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))

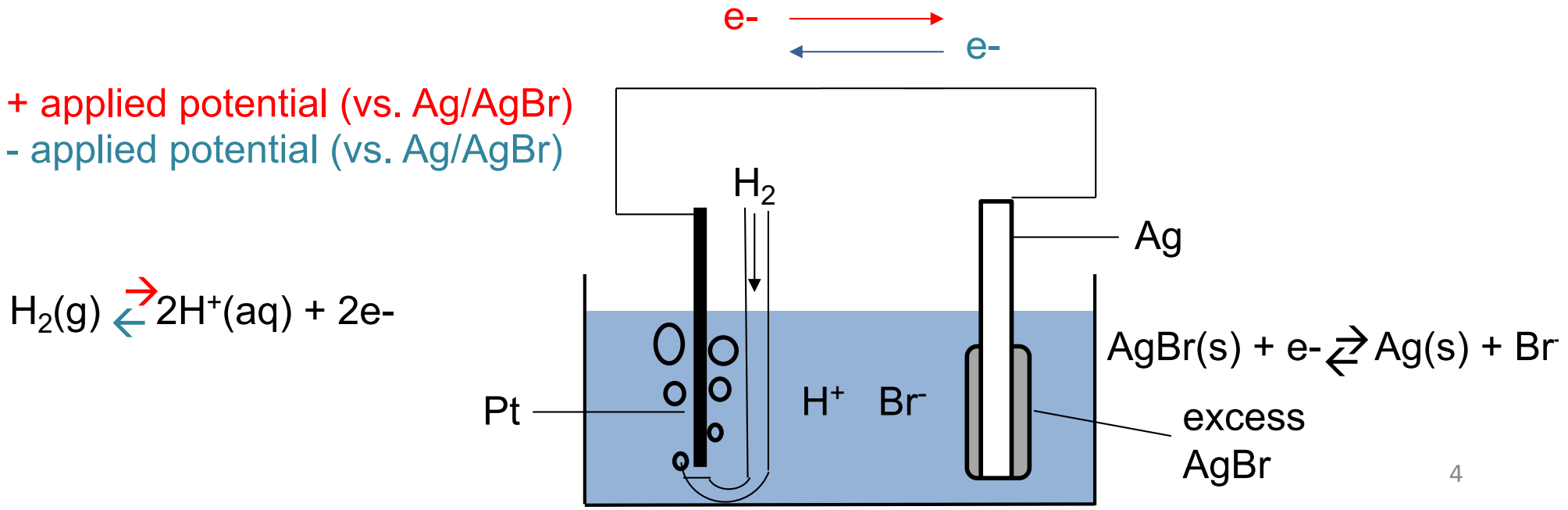
j : current density

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

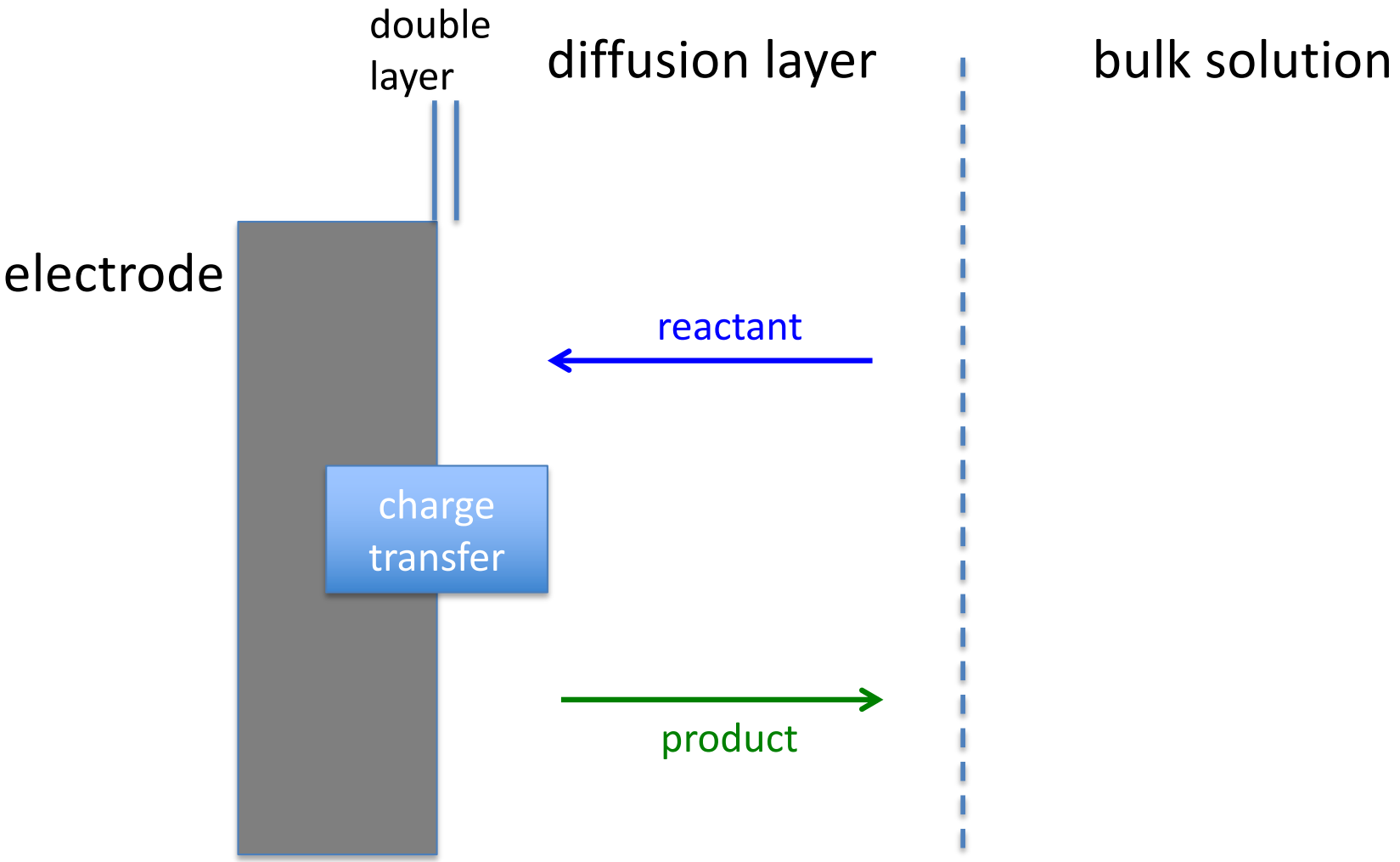
Voltage (E_{cell}) is an **intensive variable** (independent of the amount reacted). Current (j or i) is an **extensive variable** (depends on the **amount**. F = charge **per mol**).

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**.

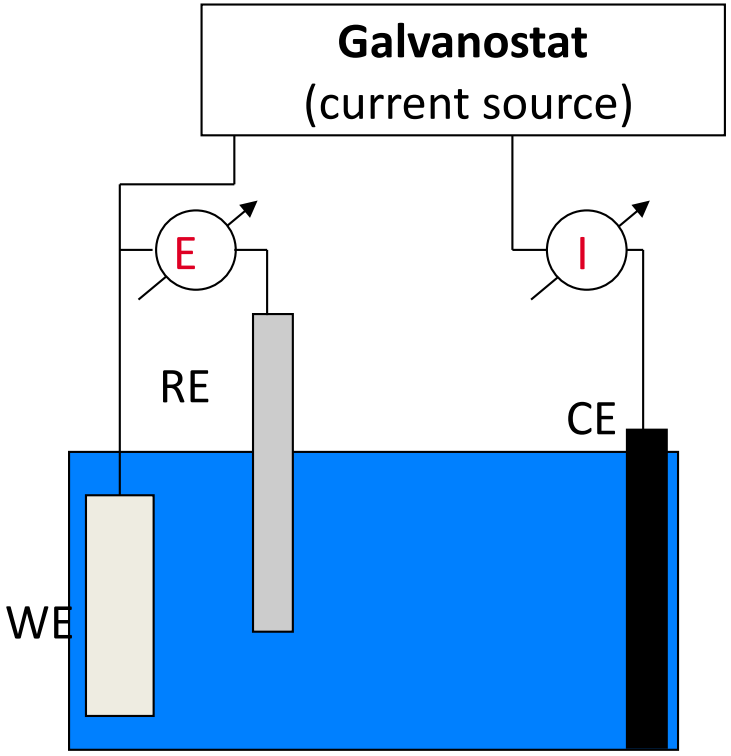


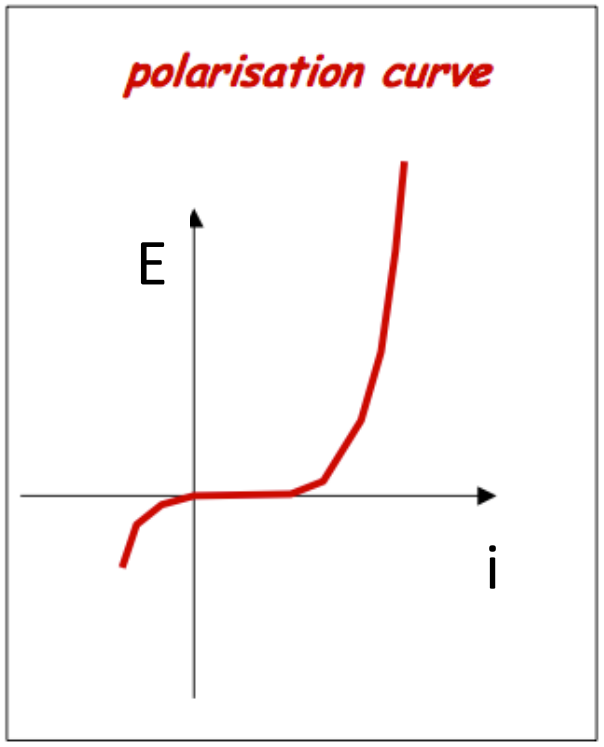
Rate determining steps (rds) in electrochemical reactions



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.

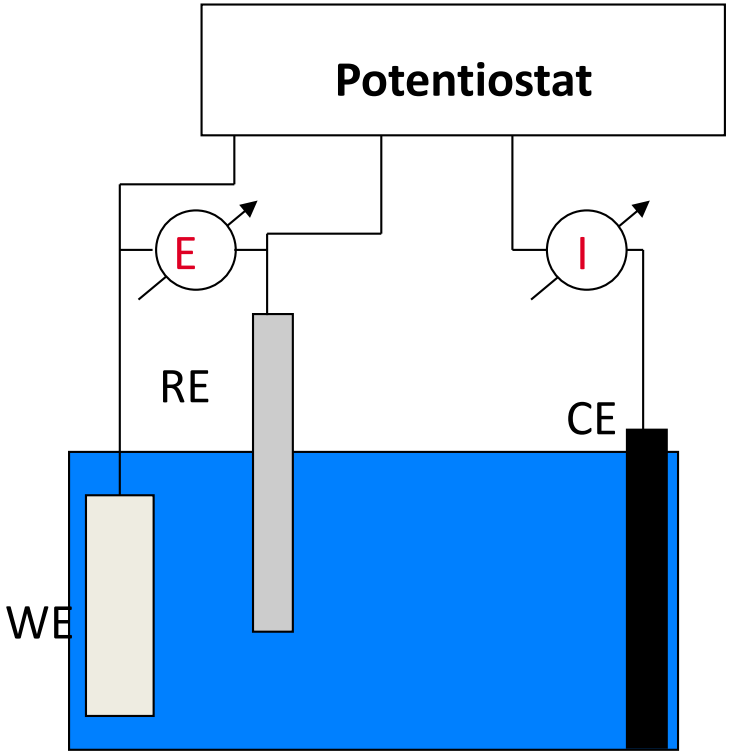


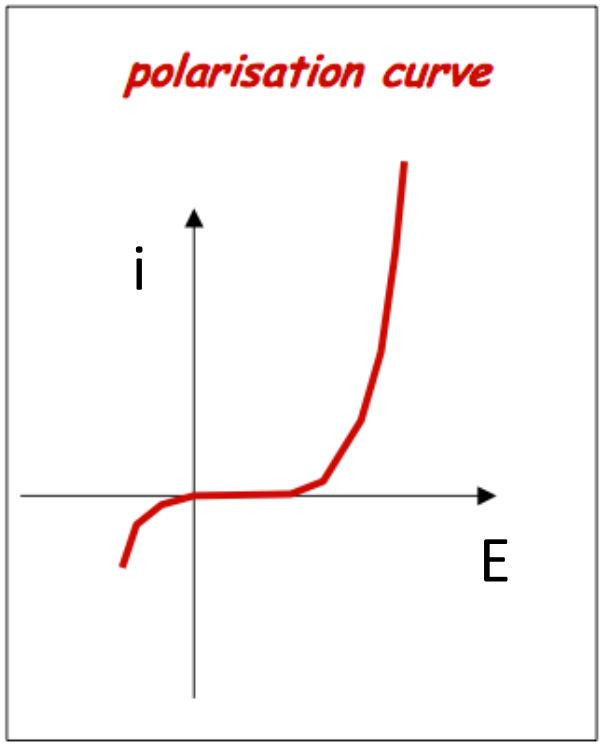


Methods for measurement of polarisation curves (j-V curves)

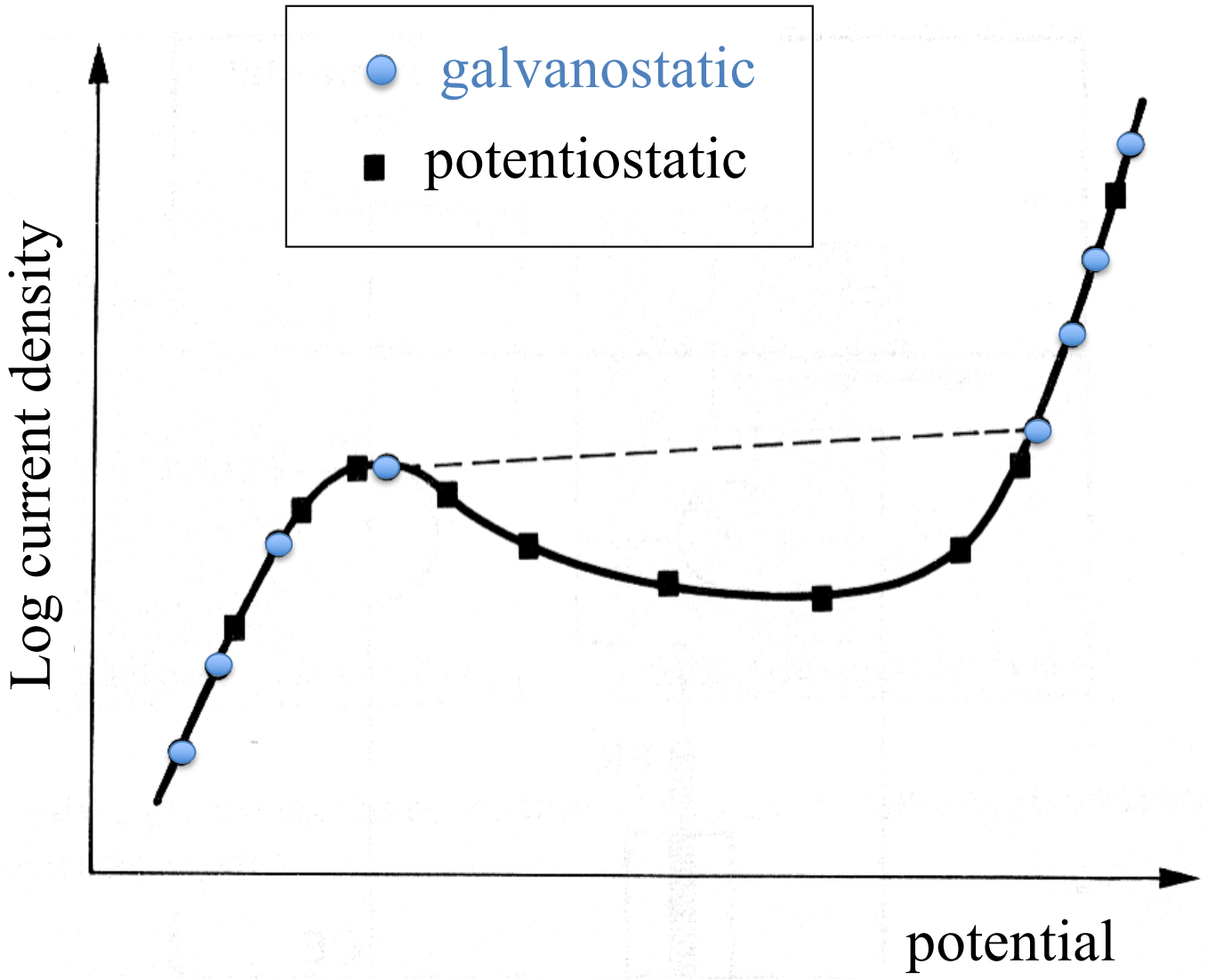
POTENTIOSTAT: electronic device that maintains a selected potential E between RE and WE by passing an appropriate current I between WE and CE.

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





Galvanostatic and potentiostatic polarisation (j-V) curves



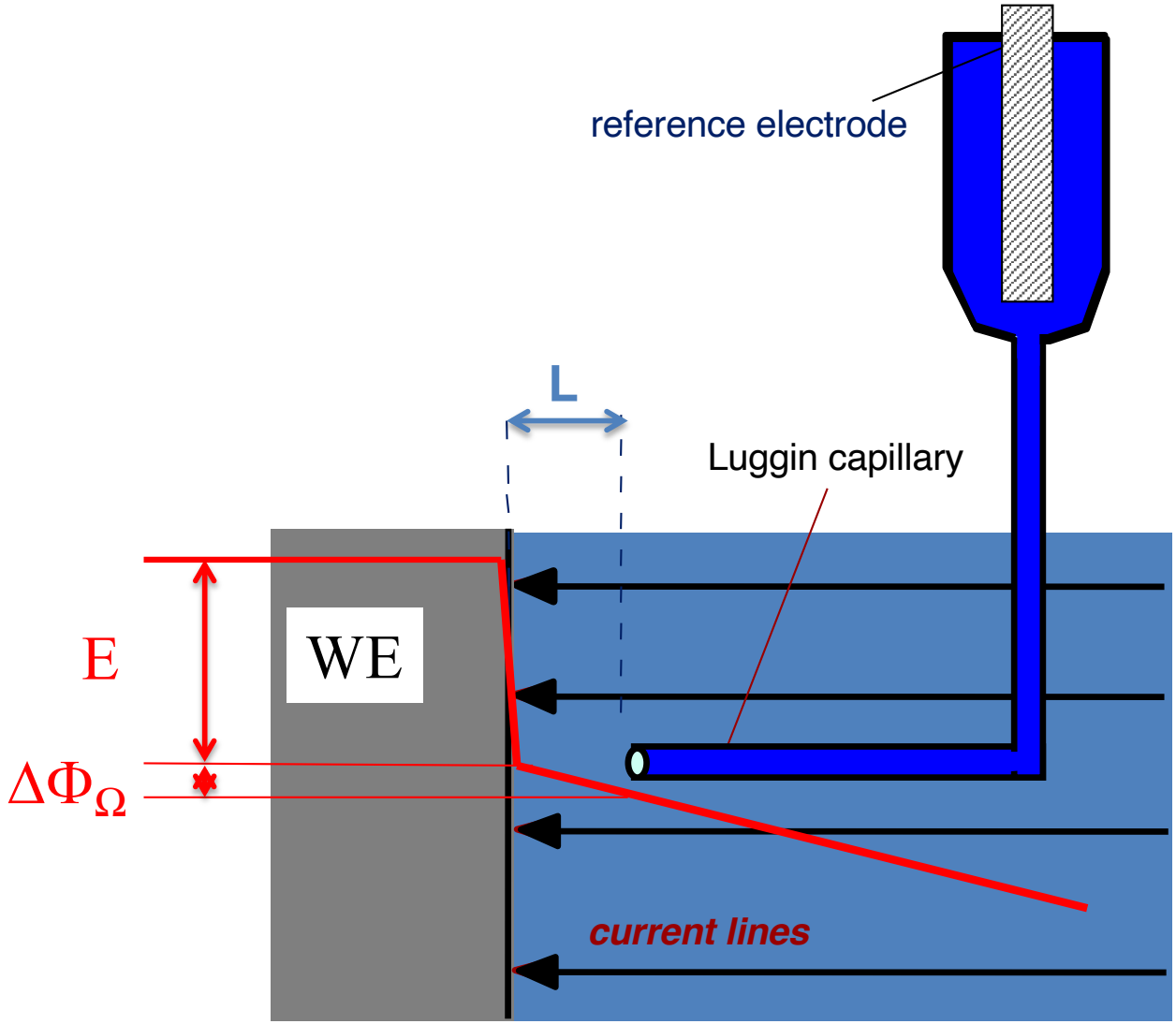
Reference electrode with Luggin capillary

