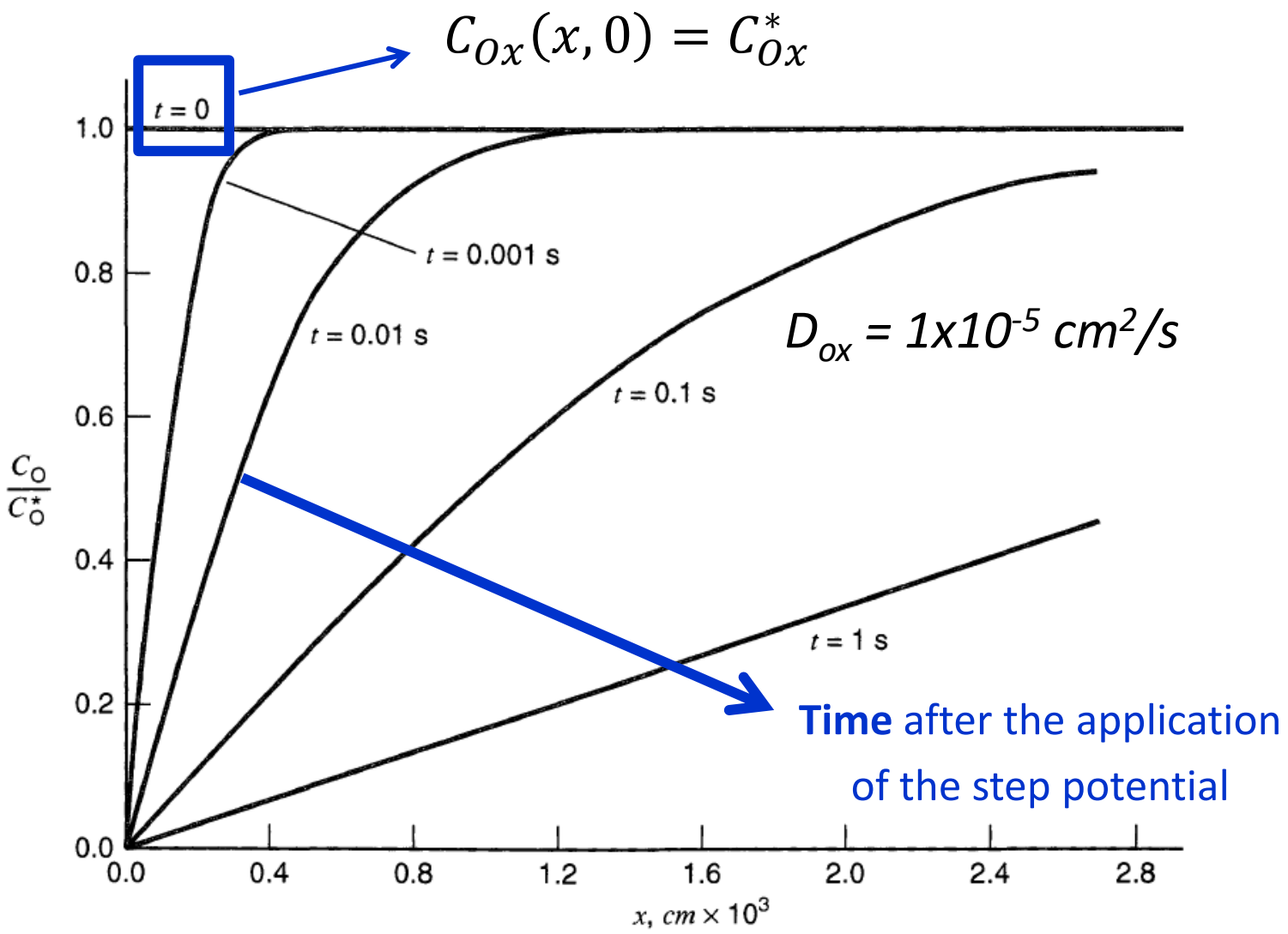
The concentration profiles

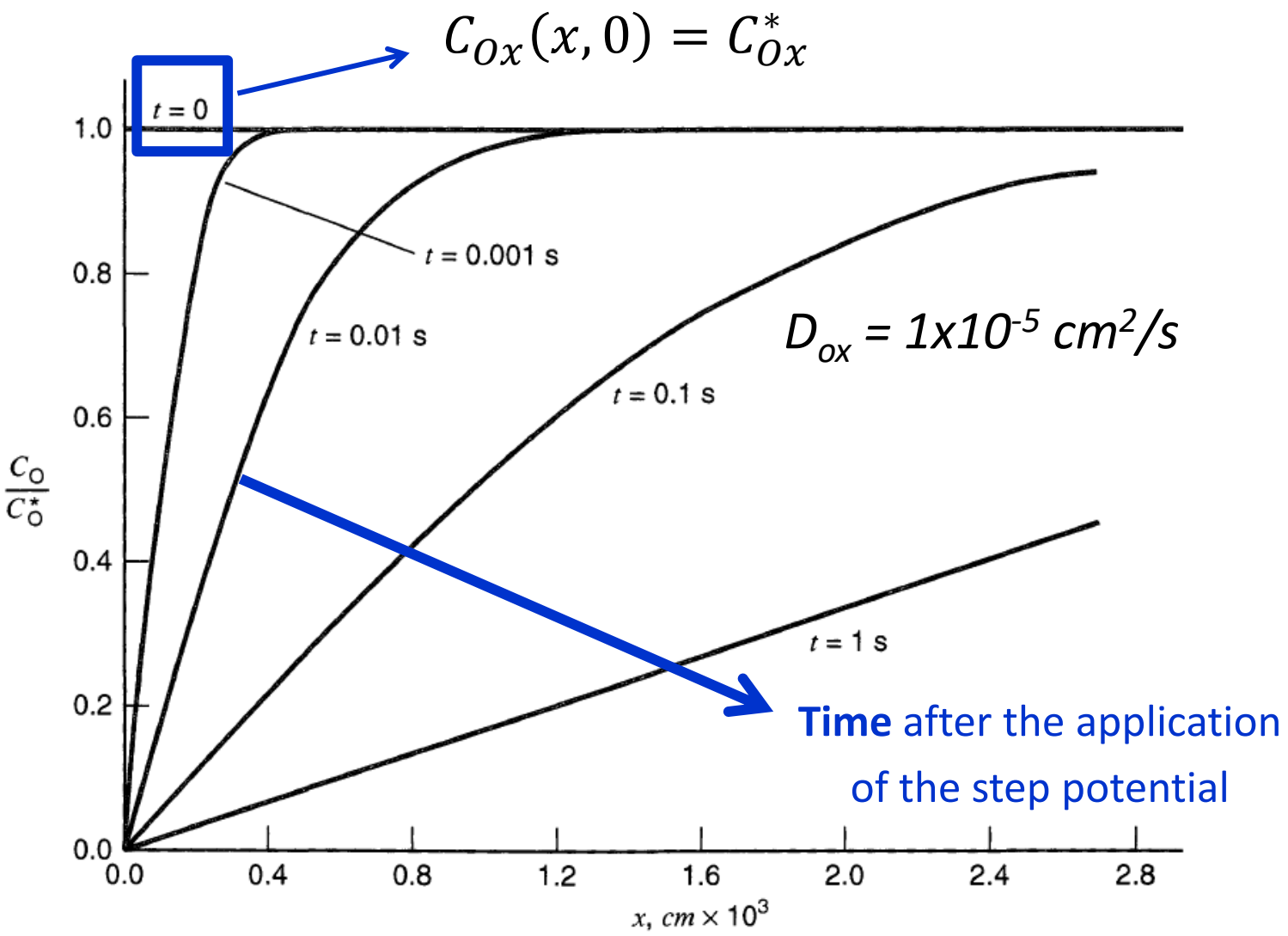


Bard & Faulkner, 2nd Ed., Wiley, 2001

$$C_{ox}(x,t) = C^*_{Ox}\, erf\left[\frac{x}{2\sqrt{D_{Ox}t}}\right]$$

- **Time-dependent concentration profiles** near the electrode surface (as a function of the distance)
- Ox depletion at the surface with increasing times
- The **slope** of each concentration profile indicates the Ox **concentration gradient** $(\partial C_{Ox}(x,t)/\partial x)$ at various t

The concentration profiles



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

$$C_{ox}(x,t) = C^*_{Ox}\ erf\left[\frac{x}{2\sqrt{D_{Ox}t}}\right]$$

- Profiles asymptotically tend to C_{Ox}^* value

