Solar Energy Conversion Devices and Plants

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Outline

- Electrochemistry basics:
  - Electrochemical Thermodynamics
  - Electrochemical Kinetics
  - Transport Phenomena

- This module based on:

  A. Boghossian, Lecture notes for the course *Electrochemical engineering*, EPFL

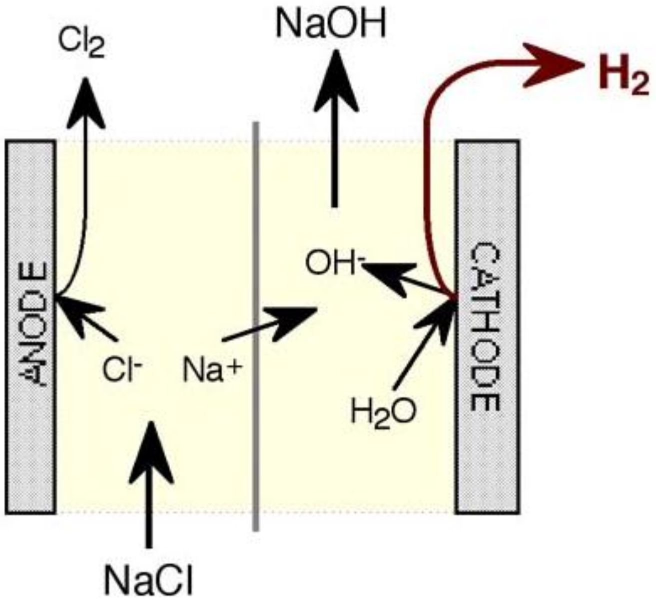
Electrochemistry

- **Electrochemistry** is a branch of chemistry that studies chemical reactions which take place in a solution at the interface of an electron conductor (a metal or a semiconductor) and an ionic conductor (the electrolyte), and which involve electron transfer between the electrode and the electrolyte or species in solution.

- **Electrochemistry** is the study and utilization of electrochemical cells - devices that allow redox reactions to occur in physically separated locations.

Examples of large-scale electrochemistry

- The **chloralkali process** (also chlor-alkali and chlor alkali) is an industrial process for the electrolysis of sodium chloride solution (brine). Depending on the method, several products besides hydrogen can be produced. If the products are separated, **chlorine and sodium hydroxide (caustic soda) are the products**; by mixing, sodium hypochlorite or sodium chlorate are produced, depending on the temperature. The process has a high energy consumption, for example over 4 billion kWh per year in West Germany in 1985. Chlor-alkali ECRs currently consume about two percent of the United States' electrical power.



Examples of large-scale electrochemistry

Working Principle of a Fuel Cell

excess fuel out

water + heat out

fuel in (H_2)

air in

Fuel + Oxidant = Products

Step 1: Thermodynamics

Gibbs free energy

- For electrochemistry

Spontaneous reactions ($\Delta G < 0$)

- Fuel cells
- Batteries
- Corrosion

Non-spontaneous reactions ($\Delta G > 0$)

- Electrolysis
- Electroplating
- Electrosynthesis
- Electrowinning
- Electrorefining

Gibbs free energy

- Related to the H and S

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

- ΔG : Related to energy production (or consumption)

- ΔH : Total heat content of a system (internal energy + product of pressure and volume); energy required to create a system and make room for it by displacing its environment and establishing volume and pressure

- TΔS : Heat/energy that is released

Cell potential

- ΔG° is not directly measureable. How does it relate to a measureable parameter for a fuel cell?

$$\Delta G^\circ = -z\, F\, E^\circ$$

\# e- transferred
per mole product

Faraday’s constant:
9.6×10^4 C/mol e-

- For the fuel cell:

Oxidation half-reaction (anode)
$H_2(g) \rightarrow 2H^+ + 2e^-$

Reduction half-reaction (cathode)
$1/2O_2\,(g) + 2e^- + 2H^+(g) \rightarrow H_2O(l)$

$$E^\circ = E^\circ_{\text{oxidation}} + E^\circ_{\text{reduction}}$$

Thermodyanmic efficiency

$$\Delta G = \Delta H - T\Delta S$$

electrical energy

chemical energy

heat released/absorbed by the environment

$$\eta_{th,\text{fuel cell}} = \frac{\Delta G}{\Delta H} < 1$$

$$\eta_{th,\text{electrolysis}} = \frac{\Delta H}{\Delta G} > 1$$

Dependence of fuel cell efficiency on temperature

Conversion and electrochemical efficiency

For a fuel cell, we can calculate the maximum theoretical thermodynamic efficiency of the cell assuming reaction completion and no voltage losses

$$\eta_{th,\text{fuel cell}} = \frac{\Delta G^\circ}{\Delta H^\circ}$$

But in practice, we do not achieve 100% conversion of reactants into products. So we define a conversion efficiency (η_c)

$$\eta_c = \frac{\text{Amount of fuel reacted}}{\text{Amount of fuel provided}}$$

Similarly, the measured cell potential is less than the thermodynamic cell potential due to potential losses. So we define an electrochemical efficiency (η_{el})

$$\eta_{el} = \frac{E}{E_{cell}} \quad \begin{matrix} \leftarrow \text{Measured potential} \\ \leftarrow \text{Calculated from } \Delta G \end{matrix}$$

Potential

Reduction potential is a measure of a tendency of a chemical species to **acquire electrons**.

Other names: Reduction-oxidation potential
Redox potential
Midpoint potential

The **more positive** the reduction potential, the **more favorable** the reduction reaction

More thermodynamically favored

Based on the values provided in the Standard Reduction table…

$Au^{3+}(aq) + 3e^{-} \rightarrow Au(s)$ $E° = +1.50\ V$

$Fe^{3+}(aq) + e^{-} \rightarrow Fe^{2+}(aq)$ $E° = +0.77\ V$

Potential

Reduction potential is a measure of a tendency of a chemical species to **acquire electrons**.

The oxidation potential is just the reverse reaction, which has the opposite sign → $(E_{oxidation})_{reactionA} = -(E_{reduction})_{reactionA}$

Based on the values provided in the Standard Reduction table…

More thermodynamically favored

$Au^{3+}(aq) + 3e^- \leftarrow Au(s) \qquad E° = -1.50\ V$

$$\boxed{Fe^{3+}(aq) + e^- \leftarrow Fe^{2+}(aq) \qquad E° = -0.77\ V}$$

Potential

Reduction potential is a measure of a tendency of a chemical species to **acquire electrons**.

The oxidation potential is just the reverse reaction, which has the opposite sign → $(E_{oxidation})_{reactionA} = -(E_{reduction})_{reactionA}$

$$A_{ox} + ze^- \underset{E_{oxidation}}{\overset{E_{reduction}}{\rightleftharpoons}} A_{red}$$

$E_{reduction} > 0$, reduction favored

$$\left.\begin{array}{l} E_{reduction} < 0 \\ E_{oxidation} > 0 \end{array}\right\} \text{oxidation favored}$$

Potential

Reduction potential is measured relative to a reference reaction (**reference electrode**).

vs. Standard Hydrogen Electrode (SHE)

$Au^{3+}(aq) + 3e^- \rightarrow Au(s)$ E° = +1.50 V

$2H^+(aq) + 2e^- \rightarrow H_2(g)$ E° = 0.0 V

vs. Ag/AgCl/saturated KCl

$Au^{3+}(aq) + 3e^- \rightarrow Au(s)$ E° = +1.303 V

$2H^+(aq) + 2e^- \rightarrow H_2(g)$ E° = -0.197 V

$AgCl(s) + e^- \rightarrow Ag(s) + Cl^-$ E° = 0.0 V

Potential

Absolute potential is the electrode potential of a metal measured with respect to a universal reference system that neglects the metal-solution interface. It is the difference in electronic energy between a point inside the metal of an electrode and a point outside the electrolyte in which the electrode is submerged (an electron at rest in vacuum).

The absolute potential is difficult to determine accurately, so the standard hydrogen electrode (SHE) is typically used as a reference potential. The SHE is one of the few systems for which the absolute potential has been accurately determined.

vs. vacuum (absolute potential)

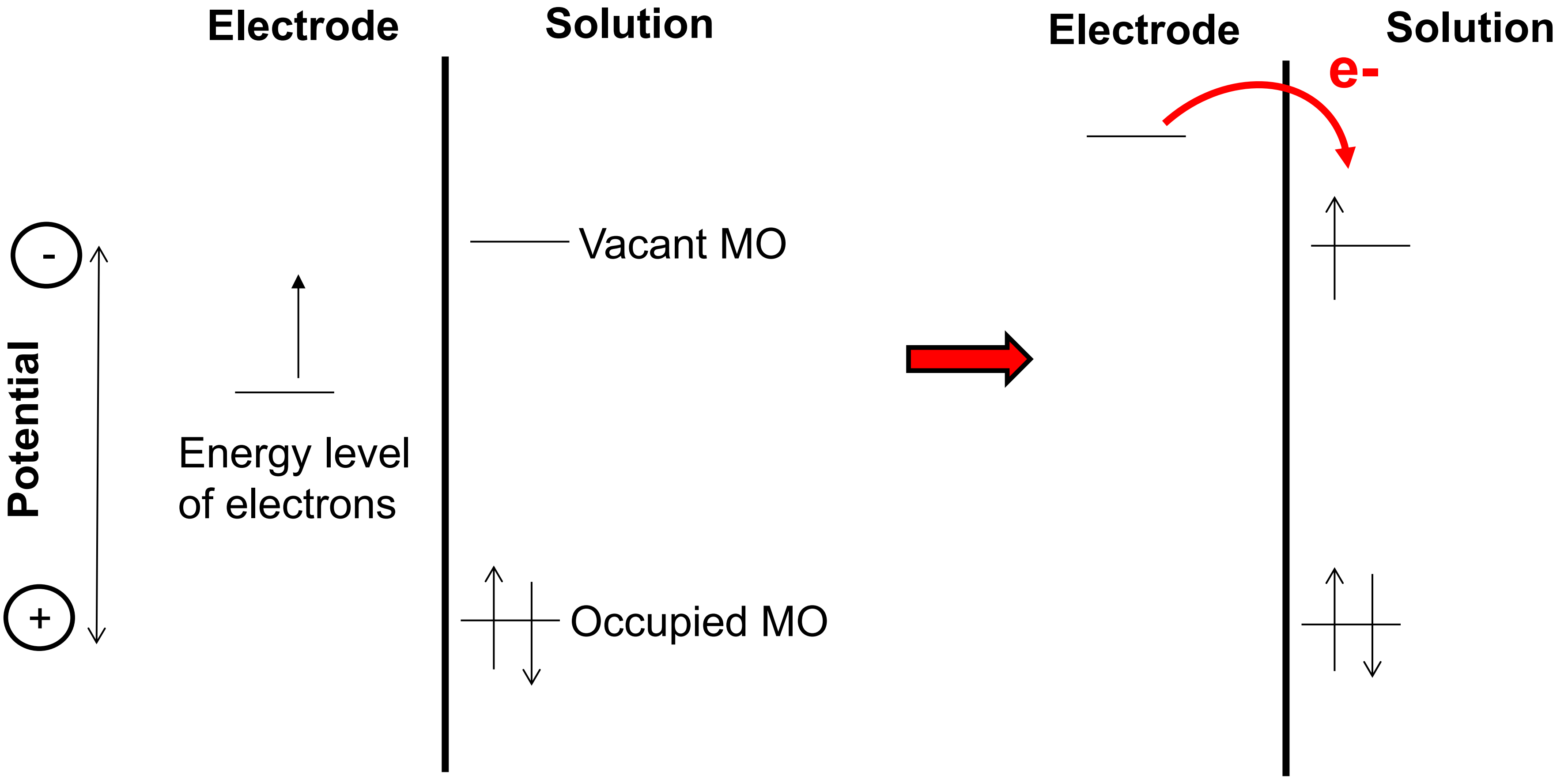
$Au^{3+}(aq) + 3e^{-} \rightarrow Au(s)$	$E° = +5.94$ V
$2H^{+}(aq) + 2e- \rightarrow H_2(g)$	$E° = +4.44$ V
$M^{+}_{solution} + e\text{-}(g) \rightarrow M_{metal}$	$E° = 0.0$ V

Related to work function of the metal

Potential

Reduction process of a species at an electrode

MO = Molecular Orbital



Electrode

Solution

Electrode

Solution

e-

Vacant MO

Potential

-

+

Energy level of electrons

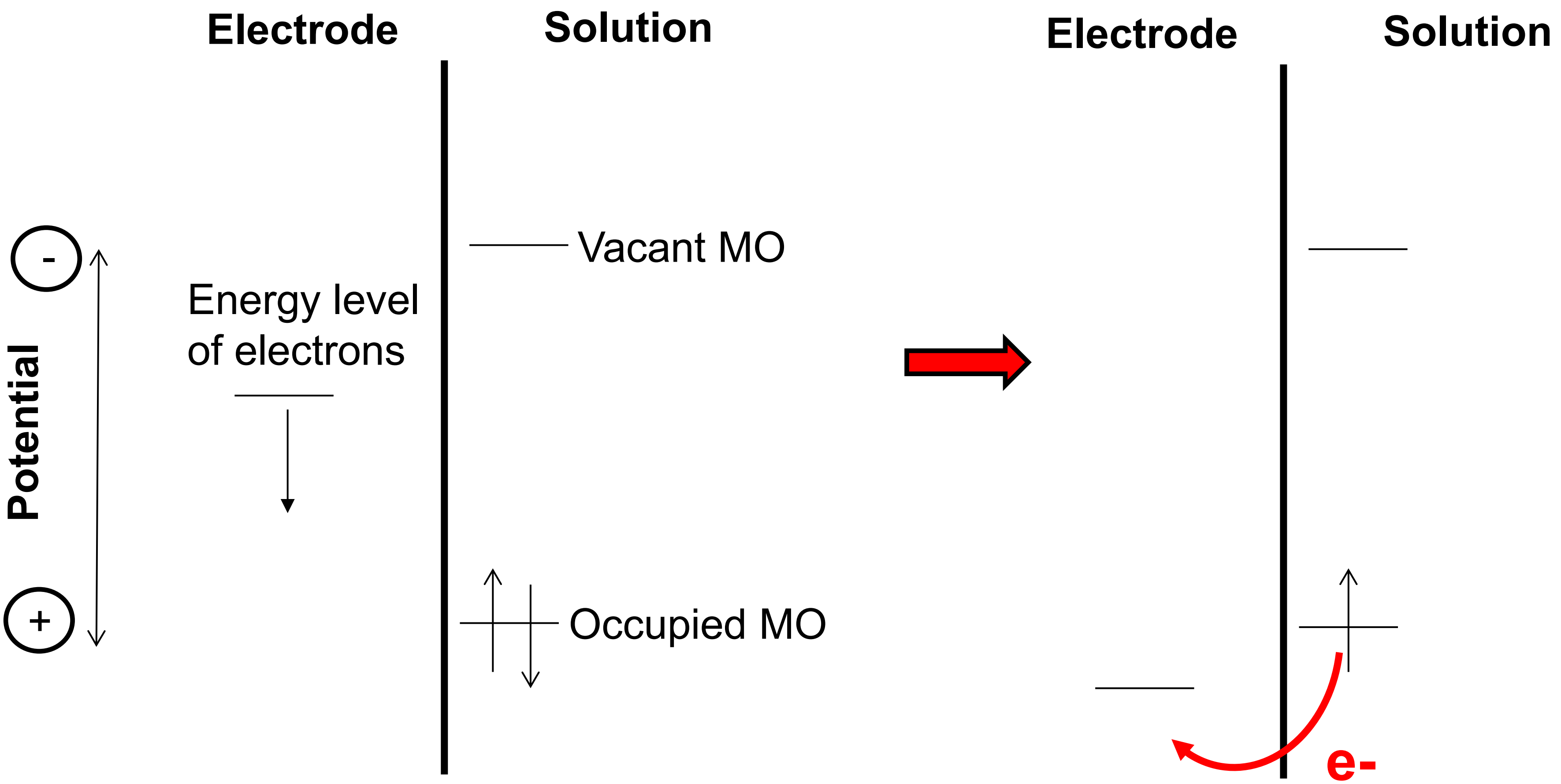
Occupied MO

$A + e^- \rightarrow A^-$

Potential

Oxidation process of a species at an electrode

MO = Molecular Orbital



Electrode

Solution

Electrode

Solution

Vacant MO

Energy level of electrons

Potential

-

+

Occupied MO

e-

$A^- \rightarrow A + e^-$

What is current?

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

i : current

units of amperes (A), which is 1 coulomb/s (C/s)

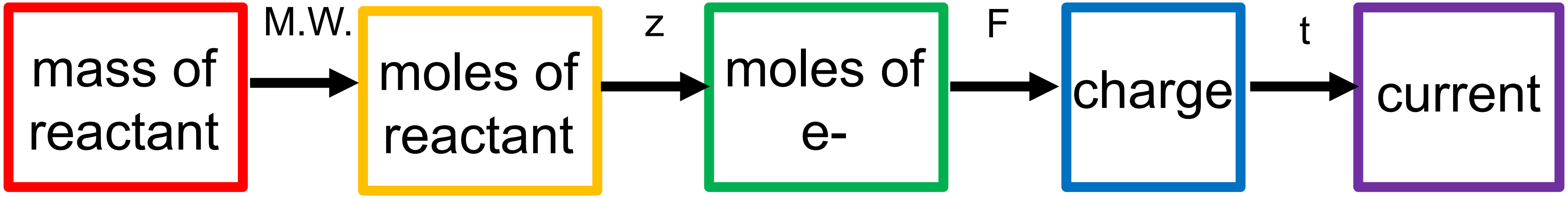
j : current density

units of amperes/surface area (A/m^2)

Whereas voltage (E_{cell}) is an **intensive variable** (independent of the amount reacted), current (j or i) is an **extensive variable** (depends on the amount).

Relationship Current and Reactant Conversion

Current can be calculated from the amount of reactant reacted



mass of reactant $\xrightarrow{\text{M.W.}}$ moles of reactant $\xrightarrow{z}$ moles of e- $\xrightarrow{F}$ charge $\xrightarrow{t}$ current

$$[\text{g}] \quad \frac{[\text{mol}]}{[\text{g}]} \quad [\text{mol}] \quad \frac{[\text{mol e-}]}{[\text{mol}]} \quad [\text{mol e-}] \quad \frac{[\text{C}]}{[\text{mol e-}]} \quad [\text{C}] \quad \frac{[1]}{[\text{s}]} \quad \frac{[\text{C}]}{[\text{s}]}$$

$$\boxed{i = \frac{(\#\ \text{moles})(z)(F)}{t}}$$

Relationship Between Current, Heat, and Power

Current can be used to determine the total amount of heat released (or absorbed)

$$E_{thn} = E_{cell} - \frac{T\Delta S}{z\,F} \longrightarrow T\Delta S = (E_{cell}-E_{thn})\cdot z\cdot F$$

$$\frac{[J]}{[mol]} = [V] \cdot \frac{[mol\ e\text{-}]}{[mol]} \cdot \frac{[C]}{[mol\ e\text{-}]}$$

$$\text{Total heat in [J]} = (E_{cell}-E_{thn})\cdot z\cdot F \ \times\ \#\ \text{moles} \qquad \#\ \text{moles} = \frac{i\cdot t}{z\cdot F}$$

$$\boxed{\text{Total heat in [J]} = (E_{cell}-E_{thn})\cdot i\cdot t}$$

Relationship Between Current, Heat, and Power

Power (P) is the rate, per unit time, at which electrical energy is transferred by an electrical current. The SI unit of power is the watt, [W] = 1 J/s.

$$P = i \cdot V$$

i = current

V = voltage

The power output of a device (P_{output}) is less than the theoretical maximum output (P_{max}) due to losses.

