Current-reversal chronopotentiometry at a dropping mercury electrode

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ABSTRACT

A theoretical study for a slow charge-transfer reaction, in current-reversal chronopotentiometry at a DME, using a preceding blank period, is presented. When \( t_1 \gg t \), the equations obtained here become those reported in the literature at stationary plane electrodes. In addition, an easy method of determining the kinetic parameters of the electrode reaction and the formal standard reduction potential is presented.

INTRODUCTION

As has been recently demonstrated [1], the development of a generalized theory for chronopotentiometry with different current–time functions, after a blank period \( (t_1) \), at a DME offers, among other advantages, the possibility of applying a current step to this electrode, which had not been possible up till then. So, if \( t_1 = 0 \), when a constant current is applied a high current density in the earlier stage of drop life is obtained, which represents a serious drawback [2,3].

Chronopotentiometry with current reversal is very useful in the evaluation of thermodynamic and kinetic electrode parameters for both reduction and re-oxidation processes. However, until now the corresponding theoretical development has been limited to stationary electrodes [4–17].

In this paper we develop the theory concerning chronopotentiometry with current reversal at a DME using this blank period. General equations for transition times, concentration profiles and potential–time curves are derived, adopting for the DME the expanding plane electrode model. These equations become those obtained by Berzins and Delahay [4], Macero and Anderson [5,6] and Murray and Reilley [7] when \( t_1 \gg t \). Moreover, a simple method of determining the kinetic parameters and the formal standard reduction potential of a charge-transfer reaction, when this behaves as totally irreversible, is presented.
THEORY

If we consider a slow charge-transfer reaction and a constant current, \( I_o \), is applied to the DME after a blank period, \( t_i \), the surface concentrations of electroactive species, A and B, and the transition time are given by the following expressions [1] (see Notation/Definitions):

\[
c_A(0, t)/c_A^* = 1 - N_i t^{-1/6} F(\beta) \\
c_B(0, t)/c_B^* = \mu + \gamma N_i t^{-1/6} F(\beta) \\
\tau^{1/2} = (t_i + \epsilon)^{1/2} / N_i F(\beta) \\
F(z) = \frac{1}{\sqrt{\pi}} \{ 1 + \frac{4}{5} z^3 + \frac{32}{75} z^5 + \frac{64}{315} z^7 \}
\]

Equations (1) and (2) are valid for \( 0 \leq t \leq \tau \).

At time \( t_2 \leq \tau \), the current through the cell is reversed and now the anodic process proceeds at \( I_0' \), which may not necessarily be the same as the current \( I_o \) during the cathodic process. For \( t > t_2 \), we may write

\[
t = t_2 + t'
\]

and so eqns. (1) and (2) in ref. 1 remain valid if we replace \( t \) by \( t' \) and \( t_i \) by \( t_2 + t' \). In turn, the boundary value problem is now given by (see Notation/Definitions)

\[
t' = 0, \quad x > 0 \\
t' > 0, \quad x \rightarrow \infty \\
c_A(x, t) = c_A(s_A, x, \beta) \\
c_B(x, t) = c_B(s_B, x, \beta)
\]

Equations (6) through (8) are now

\[
D_A \frac{\partial c_A}{\partial x} |_{x=0} = -D_B \frac{\partial c_B}{\partial x} |_{x=0} = \frac{-I_0'}{n F A_0} \\
I_0'/n F A_0 \tau^{1/2} = k_6 c_A(0, t' - t_i c_A(0, t'))
\]

where \( t_i \) is now

\[
t_i = t_f + t_2 + t'
\]

The solution of eqn. (2) in ref. 1 (with \( t' \) instead of \( t \) and \( t_i \) given by eqn. 9) can be obtained by proceeding as follows [18].

Using the transformations

\[
s' = x/\sqrt{2(D_A t')^{1/2}} \\
\Omega = (2(I_0 + I_0' t')^{-1/6})/(n F A_0 D_A^{1/2} c_A^*) \\
e = (t'/t_i)^{1/3}
\]

supposing that \( c_A \) and \( c_B \) have the form

\[
c_A = c_A(s_A, x, \beta) + \sum_{i,j} p_{ij} (s_A^0) \Omega \epsilon^j \\
c_B = c_B(s_B, x, \beta) + \sum_{i,j} q_{ij} (s_B^0) \Omega \epsilon^j
\]

and proceeding as in the previous paper [1] (see Appendix), we obtain for the surface concentrations of species A and B, after application of current reversal, the following expressions:

\[
c_A(0, t')/c_A^* = \mu + \gamma N_i t^{-1/6} F(\beta) - \gamma (N_i + N_i^*) \epsilon^2 (t')^{-1/6} F(\epsilon) \\
c_B(0, t')/c_B^* = 1 - N_i t^{-1/6} F(\beta) + (N_i + N_i^*) \epsilon^2 (t')^{-1/6} F(\epsilon)
\]

where

\[
N_i^* = 2I_0'/n F A_0 D_A^{1/2} c_A^*
\]