$$\frac{\partial C_{Ox}(x,t)}{\partial x} = 0 \Rightarrow C_{Ox}(x,t) = C^*_{Ox}$$

- Time-dependent **thickness of the diffusion layer**, which can be defined in terms of $\sqrt{D_{ox}t}$ ($\approx 6\sqrt{D_{Ox}t}$)

The Cottrell Equation

$$-J_{Ox}(0,t) = \frac{i}{nFA} = D_{Ox}\left(\frac{\partial C_{Ox}(x,t)}{\partial x}\right)_{x=0}$$

$$\bar{C}_{Ox}(x,s) = \frac{C^*_{Ox}}{s} - \frac{C^*_{Ox}}{s} e^{\left[-\sqrt{\frac{s}{D_{Ox}}}x\right]}$$

$\mathcal{L}$ ⇓

$$\frac{\bar{\imath}(s)}{nFA} = D_{Ox}\left(\frac{\partial \bar{C}_{Ox}(x,s)}{\partial x}\right)_{x=0} = D_{Ox}\left[-\frac{C^*_{Ox}}{s}\left(-\frac{s^{1/2}}{D_{Ox}^{1/2}}\right) e^{\left[-\sqrt{\frac{s}{D_{Ox}}}x\right]}\right]_{x=0} = D_{Ox}\left(\frac{C^*_{Ox}}{s^{1/2} D_{Ox}^{1/2}}\right)$$

