Electrochemistry for materials technology

Chapter 3

Electrode kinetics

A. Charge transfer limitation

(Butler-Volmer equation)

Recap of cell potentials definition

$$E_{cell} = E^{\circ}_{cell,T} - \frac{RT}{zF} \ln Q$$

Standard cell potential: the theoretical Nernst ΔV for a redox reaction, when the activities of all the reactants and products are one (= standard).

Equilibrium potential: ΔV of the cell taking into account the activities according to the Nernst equation.

'Activities': - concentrations for solutions (e.g. Fe^{3+}, Cu^{2+},…)
- partial pressures for gases (e.g. H_2, O_2,..)

Open circuit voltage (OCV):

- = Experimental measurement of maximum ΔV at current density j=0 (in principle equal to theoretical ΔV calculated from ΔG, but usually less).
- Useful for characterizing device performance. (Significant deviation from theoretical ΔV is indicative of side reactions, f.ex. PEMFC)
- ΔV decreases as current flows through the system, due to ohmic (= R.I) and non-ohmic losses (= charge transfer + mass transfer).

Current I or j

Electric current (i or j) is the flow of electric charge (C/s). This charge is carried by *electrons* in a wire or by *ions* in an **electrolyte**.

i : current (in Amperes (A), or Coulomb/s (C/s))

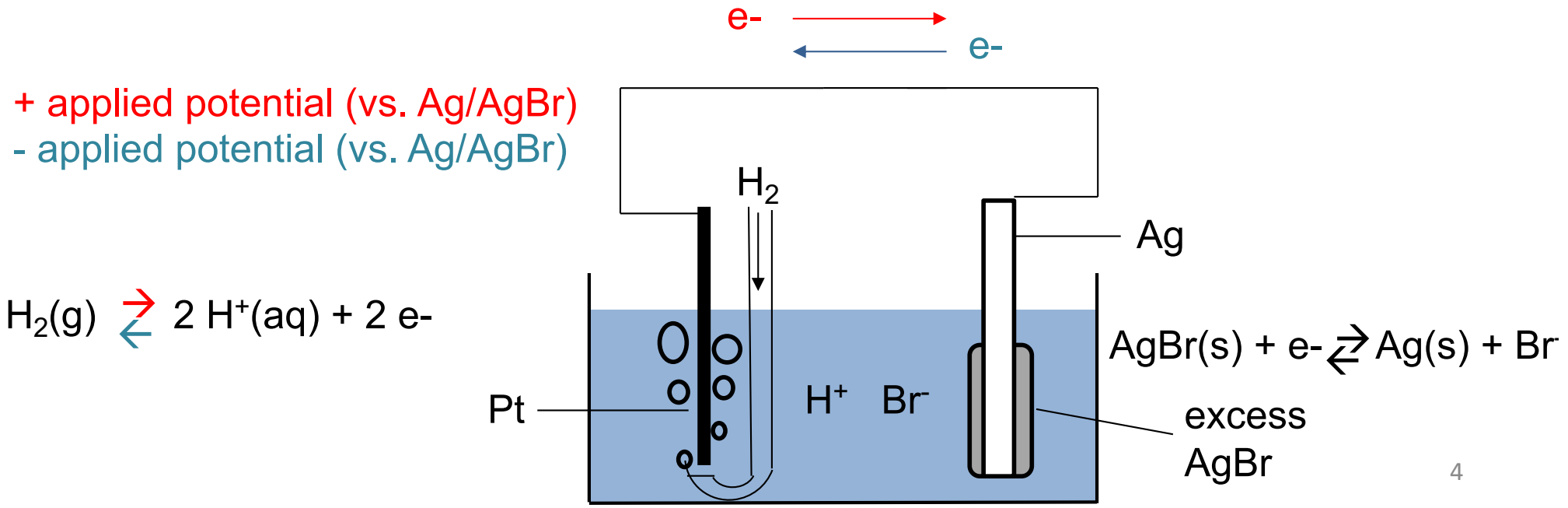
j : current density

units of A/surface area (cm^2 or m^2)

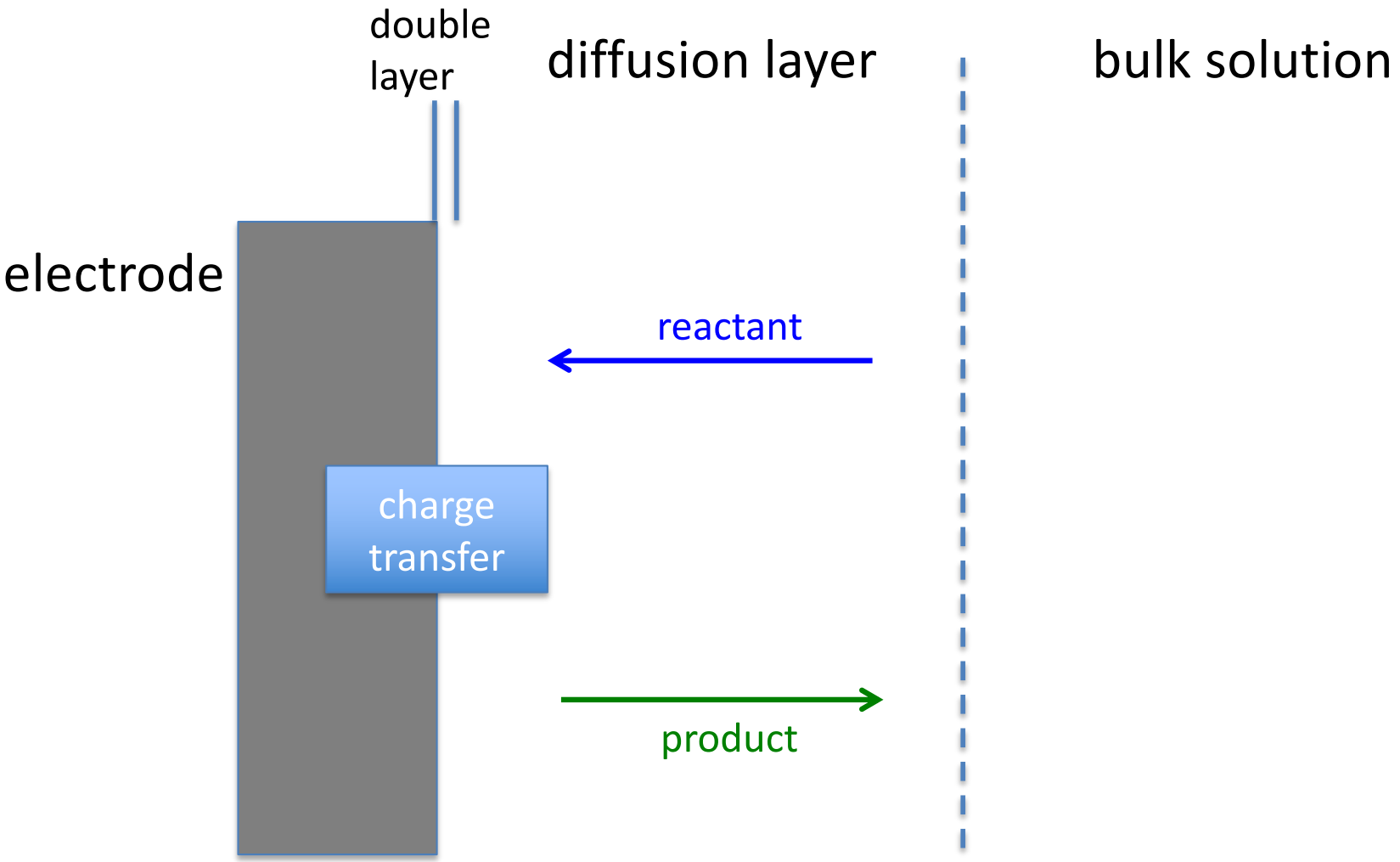
Voltage (E_{cell}) is an **intensive variable** (independent of the amount reacted). Current (j or i) is an **extensive variable** (depends on the **amount**. F = charge **per mol**).

Sign convention for current

- *Electrons* (e^-), in the *external* circuit, **always** flow from anode (oxidation) to cathode (reduction).
- *Current* **always** flows from cathode to anode (opposite to e^-).
- The only difference occurs, *in a current vs. voltage plot of a working electrode (WE) vs. a reference electrode (RE)*, when applying a positive potential to the WE to drive an oxidation (anodic reaction), or a negative potential to drive a reduction (cathodic reaction), if the resulting current is considered positive or negative in sign **in a plot**.

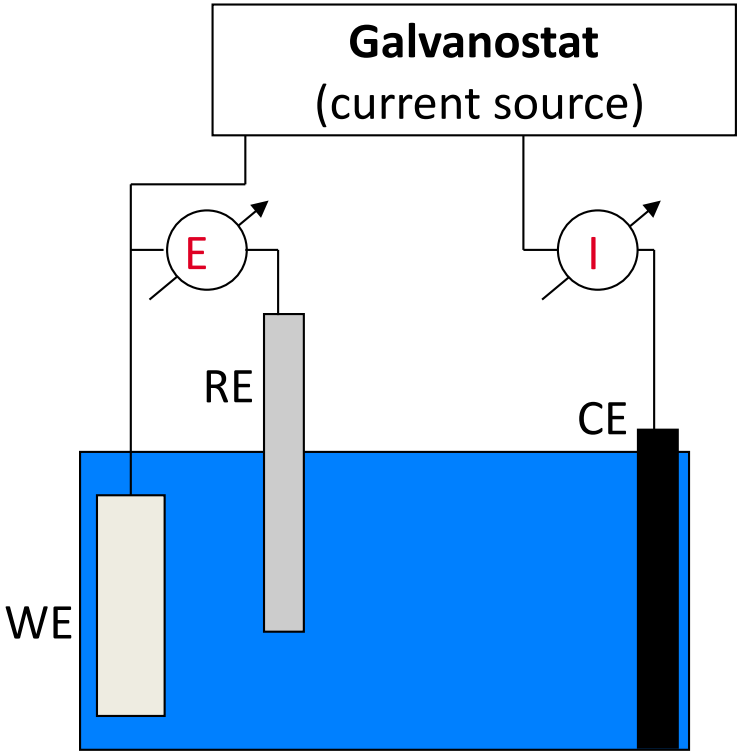


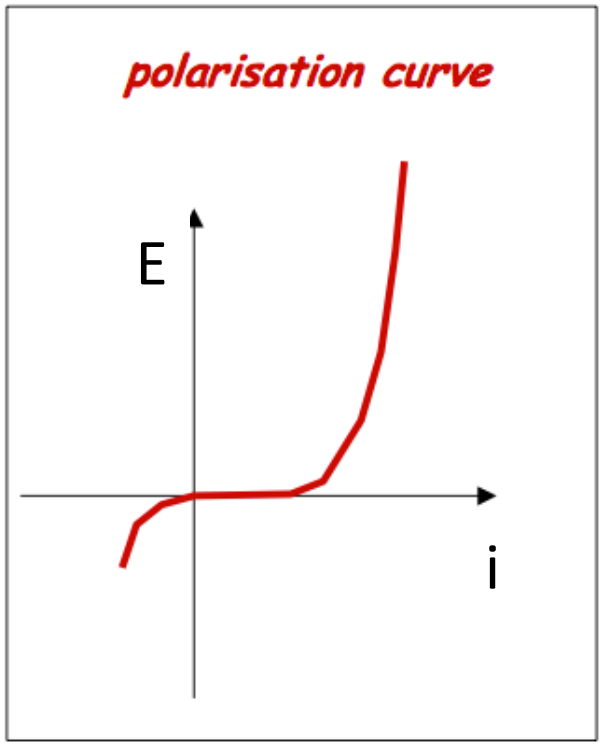
Rate determining steps (rds) in electrochemical reactions



Methods for measurement of polarisation curves (j-V curves)

GALVANOSTAT: current source that forces a selected current I to pass from the working electrode WE (i.e. the electrode under investigation) to the counter electrode CE. The resulting potential E is measured using a reference electrode RE.

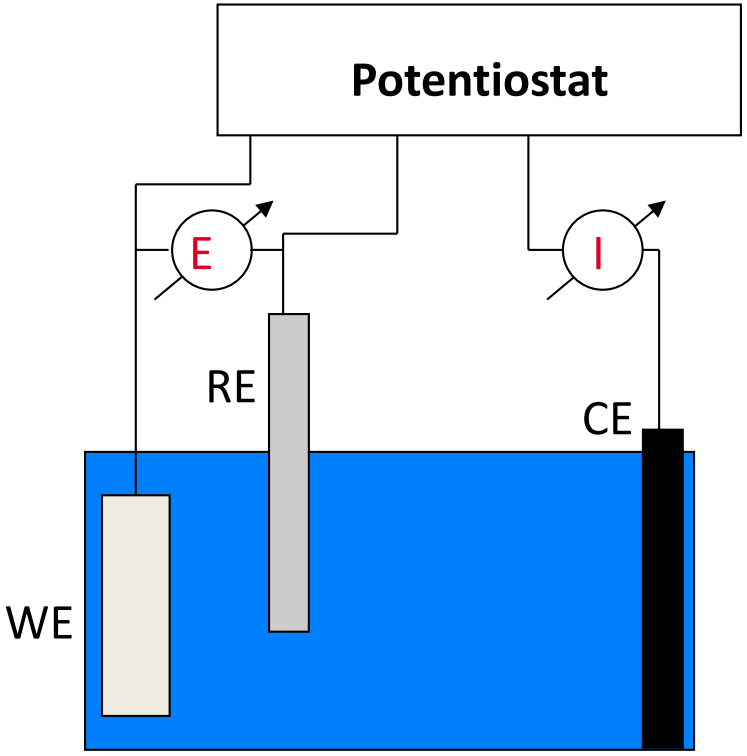


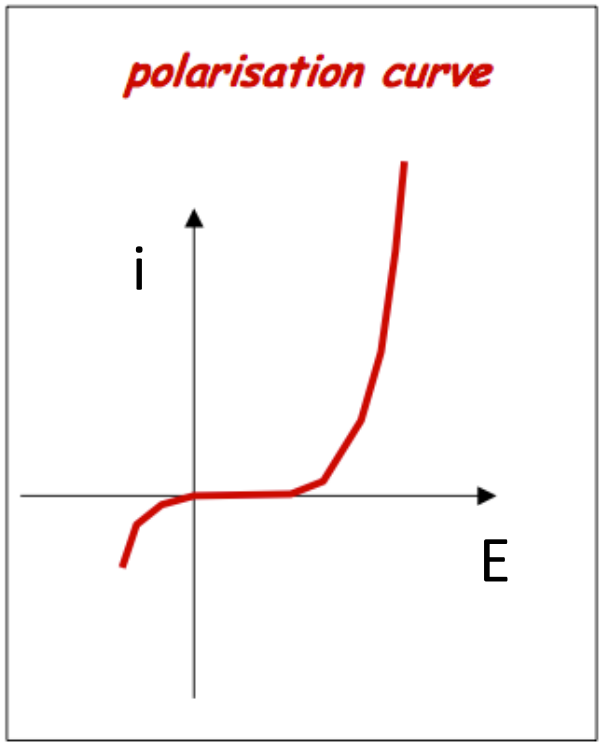


Methods for measurement of polarisation curves (j-V curves)

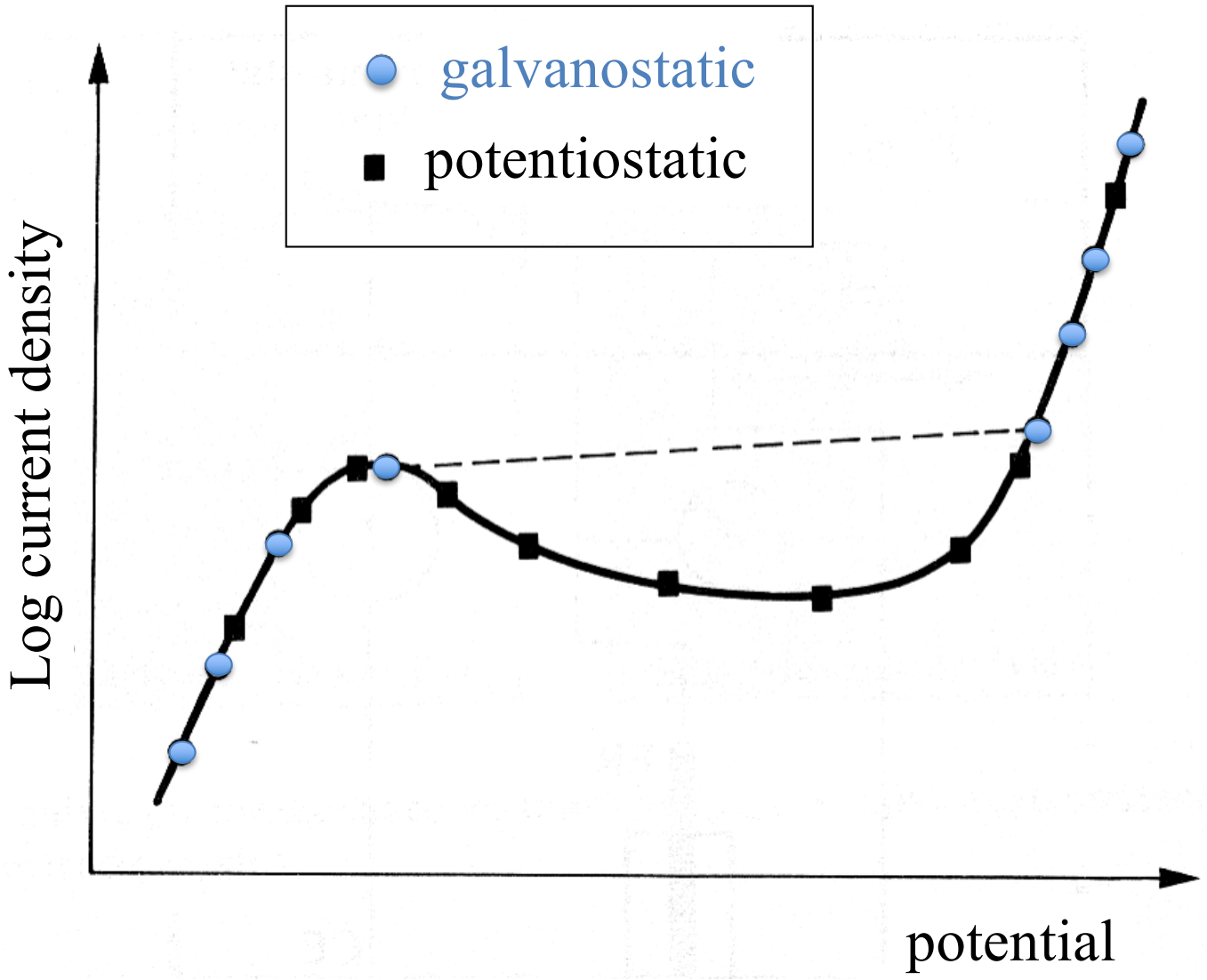
POTENTIOSTAT: electronic device that maintains a selected potential E between RE and WE by passing an appropriate current I between WE and CE.

RE: reference electrode, CE: counter electrode, WE: working electrode





Galvanostatic and potentiostatic polarisation (j-V) curves



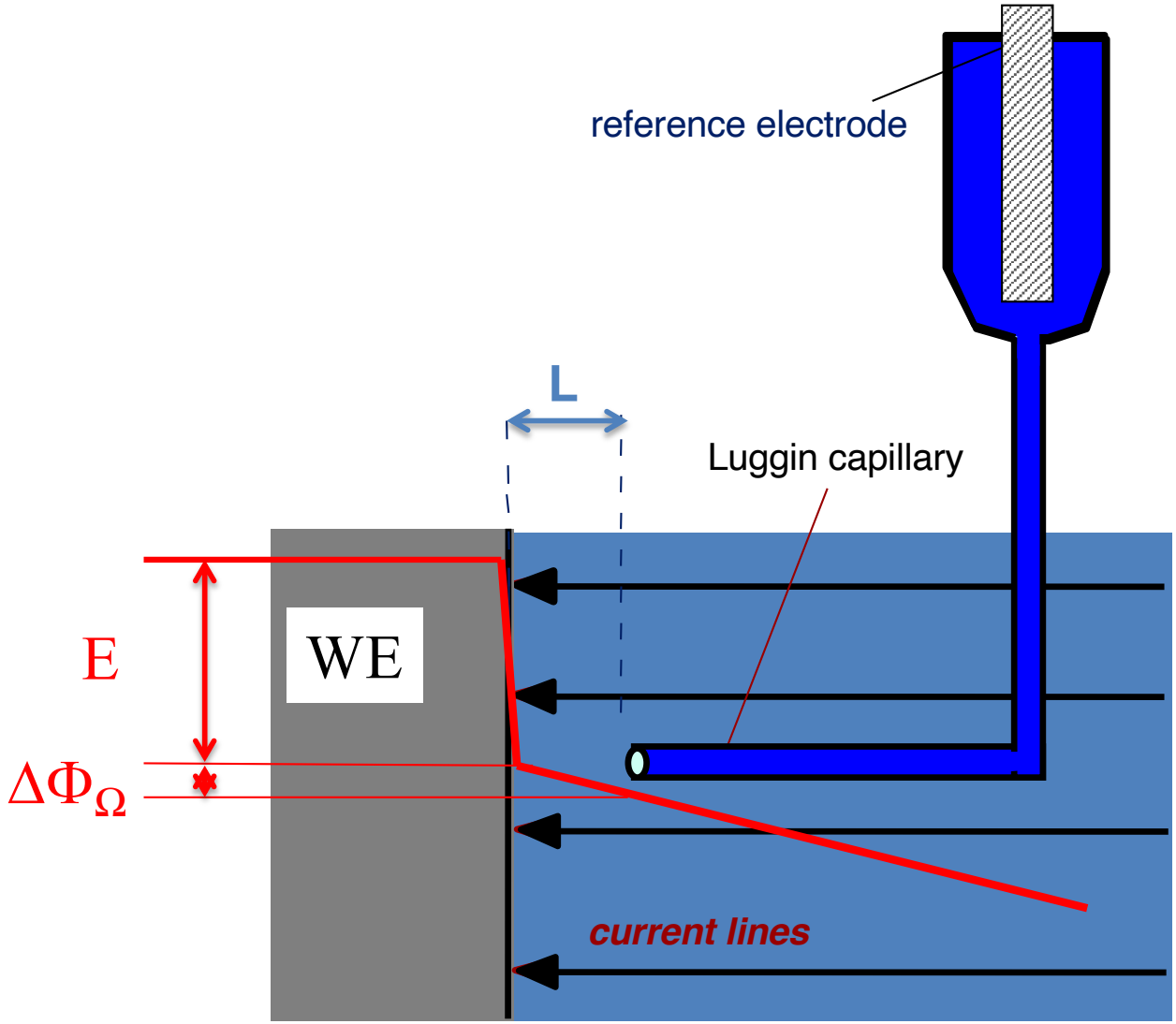
Reference electrode with Luggin capillary

