THE OPEN-CIRCUIT DECAY BEHAVIOUR OF CHLORINE-EVOLVING ELECTRODES

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Abstract—The open-circuit decay behaviour of a previously chlorine-evolving electrode, has been studied. It has been stated that the rate of the chlorine evolution on open circuit is determined by the parameters of the rate equation of the chlorine evolution and the diffusion of atomic chlorine out of the electrode. Both possible mechanisms *viz.* the Volmer–Tafel and the Volmer–Heyrovsky mechanism have been considered.

Numerically calculated relations have been given between the overpotential on open circuit, the rate of the chlorine evolution on open circuit and time. Moreover, theoretical relations are calculated between the overpotential during the anodic polarisation and the overpotential on open circuit at the moment of, and 1 s after, switching off the polarising current, and the total quantity of chlorine evolved on open circuit, divided by the rate of the exchange reaction of the chlorine evolution.

Earlier experimental results on the behaviour on open circuit, of the chlorine–chloride electrode in chloride melts and in aqueous acidic sodium chloride solutions have been compared with the calculated theoretical relations. It has been found that some earlier conclusions on the behaviour of the chlorine–chloride electrode need correction.

NOMENCLATURE

$c(x, t_n)$	concentration of atomic chlorine present in an electrode at a distance x at time t_n after switching off the polarisation current
c_0	$c(x, 0)$ at $x \geq 0$ or $c(\infty, t_n)$ at $t_n \geq 0$
D	diffusion coefficient of atomic chlorine
E	electrode potential <i>vs sce</i>
F	Faraday constant
h	the slope of the linear part of the $\eta_n/\log t_n$ curve
j	real <i>cd</i>
j_0	real exchange <i>cd</i>
p	constant factor; $p = \theta/c$
$\dot{q}$	$\int_0^{t_n} \frac{j_n}{j_0} dt_n$
R	gas constant
T	temperature
t_n	time after switching off the polarisation current
x	distance in the electrode measured from the boundary electrode surface–electrolyte

Greek symbols

α	transfer coefficient
η	overpotential during anodic polarisation
η_n	overpotential on open circuit; $\eta_n = E_n - E_r$
$\eta_n(0)$	η_n at $t_n = 0$
$\eta_n(1)$	η_n at $t_n = 1$ s
θ	degree of coverage with atomic chlorine
θ_0	θ at $t_n = 0$; this being equal to the degree of coverage at the potential of the electrode on current flow

Subscripts

i	current flow conditions
n	open circuit conditions
r	thermodynamic conditions
H	Heyrovsky reaction
T	Tafel reaction
V	Volmer reaction

INTRODUCTION

Investigation of the time-dependent decay of potential after polarisation of an electrode provides information

complementary to that obtained by the investigation of potential–current density relations and its modifications. The potential decay behaviour can be used successfully to elucidate the mechanism of the electrode reactions[1–6].

Theoretically potential decay curves have been obtained by numerical calculations with computers. At practically the same time these calculations have been performed for the H_2/H^+ [3] and for the Cl_2/Cl^- electrode process[4].

Tilak and Conway[3] have examined the potential decay behaviour assuming that the chemisorbed intermediate is only present at the surface of the electrode, whereas Janssen *et al*[4] have assumed that the chemisorbed intermediate is also present in the bulk of the electrode material by diffusion and diffuses out of this material during the potential decay. The diffusion of the intermediate out of the electrode material strongly affects potential decay behaviour[2, 4, 7].

The calculated theoretical curves given in the literature are only useful at overpotentials greater than about 60 mV, owing to the neglect of the back reaction[3, 4]. Also, the difference between the overpotential $\eta_n(0)$ on open circuit at the moment of switching off the polarising current ($t_n = 0$) and the overpotential η_n on open circuit was calculated[4].

In the present paper, theoretical η_n/t_n -relations are derived for the Cl_2/Cl^- -process at $\eta_n > 5$ mV, the other conditions being the same as those in the literature[4]. Moreover, relations between overpotentials during the electrolysis and overpotential on open circuit are given.

2. THEORY

For an electrode process, involving chemisorbed intermediates, switching off the polarising current leads to a change of electrode potential E with time t_n . The decay of electrode potential depends on both the discharge of the ionic double-layer and the decrease in

the degree of coverage of the electrode surface by the intermediate of the electrode reactions.

