Thanks are due to Dr D. K. Majumdar for his interest in the work.

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Chronopotentiometry with Programmed Current: Theoretical Study of an Electrode Process Complicated by a Catalytic Reaction

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Theoretical chronopotentiometric equation for an electrode process complicated by a catalytic process is given for ramp current (current varying linearly with time) and ac chronopotentiometry.

PROGRAMMED current chronopotentiometry[1-4] provides useful information on the chronopotentiometric behaviour of various kinetic schemes. In the present note theoretical equations for electrode processes complicated by catalytic reaction are solved for the following current impulses: (a) the current varying linearly with time (ramp current); and (b) alternating current of small amplitude is superimposed over a constant electrolysis current (ac chronopotentiometry).

Theoretical analysis — For the kinetic scheme

$$O + ne \rightarrow R$$
$$R + Z \rightleftharpoons O$$
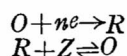
in which Z reacts with R, but is itself not involved in the electrode process, Fick's[5] second law equations are

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

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

If the bulk concentration of the species Z (C_Z^0) is much larger than that of the electroactive species O, $C_Z(x, t)$ can then be replaced by C_Z^0 in Fick's

equations. For a simple case the rate of backward chemical reaction is negligible, $D_O = D_R = D$, and R is not present initially, the above equations reduced to

$$\frac{\partial C_O(x, t)}{\partial t} = D \frac{\partial^2 C_O(x, t)}{\partial x^2} + k_f C_Z^0 C_R(x, t) \qquad \text{...(1)}$$

$$\frac{\partial C_R(x, t)}{\partial t} = D \frac{\partial^2 C_R(x, t)}{\partial x^2} - k_f C_Z^0 C_R(x, t) \qquad \text{...(2)}$$

The initial conditions are

$$\left.\begin{array}{l} C_O(x, 0) = C^0 \\ C_R(x, 0) = 0 \end{array}\right\} \qquad \text{...(3)}$$

$$\left.\begin{array}{l} C_R(x, t) = 0 \\ C_O(x, t) = C^0 \end{array}\right\} x \rightarrow \infty \qquad \text{...(4)}$$

Also the boundary condition is obtained by equating the sum of fluxes of O and R at the electrode surface to zero

$$D\left\{\frac{\partial C_O(x, t)}{\partial x}\right\}_{x=0} + D\left\{\frac{\partial C_R(x, t)}{\partial x}\right\}_{x=0} = 0 \qquad \text{...(5)}$$

(a) *Ramp current* ($i = \theta t$) — When the electrolysis current is varying linearly with time (ramp current), the flux of the reducible species O is given as

$$\left\{\frac{\partial C_O(x, t)}{\partial x}\right\}_{x=0} = \frac{\theta t}{nFAD} \qquad \text{...(6)}$$

For solving Eqs. (1) and (2) under the initial and boundary conditions (3)-(6), the following transformation is made

$$\Psi(x, t) = C_O(x, t) + C_R(x, t) \qquad \text{...(7)}$$

Solving the Laplace transform of diffusion Eqs. (1) and (2), under condition (7), one obtains

$$\overline{\Psi}(x, S) = C^0/S + M \exp\left[-x \frac{S^{\frac{1}{2}}}{D^{\frac{1}{2}}}\right] \qquad \text{...(8)}$$

and

$$\overline{C}_R(x, S) = N \exp\left[-x \frac{(S + k_f C_Z^0)^{\frac{1}{2}}}{D^{\frac{1}{2}}}\right] \qquad \text{...(9)}$$

where M and N are integration constants whose values are to be determined from the initial and boundary conditions (see Appendix). Thus

$$\overline{\Psi}(x, S) = C_O^0/S \qquad \text{...(10)}$$

$$\overline{C}_R(x, S) = \frac{\theta}{nFAD^{\frac{1}{2}}S^2(S + k_f C_Z^0)^{\frac{1}{2}}} \exp\left[-x \frac{(S + k_f C_Z^0)^{\frac{1}{2}}}{D^{\frac{1}{2}}}\right] \qquad \text{...(11)}$$

At $x = 0$, Eqs. (10) and (11) reduce to

$$\overline{\Psi}(0, S) = C_O^0/S \qquad \text{...(12)}$$

$$\overline{C}_R(0, S) = \frac{\theta}{nFAD^{\frac{1}{2}}S^2(S + k_f C_Z^0)^{\frac{1}{2}}} \qquad \text{...(13)}$$

