PERGAMON

Electrochimica Acta 47 (2002) 1137–1144

ELECTROCHIMICA Acta

www.elsevier.com/locate/electacta

Kinetic study of the chlorine electrode reaction on Ti/RuO$_2$ through the polarisation resistance

Part II: mechanistic analysis

J.L. Fernández, M.R. Gennero de Chialvo, A.C. Chialvo *,[1]

Programa de Electroquímica Aplicada e Ingeniería Electroquímica (PRELINE), Facultad de Ingeniería Química,
Universidad Nacional del Litoral, Santiago del Estero 2829, 3000 Santa Fe, Argentina

Received 2 July 2001; received in revised form 27 September 2001

Abstract

A new methodology for the kinetic treatment of electrode reactions is presented. It is based on a theoretical analysis of the predictive capability of different mechanisms for the dependence of the polarisation resistance on the different operative variables. This procedure is applied in this case to the analysis of the chlorine electrode reaction on Ti/RuO$_2$, for which the variation of the polarisation resistance on the activity of the chloride ions and on the partial pressure of the chlorine gas is derived. The descriptive capability of the mechanisms under discussion at present for this reaction is discussed and the theoretical dependences are compared with experimental data. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Chlorine electrode reaction; Ti/RuO$_2$ electrode; Polarisation resistance; Kinetic mechanisms

1. Introduction

The polarisation resistance (Rp) has been occasionally used for the kinetic analysis of electrode reactions that can be studied around the equilibrium potential, such as those of hydrogen (HER) and chlorine (ClER) on several electrode materials like noble metals [1–3] and oxides [4–6]. The expression relating the polarisation resistance with the elementary kinetic parameters involved in the Volmer–Heyrovsky–Tafel (VHT) mechanism has been recently derived for the HER [7]. However, the potentiality of this variable for a complete kinetic study of an electrodic reaction has not been explored yet. Therefore, a complete aprioristic analysis of the descriptive capability of a given mechanism, guided to obtain the functionality of the polarisation resistance with the operative variables, should be of interest.

The present analysis is focused in the ClER on Ti/RuO$_2$, as the experimental dependences of Rp on the activity of the chloride ions ($a_{\mathrm{Cl}^-}^{o'}$) and the partial pressure of chlorine ($\bar{p}_{\mathrm{Cl}_2}$) were determined [8]. The theoretical relationships $Rp = Rp(a_{\mathrm{Cl}^-}^{o'}, p_1^k, \ldots, p_n^k)$ and $Rp = Rp(\bar{p}_{\mathrm{Cl}_2}, p_1^k, \ldots, p_n^k)$ are derived for different mechanisms, being p_i^k the kinetic parameters of the elementary steps corresponding to the k mechanism. On this basis, the kinetic parameters p_i^k are evaluated by regression of one type of experimental data, for example Rp versus $a_{\mathrm{Cl}^-}^{o'}$. Then, substituting them in $Rp = Rp(\bar{p}_{\mathrm{Cl}_2}, p_1^k, \ldots, p_n^k)$, the Rp versus $\bar{p}_{\mathrm{Cl}_2}$ dependence is predicted and compared with the experimental results. This procedure, which can be also applied viceversa, gives strong evidence in order to validate a given kinetic mechanism, much more accurate than the simple correlation of experimental data.

The ClER depends directly on the variables $a_{\mathrm{Cl}^-}^{o'}$ and $\bar{p}_{\mathrm{Cl}_2}$, as it is already stated. However, it is known that the reaction rate is also influenced by pH [8,9]. On this sense, it has been demonstrated that the effect of this variable can be satisfactorily explained on the basis of a surface model that takes into account the inhibition of active sites by protons [8]. Therefore, the mechanisms

---

* Corresponding author. Tel.: +54-342-4571-164; fax: +54-342-4571-162.

E-mail address: achialvo@fiqus.unl.edu.ar (A.C. Chialvo).

[1] ISE member.

0013-4686/02/$ - see front matter © 2002 Elsevier Science Ltd. All rights reserved.
PII: S0013-4686(01)00838-6

under study are Volmer–Heyrovsky–Tafel and Volmer–Krishtalik, which do not involve protonated intermediates.

2. Theoretical analysis

2.1. Fundamentals

The expression of the intrinsic polarisation resistance (Rp_o), independent of pH, as a function of the equilibrium reaction rates can be obtained from the derivative of the theoretical expression of the dependence of the current density on overpotential. This is derived from the mass balances of the global reaction in stationary state [10], assuming a given behaviour for the adsorption of the intermediate species, as it was carried out for the HER under the mechanism of VHT [7]. Nevertheless, this expression can also be deduced from a general treatment based on the formalism of the Thermodynamics of the irreversible processes [11]. Basically, the relationship between the rate (V) and the electrochemical affinity (A) of the global reaction is obtained through the relationships between the rates and affinities of the elementary steps, respectively [7,11]. In this context, the following equality is considered [7]:

$$\lim_{\eta \to 0} \frac{V}{A} = \frac{1}{(nF)^2 Rp_o} \tag{1}$$

where η is the overpotential, n is the number of transferred electrons and F is the Faraday constant. Therefore, applying Eq. (1) to a given kinetic mechanism the expression of Rp_o as a function of the equilibrium reaction rates is obtained. Finally, from the corresponding expressions of the reaction rates of the elementary steps [12], the dependences of Rp_o on the operative variables can also be derived.

2.2. Volmer–Heyrovsky–Tafel mechanism

2.2.1. Reaction rate on steady state

The application of the mechanism of Volmer–Heyrovsky–Tafel (VHT) to the ClER involves the following elementary reaction steps:

$$-\mathrm{S}^Z + \mathrm{Cl}^- \leftrightarrows -\mathrm{SCl}^Z + \mathrm{e}^- \tag{V}$$

$$-\mathrm{SCl}^Z + \mathrm{Cl}^- \leftrightarrows -\mathrm{S}^Z + \mathrm{Cl}_{2(g)} + \mathrm{e}^- \tag{H}$$

$$-\mathrm{SCl}^Z + -\mathrm{SCl}^Z \leftrightarrows 2\text{-}\mathrm{S}^Z + \mathrm{Cl}_{2(g)} \tag{T}$$

The following relationships between the global reaction rate and the corresponding rates of the elementary steps was obtained by means of a mass balance of the reaction in stationary state [10]:

$$2V = v_\mathrm{V} + v_\mathrm{H} = 2(v_\mathrm{H} + v_\mathrm{T}) = 2(v_\mathrm{V} - v_\mathrm{T}) \tag{2}$$

being $v_i = v_{+i} - v_{-i}$, where the subscript i refers to an elementary step.