Tilak and Conway[4] found that the effect of the double-layer capacitance upon the potential decay behaviour is insignificant. Their conclusion is surely correct for the case discussed here. The time constant for the discharge of the ionic double layer for an electrode process, not involving chemisorbed intermediates, is about 5×10^{-3} s at an exchange-current density of about 0.1 mA/cm^2 [8].

In this paper the Cl_2/Cl^- -electrode process is considered. The results obtained can be applied to analogous processes for instance the H_2/H^+ electrode process. The latter is generally discussed in the literature. The chlorine formation by the electrochemical oxidation of chloride ions can occur according to two different reaction mechanisms, viz the Volmer-Tafel mechanism and the Volmer-Heyrovsky mechanism.

It is assumed that, at the moment of switching off the polarisation current, atomic chlorine — the intermediate of the Cl_2/Cl^- electrode process — is also present in the bulk of the electrode material and reacts to molecular chlorine on the electrode surface according to both the Tafel and/or the Heyrovsky reaction.

2.1 Volmer-Tafel mechanism

The Volmer-Tafel mechanism consists of two reactions, viz the Volmer reaction ($\text{Cl}^- \rightleftharpoons \text{Cl}_{\text{ad}} + e^-$) and the Tafel reaction ($2 \text{Cl}_{\text{ad}} \rightleftharpoons \text{Cl}_2$). The potential on open circuit is determined by the equilibrium between the cathodic and the anodic Volmer reaction. The rate of the formation of molecular chlorine depends on the net rate of the Tafel reaction. The rate of the removal of atomic chlorine can be deduced from the rate equations of the Tafel reaction[9]. This rate can be expressed as a current density.

$$j_{n,T} = j_{0,T} \left[\frac{\theta_n^2}{\theta_r^2} - \frac{(1 - \theta_n)^2}{(1 - \theta_r)^2} \right] \quad (1)$$

It is assumed that the diffusion of chlorine atoms out of the bulk of the electrode material can be described as a

one-dimensional diffusion process and satisfies the second equation of Fick.

$$\frac{\delta c(x, t_n)}{\delta t_n} = D \frac{\delta^2 c(x, t_n)}{\delta x^2} \quad (2)$$

This equation is solved with the following boundary conditions

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

$$c(\infty, t_n) = c_0 \quad \text{for } t_n \geq 0$$

$$D \frac{\delta c(x, t_n)}{\delta x} = \frac{j_{0,T}}{F} \left(\frac{c^2(0, t_n)}{c_r^2} - \frac{(1 - pc(0, t_n))^2}{(1 - pc_r)^2} \right)$$

where $\theta = pc$ and p is a constant factor. The latter boundary condition denotes that the rate of the diffusion of atomic chlorine out of the bulk of the electrode is equal to the rate of the removal of atomic chlorine on the electrode surface, see (1). The boundary conditions are the same as those in the literature with the exception of the last term on the right hand side. The additional term represents the influence of the dissociation reaction of molecular chlorine upon the removal of atomic chlorine.

The relation between $c(0, t_n)/c_r$ and t_n was calculated as described[4]; this relation is equal to that between θ_n/θ_r and t_n . After rearrangement of the relation between θ_n and η_n given in[7], it follows that

$$\frac{\theta_n}{\theta_r} = \frac{1}{\theta_r + (1 - \theta_r) \exp - \left[\frac{F \eta_n}{RT} \right]} \quad (3)$$

Calculated relations between η_n and $\log t_n$ are shown in Figs. 1 and 2. η_n is plotted vs $\log t_n$ for $j_{0,T} = 10^{-4} \text{ A/cm}^2$, $D = 10^{-5} \text{ cm}^2/\text{s}$, $\theta_r = 10^{-2}$ and various values of θ_0 in Fig. 1. The influence of $j_{0,T}$, D and θ_r upon the $\eta_n/\log t_n$ relation are shown in Fig. 2. In all our calculations $T = 298 \text{ K}$, and $p = 10^5 \text{ cm}^3/\text{mol}$ were used. The calculation was done by means of a Crank-Nicholson difference scheme with nonlinear boundary conditions[12] on a Burroughs B7600 com-

