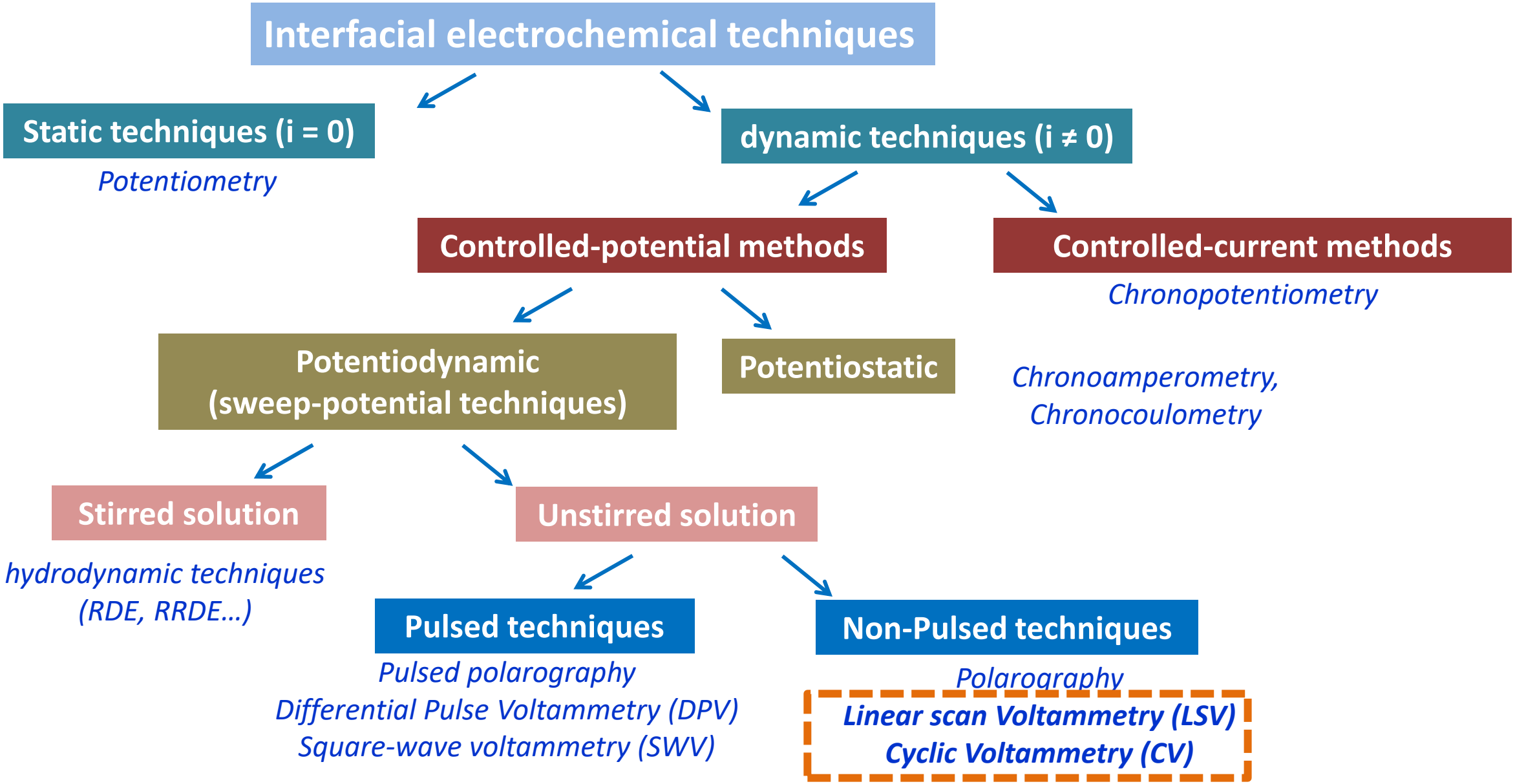
Basic classification of electrochemical methods



Potential sweep electrochemical methods: voltammetry

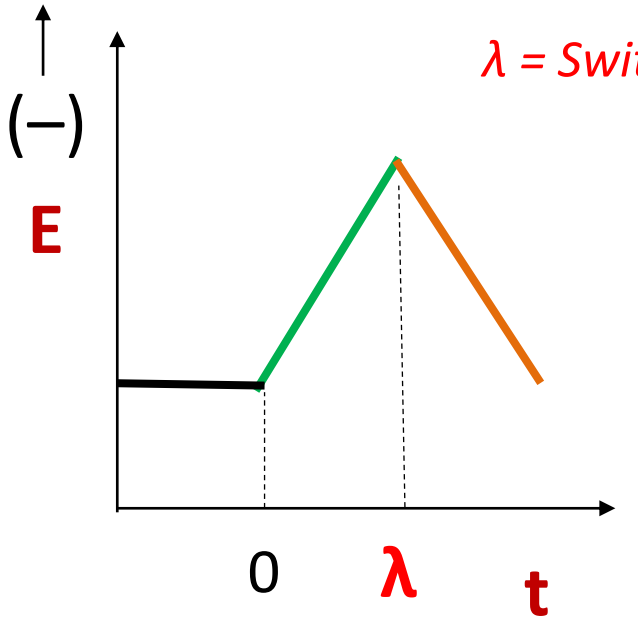
$(0 < t \leq \lambda)$ $\quad E(t) = E_i - vt$ Linear Scan Voltammetry (LSV)

$(t > \lambda)$ $\quad E(t) = E_i - 2v\lambda + vt$ Cyclic Voltammetry (CV)

