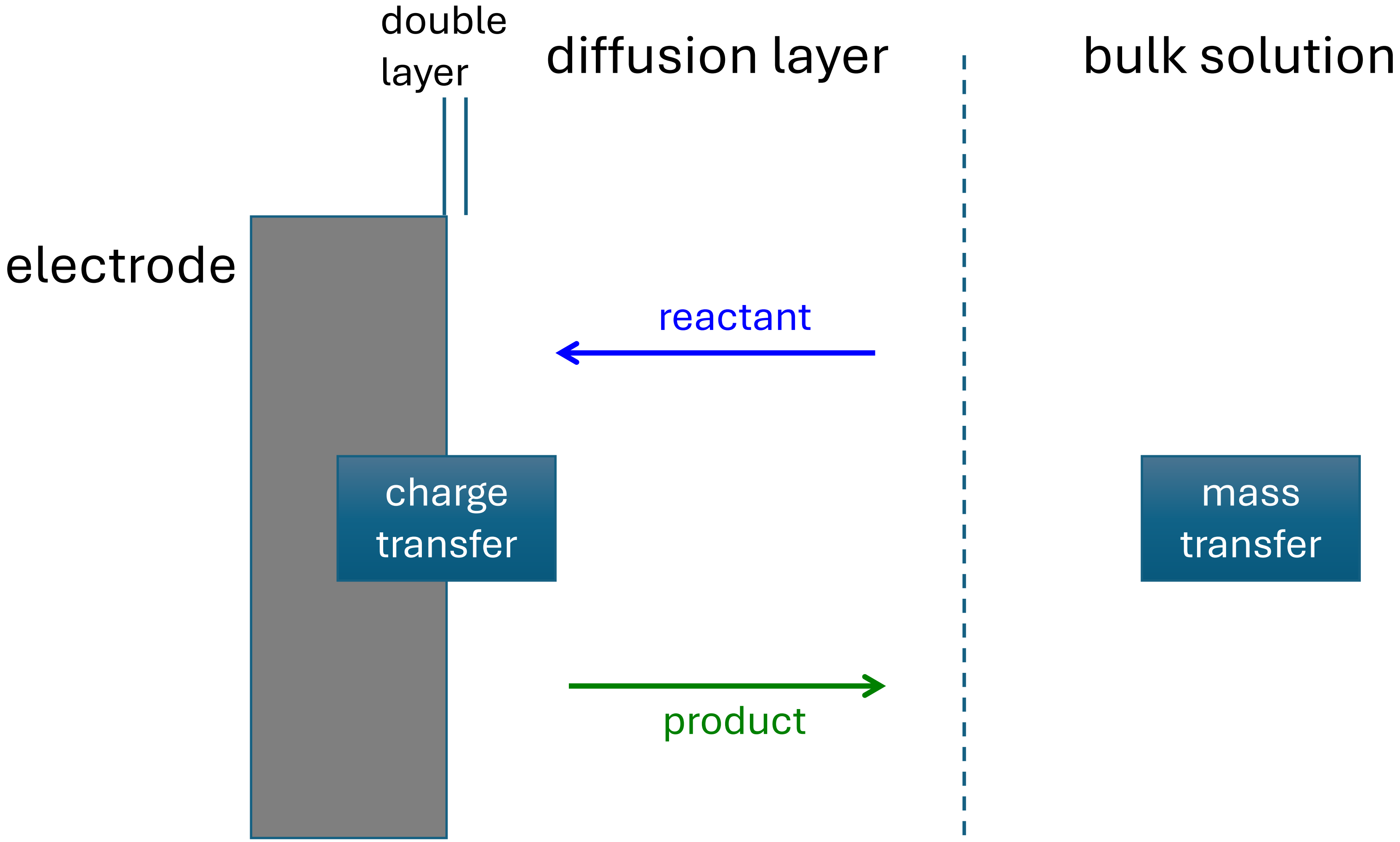
Electrochemistry for materials technology

Chapter 4

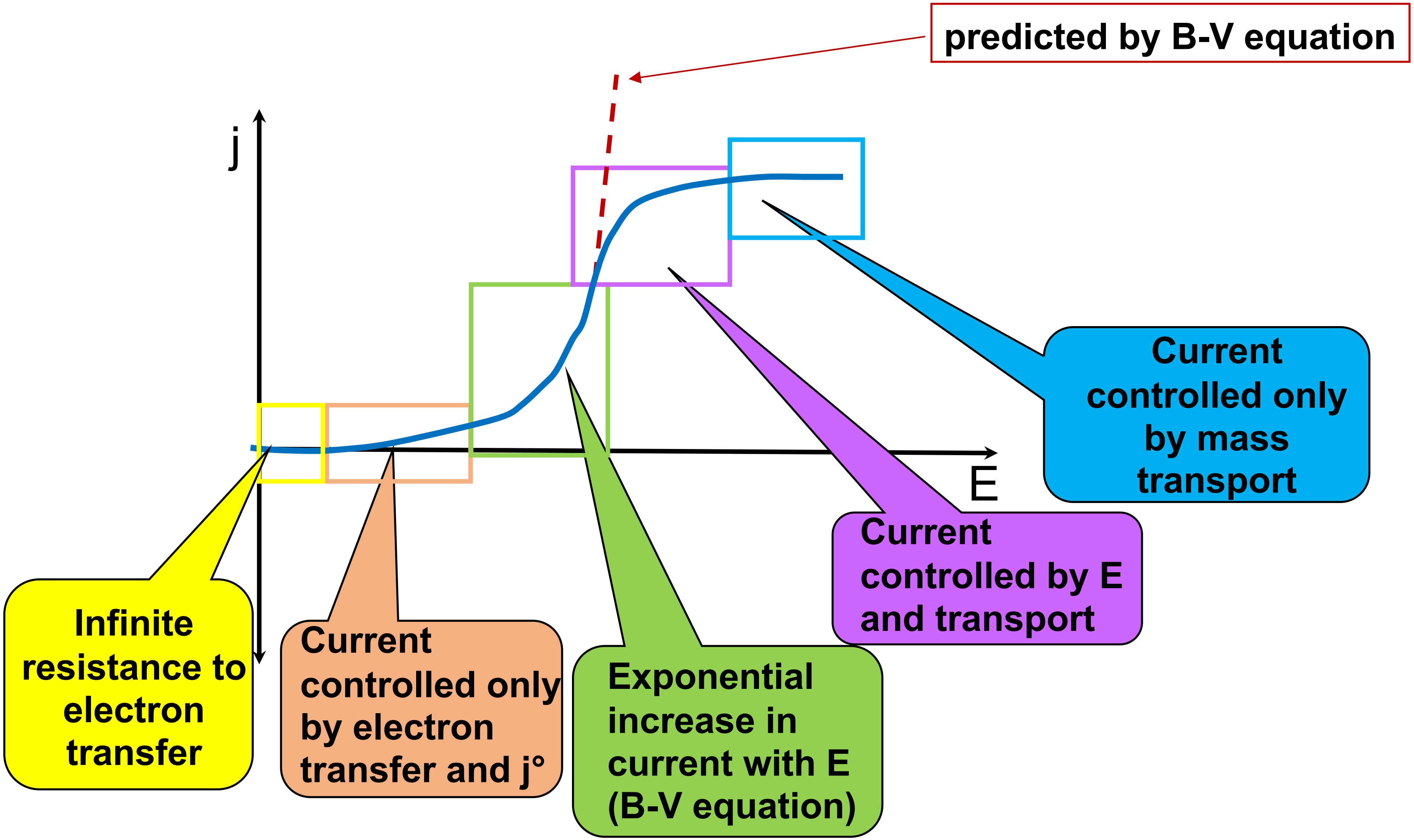
Electrode kinetics

B. Mass transfer limitation

Rate determining steps in electrochemical reactions



Observed j-V plot



predicted by B-V equation

Infinite resistance to electron transfer

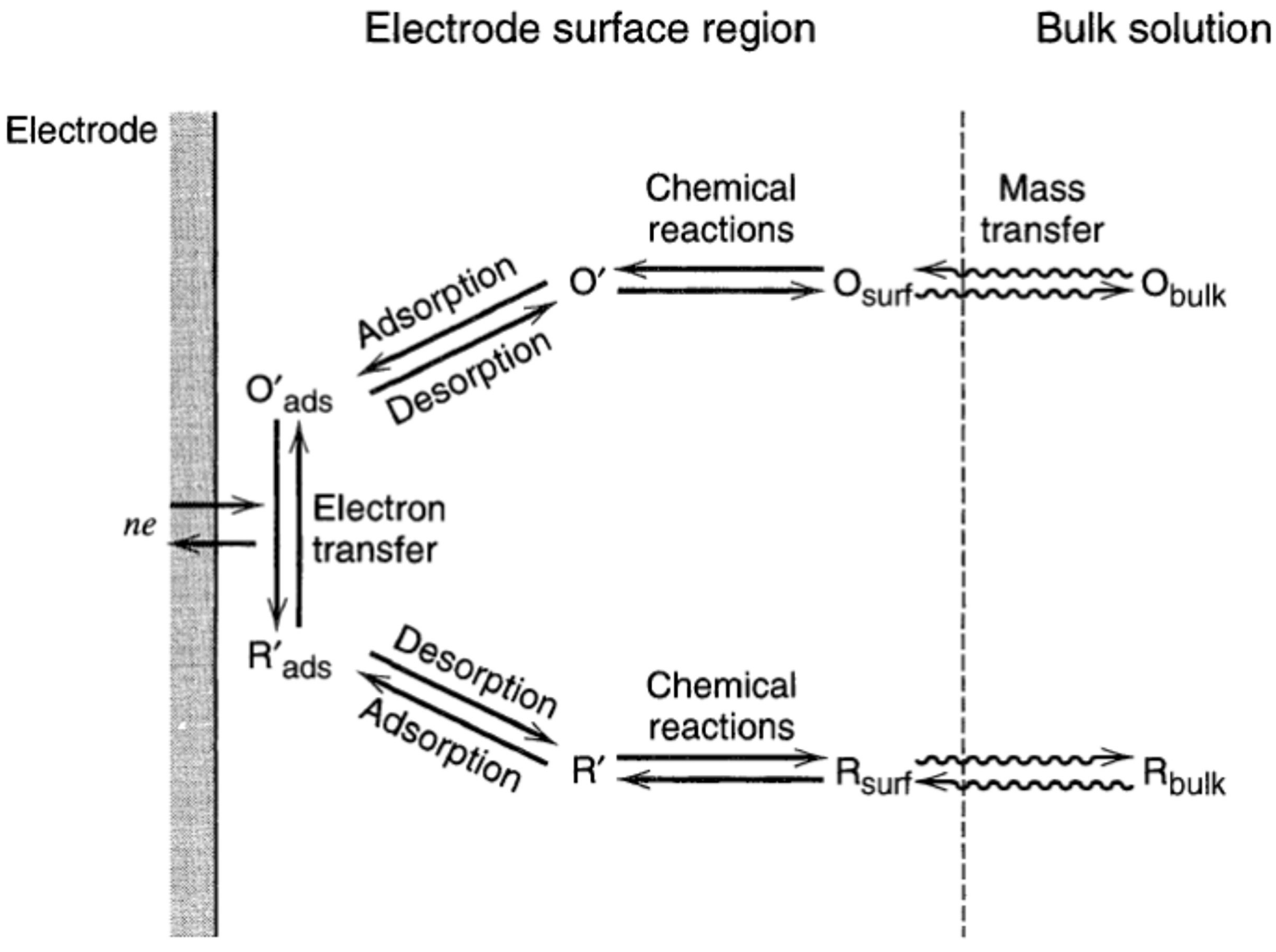
Current controlled only by electron transfer and j°

Exponential increase in current with E (B-V equation)

