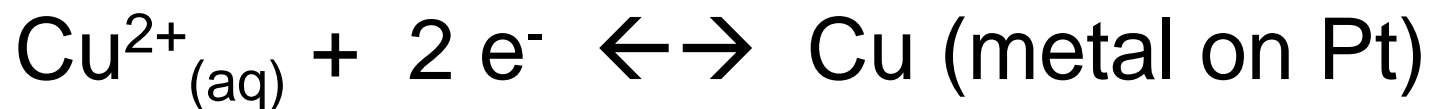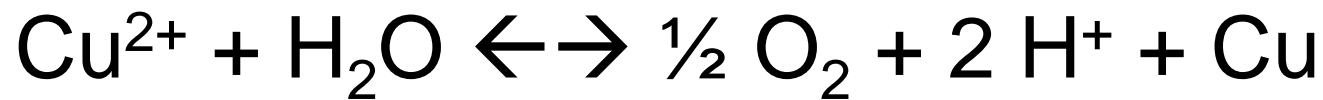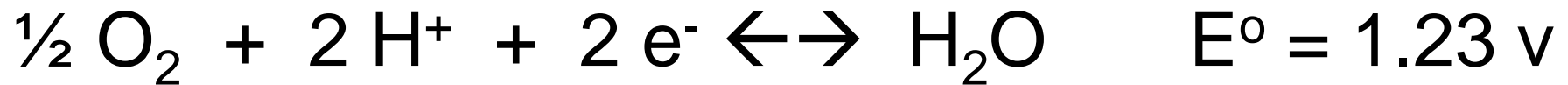# Electrogravimetry
(Controlled Potential Electrolysis)

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

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

    $Cu^{2+}_{(aq)} + 2\ e^- \longleftrightarrow Cu$ (metal on Pt)

- Change in weight of dried cathode before & after deposition = amount of Cu in sample

- Assumptions:
    - All Cu is plated out
    - Nothing else plates out

$$Cu^{2+}_{(aq)} + 2\ e^- \longleftrightarrow Cu \qquad E^o = 0.34\ v$$

$$\tfrac{1}{2}\ O_2 + 2\ H^+ + 2\ e^- \longleftrightarrow H_2O \qquad E^o = 1.23\ v$$

$$Cu^{2+} + H_2O \longleftrightarrow \tfrac{1}{2}\ O_2 + 2\ H^+ + Cu$$

For zero current $\qquad E_{cell} = E_{Cu} - E_{O_2,H_2O}$

Use Nernst Equation with $E^{o's}$ & concentrations

$$E_{cell} = \left(0.34 - \frac{0.059}{2} \log \frac{1}{[Cu^{2+}]}\right) -$$

$$\left(1.23 - \frac{0.059}{2} \log \frac{1}{(P_{O_2})^{0.5}[H^+]^2}\right) = -\ 0.91\ v$$

- Apply potential more negative than – 0.91 v to force system to reach an equilibrium where $[Cu^{2+}]$ is small (like 99.9% lower than the approximate starting concentration)
- Choose cathode potential to reduce equilibrium $[Cu^{2+}]$ 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

