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Kinetic study of the chlorine electrode reaction on Ti/RuO₂ through the polarisation resistance Part III: proposal of a reaction mechanism

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Abstract

A kinetic mechanism for the chlorine electrode reaction (CIER) on Ti/RuO₂ electrodes is proposed. The first step is the oxidation of the superficial sites, where the chloride ion is electroadsorbed giving the atomic chlorine intermediate. The later discharge of chlorine can take place either by recombination of two adsorbed intermediates or by the reaction between the intermediate and the chloride ion, being both chemical steps. The expression of the intrinsic polarisation resistance Rp_o as a function of the activity of chloride $a_{CI-}^{o'}$ and the partial pressure of chlorine \vec{p}_{Cl_2} was obtained from the resolution of the kinetic mechanism and it was compared with experimental data. The correlations of the independent experimental relationships Rp_o versus $a_{CI-}^{o'}$ and Rp_o versus \vec{p}_{Cl_2} were remarkably good, giving strong evidence that the CIER takes place through the proposed mechanism on the RuO₂ electrodes. The kinetic constants obtained from the correlations were used for the simulation of the dependences of the current density and the surface coverages on overpotential. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Chlorine electrode reaction; Ti/RuO₂ electrode; Polarisation resistance; Kinetic mechanism

1. Introduction

The chlorine electrode reaction (ClER) on Ti/RuO₂ electrodes has been studied by the use of the polarisation resistance (*Rp*) [1,2]. In part I [1], the conditions where it is possible to make this analysis were established and the results obtained in the measurements of *Rp* as a function of pH, the activity of chloride $(a_{Cl}^{o'})$ and the partial pressure of chlorine (\bar{p}_{Cl_2}) were reported. It was also possible to explain the effect of acidity $(a_{H^+}^{o'})$ by means of an inhibition model based in the superficial acid–base equilibrium of the oxide. Starting from this model the intrinsic polarisation resistance (*Rp*_o), independent of the solution pH, was obtained.

For the interpretation of the variation of Rp_0 on the operative variables, a theoretical analysis of the main

mechanisms proposed for the ClER was carried out and described in Part II [2]. The dependences of Rp_o on $a_{Cl-}^{o'}$ and \bar{p}_{Cl_2} for each mechanism were derived and compared with the experimental results. It was verified that the Volmer–Krishtalik mechanism (modified scheme) partially describes the experimental results, although another elementary kinetic process should be involved in the reaction. Therefore, this third part deals with a proposal of a sequence of elementary steps that configure a mechanism for the ClER on RuO₂, which is in agreement with the obtained experimental evidences.

2. Theoretical aspects

2.1. Proposal of a kinetic mechanism for the ClER on Ti/RuO_2 electrodes

The first aspect to be taken into account in the proposal of a mechanism for the ClER on Ti/RuO_2 electrodes, which was already mentioned in Part I [1], is

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that there are strong evidences in favour of a change in the oxidation state of the superficial sites of the ruthenium oxide. They would increase their oxidation state at slightly smaller potentials than those at which the CIER takes place [3-5]. Burke and O'Neill [3] demonstrated that this process is indifferent to the presence of chloride ions. Thus, the oxidation of these sites can be written as:

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

where $-S^{Z}$ and $-S^{Z+1}$ are the non-oxidised and oxidised superficial sites respectively. It should be noticed that this step is intrinsic to the oxide, and therefore it is common to any reaction that can take place in the same potential region, such as the oxygen electrode reaction. There are evidences that reaction (1) is only one of successive oxidation steps, which could lead to the break-up of the ruthenium oxide, producing species of high oxidation states like RuO₄ or oxichlorides of Ru(VI) and Ru(VII) at high overpotentials [6-9]. It has been recently demonstrated [9] that these species exist in solution in a proportion depending on pH and their presence can be detected by the application of a fast potentiodynamic sweep towards the cathodic direction immediately after the evolution of chlorine, as it is shown in the voltammograms of Fig. 1.

The formation of the chlorine adsorbed intermediate from the chloride ions should take place preferably on the oxidised sites, which are generated together with the chlorine evolution:

$$-S^{Z+1} + Cl^{-} \leftrightarrows -SCl^{Z+1} + e^{-}$$
⁽²⁾



Fig. 1. Voltamperometric responses of a Ti/RuO₂ electrode after chlorine evolution at $\eta = 0.1$ V during 30 s. Sweep rate: 0.5 V s⁻¹. Electrolyte solution: NaCl (4 – x) M + HCl xM. T = 30 °C. pH: 2.18 (a), 0.91 (b), 0.53 (c), 0.09 (d). (1) First cycle, (2) Successive cycles. Reference electrode: chlorine electrode (CIE), E vs. SCE = 1.092 V.