2.2.2. Dependence of the polarisation resistance on the equilibrium parameters

The expression of Rp_o as a function of the equilibrium reaction rates has been previously obtained for the HER [7] and is identical for the ClER:

$$Rp_o = \frac{RT}{4F^2}\left(\frac{4v_\mathrm{T}^\mathrm{e} + v_\mathrm{H}^\mathrm{e} + v_\mathrm{V}^\mathrm{e}}{v_\mathrm{V}^\mathrm{e} v_\mathrm{H}^\mathrm{e} + v_\mathrm{V}^\mathrm{e} v_\mathrm{T}^\mathrm{e} + v_\mathrm{H}^\mathrm{e} v_\mathrm{T}^\mathrm{e}}\right) \tag{3}$$

where v_i^e is the equilibrium reaction rate of the step i.

2.2.3. Dependence of the polarisation resistance on the operative variables

From the dependences of the reaction rates of the elementary steps on the electrode potential [12] and considering a Langmuir type adsorption for the reaction intermediate, the expressions of the corresponding equilibrium reaction rates can be written as:

$$v_\mathrm{V}^\mathrm{e} = k_{+\mathrm{V}}(1-\theta^\mathrm{e})a_{\mathrm{Cl}^-}^{\mathrm{o'}} \mathrm{e}^{\alpha f E^\mathrm{e}} = k_{-\mathrm{V}}\theta^\mathrm{e}\mathrm{e}^{-(1-\alpha)fE^\mathrm{e}} \tag{4}$$

$$v_\mathrm{H}^\mathrm{e} = k_{+\mathrm{H}}\theta^\mathrm{e} a_{\mathrm{Cl}^-}^{\mathrm{o'}} \mathrm{e}^{\alpha f E^\mathrm{e}} = k_{-\mathrm{H}}(1-\theta^\mathrm{e})\bar{p}_{\mathrm{Cl}_2}\mathrm{e}^{-(1-\alpha)fE^\mathrm{e}} \tag{5}$$

$$v_\mathrm{T}^\mathrm{e} = k_{+\mathrm{T}}(\theta^\mathrm{e})^2 = k_{-\mathrm{T}}(1-\theta^\mathrm{e})^2\bar{p}_{\mathrm{Cl}_2} \tag{6}$$

where k_{+i} and k_{-i} are, respectively, the constants of the forward and backward reaction rates of the step i, α is the symmetry factor (supposed equal for all the elementary steps), $f = F/RT$, E^e is the equilibrium potential, θ^e is the equilibrium surface coverage of the adsorbed Cl intermediate.

The dependence of θ^e on the chlorine partial pressure can be obtained from Eq. (6):

$$\theta^\mathrm{e} = \frac{\bar{p}_{\mathrm{Cl}_2}^{1/2}}{\bar{p}_{\mathrm{Cl}_2}^{1/2} + K_\mathrm{T}^{1/2}} \tag{7}$$

The linking relationships between the equilibrium constants of the elementary steps can be also derived considering a Nernstian behaviour of the equilibrium potential:

$$\frac{K_V K_T}{K_H} = 1, \quad K_\mathrm{V} K_\mathrm{T}^{1/2} = \mathrm{e}^{-fE^\circ}, \quad \frac{K_\mathrm{H}}{K_\mathrm{T}^{1/2}} = \mathrm{e}^{-fE^\circ} \tag{8}$$

where $K_i = k_{+i}/k_{-i}$ is the equilibrium constant of the step i and E° is the standard potential of the ClER.

Rearranging Eqs. (4)–(6), substituting Eq. (7) in them and taking into account the relationships (8), the expressions of the equilibrium reaction rates are obtained as a function of the variables $a_{\mathrm{Cl}^-}^{\mathrm{o'}}$ and $\bar{p}_{\mathrm{Cl}_2}$:

$$v_\mathrm{V}^\mathrm{e} = k_{+\mathrm{V}} K_\mathrm{T} \mathrm{e}^{\alpha f E^\circ} \frac{a_{\mathrm{Cl}^-}^{o'(1-\alpha)} \bar{p}_{\mathrm{Cl}_2}^{\alpha/2}}{(\bar{p}_{\mathrm{Cl}_2}^{1/2} + K_\mathrm{T}^{1/2})} \tag{9}$$

$$v_\mathrm{H}^\mathrm{e} = k_{+\mathrm{H}} \mathrm{e}^{\alpha f E^\circ} \frac{a_{\mathrm{Cl}^-}^{\mathrm{o'}(1-\alpha)} \bar{p}_{\mathrm{Cl}_2}^{\frac{(1+\alpha)}{2}}}{(\bar{p}_{\mathrm{Cl}_2}^{1/2} + K_\mathrm{T}^{1/2})} \tag{10}$$

$$v^{\mathrm{e}}_{\mathrm{T}} = k_{+\mathrm{T}} \frac{\bar{p}_{\mathrm{Cl_2}}}{(\bar{p}^{1/2}_{\mathrm{Cl_2}} + K^{1/2}_{\mathrm{T}})^2} \tag{11}$$

The corresponding expression of Rp_{o}, obtained replacing Eqs. (9)–(11) into Eq. (3), is:

$$Rp_{\mathrm{o}} = \frac{RT}{4F^2}\left[\frac{4\dfrac{k_{+\mathrm{T}}\bar{p}^{(1-\alpha/2)}_{\mathrm{Cl_2}}}{k_{\mathrm{V}}a^{\mathrm{o'}(1-\alpha)}_{\mathrm{Cl^-}}} + (\bar{p}^{1/2}_{\mathrm{Cl_2}} + K^{1/2}_{\mathrm{T}})\left(\dfrac{k_{\mathrm{H}}}{k_{\mathrm{V}}}\bar{p}^{1/2}_{\mathrm{Cl_2}} + K_{\mathrm{T}}\right)}{4\dfrac{k_{+\mathrm{T}}\bar{p}^{(1-\alpha/2)}_{\mathrm{Cl_2}}}{k_{\mathrm{V}}a^{\mathrm{o'}(1-\alpha)}_{\mathrm{Cl^-}}}\left(\dfrac{k_{\mathrm{H}}}{k_{\mathrm{V}}}\bar{p}^{1/2}_{\mathrm{Cl_2}} + K_{\mathrm{T}}\right) + \dfrac{k_{\mathrm{H}}}{k_{\mathrm{V}}}\bar{p}^{1/2}_{\mathrm{Cl_2}}(\bar{p}^{1/2}_{\mathrm{Cl_2}} + K^{1/2}_{\mathrm{T}})}\right]\frac{(\bar{p}^{1/2}_{\mathrm{Cl_2}} + K^{1/2}_{\mathrm{T}})}{k_{\mathrm{V}}K_{\mathrm{T}}a^{\mathrm{o'}(1-\alpha)}_{\mathrm{Cl^-}}\bar{p}^{\alpha/2}_{\mathrm{Cl_2}}} \tag{12}$$

where $k_{\mathrm{V}} = k_{+\mathrm{V}}\mathrm{e}^{\alpha f E^\circ}$ and $k_{\mathrm{H}} = k_{+\mathrm{H}}\mathrm{e}^{\alpha f E^\circ}$. Eq. (12) contains the constants of the forward reaction rates of the elementary steps and the equilibrium constant of the Tafel step. The other equilibrium constants are related to this through the relationships (8).

