Basic potential step methods (Ch. 5)

Overview of step experiments
Potential step under diffusion control
Diffusion-controlled currents at ultramicroelectrodes
Sampled-current voltammetry for reversible electrode reactions

Sampled-current voltammetry for quasireversible & irreversible electrode reactions

Multicomponent systems & multistep charge transfers
Chronoamperometric reversal techniques
Chronocoulometry
Special applications of ultramicroelectrodes

Step-functional changes in WE potential & mass transport only by diffusion

Overview of step experiments
Types of techniques
Potentiostat: control of potential

Basic potential step experiment: O + e → R   (unstirred solution, E_2: mass-
transfer (diffusion)-limited value (rapid kinetics → no O on surface))
chronoamperometry (i vs. t)

-Series of step experiments (between each step: stirring for same initial condition)
4, 5: mass-transfer (diffusion)-limited (no O on electrode surface))

sampled-current voltammetry ($i(\tau)$ vs. E)

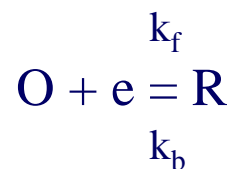Potential step: $E_1 \rightarrow E_2 \rightarrow E_1$ (reversal technique)

double potential step chronoamperometry

Current-potential characteristics

Controlled potential experiment for the electrode reaction

$$O + e \overset{k_f}{\underset{k_b}{=}} R$$

Current-potential characteristic

$$i = FAk^0[C_O(0,t)e^{-\alpha f(E - E0´)} - C_R(0,t)e^{(1 - \alpha)f(E - E0´)}$$

Fick's law $\rightarrow$ time-dependent surface conc $C_O(0, t)$ & $C_R(0, t)$

(a) Large-amplitude potential step (to mass-transfer controlled region)
$C_O(0, t) \sim 0$, current is totally controlled by mass transfer & electrode kinetics no
    longer influence the current $\rightarrow$ I is independent of E

(b) small-amplitude potential changes
For small η, $i = -i_0 f\eta$ (Eq. 3.4.2 in p.102)

(c) Reversible (Nernstian) electrode process
For very rapid electrode kinetics, i-E relation $\rightarrow$ Nernst form
        $E = E^{0'} + (RT/nF)\ln[C_O(0, t)/C_R(0, t)]$ (Eq. 3.4.28 in p. 106)
No kinetic parameter (k^0 & α) involved

(d) Totally irreversible e-transfer
If electrode kinetics are very sluggish (very small k^0), anodic & cathodic terms
    are never simultaneously significant $\rightarrow$ Tafel region   (Sec. 3.4.3)

(e) Quasireversible systems

Potential step under diffusion control
A planar electrode
For diffusion-limited, concentration profile, $C_O(x, t)$

$$\partial C_O(x, t)/\partial t = D_O(\partial^2 C_O(x, t)/\partial x^2)$$

$\rightarrow$ boundary conditions: $C_O(x, 0) = C_O{}^*$
$$\lim_{x \to \infty} C_O(x, t) = C_O{}^*$$

$$C_O(0, t) = 0 \quad (\text{for } t > 0)$$

$-J_O(0, t) = i(t)/nFA = D_O[\partial C_O(x, t)/\partial x]_{x = 0}$

Laplace transformation
$\rightarrow$ i vs. t

$$i(t) = i_d(t) = (nFAD_O{}^{1/2}C_O{}^*)/(\pi^{1/2} t^{1/2}) \qquad \text{Cottrell equation}$$

$i_d(t)$: diffusion-limited current

Instrumental & experimental limitations of i-t behavior under Cottrell conditions
(a) Potentiostat limitations: very high current at short times
(b) Recording device limitations
(c) Limitations by R_u & C_d: overlap with nonfaradaic current (time constant
    R_uC_d) Fig.1.2.7 (p. 16). t > 5R_uC_d
(d) Limitations due to convection: convective effect > 300 s or 20 s

<u>Concentration profile</u>

$$C_O(x, t) = C_O*erf[x/2(D_Ot)^{1/2}]$$ (erf(x): page 779)

