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Janssen, L.J.J.; Starmans, L.M.C.; Visser, J.G.; Barendrecht, E.

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MECHANISM OF THE CHLORINE EVOLUTION ON A RUTHENIUM OXIDE/TITANIUM OXIDE ELECTRODE AND ON A RUTHENIUM ELECTRODE

L. J. J. JANSEN,* L. M. C. STARMANS,* J. G. Vimeo and E. BARENDRECHT*
* Department of Electrochemistry, Eindhoven University of Technology and
† Computing Centre, Eindhoven University of Technology, Eindhoven, The Netherlands

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Abstract—The mechanism of the chlorine evolution on titanium electrodes coated with a layer of ruthenium oxide and titanium oxide under different experimental conditions, and on a ruthenium electrode, both in acidic chloride solution, has been investigated. Potentiodynamic current density—potential curves were recorded as a function of the time of anodic pre-polarisation, the composition of the solution and the temperature. Moreover, potential decay curves were determined. Theoretical potential decay curves were deduced for both the Tafel reaction (2Cl^- → Cl_2) and the Heyrovsky reaction (Cl^- + Cl_2 → Cl_2 + e^-) as a rate determining step in the formation of molecular chlorine. They were compared with those found experimentally. The influence of possible diffusion of atomic chlorine out of the electrode was also taken into consideration. It was found that for all the electrodes investigated, molecular chlorine is formed both at anodic polarisation and on open circuit according to the Volmer—Heyrovsky mechanism, where the Heyrovsky reaction is the rate-determining step. The transfer coefficient is 0.5 for the chlorine evolution at an “ideal” ruthenium oxide titanium oxide electrode and at a ruthenium electrode.

NOMENCLATURE

- b: Tafel slope of the E/log J curve
- c(x, t): concentration of atomic chlorine present in an electrode at a distance x at time t after switching off the polarisation current
- c_0: c(x, 0) at x ≥ 0 or c(x, t) at t = 0
- D: diffusion coefficient of atomic chlorine
- E: electrode potential vs see
- E_a: electrode potential on open circuit
- E_r: reversible electrode potential vs see
- F: Faraday constant
- k_T; k_H: the slope of the linear part of the (log E - log J) curve for respectively the Tafel and the Heyrovsky reactions
- J_ge metric exchange cd
- J: real exchange cd
- j_0; j_0,T; j_0,H: j_0 for respectively the Tafel and the Heyrovsky reactions
- k_T; k_H: reaction constant of respectively the Tafel and the Heyrovsky reactions
- k_T^p; k_H^p: p = θ/c
- constant factor
- R: gas constant
- r: roughness factor
- T: temperature in °C or K
- T_F: the firing temperature
- t_a: time of anodic polarisation
- t_A: the firing time
- t_s: time after switching off the polarisation current
- u_T; u_H: rate of chlorine evolution for respectively the Tafel and the Heyrovsky reaction
- x: distance in the electrode measured from the boundary electrode surface/electrolyte
- α: transfer coefficient
- η_H: overpotential during anodic polarisation
- η_o(0): overpotential on open circuit; η_a = E_a - E_r
- θ: degree of coverage with atomic chlorine
- θ_0: θ at t = 0; this being equal to the degree of coverage at the potential of the electrode on current flow
- ω: θ at E_r

1. INTRODUCTION

A few years ago the titanium electrode coated with a layer of mixed oxides of titanium, ruthenium and/or other noble metals was introduced into the chlorine—alkali industry.

Several investigators[1-4] have already examined the behaviour of this anode material in concentrated acidic chloride solutions. Moreover, the mechanism of the chlorine evolution has also been studied[2, 5, 7].