2.3. Volmer–Krishtalik mechanism

The mechanism of Volmer–Krishtalik (VK) is known in two kinetically equivalent schemes [13], which will be called original (o) and modified (m) respectively.

$$-\mathrm{SCl}^{Z} \leftrightarrows -\mathrm{SCl}^{Z+1} + \mathrm{e}^- \tag{o1}$$

$$-\mathrm{S}^{Z} + \mathrm{Cl}^- \leftrightarrows -\mathrm{SCl}^{Z} + \mathrm{e}^- \tag{o2}$$

$$-\mathrm{SCl}^{Z+1} + \mathrm{Cl}^- \leftrightarrows -\mathrm{S}^{Z} + \mathrm{Cl}_{2(\mathrm{g})} \tag{o3}$$

$$-\mathrm{S}^{Z} \leftrightarrows -\mathrm{S}^{Z+1} + \mathrm{e}^- \tag{m1}$$

$$-\mathrm{S}^{Z+1} + \mathrm{Cl}^- \leftrightarrows -\mathrm{SCl}^{Z+1} + \mathrm{e}^- \tag{m2}$$

$$-\mathrm{SCl}^{Z+1} + \mathrm{Cl}^- \leftrightarrows -\mathrm{S}^{Z} + \mathrm{Cl}_{2(\mathrm{g})} \tag{m3}$$

Ignoring the nature of the involved species, it is verified that step (o1) is equivalent to (m1), steps (o2) to (m2) and steps (o3) to (m3). Therefore, both mechanisms lead to the same expressions for the surface coverage of the intermediate species and for j versus η, which were previously obtained [14]. The corresponding equations for the polarisation resistance as a function of the equilibrium reaction rates are also the same. Nevertheless, it should be taken into account that the surface coverages are referred to different species. Moreover, the equilibrium constants and thus Rp_{o} have different dependences on the experimental variables. It can be observed that both outlines consider a step of oxidation of the superficial sites, (o1) and (m1) respectively, and the difference among them resides in their nature. While in the modified scheme the loss of electrons takes place in an empty site generating an active site, in the original the site with the intermediate already adsorbed is oxidised.

2.3.1. Reaction rate on steady-state

For each one of the schemes under analysis, the reaction mechanism has three elementary steps and two intermediate species, so that only one linearly independent route can be considered. The relationship between the global reaction rate and the corresponding reaction rates of the elementary steps are [14]:

$$2V = v_1 + v_2 = v_1 + v_3 = v_2 + v_3 = 2v_1 = 2v_2 = 2v_3 \tag{13}$$

where the subscript is referred to the step oi or mi ($i = 1, 2, 3$).

2.3.2. Dependence of the polarisation resistance on the equilibrium rates

The relationship between the electrochemical affinity of the global reaction rate and those of the elementary steps is:

$$A = A_1 + A_2 + A_3 \tag{14}$$

The relationship between A and V is obtained from Eqs. (13) and (14) and taking into account the relationship between the affinity and the reaction rate of an elementary step when the system is near the equilibrium state [11]:

$$A = RT\left(\frac{1}{v^{e}_{1}} + \frac{1}{v^{e}_{2}} + \frac{1}{v^{e}_{3}}\right)V \tag{15}$$

Finally, the expression of the polarisation resistance as a function of the equilibrium reaction rates for both schemes of the VK mechanism is achieved from Eq. (1) to Eq. (15):

$$Rp_{\mathrm{o}} = \frac{RT}{4F^2}\left(\frac{1}{v^{\mathrm{e}}_{1}} + \frac{1}{v^{\mathrm{e}}_{2}} + \frac{1}{v^{\mathrm{e}}_{3}}\right) \tag{16}$$

Eq. (16) can also be obtained evaluating the derivative at $\eta = 0$ of the expression of the current density on overpotential [14].

2.3.3. Dependence of the polarisation resistance on the operative variables. Original scheme

The expressions of the equilibrium reaction rates of the elementary steps are:

$$v^{\mathrm{e}}_{1} = k_{+1}\theta^{\mathrm{e}}_{\mathrm{I}}\mathrm{e}^{\alpha f E^{\mathrm{e}}} = k_{-1}\theta^{\mathrm{e}}_{\mathrm{II}}\mathrm{e}^{-(1-\alpha)fE^{\mathrm{e}}} \tag{17}$$

$$v^{\mathrm{e}}_{2} = k_{+2}(1-\theta^{\mathrm{e}})a^{\mathrm{o'}}_{\mathrm{Cl^-}}\mathrm{e}^{\alpha f E^{\mathrm{e}}} = k_{-2}\theta^{\mathrm{e}}_{\mathrm{I}}\mathrm{e}^{-(1-\alpha)fE^{\mathrm{e}}} \tag{18}$$

$$v^{\mathrm{e}}_{3} = k_{+3}\theta^{\mathrm{e}}_{\mathrm{II}}a^{\mathrm{o'}}_{\mathrm{Cl^-}} = k_{-3}(1-\theta^{\mathrm{e}})\bar{p}_{\mathrm{Cl_2}} \tag{19}$$

where θ_{I} is the surface coverage of adsorbed Cl on the non-oxidised sites ($-\mathrm{SCl}^{Z}$), θ_{II} is the surface coverage of adsorbed Cl on the oxidised sites ($-\mathrm{SCl}^{Z+1}$), $\theta = \theta_{\mathrm{I}} + \theta_{\mathrm{II}}$, $(1-\theta)$ is the fraction of non-oxidised free sites ($-\mathrm{S}^{Z}$) and the superscript e is referred to equilibrium values.