$$\bar{\imath}(s) = \frac{nFAD_{Ox}^{1/2} C^*_{Ox}}{s^{1/2}}$$

$\mathcal{L}^{-1}$ ⇒

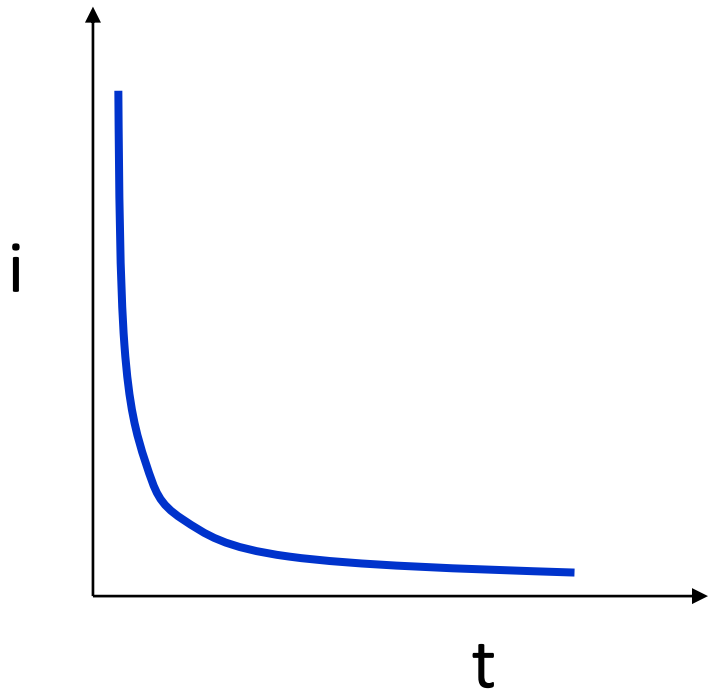
$$i(t) = \frac{nFAD_{Ox}^{1/2} C^*_{Ox}}{\pi^{1/2} t^{1/2}}$$

Cottrell Equation

The Cottrell Equation

$$i(t) = \frac{nFAD_{Ox}^{1/2}C_{Ox}^{*}}{\pi^{1/2}t^{1/2}}$$

F. G. Cottrell
(1877 - 1948)



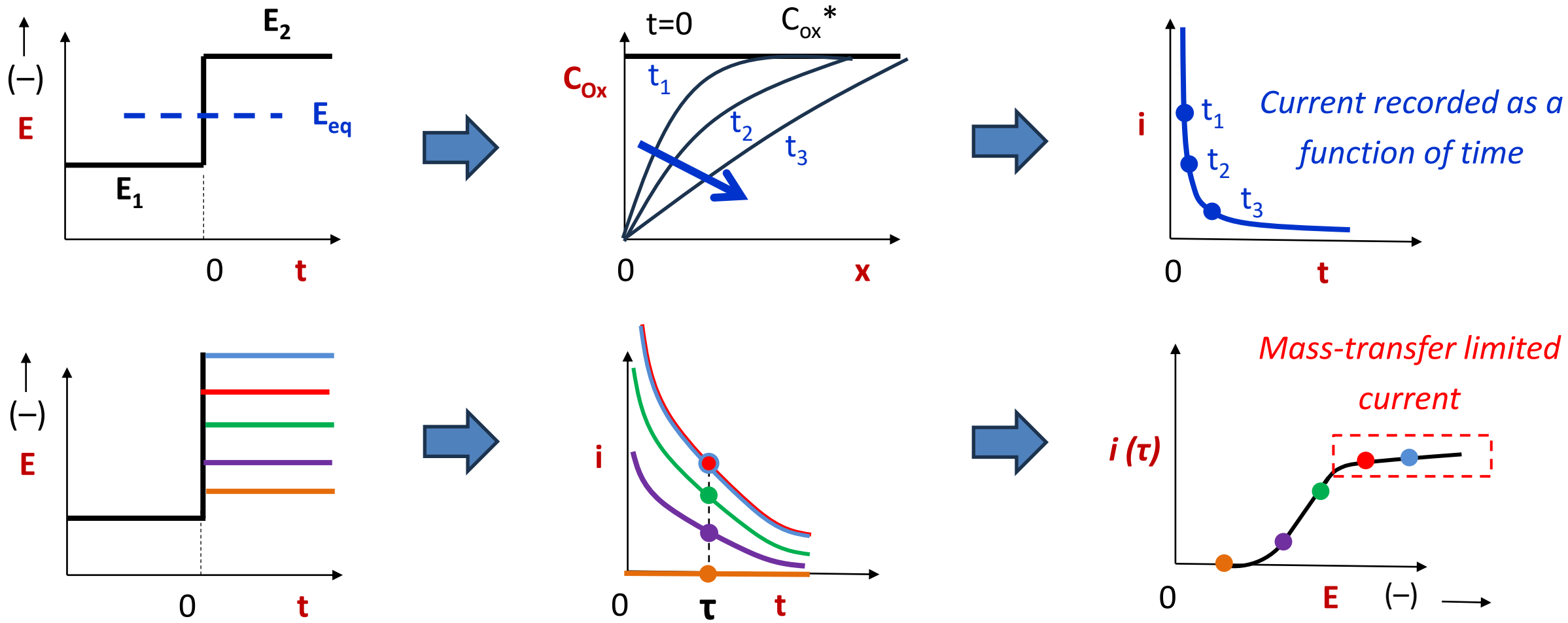
- Effect of depletion of Ox near the surface
- ***Faradaic*** **current inversely proportional to** $t^{1/2}$ (i decrease with time)
- The **linear** dependence of **i vs.** $1/t^{1/2}$ is **diagnostic test** for diffusion-controlled electrochemical process
- Cottrell behaviour not observed at **very short times** due to **capacitive or *non-faradaic* current** (“charging” current),

