

# A CONTRIBUTION TO THE THEORY OF THE POTENTIAL SWEEP METHOD: CHARGE TRANSFER REACTIONS WITH UNCOMPENSATED CELL RESISTANCE

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**Abstract**—The effect of uncompensated cell resistance on current-potential curves obtained with the potential sweep method is presented for simple electrochemical reactions in conditions of a constant ionic activity and with the product entirely adsorbed on the electrode surface under either quasi-equilibrium or Tafel conditions. First and second order processes are considered. Results obtained for the latter are referred to the electrochemical reduction of platinum oxide film in 1*N* sulphuric acid at room temperature.

## INTRODUCTION

The theory of the potential sweep method has been developed for electrochemical processes of different type, such as, Nernstian charge transfer with pure diffusion control, for slow charge transfer, for dimerisation and polymerisation processes[1-15]. When a faradaic current flows through the working electrode, the cell resistance provokes the following distortion of the voltogram: (i) the current peak potentials are shifted toward larger values; (ii) the height of the current peaks is lowered, and (iii) the peak widths are broader. The magnitude of these effects increases with the cell resistance, the electrode area, the potential sweep rate and depolariser concentration. Therefore, the distortion of the voltograms by uncompensated cell resistance and the dependence of this effect on potential sweep rate and depolariser concentration, indicate the convenience of establishing mathematical relationships describing the voltammetric current-potential curves, in order to determine kinetic measurements aimed for mechanistic conclusions.

The effect of ohmic drop is of particular significance in three limiting cases: (i) when high potential sweep rates are used; (ii) when the reaction occurs in a system of relatively low conductance, as often happens when non-aqueous electrolyte solutions are studied, and (iii) when the reaction product yielded by the electrochemical reaction is a non-conducting species which accumulates on the electrode surface, as often occur in phenomena related to passivity.

The present paper is mainly devoted to study the possible effect of the uncompensated ohmic resistance on linear sweep voltammograms without, taking into account the double layer charging current, for simple electrochemical reactions in conditions where the

activity of the ionic species is constant and the product is entirely adsorbed on the electrode surface.

## THEORETICAL DERIVATION

Let us consider that a simple electron transfer reaction of the type:



occurs at the electrode, involving the formation of the adsorbed species *X*. It is assumed that reaction (1) in both directions is under activation control and species *X*, within the potential range to be considered, can be removed only by the ionisation process from the electrode surface. The concentration of the ionic species is considered as a constant from the outer Helmholtz plane throughout the bulk of the solution. Diffuse double layer effects are neglected. Then, the potential drop across the Helmholtz layer will differ from the potential applied between the working electrode and the reference electrode only by a constant term.

### 1. Reaction (1) under quasi-equilibrium

When an anodic potential sweep is applied to a system where reaction (1) occurs under quasi-equilibrium conditions, the anodic faradaic current is given by:

$$i_F = k_1(1 - \theta)a_X \exp\left(\frac{\beta FV}{RT}\right) - k_{-1}\theta \exp\left(-\frac{(1 - \beta)FV}{RT}\right). \quad (2)$$

where  $k_1$  and  $k_{-1}$  are the specific rate constants in the forward and backward directions when the potential difference,  $V$ , at the metal-solution interface is null, and  $\theta$  is the degree of surface coverage of the electrode by species  $X$ . When a linear potential sweep is applied both  $V$  and  $\theta$  certainly change with time. The expressions for the potential dependence of both the adsorption pseudo-capacitance and degree of surface coverage for reaction (1) under a linear potential sweep were derived, in the absence of ohmic polarisation, by different authors[7-10, 13]. The conditions for this case are expressed as:

$$i_F \ll k_1 a_X (1 - \theta) \exp\left(\frac{\beta FV}{RT}\right) \quad (3)$$

and

$$|i_F| \ll k_{-1} \theta \exp\left(-\frac{(1 - \beta)FV}{RT}\right). \quad (4)$$

Taking into account (3) and (4) with (2):

$$k_1(1 - \theta)a_X \exp\left(\frac{\beta FV}{RT}\right) - k_{-1}\theta \exp\left(-\frac{(1 - \beta)FV}{RT}\right) = 0. \quad (5)$$

