theoretical and experimental voltammograms to explore the plasticity of the model.

### 2. The reaction rate *k* as function of temperature

In order to put forward and expression for the reaction rate k in terms of the temperature, we will follow a course that starts with the identification of all factors (variables and parameters) affected by the thermal conditions observed in the electrolytic cell. The next step will be to find a convenient relationship among these factors; such that the final expression for the currents attends all features present in the experimental curves obtained at different temperatures.

To define the effect of temperature on the system, we must recall that we assumed that the electrochemical deposition process evolves through a two-step type mechanism [26,27]. The ions diffuse towards the electrode surface to be incorporated by the growing deposit by reaction that has a probability to occur at an electro-active point on the surface. The temperature through different parameters influences both these mechanisms, diffusion and reaction.

While it is easy to state that diffusion is sensitive to a change in temperature through the magnitude of its transport coefficient, it is not so simple to discriminate the effects produced by temperature on the charge transfer reaction. However, because this reaction is strongly determined by the available charge to be transferred at the electrode/electrolyte interface, we have chosen the population of conduction band electrons, on the electrode surface, as a relevant parameter. At this interface the electrical resistivity of the electrolytic solution must be considered as one of the factors that affects the charge transfer rates. Finally, we realize a last effect that should affect the reaction rate. Because of charge transfer reactions are conditioned by an activation energy, which represents the minimum amount of energy necessary to the electrons to surmount the energy barrier for reduction of the ions, a thermal contribution from the bath should be included as aiding the activation energy. That is, the bath temperature also influences the barrier height for electron transfer at the electrode surface, affecting the potential onset of the reduction reactions.

Assuming that these are the relevant factors related to temperature that produce significant changes in the reaction rate, we just need to explicit their dependence on temperature and write an expression for k.

By inspecting Eq. (3) it is possible to see that the contribution of the diffusion constant is already included in the current density expression, obtained through the Fick's second law. Because the solvated ions has a behavior of Brownian particles we used the Stoke–Einstein relation [28] to make explicit the temperature dependence of the diffusion constant,

$$D = \left(\frac{R}{N}\frac{1}{6\pi\mu r}\right)T,\tag{5}$$

where  $\mu$  is the viscosity of the liquid and *r* is the radius of the Brownian particles.

Then, once the diffusion constant  $D_r$  is known at a particular temperature  $T_r$ , we may write a simpler expression for it, that is, D = AT, where the parameter A turns to be a constant given by  $A = D_r/T_r$ . Thus, to consider situations where T lies around the ambient temperature we use  $D_r = 1.0 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  and  $T_r = 300 \text{ K}$  to define A and,

$$D = 3.4 \times 10^{-8} T \,(\mathrm{cm}^2/\mathrm{s}). \tag{6}$$

Also, the resistivity  $\rho$  in the electrolytic medium and the population of conduction electrons in the electrode can be put as a function that depends uniquely on the temperature, as it will be shown in the next paragraph.

Following the works of Rajendran et al. [29] and Villullas et al. [30], for situations that evolve in the range 277–314 K, a simple relation connecting the resistivity with the inverse of the temperature could be used. However, this relation is only valid for electrolytes with low concentration of ionic species, because we know that the electrical resistivity depicts a nonlinear dependence with the temperature at high electrolyte concentrations [31–33]. We also know that the resistivity (conductivity) of a complex mixture of electrolytes is not available by a simple expression, however it is accepted as an inverse (linear) function of temperature for systems near the 300 K [29–33] and under conditions of low electrolyte concentration. So after Rajendran et al. [29], we assume,

$$\rho = \left(\frac{1}{1.08 \times 10^{-4}T}\right) (\text{cm/S}).$$
(7)

To complete the list of physical parameters affected by the temperature that enters in the description of the reaction rate, we will write below the expression for the population of electrons in the conduction band of a semiconductor. From current textbooks [34] we find,

$$N = 4.83 \times 10^{15} \sqrt{T^3} \exp\left(-\frac{E_g}{2k_B T}\right) \frac{1}{\text{cm}^3},$$
(8)

where  $E_g$  is the energy band gap and  $k_B$  is the Boltzmann constant.