The formation of molecular chlorine should take place by the reaction of a chlorine adsorbed intermediate and a chloride ion:

$$-\mathbf{SCl}^{Z+1} + \mathbf{Cl}^{-} \leftrightarrows -\mathbf{S}^{Z} + \mathbf{Cl}_{2}$$
(3)

It should be noticed that reactions (1), (2) and (3) constitute the modified scheme of the Volmer–Krishtalik mechanism [2,16], which has been analysed in Part II [2]. In addition to these steps, it cannot be ignored the well-known capacity of RuO_2 for the adsorption/ desorption of chlorine in aqueous solution [10]. Then, the possibility of formation of adsorbed chlorine from the molecular chlorine dissolved in the solution near the reaction plane should be considered:

$$2-S^{Z+1} + Cl_2 \leftrightarrows 2-SCl^{Z+1} \tag{4}$$

Eq. (4) is the Tafel step written in the inverse direction with respect to that commonly used. The direction in which this step is taking place at a given overpotential is governed exclusively by the relative values of the following relationships: the surface coverage of adsorbed Cl with respect to its value at equilibrium and the fraction of oxidised sites with respect to its corresponding equilibrium value (see Eq. (21) later on). Therefore, it is possible that molecular chlorine can be also produced by recombination of two chlorine adsorbed intermediates. Although the Tafel step is accepted as taking part in the ClER mechanism on platinum [11-13], certain doubts were stated about its existence on oxides, based on the analysis of reaction orders and Tafel slopes. Nevertheless, the existence of a non-electrochemical step without the participation of chloride ions has been emphasised [14] and also evidences of the presence of this step during the ClER on RuO_2 electrodes have been given [15].

It should be reasonable to call the resulting kinetic mechanism, constituted by steps (1-4), as the Volmer–Krishtalik–Tafel mechanism.

2.2. Theoretical analysis of the Volmer–Krishtalik–Tafel mechanism

The same generalised treatment described in the Part II [2] was used here to obtain the expression of the polarisation resistance for the Volmer–Krishtalik–Tafel mechanism. As it consists of four elementary steps and two reaction intermediates, two linearly independent routes can be outlined. Making a mass balance of the global reaction in stationary state, the following expression for the global reaction rate (V) as a function of the rates of the elementary steps is obtained:

$$2V = v_1 + v_2 = v_2 + v_3 = 2(v_1 - v_4) = 2(v_3 - v_4)$$

= 2(v_2 + v_4) (5)

being $v_i = v_{+i} - v_{-i}$, where the subscripts *i* refers to the elementary step (*i* = 1, 2, 3, 4).

The following implicit relationships between the rates of the elementary steps are involved in Eq. (5):

$$v_1 = v_3 = v_2 + 2v_4 \tag{6}$$

The corresponding relationships between the electrochemical affinity of the global reaction (A) and those of the elementary steps (A_i) are:

$$A = A_1 + A_2 + A_3 = 2(A_1 + A_3) + A_4 = 2A_2 - A_4$$
(7)

Combining Eqs. (6) and (7) and taking into account the relationship between A_i and v_i [17], the following expressions for the electrochemical affinities of the elementary steps are obtained:

$$A_{1} = \frac{\frac{2}{v_{1}^{e}}(v_{4}^{e}+1)}{1 + (4v_{4}^{e}+v_{2}^{e})\left(\frac{1}{e}+\frac{1}{e}\right)}A$$
(8)

$$A_{2} = \frac{1 + 2v_{4}^{e} \left(\frac{1}{v_{1}^{e}} + \frac{1}{v_{3}^{e}}\right)}{1 + (4v_{4}^{e} + v_{2}^{e}) \left(\frac{1}{v_{1}^{e}} + \frac{1}{v_{3}^{e}}\right)} A$$
(9)

$$A_{3} = \frac{\frac{2}{v_{3}^{e}}(v_{4}^{e}+1)}{(1-1)^{2}}A$$
(10)

$$\frac{1}{1 + (4v_4^e + v_2^e) \left(\frac{1}{v_1^e} + \frac{1}{v_3^e}\right)^A}$$

$$\frac{1}{1 + (4v_4^e + v_2^e) \left(\frac{1}{v_1^e} + \frac{1}{v_3^e}\right)^A}$$
(10)

$$A_{4} = \frac{1 - v_{2}^{e} \left(\frac{1}{v_{1}^{e}} + \frac{1}{v_{3}^{e}} \right)}{1 + (4v_{4}^{e} + v_{2}^{e}) \left(\frac{1}{v_{1}^{e}} + \frac{1}{v_{3}^{e}} \right)} A$$
(11)

where $v_i^e = v_{+i}^e = v_{-i}^e$ is the equilibrium rate of step *i*.

