

In all electrochemical methods, the rate of oxidation & reduction depend on:

1) rate & means by which soluble species reach electrode surface (**mass transport**)

2) kinetics of the electron transfer process at electrode surface (**electrode kinetics**), which depend on:

a) nature of the reaction

b) nature of electrode surface

c) temperature

(we don't have much control over #2)

Mass Transport or Mass Transfer

1) **Migration** – movement of a charged particle in a potential field – generally bad (important for conductance & electrophoresis)

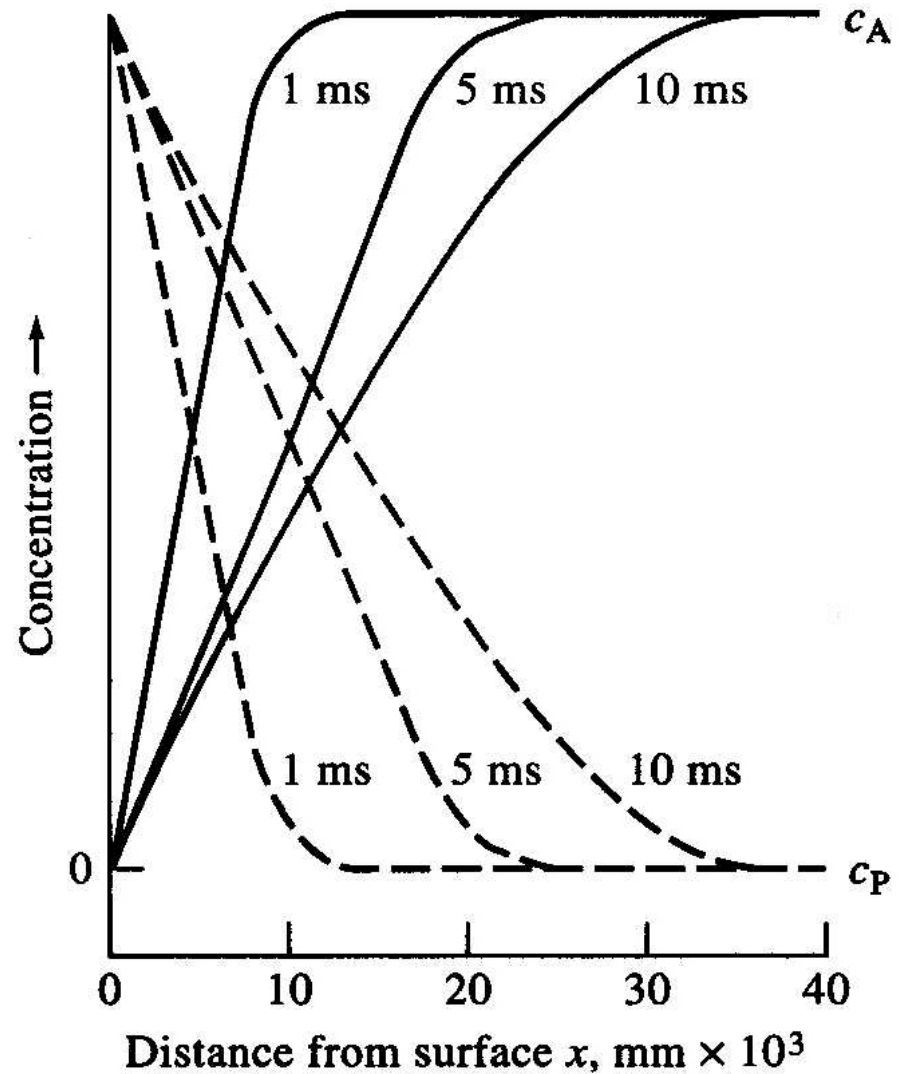
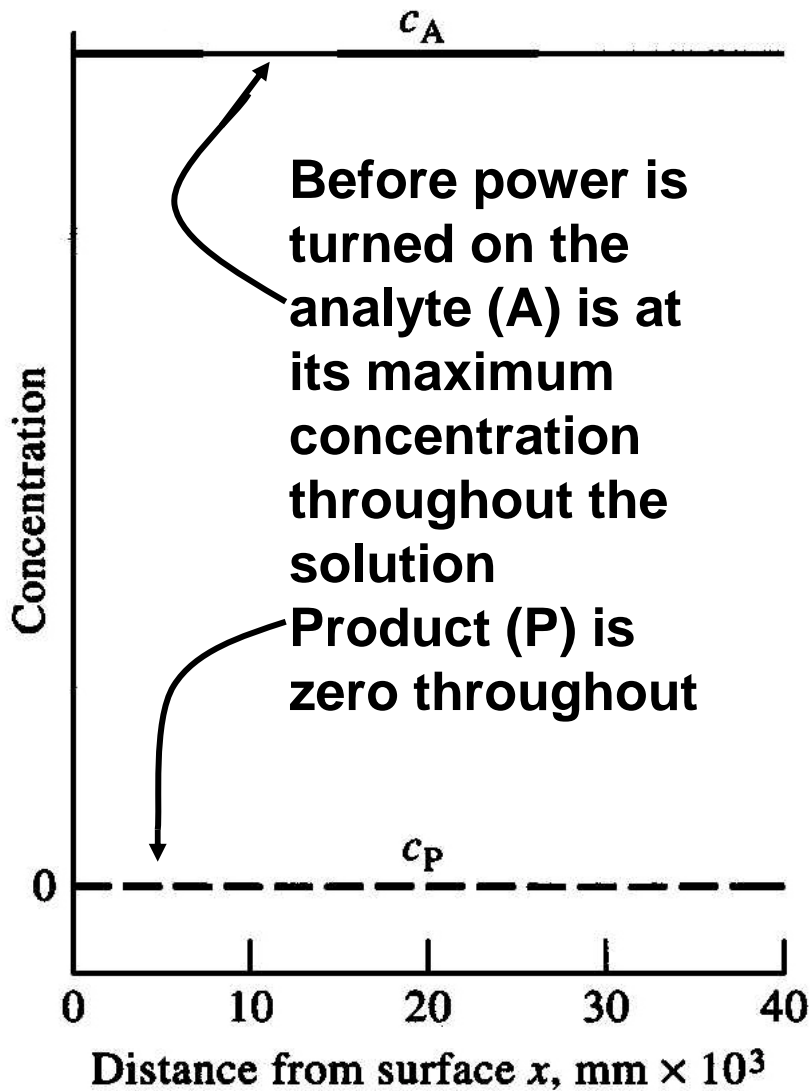
In most cases migration is undesirable and can be eliminated by adding a 100 fold excess of an inert electrolyte (i.e., electrochemically inert – not oxidized or reduced) Inert electrolyte does the migrating, not the analyte