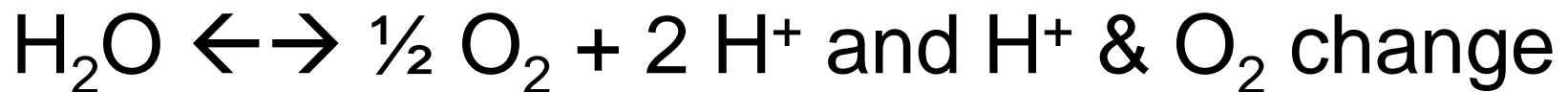# Cell for Electrogravimetry

Pt Electrodes
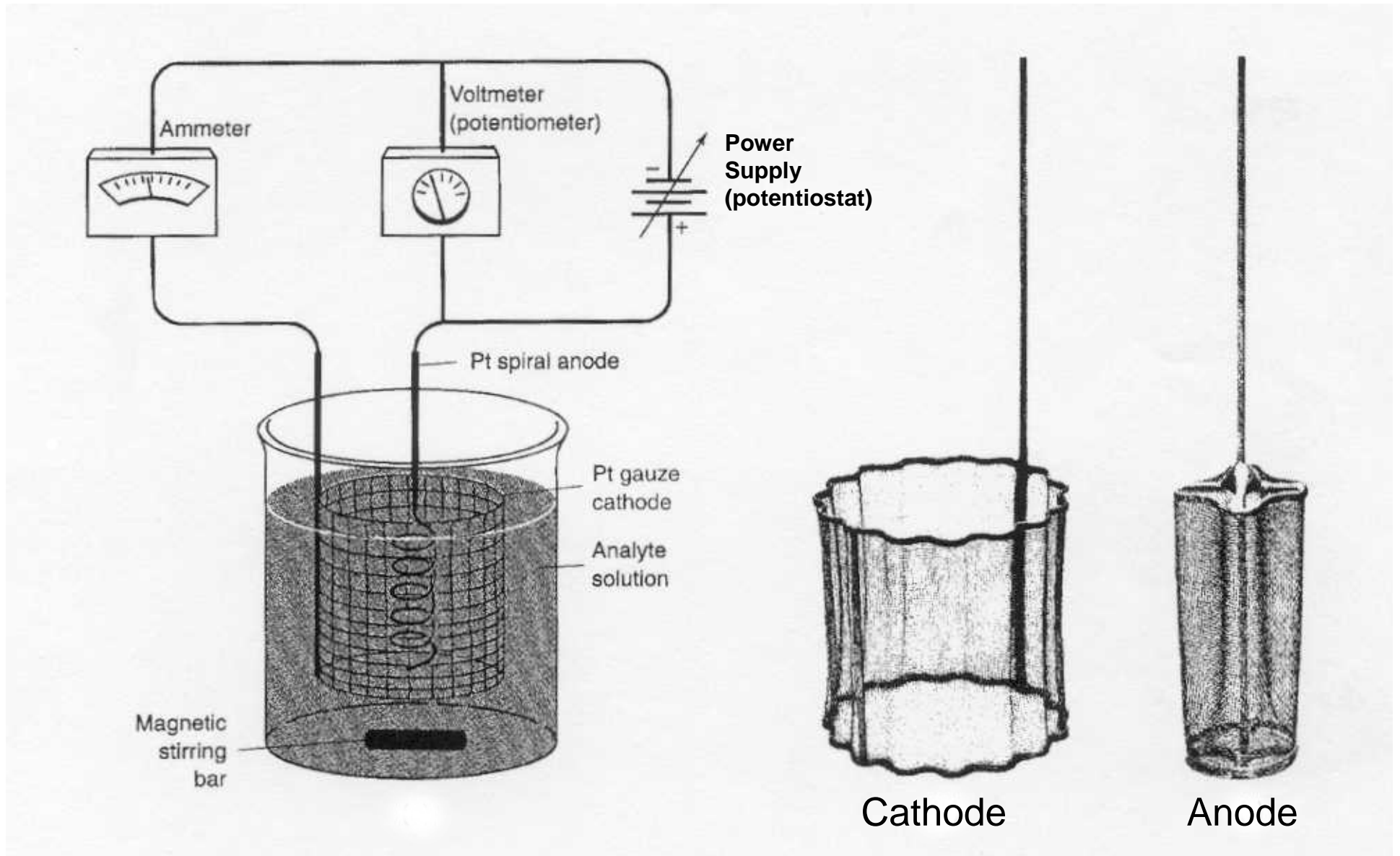
Cathode   Anode

Problem with simple electrogravimetry system is that the potential of the cathode is not accurately known