From (5) the adsorption isotherm is obtained:

$$\frac{\theta}{1 - \theta} = K_1 a_X \exp\left(\frac{FV}{RT}\right), \quad (6)$$

where  $K_1 = k_1/k_{-1}$ . Hence, the degree of surface coverage is derived from equation (6):

$$\theta = \frac{K_1' \exp\left(\frac{FV}{RT}\right)}{1 + K_1' \exp\left(\frac{FV}{RT}\right)} = \frac{K_1'}{\exp\left(-\frac{FV}{RT}\right) + K_1'}, \quad (7)$$

with  $K_1' = K_1 \cdot a_X$ . The expression for  $\theta$  allows a different expression for the net faradaic current; it would be convenient to visualise the behaviour of the latter during the transient. Thus,

$$i_F = k \frac{d\theta}{dt}, \quad (8)$$

where  $k$  corresponds to the charge required to obtain a monolayer of adsorbed intermediates according to reaction (1). Equation (8) involves the rate of change of the degree of surface coverage, the latter depending on the applied potential, which is a function of time. The potential  $V$  at time  $t$  is expressed by:

$$V = V_i + vt - i_F R_u, \quad (9)$$

where  $V_i$  is the initial potential, in  $V$ ;  $v$  the potential sweep rate in  $V/s$  and  $R_u$  is the ohmic drop across the cell, in  $\Omega \times \text{cm}^2$ . Hence, the "true potential sweep rate,"  $v_t$ , is given by:

$$v_t = \frac{dV}{dt} = v - \frac{di_F}{dt} R_u. \quad (9')$$

Combining equations (7), (8), (9) and (9') one obtains:

$$\frac{d\theta}{dt} = \frac{K_1'}{\left[\exp\left(-\frac{FV}{RT}\right) + K_1'\right]^2} \frac{F}{RT} \times \exp\left[\left(-\frac{FV}{RT}\right)\left(v - \frac{di_F}{dt} R_u\right)\right]. \quad (10)$$

Taking into account equation (10) with (8), the net faradaic current is:

$$i_F = \frac{kK_1'}{\left[\exp\left(-\frac{FV}{RT}\right) + K_1'\right]^2} \frac{F}{RT} \times \exp\left[\left(-\frac{FV}{RT}\right)\left(v - \frac{di_F}{dt} R_u\right)\right]. \quad (11)$$

Equation (11) can be written as follows:

$$\frac{di_F}{dt} = \frac{v}{R_u} - \frac{RTi_F \left[\exp\left(-\frac{FV}{RT}\right) + K_1'\right]^2}{kK_1'FR_u \exp\left(-\frac{FV}{RT}\right)}. \quad (12)$$

and taking into account (9):

$$\frac{di_F}{dt} = \frac{v}{R_u} - \frac{RTi_F \left[\exp\left(-\frac{F(V_i + vt - i_F R_u)}{RT}\right) + K_1'\right]^2}{kK_1'FR_u \left[\exp\left(-\frac{F(V_i + vt - i_F R_u)}{RT}\right)\right]}. \quad (13)$$

This equation can be solved by applying a numerical method, such as the Runge-Kutta procedure, only if  $R_u \neq 0$ . The program was fed to a Hewlett-Packard calculator, the results being available from an X-Y plotter (Fig. 1) for a particular set of fixed conditions, as indicated in Table 1. Equation (13) implies the current peak potential shifts with potential as indicated in Fig. 2.

Equation (13) has, as a limiting case when  $R_u \rightarrow 0$  ( $R_u \neq 0$ ), the kinetic equations derived by Srinivasan and Gileadi for the same type of process[7]. For the quasi-reversible case, when  $R_u = 0$ , the current peak height changes linearly with the potential sweep rate and the potential at the current peak is independent of the potential sweep rate.