Mass Transport or Mass Transfer

- 2) **Diffusion** – movement due to a concentration gradient. If electrochemical reaction depletes (or produces) some species at the electrode surface, then a concentration gradient develops and the electroactive species will tend to diffuse from the bulk solution to the electrode (or from the electrode out into the bulk solution)

Concentration polarization

Reaction is $A + e^- \rightarrow P$



Fick's Laws describe diffusion

1st Law

$$J = -D \frac{\partial C(x,t)}{\partial x}$$

Where

J = flux of material i.e., moles passing a 1 cm² plane at point x & time t (mol/cm²/sec)

D = diffusion coefficient (cm²/sec)

C = concentration

t = time (sec) from when power is turned on

x = distance from electrode surface (cm)

Skipping to the Electrochemical Solution

Number of
electrons

Faraday's
constant

Electrode
area

Concentration

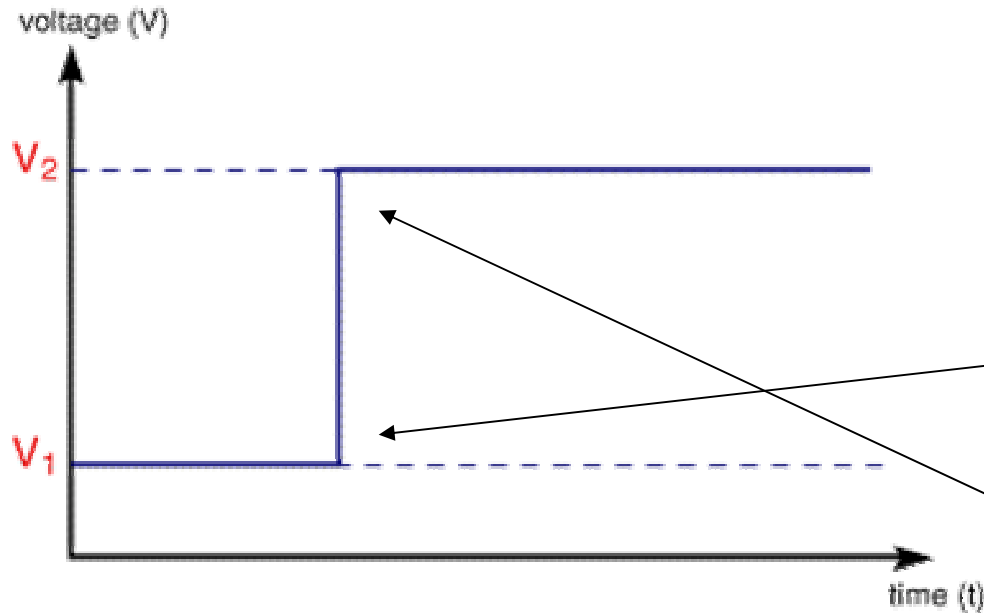
$$I = n F A c_o \sqrt{\frac{D}{\pi t}}$$

The Cottrell equation

Diffusion
coefficient

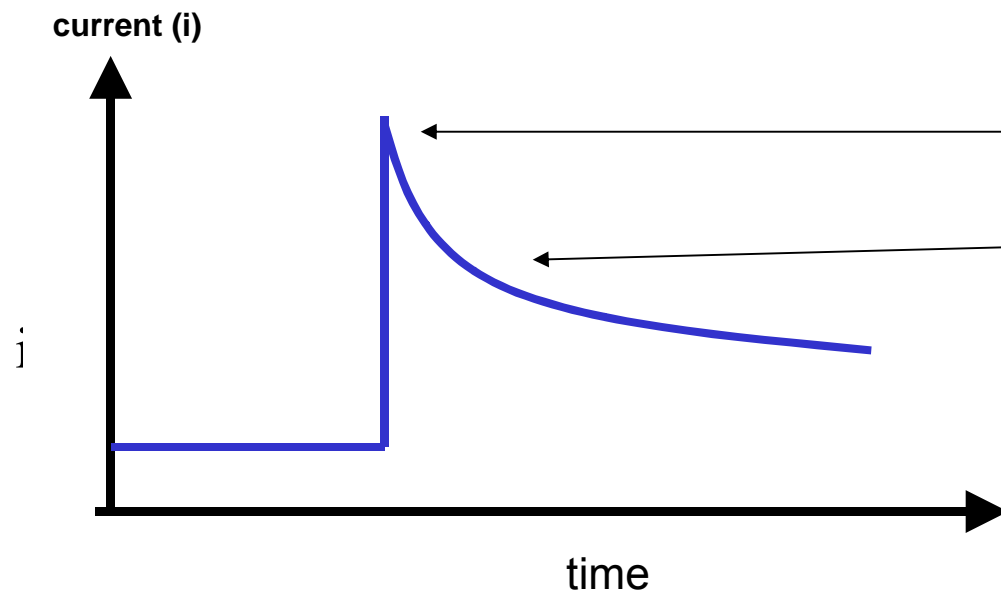
Time

Current is the flux
of electrons at the
electrode surface



Experiment showing how Cottrell equation describes current as a function of time

Voltage applied to cell begins at V_1 where no reaction occurs and is stepped up to V_2 causing electrode process to begin and a current spike results.



Current drops off with time according to the Cottrell equation since material must diffuse to the electrode surface in order to react.