Relationship Between Current, Heat, and Power

Joule heating (ohmic heating, resistive heating) is the process by which the passage of an electric current through a conductor produces heat.

$$P_{output} = P_{max} - P_{heat}$$

$$P_{heat} = i \cdot \Delta V$$

P_{output} = actual power output

P_{max} = maximum power

P_{heat} = power converted to heat

ΔV = voltage drop

Using Ohm's law ($V=iR$), we can relate power loss to current

$$P_{heat} = i^2 \cdot R$$

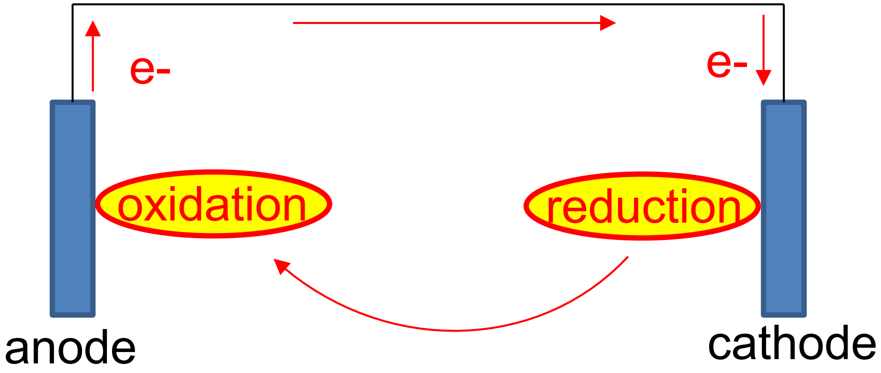
R = resistance

The SI unit of resistance is the ohm, [Ω] = 1 V/A

Sign Convention for Current

Convention used in this course:

reduction (**cathodic**) current is taken as **positive**
oxidative (**anode**) current is taken as **negative**



Recall:

- applying a positive potential to an electrode oxidizes the electrolyte (happens at the anode)
- applying a negative potential to an electrode reduces the electrolyte (happens at the cathode)

Cell Potential at Equilibrium

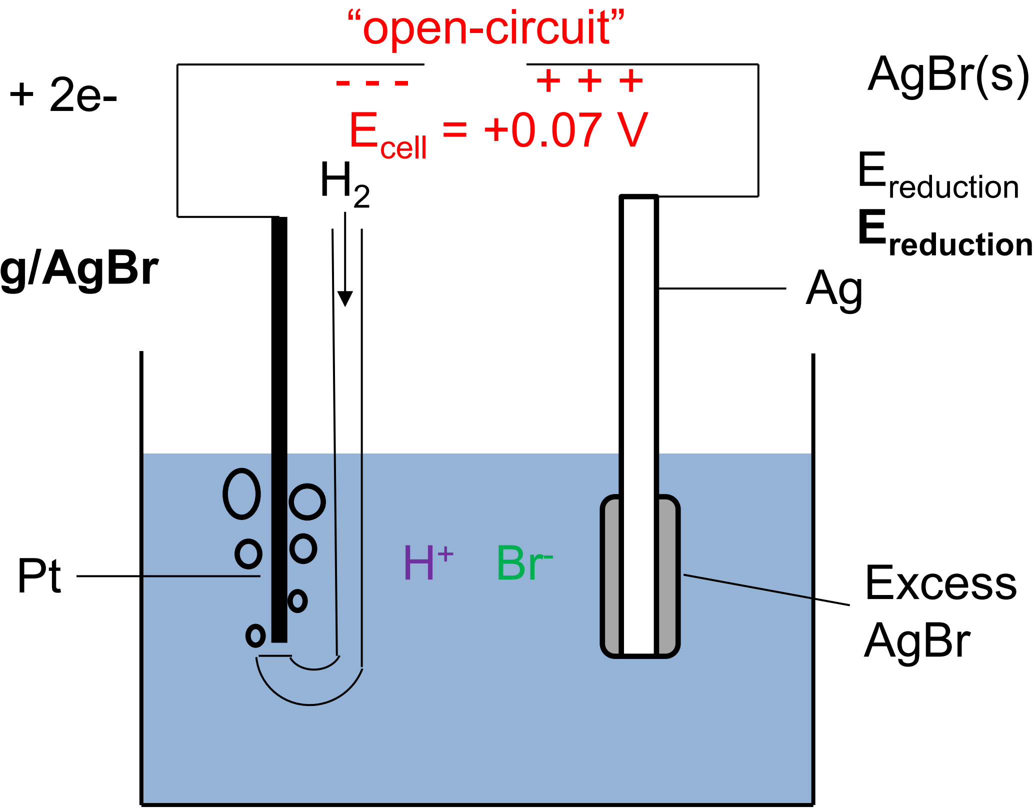
Equilibrium is established:

H^+ and H_2 is present at one electrode
Ag and AgBr is present at the other electrode

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

$E_{oxidation}$= 0 vs NHE

$E_{oxidation}$=-0.07 vs. Ag/AgBr



E_{cell} = +0.07 V

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

$E_{reduction}$ = +0.07 vs NHE

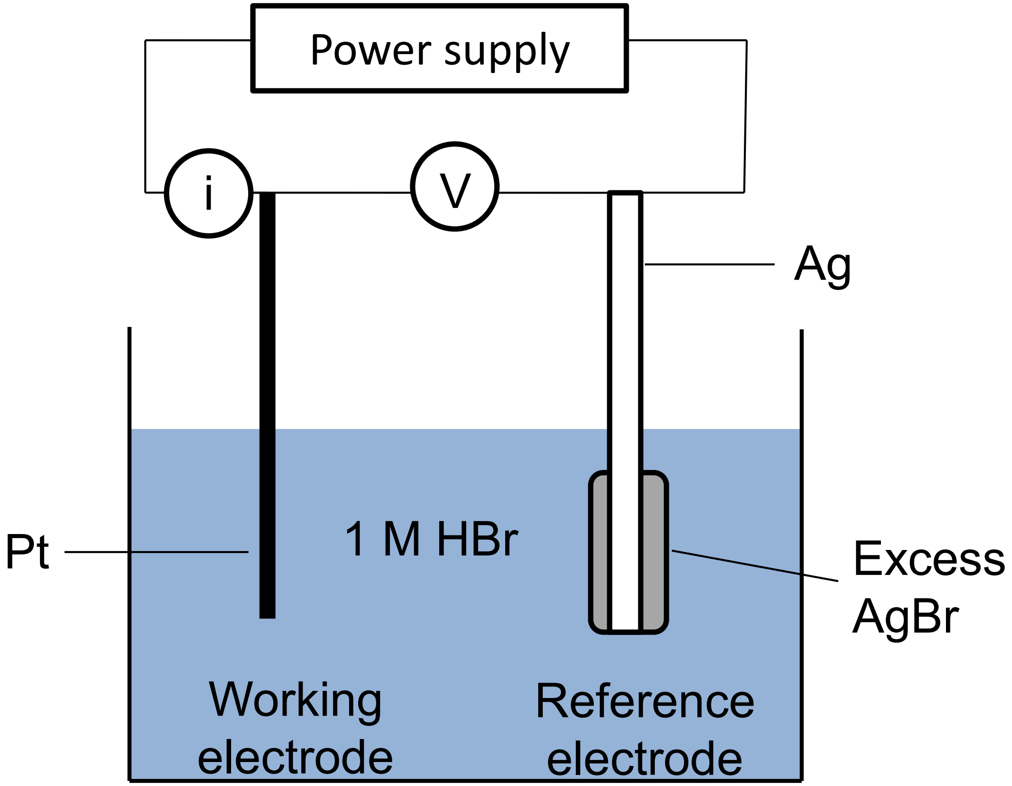
$E_{reduction}$ = 0 vs. Ag/AgBr

Net Current Production Under Non-equilibrium Conditions

Consider a electrochemical experiment where a working electrode and a reference electrode are immersed in a solution, and the potential difference between the electrodes is varied by means of an external power supply

Working electrode: electrode where reaction of interest occurs

Reference electrode: electrode made up of phases having essentially constant compositions→ this potential is fixed



Net Current Production Under Non-equilibrium Conditions

If we apply a **negative potential** to the Pt electrode relative to the Ag/AgBr electrode, eventually we get a reduction reaction

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

- The flow of electrons is from the electrode to the solution, so a reduction (cathodic) current flows.
- While this happens, Ag(s) is oxidized in the presence of Br^{-} to form AgBr at the Ag/AgBr electrode. Since [Br-] remains constant near the electrode at modest currents, the potential of the Ag/AgBr electrode will be almost the same as at open circuit.

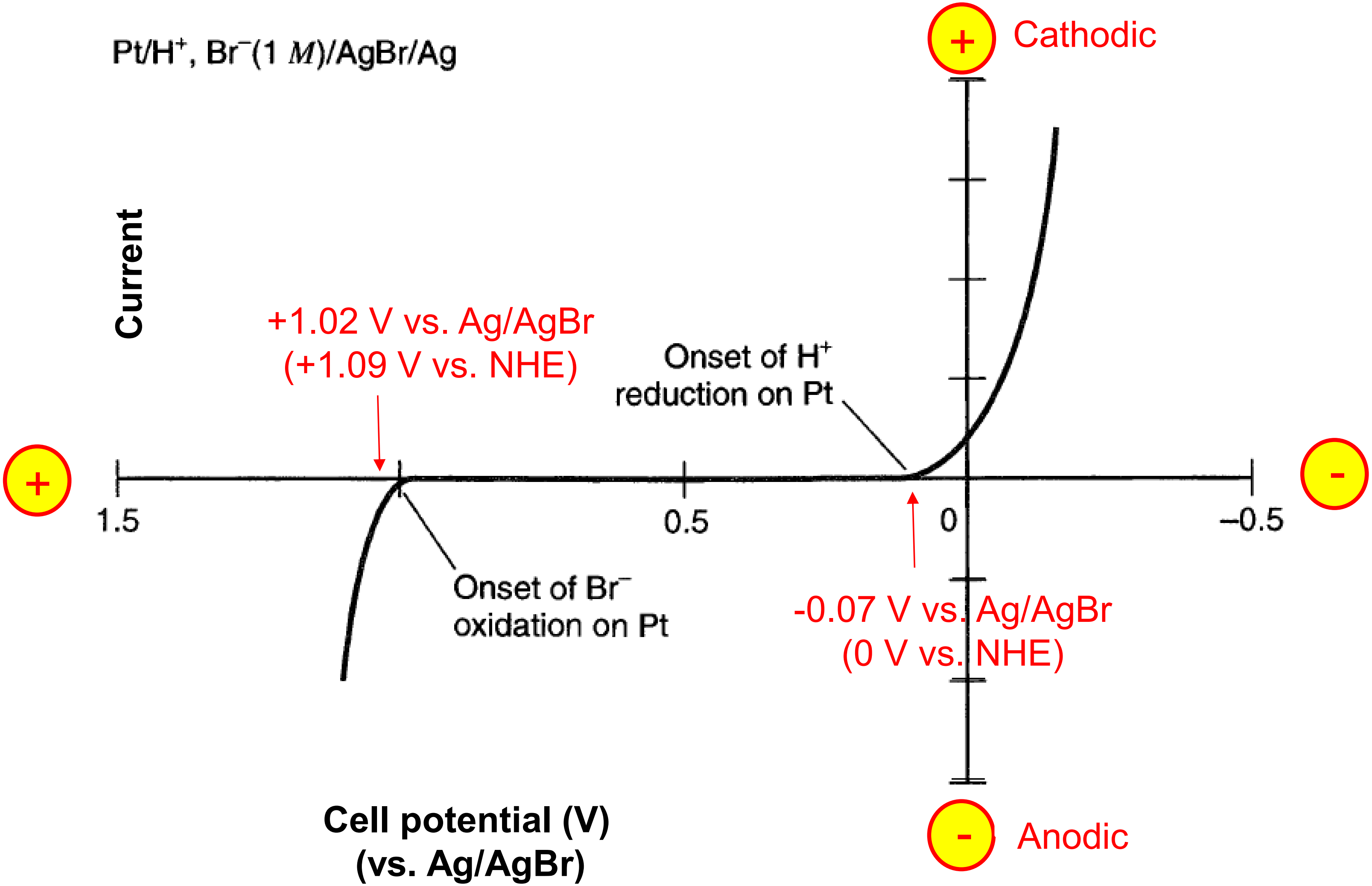
Net Current Production Under Non-equilibrium Conditions

If we apply a **positive potential** to the Pt electrode relative to the Ag/AgBr electrode, eventually we get an oxidation reaction

$$2Br^{-}(aq) \rightarrow Br_2(g) + 2e-$$

- The flow of electrons is from the solution to the electrode, so an oxidation (anodic) current flows
- While this happens, AgBr(s) at the Ag/AgBr electrode is reduced to Ag, and Br^{-} is liberated into the solution. Since [Br-] remains constant near the electrode at modest currents, the potential of the Ag/AgBr electrode will be almost the same as at open circuit

Current-Voltage Plot Curve



Effect of Electrode Material on Current-Voltage Plot

Same system, but different working electrode

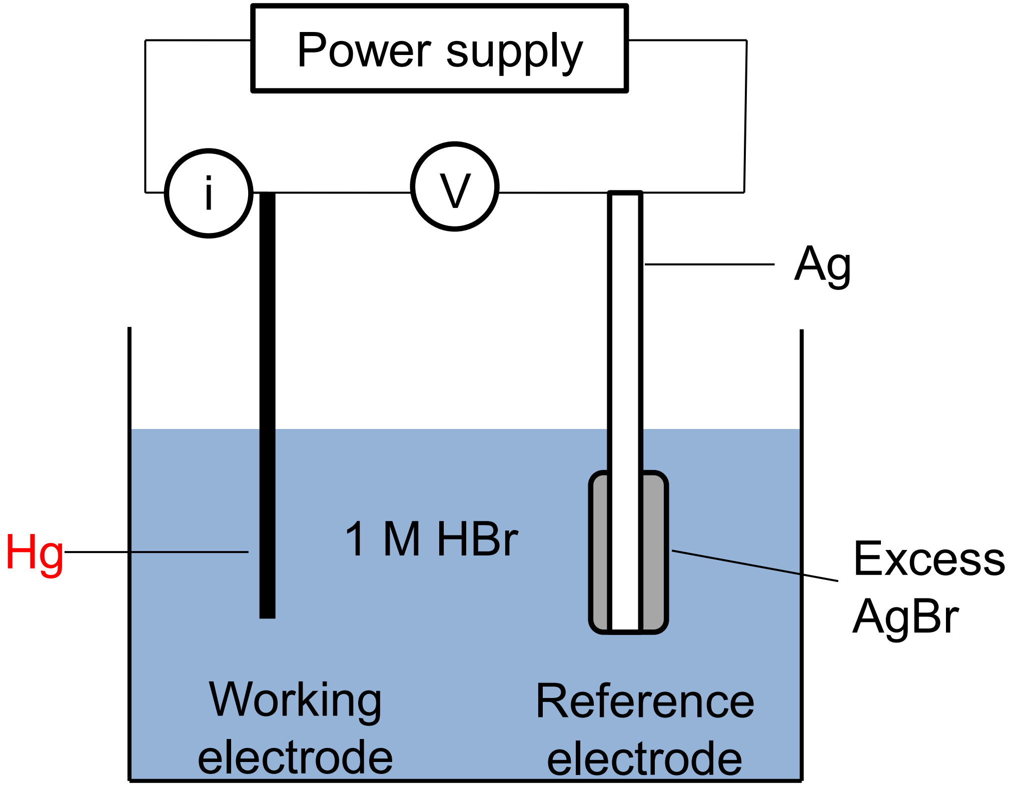
Reference electrode is in equilibrium

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

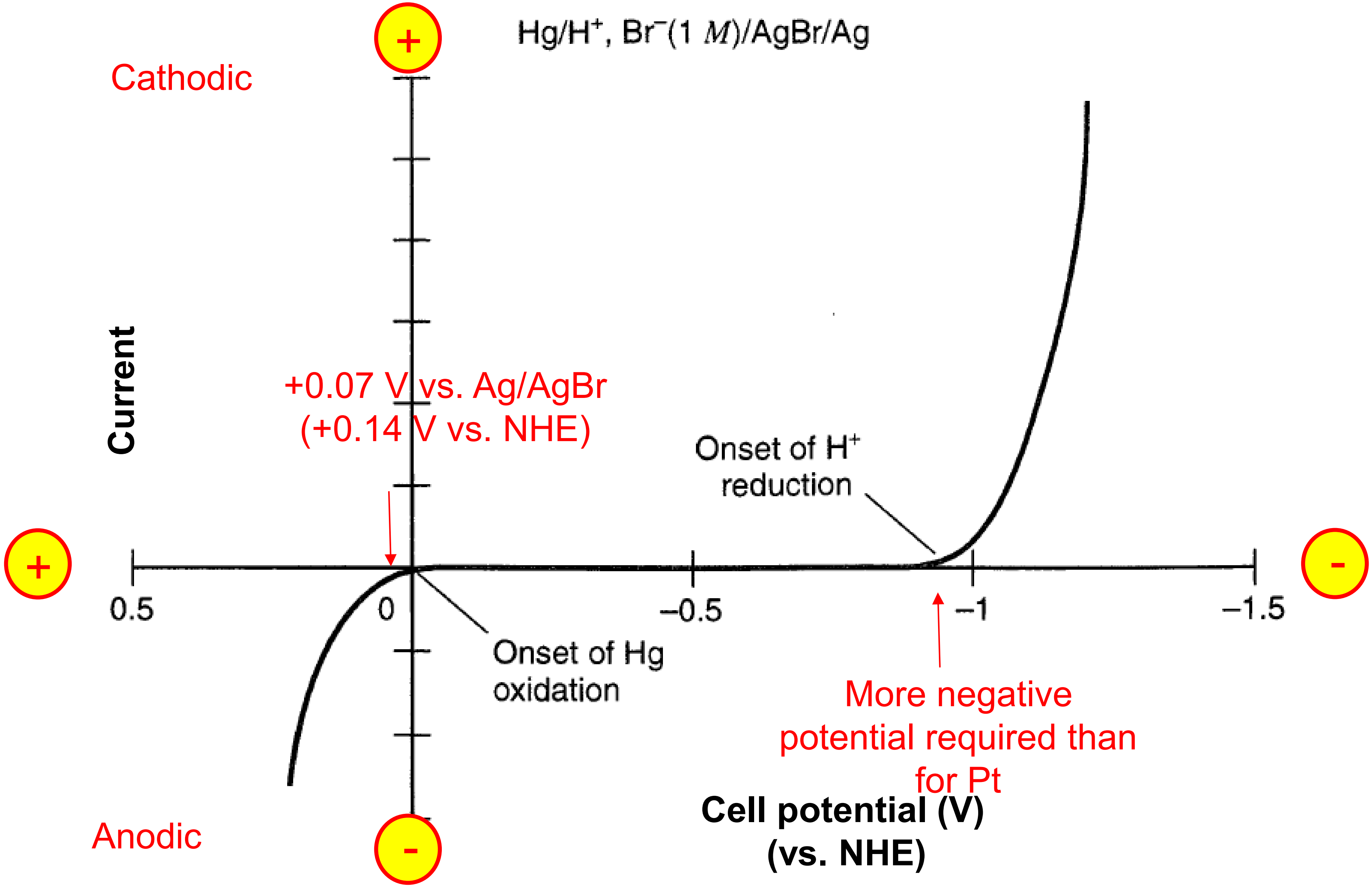
[Br-] is known → Calculated potential from Nernst equation

