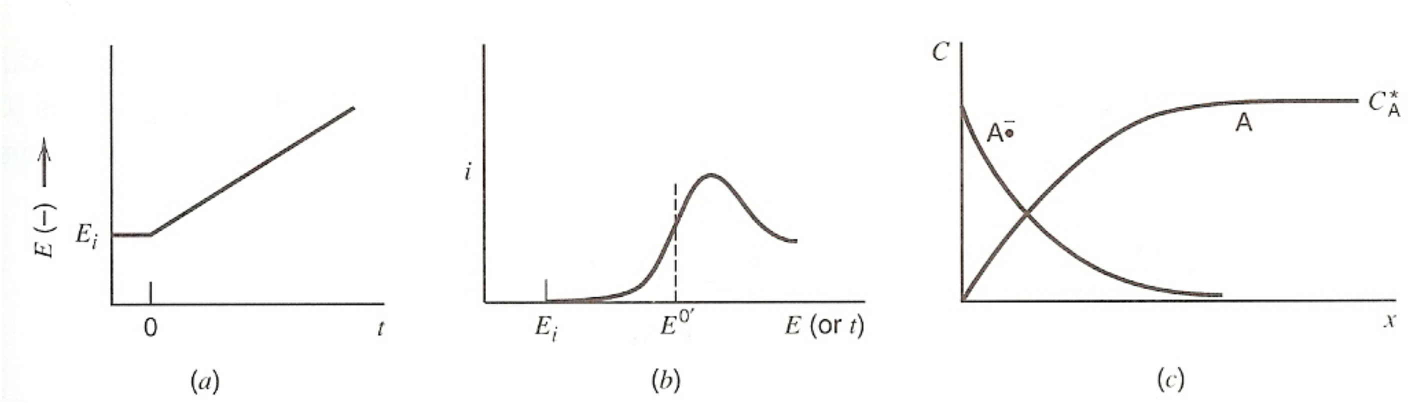
Potential Sweep Methods (Ch. 6)

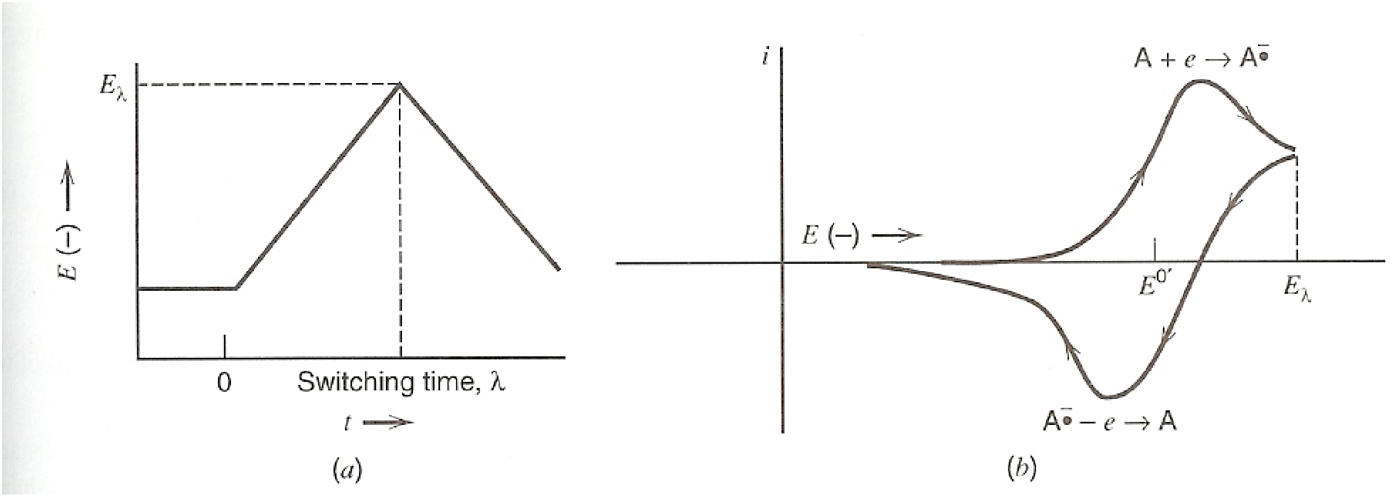
Nernstian (reversible) systems
Totally irreversible systems
Quasireversible systems
Cyclic voltammetry
Multicomponent systems & multistep charge transfers

Introduction

Linear sweep voltammetry (LSV)



Cyclic voltammetry (CV)



Nernstian (reversible) systems

Solution of the boundary value problem

O + ne = R (semi-infinite linear diffusion, initially O present)

$$E(t) = E_i - vt$$

Sweep rate (or scan rate): v (V/s)

Rapid e-transfer rate at the electrode surface

$$C_O(0, t)/C_R(0, t) = f(t) = \exp[nF\,(E_i - vt - E^{0\prime})/RT]$$

$$i = nFAC_O^*(\pi D_O \sigma)^{1/2}\chi(\sigma t)$$

$\sigma = (nF/RT)v$

TABLE 6.2.1 Current Functions for Reversible Charge Transfer (3)[a,b]

$\frac{n(E-E_{1/2})}{RT/F}$	$n(E-E_{1/2})$ mV at 25°C	$\pi^{1/2}\chi(\sigma t)$	$\phi(\sigma t)$	$\frac{n(E-E_{1/2})}{RT/F}$	$n(E-E_{1/2})$ mV at 25°C	$\pi^{1/2}\chi(\sigma t)$	$\phi(\sigma t)$
4.67	120	0.009	0.008	−0.19	−5	0.400	0.548
3.89	100	0.020	0.019	−0.39	−10	0.418	0.596
3.11	80	0.042	0.041	−0.58	−15	0.432	0.641
2.34	60	0.084	0.087	−0.78	−20	0.441	0.685
1.95	50	0.117	0.124	−0.97	−25	0.445	0.725
1.75	45	0.138	0.146	−1.109	−28.50	0.4463	0.7516
1.56	40	0.160	0.173	−1.17	−30	0.446	0.763
1.36	35	0.185	0.208	−1.36	−35	0.443	0.796
1.17	30	0.211	0.236	−1.56	−40	0.438	0.826
0.97	25	0.240	0.273	−1.95	−50	0.421	0.875
0.78	20	0.269	0.314	−2.34	−60	0.399	0.912
0.58	15	0.298	0.357	−3.11	−80	0.353	0.957
0.39	10	0.328	0.403	−3.89	−100	0.312	0.980
0.19	5	0.355	0.451	−4.67	−120	0.280	0.991
0.00	0	0.380	0.499	−5.84	−150	0.245	0.997