$$i_C \propto 1/\exp(t)$$

Chronoamperometry

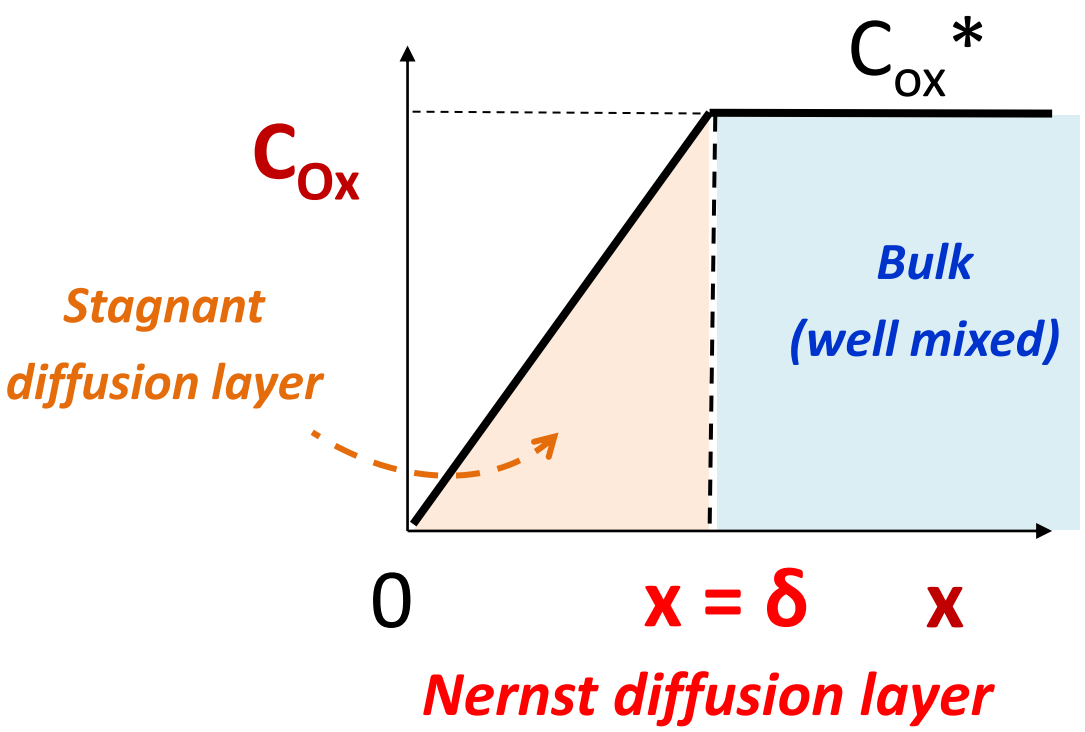
$$i(t) = \frac{nFAD_{Ox}^{1/2}C_{Ox}^{*}}{\pi^{1/2}t^{1/2}}$$

Diffusion-limited current at E_2



Steady-state mass transfer: limiting current

Steady-state conditions: the species concentrations do not vary over time (but only with the distance from the electrode surface), i.e. the overall reaction rate (current) is time-independent



$$v_{mt} = D_{Ox}\left(\frac{\partial C_{Ox}(x)}{\partial x}\right)_{x=0}$$

Rate of mass transfer

Ox concentration gradient at the surface

$$v_{mt} = \frac{\boldsymbol{D_{Ox}}}{\boldsymbol{\delta}}\left(C^*_{Ox} - C_{Ox}(x=0)\right)$$

Mass transfer coefficient (m_T) [cm/s] ***Same units as k^0!!***

Steady-state mass transfer: limiting current

$$v_{mt} = \frac{\boldsymbol{D_{Ox}}}{\boldsymbol{\delta}}\left(C^*_{Ox} - C_{Ox}(x=0)\right) = \boldsymbol{m_{T,Ox}}\left(C^*_{Ox} - C_{Ox}(x=0)\right)$$

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

$$v_{mt} = \boldsymbol{m_{T,Ox}}\left(C^*_{Ox} - C_{Ox}(x=0)\right) = \frac{i}{nFA}$$

$$\boldsymbol{m_{T,Red}}\left(C_{Red}(x=0) - C^*_{Red}\right) = \frac{i}{nFA}$$

Potential-dependent terms

Red is produced

($C_{x=0} > C^*$)

Steady-state mass transfer: limiting current

$\eta \rightarrow -\infty$ ⇒ $C_{Ox}(x=0) = 0$ ⇒ *Maximum* $\mathbf{v_{mt}}$, *maximum* $i = i_L$

$$i_L = nFA\, m_{T,Ox}\, C_{Ox}^{*} = \frac{nFA D_{Ox} C_{Ox}^{*}}{\delta}$$

Limiting current

$$\frac{C_{Ox}(x=0)}{C_{Ox}^{*}} = 1 - \frac{i}{i_L}$$

- *maximum rate of the electrode process (**dictated by mass-transfer kinetics**)*
- *Ox gets reduced immediately as it reaches x = 0 (**fast ET kinetics**)*