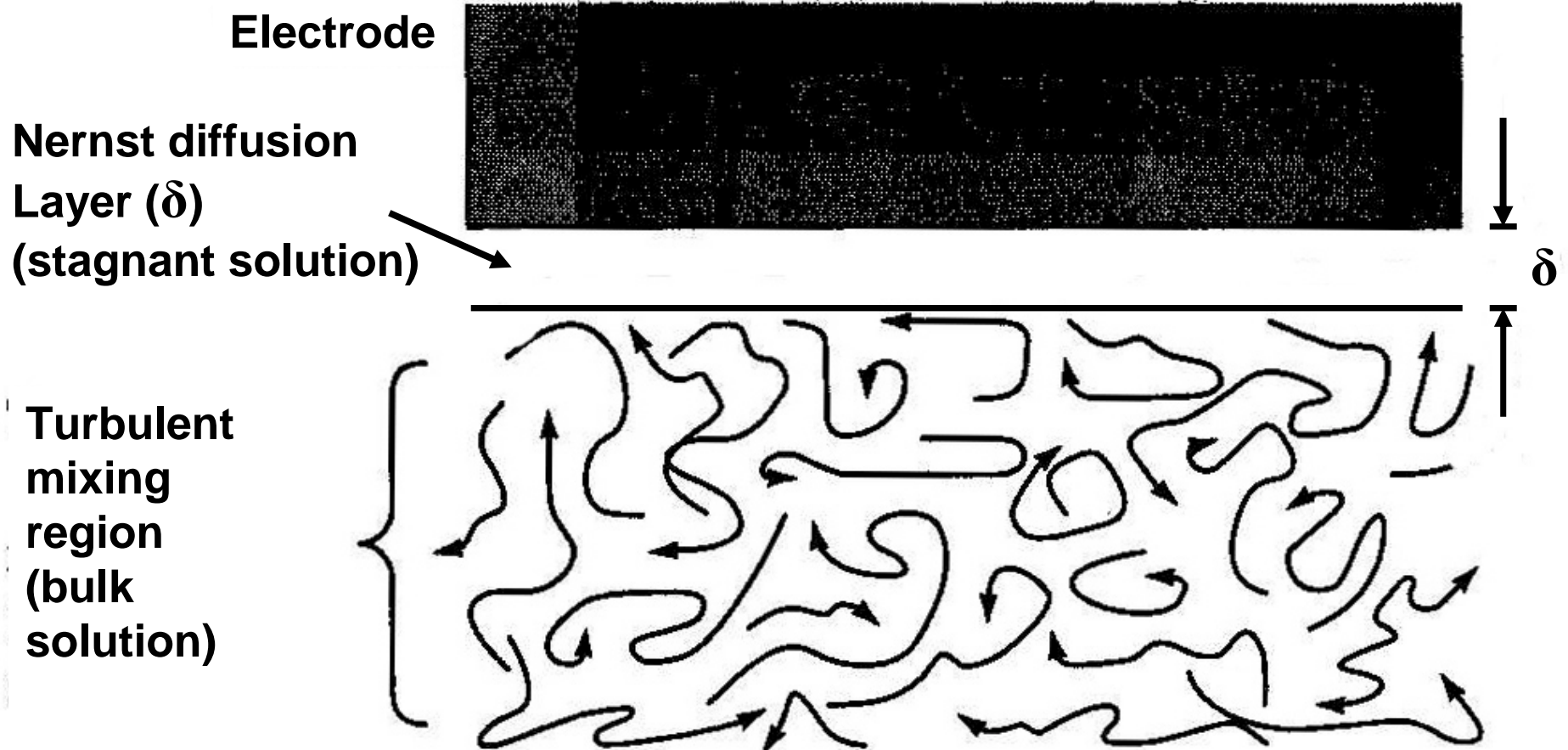
Mass Transport or Mass Transfer

- 3) **Convection** – mass transfer due to stirring. Achieved by some form of mechanical movement of the solution or the electrode i.e., stir solution, rotate or vibrate electrode

Difficult to get perfect reproducibility with stirring, better to move the electrode