Fig. 1. Potential decay curves for the chlorine formation on open-circuit according to the Volmer-Tafel mechanism at various values of θ_0/θ_r and $\eta_n(0)$ and at $j_{0,T} = 10^{-4} \text{ A/cm}^2$, $\theta_r = 10^{-2}$ and $D = 10^{-5} \text{ cm}^2/\text{s}$.

curve	θ_0/θ_r	$\eta_n(0) \text{ mV}$
1	80	154
2	40	108
3	20	83
4	8	55
5	4	36
6	2	18

Fig. 2. Potential decay curves for the chlorine formation on open-circuit according to the Volmer-Tafel mechanism at various values of $j_{0,T}$, θ_r , $\eta_n(0)$ and D and for $\theta_0/\theta_r = 80$.

curve	$j_{0,T}$ A/cm ²	D cm ² /s	θ_r	$\eta_n(0)$ mV
1	10^{-7}	10^{-5}	10^{-2}	154
2	10^{-6}	10^{-5}	10^{-2}	154
3	10^{-5}	10^{-5}	10^{-2}	154
4	10^{-4}	10^{-5}	10^{-3}	115
5	10^{-4}	10^{-4}	10^{-2}	154
6	10^{-4}	10^{-5}	10^{-2}	154
7	10^{-4}	10^{-6}	10^{-2}	154
8	10^{-3}	10^{-5}	10^{-2}	154

puter. The time step size we used was $\Delta t = 0.01$ s and for the x -coordinate 640 gridpoints from 0– ∞ were taken. In the literature[2, 6, 7] the rate of the gas evolution or the total volume of gas evolved is given as a function of the time after switching off the polarising current and even so the total volume of gas evolved as a function of the potential on open circuit.

From the calculated relation between θ_n and t_n (Fig. 2) and from (1), the relation between $j_{n,T}$ and t_n was calculated. $\log(j_{n,T}/j_{0,T})$ is plotted vs $\log t_n$ in Fig. 3 for various values of $j_{0,T}$ and for $D = 10^{-5}$ cm²/s, $\theta_r = 10^{-2}$, $\theta_0 = 0.8$ and $\eta_n(0) = 154$ mV. Figure 4 shows the relation between η_n and $j_{0,T}q_T$, where q_T is proportional to the total volume of evolved gas during the time t_n after switching off the polarising current. This value was determined by graphical integration of the $j_{n,T}/t_n$ curve.

The behaviour of the electrode after switching off the polarising current is closely related to the behaviour of the electrode during anodic polarisation, as shows the relation between η_i and $\eta_n(0)$. This relation can be calculated from the theoretical relations between η_i and θ_i [9] and between η_n and θ_n [3] with substitution of θ_n by $\eta_n(0)$ and of θ_i by θ_0 .

In Figure 5 $\eta_n(0)$ is plotted vs η_i for $\theta_r = 10^{-2}$, $j_{0,T} = 10^{-4}$ A/cm² and for various values of $j_{0,T}/j_{0,v}$. This figure shows that $\eta_n(0) = \eta_i$ when $j_{0,T}/j_{0,v} \rightarrow 0$; this means that in this case the Volmer reaction has no influence at all upon the $\eta_i/\log j_i$ relation which is then completely determined by the Tafel reaction.

To elucidate the rate-determining step of the Cl_2/Cl^- reaction, the $\eta_n(0)/\eta_i$ relation should be useful. However, the experimental determination of $\eta_n(0)$ is often not easily done owing to both the discharge of the ionic double-layer and the sharp decrease of η_n directly

after switching off the polarising current. That means in many cases $\eta_n(0)$ cannot be used for elucidation of the reaction mechanism. However, the overpotential on open circuit at more or less arbitrary $t_n = 1$ s, $\eta_n(1)$, appears to be the more useful.

The $\eta_n(1)/\eta_i$ -relation can be deduced from the η_i/θ_i ,

Fig. 3. $j_{n,T}/j_{0,T}$ vs the time after switching off the polarising current for the chlorine formation according to the Volmer-Tafel mechanism at various values of $j_{0,T}$ and at $D = 10^{-5}$ cm²/s, $\theta_r = 10^{-2}$, $\theta_0 = 0.8$ and $\eta_n(0) = 154$ mV.