The corresponding equations of the surface coverage of the intermediate species can be derived from Eq. (17) to Eq. (19):

$$\theta^{\mathrm{e}}_{\mathrm{I}} = \frac{K_2\mathrm{e}^{fE^\circ}\bar{p}^{1/2}_{\mathrm{Cl}_2}a^{\mathrm{o}'}_{\mathrm{Cl}-}}{K_2\mathrm{e}^{fE^\circ}\bar{p}^{1/2}_{\mathrm{Cl}_2}(a^{\mathrm{o}'}_{\mathrm{Cl}-} + K_1\mathrm{e}^{fE^\circ}\bar{p}^{1/2}_{\mathrm{Cl}_2}) + a^{\mathrm{o}'}_{\mathrm{Cl}-}} \tag{20}$$

$$\theta^{\mathrm{e}}_{\mathrm{II}} = \frac{K_1K_2\mathrm{e}^{2fE^\circ}\bar{p}_{\mathrm{Cl}_2}}{K_2\mathrm{e}^{fE^\circ}\bar{p}^{1/2}_{\mathrm{Cl}_2}(a^{\mathrm{o}'}_{\mathrm{Cl}-} + K_1\mathrm{e}^{fE^\circ}\bar{p}^{1/2}_{\mathrm{Cl}_2}) + a^{\mathrm{o}'}_{\mathrm{Cl}-}} \tag{21}$$

as well as the following linking relationship between the equilibrium constants of the elementary steps:

$$K_1K_2K_3 = \mathrm{e}^{-2fE^\circ} \tag{22}$$

Rearranging Eqs. (17)–(19), substituting Eqs. (20) and (21) in them and taking into account Eq. (22), the expressions of the equilibrium reaction rates as a function of the operative variables are derived:

$$v^{\mathrm{e}}_1 = \frac{k_{+1}K_2\mathrm{e}^{(1+\alpha)fE^\circ}a^{\mathrm{o}'(1-\alpha)}_{\mathrm{Cl}-}\bar{p}^{\frac{1+\alpha}{2}}_{\mathrm{Cl}_2}}{K_2\mathrm{e}^{fE^\circ}\bar{p}^{1/2}_{\mathrm{Cl}_2}(a^{\mathrm{o}'}_{\mathrm{Cl}-} + K_1\mathrm{e}^{fE^\circ}\bar{p}^{1/2}_{\mathrm{Cl}_2}) + a^{\mathrm{o}'}_{\mathrm{Cl}-}} \tag{23}$$

$$v^{\mathrm{e}}_2 = \frac{k_{+2}\mathrm{e}^{\alpha fE^\circ}a^{\mathrm{o}'(2-\alpha)}_{\mathrm{Cl}-}\bar{p}^{\alpha/2}_{\mathrm{Cl}_2}}{K_2\mathrm{e}^{fE^\circ}\bar{p}^{1/2}_{\mathrm{Cl}_2}(a^{\mathrm{o}'}_{\mathrm{Cl}-} + K_1\mathrm{e}^{fE^\circ}\bar{p}^{1/2}_{\mathrm{Cl}_2}) + a^{\mathrm{o}'}_{\mathrm{Cl}-}} \tag{24}$$

$$v^{\mathrm{e}}_3 = \frac{k_{-3}a^{\mathrm{o}'}_{\mathrm{Cl}-}\bar{p}_{\mathrm{Cl}_2}}{K_2\mathrm{e}^{fE^\circ}\bar{p}^{1/2}_{\mathrm{Cl}_2}(a^{\mathrm{o}'}_{\mathrm{Cl}-} + K_1\mathrm{e}^{fE^\circ}\bar{p}^{1/2}_{\mathrm{Cl}_2}) + a^{\mathrm{o}'}_{\mathrm{Cl}-}} \tag{25}$$

Finally, replacing Eqs. (23)–(25) into Eq. (16) and grouping constants, the corresponding expression of the polarisation resistance for the original scheme of the VK mechanism is obtained:

$$Rp_{\mathrm{o}} = \frac{RT}{4F^2}\left[\frac{a^{\mathrm{o}'}_{\mathrm{Cl}-}}{k_1K'_2\bar{p}^{(1-\alpha)/2}_{\mathrm{Cl}_2}} + \frac{1}{k_2a^{\mathrm{o}'}_{\mathrm{Cl}-}\bar{p}^{\alpha/2}_{\mathrm{Cl}_2}} + \frac{1}{k_{-3}\bar{p}_{\mathrm{Cl}_2}}\right]\left(K'_1K'_2\frac{\bar{p}_{\mathrm{Cl}_2}}{a^{\mathrm{o}'}_{\mathrm{Cl}-}} + K'_2\bar{p}^{1/2}_{\mathrm{Cl}_2} + 1\right) \tag{26}$$

where $k_1 = k_{+1}\mathrm{e}^{\alpha fE^\circ}$, $k_2 = k_{+2}\mathrm{e}^{\alpha fE^\circ}$, $K'_1 = K_1\mathrm{e}^{fE^\circ}$ and $K'_2 = K_2\mathrm{e}^{fE^\circ}$.

It should be noticed that although Eq. (26) involves only some of the kinetic and equilibrium constants of the elementary steps, the other can be calculated by Eq. (22).

2.3.4. Dependence of the polarisation resistance on the operative variables. Modified scheme

The equilibrium reaction rates of the elementary steps are:

$$v^{\mathrm{e}}_1 = k_{+1}(1-\theta^{\mathrm{e}})\mathrm{e}^{\alpha fE^{\mathrm{e}}} = k_{-1}\theta^{\mathrm{e}}_{\mathrm{I}}\mathrm{e}^{-(1-\alpha)fE^{\mathrm{e}}} \tag{27}$$

$$v^{\mathrm{e}}_2 = k_{+2}\theta^{\mathrm{e}}_{\mathrm{I}}a^{\mathrm{o}'}_{\mathrm{Cl}-}\mathrm{e}^{\alpha fE^{\mathrm{e}}} = k_{-2}\theta^{\mathrm{e}}_{\mathrm{II}}\mathrm{e}^{-(1-\alpha)fE^{\mathrm{e}}} \tag{28}$$

$$v^{\mathrm{e}}_3 = k_{+3}\theta^{\mathrm{e}}_{\mathrm{II}}a^{\mathrm{o}'}_{\mathrm{Cl}-} = k_{-3}(1-\theta^{\mathrm{e}})\bar{p}_{\mathrm{Cl}_2} \tag{29}$$

In this case θ_{I} is the fraction of oxidised sites ($-\mathrm{S}^{Z+1}$) while θ_{II} and $(1-\theta)$ have the same meaning as in the original scheme.