$$E_{applied} = E_{cathode} - E_{anode} - E_{IR} - E_{overvoltage}$$
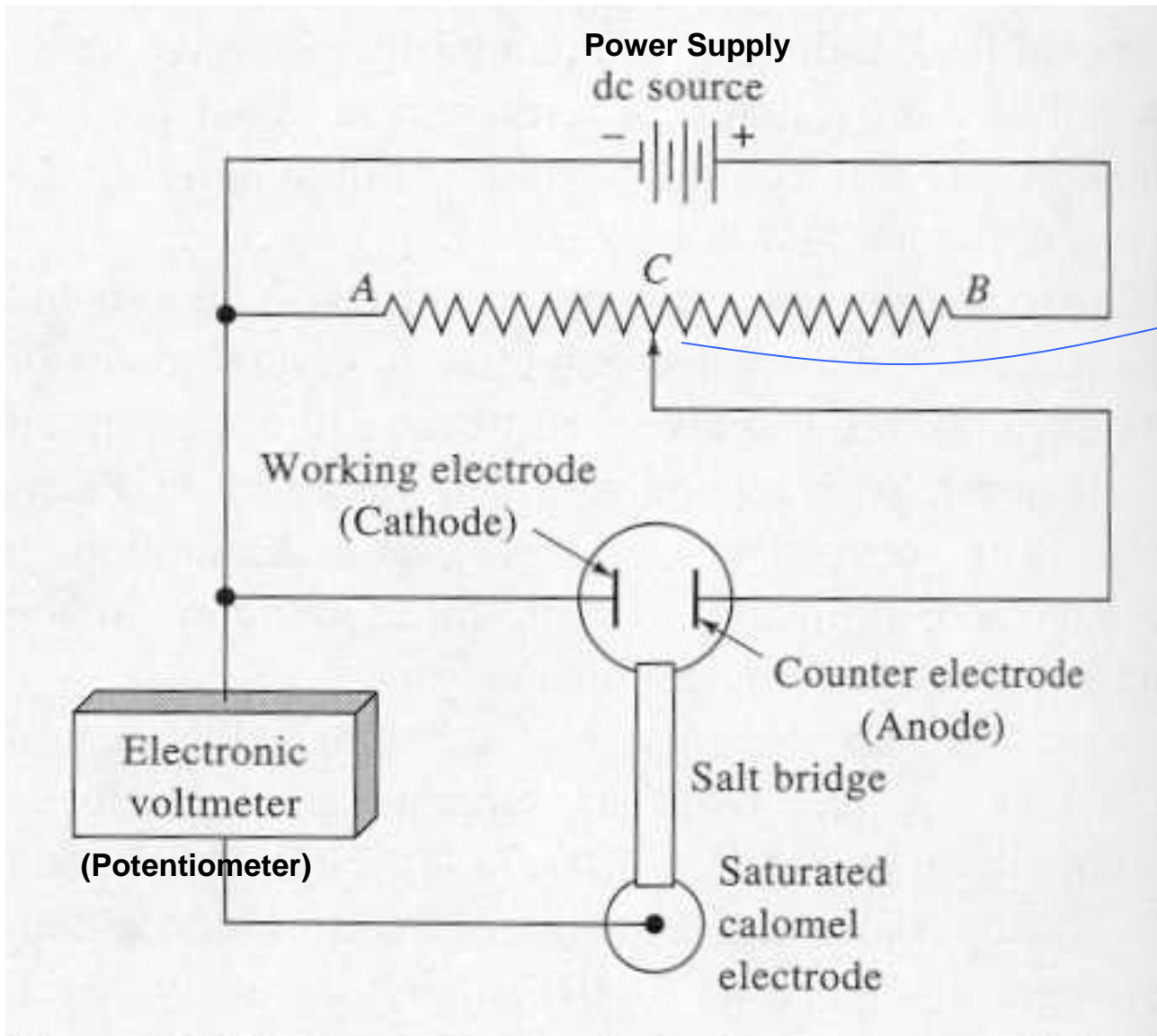
E_J is insignificant and can be ignored here

Don't know the magnitude of E_{IR} or $E_{overvoltage}$ & E_{IR} changes throughout experiment

A similar problem exists at the anode since $H_2O \longleftrightarrow \frac{1}{2} O_2 + 2 H^+$ and H^+ & O_2 change during electrolysis so anode potential change

Much of this problem can be eliminated by using a three electrode system

Power Supply
dc source

A — C — B

Working electrode
(Cathode)

Electronic
voltmeter
(Potentiometer)

Counter electrode
(Anode)

Salt bridge

Saturated
calomel
electrode

Use potentiometer to measure potential of cathode relative to reference electrode then manually adjust slidewire contact to hold $E_{cathode}$ at desired value. This operation must be repeated at intervals during the electrodeposition because the current changes with conc.

Bulk current still flows from cathode to anode, but anode potential is no longer important.

Three Electrode Configuration

1) Reference electrode – maintains fixed potential despite changes in solution comp.