Given that we have identified and made explicit the relation between each physical variable and the temperature, we should now conclude the task by relating  $\rho$ , N and D together, in order to define the arbitrary parameter  $\alpha$  and the argument of the exponential function that appears in the second bracket of Eq. (4). There is no formal prescription to attain this goal. We will assume the naïve hypothesis that Ohm's law is valid on both sides of the electrode/liquid interface. It is not a problem if the current that flows through the interface does not obey Ohm's law. We assert that before deposition, as the potential is turned on, there is a charge arrangement in both sides of the interface relating the electric field *E*, the resistivity  $\rho$  and the current density in the usual way, that is  $E = \rho J$ . Inside the electrode it reads  $E_s = \rho_s J_s$ , and similarly in the liquid side, near the electrode surface, we have  $E_1 = \rho_1 J_1$  (the subscripts identify the medium, s for silicon and 1 for the liquid).

Because the electric charges on the electrode side induce an equal amount of charge on the liquid side, we conjecture that the current densities are proportional, i.e.,  $J_s \propto J_1$ . Now, invoking the classical image of a parallel plate capacitor of width  $\delta$  and capacitance  $C_A$ , defined and charged in the liquid side, just on the electrode surface, we write,

$$\frac{\Delta E}{k_{\rm B}T} = \frac{Q\Delta V}{RT} = C_{\rm A}\rho_{\rm I}\delta_{\rm I}J_{\rm I}\frac{\Delta V}{RT},\tag{9}$$

where we have used the resistance in the form  $R_1 = \rho_1 \delta_1 / A$ .

To relate  $\delta_I J_1$  (whose dimension is molar charge per length per second) to our selected parameters (*N* and *D*) we consider the flux of ions near the electrode surface ( $J_1 \propto D(\partial c/\partial x)$ )) and assume that  $\delta_1(\partial c/\partial x) \propto N$  and  $\delta_1 J_1 \propto D\delta_1(\partial c/\partial x) \propto DN$ . That means that the concentration gradient in the solution, in the close proximity of the interface, is proportional to the electronic density on the electrode surface. Thus we propose,

$$\frac{\Delta E}{k_{\rm B}T} = C_{\rm A}\rho_{\rm l}NDzF\frac{\Delta V}{RT}.$$
(10)

Using Eq. (10) we write again Eq. (4), that reads,

$$k = [1 + \exp\{b(V - V_k)\}]^{-1}$$
$$\times \left[1 + \exp\left(\frac{zFC_A\rho_l ND(V - V_l)}{RT}\right)\right]^{-1}.$$
 (11)

This expression gives the reaction rate in terms of the temperature apart from a last ingredient. Temperature, besides the effects produced on D, N and  $\rho$ , as shown by Eqs. (6)–(8), also affects the reaction rate through a change on the activation energy required for the charge transfer. In the present case depicting a twofold contribution. One of these consists in the self-evident distortion of the potential barrier after an increment on the temperature. In Fig. 1 we demonstrate schematically the concept. In this figure  $\Delta U$  and  $\Delta U^I$  represent the magnitude of the energy barriers at the reference temperature and at a higher one, respectively. In Eq. (11)  $\Delta U$  is given by  $b(V - V_k)$  and  $zFC_A\rho_1ND(V - V_1)$ , two terms with similar meaning that we will represent by  $Q(V - V_1)$  for brevity. To make simpler our explanation we will just examine the representative relation,

$$k \propto \left[1 + \exp\left(\frac{Q(V-V_l)}{RT}\right)\right],$$
 (12)

that corresponds to Eq. (11) with just one of the bracket in an explicit form. It is enough to examine this generic bracket



Fig. 1. Double-well potential that represents the potential energy to be surmount in a charge transfer "reaction" that imply the reduction of ionic specie on the electrode surface. The sketch mimics the changes on the potential barrier by effect of temperature ( $T_s > T_c$ ) when we look the same region in the space of parameters.

because all the effects verified there have a similar effect on the other. Assuming that  $V_1$  is a characteristic and constant potential in Eq. (12), it follows that and increasing in T requires a lower numerator (on the exponential argument) in order to that corresponds to Eq. (11) with just one of the bracket in an explicit form. It is enough to maintain the same magnitude for k, and that means we attain this magnitude for the reaction rate at a lower value for the variable potential V. However we realize another contribution coming from the temperature control, it redefines,  $V_1$ , the potential that triggers the deposition process. To explain this assertion we remember that, in the electrolytic solution, the polarized water molecules encapsulate the ions by many solvation shells. Thus, it is natural to assume a redox process requires these shells to be broken or to be found in an unstable state in order to allows permeability for electron transport. Thus an increase on the temperature also increases the probability that charges permeate the solvation shells, reducing the ion. In our schematic description, depicted in Fig. 1, this effect is visualized as a lowering of  $V_1$ , the potential yield that sets the beginning of the reaction. The theoretical model follows the simplest prescription, assuming that  $V_1$  changes with the inverse of temperature. Once the range of variations on T is short we follow the current dependence chosen for all parameters in this paper (except to N) assuming in this case an inverse linear dependence with temperature. Because all variations are computed in terms of a reference temperature  $T_r$ , to take account of this effect we change  $V_l$  by  $(T_r/T)V_1$ , in Eq. (11). As a consequence, the final expression for the reaction rate reads,