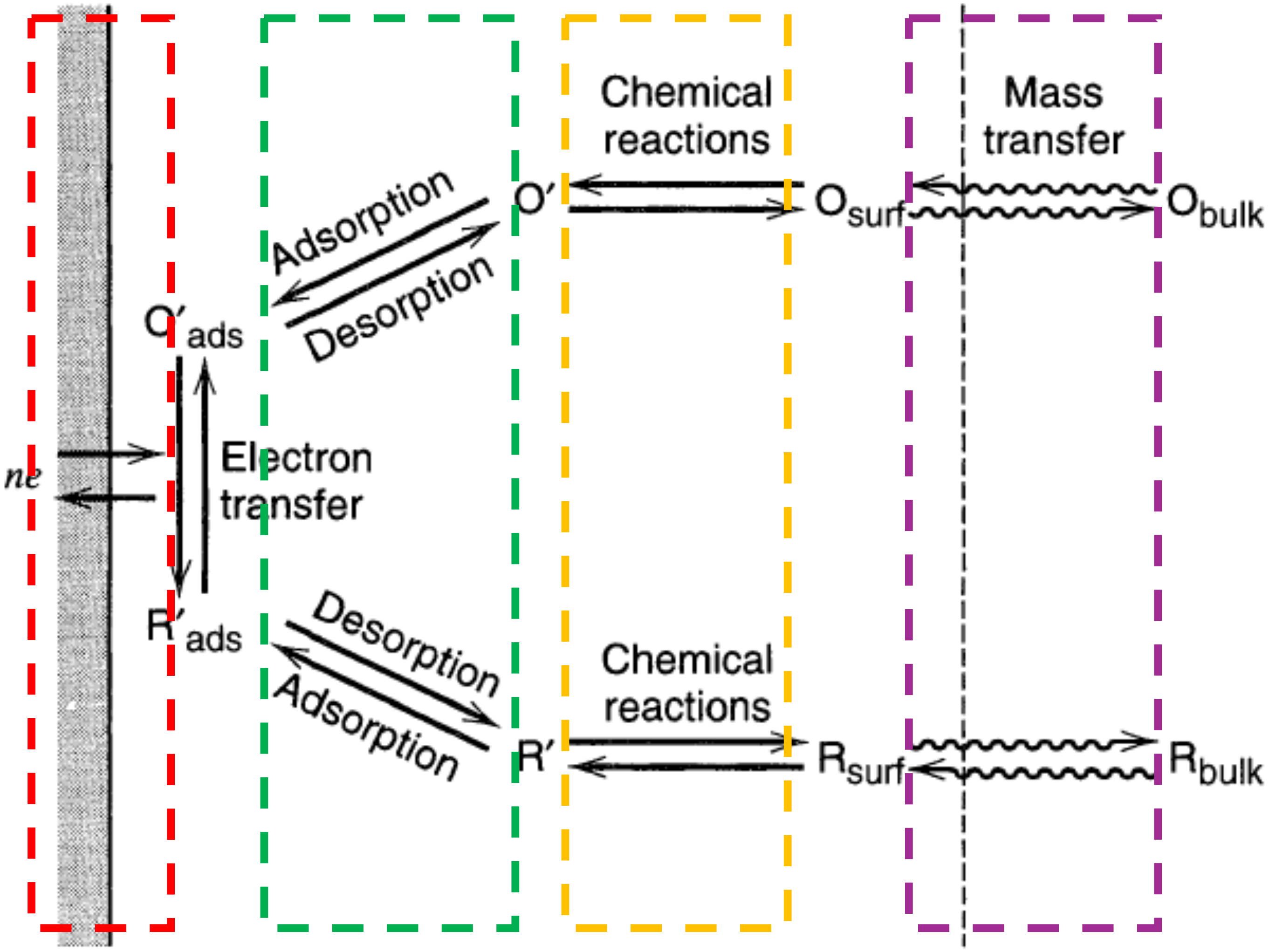
Current controlled by E and transport

Current controlled only by mass transport

B-V model with mass transport



B-V model with mass transport



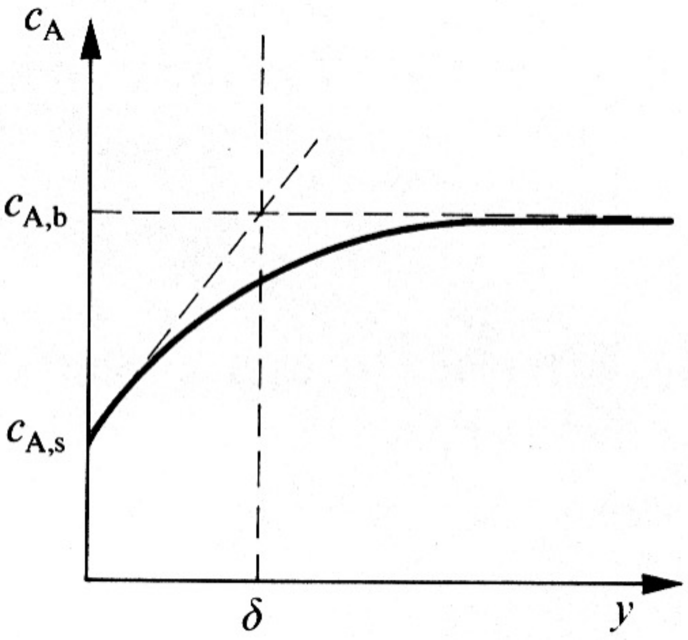
charge transfer

electric double layer

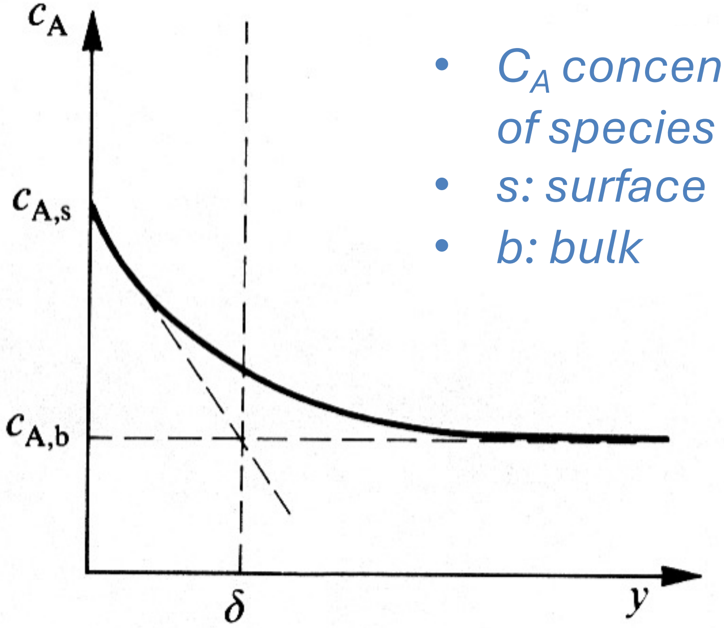
multi-step mechanisms

transport

Concentration profiles near the electrode surface



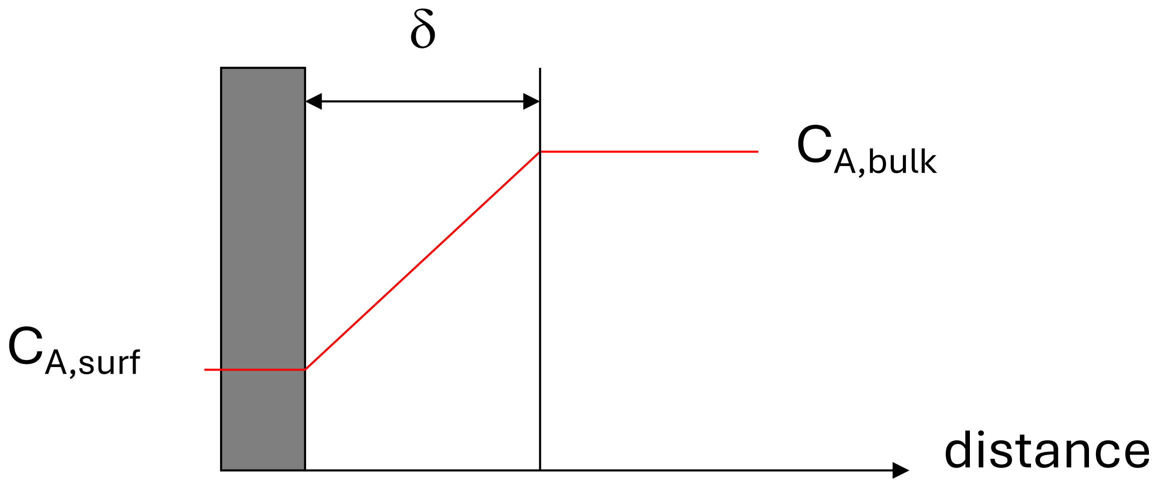
mass transport of
reactant A



mass transport of
product A

- *C_A concentration of species A*
- *s: surface*
- *b: bulk*

Flux N_A of species A normal to the electrode surface : simple scheme



$$N_A = - D_A \frac{C_{A,bulk} - C_{A,surf}}{\delta} \qquad (mol/m^2\ s)$$

D_A : coefficient of diffusion (m^2/s)

δ : thickness of Nernst diffusion layer (m)

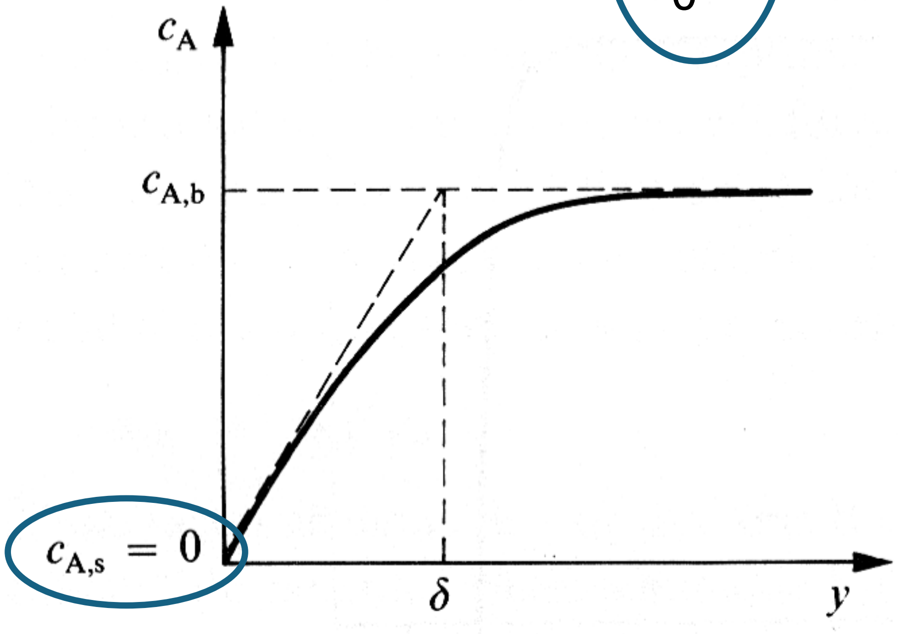
Cathodic and anodic current densities in case of mass transport limited reactions

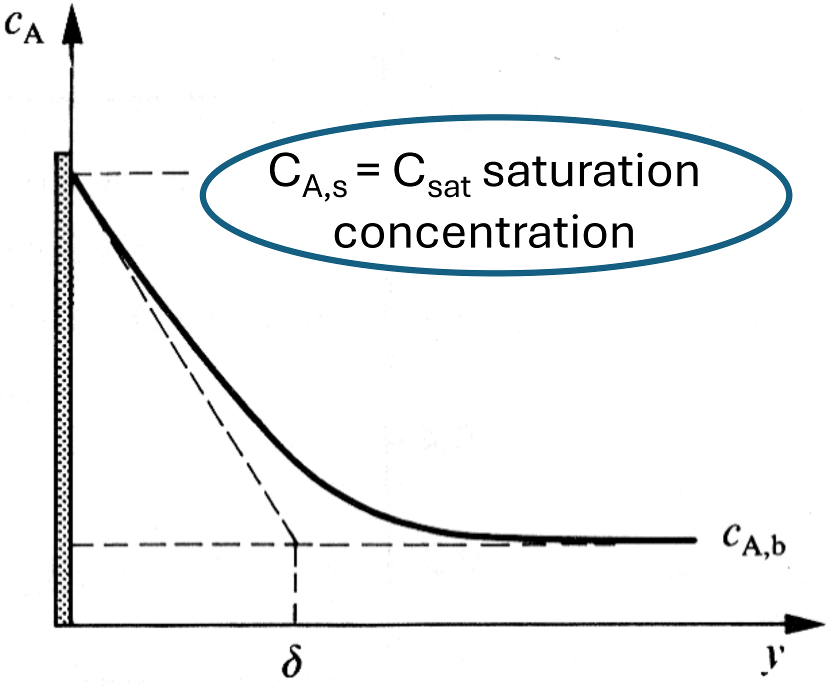
Current density	Transport of		A	N_A	i
$i_a = - n F N_A$	reactant	$Fe^{2+} \rightarrow Fe^{3+}$ oxidation	Fe^{2+}	<0	pos.
$i_a = + n F N_A$	product		Fe^{3+}	>0	pos.
$i_c = + n F N_A$	reactant	$Fe^{3+} \rightarrow Fe^{2+}$ reduction	Fe^{3+}	<0	neg.
$i_c = - n F N_A$	product		Fe^{2+}	<0	neg.

with $N_A = -D_A (C_{A,b} - C_{A,s}) / \delta$

Concentration profiles near electrode surface at the **limiting current**

with $N_A = -D_A (C_{A,b} - \underset{=0}{\boxed{C_{A,s}}}) / \delta$





$C_{A,s} = C_{sat}$ saturation concentration

$i_a = - n F N_A$

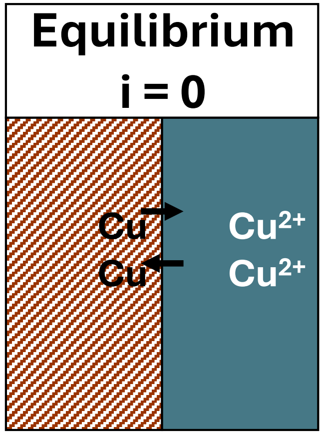
reactant

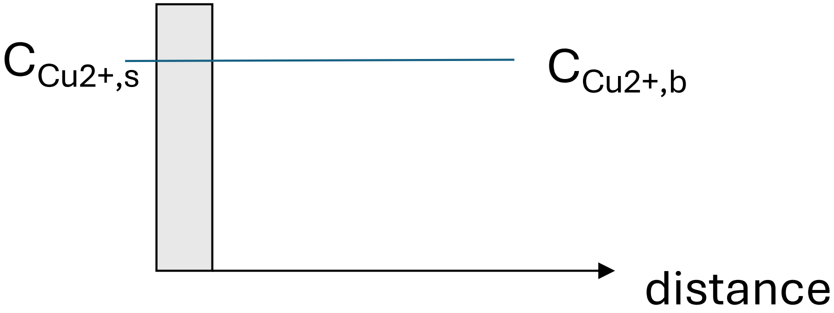
product

$i_l = +/- n F D_A c_{A,b} / \delta$

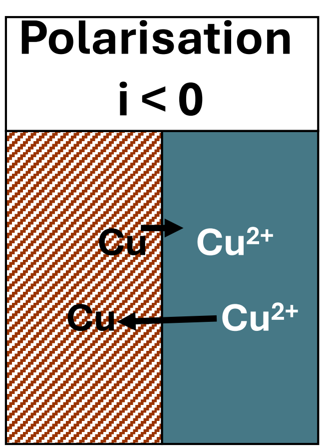
$i_l = +/- n F D_A (\boxed{c_{sat}} - c_{A,b}) / \delta$