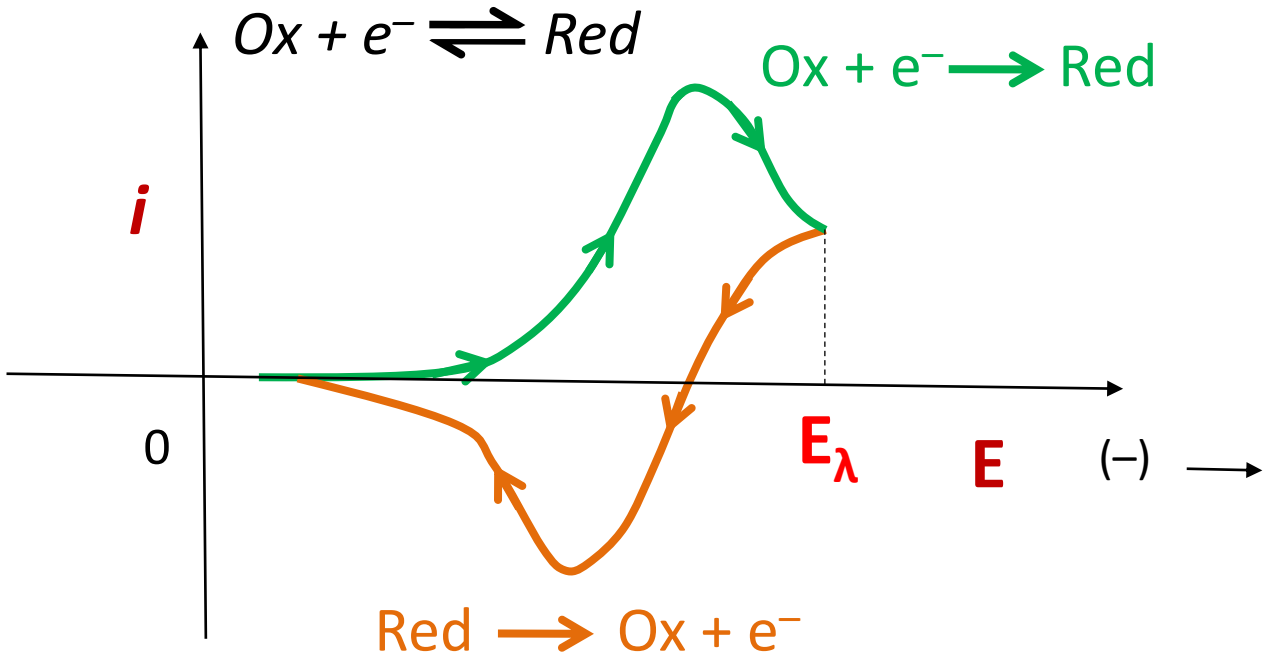
$$v = \frac{dE(t)}{dt}$$

Scan rate (V/s)

Peak-shaped i-E curves



λ = Switching potential



Linear Scan Voltammetry: boundary conditions

$$Ox + e^- \rightleftharpoons Red$$

- Planar electrode
- **Initial conditions (1)** $C_{Ox}(x,0) = C_{Ox}^*$ $C_{Red}(x,0) = 0$ for $t = 0$
- **Semi-infinite conditions (2)** (linear diffusion) $\lim_{x\to\infty} C_{Ox}(x,t) = C_{Ox}^*$
- **Flux balance (3)**

$$J_{Ox}(0,t) = -J_{Red}(0,t)$$

$$D_{Ox}\left(\frac{\partial C_{Ox}(x,t)}{\partial x}\right)_{x=0} + D_{Red}\left(\frac{\partial C_{Red}(x,t)}{\partial x}\right)_{x=0} = 0$$

Common boundary conditions to potential step techniques

Linear Scan Voltammetry: boundary conditions

- **Linear potential scan with time (LSV) (4)**

$$\boldsymbol{E(t) = E_i - \nu t} \qquad \textit{for } 0 < t \leq \lambda$$

Surface concentration condition

$$\frac{C_{Ox}(0,t)}{C_{Red}(0,t)} = exp\left[\frac{nF}{RT}(E - E^{0\prime})\right]$$

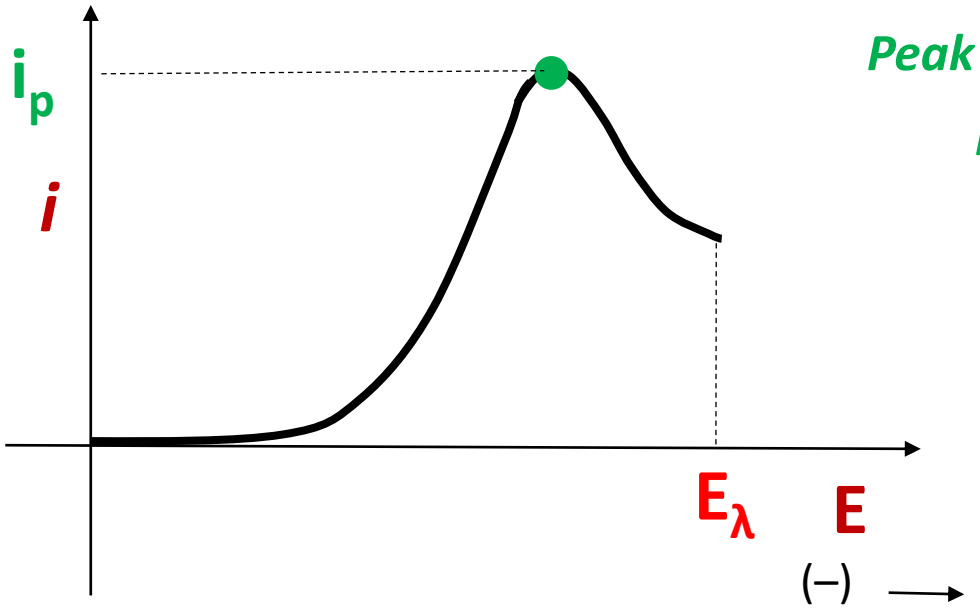
Nernstian redox system (reversible)

$$\boxed{\frac{C_{Ox}(0,t)}{C_{Red}(0,t)} = f(t) = exp\left[\frac{nF}{RT}(E_i - \nu t - E^{0\prime})\right]}$$