Working electrode is not in equilibrium

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



Effect of Electrode Material on Current-Voltage Plot



Effect of Electrode Material on Current-Voltage Plots

The thermodynamics of the system stays the same

If we apply a negative potential to the Hg electrode relative to the Ag/AgBr electrode, eventually we get a reduction reaction

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

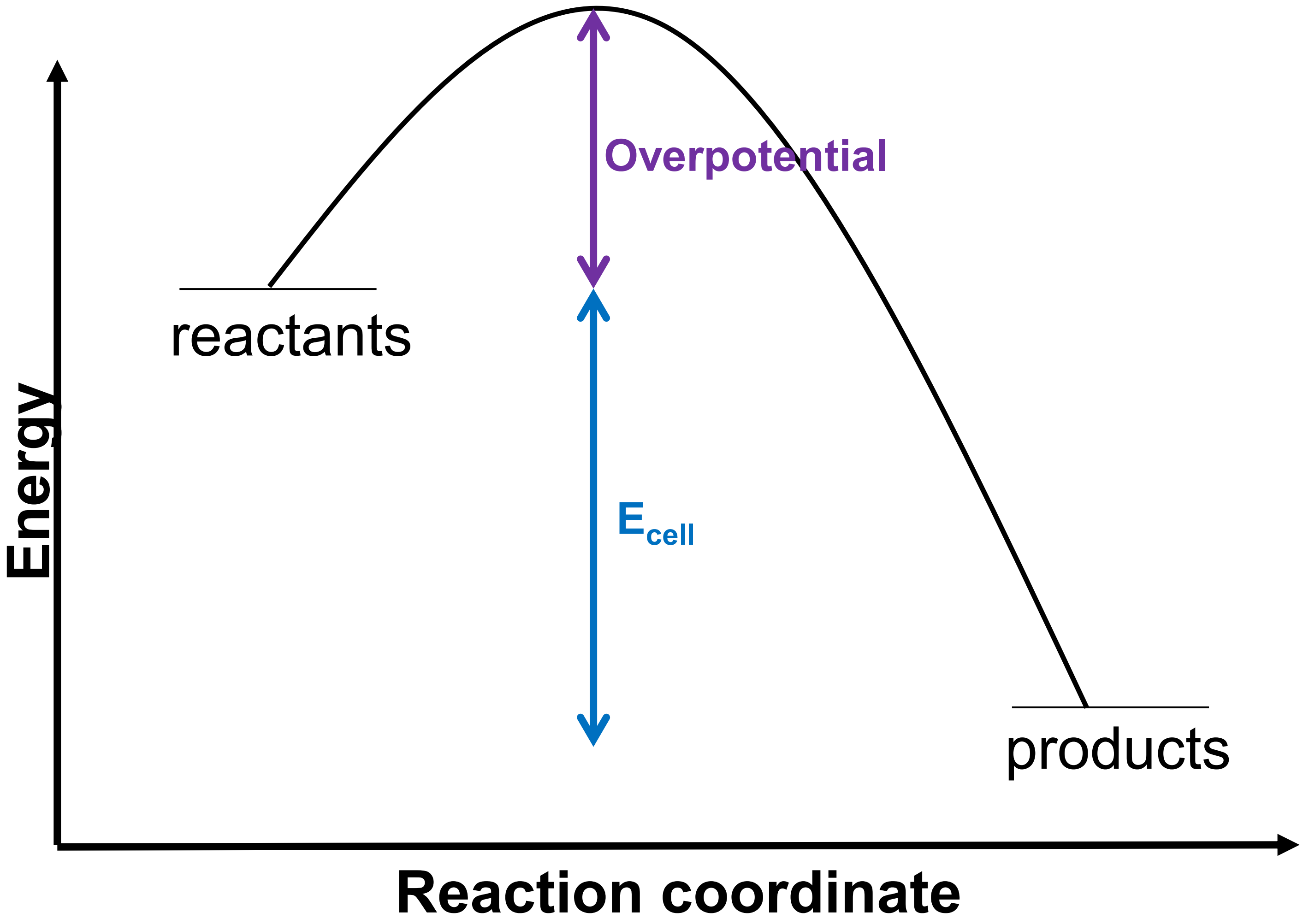
The equilibrium potential of this half reaction is independent of the metal

In the case of Hg, a more negative potential (higher electron energies) is needed to allow the reaction to occur at a measureable rate.

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

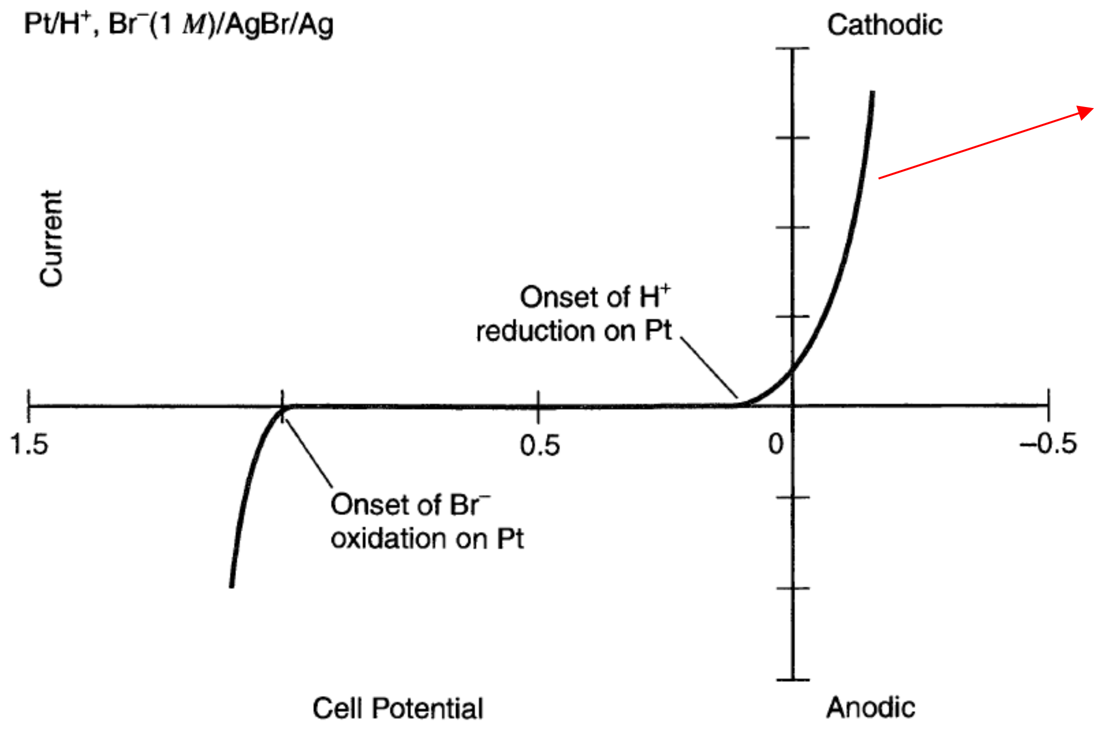
“Mercury shows a high overpotential for the hydrogen evolution reaction”

Kinetics


Overpotential
reactants
Energy
E_{cell}
products
Reaction coordinate

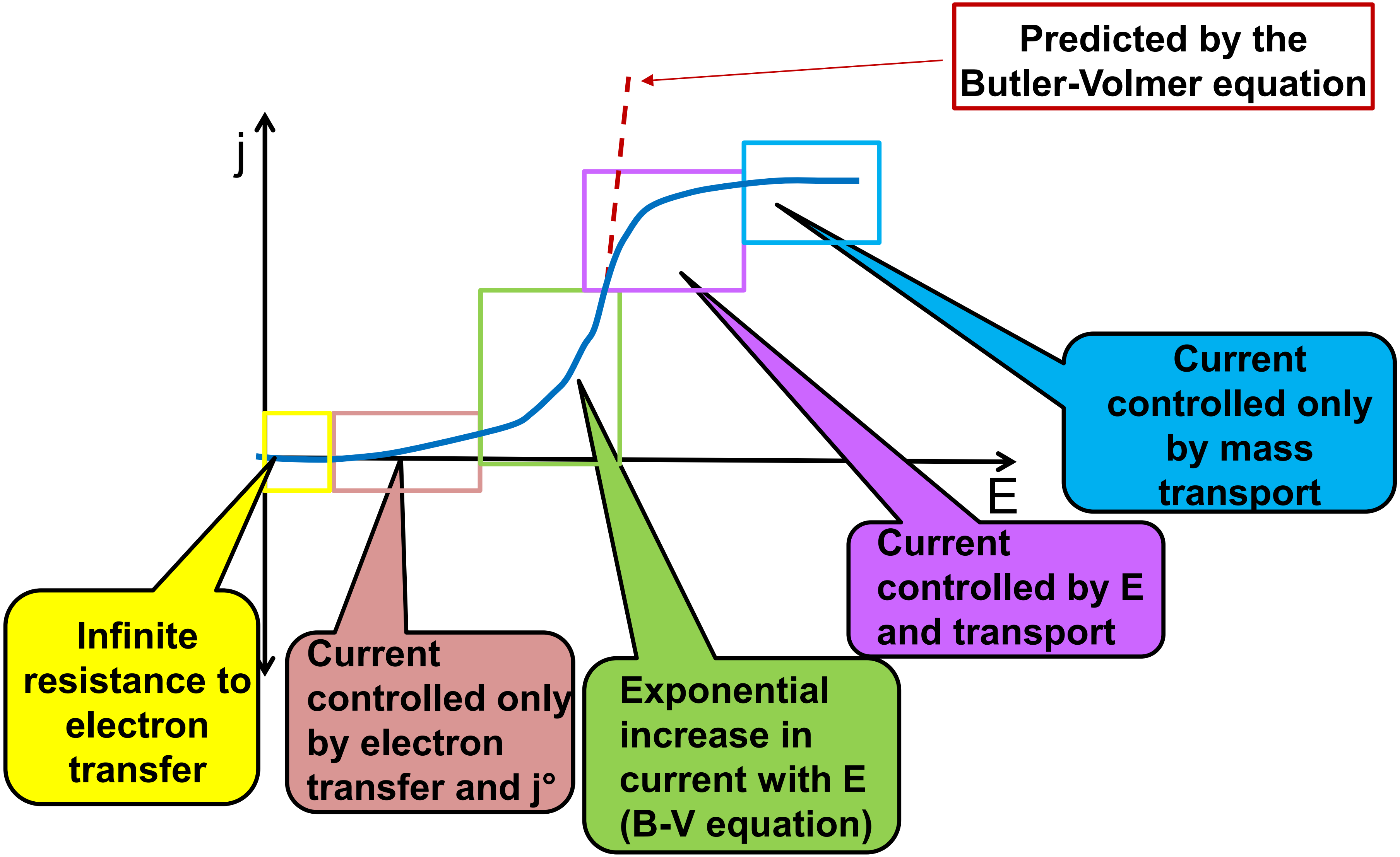
Analytical Expression for the Current-Voltage Curves

Now that we have a qualitative understanding of current potential curves, can we derive an analytical expression relating current to voltage?



What is the equation for this plot?

Analytical Expression for the Current-Voltage Curves



Predicted by the Butler-Volmer equation

Infinite resistance to electron transfer

Current controlled only by electron transfer and j°

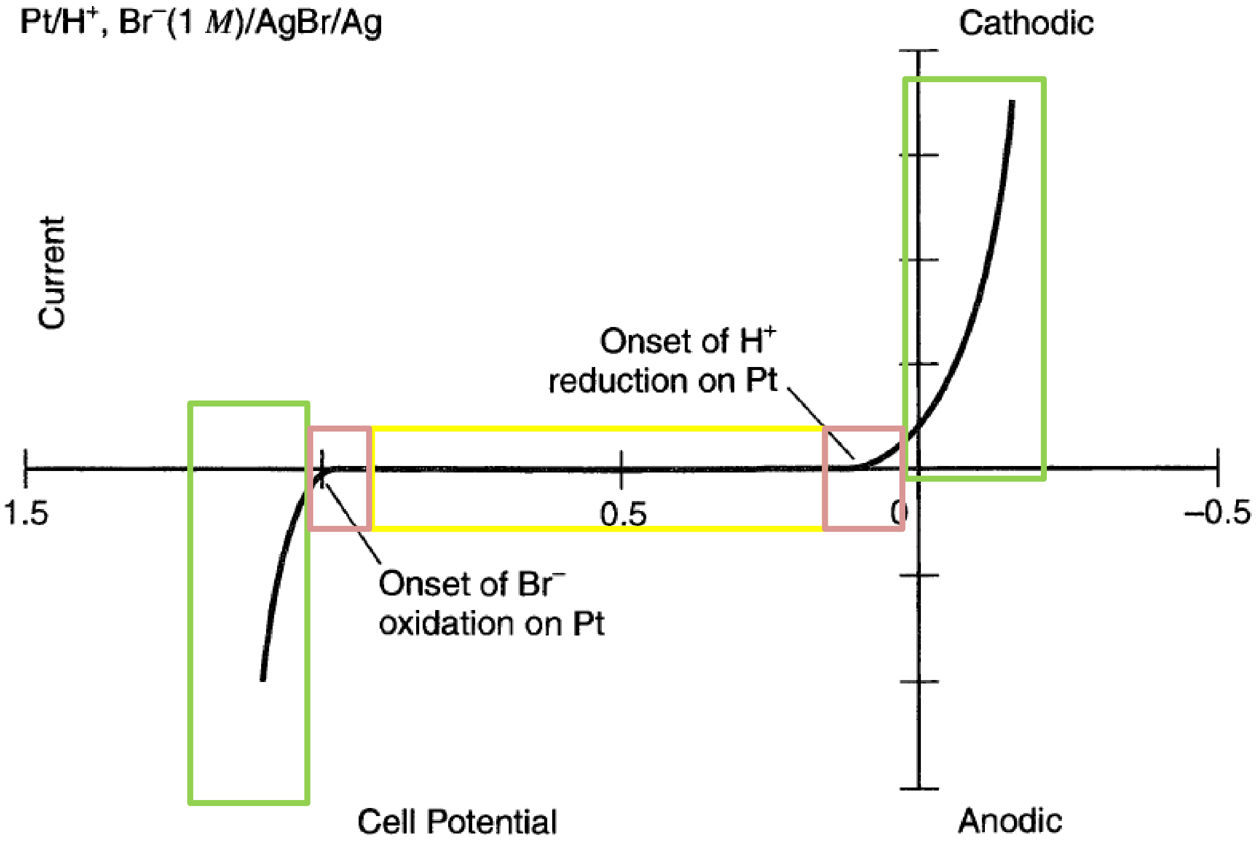
Exponential increase in current with E (B-V equation)

Current controlled by E and transport

Current controlled only by mass transport

Analytical Expression for the Current-Voltage Curves

- First:

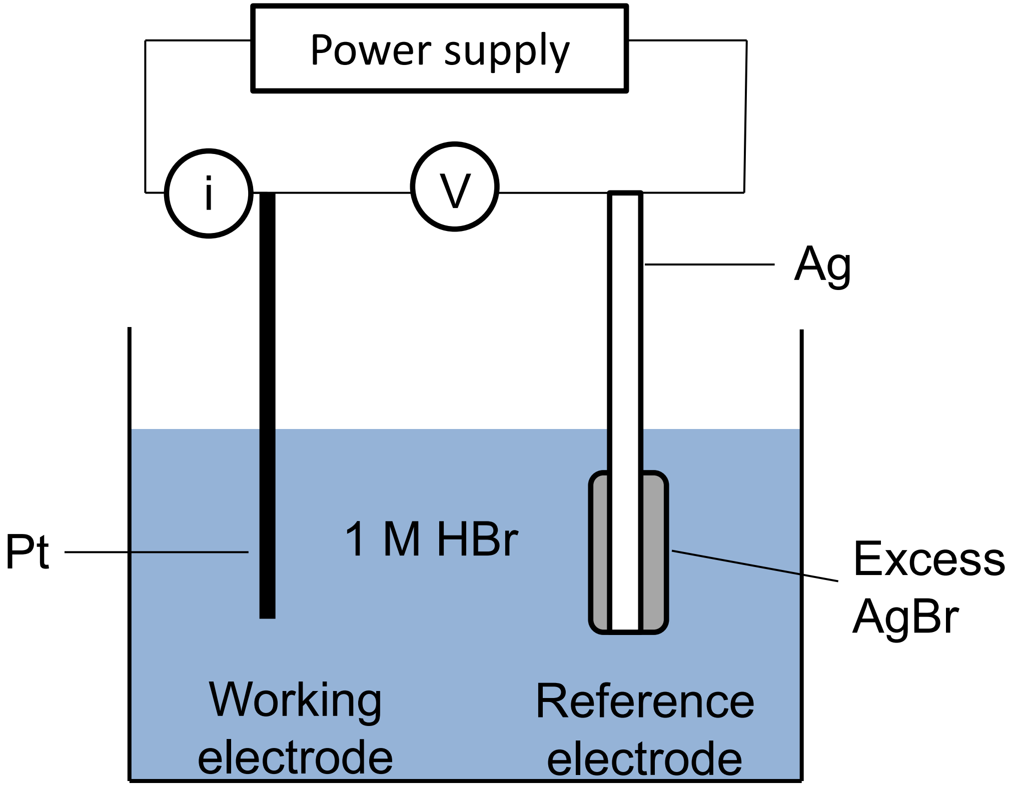


Net Current Production Under Non-equilibrium Conditions

Consider a electrochemical experiment where a working electrode and a reference electrode are immersed in a solution, and the potential difference between the electrodes is varied by means of an external power supply

Working electrode: electrode where reaction of interest occurs

Reference electrode: electrode made up of phases having essentially constant compositions→ this potential is fixed



Net Current Production Under Non-equilibrium Conditions

If we apply a bias relative to the reference electrode, we get a current.