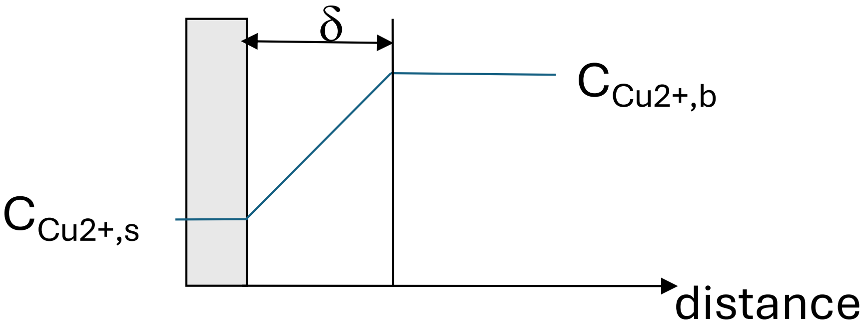
Origin of concentration overvoltage (mass transport limitation)





$$E_{i=0} = E^0 + RT/2F \ \ln c_{Cu,b}$$





reduction;
Cu plating;
i < 0

$$E_{i<0} = E^0 + RT/2F \ \ln c_{Cu,s}$$

Concentration overvoltage

Overvoltage $\eta = E - E_{rev} = RT/2F \ \ln \boxed{(c_{Cu2+,s} / c_{Cu2+,b})}$

$i = n F N_{Cu2+} = - n F D_{Cu2+} (c_{Cu2+,b} - c_{Cu2+,s}) / \delta$

reduction;
Cu plating;
$i < 0$
$\eta < 0$

$C_{bulk} > C_{surface}$

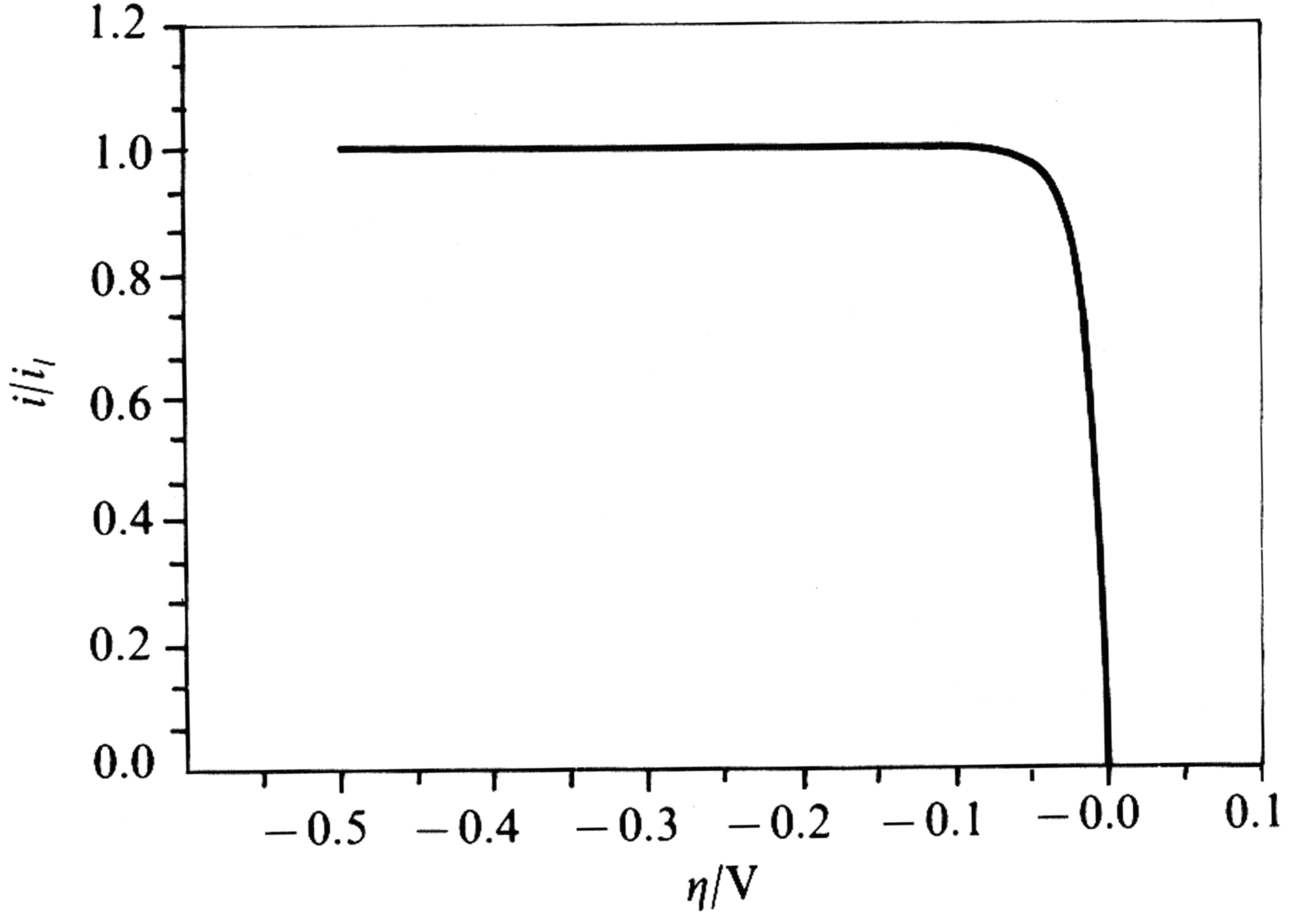
$i_l = n F N_{max,\ Cu2+} = - n F D_{Cu2+} c_{Cu2+,b} / \delta$

$C_{Cu2+,s} = 0$

$i / i_l = 1 - \boxed{(c_{Cu2+,s} / c_{Cu2+,b})}$

➡ $\mathbf{i = i_l (1 - \exp (2F/RT\ \eta))}$

Theoretical polarization curve for cathodic deposition with only concentration overvoltage



Formalism for *mixed* control: charge transfer + mass transport

Butler-Volmer (cathodic):

$[O_s]$

$$i_{c,\ Cu2+} = -\ i_{0,\ Cu2+} \frac{c_{Cu2+,\ s}}{c_{Cu2+,\ b}} \exp\left(-\ \eta / \beta_c\right)$$

$[O^*]$

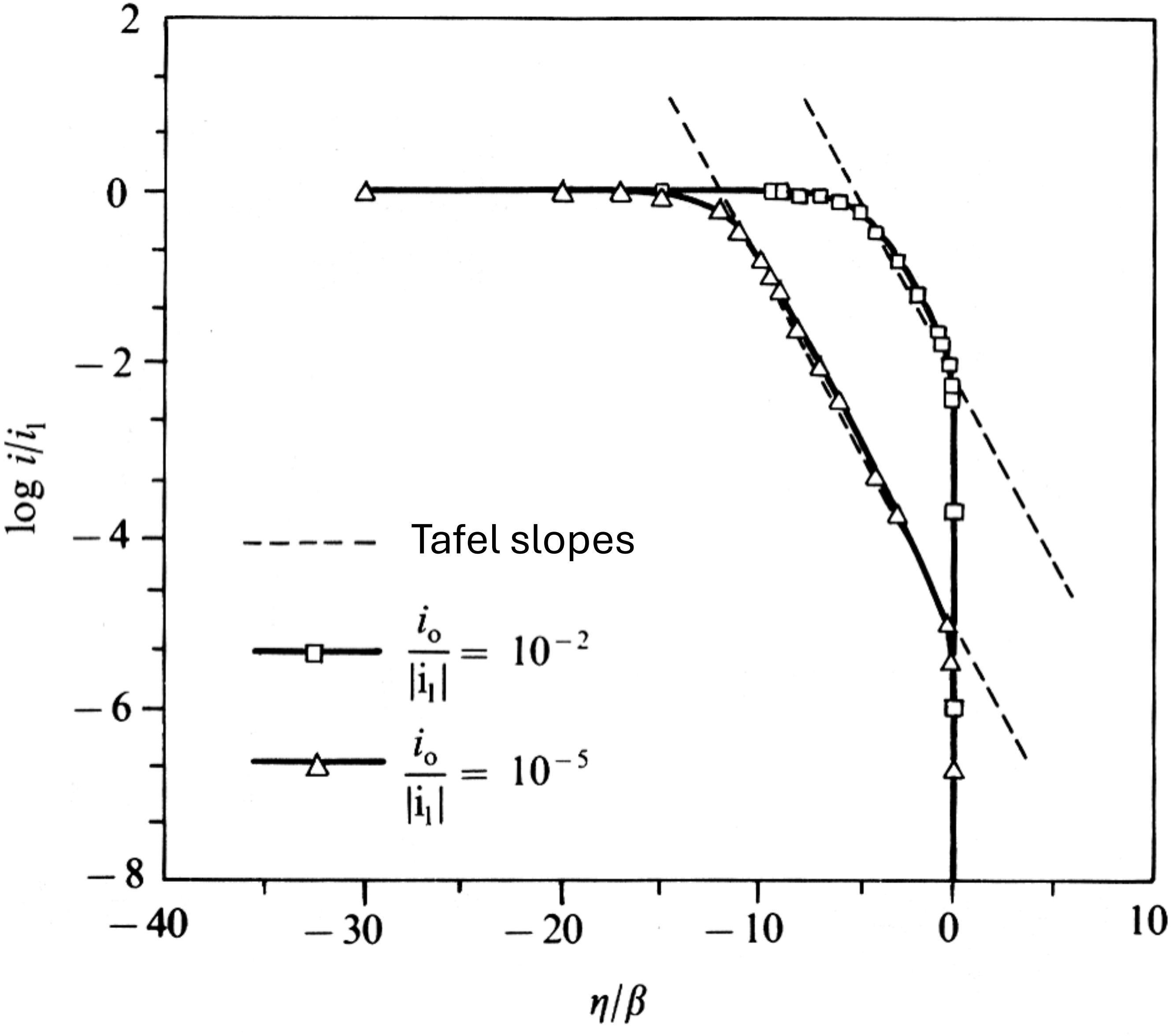
Mass transport:

$$i_c / i_l = 1 - \frac{c_{Cu2+,\ s}}{c_{Cu2+,\ b}}$$

Mixed :

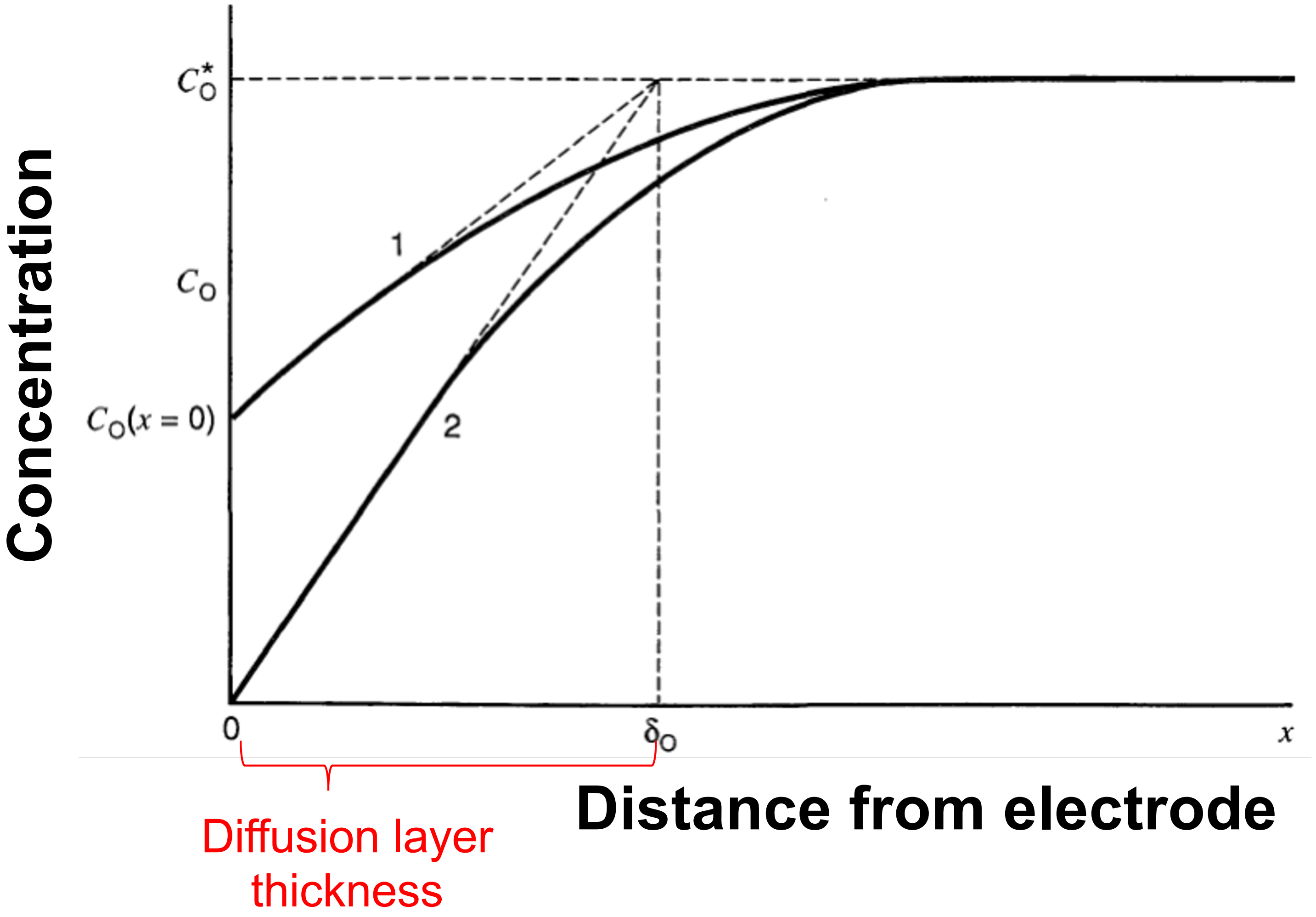
$$i_c = -\ \frac{(i_0 / i_l) \exp\left(-\ \eta / \beta_c\right)}{1 - (i_0 / i_l) \exp\left(-\ \eta / \beta_c\right)}$$