Time-dependent Nernst-type equation

(more complicated rigorous mathematical treatment for solving the equations)

Linear Scan Voltammetry for a nernstian system



Randles-Sevcik equation

Peak current *[A]*

$$i_p = 0.4463 \left(\frac{F^3}{RT}\right)^{1/2} n^{3/2} A\, D_{Ox}^{1/2} C_{Ox}^{*} v^{1/2}$$

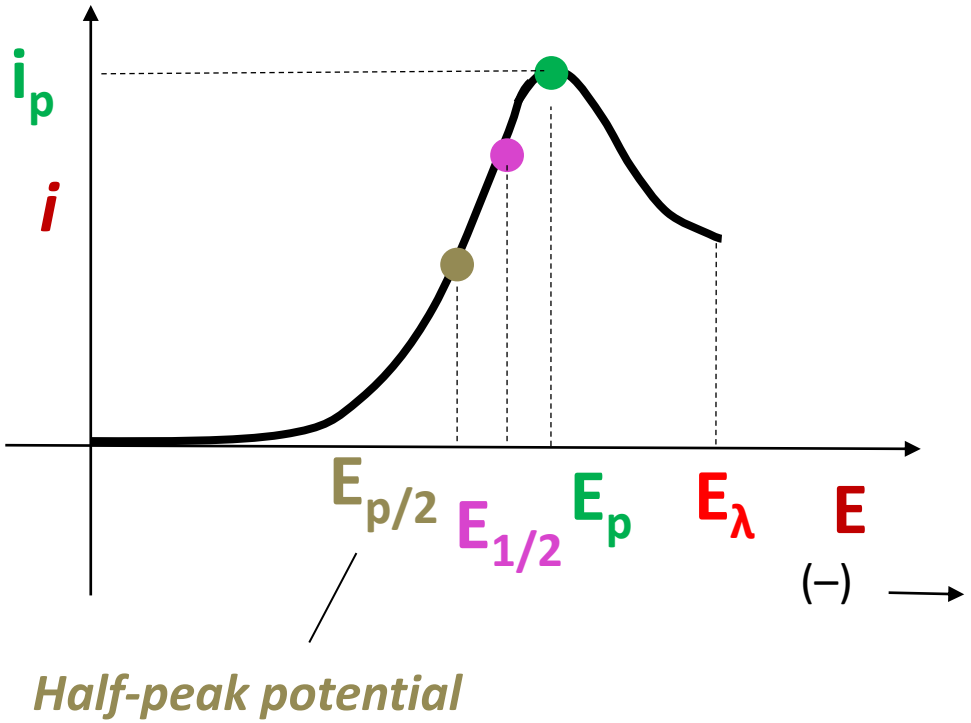
Number of electrons — *Area* *[cm²]* — *Diffusion coefficient* *[cm²/s]* — *Bulk Ox concentration* *[mol/cm³]* — *Scan rate* *[V/s]*

At T = 25°C

$$i_p = (2.69 \times 10^5)\, n^{3/2} A\, D_{Ox}^{1/2} C_{Ox}^{*} v^{1/2}$$

- $i_p \propto v^{1/2}$: for a reversible wave, it indicates a **diffusion control** (Cottrellian $i_d \propto t^{-1/2}$)
- D_{Ox} can be estimated from $i_p / v^{1/2} C_{Ox}^{*}$ (if A and n are known)
- n can be estimated from $i_p / v^{1/2} C_{Ox}^{*}$ (if A and D_{Ox} are known)

Linear Scan Voltammetry for a nernstian system



Half-peak potential

$$E_p - E_{1/2} = -1.109\frac{RT}{nF} = -28.5\ mV \quad (25°C,\ n=1)$$

Peak potential

(independent on v!!!)