Diffusion layer thickness: $(D_Ot)^{1/2}$
(다양하게 정의됨)

e.g., $D_O = 1 \times 10^{-5}$ cm^2/s
→ $(D_Ot)^{1/2} = 30$ μm for 1 s

Semi-infinite spherical diffusion

e.g., hanging mercury drop

$$\partial C_O(r, t)/\partial t = D_O[(\partial^2 C_O(r, t)/\partial r^2) + (r/2)(\partial C_O(r, t)/\partial r)]$$

r: radial distance from electrode center

→ boundary conditions: $C_O(r, 0) = C_O^*$ $(r > r_0)$

$$\lim_{r \to \infty} C_O(r, t) = C_O^*$$

$$C_O(r_0, t) = 0 \quad (\text{for } t > 0)$$

r_0: radius of the electrode

→ i vs. t

$$i_d(t) = (nFAD_O C_O^*)\{[1/(\pi D_O t)^{1/2}] + (1/r_0)\}$$

$$i_d(\text{spherical}) = i_d(\text{linear}) + (nFAD_O C_O^*)/r_0$$

For a planar electrode $\lim_{t \to \infty} i_d = 0$

For a spherical case $\lim_{t \to \infty} i_d = (nFAD_O C_O^*)/r_0$

Concentration profile

$$C_O(r, t) = C_O * \{ 1 - (r_0/r) \text{erfc}[(r - r_0)/2(D_O t)^{1/2}] \}$$

- Diffusion layer grows much larger than r_0 (e.g., UME): $(r - r_0) << 2(D_O t)^{1/2}$

$$C_O(r, t) = C_O * [1 - (r_0/r)]$$

$\rightarrow$ conc profile: independent of time

- Linear diffusion approximation

Within a% error: 2nd term/1st term $\leq$ a/100

$$i_d(t) = (nFAD_O C_O *) \{ [1/(\pi D_O t)^{1/2}] + (1/r_0) \}$$

Microscopic & geometric areas
   (A_m)   **(A_g)**

Roughness factor $\rho = A_m/A_g$

Typically 2~3
Smooth single crystal < 1.5

In chronoamperometry

long time (1 ms to 10 s)
diff. layer: 10 ~ 100 μm
Geometric area for Cottrell eqn

short time (~100 ns)
diff. layer: 10 nm
microscopic area

Electrode
with active/inactive areas

Time

Area for Cottrell eqn

Diffusion-controlled currents at ultramicroelectrodes

UME: < 25 µm ~ 10 nm (nanodes)

Types of UME: disk, spherical, hemispherical, band, cylindrical

Responses to a <u>large-amplitude</u> potential step

(a) <u>Spherical or hemispherical UME</u>

For spherical

i vs. t

$$i = [(nFAD_O^{1/2}C_O*)/(\pi^{1/2}t^{1/2})] + [nFAD_OC_O*/r_0]$$

Short time: 1st term dominates (= Cottrell eqn) (diff. layer is thin vs. r_0)

Long time: 2nd term dominates $\rightarrow$ steady-state current (i_{ss})

$$i_{ss} = nFAD_OC_O*/r_0 = 4\pi nFD_OC_O*r_0$$

Hemispherical UME: half of the current of sphere UME

(b) <u>Disk UME</u> (practically most important!)

Diffusion equation

cf. General formulation of Fick's 2nd law (Ch. 4)

$$\partial C_O / \partial t = D_O \nabla^2 C_O$$

r: radial distance from electrode center
z: linear normal to the plane

$\rightarrow$ boundary conditions:

$C_O(r, z, 0) = C_O*$

$\lim_{r\to\infty} C_O(r, z, t) = C_o*$

$\lim_{z\to\infty} C_O(r, z, t) = C_o*$

$\partial C_O(r, z, t)/\partial z \big|_{z=0} = 0 \quad (r > r_0)$
$C_O(r, 0, t) = 0 \ (r \leq r_0, t > 0)$

$i = 4nFAD_OC_O*f(\tau)/\pi r_0$

$\tau = 4D_Ot/r_O^{1/2}$
$f(\tau) = 0.88623\tau^{-1/2} + 0.78540 + 0.094\tau^{1/2} \quad$ when $\tau < 1$ (at short times)
$f(\tau) = 1 + 0.71835\tau^{-1/2} + 0.05626\tau^{-3/2} \dots$ when $\tau > 1$ (at long times)