Theoretical polarization curves for a cathodic reaction under mixed control



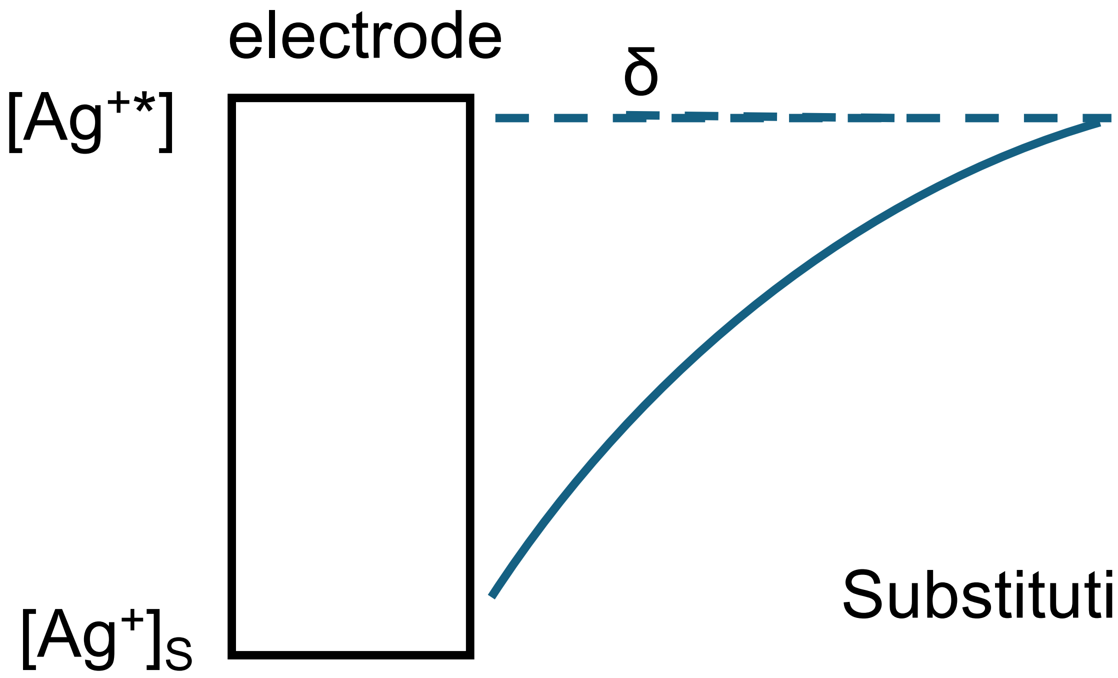
Mass transport contribution to B-V equation

- Surface concentration is determined by kinetics or Nernst Equation
- If surface reaction is fast, current is diffusion limited



Mass transport contribution to B-V equation

$Ag^+ + e^- \rightarrow Ag$



molar flux

$$J = D\,\frac{\Delta C}{\delta}$$

diffusion coefficient

Nernst thickness

Relationship between J and j:

$$j = J \cdot z \cdot F$$

$$\left[\frac{C}{s\cdot m^2}\right] = \left[\frac{mol}{s\cdot m^2}\right] \cdot \left[\frac{mol\ e-}{mol}\right] \cdot \left[\frac{C}{mol\ e-}\right]$$

Substituting the expression for flux:

$$j = \underbrace{\frac{D}{\delta}}_{\text{mass-transfer coefficient } (k_m)} \Delta C \cdot z \cdot F$$

(units of velocity m/s)

Mass transport contribution to B-V equation

$$j = \frac{D}{\delta} \Delta C \cdot z \cdot F$$

$$j = k_m([C^*]-[C]_S) \cdot z \cdot F$$

For limiting case where $[C]_S=0$: $j_{lim} = k_m[C^*] \cdot z \cdot F$

C* : bulk concentration

By substituting for k_m and rearranging,

$$\frac{[C]_S}{[C^*]} = 1 - \frac{j}{j_{lim}}$$

Notes about the mass transfer coefficient k_m :

- Mass transfer coefficients are measurement technique-dependent (e.g. stirring), and, in some cases, time-dependent.
- Both k° (frequency factor, Ch. 3 slides 46-47) and k_m have units of [cm/s]
- When $k° >> k_m$, j-V curves are controlled by mass transport
- When $k° << k_m$, j-V curves are controlled by charge transfer kinetics

Mass transport contribution to B-V equation

If we consider the two different species, [R] and [O], which affect the anode and cathode, then (chapter 3, p.82):

$$\frac{j}{j^{\circ}} = \frac{[R]_s}{[R^*]}\, e^{\frac{\alpha_a zF}{RT}\acute{\eta}} - \frac{[O]_s}{[O^*]}\, e^{\frac{-(1-\alpha_a)zF}{RT}\acute{\eta}}$$

Limiting current for anodic reaction $j_{lim,a}$:

$$\frac{[R]_S}{[R^*]} = 1 - \frac{j}{j_{lim,a}}$$

Limiting current for cathodic reaction $j_{lim,c}$:

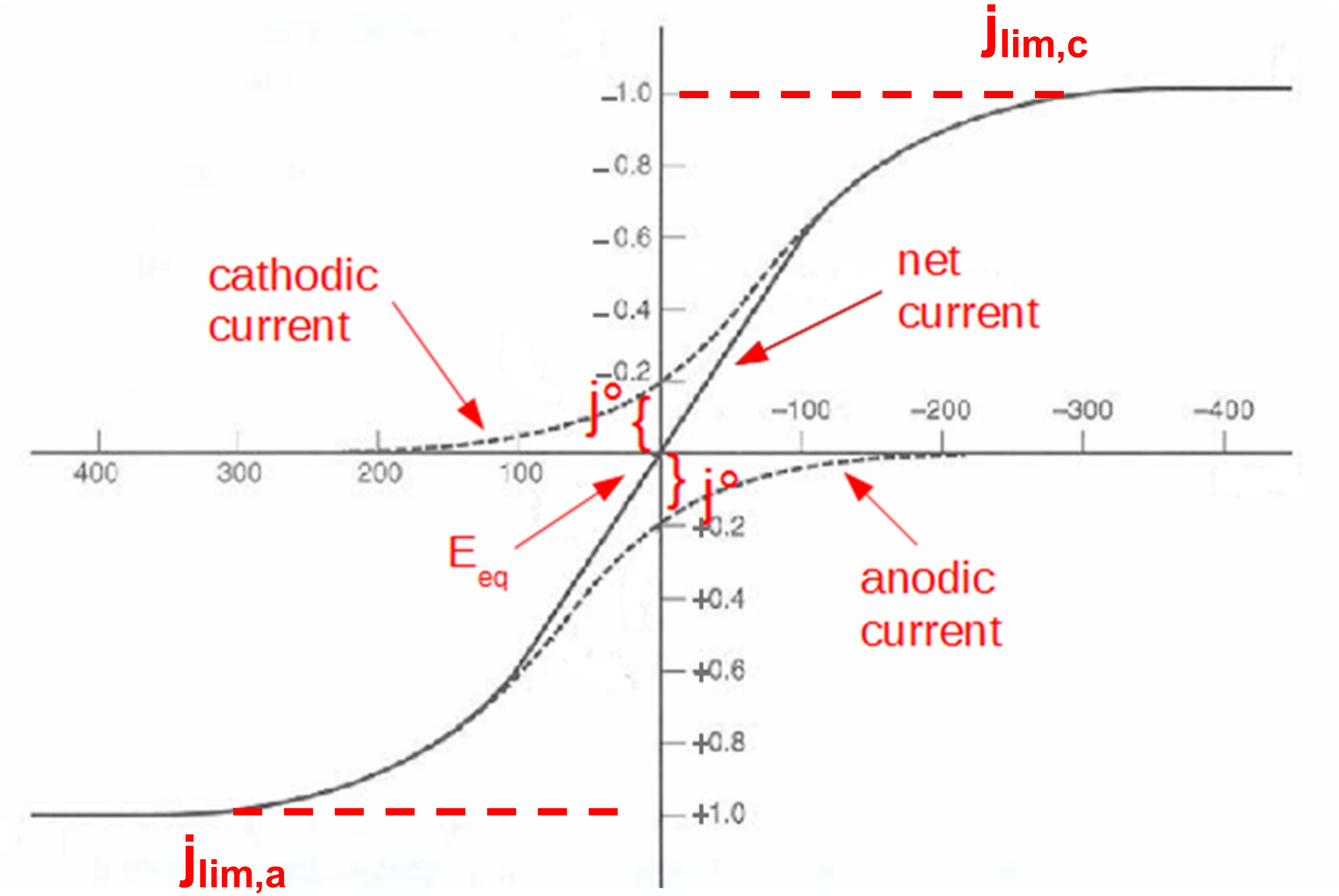
$$\frac{[O]_S}{[O^*]} = 1 - \frac{j}{j_{lim,c}}$$

Substitution

Butler-Volmer model with Mass Transport limitations

$$\boxed{\frac{j}{j^{\circ}} = \left[1 - \frac{j}{j_{lim,a}}\right] e^{\frac{\alpha_a zF}{RT}\acute{\eta}} - \left[1 - \frac{j}{j_{lim,c}}\right] e^{\frac{-(1-\alpha_a)zF}{RT}\acute{\eta}}}$$

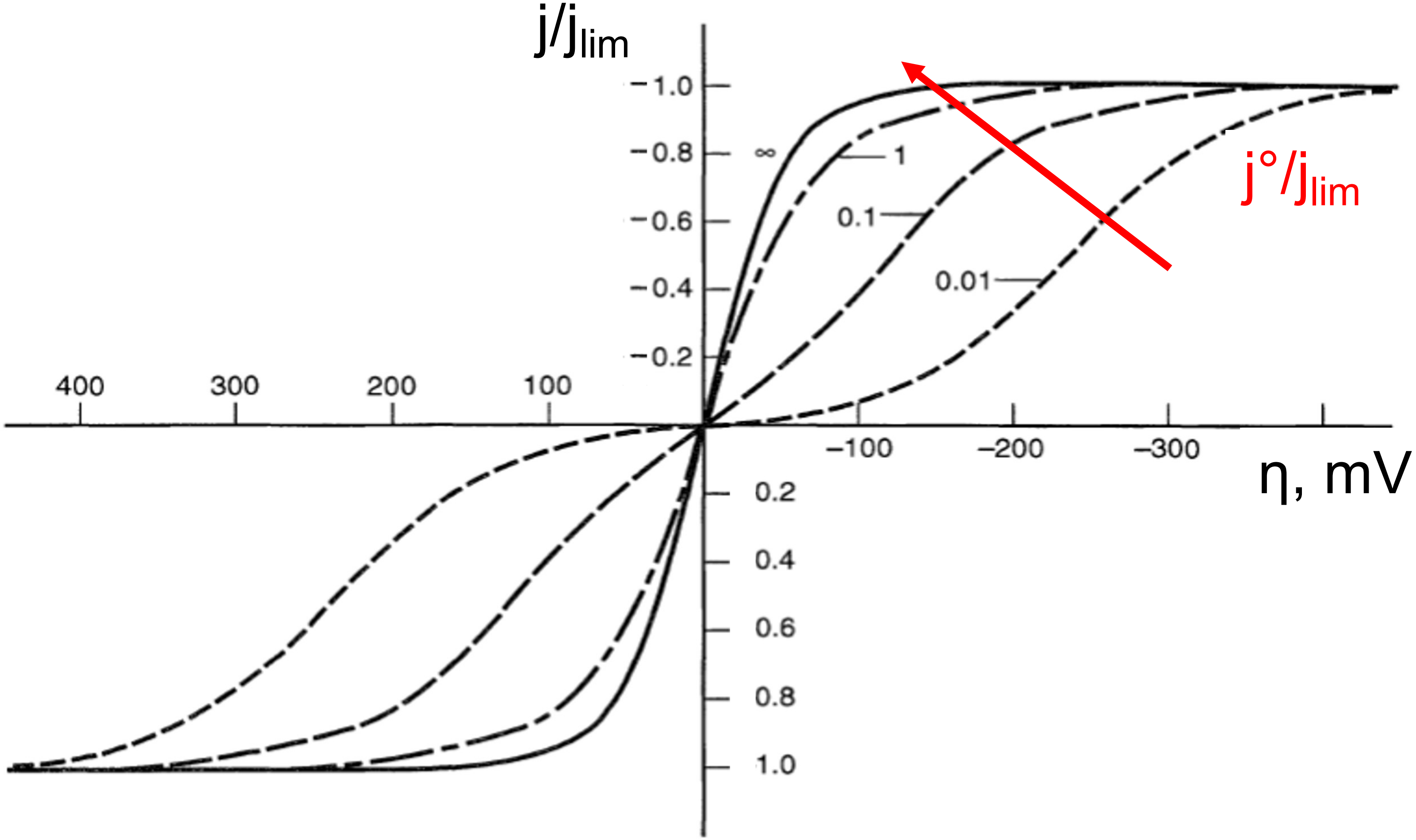
Mass transport contribution to B-V equation