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

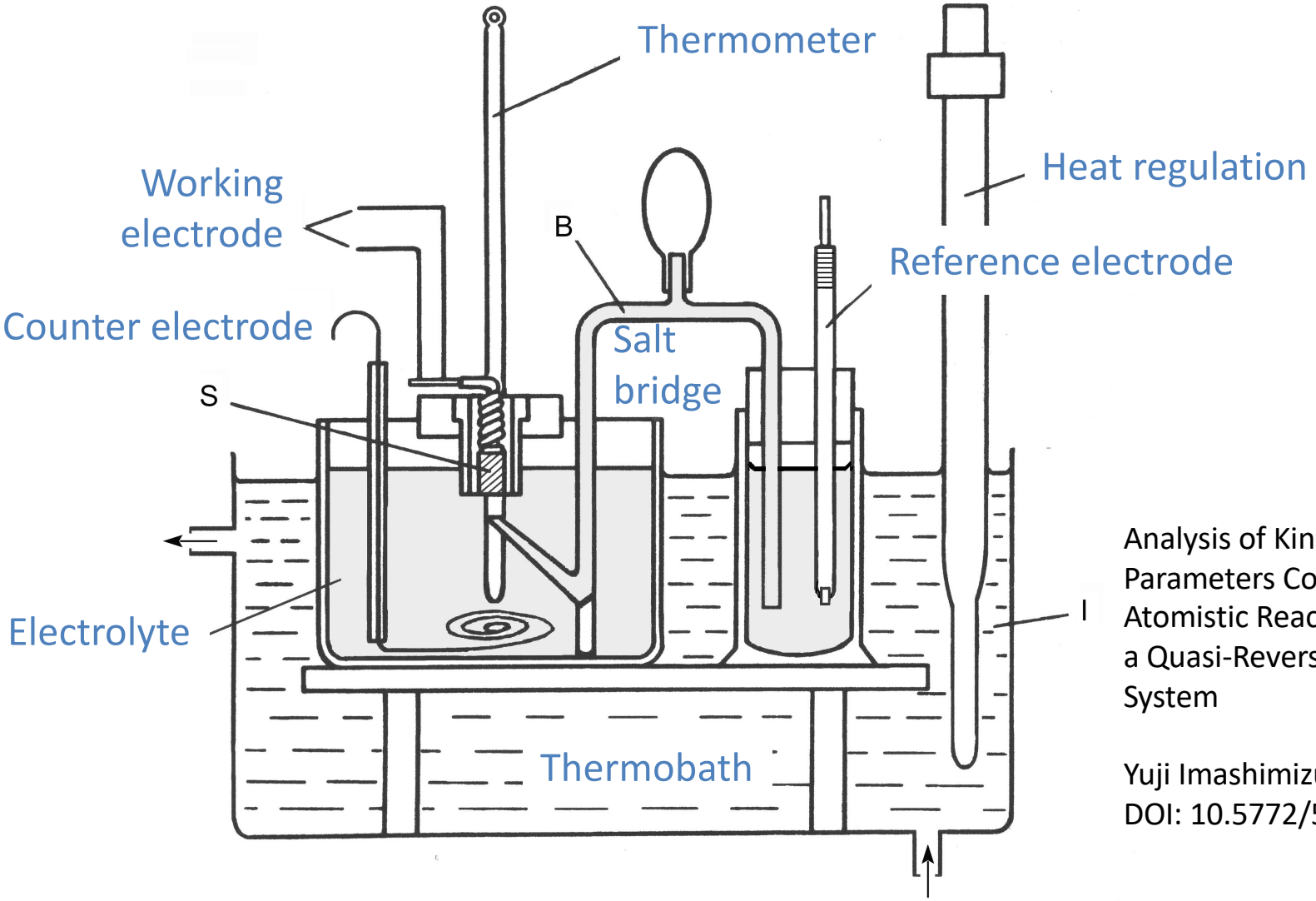
$$E_{measured} = E + \Delta\Phi_\Omega$$

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

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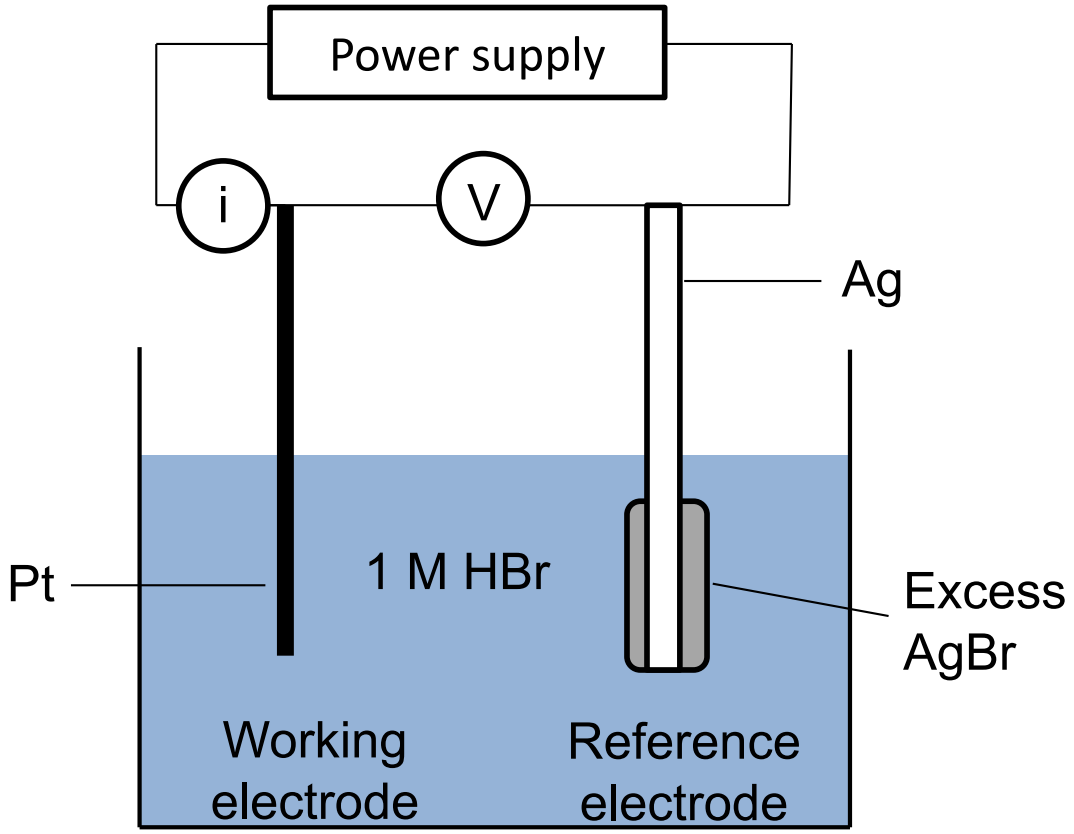
Net current flow under **non-equilibrium** conditions

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

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

- The flow of electrons is from the solution (Br^- anions at the Pt surface) into 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.

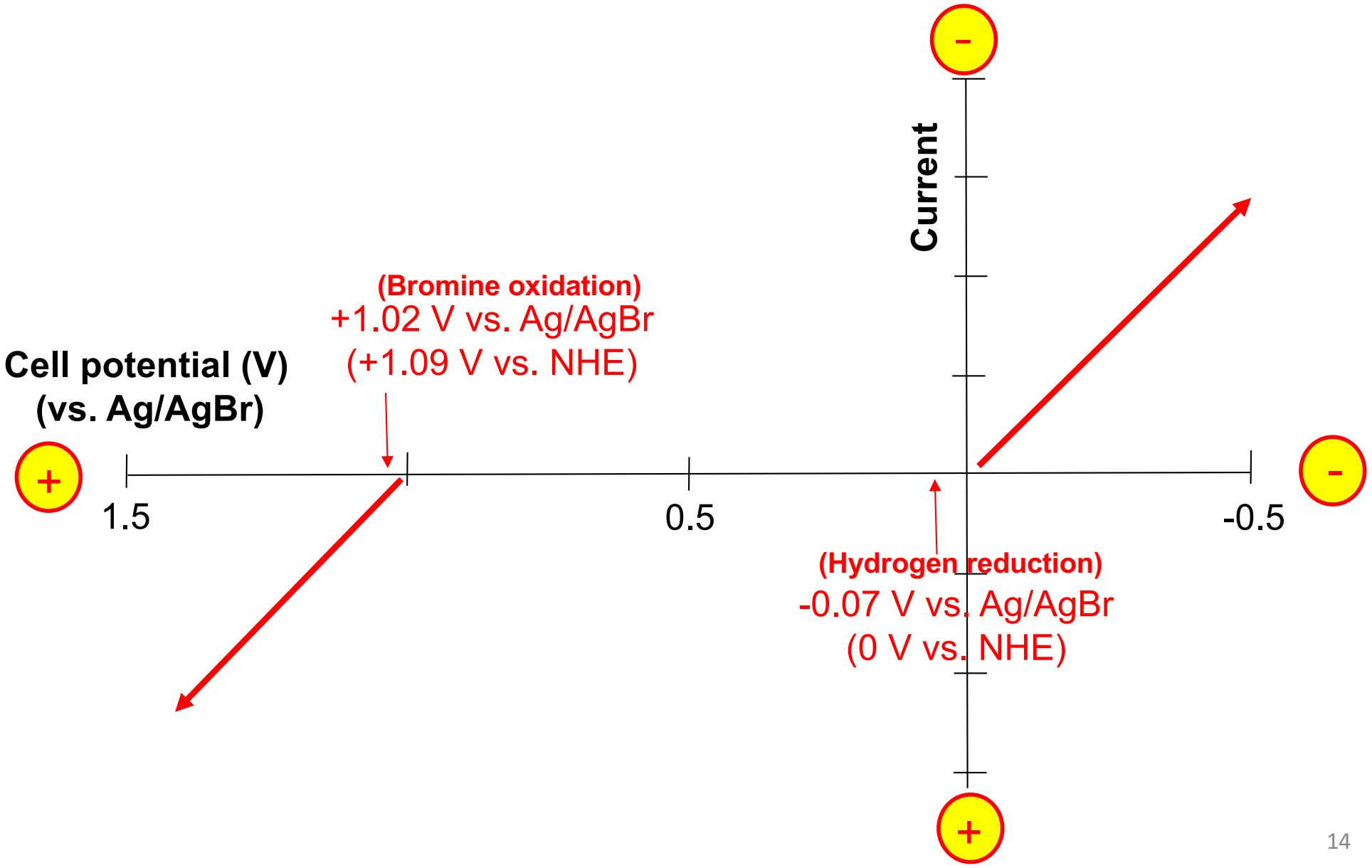
Net current flow under non-equilibrium conditions

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

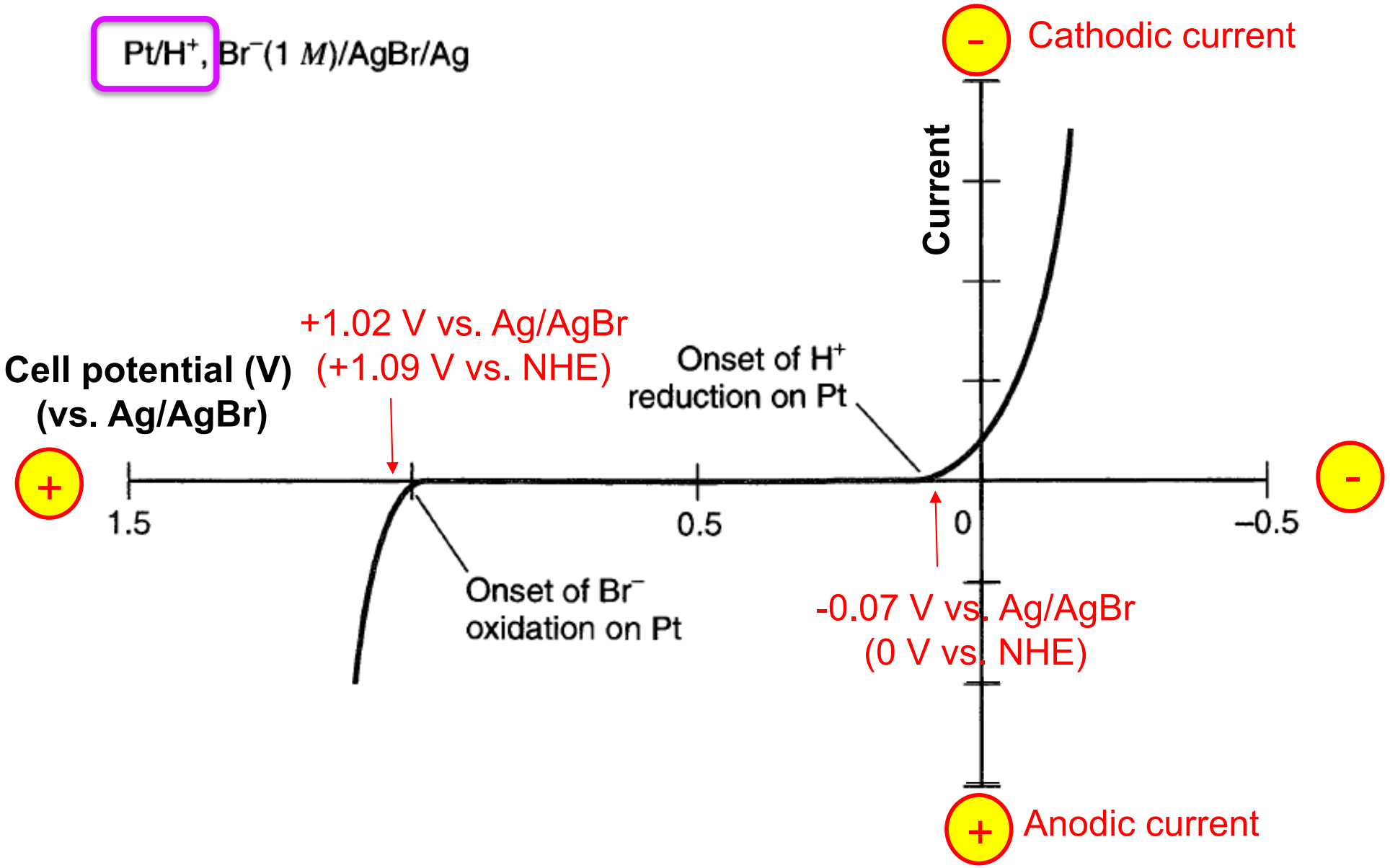
$$2\ H^+(aq) + 2\ e^- \rightarrow H_2(g) \qquad E_{reduction} = -0.07\ V\ vs\ Ag/AgBr$$

- 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

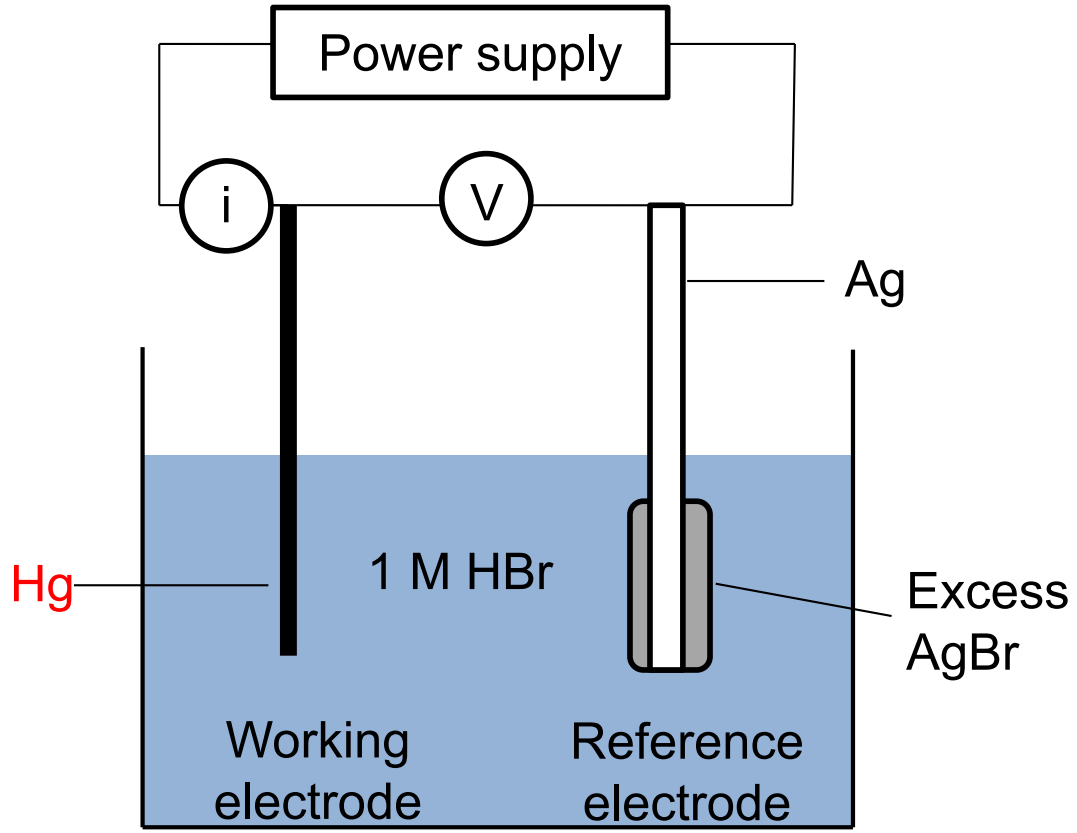
$AgBr(s) + e^- \rightleftarrows Ag(s) + Br^-$

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

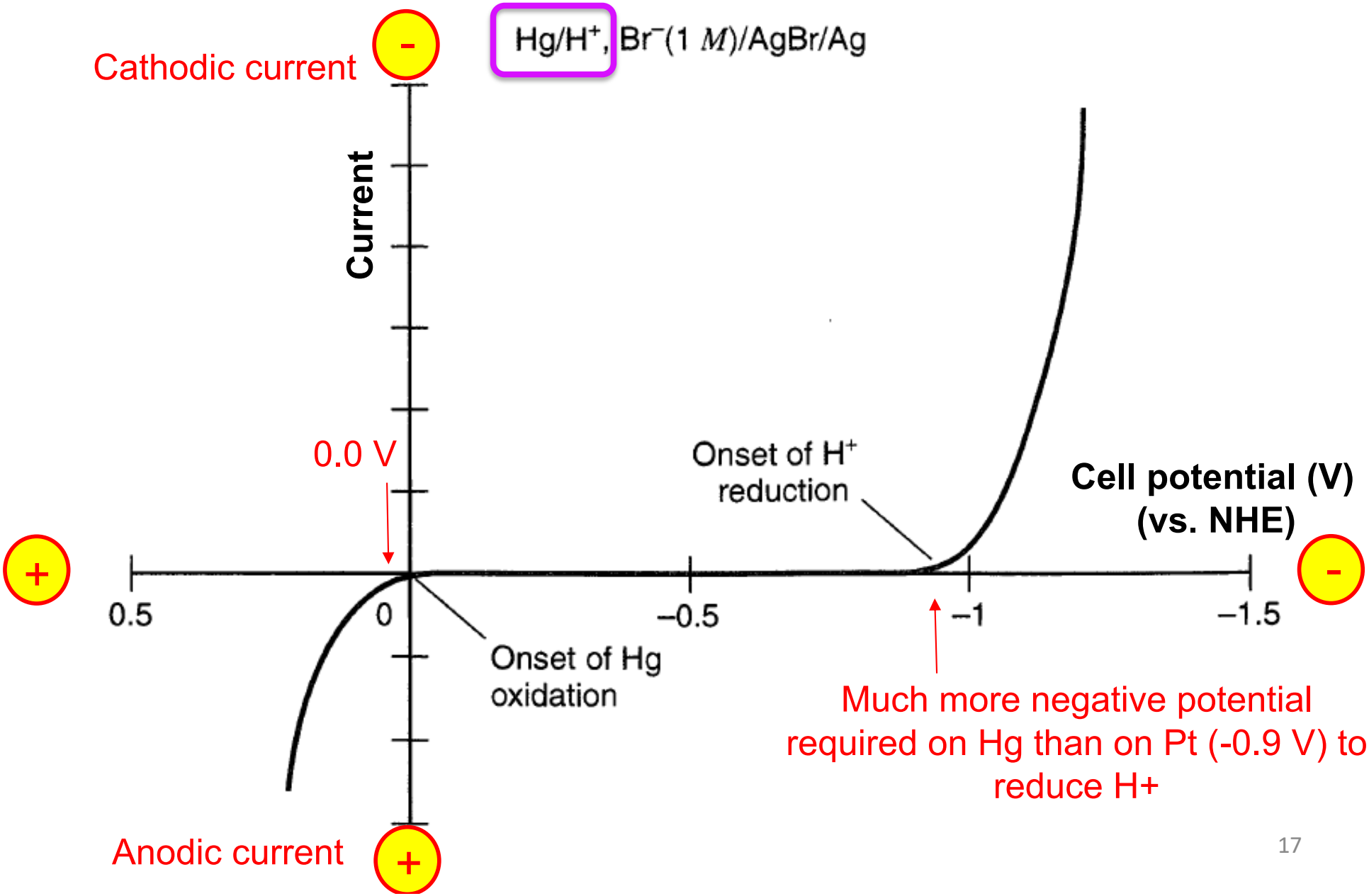
Working electrode is not in equilibrium

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 :