The value of \( \tau' \) (transition time for the reoxidation process) is readily deduced from eqn. (15) by introducing the condition \( c_B(0, \tau') = 0 \):

\[
(t')^{1/2} = \frac{\mu (t_2 + \epsilon) + \gamma (N_i + N_i^*)} {\gamma (N_i + N_i^*)} \frac{n F A_0^{1/2} I_0} {2 I_0'}
\]

where \( \beta_{t_2, \tau} \) and \( \epsilon \) are the values of variables \( \beta \) and \( \epsilon \) for \( t = t_2 + \tau' \) and \( t' = \tau' \), respectively.

If \( t_1 \gg t \) (stationary plane electrode) \( F(\beta_{t_2, \tau}) = F(\beta_2) = 1/\sqrt{\pi} \), eqn. (18) becomes

\[
(t_2 + \epsilon) - \epsilon^{-1/2} = c_A^* \sqrt{n F A_0} / 2 I_0
\]

where

\[
a = I_0'/I_0
\]

If \( a = 1 \), eqn. (19) simplifies to that obtained for a stationary plane electrode by Murray and Reiley [7].

When the electrode product is not present at the beginning of the electrolysis (\( c_A^* = 0 \)), eqn. (19) gives

\[
(t')^{1/2} = \sqrt{t_2} (a + 2) \quad t_i \leq \tau
\]

which is the equation deduced by Berzins and Delahay [4] and Macero and Anderson [5] for a stationary plane electrode when \( t_2 \sim \tau \).

On the other hand, the expression of the potential–time functions for the reoxidation process is obtained, in a dimensionless form, by introducing eqns. (15) and (16) in eqn. (8) and making the following substitutions:

\[
N(t, \beta) = N_i (t_2 + \epsilon)^{-1/6} \beta^2 \\
N' (t', \epsilon) = N_i' (t')^{-1/6} \epsilon^2 \\
M(t', \epsilon) = (N_i + N_i^*) (t')^{-1/6} \epsilon \\
\theta(t') = \theta \epsilon \\
\theta_0 = 4k_6^2 / D_A \\
\eta(t') = n F / RT \ln [E(t') - E^*]
\]
Thus, we have after some rearrangement
\[
\theta(t')^{-1/2}N'(t', \epsilon) = 10^{\text{10+4.5}} \left\{ \frac{\mu + \gamma N(t', \beta) F(\beta) - \gamma M(t', \epsilon) F(\epsilon)}{1 - N(t', \beta) F(\beta) + M(t', \epsilon) F(\epsilon)} \right\} 
\]
(28)

For a reversible process \((k_s \gg 1)\), eqn. (28) simplifies to
\[
\eta(t') = \log \frac{1 - N(t', \beta) F(\beta) + M(t', \epsilon) F(\epsilon)}{\mu + \gamma N(t', \beta) F(\beta) - \gamma M(t', \epsilon) F(\epsilon)} 
\]
(29)

Conversely, if the charge-transfer reaction is totally irreversible \((k_s \ll 1)\), we find that
\[
\eta(t') = \log \frac{\theta(t')^{-1/2}N'(t', \epsilon)}{\mu + \gamma N(t', \beta) F(\beta) - \gamma M(t', \epsilon) F(\epsilon)} 
\]
(30)

Finally, if \(t_1 \gg t\) (stationary plane electrode), \(I_0 = I_0^c\) and \(\mu = 0\), eqns. (28), (29) and (30) are identical to eqns. (4), (6b) and (8b), respectively, obtained by Anderson and Macero in ref. 6.

RESULTS AND DISCUSSION

Table 1 shows the transition times obtained from eqn. (18) for the reoxidation process with a fixed value of \(N_s\) and different values of \(N_s'\) and \(t_i\). For each value of the two variables, two values of \(\tau'\), corresponding to \(t_2 < \tau\) and \(t_2 = \tau\), respectively, are calculated. As can be observed, both \(\tau\) and \(\tau'\) increase with \(t_i\), fulfilling in any case
\[
\tau'/t_2 > 1/\log(a = 2) 
\]
(31)

This result differs from that obtained with a stationary plane electrode (see eqn. 21).