Short time

Diff. layer: thin vs. r_0

→ Cottrell current

Triangle: Cottrell current

Filled square: τ → 0

Intermediate time

Long time

dashed line: $i/i_{ss} = 1$

(steady-state)

$i_{ss} = 4nFAD_OC_O*/(\pi r_0)$

$\quad = 4nFD_OC_O*r_0$

(c) <u>Cylindrical UME</u>
(d) <u>Band UME</u>

Summary of behavior at UME
- At short time: any UME $\rightarrow$ Cottrell equation!
- At long time: UME approaches a steady state

$$i_{ss} = nFAm_O C_O*$$

m_O: mass-transfer coefficient

Sampled-current voltammetry for reversible electrode reactions

Voltammetry based on linear diffusion at a planar electrode

(a) A step to an arbitrary potential

O + ne = R & assume rapid charge-transfer kinetics

$$E = E^{0'} + (RT/nF)\ln[C_O(0, t)/C_R(0, t)]$$

$\rightarrow$ $$\Theta = C_O(0, t)/C_R(0, t) = \exp[nF (E - E^{0'})/RT]$$

$$\color{red} i(t) = [nFAD_O^{1/2}C_O^*]/[\pi^{1/2}t^{1/2}(1 + \zeta\Theta)]$$

$\zeta = (D_O/D_R)^{1/2}$

Cottrell equation is a special case for the diffusion-limited region (very negative
    $E - E^{0'}$: $\Theta \rightarrow 0$) : Cottrell current as $i_d(t)$

$$\color{red} i(t) = i_d(t)/(1 + \zeta\Theta)$$

For very positive E ; $\Theta \rightarrow \infty$; $i(t) \rightarrow 0$ $i(t)$: 0 to $i_d(t)$ (Fig. 5.1.3 in p. 158)

(b) <u>Shape of i-E curve</u>

For a fixed sampling time τ

$$i(\tau) = i_d(\tau)/(1 + \zeta\Theta)$$

$\rightarrow$ $\zeta\Theta = [i_d(\tau) - i(\tau)]/i(\tau)$

$\rightarrow$ $E = E^{0'} + (RT/nF)\ln[D_R^{1/2}/D_O^{1/2}] + (RT/nF)\ln\{[i_d(\tau) - i(\tau)]/i(\tau)\}$

When $i(\tau) = i_d(\tau)/2$, 3rd term $\rightarrow$ 0

Half-wave potential, $E_{1/2} = E^{0'} + (RT/nF)\ln[D_R^{1/2}/D_O^{1/2}]$

$$E = E_{1/2} + (RT/nF)\ln\{[i_d(\tau) - i(\tau)]/i(\tau)\}$$

For reversibility

E vs. $\log\{[i_d(\tau) - i(\tau)]/i(\tau)\}$ $\rightarrow$

Linear with a slope of

2.303RT/nF or 59.1/n mV

$$D_R \neq D_O \rightarrow E_{1/2} \neq E^{0'}$$

(c) <u>Concentration profile</u>

$$C_O(0, t) = C_O*\{1 - [i(t)/ i_d(t)]\}$$
$$C_R(0, t) = \zeta C_O*[i(t)/i_d(t)]$$

Steady-state voltammetry at a UME

<u>A step to an arbitrary potential at a spherical electrode</u>

$$O + ne = R \text{ \& reversible}$$

$$\Theta = C_O(r_0, t)/C_R(r_0, t) = \exp[nF(E - E^{0'})/RT]$$

Steady-state regime

$$i = nFAD_O C_O*/(1 + \zeta^2\Theta)r_0$$

Steady-state limiting current is the special case for the diffusion limited region ($\Theta \rightarrow 0$)