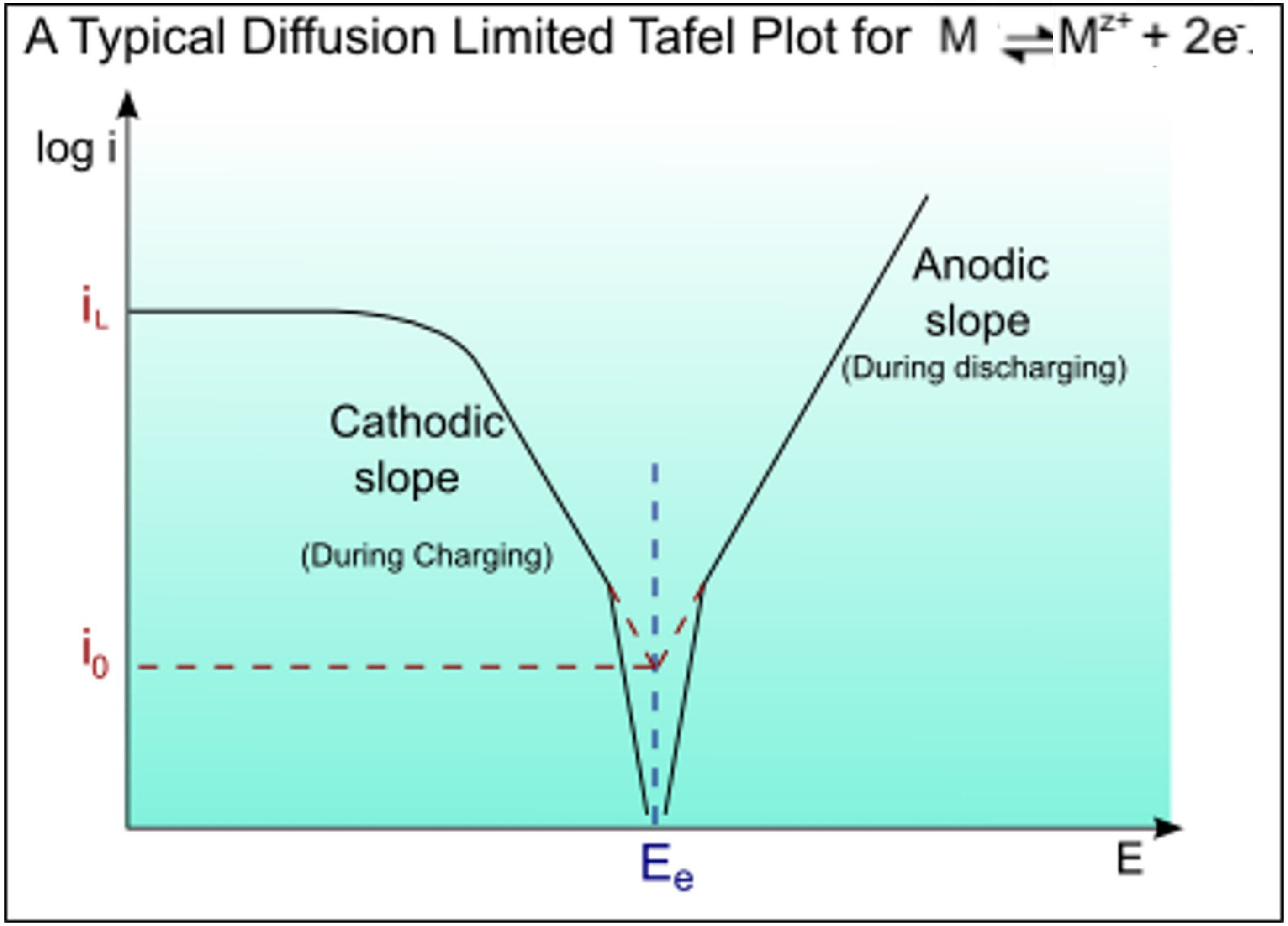
Mass transport contribution to B-V equation

Increasing $j°/j_{lim}$ decreases the onset potential at which current is observed.
All curves with high $j°/j_{lim}$ look the same (mass transfer limited)

→ No kinetic information can be derived from them



Mass transport contribution to B-V equation



Deposition is typically limiting, whereas dissolution is not.
Same for e.g. H^+ reduction or O_2 reduction (limited), whereas H_2 evolution or O_2 evolution are not.

Simplification for mass transport form of B-V equation: 1. small η

Analogous simplifications as before hold for

($\acute{\eta} \sim 0$, $\acute{\eta} << 0$, $\acute{\eta} >> 0$)

For $\acute{\eta} \sim 0$, linearization via Taylor series

$$\acute{\eta} = \frac{j}{f}\left[\frac{1}{j^{\circ}} + \frac{1}{j_{lim,a}} - \frac{1}{j_{lim,c}}\right] = j\left[\frac{RT}{j^{\circ}zF} + \frac{RT}{j_{lim,a}zF} - \overbrace{\frac{RT}{\underbrace{j_{lim,c}}_{<0}zF}}^{>0}\right]$$

$f = zF/RT$

$$\acute{\eta} = j \cdot [R_{ct} + R_{mt,a} + R_{mt,c}]$$

charge transfer resistance

$$R_{ct} = \frac{RT}{j^{\circ}zF}$$

mass transfer resistance @ anode

$$R_{mt,a} = \frac{RT}{j_{lim,a}zF}$$

mass transfer resistance @ cathode

$$R_{mt,c} = \frac{RT}{|j_{lim,c}|zF}$$

Simplification for mass transport form of B-V equation: 2. large η

For large $E\text{-}E_{eq}$ → $|ή| >> \frac{RT}{zF}$

Depending on whether a positive or negative potential is applied, we have either

$e^{\alpha_a f ή} >> e^{-(1-\alpha_a) f ή}$

if ή > 0

or

$e^{\alpha_a f ή} << e^{-(1-\alpha_a) f ή}$

if ή < 0

Simplification for mass transport form of B-V equation: 2. large η

$$\boxed{\text{For large } E\text{-}E_{eq} \rightarrow |\acute{\eta}| >> \frac{RT}{zF}}$$

for ή > 0
(anodic)

$$e^{\alpha_a f\acute{\eta}} >> e^{-(1-\alpha_a)f\acute{\eta}}$$

$$j = j^{\circ}\left[\left[1 - \frac{j}{j_{lim,a}}\right]e^{\frac{\alpha_a zF}{RT}\acute{\eta}} - \cancel{\left[1 - \frac{j}{j_{lim,c}}\right]e^{\frac{-(1-\alpha_a)zF}{RT}\acute{\eta}}}\right]$$

$$j \sim j^{\circ}\left[1 - \frac{j}{j_{lim,a}}\right]e^{\frac{\alpha_a zF}{RT}\acute{\eta}} \Rightarrow \frac{j}{j^{\circ}\left[1 - \frac{j}{j_{lim,a}}\right]} = e^{\frac{\alpha_a zF}{RT}\acute{\eta}}$$

$$\frac{j \cdot j_{lim,a}}{j^{\circ}(j_{lim,a} - j)} = e^{\frac{\alpha_a zF}{RT}\acute{\eta}}$$

Simplification for mass transport form of B-V equation: 2. large η

$$\frac{j \cdot j_{lim,a}}{j^{\circ}(j_{lim,a} - j)} = e^{\frac{\alpha_a zF}{RT}\acute{\eta}}$$

$$\frac{j_{lim,a}}{j^{\circ}} \cdot \frac{j}{j_{lim,a} - j} = e^{\frac{\alpha_a zF}{RT}\acute{\eta}}$$

$$\ln\frac{j_{lim,a}}{j^{\circ}} + \ln\frac{j}{j_{lim,a} - j} = \frac{\alpha_a zF}{RT}\acute{\eta}$$

$$\eta = a + b \ln\frac{j}{j_{lim,a} - j}$$

Tafel plot form

$$\boxed{\acute{\eta} = \overbrace{\frac{RT}{\alpha_a zF}\ln\frac{j_{lim,a}}{j^{\circ}}}^{a} + \overbrace{\frac{RT}{\alpha_a zF}}^{b}\ln\frac{j}{j_{lim,a} - j}}$$

$$\frac{j_{lim,a}}{j_{lim,a} - j} \cdot \frac{j}{j^{\circ}} = e^{\frac{\alpha_a zF}{RT}\acute{\eta}}$$

$$\ln\frac{j_{lim,a}}{j_{lim,a} - j} + \ln\frac{j}{j^{\circ}} = \frac{\alpha_a zF}{RT}\acute{\eta}$$

Overpotential form

$$\boxed{\acute{\eta} = \overbrace{\frac{RT}{\alpha_a zF}\ln\frac{j_{lim,a}}{j_{lim,a} - j}}^{\text{concentration overpotential } (\eta_{conc})} + \overbrace{\frac{RT}{\alpha_a zF}\ln\frac{j}{j^{\circ}}}^{\text{activation overpotential } (\eta_{act})}}$$

Simplifications for mass transport form of B-V equation: 2. large η

Concentration overpotential is the overpotential required to produce a current that involves the depletion of charge-carriers at the electrode surface (mass transfer limited).

As $j \rightarrow 0$,
$\eta_{conc} \rightarrow 0$

As $j \rightarrow j_{lim}$,
$\eta_{conc} \rightarrow$ dominates

Activation overpotential is the overpotential required to produce a current that depends on the activation energy of the redox reaction.

As $j \rightarrow 0$,
$\eta_{act} \rightarrow$ dominates

As $j \rightarrow j_{lim}$,
$\eta_{act} \rightarrow$ constant

Simplifications for mass transport form of B-V equation: 2. large η

For large $E\text{-}E_{eq}$ → $|ή| >> \frac{RT}{zF}$

Depending on whether a positive or negative potential is applied, we have either

$$e^{\alpha_a f ή} >> e^{-(1-\alpha_a) f ή}$$

if ή > 0

or

$$e^{\alpha_a f ή} << e^{-(1-\alpha_a) f ή}$$

if ή < 0

Simplifications for mass transport form of B-V equation: 2. large η

$$\boxed{\text{For large } E\text{-}E_{eq} \rightarrow |\acute{\eta}| >> \frac{RT}{zF}}$$

for $\acute{\eta} < 0$
(cathodic)

$$e^{\alpha_a f \acute{\eta}} << e^{-(1-\alpha_a) f \acute{\eta}}$$

via analogous derivation as for $\acute{\eta} > 0$ (anodic)….

$$\eta = a + b \ln \frac{|j - j_{limc}|}{|j|}$$

Tafel plot form

$$\boxed{\acute{\eta} = \overbrace{\frac{RT}{(1-\alpha_a)zF} \ln \frac{|j°|}{|j_{lim,c}|}} + \overbrace{\frac{RT}{(1-\alpha_a)zF}} \ln \frac{|j - j_{lim,c}|}{|j|}}$$

Overpotential form

$$\boxed{\acute{\eta} = \overbrace{\frac{RT}{(1-\alpha_a)zF} \ln \frac{|j - j_{lim,c}|}{|j_{lim,c}|}}^{\text{concentration overpotential } (\eta_{conc})} + \overbrace{\frac{RT}{(1-\alpha_a)zF} \ln \frac{|j°|}{|j|}}^{\text{activation overpotential } (\eta_{act})}}$$

Simplifications of B-V equation: large η

for η > 0 (anodic)

$$\acute{\eta} = \frac{RT}{\alpha_a zF} \ln \frac{j_{lim,a}}{j°} + \frac{RT}{\alpha_a zF} \ln \frac{j}{j_{lim,a} - j}$$

Tafel plot form

$$\acute{\eta} = \frac{RT}{\alpha_a zF} \ln \frac{j_{lim,a}}{j_{lim,a} - j} + \frac{RT}{\alpha_a zF} \ln \frac{j}{j°}$$

Overpotential form

for η < 0 (cathodic)

$$\acute{\eta} = \frac{RT}{(1-\alpha_a)zF} \ln \frac{|j°|}{|j_{lim,c}|} + \frac{RT}{(1-\alpha_a)zF} \ln \frac{|j - j_{lim,c}|}{|j|}$$

Tafel plot form

$$\acute{\eta} = \frac{RT}{(1-\alpha_a)zF} \ln \frac{|j - j_{lim,c}|}{|j_{lim,c}|} + \frac{RT}{(1-\alpha_a)zF} \ln \frac{|j°|}{|j|}$$

Overpotential form

Total overpotential and interpretation of its components

Recall:

Overpotential represents the extra energy required to overcome reaction energy barriers

→ Increases minimum voltage required for electrolysis / battery charge

→ Decreases the maximum voltage obtained from a fuel cell / battery discharge

We usually want to minimize the overpotential of a device

$$\eta_{\text{total overpotential}} = \sum |\acute{\eta}_{\text{individual overpotentials}}|$$

Galvanic (fuel) cell:

$$E_{\text{overall}} = E_{\text{eq}} - |\acute{\eta}_{\text{total overpotential}}|$$

Faradaic (electrolysis) cell:

$$E_{\text{overall}} = E_{\text{eq}} + |\acute{\eta}_{\text{total overpotential}}|$$

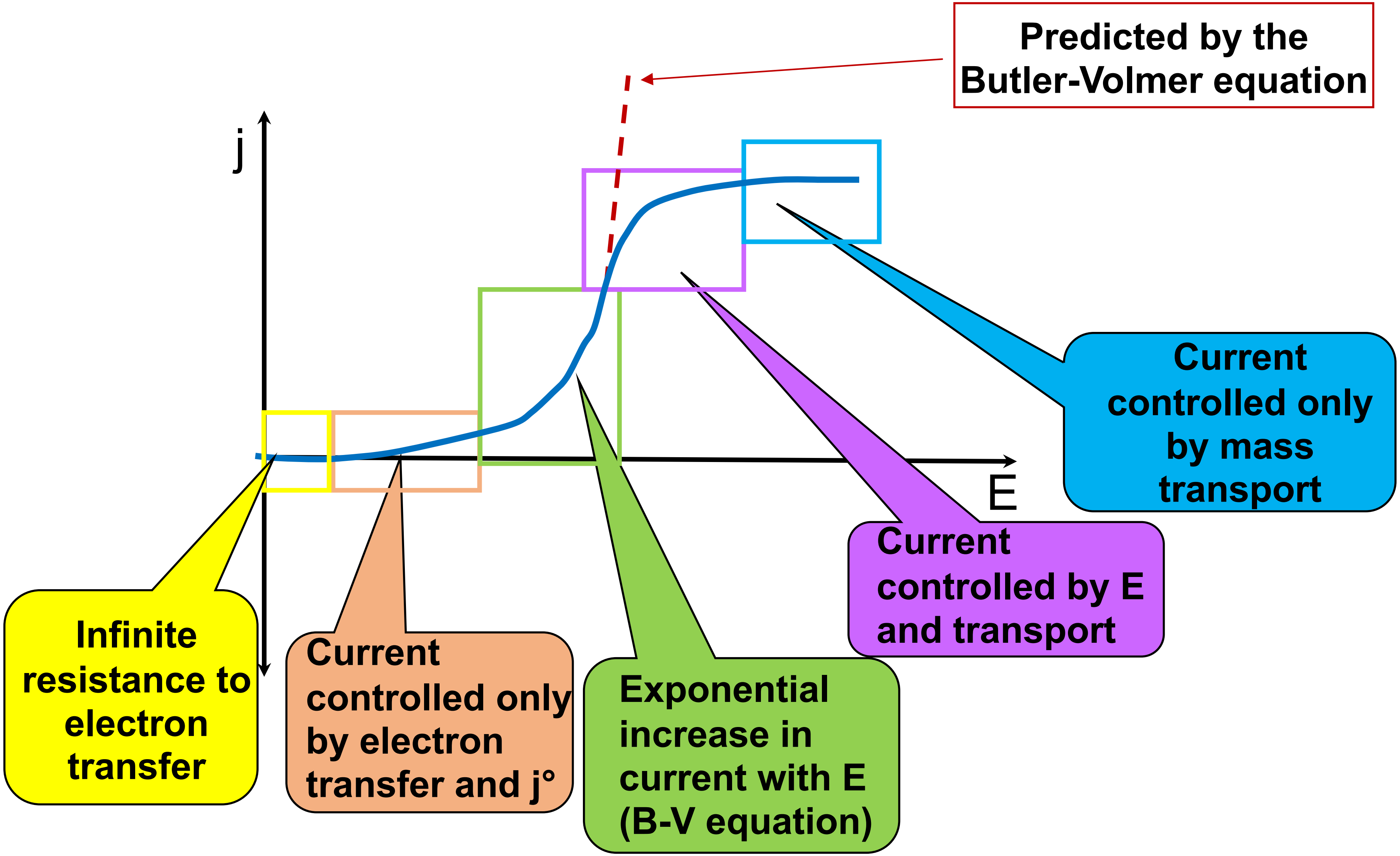
Total overpotential and interpretation of its components

$$E_{overall} = E_{eq} - |\acute{\eta}_{total\ overpotential}| = E_{eq} - \sum|\acute{\eta}_{individual\ overpotentials}|$$

