Programmed Current Chronopotentiometry: Part II-Theoretical Study of an Electrode Process Followed by a Chemical Reaction[†]

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Theoretical chronopotentiometric equations for electrode process followed by a chemical reaction are given for a ramp current impulse.

PROGRAMMED current chronopotentiometry¹⁻⁵ is useful for the identification of kinetics of reactions occurring at the electrode surface and/or in solution. The electrode process followed by a chemical reaction has been studied by polarography⁶⁻⁸ and data interpretted using the theoretical treatments of Kern⁹ and Kivalo¹⁰. Delahay *et al.*¹¹⁻¹⁴ have developed theoretical treatment for such processes using a constant electrolysis current. In continuation of our earlier study¹⁵, theoretical equations for the above electrode process using a ramp electrolysis current are given here.

Theoretical Analysis

Let us consider the process (1)

$$0 \xrightarrow{\text{ne}} \mathbf{R} \stackrel{k_f}{\underset{k_i}{\leftarrow}} \mathbf{Z} \qquad \dots (1)$$

wherein O is reduced to R at the electrode surface and R is transformed to Z by chemical reaction; Z is neither reduced nor oxidized at the potential at which O is reduced.

Fick's equation¹⁶ of diffusion must, therefore, be modified to account for the transformation of Rto Z. Thus for R and Z, Fick's equations are:

$$\frac{\partial C_{\mathrm{R}}(x,t)}{\partial t} = D_{\mathrm{R}} \frac{\partial C_{\mathrm{R}}(x,t)}{\partial x^{2}} - k_{f}C_{\mathrm{R}}(x,t) + k_{b}C_{z}(x,t)$$
...(2)

$$\frac{\partial C_z(x,t)}{\partial t} = D_z \frac{\partial C_z(x,t)}{\partial x^2} + k_f C_R(x,t) - k_b C_z(x,t)$$
...(3)

The initial conditions are:

$$C_{\rm R}(x, 0) = C_{\rm z}(x, 0) = 0$$

$$C_{\rm R}(\infty, t) = C_{\rm z}(\infty, t) = 0$$

and the boundary conditions for the ramp current is,

$$D_{\rm R} \left(\frac{\partial C_{\rm R}}{\partial x} \frac{(x,t)}{x} \right)_{x=0} = -\frac{It}{nFA} \qquad \dots (6)$$

and, also

$$D_{z} \left(\frac{\partial C_{z} \left(x, t \right)}{\partial x} \right)_{x=0} = 0 \qquad \dots (7)$$

†Part I, see ref. 15.

[†]Present address: Chemistry Department, Rajdhani College (University of Delhi), Raja Garden, Delhi 110015. §Present address: Chemistry Department, K.M. College (University of Delhi), Delhi 110007. The concentration of species 0 at the electrode surface will be unaffected by the chemical reaction, and is given by the equation⁴

$$C_{\rm O}(0,t) = C_{\rm O}^{\,0} - \frac{4It^{3/2}}{3\pi^{\frac{1}{2}}nFAD_{\rm O}^{\frac{1}{2}}} \qquad \dots (8)$$

Introducing the new functions such that

$$\psi(x, t) = C_{\rm R}(x, t) + C_{z}(x, t)$$
 ...(9)

$$\phi(x,t) = C_z(x,t) - \frac{\kappa_f}{k_b} C_R(x,t) \qquad ...(10)$$

and assuming that $D_{\rm R} = D_z = D$, Eqs. (2) and (3) reduce to

$$\frac{\partial \psi(x,t)}{\partial t} = D \frac{\partial^2 \psi(x,t)}{\partial x^2} \qquad \dots (2a)$$

$$\frac{\partial \phi(x, t)}{\partial t} = D \frac{\partial^2 \phi(x, t)}{\partial x^2} - (k_f + k_b) \phi(x, t) \qquad \dots (3a)$$

The new initial and boundary conditions then become

$$\begin{aligned} \Psi(x, 0) &= \phi(x, 0) = 0 & \dots(4a) \\ \left\{ \frac{\partial \Psi(x, t)}{\partial x} \right\}_{x=0} &= -\frac{It}{nFAD} \left(1 + \frac{k_f}{k_b} \right) & \dots(6a) \end{aligned}$$

and

... (4)

...(5)

$$\begin{cases} \frac{\partial \phi(x,t)}{\partial x} \\ x = 0 \end{cases} = -\frac{k_f}{k_b} \begin{cases} \frac{\partial \Psi(x,t)}{\partial x} \\ x = 0 \end{cases} \qquad \dots (7a)$$

Laplace transform of partial differential Eqs. (2a) and (3a) are

$$D\left[\frac{d^2\overline{\Psi}(x,s)}{dx^2}\right] = -\Psi(x,0) + s\overline{\Psi}(x,s) \qquad \dots (2b)$$
$$= s\overline{\Psi}(x,s)$$

and

$$D\begin{bmatrix} \frac{d^2\phi(x,s)}{dx^2} \end{bmatrix} = -\phi(x,0) + s\overline{\phi}(x,s) + (k_f + k_b) \ \overline{\phi}(x,s)$$
$$= (s + k_f + k_b)\overline{\phi}(x,s) \qquad \dots (3b)$$

The general solutions of (2b) and (3b) under boundary conditions are given by Eqs. (11) and (12) $\overline{\Psi}(x, s) = M \exp(-xs^{1/2}/D^{1/2})$...(11) $\overline{\phi}(x, s) = N \exp[-x(s+k_f+k_b)^{1/2}/D^{1/2}]$...(12)