The experimental results are often contradictory. For instance, the following Tafel slopes were found: 32 mV for a coating of oxides of Ti, Ir and Ru, 108 mV[4] and 40 mV[7] for a coating of RuO_2 and 35 mV for a coating of RuO_2 and TiO_2[6]. The differences in Tafel slopes cannot be explained only in terms of chemical composition of the oxide layer. Possible important factors may be the conditions used in the preparation and the electrochemical pre-treatment of the electrode. The influence of these factors are presented in this paper for two different types of electrodes, namely for a titanium electrode coated with an oxide mixture composed of 30 mole% RuO_2 and 70 mole% TiO_2 and for a pure ruthenium electrode. The mechanisms proposed in the literature are mainly based on E/log J curves. In addition, we also examined potential decay curves for elucidating the mechanism of the chlorine evolution.
2. EXPERIMENTAL

2.1 Preparation of the RuO$_2$/TiO$_2$-electrode and the Ru-electrode

The RuO$_2$/TiO$_2$ electrodes were prepared by coating titanium sheets (40 $\times$ 5 $\times$ 0.5 mm, purity of Ti 98–99%) with a layer of ruthenium oxide and titanium oxide. The RuO$_2$ content of the coating was 30%. The titanium sheets were cleaned with acetone and subsequently etched in concentrated hydrochloric acid at 80° for 10 min.

The coating was achieved by painting the titanium sheet with an aqueous solution consisting of 1.4 ml TiCl$_4$, 3 ml H$_2$O, 0.5 ml 30% H$_2$O$_2$ and 120 mg RuCl$_3$·3 H$_2$O and then by drying in air at about 80°. Thereafter the coated sheet was fired at 500° for 1 h, except when otherwise stated. In applying multilayer coatings the procedure was repeated. Unless otherwise stated RuO$_2$/TiO$_2$ electrodes with two coating layers were used.

For comparison, a pure ruthenium rod was used; a disc having a geometric area of 1.00 cm$^2$ was the exposed electrode surface; the cylinder part of the rod was completely isolated with a Perspex cylinder.

2.2 Experimental techniques and apparatus

Two different electrolytic cells were used. The measuring cell, a normal H-shaped diaphragm cell (volume of both compartments was 100 ml), was applied for the determination of the potential–current curves, the potential–time curves and of the capacitance of the electrodes. This cell was thermostatted (unless otherwise stated at 25°). The other cell, a vessel divided into an anodic compartment of 5000 ml and a cathodic compartment of 2000 ml was used for the anodic polarisation of the electrodes for long periods. In both cases, platinum electrodes served as counterelectrodes. The voltammograms were measured with the usual setup.

The capacitance of the electrode was determined in the usual way. The magnitude of the potential-pulse was 50 mV.

As a reference electrode a sce was used. The reversible potential of the Cl$_2$/Cl$^-$ redox system was determined with a platinum electrode, activated by a chlorine evolution for a short period.

It appeared that the activity of the RuO$_2$/TiO$_2$ electrodes depends on the polarisation time. To determine this effect the electrode was polarised with a constant current density, viz 25 mA/cm$^2$. After a fixed polarisation time the electrode was removed from the great electrolytic cell and was put into the small H-shape cell containing a 4 M NaCl + 1 M HCl solution, saturated with chlorine. The voltammogram was recorded after a sweep period of about 10 min. Thereafter the electrode was again polarised anodically in the great electrolytic cell for a fixed period. This procedure was applied to minimise the change of the composition of the electrolyte during the long continued electrolysis.

3. RESULTS

3.1 Roughness of the electrodes

The capacitance determined by the potential-pulse method[8] was used as a measure for the roughness of the RuO$_2$/TiO$_2$ electrode.

It appeared that in the investigated range from 800 to 1000 mV, both the direction and the amplitude of the potential-pulse had no influence upon the capacitance. Assuming that the capacitance measured is equal to the double layer capacitance (viz 17.4 µF/cm$^2$ determined at a mercury electrode in a 4 M NaCl + 1 M HCl solution), the roughness factor of the different RuO$_2$/TiO$_2$ electrodes varied between 20 and 40. No systematic increase of the roughness of the electrodes was found with increasing numbers of coating layers.

