CHRONOPOTENTIOMETRY WITH NON-LINEAR PERTURBATION
FUNCTIONS AT THE DME WITH A PRECEDING BLANK PERIOD

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ABSTRACT

A theoretical study on the use of non-linear perturbation functions of the form $I(t) = I_0 e^{\alpha t}$ ($\alpha > 0$) after a blank period, $t_1$, at the DME, is presented. Equations for the potential–time curves are derived and discussed. The general equation obtained here becomes Galvez’s equation when $t_1 \rightarrow 0$ and also the generalized Sand equation when $t_1 \gg t$.

INTRODUCTION

The theory concerning the chronopotentiometric study of electrode processes with non-linear current–time functions (ctf) has been largely developed both for the stationary electrode [1,2] and for the DME [3–5].

However, serious problems appear when this theory is applied. Thus, stationary electrodes show a poorly reproducible surface and tend to accumulate contaminations on the electrode–solution interface [6], in contrast to the DME, which shows a clean, perfectly reproducible and contamination-free surface. Nevertheless, the use, with the DME, of the first stage of the drop life, causes several errors due fundamentally to the following reasons [7,8]: (1) High capillary back-pressure; (2) drop cannot be approximated by a sphere; (3) convection, due to the fall of the preceding drop; (4) high demands on the adjustment of the different relays, which would be necessary if the different functions were synchronized.

Therefore, the optimum situation will be achieved with the use of a DME with a blank period. This feature is imperative when the electrolysis time is short.

As far as we know, the only attempt carried out in this sense is that of Kies [8,9], who used a perturbation of the type $I(t) = I_0 (t_1 + t)^{2/3}$, where $t_1$ is a blank period.

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The aim of this paper is the development of a more generalized theory for chronopotentiometry with a programmed current (using as the cft $I(t) = I_{d}e^{-w}$, $w \geq 0$), after a blank period ($t_{b}$). In addition to the elimination of the experimental problems mentioned above this technique offers the possibility of applying a current step, which has not been possible up to now with a normal DME.

The general equation obtained here, becomes Gálvez's equation [3] when $t_{b} \rightarrow 0$, and also the generalized Sand equation [1] when $t_{b} \gg t$.

THEORY

A simple charge transfer reaction (ctr) can be written as

$$A + n e^{-} \rightarrow B$$

If $D_{t}$ is the operator

$$D_{t} = \frac{\partial}{\partial t} - \frac{D_{0}}{\partial x^{2}} + \frac{2x}{3(t_{1} + t)} \frac{\partial}{\partial x}$$

(1)

the boundary value problem (bvp), if double-layer effects are neglected, may be written as

$$D_{t}c_{A} = D_{t}c_{B} = 0$$

(2)

$$t = 0, \ x \gg 0 \quad (c_{A} = c_{A}^{*}, \ c_{B} = c_{B}^{*})$$

(3)

$$t > 0, \ x = \infty$$

$$I(t)/nFA(t_{b}) = k_{e}c_{A}(0, t) - k_{b}c_{B}(0, t)$$

(4)

$$D_{A}(\frac{\partial c_{A}}{\partial x})_{0} = \frac{D_{B}(\frac{\partial c_{B}}{\partial x})_{0}}{nFA(t_{b})}$$

(5)

where

$$I(t) = I_{d}e^{-w}$$

(6)

$$k_{e} = k_{e} \exp\left(-\alpha nF/RT\right) \left[(E(t) - E_{0})\right]$$

(7)

$$k_{b} = k_{b} \exp\left[1 - \alpha\left(nF/RT\right)(E(t) - E_{0})\right]$$

(8)

with the variables

$$s_{i} = \frac{1}{2[D_{t}]^{1/3}}$$

(9)

$$\beta = \frac{2I_{d}e^{-w-1/6}}{nFA_{0}D_{A}c_{A}^{*}}$$

$$\chi = \frac{2\beta}{\partial^{2}c_{A}/\partial x^{2} + \frac{2x}{3(t_{1} + t)} \frac{\partial}{\partial x}}$$