$C_{Ox}(x=0) = 0$ for $i = i_L$ (max i, $\eta \rightarrow -\infty$)

$C_{Ox}(x=0) = C_{Ox}^{*}$ for $i = 0$ ($\eta \rightarrow 0$)

…Recall…

$$E = E^{0'} + \frac{RT}{nF} ln\left(\frac{C_{Ox}(0,t)}{C_{Red}(0,t)}\right)$$

Nernst-type Equation

Nernstian redox system

Steady-state i-E curves for a Nernstian redox system

CASE STUDY – only Ox is present at t = 0 *(both Ox and Red are soluble)*

Ox

1) $i_L = nFA\, m_{T,Ox}\, C^*_{Ox}$

2) $\dfrac{C_{Ox}(x=0)}{C^*_{Ox}} = 1 - \dfrac{i}{i_L}$ ⇒ $C_{Ox}(x=0) = \left(\dfrac{i_L - i}{nFA m_{T,Ox}}\right)$

Red

$m_{T,Red}(C_{Red}(x=0) - \cancel{C^*_{Red}}) = \dfrac{i}{nFA}$ ⇒ $C_{Red}(x=0) = \dfrac{i}{nFA m_{T,Red}}$

substitution

$E = E^{0'} + \dfrac{RT}{nF} ln\left(\dfrac{C_{Ox}(x=0)}{C_{Red}(x=0)}\right)$ ⇒ $E = E^{0'} + \dfrac{RT}{nF} ln\left(\dfrac{i_L - i}{\cancel{nFA} m_{T,Ox}}\right)\left(\dfrac{\cancel{nFA} m_{T,Red}}{i}\right)$ …

Steady-state i-E curves for a Nernstian redox system

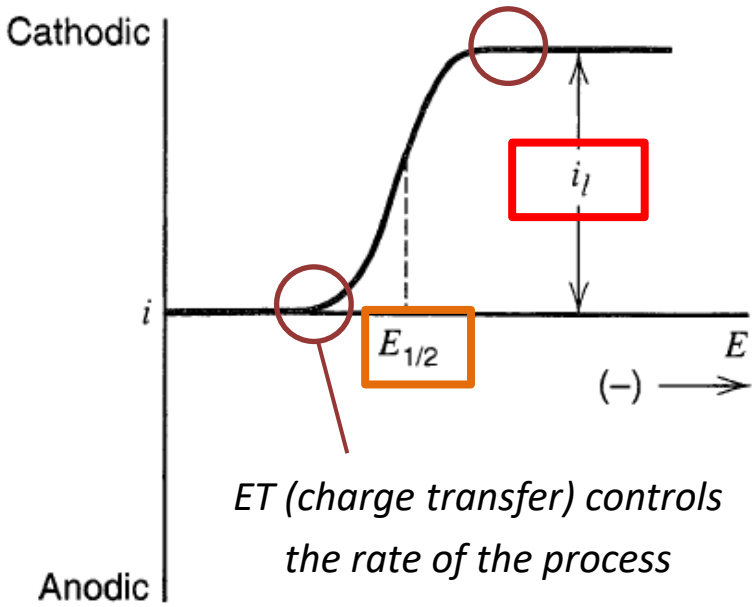
$$\ldots \quad E = E^{0'} - \frac{RT}{nF} ln\left(\frac{m_{T,Ox}}{m_{T,Red}}\right) + \frac{RT}{nF} ln\left(\frac{i_L - i}{i}\right)$$

Half-wave potential

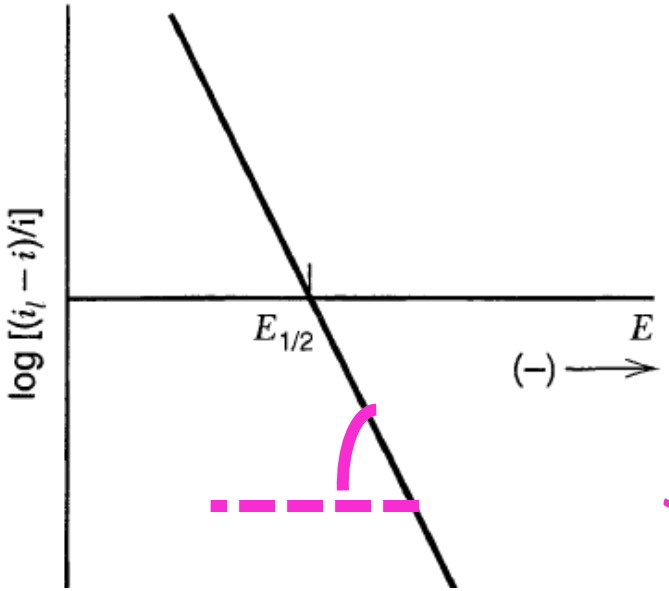
$$E = E_{1/2} + \frac{RT}{nF} ln\left(\frac{i_L - i}{i}\right)$$

$E_{1/2}$ *is* ***independent on the Ox/Red concentrations*** *and is therefore characteristic of the Ox/Red couple*