Peak current and potential

Peak current: $\pi^{1/2}\chi(\sigma t) = 0.4463$

$$i_p = 0.4463(F^3/RT)^{1/2} n^{3/2} A D_O^{1/2} C_O^{*} v^{1/2}$$

At 25°C, for A in cm^2, D_O in cm^2/s, C_O^* in mol/cm^3, v in V/s → i_p in amperes

$$i_p = (2.69 \times 10^5) n^{3/2} A D_O^{1/2} C_O^{*} v^{1/2}$$

Peak potential, E_p

$$E_p = E_{1/2} - 1.109(RT/nF) = E_{1/2} - 28.5/n \quad \text{mV at } 25^\circ\text{C}$$

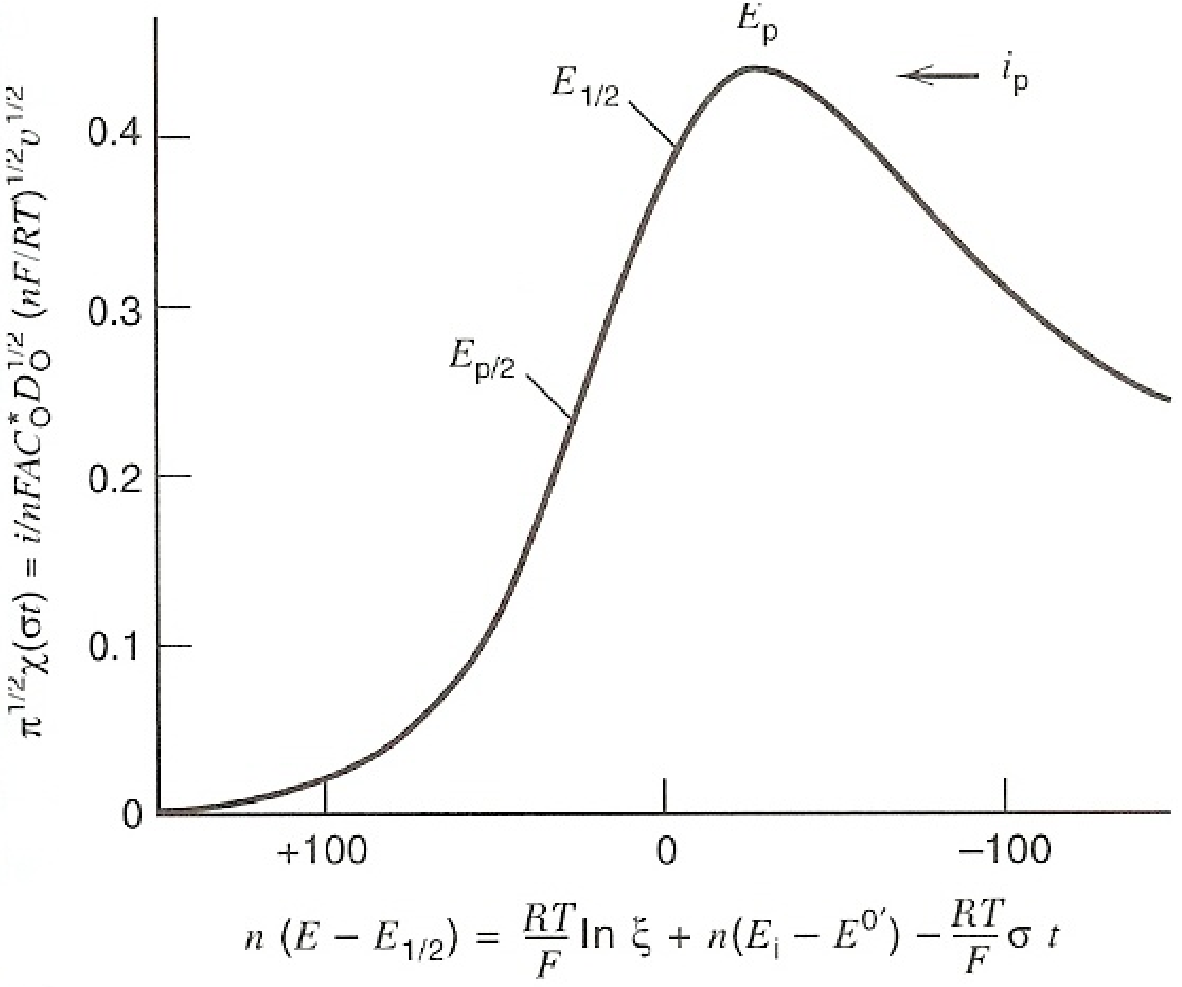
Half-peak potential, $E_{p/2}$

$$E_{p/2} = E_{1/2} + 1.09(RT/nF) = E_{1/2} + 28.0/n \quad \text{mV at } 25^\circ\text{C}$$

$E_{1/2}$ is located between E_p and $E_{p/2}$

$$|E_p - E_{p/2}| = 2.20(RT/nF) = 56.5/n \quad \text{mV at }^\circ\text{C}$$

For reversible wave, <u>E_p is independent of scan rate, i_p is proportional to $v^{1/2}$</u>



E_p
$E_{1/2}$
i_p
$E_{p/2}$
0.4
0.3
0.2
0.1
0
+100
0
−100
$\pi^{1/2}\chi(\sigma t) = i/nFAC_O^* D_O^{1/2} (nF/RT)^{1/2} v^{1/2}$
$n\,(E - E_{1/2}) = \frac{RT}{F} \ln \xi + n(E_i - E^{0'}) - \frac{RT}{F} \sigma\, t$

Spherical electrodes and UMEs

Spherical electrode (e.g., a hanging mercury drop)

$$i = i(\text{plane}) + nFAD_OC_O{}^*\phi(\sigma t)/r_0$$

$\phi(\sigma t)$: tabulated function (Table 6.2.1)