Inverse transforms of Eqs. (12) and (13) are

$$\Psi(0, t) = C_O^0 \qquad \text{...(14)}$$

and

$$C_R(0, t) = \frac{\theta}{\pi^{\frac{1}{2}}nFAD^{\frac{1}{2}}}\left[\frac{\pi^{\frac{1}{2}}(2k_f C_Z^0 t - 1)}{(k_f C_Z^0)^{3/2}} \operatorname{erf}(k_f C_Z^0 t)^{\frac{1}{2}} + \frac{t^{\frac{1}{2}} \exp(-k_f C_Z^0 t)}{(k_f C_Z^0)}\right] \qquad \text{...(15)}$$

and using Eq. (7), expression for $C_O(0, t)$ is

$$C(0_O, t) = C_O^0 - \frac{\theta}{\pi^{\frac{1}{2}} nFAD^{\frac{1}{2}}} \left[\frac{\pi^{\frac{1}{2}}(2k_fC_Z^0t-1)}{(k_fC_Z^0)^{3/2}} \, \text{erf}(k_fC_Z^0t)^{\frac{1}{2}} + \frac{t^{\frac{1}{2}} \exp \, (-k_fC_Z^0t)}{(k_fC_Z^0)} \right] \quad \ldots(16)$$

Eqs. (15) and (16) represent the concentrations of species O and R at the electrode surface at any time t.

By definition, at the transition time $(t = \tau_c)$, the concentration of O at the electrode surface is zero, giving

$$\tau_c^{3/2} = \frac{\pi^{\frac{1}{2}} nFAD^{\frac{1}{2}}C_O^0}{\theta}$$

$$\times \left[\frac{1}{\frac{\pi^{\frac{1}{2}}(2k_fC_O^0\tau-1)}{2(k_fC_Z^0\tau)^{3/2}} \, \text{erf}(k_fC_Z^0\tau)^{\frac{1}{2}} + \frac{\exp(-k_fC_Z^0\tau)}{k_fC_Z^0\tau}} \right] \quad \ldots(17)$$

It is convenient to compare τ_c with transition time in the absence of catalytic effect (τ_d), which is given by

$$\tau_d^{3/2} = \frac{3nFAD_O^{\frac{1}{2}}\pi^{\frac{1}{2}}C_O^0}{4\theta} \quad \ldots(18)$$

Thus

$$\left(\frac{\tau_c}{\tau_d}\right)^{3/2} = \frac{4}{3} \left[\frac{1}{\frac{\pi^{\frac{1}{2}}(2k_fC_Z^0\tau-1)}{2(k_fC_Z^0\tau)^{3/2}} \, \text{erf}(k_fC_Z^0\tau)^{\frac{1}{2}} + \frac{\exp(-k_fC_Z^0\tau)}{k_fC_Z^0\tau}} \right] \quad \ldots(19)$$

The r.h.s. of Eq. (19) approaches unity for $(k_fC_Z^0\tau) = 0$. Experimentally this is achieved at low values of $k_fC_Z^0$ or τ or high current density i_0.

(b) *Ac chronopotentiometry* — When ac of small amplitude is superimposed over a constant electro lysis current, the current excitation may be denoted as

$$i(t) = \theta + B \sin \omega t$$

Analogues of Eqs. (12) and (13) are

$$\overline{\Psi}(0, S) = C^0/S$$

$$\overline{C}_R(0, S) = \frac{1}{nFAD^{\frac{1}{2}}(S+k_fC_Z^0)^{\frac{1}{2}}} \left\{ \frac{\theta}{S} + \frac{B\omega}{\omega^2+S^2} \right\} \quad \ldots(20)$$

the corresponding inverse transforms being

$$\Psi(0, t) = C^0$$

$$C_R(0, t) = \frac{\theta}{nFAD^{\frac{1}{2}}(k_fC_Z^0)^{\frac{1}{2}}} \, \text{erf}[t^{\frac{1}{2}}(k_fC_Z^0)^{\frac{1}{2}}]$$

$$+ \frac{B}{nFAD^{\frac{1}{2}}[(k_fC_Z^0)^2+\omega^2]^{\frac{1}{2}}}$$

$$\times \left[\frac{\pm \omega \sin \omega t \pm [\{(k_fC_Z^0)^2+\omega^2\}^{\frac{1}{2}} - k_fC_Z^0] \cos \omega t}{[2\{(k_fC_Z^0)^2+\omega^2\}^{\frac{1}{2}} - 2(k_fC_Z^0)]^{\frac{1}{2}}} \right] \quad \ldots(21)$$