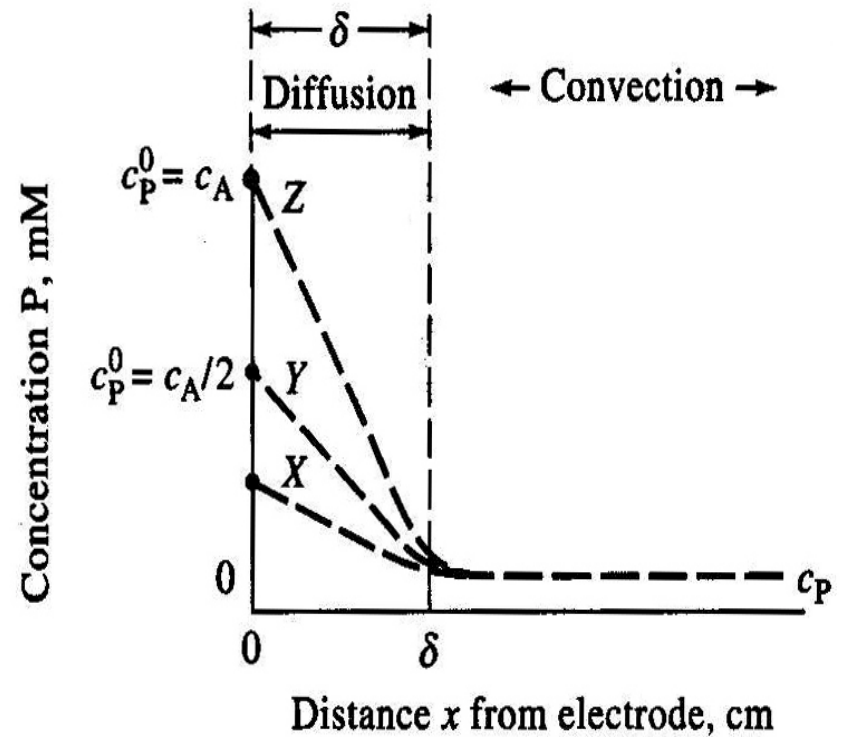
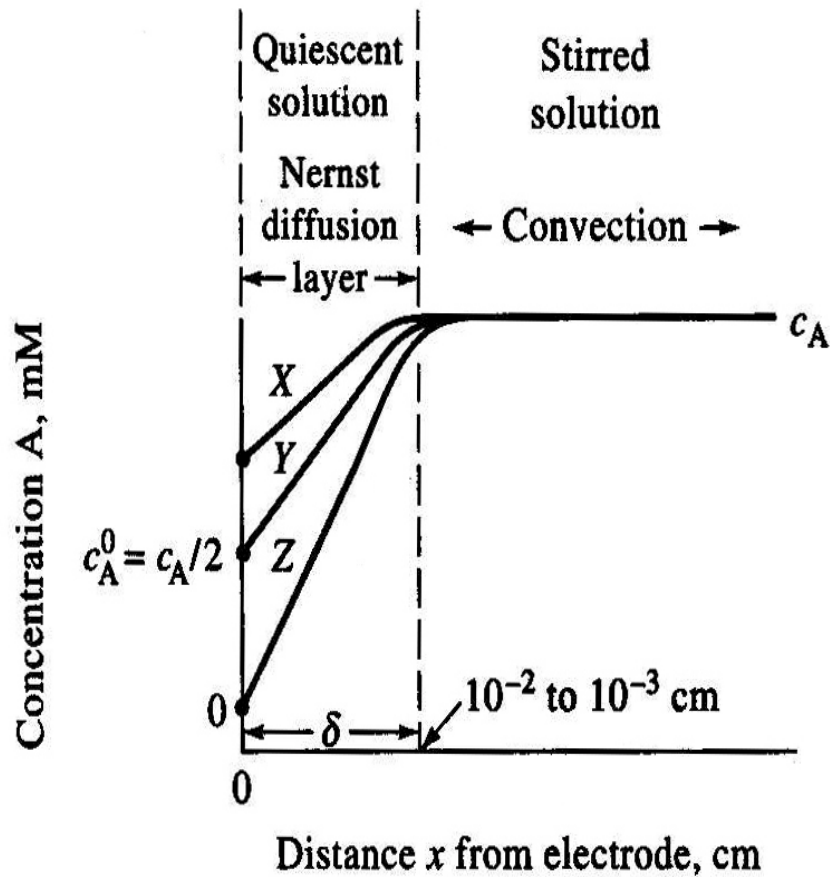
Convection is considerably more efficient than diffusion or migration = higher currents for a given concentration = greater analytical sensitivity