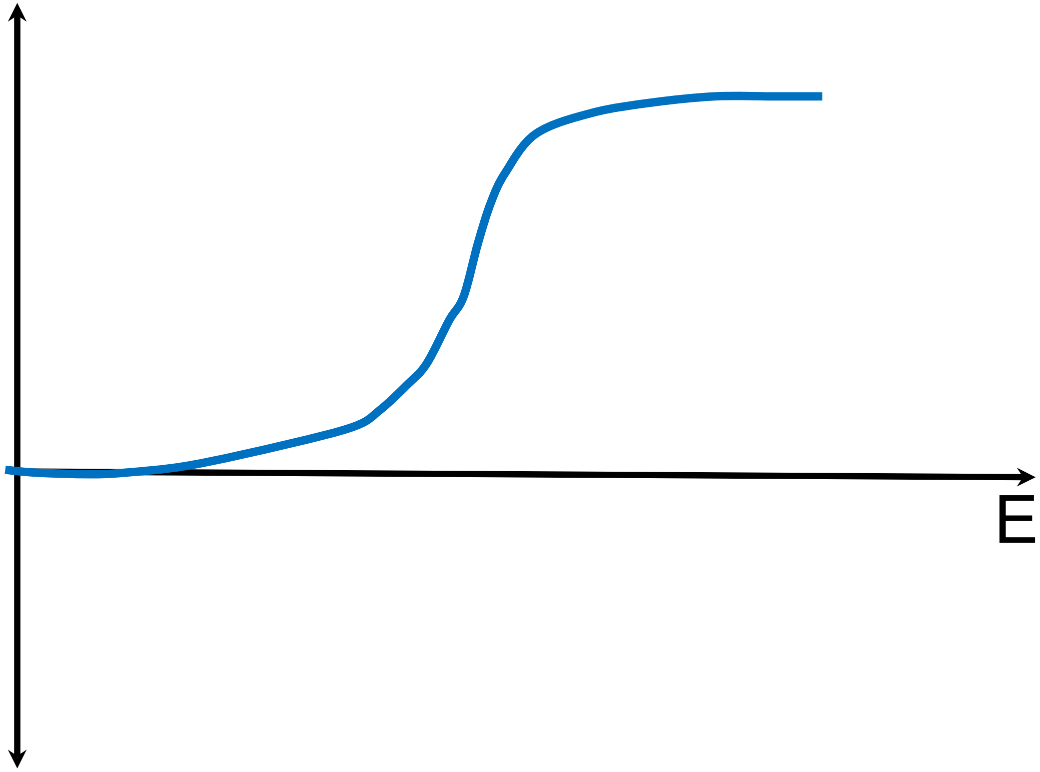
Individual overpotentials include cathodic, anodic, and electrolytic (=ohmic) components

$$E_{overall} = E_{eq} \underbrace{- \overbrace{|\acute{\eta}_{conc,c}| - |\acute{\eta}_{act,c}|}^{\text{cathodic overpotential}} - \overbrace{|\acute{\eta}_{conc,a}| - |\acute{\eta}_{act,a}|}^{\text{anodic overpotential}} - \overset{\text{electrolytic ohmic drop}}{|\acute{\eta}_{ohm}|}}_{- \left|\frac{RT}{(1-\alpha_a)zF} \ln \frac{|j - j_{lim,c}|}{|j_{lim,c}|}\right| - \left|\frac{RT}{(1-\alpha_a)zF} \ln \frac{|j^{\circ}|}{|j|}\right| - \left|\frac{RT}{\alpha_a zF} \ln \frac{j_{lim,a}}{j_{lim,a} - j}\right| - \left|\frac{RT}{\alpha_a zF} \ln \frac{j}{j^{\circ}}\right| - |j\overset{\text{electrolyte resistance}}{\boxed{AR_{ohm}}}|}$$

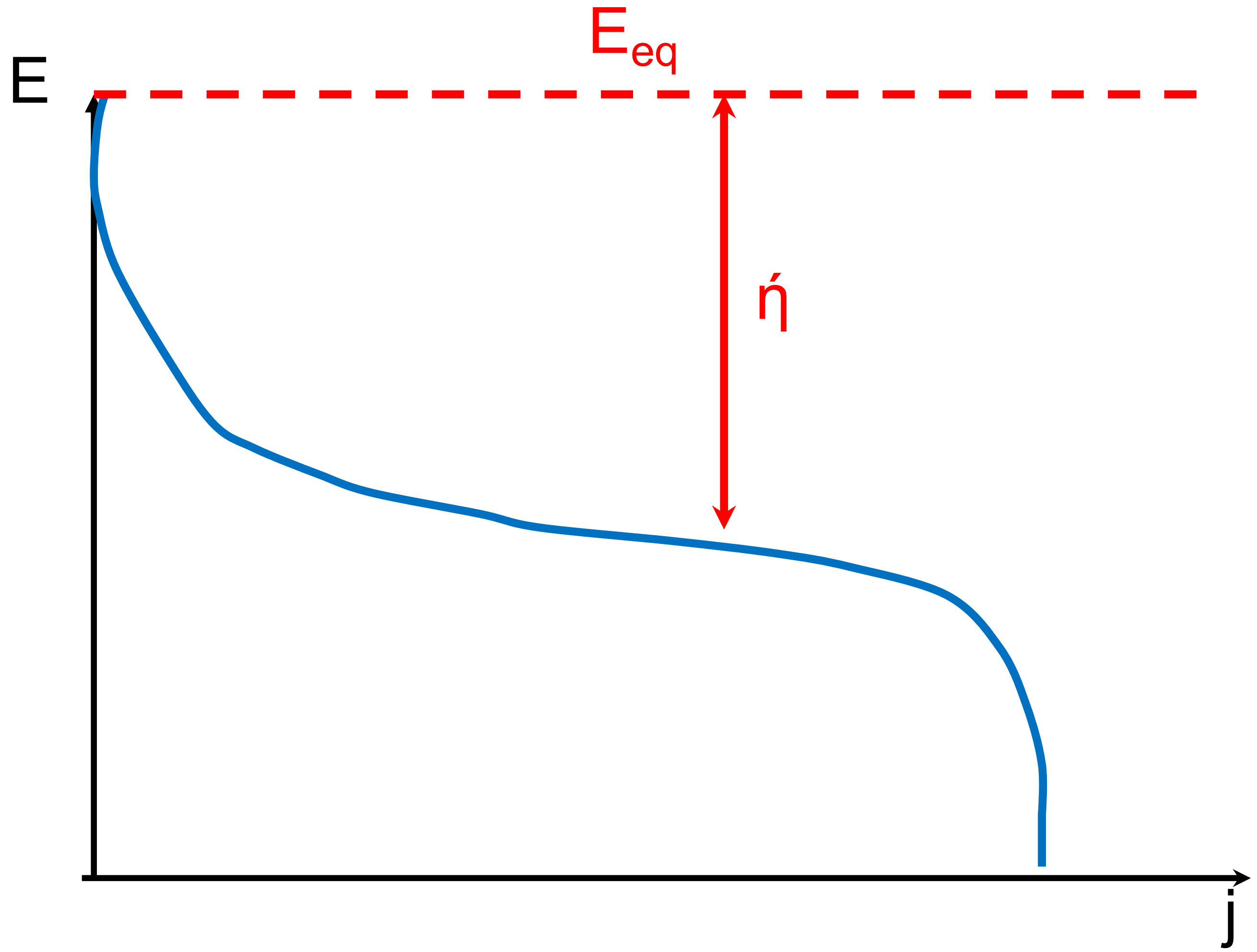
Total overpotential and interpretation of its components



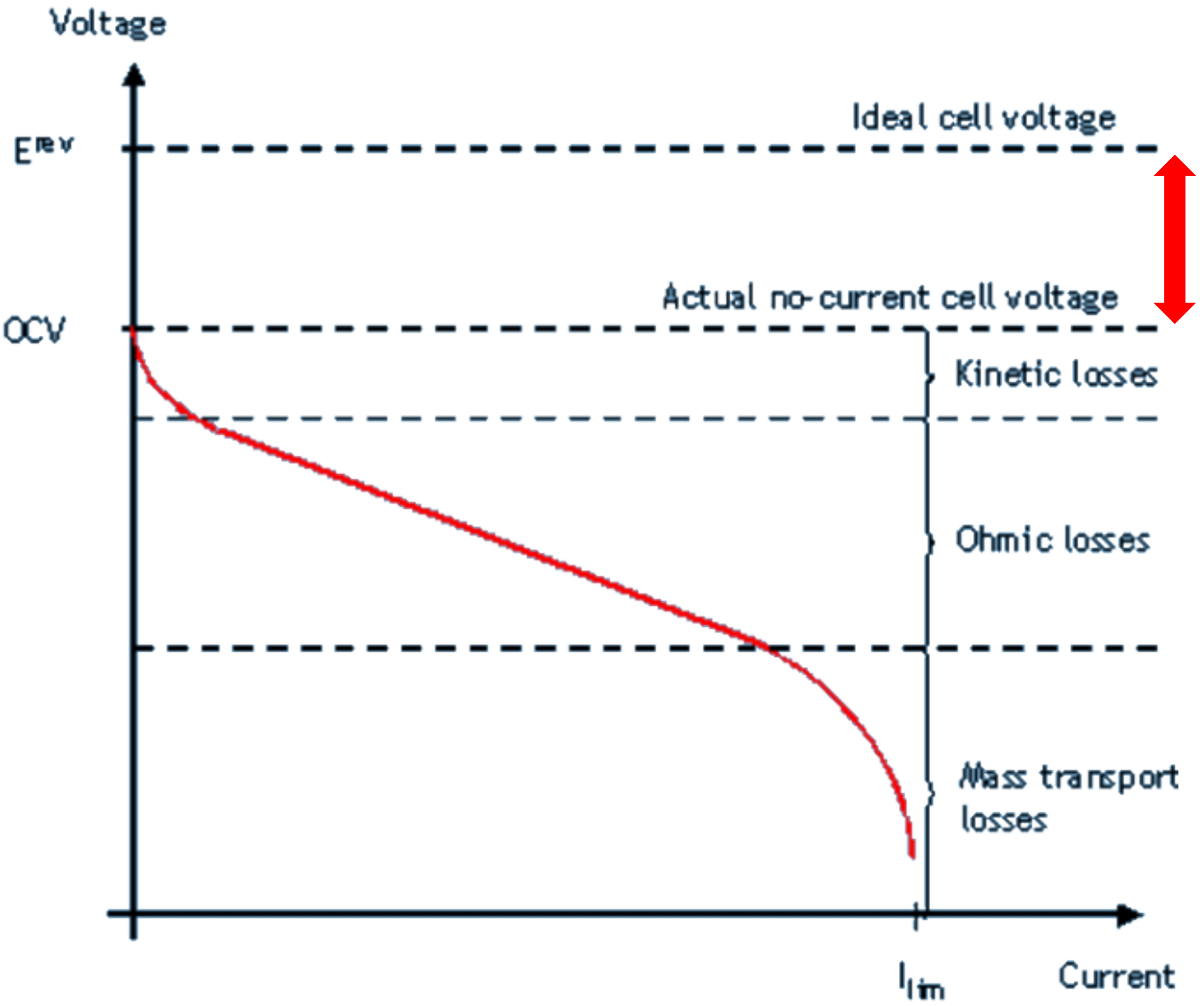
Total overpotential and interpretation of its components