The following expressions of the surface coverages of the intermediate species, the equilibrium reaction rates and the polarisation resistance as a function of $a^{\mathrm{o}'}_{\mathrm{Cl}-}$ and $\bar{p}_{\mathrm{Cl}_2}$were obtained by the procedure described previously:

$$\theta^{\mathrm{e}}_{\mathrm{I}} = \frac{K_1\mathrm{e}^{fE^\circ}\bar{p}^{1/2}_{\mathrm{Cl}_2}}{K_1\mathrm{e}^{fE^\circ}\bar{p}^{1/2}_{\mathrm{Cl}_2}(1 + K_2\mathrm{e}^{fE^\circ}\bar{p}^{1/2}_{\mathrm{Cl}_2}) + a^{\mathrm{o}'}_{\mathrm{Cl}-}} \tag{30}$$

$$\theta^{\mathrm{e}}_{\mathrm{II}} = \frac{K_1K_2\mathrm{e}^{2fE^\circ}\bar{p}_{\mathrm{Cl}_2}}{K_1\mathrm{e}^{fE^\circ}\bar{p}^{1/2}_{\mathrm{Cl}_2}(1 + K_2\mathrm{e}^{fE^\circ}\bar{p}^{1/2}_{\mathrm{Cl}_2}) + a^{\mathrm{o}'}_{\mathrm{Cl}-}} \tag{31}$$

$$v^{\mathrm{e}}_1 = \frac{k_{+1}\mathrm{e}^{\alpha fE^\circ}a^{\mathrm{o}'(1-\alpha)}_{\mathrm{Cl}-}\bar{p}^{\alpha/2}_{\mathrm{Cl}_2}}{K_1\mathrm{e}^{fE^\circ}\bar{p}^{1/2}_{\mathrm{Cl}_2}(1 + K_2\mathrm{e}^{fE^\circ}\bar{p}^{1/2}_{\mathrm{Cl}_2}) + a^{\mathrm{o}'}_{\mathrm{Cl}-}} \tag{32}$$

$$v^{\mathrm{e}}_2 = \frac{k_{+2}K_1\mathrm{e}^{(1+\alpha)fE^\circ}a^{\mathrm{o}'(1-\alpha)}_{\mathrm{Cl}-}\bar{p}^{\frac{1+\alpha}{2}}_{\mathrm{Cl}_2}}{K_1\mathrm{e}^{fE^\circ}\bar{p}^{1/2}_{\mathrm{Cl}_2}(1 + K_2\mathrm{e}^{fE^\circ}\bar{p}^{1/2}_{\mathrm{Cl}_2}) + a^{\mathrm{o}'}_{\mathrm{Cl}-}} \tag{33}$$

$$v^{\mathrm{e}}_3 = \frac{k_{-3}a^{\mathrm{o}'}_{\mathrm{Cl}-}\bar{p}_{\mathrm{Cl}_2}}{K_1\mathrm{e}^{fE^\circ}\bar{p}^{1/2}_{\mathrm{Cl}_2}(1 + K_2\mathrm{e}^{fE^\circ}\bar{p}^{1/2}_{\mathrm{Cl}_2}) + a^{\mathrm{o}'}_{\mathrm{Cl}-}} \tag{34}$$

$$Rp_{\mathrm{o}} = \frac{RT}{4F^2}\left[\left(\frac{1}{k_1} + \frac{1}{k_2K'_1\bar{p}^{1/2}_{\mathrm{Cl}_2}}\right)\frac{a^{\mathrm{o}'\alpha}_{\mathrm{Cl}-}}{\bar{p}^{\alpha/2}_{\mathrm{Cl}_2}} + \frac{1}{k_{-3}\bar{p}_{\mathrm{Cl}_2}}\right]\left[K'_1\frac{\bar{p}^{1/2}_{\mathrm{Cl}_2}}{a^{\mathrm{o}'}_{\mathrm{Cl}-}}(1 + K'_2\bar{p}^{1/2}_{\mathrm{Cl}_2}) + 1\right] \tag{35}$$

where $k_1 = k_{+1}\mathrm{e}^{\alpha fE^\circ}$, $k_2 = k_{+2}\mathrm{e}^{\alpha fE^\circ}$, $K'_1 = K_1\mathrm{e}^{fE^\circ}$ and $K'_2 = K_2\mathrm{e}^{fE^\circ}$. It should be noticed that Eq. (35) establishes different dependences of Rp_{o} on $a^{\mathrm{o}'}_{\mathrm{Cl}-}$ and $\bar{p}_{\mathrm{Cl}_2}$with respect to the original scheme. It should be mentioned that the linking relationship between the equilibrium constants of the elementary steps is the same as the original scheme, given by Eq. (22).

3. Analysis of the descriptive capability of the studied mechanisms

Holding one of the two variables ($a^{\mathrm{o}'}_{\mathrm{Cl}-}$or $\bar{p}_{\mathrm{Cl}_2}$) constant, particular expressions of Eqs. (12), (26) and (35) are obtained. The descriptive capability of each one of these equations was evaluated for different values of the kinetic parameters in the range of Rp values less than 10 kΩ cm^{-2}, which corresponds to the domain of experimental determinations. Some of these simulations are shown in Fig. 1 for the three mechanisms under study. It should be noticed that for a given set of constants, each mechanism establishes unique dependences Rp_{o} versus $a^{\mathrm{o}'}_{\mathrm{Cl}-}$and Rp_o versus $\bar{p}_{\mathrm{Cl}_2}$.

It has been determined that all mechanisms have the capability to describe increasing or decreasing dependences of Rp_{o} on $\bar{p}_{\mathrm{Cl}_2}$ in the range of pressures analysed, but it is not so for the dependences Rp_{o} versus $a^{\mathrm{o}'}_{\mathrm{Cl}-}$. In this case, the mechanism VHT can only predict a decreasing behaviour of Rp_{o} on $a^{\mathrm{o}'}_{\mathrm{Cl}-}$, independently of the values assigned to the parameters. Meanwhile, both schemes of the VK mechanism can predict also decreasing responses, which can present a minimum depending on the values of the kinetic parameters.