From the first and fourth term of Eq. (5) and taking into account Eqs. (8) and (11), the expression of the global reaction rate is derived: It should be noticed that if the Tafel step is negligible, $v_4^e = 0$, Eq. (13) becomes equal to the expression of Rp_o corresponding to the Volmer–Krishtalik mechanism [2]. Assuming a Langmuirian adsorption for the reaction intermediates, the expressions for the equilibrium surface coverages (θ_1^e , θ_{II}^e) as well as those of the equilibrium reaction rates of the elementary steps (1), (2) and (3) are the same as those derived by the modified scheme of the Volmer–Krishtalik mechanism, Eqs. (30)–(34) of the Part II [2]. The following relationships between the equilibrium constants of the four elementary steps are verified:

$$K_1 K_2 K_3 = e^{-2fE_o}; \quad \frac{K_1 K_3 K_4}{K_2} = 1; \quad \frac{K_2^2}{K_4} = e^{-2fE_o}$$
(14)

where K_i is the equilibrium constant of the step *i*, E_o is the standard potential of the CIER and f = F/RT.

The equilibrium reaction rate of the step (4) is:

$$v_4^{\rm e} = k_{+4} (\theta_{\rm I}^{\rm e})^2 \bar{p}_{\rm Cl_2} = k_{-4} (\theta_{\rm II}^{\rm e})^2$$
(15)

where $\theta_{\rm I}$ is the fraction of oxidised sites $(-S^{Z+1})$, $\theta_{\rm II}$ is the surface coverage of adsorbed Cl on the oxidised site $(-SCl^{Z+1})$, k_{+i} , k_{-i} are the constants of the forward and backward reaction rates respectively of the step *i*. Substituting the expression of $\theta_{\rm I}^{\rm e}$ in Eq. (15) and taking into account Eq. (14), the equilibrium reaction rate of step (4) is obtained as a function of the operative variables $a_{\rm CI-}^{\rm o}$ and $\bar{p}_{\rm CI_2}$:

$$v_{4}^{e} = \frac{k_{+4}K_{1}^{2}e^{2/E_{o}}\bar{p}_{Cl_{2}}^{2}}{[K_{1}e^{fE_{o}}\bar{p}_{Cl_{2}}^{1/2}(1+K_{2}e^{fE_{o}}\bar{p}_{Cl_{2}}^{1/2})+a_{Cl^{-}}^{o^{*}}]^{2}}$$
(16)

The expression of Rp_o for the Volmer–Krishtalik– Tafel mechanism is derived by substitution of the corresponding equilibrium reaction rates into Eq. (13):

$$Rp_{o} = \frac{RT}{4F^{2}} \left\{ \frac{\left[\left(\frac{1}{k_{1}} + \frac{1}{k_{2}K_{1}'\bar{p}_{\text{Cl}_{2}}^{1/2}} \right) \frac{a_{\text{Cl}_{2}}^{\circ,\alpha}}{\bar{p}_{\text{Cl}_{2}}^{\circ,2}} + \frac{1}{k_{-3}\bar{p}_{\text{Cl}_{2}}} \right] \left[K_{1}' \frac{\bar{p}_{\text{Cl}_{2}}^{1/2}}{a_{\text{Cl}_{-}}^{\circ,\circ}} (1 + K_{2}'\bar{p}_{\text{Cl}_{2}}^{1/2}) + 1 \right] + \frac{4k_{+4}K_{1}'\bar{p}_{\text{Cl}_{2}}^{(1-\alpha)/2}}{k_{2}a_{\text{Cl}_{-}}^{\circ,\circ}} \left(\frac{\bar{p}_{\text{Cl}_{2}}^{(1-\alpha)/2}}{k_{1}} + \frac{1}{k_{-3}} \right) \right] \\ \left. 1 + \frac{k_{+4}K_{1}'\bar{p}_{\text{Cl}_{2}}^{1/2}}{a_{\text{Cl}_{-}}^{\circ,\circ} - \left[K_{1}'\bar{p}_{\text{Cl}_{2}}^{1/2} + K_{2}'\bar{p}_{\text{Cl}_{2}}^{1/2} + a_{\text{Cl}_{-}}^{\circ,\circ} \right]} \left[\left(\frac{1}{k_{1}} + \frac{1}{k_{2}K_{1}'\bar{p}_{\text{Cl}_{2}}^{1/2}} \right) \frac{a_{0}'^{\alpha}}{\bar{p}_{\text{Cl}_{2}}^{\alpha}} + \frac{1}{k_{-3}\bar{p}_{\text{Cl}_{2}}} \right] \right] \right\}$$
(17)

$$V = \left\{ \frac{1 + v_4^{\rm e} \left(\frac{1}{v_1^{\rm e}} + \frac{1}{v_2^{\rm e}} + \frac{1}{v_3^{\rm e}}\right)}{\frac{1}{v_1^{\rm e}} + \frac{1}{v_3^{\rm e}} + \frac{1}{v_2^{\rm e}} \left[4v_4^{\rm e} \left(\frac{1}{v_1^{\rm e}} + \frac{1}{v_3^{\rm e}}\right) + 1 \right] \right\} \frac{A}{RT}$$
(12)

