

## 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.

**P**ROGRAMMED current chronopotentiometry<sup>1-5</sup> 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 polarography<sup>6-8</sup> and data interpreted using the theoretical treatments of Kern<sup>9</sup> and Kivalo<sup>10</sup>. Delahay *et al.*<sup>11-14</sup> have developed theoretical treatment for such processes using a constant electrolysis current. In continuation of our earlier study<sup>15</sup>, theoretical equations for the above electrode process using a ramp electrolysis current are given here.

### Theoretical Analysis

Let us consider the process (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 equation<sup>16</sup> of diffusion must, therefore, be modified to account for the transformation of R to Z. Thus for R and Z, Fick's equations are:

$$\frac{\partial C_R(x,t)}{\partial t} = D_R \frac{\partial C_R(x,t)}{\partial x^2} - k_f C_R(x,t) + k_b C_Z(x,t) \quad \dots(2)$$

$$\frac{\partial C_Z(x,t)}{\partial t} = D_Z \frac{\partial C_Z(x,t)}{\partial x^2} + k_f C_R(x,t) - k_b C_Z(x,t) \quad \dots(3)$$

The initial conditions are:

$$C_R(x,0) = C_Z(x,0) = 0 \quad \dots(4)$$

$$C_R(\infty,t) = C_Z(\infty,t) = 0 \quad \dots(5)$$

and the boundary conditions for the ramp current is,

$$D_R \left( \frac{\partial C_R(x,t)}{\partial x} \right)_{x=0} = - \frac{It}{nFA} \quad \dots(6)$$

and, also

$$D_Z \left( \frac{\partial C_Z(x,t)}{\partial x} \right)_{x=0} = 0 \quad \dots(7)$$

The concentration of species 0 at the electrode surface will be unaffected by the chemical reaction, and is given by the equation<sup>4</sup>

$$C_0(0,t) = C_0^0 - \frac{4It^{3/2}}{3\pi^{3/2}nFAD^{3/2}} \quad \dots(8)$$

Introducing the new functions such that

$$\psi(x,t) = C_R(x,t) + C_Z(x,t) \quad \dots(9)$$

$$\phi(x,t) = C_Z(x,t) - \frac{k_f}{k_b} C_R(x,t) \quad \dots(10)$$

and assuming that  $D_R = D_Z = D$ , Eqs. (2) and (3) reduce to

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

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

The new initial and boundary conditions then become

$$\Psi(x,0) = \phi(x,0) = 0 \quad \dots(4a)$$

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

and

$$\left\{ \frac{\partial \phi(x,t)}{\partial x} \right\}_{x=0} = - \frac{k_f}{k_b} \left\{ \frac{\partial \Psi(x,t)}{\partial x} \right\}_{x=0} \quad \dots(7a)$$

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

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

and

$$D \left[ \frac{d^2 \bar{\phi}(x,s)}{dx^2} \right] = -\phi(x,0) + s\bar{\phi}(x,s) + (k_f + k_b)\bar{\phi}(x,s) = (s + k_f + k_b)\bar{\phi}(x,s) \quad \dots(3b)$$

The general solutions of (2b) and (3b) under boundary conditions are given by Eqs. (11) and (12)

$$\bar{\Psi}(x,s) = M \exp(-xs^{1/2}/D^{1/2}) \quad \dots(11)$$

$$\bar{\phi}(x,s) = N \exp[-x(s + k_f + k_b)^{1/2}/D^{1/2}] \quad \dots(12)$$

†Part I, see ref. 15.

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

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

and

$$\left\{ \frac{d\bar{\phi}(x, s)}{dx} \right\}_{x=0} = -\frac{k_f}{k_b} \left\{ \frac{d\bar{\Psi}(x, s)}{dx} \right\}_{x=0} \dots (14)$$

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

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

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

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

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

and

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

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

$$C_R(0, t) = \frac{IK}{nFAD^{1/2}(1+K)} \left[ \frac{4t^{3/2}}{3\pi^{1/2}K} + \frac{\{2(k_f+k_b)t-1\}}{(k_f+k_b)^{3/2}} \operatorname{erf}\{(k_f+k_b)t\}^{1/2} + \frac{t^{1/2} \exp\{-(k_f+k_b)t\}}{\pi^{1/2}(k_f+k_b)} \right] \dots (19)$$

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, potential-time curves are obtained by substituting  $C_O(0, t)$  and  $C_R(0, t)$  terms in Nernst equation. Thus

$$E = E_{1/2} + \frac{RT}{nF} \ln \frac{C_O^0 - \frac{4It^{3/2}}{3\pi^{1/2}nFAD^{1/2}}}{\frac{IK}{nFAD^{1/2}(1+K)} \left[ \frac{4t^{3/2}}{3\pi^{1/2}K} + \frac{\{2(k_f+k_b)t-1\}}{(k_f+k_b)^{3/2}} \operatorname{erf}\{(k_f+k_b)t\}^{1/2} + \frac{t^{1/2} \exp\{-(k_f+k_b)t\}}{\pi^{1/2}(k_f+k_b)} \right]} \dots (20)$$

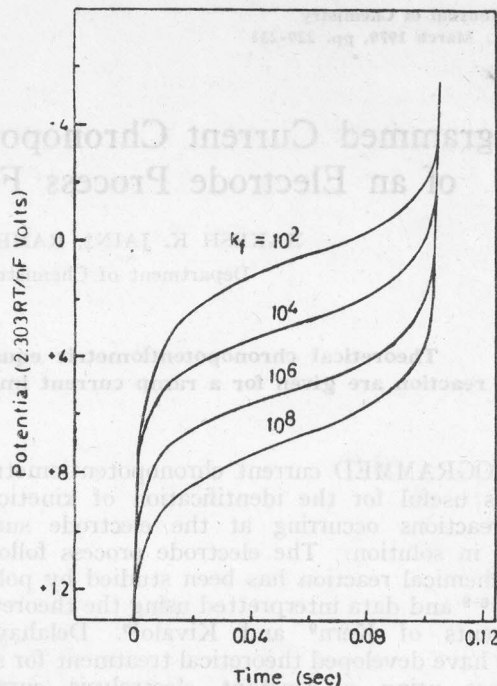


Fig. 1 — Effect of rate constant,  $k_f$  on potential-time curves for an electrochemical reaction followed by chemical transformation

which on rearrangement yields

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

where

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

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

$$E_{0.636\tau} = E_{\frac{1}{2}} - \frac{RT}{nF} \ln \eta_{0.636\tau} \dots (23)$$

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  $\tau$  is large the argument of error function is larger than 2. The Eq. (21) then reduces to

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

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

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

$$[(k_f+k_b)t], \eta \text{ will practically reduce to } \left( 1 + \frac{1}{1+K} \right)$$

which shows that there is practically little transformation ( $K \gg 1$ )  $R \rightleftharpoons Z$  during electrolysis.