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

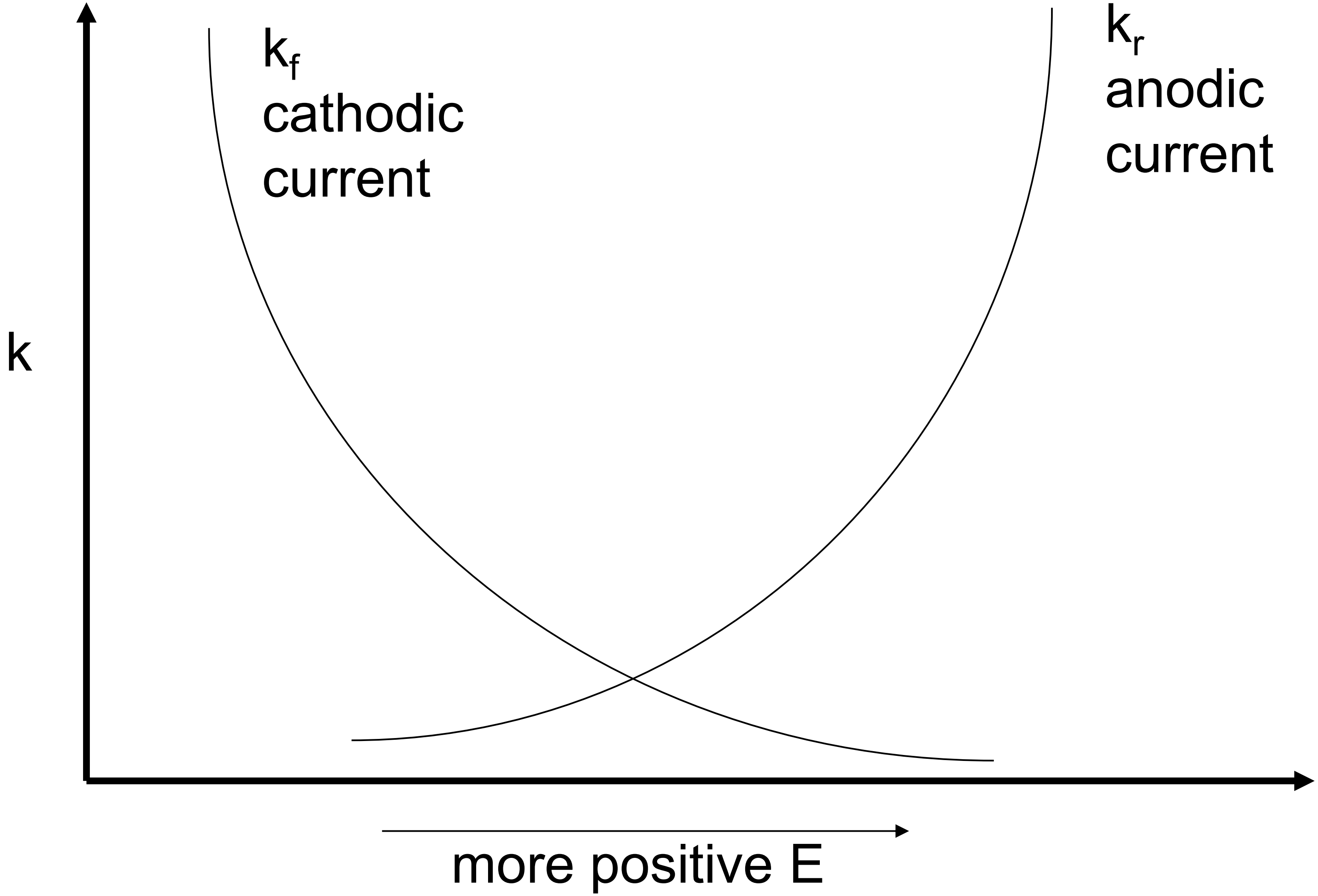
O: oxidized species in the electrolyte
R: reduced species in the electrolyte
e-: electrons being transferred to/from the working electrode

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

Forward reaction: rate **increases** as electrode becomes more **negative** (e.g. electrode can be more easily oxidized to reduce O)

Reverse reaction: rate **increases** as electrode becomes more **positive** (e.g. electrode can be more easily reduced to oxidize R)

Net Current Production Under Non-equilibrium Conditions



Derivation of Butler-Volmer Equation

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

cathode : $$\text{rate}_f := k_f[O]_s = \frac{i_c}{zFA} = \frac{j_c}{zF}$$

anode : $$\text{rate}_r := k_r[R]_s = \frac{|i_a|}{zFA} = \frac{|j_a|}{zF}$$

depends on potential!

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

Derivation of Butler-Volmer Equation

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

At equilibrium:

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

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

Nernst Equation:

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

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

Derivation of Butler-Volmer Equation

Substituting the expression from the Nernst Equation into the equilibrium expression

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

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

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

Derivation of Butler-Volmer Equation

After a few manipulations…

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

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

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

Derivation of Butler-Volmer Equation

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

Defined with respect to the cathode (forward reaction)

Derivation of Butler-Volmer Equation

$$\alpha_c = \frac{d}{dE}\left[\frac{RT}{zF}\ln\frac{1}{k_f}\right] \Rightarrow \alpha_c E = \left[\frac{RT}{zF}\ln\frac{1}{k_f}\right] + C$$

or….

$$\ln\frac{1}{k_f} = \frac{\alpha_c zFE}{RT} + C'$$

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

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

Derivation of Butler-Volmer Equation

Similarly, for the oxidation reaction,

$$1 - \alpha_c = \frac{d}{dE}\left[\frac{RT}{zF}\ln k_r\right] \Rightarrow (1-\alpha_c)E = \frac{RT}{zF}\ln k_r + C$$

or….

$$\ln k_r = \frac{(1-\alpha_c)zFE}{RT} + C'$$

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

$k_r = k_r^\circ$ when $E = E^\circ$

Derivation of Butler-Volmer Equation

Now let's plug in the derived expressions for the forward and reverse rate constants to determine overall current:

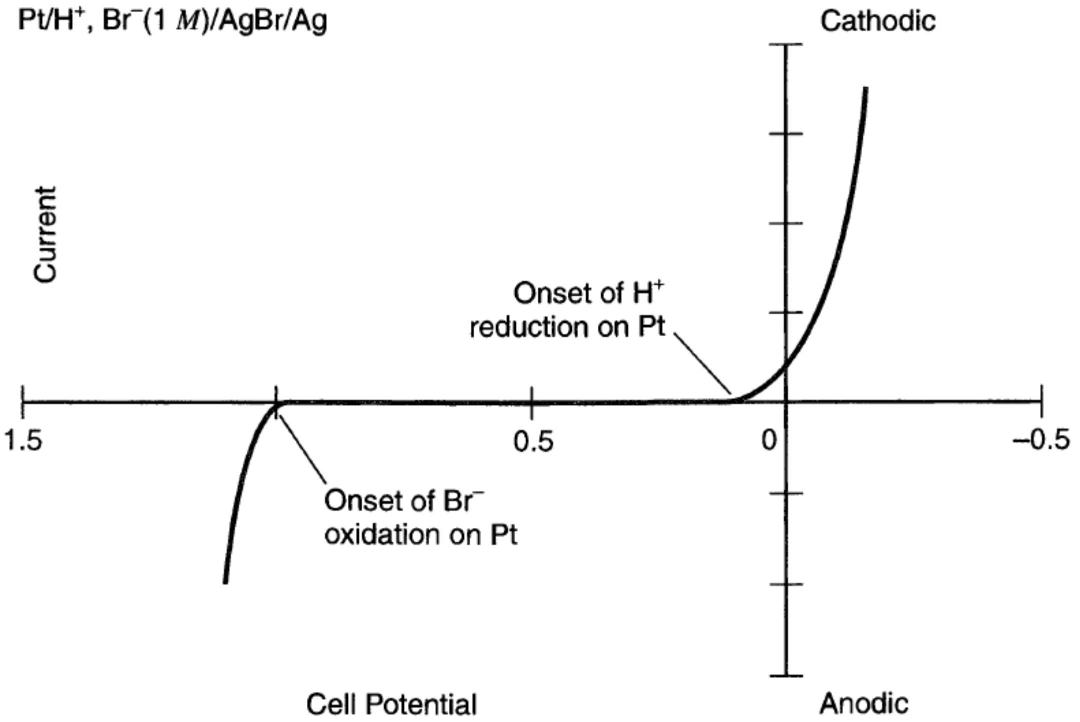
$$\frac{j}{zF} = k_f[O]_s - k_r[R]_s = \boxed{k_f^\circ\, e^{-\frac{\alpha_c zF}{RT}(E-E^\circ)}}\,[O]_s - \boxed{k_r^\circ\, e^{\frac{(1-\alpha_c)zF}{RT}(E-E^\circ)}}\,[R]_s$$

Assuming $k_f^\circ = k_r^\circ = k^\circ$

Butler-Volmer Equation

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

Derivation of Butler-Volmer Equation



$$j = zFk^\circ \left[\underbrace{[O]_s\, e^{-\frac{\alpha_c zF}{RT}(E-E^\circ)}}_{\text{cathodic current } (j_c) \text{ term}} - \underbrace{[R]_s\, e^{\frac{(1-\alpha_c)zF}{RT}(E-E^\circ)}}_{\text{anodic current } (j_a) \text{ term}} \right]$$

Simplifications of the Butler-Volmer Equation: Small η

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

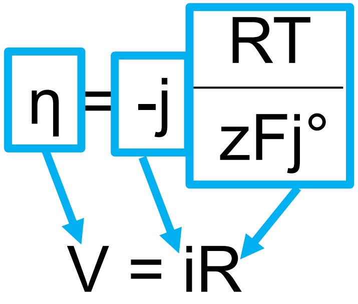
Substituting Taylor series approximations into corresponding exponential terms

Recall: simplification from assuming uniform concentrations

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

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

Solving for η and substituting for f



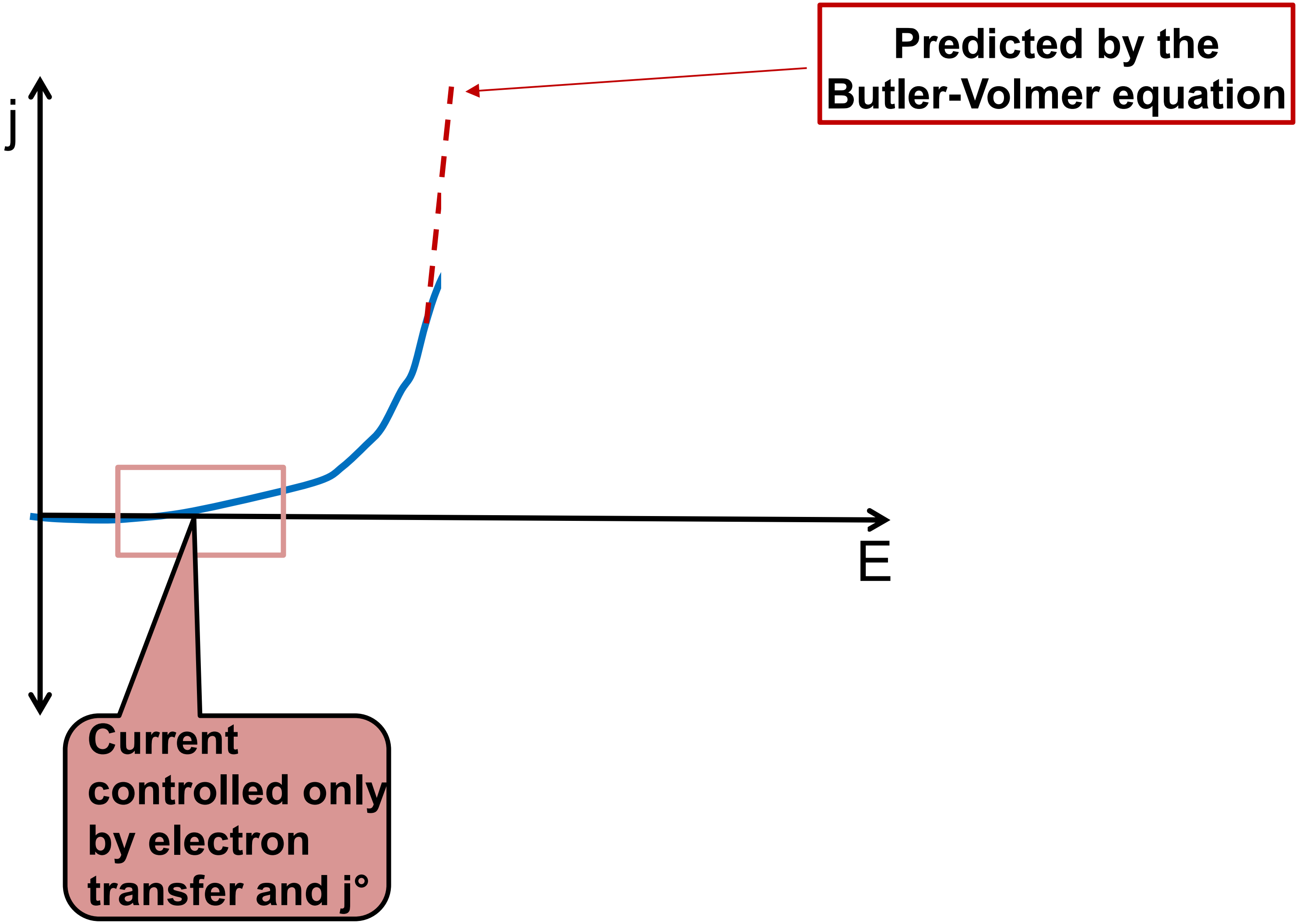
$$\boxed{\eta} = \boxed{-j}\boxed{\frac{RT}{zFj^\circ}}$$

Ohm's law : $V = iR$

Charge transfer resistance

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

Analytical Expression for the Current-Voltage Curves



Predicted by the Butler-Volmer equation

Current controlled only by electron transfer and j°

Simplifications of the Butler-Volmer Equation: Large η

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

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

$$e^{-\alpha_c f\eta} \gg e^{(1-\alpha_c)f\eta} \qquad \text{or} \qquad e^{-\alpha_c f\eta} \ll e^{(1-\alpha_c)f\eta}$$

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

Simplifications of the Butler-Volmer Equation: Large η

For large E-E° → $|\eta| \gg \dfrac{RT}{zF}$

for $\eta < 0$
(cathodic)

$$e^{-\alpha_c f\eta} \gg e^{(1-\alpha_c) f\eta}$$

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

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

Getting this into linear form…

$\eta = a + b \ln j$

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

Simplifications of the Butler-Volmer Equation: Large η

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

for η > 0
(anodic)

$$e^{-\alpha_c f\eta} \ll e^{(1-\alpha_c)f\eta}$$

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

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

Getting this into linear form…

$\eta = a + b \ln j$

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

Simplifications of the Butler-Volmer Equation: Large η

for η < 0
(cathodic)

$$\eta = \frac{RT}{zF\alpha_c} \ln j° - \frac{RT}{zF\alpha_c} \ln j$$

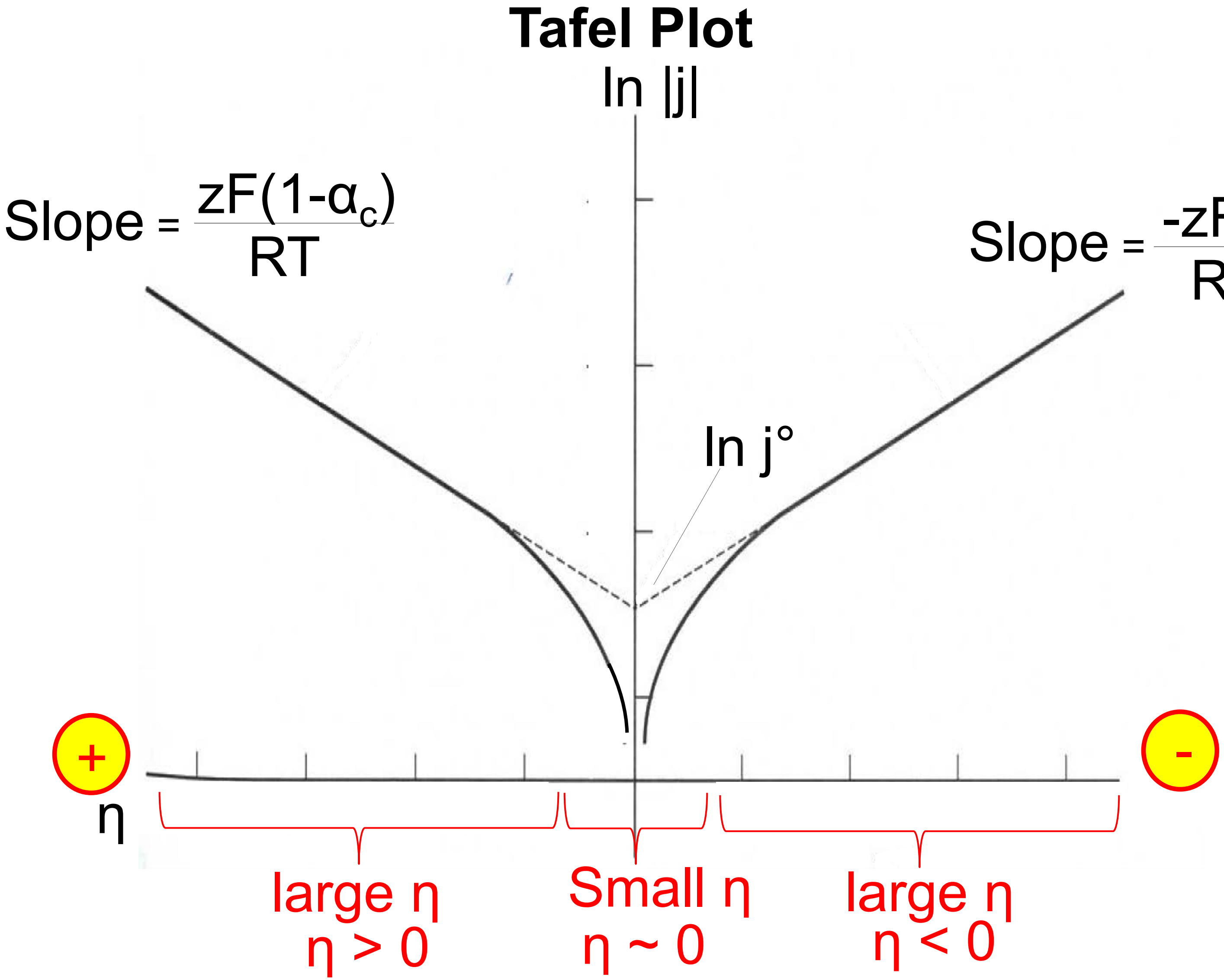
$$\boxed{\ln j = \ln j° - \frac{zF\alpha_c}{RT} \eta}$$

for η > 0
(anodic)