3.2 Influence of the sweep rate and of the scanning potential range on the E/J curves

To investigate the effect of the sweep rate on the morphology of the E/J curve, this curve was measured at a sweep rate varying between 0.5 and 50 mV/s. A typical E/J curve for a RuO$_2$/TiO$_2$ electrode is represented in Fig. 1. For these electrodes hysteresis occurs; however, at sweep rates lower than 2 mV/s the hysteresis disappeared practically. The E/J curves were determined in the potential range from 1050 to 1500 mV. This potential range was chosen to prevent a change of the nature of the electrode surface during the sweeping of the potential. The minimum potential $E_{\text{min}}$ was varied between 1050 and 1250 mV and the maximum potential $E_{\text{max}}$ between 1200 and 1500 mV. It appeared that the shape of the E/J curve remained the same and that only some hys-
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Fig. 2. The current density $J$ at an overpotential of 90 mV and the Tafel slope $b$ for a RuO$_2$/TiO$_2$-electrode as a function of the total electrolysis time $t_A$. The RuO$_2$/TiO$_2$-electrode was formed by firing at 500°C for 2 h.

The current density and the Tafel slope occurred Its effect depended on the difference between $E_{\text{min}}$ and $E_{\text{max}}$.

Owing to the preceding results, the following potentiodynamic $E/J$ curves were determined at a sweep rate of 1.25 mV/s and at a potential range of 1050–1300 mV.

3.3 The nature of the electrode surface

3.3.1 Time of anodic polarisation. The influence of the anodic polarisation on the behaviour of the Ru-electrode and the RuO$_2$/TiO$_2$-electrode evolving chlorine were investigated by determining potentiodynamic $E/J$ curves after the electrodes have been polarised for several times in succession. In Fig. 2, for a RuO$_2$/TiO$_2$ electrode the current density at a constant overpotential and the Tafel slope $b$ of the $E$/log $J$ curve are plotted versus the total time $t_A$ of anodic polarisation of the electrode.

The shapes of both curves of Fig. 2 are characteristic. The decrease of both the current density and the Tafel slope occurred mainly during the first 20 h. This phenomenon occurred most markedly for electrodes formed by firing at 350°C for 15 min. For a Ru-electrode the $J/t_A$ and the $b/t_A$ relation are represented in Fig. 3.

In the following only the current density and the Tafel slope are given for electrodes of which the nature of the surface has become constant.

3.3.2 Temperature of the firing process. The effect of the temperature of the firing process was investigated for RuO$_2$/TiO$_2$ electrodes formed at 500°C for times varying between 0.25 and 6 h.

The RuO$_2$/TiO$_2$ layer on the electrode fired for 6 h started to scale off after electrolysis of 100 h and had practically disappeared after a 150 h electrolysis. It appeared that the current density and the Tafel slope are practically independent of the firing time.

Kuhn and Mortimer[4] found also no systematic variation in the activity of the electrodes fired at 400°C for 1–50 h.

3.3.3 Thickness of the coating layer. The thickness of the coating layer of the RuO$_2$/TiO$_2$ electrode was varied by covering the electrodes 1, 2, 5 and 10 times with the RuCl$_3$/HCl solution. After a pre-electrolysis for about 150 h, both the $E$/$J$ curve and the capacitance were determined. From these experiments it followed that the thickness of the electrode had no significant influence upon the Tafel slope and upon the ratio between the current density and the capacitance of the electrode. The exchanged current density $J_0$ was determined by extrapolation of the linear section of the $E$/log $J$ curve. The electrochemical surface area was calculated from the capacitance of the electrode and the capacitance of the double layer.

The obtained value varied between $8 \times 10^{-5}$ and $20 \times 10^{-5}$ mA/cm$^2$, the average value of $J_0$ was $13 \times 10^{-5}$ mA/cm$^2$.

3.4 Electrolytic conditions

3.4.1 Composition of the solution. For solutions with a chloride concentration of 5 M and a pH varying between 0 and 3, it appeared that the $E/J$ curve does not depend on the pH. The influence of the chloride concentration on the $E/J$ curve was investigated for NaCl/HCl solutions of which the ratio between the
NaCl and the HCl concentration was equal to 4, and the total chloride concentration varied between 0.5 and 5 M. For a RuO$_2$/TiO$_2$-electrode it appeared that the chloride concentration has no influence upon the current density at $E = 1250$ mV; this potential is minimal 50 mV higher than the reversible potential of the Cl$^-$/Cl$_2$ couple obtained the results were in agreement with those of Kuhn and Mortimer$[4]$ and those of Erenburg et al.$[7]$.