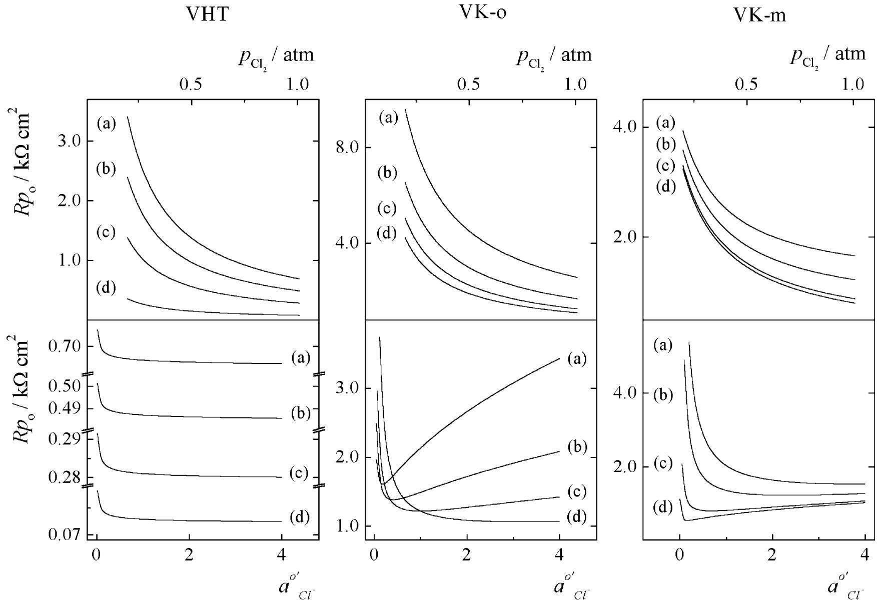

Fig. 1. Simulations of the dependences Rp_o vs. $\bar{p}_{Cl_2}$(C_{Cl^-} = 2 M) and Rp_o vs. $a^{o'}_{Cl^-}$($\bar{p}_{Cl_2}$ = 1 atm) for the ClER through the Volmer–Heyrovsky–Tafel, original Volmer–Krishtalik and modified Volmer–Krishtalik mechanisms. T = 30 °C. Kinetics parameters: VHT: $k_V = 10^{-15}$, $k_H = 10^{-5}$, $k_{+T} = 10^{-6}$, $K_T = 10^3$ (a), 4×10^3 (b), 7×10^3 (c), 10^4 (d); original VK: $k_1 = 10^3$, $k_2 = 10^3$, $k_{-3} = 10^{-10}$, $K'_1 = 10^{12}$, $K'_2 = 5 \times 10^{-14}$ (a), 10^{-13} (b), 2×10^{-13} (c), 5×10^{-13} (d); modified VK: $k_1 = 1$, $k_2 = 10^3$, $k_{-3} = 2 \times 10^{-10}$, $K'_1 = 2 \times 10^{-13}$, $K'_2 = 10^{13}$ (a), 5×10^{12} (b), 10^{12} (c), 10^{11} (d). k_i in mol s^{-1} cm^{-2}.

4. Analysis of experimental results

In the first part [8], the experimental measurements of the polarisation resistance were described. It was also analysed the influence of pH, so that the calculated values of Rp_o are free from the influence of this variable. The dependences of Rp_o on $\bar{p}_{Cl_2}$ and $a^{o'}_{Cl^-}$ are shown in Fig. 2. It can be observed an increase in the polarisation resistance as the activity of chloride ions increases, seeming that the curve passes through a minimum in the range $0.1 < a^{o'}_{Cl^-} < 1$.

4.1. Analysis by the Volmer–Heyrovsky–Tafel mechanism

It has been indicated in a previous item that Eq. (12) cannot predict an increasing dependence of Rp_o on $a^{o'}_{Cl^-}$, as it is observed experimentally, independently of the values assigned to the constants. Consequently, this mechanism should be discarded for the description of the ClER on Ti/RuO$_2$ electrodes.

4.2. Analysis by the Volmer–Krishtalik mechanism (original scheme)

Following the proposed methodology, the parameters involved in Eq. (26) were evaluated by fitting the experimental dependences Rp_o versus $\bar{p}_{Cl_2}$ at $a^{o'}_{Cl^-}$ constant, taking the symmetry factor $\alpha = 0.5$. It can be observed in Fig. 3I that the correlations corresponding to three different chloride concentrations (2, 3 and 4 M) can be considered acceptable. The corresponding kinetic constants obtained from these correlations are shown in Table 1(a, b and c). Nevertheless, when starting from these results the dependence Rp_o versus $a^{o'}_{Cl^-}$ at $\bar{p}_{Cl_2} = 1$ atm is predicted (Fig. 3II), the resulting values of Rp_o are almost independent of $a^{o'}_{Cl^-}$, although they are in the order of the experimental values. Correlations were also carried out with other values of α, but

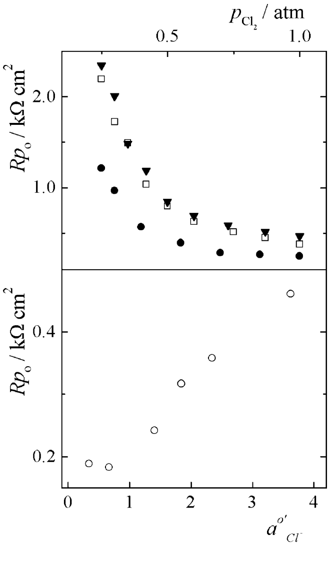

Fig. 2. Experimental dependences Rp_o vs. $\bar{p}_{Cl_2}$ and Rp_o vs. $a^{o'}_{Cl^-}$ for the ClER in NaCl–HCl solutions saturated with Cl$_{2(g)}$. C_{Cl^-} = 2 M (●), 3 M (□), 4 M (▼); $\bar{p}_{Cl_2}$ = 1 atm (○). T = 30 °C.

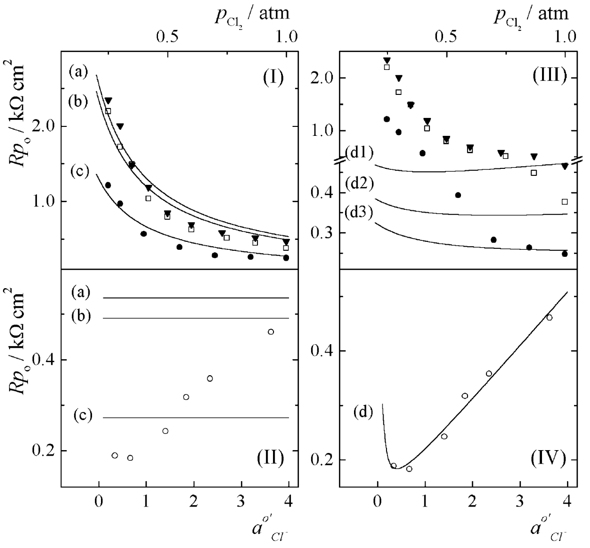

Fig. 3. Correlations of the experimental dependences Rp_o vs. $\bar{p}_{Cl_2}$ (I) and Rp_o vs. $a^{o'}_{Cl-}$ (IV) for the ClER by the original VK mechanism, and their corresponding simulations of the dependences Rp_o vs. $a^{o'}_{Cl-}$(II) and Rp_o vs. $\bar{p}_{Cl_2}$ (III) using the kinetic parameters obtained from each fitting (Table 1). Correlations: C_{Cl-} = 4 M (a), 3 M (b), 2 M (c); $\bar{p}_{Cl_2}$ = 1 atm (d). Simulations: $\bar{p}_{Cl_2}$ = 1 atm (a, b, c); C_{Cl-} = 4 M (d1), 3 M (d2), 2 M (d3).