Nernst Diffusion Layer Concept for stirred solution & stationary electrode



Convective Mass Transport

Electrode converts $A + e^- \rightarrow P$ at surface



Fick's first law applied to stagnant layer

$$\frac{\partial C(x,t)}{\partial x} = \frac{C_{bulk} - C_{surface}}{\delta}$$

$$i = nFAD \frac{C_{bulk} - C_{surface}}{\delta}$$

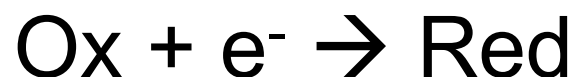
For stirred solutions

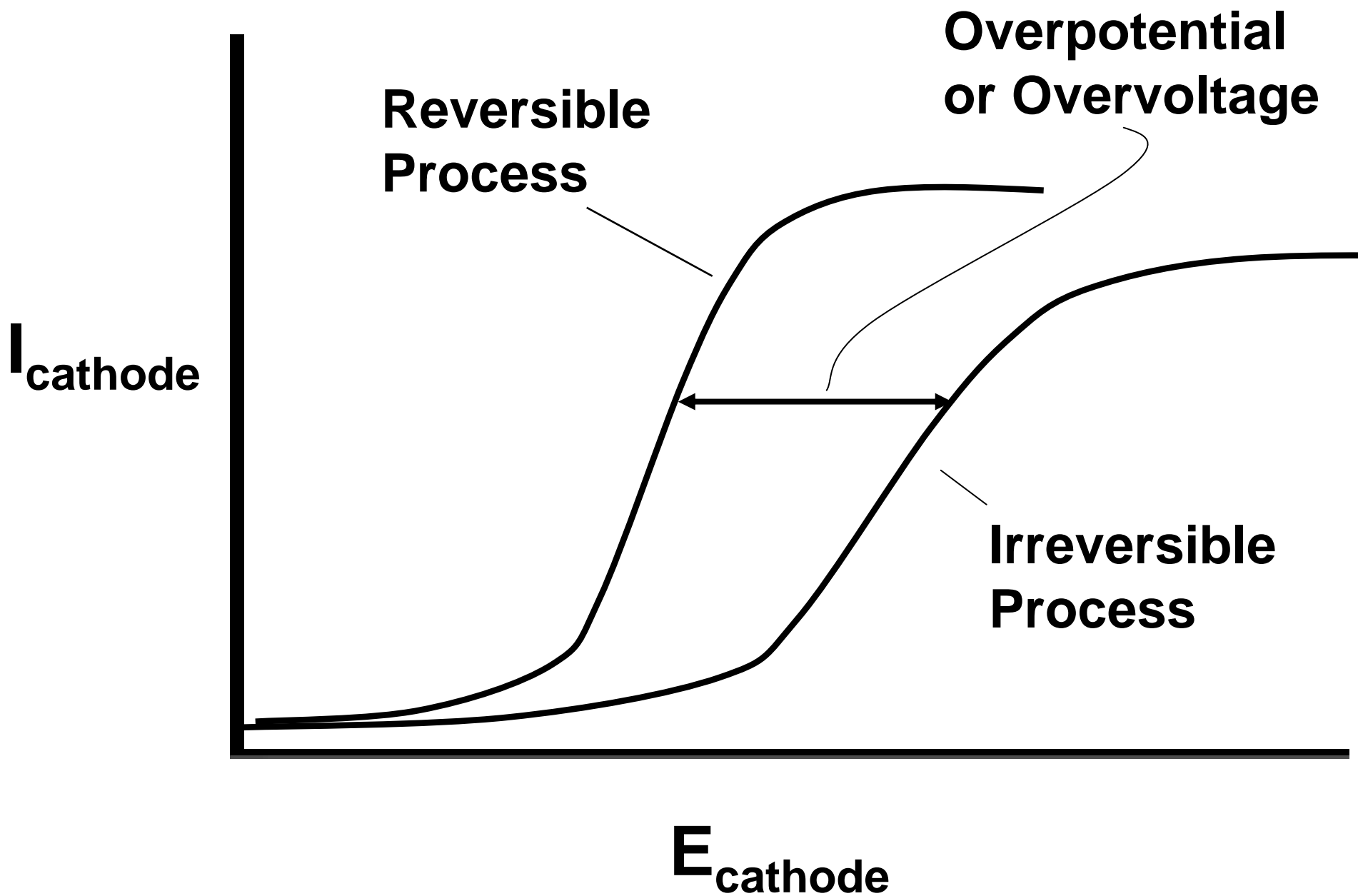
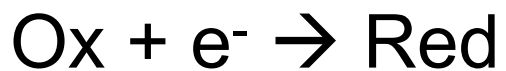
$$i = nFAD \frac{C_{bulk}}{\delta}$$