3.4.2 Temperature. The temperature was varied between 2 and 70$^\circ$ to establish the effect of the temperature of the electrolysis on the $E/J$ relation for a RuO$_2$-electrode. From the Tafel slope $b$ the transfer coefficient $\alpha = (2.3RT/bF) - 1$ was calculated. This equation is used when the Heyrovsky reaction is the rate-determining step$[10]$. It appeared that $\alpha$ is independent of the temperature. The average value of the transfer-coefficient was $0.45 \pm 0.05$.

In Fig. 5 the current density at an overpotential of 60 mV is plotted vs the reciprocal absolute temperature. From the slope of the straight line of this figure it was calculated that the activation energy is 6.5 kcal/mol at an overpotential of 60 mV.

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in this case decreased more strongly and no gas evolution could be observed, it is obvious that otherwise the behaviour of the RuO$_2$/TiO$_2$-electrode is comparable to that of the graphite electrode.

The chlorine, evolved at the electrode on open circuit is formed from atomic chlorine. Chlorine can be formed according to two mechanisms.

4.1 Tafel mechanism

The Tafel mechanism refers to the reaction $2\text{Cl}_2 \rightarrow \text{Cl}_2$. The potential on open circuit is determined by the equilibrium between the cathodic and the anodic Volmer reaction

$$\text{Cl}^- \rightarrow \text{Cl}_2 + e^-.$$ 

First we discuss the case where atomic chlorine is present only on the outer surface of the electrode. Moreover, we neglect the dissociation reaction of molecular chlorine. For this case it can be deduced that $\theta = \frac{2k_T0}{1 + 2k_T0t_a}$. 

Integration of equation (1) gives:

$$\theta = \frac{\theta_0}{1 + 2k_T0t_a}.$$ 

The rate of the chlorine evolution, $v_r$, according to the Tafel reaction is equal to:[10]

$$v_r = \frac{j_0}{F} \frac{2z}{\theta^2}.$$ 

Neglecting the current due to the discharge of the capacitance of the double layer, the rate of the cathodic Volmer reaction is then equal to the rate of anodic Volmer reaction. So, it follows that the degree of coverage with atomic chlorine, $\theta$, is given by[11]

$$\theta = \frac{1}{1 + \left\{\left(1 - \theta_0\right)/\theta_0\right\} \exp \left(\frac{F\eta}{RT}\right)}.$$ 

If $\theta_0 \ll 1$, then for $\theta$ at low overpotentials,

$$\theta \approx \theta_0 \exp \left(\frac{F\eta}{RT}\right).$$ 

From (2) and (5) it follows that

$$\eta = -\frac{RT}{F} \ln \left(2k_T0t_a + \frac{\theta}{\theta_0}\right).$$ 

If $2k_T0t_a \gg \theta_0$, equation (6) shows that the slope of the $\eta/\ln t_a$ curve is $-RT/F$.

In extension we now suppose that atomic chlorine is also present in the bulk of the anode material. This means that atomic chlorine diffuses out of the bulk of the anode material and reacts to molecular chlorine according to the Tafel reaction.

We suppose that the diffusion of chlorine atoms can be described as a one-dimensional diffusion problem. Consequently, the diffusion satisfies to the following second equation of Fick,

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}.$$ 

Moreover, it is supposed that at $t_a = 0$ the concentration of atomic chlorine is independent of the distance $x$ and that the total thickness is so great that this thickness can be considered as infinity. The boundary conditions are then:

$$c(x, 0) = c_0 \quad \text{for} \quad x > 0$$

$$c(x, t_a) = c_0 \quad \text{for} \quad t_a > 0$$

and the degree of coverage $\theta = p\theta_0$.

The relation between $c(0, t_a)c_0$ and $t_a$ was calculated for different values of $D$, $k_T$, and $c_0$. The calculation was done by means of a Crank–Nicolson difference scheme with nonlinear boundary conditions[15] on a Burroughs B6700 computer. The time step size we used was $\Delta t = 0.01$ s and for the $x$-coordinate 640 gridpoints from 0 to infinity were taken.