The following generalised expression for the polarisation resistance of the Volmer–Krishtalik–Tafel mechanism is obtained from the relationship between Rp_o and V/A in the limit for the overpotential η tending to zero [2,17] and taking into account Eq. (12):

$$Rp_{o} = \frac{RT}{4F^{2}} \left[\frac{\frac{1}{v_{1}^{e}} + \frac{1}{v_{2}^{e}} + \frac{1}{v_{3}^{e}} + \frac{4v_{4}^{e}}{v_{2}^{e}} \left(\frac{1}{v_{1}^{e}} + \frac{1}{v_{3}^{e}}\right)}{1 + v_{4}^{e} \left(\frac{1}{v_{1}^{e}} + \frac{1}{v_{2}^{e}} + \frac{1}{v_{3}^{e}}\right)} \right]$$
(13)

where $k_1 = k_{+1}e^{\alpha/E_o}$, $k_2 = k_{+2}e^{\alpha/E_o}$, $K'_1 = K_1e^{/E_o}$ and $K'_2 = K_2e^{\beta/E_o}$. It can be observed that this equation involves the kinetic constants of the forward reaction of steps (1), (2) and (4) and the kinetic constant of the backward reaction of step (3), as well as the equilibrium constants of steps (1) and (2). The other constants can be calculated from those involved in Eq. (17), taking into account Eq. (14) and that $K_i = k_{+i}/k_{-i}$.

3. Results

3.1. Analysis of the experimental data $Rp_o vs. \bar{p}_{Cl_2}$ and $Rp_o vs. a_{Cl^-}^{o'}$

The experimental data were correlated with Eq. (17)



Fig. 2. Correlations of the dependences Rp_o vs. \bar{p}_{Cl_2} (I) and Rp_o vs. $a_{Cl^-}^{\circ}$ (IV), and simulations of the dependences Rp_o vs. $a_{Cl^-}^{\circ}$ (II) and Rp_o vs. \bar{p}_{Cl_2} (III), respectively, by means of the Volmer–Krishtalik–Tafel mechanism. Experimental conditions: NaCl–HCl, C_{Cl^-} : 2 M (•), 3 M (\Box), 4 M (∇); $\bar{p}_{Cl_2} = 1$ atm (\bigcirc). T = 30 °C. Dashed line in (II): simulation with the average constants (Table 1e).

using a non-linear least squares method. The value of the symmetry factor α was fixed at 0.5 and one of the operative variables, $a_{Cl-}^{o'}$ or \bar{p}_{Cl_2} , was kept constant. The aim of this correlation was to find the set of kinetic parameters that better reproduces the experimental results.

The correlations of the experimental dependences Rp_o versus \bar{p}_{Cl_2} at three different concentrations of chloride ions are shown in Fig. 2I, where it can be verified that a good correlation is achieved in all cases. A fitting with this accuracy could not be obtained through any of the previously analysed mechanisms [2]. The kinetic constants obtained in each correlation are shown in Table 1(a-c), which are very similar for the three concentrations. As a self-consistency test, with these kinetic constants the dependences Rp_o versus $a_{Cl-}^{o'}$ were simulated. The corresponding curves are shown in Fig. 2II, where a notable agreement between the simulations and the experimental response is observed. A simulation of this accuracy could not be obtained

through the mechanisms already discussed [2], even using different adsorption isotherms for the description of the reaction intermediates.

On the other hand, the correlation made on the experimental dependence Rp_o versus $a_{Cl-}^{o'}$ at a chlorine partial pressure equal to 1 atm is illustrated in Fig. 2IV, where it can be also observed that the present mechanism can describe appropriately the experimental data. The resulting parameter values are shown in Table 1(d). In the same way, the curves Rp_o versus \bar{p}_{Cl_2} were simulated with these parameters at different chloride concentrations, which are shown in Fig. 2III. A very good agreement between the simulations and the experimental responses is again obtained, better than that of the other mechanisms [2].

It should be noticed in Table 1 the similarity between the different values of the kinetic constants, which were obtained from two different sets of experimental data. Thus, it was possible the calculation of average values, which are shown in Table 1(e). It should be taken into account that the parameters used in a simulation were obtained by correlation of a completely independent data set. Moreover, the expressions used in both, correlation and simulation respectively, have in common only the mechanism that originated them. In this context, the excellent agreement between simulations and experimental data constitutes strong evidence in favour of the proposed mechanism.