Equations (2) after rearrangement, become

$$\frac{\partial^{2}c_{A}}{\partial x^{2}} + \frac{\partial c_{A}}{\partial x} - 4m \frac{\partial c_{A}}{\partial x} = \frac{4}{3} \frac{\partial c_{A}}{\partial x} - \frac{8}{3} \frac{\partial c_{A}}{\partial x} + \frac{8}{3} \frac{\partial c_{A}}{\partial x}$$

(10)

$$\frac{\partial^{2}c_{B}}{\partial x^{2}} + \frac{\partial c_{B}}{\partial x} - 4m \frac{\partial c_{B}}{\partial x} = \frac{4}{3} \frac{\partial c_{B}}{\partial x} - \frac{8}{3} \frac{\partial c_{B}}{\partial x} + \frac{8}{3} \frac{\partial c_{B}}{\partial x}$$

(11)

where

$$m = w - 1/6$$

and the bvp may be rewritten as

$$\gamma D_{A}(\partial c_{A}/\partial s_{A}) = \chi \frac{\partial c_{A}}{\partial x}$$

(13)

$$\gamma (\partial c_{B}/\partial s_{B}) = -\gamma (\partial c_{B}/\partial s_{B})$$

(14)

$$\gamma = \frac{D_{A}/D_{B})^{1/2}}{nFA_{0}}$$

(15)

Expanding $c_{A}$ and $c_{B}$ as

$$c_{A} = c_{A}^{*} + \sum_{i,j=0} \alpha_{i,j}(s_{A}) \chi^{i} \beta^{j}$$

(16)

$$c_{B} = c_{B}^{*} + \sum_{i,j=0} \phi_{i,j}(s_{B}) \chi^{i} \beta^{j}$$

eqns. (10) and (11) are transformed to

$$\alpha_{i,j}(s_{A}) + 2s_{A} \alpha_{i,j}(s_{A})^{2} - 2m \alpha_{i,j}(s_{A}) = -\frac{8}{3} \chi \phi_{i,j-1}(s_{A}) - \frac{8}{3} \chi \phi_{i,j-1}(s_{A})$$

(17)

$$\phi_{i,j}(s_{B}) + 2s_{B} \phi_{i,j}(s_{B})^{2} - 2m \phi_{i,j}(s_{B}) = -\frac{8}{3} \chi \phi_{i,j-1}(s_{B}) - \frac{8}{3} \chi \phi_{i,j-1}(s_{B})$$

and

$$s_{A}, s_{B} \rightarrow \infty$$

$$s_{A}, s_{B} \rightarrow 0$$

$$s_{i,j}(0) = 0$$

$$s_{i,j}(0) = 0$$

$$\alpha_{i,j}(0) = c_{A}^{*}$$

$$\phi_{i,j}(0) = -\phi_{i,j}(0)$$

(18)

(19)

(20)

(21)

By following the procedures described in ref. [10], we obtain for the surface concentrations of $A$ and $B$ the following functions with time (see appendix)

$$c_{A}(0, t) = c_{A}^{*} - c_{A}^{*}N_{s}e^{-2m}e^{2F(m, \beta)}$$

(22)

$$c_{B}(0, t) = c_{B}^{*} - c_{B}^{*}N_{s}e^{-2m}e^{2F(m, \beta)}$$

(23)
where

$$N_s = 2I_0/nF \frac{D_a}{D_a} A_0 c_s$$ (24)

$$F(m, \beta) = \frac{1}{P_{m, A}} A \left( \frac{m}{6} \right) \beta^3 + \frac{B(m)}{108} \frac{\beta^6 - C(m)}{8748} \beta^4 + \ldots$$ (25)