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Values of integration constants M and N are obtained from boundary conditions (6a) and (7a), which in Laplace transforms are

$$\begin{cases} \frac{d\overline{\Psi}(x, s)}{dx} \\ x=0 \end{cases} = -\frac{I}{nFADs^2} \left(1 + \frac{k_f}{k_b}\right) \dots (13)$$

and

 $\left\{\frac{d\phi(x,s)}{dx}\right\} = -\frac{k_f}{k_b} \left\{\frac{d\overline{\Psi}(x,s)}{dx}\right\} \dots \dots (14)$

Using Eqs. (11) and (12) with (13) and (14) one obtains

$$M = \frac{I}{nFAD^{1/2}s^{5/2}}$$

and

$$N = \frac{(k_f/k_b)I}{nFAD^{1/2}s^2(s+k_b+k_f)^{1/2}}$$

Thus Eqs. (11) and (12) become

$$\overline{\Psi}(x,s) = \frac{I}{nFAD^{1/2}s^{5/2}} \exp(-xs^{1/2}/D^{1/2}) \qquad \dots (15)$$

$$(k_s/k_s)I$$

$$\overline{\phi}(x, s) = \frac{(\kappa_f/\kappa_b)}{nFAD^{1/2}s^2(s+k_f+k_b)^{1/2}} \exp(-xs^{1/2}/D^{1/2}) \dots (16)$$

whose inverse transforms are obtained at x = 0 using convolution method

$$\Psi(0,t) = \frac{4It^{5/2}}{3nFAD^{1/2}\pi^{1/2}} \qquad \dots (17)$$

and

$$\phi(0,t) = -\frac{I(k_f/k_b)}{nFAD^{1/2}} \left[\frac{2(k_f+k_b)t-1}{(k_f+k_b)^{3/2}} \operatorname{erf}\{(k_f+k_b)t\}^{1/2} + \frac{t^{1/2}}{\pi^{1/2}} \frac{\exp\{-(k_f+k_b)t\}}{(k_f+k_b)} \right] \dots (18)$$

Thus the concentration of R at the electrode surface at time t is given by Eq. (19)

$$C_{\mathbf{R}}(0,t) = \frac{IK}{nFAD^{1/2}(1+K)} \left[\frac{4t^{3/2}}{3\pi^{1/2}K} + \frac{\{2(k_f+k_b)t-1\}}{(k_f+k_b)^{3/2}} \right]$$

erf{ $(k_f+k_b)t$ }^{1/2} + $\frac{t^{1/2}}{\pi^{1/2}} \frac{\exp\{-(k_f+k_b)t\}}{(k_f+k_b)}$...(19)

where $K = k_f/k_b$ is the equilibrium constant. Similarly value of $C_z (0, t)$ can be obtained.

For a totally irreversible electrode process, potential-time curves for reduction of O are not affected by the chemical transformation $R \rightleftharpoons Z$. For a completely reversible electrode process, potentialtime curves are obtained by substituting $C_0(0, t)$ and $C_R(0, t)$ terms in Nernst equation. Thus

$$E = E_{1/2} + \frac{RT}{nF} \ln \frac{C_{\circ}^{\circ} - \frac{4It^{3/2}}{3\pi^{1/2}nFAD^{1/2}}}{\frac{IK}{nFAD^{1/2}(1+K)} \left[\frac{4t^{3/2}}{3\pi^{1/2}K} + \frac{\{2(k_f + k_b)t - 1\}}{(k_f + k_b)^{3/2}}erf\{(k_f + k_b)t\}^{1/2}} + \frac{t_{1/2}}{\pi^{1/2}}\frac{\exp\{-(k_f + k_b)t\}}{(k_f + k_b)} \right] \dots (20)$$





which on rearrangement yields

$$E = E_{1/2} + \frac{RT}{nF} \ln \frac{\tau^{3/2} - t^{3/2}}{t^{3/2}} - \frac{RT}{nF} \ln \eta \qquad \dots (21)$$

where

$$\eta = \frac{1}{1+K} + \left(\frac{K}{1+K}\right) \frac{3\pi^{1/2} \{2(k_f + k_b)t - 1\}}{4(k_f + k_b)^{3/2} t^{3/2}}$$

erf{ $(k_f + k_b)t$ }^{1/2} + $\frac{3}{4t} \left(\frac{K}{1+K}\right) \frac{\exp\{-(k_f + k_b)t\}}{(k_f + k_b)} \dots (22)$

The effect of k_f on potential-time curves is shown in Fig. 1 for a hypothetical case where $\tau = 0.1$ sec and K = 1000.

At
$$t = 0.636\tau$$
, Eq. (21) reduces to
 $E_{0.636\tau} = E_{\frac{1}{2}} - \frac{RT}{nF} \ln \eta_{0.636\tau} \qquad \dots (23)$

When there is no transformation of R to Z, $E_{0.636\tau}$ is identical to $E_{\frac{1}{2}}$.

Influence of current density and equilibrium constant — When the current density is sufficiently low or τ is large the argument of error function is larger than 2. The Eq. (21) then reduces to

$$E = E_{1/2} + \frac{RT}{nF} \ln \frac{\tau^{3/2} - t^{3/2}}{t^{3/2}} + \frac{RT}{nF} \ln (1+K) \qquad \dots (24)$$

Equation (24) will also hold, in general, when the chemical reaction is reversible and rapid.

For a sufficiently high current density or small τ , argument of error function will be low and error function can be expanded for a sufficiently low argument,

$$[(k_f+k_b)t]$$
, η will practically reduce to $\left(1+\frac{1}{1+K}\right)$
which shows that there is practically little trans-
formation $(K\gg1)$ R=Z during electrolysis

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