## 2. Reaction (1) under irreversible conditions

Let us consider the possibility that this reaction is highly irreversible so that the reverse reaction can be neglected. Then the rate of the faradaic process is nearly equal to the rate of the forward reaction. Under these conditions, the applied potential is far from

Table 1. Data used to calculate E/I curves for reaction (1) under quasi-equilibrium conditions.  $A = v/R_u'$ ;  $Z = B/kK_1R_u'$ ;  $B = RT/\beta F$ ;  $K_1 = 7.0685 \times 10^{-4}$ ;  $k = 13.56$  mC/cm<sup>2</sup>;  $t_0 = [(i_F)_{t=0} \text{ Area } R_u'/v]$ ;  $T = 473^\circ\text{K}$ ;  $B = 41.3525$  mV; Electrode Area: 1 cm<sup>2</sup>

$R_u'$ $\Omega$	$v$ mV/s	$A$	$Z$	$\Delta t$ s	$(i_F)_{t=0}$ mA/cm <sup>2</sup>	$t_0$ s
5	10	2.00	$8.6293 \times 10^2$	$2.5 \times 10^{-4}$	$2.318 \times 10^{-3}$	$1.159 \times 10^{-3}$
50	10	$5.0 \times 10^{-1}$	$8.6293 \times 10^1$	$2.5 \times 10^{-3}$	$2.318 \times 10^{-3}$	$1.159 \times 10^{-2}$
100	10	$1.0 \times 10^{-2}$	$4.3146 \times 10^1$	$5 \times 10^{-3}$	$2.318 \times 10^{-3}$	$2.318 \times 10^{-2}$
200	10	$5.0 \times 10^{-2}$	$2.1573 \times 10^1$	$1 \times 10^{-2}$	$2.318 \times 10^{-3}$	$4.636 \times 10^{-2}$
300	10	$3.33 \times 10^{-2}$	$1.4382 \times 10^1$	$1.5 \times 10^{-2}$	$2.318 \times 10^{-3}$	$6.954 \times 10^{-2}$

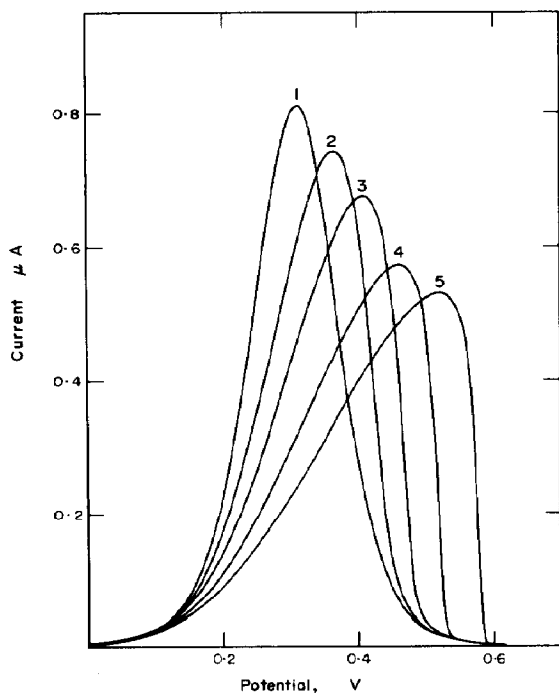


Fig. 1. Anodic current-potential curves obtained from equation (13), with data assembled in Table 1.  $R_u' = 5 \Omega$  (1);  $50 \Omega$  (2);  $100 \Omega$  (3);  $200 \Omega$  (4);  $300 \Omega$  (5);  $500 \Omega$  (6).

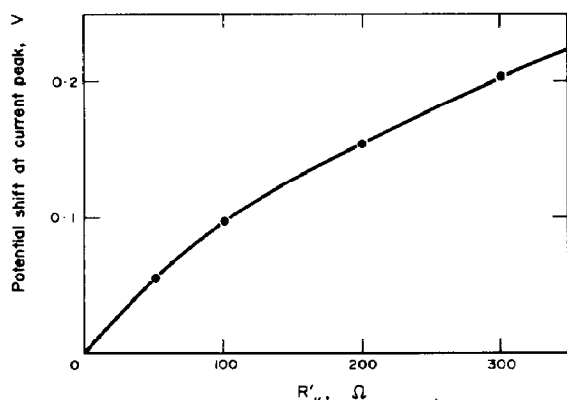


Fig. 2. Shift of the potential at peak current with ohmic resistance. The shifts are referred to the potential at current peak for  $R_u' = 0 \Omega$ .