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

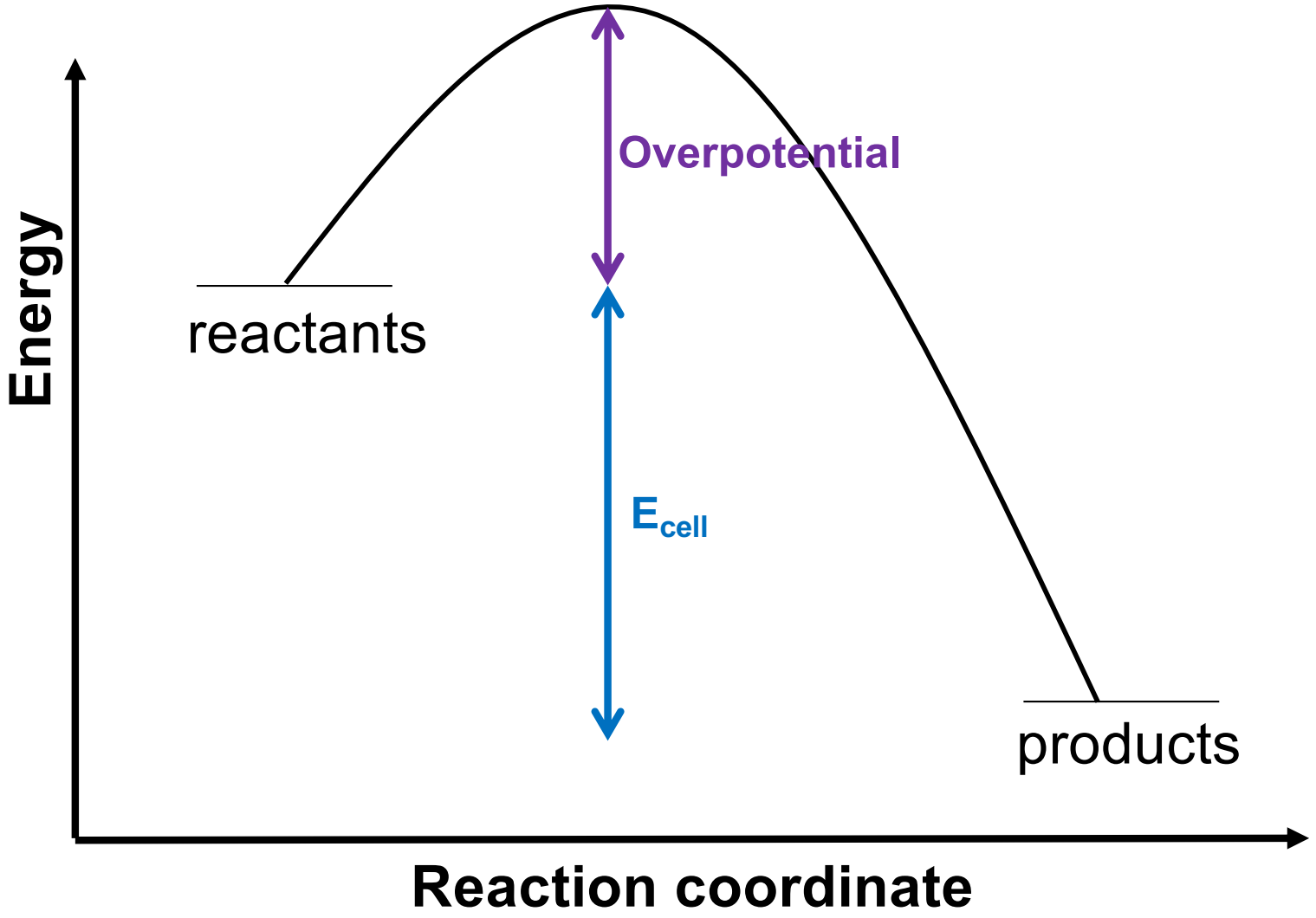
The equilibrium potential of this half reaction is independent of the electrode material.

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

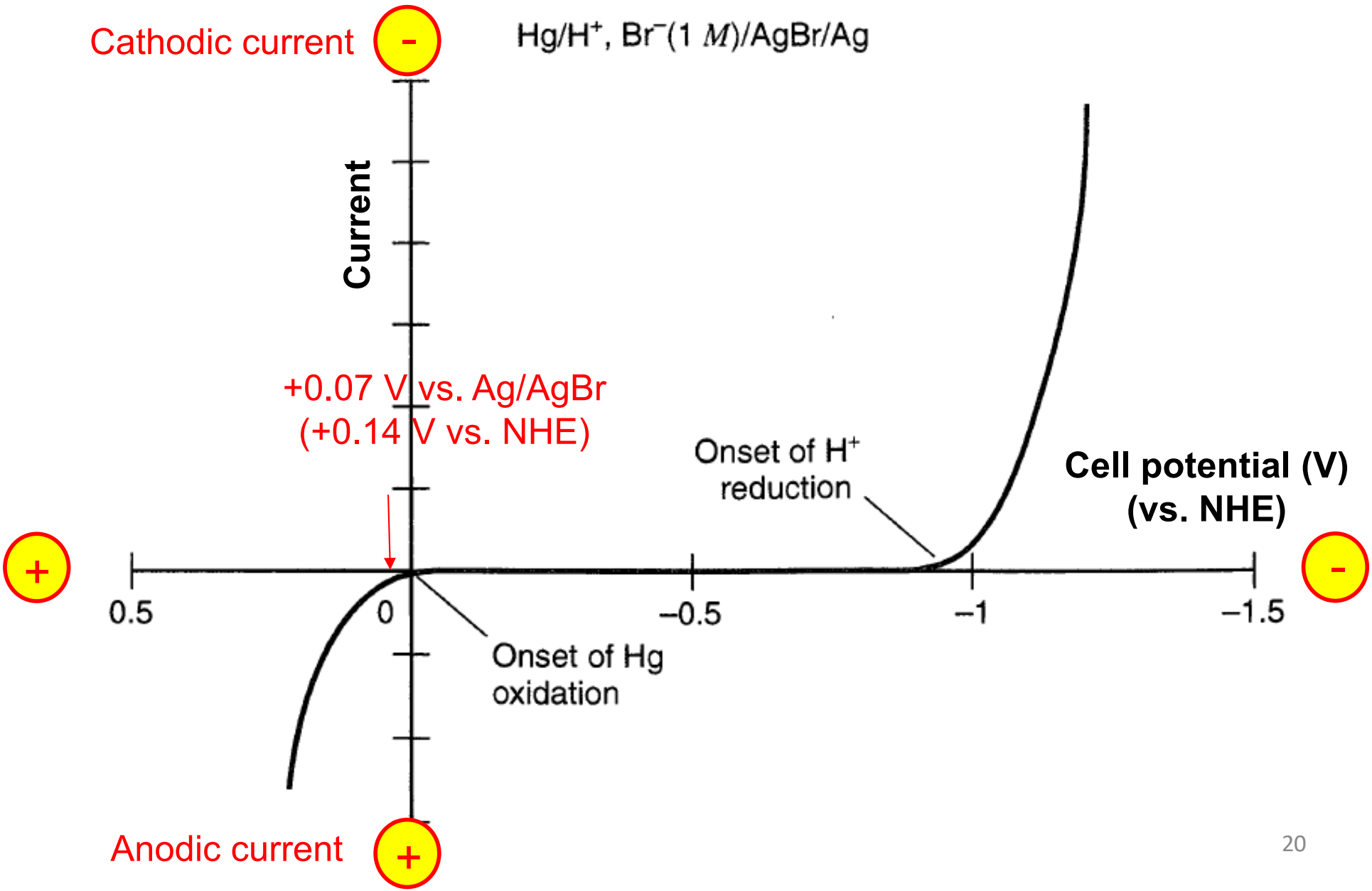
The additional potential (beyond the thermodynamic requirement) needed to drive a reaction at a certain rate is called the **overpotential**.

=> 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

<u>Same system, but different working electrode</u> (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).

<u>Observation</u>:
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

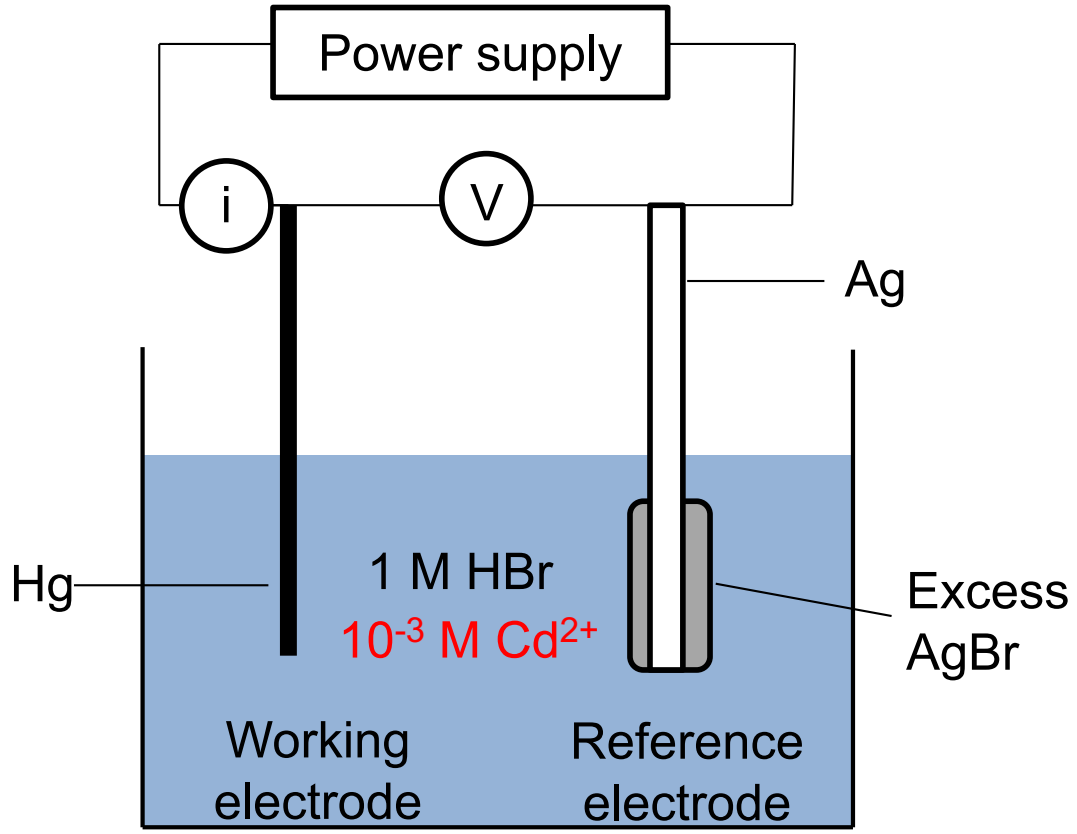
$AgBr(s) + e^- \rightleftarrows Ag(s) + Br^-$

[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

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

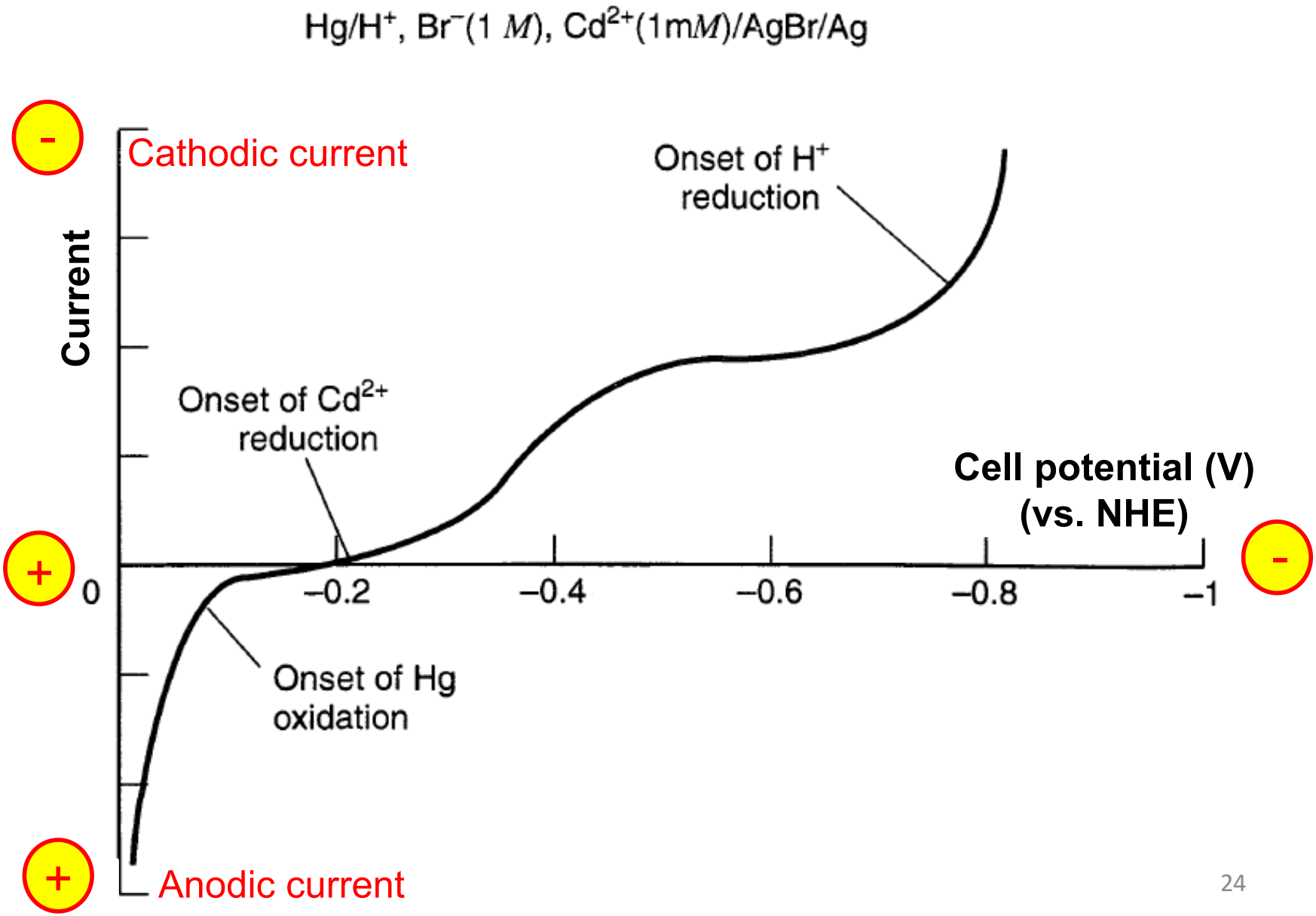
Apply a very **positive** potential to the Hg electrode relative to the Ag/AgBr electrode => **oxidation** reaction

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

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

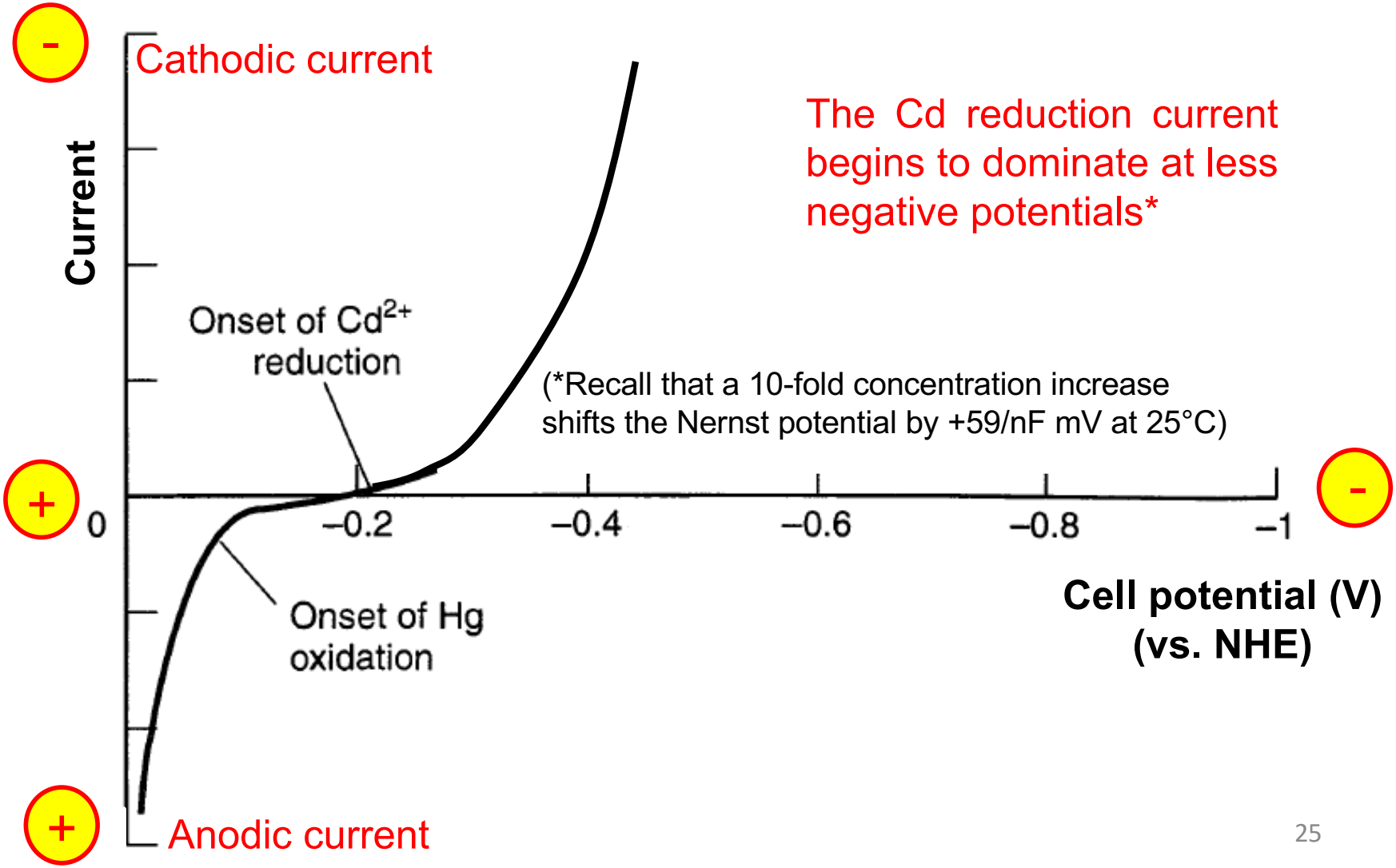
$$CdBr_4^{2-} + 2e^- \xrightarrow{Hg} Cd\ (Hg) + 4\ Br^- \qquad E_{onset} \sim -0.4\ V\ vs.\ NHE$$

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



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

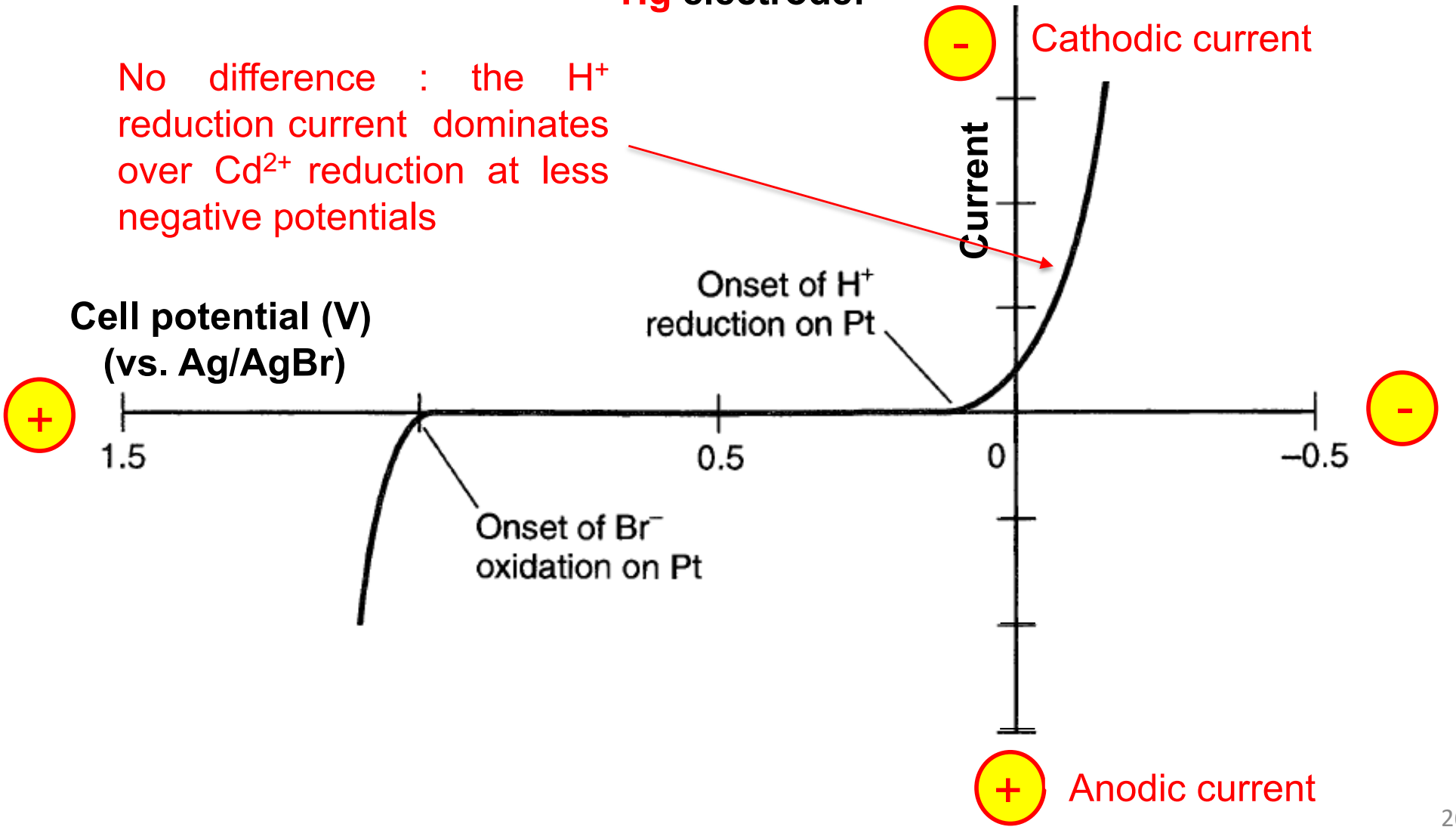
When adding higher concentration of Cd^{2+} to the solution :