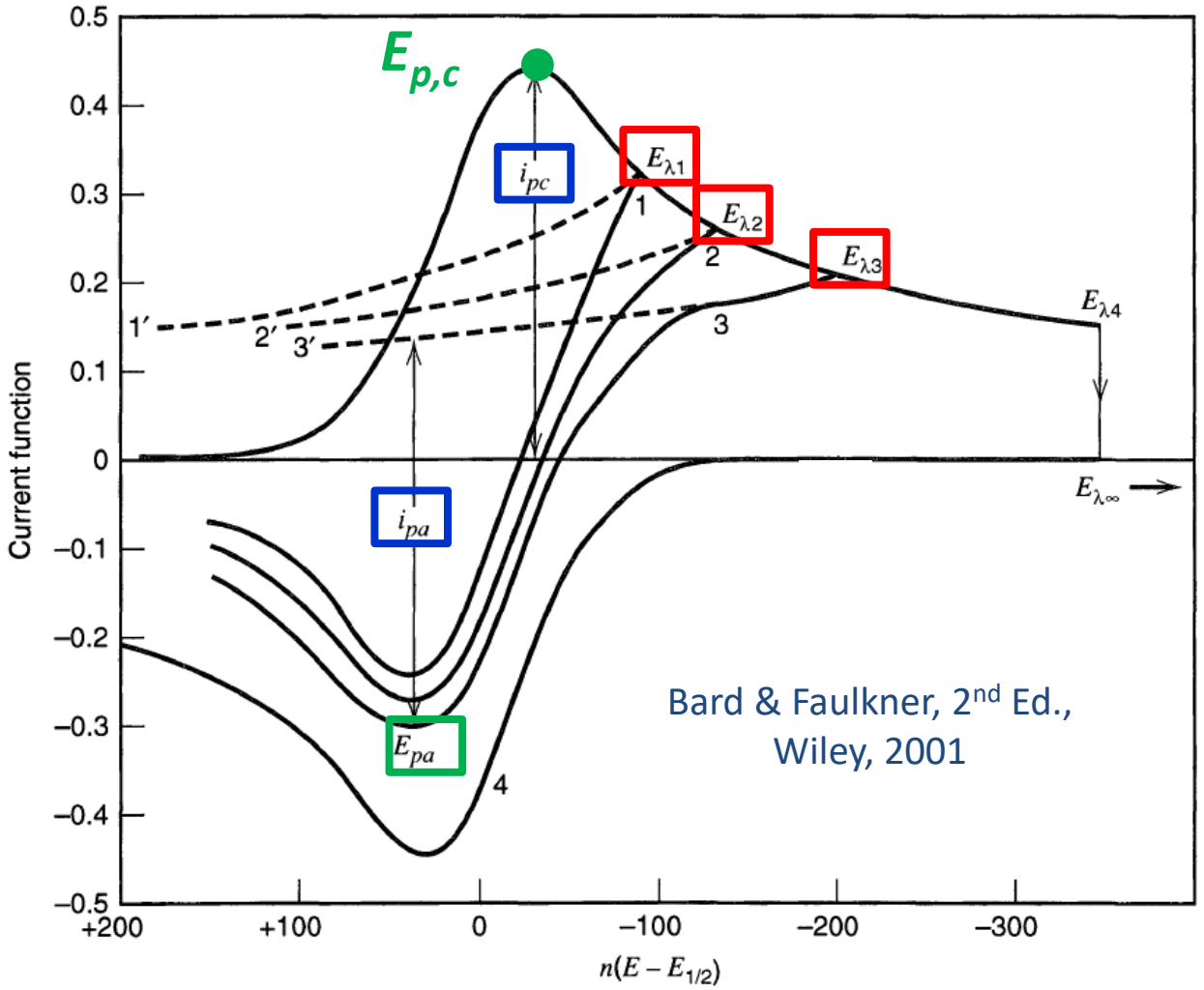
≈ midway between E_p and $E_{p/2}$

$$|E_p - E_{p/2}| = 2.20\frac{RT}{nF} = 56.5\ mV \quad (25°C,\ n=1)$$

Peak width *(independent on v)*

Cyclic Voltammetry (CV): a reversible nernstian system

i-E cyclic voltammograms (CVs)



Bard & Faulkner, 2nd Ed., Wiley, 2001

Cyclic Voltammetry (CV) (Reversal technique)

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

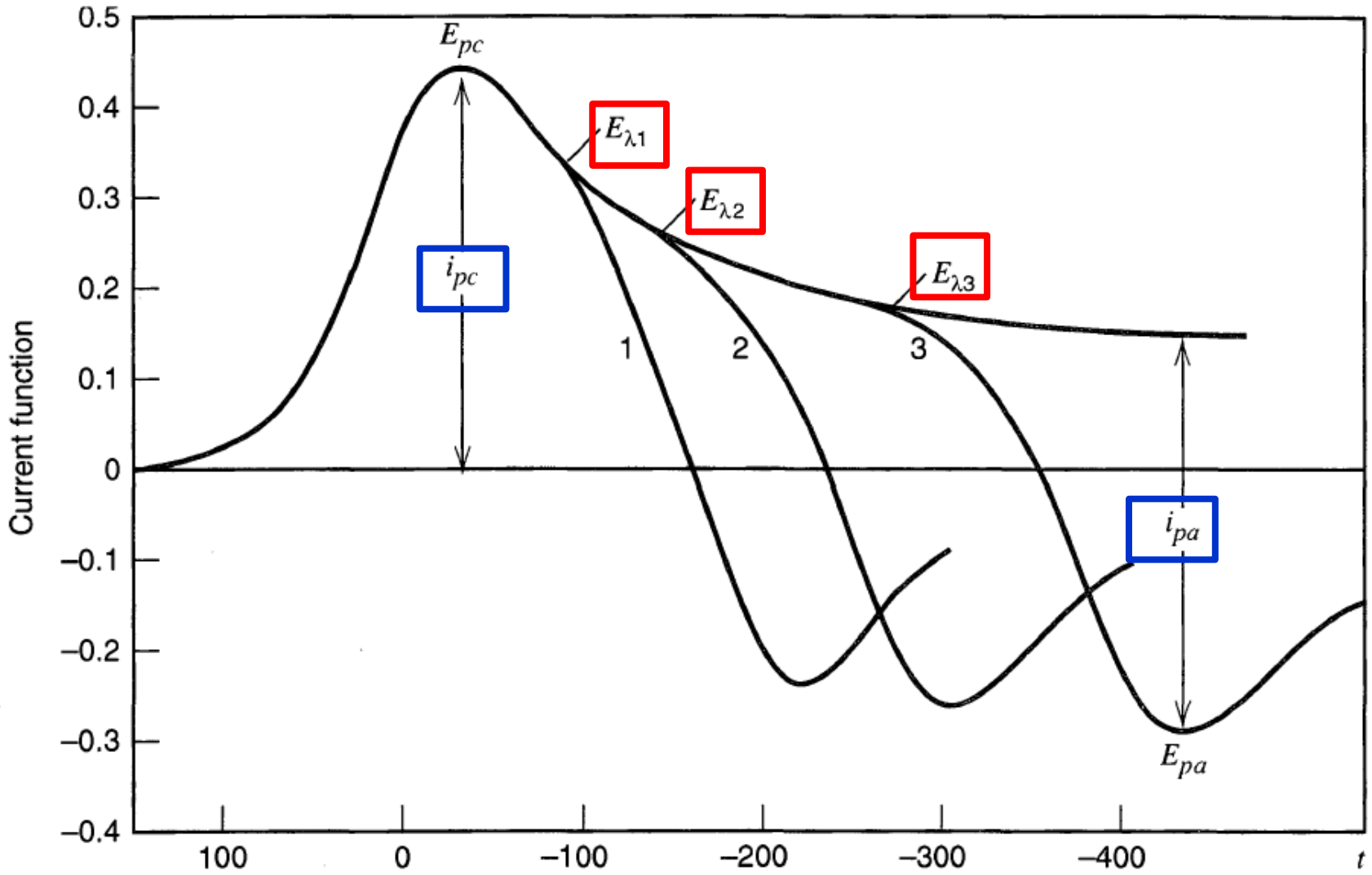
$(t > \lambda)$ $\quad E(t) = E_i - 2v\lambda + vt$