the equilibrium potential and a Tafel relationship between  $V$  and  $i_F$  is fitted:

$$i_F = k_1 a_X (1 - \theta) \exp\left(\frac{\beta F V}{RT}\right). \quad (14)$$

Taking into account (9), the rate equation in the differential form is:

$$\frac{di_F}{dt} = k_1'(1 - \theta) \frac{d}{dt} \left[ \exp\left(\frac{\beta F}{RT} (V_i + vt - i_F R_u)\right) \right] - k_1 \exp\left(\frac{\beta F V}{RT}\right) \frac{d\theta}{dt} \quad (15)$$

$$= k_1'(1 - \theta) \exp\left(\frac{\beta F V}{RT}\right) \frac{\beta F}{RT} \left( v - \frac{di_F}{dt} R_u \right) - \frac{k_1'}{k} i_F \exp\left(\frac{\beta F V}{RT}\right), \quad (16)$$

where  $k_1' = k_1 a_X$ . From (15) one obtains:

$$1 - \theta = \frac{\frac{di_F}{dt} + \frac{k_1'}{k} i_F \exp\left(\frac{\beta F V}{RT}\right)}{k_1' \exp\left(\frac{\beta F V}{RT}\right) \frac{\beta F V}{RT} \left( v - \frac{di_F}{dt} R_u \right)}. \quad (17)$$

Considering equations (14) and (17), the net faradaic current is given by the expression:

$$i_F = \left[ \frac{di_F}{dt} + \frac{k_1'}{k} i_F \exp\left(\frac{\beta F V}{RT}\right) \right] \left[ \left( v - \frac{di_F}{dt} R_u \right) \frac{\beta F}{RT} \right]^{-1}. \quad (18)$$

From (18) the explicit differential expression is:

$$\frac{di_F}{dt} = \frac{i_F \frac{\beta F}{RT} v - \frac{k_1'}{k} \exp\left(\frac{\beta F V}{RT}\right) i_F}{1 + i_F R_u \frac{\beta F}{RT}}. \quad (19)$$

This equation, replacing the expression for  $V$ , from (9), becomes:

$$\frac{di_F}{dt} = \frac{i_F v \frac{\beta F}{RT} - \frac{i_F k_1'}{k} \exp\left(\frac{\beta F}{RT} (V_i + vt - i_F R_u)\right)}{1 + i_F R_u \frac{\beta F}{RT}}. \quad (20)$$

To solve equation (20), the numerical procedure for the evaluation of equation (13) was again used. Solutions for any value of  $R_u'$ , including  $R_u' = 0$ , can be obtained. The kinetic parameters used are assembled in Table 2; they correspond to parathiocyanogen formation on platinum at 190°C in molten potassium

thiocyanate. Results are shown in Fig. 3, as given by the X-Y plotter.

If the current maximum is  $i_{F, \max}$  and the corresponding potential is  $V_{\max}$ , the condition  $(di_F/dt) = 0$  implies:

$$\frac{\beta F v}{RT} = \frac{k_1'}{k} \exp \left[ \frac{\beta F V_{\max}}{RT} \right]. \quad (21)$$

Therefore:

$$V_{\max} = \frac{RT}{\beta F} \ln \frac{\beta F k}{RT k_1'} + \frac{RT}{\beta F} \ln v + I_{\max} R_u' \quad (22)$$

According to (22) the potential at the peak current, at a constant  $R_u'$  value, increases linearly with the logarithm of the potential sweep rate (Fig. 4).  $R_u'$  is the ohmic drop across the cell in  $\Omega$ . The ohmic drop appears as a term which depends on  $v$ , as the maximum current does. Consequently a  $V_{\max}$  vs  $\ln v$  plot does not give a straight line if the quantity of  $R_u'$  is appreciable. Equation (22), when  $R_u' = 0$ , produces the equation derived by Gileadi and Srinivasan[7].