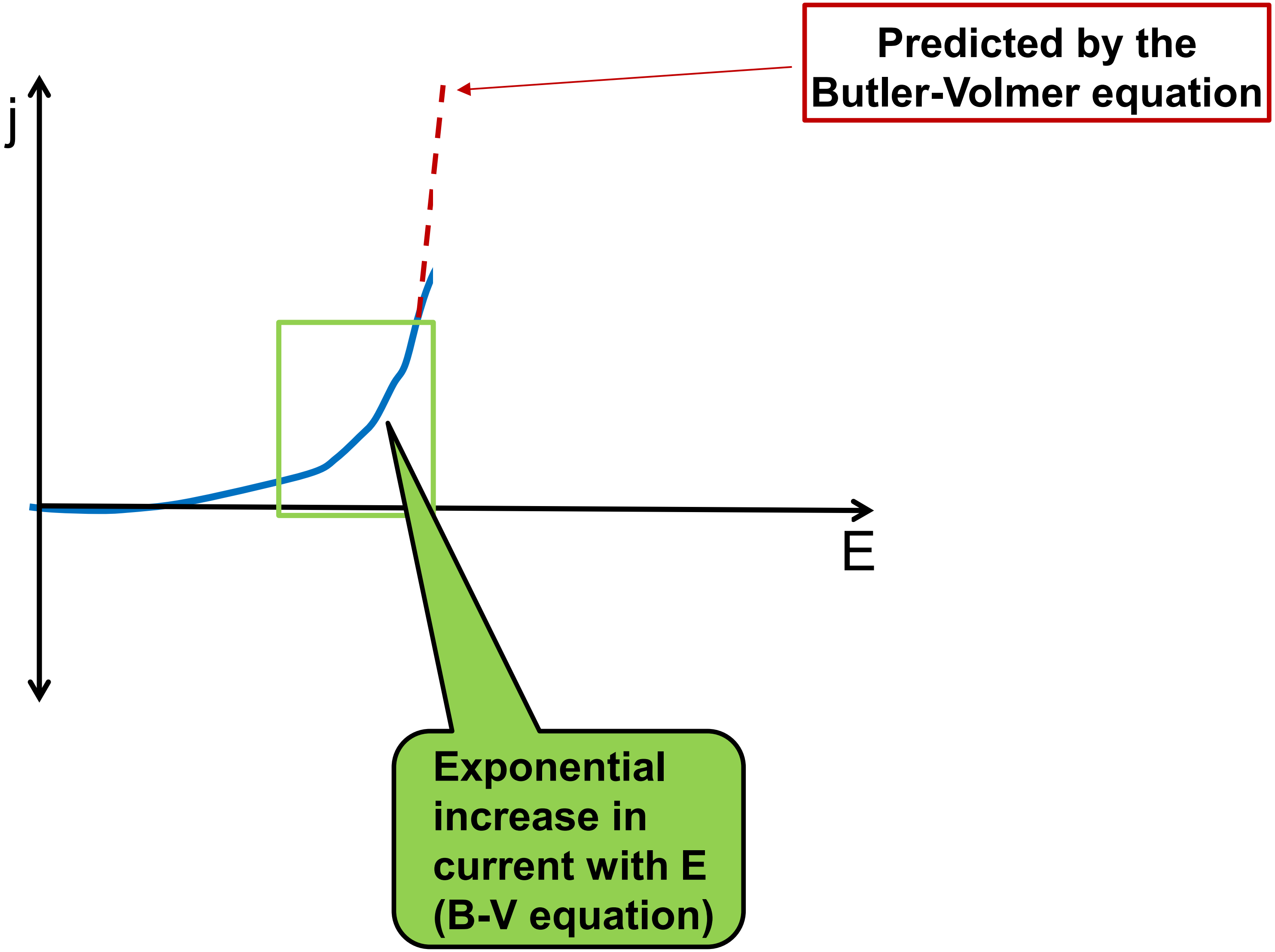
$$\eta = \frac{RT}{zF(1-\alpha_c)} \ln |j| - \frac{RT}{zF(1-\alpha_c)} \ln |j°|$$

$$\boxed{\ln |j| = \ln |j°| + \frac{zF(1-\alpha_c)}{RT} \eta}$$

Simplifications of the Butler-Volmer Equation: Large η



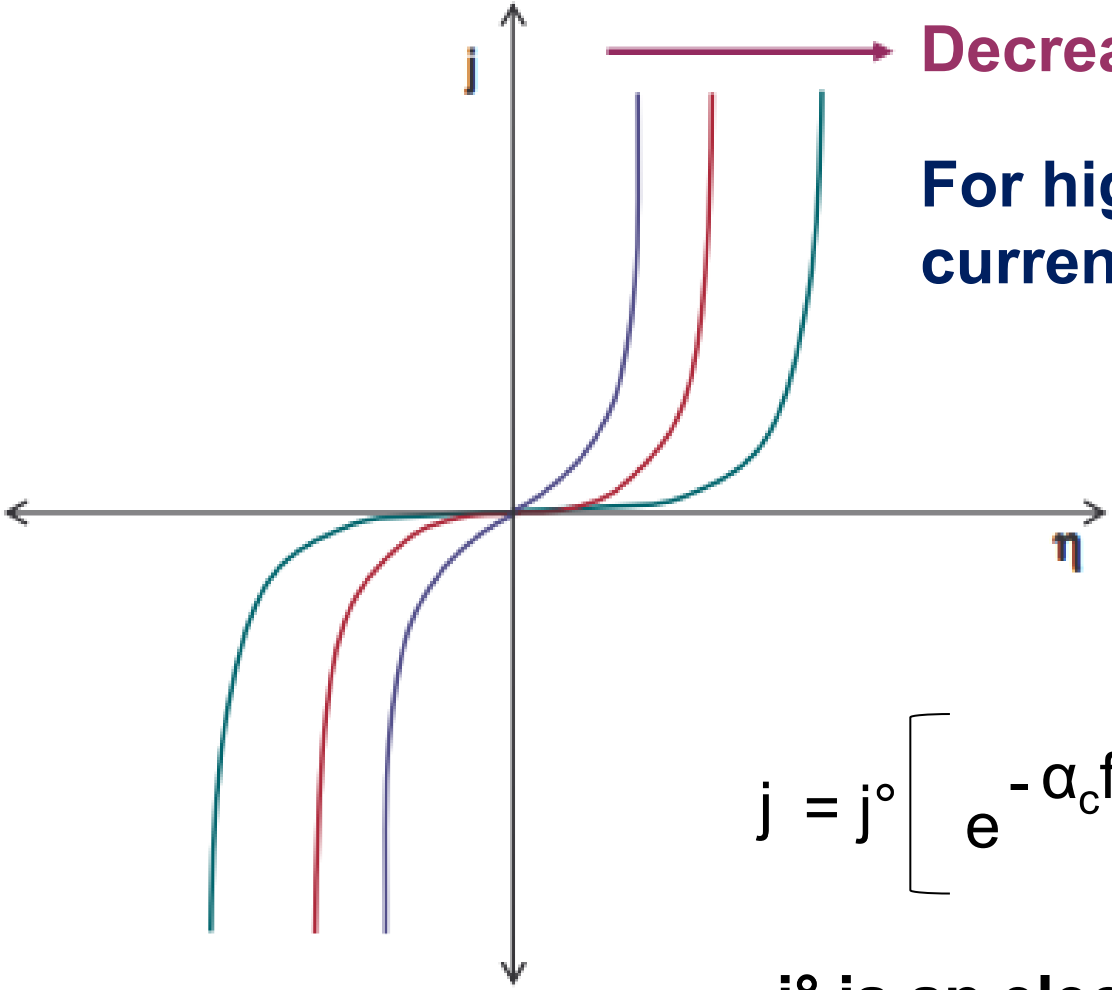
Analytical Expression for the Current-Voltage Curves



Predicted by the Butler-Volmer equation

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

Effect of j° on Current-Voltage Plot



Decreasing j°

For high j°: observable current at low η

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

j° is an electrode property

Total Overpotential and Its Components

Recall:
Overpotential represents the extra energy required to overcome reaction energy barrier
→ Increases minimum voltage required for electrolysis
→ Decreases the maximum voltage obtained from fuel cell

We always want to minimize the overpotential of a device

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

Galvanic (fuel) cell:

Faradaic (electrolytic) cell:

Total Overpotential and Its Components

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

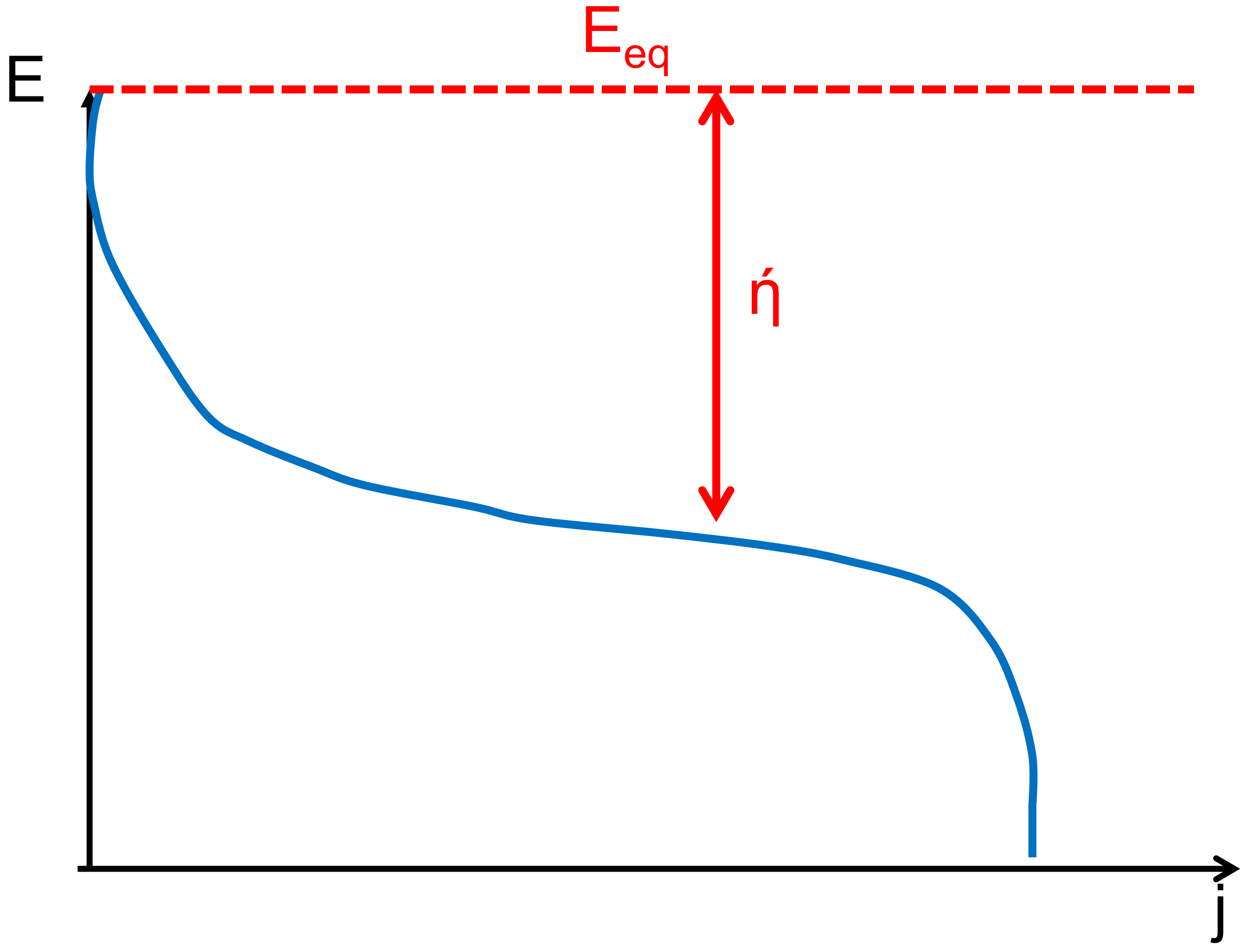
If both anodic and cathodic reactions are running under Tafel conditions

$$E_{overall} = E_{eq} \underbrace{\overbrace{- |\acute{\eta}_{conc,c}| - |\acute{\eta}_{act,c}|}^{\text{cathodic overpotential}} \overbrace{- |\acute{\eta}_{conc,a}| - |\acute{\eta}_{act,a}|}^{\text{anodic overpotential}} \overbrace{- |\acute{\eta}_{ohm}|}^{\text{electrolytic overpotential}}}$$

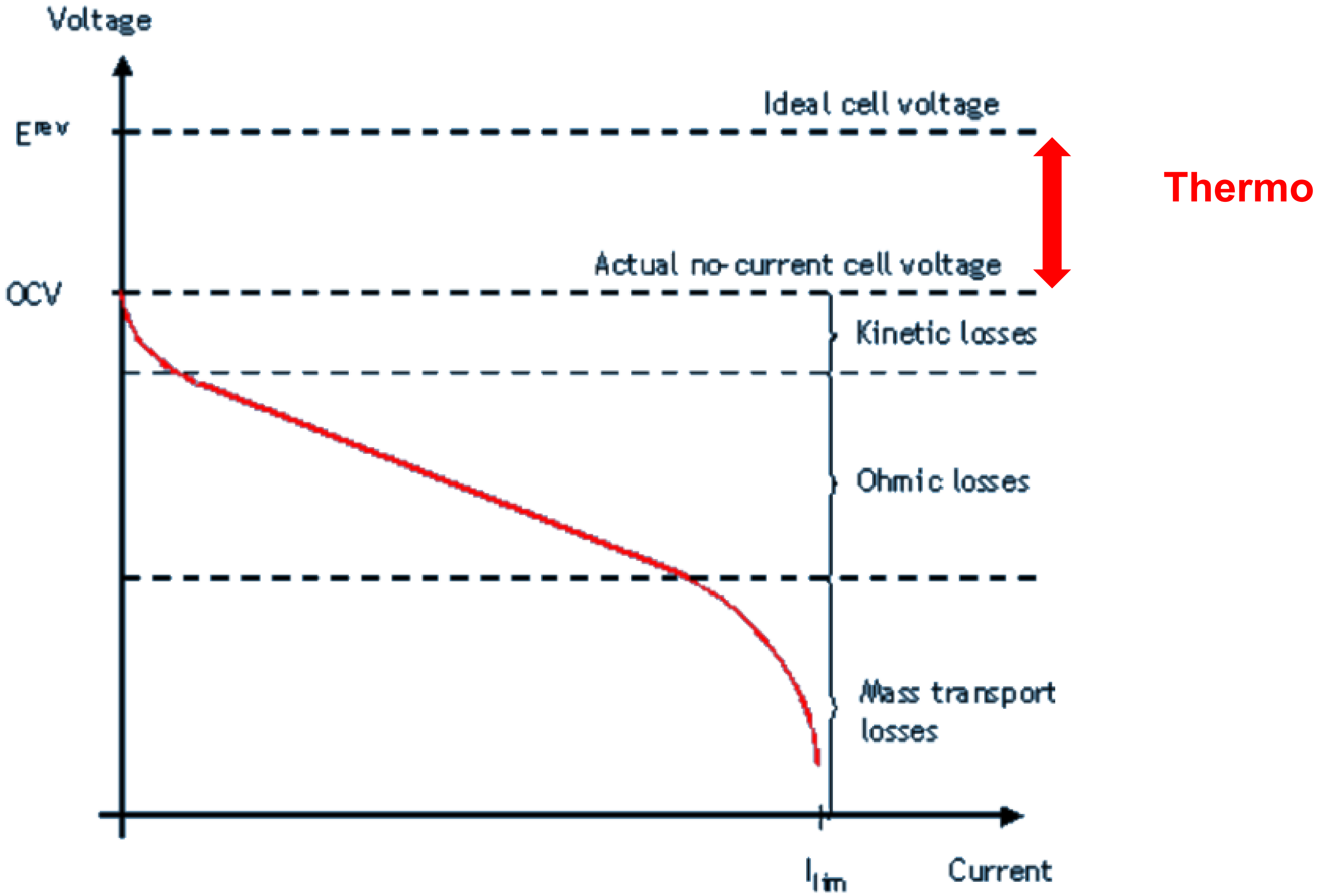
$$- \left|\frac{RT}{\alpha_c zF} \ln \frac{j_{lim,c} - j}{j_{lim,c}}\right| - \left|\frac{RT}{\alpha_c zF} \ln \frac{j°}{j}\right| - \left|\frac{RT}{(1-\alpha_c)zF} \ln \frac{|j_{lim,a}|}{|j_{lim,a} - j|}\right| - \left|\frac{RT}{(1-\alpha_c)zF} \ln \frac{|j|}{|j°|}\right| - |jAR_{ohm}|$$

electrolyte resistance

Total Overpotential and Its Components



Total Overpotential and Its Components



Total Overpotential and Its Components

Low j

($j << j_{lim}$)

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

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

Higher j

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

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

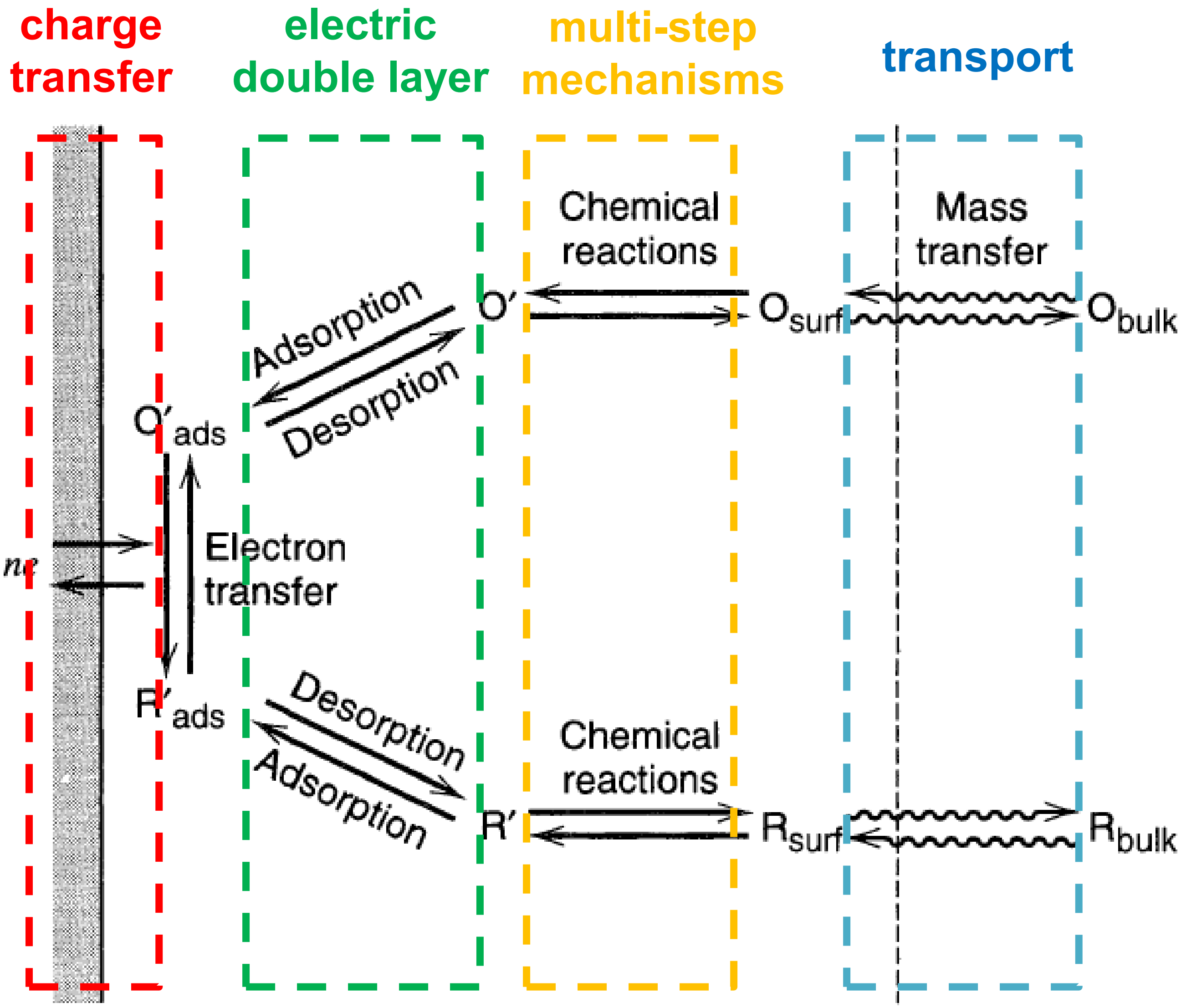
High j

($j \rightarrow j_{lim}$)

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

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

B-V Model with Mass Transport



Modes of Mass Transfer

Diffusion : Movement of a species under the influence of a gradient of chemical potential (i.e., a concentration gradient).

Migration : Movement of a charged body under the influence of an electric field (a gradient of electrical potential).

Convection : Stirring or hydrodynamic transport (may be characterized by stagnant regions, laminar flow, or turbulent flow).

Modes of Mass Transfer

Mass transfer to an electrode is governed by the **Nernst Planck equation** written for one-dimensional mass transfer along the x-axis as

$$J_i(x) = -\underbrace{D_i \frac{\partial C_i(x)}{\partial x}}_{\text{diffusion}} - \underbrace{\frac{z_i F}{RT} D_i C_i \frac{\partial \Phi(x)}{\partial x}}_{\text{migration}} + \underbrace{C_i v(x)}_{\text{convection}}$$

$J_i(x)$: flux of species i at a distance x from the surface [mol s^{-1} cm^{-2}]

$D_i(x)$: diffusion coefficient of species i [cm^2/s]

$\frac{\partial C_i(x)}{\partial x}$: concentration gradient at distance x

$\frac{\partial \Phi(x)}{\partial x}$: potential gradient at distance x

z_i : charge of species i (not to be confused with z, which is mol e- /mol reactant)

C_i : concentration of species i [mol cm^{-3}]

v(x): velocity with which a volume element in solution moves along the axis [cm s^{-1}]

Modes of Mass Transfer

A rigorous solution is not very easy when all 3 forms of mass transfer are in effect; hence electrochemical systems are frequently designed so that one or more of the contributions to mass transfer are negligible.