- Shape of CVs depends on E_λ
- For $E_\lambda - E_{p,c} > (35/n)$ **mV**, the reverse peak has the same shape as the forward one
- For a reversible wave, $i_{p,a}/i_{p,c} = 1$ (**independent on *v***)
- $i_{p,a}$ is measured from the decaying cathodic current as baseline
- ΔE_p only slightly depends on E_λ

$$\Delta E_p = E_{p,a} - E_{p,c} = 2.3\frac{RT}{nF} \sim 57\ mV \quad (25°C, n=1)$$

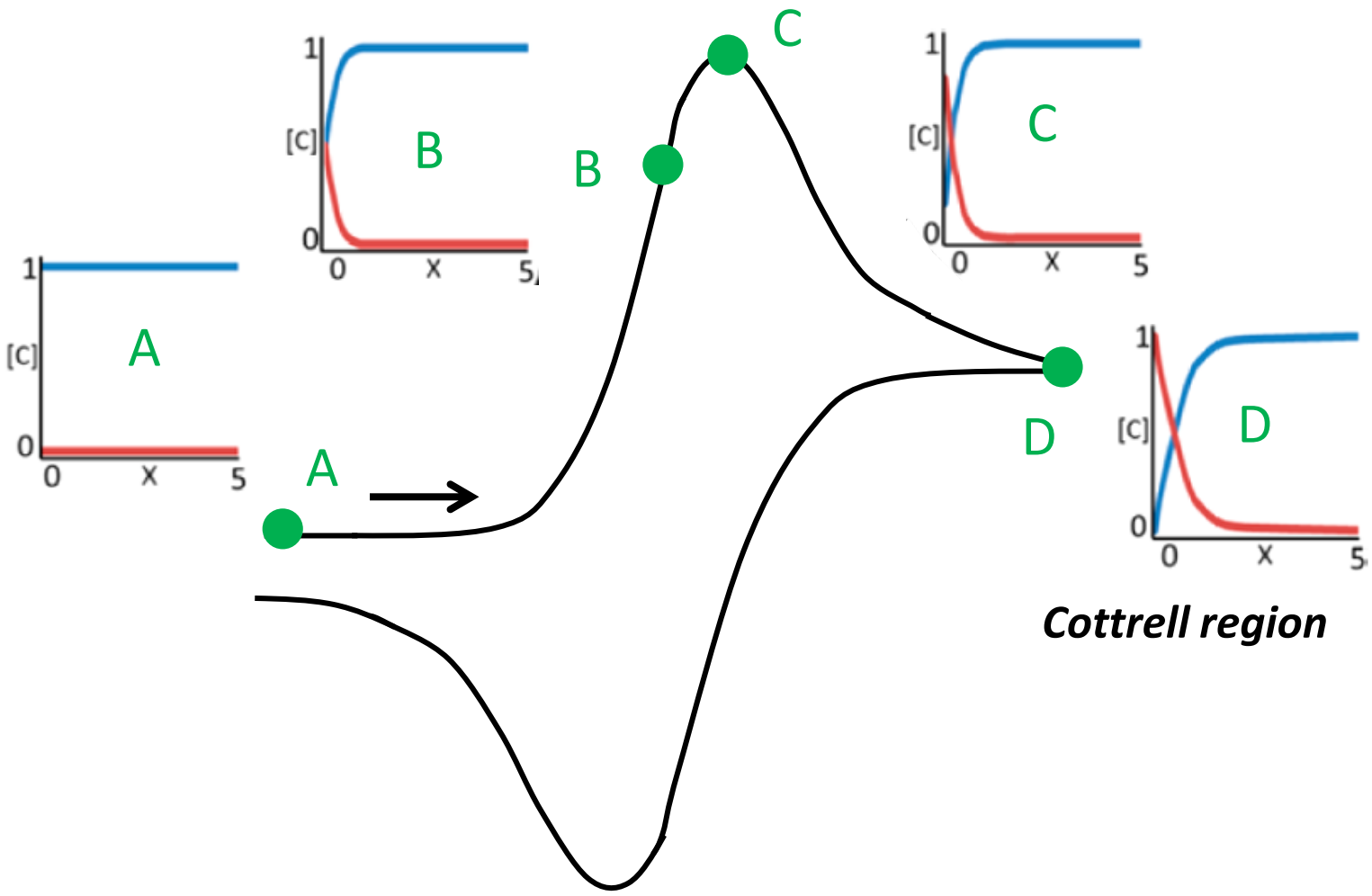
Cyclic Voltammetry (CV): a reversible nernstian system