3.2. Simulations of dependences log j, θ_I and θ_{II} vs. η

The dependence of the current density j on overpotential η for the CIER on a Ti/RuO₂ electrode free from any mass transfer process can be simulated with the kinetic constants calculated as it was indicated in the previous item. It should be noticed that, as the kinetic parameters were obtained from experimental data related to the real area of the electrodes [1], the simulated responses correspond to a smooth surface. The expressions of the surface coverages θ_{I} and θ_{II} and that of the relationship j vs. η corresponding to the Volmer– Kristhalik–Tafel mechanism must be derived to carry out such simulations. Although it is likely that the variation of the surface coverage of the adsorbed chlo-

Table 1

Kinetic and equilibrium constants of the elementary steps of the CIER obtained from the correlation of the experimental data Rp_o vs. \bar{p}_{Cl_2} (a, b and c) and Rp_o vs. $a_{Cl_2}^{o'}$ (d) by the Volmer–Krishtalik–Tafel mechanism (average values: (e))

	$k_{+1} e^{\alpha f E_o}$	$k_{+2} \mathrm{e}^{\alpha / E_o} \times 10^3$	$k_{-3} \times 10^{11}$	k_{+4}	$K_1 e^{fE_o} \times 10^6$	$K_2 e^{fE_o}$
(a)	2.2603	1.623	6.954	157.046	3.208	240597.7
(b)	2.3237	1.318	7.210	161.116	3.266	244982.8
(c)	2.6122	1.212	5.870	239.604	4.653	349019.5
(d)	2.6644	1.011	10.407	121.331	4.001	212101.5
(e)	2.4652	1.291	7.610	169.774	3.782	261675.4

 k_{+i} in mol s⁻¹ cm⁻².

rine intermediate on overpotential could be significant, a Langmuirian behaviour is considered as a first approximation.

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

$$v_{1} = v_{1}^{e} \left[\frac{(1-\theta)}{(1-\theta^{e})} e^{\alpha f \eta} - \frac{\theta_{1}}{\theta_{1}^{e}} e^{-(1-\alpha)f \eta} \right]$$
(18)

$$v_{2} = v_{2}^{e} \left[\frac{\theta_{I}}{\theta_{I}^{e}} e^{\alpha f \eta} - \frac{\theta_{II}}{\theta_{II}^{e}} e^{-(1-\alpha)f \eta} \right]$$
(19)

$$v_3 = v_3^{\rm e} \left[\frac{\theta_{\rm II}}{\theta_{\rm II}^{\rm e}} - \frac{(1-\theta)}{(1-\theta^{\rm e})} \right]$$
(20)

$$v_4 = v_4^{e} \left[\frac{\theta_1^2}{\theta_1^{e^2}} - \frac{\theta_{II}^2}{\theta_{II}^{e^2}} \right]$$
(21)

The following relationship between θ_{I} and θ_{II} can be obtained from the first two members of Eq. (6):

$$\theta_{\rm II} = \frac{(e^{\alpha f \eta} + m_3) - \left[\frac{(1 - \theta^{\rm e})}{\theta_{\rm I}^{\rm e}} e^{-(1 - \alpha)f \eta} + (e^{\alpha f \eta} + m_3)\right] \theta_{\rm I}}{e^{\alpha f \eta} + m_3 \frac{(1 - \theta_{\rm I}^{\rm e})}{\theta_{\rm II}^{\rm e}}}$$
(22)

$$c = \left\{ \left[\frac{1}{(1-\theta^{e})} - \frac{m_{2}}{\theta^{e}_{II}} e^{-f\eta} \right] \theta^{e}_{II} e^{\alpha f\eta} - \frac{2m_{4}(e^{\alpha f\eta} + m_{3})}{\left[(1-\theta^{e})m_{3} + \theta^{e}_{II}(m_{3} + e^{\alpha f\eta})\right]} \right\} \times \frac{(e^{\alpha f\eta} + m_{3})}{\left[(1-\theta^{e})m_{3} + \theta^{e}_{II}(m_{3} + e^{\alpha f\eta})\right]} - \frac{e^{\alpha f\eta}}{(1-\theta^{e})}$$
(27)

It can be demonstrated that only the following root has a physical meaning:

$$\theta_1 = \frac{-b + \sqrt{b^2 - 4ac}}{2a} \tag{28}$$

From the first and third term of Eq. (5) and taking into account Eqs. (19) and (20), the expression of V is:

$$2V = \left[\frac{v_2^e}{\theta_{\rm I}^{\rm e}} e^{\alpha f \eta} + \frac{v_3^e}{(1-\theta^{\rm e})}\right] \theta_{\rm I} + \left[v_3^e \left(\frac{1}{\theta_{\rm II}^{\rm e}} + \frac{1}{1-\theta^{\rm e}}\right) - \frac{v_2^e}{\theta_{\rm II}^{\rm e}} e^{-(1-\alpha)f \eta}\right] \theta_{\rm II} - \frac{v_3^e}{(1-\theta^{\rm e})}$$
(29)