Again using Eq. (7), concentration $C_O(0, t)$ is obtained

from Eq. (20)

$$C_O(0,t) = C_O^0 - \frac{\theta}{nFAD^{\frac{1}{2}}(k_fC_Z^0)^{\frac{1}{2}}} \, \text{erf} \, [t^{\frac{1}{2}}(k_fC_Z^0)^{\frac{1}{2}}]$$

$$+ \frac{B}{nFAD^{\frac{1}{2}}[(k_fC_Z^0)^2+\omega^2]^{\frac{1}{2}}}$$

$$\times \left[\frac{\pm \omega \sin \omega t \mp [\{(k_fC_Z^0)^2+\omega^2\}^{\frac{1}{2}} - k_fC_Z^0] \cos \omega t}{[2\{(k_fC_Z^0)^2+\omega^2\}^{\frac{1}{2}} - 2(k_fC_Z^0)]^{\frac{1}{2}}} \right] \quad \ldots(22)$$

Defining the catalytic transition time, τ_c, by the equation

$$\tau_c^{\frac{1}{2}} = \frac{nFD^{\frac{1}{2}}AC_O^0(k_fC_Z^0\tau_c)^{\frac{1}{2}}}{\theta \, \text{erf} \, (k_fC_Z^0\tau_c)^{\frac{1}{2}}} \quad \ldots(23)$$

as in the dc chronopotentiometry[6], under similar conditions, potential time curves for reversible, irreversible and quasi-reversible processes can be obtained using Eqs. (21) and (22). Potential-time equations for reversible and irreversible with or without chemical reaction followed by electrode process are already available[7-10].

APPENDIX

The function $\Psi(x, t)$ is defined by Eq. (7). The value of $C_O(x, t)$ in terms of new function $\Psi(x, t)$ is

$$C_O(x, t) = \Psi(x, t) - C_R(x, t) \quad \ldots(i)$$

Using the newly defined function $\Psi(x, t)$, the differential Eqs. (1) and (2) become

$$\frac{\partial \Psi(x, t)}{\partial t} = D \frac{\partial^2 \Psi(x, t)}{\partial x^2} \quad \ldots(ii)$$

$$\frac{\partial C_R(x, t)}{\partial t} = D \frac{\partial^2 C_R(x, t)}{\partial x^2} - k_fC_Z^0C_R(x, t) \quad \ldots(iii)$$

Rewriting initial and boundary conditions in terms of function $\Psi(x, t)$

$$\left. \begin{array}{l} \Psi(x, 0) = C^0 \\ C_R(x, 0) = 0 \\ \Psi(\infty, t) = C^0 \\ C_R(\infty, t) = 0 \\ \left\{ \dfrac{\partial \Psi(x, t)}{\partial x} \right\}_{x=0} = 0 \end{array} \right\} \quad \ldots(iv)$$

The current excitations for ramp current and ac chronopotentiometry being

$$\left\{ \frac{\partial C_R(x, t)}{\partial x} \right\}_{x=0} = -\frac{\theta t}{nFAD} \quad \ldots(vi)$$

and

$$\left\{ \frac{\partial C_R(x, t)}{\partial x} \right\}_{x=0} = -\frac{\theta}{nFAD} - \frac{B \sin \omega t}{nFAD} \quad \ldots(vii)$$

Laplace transform of differential Eqs. (ii) and (iii) are

$$\frac{d\overline{\Psi}(x, S)}{dt} = D \frac{d^2\overline{\Psi}(x, S)}{dx^2}$$

and

$$\frac{d\overline{C}_R(x, S)}{dt} = D \frac{d^2\overline{C}_R(x, S)}{dx^2} - k_fC_Z^0\overline{C}_R(x, S)$$

whose general solutions are given by Eqs. (8) and (9).