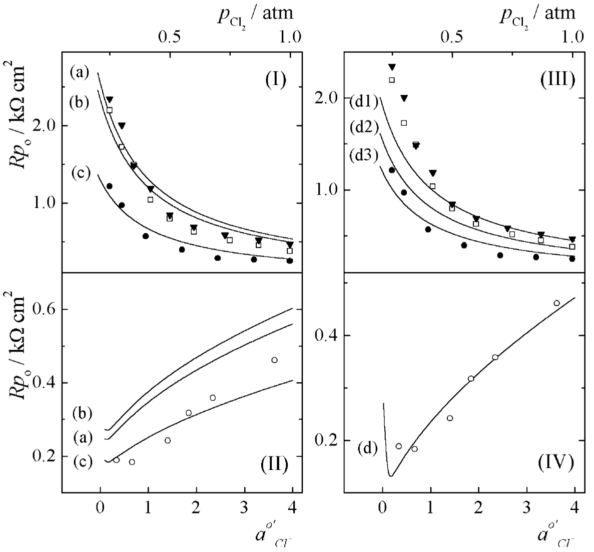

Fig. 4. Correlations of the experimental dependences Rp_o vs. $\bar{p}_{Cl_2}$ (I) and Rp_o vs. $a^{o'}_{Cl-}$ (IV) for the ClER by the modified VK mechanism, and their corresponding simulations of the dependences Rp_o vs. $a^{o'}_{Cl-}$(II) and Rp_o vs. $\bar{p}_{Cl_2}$ (III) using the kinetic parameters obtained from each fitting (Table 2). Correlations: C_{Cl-} = 4 M (a), 3 M (b), 2 M (c); $\bar{p}_{Cl_2}$ = 1 atm (d). Simulations: $\bar{p}_{Cl_2}$ = 1 atm (a, b, c); C_{Cl-} = 4 M (d1), 3 M (d2), 2 M (d3).

the descriptive capability of Eq. (26) were not improved.

On the other hand, if the order of the analysis is inverted, that is the experimental Rp_o versus $a^{o'}_{Cl-}$-plot is correlated, the results are good (Fig. 3IV) and the corresponding values of the obtained constants are indicated in Table 1(d). However, the simulations of the dependence Rp_o versus $\bar{p}_{Cl_2}$(Fig. 3III) with these parameters are unacceptable. The range of variation of the simulated values of Rp_o (~ 0.038 kΩ cm² atm^{-1}) is almost one order of magnitude less than that of the corresponding experimental values. Moreover, for the highest concentrations of Cl$^-$, the simulations cannot even describe the experimental decreasing variations.

It should be noticed that the equilibrium surface coverages θ^e_I and θ^e_{II} evaluated from Eqs. (20) and (21) have a maximum variation of $\Delta\theta^e_I < 0.1$ and $\Delta\theta^e_{II} < 0.1$ in the whole range of $\bar{p}_{Cl_2}$and $a^{o'}_{Cl-}$ values.

4.3. Analysis by the Volmer–Krishtalik mechanism (modified scheme)

The correlation of the experimental data through Eq. (35), following the proposed methodology, are shown in Fig. 4I, IV. The corresponding values of the kinetic parameters are illustrated in Table 2. The response of this mechanism in relation to the correlation of the dependence of Rp_o on $\bar{p}_{Cl_2}$is similar to that of the original scheme. The description of the experimental Rp_o versus $a^{o'}_{Cl-}$-plot with the parameters obtained in the previous correlation is again not acceptable. Nevertheless, the correlation of the experimental data Rp_o versus $a^{o'}_{Cl-}$-is good and the resulting parameters lead to a description of the dependence Rp_o versus $\bar{p}_{Cl_2}$much more accurate than that of the original scheme, especially at the higher values of $\bar{p}_{Cl_2}$. This should be due to the parameters were calculated at 1 atm. The equi-

Table 1

Kinetic and equilibrium constants of the elementary steps of the ClER obtained from the correlation of the experimental data Rp_o vs. $\bar{p}_{Cl_2}$ (a, b and c) and Rp_o vs. $a^{o'}_{Cl-}$ (d) by the original VK mechanism

	$k_{+1}e^{\alpha f E_o}$	$k_{+2}e^{\alpha f E_o}$	k_{-3}	$K_1 e^{f E_o}$	$K_2 e^{f E_o}$
(a)	7.25×10^{25}	5.51×10^{6}	1.26×10^{-10}	362.70	10^{-18}
(b)	2.11×10^{25}	1.20×10^{7}	1.38×10^{-10}	2.29	1.1×10^{-17}
(c)	1.41×10^{29}	8.65×10^{9}	2.49×10^{-10}	92.66	2×10^{-18}
(d)	6.78×10^{-10}	2.39×10^{-4}	1.61×10^{-5}	0.07245	23417.12

$k_{\pm i}$ in mol s^{-1} cm^{-2}.

librium surface coverages $\theta_{\mathrm{I}}^{\mathrm{e}}$ and $\theta_{\mathrm{II}}^{\mathrm{e}}$ evaluated from Eqs. (30) and (31) have a maximum variation of $\Delta\theta_{\mathrm{I}}^{\mathrm{e}} < 10^{-7}$ and $\Delta\theta_{\mathrm{II}}^{\mathrm{e}} < 0.1$ in the whole range of $\bar{p}_{\mathrm{Cl}_2}$and $a_{\mathrm{Cl}^-}^{\mathrm{o'}}$ values.

5. Discussion

A kinetic study carried out on porous electrode materials such as oxides obtained by thermal decomposition is intrinsically complex. Therefore, it should be done under special conditions, such as near the equilibrium potential of the reaction under evaluation. The polarisation resistance is the appropriate kinetic variable for this case, as it can be measured directly and free of any aprioristic restriction. However, the kinetic expressions habitually used for describing the j versus η plot were derived under a series of approaches, such as rate-determining step criteria or quasi-equilibrium assumption, which make these equations inapplicable near the equilibrium conditions. Nevertheless, kinetic expressions can be obtained in the framework of an analysis without the classical approximations [7,10]. Such expressions were derived and applied to the most important mechanisms outlined for the ClER on $\mathrm{RuO_2}$ electrodes.

The theoretical dependences of the polarisation resistance on the variables that influence the electrodic reaction were obtained for each mechanism under study. On this basis, an aprioristic analysis of the predictive capability of a given mechanism can be carried out in order to determine if it is intrinsically accurate for the correlation of experimental data. From the independent fitting of the variation of Rp on one of these variables, a set of kinetic parameters (p_i^k) is obtained. Then, it is verified if this set can reproduce appropriately the experimental variations of Rp on the other variables. This procedure introduces a strong restriction that makes this methodology highly reliable, as it is unlikely that an inappropriate mechanism can overcome this test successfully.

On this context, taking into account that experimental data of the intrinsic polarisation resistance as a function of the chloride ions concentration and the chlorine partial pressure were obtained and described in the part I [8], expressions of the dependences of Rp_{o} on $a_{\mathrm{Cl}^-}^{\mathrm{o'}}$ and $\bar{p}_{\mathrm{Cl}_2}$ were derived for the Volmer–Heyrovsky–Tafel mechanism and for both schemes, original and modified respectively, of the Volmer–Krishtalik mechanism. It has been considered a Langmuirian behaviour for the adsorbed intermediates. Taken into account that the variation of the equilibrium surface coverages in the experimental conditions was not significant, the reaction kinetics should be almost indifferent to the behaviour of the adsorbed intermediates. Therefore, the use of another adsorption isotherm should not introduce changes in the results obtained.