The relationship *j* versus η is obtained replacing Eq. (22) into Eq. (29) and taking into account that the current density is j = 2FV:

$$j/F = \frac{\theta_{\rm II}^{\rm e}(v_3^{\rm e} + v_1^{\rm e}e^{\varkappa/\eta}) \left[v_3^{\rm e} \left(\frac{1}{\theta_{\rm II}^{\rm e}} + \frac{1}{1 - \theta^{\rm e}} \right) - \frac{v_2^{\rm e}}{\theta_{\rm II}^{\rm e}} e^{-(1 - \varkappa)f\eta} \right]}{\left[(1 - \theta^{\rm e})v_3^{\rm e} + \theta_{\rm II}^{\rm e}(v_3^{\rm e} + v_1^{\rm e}e^{\varkappa/\eta}) \right]} - \frac{v_3^{\rm e}}{(1 - \theta^{\rm e})} - \frac{v_3^{\rm e}}{(1 - \theta^{\rm e})} + \left\{ v_2^{\rm e}e^{\varkappa/\eta} + v_3^{\rm e} \frac{\theta_{\rm II}^{\rm e}}{(1 - \theta^{\rm e})} - \frac{\left[v_3^{\rm e} \left(1 + \frac{\theta_{\rm II}^{\rm e}}{1 - \theta^{\rm e}} \right) - v_2^{\rm e}e^{-(1 - \varkappa)f\eta} \right] \left[v_1^{\rm e}(1 - \theta)e^{-(1 - \varkappa)f\eta} + \theta_{\rm II}^{\rm e}(v_3^{\rm e} + v_1^{\rm e}e^{\varkappa/\eta}) \right]} \right\} \frac{\theta_{\rm II}}{\left[v_3^{\rm e}(1 - \theta^{\rm e}) + \theta_{\rm II}^{\rm e}(v_3^{\rm e} + v_1^{\rm e}e^{\varkappa/\eta}) \right]} \right\}}$$
(30)

where $m_i = v_i^e / v_1^e$. Then, from the first and last members of Eq. (6):

$$2m_{4}\left(\frac{1}{\theta_{\mathrm{I}}^{\mathrm{e2}}} - \frac{1}{\theta_{\mathrm{II}}^{\mathrm{e2}}}\right)\theta_{\mathrm{I}}^{2} + \left[\frac{(\mathrm{e}^{-f\eta} + m_{2})}{\theta_{\mathrm{I}}^{\mathrm{e}}} + \frac{1}{(1 - \theta^{\mathrm{e}})}\right]\mathrm{e}^{\alpha f\eta}\theta_{\mathrm{I}} + \left[\frac{1}{(1 - \theta^{\mathrm{e}})} - \frac{m_{2}}{\theta_{\mathrm{II}}^{\mathrm{e}}}\mathrm{e}^{-f\eta}\right]\mathrm{e}^{\alpha f\eta}\theta_{\mathrm{II}} - \frac{\mathrm{e}^{\alpha f\eta}}{(1 - \theta^{\mathrm{e}})} = 0$$
(23)

The expression for θ_{I} is obtained substituting Eq. (22) into Eq. (23):

$$a\theta_{\rm I}^2 + b\theta_{\rm I} + c = 0 \tag{24}$$

where

$$a = \frac{2m_4}{\theta_1^{e2}} \left\{ 1 - \left[\frac{(1 - \theta^e) e^{-(1 - \alpha)f\eta} + \theta_1^e(m_3 + e^{\alpha f\eta})}{(1 - \theta^e)m_3 + \theta_{II}^e(m_3 + e^{\alpha f\eta})} \right]^2 \right\}$$
(25)

$$b = \left\{ \frac{(e^{-f\eta} + m_2)}{\theta_{\rm I}^{\rm e}} + \frac{1}{(1 - \theta^{\rm e})} - \frac{\theta_{\rm II}^{\rm e}}{\theta_{\rm I}^{\rm e}} \left[\frac{1}{(1 - \theta^{\rm e})} - \frac{m_2}{\theta_{\rm II}^{\rm e}} e^{-f\eta} \right] \right. \\ \times \left[\frac{(1 - \theta^{\rm e})e^{-(1 - \alpha)f\eta} + \theta_{\rm I}^{\rm e}(m_3 + e^{\alpha f\eta})}{(1 - \theta^{\rm e})m_3 + \theta_{\rm II}^{\rm e}(m_3 + e^{\alpha f\eta})} \right] \right\} e^{\alpha f\eta} \\ + \frac{2m_4(e^{\alpha f\eta} + m_3)[(1 - \theta)e^{-(1 - \alpha)f\eta} + \theta_{\rm II}^{\rm e}(m_3 + e^{\alpha f\eta})]}{\theta_{\rm II}^{\rm e}[(1 - \theta^{\rm e})m_3 + \theta_{\rm II}^{\rm e}(m_3 + e^{\alpha f\eta})]^2}$$
(26)

where θ_{I} is defined by Eqs. (25)–(28).