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:

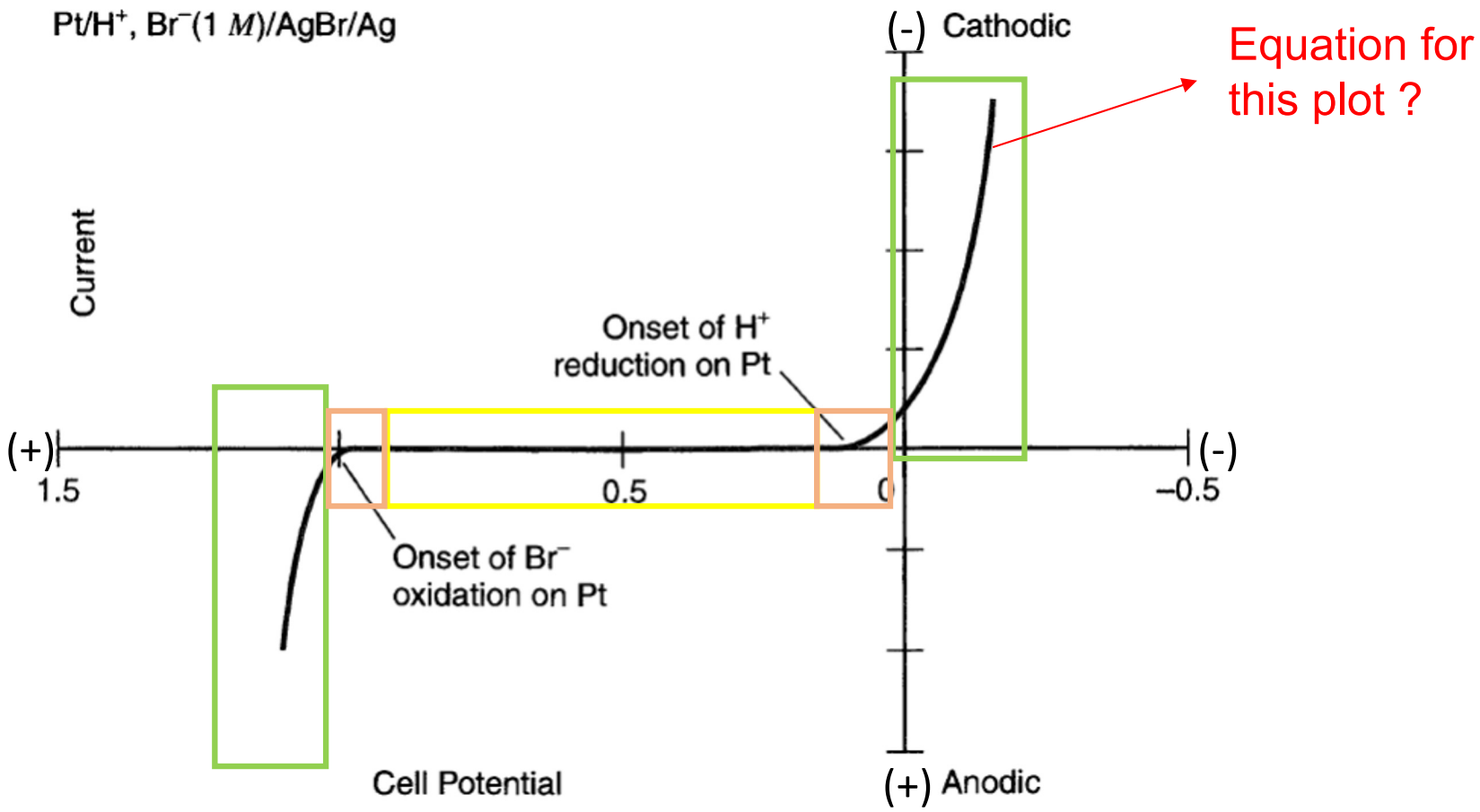
- When an electrode is moved from its open-circuit value towards more **negative** potentials (negative currents), the substance **reduced** first (=easiest to reduce = to pick up e-) has the least negative (or more positive) E°.
  Example: H^+ reduction before Cd^{2+} reduction on a Pt electrode system

- 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

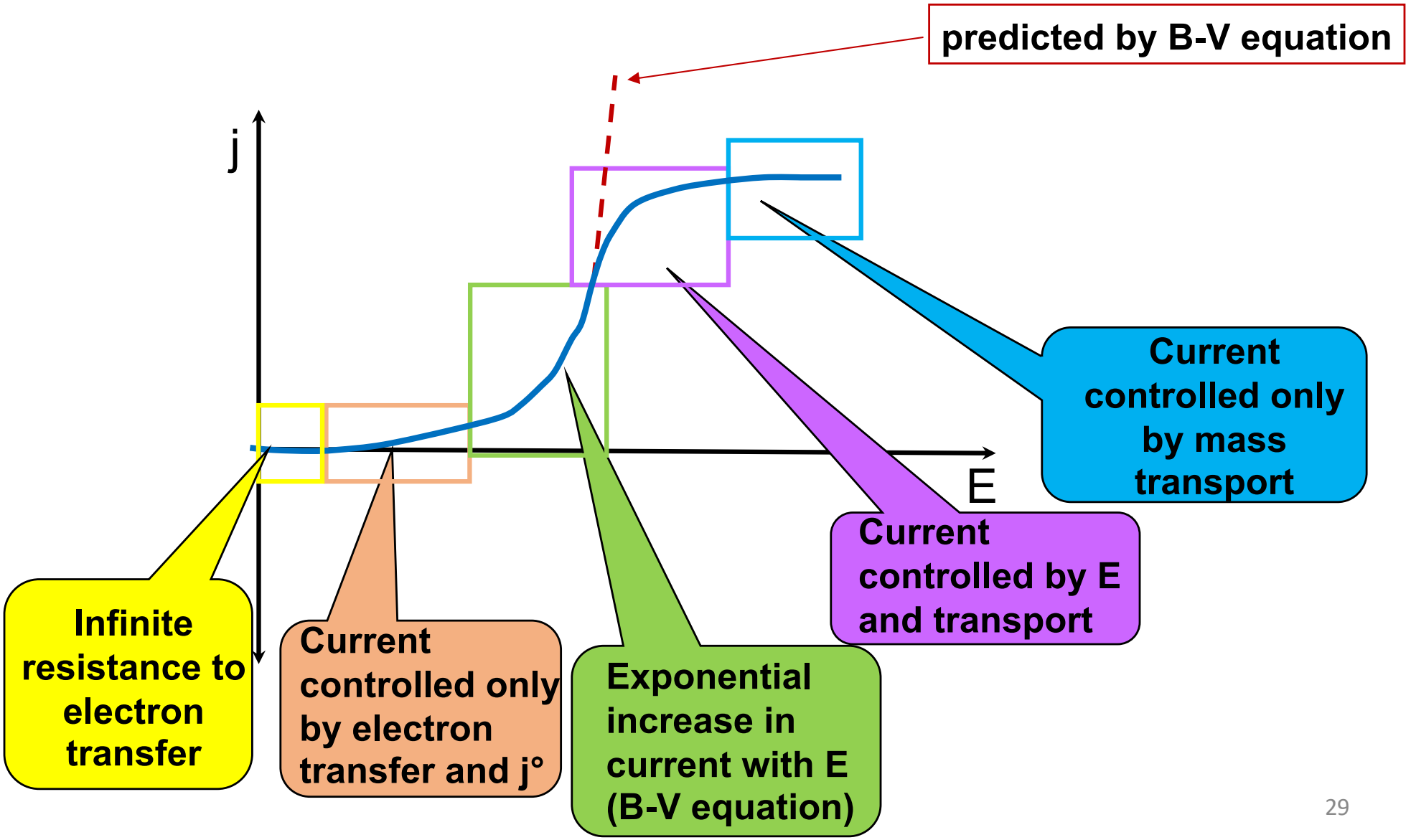
- (small) quantities of an added substance may contribute an additional peak.
  Example: small concentrations of Cd^{2+} added to Hg electrode system

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

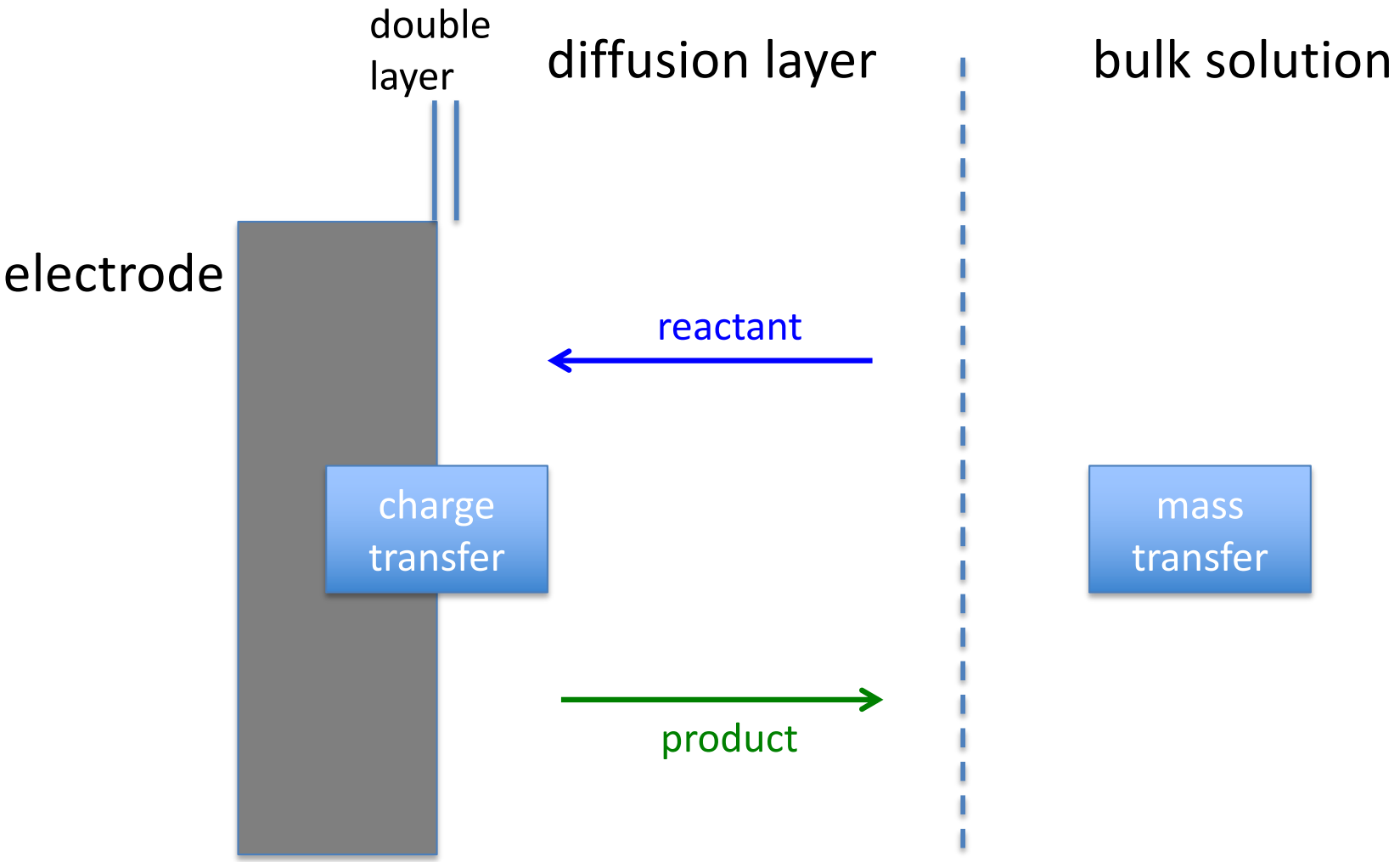
Deriving an analytical expression for observed j-V plot



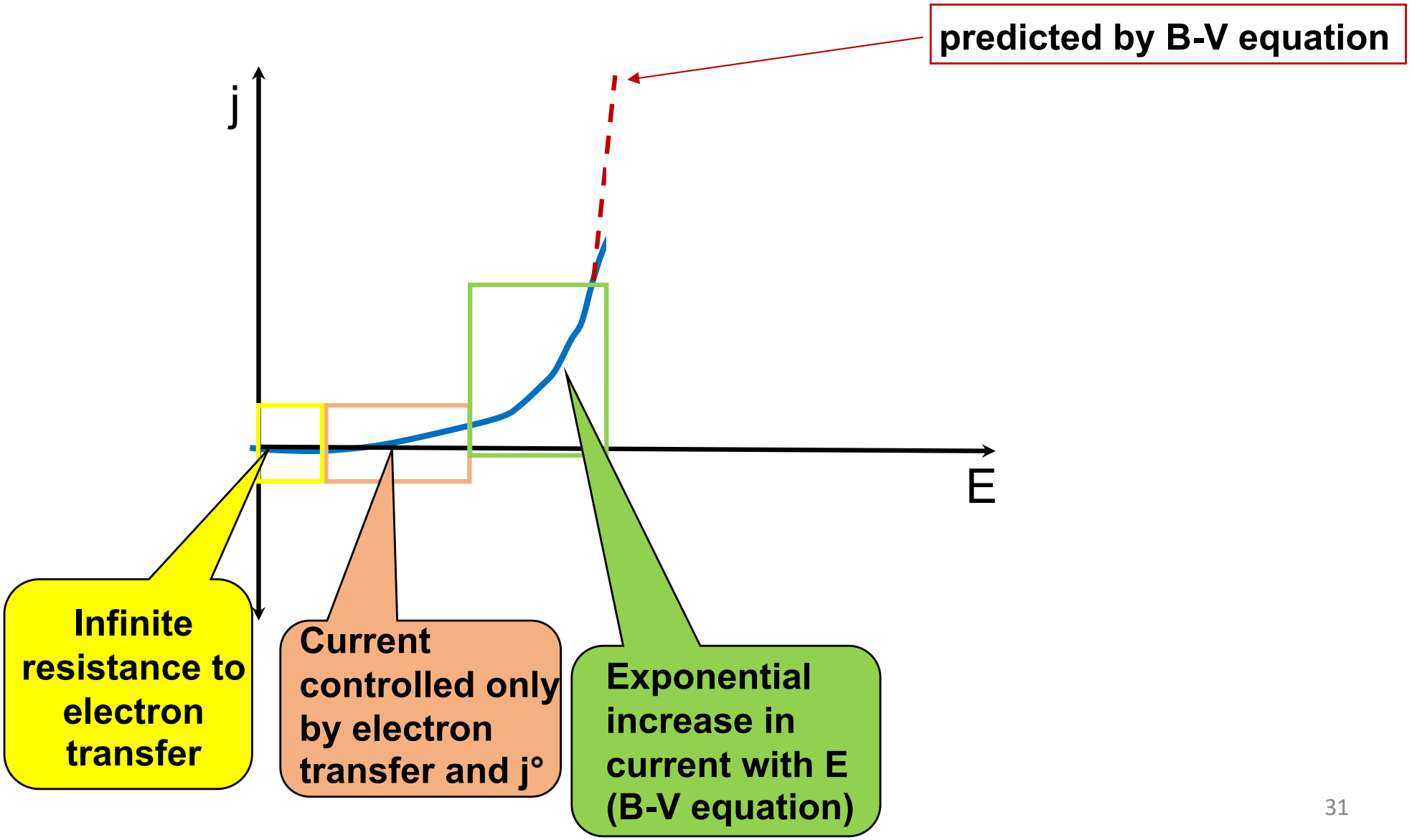
Deriving an analytical expression for observed j-V plot



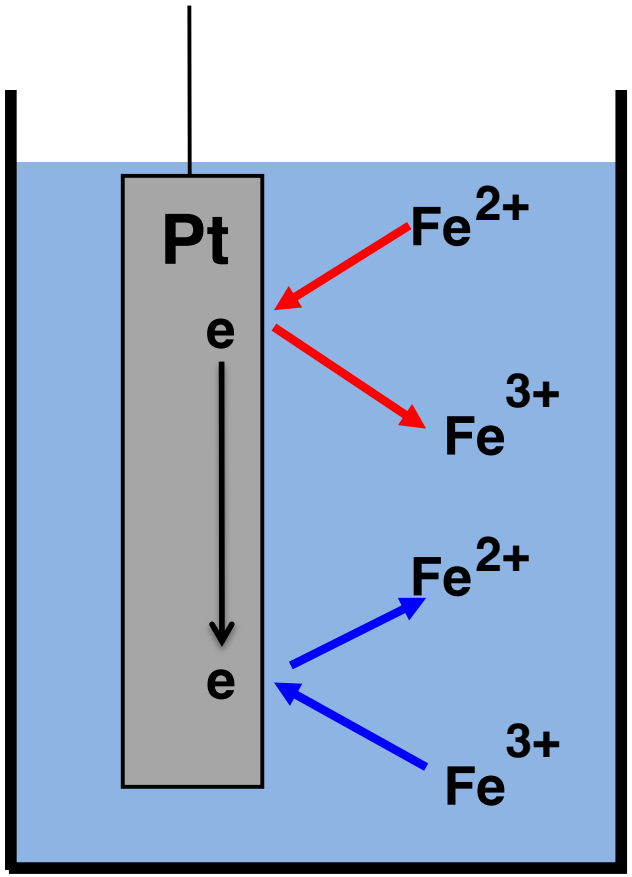
Rate determining steps in electrochemical reactions



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 :

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

Recall:

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

Hyp. : 1st order kinetics

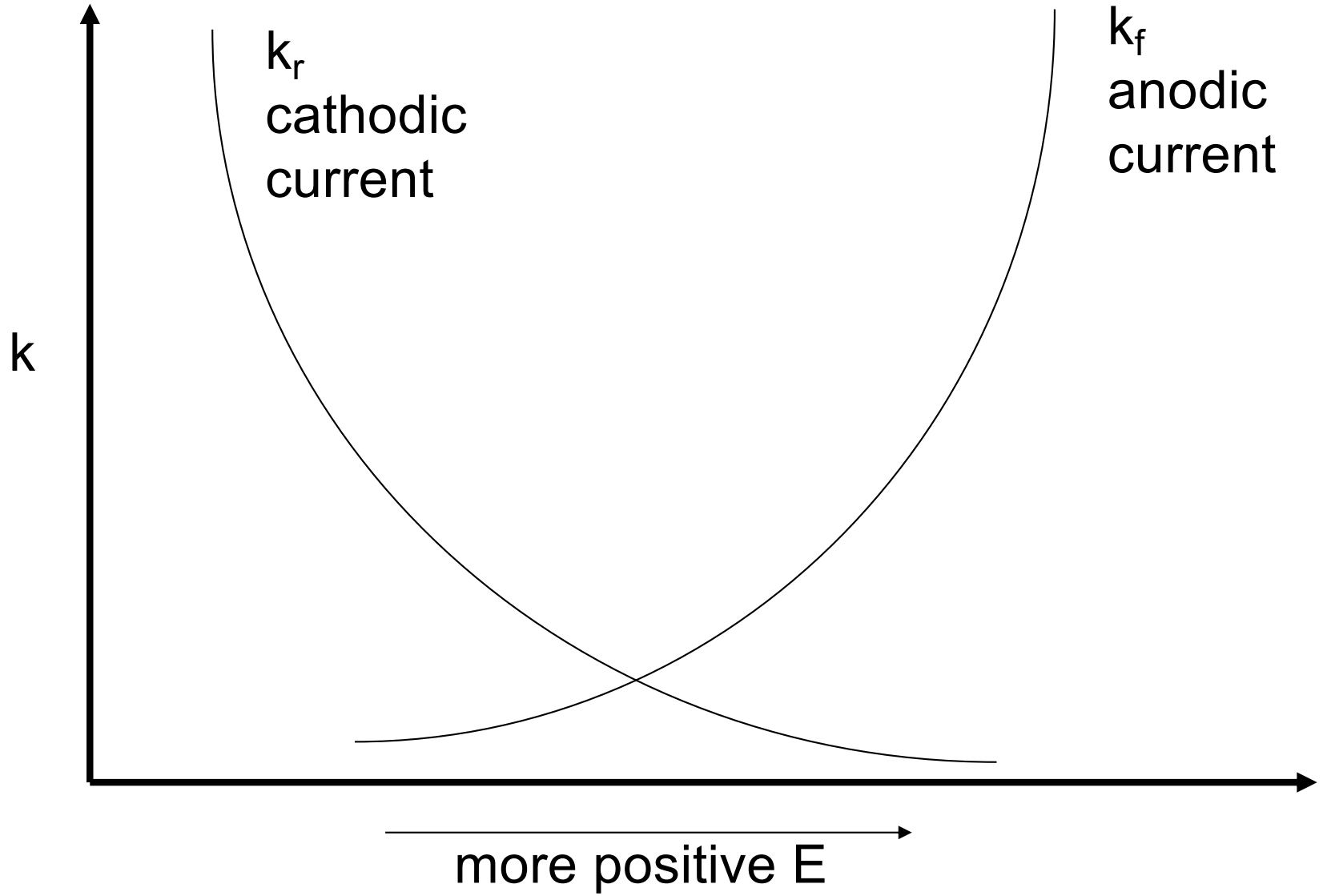
forward

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

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

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

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

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

depends on potential !