$$k = \left[1 + \exp\left\{b\left(V - \frac{T_{\rm r}}{T}V_k\right)\right\}\right]^{-1} \times \left[1 + \exp\left(\frac{zFC_{\rm A}\rho ND(V - T_{\rm r}/T)V_{\rm l}}{RT}\right)\right]^{-1}.$$
 (13)

In this formulation the reaction rate k (given by Eq. (13)) is a function of the temperature T and the potential V, given that the resistivity, the diffusion coefficient and the population

of electrons are now functions of *T* as shown by Eqs. (6)–(8). As a consequence, the current density, given by Eq. (3), is now in the general formula  $I = I(c_b, \omega, T, V)$ , as announced in the introduction of the paper.  $\omega$  is included to account for the scan rate that relates the potential *V* to the time *t*.

#### 3. Effect of temperature on the voltammograms

Through the algorithm given in the Appendix B we use the expression,

$$I = -I_{\text{sta}} \left[ 1 - \exp(-kt) + 2k \sum_{i=1}^{\infty} \frac{\exp(-kt - \exp(-\lambda_i^2 t))}{\lambda_i^2 - k} \right],$$
(14)

which generate all the theoretical current–potential curves shown in this work.

Eq. (14) is identical to Eq. (3), but now the reaction rate k(V, T) is specified by Eq. (13) and the time  $t(V, \omega)$  is substituted by a function of the potential and the scan rate through the relation  $V = V_0 + \omega t$ .

Before continuing we must observe that in spite of our effort to avoid arbitrary assumptions on the definition of the current expressions, we are faced to our incapability to define a precise value for the stationary concentration on the electrode surface,  $c_{\rm s}$ , as function of the temperature as well as the impossibility to define a precise value for the resistivity and the capacitance in systems composed by complex electrolyte mixtures. We also assume that  $\delta$  goes with the inverse of temperature because thermal agitation tends to reduce the region where the induced dipoles are lined up to the electric field. So we wrote  $\delta = \delta_r(T_r/T)$ , with the subindex meaning the reference values. Thus, to evaluate the adequacy of our description we will proceed as follow. We adjust the theoretical results to the experimental data at T = 300 K, in order to fix these parameters. Once it is done, nothing but temperature is changed to produce the curves. In Table 1 it is given the magnitude of all parameters used for  $T = T_r = 300$  K.

We search for a theoretical approach suitable for the description of the voltammograms. That means we are pursuing for a qualitative description of the experimental profiles, which could be achieved in terms of real variables and with a minimum requirement of free parameters. In Fig. 2 we show the current–potential profiles obtained from Eq. (14). All the curves are defined by the same set of parameters, except for the temperature. In this figure we see how the theoretical model reveals the main effects produced by increments on the bath temperature, namely the increase of the current peak yield and the increase of the stationary current (represented by the plateau)

Table 1 Values used to generate the voltammograms

| U  | e |   |
|--|---|---|
| $c_b = 26 \text{ mM}$                              |   | $V_k = 0.89 \text{ V}$  |
| $c_s = 14 \text{ mM}$                              |   | $V_{k(\text{return})} = 0.87 \text{ V}$                                     |
| $\delta = 3 \times 10^{-2} \text{ cm}$             |   | $V_l = 0.91 \text{ V}$  |
| $D = 1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ |   | $\omega = 10 \mathrm{mVs^{-1}}$   |
| $b = 200 \mathrm{V}^{-1}$                          |   | $\rho C_{\rm A} = 1.79 \times 10^{-6} \mathrm{cm}\mathrm{F}\mathrm{S}^{-1}$ |
| $b_{\rm return} = 32  {\rm V}^{-1}$                |   | $N = 1.43 \times 10^{10} \text{ cm}^{-3}$                                   |



Fig. 2. Theoretical voltammograms obtained from Eq. (14). They represent systems, which are defined by the same parameters except temperature. To generate the curves we used a  $10 \text{ mV s}^{-1}$  scan rate, 0.03 cm as the width of the stationary diffusion layer and  $\rho$ , *N* and *D* as defined in the Table 1.

on the voltammograms. Alterations on the nucleation loop and on the potential that triggers the deposition current are also verified. It is particularly apparent the shift, of the potential that triggers deposition, to less negative values when temperature is increased. All the effects identified in the voltammograms are very often observed in experimental voltammograms.