$$i = i_d/(1 + \zeta^2\Theta)$$

<u>Shape of the wave</u>

Reversible steady-state voltammogram

$$E = E^{0'} + (RT/nF)\ln[D_R/D_O] + (RT/nF)\ln[(i_d - i)/i]$$

Half-wave potential, $\quad E_{1/2} = E^{0'} + (RT/nF)\ln[D_R/D_O]$

Concentration profile

$$C_O(r_0, t) = C_O*[1 - (i/i_d)]$$
$$C_R(r_0, t) = \zeta^2 C_O*(i/i_d)$$

Sampled-current voltammetry for quasi- & irreversible electrode rxns
Responses based on linear diffusion at a planar electrode
(a) Current-time behavior
O + ne = R & governed by both mass transfer & charge-transfer kinetics
For the quasireversible one-step, one-electron case

$$i/FA = D_O(\partial C_O(x, t)/\partial x)_{x=0} = k_f C_O(0, t) - k_b C_R(0, t)$$

where $k_f = k^0 e^{-\alpha f(E - E0')}$ & $k_b = k^0 e^{(1 - \alpha)f(E - E0')}$, $f = F/RT$

$\rightarrow$ $\qquad$ $i(t) = FAk_f C_O^* \exp(H^2 t) erfc(Ht^{1/2})$

where $H = (k_f/D_O^{1/2}) + (k_b/D_R^{1/2})$

Using erf(x) & erfc(x) = 1- erf(x) in page 779
$\exp(H^2 t) erfc(Ht^{1/2})$: 1 for $Ht^{1/2} = 0$, but approaches 0 as $Ht^{1/2} \uparrow$

Current-time curve (with R initially absent)
- Kinetics limit the current at t = 0 to a finite value proportional to k_f

(d) <u>Sampled-current voltammetry</u>

    - Very facile kinetics, large $k^0 \rightarrow$
        reversible shape, $E_{1/2} \sim E^{0'}$ ' ' '
    - Smaller $k^0 \rightarrow$ kinetics driven:
        displaced potentials, broadened
        wave

Multicomponent systems & multistep charge transfers

For O + ne $\rightarrow$ R & O´ + n´e $\rightarrow$ R´

For chronoamperometry or sampled-current voltammetry based on linear diff

$$(i_d)_{total} = (FA/\pi^{1/2}t^{1/2})(nD_O^{1/2}C_O^* + n'D_{O'}^{1/2}C_{O'}^*)$$

For sampled-current voltammetry based on steady-state at UME

$$(i_d)_{total} = FA(nm_O C_O^* + n'm_{O'}C_{O'}^*)$$

$$(i_d)_{total} = i_d + i_{d'}$$

Chronoamperometric reversal techniques

$E(t) = E_f + S_\tau(t)(E_r - E_f)$ $(t > 0)$ $S_\tau(t)$ is 0 for $t \leq \tau$, and 1 for $t > \tau$

Initial: $C_O(x, 0) = C_O{}^*$, $C_R(x, 0) = 0$

Forward step: $C_O(0, t) = C_O{}'$, $C_R(0, t) = C_R{}'$

   $C_O{}' = \theta' C_R{}'$ (O/R couple: nernstian)

Where $\theta' = \exp[nf(E_f - E^{0'})]$

Reversal step: $C_O(0, t) = C_O{}''$, $C_R(0, t) = C_R{}''$

   $C_O{}'' = \theta'' C_R{}''$

Where $\theta'' = \exp[nf(E_r - E^{0'})]$

$$\lim_{x \to \infty} C_O(x, t) = C_O*$$

$$\lim_{x \to \infty} C_R(x, t) = 0$$

$$J_O(0, t) = -J_R(0, t)$$

Current-time response

For $0 \leq t \leq \tau$

$$i_f(t) = [nFAD_O^{1/2}C_O*]/[\pi^{1/2}t^{1/2}(1+ \zeta\theta')]$$

Stepping in forward phase to diffusion plateau ($\theta' \sim 0$, $C_O' \sim 0$), then reversing to the diffusion plateau for reoxidation ($\theta'' \to \infty$, $C_R'' \sim 0$)

$$-i_r(t) = (nFAD_O^{1/2}C_O*/\pi^{1/2})[1/(t - \tau)^{1/2} - 1/t^{1/2}] \quad \text{Kambara eqn}$$

*could be derived under $C_O'' = 0$ & $C_R'' = 0$ (also for irreversible system)