MT (diffusion) controls the rate of the process



ET (charge transfer) controls the rate of the process



$$i = i_L/2 \Rightarrow E = E_{1/2}$$

Half-wave

$$m_{T,Ox} \approx m_{T,Red} \Rightarrow E_{1/2} \approx E^{0'}$$

$$\text{Slope} = \frac{nF}{2.3RT} \approx \frac{n}{59\ mV} \quad (T = 298\ K)$$

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

Effect of mass transfer on the i-η curves

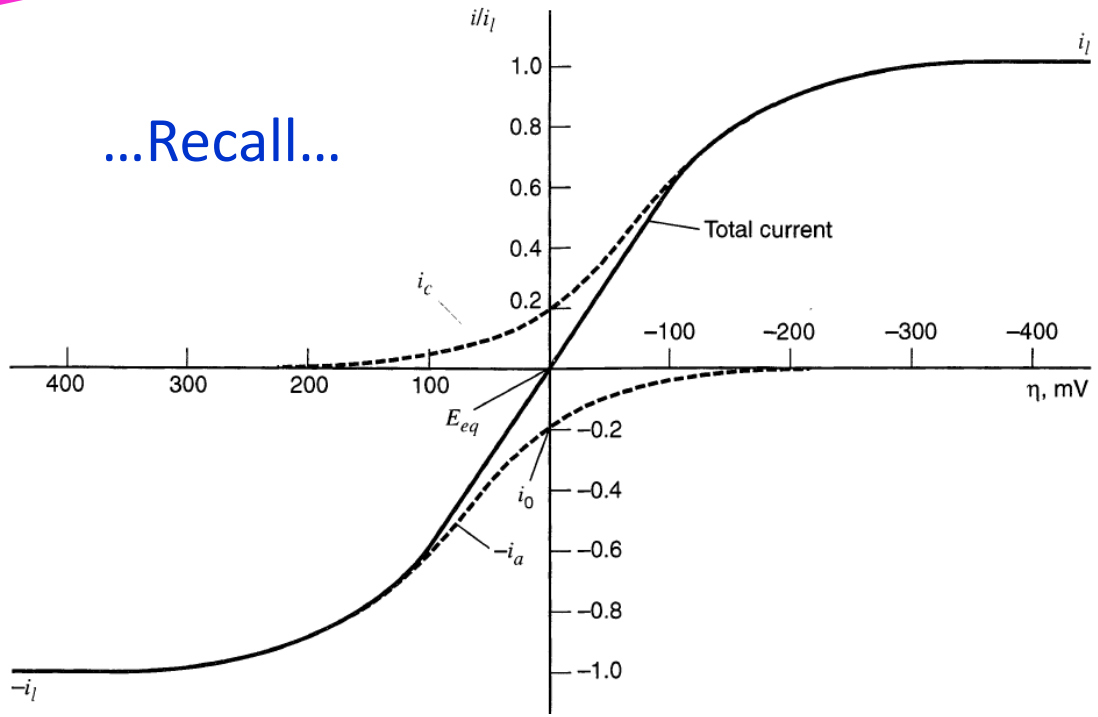
Butler-Volmer

$$i = i_0\left[\frac{C_{Ox}(0,t)}{C^*_{Ox}}e^{-\alpha\frac{nF}{RT}\eta} - \frac{C_{Red}(0,t)}{C^*_{Red}}e^{(1-\alpha)\frac{nF}{RT}\eta}\right]$$

Mass transfer (diffusion)

Charge transfer

…Recall…



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

Effect of mass transfer on the i-η curves

Butler-Volmer

$$i = i_0\left[\frac{C_{Ox}(0,t)}{C^*_{Ox}}e^{-\alpha\frac{nF}{RT}\eta} - \frac{C_{Red}(0,t)}{C^*_{Red}}e^{(1-\alpha)\frac{nF}{RT}\eta}\right]$$