For example,

Migration can be considered negligible by the addition of inert electrolyte (i.e. a supporting electrolyte) at a concentration much larger than that of the electroactive species.

Convection can be considered negligible by preventing stirring and vibrations in the electrochemical cell.

Modes of Mass Transfer

Mass transfer to an electrode is governed by the **Nernst Planck equation** written for one-dimensional mass transfer along the x-axis as

$$J_i(x) = -\underbrace{D_i \frac{\partial C_i(x)}{\partial x}}_{\text{diffusion}} - \underbrace{\frac{z_i F}{RT} D_i C_i \frac{\partial \Phi(x)}{\partial x}}_{\text{migration}}$$

If the species i is charged, then the flux, J_i, is equivalent to the current density.

$$-J_i = \frac{j_i}{z_i F} = \underbrace{\frac{j_{d,i}}{z_i F}}_{\substack{\text{flux due to}\\ \text{diffusion}}} + \underbrace{\frac{j_{m,i}}{z_i F}}_{\substack{\text{flux due to}\\ \text{migration}}}$$

Migration-Limited Case

In the bulk solution (away from the electrode) concentration gradients are generally small, and the total current is carried mainly by migration of all charged species.

$$J_i(x) = -D_i \cancel{\frac{\partial C_i(x)}{\partial x}} - \underbrace{\frac{z_i F}{RT} D_i C_i \frac{\partial \Phi(x)}{\partial x}}_{\text{migration}} + \cancel{C_i v(x)}$$

Small concentration gradient

No stirring

$$-J_i(x=0,t) = \frac{j_{m,i}}{z_i F} = \frac{z_i F}{RT} D_i C_i \frac{\partial \Phi(x)}{\partial x} \Longrightarrow j_{m,i} = j_i = \frac{z_i^2 F^2}{RT} D_i C_i \frac{\partial \Phi(x)}{\partial x}$$

charge of species i

Migration-Limited Case

$$j_i = \frac{z_i^2 F^2}{RT} D_i C_i \frac{\partial \Phi(x)}{\partial x}$$

Mobility of a species i (u_i) is the ability of a charged particle to move through a medium in response to an electric field.

$$u_i = \frac{|z_i| F D_i}{RT}$$

By substituting for D_i,

Assuming linear change in potential (ΔE) over distance L

$$j_i = |z_i| F u_i C_i \frac{\partial \Phi(x)}{\partial x} \quad \Longrightarrow \quad j_i = \frac{|z_i| F u_i C_i \Delta E}{L}$$

$$\frac{\partial \Phi(x)}{\partial x} \sim \frac{\Delta E}{L}$$

Migration-Limited Case

If multiple species contribute to current, the total current is the sum all the individual contributions.

$$j = \sum_i j_i = \frac{F \Delta E}{L} \sum_i |z_i| u_i C_i$$

The **transference number** of species i (t_i) is the fraction of the total migration current that a given ion i carries.

$$t_i = \frac{j_i}{j} = \frac{|z_i| u_i C_i}{\sum_k |z_k| u_k C_k}$$

Diffusion-Limited Case

Consider the reaction

$$O + ze^- \longrightarrow R$$

when the reduction of O begins, $[O]_S \ll [O]^*$

$$J_i(x) = \underbrace{- D_i \frac{\partial C_i(x)}{\partial x}}_{\text{diffusion}} - \cancel{\frac{z_i F}{RT} D_i C_i \frac{\partial \Phi(x)}{\partial x}} + \cancel{C_i v(x)}$$

Assume there is an excess of supporting electrolyte

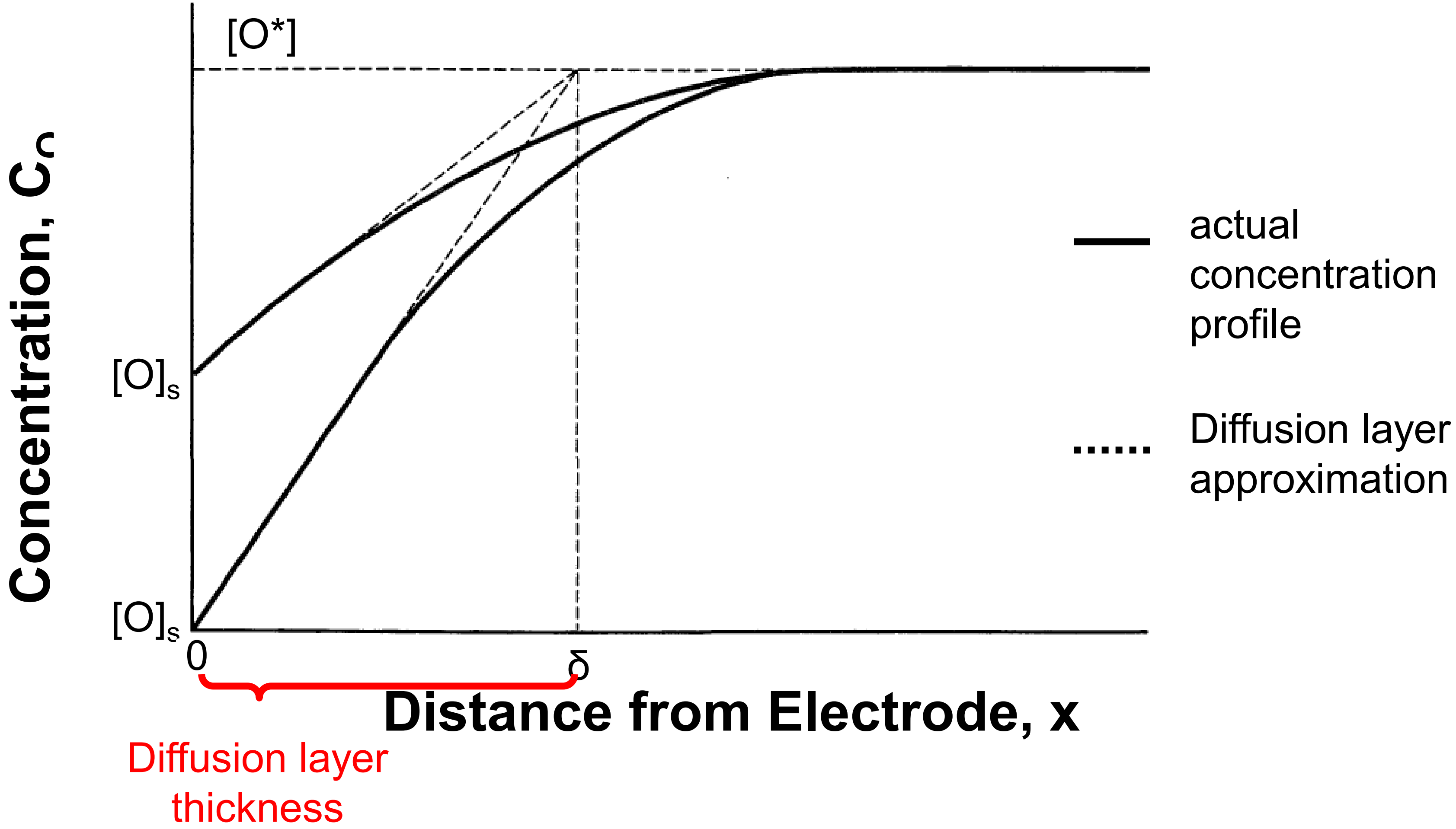
Assume stirring is ineffective at the electrode surface

Rate of mass-transfer (v_{mt}) is proportional to the concentration gradient

$$v_{mt} \,\alpha\, D_O \left.\frac{\partial C_O(x)}{\partial x}\right|_{x=0} \xrightarrow{\text{Assuming linear variation}} D_O \frac{[O]^* - [O]_S}{\delta}$$

(at the surface)

Diffusion-Limited Case



Diffusion-Limited Case

To solve these problems analytically, we need to define 3 conditions:

1. Initial conditions of your system at $t = 0$.

2. Conditions at far distances from your electrode ($x >> 0$).

3. Conditions at the surface of your electrode ($x = 0$).

Diffusion-Limited Case / Boundary Conditions: Initial condition

$$O + ze^- \rightleftarrows R$$

- Usually of the form,

$$C_O(x,0) = f(x)$$

- If [O*] is uniform at t = 0,

$$C_O(x,0) = [O^*]$$

- If R is absent at t =0,

$$C_R(x,0) = 0$$

Diffusion-Limited Case / Boundary Conditions: Semi-Infinite (BC1)

When the electrolytic cell is large compared to the diffusion length, the solution at the walls of the cell are not affected by the presence of an electrode. At large distances ($x \rightarrow \infty$), the concentration reaches a constant value, typically the initial concentration.

$$\lim_{x \rightarrow \infty} C_O(x,t) = [O^*]$$

$$\lim_{x \rightarrow \infty} C_R(x,t) = 0$$

For thin-layer electrolytic cells where the cell wall is at a distance and L is of the order of the diffusion length, one must use the boundary conditions at $x = L$ instead of $x \rightarrow \infty$.

Diffusion-Limited Case / Boundary Conditions: Electrode Surface

If the potential is controlled in an experiment,

$$C_O(0,t) = \boxed{f(E)}$$

$$\frac{C_O(0,t)}{C_R(0,t)} = \boxed{f(E)}$$

Some general current-potential characteristic or, in special cases, the Nernst Equation

If the current is controlled in an experiment, the boundary condition is expressed in terms of the flux at x=0,

$$\frac{j}{zF} = -J_O(x=0,t) = D_O \left.\frac{\partial C_O(x,t)}{\partial x}\right|_{x=0} = f(t)$$

(at the surface)

Diffusion-Limited Case / Boundary Conditions: Electrode Surface

Conservation of mass at an electrode surface

When O is converted to R and both O and R are soluble in the solution phase, then for each O that undergoes electron transfer at the electrode, an R must be produced:

$$D_O \left.\frac{\partial C_O(x,t)}{\partial x}\right|_{x=0} + D_R \left.\frac{\partial C_R(x,t)}{\partial x}\right|_{x=0} = 0$$

Diffusion-Limited Case / Simplification of Diffusion Equations

The analytical mathematical methods for solving these problems sometimes include numerical methods or simulations. Several special cases will be presented.

For example, at steady-state:

$$\cancel{\frac{\partial C_i(x,t)}{\partial t}} = D_i \nabla^2 C_i = 0$$

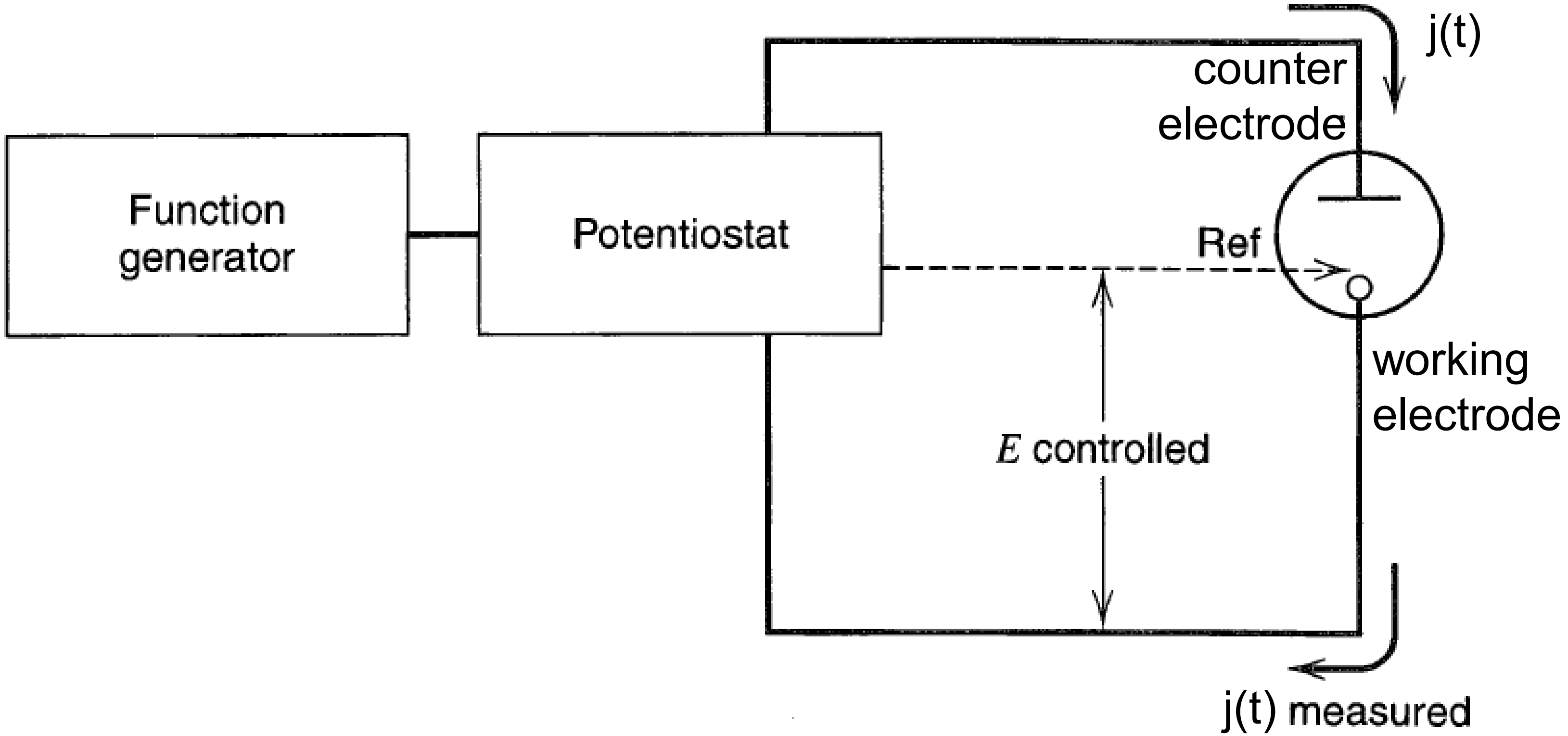
Potential Step Methods Under Diffusion Control

- We will consider systems in which the mass transport of electroactive species occurs only by diffusion and we implement step-functional changes in the working electrode.

- Assume electrode area (A) << solution volume (V) (small A/V conditions) such that the passage of current does not alter the bulk concentration of the electroactive species.

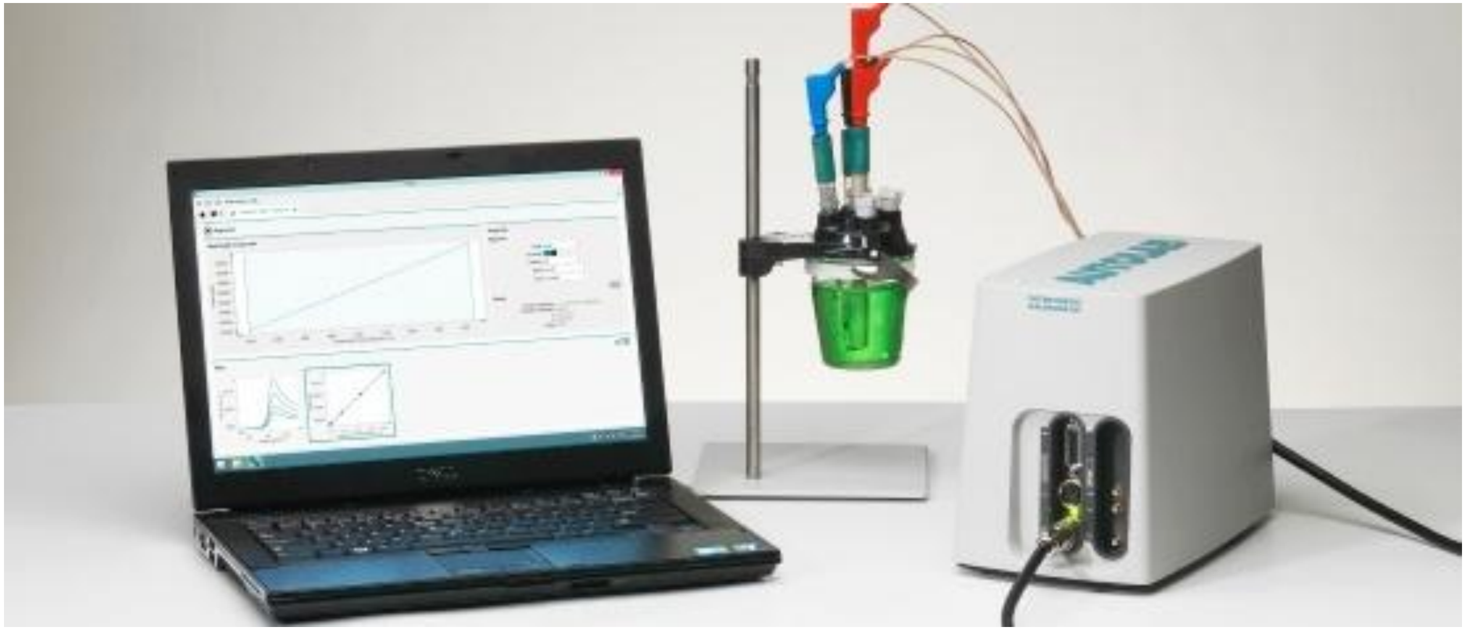
Potential Step Methods Under Diffusion Control

A **potentiostat** is used for controlled-potential experiments



Potential Step Methods Under Diffusion Control

A **potentiostat** is used for controlled-potential experiments



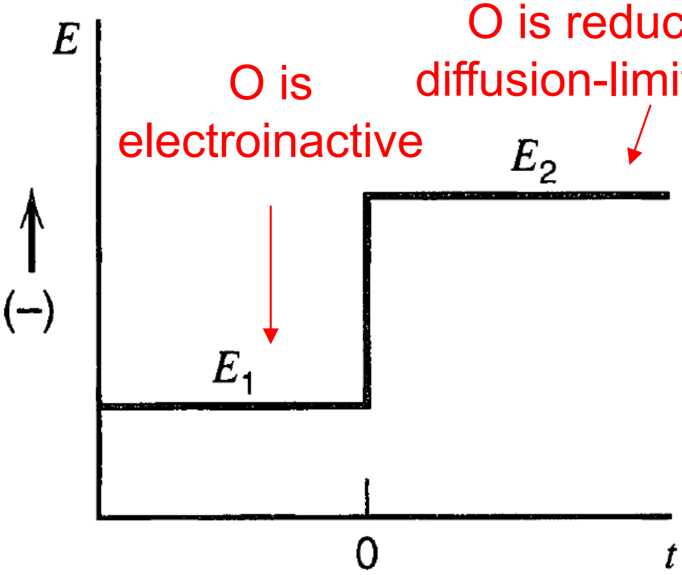
Potential Step Methods Under Diffusion Control

Imagine an experiment where we start with a potential (E_1) where no faradaic (i.e. charge transfer) processes take place and then instantaneously adjust to a potential (E_2) where we are mass-transfer limited (no reactant on the electrode surface).