$$A(m) = p_{m, 1/3}^2 - 2p_{m, 1/3} + p_{m, 13}$$

$$B(m) = -2(9m + 14)p_{m, 13} + 36(m + 2)p_{m, 13} - 2(12m + 35)p_{m, 13}$$

$$+ (6m + 23)p_{m, 19}$$

$$C(m) = 2(540m^2 + 2124m + 1851)p_{m, 1} - 12(180m^2 + 870m + 1031)p_{m, 13}$$

$$+ 27(60m^2 + 400m + 659)p_{m, 13} - 36(18m^2 + 153m + 322)p_{m, 19}$$

$$+ 12(9m^2 + 93m + 238)p_{m, 25}$$ (26)

$$P_{m, A} = \frac{21}{3} \left( 1 + \frac{6m + A}{6} \right)$$ (27)

Equations (22)-(27) are valid for \(m \geq -1/6\) \((w \geq 0)\). This is in contrast with the equations obtained when \(t_1 = 0\) (in this case \(w \geq 1/6\), [3]); this fact is due to the particular characteristics of our perturbation.

**Transition time**

The transition time, \(\tau\), is obtained from eqn. (22) by writing \(c_s(0, \tau) = 0\). Thus, we have

$$\tau^m = 1/N_0 \beta_s^3 F(m, \beta_r)$$ (28)

where \(\beta_r\) is the value of the variable \(\beta\) for \(t = \tau\).

If \(t_1 = 0\) (\(\beta = \beta_r = 1\)) we obtain:

$$\tau^m = 1/N_0 F(m, 1)$$ (29)

This equation is in agreement with that obtained by Gálvez [3] (see below). Also interesting is the situation when \(m = 0\) \((w = 1/6)\). From eqns. (22) and (28), we obtain

$$\beta_r^3 \left( \frac{1}{P_{a/3}} - \frac{A(0)}{6} \beta_r^3 + \frac{B(0)}{108} \frac{\beta_r^6 - C(0)}{8748} \beta_r^4 + \ldots \right) = \frac{1}{N_s}$$ (30)

where

$$A(0) = -3/5p_{a/3}$$

$$B(0) = 189/80p_{a/3}$$

$$C(0) = -2187/44p_{a/3}$$ (31)

It is obvious, that if a suitable value of \(N_s\) is used, it is possible to obtain a \(\tau\) value according to eqn. (30), as opposed to the situation observed when \(t_1 = 0\).

On the other hand, if \(m = -1/6\), \((w = 0\), current step\) eqn. (28) becomes

$$\tau^m_{1/6} = N_0 \beta_r^3 \left( \frac{1}{P_{1/6}} - \frac{A(-1/6)}{6} \beta_r^3 + \frac{B(-1/6)}{108} \frac{\beta_r^6 - C(-1/6)}{8748} \beta_r^4 + \ldots \right)$$ (32)

$$A(-1/6) = -\frac{2}{3p_1}$$

$$B(-1/6) = \frac{14}{5p_1}$$

$$C(-1/6) = -\frac{432}{7p_1}$$ (33)

Finally, if \(t_1 \gg \tau\) (stationary electrode), eqns. (22) and (28) are

$$\tau^{w+1/2} = \left( nFA^2 / \epsilon \right) c_s / 2I_0$$ (34)

where \(A\) is the electrode area when current is applied \((= A_0 \sqrt{\epsilon / \sigma})\). This equation is identical to the so-called “generalized Sand equation” [1]. When \(w = 0\), it is the ordinary Sand equation.

**Potential-time functions (ptfs)**

Making the following substitutions:

$$N(m, t, t_1) = \beta^2 N_3 t^m$$ (35)

$$\theta(t) = \theta_0 t$$ (36)

$$\theta_0 = 4kT / D_a$$ (37)

$$\eta(t) = (nF / RT) \ln 10 \left( (E(t) - E^0) \right)$$ (38)

$$\mu = c_s / \epsilon_s$$ (39)

and inserting eqns. (22) and (23) in eqn. (4), we obtain the corresponding ptfs in a dimensionless form

$$\theta(t)^{-1/2} N(m, t, t_1) 10^{\eta(t)}$$

$$= 1 - N(m, t, t_1) F(m, \beta) - 10^{\eta(t)} \left[ \mu + \gamma N(m, t, t_1) F(m, \beta) \right]$$ (40)