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

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

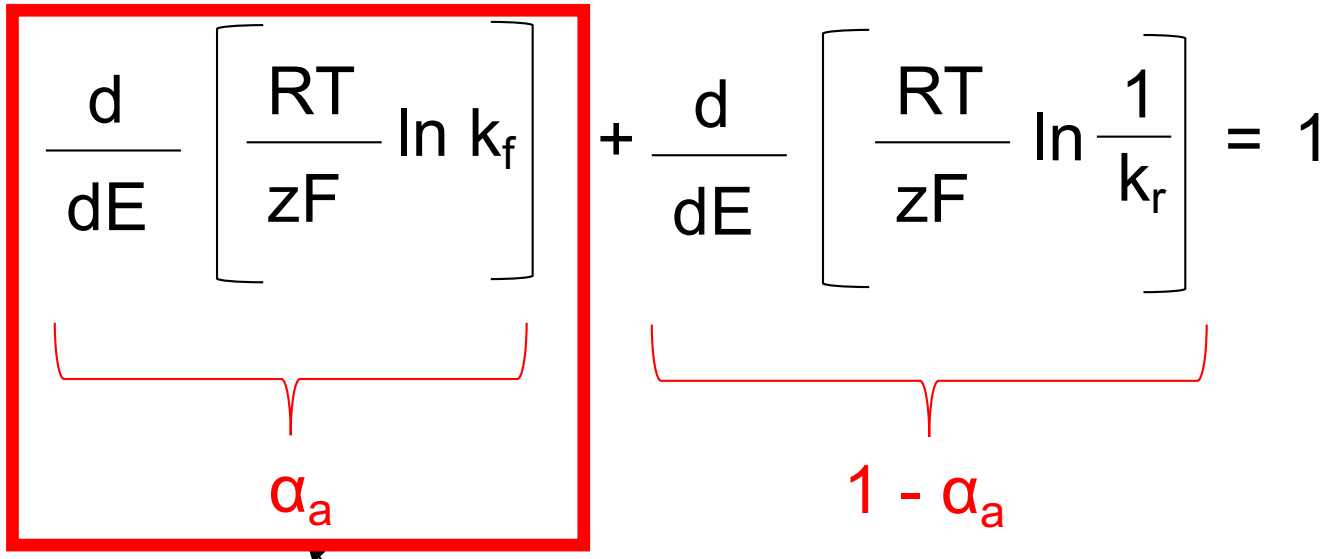
$$\ln \frac{[O]_s}{[R]_s} = \frac{(E_{cell} - E°_{cell,T})zF}{RT}$$

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

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

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

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


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

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

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

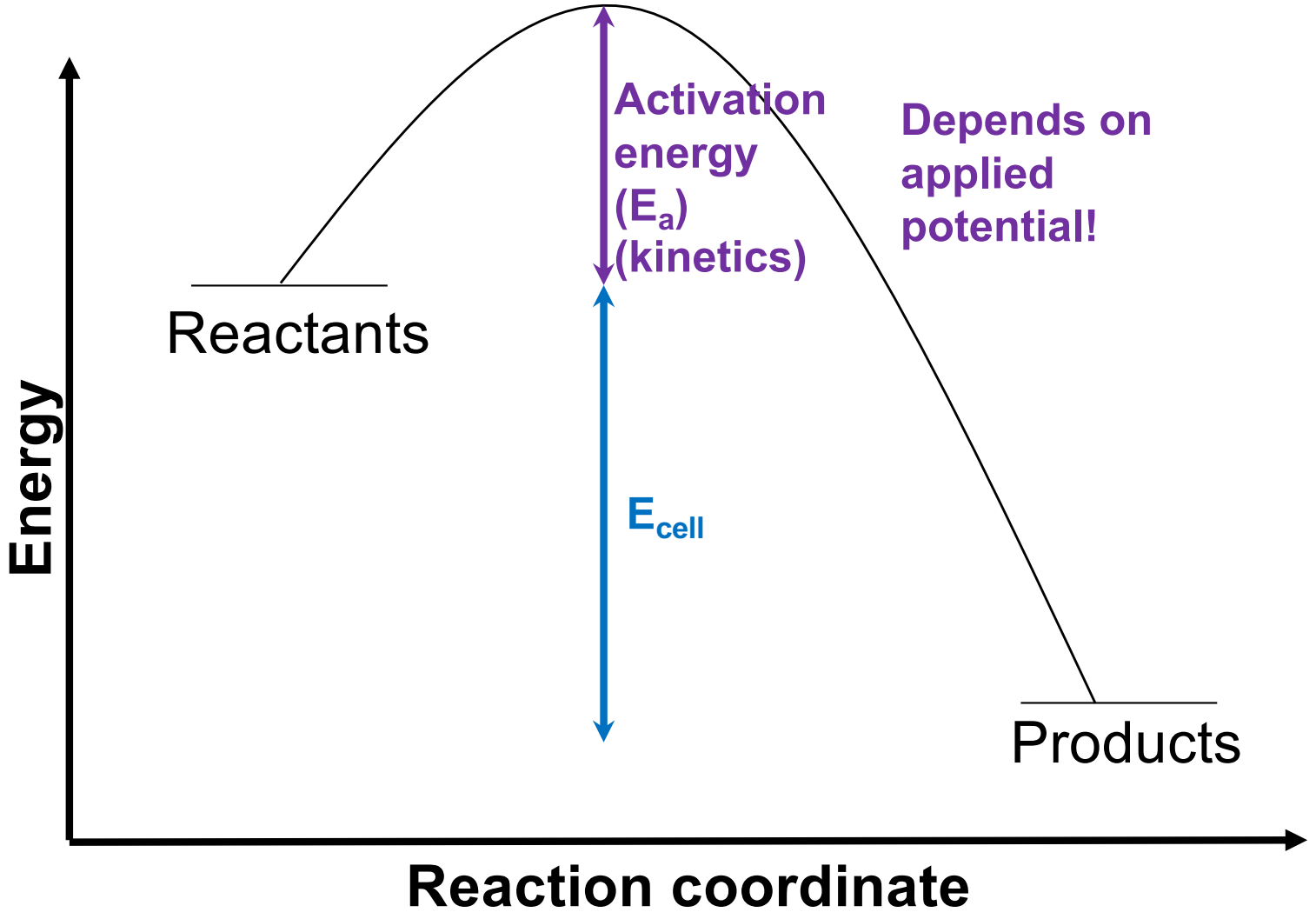
$$k_f = k_f^\circ \, e^{\frac{\alpha_a zF}{RT}(E-E^\circ)}$$

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

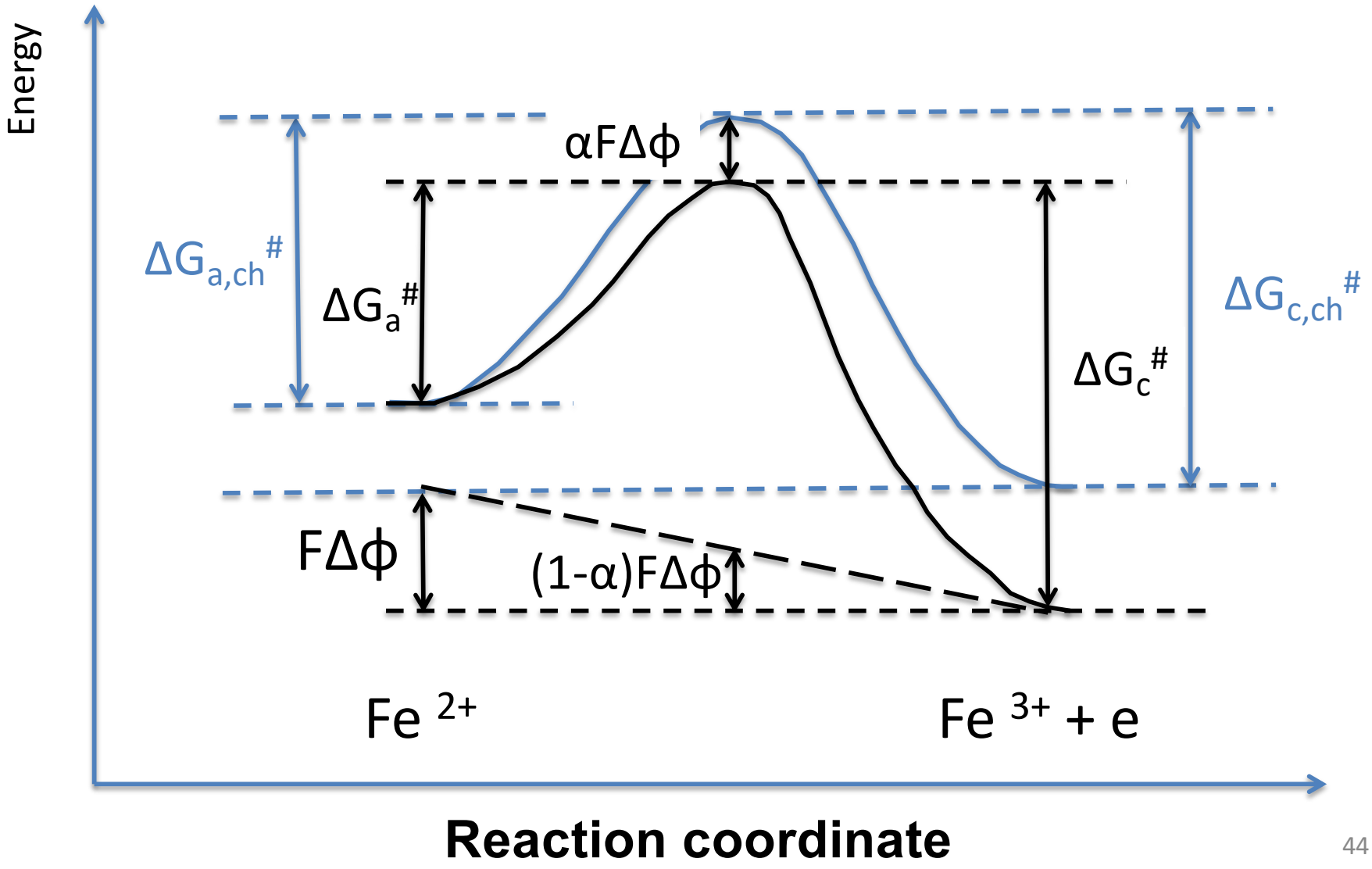
cf. Arrhenius expression:

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

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 occurance = 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:

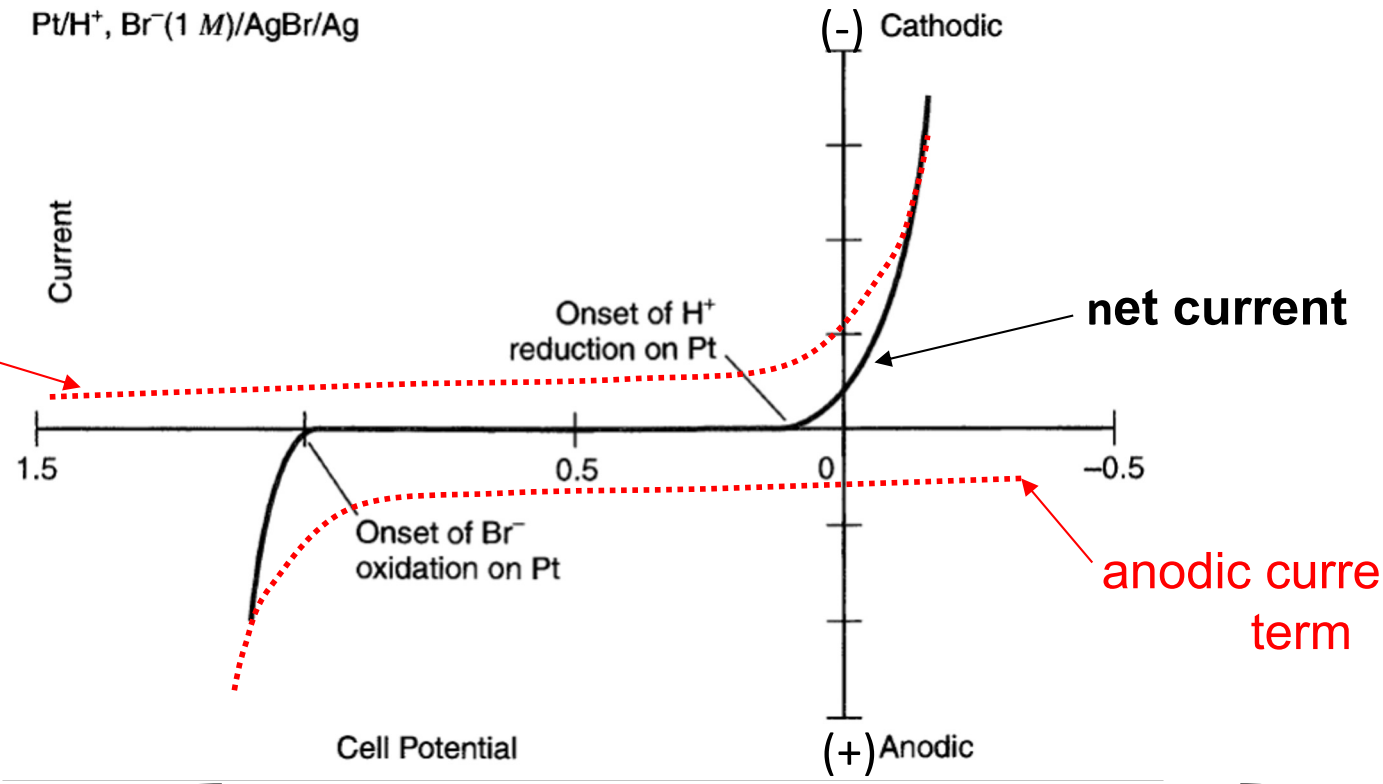
$$\frac{j}{zF} = k_f[R]_s - k_r[O]_s = k_f^\circ e^{\frac{\alpha_a zF}{RT}(E-E^\circ)}[R]_s - k_r^\circ e^{-\frac{(1-\alpha_a)zF}{RT}(E-E^\circ)}[O]_s$$

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)