The integration constants M and N are evaluated from the initial and boundary conditions (iv)-(vii). Laplace transforms of conditions (iv)-(vii) are

$$\overline{\Psi}(x, 0) = C^0/S; \ \overline{\Psi}(\infty, t) = C^0/S \atop \overline{C}_R(x, 0) = 0; \ \overline{C}_R(\infty, t) = 0 \right\} \quad \text{...(iva)}$$

$$\left\{ \frac{d\overline{\Psi}(x, S)}{dx} \right\}_{x=0} = 0 \quad \text{...(va)}$$

$$\left\{ \frac{d\overline{C}_R(x, S)}{dx} \right\}_{x=0} = -\frac{\theta}{nFADS^2} \text{(ramp current)} \quad \text{...(via)}$$

$$\left\{ \frac{d\overline{C}_R(x,S)}{dx} \right\}_{x=0} = -\frac{1}{nFAD} \left\{ \frac{\theta}{S} + \frac{B\omega}{\omega^2+S^2} \right\}$$

(ac chronopotentiometry)   ...(viia)

Differentiation of Eqs. (8) and (9) with respect to x under conditions (iva)-(viia) leads to the values M and N

$$M = 0$$

$$N = \frac{\theta}{nFAD^{\frac{1}{2}}S^2(S+k_fC_Z^0)^{\frac{1}{2}}}$$

and

$$N = \frac{1}{nFAD^{\frac{1}{2}}(S+k_fC_Z^0)^{\frac{1}{2}}} \left(\frac{\theta}{S} + \frac{B\omega}{\omega^2+S^2} \right)$$

for ramp and ac chronopotentiometry respectively. Inverse transform of Eq. (12) is available in standard tables; that for Eqs. (13) and (20) are evaluated by convolution.

Nomenclature

A	= area of the electrode
B	= amplitude of ac. of frequency w
$C_i(x,t)$	= concentration of the species i at a distance x from the electrode surface at a time t after the start of electrolysis
C_i^0	= initial concentration of i species
D_O, D_R	= diffusion coefficient of O and R respectively
erf	= the error function defined as $\text{erf}(\lambda) = 2/\pi \int_0^\lambda \exp(-Z^2)dZ$
θ	= magnitude of impulse current
t	= time of electrolysis
k_f, k_b	= the formal rate constants for the forward and backward processes respectively

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Ion Adsorption Properties of Molybdenum Ferrocyanide, Tungsten Ferrocyanide & Multiloaded Molybdenum Ferrocyanide-Dowex Exchangers

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Adsorption of alkali, alkaline earth metal ions and some di-, ter and tetravalent cations on ferrocyanide molybdate (FeMo), ferrocyanide tungstate (FeW) and Dowex-1 loaded with FeMo has been studied. Adsorption decreases with increase in the hydrated radii of the alkali ions. FeMo loaded on Dowex-1 has lower adsorption capacity as compared to unsupported FeMo.

SINCE the revival of interest in the field of inorganic ion exchangers[1], considerable work has appeared in the literature[2] on the ion exchange properties of inorganic ferrocyanide compounds. In a search for an inorganic ion exchanger for the removal of Cs and Sr, Baetsle and coworkers synthesized molybdenum ferrocyanide or ferrocyanide molybdate[3] (FeMo) and the more acid-resistant ferrocyanide tungstate[4,5] (FeW). Krtil prepared tungsten ferrocyanide and studied its ion exchange properties[6]. Watari and coworkers have done considerable amount of work on inorganic ion exchangers loaded on organic resins (multi-loaded metal salt ion exchangers) and have studied the behaviour of copper, iron, nickel ferrocyanides[7,8]. In the present investigation ion adsorption properties of FeMo and FeW and resins loaded with FeMo were studied.

Ferrocyanide molybdate (FeMo) — Ferrocyanic acid was prepared by passing a known concentration of potassium ferrocyanide through Dowex-50 in the H+-form. To this solution requisite amount of sodium molybdate was added to get a Mo/Fe ratio of 2, 3 and 4, and the pH of the mixture adjusted to 3 and was allowed to stand for 6 hr. The FeMo gel was washed with $0.1M$ HCl, decanted and later filtered and dried at 50°. It was then treated with $1M$ HCl, filtered and dried.

Ferrocyanide tungstate (FeW) — It was prepared by adding requisite amount of sodium tungstate to ferrocyanic acid so as to get a W/Fe ratio of 3. The final pH was adjusted to 1 and the whole mixture allowed to stand for 24 hr. The gel was washed with $1M$ HCl, filtered and dried at 70°

Multiloaded exchanger: FeMo-Dowex 1 — Dowex 1 (50-100 mesh) was equilibrated with potassium ferrocyanide and was washed with water. It was then equilibrated with necessary amount of sodium molybdate (to give Mo/Fe ratio = 3) and washed with water. This cycle of loading with FeMo was repeated five times. It was later washed and dried.

Characterization of FeMo and FeW by Mössbauer spectroscopy — Matas and Zemick[9] had studied a series of ferro- and ferricyanides. In the case of ferrocyanides, chemical shift was found to decrease