Fig. 4. Relationship between the overvoltage on open-circuit and the charge $j_{0,T} q_T$ for the chlorine formation according to the Volmer-Tafel mechanism at various values of $j_{0,T}$ and at $D = 10^{-5}$ cm²/s, $\theta_r = 10^{-2}$, $\theta_0 = 0.8$ and $\eta_n(0) = 154$ mV.

$\eta_n(0)/\theta_0$ and $\eta_n/\log t_n$ relations with $\theta_0 = \theta_i$, $\eta_n(1)/\eta_r$ relations are also plotted in Fig. 5 for various values of $j_{0,T}/j_{0,V}$ and for $\theta_r = 10^{-2}$, $j_{0,T} = 10^{-4}$ A/cm² and $D = 10^{-5}$ cm²/s.

In Figure 6 $\eta_n(1)/\eta_i$ curves are shown for

The potential on open circuit can also be determined by this mechanism. The relation between the degree of coverage and the overpotential on open circuit is rather complex. Assuming that $\alpha_V = \alpha_H$, it has been deduced[6] that

$$\theta_n = \frac{j_{0,V} - j_{0,H} \exp\left(-\frac{F\eta_n}{RT}\right)}{j_{0,V} - j_{0,H} \frac{1 - \theta_r}{\theta_r} + \left(\frac{1 - \theta_r}{\theta_r} j_{0,V} - j_{0,H}\right) \exp\left(-\frac{F\eta_n}{RT}\right)} \quad (4)$$

$j_{0,T}/j_{0,V} \rightarrow 0$, $\theta_r = 10^{-2}$, $c_r = 10^{-7}$ mol/cm³ and various values of $j_{0,T}$ and D .

2.2 Volmer-Heyrovsky mechanism

This mechanism consists of the Volmer reaction ($\text{Cl}^- \rightleftharpoons \text{Cl}_{ad} + e^-$) and the Heyrovsky reaction ($\text{Cl}^- + \text{Cl}_{ad} \rightleftharpoons \text{Cl}_2 + e^-$).

Neglecting the discharge of the double-layer as before, the net polarising current on open circuit is zero and the absolute value of the net rate of the Heyrovsky reactions is then equal to that of the Volmer reaction; this means that $j_H = -j_V$.

The rate of the removal of atomic chlorine can be deduced from the rate equation for the anodic and

Fig. 5. Relationship between the overvoltage on open-circuit at the moment of switching off the polarising current and the overvoltage on current flow (—) and relationship between the overvoltage on open-circuit at 1 s after switching off the polarising current and the overvoltage on current-flow (---). Both relationships are given for the chlorine formation according to the Volmer-Tafel mechanism at various values of $j_{0,T}/j_{0,V}$ and at $j_{0,T} = 10^{-4}$ A/cm², $\theta_r = 10^{-2}$ and $D = 10^{-5}$ cm²/s.

Fig. 6. Overvoltage on open-circuit at 1 s after switching off the polarising current vs overvoltage on current flow for the chlorine formation according to the Volmer-Tafel mechanism at various values of $j_{0,T}$ and D and at $\theta_r = 10^{-2}$ and $j_{0,T}/j_{0,V} \rightarrow 0$.

curve	$j_{0,T} \text{ A/cm}^2$	$D \text{ cm}^2/\text{s}$
1	10^{-6}	10^{-5}
2	10^{-5}	10^{-5}
3	10^{-4}	10^{-4}
4	10^{-4}	10^{-5}
5	10^{-4}	10^{-6}
6	10^{-3}	10^{-5}

cathodic Heyrovsky reaction. It follows that

$$j_H = j_{0,H} \left(\frac{\theta_n}{\theta_r} \exp \frac{\alpha_H F \eta_n}{RT} - \frac{(1 - \theta_n)}{(1 - \theta_r)} \right)$$

Fig. 7. Potential decay curves for the chlorine formation on open-circuit according to the Volmer-Heyrovsky mechanism at various values of θ_0/θ_r and $\eta_n(0)$ mV and at $j_{0,H}/j_{0,V} \rightarrow 0$, $j_{0,H} = 5 \times 10^{-6} \text{ A/cm}^2$, $\theta_r = 10^{-3}$ and $D = 10^{-5} \text{ cm}^2/\text{s}$.