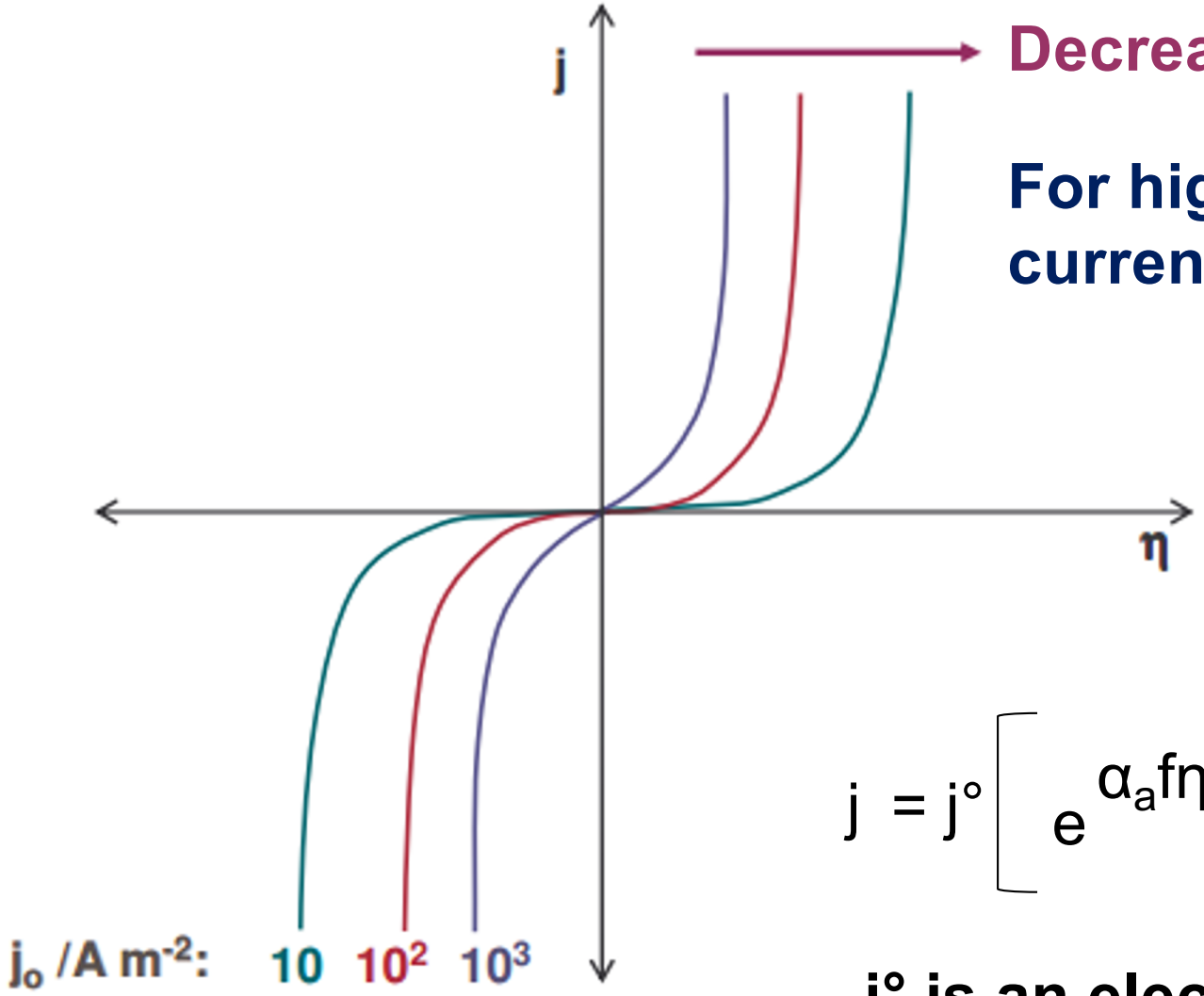
$f = \frac{zF}{RT}$

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

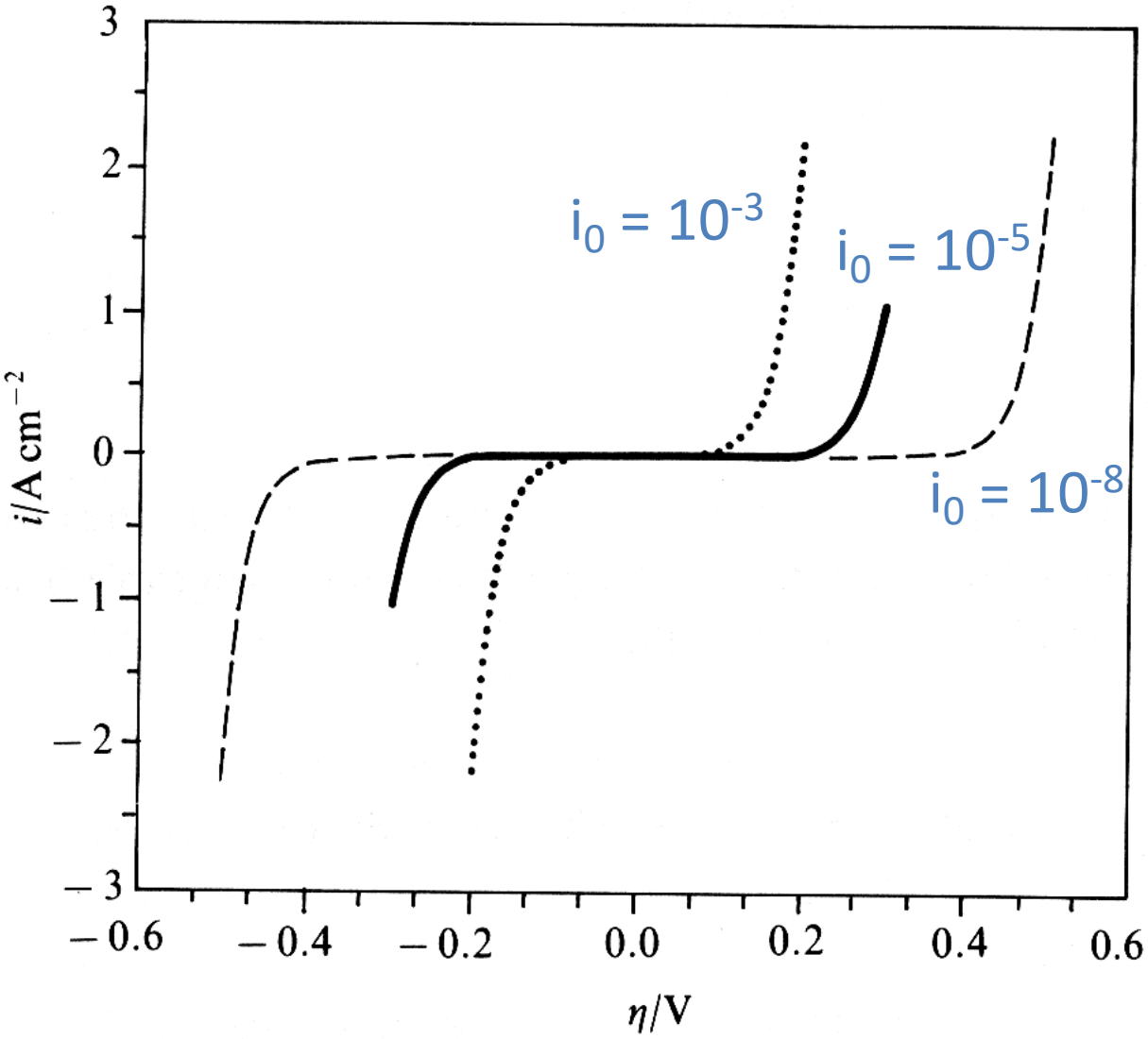


For high j°: observable current at low η

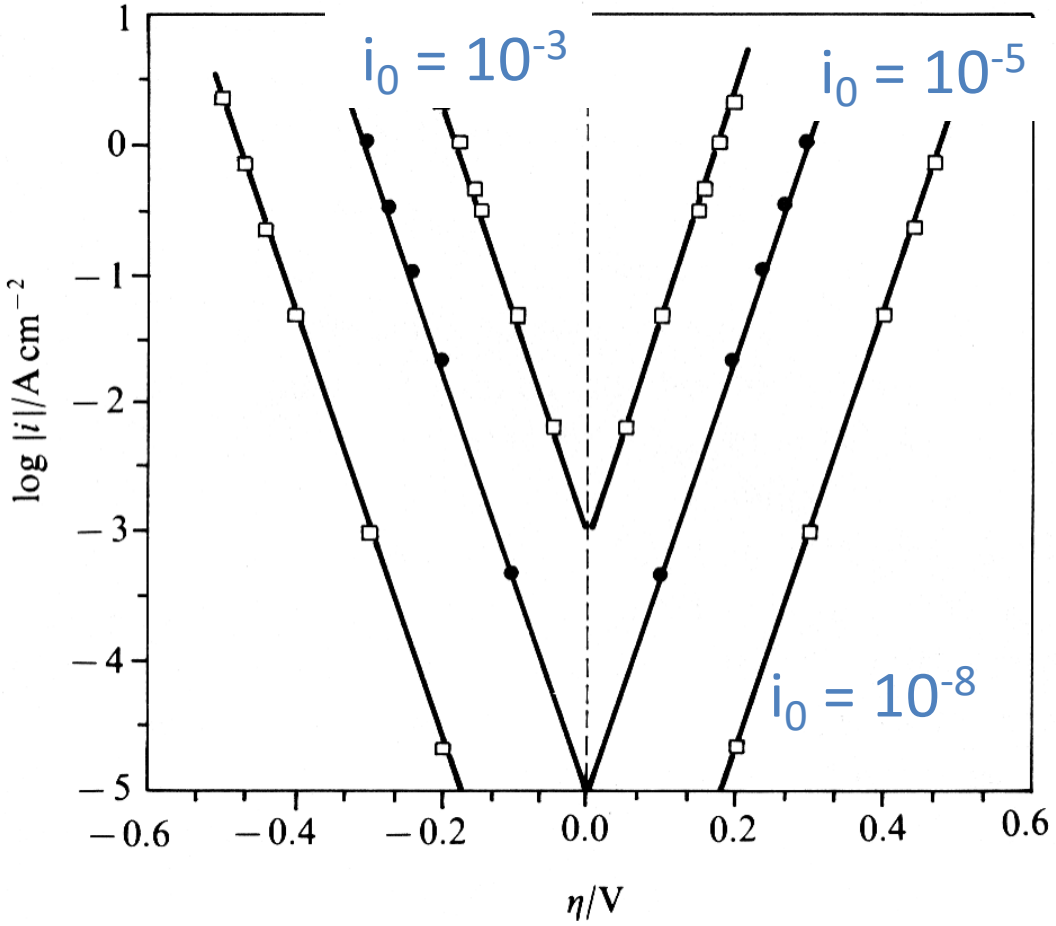
$$j = j^\circ \left[e^{\alpha_a f \eta} - e^{-(1-\alpha_a) f \eta} \right]$$

j° is an electrode property

Effect of exchange current i_0 on polarisation behaviour (linear scale)



Effect of exchange current i_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.

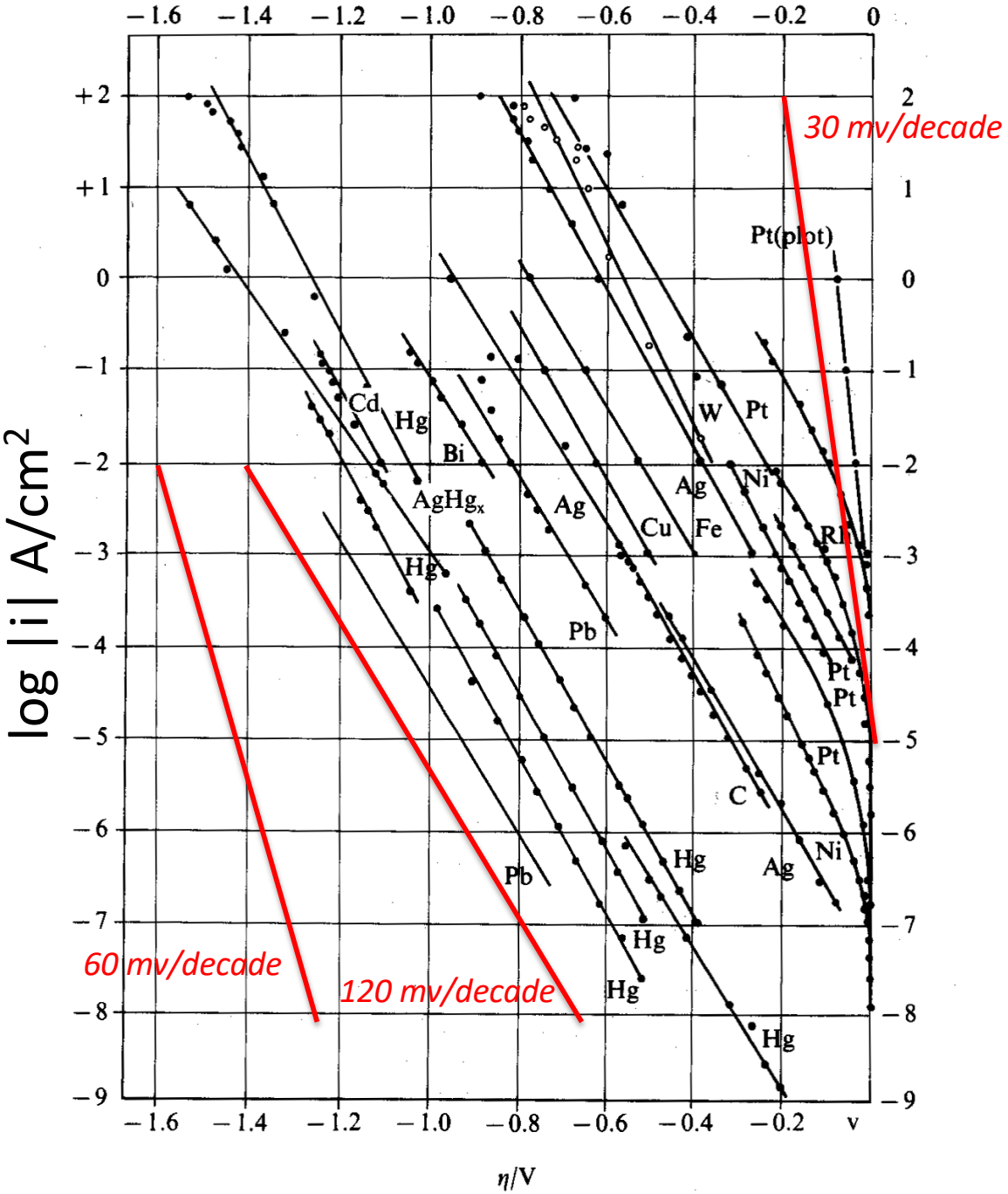
Parameters affecting charge transfer current densities

Exchange current density i_0 of the reaction

$2H^+ + 2e^- \Rightarrow H_2$ (20°C)

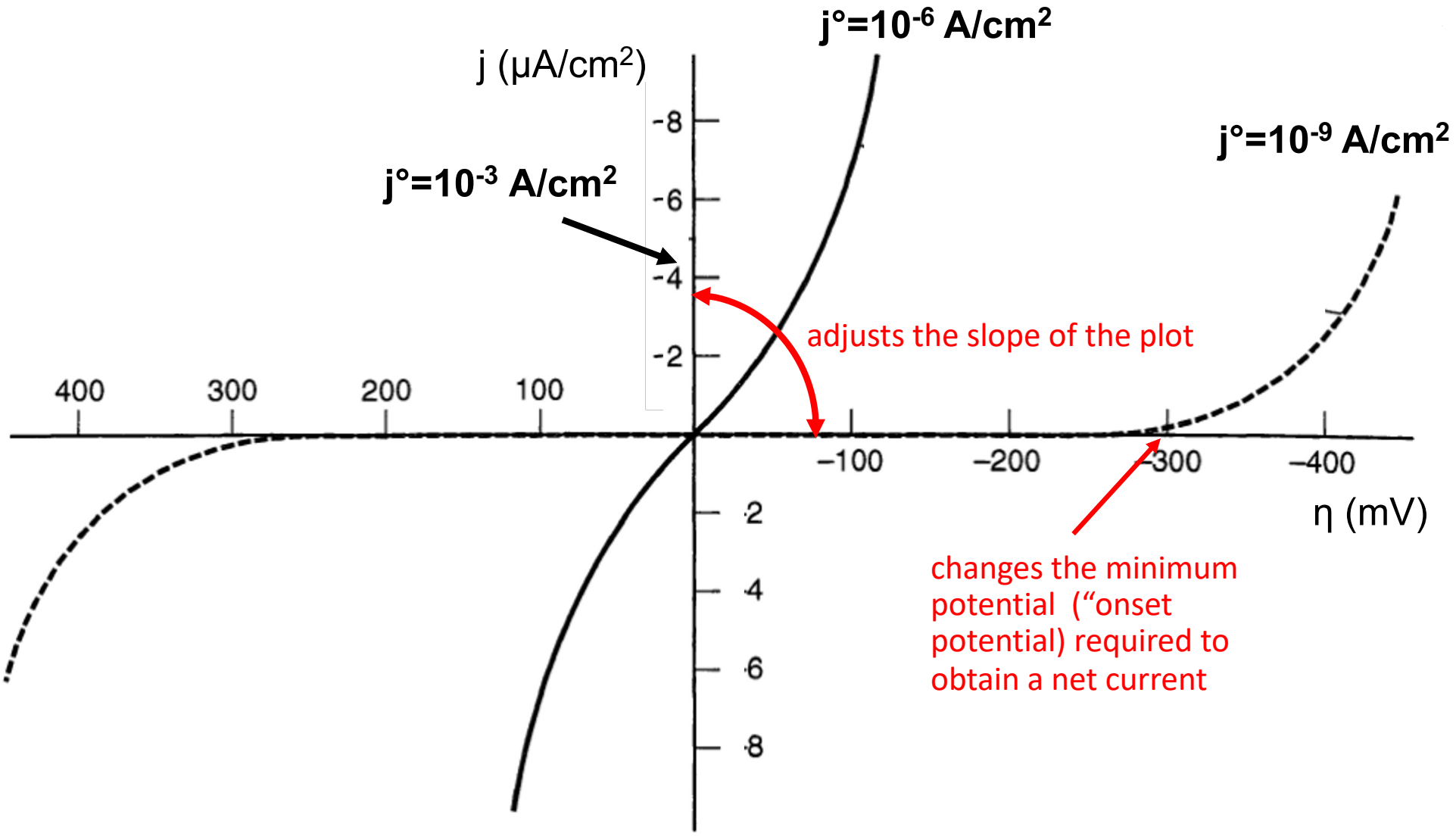
Metal	Solution	i_0 [A/cm^2]
Pt	1 M HCl	$1\ 10^{-3}$
Pb	1 M HCl	$2\ 10^{-13}$
Cu	0.14 M HCl	$2\ 10^{-7}$
Cu	0.15 M NaOH	$1\ 10^{-6}$

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



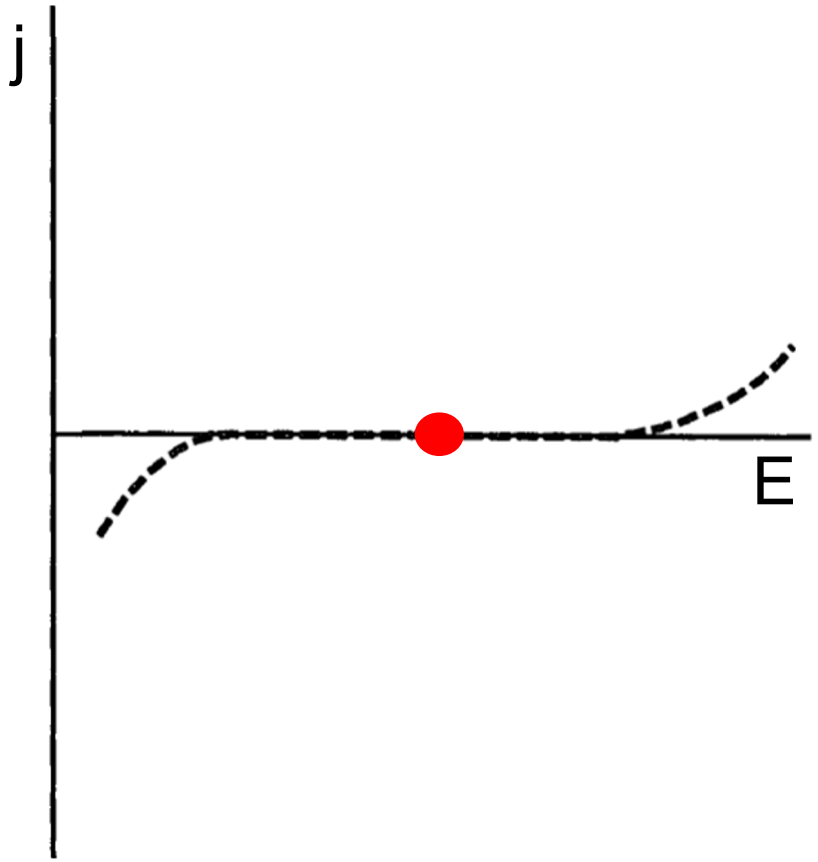
Cathodic polarization curves of hydrogen evolution on different metals in sulfuric acid

Effect of j° on ‘polarizability’

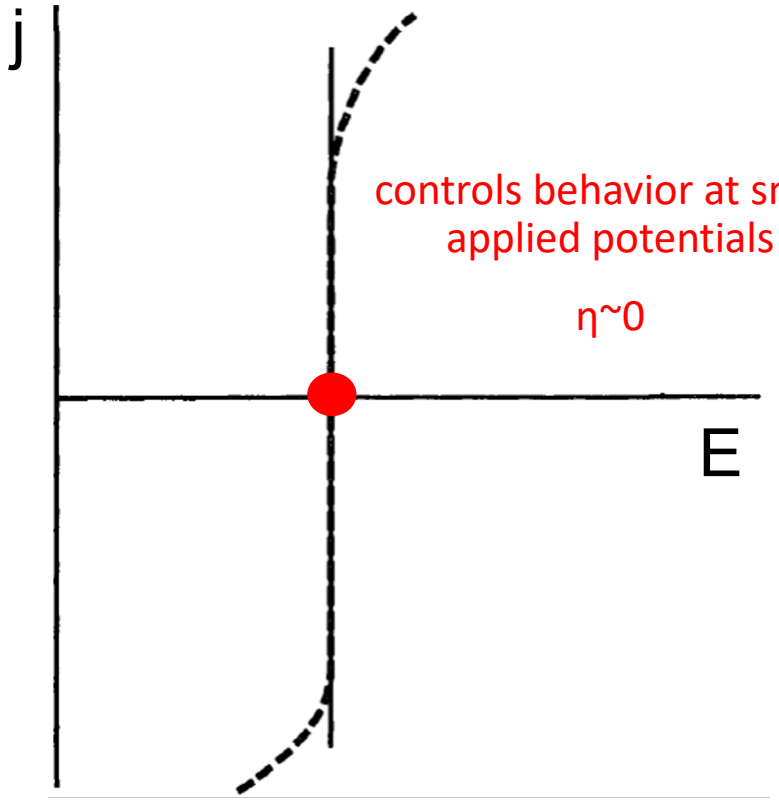


Effect of j° on polarizability

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

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

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

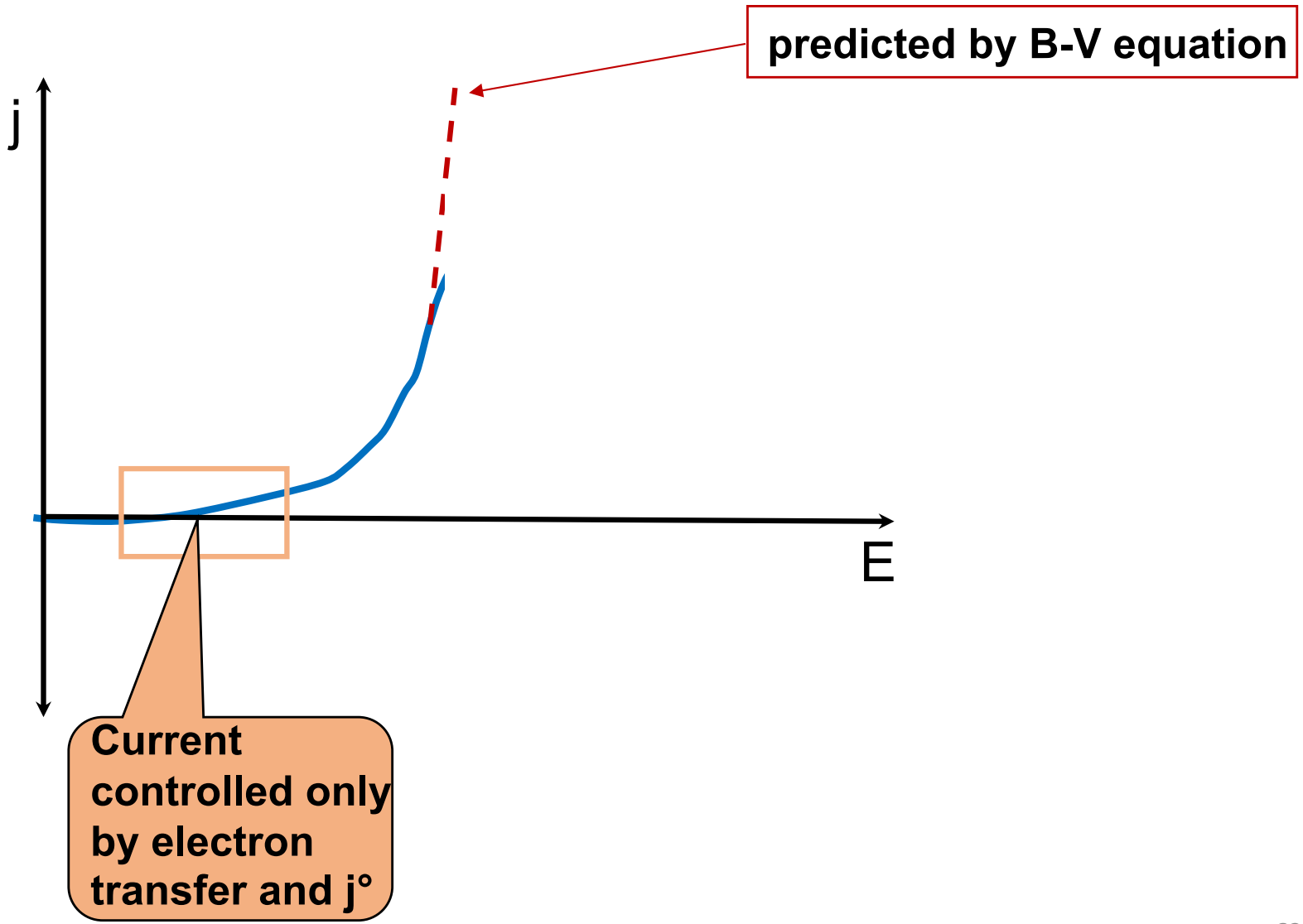
Solving for η and substituting for f

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

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

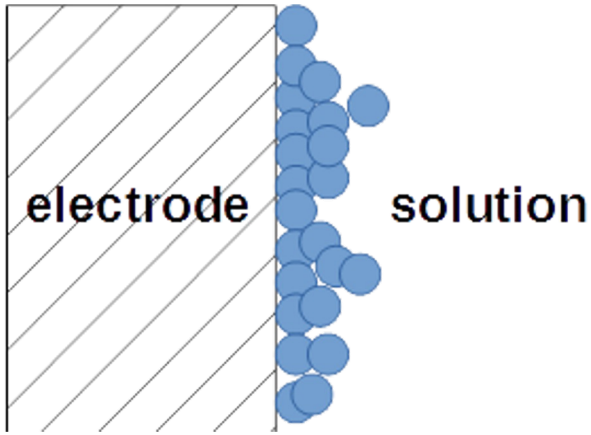
An **ideal polarizable electrode** is an electrode at which no charge transfer occurs across the metal-solution interface, regardless of the potential imposed.