$$O + ze^- \longrightarrow R$$

Potential Step Methods Under Diffusion Control

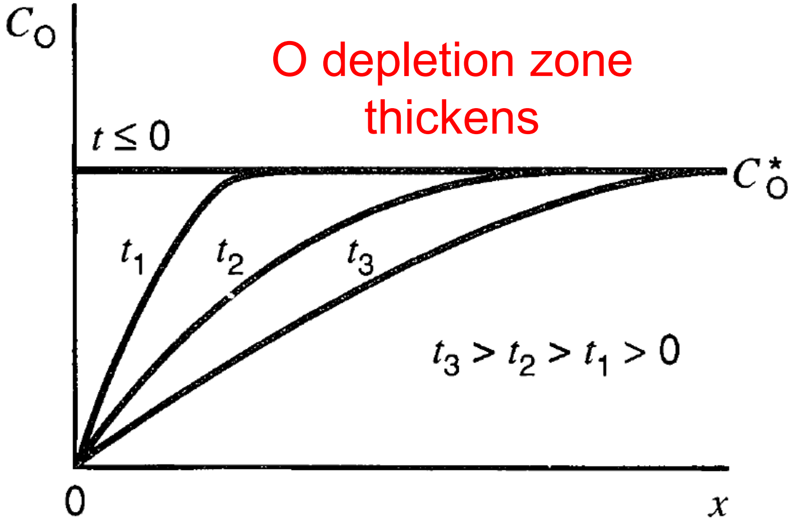
Potential change



O is electroinactive

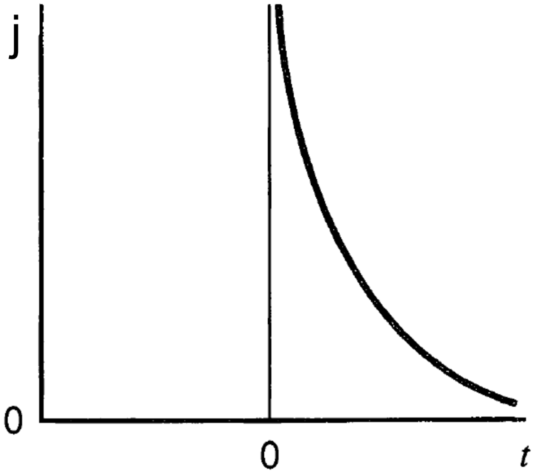
O is reduced at diffusion-limited rate

Corresponding concentration profile



O depletion zone thickens

Current flow vs. time



Current is proportional to the concentration gradient at the surface "chronoamperometry"

Potential Step Methods Under Diffusion Control

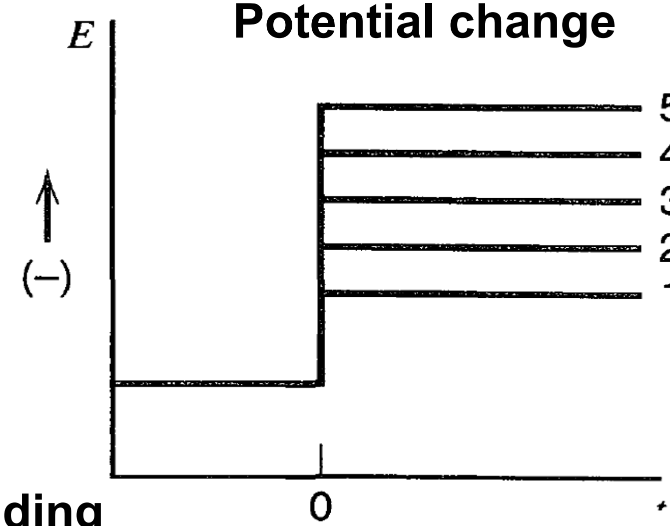
$$O + ze^- \longrightarrow R$$

As before, imagine an experiment where we start with a potential where no faradaic (i.e. charge transfer) processes take place and then instantaneously adjust to a potential where

1. No faradaic processes occur.
2. Some O is reduced, but not so effectively that $[O]_S=0$.
3. Some more O is reduced, but not so effectively that $[O]_S=0$.
4. Mass-transfer-limited regime is approached such that $[O]_S=0$.
5. Mass-transfer-limited regime is approached at an even higher potential such that $[O]_S=0$.

Potential Step Methods Under Diffusion Control

Potential change

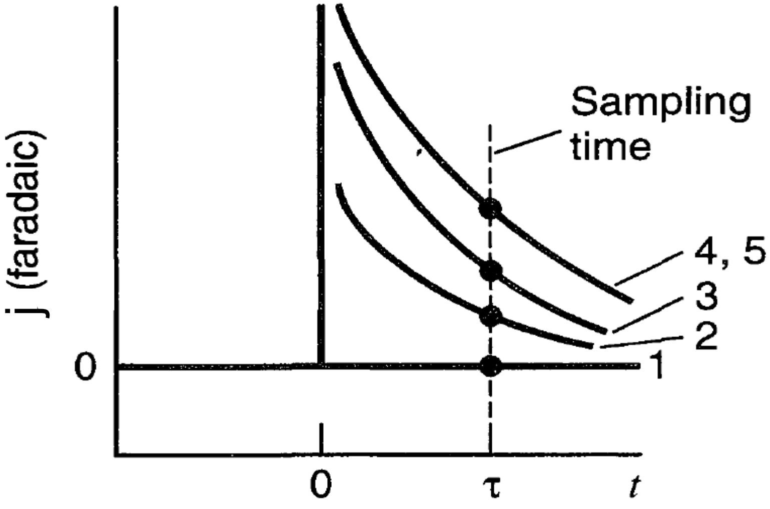


mass transfer-limited

some charge-transfer

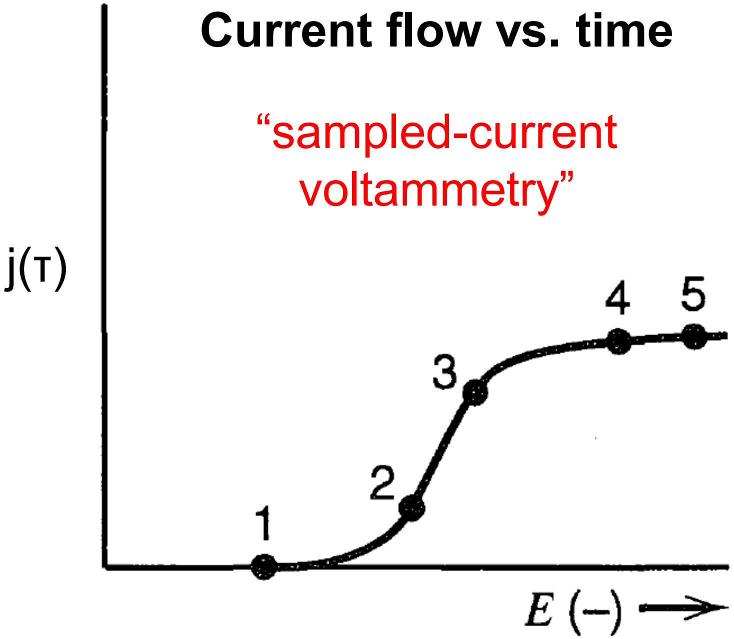
no charge-transfer

Corresponding concentration profile



Current flow vs. time

“sampled-current voltammetry”



Potential Step Methods Under Diffusion Control: Planar Diffusion

$$O + ze^- \longrightarrow R$$

Consider the first case where we apply a step potential to go from a non-faradaic process to a mass-transport limited process.

Linear Diffusion

$$\frac{\partial C_O(x,t)}{\partial t} = D_O \frac{\partial^2 C_O(x,t)}{\partial x^2}$$

Boundary Conditions

$$\text{IC} : C_O(x,0) = [O^*]$$

$$\text{BC1} : \lim_{x \to \infty} C_O(x,t) = [O^*]$$

$$\text{BC2} : C_O(0,t) = 0 \quad (t > 0)$$

Potential Step Methods Under Diffusion Control: Planar Diffusion

$$\frac{\partial C_O(x,t)}{\partial t} = D_O \frac{\partial^2 C_O(x)}{\partial x^2} \xrightarrow[\text{(see notes)}]{\text{Laplace transform}} \overline{C_O}(x,s) = \frac{[O^*]}{s} + A(s)\cdot \exp\left(-x\sqrt{\frac{s}{D_O}}\right)$$

Transforming BC2,

$$\text{BC2} : C_O(0,t) = 0 \quad (\text{for } t > 0) \Longrightarrow \text{BC2} : \overline{C_O}(0,s) = 0$$

Evaluating and substituting for A(s),

$$\overline{C_O}(x,s) = \frac{[O^*]}{s} - \frac{[O^*]}{s} \exp\left(-x\sqrt{\frac{s}{D_O}}\right)$$

Potential Step Methods Under Diffusion Control: Planar Diffusion

Recall the relationship between flux and current

$$\frac{j(t)}{zF} = D_O \left.\frac{\partial C_O(x,t)}{\partial x}\right|_{x=0}$$

(at the surface)

Which is transformed to

$$\frac{\bar{j}(s)}{zF} = D_O \left.\frac{\partial \bar{C}_O(x,s)}{\partial x}\right|_{x=0}$$

(at the surface)

Differentiation of the expression

$$\frac{\partial}{\partial x}\left[\bar{C}_O(x,s) = \frac{[O^*]}{s} - \frac{[O^*]}{s}\exp\left(-x\sqrt{\frac{s}{D_O}}\right)\right]$$

$$\bar{j}(s) = \frac{zFD_O^{0.5}[O^*]}{s^{0.5}}$$

inversion….

$$\boxed{j_d(t) = \frac{zFD_O^{0.5}[O^*]}{\pi^{0.5}t^{0.5}}}$$

Cottrell equation

$t^{-0.5}$ dependency is a mark of diffusive control over electrolysis

Potential Step Methods Under Diffusion Control: Planar Diffusion

To find the concentration profile for $C_O(x,t)$,

$$\overline{C_O}(x,s) = \frac{[O^*]}{s} - \frac{[O^*]}{s} \exp\left(-x\sqrt{\frac{s}{D_O}}\right)$$

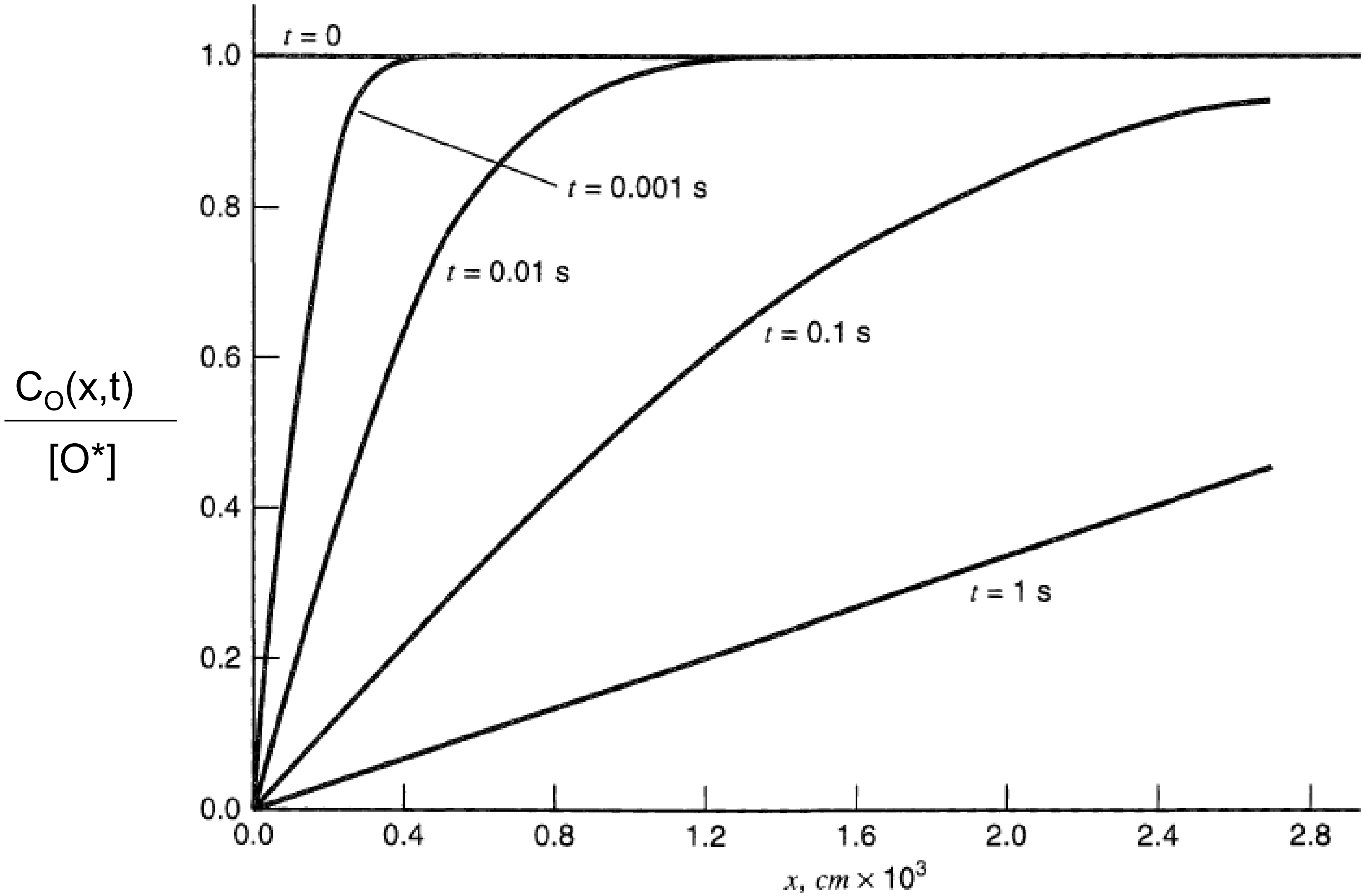
inversion….

$$C_O(x,t) = [O^*] \left[1 - \mathrm{erfc}\left[\frac{x}{2(D_O t)^{0.5}}\right]\right]$$

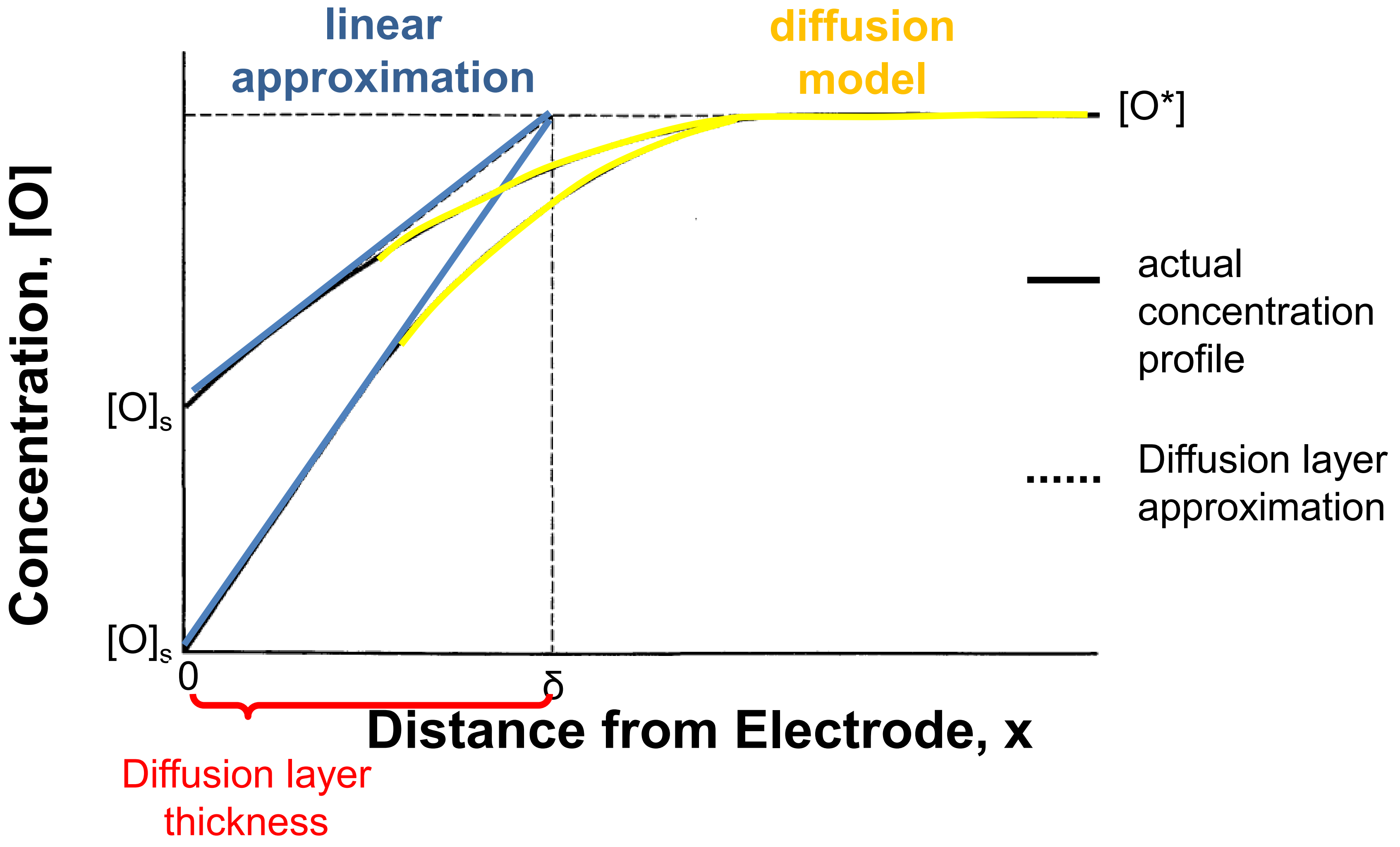
or

$$\boxed{C_O(x,t) = [O^*] \left[\mathrm{erf}\left[\frac{x}{2(D_O t)^{0.5}}\right]\right]}$$