**Reversible process:** If \(k_\gamma \to \infty\), eqn. (40) is simplified to

$$\eta(t) = \log \frac{1 - N(m, t, t_1) F(m, \beta)}{\mu + \gamma N(m, t, t_1) F(m, \beta)}$$ (41)

If \(t \to 0\), eqn. (41) becomes

$$\left[ \eta(t) \right]_{t \to 0} = \log \frac{1}{\mu} \quad m \geq -1/6$$ (42)
Irreversible process: If \( k_c \ll 1 \) in eqn. (40):

\[
\eta(t) = \frac{1}{\alpha} \log \frac{1 - N(m, t, t_1)F(m, \beta)}{N(m, t, t_1)\theta(t)^{-1/2}}
\]  
(43)

After some manipulations, this equation may be rewritten as

\[
E(t) - E^0 = \left(\frac{RT}{anF}\right) \ln(nFA_0e^{\frac{E}{R}}/I_0) + \left(\frac{RT}{anF}\right) \ln\left\{1/\left(1 - \frac{1}{\beta^2} - N^1/2F(m, \beta)\right)^{1/2}\right\}
\]  
(44)

If \( \beta = 1 \) and \( m - 1/2 \) (\( w = 2/3 \)), we obtain (see eqn. 29):

\[
E(t) - E^0 = \frac{RT}{anF} \ln\left(\frac{nFA_0e^{\frac{E}{R}}/I_0}{I_0}\right) + \frac{RT}{anF} \ln\left\{1 - \frac{1}{\tau^{1/2}}\right\}
\]  
(45)

which is the same as obtained previously by Delahay and Berzins [11] and Gálvez [3].

On the other hand, for a current step, eqn. (43) becomes

\[
\eta(t) = \frac{1}{\alpha} \log \theta(t)^{-1/2}\left\{\frac{(t_1 + t)^{1/3}}{N_s} - \tau^{1/2}F\left(-1/6, \beta\right)\right\}
\]  
(46)

and

\[
[\eta(t)]_{t \to 0} = \frac{1}{\alpha} \log \frac{nFA_0e^{\frac{E}{R}}k_c/I_0^{1/3}}{I_0}
\]  
(47)

while if \( m > -1/6 \) (eqn. 43)

\[
[\eta(t)]_{t \to 0} = \infty
\]  
(48)

RESULTS AND DISCUSSION

Transition time

If \( \beta = 1 \), the equation obtained in this paper coincides with that obtained by Gálvez. The following condition is fulfilled [3]:

\[
F(m, 1) \to (3/\tau)^{3/2}/P_{sat}^{3/2}
\]  
(49)

In order to determine the number of terms which are needed for \( F(m, \beta) \) in calculations, we have obtained (see Table 1) the transition time by taking up to four (\( \tau \)) or three (\( \tau' \)) terms in the case in which more terms are necessary, i.e., when \( \beta = 1 \), and its ratio with that obtained by using eqn. (26) in ref. 3 (\( \tau_1 \)). As shown, the maximum deviation observed by using only three terms in \( F(m, \beta) \), is lower than 0.7\% if \( w > 1/2 \). If \( t_1 > 0 \) (\( \beta < 1 \)), the use of three terms in the P/t or transition time calculations is also sufficiently accurate with deviations lower than 1\%, independently of the value of \( w \).

Table 2 shows the transition time obtained from eqn. (28) for several values of \( t_1 \) and \( w \). As can be observed, the transition time is more strongly dependent on \( t_1 \) for

<table>
<thead>
<tr>
<th>( \eta )/s</th>
<th>( \tau )/s</th>
<th>( \tau' )/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.7774</td>
<td>1.7627</td>
</tr>
<tr>
<td>2/3</td>
<td>2.0993</td>
<td>2.0775</td>
</tr>
<tr>
<td>1/2</td>
<td>2.4258</td>
<td>2.4005</td>
</tr>
<tr>
<td>1/3</td>
<td>3.6874</td>
<td>3.5961</td>
</tr>
</tbody>
</table>

lower values of \( w \). Similarly, \( \tau \) is strongly dependent on \( N_s \) under these conditions (Table 3).