All these three factors have a great influence upon the log $c(0, t_a)c_0$/log $t_a$ curves. Since the concentration of atomic chlorine at the electrode surface is proportional to exp ($F\eta/RT$), $\eta_0(t_a) - \eta_0$ instead of log $c(0, t_a)c_0$ is represented graphically. The results of the calculations are shown in Figs. 8 and 12. In Fig. 8 $\eta_0(t_a) - \eta_0$ is plotted as log $t_a$ for $c_0 = 10^{-5}$ mole/cm$^3$, $D = 10^{-4}$ cm$^2$/s and various values of $k_T$.

In Fig. 9 for $c_0 = 10^{-7}$ mole/cm$^3$, $k_T = 10^6$ cm$^4$/mole s and various values of $D$; and in Fig. 10 for $D = 10^{-3}$ cm$^2$/s, $k_T = 10^6$ cm$^4$/mole s and various values of $c_0$.

From the theoretical $(\eta_0(t_a) - \eta_0)/\log t_a$-relations, (5) and from the proportionality between $c$ and $\theta$ it follows that in the range 20 mV $< \eta_0$ (0) $< 120$ mV at 0.1 s $< t_a$ $< 10$ s the $(\eta_0(0) - \eta_0)/\log t_a$-curve is practically linear, its slope $h_T$ is generally...
practically independent of $c_0$ and $k_f$, whereas $D$ can vary from $10^{-4}$ to $10^{-5}$ cm$^2$/s. The slope $h_T$ is then equal to about 14 mV at 25°. At smaller values of $D$ however, the slope of the $(\eta_n(0) - \eta_n)/\log t_n$-curve changes strongly with increasing log $t_n$.

4.2 Volmer–Heyrovsky mechanism

The other mechanism according to which molecular chlorine is formed on open circuit, is the Volmer–Heyrovsky mechanism, consisting of

$$\text{Cl}_2 + \text{Cl}^- \rightarrow \text{Cl}_2 + e^-$$

anodic Heyrovsky reaction;

$$\text{Cl}_2 + e^- \rightarrow \text{Cl}^-$$

cathodic Volmer reaction.

As mentioned before, the rate of the chlorine evolution is determined by the anodic Heyrovsky reaction, while neglecting the cathodic Heyrovsky reaction. First we discuss the case where only atomic chlorine is present on the electrode surface. The rate of the decrease of the degree of coverage is given by

$$- \frac{d\theta}{dt_n} = 2 k_B \theta \exp \frac{a \mu F \eta_n}{RT}.$$  \hspace{1cm} (8)

If $\theta < 1$, then $\theta$ at low overpotentials can be calculated with equation (5). Substitution of $\theta$ from (5) into (8), followed by integration and rearrangements, deliver us the following expression

$$\eta_n = - \frac{RT}{a \mu F} \ln \left[ 2 k_B t_n \exp \frac{a \mu \eta_n(0)}{RT} \right]$$ \hspace{1cm} (9)

In extension, we discuss in the following also the case when atomic chlorine diffuses out of the bulk of the electrode material. We apply also the one dimensional second equation of Fick with the following boundary
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Fig. 13. Potential decay curves for the chlorine formation on open circuit according to the Volmer–Heyrovsky mechanism at $D = 10^{-5}$ cm$^2$/s, $k_H^* = 10^{3/2}$ cm$^{3/2}$/mole$^1$ s and various $c_0$.

conditions

\[ c(x,0) = c_0 \quad \text{and} \quad x \geq 0, \]

\[ c(x, t_n) = c_0 \quad \text{for} \quad t_n \geq 0, \]

\[ D \frac{\delta c(x, t_n)}{\delta x} = k_H^* c(0, t_n)^{3/2}. \]

The latter condition can be deduced from the rate of the chlorine evolution on open circuit, $v_H$ = $j_0, H \theta^{1+s_H}$, according to the Volmer–Heyrovsky mechanism. The rate is given by

\[ v_H = j_0, H \theta^{1+s_H} F \theta^{-s_H}. \]

where $j_0, H$ is the exchange current density of the Heyrovsky reaction. Since $\theta = \nu c$ and assuming $s_H = 0.5$, we get $v_H = k_H^* c(0, t_n)^{3/2}$ where

\[ k_H^* = \frac{j_0, H}{F \theta^{1/2}}. \]

For this case also the ratio between $c(0, t_n)/c_0$ and \( t_n \) was calculated for different $D$, $k_H^*$ and $c_0$ values.