Potential Step Methods Under Diffusion Control: Planar Diffusion

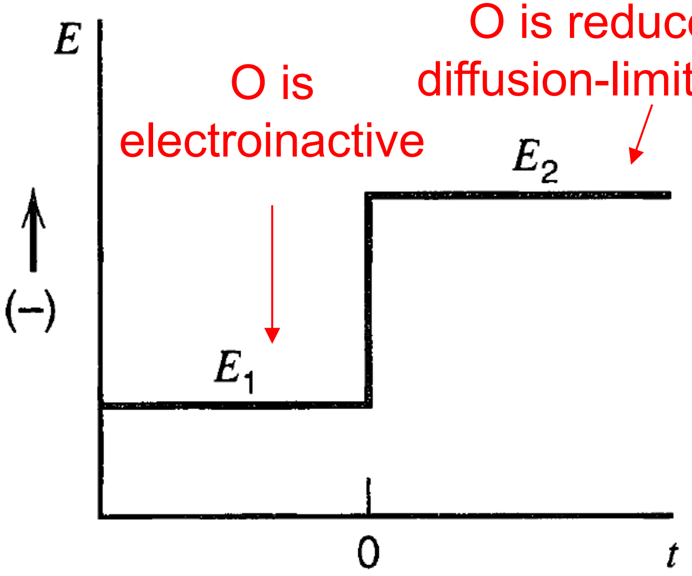


Diffusion-Limited Case



Potential Step Methods Under Diffusion Control

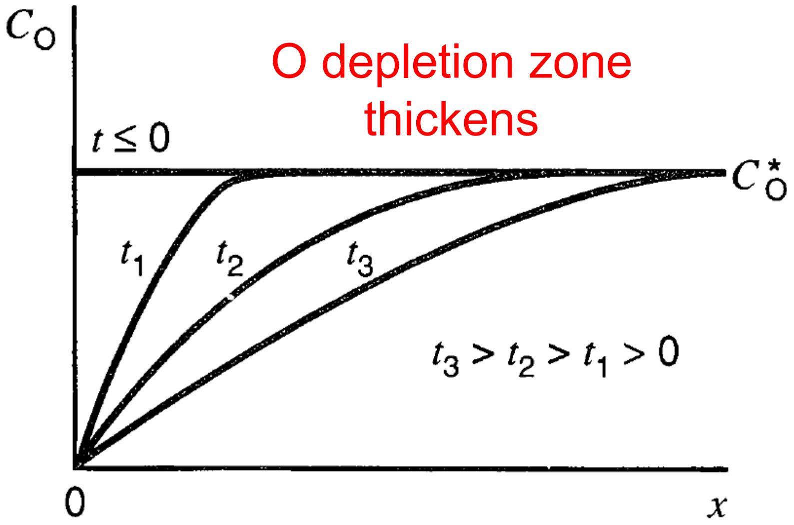
Potential change



O is electroinactive

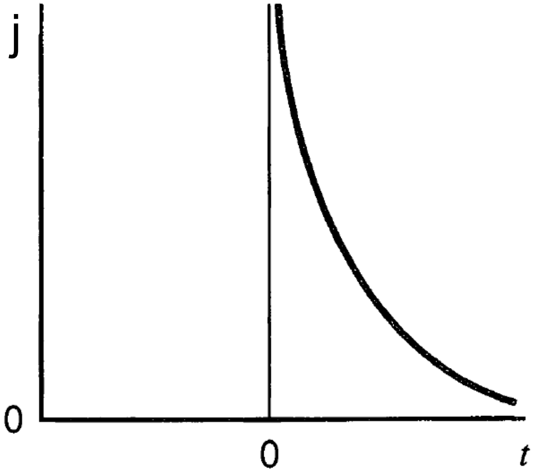
O is reduced at diffusion-limited rate

Corresponding concentration profile



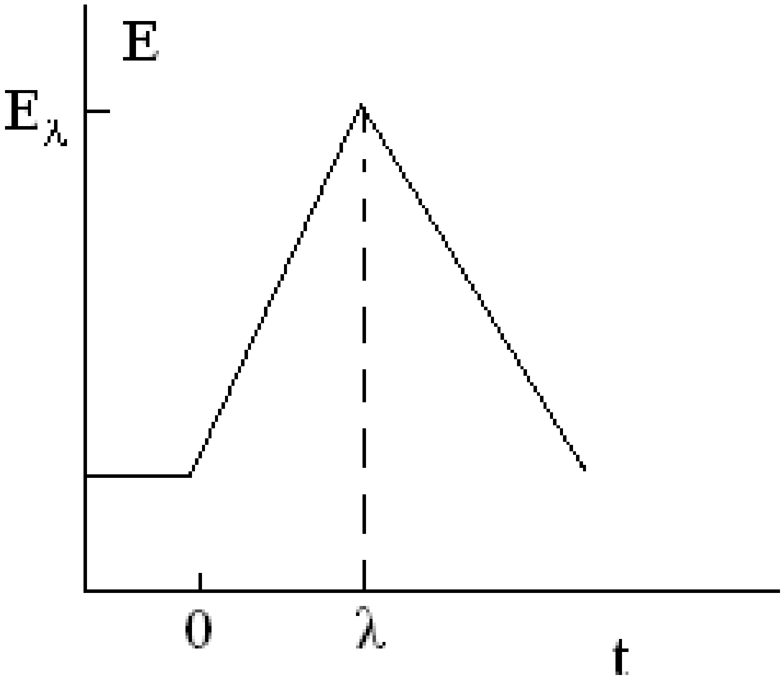
O depletion zone thickens

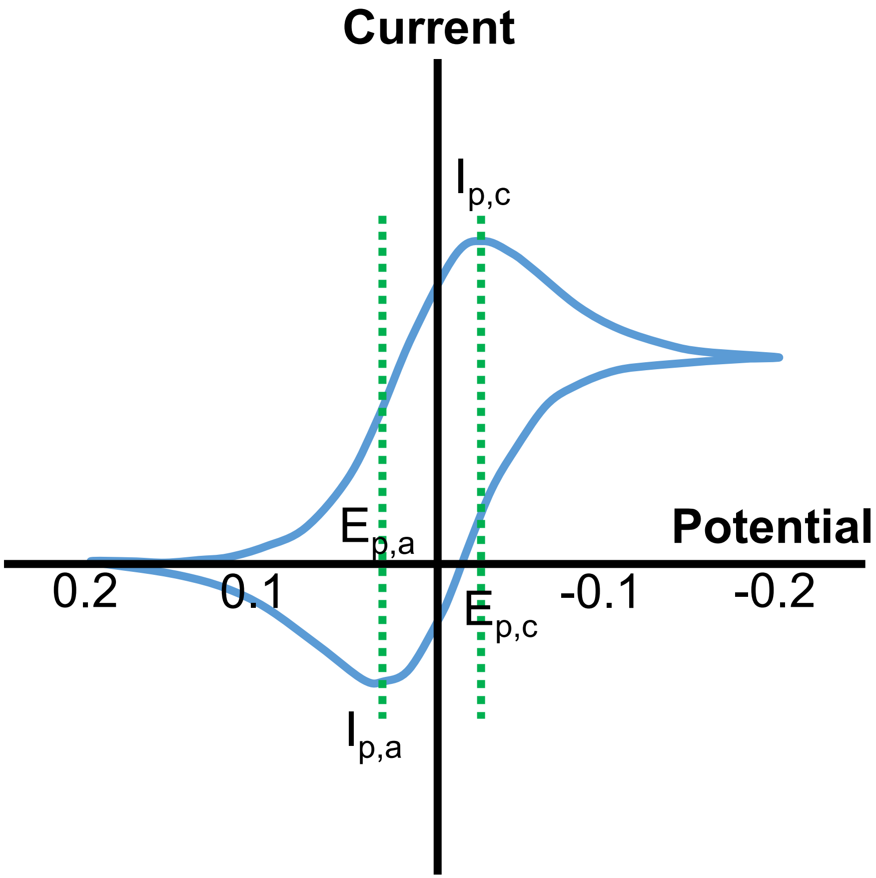
Current flow vs. time



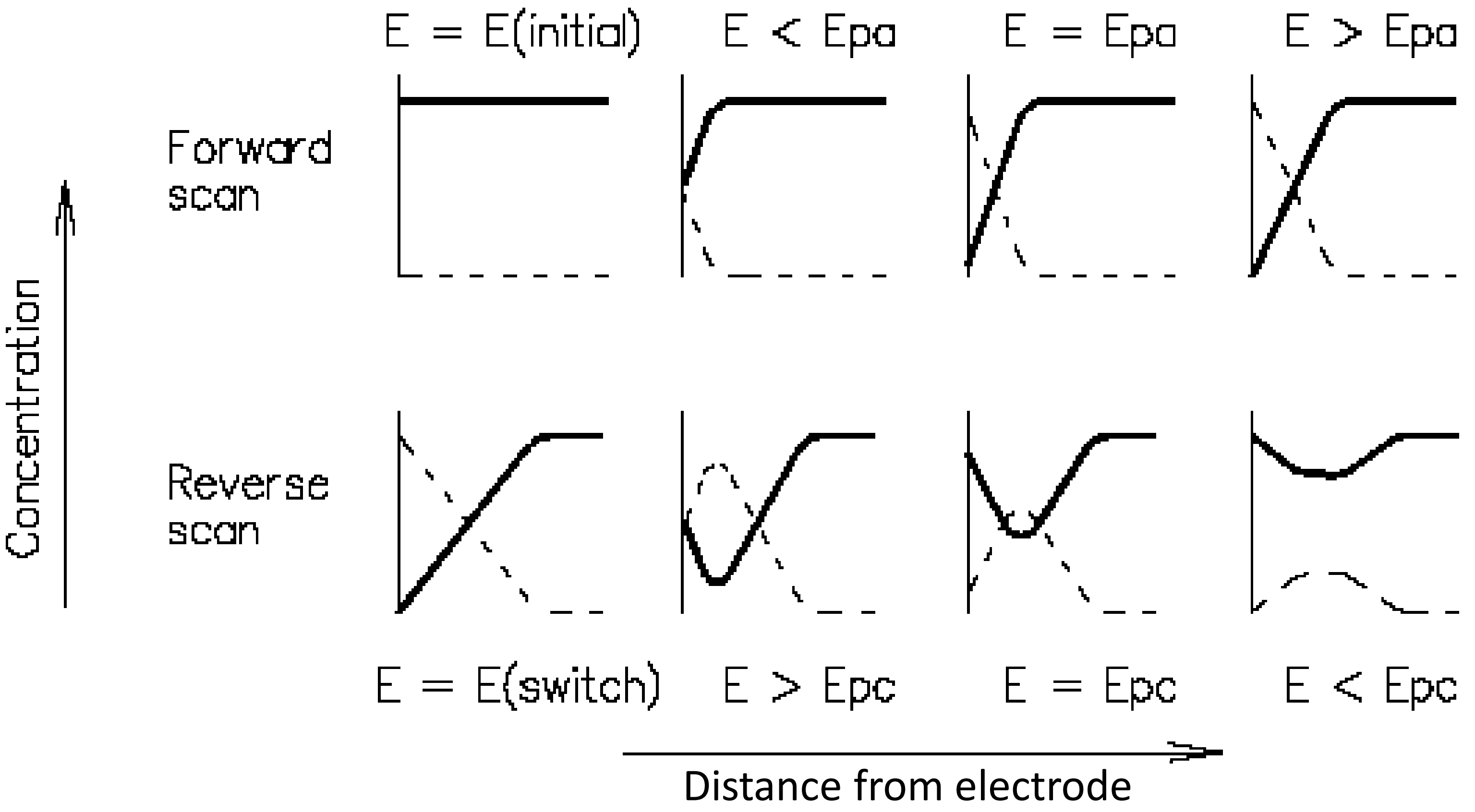
Current is proportional to the concentration gradient at the surface “chronoamperometry”

Current-Voltage (CV) Curve





Current-Voltage (CV) Curve



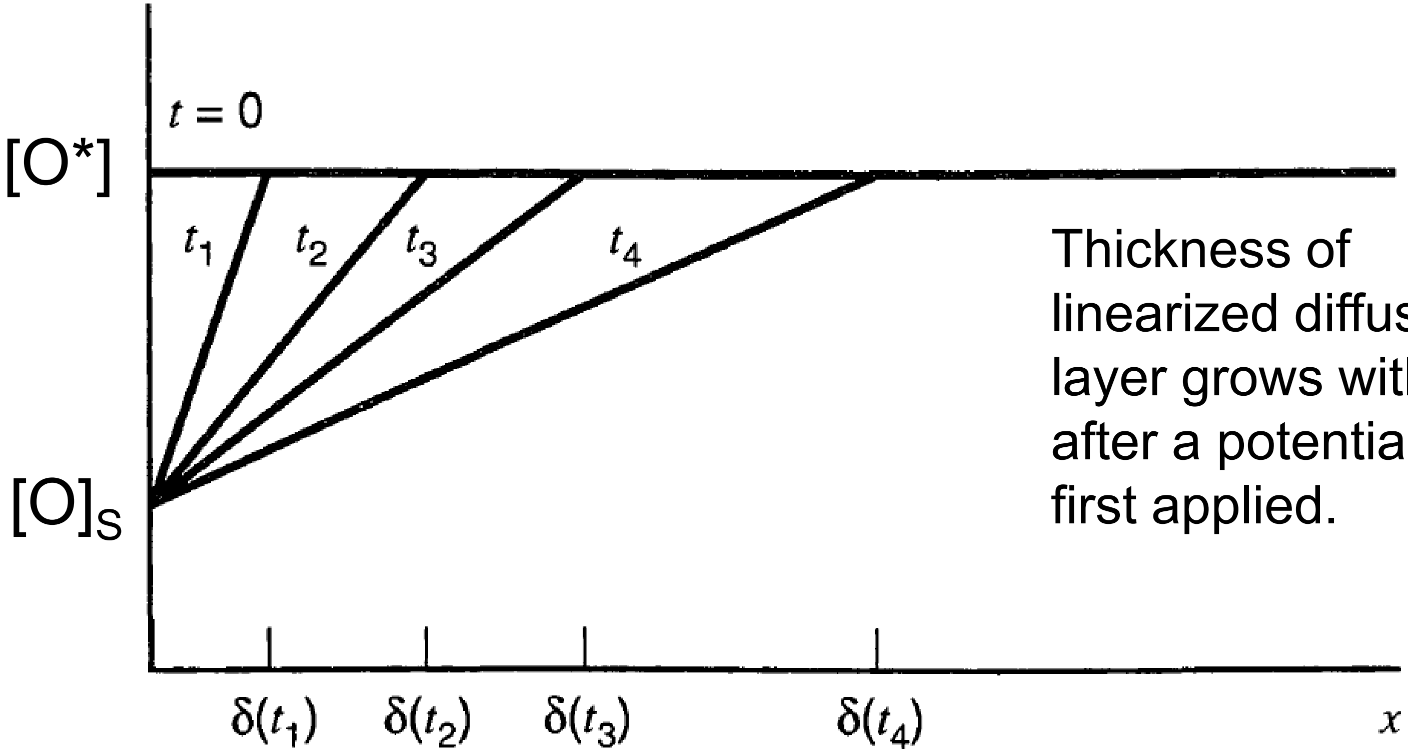
— Solid lines correspond to reducing species

···· Dotted lines correspond to oxidizing species

Current-Voltage (CV) Curve

There is no stirring in CV, so the thickness of the diffusion layer increases as the experiment unfolds (C will have to diffuse further from the bulk)

Shorter diffusion layer ←→greater current
Shorter diffusion layer ←→ faster scan rate



Thickness of linearized diffusion layer grows with time after a potential E is first applied.

Current-Voltage (CV) Curve

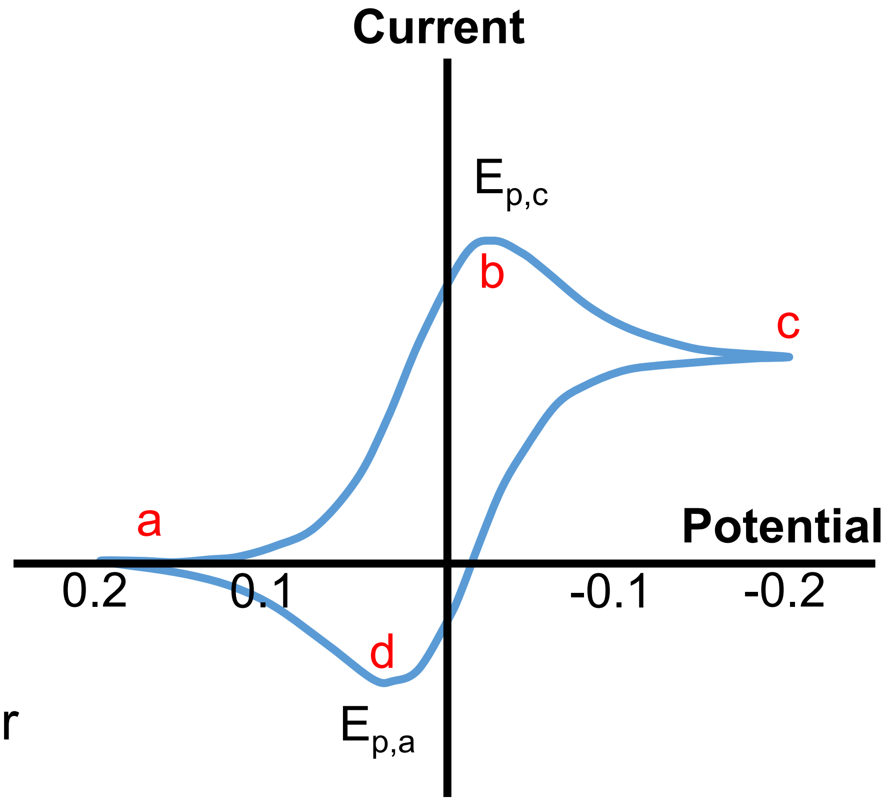
The Randles-Sevcik equation can be applied to stationary electrodes that are scanned across different potentials (CV curve). It relates the peak current with the scan rate [V s^{-1}].

$$j_p = 0.4463zF[C^*]\left[\frac{zF\underline{v}\,D}{RT}\right]^{1/2}$$

j_p = peak current
z = mol e-/mol reactant
[C*] = bulk density of reactant
D = diffusion coefficient
$\underline{v}$ = scan rate [V s^{-1}]

Current-Voltage (CV) Curve

- At a potential positive of E°, only non-faradaic current flows.
- When the potential reaches E°, reduction begins and current starts to flow.
- As the potential continues to grow more negative, $[O]_S$ begins to drop, and hence the flux to the surface and the current increase.
- As the potentials moves past $E_{p,c}$, the surface concentration drops near 0 and mass transfer reaches a maximum rate.
- Then it declines as the depletion effect sets in.



$$E° = (E_{p,a} + E_{p,c})/2$$

a : onset potential
b,d : peak potential
c : switching potential

Current-Voltage (CV) Curve

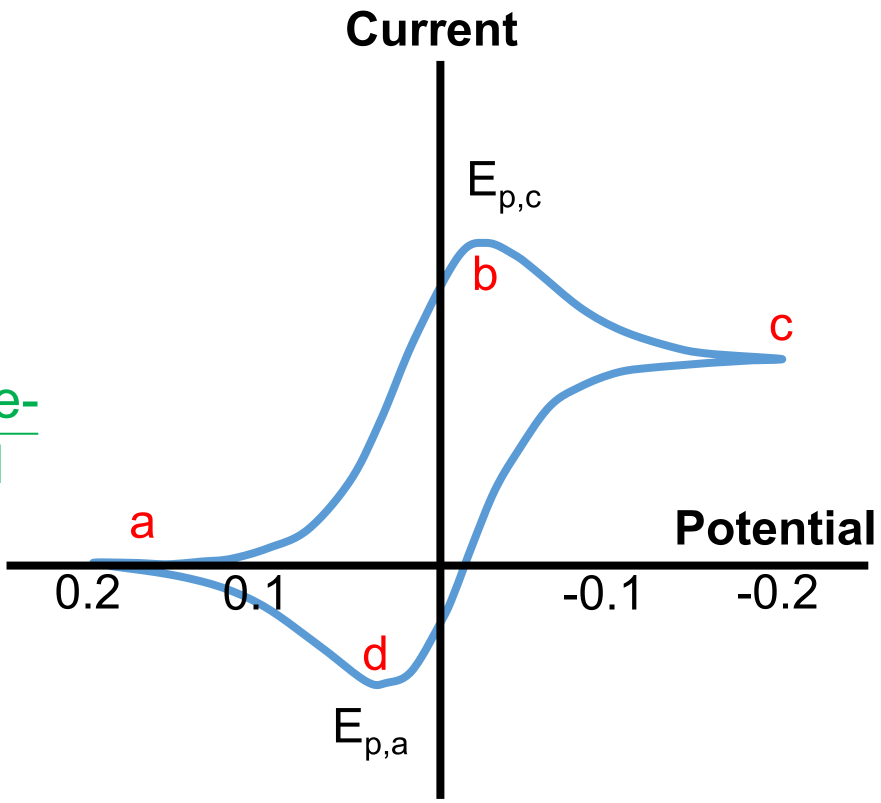
For a reversible reaction, the separation between the two peaks is defined as

$$|E_{p,a} - E_{p,c}| = \Delta E_p = \frac{0.058\ \text{V}}{z}$$

$$z \rightarrow \frac{\text{mol e-}}{\text{mol}}$$

- ΔE_p is independent of the scan rate for a fast electron transfer reaction.

- Increasing values of ΔE_p as a function of increasing scan rate indicates the presence of electrochemical irreversibility.



$$E° = (E_{p,a} + E_{p,c})/2$$

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Outline

- Additional reading:

Electrochemical Methods – Fundamental and Applications by Bard and Faulkner by Wiley.