For large v in conventional-sized electrode → i(plane) >> 2^{nd} term

Same for hemispherical & UME at fast scan rate

For UME at very small v: r_0 is small → i(plane) << 2^{nd} term

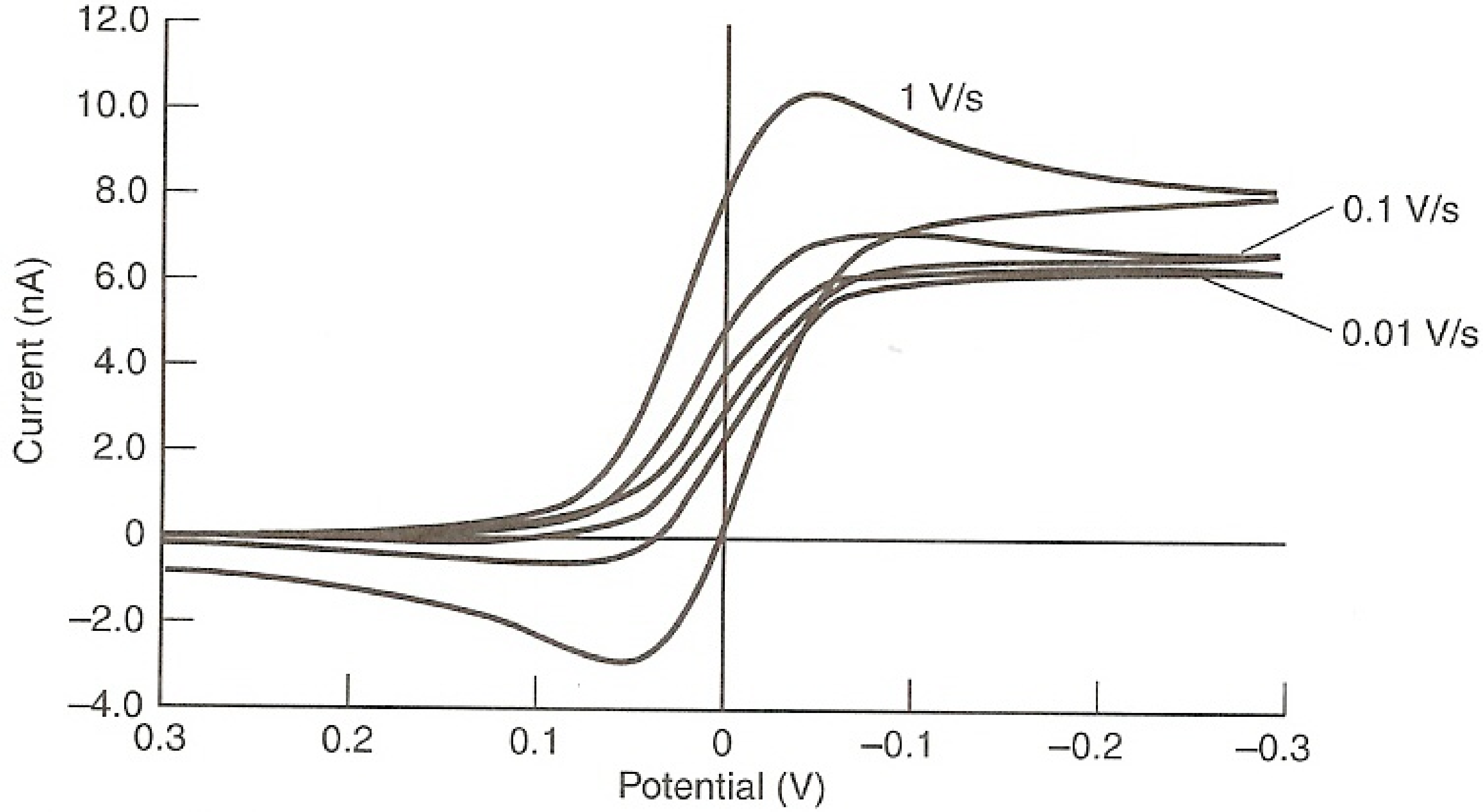
→ voltammogram is a steady-state response independent of v

→ $v \ll RTD/nFr_0^2$

$r_0 = 5\ \mu m$, $D = 10^{-5}\ cm^2/s$, T = 298 K → steady-state voltammogram at v < 1 V/s

$r_0 = 0.5\ \mu m$ → steady-state behavior up to 10 V/s

Transition from typical peak-shaped voltammograms at fast v to steady-state voltammograms at small v



12.0
10.0
8.0
6.0
4.0
2.0
0
−2.0
−4.0
Current (nA)
0.3
0.2
0.1
0
−0.1
−0.2
−0.3
Potential (V)
1 V/s
0.1 V/s
0.01 V/s

cf. For potential sweep (Ch.1)

Linear potential sweep with a sweep rate v (in V/s)

$$E = vt$$

$E = E_R + E_C = iR_s + q/C_d$

$$vt = R_s(dq/dt) + q/C_d$$

If q = 0 at t = 0, $i = vC_d[1 - \exp(-t/R_sC_d)]$

- Current rises from 0 and attains a steady-state value (vC_d): <u>measure C_d</u>

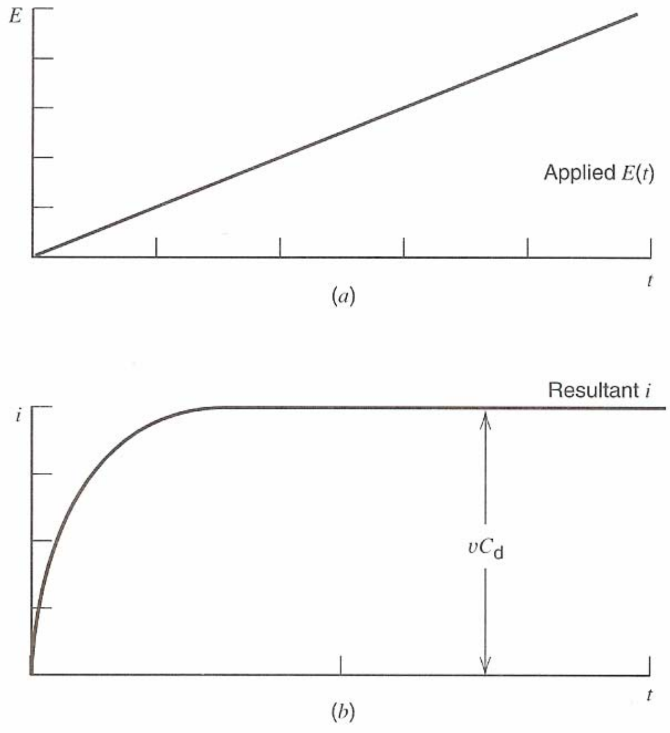


Figure 1.2.10 Current-time behavior resulting from a linear potential sweep applied to an *RC* circuit.

