

Controlled-current techniques (Ch. 8)

General theory of controlled-current methods
E-t curves in constant current electrolysis

Introduction

Chronopotentiometric (E vs. t) technique or *galvanostatic* technique:
controlled current between WE and auxiliary electrode with a current source
(called Galvanostat) → E between WE and RE

Controlled-i vs. controlled-E

(+)

Controlled-i is simpler

Mathematics solving diffusion equations are much simpler

(-)

Double-layer charging effect is larger & is not easy to be corrected

Multicomponent systems & multistep rxns are more complicated

Classification

Constant-current chronopotentiometry

Programmed current chronopotentiometry

Current reversal chronopotentiometry

Cyclic chronopotentiometry

General theory of controlled-current methods

Mathematics of semi-infinite linear diffusion

O + ne = R (planar electrode, unstirred, only O initially present (C_O^*))

$$\frac{\partial C_O(x, t)}{\partial t} = D_O[\partial^2 C_O(x, t)/\partial x^2]$$

$$\frac{\partial C_R(x, t)}{\partial t} = D_R[\partial^2 C_R(x, t)/\partial x^2]$$

At $t = 0$ (for all x) & as $x \rightarrow \infty$ (for all t): $C_O(x, t) = C_O^*$ $C_R(x, t) = 0$

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

Constant-current electrolysis-the Sand equation

At the transition time, τ , $C_O(0, t)$ drops to zero

Sand equation

$$i\tau^{1/2}/C_O^* = (nFAD_O^{1/2}\pi^{1/2})/2 = 85.5nD_O^{1/2}A \text{ (mA}\cdot\text{s}^{1/2}/\text{mM) (with A in cm}^2\text{)}$$

↑

Transition time constant

For $0 \leq t \leq \tau$

$$C_O(0, t)/C_O^* = 1 - (t/\tau)^{1/2}$$

$$C_R(0, t) = (2it^{1/2})/(nFAD_R^{1/2}\pi^{1/2}) = \xi(t/\tau)^{1/2}C_O^*$$

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

For various t/τ

Potential-time curves in constant-current electrolysis

Reversible (Nernstian) waves

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

$$E = E_{\tau/4} + (RT/nF)\ln[(\tau^{1/2} - t^{1/2})/t^{1/2}]$$

Where $E_{\tau/4}$ (quarter-wave potential),

$$E_{\tau/4} = E^{0'} - (RT/2nF)\ln(D_O/D_R)$$

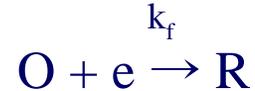
Reversibility: E-t curve

E vs. $\log[(\tau^{1/2} - t^{1/2})/t^{1/2}]$

→ slope $59/n$ mV

Totally irreversible waves

For a totally irreversible one-step, one electron reaction



$$E = E^{0'} + (RT/\alpha F) \ln[FA C_O^* k^0 / i] + (RT/\alpha F) \ln[1 - (t/\tau)^{1/2}]$$

Using Sand equation

$$E = E^{0'} + (RT/\alpha F) \ln[2k^0 / (\pi D_O)^{1/2}] + (RT/\alpha F) \ln[\tau^{1/2} - t^{1/2}]$$

Totally irreversible reduction wave: E-t wave \rightarrow shift toward more negative potentials with $i \uparrow$, with $\times 10 \uparrow$ in i causing $2.3RT/\alpha F$ shift (or $59/\alpha$ mV at 25°C)

Quasireversible waves