Electrolyte solution
= ohmic drop $\Delta\Phi_\Omega$

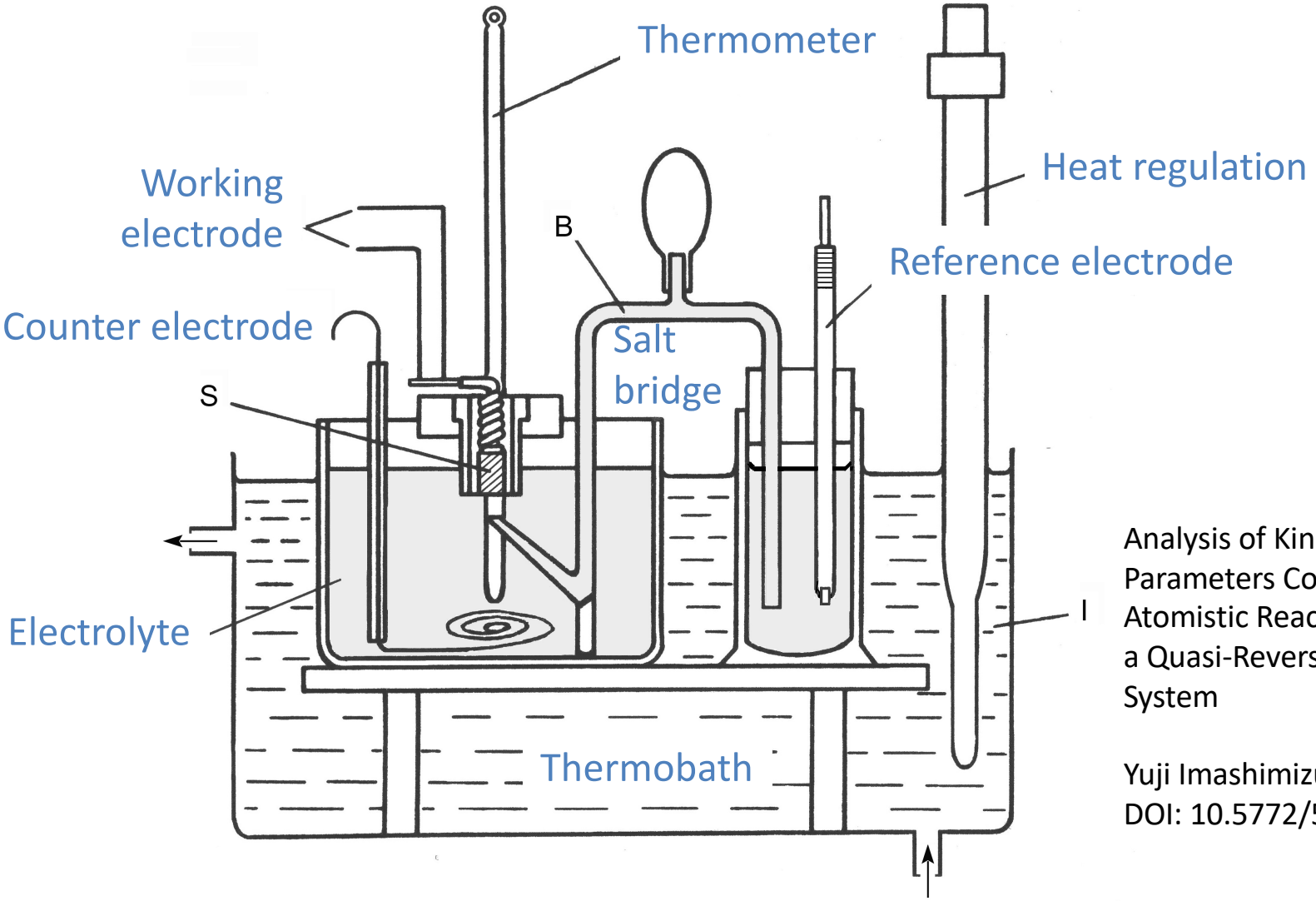
$$E_{measured} = E + \Delta\Phi_\Omega$$

$$\Delta\Phi_\Omega = i\,L / \kappa$$

κ = electrolyte conductivity



Schematic diagram of an electrolytic cell for polarisation experiments



Analysis of Kinetic Parameters Controlling Atomistic Reaction Process of a Quasi-Reversible Electrode System

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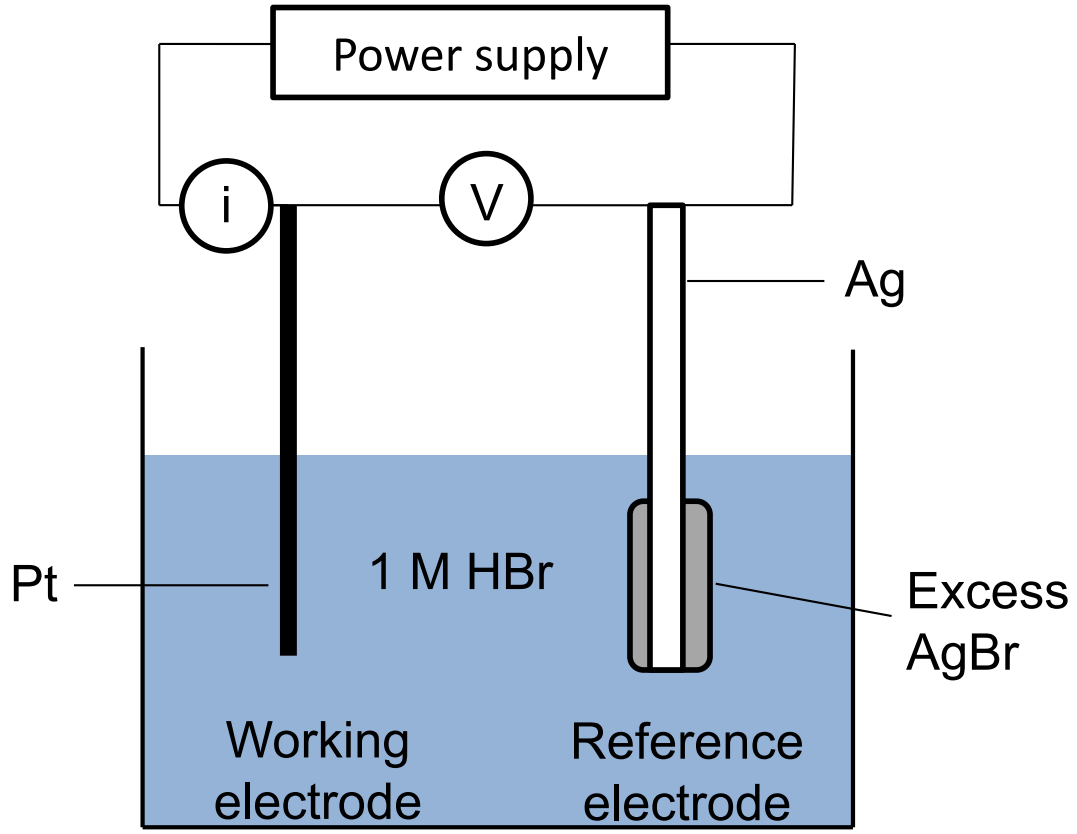
DOI: 10.5772/51896

Net current flow under **non-equilibrium** conditions

Consider an electrochemical experiment where a WE (Pt) and RE (AgBr) are immersed in a solution, and the potential difference between the 2 electrodes is varied by means of an external power supply.

Working electrode (WE): electrode where the reaction of interest occurs

Reference electrode (RE): electrode made up of phases having essentially constant compositions → its potential is fixed



Net current flow under non-equilibrium conditions

1. Apply more **positive potentials** to the Pt electrode relative to the Ag/AgBr electrode => **oxidation** reaction

$$2\ Br^-(aq) \rightarrow Br_2(g) + 2\ e^-$$ $E_{reduction}$ = +1.02 V vs Ag/AgBr

- The flow of electrons is from the solution (Br^- anions at the Pt surface) to the electrode = **oxidation** (anodic current)
- While this happens, AgBr(s) at the Ag/AgBr electrode is **reduced** to Ag^0, and Br^- is liberated into the solution. As [Br-] remains constant near the electrode at modest currents, the potential of the Ag/AgBr electrode remains ≈ the same as at open circuit.

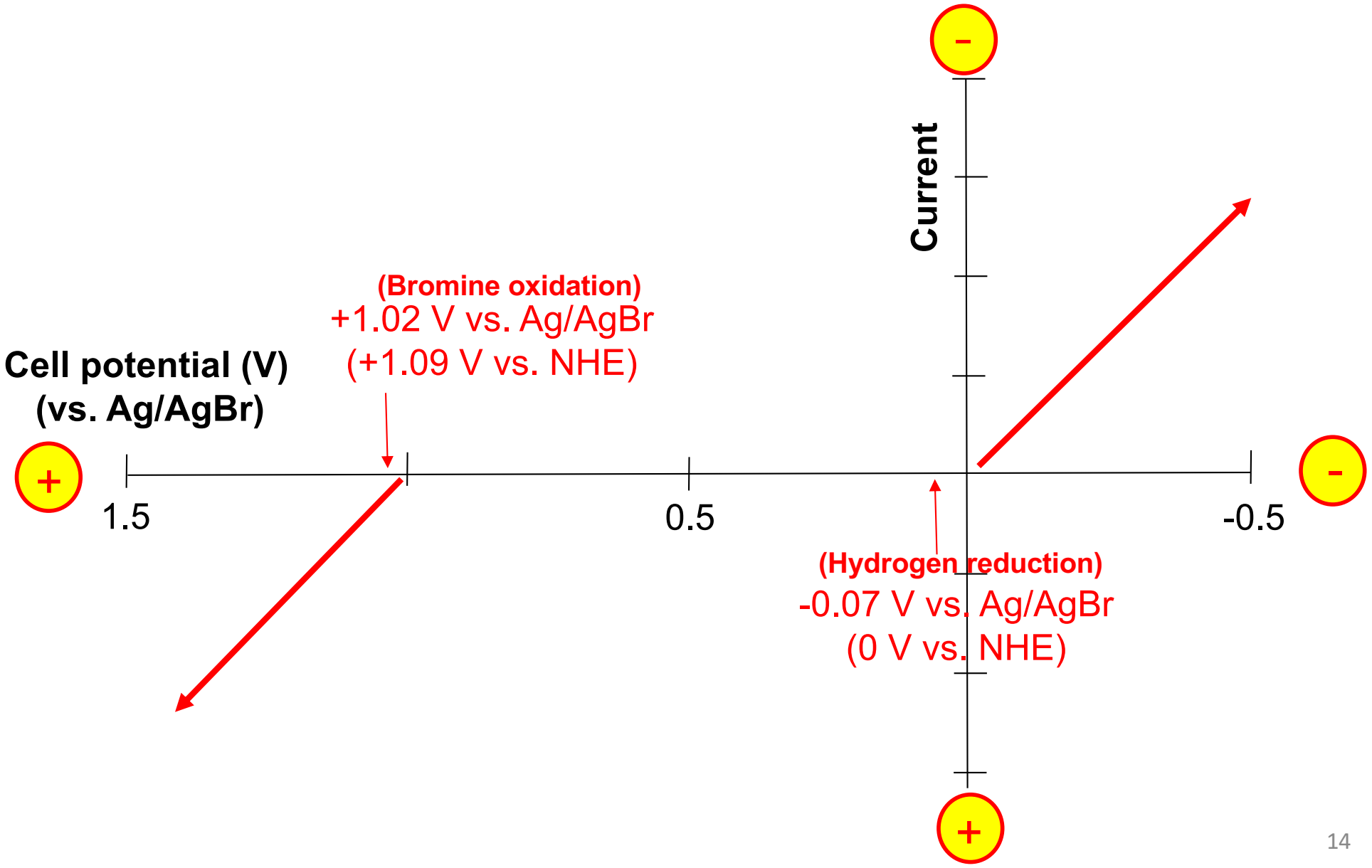
Net current flow under non-equilibrium conditions

2. Apply more **negative potentials** to the Pt electrode relative to the Ag/AgBr electrode => **reduction** reaction

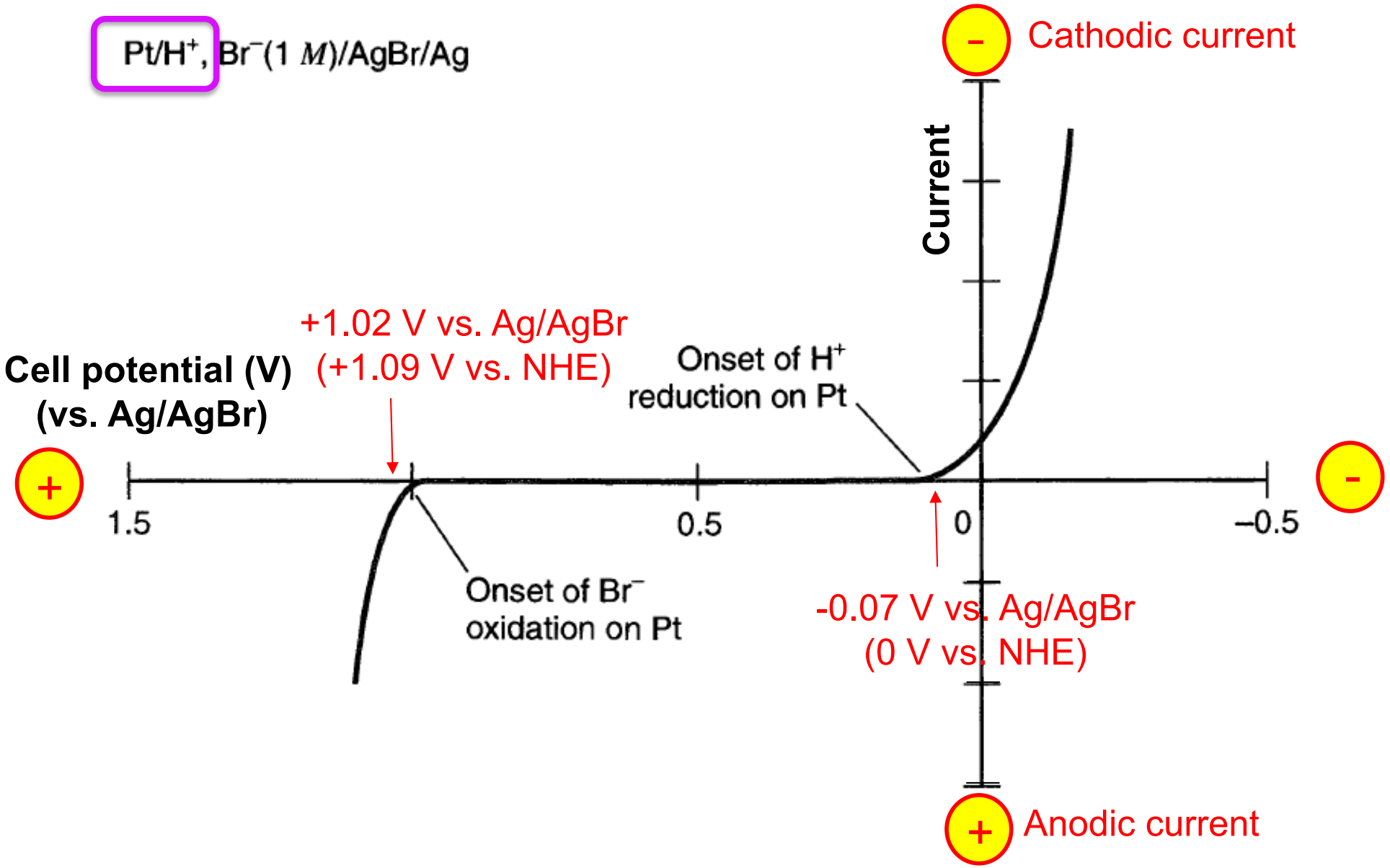
$$2\ H^+(aq) + 2\ e^- \rightarrow H_2(g) \qquad E_{reduction} = -0.07\ V\ vs\ Ag/AgBr$$

- The flow of electrons is from the electrode into the solution (H^+ at the Pt surface) = **reduction** (cathodic current)
- While this happens, Ag(s) is **oxidized** in the presence of Br^- to form AgBr at the Ag/AgBr electrode. As [Br-] remains constant near the electrode at modest currents, the potential of the Ag/AgBr electrode remains ≈ the same as at open circuit.

Current-voltage (j-V) plot : expected trend



Current-voltage (j-V) plot : observed



Effect of electrode material on j-V plot

Same system, but different working electrode WE (Pt replaced by Hg)

Reference electrode is in equilibrium

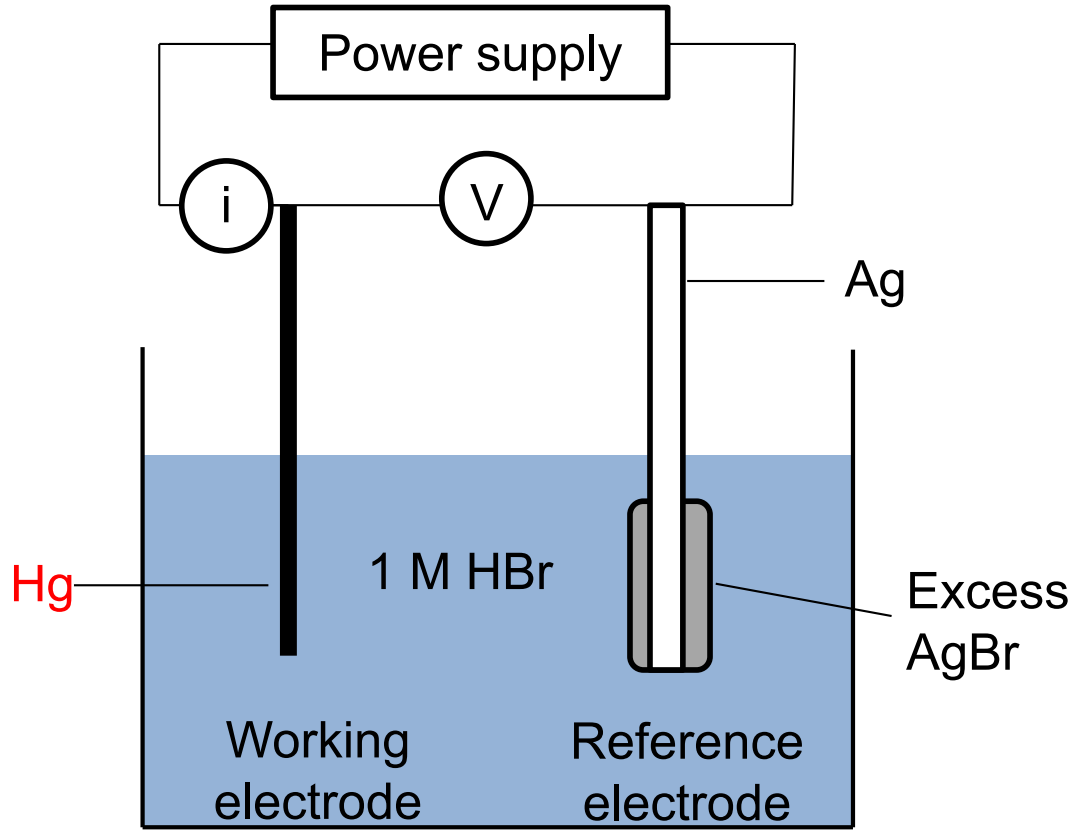
$AgBr(s) + e^- \rightleftarrows Ag(s) + Br^-$

[Br-] is known → calculated potential from Nernst equation

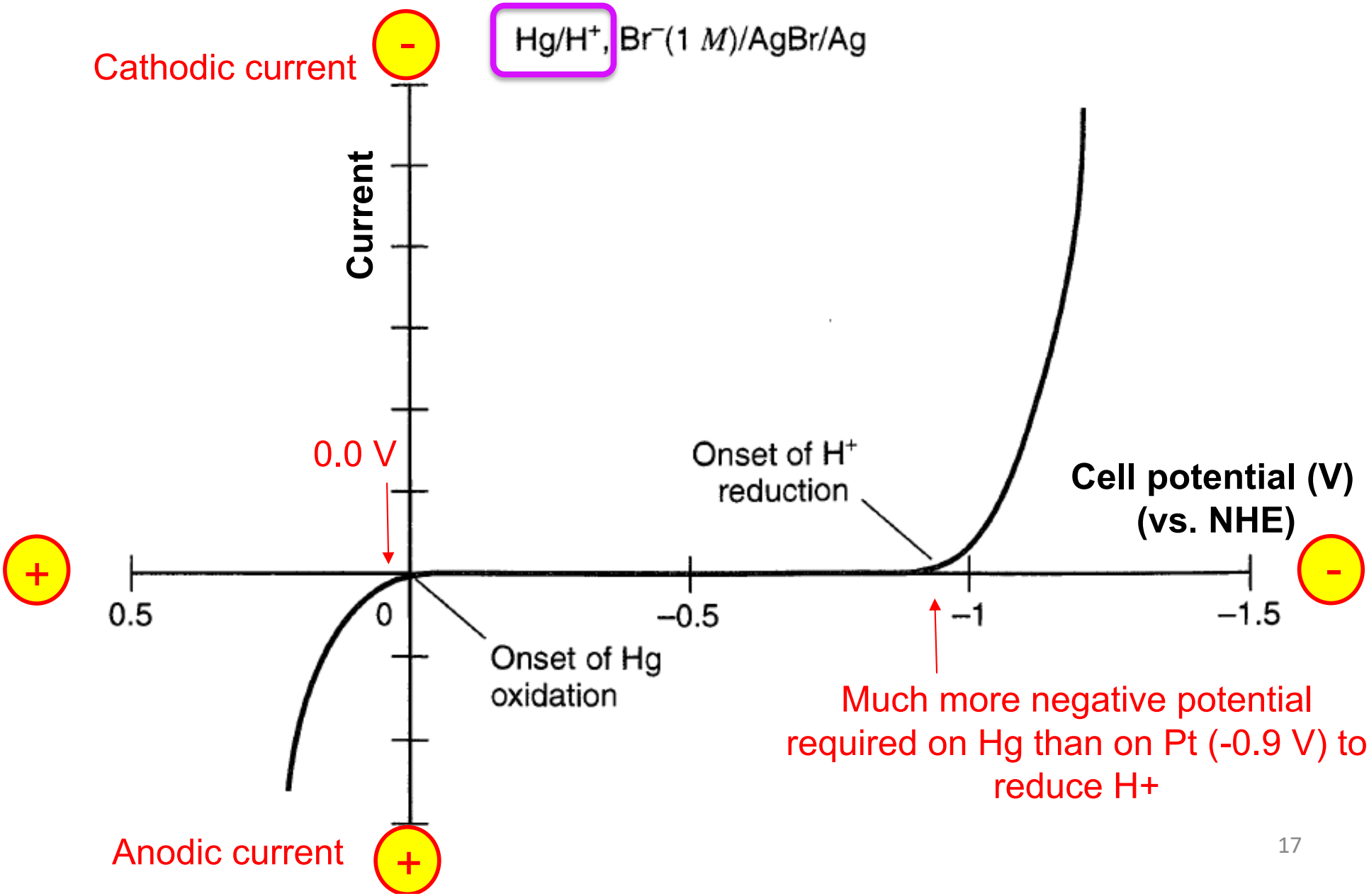
Working electrode is not in equilibrium

There is no redox couple (H_2/H^+ nor O_2/H_2O) present

(H_2 or O_2 missing)



Effect of electrode material on j-V plot



Effect of electrode material on j-V plots

The thermodynamics of the system stay the same

Apply a **negative** potential to the Hg electrode relative to the Ag/AgBr electrode,
=> **reduction** reaction :

$$2\ H^+(aq) + 2e^- \rightarrow H_2(g)$$

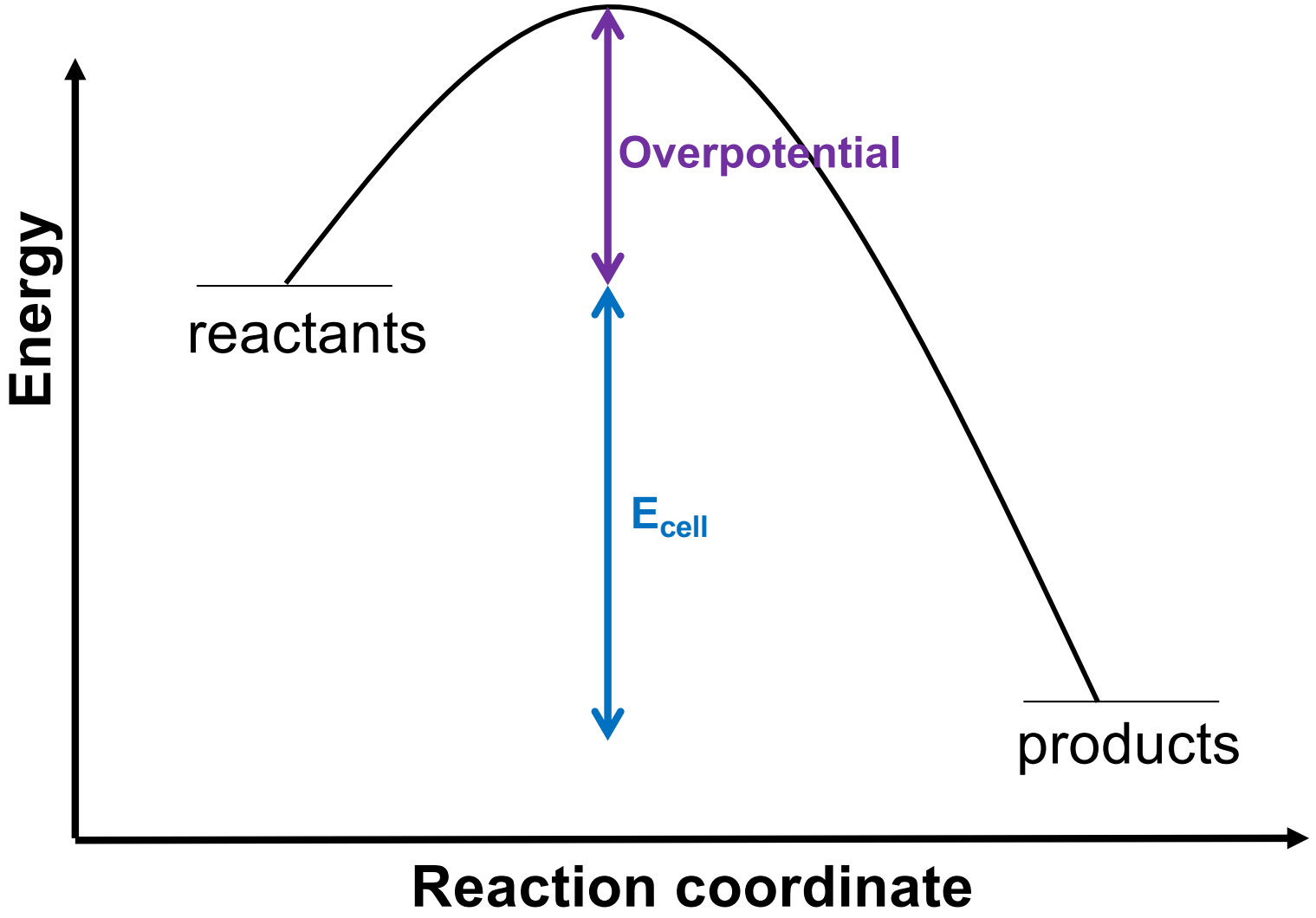
The equilibrium potential of this half reaction is independent of the electrode material.