The dependence of the surface concentrations of species A and B on \(\tau\) and the concentration profiles of B at different values of \(t'\) are shown in Figs. 1 and 2.

<table>
<thead>
<tr>
<th>(N_s'/s^{1/2})</th>
<th>(\tau_1/t_2) ((t_2 = 0.5) s)</th>
<th>(\tau_2/t_2) ((t_2 = 1.5) s)</th>
<th>(\tau_1/t_2) ((t_2 = \tau_2))</th>
<th>(\tau_2/t_2) ((t_2 = \tau_2))</th>
</tr>
</thead>
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<tr>
<td>1.0</td>
<td>0.739</td>
<td>0.891</td>
<td>2.282</td>
<td>2.949</td>
</tr>
<tr>
<td>1.5</td>
<td>0.451</td>
<td>0.544</td>
<td>1.393</td>
<td>1.802</td>
</tr>
<tr>
<td>2.0</td>
<td>0.331</td>
<td>0.378</td>
<td>0.969</td>
<td>1.253</td>
</tr>
<tr>
<td>2.5</td>
<td>0.235</td>
<td>0.283</td>
<td>0.724</td>
<td>0.936</td>
</tr>
<tr>
<td>3.0</td>
<td>0.184</td>
<td>0.221</td>
<td>0.567</td>
<td>0.733</td>
</tr>
<tr>
<td>3.5</td>
<td>0.149</td>
<td>0.179</td>
<td>0.458</td>
<td>0.593</td>
</tr>
<tr>
<td>4.0</td>
<td>0.123</td>
<td>0.148</td>
<td>0.380</td>
<td>0.491</td>
</tr>
</tbody>
</table>

Fig. 1. Surface concentrations of species A (-- -- --) and B (-----), eqns. (1)–(2) and (15)–(16). \(t_1 = 2\) s, \(\mu = 0\), \(\gamma = 1\), \(N_s = 3 s^{1/2}\), \(t_2 = \tau = 1.908\) s. The values of \(N_s'/s^{1/2}\) and \(\tau'\) (s) respectively were: (a) 1, 2.943; (b) 2, 1.253; (c) 4, 0.491.

Fig. 2. Dependence of the concentration profiles of species B on \(\tau'\) (eqn. 14): \(t_1 = 2\) s, \(\mu = 0\), \(\gamma = 1\), \(t_2 = 1.275\) s, \(N_s = 2.1 s^{1/2}\), \(N_s' = 0.7 s^{1/2}\), \(\tau' = 2.072\) s. \(\tau'/\tau\): (a) 0; (b) 0.1; (c) 0.5; (d) \(\tau'\).

Fig. 3. Potential–time curves for a reversible process \((k_s \gg 1)\) (eqn. 41 in ref. 1 for \(t < t_2\) and eqn. 29 in this paper for \(t > t_2\)): \(t_1 = 2\) s, \(\mu = 0\), \(\gamma = 1\), \(T = 298\) K, \(n = 1\), \(N_s = 3 s^{1/2}\), \(t_2 = \tau\). \(N_s'/s^{1/2}\): (a) 1, (b) 1.5, (c) 3.
respectively. This last figure is qualitatively similar to that obtained by Berzins and Delahay for a stationary plane electrode [4]. However, in Fig. 2 the slope of the curves at \( x = 0 \) is dependent on \( t' \) according to (see eqn. 7):

\[
\begin{align*}
\left( \frac{\partial c_B}{\partial x} \right)_{x=x_0} & = \left( \frac{t_{s,2}}{t_{s,1}} \right)^{2/3}, \\
\text{where } t_{s,1} & = t_1 + t_2 + t_3.
\end{align*}
\]  
(32)

Meanwhile the above relation is equal to unity for stationary electrodes.