As a consequence, when applying the current to grown drops, no transition time is observed below a \( N_s \) minimum, for the lower values of \( w \). This \( (N_s)_{min} \) is highly

<table>
<thead>
<tr>
<th>( N_s )/s</th>
<th>( \tau_1 )/s</th>
<th>( \tau_2 )/s</th>
<th>( \tau_1/\tau_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>w</td>
<td>0</td>
<td>2.85</td>
<td>0.722</td>
</tr>
<tr>
<td>3.00</td>
<td>0.595</td>
<td>1.908</td>
<td>4.197</td>
</tr>
<tr>
<td>3.25</td>
<td>0.456</td>
<td>1.357</td>
<td>2.698</td>
</tr>
<tr>
<td>3.50</td>
<td>0.365</td>
<td>1.042</td>
<td>1.986</td>
</tr>
<tr>
<td>3.75</td>
<td>0.301</td>
<td>0.837</td>
<td>1.556</td>
</tr>
</tbody>
</table>

When \( w = 1/6 \) | 2.10 | 3.539 | 7.079 | 10.619 |
| 2.50 | 1.626 | 3.251 | 4.877 |
| 3.00 | 0.934 | 1.867 | 2.801 |
| 3.50 | 0.638 | 1.276 | 1.914 |
| 3.75 | 0.546 | 1.093 | 1.639 |
dependent on \( t_1 \) and \( w \). So, if \( t_1 = 2 \text{ s} \) and \( w = 0 \), \( (N_a)_{\text{min}} = 2.63 \text{ s}^{1/6} \); if \( t_1 = 2 \text{ s} \) and \( w = 1/6 \), \( (N_a)_{\text{min}} = 1.77 \).

**Potential–time functions**

In Figs. 1, 2 and 3 we have plotted \( \Delta E = E(t) - E^0 \) vs. \( t \) for \( N_a = 2.67 \text{ s}^{-m} \) and different values of \( w \) and for \( D_\alpha = 10^{-5} \text{ cm}^2 \text{ s}^{-1} \). The dependence of the ptf on \( \theta_0 \) and \( \alpha \) is similar to that obtained in ref. 3. Thus, if \( 0.2 < \theta_0 < 2000 \text{ s}^{-1} \) (\( 10^{-3} < k_5 < 0.1 \text{ cm s}^{-1} \)), the cfr must be considered as quasi-reversible and no simplification is possible, in eqn. (40). If \( \theta_0 < 0.2 \text{ s}^{-1} \) (\( k_5 < 10^{-3} \text{ cm s}^{-1} \)), eqn. (40) agrees well with eqn. (43) and the cfr is considered as totally irreversible. Finally, for values of \( \theta_0 > 2000 \text{ s}^{-1} \) (\( k_5 > 0.1 \text{ cm s}^{-1} \)), the cfr is reversible and eqn. (41) may be used.

However, the shape of the ptf is obtained with this technique is substantially different from those observed when \( t_1 = 0 \), particularly in the lower values of \( t \).

Finally, it is shown in Figs. 2 and 3 (cfr quasi-reversible and irreversible, respectively) that the corresponding curve for \( m = -1/6 \) (\( w = 0 \)) intercepts the ordinate axis in a characteristic point. The value of this point for an irreversible process is (see eqn. 46)

\[
\Delta E = \left( RT/a_nF \right) \ln \left( FA \nu_a^a k_i \frac{t_f}{t_i} J_0 \right)
\]  

(50)

Fig. 1. Potential–time curves for a reversible process (\( \theta_0 \rightarrow \infty \)), \( t_1 = 2 \text{ s} \), \( N_a = 2.67 \text{ s}^{-m} \), \( T = 298 \text{ K} \), \( \alpha = 1 \), \( \gamma = 1 \), \( \beta = 0 \). \( w \) values are: (a) 1, (b) 2/3, (c) 1/2, (d) 1/3, (e) 1/6, (f) 0.