In the case of Hg, however, a much more negative potential (higher electron energy) is needed to observe the first small (measurable) current flow.

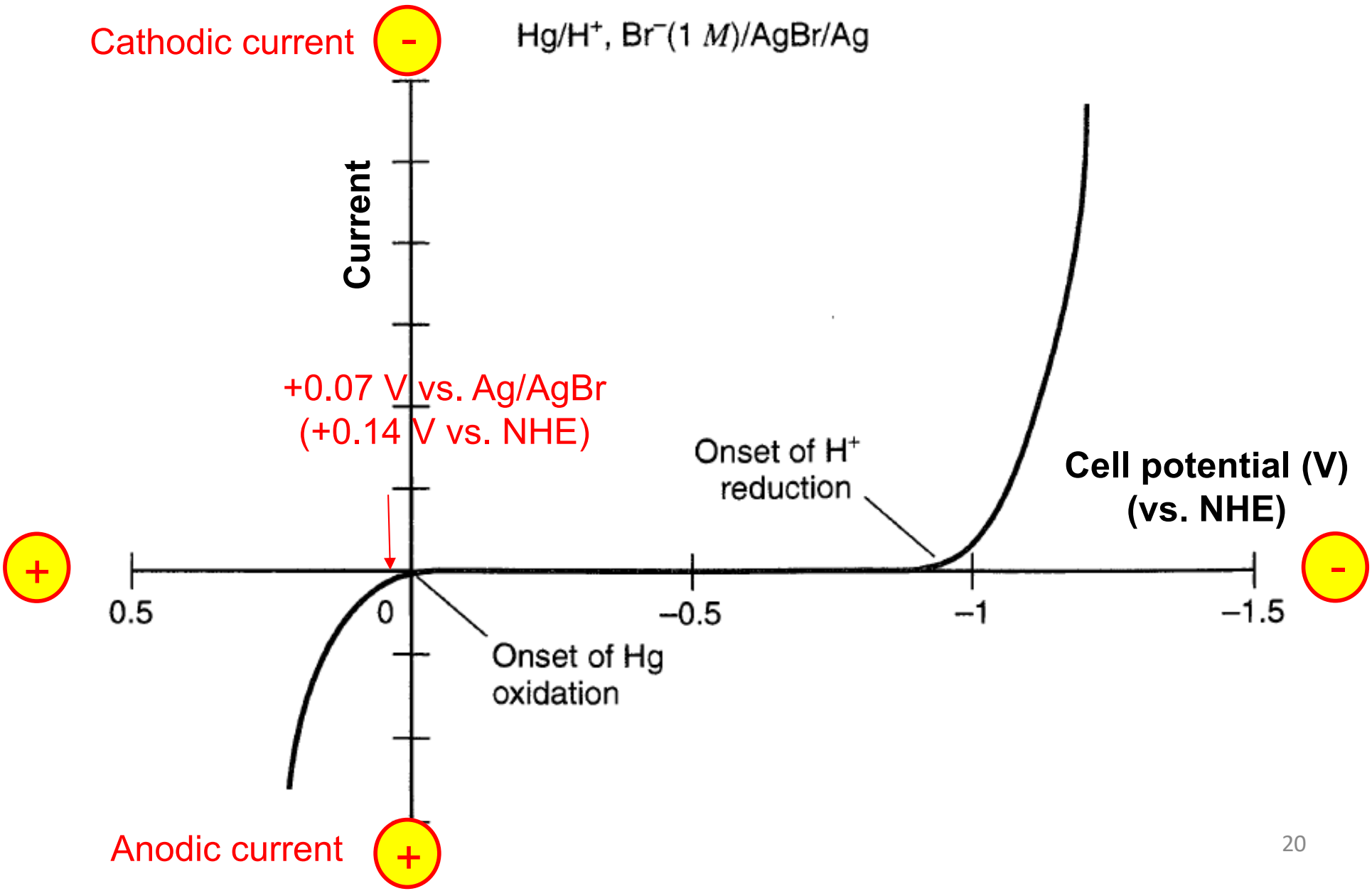
The additional potential (beyond the thermodynamic requirement) needed to drive a reaction at a certain rate is called the **overpotential**.

=> mercury (Hg) shows a very high overpotential for the hydrogen evolution reaction

Analogy between chemical reactivity and electrochemistry



Effect of electrode material on j-V plot



Effect of electrode material on j-V plot

Same system, but different working electrode (Pt replaced by Hg)

Apply a **positive** potential to the Hg electrode relative to the Ag/AgBr electrode => **oxidation** reaction

$$2\ Hg + 2\ Br^-(aq) \rightarrow Hg_2Br_2 + 2\ e^-$$

This reaction proceeds at a much lower potential (+0.14 V vs NHE) than the Br- oxidation reaction (+1.07 V vs. NHE).

Observation:
the onset potential (E_{onset}) at which measurable oxidation (or reduction) current flow occurs depends both :
(a) on the electrode material (e.g. overpotential of Hg vs Pt electrode for hydrogen evolution) and
(b) on the solution employed (e.g. Br^- ion redox reaction with Hg vs Pt).

Effect of additional electrolyte (/ions) on j-V plot

Same system, but additional electrolyte (ions) added

Reference electrode is in equilibrium

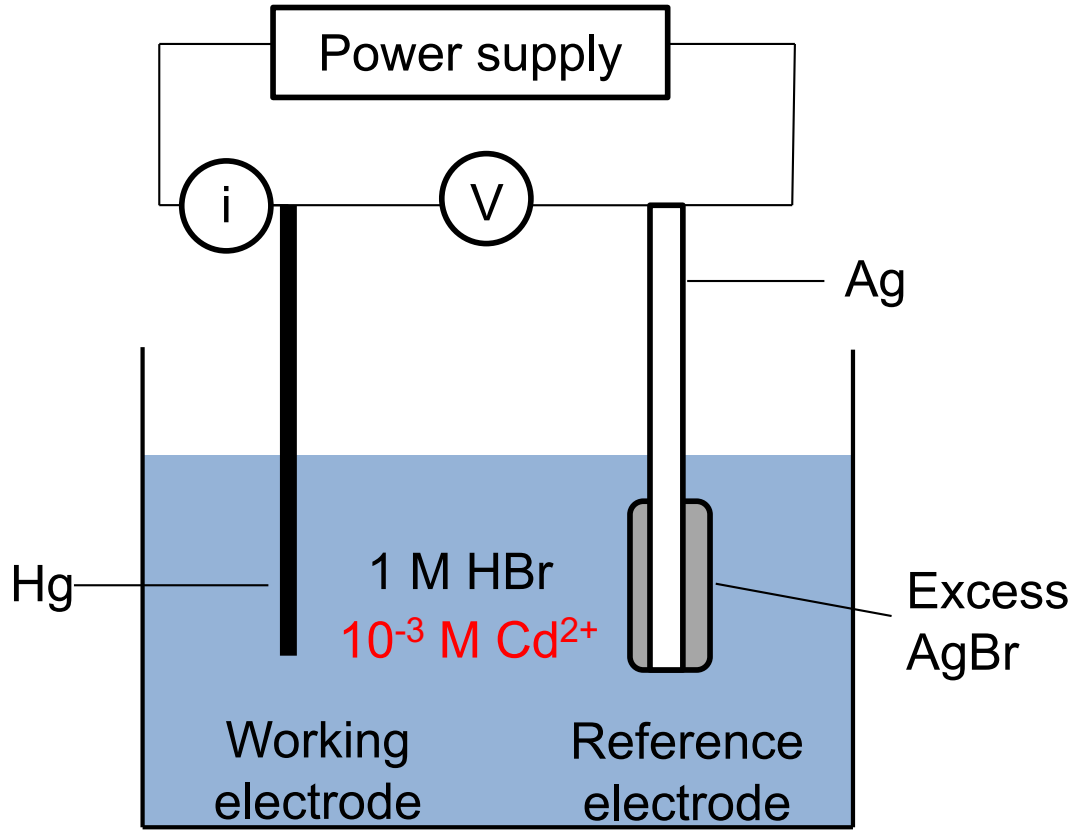
$AgBr(s) + e^- \rightleftarrows Ag(s) + Br^-$

[Br-] is known → calculated potential from Nernst equation

Working electrode is not in equilibrium

There is no redox couple (H_2/H^+ nor O_2/H_2O) present

small concentration of Cd^{2+} added



Effect of additional electrolyte (/ions) on j-V plot

Apply a very **negative** potential to the Hg electrode relative to the Ag/AgBr electrode => **reduction** reaction

$$2\ H^+(aq) + 2\ e^- \rightarrow H_2(g) \qquad E_{onset} < -0.8\ V\ vs.\ NHE$$

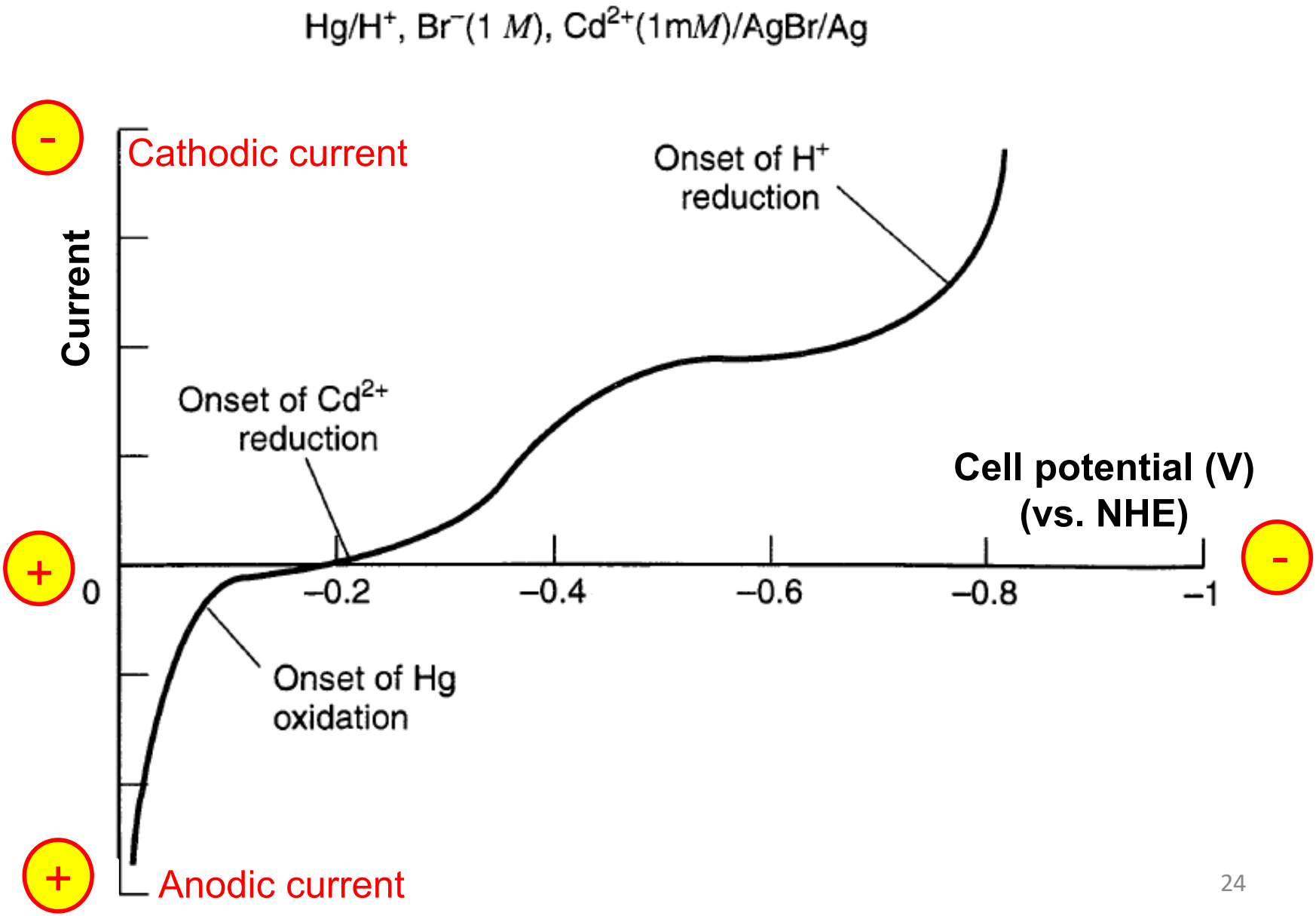
Apply a very **positive** potential to the Hg electrode relative to the Ag/AgBr electrode => **oxidation** reaction

$$2\ Hg + 2\ Br^-(aq) \rightarrow Hg_2Br_2 + 2\ e^- \qquad E_{onset} > -0.1\ V\ vs.\ NHE$$

At ***intermediate*** negative potentials applied to the Hg electrode relative to the Ag/AgBr electrode => intermediate, additional, reduction reaction

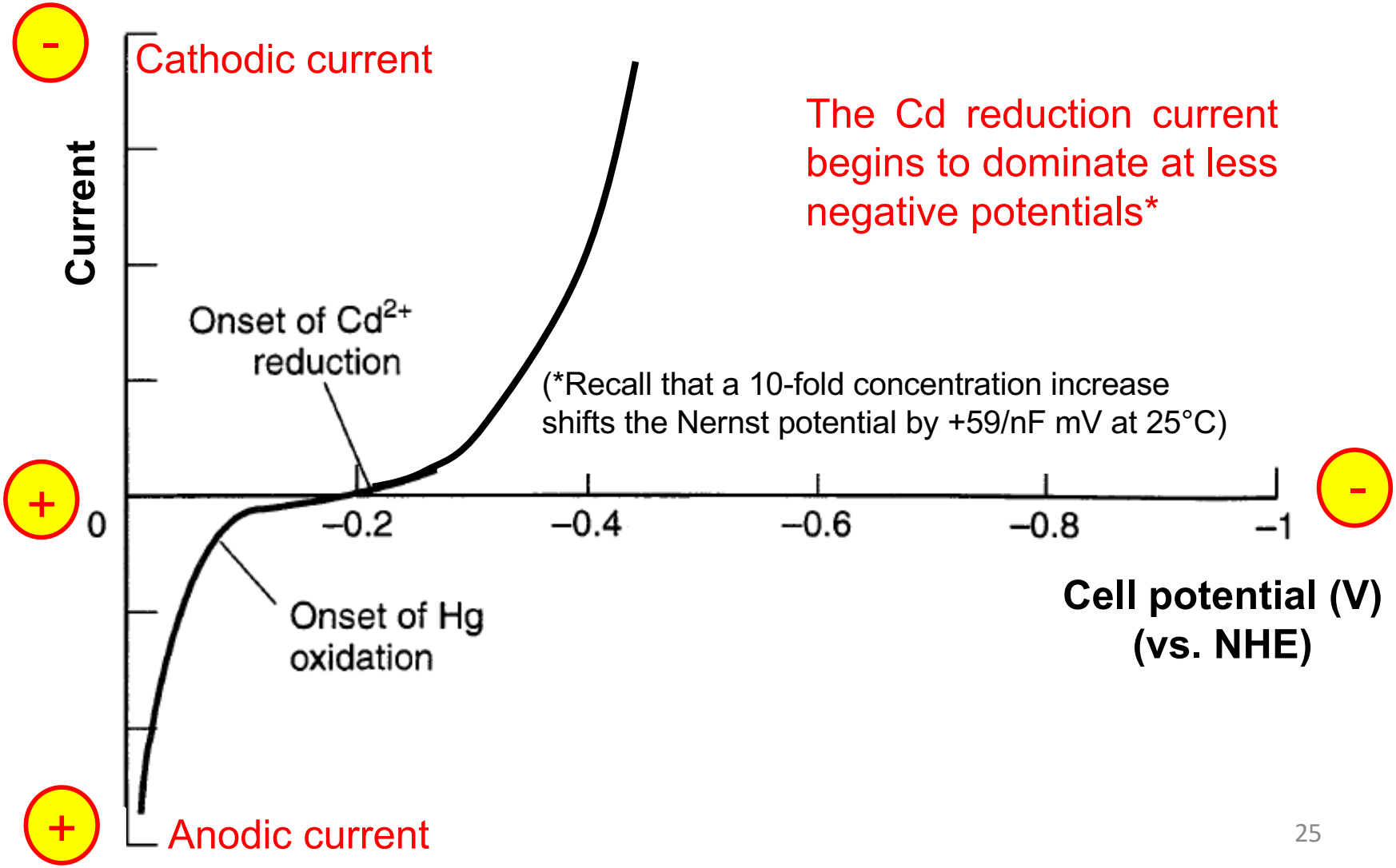
$$CdBr_4^{2-} + 2e^- \xrightarrow{Hg} Cd\ (Hg) + 4\ Br^- \qquad E_{onset} \sim -0.4\ V\ vs.\ NHE$$

Effect of additional electrolyte (/ions) on j-V plot



Effect of additional electrolyte (/ions) on j-V plot

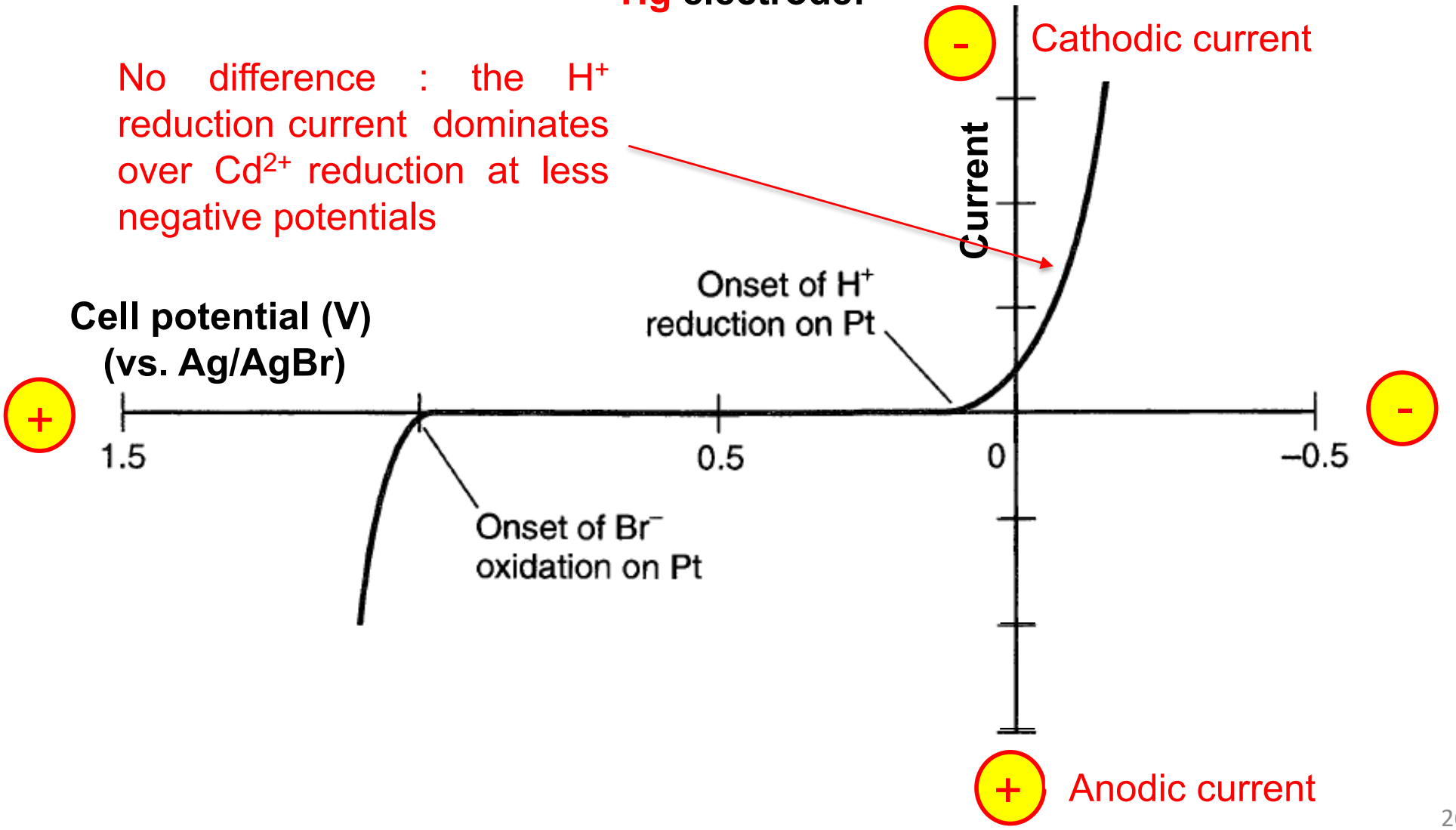
When adding higher concentration of Cd^{2+} to the solution :



Effect of additional electrolyte (/ions) on j-V plot

When adding Cd^{2+} to the solution with the Pt electrode instead of the Hg electrode:

No difference : the H^+ reduction current dominates over Cd^{2+} reduction at less negative potentials



General rules for j-V plots

In the absence of high overpotentials, in general:

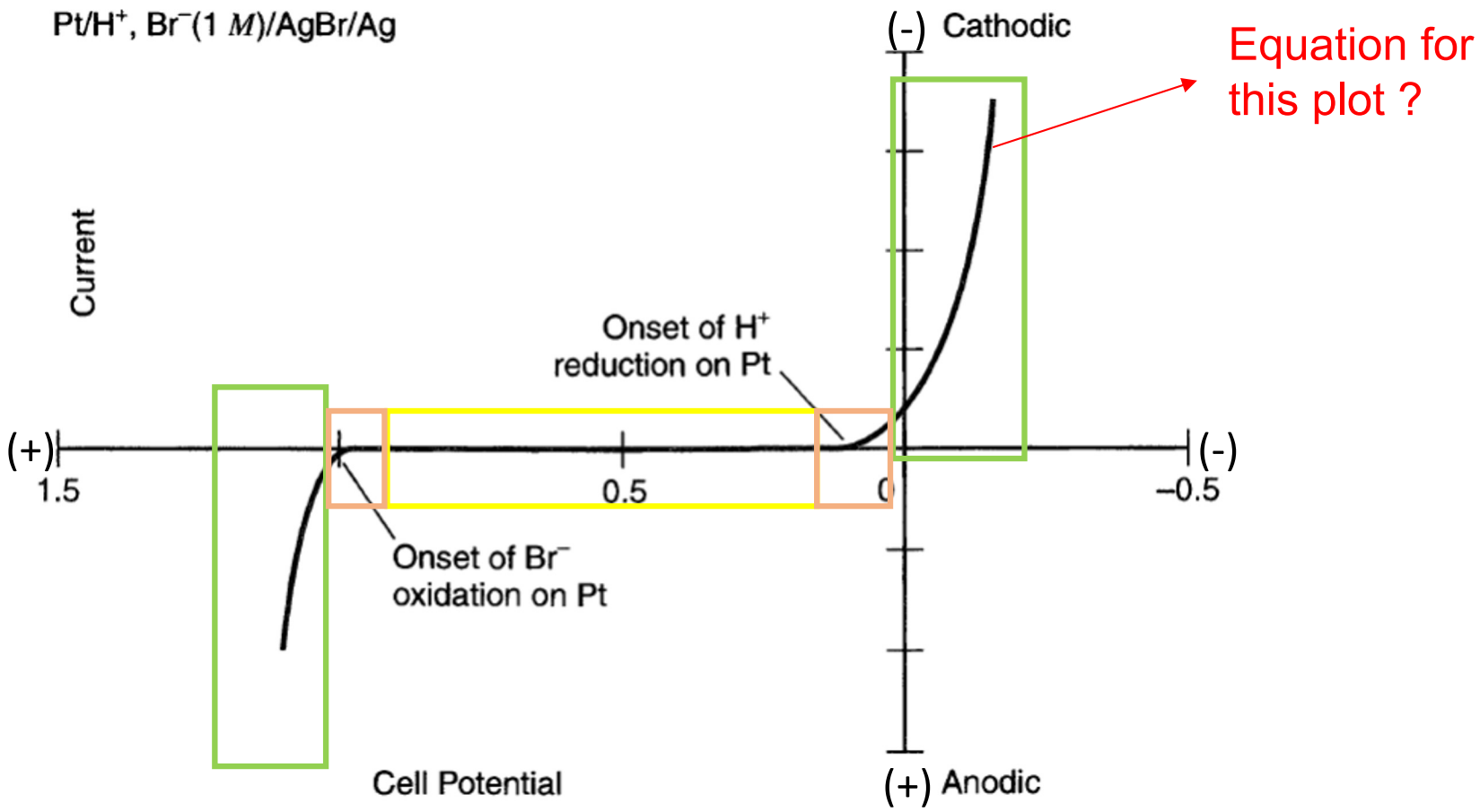
- When an electrode is moved from its open-circuit value towards more **negative** potentials (negative currents), the substance **reduced** first (=easiest to reduce = to pick up e-) has the least negative (or more positive) E°.
  Example: H^+ reduction before Cd^{2+} reduction on a Pt electrode system

- When an electrode is moved from its open-circuit value towards more **positive** potentials (positive currents), the substance **oxidized** first (=easiest to oxidize = to loose e-) has the least positive (or more negative) E°.
  Example: Hg oxidation before Br- oxidation on a Hg electrode system

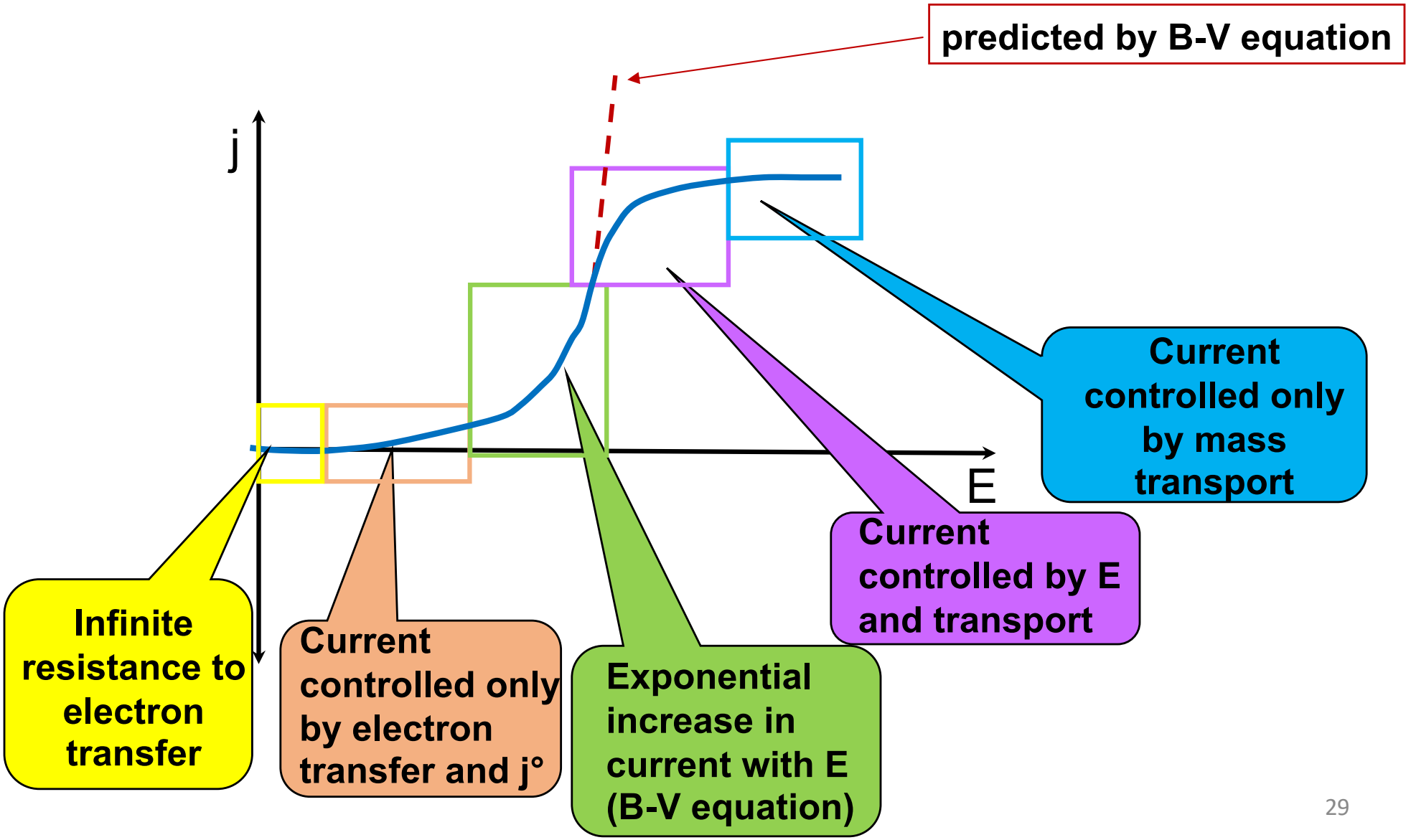
- (small) quantities of an added substance may contribute an additional peak.
  Example: small concentrations of Cd^{2+} added to Hg electrode system

These predictions are based on thermodynamic considerations, and slow kinetics (e.g. large overpotentials) might prevent a reaction from occurring at a significant rate in a region where the E° would suggest the reaction to be possible.
Example: H^+ reduction on Hg vs. Pt electrode

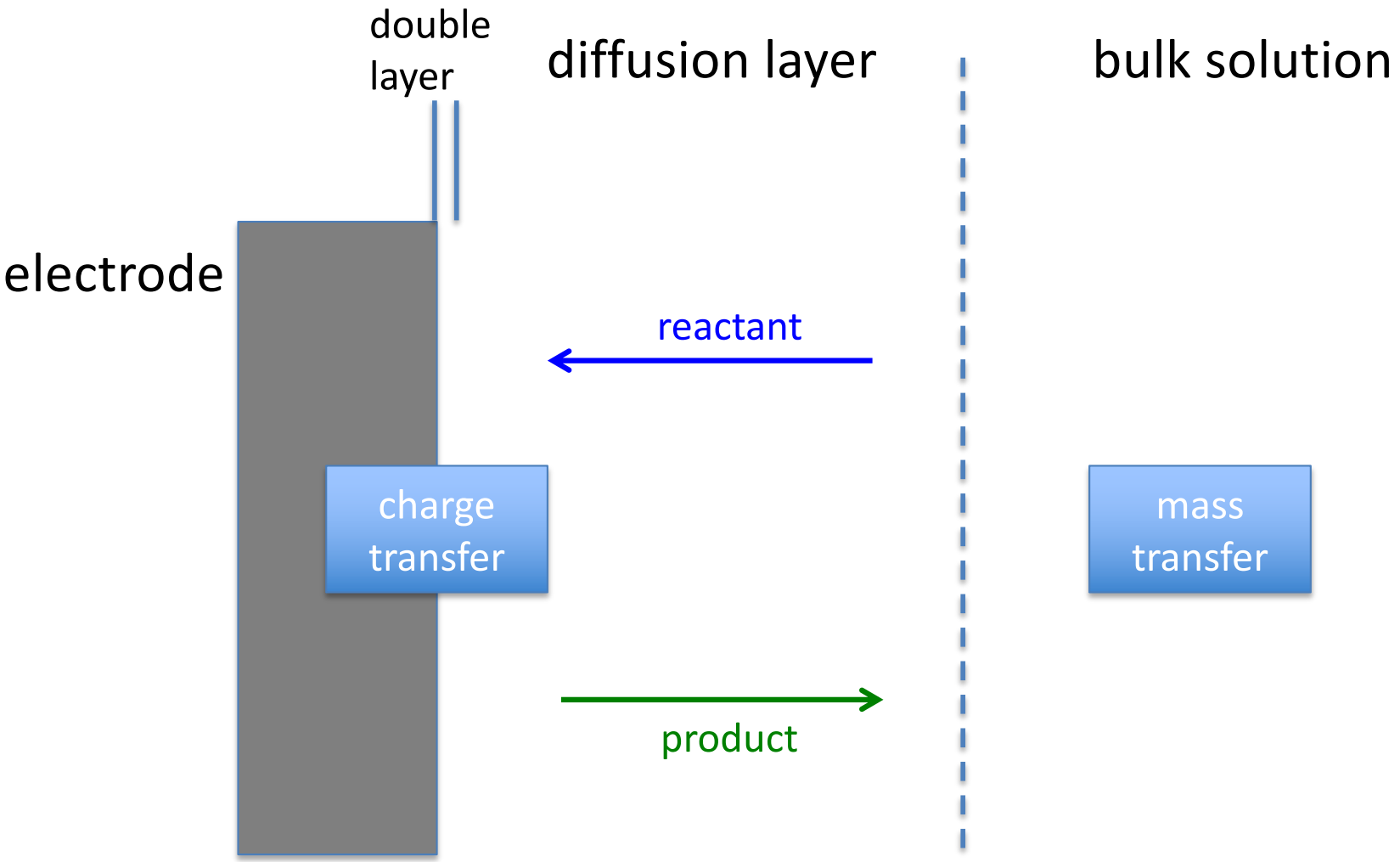
Deriving an analytical expression for observed j-V plot



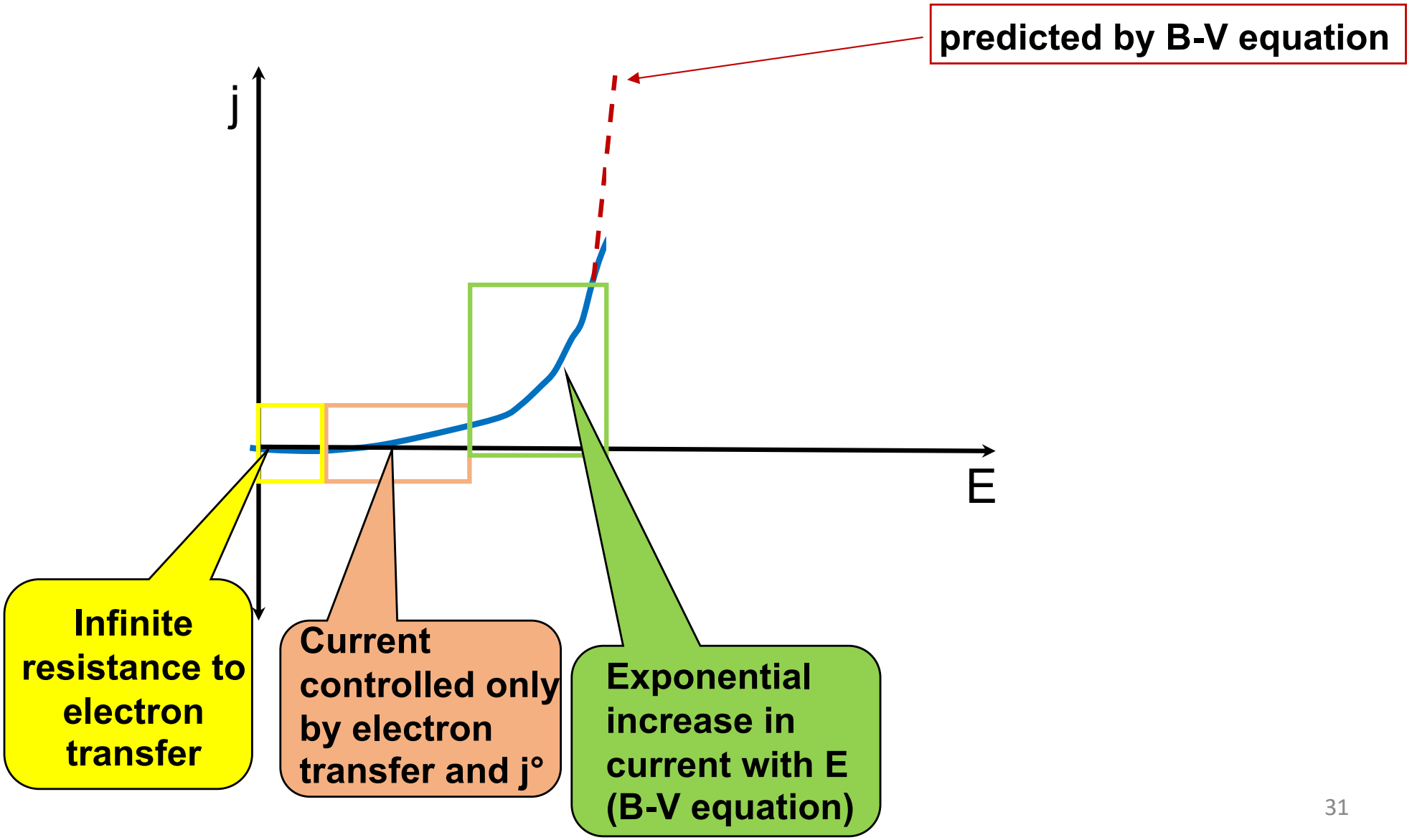
Deriving an analytical expression for observed j-V plot



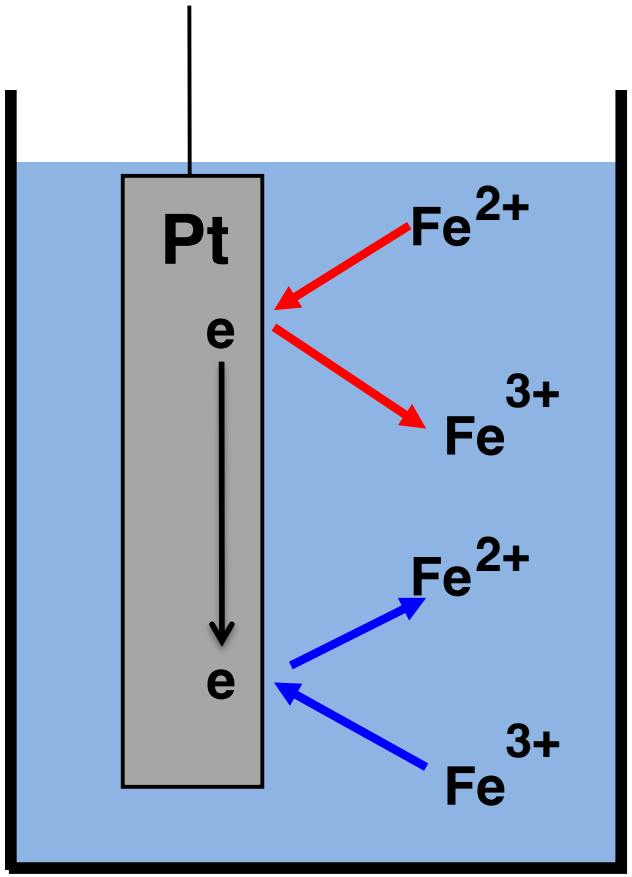
Rate determining steps in electrochemical reactions



Deriving an analytical expression for observed j-V plot



General equation for charge transfer reaction : Butler-Volmer



$$Fe^{2+} \underset{v_c}{\overset{v_a}{\rightleftharpoons}} Fe^{3+} + e$$

V_a: anodic reaction rate
V_c: cathodic reaction rate

Hypotheses:

- **first order** kinetics ($v \propto$ concentration)
- **Arrhenius** law

$$v_a = k_a \, c_{Fe\,2+,s} \, \exp\left(-\Delta G_a^{\#} / RT \right)$$

$$v_b = k_b \, c_{Fe\,3+,s} \, \exp\left(-\Delta G_c^{\#} / RT \right)$$

Net current flow under non-equilibrium conditions

Apply a bias relative to a reference electrode => current flow

$$R \underset{k_r}{\overset{k_f}{\rightleftharpoons}} O + ze^-$$

Recall:
$E_{red} > 0$: reduction favored
$E_{red} < 0$: oxidation favored

O : oxidized species in the electrolyte
R : reduced species in the electrolyte
e- : electrons being transferred to/from the working electrode

Forward reaction: rate k_f **increases** as electrode becomes more **positive** (easier to oxidize R to O)
Reverse reaction: rate k_r **increases** as electrode becomes more **negative** (easier to reduce O to R)

Derivation of Butler-Volmer equation

$$R \underset{k_r}{\overset{k_f}{\rightleftharpoons}} O + ze^-$$

[moles reacted] / [time·area]

anode :

$$rate_f := k_f [R]_s = \frac{i_a}{zFA} = \frac{j_a}{zF}$$

anode

Recall:

$$j = \frac{i}{A}$$

Hyp. : 1st order kinetics

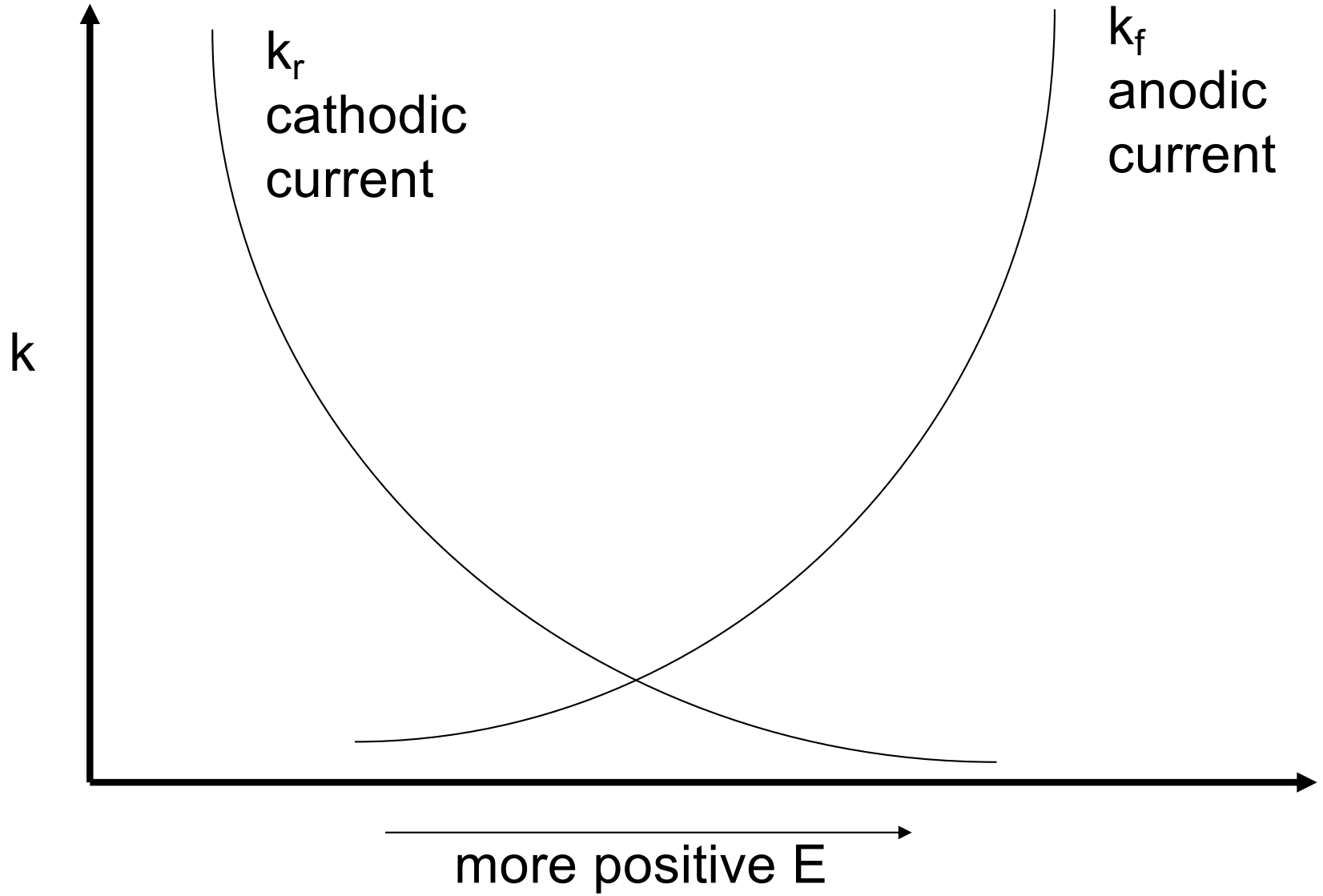
forward

surface concentration

reaction rate (mol/s.cm^2)

$$i = \frac{(\#\ moles)(z)(F)}{t} \Rightarrow \frac{(\#\ moles)}{t \cdot A} = \frac{i}{(z)(F)(A)}$$

Net current flow under non-equilibrium conditions



Derivation of Butler-Volmer equation

$$R \underset{k_r}{\overset{k_f}{\rightleftharpoons}} O + ze^-$$

anode : $\quad rate_f := k_f [R]_s = \frac{i_a}{zFA} = \frac{j_a}{zF}$

cathode : $\quad rate_r := k_r [O]_s = \frac{|i_c|}{zFA} = \frac{|j_c|}{zF}$

cathode

reverse

surface concentration

Derivation of Butler-Volmer equation

$$R \underset{k_r}{\overset{k_f}{\rightleftharpoons}} O + ze^-$$

anode : $\quad rate_f := k_f [R]_s = \frac{i_a}{zFA} = \frac{j_a}{zF}$

cathode : $\quad rate_r := k_r [O]_s = \frac{|i_c|}{zFA} = \frac{|j_c|}{zF}$

$$rate_{net} = rate_f - rate_r = \frac{j}{zF} = \frac{j_a - |j_c|}{zF} = k_f [R]_s - k_r [O]_s$$

depends on potential ! see p.35

Derivation of Butler-Volmer equation

$$\text{rate}_{net} = \text{rate}_f - \text{rate}_r = \frac{j}{zF} = \frac{j_a - |j_c|}{zF} = k_f [R]_s - k_r [O]_s$$

At equilibrium:

$$\text{rate}_f = \text{rate}_r \; ; \; j_a = |j_c|$$

$$k_f [R]_s = k_r [O]_s \rightarrow \frac{k_f}{k_r} = \frac{[O]_s}{[R]_s} \rightarrow \ln k_f - \ln k_r = \ln \frac{[O]_s}{[R]_s}$$