In Figs. 3–5 we have plotted \( \Delta E = (E - E^0) \) vs. \( t \) for a reversible, quasi-reversible and irreversible charge-transfer reaction, respectively, for \( \mu = 0, \text{ and } t_2 = \tau, \) \( N' = 3 \) \( s^{1/3} \) and three different values of \( N' \). As could be expected, as the process becomes more irreversible, i.e. when \( k_i \) decreases, the separation of the forward and reverse \( E/t \) curves increases. However, both the forward and the reverse \( E/t \) curves are shifted in the same direction along the potential axis by variations in \( \alpha \). Consequently, the separation between these two curves is slightly affected by the \( \alpha \) values. Moreover, the influence exerted by \( \alpha \) on the shape of these curves is qualitatively similar to that described in ref. 6. So, an increase of \( \alpha \) decreases the slope of the \( E/t \) curve corresponding to the forward process and increases that of the reverse one.

If the process is reversible \( (k_i > 0.1 \text{ cm s}^{-1}, \text{ Fig. 3}), \) when \( \mu = 0 \) is fulfilled

\[
(E - E^0)_{v = 0} = -(E - E^0)_{v = 0} = -\infty
\]  
(33)

In this case, the determination of the reversible polarographic half-wave potential, \( E_{1/2} \), could be carried out as shown in ref. 19.

![Fig. 4. Potential-time curves for a quasi-reversible process (\( k_i = 5 \times 10^{-3} \text{ cm s}^{-1} \)) (eqn. 40 in ref. 1 for \( t < t_2 \) and eqn. 28 in this paper for \( t > t_2 \), \( \alpha = 0.5 \). Other conditions as in Fig. 3.](image)

![Fig. 5. Potential-time curves for an irreversible process (\( k_i = 10^{-3} \text{ cm s}^{-1} \)) (eqn. 43 in ref. 1 for \( t < t_2 \) and eqn. 30 in this paper for \( t > t_2 \)). \( \alpha = 0.5 \). Other conditions as in Fig. 3.](image)

![Fig. 6. (I) Dependence of \( E_t \) on \( \ln g(-1/6, \beta) \) (eqn. 51 in ref. 3). (II) Dependence of \( E_t \) on \( \ln g(1/3, \beta, \epsilon) \) (eqn. 36 in this paper). \( k_i = 10^{-3} \text{ cm s}^{-1}, E^0 = 0 \text{ V}, \alpha = 0.5, N' = 3 \). (a) 2; (b) 3; (c) 5. Other conditions as in Fig. 3.](image)

Conversely, if the process is irreversible \( (k_i < 10^{-3} \text{ cm s}^{-1}, \text{ Fig. 4}), \) for \( \mu = 0 \) and \( t_2 = \tau \) we obtain

\[
(E)_{v = 0} = E^0 + \frac{RT}{(1 - \alpha)nF} \ln \left( \frac{adB_t^{1/2}}{2k_i^{1/3}sF(\beta_i)} \right)
\]  
(34)

Taking into account this expression and the \( (E)_{v = 0} \) value obtained for the forward process [1], it is possible, using different values of \( I_0 \) and/or \( I_0' \), to obtain approximate values of \( \alpha, k_i \) and \( E^0 \).

On the other hand, eqn. (30), after some manipulation, may be rewritten as

\[
E(t') = E^0 + \frac{RT}{(1 - \alpha)nF} \ln \frac{I_0'}{\gamma nF\alpha^{1/3}k_i} - \frac{RT}{(1 - \alpha)nF} \ln \left( g(t', \beta, \epsilon) \right)
\]  
(35)

where

\[
g(t', \beta, \epsilon) = (\mu/\gamma)I_0^{1/3} + N' (t_2 + t')^{1/3} F(\beta) - (N' + N'_i)(t')^{1/3} F(\epsilon)
\]  
(36)

If we plot \( E \) vs. \( \ln \left( g(t', \beta, \epsilon) \right) \) and we make a similar representation for the preceding cathodic process (\( E \) vs. \( \ln \left( g(-1/6, \beta) \right) \), it is possible to obtain accurate values of \( \alpha, k_i \) and \( E^0 \). So, we obtain from the slopes of the cathodic and
anodic processes \( \alpha \) and \((1 - \alpha)\), respectively. It is possible to verify by the present method that the sum \( \alpha + (1 - \alpha) \) is indeed equal to unity. If there are kinetic complications (consecutive electrochemical reactions, dismutation, etc.), this sum will generally be different from unity, and such complications can therefore be detected.