2) Working electrode – electrode of interest which is the cathode in this system

3) Counter electrode (Auxiliary electrode) – third electrode taking most of current flow (acts as current sink)

Advantages of 3 electrode system

1) Changes in concentration at counter electrode are not important, no effect on working electrode potential

2) No current flows through reference → no IR drop (its potential is constant)

Applications of Electrogravimetry
(Controlled Potential Electrolysis)

1) Quantitative analysis (electrogravimetry) – very accurate & precise, weighing is the only measurement operation, can control degree of completion for the deposition reaction by proper choice of potential, some degree of selectivity using potential

2) Separations – separate one species from another in solution by selectively plating it out and removing it from solution. This method is used to remove interferences particularly in electrochemical methods

3) Preconcentration – plating out metals from a large volume of solution ($\geq$ 1 L) onto a small electrode effectively increases their concentration. Can also reoxidize metals back into a small volume of solution (e.g., 1 mL) & the ratio of volumes gives preconcentration factor (i.e., 1000). Can also use other methods for analysis of metal on solid electrode surface (e.g., AA, ICP, XRF, XPS).

4) Electrosynthesis (controlled potential electrolysis) – used by organic chemists to perform oxidation or reduction reactions at bench scale. Take advantage of ability to control potential & produce any oxidizing or reducing strength desired.

5) Purification – to remove trace metals from reagents by plating them out of solution onto a large Hg pool electrode. This cell can also be used for electrosynthesis, etc.
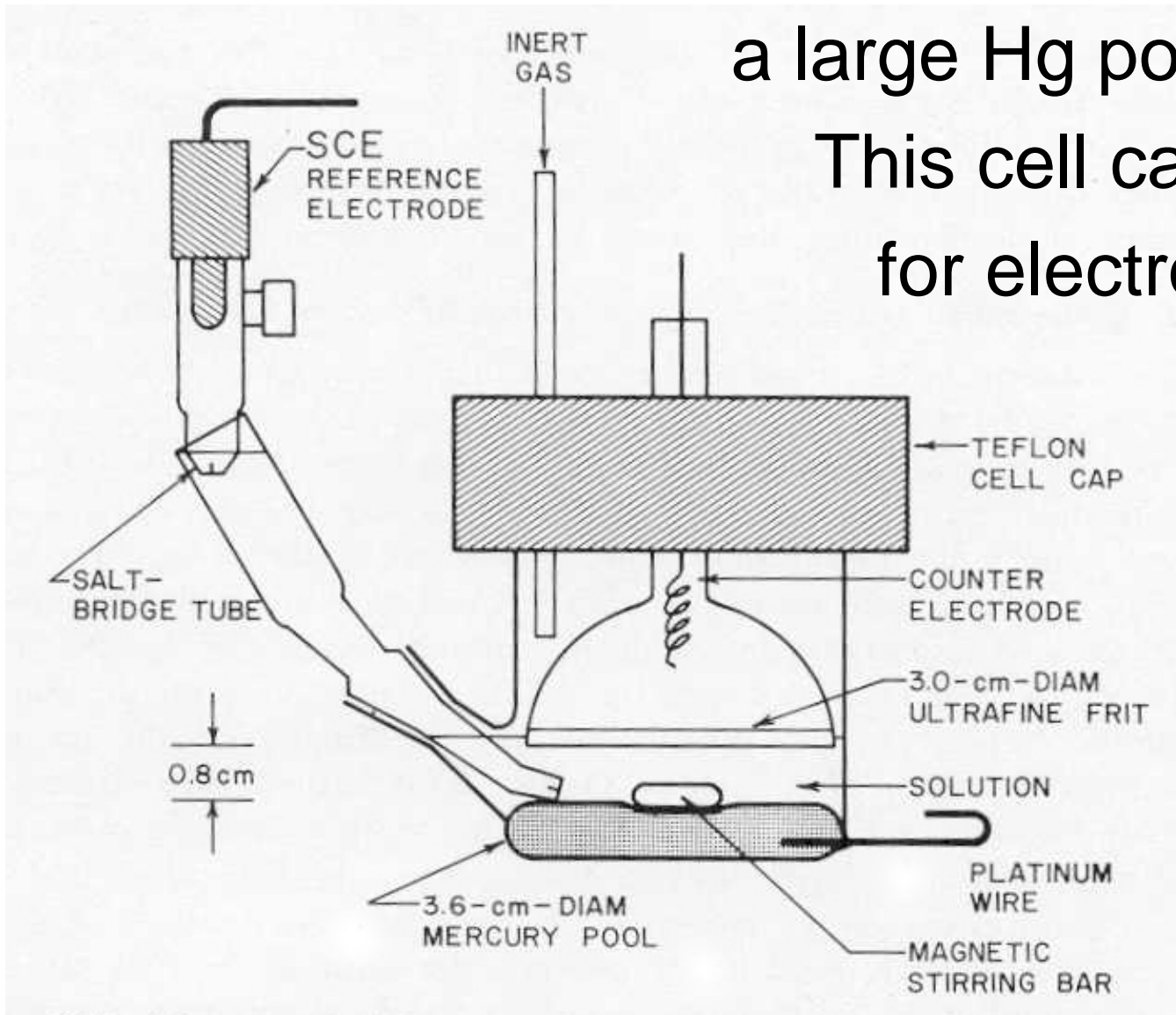
Chronoamperometry