Nernst Equation:

$$E_{cell} = E^\circ_{cell,T} - \frac{RT}{zF} \ln \frac{[R]_s}{[O]_s} = E^\circ_{cell,T} + \frac{RT}{zF} \ln \frac{[O]_s}{[R]_s}$$

$$\ln \frac{[O]_s}{[R]_s} = \frac{(E_{cell} - E^\circ_{cell,T})zF}{RT}$$

Substituting the expression from the Nernst Equation into the equilibrium expression

$$\ln k_f - \ln k_r = \ln \frac{[O]_s}{[R]_s}$$

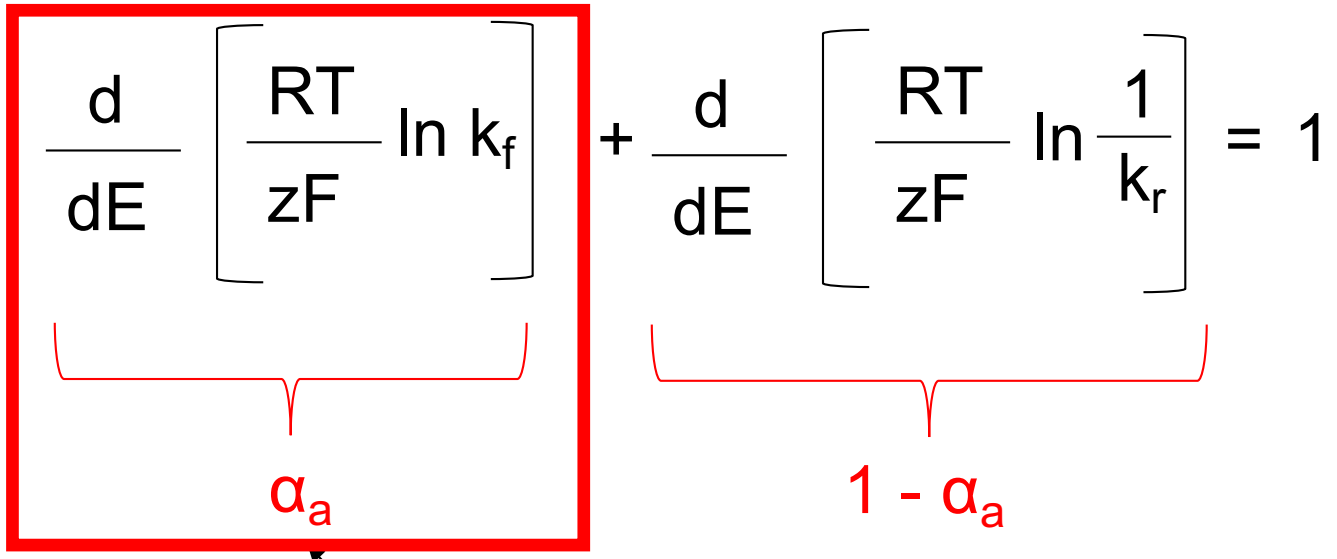
$$\ln \frac{[O]_s}{[R]_s} = \frac{(E_{cell} - E°_{cell,T})zF}{RT}$$

$$\ln k_f - \ln k_r = \frac{(E_{cell} - E°_{cell,T})zF}{RT}$$

$$\frac{RT}{zF} \times (\ln k_f - \ln k_r) = \frac{(E_{cell} - E^\circ_{cell,T})zF}{RT} \times \frac{RT}{zF}$$

$$\frac{d}{dE}\left[\frac{RT}{zF}\ln k_f - \frac{RT}{zF}\ln k_r\right] = \left[(E_{cell} - E^\circ_{cell,T})\right]\frac{d}{dE}$$

$$\frac{d}{dE}\left[\frac{RT}{zF}\ln k_f\right] \overset{+}{-} \frac{d}{dE}\left[\frac{RT}{zF}\ln \frac{1}{k_r}\right] = 1$$


$\frac{d}{dE}\left[\frac{RT}{zF}\ln k_f\right] + \frac{d}{dE}\left[\frac{RT}{zF}\ln\frac{1}{k_r}\right] = 1$
α_a
$1 - \alpha_a$
Defined with respect to the anode (forward reaction)

$$\alpha_a = \frac{d}{dE}\left[\frac{RT}{zF}\ln k_f\right] \Rightarrow \alpha_a E = \left[\frac{RT}{zF}\ln k_f\right] + C$$

or $$\ln k_f = \frac{\alpha_a zFE}{RT} + C'$$

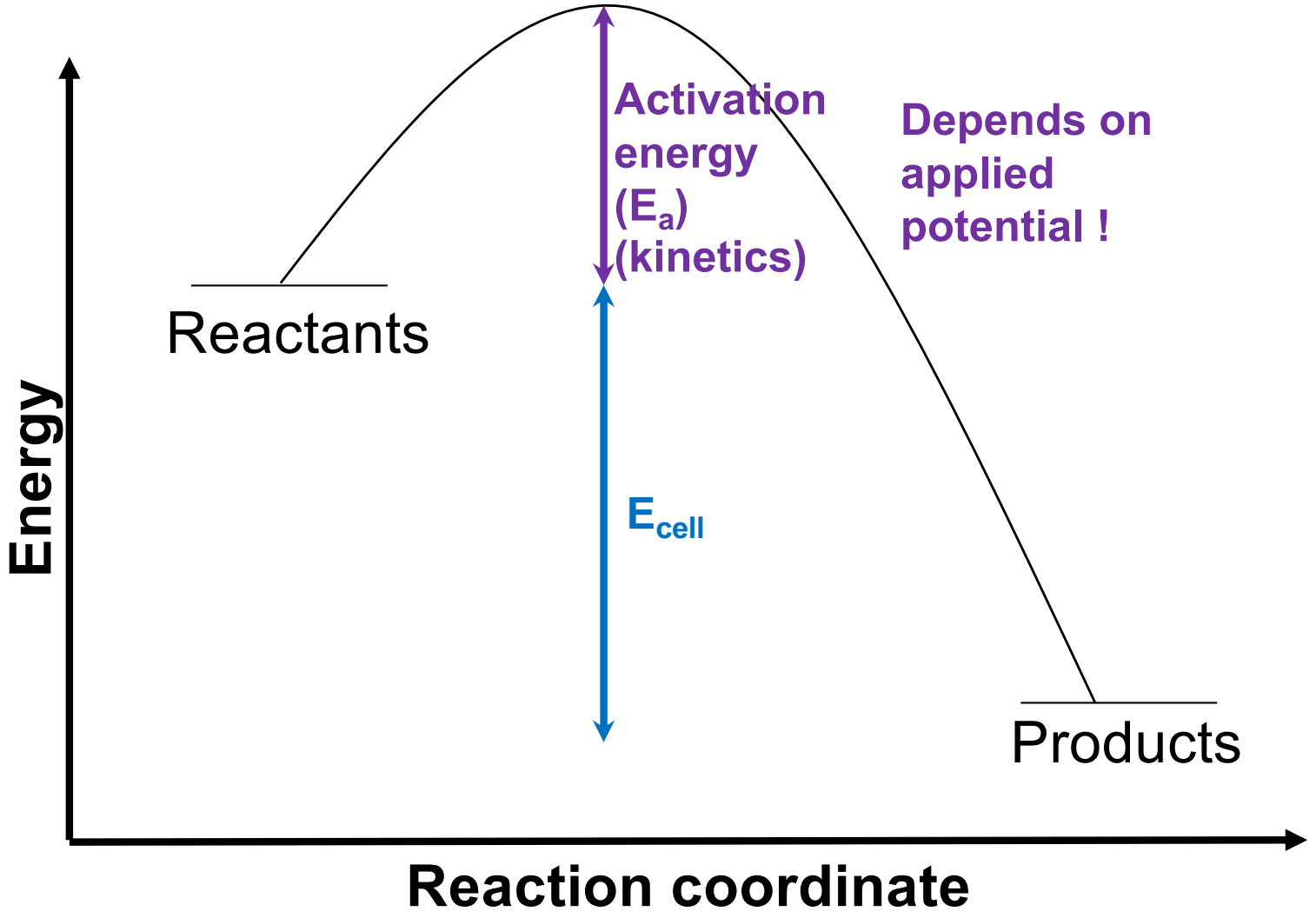
$$k_f = k_f^\circ \, e^{\frac{\alpha_a zF}{RT}(E-E^\circ)}$$

$k_f = k_f^\circ$ when $E = E^\circ$

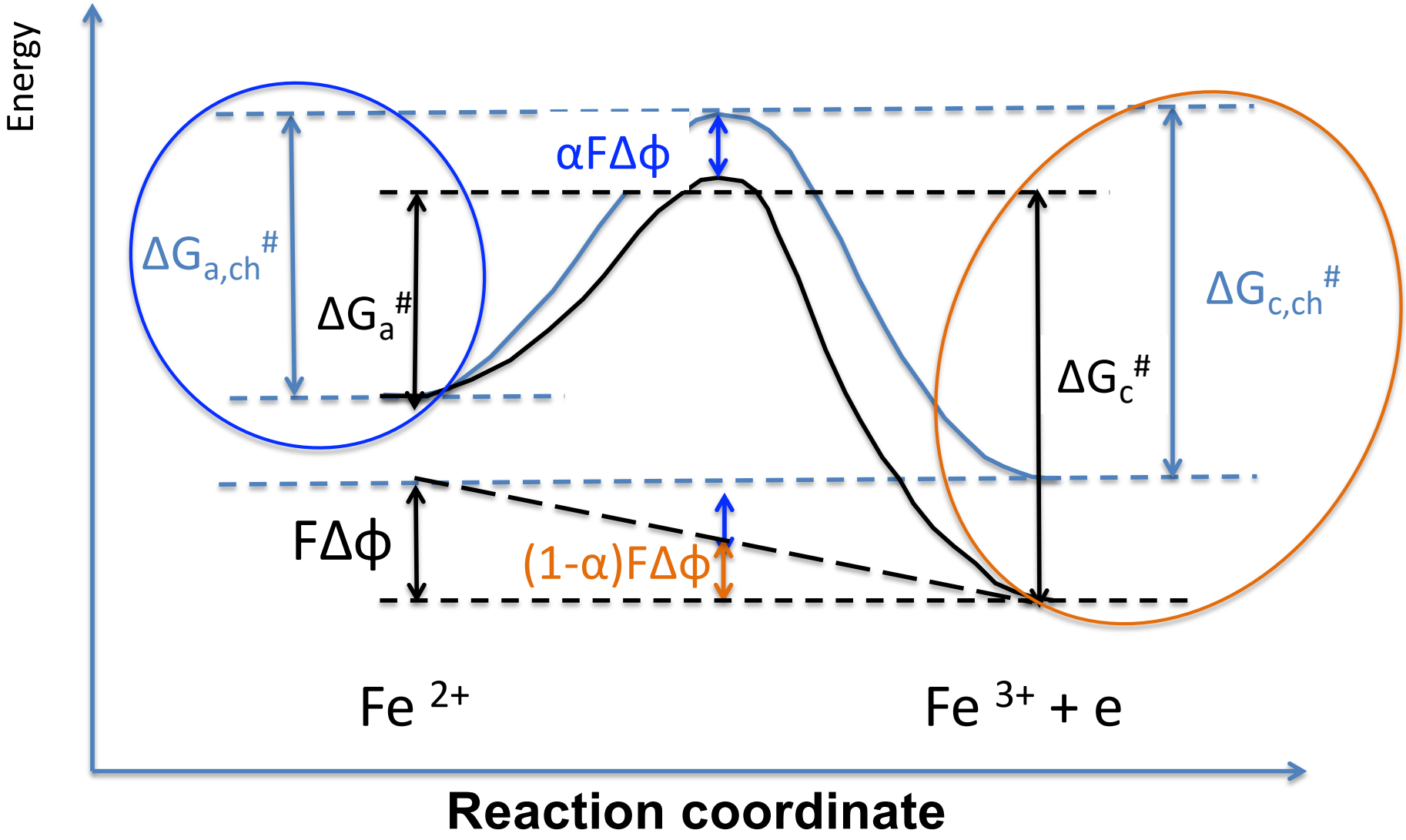
cf. Arrhenius expression:

$$k = A\, e^{-\frac{E_a}{RT}}$$

Analogy chemical reactivity and electrochemistry



Activation energy for charge transfer at electrode-electrolyte interface



Explanations:

- **Blue** is for the oxidation of Fe^{2+} ion in solution without applied electrical potential
- **Black** is for the redox reaction at a solid electrode interface that provides a potential difference $\Delta\phi$ to the solution.
- The applied potential is positive (anodic) since the oxidation of Fe^{2+} to Fe^{3+} is facilitated, the final energy of the product side (Fe^{3+}) is lowered (shifted down by $F\Delta\phi$). (The electrode takes up an electron from the dissolved Fe^{2+} , hence it is an oxidation (anodic)).
- This distorts the reaction path from the **blue** to the **black** curve, changing the **activation energy E_A ($\Delta G^{\#}$)** in both directions.
- E_A for the oxidation (left to right) is lowered by a factor $\alpha.F\Delta\phi$ (easier to oxidize thanks to the applied potential), while E_A for the reduction (right to left) is increased by a factor $(1-\alpha)F\Delta\phi$ (more difficult to reduce than before).
- The relative ease depends on the transfer number α, which is defined as 0.5 for a 'symmetrical' reaction.

Interpretation of k°

k° is a **frequency factor**. If the exponential term in an Arrhenius relation expresses the probability of surmounting the activation barrier E_A, k° is seen as the frequency of attempts on it.

$$k = k^\circ e^{f(\alpha,E)}$$

reaction occurrence = number of trials x probability of success

Values of k° depend on reaction complexity

$O_2 + 4\ H^+ + 4\ e^- \rightarrow H_2O$ (smaller k°)

$H_2 \rightarrow 2\ H^+ + 2e^-$ (larger k°)

k° for H-oxidation >> k° for O-reduction

Interpretation of k°

Even with a given value of k°, we can still change k

$$k = k^\circ e^{f(\alpha,E)}$$

- We can apply a large potential E to maintain a higher k for a small given value for k°

→ applying a large overpotential leads to lower net cell voltage (= less efficient)

- A better approach is to increase k° by reducing the reaction complexity or by improving the probability of reaction by orienting molecules favorably

→ approach to improving the oxygen reduction kinetics in existing devices

2nd term of Butler-Volmer equation

$$\frac{d}{dE}\left[\frac{RT}{zF}\ln k_f\right] + \frac{d}{dE}\left[\frac{RT}{zF}\ln\frac{1}{k_r}\right] = 1$$

α_a $\qquad$ $1 - \alpha_a$

via similar derivations as for k_f

$$k_r = k_r^\circ \, e^{-\frac{(1-\alpha_a)zF}{RT}(E-E^\circ)}$$

Overall Butler-Volmer equation

Combine the expressions for the **forward** and **reverse** rate constants to determine overall current:

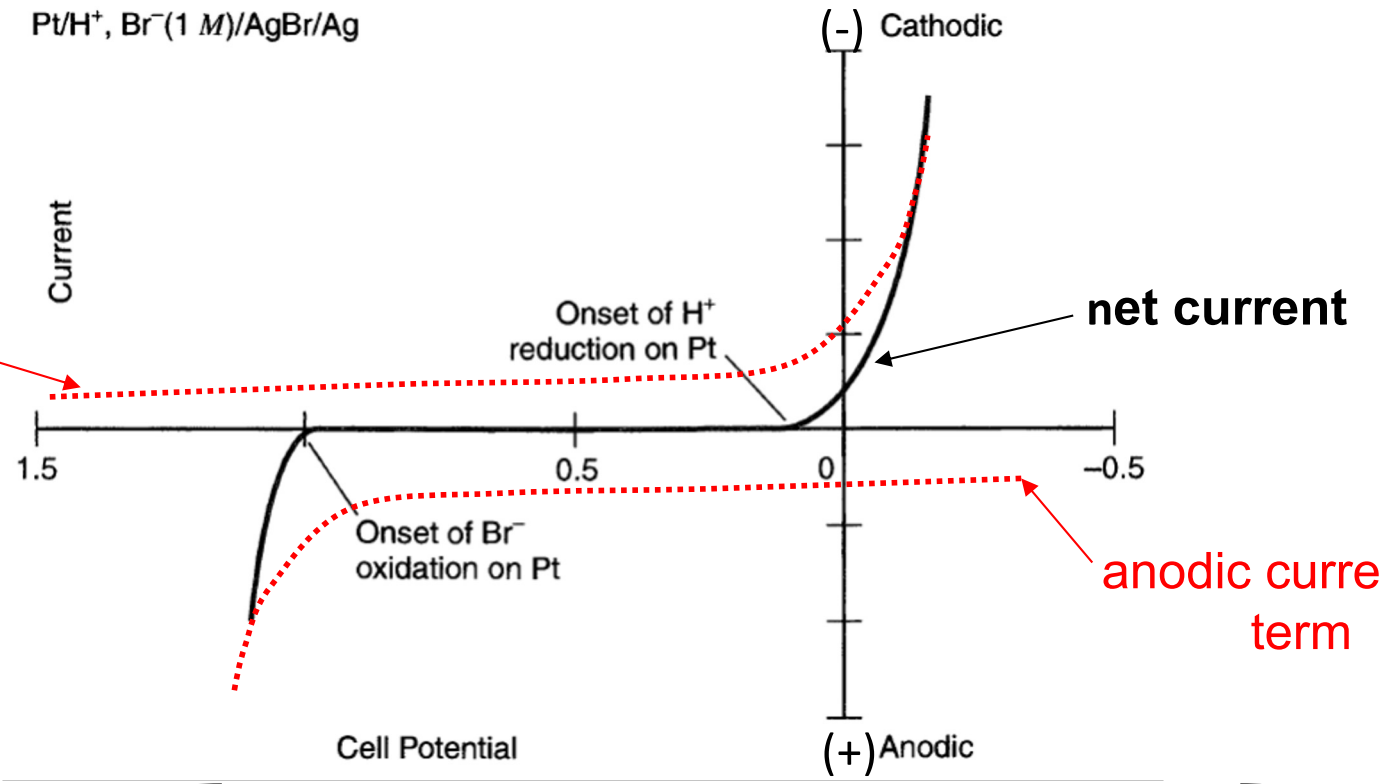
$$\frac{j}{zF} = k_f[R]_s - k_r[O]_s = k_f^\circ e^{\frac{\alpha_a zF}{RT}(E-E^\circ)}[R]_s - k_r^\circ e^{-\frac{(1-\alpha_a)zF}{RT}(E-E^\circ)}[O]_s$$

Assuming $k_f^\circ = k_r^\circ = k^\circ$ (1^{st} order kinetics)

Butler-Volmer Equation

$$j = zFk^\circ \left[[R]_s e^{\frac{\alpha_a zF}{RT}(E-E^\circ)} - [O]_s e^{-\frac{(1-\alpha_a)zF}{RT}(E-E^\circ)} \right]$$

Empirical example



cathodic current (j_c) term

anodic current (j_a) term

$$j = zFk^\circ \left[[R]_s \, e^{\frac{\alpha_a zF}{RT}(E-E^\circ)} - [O]_s \, e^{-\frac{(1-\alpha_a)zF}{RT}(E-E^\circ)} \right]$$

anodic current (j_a) term

cathodic current (j_c) term

Simplification of B-V equation: 1. Equilibrium

$$j = zFk^\circ \left[[R]_s \, e^{\frac{\alpha_a zF}{RT}(E-E^\circ)} - [O]_s e^{-\frac{(1-\alpha_a)zF}{RT}(E-E^\circ)} \right]$$

At equilibrium, $j = 0$ ($j_a = |j_c|$)

$$[R]_s \, e^{\frac{\alpha_a zF}{RT}(E_{eq}-E^\circ)} = [O]_s e^{-\frac{(1-\alpha_a)zF}{RT}(E_{eq}-E^\circ)}$$

$$\frac{[O]_s}{[R]_s} = e^{\frac{zF}{RT}(E_{eq}-E^\circ)}$$

simplifies to Nernst Equation ✓

$$\ln \frac{[O]_s}{[R]_s} = \frac{zF}{RT}(E_{eq}-E^\circ) \quad \Rightarrow \quad \boxed{E_{eq} = E^\circ + \frac{RT}{zF} \ln \frac{[O]_s}{[R]_s}}$$

Simplification of B-V equation: 2.Uniform concentration and j°

$$j = zFk^\circ \left[[R]_s \, e^{\frac{\alpha_a zF}{RT}(E-E^\circ)} - [O]_s e^{-\frac{(1-\alpha_a)zF}{RT}(E-E^\circ)} \right]$$

Assuming $[O]_s = [O]_{bulk} = [R]_s = [R]_{bulk} = [C]$

no mass transfer limitations

$$\Rightarrow \quad j = zFk^\circ[C] \left[e^{\frac{\alpha_a zF}{RT}(E-E^\circ)} - e^{-\frac{(1-\alpha_a)zF}{RT}(E-E^\circ)} \right]$$

Define:

$\eta = E - E^\circ$ (overpotential)

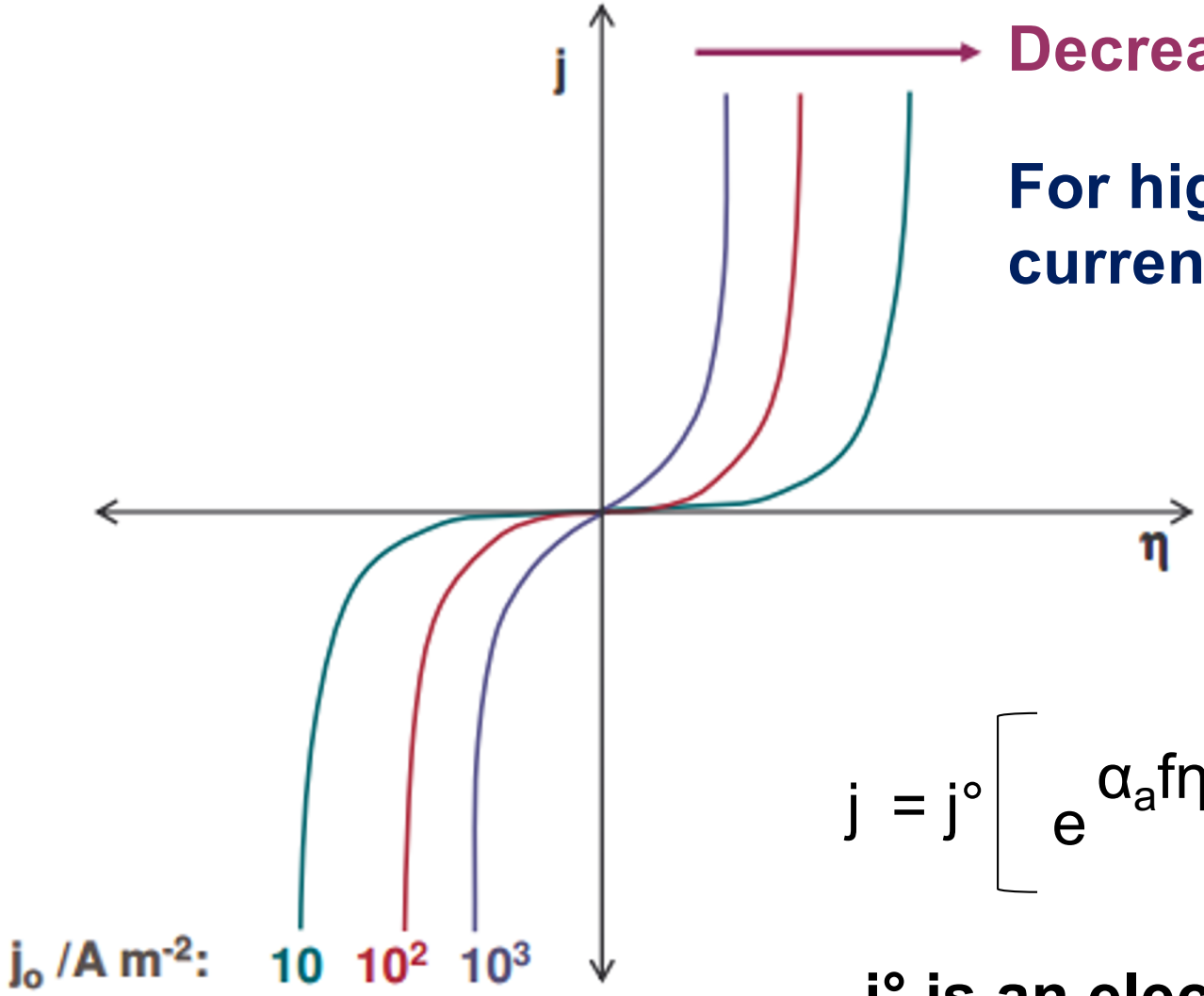
$f = \frac{zF}{RT}$

$j^\circ = zFk^\circ[R]^{1-\alpha}[O]^{\alpha}$ for 1:1 stoichiometric O : R reactions