The expressions of the limiting anodic and cathodic kinetic current densities, as well as the limiting values of the surface coverages can be also obtained:

$$\theta_{\mathrm{I}(+)} = \lim_{\eta \to \infty} \theta_{\mathrm{I}} = 0; \quad \theta_{\mathrm{I}(-)} = \lim_{\eta \to -\infty} \theta_{\mathrm{I}} = 0$$
(31)

$$\theta_{\mathrm{II}(+)} = \lim_{\eta \to \infty} \theta_{\mathrm{II}} = 1; \quad \theta_{\mathrm{II}(-)} = \lim_{\eta \to -\infty} \theta_{\mathrm{II}} = 0 \tag{32}$$

$$\lim_{\eta \to \infty} j = \frac{2F}{\theta_{\mathrm{II}}^{\mathrm{e}}} \left(v_{3}^{\mathrm{e}} + \frac{v_{4}^{\mathrm{e}}}{\theta_{\mathrm{II}}^{\mathrm{e}}} \right); \quad \lim_{\eta \to -\infty} j = -\frac{2Fv_{3}^{\mathrm{e}}}{(1 - \theta^{\mathrm{e}})}$$
(33)

Taking into account the dependence of the experimental current density (j^*) on pH, Eqs. (9) and (12) in Part I [1], using the average kinetic constants given in Table 1(e) and the Eqs. (22), (25)–(28) and (30), the curves $\log j^*$ versus η and θ_i versus η were obtained at different conditions (T = 30 °C). From the analysis of the variation of Rp on pH, it can be concluded that the fraction of non-inhibited surface area is independent of potential in the range of the experimental measurements ($\Delta E < 0.05$ V) [1]. This invariance was considered to be valid in the range of overpotentials used in the simulations ($\Delta \eta = 0.35$ V). Fig. 3 shows the effect of the chloride ions concentration at a given pH while Fig. 4 illustrates the effect of the chlorine partial pressure.



Fig. 3. Simulations of the dependences $\log j^*$, θ_1 and θ_{11} vs. η . $\bar{p}_{Cl_2} = 1$ atm, pH 0.75, C_{Cl-} (M): 0.5 (a), 1 (b), 2 (c), 3 (d), 4 (e).

Furthermore, the effect of the pH value is shown in Fig. 5. As it is already stated, these dependences represent the behaviour that should have a RuO_2 electrode with a smooth surface operating under activated control in stationary state. It should also be very interesting to visualise the magnitude of the contribution of each elementary step to the total response. Fig. 6 illustrates the dependences of the rates of each step and that of the global reaction on η .

4. Discussion

The aim of improving the description of the experi-







Fig. 5. Simulations of the dependences $\log j^*$, θ_1 and θ_{II} vs. η . $C_{CI-} = 3$ M, $\bar{p}_{CI_2} = 1$ atm, pH: 1.0 (a), 0.75 (b), 0.5 (c), 0.25 (d).

mental results reached by means of the modified VK mechanism, leaded to the proposition of a new possible sequence of elementary steps. In this context, two facts are decisive in order to achieve the final outline. One of them is the almost unquestionable simultaneity of two processes, the superficial oxidation of the electrode material and the chlorine evolution. This fact had already been recognised two or three decades ago [5,18], when the formation of a reaction intermediate in an oxidised state was proposed. Later on, the advances achieved in the understanding of the superficial behaviour of oxides introduced several improvements [14,16,19]. Thus, it was considered reasonable to propose the oxidation of the superficial sites as the first step, which should fulfil two boundary conditions. One is related to its independence on the chloride ion concentration, based in experimental evidence [2]. The other is the independence on pH, since the resulting



Fig. 6. Simulations of the dependences of the global reaction rate V = j/2F (a) and of the rates of the elementary steps 1 (b), 2 (c), 3(b) and 4 (d), on η for the Volmer–Krishtalik–Tafel mechanism. $C_{\rm Cl-} = 1$ M, $\bar{p}_{\rm Cl_2} = 1$ atm. Inset graph: enlarged scale.

mechanism should not involve this last variable. Then, the active surface is occupied by oxidised and non-oxidised sites and the formation of the adsorbed chlorine intermediate will take place on those that minimise the global energy of the system. Moreover, it seemed to be that this oxidation step makes possible the chlorine evolution, as it is more likely that the adsorbed intermediate is formed on the oxidised sites.

At this point, the second decisive aspect is the way in which the chlorine intermediate is formed, being the most common the electroadsorption of chloride ions (Volmer step). Nevertheless, it should also be natural to outline the possibility of the adsorbed chlorine formation from the dissolved molecular chlorine. There are evidences that this dissociative adsorption takes place at cathodic potentials [10]. On the other hand, the formation of molecular chlorine through the recombination of two adsorbed chlorine (Tafel step) occurs on metals like platinum [11-13] and it should also take place on RuO₂. Therefore, it was considered appropriate to include step (4) in order to take into account the interrelation between the adsorbed atomic chlorine and the molecular chlorine. It should be emphasised that the direction indicated for a given step is not necessarily the correct one, as it is established for the sign of the corresponding reaction rate at a given overpotential.