### 3. A second order electrochemical process under irreversible conditions

Let us consider a second order electrochemical reaction under activation control represented by:

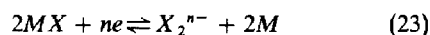


Table 2. Data used to calculate E/I curves for reaction (1) under irreversible conditions.  $M = (RT/\beta F) \times (k_1/kv)$ ;  $k_1 = 1.532 \times 10^{-15}$  A/cm<sup>2</sup>;  $k = 28.98$  mC/cm<sup>2</sup>; Electrode area: 0.102 cm<sup>2</sup>. Numerical data taken from ref. [18].

$t_0 = [(i)_{t=0} \text{ Area } R_u'/v]$ ;  $(i)_{t=0} = k_1$ ;  $v = 15$  mV/s;  $M = 7.01 \times 10^{-14}$

$R_u'$ $\Omega$	$\Delta t$ s	$t_0$ s
0	$5 \times 10^{-2}$	0
10	$2 \times 10^{-2}$	$1.042 \times 10^{-13}$
56	$2 \times 10^{-2}$	$5.834 \times 10^{-13}$
100	$2 \times 10^{-2}$	$1.0213 \times 10^{-12}$
150	$1 \times 10^{-2}$	$1.532 \times 10^{-12}$
220	$1 \times 10^{-2}$	$2.2469 \times 10^{-12}$
330	$1 \times 10^{-3}$	$3.4725 \times 10^{-12}$
470	$1 \times 10^{-3}$	$4.9024 \times 10^{-12}$
1000	$1 \times 10^{-3}$	$1.0213 \times 10^{-11}$
2000	$1 \times 10^{-3}$	$2.0427 \times 10^{-11}$

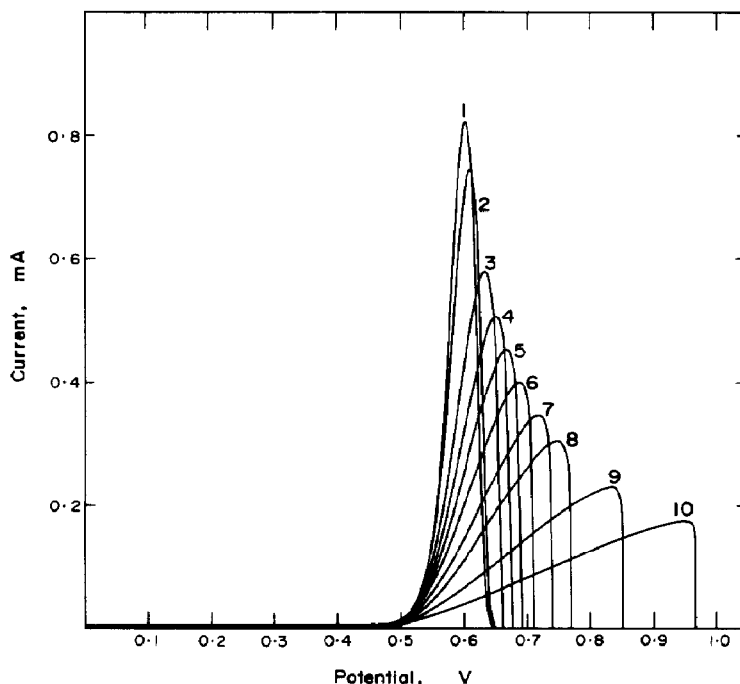


Fig. 3. Anodic current-potential curves obtained from equation (20), with data assembled in Table 2.  $R_u' = 0 \Omega$  (1); 10  $\Omega$  (2); 56  $\Omega$  (3); 100  $\Omega$  (4); 150  $\Omega$  (5); 220  $\Omega$  (6); 330  $\Omega$  (7); 470  $\Omega$  (8); 1000  $\Omega$  (9); 2000  $\Omega$  (10).