$$\frac{C_{Ox}(x=0)}{C^*_{Ox}} = 1 - \frac{i}{i_{L,c}}$$

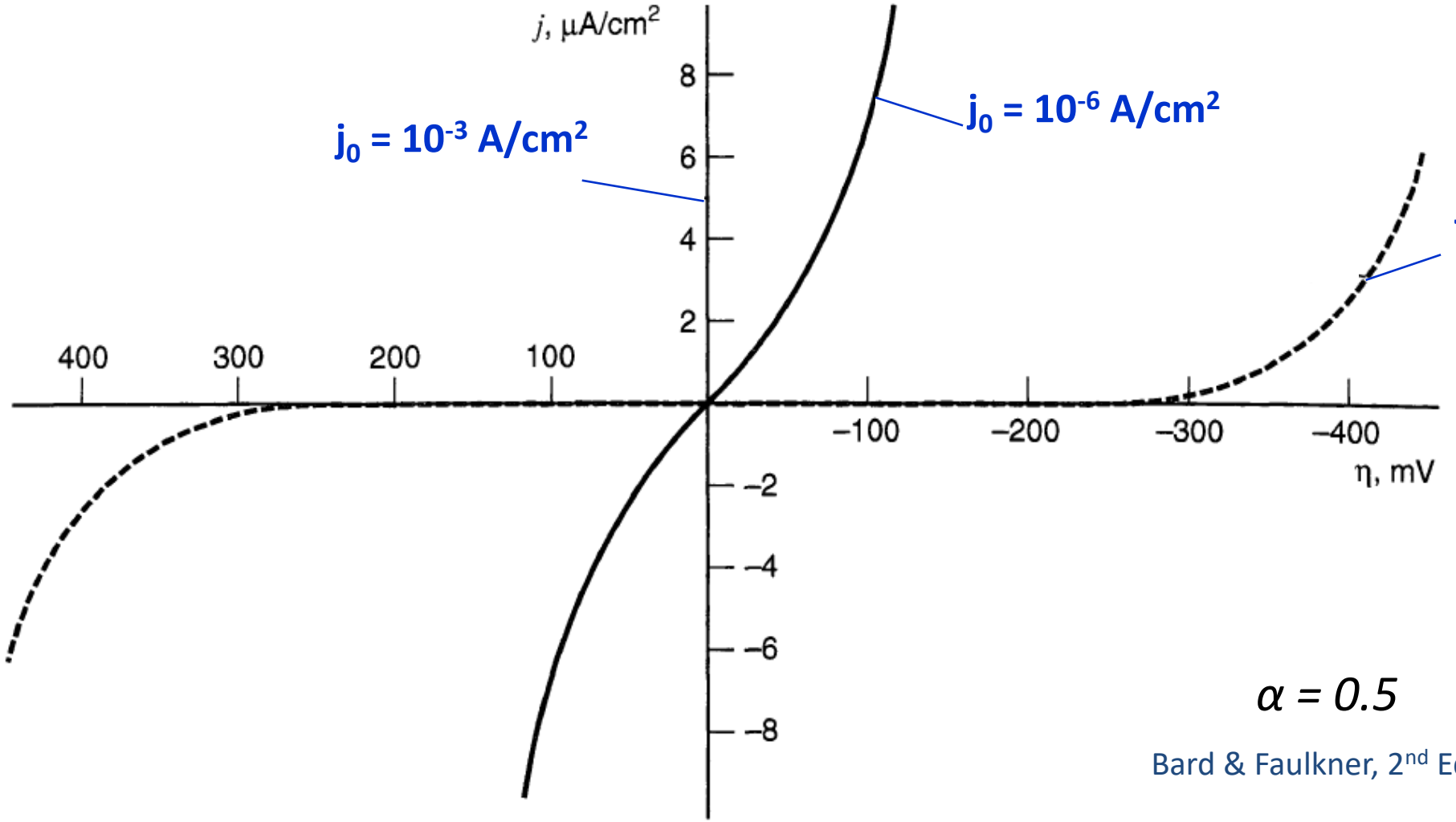
$$\frac{C_{Red}(x=0)}{C^*_{Red}} = 1 - \frac{i}{i_{L,a}}$$

$$\frac{i}{i_0} = \left(1 - \frac{i}{i_{L,c}}\right)e^{-\alpha\frac{nF}{RT}\eta} - \left(1 - \frac{i}{i_{L,a}}\right)e^{(1-\alpha)\frac{nF}{RT}\eta}]$$