Step (3) consists in the combination of adsorbed chlorine with the chloride ions in solution, producing molecular chlorine and regenerating the non-oxidised sites (step 3). In place of this chemical step, the interaction between the adsorbed chlorine and the chloride ion through the Heyrovsky step, regenerating the oxidised site with the transfer of one electron could be proposed. In such case, the site oxidation should be at equilibrium without participating of the reaction mechanism. This scheme would correspond to the Volmer-Heyrovsky-Tafel mechanism, with an acid-base and a redox equilibrium previous to the kinetic mechanism [14]. However, it has been demonstrated in part I [1] that only the acid-base equilibrium is external to the reaction mechanism and explains itself the dependence of the reaction rate on pH.

The expression of the polarisation resistance as a function of $a_{Cl-}^{o'}$ and \bar{p}_{Cl_2} was obtained from the resolution of the kinetic mechanism formed by the four elementary steps and then it was compared with the experimental data. It has been demonstrated that the correlation of both independent experimental plots Rp_o versus $a_{Cl-}^{o'}$ and Rp_o versus \bar{p}_{Cl_2} was remarkably good. Furthermore, these results can be reproduced through a unique set of kinetic constants of the elementary steps. This is a very restrictive test that the mechanism could overcome and therefore is a strong evidence that the CIER takes place through it on the RuO₂ electrodes.

The kinetic constants obtained from this analysis were used to simulate the dependences $\log j^*$, θ_I and θ_{II}

cal expressions, and the obtained results were illustrated in Figs. 3-5. It can be observed that the fraction of oxidised sites tends to zero in both anodic and cathodic directions (Eq. (31)), going through a maximum slightly up the equilibrium potential. Besides, the surface coverage of the adsorbed chlorine goes respectively to zero and one in the cathodic and anodic direction (Eq. (32)). The dependence $\log j^*$ versus η presents three remarkable characteristics. One of them is the non-existence of rigorous Tafelian regions, reaching quickly limiting kinetic current densities in both directions (Eq. (33)). Another aspect is the low current densities, which does not overcome 10^{-3} A cm⁻², which contrasts with the usually reported values between 0.1 and 1 A cm⁻² [3,7,15,16,20-32]. Nevertheless, it should be bear in mind that in general these values correspond to apparent current densities (related to the geometric area), being obtained on electrodes with roughness factors ranging between 100 and 1000 [33-38]. Therefore, if the polarisation curves described here are referred to the geometric area of an electrode with such roughness factor, they will be increased in two or three orders of magnitude. Moreover, some curves obtained on smooth surfaces show similar current densities to those of the present simulations [39]. The third characteristic is the presence of a non-diffusional maximum in the cathodic region, which magnitude decreases when the concentration of chloride increases and when the chlorine partial pressure decreases. After that, a limiting kinetic current is achieved. The presence of such cathodic maximum in the ClER on ruthenium oxide based electrodes was reported by Erenburg et al. [18], who referred it to changes in the oxide surface with time. Likewise, the existence of the limiting kinetic current was clearly demonstrated by Evdokimov et al. on RuO₂ rotating disc electrodes [19,20]. It should be taken into account that the simulated curves represent the responses of a smooth RuO₂ electrode where the CIER operates exclusively under activated control in the whole interval of the evaluated overpotentials, a fact that is rather difficult to be fulfilled in this type of materials. Finally, from the observation of the resulting dependences for the rates of the elementary steps on η , it can be concluded that steps (1), (2) and (3) take place in the proposed direction, but step (4) occurs in the inverse direction and thus molecular chlorine is generated by recombination of two adsorbed chlorine atoms.

on η , after the derivation of the corresponding analyti-

5. Conclusions

On the basis of the use of the polarisation resistance, a complete kinetic analysis was carried out, giving solid evidences about the mechanism through which the chlorine electrode reaction takes place on Ti/RuO_2 electrodes. This involve the following sequence of steps:

$$-S^{Z} + H^{+} \Leftrightarrow -SH^{Z+1}$$

$$-S^{Z} \Leftrightarrow -S^{Z+1} + e^{-}$$

$$-S^{Z+1} + Cl^{-} \Leftrightarrow -SCl^{Z+1} + e^{-}$$

$$-SCl^{Z+1} + Cl^{-} \Leftrightarrow -S^{Z} + Cl_{2(g)}$$

$$2-SCl^{Z+1} \Leftrightarrow 2-S^{Z+1} + Cl_{2(g)}$$

The first is an equilibrium step independent of the ClER, being an intrinsic property of the oxide. This step explains the dependence of the electrode behaviour on pH. The following four steps configure the mechanism of the ClER, that can be denominated the Volmer–Krishtalik–Tafel mechanism. This involves a first step of oxidation of the superficial sites, which generate the active sites where the adsorbed chlorine intermediate is formed from the chloride ions. The later discharge of chlorine can occur either by the reaction of an intermediate with a chloride ion.

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