This reaction implies the desorption and electrochemical reduction of the species  $X$ , which is initially adsorbed on the electrode surface, the step involving the simultaneous transfer of  $n$  charges. As in case (2), at potentials far from equilibrium the rate of the faradaic process in the forward direction under stationary conditions is:

$$i_F = -k_2 \theta^2 \exp\left(-\frac{\alpha_2 n F V}{RT}\right). \quad (24)$$

Taking into account the equation for the applied potential:

$$V = V_i - vt + i_F R_u, \quad (25)$$

one obtains:

$$i_F = -k_2 \theta^2 \exp\left[\frac{(V_i + vt - i_F R_u)\alpha_2 n F}{RT}\right] \quad (26)$$

and differentiation yields:

$$\begin{aligned} \frac{di_F}{dt} &= -k_2 2\theta \frac{d\theta}{dt} \exp\left(\frac{(V_i + vt - i_F R_u)\alpha_2 n F}{RT}\right) \\ &\quad - \frac{k_2 \theta^2 \alpha_2 n F}{RT} \left(v - \frac{di_F}{dt} R_u\right) \\ &\quad \times \exp\left[\frac{(V_i + vt - i_F R_u)\alpha_2 n F}{RT}\right] \\ &= -2 \frac{k_2^{1/2}}{k} i_F^{3/2} \exp\left[\frac{(V_i + vt - i_F R_u)\alpha_2 n F}{2RT}\right] \\ &\quad + \frac{i_F \alpha_2 n F}{RT} \left(v - \frac{di_F}{dt} R_u\right) \\ &= -\left\{\frac{2k_2^{1/2}}{k} i_F^{3/2} \exp\left[\frac{(V_i + vt - i_F R_u)\alpha_2 n F}{2RT}\right] \right. \\ &\quad \left. - \frac{i_F v \alpha_2 n F}{RT}\right\} \left(1 + \frac{i_F R_u \alpha_2 n F}{RT}\right)^{-1}. \quad (27) \end{aligned}$$

The condition for the current peak,  $(di_F/dt) = 0$ , is fulfilled when:

$$\frac{2k_2^{1/2}}{k} i_{\max}^{1/2} \exp\left[\frac{(V_i + vt - i_{\max} R_u)\alpha_2 n F}{2RT}\right] = \frac{\alpha_2 n F v}{RT}. \quad (28)$$

Therefore:

$$\begin{aligned} (V_i + vt)_{\max} - i_{\max} R_u \\ = \frac{2RT}{\alpha_2 n F} \ln \frac{\alpha_2 n F v}{RT k_2^{1/2}} + \frac{2RT}{\alpha_2 n F} \ln \frac{k}{2i_{\max}^{1/2}}, \quad (29) \end{aligned}$$

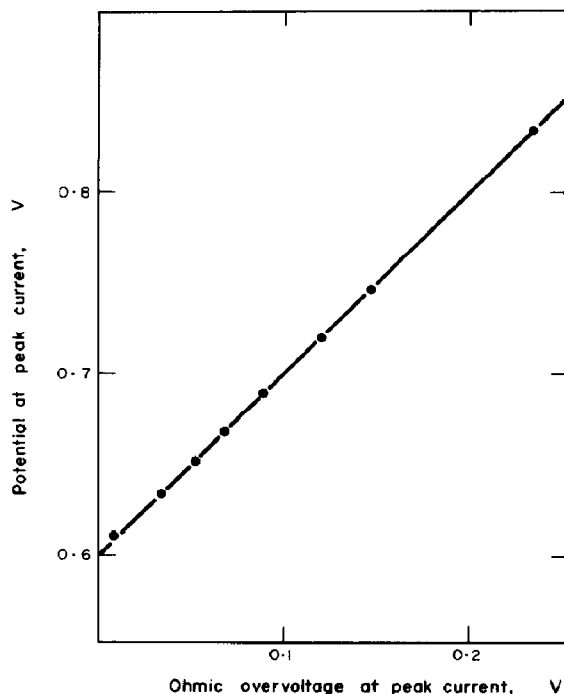


Fig. 4. Dependence of the potential at peak current on ohmic overvoltage according to (22). Data taken from Fig. 3.