Effect of double-layer capacitance & uncompensated resistance

Charging current at potential sweep

$$|i_c| = AC_dv$$

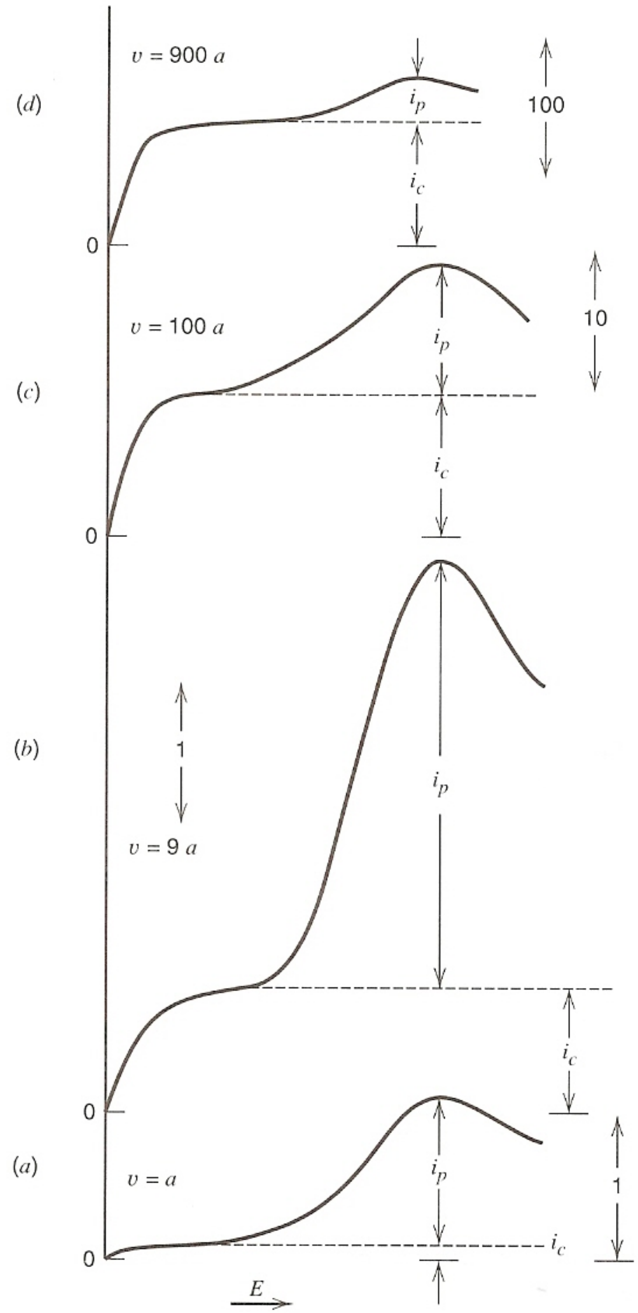
Faradaic current measured with baseline of i_c

i_p varies with $v^{1/2}$, i_c varies with $v \rightarrow$ <u>i_c more important at faster v</u>

$$|i_c|/i_p = [C_d v^{1/2}(10^{-5})]/[2.69n^{3/2}D_O^{1/2}C_O^*]$$

At high v & low $C_O^* \rightarrow$ severe distortion of the LSV wave

R_u cause E_p to be a function of v



(d)
v = 900 a
100
(c)
v = 100 a
10
(b)
1
v = 9 a
(a)
v = a
1
E

Totally irreversible systems

Solution of the boundary value problem

Totally irreversible one-step, one-electron reaction: $O + e \xrightarrow{k_f} R$

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

Where $k_f = k^0 e^{-\alpha f(E(t) - E0')}$, $E(t) = E_i - vt$

$\rightarrow$

$$k_f(t)C_O(0, t) = k_{fi}C_O(0, t)e^{bt}$$

Where $b = \alpha fv$ & $k_{fi} = k^0\exp[-\alpha f(E_i - E^{0'})]$

$$i = FAC_O^*D_O^{1/2}v^{1/2}(\alpha F/RT)^{1/2}\chi(bt)$$

$\chi(bt)$ (Table 6.3.1). i varies with $v^{1/2}$ and C_O^*

For spherical electrodes

$$i = i(\text{plane}) + FAD_OC_O^*\phi(bt)/r_0$$

TABLE 6.3.1 Current Functions for Irreversible Charge Transfer (3)[a]

Dimensionless Potential[b]	Potential[c] mV at 25°C	$\pi^{1/2}\chi(bt)$	$\phi(bt)$	Dimensionless Potential[b]	Potential[c] mV at 25°C	$\pi^{1/2}\chi(bt)$	$\phi(bt)$
6.23	160	0.003		0.58	15	0.437	0.323
5.45	140	0.008		0.39	10	0.462	0.396
4.67	120	0.016		0.19	5	0.480	0.482
4.28	110	0.024		0.00	0	0.492	0.600
3.89	100	0.035		−0.19	−5	0.496	0.685
3.50	90	0.050		−0.21	−5.34	0.4958	0.694
3.11	80	0.073	0.004	−0.39	−10	0.493	0.755
2.72	70	0.104	0.010	−0.58	−15	0.485	0.823
2.34	60	0.145	0.021	−0.78	−20	0.472	0.895
1.95	50	0.199	0.042	−0.97	−25	0.457	0.952
1.56	40	0.264	0.083	−1.17	−30	0.441	0.992
1.36	35	0.300	0.115	−1.36	−35	0.423	1.000
1.17	30	0.337	0.154	−1.56	−40	0.406	
0.97	25	0.372	0.199	−1.95	−50	0.374	
0.78	20	0.406	0.253	−2.72	−70	0.323	

Peak current and potential

Maximum $\chi(bt)$ at $\pi^{1/2}\chi(bt) = 0.4958$

Peak current

$$i_p = (2.99 \times 10^5)\alpha^{1/2} A C_O^* D_O^{1/2} v^{1/2}$$

n-electron process with RDS: n in right side

Peak potential

$$\alpha(E_p - E^{0\prime}) + (RT/F)\ln[(\pi D_O b)^{1/2}/k^0] = -0.21(RT/F) = -5.34 \text{ mV at } 25^\circ\text{C}$$