The \( k_i \) and \( E^\circ \) values can be calculated from the slopes and intercepts of both representations, obtaining

\[
\ln k_i = \frac{RT}{nFp} \left( \frac{Q_0 - Q_A}{P_B} + \ln \frac{\alpha}{\gamma} \right) + \ln \frac{I_0}{nFAC_A} \quad (37)
\]

\[
E^\circ = \frac{P_0Q_A - P_0Q_B + P_A P_0 \ln(\gamma/\alpha)}{P_B - P_A} \quad (38)
\]

where \( Q_0 \) and \( P_0 \) are the intercepts and slopes for the cathodic \( (i = A) \) and anodic \( (i = B) \) processes, respectively. As an example, in Fig. 6 these plots are reproduced for a process with \( k_i = 10^{-3} \) cm s \(^{-1}\), \( \gamma = 0.5 \) and \( E^\circ = 0 \) V, in which the three parallel straight lines correspond to three different values of \( N_i^e \).

Finally, for a quasi-reversible process the determination of the kinetic and thermodynamic parameters for a charge-transfer reaction can be carried out by a non-linear regression analysis in a similar way to that described by Anderson and Macero [6].

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APPENDIX

The functions \( \delta_{ij}(s_B) \) and \( \rho_{ij}(s_A) \) are:

\[
\delta_{1,2}(s_B) = -\frac{\gamma e^{-i\phi}}{\sqrt{\pi}} \Psi_1(s_B) \quad (A2)
\]

\[
\delta_{1,3}(s_B) = \frac{\gamma e^{-i\phi}}{\sqrt{\pi}} \left\{ 3 e^{-i\phi^2} - 12 \Psi_1(s_B) + 8 \Psi_3(s_B) \right\} \quad (A3)
\]

\[
\delta_{1,8}(s_B) = -\frac{e^{-i\phi}}{270 \sqrt{\pi}} \left\{ -125 e^{-i\phi^2} + 30 s_B^2 e^{-i\phi^2} + 660 \Psi_1(s_B) \right. \\
\left. - 880 \Psi_3(s_B) + 352 \Psi_5(s_B) \right\} \quad (A4)
\]

\[
\delta_{1,11}(s_B) = \frac{e^{-i\phi}}{5670 \sqrt{\pi}} \left\{ 4095 e^{-i\phi^2} - 1120 s_B^2 e^{-i\phi^2} + 1403 s_B^4 e^{-i\phi^2} - 27720 \Psi_1(s_B) \right. \\
\left. + 55440 \Psi_3(s_B) - 44352 \Psi_5(s_B) + 12672 \Psi_7(s_B) \right\} \quad (A5)
\]

\[
\rho_{1,0}(s_A) = -\frac{1}{\gamma} \delta_{1,0}(s_A) \quad (A6)
\]

where the \( \Psi_i \) are the functions defined by Koutecký (for their properties see Appendix A of ref. 20).

NOTATION/DEFINITIONS

\[
c_i(s, \chi, \beta) \quad \text{eqn. (16) in ref. 1, for } w = 0 \ (i = A \text{ or } B)
\]

\( x \) \quad \text{distance from electrode surface}

\( c_i^- \), \( c_i^+ \) \quad \text{initial concentrations of } A \text{ and } B

\( \mu \) \quad \frac{c_i^-}{c_i^+}

\( \chi \) \quad \frac{D_i A}{D_B}

\( \gamma \) \quad \frac{D_i}{D_B}

\( \beta \) \quad \frac{D_i}{D_B}

\( \beta_i \) \quad = \text{value of } \beta \text{ for } \tau = t

\( N_i^e \) \quad \text{electrode area at } t_i = 1 \text{s}

\( A_0 \), \( I'_0 \) \quad \text{forward and reverse constant, respectively}

\( a \) \quad = \frac{I'_0}{I_0}

\( E^\circ \) \quad \text{formal standard potential of electroactive couple}

\( E \) \quad \text{time-dependent electrode potential}

\( E_{t_2}, E_{t_2} \) \quad \text{time-dependent electrode potentials at } t < t_2 \text{ and } t > t_2, \text{ respectively (see Fig. 6)}

\( t_2, t_2' \) \quad \text{transition times of reduction and reoxidation processes, respectively}

\( k_i, k_i' \) \quad \text{heterogeneous rate constants of the forward and the reverse charge-transfer reactions}

\( k_s \) \quad \text{apparent heterogeneous rate constant of charge transfer at } E^\circ

\alpha \quad \text{electro-transport coefficient}

Other definitions are conventional.

REFERENCES

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Chronopotentiometry with current reversal is very useful in the evaluation of thermodynamic and kinetic electrode parameters for both reduction and re-oxidation processes. However, until now the corresponding theoretical development has been limited to stationary electrodes [4–17].

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