Total overpotential and interpretation of its components

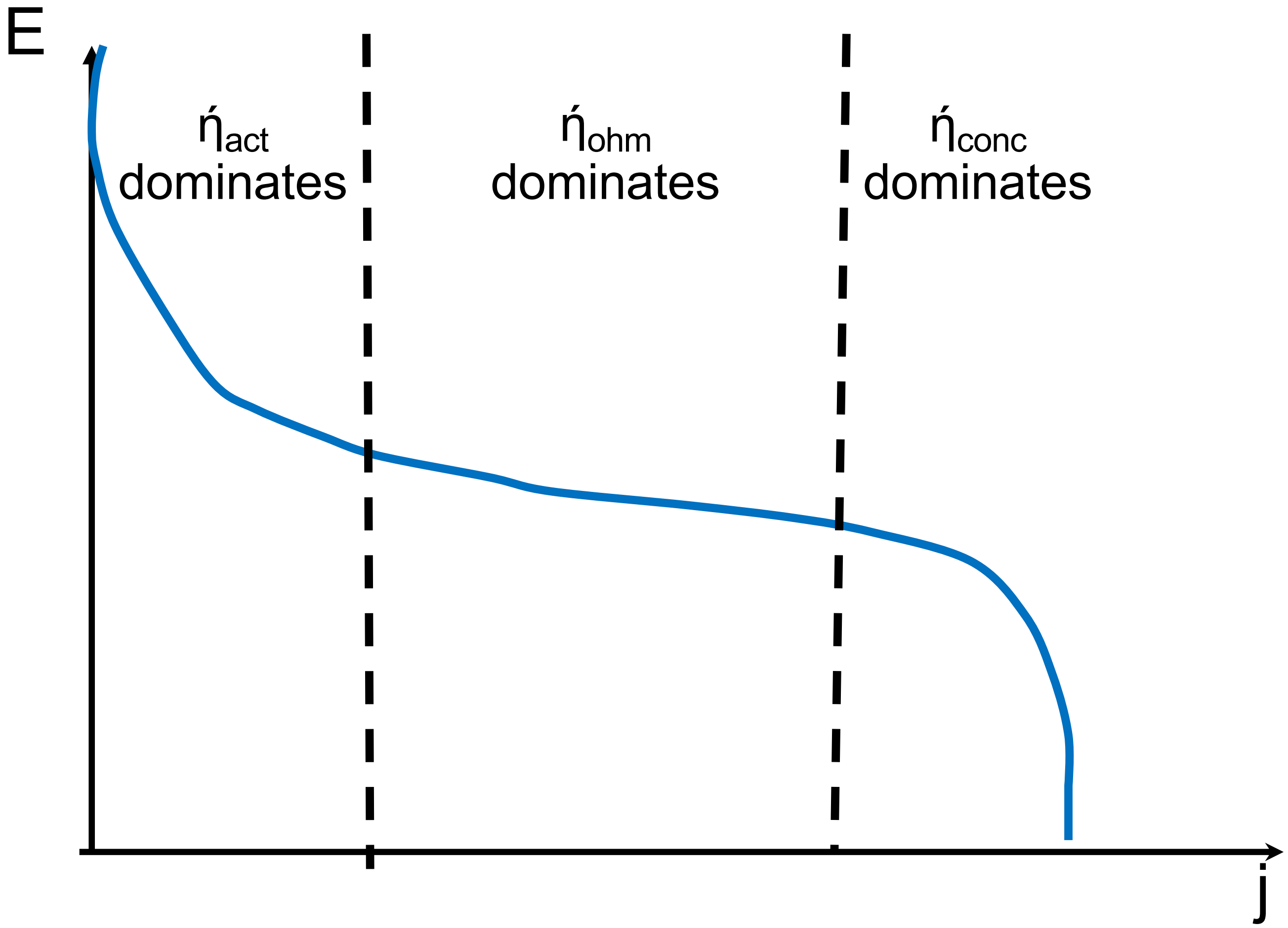


Total overpotential and interpretation of its components



Other loss (leakage, corrosion,…)

Total overpotential and interpretation of its components



Total overpotential and interpretation of its components

Low j

($j << j_{lim}$)

ή$_{act}$ dominates

$$E_{overall} \approx E_{eq} - \left| \frac{RT}{(1-\alpha_a)zF} \ln \frac{|j°|}{|j|} \right| - \left| \frac{RT}{\alpha_a zF} \ln \frac{j}{j°} \right|$$

Higher j

ή$_{ohm}$ dominates

$$E_{overall} \approx E_{eq} - const - jAR_{ohm}$$

Highest j

($j \rightarrow j_{lim}$)

ή$_{conc}$ dominates

$$E_{overall} \approx E_{eq} - const. - \left| \frac{RT}{(1-\alpha_a)zF} \ln \frac{|j - j_{lim,c}|}{|j_{lim,c}|} \right| - \left| \frac{RT}{\alpha_a zF} \ln \frac{j_{lim,a}}{j_{lim,a} - j} \right|$$

Simplifications for Mass Transport Form of the Butler-Volmer Equation: large η

As $j \rightarrow 0$,

$\eta_{conc} \rightarrow 0$

$\eta_{act} \rightarrow$ dominates

As $j \rightarrow j_{lim}$,

$\eta_{conc} \rightarrow$ dominates

$\eta_{act} \rightarrow$ constant

$$- \underbrace{\left| \frac{RT}{(1-\alpha_a)zF} \ln \frac{|j - j_{lim,c}|}{|j_{lim,c}|} \right|}_{\eta_{conc}} - \underbrace{\left| \frac{RT}{(1-\alpha_a)zF} \ln \frac{|j^{\circ}|}{|j|} \right|}_{\eta_{act}} - \underbrace{\left| \frac{RT}{\alpha_a zF} \ln \frac{j_{lim,a}}{j_{lim,a} - j} \right|}_{\eta_{conc}} - \underbrace{\left| \frac{RT}{\alpha_a zF} \ln \frac{j}{j^{\circ}} \right|}_{\eta_{act}}$$

Total overpotential and interpretation of its components

Low j

($j << j_{lim}$)

$\acute{\eta}_{act}$ dominates

$$E_{overall} \approx E_{eq} - \left| \frac{RT}{(1-\alpha_a)zF} \ln \frac{|j°|}{|j|} \right| - \left| \frac{RT}{\alpha_a zF} \ln \frac{j}{j°} \right|$$

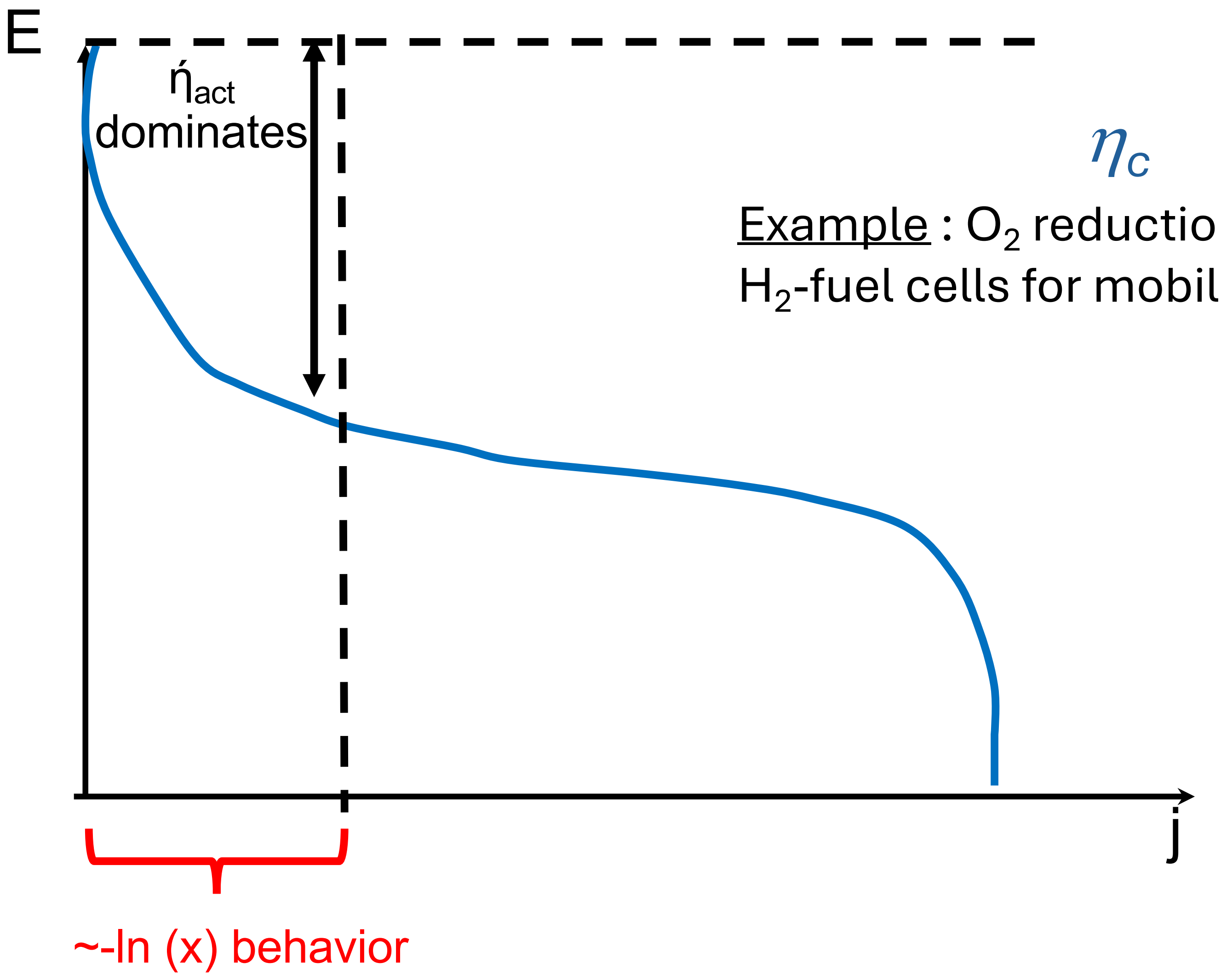
$$- \underbrace{\cancel{\left| \frac{RT}{(1-\alpha_a)zF} \ln \frac{|j - j_{lim,c}|}{|j_{lim,c}|} \right|}}_{\text{approaches 0}} - \underbrace{\left| \frac{RT}{(1-\alpha_a)zF} \ln \frac{|j°|}{|j|} \right|}_{\eta_c \Downarrow} - \underbrace{\cancel{\left| \frac{RT}{\alpha_a zF} \ln \frac{j_{lim,a}}{j_{lim,a} - j} \right|}}_{\text{approaches 0}} - \underbrace{\left| \frac{RT}{\alpha_a zF} \ln \frac{j}{j°} \right|}_{\eta_\alpha \Downarrow} \underbrace{- |jAR_{ohm}|}_{\text{assume negligible ohmic losses}}$$

The ln of a very large (or very small) number is a very positive (or negative) value.

η_{act} represents energy needed to just barely start producing current

Effect is clearly seen when $j << j_{lim}$, $j << j°$, and R_{ohm} is very small.

Total overpotential and interpretation of its components



Example : O_2 reduction reaction in H_2-fuel cells for mobility

Total overpotential and interpretation of its components

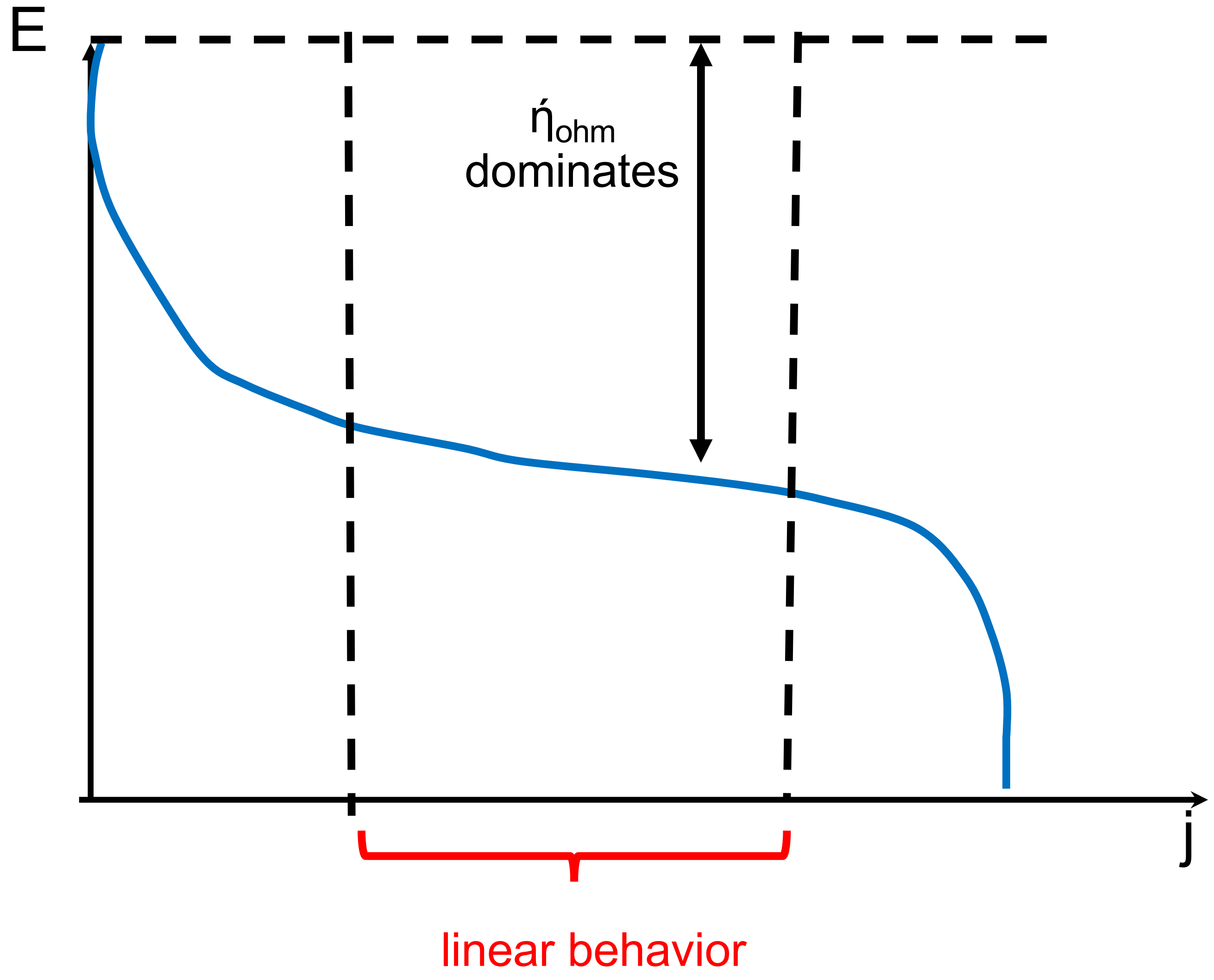
Higher j

$ή_{ohm}$ dominates

$$E_{overall} \approx E_{eq} - \text{const} - jAR_{ohm}$$

$$\underbrace{- \left| \frac{RT}{(1-\alpha_a)zF} \ln \frac{|j - j_{lim,c}|}{|j_{lim,c}|} \right| - \left| \frac{RT}{(1-\alpha_a)zF} \ln \frac{|j°|}{|j|} \right| - \left| \frac{RT}{\alpha_a zF} \ln \frac{j_{lim,a}}{j_{lim,a} - j} \right| - \left| \frac{RT}{\alpha_a zF} \ln \frac{j}{j°} \right|}_{\text{constant}} - |jAR_{ohm}|$$