It has been proved that the VHT mechanism is unable to reproduce the observed behaviour, particularly the experimental Rp_{o} versus $a_{\mathrm{Cl}^-}^{\mathrm{o'}}$ plot, which shows a minimum. This solid argument confirms that this mechanism is not appropriate for the ClER on $\mathrm{RuO_2}$ electrodes. The main failure should be that the oxidation of the superficial sites of ruthenium dioxide at the potentials of the ClER [15,16] is not taken into account. Precisely, this step is the main difference between the mechanisms VHT and VK, being the nature of these oxidised sites the difference among the two schemes of this last mechanism. Both of them are qualitatively able to predict the observed behaviour of Rp_{o} as a function of $a_{\mathrm{Cl}^-}^{\mathrm{o'}}$ and $\bar{p}_{\mathrm{Cl}_2}$. A good agreement is achieved between the experimental and the theoretical response for the dependence Rp_{o} versus $a_{\mathrm{Cl}^-}^{\mathrm{o'}}$by means of the original scheme, from which a set of kinetic constants were calculated through least squares (Table 1d). Nevertheless, the self-consistency is not achieved on the description of the relationship Rp_{o} versus $\bar{p}_{\mathrm{Cl}_2}$, since the simulation using the kinetic constants obtained from the correlation of the Rp_{o} versus. $a_{\mathrm{Cl}^-}^{\mathrm{o'}}$data is not in agreement with the experimental results. On the other hand, the set of parameters (Table 2d) obtained with the modified scheme reproduces fairly well both dependences. The main failure of this scheme is the description of the dependence Rp_{o} versus $\bar{p}_{\mathrm{Cl}_2}$, especially for the lower values of $\bar{p}_{\mathrm{Cl}_2}$. This result suggests that there are probably certain aspects in the modelling of the effect of the chlorine partial pressure that were not appropriately taken into account. On this sense, the improvement of the predictive capability of the modified VK mechanism was intended through the adoption of a Frumkian behaviour for the adsorbed intermediates. However, the correlations were only

Table 2
Kinetic and equilibrium constants of the elementary steps of the ClER obtained from the correlation of the experimental data Rp_{o} vs. $\bar{p}_{\mathrm{Cl}_2}$ (a, b and c) and Rp_{o} vs. $a_{\mathrm{Cl}^-}^{\mathrm{o'}}$ (d) by the modified VK mechanism

	$k_{+1}\mathrm{e}^{\alpha fE_{\mathrm{o}}}$	$k_{+2}\mathrm{e}^{\alpha fE_{\mathrm{o}}}$	k_{-3}	$K_1\mathrm{e}^{fE_{\mathrm{o}}}$	$K_2\mathrm{e}^{fE_{\mathrm{o}}}$
(a)	1.44×10^{-7}	6.6×10^{-4}	1.15×10^{-7}	4.738×10^{-7}	10176.1
(b)	4.74×10^{-8}	6.4×10^{-4}	1.07×10^{-7}	4.641×10^{-7}	9845.1
(c)	1.29×10^{-8}	8.4×10^{-4}	1.35×10^{-7}	5.624×10^{-7}	9272.7
(d)	4.23×10^{-9}	6.9×10^{-4}	3.67×10^{-7}	5.0×10^{-7}	46371.3

scarcely improved, needing an extremely high value of the interaction coefficient (~ 6000), which is meaningless. Besides, the self-consistency in the simultaneous description of both dependences was again not achieved. These facts indicate that the change of the adsorption isotherm only adds one fitting parameter, which improves the description of both dependences, but do not modify the descriptive capability of the mechanism. Therefore, it is likely that a more complete mechanism, involving the modified scheme of the Volmer–Krishtalik mechanism should describe accurately the chlorine electrode reaction.

6. Conclusions

A new methodology for the kinetic analysis of electrode reactions has been proposed, based in the dependence of the polarisation resistance on the experimental variables. Its application to different mechanisms proposed for the ClER on Ti/RuO_2 electrodes was described. On the basis of the present results, it can be concluded that the Volmer–Krishtalik mechanism, particularly the modified scheme, could partially describe the experimental dependences of the polarisation resistance on the operative variables. However, certain deficiencies were observed indicating that another elementary process could take place simultaneously. These aspects will be analysed in part III [17].

Acknowledgements

The financial support of Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Agencia Nacional de Promoción Científica y Tecnológica (ANPCYT) and Universidad Nacional del Litoral (UNL) is gratefully acknowledged.

References

[1] S. Schuldiner, J. Electrochem. Soc. 106 (1959) 891.
[2] M. Enyo, T. Yokoyama, J. Head. Inst. Catal., Hokkaido Univ. 17 (1969) 1.
[3] T. Sasaki, A. Matsuda, J. Head. Inst. Catal., Hokkaido Univ. 21 (1973) 157.
[4] R.G. Érenburg, L.I. Krishtalik, V.I. Bystrov, Élektrokhimiya 8 (1972) 1740.
[5] B.V. Tilak, J. Electrochem. Soc. 126 (1979) 1343.
[6] R. Boggio, A. Carugatti, G. Lodi, S. Trasatti, J. Appl. Electrochem. 15 (1985) 335.
[7] M.R. Gennero de Chialvo, A.C. Chialvo, J. Electroanal. Chem. 415 (1996) 97.
[8] J.L. Fernández, M.R. Gennero de Chialvo, A.C. Chialvo, Electrochim. Acta 47 (2002) 1129.
[9] R.G. Érenburg, L.I. Krishtalik, N.P. Rogozhina, Élektrokhimiya 20 (1984) 1183.
[10] M.R. Gennero de Chialvo, A.C. Chialvo, J. Electroanal. Chem. 372 (1994) 209.
[11] R. Haase, Thermodynamics of Irreversible Processes, Dover, New York, 1990.
[12] K.J. Vetter, Electrochemical Kinetics: Theoretical and Experimental Aspects, Academic Press, New York, 1967.
[13] L.I. Krishtalik, Electrochim. Acta 26 (1981) 329.
[14] J.L. Fernández, M.R. Gennero de Chialvo, A.C. Chialvo, Electrochem. Commun. 2 (2000) 630.
[15] J. Augustynski, L. Balsenc, J. Hinden, J. Electrochem. Soc. 125 (1978) 1093.
[16] E.W. Tsai, K. Rajeshwar, Electrochim. Acta 36 (1991) 27.
[17] J.L. Fernández, M.R. Gennero de Chialvo, A.C. Chialvo, Electrochim. Acta 47 (2002) 1145.