$$R_{ct} = \frac{RT}{zF|i°|}$$

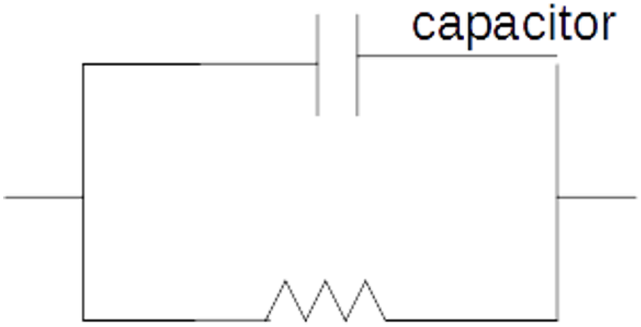
- As R_{ct} approaches zero, the interface is said to be ideally non-polarizable, i.e. its potential cannot be changed
- A **reference electrode** should be ideally polarizable over the current range in the experiment

Effect of j° and R_{ct} on polarizability

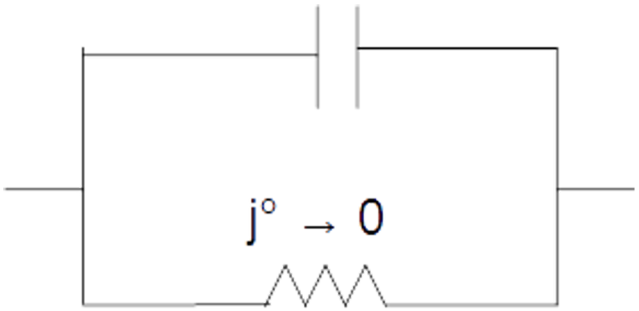
Electrified interface



Its equivalent circuit

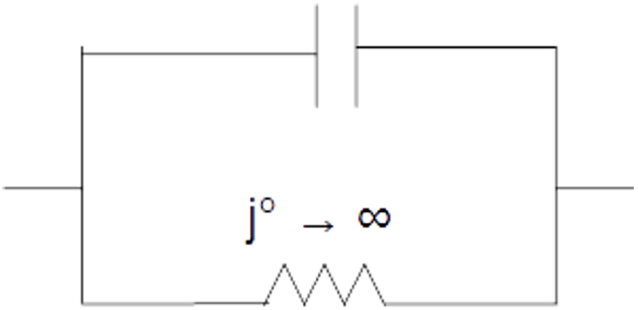


Equivalent circuit of ideally polarizable interface

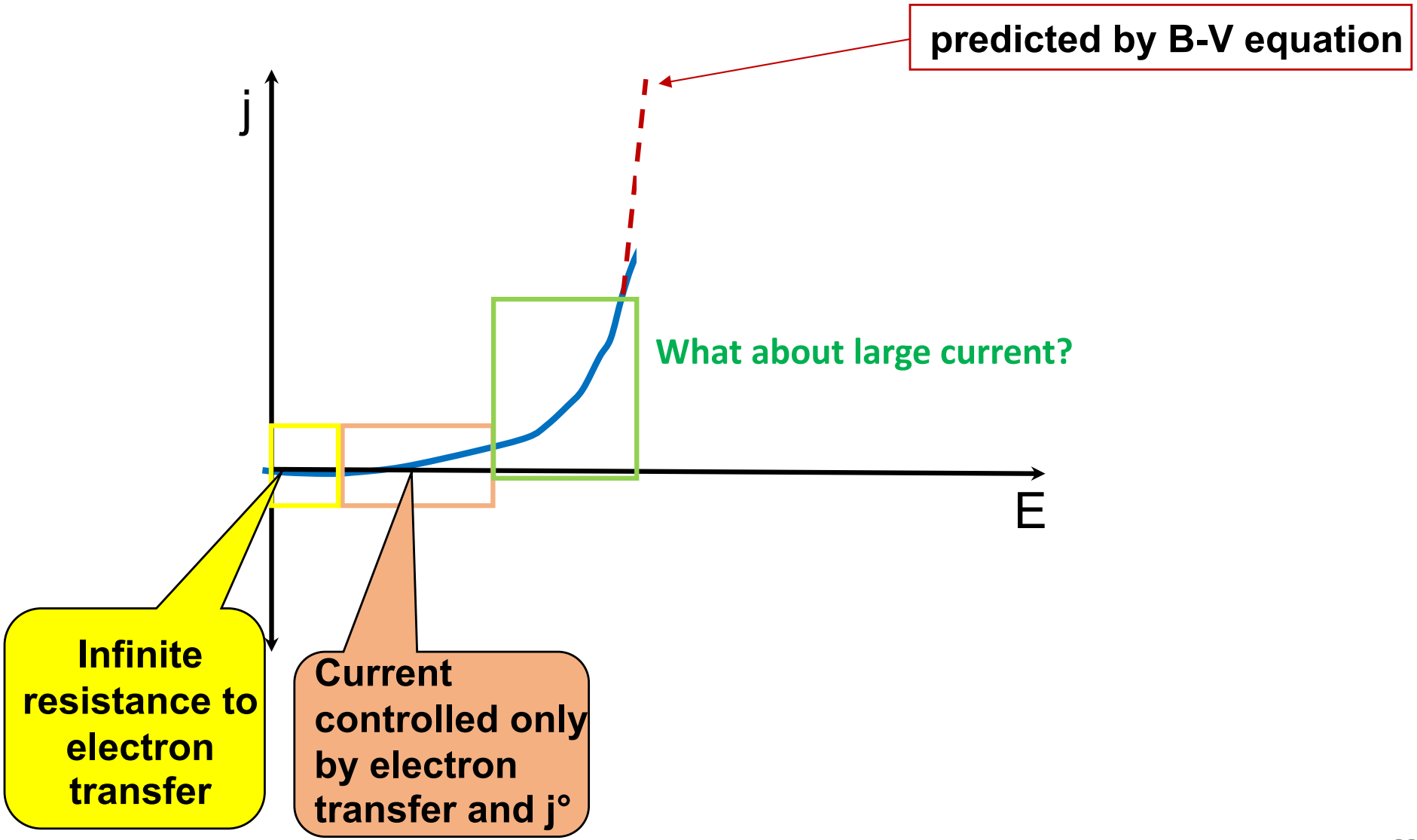


R → ∞

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

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

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

or

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

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

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

if $\eta >> 0$

or

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

if $\eta << 0$

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 :

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

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

for η >> 0 (anodic)

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

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

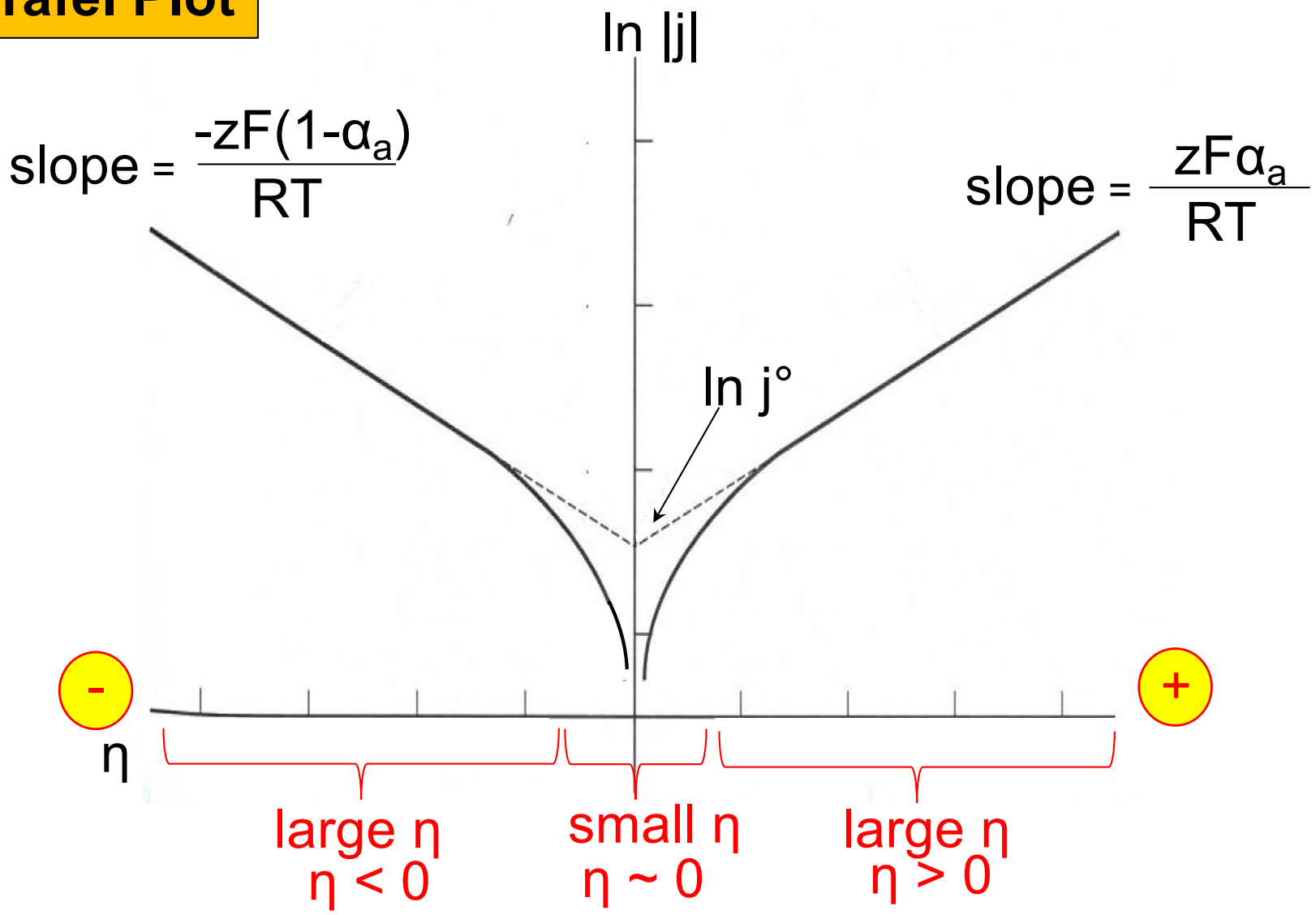
for η << 0 (cathodic)

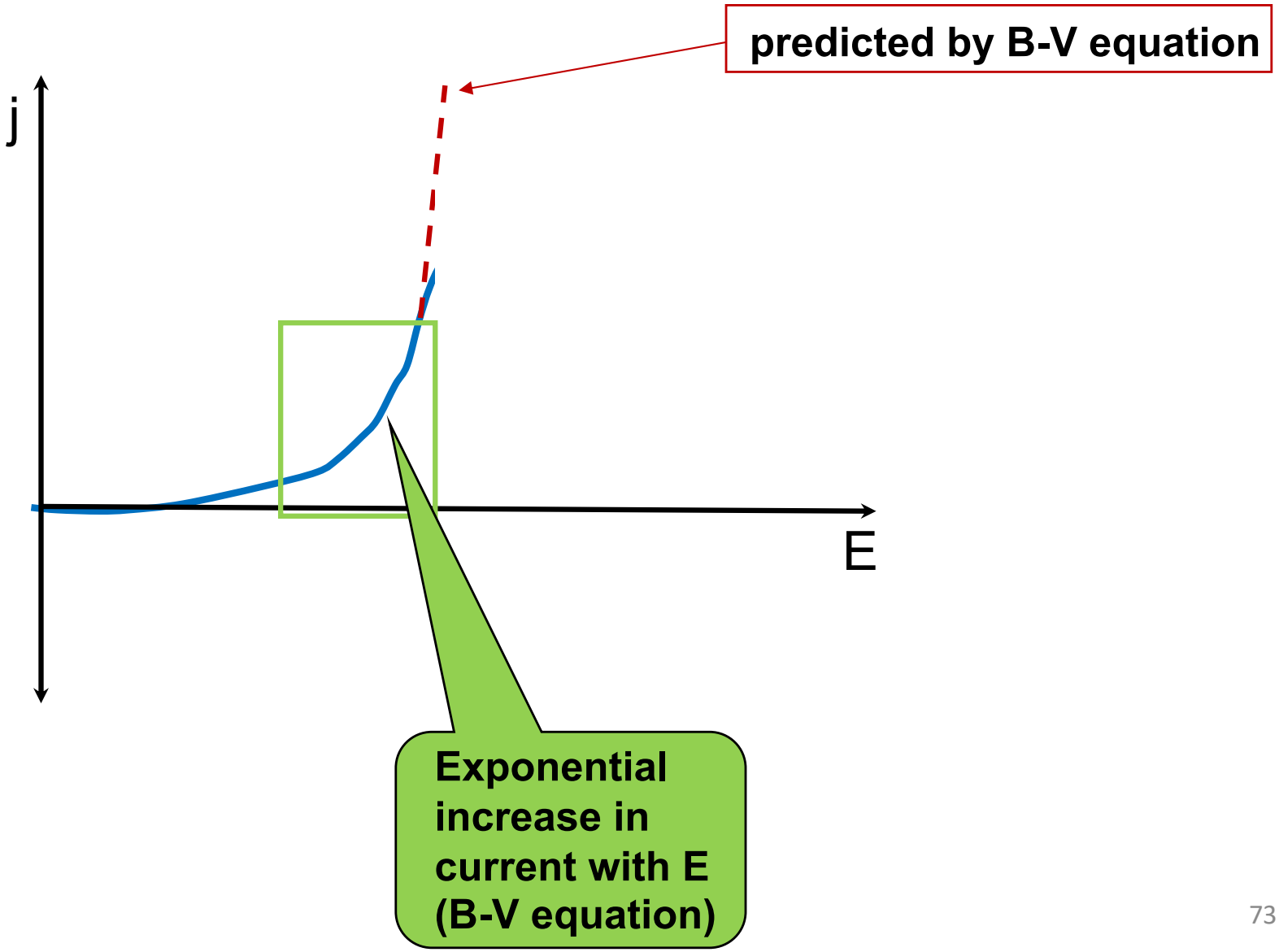
$$\eta = -\frac{RT}{zF(1-\alpha_a)} \ln |j| + \frac{RT}{zF(1-\alpha_a)} \ln |j^\circ|$$

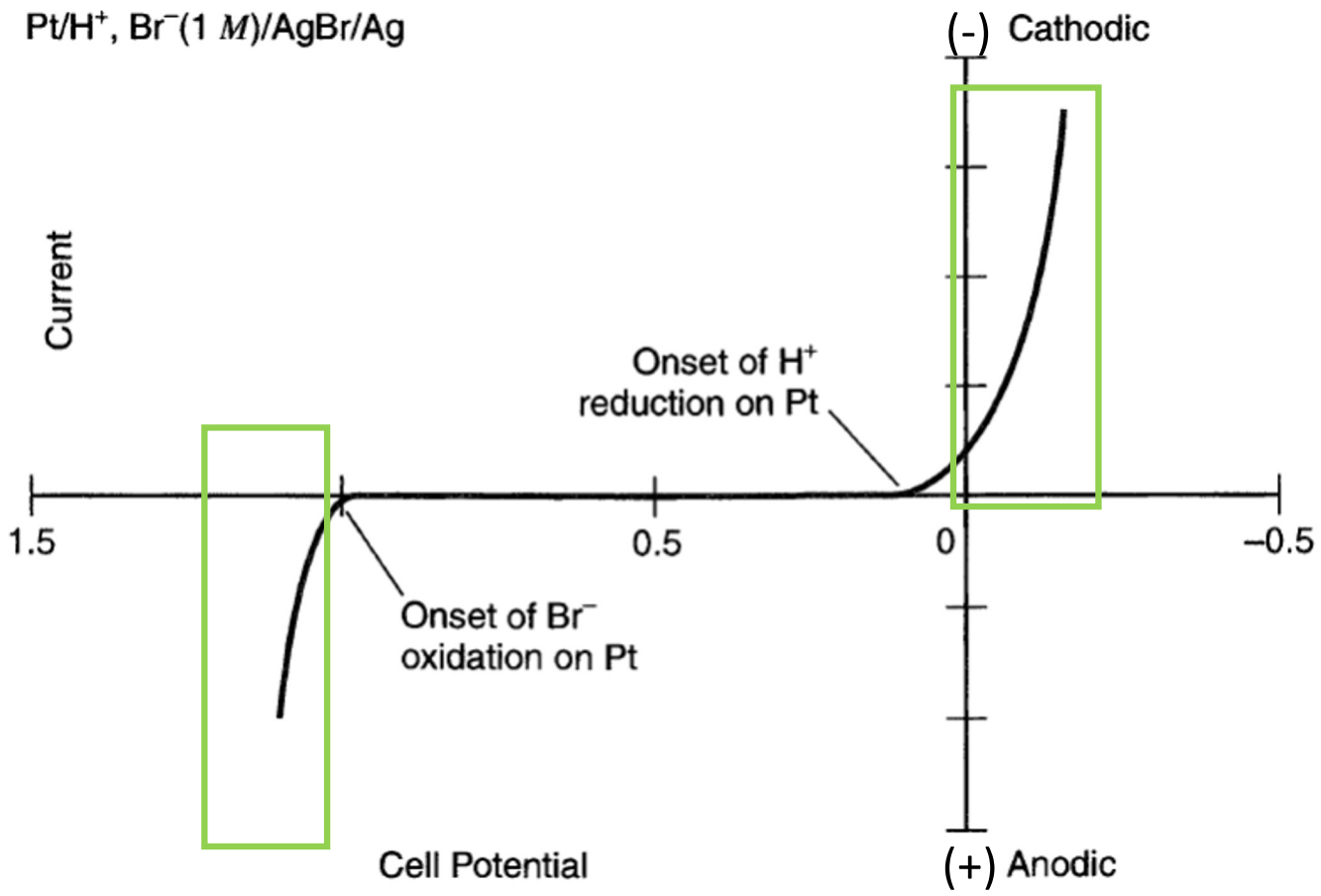
$$\ln |j| = \ln |j^\circ| - \frac{zF(1-\alpha_a)}{RT} \eta$$