Or

$$E_p = E^{0\prime} - (RT/\alpha F)[0.780 + \ln(D_O^{1/2}/k^0) + \ln(\alpha F v/RT)^{1/2}]$$

$$|E_p - E_{p/2}| = 1.857RT/\alpha F = 47.7/\alpha \text{ mV at } 25^\circ\text{C}$$

E_p: ftn of v $\rightarrow$ for reduction, $1.15RT/\alpha F$ (or $30/\alpha$ mV at 25°C) negative shift for tenfold increase in v

$$i_p = 0.227FAC_O^* k^0 \exp[-\alpha f(E_P - E^{0\prime})]$$

$\rightarrow$ i_p vs. $E_p - E^{0\prime}$ plot at different v: slope of $-\alpha f$ and intercept proportional to k^0

n-electron process with RDS: n in right side

Quasireversible systems

For one-step, one-electron system

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

For the quasireversible one-step, one-electron case (5.5.3, p. 191)

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

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

The shape of peak & peak parameters → ftns of α & Λ

$$\Lambda = k^0/(D_O^{1-\alpha} D_R^{\alpha} f v)^{1/2}$$

Or for $D_O = D_R = D$

$$\Lambda = k^0/(Dfv)^{1/2}$$

Current $$i = FAD_O^{1/2} C_O^* f^{1/2} v^{1/2} \Psi(E)$$

Ψ(E) (Fig. 6.4.1): <u>Λ > 10 → approach to the reversible</u>

$\Psi(E)$

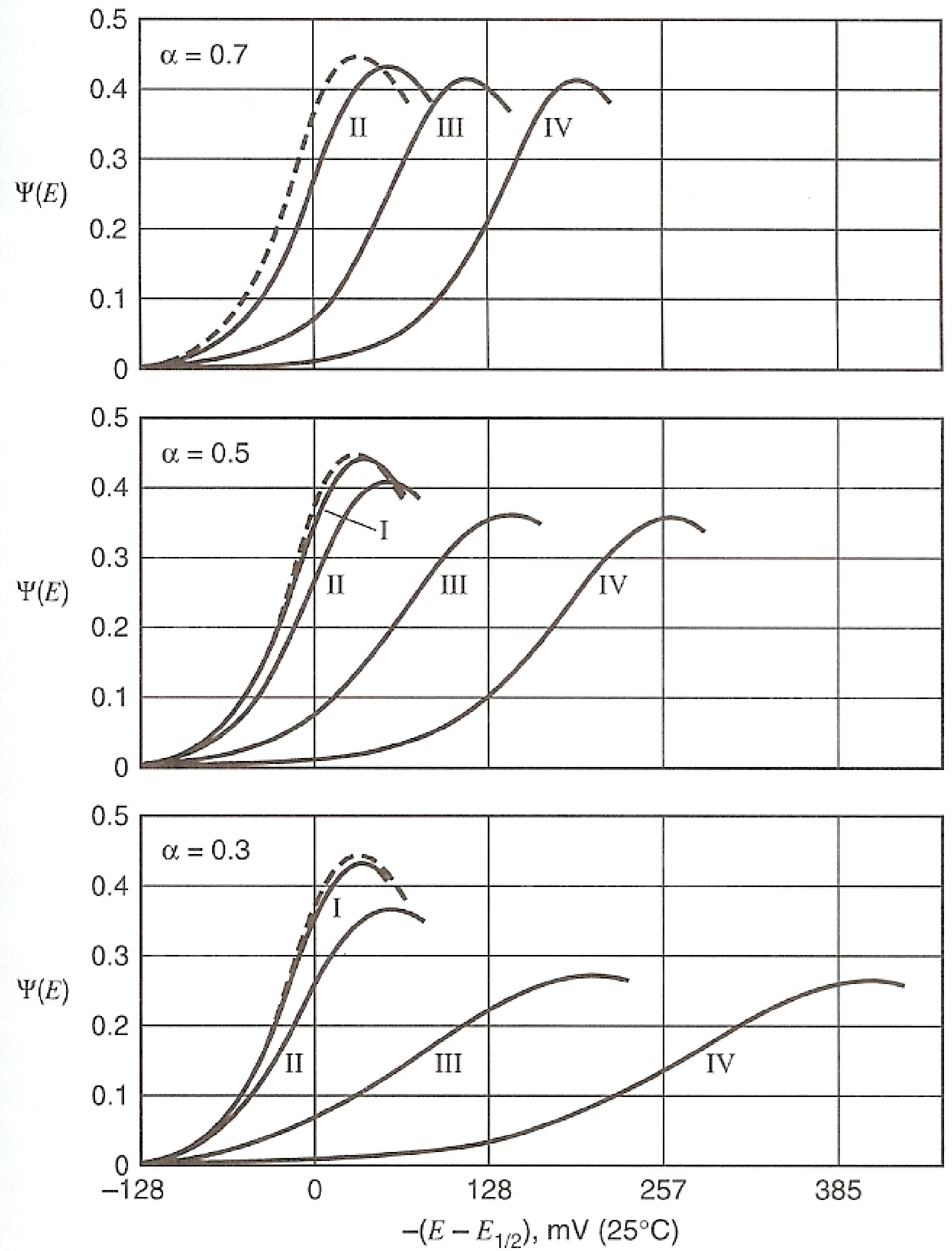
I. $\Lambda = 10$

II. $\Lambda = 1$

III. $\Lambda = 0.1$

IV. $\Lambda = 0.01$

Dashed line: reversible



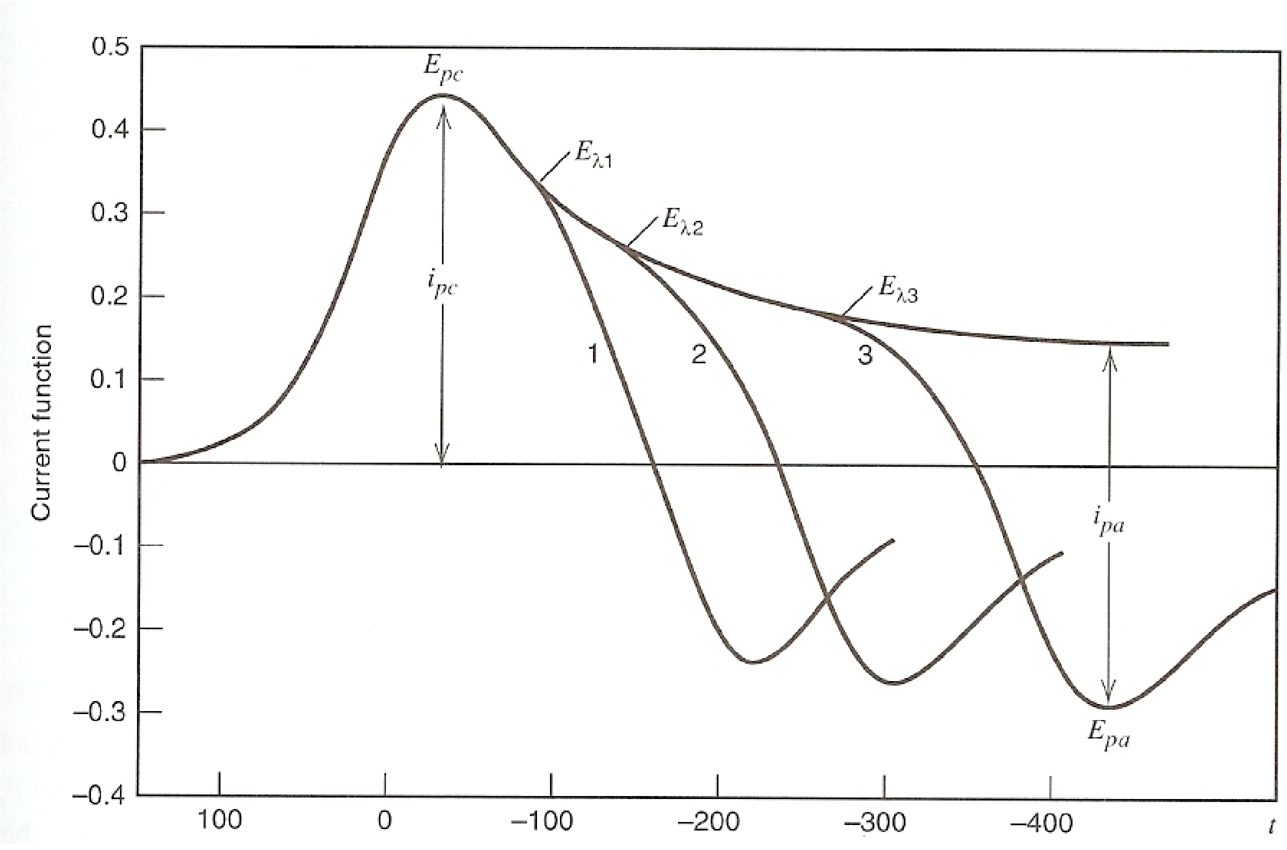
Cyclic voltammetry

$(0 < t \leq \lambda)$ $E = E_i - vt$

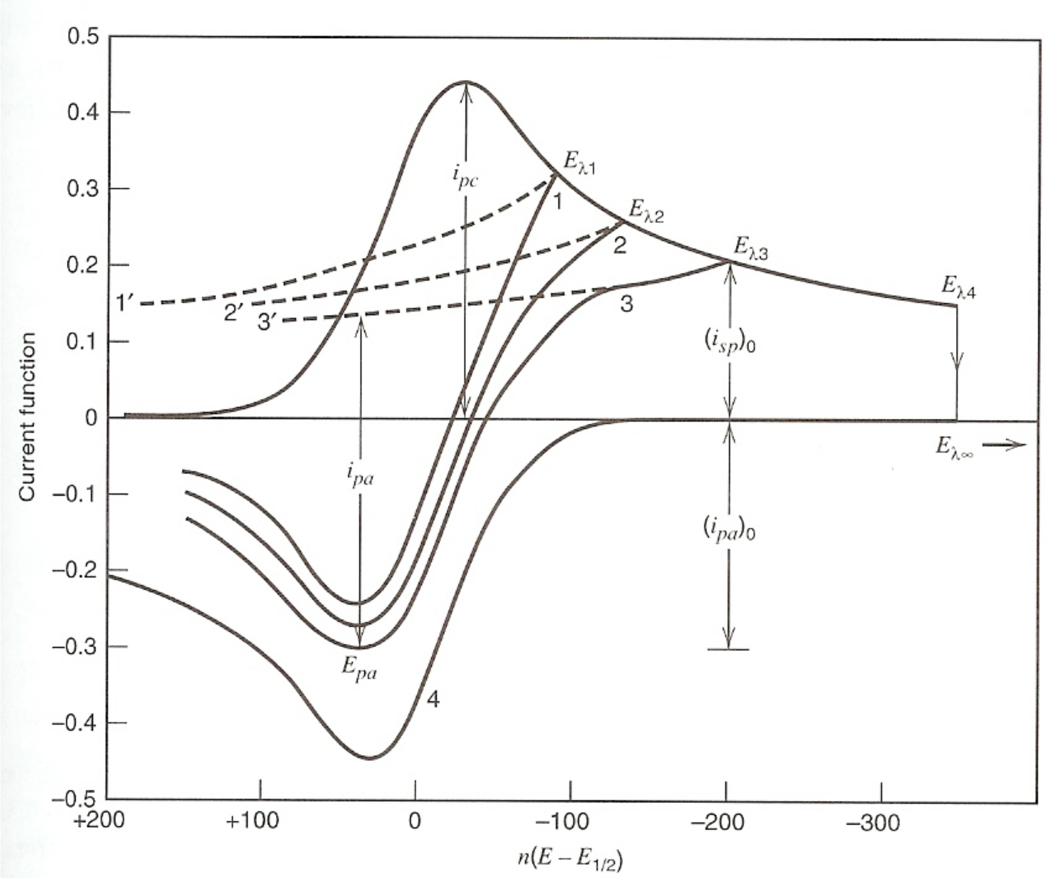
$(t > \lambda)$ $E = E_i - 2v\lambda + vt$

Nernstian systems

i-t curve at different E_λ



i-E curve (CV) at different E_λ



(1) E_λ (1) $E_{1/2}$ – 90/n, (2) $E_{1/2}$ – 130/n, (3) $E_{1/2}$ – 200/n mV, (4) after $i_{pc} \rightarrow 0$

i_{pa}/i_{pc} = 1 for nernstian regardless of scan rate, E_λ (> 35/n mV past E_{pc}), D