Mass Transport vs Electrode Kinetics

- Experimentally rate of electron transfer is fast for many processes so can assume:
 - current depends only on mass transfer
 - surface concentrations are in equilibrium with applied potential as expressed by the Nernst equation
- Processes which satisfy these assumptions are known as electrochemically **reversible**

- A process may be reversible under one set of conditions and irreversible under other conditions
- Process is more likely to be irreversible if
 - it involves a high current
 - employs a rapid potential scan
- If a process is irreversible, then the rate of reaction at the electrode surface (i.e., current) will be slower than predicted from mass transfer considerations alone
- Varying potential (E) linearly at a stationary electrode in a stirred solution for



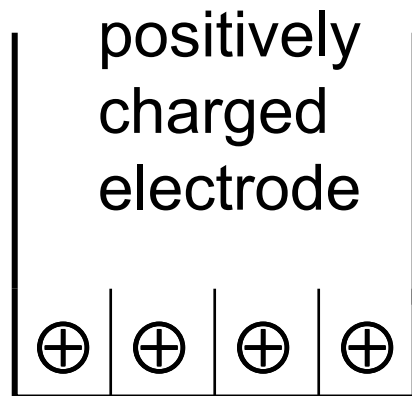


- Overpotential (overvoltage) = potential to achieve the same current as if process was reversible
- Large overvoltage → process more irreversible
- For reversible processes $E_{\text{overpotential}} = 0$
- Overvoltage characteristics:
 - 1) increases with current density (current/area)
 - 2) decreases with increasing temp
 - 3) high for reactions producing gases
 - 4) depends on electrode composition
 - 5) difficult to specify exactly – electrode surface

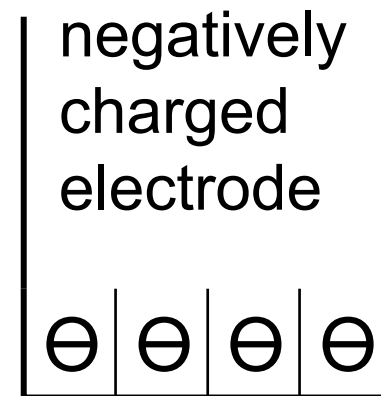
Other Electrochemistry Fundamentals

1) Kinds of current

- a) Faradaic current = current due to electron transfer (usually what we are interested in)
- b) Capacitive current = current that flows as electrode surface charges up like a capacitor



attracts negative
ions to surface



attracts positive
ions to surface

- If we change the electrode potential → current flows to carry charge to the surface & charge up electrode = capacitive current
- Capacitances are significant, often 40 – 60 $\mu\text{F}/\text{cm}^2$ of electrode area
- In methods involving potential scan, capacitive current is the major source of background → detection limits occur at those concentrations where Faradaic current is too small to be adequately distinguished from $I_{\text{capacitive}}$

2) Kinds of Potentials

- a) Junction Potentials – already discussed
- b) Potential Due to IR Drop – when current flows, solution has some electrical resistance, therefore there is an IR drop across the solution (i.e., between electrodes) → $V = IR$

Three ways to handle this interfering potential:

- 1) work at low currents so V is small
- 2) Minimize R using a supporting electrolyte which in turn minimizes V
- 3) Correct for V by making a single measurement of R and measuring I throughout the experiment (not usually done)

3) Kinds of Electrodes

- a) Stationary – e.g., Pt wire in solution
- b) Self-Renewing – e.g., dropping Hg electrode
- c) Hydrodynamic – rotating, vibrating, wall-jet

4) Electrode Materials

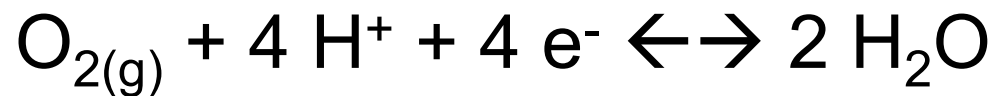
- Want an electrode material that is not easily oxidized or reduced
 - Most common materials: Hg, Pt, Au, C (graphite)
 - Available potential range –
max cathodic potential limited by reduction of solvent
e.g., for H₂O
- $2 \text{H}^+ + 2 \text{e}^- \leftrightarrow \text{H}_{2(\text{g})}$
- potential is
pH dependent

Electrode Materials (cont.)

