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^*))

$$\partial C_O(x, t)/\partial t = D_O[\partial^2 C_O(x, t)/\partial x^2]$$
$$\partial C_R(x, t)/\partial t = D_R[\partial^2 C_R(x, t)/\partial x^2]$$

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

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

Constant-current electrolysis-the Sand equation

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

Sand equation

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

↑

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

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

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

$\rightarrow$ slope 59/n mV

Totally irreversible waves

For a totally irreversible one-step, one electron reaction

$$O + e \xrightarrow{k_f} R$$

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

Using Sand equation

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

Totally irreversible reduction wave: E-t wave → shift toward more negative potentials with i↑, with x10↑ in i causing 2.3RT/αF shift (or 59/α mV at 25°C)

Quasireversible waves