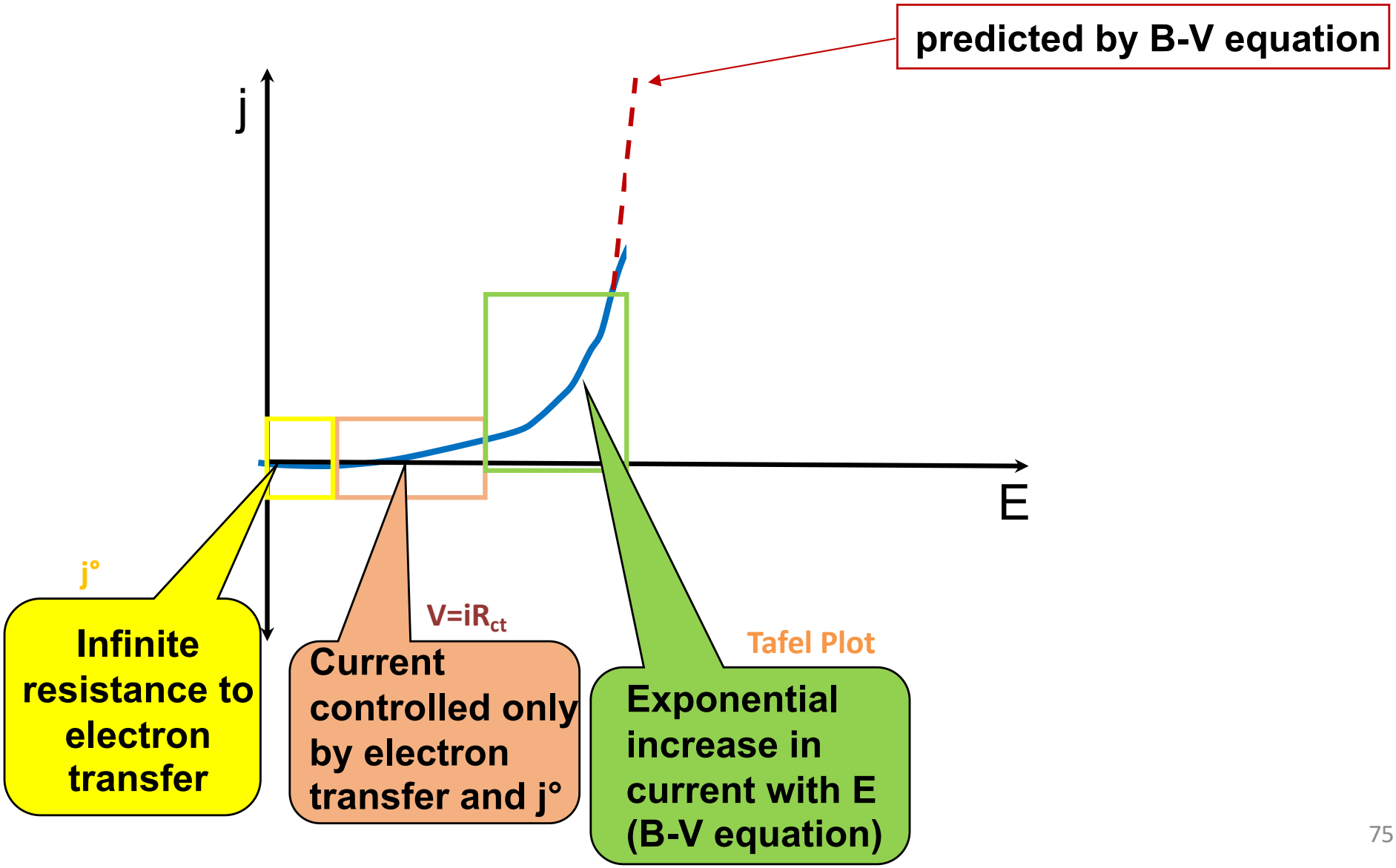
Simplification of B-V equation: 4. large overpotential η

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**

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

  1:1 O : R ratio

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

  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)

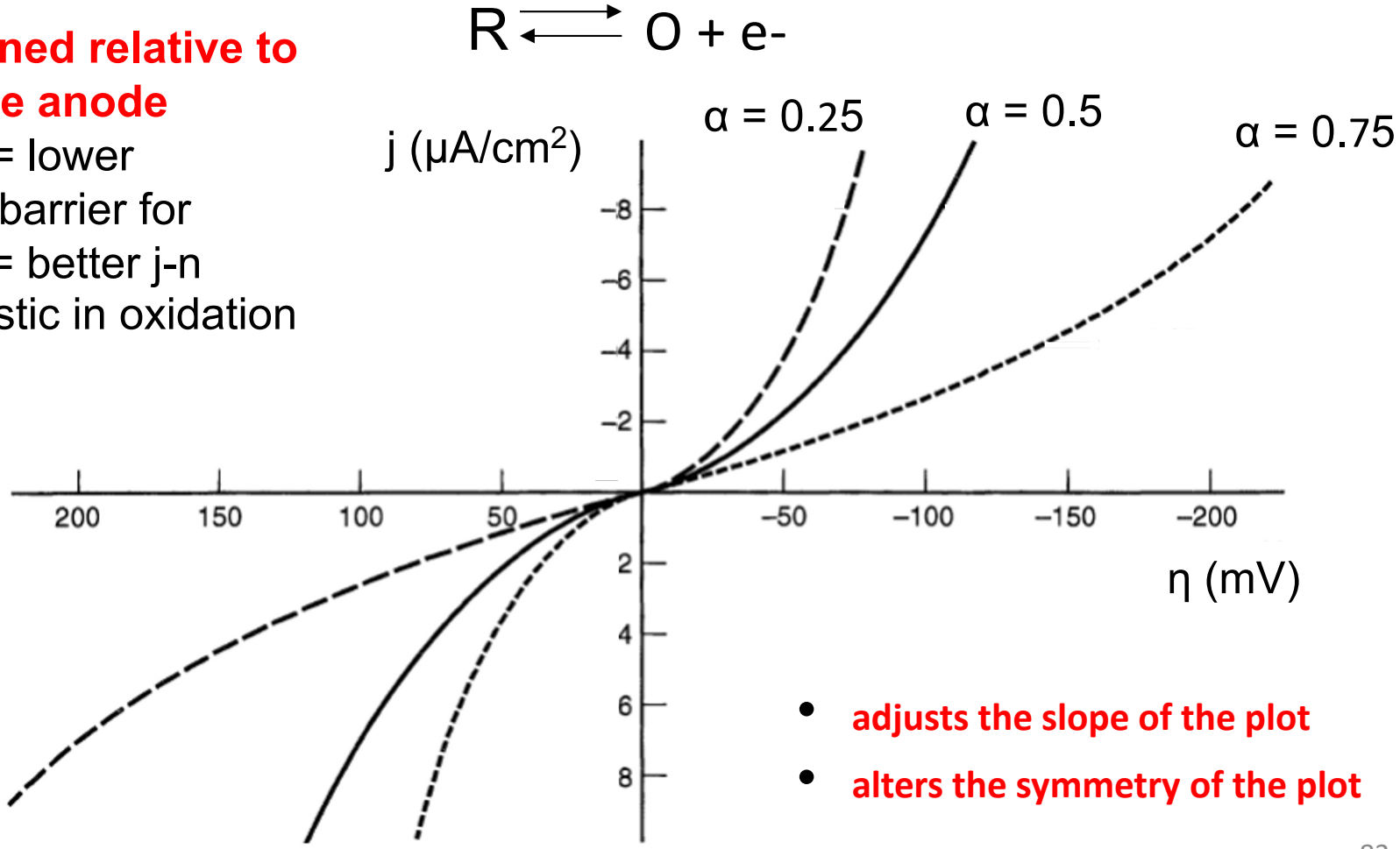
$$\frac{j}{j^{\circ}} = \frac{[R]_s}{[R^*]}\, e^{\frac{\alpha_a zF}{RT}\underbrace{(E-E_{eq})}_{\acute{\eta}}} - \frac{[O]_s}{[O^*]}\, e^{\frac{-(1-\alpha_a)zF}{RT}\underbrace{(E-E_{eq})}_{\acute{\eta}}}$$

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

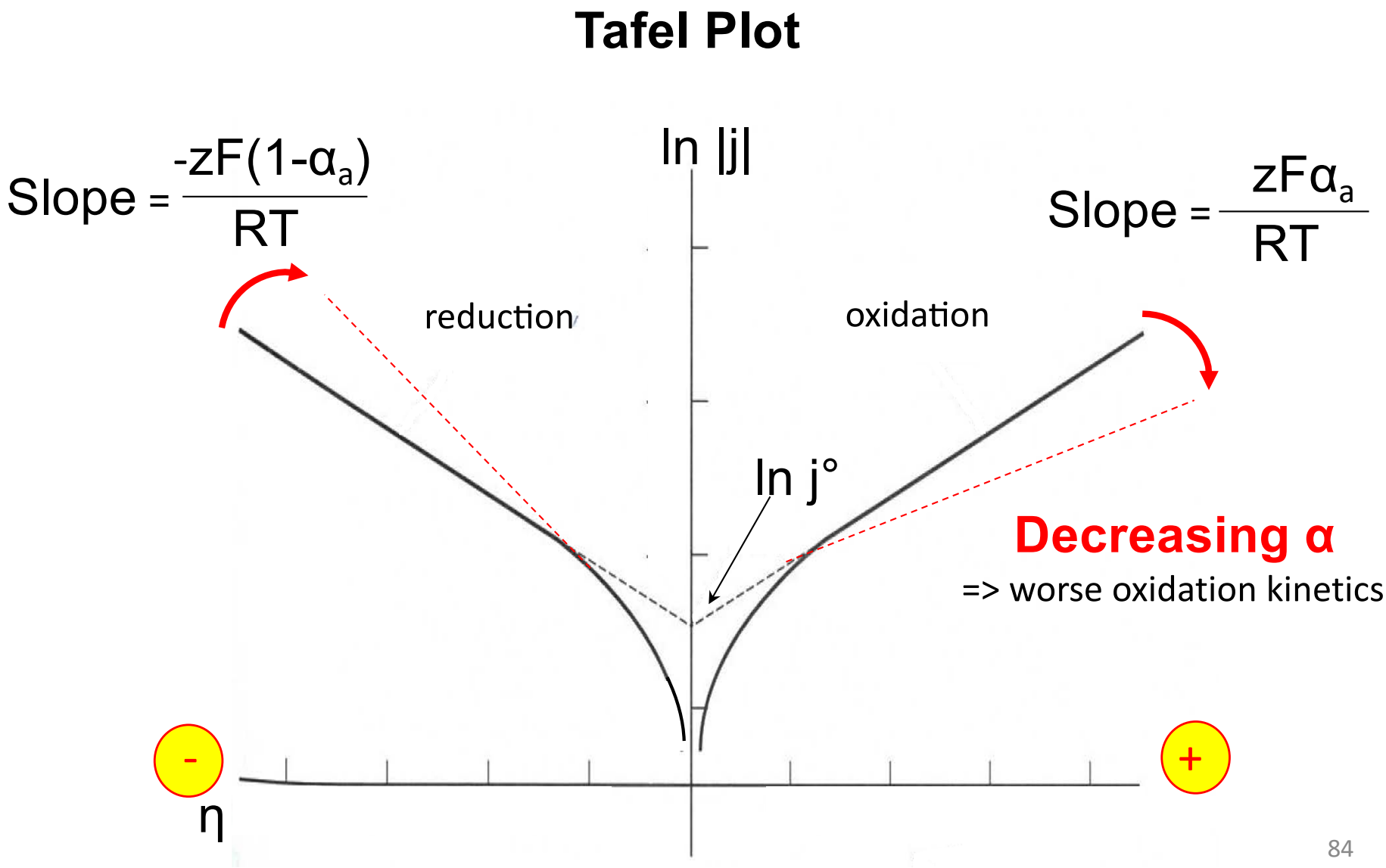
α is defined relative to the anode

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

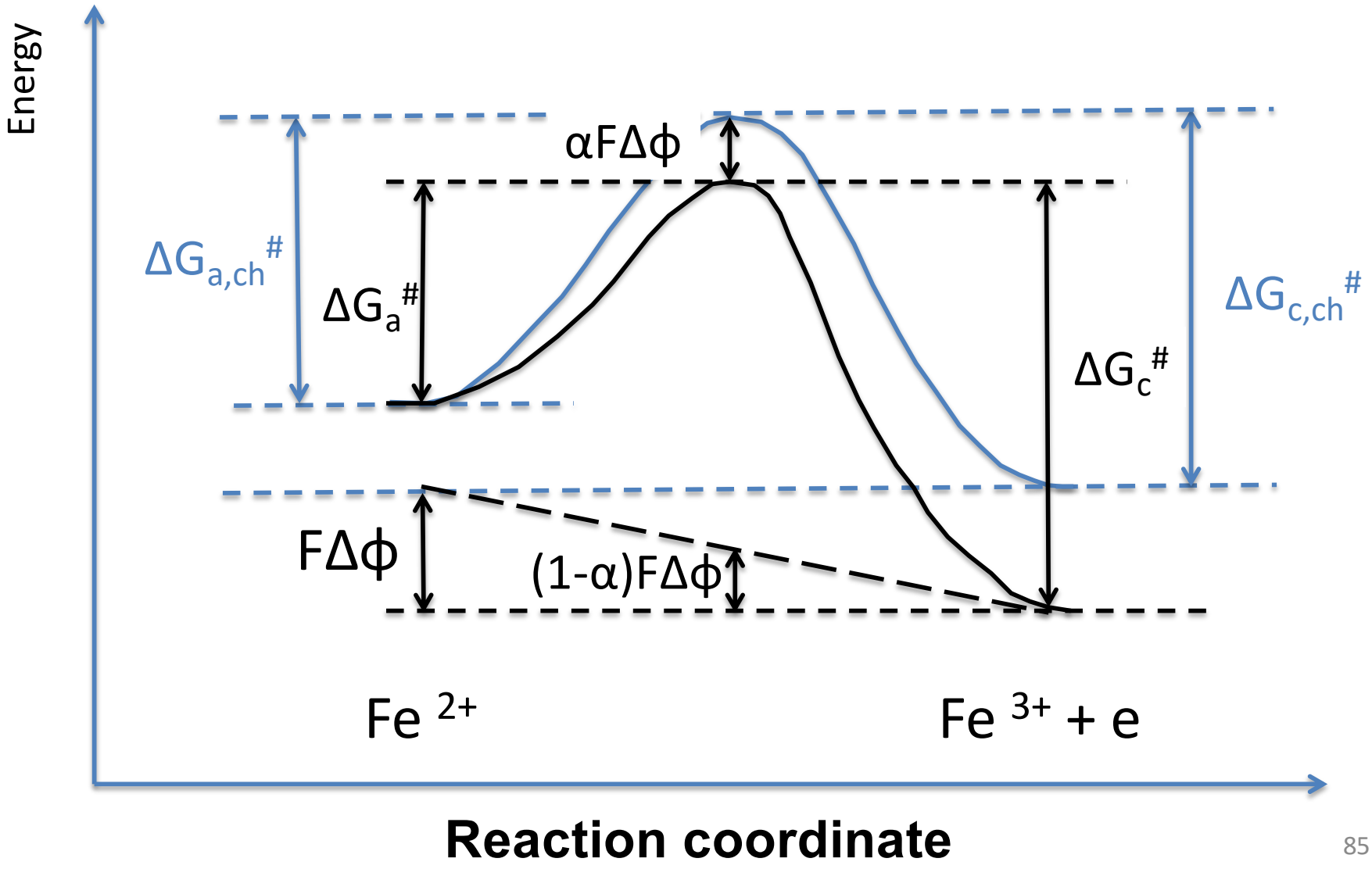


- **adjusts the slope of the plot**
- **alters the symmetry of the plot**

Effect of α

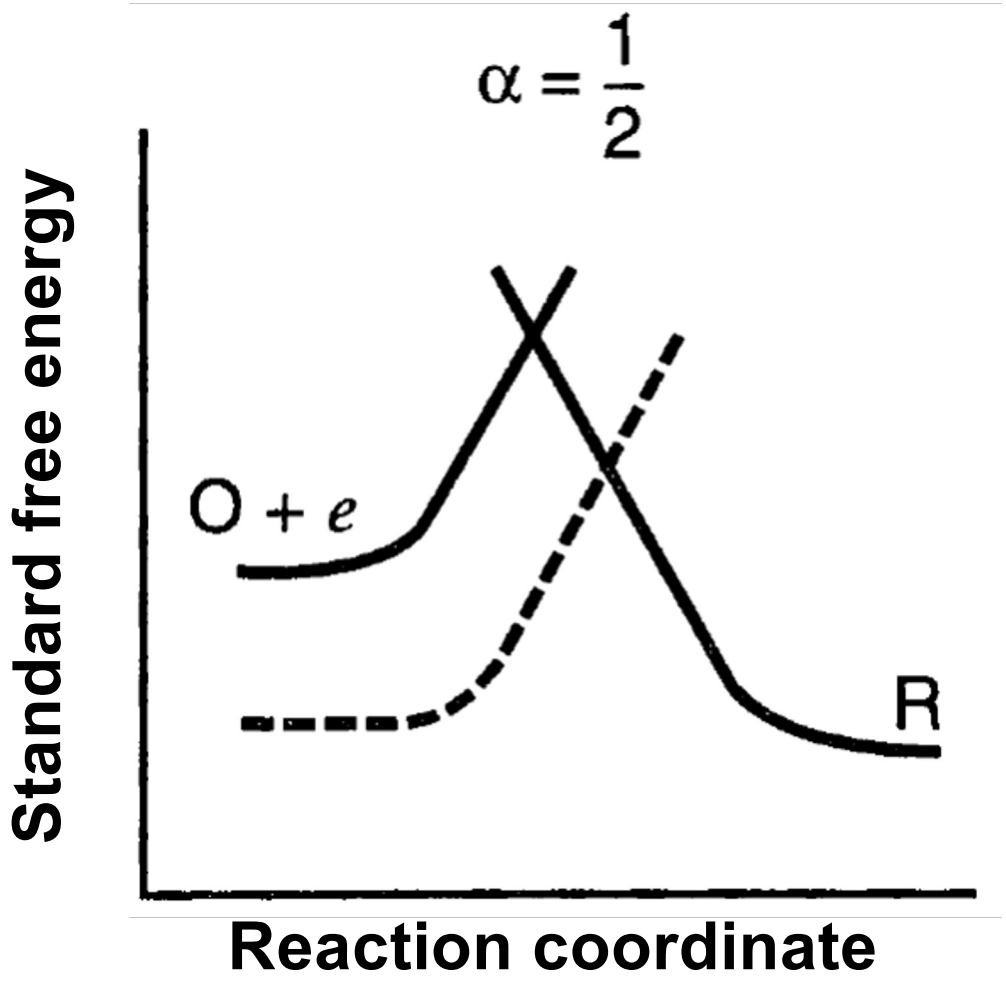

Tafel Plot
Slope = -zF(1-αa) / RT
ln |j|
Slope = zFαa / RT
reduction
oxidation
ln j°
Decreasing α
=> worse oxidation kinetics
-
+
η

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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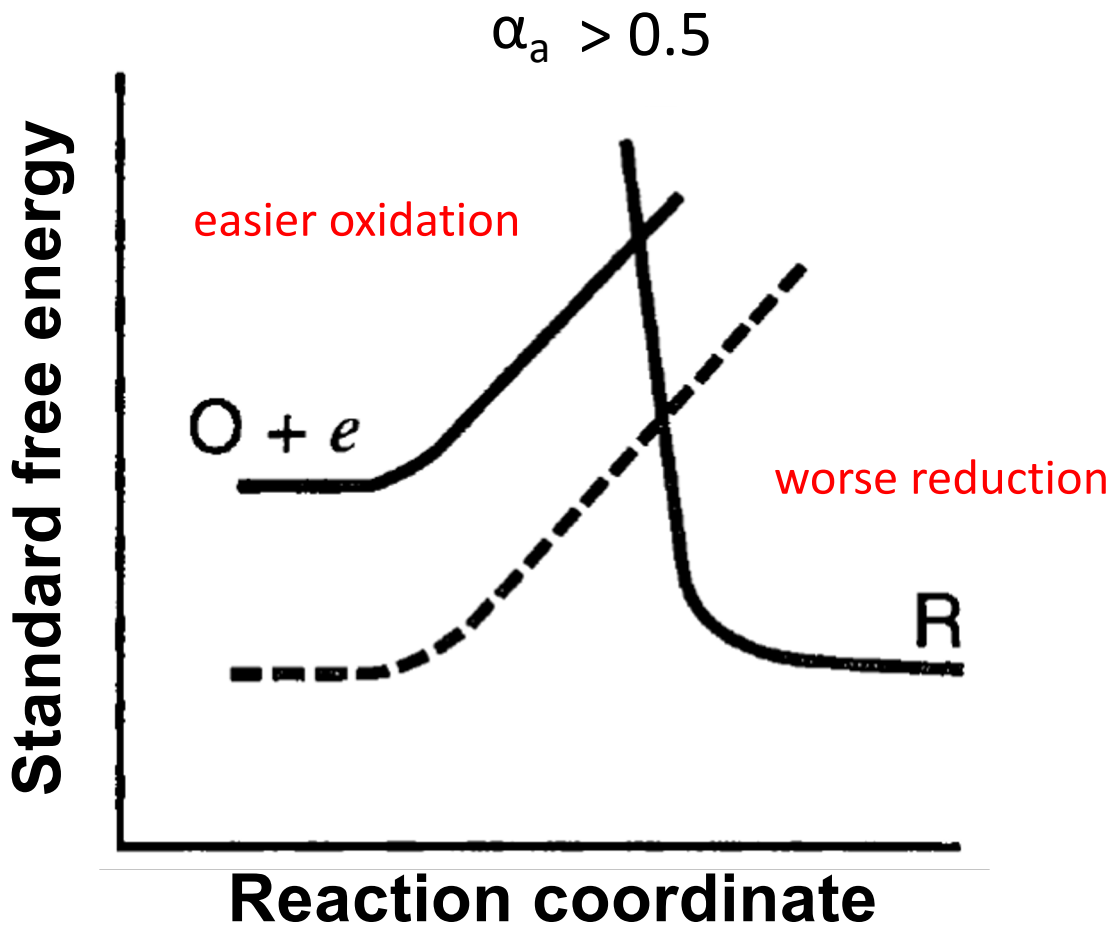

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