For Pt, Au, C

max anodic potential limited by solvent oxidation

e.g., for H₂O



potential is

pH dependent

For Hg

max anodic potential limited by oxidation of Hg

Large usable potential range because of high overvoltage for production of gaseous products

Because Hg is a liquid which has a very smooth surface, it has a particularly high overvoltage for H⁺ reduction, therefore it is possible to go to more cathodic potentials with Hg than for Pt, Au, or C

The purer the Hg, the higher the overpotential for H₂ evolution

For C (graphite)

Using graphite electrodes, necessary to impregnate pores with wax or other hydrophobic material to prevent solution from seeping in and changing the electrode surface area with time

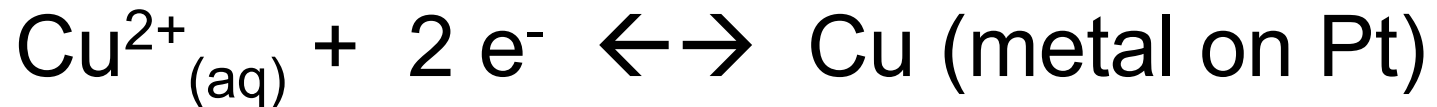
Carbon paste electrodes can be prepared by mixing carbon powder with Nujol (of Nujol mull fame)

Glassy carbon electrodes are the more modern version of carbon electrodes

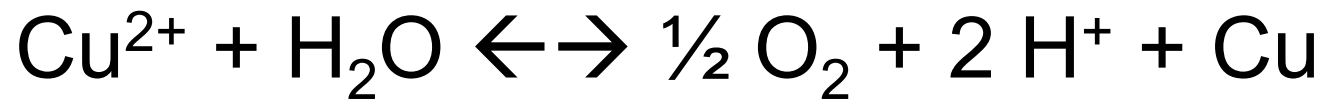
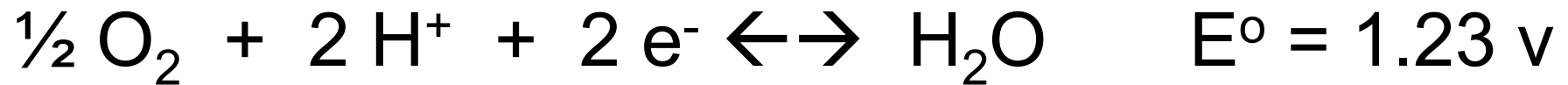
Electrogravimetry

- Apply potential to cause a soluble species to reduce or deposit on a solid electrode

e.g., reduce Cu^{2+} onto Pt cathode



- Change in weight of dried cathode before & after deposition = amount of Cu in sample
- Assumptions:
 - All Cu is plated out
 - Nothing else plates out



For zero current $E_{\text{cell}} = E_{\text{Cu}} - E_{\text{O}_2, \text{H}_2\text{O}}$

Use Nernst Equation with E° 's & concentrations

$$E_{\text{cell}} = \left(0.34 - \frac{0.059}{2} \log \frac{1}{[\text{Cu}^{2+}]} \right) - \left(1.23 - \frac{0.059}{2} \log \frac{1}{(\text{P}_{\text{O}_2})^{0.5} [\text{H}^{+}]^2} \right) = -0.91 \text{ v}$$

- Apply potential more negative than -0.91 v to force system to reach an equilibrium where $[\text{Cu}^{2+}]$ is small (like 99.9% lower than the approximate starting concentration)
- Choose cathode potential to reduce equilibrium $[\text{Cu}^{2+}]$ to any desired value
- Must be cautious not to set potential too far negative to make sure nothing else is reduced
- Normally set conditions so that reduction is complete in a reasonably short period of time