Fig. 3 shows, similarly to Fig. 2, three voltammograms obtained at three different temperatures. The experimental procedure to obtain the data is described in detail at the Appendix A. The features in the nucleation loops, stationary current and shift in the potential onset are easily observed and the similarities between theoretical and experimental curves allow us to explain the reasons that are behind every one of the changes introduced



Fig. 3. Experimental voltammograms obtained during electrochemical deposition of Co on *n*-silicon electrode. The electrolytic medium was formed by an aqueous solution containing 26 mM of CoSO<sub>4</sub> and 0.5 M of Na<sub>2</sub>SO<sub>4</sub>, and the scan rate was 10 mV/s. The current profiles were obtained at different temperatures as indicated in the figure.

by effect of the temperature. For instance we could explain the growth verified on the stationary current (the intensity of the current plateaus) with a temperature increment as a consequence of the increment on the diffusion constant and a reduction of the depth of the depletion layer. However, the strong fluctuations observed in the stationary current, particularly for the temperature of 314 K, are not described by the model developed in this work since they are a consequence of non-regular natural convection movements inside the electrolytic cell, an effect not included into the model yet. Despite some imperfections, the general behavior depicted by the theoretical curves agrees quite well with the experimental ones.

Also, according to the model, the changes on the nucleation loops are related to the changes promoted by the temperature in the magnitude of the diffusion constant, the conductivity of the electrolytic solution and the way it re-scales the magnitude of the potential that start the deposition process.

Another point to be discussed is related to the coupling between the current peaks and the current plateaus. The intensity of the current peaks depend on both, the magnitude of the stationary current  $I_{sta}$  and the magnitude of the function that appears inside the brackets, in Eq. (14), which is defined by the magnitude of the reaction rate k. Because  $I_{sta}$  is defined in terms of T, as it occurs to be with k and with the function inside the brackets, the magnitude of the current peaks and that of the current plateaus are proportional. This proportionality could be confirmed comparing profiles (voltammograms) that are normalized by two different procedures. If we normalize each voltammogram by its current peak, we will see that the plateaus merge on a same current value. On the other hand, if we normalize each voltammogram by its current plateau value, then the current peaks will attain equal magnitude. This behavior, not explicitly shown here, is a common feature of theoretical and experimental voltammograms and proves the proportionality between peaks and plateaus. This benefit put forward by the model, allows us to consider the relationship between the stationary currents measured through voltammograms and the ones measured through current transients (current-time profiles). In fact, we verified the coincidence among the stationary current values obtained from the voltammograms (the plateau intensity) and the stationary currents given by the current transients (the current intensity after a long deposition time). This result, evidenced by the experimental data and confirmed by the theoretical model, shows (see Eq. (3)) that  $I_{sta} = -zFD(c_b - c_s)/\delta$ is a function that depends merely on temperature. Then, if the current transient profiles are taken at just one temperature (no matter what the deposition potential is), the stationary current value depicted by the curves should coincide with the current intensities shown by the voltammogram measured at the same temperature. In Fig. 4 we show current transients obtained at different potential values, but at the same temperature (T = 289 K). These transients displays stationary currents that merge to a current value  $I_{sta}$  that corresponds to the one defined by the plateau in the voltammogram measured at the same temperature and depicted in Fig. 3. The theoretical model gives us a result (not shown) that is in close agreement with that conclusion, whose merit is to emphasize the correspondence between both descrip-



Fig. 4. Experimental current-time curves. The transients were generated at three different potential as indicated in the figure. The temperature of the samples during the acquisition of the data was 289 K and we indicate the magnitude of the current density at the peak of the profiles.

tions of the current profiles  $I(c_b, T, t)$  and  $I(c_b, T, V)$ , prescribed by the model.