which can be rearranged as follows:

$$\begin{aligned} V_{\max} = i_{\max} R_u + \frac{2RT}{\alpha_2 n F} \ln \frac{\alpha_2 n F v}{RT} \\ - \frac{RT}{\alpha_2 n F} \ln k_2 + \frac{2RT}{\alpha_2 n F} \ln \frac{k}{2i_{\max}^{1/2}}. \quad (30) \end{aligned}$$

Equation (30) implies a relationship between  $V_{\max}$  and  $v$  which depends on  $i_{\max}$  through a linear term and a logarithmic term, the latter depending on the order of the electrode reaction. When reaction (30) is compared to the one deduced in the absence of the ohmic polarisation term, we obtain:

$$\begin{aligned} V_{\max} = (V_{\max})_{R_u=0} + \frac{RT}{\alpha_2 n F} \ln \frac{\alpha_2 n F v}{RT q_0} \\ + \frac{RT}{\alpha_2 n F} \ln \frac{k^2}{4nF i_{\max}} + i_{\max} R_u, \quad (31) \end{aligned}$$

where,  $q_0$  is the number of mole/cm<sup>2</sup> initially placed at the electrode surface. If  $k_2$  is the second order rate constant, expressed as a current density, the following relationship is satisfied:

$$k_2 = nFq_0^2 k_{11} \quad (32)$$

$k_{11}$  being the second order rate constant in cm<sup>2</sup>/s.mole.

A set of theoretical voltammetric  $E/I$  curves, computed from (27), for a cathodic second order desorption plus electron transfer process, obtained for different

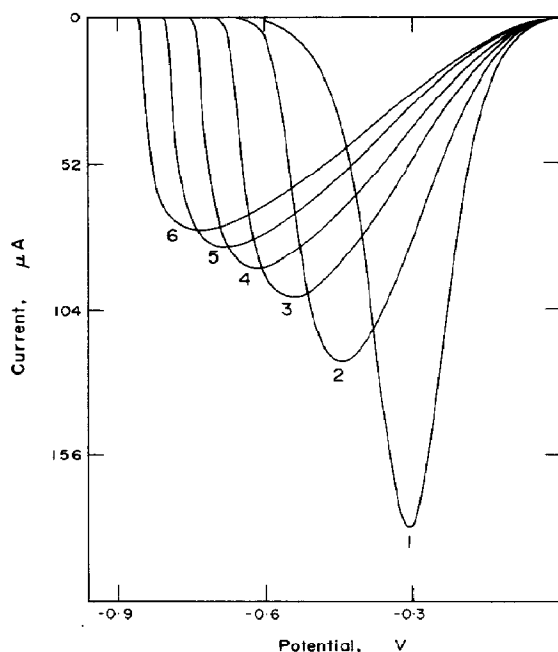


Fig. 5. Experimental cathodic current-potential curves for the electrochemical reduction of platinum oxide in 1N sulphuric acid at room temperature, at 300 mV/s.  $R_u' = 0 \Omega$  (1); 1947  $\Omega$  (2); 4000  $\Omega$  (3); 6312  $\Omega$  (4); 7937  $\Omega$  (5); and 10,000  $\Omega$  (6). See Tables 3 and 4.

Table 3. Data used for computation of the voltammetric E/I curves with equation (27) for the reduction of platinum oxide in 1N sulphuric acid at 294.2°K

$k = 0.564 \times 10^{-3} \text{ C/cm}^2$
$\alpha_2 = 0.26$ (from [17])
$v = 0.3 \text{ V/s}$
$(RT/\alpha_2 nF) = 48.72 \times 10^{-3} \text{ V}$
$(V_i + vt)_{\max} = -0.3 \text{ V}$ (arbitrary fixed)
$k_2 = (\alpha_2 nFkv/RT) \exp[(V_i + vt)_{\max} \alpha_2 nF/RT]$
$= 7.35 \times 10^{-6} \text{ A/cm}^2$
$(2k_2^{1/2}/k) = 0.304 \text{ cm/(s.C)}^{1/2}$
$(\alpha_2 nFv/RT) = 6.158/\text{s}$
Electrode Area: 0.1037 $\text{cm}^2$
$R_u'$ from 0 $\Omega$ to 10000 $\Omega$

values of  $R_u'$  are showed in Fig. 5. The values of the constants used are assembled in Table 3. The  $\alpha_2 n$  value for the reduction of platinum oxide was taken from the paper by Ohashi, Sasaki and Nagaura[17].