In analogy with the Tafel treatment, $\eta_n(0) - \eta_n$ is plotted vs $\log t_n$ for $c_0 = 10^{-5}$ mole/cm$^3$, $D = 10^{-4}$ cm$^2$/s and various $k_H^*$ (see Fig. 11); for $c_0 = 10^{-6}$ mole/cm$^3$, $k_H^* = 10^{-2}$ cm$^{3/2}$/mole$^1$ s and various $D$ (see Fig. 12) and for $D = 10^{-5}$ cm$^2$/s, $k_H^* = 10^{3/2}$ cm$^{3/2}$/mole$^1/2$ s and various $c_0$ (see Fig. 13). The slope $h_n$ of the $(\eta_n(0) - \eta_n) log t_n$ curve at $20$ mV $< \eta_n(0) - \eta_n < 120$ mV and at $0.1$ s $< t_n < 10$ s is also practically independent of $c_0$, $k_H^*$ and of $D$ varying from $10^{-4}$ to $10^{-5}$ cm$^2$/s. The slope $h_n$ is then equal to about $20$ mV.

5. DISCUSSION

5.1 The mechanism of the chlorine formation

5.1.1 The Tafel slope of the $E$/log $J$ curve. The Tafel slope, $b$, generally used to elucidate the mechanism of the chlorine formation. It appears that the slope $b$ for a RuO$_2$/TiO$_2$-electrode is influenced by the temperature of the firing process at the preparation of this electrode (Fig. 4) and by the temperature of the electrolysis (3.4.2). At the firing temperature of $500^\circ$ the slope $b$ has a minimum value. For one series of experiments, this value is about $41$ mV and for another series about $50$ mV. Mostly, a minimum value of about $40$ mV at $25^\circ$ was found for RuO$_2$/TiO$_2$-electrode fired at $500^\circ$. It is already mentioned that the Tafel slope increases linearly with the absolute temperature (3.4.2). Taking into account that $\alpha = 0.45 \pm 0.05$ for the series of experiments, mentioned in section 3.4.2., and that the Tafel slope at $25^\circ$ for an ‘ideal’ RuO$_2$/TiO$_2$-electrode, is about $40$ mV, it follows that $\alpha = 0.5$ for the chlorine evolution at an ‘ideal’ RuO$_2$/TiO$_2$-electrode.

For a Ru-electrode pre-electrolysed with an anodic current density of $25$ mA/cm$^2$ for $1$ day, the Tafel slope at $25^\circ$ was also about $40$ mV.

Comparing a slope of $40$ mV with the theoretical ones for the possible reaction mechanism[10], it follows that chlorine is formed according to the Volmer–Heyrovsky mechanism and that the Heyrovsky reaction is the rate-determining step.

A slope higher than $40$ mV may be caused by a bad electrical contact between the RuO$_2$/TiO$_2$ coating layer and the titanium sheet of the electrode. It is possible that the experimental value of $40$ mV is not the true minimum value of the Tafel slope. In the literature smaller values of the Tafel slope are given. Faita and Fiori[2] found a slope of about $30$ mV for electrodes consisting of oxides of Ru, Ti and Ir. Bondar et al[3] obtained a slope of $34$ mV for a Ti/RuO$_2$ electrode with $90\%$ Ti and $10\%$ Ru in theactive layer. A slope of $30$ mV pertains to the Tafel reaction as the rate-determining step[10]. The difference in experimental values of the Tafel slope may be explained by a different composition of the electrode.