$= zFk^\circ[C]$ when $[O] = [R] = [C]$

$$j = j^\circ \left[e^{\alpha_a f \eta} - e^{-(1-\alpha_a) f \eta} \right]$$

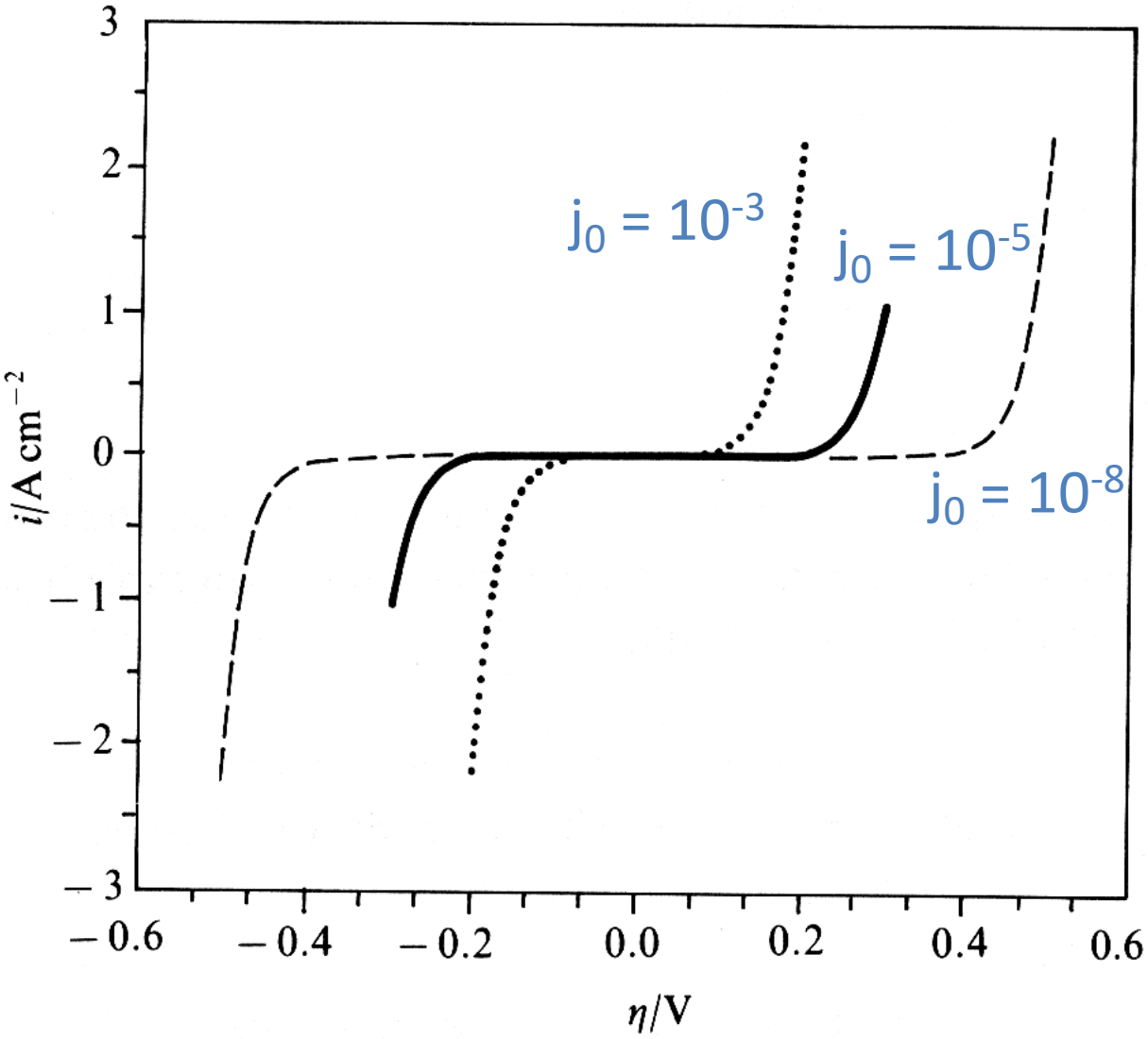
Effect of j° on j-V plot



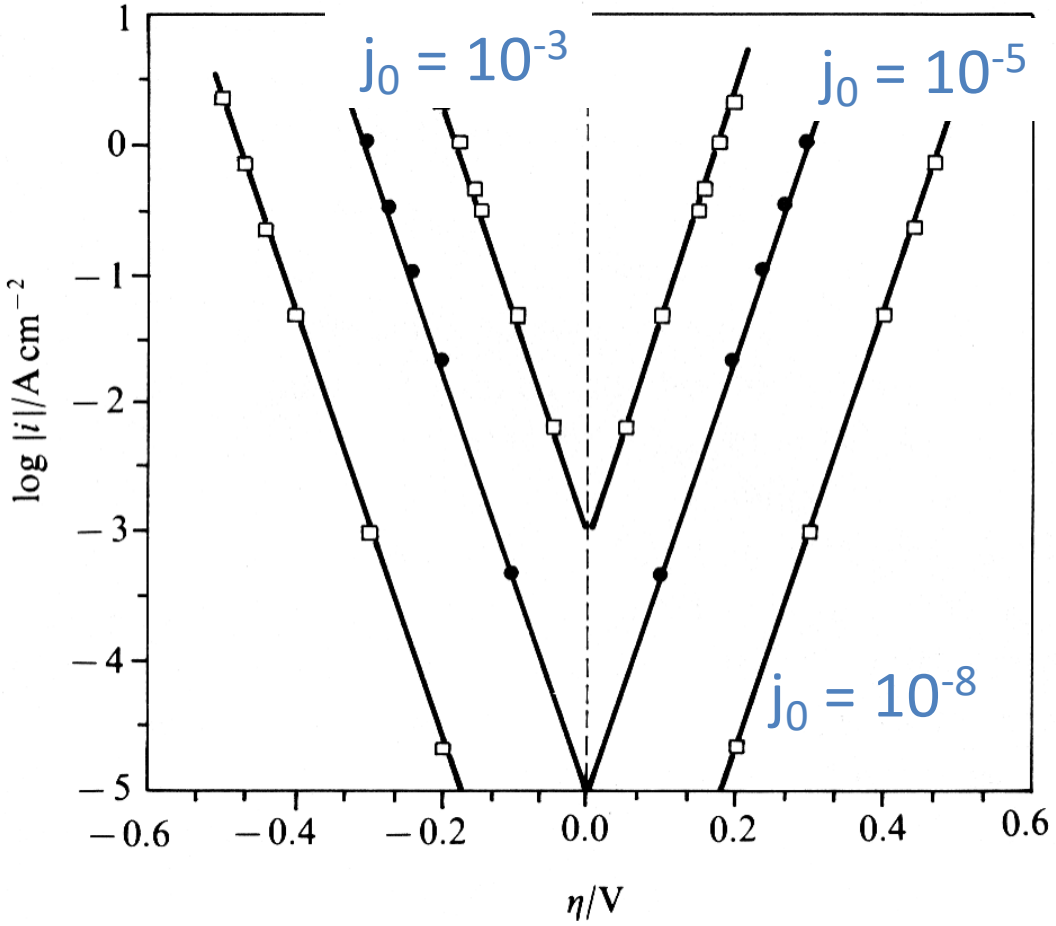
$$j = j^\circ \left[e^{\alpha_a f \eta} - e^{-(1-\alpha_a) f \eta} \right]$$

j° is an electrode property

Effect of exchange current j_0 on polarisation behaviour (linear scale)



Effect of exchange current j_0 on polarisation behaviour (log scale)



Physicochemical interpretation of j°

The **exchange current density** (j°) is defined as the anodic or cathodic current density which flows through the interface at equilibrium (zero net current)

$$R \underset{(j^\circ)}{\overset{(j^\circ)}{\rightleftharpoons}} O + ze^-$$

j° is a property of the electrode material.
It represents its catalytic activity for the reaction of interest.

Physicochemical interpretation of j°

Influence of electrode material on j° for the redox couple H^+/H_2 :

Metal	Log10 j° (A/cm²)
Pb, Hg	-13
Zn	-11
Sn, Al, Be	-10
Ni, Ag, Cu, Cd	-7
Fe, Au, Mo	-6
W, Co, Ta	-5
Pd, Rh	-4
Pt	-2

Pt is 11 orders of magnitude more catalytic than Hg for the redox couple H^+/H_2.

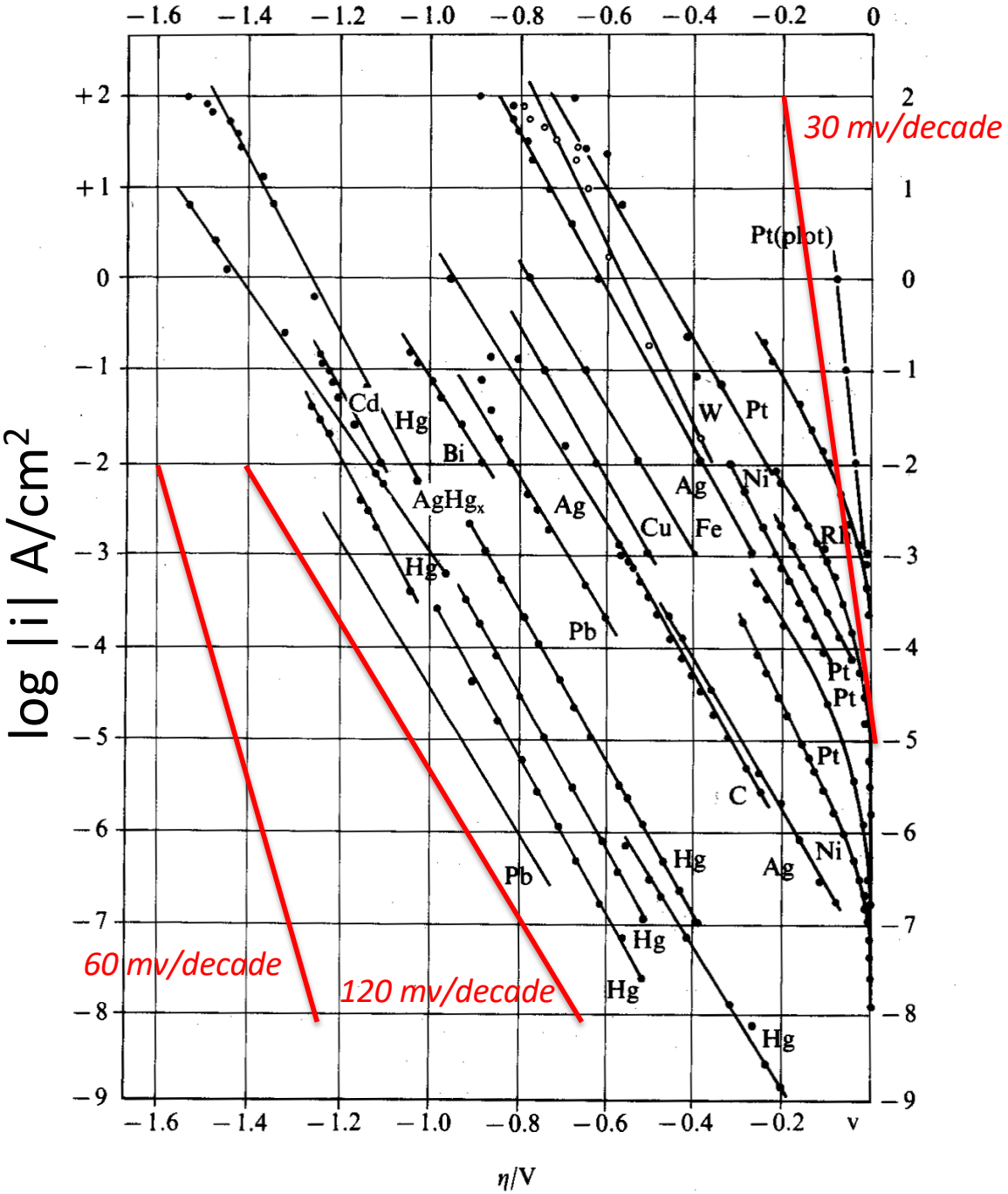
Parameters affecting charge transfer current densities

Exchange current density j_0 of the reaction

$2H^+ + 2e^- \Rightarrow H_2$ (20°C)

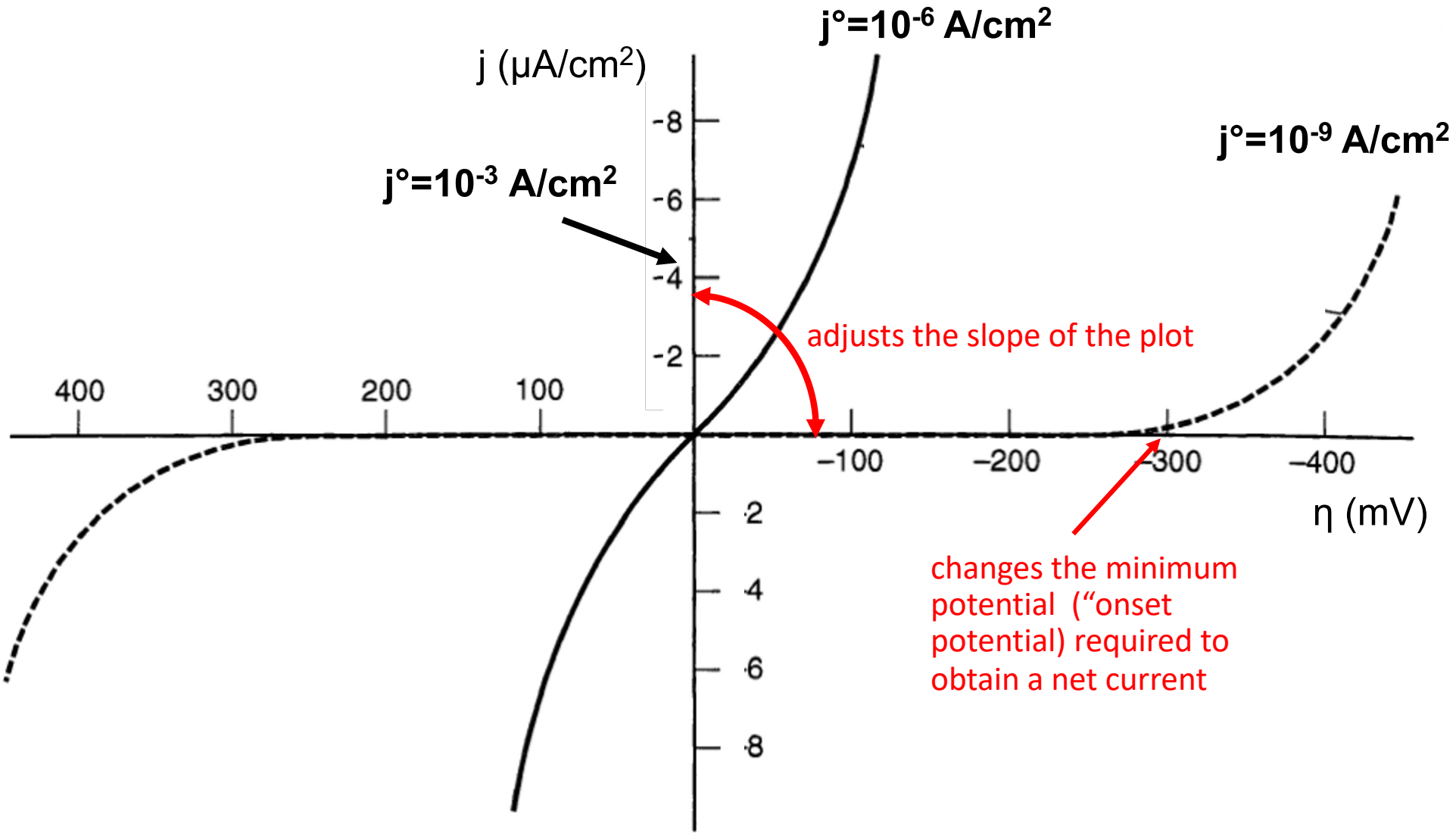
Metal	Solution	j_0 [A/cm^2]
Pt	1 M HCl	$1\ 10^{-3}$
Pb	1 M HCl	$2\ 10^{-13}$
Cu	0.14 M HCl	$2\ 10^{-7}$
Cu	0.15 M NaOH	$1\ 10^{-6}$

Tafel coefficients: β_a and $\beta_c \approx 30 - 60$ mV



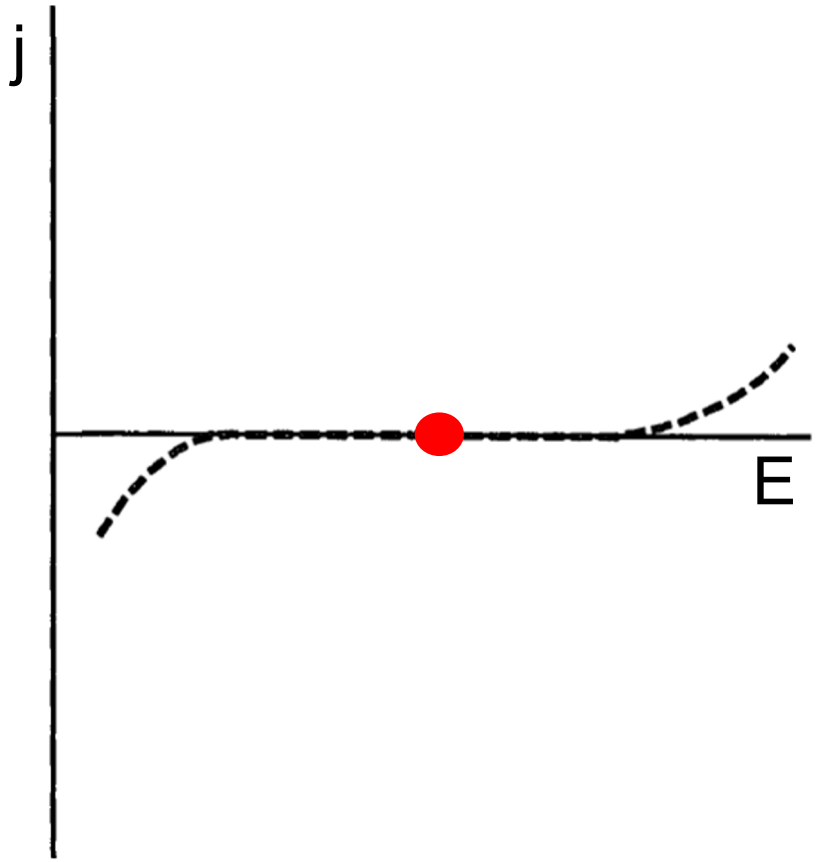
Cathodic polarization curves of hydrogen evolution on different metals in sulfuric acid

Effect of j° on ‘polarizability’

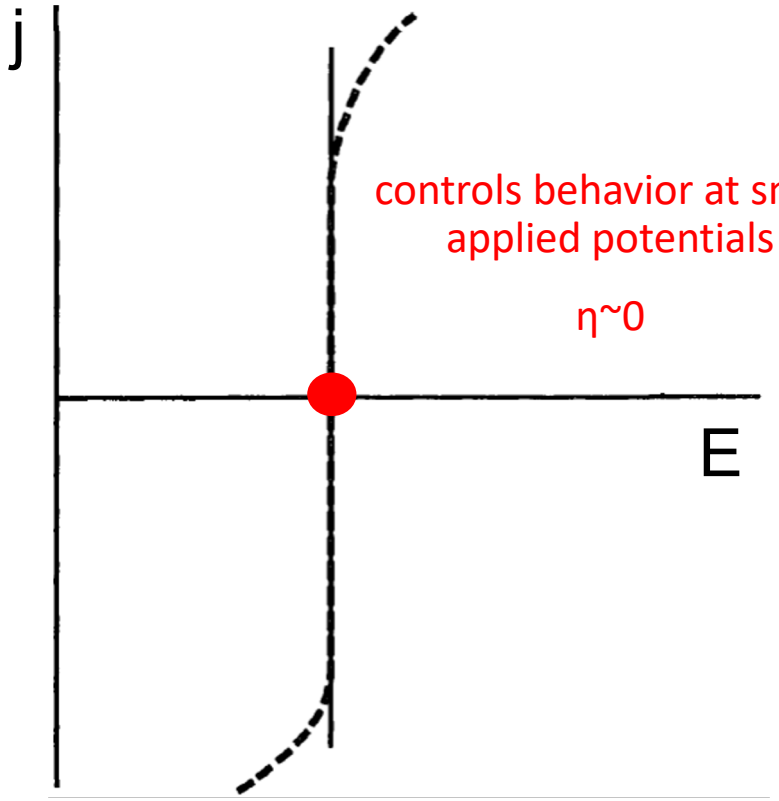


Effect of j° on polarizability

An **ideal polarizable electrode** is an electrode at which no charge transfer occurs across the metal-solution interface, regardless of the potential imposed.



polarizable electrode



non-polarizable electrode

Simplification of B-V equation: 3. small overpotential η

For small E-E° → $|\eta| << \frac{RT}{zF}$

Substituting **Taylor series approximation** into corresponding exponential terms

$$j = j^\circ \left[e^{\alpha_a f \eta} - e^{-(1-\alpha_a) f \eta} \right]$$

$$\frac{j}{j^\circ} = (1+\alpha_a f\eta) - (1-(1-\alpha_a) f\eta) = f\eta$$

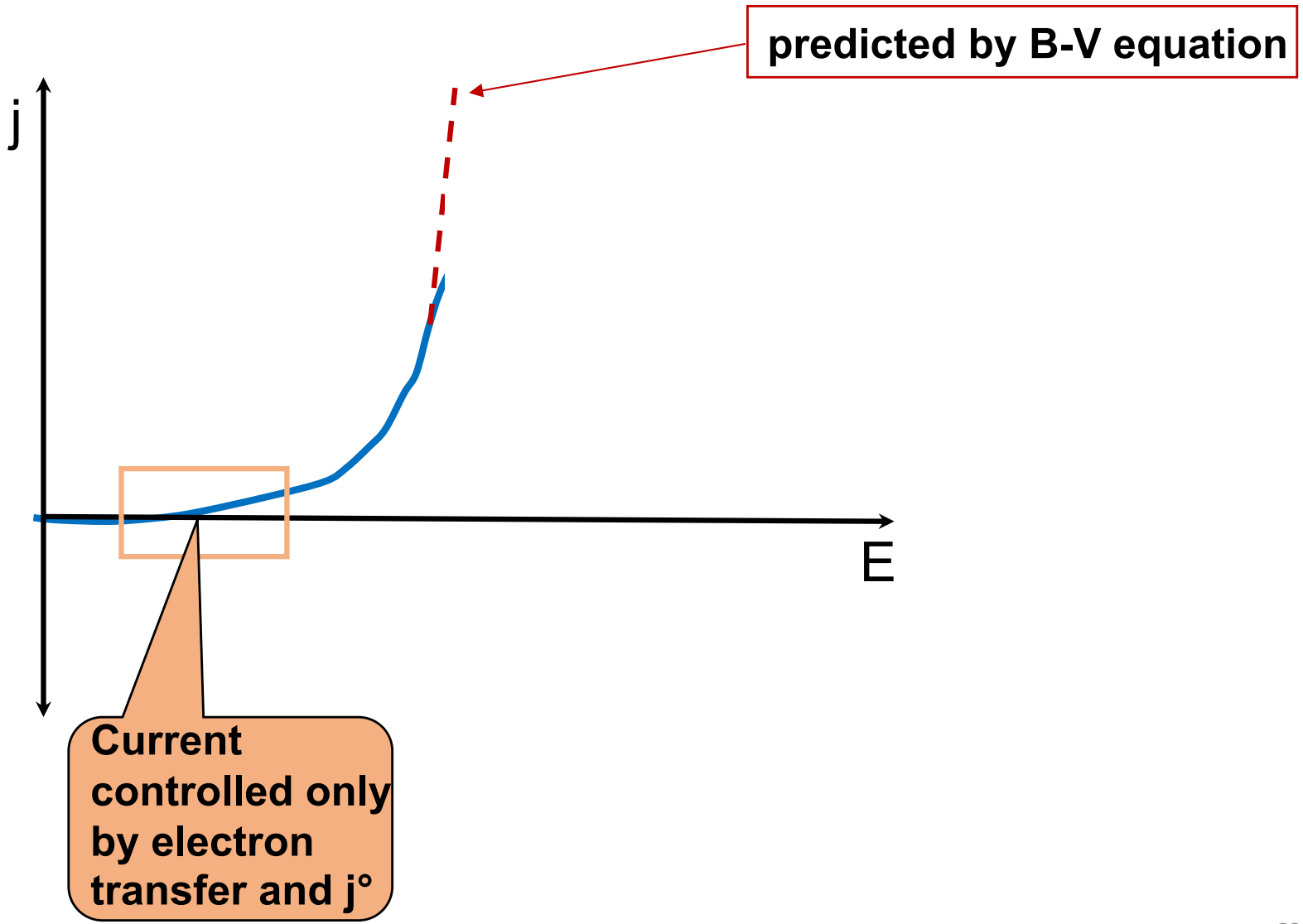
Solving for η and substituting for f

$$\eta = j \frac{RT}{zFj^\circ}$$

Ohm's law : $V = iR$

charge transfer resistance

$$R_{ct} = \frac{RT}{zF|i^\circ|}, \quad \rho_{ct} = \frac{RT}{zF|j^\circ|}$$


predicted by B-V equation
j
E
Current controlled only by electron transfer and j°