curve	θ_0/θ_r	$\eta_n(0) \text{ mV}$
1	800	213
2	400	167
3	200	142
4	80	115
5	40	96
6	20	78
7	8	54
8	4	36
9	2	18

$$\times \exp - \frac{(1 - \alpha_H) F \eta_n}{RT} \quad (5)$$

As in section 2.1, it is assumed that atomic chlorine diffuses out of the bulk of the electrode material. So, the one-dimensional second equation of Fick can be applied. The boundary conditions used are

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

$$c(\infty, t_n) = c_0 \quad \text{for} \quad t_n \geq 0,$$

$$D \frac{\delta c(x, t_n)}{\delta x} = \frac{2j_{0,H}}{F} \left(\frac{c(0, t_n)}{c_r} \right) \times \exp \frac{F \eta_n}{2RT} - \frac{1 - pc(0, t_n)}{1 - pc_r} \exp - \frac{F \eta_n}{2RT}$$

where $\theta = pc$ and $\alpha_H = 0.5$. For this case, the relation between $c(0, t_n)/c_r$ and t_n and that between η_n and t_n were calculated for various $j_{0,H}$, $j_{0,H}/j_{0,V}$, c_0 , c_r and D values. The relation between θ_n and n is given by (3) for $j_{0,H}/j_{0,V} \rightarrow 0$ and by (4) for the other $j_{0,V}$ values.

Calculated $\eta_n/\log t_n$ curves are shown in Figs. 7 and 8. The results are given in Fig. 7 for $j_{0,H} = 5 \times 10^{-6} \text{ A/cm}^2$, $j_{0,H}/j_{0,V} \rightarrow 0$, $D = 10^{-5} \text{ cm}^2/\text{s}$, $\theta_r = 10^{-3}$ and various θ_0 values. The influence of $j_{0,H}$, D and θ_r at $j_{0,V}/j_{0,H} \rightarrow 0$ upon the $\eta_n/\log t_n$ curves are shown in Fig. 8. The effect of $j_{0,H}/j_{0,V}$ is shown in Fig. 9, where $j_{0,H} = 5 \times 10^{-6} \text{ A/cm}^2$, $D = 10^{-5} \text{ cm}^2/\text{s}$ and $\theta_r = 10^{-2}$.

Just as for the Volmer-Tafel mechanism, the theoretical relation between the gas evolution rate on open circuit, expressed as the current density $j_{n,H}$ and the time after switching off the polarising current was determined. This relation was obtained from (5) and from the calculated $\eta_n/\log t_n$ curves. In Fig. 10 log

Fig. 8. Potential decay curves for the chlorine formation on open-circuit according to the Volmer-Heyrovsky mechanism at various values of $j_{0,H}$, θ_r , $\eta_n(0)$ and D and at $j_{0,H}/j_{0,v} \rightarrow 0$ and $\theta_o/\theta_r = 80$.

curve	$j_{0,H}$ A/cm ²	D cm ² /s	θ_r	$\eta_n(0)$ mV
1	5×10^{-6}	10^{-5}	10^{-2}	154
2	5×10^{-7}	10^{-5}	10^{-3}	115
3	5×10^{-6}	10^{-4}	10^{-3}	115
4	5×10^{-6}	10^{-5}	10^{-3}	115
5	5×10^{-6}	10^{-6}	10^{-3}	115
6	5×10^{-5}	10^{-5}	10^{-3}	115
7	5×10^{-4}	10^{-5}	10^{-3}	115

Fig. 9. Potential decay curves for the chlorine formation on open-circuit according to the Volmer-Heyrovsky mechanism at various values of $j_{0,H}/j_{0,v}$, θ_o/θ_r and $\eta_n(0)$ and for $\theta_r = 10^{-2}$ and $D = 10^{-5}$ cm²/s and $j_{0,H} = 5 \times 10^{-6}$ A/cm².

curve	$j_{0,H}/j_{0,v}$	θ_o/θ_r	$\eta_n(0)$ mV
1	0	80	154
2	10^{-3}	80	145
3	10^{-2}	80	113
4	0	8	55
5	10^{-2}	8	53
6	10^{-1}	8	40

Fig. 10. $j_n/j_{0,H}$ vs the time after switching off the polarising current for the chlorine formation according to the Volmer–Heyrovsky mechanism at various values of $j_{0,H}$ and at $D = 10^{-5} \text{ cm}^2/\text{s}$, $\theta_r = 10^{-3}$, $\theta_0 = 0.08$ and $j_{0,H}/j_{0,v} \rightarrow 0$.