Effect of mass transfer on the i-η curves

…Recall…

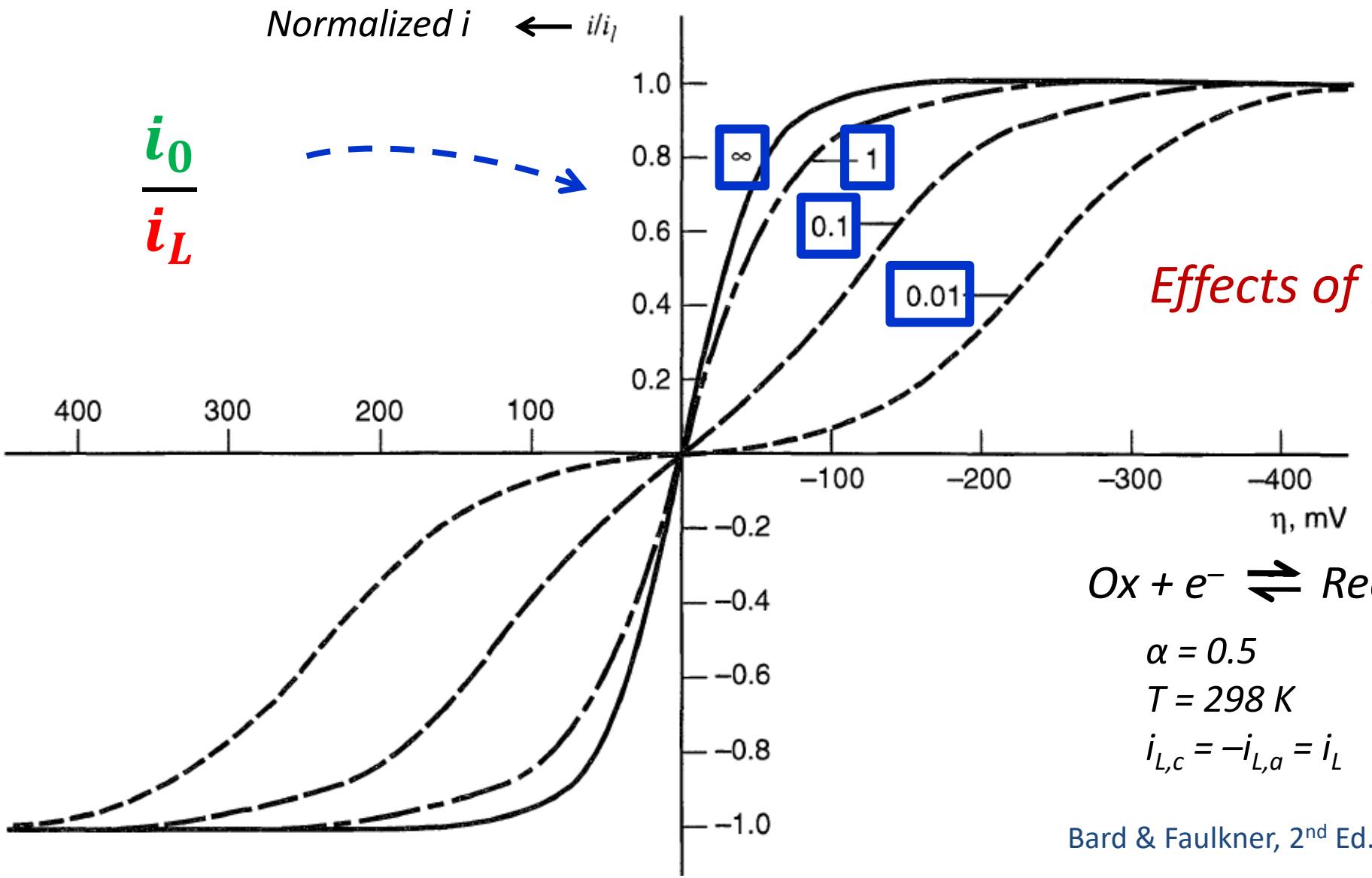
No mass transfer effect



$\alpha = 0.5$

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

Effect of mass transfer on the i-η curves



$\frac{i_0}{i_L}$

Effects of mass transfer

$Ox + e^- \rightleftharpoons Red$

$\alpha = 0.5$

$T = 298\ K$

$i_{L,c} = -i_{L,a} = i_L$

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

Charge transfer vs. Mass transfer

Butler-Volmer

$$\frac{i}{i_0} = \frac{C_{Ox}(0,t)}{C^*_{Ox}} e^{-\alpha \frac{nF}{RT}\eta} - \frac{C_{Red}(0,t)}{C^*_{Red}} e^{(1-\alpha)\frac{nF}{RT}\eta}$$

Small η approximation ⇓ *linearization (Taylor expansion)* *n = 1*

$$\frac{i}{i_0} = \frac{C_{Ox}(0,t)}{C^*_{Ox}} - \frac{C_{Red}(0,t)}{C^*_{Red}} - \frac{F}{RT}\eta$$

Considering … $\frac{C_{Ox}(0,t)}{C^*_{Ox}} = 1 - \frac{i}{i_{L,c}}$ $\frac{C_{Red}(0,t)}{C^*_{Red}} = 1 - \frac{i}{i_{L,a}}$

…we can rearrange in the form…

$$\eta = -i\frac{RT}{F}\left(\frac{1}{i_0} + \frac{1}{i_{L,c}} - \frac{1}{i_{L,a}}\right) \quad \ldots$$

Charge transfer vs. Mass transfer

…

$$\eta = -i\frac{RT}{F}\left(\frac{1}{i_0}+\frac{1}{i_{L,c}}-\frac{1}{i_{L,a}}\right) \Rightarrow \eta = -i\left(R_{ct}+R_{mt,c}+R_{mt,a}\right)$$

Charge-transfer resistance $R_{ct} = \left(\frac{RT}{nFi_0}\right)$

$$R_{mt} = \left(\frac{RT}{nF|i_L|}\right)$$

Mass-transfer resistance

$i_0 >> i_L \Rightarrow R_{ct} << R_{mt}$ (***concentration η*** *near* E_{eq})

$i_0 << i_L \Rightarrow R_{ct} >> R_{mt}$ (***activation or charge-transfer η*** *near* E_{eq})

Charge transfer vs. Mass transfer

The **shape of *i-η* curves (voltammograms)** depends on the relative values of k^0 and $m_T = D/\delta$

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

$$Ox^*_{(bulk)} \xrightarrow{m_T = D/\delta} Ox_{(x=0)} \qquad \textbf{Mass Transport}$$

$$Ox_{(x=0)} + ne^- \underset{k_{Ox}}{\overset{k_{Red}}{\rightleftharpoons}} Red_{(x=0)} \qquad \textbf{Electron transfer}$$

- **Electrochemical reversibility** ($k^0 >> m_T$) ($i_0/i_L \rightarrow \infty$): **fast ET kinetics** compared to mass transport (negligible ET activation barrier, $k^0 > 2 \cdot 10^{-4}$ m/s), so that **diffusive mass transfer is rate-limiting**
- **Electrochemical irreversibility** ($k^0 << m_T$) ($i_0/i_L \rightarrow 0$): **sluggish ET kinetics** (large ET activation barrier, $k^0 < 5 \cdot 10^{-7}$ m/s) compared to mass transport, so that **charge transfer becomes rate-limiting**
- **Electrochemical quasi-reversibility** ($k^0 \approx m_T$): intermediate cases