To examine the profound relation between the current transients  $I(c_{\rm h}, T, t)$  and the voltammograms  $I(c_{\rm h}, T, V)$ , we show in Fig. 5 theoretical current transients taken at the same potential but at different temperatures. Once again, we verify that a change in the temperature produces different stationary currents as shown by the correspondent voltammograms. It is important to stress that through the piece of the current profile shown in Fig. 5 it was not possible to verify the exact stationary value for the current as obtained by the voltammograms. However, if we take these transients for longer times we certainly will verify those values. A comparison between Figs. 4 and 5 allow us to verify that in one case (in Fig. 4) the current peak intensity depict different values because the currents were recorded under different potential whereas in Fig. 5 the reason for the difference on the peak magnitudes is just due to the temperature difference among the current transients. A result in perfect agreement



Fig. 5. Theoretical current–time curves, generated by Eq. (14). The corresponding reaction rate is computed from Eq. (13) and the temperatures are indicated in the figure.

with those shown in Figs. 2 and 3 through the corresponding voltammograms.

## 4. Conclusions

In this paper we have improved the expression that defines the reaction rate entering the description of the voltammograms and the current transients produced during electrochemical deposition processes. We have introduced the temperature as a fundamental variable to define the kinetic (diffusion and reaction) that evolves out of equilibrium conditions.

To make explicit the dependence of the reaction rate k with temperature, it was necessary to develop a dimensional analysis involving a set of parameters that depend explicitly on temperature, namely the diffusion coefficient D, the capacitance  $C_{\rm A}$ , the electrical resistivity in the electrolytic solution and the population of electrons in the conduction band of the semiconductor electrode. Because the dimensional analysis requires all this parameters to define a non-dimensional factor entering on the definition of the reaction rate k, we insist to represent the diffusion coefficient as a function of temperature, even when weakly affected by the temperature in the range considered. In comparison to previous articles [1,2] we lost a formal elegance of our early description, but we succeed for a current expression gives in terms of real parameters. In addition, to offer an analytical description of a complex phenomenon, the model allows for a qualitative comparison of theoretical and experimental data. Because the expression for the current-potential profiles were made barely explicit, as function of physics parameters, we can hope that after major improvements, descriptions like this could be used in the future as a tool to quantify  $\rho$ , D and  $C_A$  for ion migration (under diffusion control) in a great number of electrolytic solutions and under diverse conditions of temperature and ion concentration. Then electrochemistry will offer a powerful analytical procedure to quantify electrical properties and transport coefficient that characterizes bio-chemical systems.

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### Appendix A. Experimental procedure

The experimental data used in this work were obtained with a conventional three-electrode cell. The electrolyte employed was aqueous solution containing 26 mM CoSO<sub>4</sub> as the source of metal ions, 500 mM of Na<sub>2</sub>SO<sub>4</sub> as the supporting electrolyte, with pH 4.5. The temperature of the electrochemical bath were carefully controlled and fixed during the acquisition of each curve (voltammograms and current transients). The working electrode used in our experiments were silicon, obtained from single side polished, technical grade (100) oriented Si wafers n-doped (resistivity of  $1-10 \Omega$  cm). The electrical contact to the working electrode was made through eutectic GaIn back contact. A tape was used to mask off all the electrode except for a

circular area  $(0.478 \text{ cm}^2)$  of Si(100) surface which contact the electrolyte. Prior to each electrochemical experiment, a fresh electrode was prepared and its silicon surface was cleaned with 5% HF solution, then immediately transferred to the electrochemical cell. The Pt foil counter electrode was placed directly opposite the working electrode. The potentials were measured against a saturated calomel reference electrode (SCE) which was

placed as close as possible to the working electrode surface to minimize the ohmic potential drop in the electrolyte. The electrochemical experiments were performed in a dark chamber. All the electrolytes, as well as the etching solutions used to clean the samples prior to the electrochemical experiments, were prepared from distilled deionized water with a resistivity of 18  $\Omega$  cm and analytical grade reagents.

#### Appendix B. Program to compute voltammograms

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* In this program we just compute equation (14) that give us the
*current density versus the potential in a cyclic process.
******
                                              *****
**
* D=diffusion coefficient
*xL=diffusion layer depth
*t=time
*VO=maximum potential during the scan rate procedure
*TO= time spent to achieve VO
* cro=capacitance multiplied by resistivity
*xro=resistivity
*alfa=k (the reaction rate)
*******
****
*
          VARIABLES DECLARATION.
   dimension corr(0:3000),volt(0:3000)
   double precision corr,alfa,soma
*******
**
*
          RESULTING FILES
   open (1, file='poten.dat')
   open (2, file='cori.dat')
      *****
                     *********
***
779 format(f10.3)
780 format(f10.4)
800 format(e14.7)
    xpi=3.141592654
    write(*,*)'magnitude of OHL(0.03cm)'
    read(*,779)xL
    t=0.
     Too=0.0001
    salva=0.0d0
     write(*,*)'VO-maximum potential- (absolute value,1.2)'
    read(*,779)VO
     write(*,*)'Scan rate-volts/s(0.010)'
    read(*,779)TV
     write(*,*)'xnd= (1. p/ 10mV/s) (10. p/ 100mV/s)'
    read(*,779)xnd
     TO=(VO/TV)*xnd*10
     iTO=TO
     dt=1./xnd
     it=0
     ies=2*iTO
```