5.1.2 The relation between the overpotential on open circuit and the time. Section 4 shows that the relation between the overpotential on open circuit and the time can be used in order to elucidate the reaction mechanism. Owing to the conclusions in 5.1.1, we discuss the Volmer–Tafel mechanism only for the case that the Tafel reaction is the rate-determining step and the Tafel slope is $30$ mV at $25^\circ$. If on open circuit no diffusion of atomic chlorine from the bulk of the electrode material occurs the theoretical slope of the $\eta_n/log t_n$ curve is $60$ mV for a sufficiently long time. This value is much greater than the experimental value of $22$ mV. In the case that diffusion plays a role the $(\eta_n(0) - \eta_n)/log t_n$ relation is given for different values of $k_f$, $c_0$ and $D$ in the Figs. 8–10. A diffusion coefficient in the order of $10^{-5}$ cm$^2$/s is a reasonable assumption, since the diffusion of atomic chlorine occurs on the surface of the crystallites of the active layer of the RuO$_2$/TiO$_2$ and of the Ru-electrode.

The degree of coverage $\theta_0$ at the moment of switching-off the current increases with the overvoltage $\eta$ during the electrolysis according to $\theta \approx \theta_0$ exp ($F\eta/RT$). At sufficient great values of $\eta_n(0) - \eta_n$, the theoretical $(\eta_n(0) - \eta_n)/log t_n$ curve is linear and has a slope of about $14$ mV (4.1). Unfortunately, from the experimental $\eta_n/log t_n$ curves for $J > 0.75$ mA/cm$^2$, ie for $\eta > 58$ mV (Fig. 6), the determination of $\eta_n(0)$ is impossible. Especially for high overpotentials the
double layer will have a great effect on the potential decay curve \( t_s \), smaller than 0.1 s. However, for the results given in Fig. 7 and in Fig. 6 with exception of those for \( J = 0.75 \) mA/cm\(^2\), it is likely that \( \eta_0(0) - \eta_0 \) will be sufficiently great in order to obtain a linear \( \eta_0/\log t_s \) relation. The experimental slope of the \( \eta_0/\log t_s \) curve, viz 20 mV (Fig. 6) and 22 mV (Fig. 7) does not agree with the theoretical one for the Tafel mechanism.

In the following we discuss the Volmer–Heyrovsky mechanism if the Heyrovsky reaction is the rate-determining step and the Tafel slope is 40 mV at 25°. Analogous to the discussion of the Tafel mechanism we distinguish two cases viz without and with diffusion of atomic chlorine. When the diffusion is not taken into consideration, a comparison of the experimental slope of the \( \eta_0/\log t_s \) curve with the theoretical one, ie 120 mV, shows that both slopes do not coincide. However, when the diffusion is taken into consideration, the theoretical slope of the \( \eta_0/\log t_s \) at a sufficiently long time is equal to 20 mV (Figs 11–13). So, there is a very good agreement between the theoretical slope and the experimental slope. The experimental slope at a sufficiently long time is equal to 20 mV (Figs 11–13): So, there is a very good agreement between the theoretical slope and the experimental slope. The experimental slope is sufficiently long time is equal to 20 mV (Fig. 6) and 22 mV (Fig. 7) does not agree with the theoretical one for the Tafel mechanism.

It appeared that the Tafel slope \( \theta \) depends on the firing temperature. For an 'ideal' RuO\(_2\)/TiO\(_2\)-electrode we obtain a transfer coefficient of 0.5. This value is also found for the Ru-electrode. A smaller transfer-coefficient may be caused by an oxide layer. The real experiment exchange current density is equal to that of the Heyrovsky reaction. For RuO\(_2\)/TiO\(_2\)-electrodes, formed by firing at 500° for 2 h in a 4 M NaCl solution saturated with chlorine, the real exchange current density \( j_{0,H} \) of the Heyrovsky reaction is equal to 13 \times 10\(^{-5}\) mA/cm\(^2\) at 25° (3.3.4.).

At sufficient high overpotentials, for instance \( \eta > 60 \) mV, the cathodic reaction can be neglected with respect to the anodic reaction. The current density \( j \) for the Volmer–Heyrovsky reaction where the Heyrovsky reaction is the rate-determining step is given by[10]

\[
j = 2j_{0,H} \theta \exp \left( \frac{\alpha H F \eta}{RT} \right).
\]

Since the Tafel slope is about 40 mV, the literature[10] shows that \( \theta/\theta_0 \) is proportional to \( \exp \left( F\eta/RT \right) \).

References