$\to$ $\qquad\qquad -i_r/i_f = [t_f/(t_r - \tau)]^{1/2} - (t_f/t_r)^{1/2}$

For $t_r - \tau = t_f$ $\qquad\qquad -i_r/i_f = 1 - (1- \tau/t_r)^{1/2}$

$-i_r(2\tau)/i_f(\tau) = 0.293 \to$ reference to indicate complicated rxn or not

Chronocoulometry

To integrate current $\rightarrow$ charge passed as a ftn of t (Q(t))

Advantages: better signal-to-noise, distinguish contributions of double layer
    charge & adsorbed species

Large-amplitude potential step

Cottrell condition (quiescent, planar, diffusion-limited)

$$Q_d = \int i_d dt = 2nFAD_O^{1/2}C_O^* t^{1/2}/\pi^{1/2}$$

From double-layer charging & from adsorbed species,

$$Q = Q_d + Q_{dl} + nFA\Gamma_O$$

Γ_O: Surface excess of adsorbed species O (mol/cm^2)

Plot of Q vs. t$^{1/2}$ for O + supporting electrolyte & supporting electrolyte itself $\rightarrow$
    distinguish roughly Q_{dl} and $nFA\,\Gamma_O$

Reversal experiments under diffusion control

For $t > \tau$

$$-i_r(t) = (-nFAD_O^{1/2}C_O^*/\pi^{1/2})[1/(t - \tau)^{1/2} - 1/t^{1/2}] \quad \text{Kambara eqn}$$

Cumulative charge after τ

$$Q_d(t > \tau) = 2nFAD_O^{1/2}C_O^*\tau^{1/2}/\pi^{1/2} + \int i_r dt$$

$$= (2nFAD_O^{1/2}C_O^*/\pi^{1/2}) [t^{1/2} - (t - \tau)^{1/2}]$$

Removed charge in reversal

$$Q_r(t > \tau) = Q(\tau) - Q(t > \tau) = Q_{dl} + (2nFAD_O^{1/2}C_O^*/\pi^{1/2})[\tau^{1/2} + (t - \tau)^{1/2} - t^{1/2}]$$

two plots: $Q(t < \tau)$ vs. $t^{1/2}$

$\quad Q(t > \tau)$ vs. Θ ($= [\tau^{1/2} + (t - \tau)^{1/2} - t^{1/2}]$) (Anson plot)

For O is adsorbed & R is not, the difference between two intercepts: $nFA\Gamma_O$

Generally $nFA(\Gamma_O - \Gamma_R)$

$$Q_d(t \leq \tau)/Q_d(\tau) = (t/\tau)^{1/2}$$
$$Q_d(t > \tau)/Q_d(\tau) = (t/\tau)^{1/2} - [(t/\tau) - 1]^{1/2}$$

Special applications of UME
Cell time constants and fast electrochemistry
Charging dl charge: $R_u C_d$ (cell time const) $\rightarrow$ potential step requires ~$5R_u C_d$
$\rightarrow$ electrode size controls the cell time const
In disk-shaped UME, $C_d = \pi r_0^2 C_d^0$ (C_d^0: 10 ~ 50 $\mu F/cm^2$)
e.g., 1 nm radius: $C_d = 0.3$ ~ 1.5 μF. 1 μm r_0: 0.3 ~ 1.5 pF (6 orders smaller!!)

R_u (uncompensated resistance) also depends on the electrode size: $R_u = 1/4\pi\kappa r_0$

$$C_d R_u = r_0 C_d^0/4\kappa$$

Smaller electrode $\rightarrow$ much short time domains
e.g., normal size electrode: ms domain,
UME ($r_0 = 5$ μm): 170 ns
$\rightarrow$ UME (0.5 μm): < 10 ns domain

Voltammetry in media of low conductivity

Displacement of voltammetry due to iR_u

e.g.,

normal size in high conductive medium (few ohms): few mV in less than ~ mA

nonaqueous or viscous media: 0.1 M TBABF$_4$ (R_u ~ kΩ), toluene (very high!)

At UME, current is extremely small: error in potential in voltammetry is small

$\rightarrow$ negligible iR_u: low conductive media & two-electrode cells!!

Applications based on spatial resolution

UME: physically small $\rightarrow$ probe small spaces

     Scanning electrochemical microscopy (SECM) Ch. 16

     Double-band microarray electrode