i-t curves



Bard & Faulkner, 2nd Ed., Wiley, 2001

Understanding the peak shape: the concentration profiles



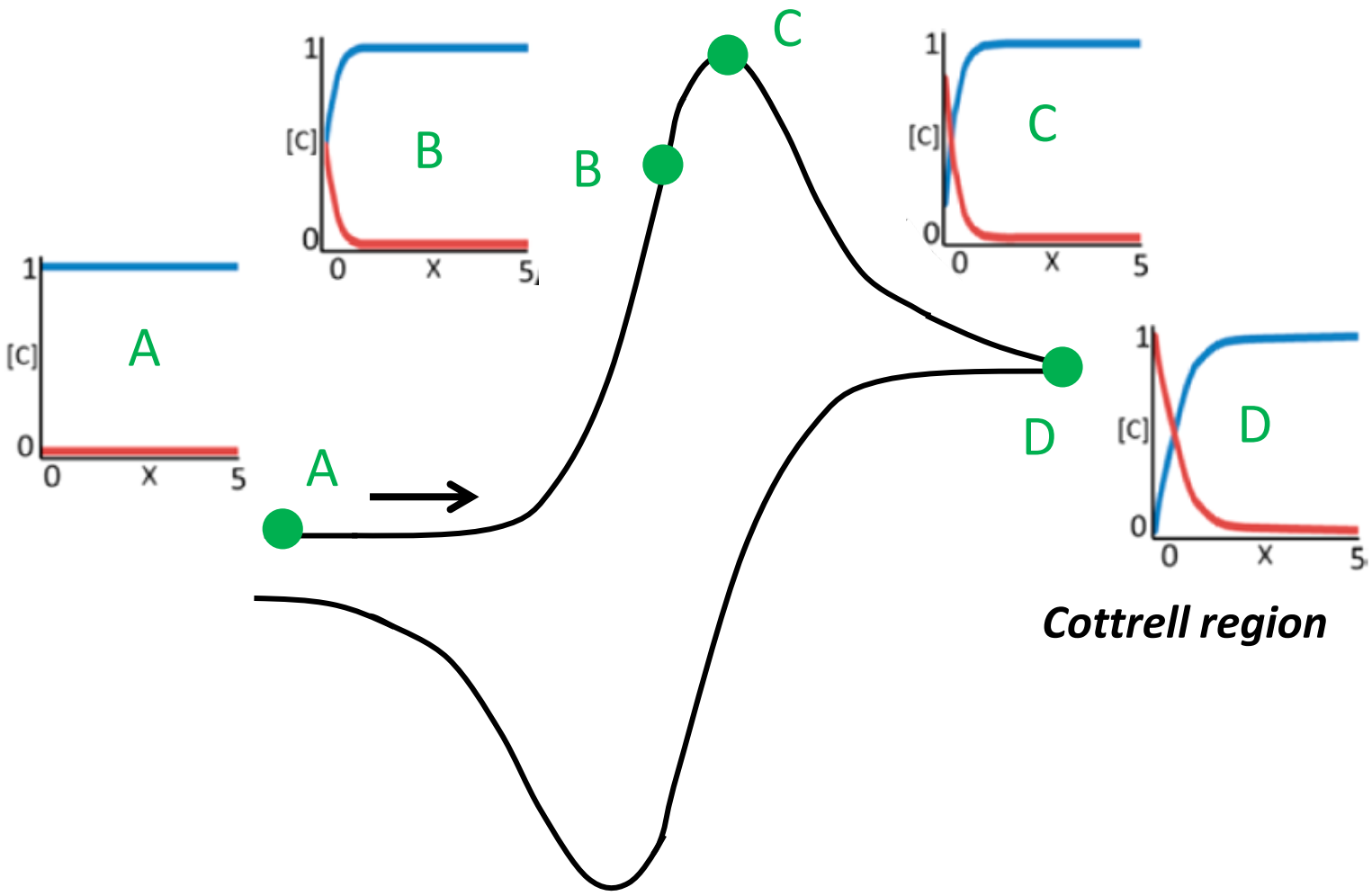
$$Ox + e^- \rightleftharpoons Red$$

$$\frac{C_{Ox}(0,t)}{C_{Red}(0,t)} = exp\left[\frac{nF}{RT}(E - E^{0\prime})\right]$$

- Concentration of the electroactive species (Ox/Red) near the electrode change over time according to the **Nernst equation**
- **A → D: cathodic scan**, **Ox is depleted** at the surface
- **C:** maximum cathodic current ($i_{p,c}$), dictated by mass transport of Ox from bulk to surface