Fig. 2. Potential–time curves for a quasi-reversible process, \( \theta_0 = 20 \text{ s}^{-1} \), \( \alpha = 0.5 \). Other conditions as in Fig. 1.

Fig. 3. Potential–time curves for a totally irreversible process, \( \theta_0 = 2 \times 10^{-3} \text{ s}^{-1} \), \( \alpha = 0.5 \). Other conditions as in Fig. 1.

Moreover, since \( F(m, \beta) > 0 \), this is the maximum value of \( \Delta E \).

It is possible to obtain \( \alpha \) and \( k_i \) values for a irreversible process (for any \( m \)), by plotting \( \Delta E \) vs. \( \ln g(m, \beta) \) (Fig. 4), where

\[
g(m, \beta) = 1/t^{m-1/2} \beta^2 - N_i^{1/2} F(m, \beta)
\]  

(51)

**APPENDIX**

The differential eqns. (17) with the bvp (18)–(21) have the following solutions [10]:

\[
\sigma_{i,j}(s_A) = \phi_{i,j}(s_B) = 0 \quad \text{unless} \quad i = 1, j = 3n + 2, n \geq 0
\]  

(1A)

\[
\sigma_{1,2}(s_A) = -\left( c_i^a / p_m \right) \nu_m A
\]  

(2A)

\[
\sigma_{1,3}(s_A) = \left( 1/6 \right) c_i^a \left( p_{m,1} \nu_m - 2p_{m,7} \nu_m A + p_{m,13} \nu_m \right)
\]  

(3A)

\[
\sigma_{1,8}(s_A) = -\left( c_i^a / 108 \right) \left( \left( 6m - 2 \right) p_{m,3} \nu_m - 2(12m + 13) p_{m,3} \nu_m A + 36(m + 2) p_{m,5} \nu_m A - 2(12m + 35) p_{m,13} \nu_m \right)
\]  

(4A)

\[
\sigma_{1,21}(s_A) = \left( c_i^a / 8748 \right) \left( 3(6m - 8)(6m - 2) p_{m,1} \nu_m - 108(6m - 2) \times (m + 1) p_{m,1} \nu_m - 18(900m^2 + 225m + 191) p_{m,1} \nu_m - 12(1800m^2 + 1031) p_{m,7} \nu_m A + 27(60m^2 + 400m) + 659p_{m,13} \nu_m - 36(18m^2 + 153m + 322) p_{m,19} \nu_m A + 12(9m^2 + 93m + 238) p_{m,23} \nu_m A \right)
\]  

(5A)
\[ \psi_{1,1}(s_A) = -\gamma \sigma_{1,1}(s_A) \quad (6A) \]

where

\[ \psi_{m,\pm A} = \psi_{(6m \pm A)/3} \quad (7A) \]

**NOTATION/DEFINITIONS**

- \( t_1 \): blank period
- \( t \): time elapsed between current application and measurement of the potential
- \( t_e \): \( t_1 + t \)
- \( A(t_e) \): time-dependent electrode area \((= A_0 t_e^{2/3})\)
- \( A_0 \): electrode area at \( t_e = 1 \) s
- \( I(t) \): time-dependent faradaic current
- \( I_0 \): value of \( I(t) \) at \( t = 1 \) s
- \( E(t) \): time-dependent electrode potential
- \( k_f, k_r \): heterogeneous rate constants of the forward and reverse charge-transfer reactions
- \( k_s \): apparent heterogeneous rate constant of charge transfer at \( E^0 \)
- \( \Gamma' \): Euler gamma function

Other definitions are conventional.

**REFERENCES**