Total overpotential and interpretation of its components



Total overpotential and interpretation of its components

High j

($j \rightarrow j_{lim}$)

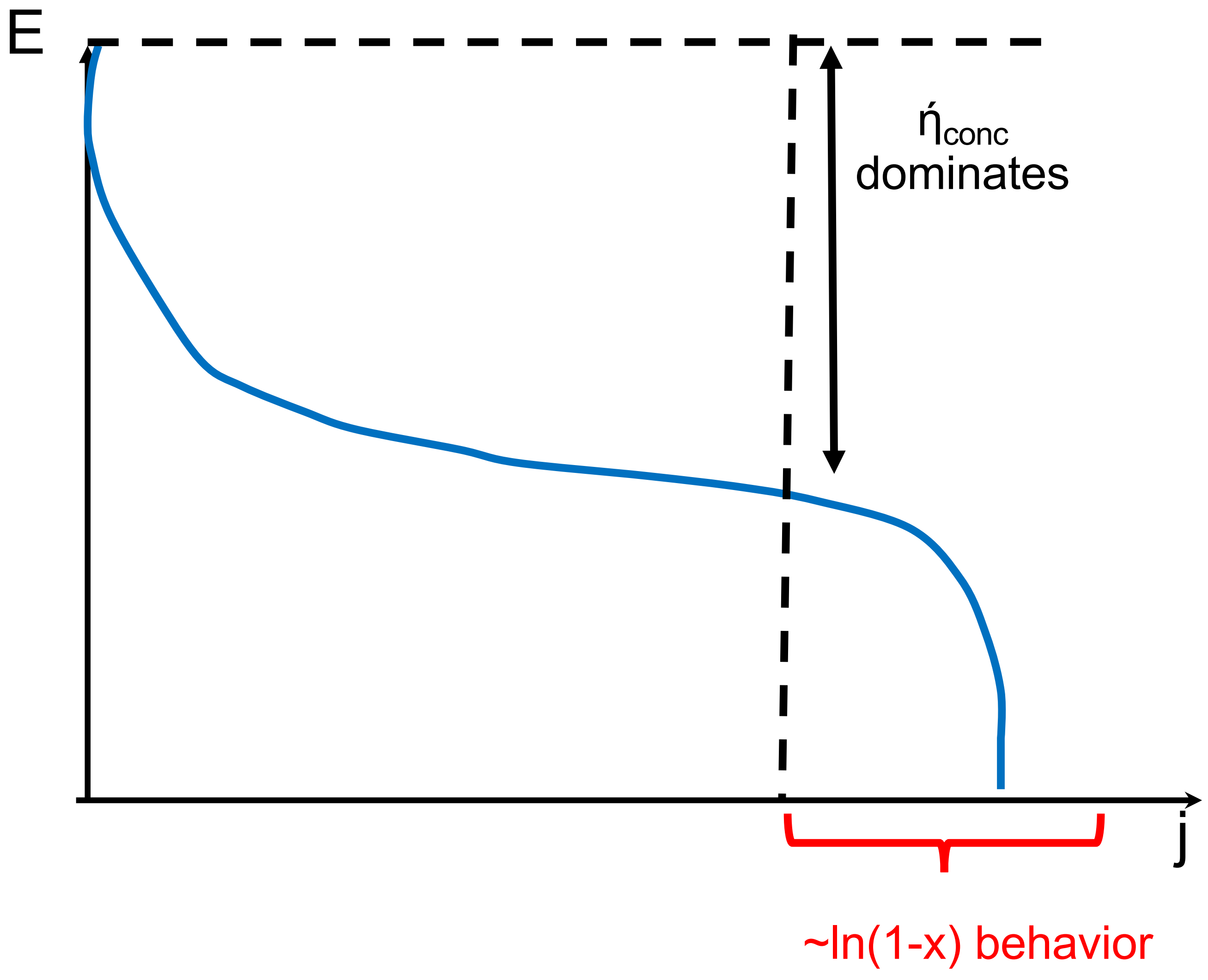
$ή_{conc}$ dominates

$$E_{overall} \approx E_{eq} - \text{const.} - \left|\frac{RT}{(1-\alpha_a)zF}\ln\frac{|j - j_{lim,c}|}{|j_{lim,c}|}\right| - \left|\frac{RT}{\alpha_a zF}\ln\frac{j_{lim,a}}{j_{lim,a} - j}\right|$$

$$-\underset{\Big\downarrow}{\left|\frac{RT}{(1-\alpha_a)zF}\ln\frac{|j - j_{lim,c}|}{|j_{lim,c}|}\right|} - \underbrace{\left|\frac{RT}{(1-\alpha_a)zF}\ln\frac{|j^{\circ}|}{|j|}\right|}_{\text{constant for } j = j_{lim}} - \underset{\Big\downarrow}{\left|\frac{RT}{\alpha_a zF}\ln\frac{j_{lim,a}}{j_{lim,a} - j}\right|} - \underbrace{\left|\frac{RT}{\alpha_a zF}\ln\frac{j}{j^{\circ}}\right| - |jAR_{ohm}|}_{\text{constant for } j = j_{lim}}$$

The ln of a number approaching infinity (or 0) is a very positive (or negative) value.

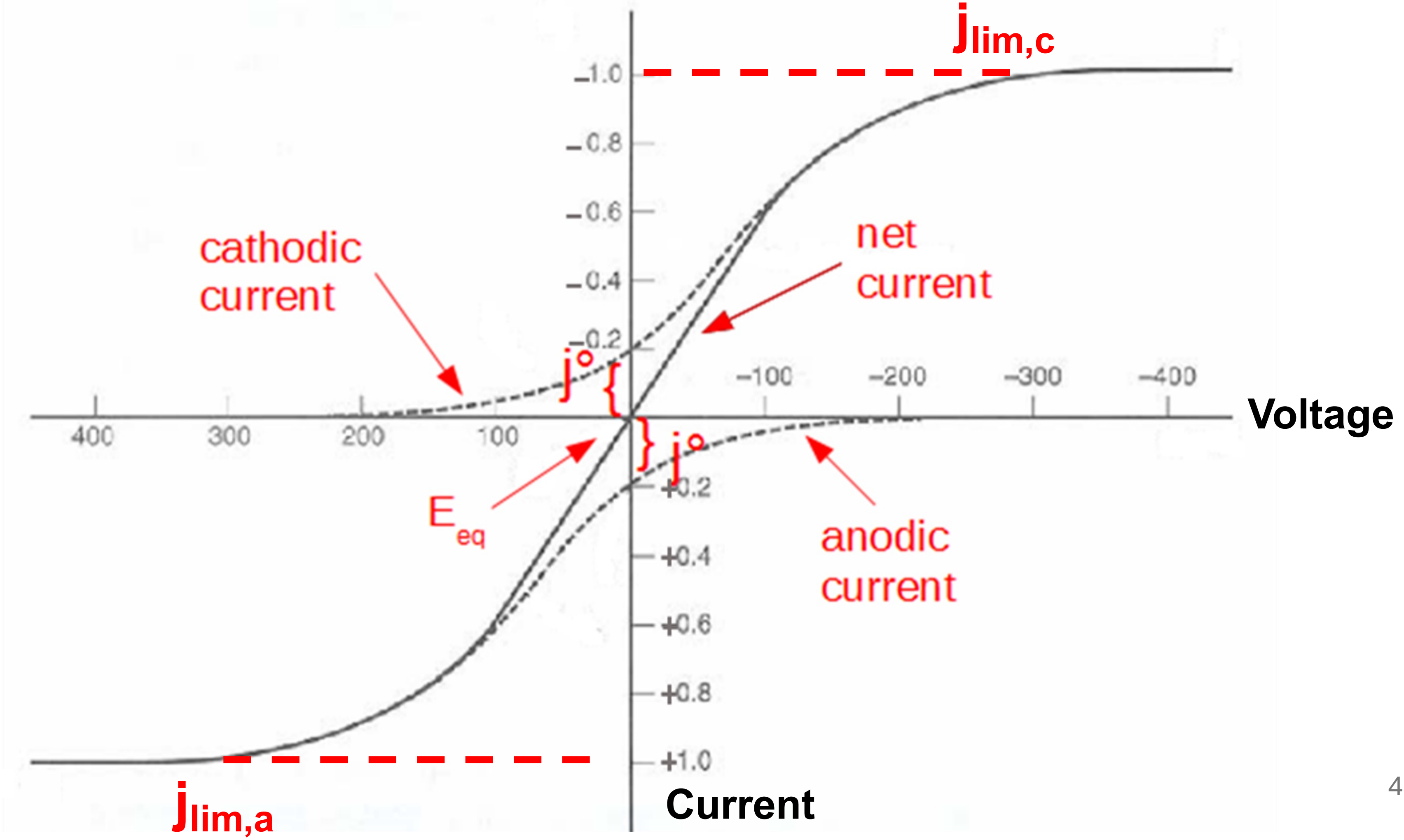
Total overpotential and interpretation of its components



Summary review of B-V Equation with Mass Transfer Effects: effect of Variables

j^0, j_{lim}

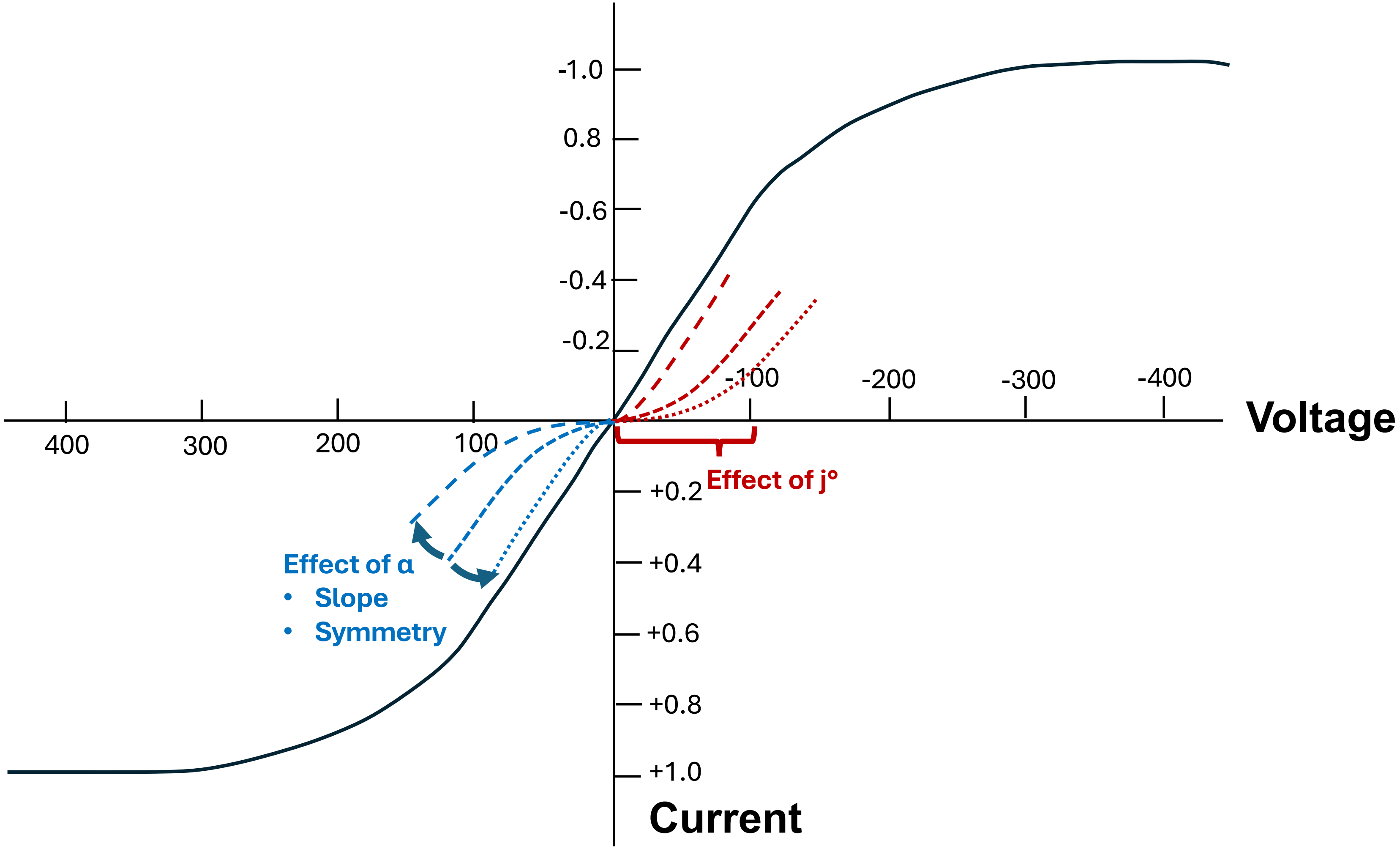
$$\frac{j}{j^\circ} = \left[1 - \frac{j}{j_{lim,a}}\right] e^{\frac{\alpha_a zF}{RT}\acute{\eta}} - \left[1 - \frac{j}{j_{lim,c}}\right] e^{\frac{-(1-\alpha_a)zF}{RT}\acute{\eta}}$$



Summary review of B-V Equation with Mass Transfer Effects: effect of Variables

α

$$\frac{j}{j^{\circ}} = \left[1 - \frac{j}{j_{lim,a}}\right] e^{\frac{\alpha_a zF}{RT} ή} - \left[1 - \frac{j}{j_{lim,c}}\right] e^{\frac{-(1-\alpha_a)zF}{RT} ή}$$



Effect of j°

Effect of α
- Slope
- Symmetry

Summary review of B-V Equation with Mass Transfer Effects: Overpotentials