J. L. Dempsey et al., *Inorg. Chem.* **2014**, 53, 9983−10002

Understanding the peak shape: the concentration profiles



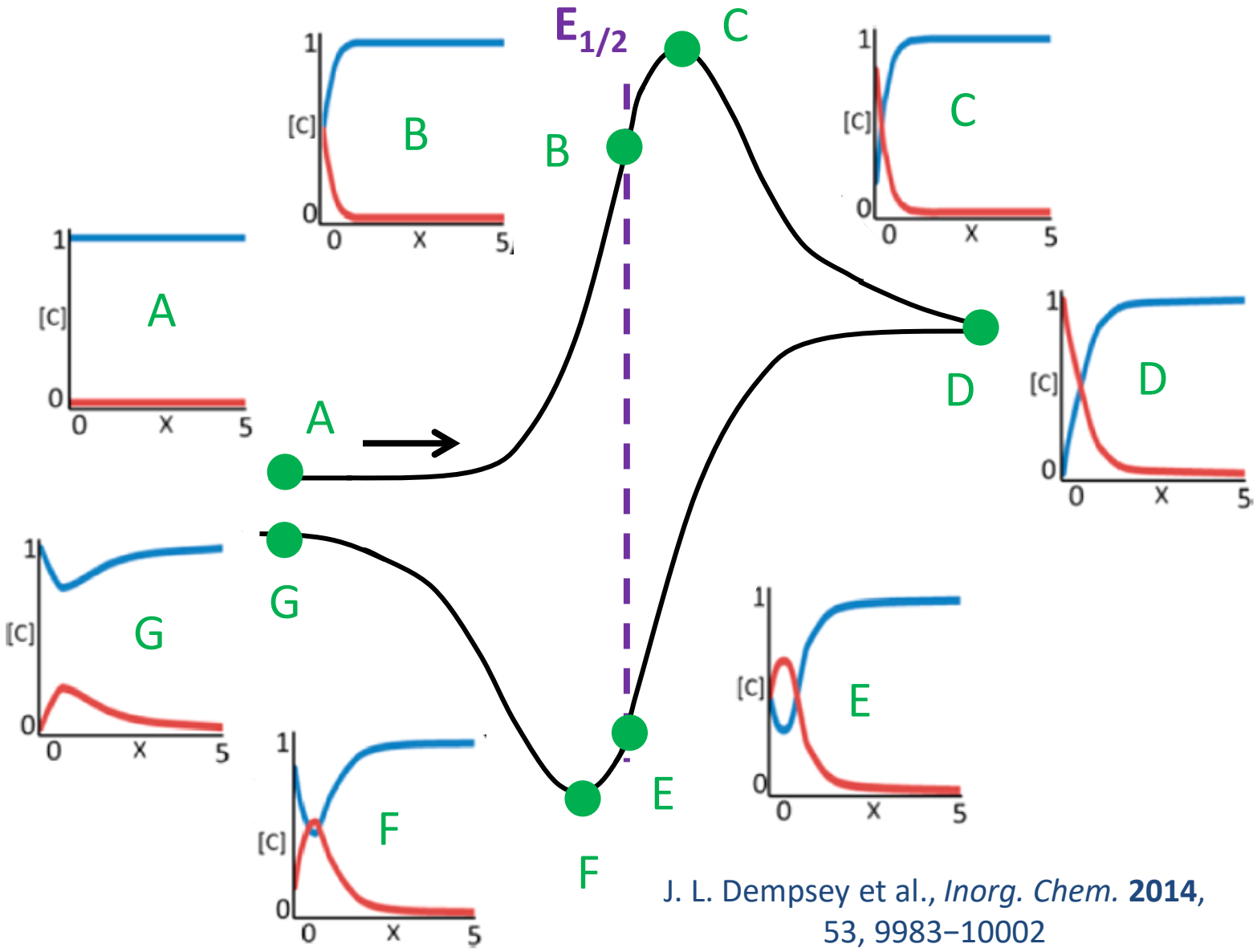
$$Ox + e^- \rightleftharpoons Red$$

$$\frac{C_{Ox}(0,t)}{C_{Red}(0,t)} = exp\left[\frac{nF}{RT}(E - E^{0\prime})\right]$$

- **Thickness of the diffusion layer (δ) grows during the scan** ($\partial C/\partial x$ diminishes) → slower mass transport from bulk to surface → *i decrease*
- δ depends on the CV timescale
- ***δ decreases with increasing scan rates*** ($\delta \sim \sqrt{Dt}$, $t \propto 1/v$)

J. L. Dempsey et al., *Inorg. Chem.* **2014**, 53, 9983−10002

Understanding the peak shape: the concentration profiles



J. L. Dempsey et al., *Inorg. Chem.* **2014**, 53, 9983−10002

$$Ox + e^- \rightleftharpoons Red$$

$$\frac{C_{Ox}(0,t)}{C_{Red}(0,t)} = exp\left[\frac{nF}{RT}(E - E^{0\prime})\right]$$

- **D → G: reverse anodic scan** (Red is oxidized to Ox as E becomes increasingly positive)
- **B and E:**

$$\mathbf{C_{Ox}\,(0,t) = C_{Red}\,(0,t)}$$

$$\mathbf{E \approx E_{1/2}}$$

$$E^{0\prime} \approx \frac{1}{2}(E_{p,c}(C) + E_{p,a}(F))$$

- **ΔE_p** is due to **the diffusive mass transport** of the electroactive species from/to surface-bulk

Reversible voltammetric waves: diagnostic criteria

Potential

- $E_{p,c}$ independent on the scan rate (v)
- $\Delta E_p = 57/n$ mV (at 25°C) independently on the scan rate (this value varies with T!!!)
- Assuming that $D_{Ox} = D_{Red}$, the **formal potential $E^{0\prime}$** can be measured as:

$$E^{0\prime} = \frac{1}{2}(E_{p,c} + E_{p,a})$$

Current

- $i_{p,c} / v^{1/2}$ constant with the scan rate (v) (freely diffusing redox species)
- $i_{p,a} / i_{p,c}$ constant and equal to 1 (independent on the scan rate)

The effect of double layer capacitance

- In potential sweep experiments, capacitive current (i_C) always flows and is **directly proportional to the scan rate** (v):

- Both the faradaic and the capacitive currents increase with the scan rate, but i_C **increases faster**

$$i_C \propto v \qquad i_p \propto v^{1/2}$$ Randles-Sevcik equation

$$\frac{|i_C|}{i_p} = \frac{(10^{-5})\, C_d v^{1/2}}{2.69\, n^{3/2} D_{Ox}^{1/2} C_{ox}^{*}}$$

- The **extraction of the faradaic component in CV at high scan rates is problematic**, especially in the presence of **low concentration** of the electroactive species (baseline correction)