```
***************
***
*Numeric procedure to compute the currents between t=0 and t=TO
***
     write(*,*)'Temperature-Tp(Kelvin, as a real number, 300.)'
     read(*,780)Tp
     aa=300./Tp
      fator=((0.218)*Tp/aa)*(0.026-0.014)
      VI=0.89*aa
     iVI=VI*TO/(VO)
     D=3.4E-8*Tp
     xro=1/(1.08E-4*Tp)
     cro=5.6E-8*xro/aa
     xLa=xL*aa
     xN=4.83E15*sqrt(Tp**3)*exp(-(6384.8/Tp))
     xp=cro*xN*7.89E-4
      write(*,*)D
     write(*,*)xN
     write(*,*)xp
      do 5 j=0,ies
      soma=0.
      if(it.gt.iTO)then
      go to 10
      else
      continue
      end if
      if(too.gt.(0.001))then
      go to 6
      else
      continue
      end if
      volt(j)=(-TV)*t
      alfa = (1./(1.exp(xp*((volt(j)/aa)+0.89)))*
     (1./(1.+\exp(200.*((volt(j)/aa)+VI))))
   1
      do 14 mi=1,1000
      xlamb2=((mi*xpi/xLa)**2)*D
      soma=soma+((exp(-alfa*t)-exp(-xlamb2*t))
   1 /(xlamb2-alfa))
  14 continue
      corr(j) = -fator*(2*alfa*soma-(exp(-alfa*t))+1.)
      corI = -corr(j)
      if(corI.lt.(15.d-3))then
      corr(j)=0
      it=it+1
      t=t+dt
      salva=corI
```

|                     | go to 5   |
|---------------------|---|
|                     | else  |
|                     | too=t   |
|                     | end if  |
| 6                   | volt(j)=(-TV)*t   |
|                     | alfa=1./(1.+exp(xp*((volt(j)/aa+0.89))))*               |
| 1                   | $(1+\exp(200.*((volt(j)/aa+VI))))$                      |
|                     | tt=t-too  |
|                     | do 15 ni=1,1000   |
|                     | xlamb2=((ni*xpi/xLa)**2)*D                              |
|                     | soma=soma+((exp(-alfa*tt)-exp(-xlamb2*tt))              |
| 1                   | /(xlamb2-alfa))   |
| 15                  | continue  |
|                     | $corr(j) = -fator^{*}(2*alfa*soma-(exp(-alfa*tt))+1.)$  |
|                     | t=t+dt  |
|                     | 1t=1t+1   |
| بله ماه ماه ماه ماه | go to 5   |
| *****               | ***************************************                 |
| *                   |   |
| *Num                | heric procedure to compute current between t=10 e t=210 |
| **                  |   |
| 10                  | aantinua  |
| 10                  |   |
|                     | u = 1 + (i) = ((TV) + i) + 2 + VO                       |
|                     | $v_{01(j)} = ((1 v)^{1} i)^{-2} v_{0}$                  |
| 1                   | $ana = 1./((1.+exp(xp^{-}((von())/aa+0.87)))))$         |
| 1                   | $(1.7(1.7 \exp(52.7)(1000)/(3a) + 0.87))))$             |
|                     | $u_{0} = 10 = 1,1000$                                   |
| G                   | $x_{1a1102} = ((111^{x}x_{1})^{x}2)^{x}D$               |
| 1                   | $/(x_1)$  |
| 16                  | (Alamoz-ana))   |
| 10                  | $corr(i) = fator*(2*a) fa*coma_(exn(-a) fa*tt))+1)$     |
|                     | t=t+dt  |
|                     | it=it+1   |
| 5                   | continue  |
| ,                   | write $(1,779)$ (volt(i),i=1,ies)                       |
| ,                   | write $(2.800)(corr(i),i=1,ies)$                        |
|                     | close(1)  |
|                     | close(2)  |
| s                   | stop  |
| e                   | end   |
|                     |   |

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