$i_{pa}/i_{pc} \rightarrow$ kinetic information
If actual baseline cannot be determined,

$$i_{pa}/i_{pc} = (i_{pa})_0/i_{pc} + 0.485(i_{sp})_0/i_{pc} + 0.086$$

Reversal charging current is same as forward scan, but opposite sign

$\Delta E_p = E_{pa} - E_{pc} \sim 2.3RT/nF$ (or 59/n mV at 25°C)

Table 6.5.1 Variation of ΔE_p with E_λ for a Nernstian System at 25°C (3)

$n(E_{pc} - E_\lambda)$ (mV)	$n(E_{pa} - E_{pc})$ (mV)
71.5	60.5
121.5	59.2
171.5	58.3
271.5	57.8
∞	57.0

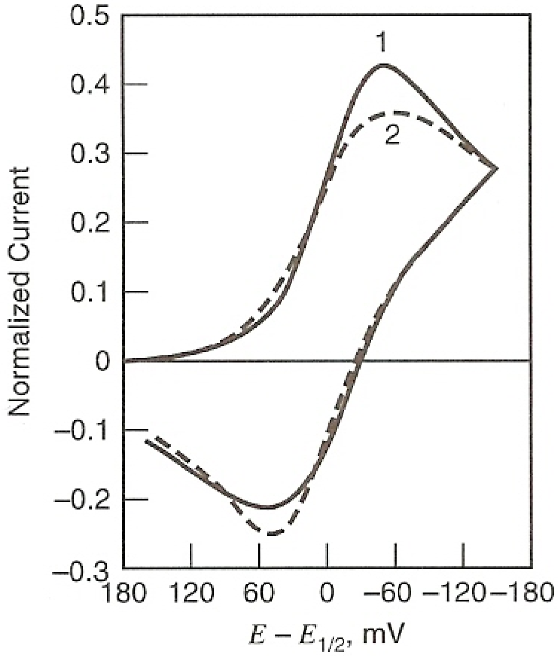
Quasireversible systems

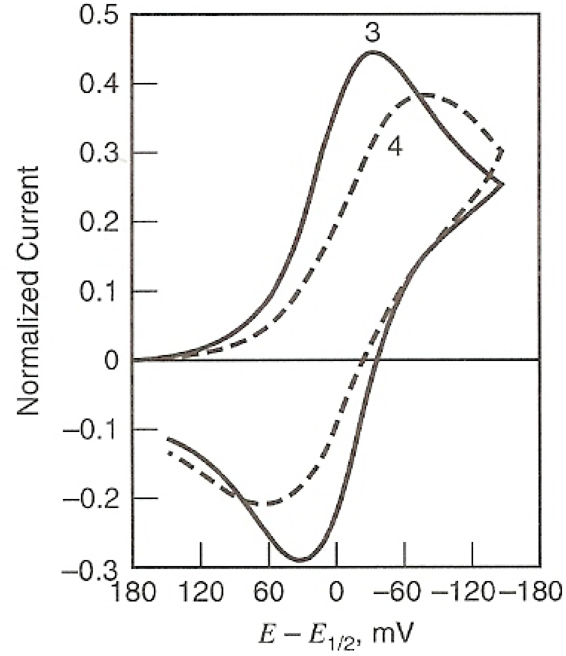
Wave shape & $\Delta E_p \rightarrow$ ftns of v, k^0, α & E_λ

If E_λ > 90/n mV beyond cathodic peak $\rightarrow$ small E_λ effect

$$\Psi = \Lambda\pi^{-1/2} = [k^0(D_O/D_R)^\alpha]/(\pi D_O f v)^{1/2}$$

(1) $\Psi = 0.5$, $\alpha = 0.7$, (2) $\Psi = 0.5$, $\alpha = 0.3$, (3) $\Psi = 7$, $\alpha = 0.5$, (4) $\Psi = 0.25$, $\alpha = 0.5$





For $0.3 < \alpha < 0.7 \rightarrow \Delta E_p$ independent of α; depend only on Ψ
$\rightarrow$ estimating k^0 in quasireversible systems

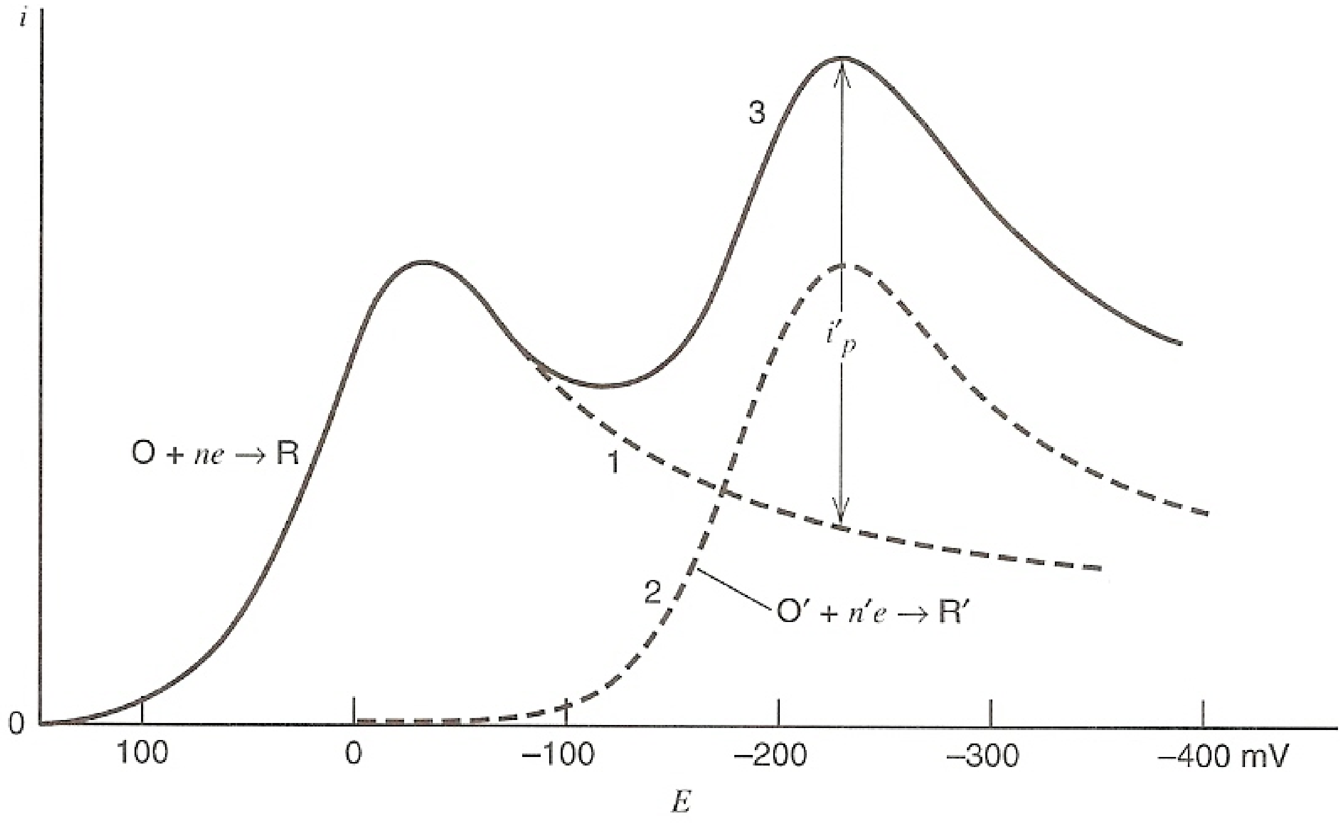
ΔE_p vs. v $\rightarrow \Delta E_p$ vs Ψ