$(j_n/j_{0,H})$ is plotted vs $\log t_n$ for $j_{0,H}/j_{0,v} \rightarrow 0$, $D = 10^{-5} \text{ cm}^2/\text{s}$, $\theta_r = 10^{-3}$, $\theta_0 = 0.08$ and various values of $j_{0,H}$. The $\eta_n/j_{0,H}q_H$ relation was obtained on the same way as that for the Tafel reaction. This relation is shown in Fig. 11 for the parameters of Fig. 10.

Analogous to the Tafel treatment, relations between η_i and $\eta_n(0)$ and between η_i and $\eta_n(1)$ can be derived. In Fig. 12, both $\eta_n(0)$ and $\eta_n(1)$ are plotted vs η_i for $j_{0,H}/j_{0,v}$. In Fig. 13 $\eta_n(1)/\eta_i$ curves are given for $\theta_r = 10^{-2}$, $j_{0,H}/j_{0,v} \rightarrow 0$ and various values of $j_{0,H}$ and D .

3. DISCUSSION

3.1 Usefulness of the investigation of decay behaviour

By comparing the experimental with the theoretical $\eta_n/\log t_n$ curves, in principle it is possible to elucidate

the reaction mechanism of the chlorine evolution. This becomes much easier when the experimental $\eta_i/\log j_i$ curves are thoroughly known.

For the two discussed mechanisms the $\eta_n/\log t_n$ as well as the $\log(j_n/j_0)/\log t_n$ curves at $\eta_n > 20 \text{ mV}$ and $\eta_n(0) - \eta_n > 20 \text{ mV}$ are practically linear for a wide range of exchange current densities, diffusion coefficients, degrees of coverage at the reversible potential and of overpotentials during anodic polarisation. From sections 2.1 and 2.2 it follows that the absolute values of the slopes of the $\eta_n/\log t_n$ and of $\log(j_n/j_0)/\log t_n$ curve at 25°C are about 14 mV and 0.5 , respectively, for the Tafel reaction as the rate determining step and about 20 mV and 0.5 , respectively, for the Heyrovsky reaction as the rate-determining step. These results agree with those in the literature[4].

The slopes of the $\log(j_n/j_{0,H})/\log t_n$ and of the $\log(j_n/j_{0,H})/\log t_n$ curves are equal. Therefore, the determination of the rate of the chlorine evolution on open circuit as a function of the time after switching off the polarising current reveals nothing about the mechanism. In the literature $\eta_n(0)$ has been determined by linear extrapolation of the relation between η_n and the quantity of hydrogen evolved on open circuit[7] and between η_n^{-1} and $t_n^{1/2}$ [6]. From the results in 2.1 and 2.2 it can be deduced that both methods of determining $\eta_n(0)$ can give erroneous results. Only at a slow potential decay during the first period after switching off the polarising current experimental determination is possible. In this case, the use of the $\eta_n/\log t_n$ relation is preferred. Moreover, $\eta_n(0)$ is equal to η_i for both mechanisms if the Volmer reaction has no effect upon the $\eta_i/\log j_i$ relation.

3.2 Application to earlier experimental results

Triacia, Solomons and Bockris[10] investigated the chlorine evolution on graphite in molten lithium chloride. From the slope of the $\eta_i/\log j_i$ curve and the stoichiometric number they concluded that chlorine is formed according to the Volmer–Tafel mechanism, where the Tafel reaction is the rate-determining step. The experimental anodic decay curves were explained by assuming a decrease of the adsorption pseudo-

Fig. 11. Relationship between the overpotential on open-circuit and the charge $j_{0,H}q_H$ for the chlorine formation according to the Volmer–Heyrovsky mechanism at various values of $j_{0,H}$ and at $j_{0,H}/j_{0,v} \rightarrow 0$, $D = 10^{-5} \text{ cm}^2/\text{s}$, $\theta_r = 10^{-3}$ and $\theta_0 = 0.08$.