The effect of double layer capacitance

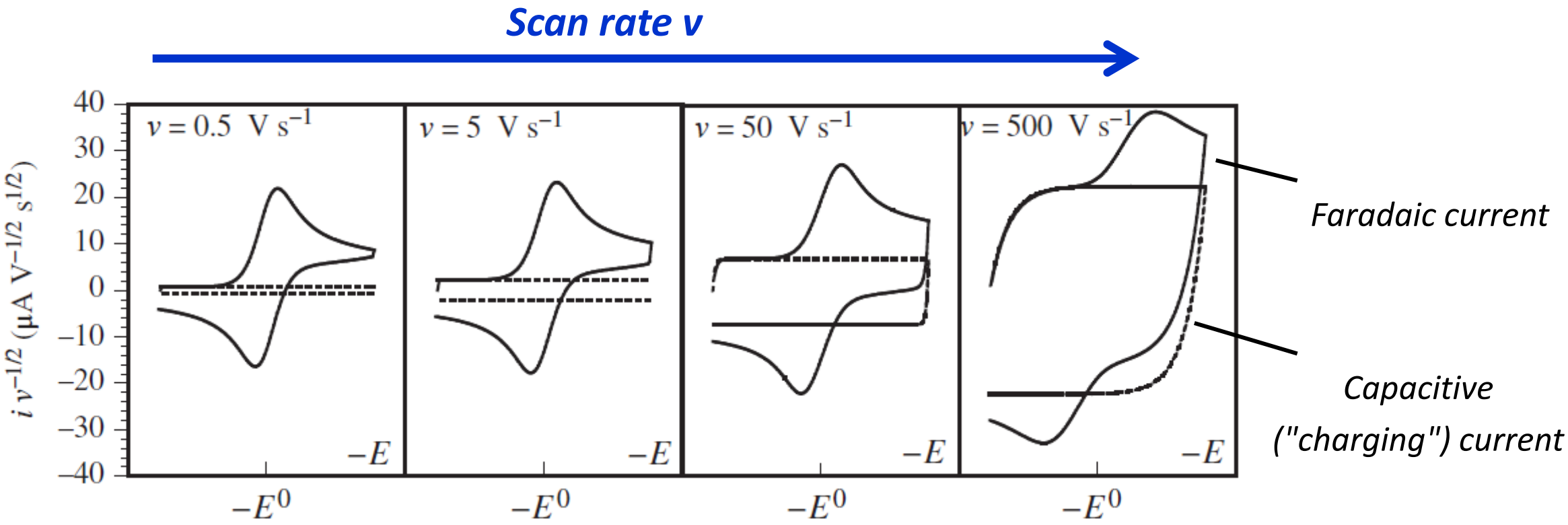
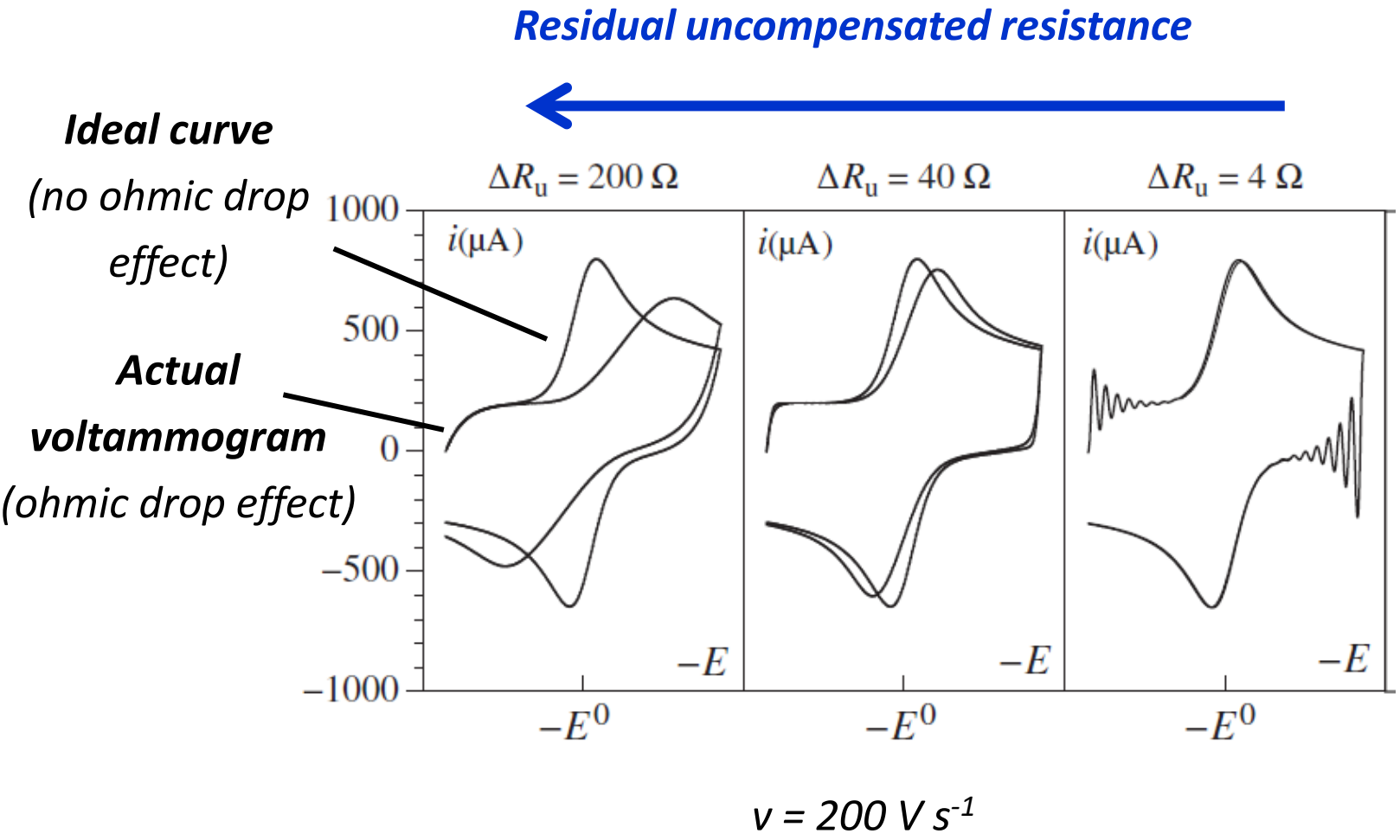


Figure 1.7 Faradaic and double-layer charging currents for a cyclic voltammetric Nernstian wave. —, total current; · · ·, capacitive component. $S = 0.05\ \text{cm}^2$, $C^0 = 5 \times 10^{-4}$ M, $C_d = 1\ \mu\text{F}$, $R_u = 100\ \Omega$.

Savéant, Elements of Molecular and Biomolecular Electrochemistry, 1st Ed., 2006

The effect of the ohmic drop



Savéant, Elements of Molecular and Biomolecular Electrochemistry, 1st Ed., 2006

- Uncompensated resistance (**iR_u**) may lead to **severe distortion** of the CV shape, typically shifting away the cathodic and anodic peaks from each other (*ΔE_p increase, lower i_p, peak broadening*)
- The effect of the ohmic drop increases at **high scan rates** (higher current), **causing E_p to be a function of *v*** (diagnostic criteria for uncompensated ohmic drop)