Table 6.5.2 Variation of ΔE_p with ψ at 25°C (14)[a]

ψ	$E_{pa} - E_{pc}$ mV
20	61
7	63
6	64
5	65
4	66
3	68
2	72
1	84
0.75	92
0.50	105
0.35	121
0.25	141
0.10	212

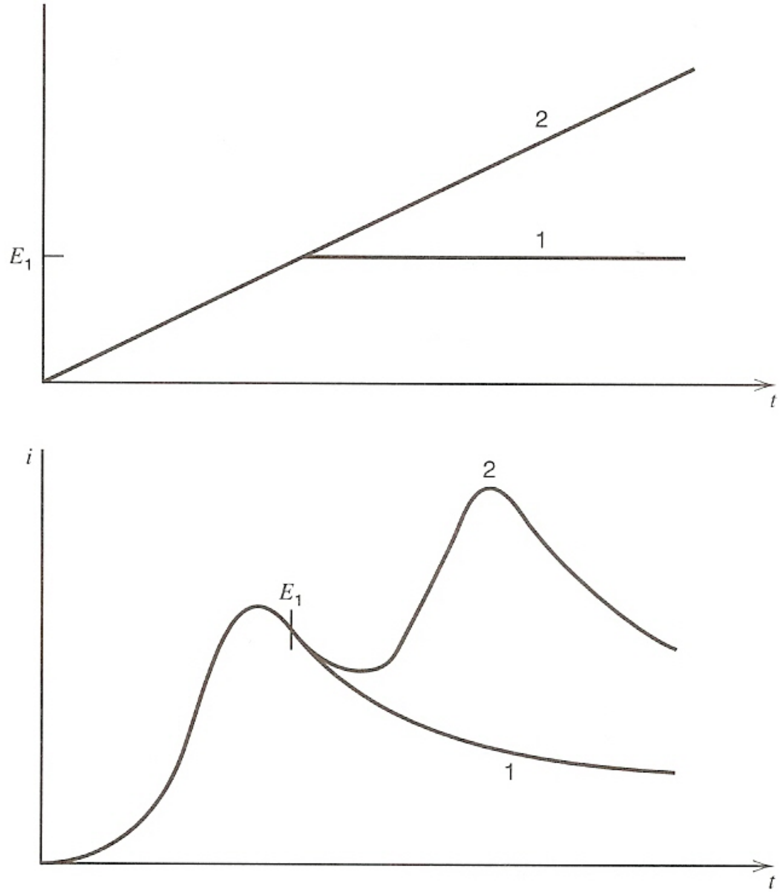
Multicomponent systems & Multistep charge transfers

O & O´ system

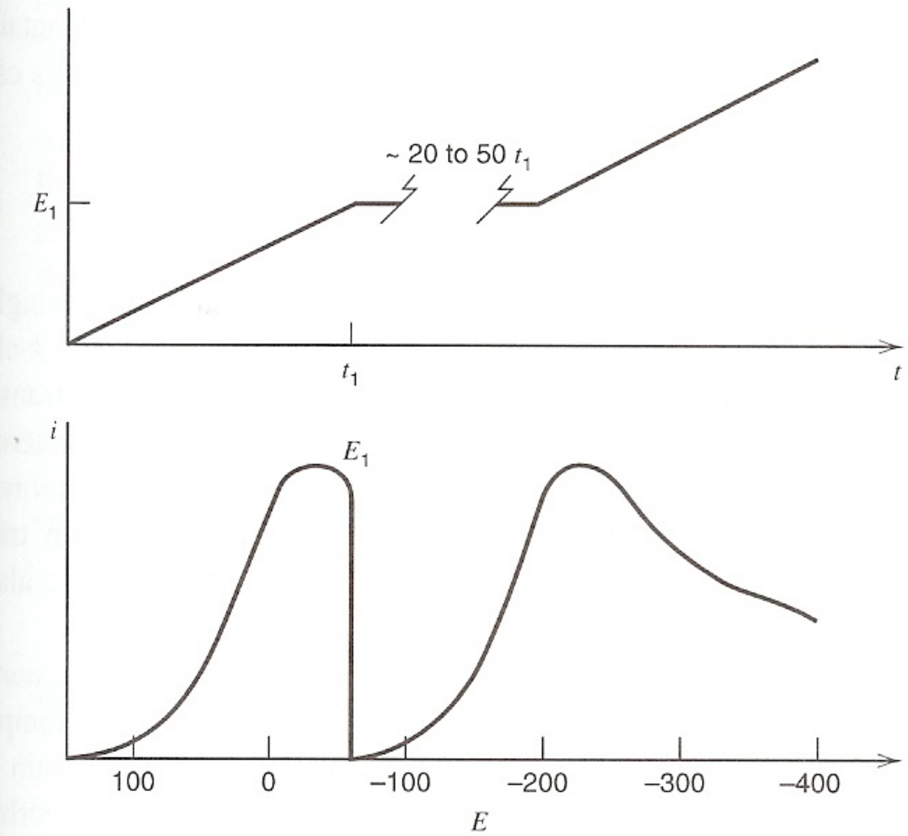


Method for obtaining baselines

Constant E after 1



Sweep stop beyond E_{p1}



In vivo applications of LSV & CV
e.g., rat brain