Effect of j° and R_{ct} on polarizability

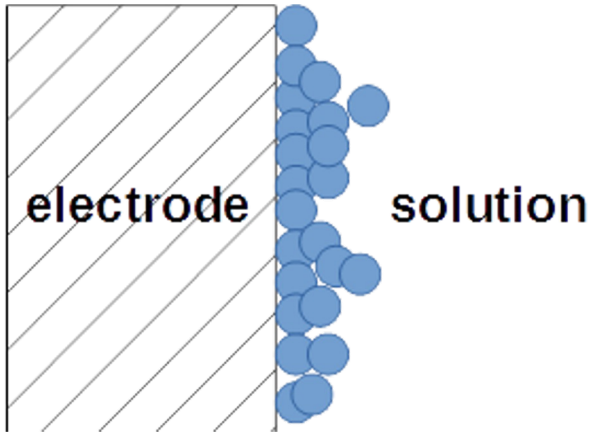
An **ideal polarizable electrode** is an electrode at which no charge transfer occurs across the metal-solution interface, regardless of the potential imposed.

$$R_{ct} = \frac{RT}{zF|i°|}$$

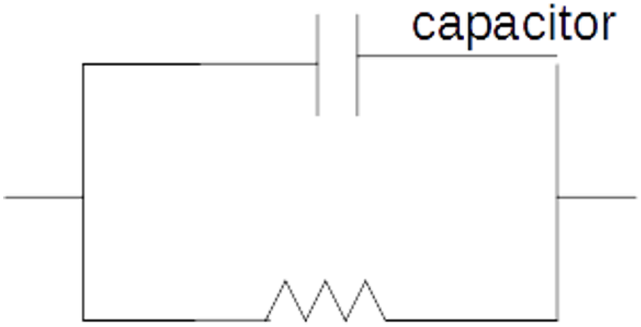
- As R_{ct} approaches zero, the interface is said to be ideally non-polarizable, i.e. its potential cannot be changed
- A **reference electrode** should be ideally polarizable over the current range in the experiment

Effect of j° and R_{ct} on polarizability

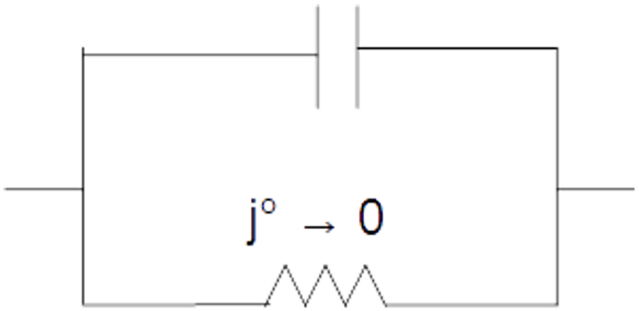
Electrified interface



Its equivalent circuit

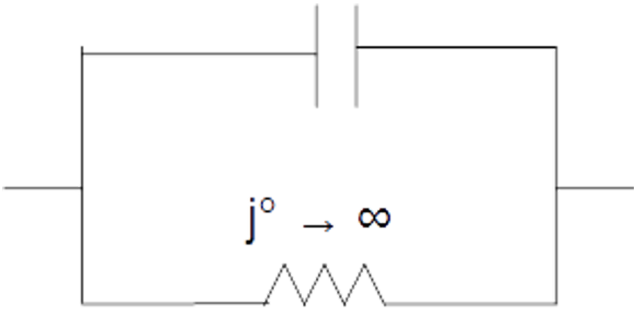


Equivalent circuit of ideally polarizable interface

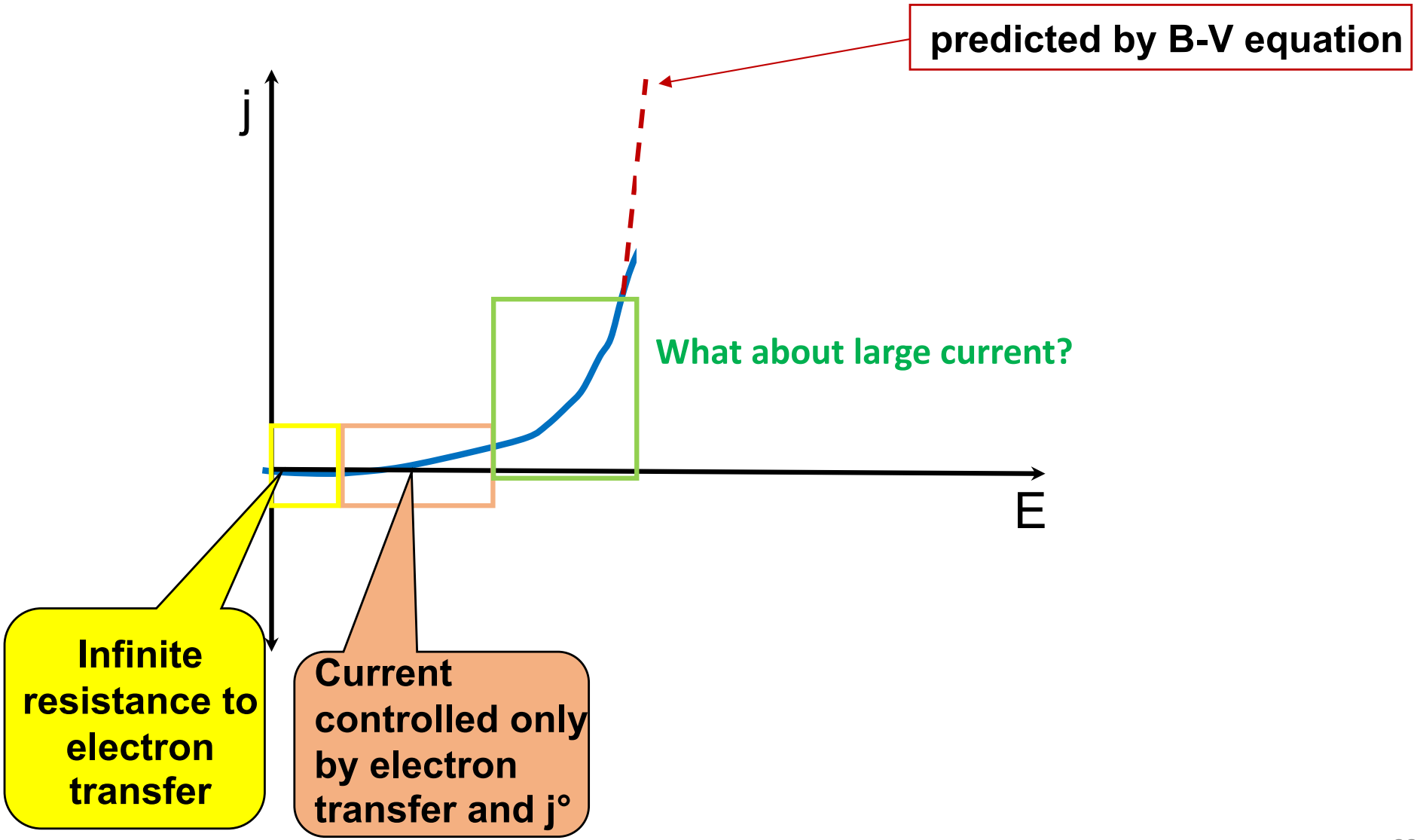


R → ∞

Equivalent circuit of ideally non-polarizable interface



R → 0


predicted by B-V equation
j
E
What about large current?
Infinite resistance to electron transfer
Current controlled only by electron transfer and j°

Simplification of B-V equation: 4. large overpotential η

For large E-E° → $|\eta| >> \frac{RT}{zF}$

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

$e^{\alpha_a f\eta} >> e^{-(1-\alpha_a)f\eta}$ if $\eta >> 0$

Anodic

or

$e^{\alpha_a f\eta} << e^{-(1-\alpha_a)f\eta}$ if $\eta << 0$

Cathodic

For large $E-E^\circ \rightarrow |\eta| >> \frac{RT}{zF}$

for $\eta > 0$ (anodic) $\quad e^{\alpha_a f\eta} >> e^{-(1-\alpha_a)f\eta}$

$$j = j^\circ \left[e^{\alpha_a f\eta} - e^{-(1-\alpha_a)f\eta} \right]$$

$$j \sim j^\circ e^{\alpha_a f\eta} \Rightarrow \frac{j}{j^\circ} = e^{\alpha_a f\eta} \Rightarrow \ln \frac{j}{j^\circ} = \alpha_a f\eta$$

$$\eta = a + b \ln j$$

Into linear form :

$$\frac{1}{\alpha_a f}(\ln j - \ln j^\circ) = \eta \Rightarrow \eta = -\frac{RT}{zF\alpha_a} \ln j^\circ + \frac{RT}{zF\alpha_a} \ln j$$

For large $E-E^\circ \rightarrow |\eta| >> \frac{RT}{zF}$

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

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

if $\eta >> 0$ if $\eta << 0$

Anodic Cathodic

For large $E-E^\circ \rightarrow |\eta| >> \frac{RT}{zF}$

for $\eta < 0$ (cathodic)

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

$$j = j^\circ \left[\cancel{e^{\alpha_a f\eta}} - e^{-(1-\alpha_a)f\eta} \right]$$

$$j \sim -j^\circ e^{-(1-\alpha_a)f\eta} \Rightarrow \frac{-j}{j^\circ} = e^{-(1-\alpha_a)f\eta} \Rightarrow \ln\left|\frac{j}{j^\circ}\right| = -(1-\alpha_a)f\eta$$

$\eta = a + b \ln j$

Into linear form :

$$\frac{-1}{(1-\alpha_a)f}\left(\ln|j| - \ln|j^\circ|\right) = \eta \Rightarrow \eta = -\frac{RT}{zF(1-\alpha_a)}\ln|j| + \frac{RT}{zF(1-\alpha_a)}\ln|j^\circ|$$

Simplification of B-V equation: 4. large overpotential η

for η >> 0 (anodic)

$$\eta = -\frac{RT}{zF\alpha_a} \ln j^\circ + \frac{RT}{zF\alpha_a} \ln j$$

$$\ln j = \ln j^\circ + \frac{zF\alpha_a}{RT} \eta$$

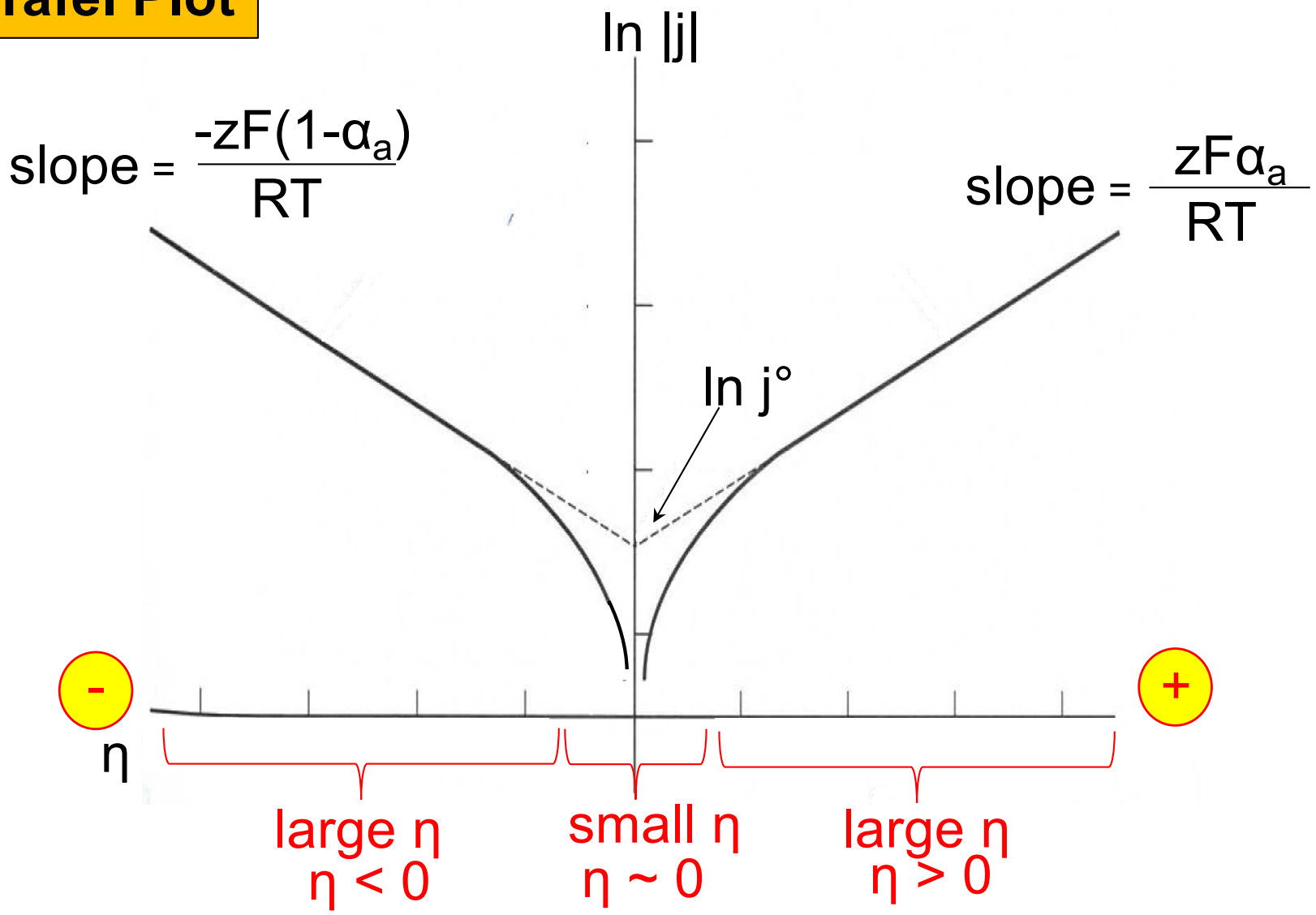
for η << 0 (cathodic)

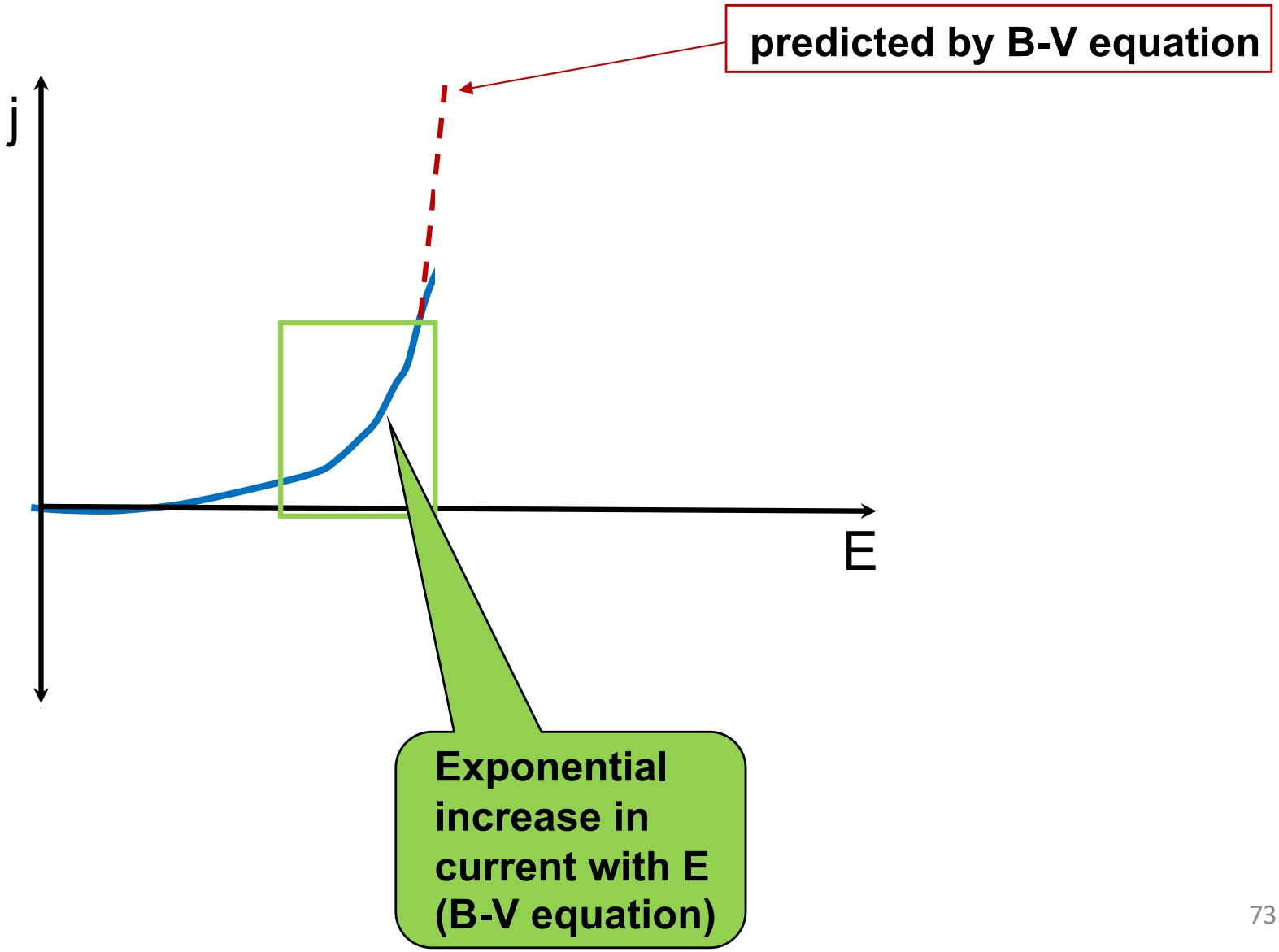
$$\eta = -\frac{RT}{zF(1-\alpha_a)} \ln |j| + \frac{RT}{zF(1-\alpha_a)} \ln |j^\circ|$$

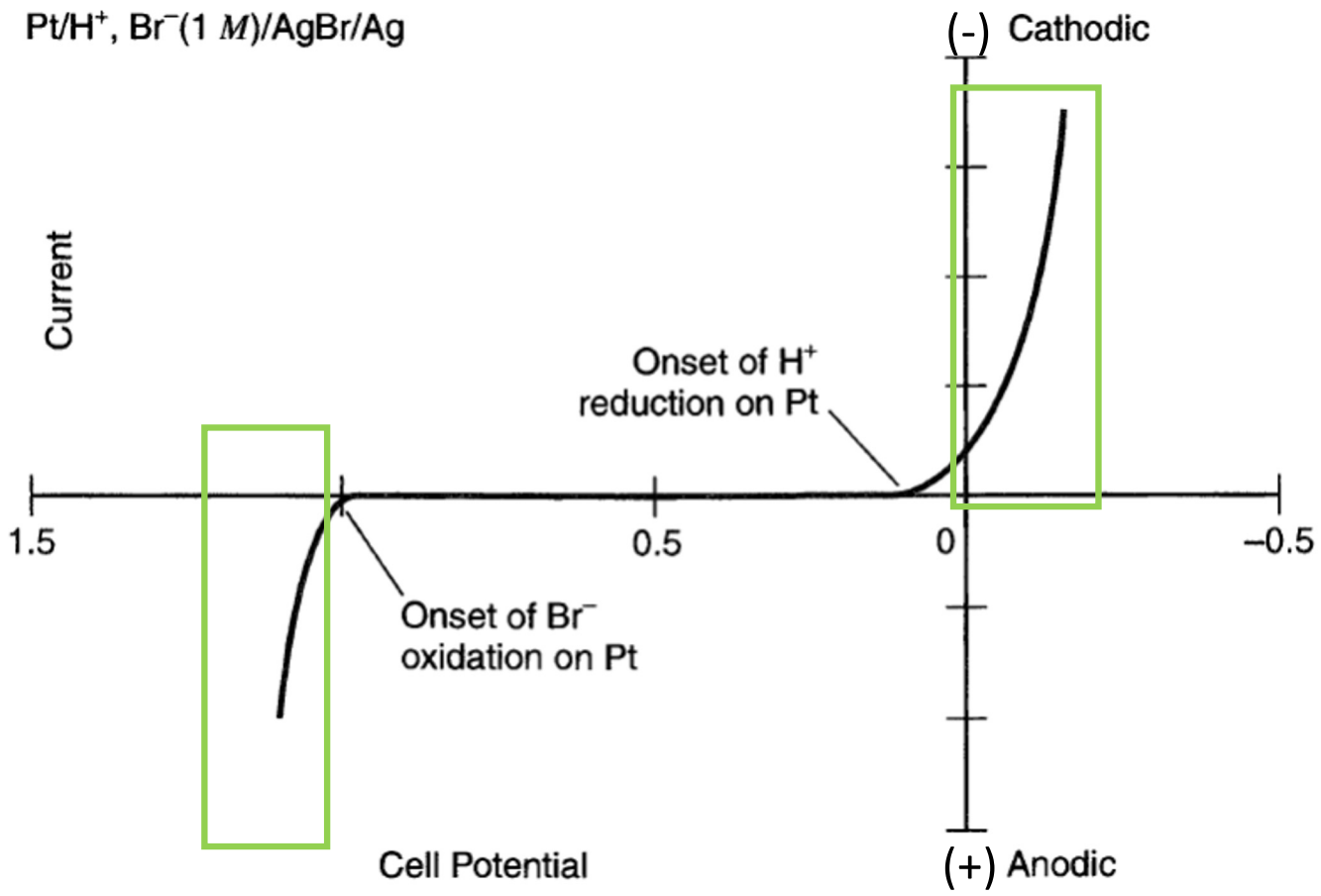
$$\ln |j| = \ln |j^\circ| - \frac{zF(1-\alpha_a)}{RT} \eta$$