In order to test the validity of equation (30), it was necessary to record new current-potential curves by cyclic voltammetry for the platinum oxide reduction in 1N  $\text{H}_2\text{SO}_4$  at room temperature as made earlier by the authors mentioned above[17]. For this purpose, a constant amount of oxide formed on a clean platinum electrode by an anodic voltammetric sweep under conditions of  $R_u' \rightarrow 0$ , was reduced by a cathodic voltammetric sweep. The cathodic reaction occurred by inserting in the circuit, by means of a rapid switching operation, a resistor of prefixed value. The potential sweep covered the voltage range from  $-0.910$  to  $+0.836 \text{ V}$ . Results are assembled in Table 4, as well as the difference,  $\Delta$ , between the experimental and the theoretical values.

### CONCLUSIONS

The mathematical analysis of current-potential transients obtained by the application of the linear potential sweep method for a simple first order adsorption step and rate controlling involving charge transfer under Langmuir isotherm, including the effect of the ohmic resistance, yields two differential equations which correspond to the following limiting cases: (i) quasi-equilibrium conditions and (ii) Tafel approximation. The solution of both equations gives the quantitative effect of the uncompensated ohmic cell resistance on the voltagrams. The errors involved in the calculations are the following: (i) for the quasi-reversible case, for  $R_u' = 300 \Omega$  and the conditions indicated in Table 1, the error in the current peak is  $6 \times 10^{-5} \text{ mA}$ . (ii) for the irreversible case, for  $R_u' = 10 \Omega$  and conditions indicated in Table 2, the error in the current peak amounts to  $7.83 \times 10^{-9} \text{ mA}$ .

The ohmic drop correction depends also on the order of the electrochemical reaction, as is clearly demonstrated with quantitative data obtained for the electrochemical reduction of platinum oxide in sulphuric acid at room temperature.

In conclusion the uncompensated ohmic effect, together with the double layer capacity effect, may

Table 4. Experimental and theoretical values of  $(V_i + vt)_{\max}$  at different  $R_u'$  for the second order electrochemical reduction of platinum oxide

$R_u'$ $\Omega$	$I_{\max}$ $\mu\text{A}$	$[(V_i + vt)_{R_u'=0} - (V_i + vt)_{R_u'=R_u'}]_{\text{exp}}$ mV	$I_{\max} R_u'$ mV	$\frac{RT}{\alpha_2 nF} \ln \frac{\alpha_2 nFkv}{4RTI_{\max}}$ mV	$[(V_i + vt)_{R_u'=0} - (V_i + vt)_{R_u'=R_u'}]_{\text{theor}}$ mV	$ \Delta $ mV
0	$90 \pm 8$	0	0	—	0	0
1947	64	$148 \pm 10$	124.6	16.63	141.2	$ +6.8  < 10$
4000	57	$259 \pm 10$	228.0	22.25	250.3	$ +8.4  < 10$
6312	53	$370 \pm 10$	334.5	25.96	360.5	$ +9.5  < 10$
7937	46	$402 \pm 10$	365.1	32.86	398.0	$ +4.0  < 10$
10000	41	$438 \pm 10$	410.0	38.30	448.3	$ -10.3  \approx 10$

produce a large distortion in the voltammetric current-potential curves so that kinetic data derived from peak currents and from the whole curve can be significantly erroneous. This effect is particularly notorious when large potential sweep rates are employed and is important for the case of Nernstian charge transfer process and for an electrochemical process, which are controlled by a charge transfer step. For the latter it can also be predicted that the influence of the uncompensated ohmic resistance term decreases when passing from a Langmuir to a Temkin isotherm condition and in this case it also decreases when the Temkin factor,  $f$ , increases for then the current at the peak becomes smaller[18].

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