Fig. 12. Relationship between the overvoltage on open-circuit at the moment of switching off the polarising current and the overvoltage on current flow (—) and relationship between the overvoltage on open-circuit at 1 s after switching off the polarising current and the overvoltage on current flow (---). Both relationships are given for the chlorine formation according to the Volmer–Heyrovsky mechanism at $j_{0,H} = 5 \times 10^{-6}$ A/cm², $D = 10^{-5}$ cm²/s, $\theta_r = 10^{-2}$ and at various values of $j_{0,H}/j_{0,V}$.

capacitance with increasing potential and a change variation of heat of adsorption with the degree of coverage by atomic chlorine. From a comparison of the experimental with the theoretical $\eta_n/\log t_n$ relation, Tilak and Conway concluded that the experimental curves can be explained by assuming a non-activated adsorption of chlorine atoms with strong repulsive

Fig. 13. Overvoltage on open-circuit at 1 s after switching off the polarising current vs overpotential on current flow for the chlorine formation according to the Volmer–Heyrovsky mechanism at various values of $j_{0,H}$ and D and at $\theta_0 = 0.08$, $\theta_r = 10^{-2}$ and $j_{0,H}/j_{0,V} \rightarrow 0$.

curve	$j_{0,H}$ A/cm ²	D cm ² /s
1	5×10^{-7}	10^{-5}
2	5×10^{-6}	10^{-4}
3	5×10^{-6}	10^{-5}
4	5×10^{-6}	10^{-6}
5	5×10^{-5}	10^{-5}
6	5×10^{-4}	10^{-5}

interaction between adsorbed chlorine atoms (3).

The experimental anodic $\eta_n/\log t_n$ curves at $t_n > 10^{-4}$ s have a slope of $-2.3(RT/4F)$ [10]. The theoretical slope h_T of the $\eta_n/\log t_n$ curves is -14 mV for the Tafel reaction as rate-determining reaction. At $\eta_n > 20$ mV, $\eta_n(0) - \eta_n > 20$ mV and at 25°C , this value of h_T is equal to $-2.3(RT/4F)$.

Consequently, corrected for temperature, both slopes are equal. Moreover, the shape of the experimental $\eta_n/\log t_n$ curve [10] agrees with that of the curve in Fig. 2 for $j_{0,T} = 10^{-7}$ A/cm². Only the time scale of the two curves is different. This difference can be eliminated by using a higher exchange-current density and diffusion coefficient in calculating the theoretical $\eta_n/\log t_n$ curve.

The formation of chlorine during anodic polarisation and on open circuit at graphite electrodes in aqueous sodium chloride hydrochloride solution was studied by Janssen and Hoogland [6, 9, 11]. They found that chlorine is formed according to the Volmer–Heyrovsky mechanism. For an aged graphite electrode the Heyrovsky reaction is the rate-determining step, whereas for a new graphite electrode both the Volmer and the Heyrovsky reactions determine the relation between potential and current density.

From the theory (2.1 and 2.2) it follows that especially the relation between η_n and t_n is important for elucidation of the mechanism. Unfortunately, this relation was not determined during the first period onto about 3 s after switching off the anodic current [6]. From Fig. 4, reference [6] it can be deduced that for an aged electrode in the investigated range of t_n , η_n is smaller than 20 mV and the slope h of the $\eta_n/\log t_n$ curve is -7.5 mV and for a new electrode the slope h is -56 mV at $\eta_n > 25$ mV. Both electrodes were previously polarised with an anodic current density of 45 mA/cm² at 25°C . These slopes can be explained by both the Volmer–Tafel and the Volmer–Heyrovsky mechanisms, although the first mechanism is preferred. This preference is based mainly on the slope of -56 mV, which agrees with the theoretical one for the Volmer–Tafel mechanism where it is mainly the atomic chlorine present on the outer surface of the electrode that determines the $\eta_n/\log t_n$ curve [4]. Addition experiments, especially at $t_n < 37$ s, are necessary if better founded conclusions are to be obtained.

The potential decay behaviour was also used to elucidate the mechanism of the chlorine formation on ruthenium oxide–titanium oxide electrodes and on ruthenium electrodes [4]. In reference [4] $\eta_n(0) - \eta_n$ have been plotted vs $\log t_n$; the questionable value of this relation lies in the great uncertainty of the value of $\eta_n(0)$. However, this has no influence upon the slope of the $\eta_n/\log t_n$ curve. Since the back reaction affects the $\eta_n/\log t_n$ curve only at very low η_n , viz $\eta_n < 20$ mV, the conclusions drawn in reference [4] are correct.

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