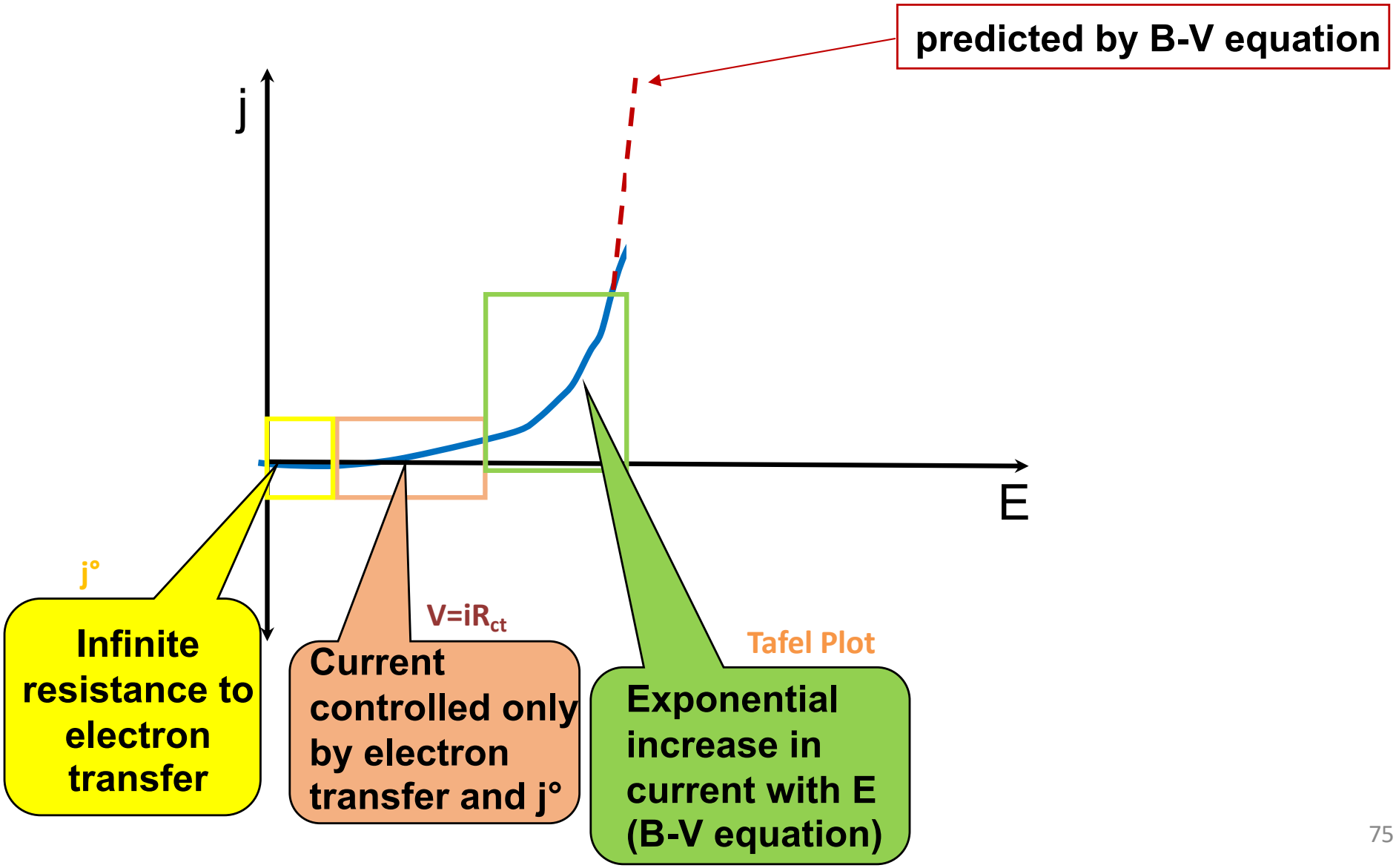
Simplification of B-V equation: 4. large overpotential η

Tafel Plot




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


Pt/H+, Br−(1 M)/AgBr/Ag
(-) Cathodic
Current
Onset of H+
reduction on Pt
1.5
0.5
0
–0.5
Onset of Br−
oxidation on Pt
Cell Potential
(+) Anodic


predicted by B-V equation
j
E
j°
Infinite resistance to electron transfer
V=iR_ct
Current controlled only by electron transfer and j°
Tafel Plot
Exponential increase in current with E (B-V equation)

Overview of B-V simplifications

$$j = zFk^\circ \left[[R]_s \, e^{\frac{\alpha_a zF}{RT}(E-E^\circ)} - [O]_s e^{-\frac{(1-\alpha_a)zF}{RT}(E-E^\circ)} \right]$$

- **Small |η| → charge transfer resistance**

  $(E-E^\circ) \sim 0$ (10 mV) $\quad R_{ct} = \dfrac{RT}{zF\,|i^\circ|}$

- **Large |η| → Tafel kinetics**

  $(E-E^\circ) >> 0$ (> 0.1 V) $\quad [R]_s \, e^{\frac{\alpha_a zF}{RT}(E-E^\circ)}$ anodic current dominates

  $(E-E^\circ) << 0$ (< - 0.1V) $\quad [O]_s \, e^{-\frac{(1-\alpha_a)ZF}{RT}(E-E^\circ)}$ cathodic current dominates

- **$i_{net} = 0$ → Nernst Equation**

  $j_a = |j_c| = j^\circ$

  $j^\circ = zFk^\circ [R]_S^{1-\alpha} [O]_S^{\alpha} = zFk^\circ [C]$

  1:1 O : R ratio

  $[O]_S = [R]_S = [C]$

  electrode property

  reaction complexity

B-V equation relative to equilibrium reference potential

$$j = zFk^{\circ}\left[[R]_s\, e^{\frac{\alpha_a zF}{RT}(E-E^{\circ})} - [O]_s\, e^{\frac{-(1-\alpha_a)zF}{RT}(E-E^{\circ})}\right]$$

arbitrary reference selected

Re-write this equation using the equilibrium potential as a reference.
(i.e., we evaluate current when a potential is applied relative to the equilibrium reference)

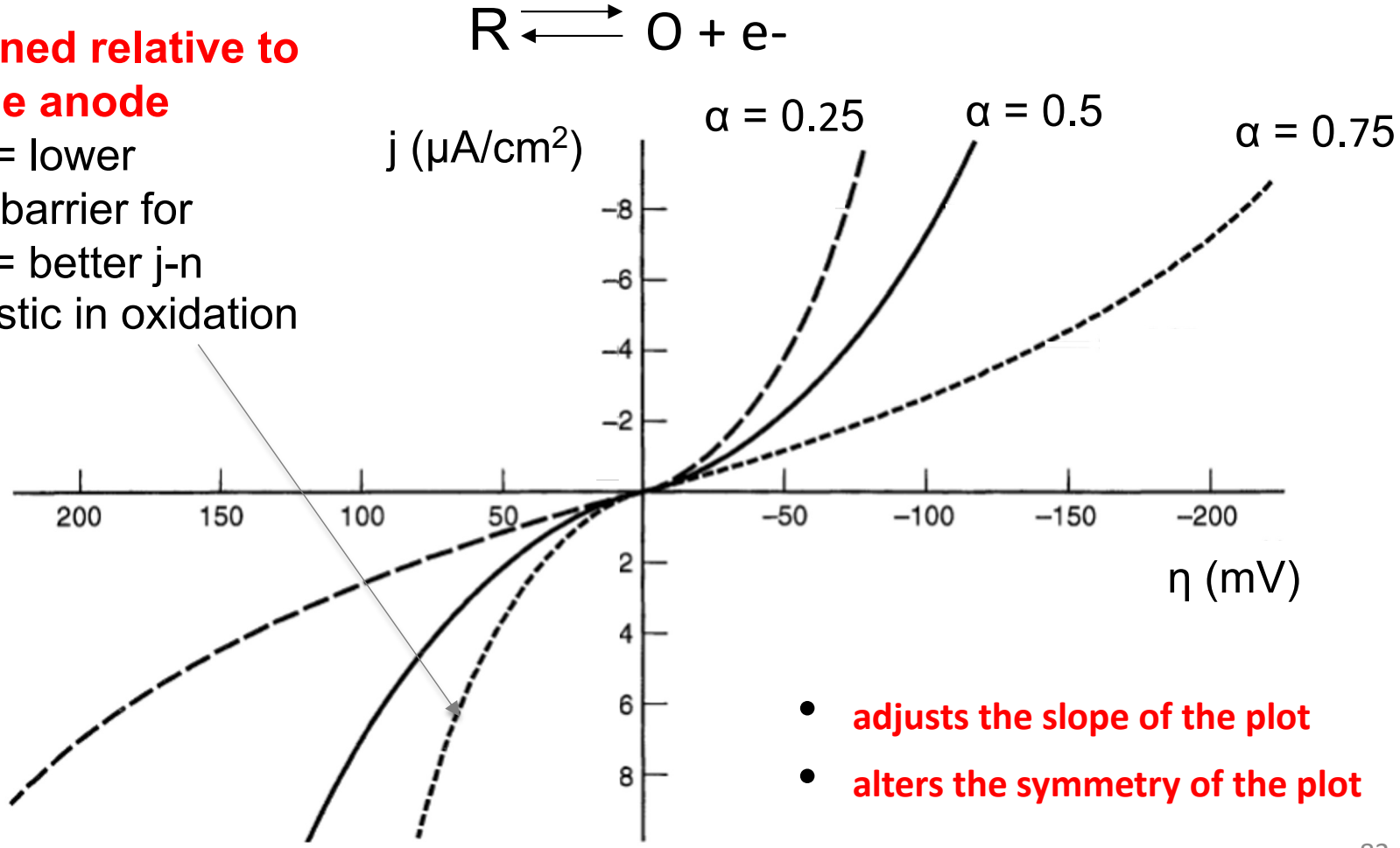
$$\frac{j}{j^{\circ}} = \frac{[R]_s}{[R^*]}\, e^{\frac{\alpha_a zF}{RT}\underbrace{(E-E_{eq})}_{\acute{\eta}}} - \frac{[O]_s}{[O^*]}\, e^{\frac{-(1-\alpha_a)zF}{RT}\underbrace{(E-E_{eq})}_{\acute{\eta}}}$$

Effect of α

If the voltammogram (current-potential curve) is charge transfer kinetically controlled (no mass transfer effects), α far from 0.5 will result in an asymmetric wave shape

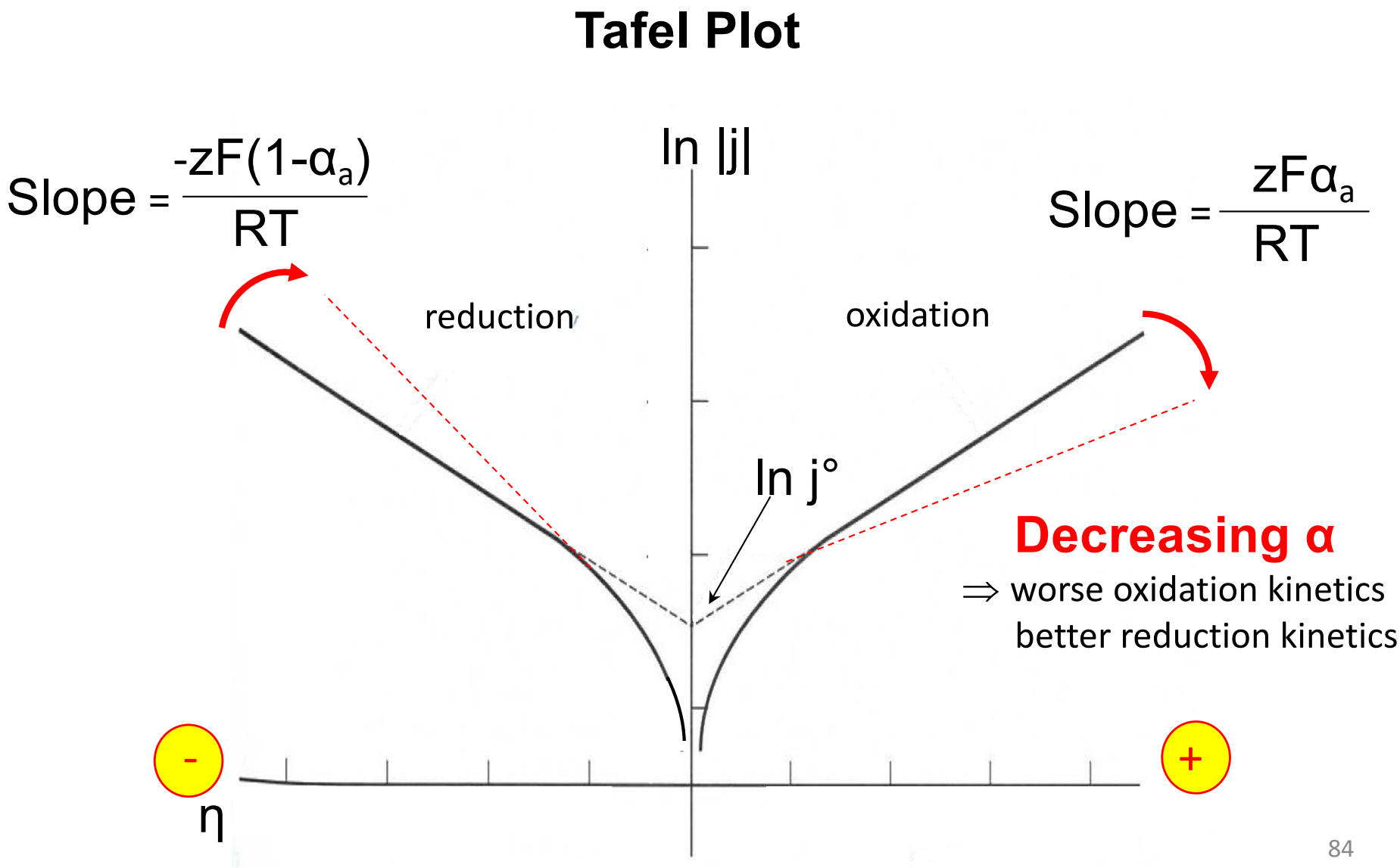
α is defined relative to the anode

(higher α = lower activation barrier for oxidation = better j-n characteristic in oxidation regime)

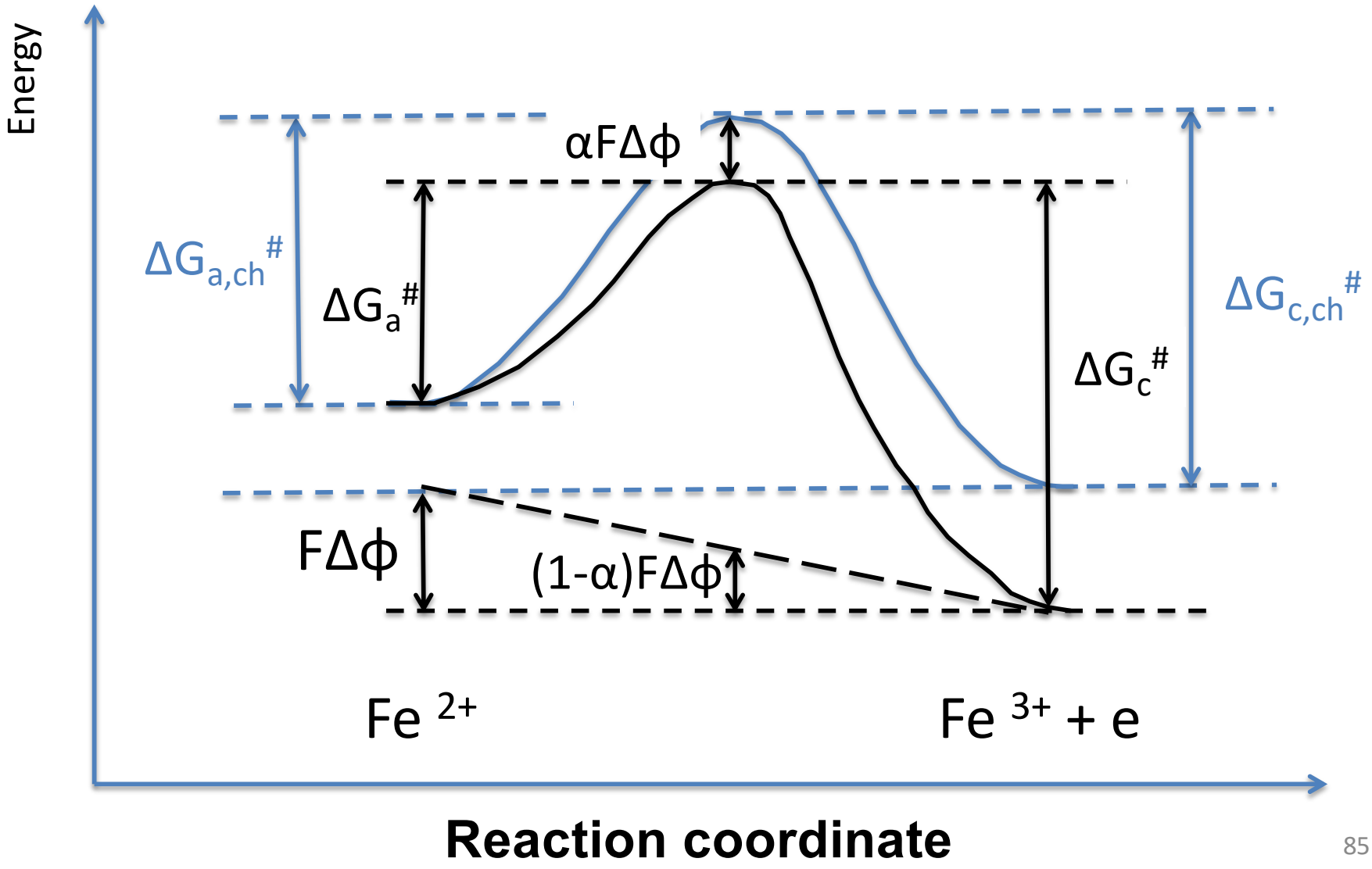


- **adjusts the slope of the plot**
- **alters the symmetry of the plot**

Effect of α

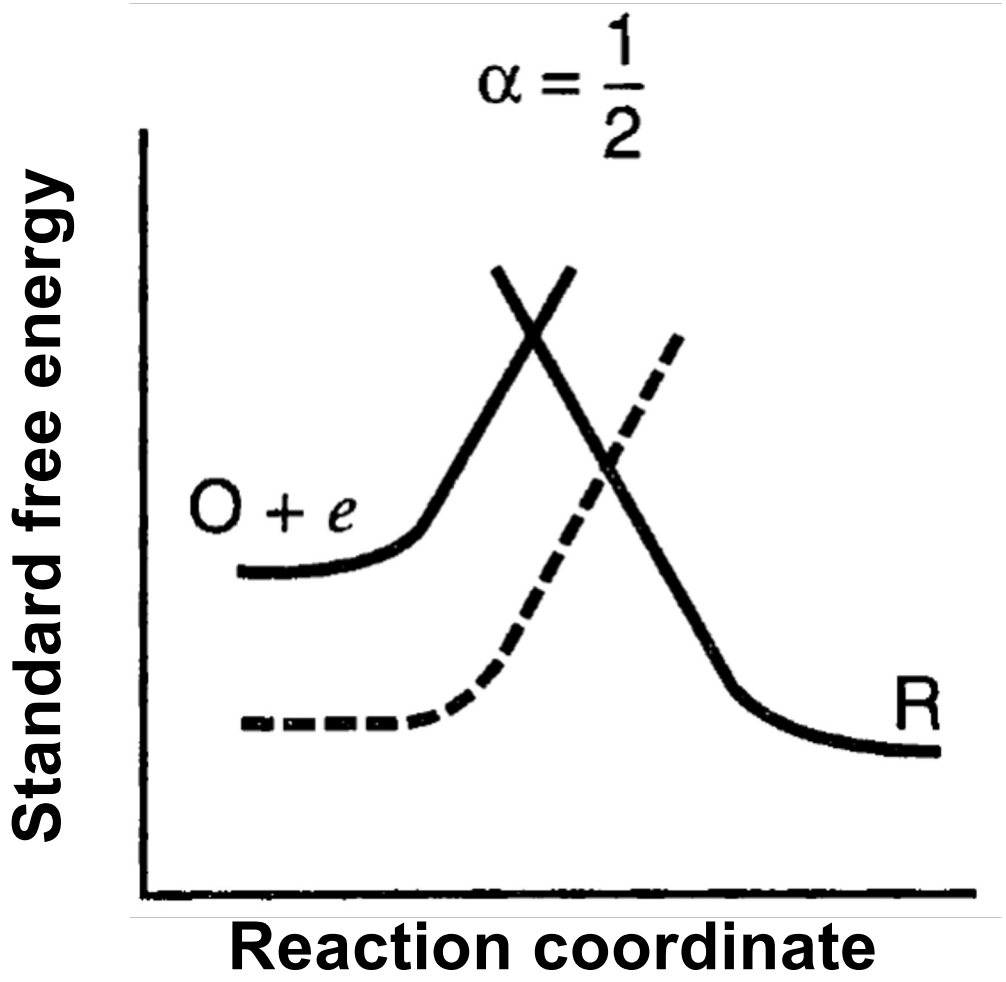

Tafel Plot
Slope = -zF(1-α_a) / RT
ln |j|
Slope = zFα_a / RT
reduction
oxidation
ln j°
Decreasing α
⇒ worse oxidation kinetics
better reduction kinetics
-
+
η

pm: Activation energy for charge transfer at electrode-electrolyte interface



Physicochemical interpretation of α

The **transfer coefficient** (α) is an indicator of the symmetry of the barrier to the reaction.



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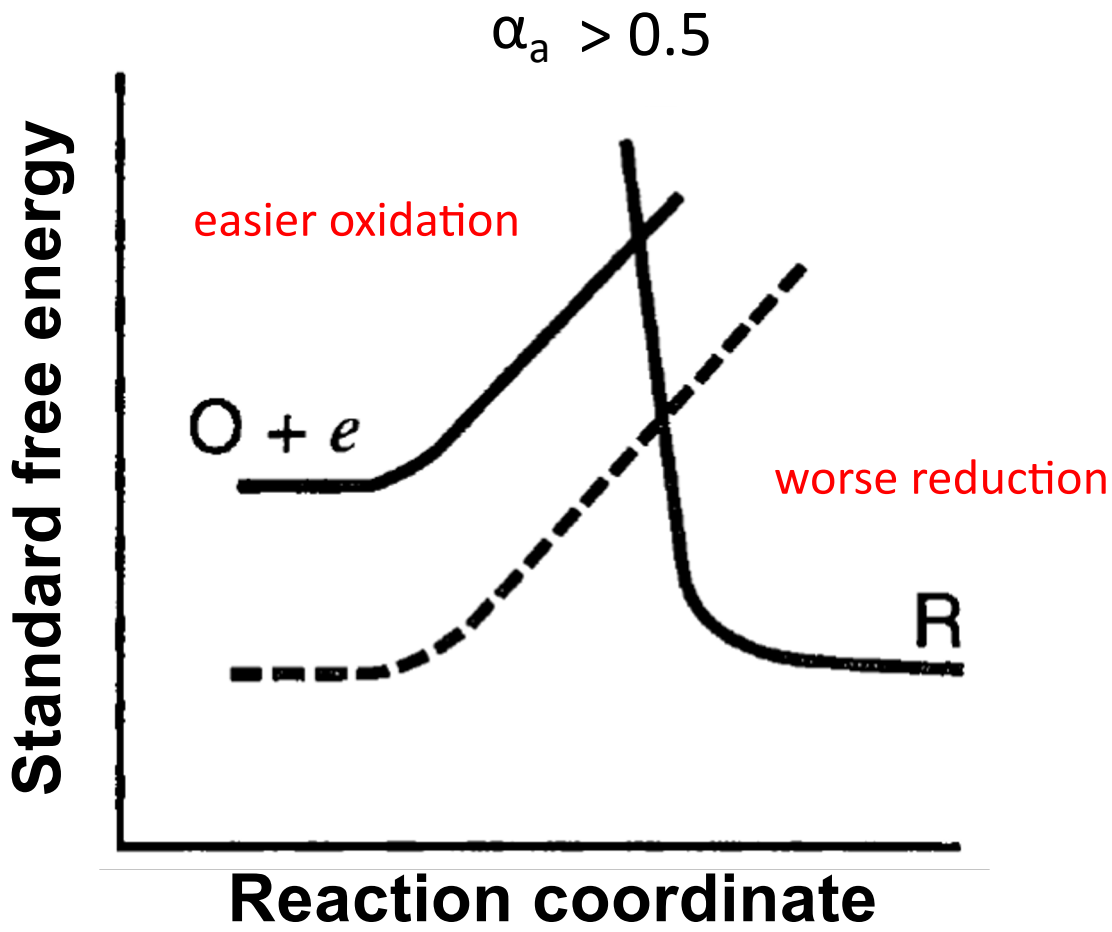

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