- Stationary electrode
- Unstirred = mass transport by diffusion
- Constant potential
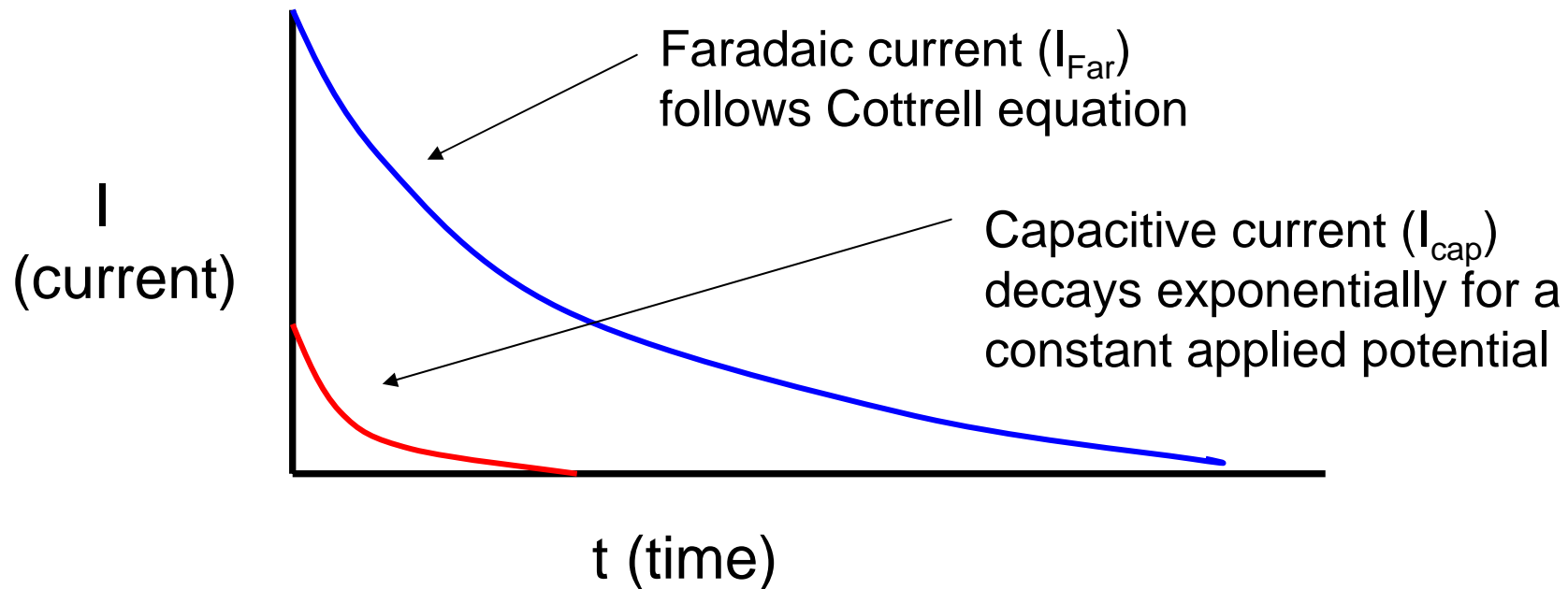- Measure current vs time

Theory

assume   Ox + n e$^-$ $\leftarrow\rightarrow$ Red

- both Ox and Red are soluble

- reversible reaction (electrochemically)

- potential set so reduction goes to
   completion at the electrode surface

Components of output signal in Chronoamperometry

I_{Far} decreases because Ox used up at electrode surface and Ox is only replenished by diffusion

Faradaic current (I_{Far}) follows Cottrell equation

Capacitive current (I_{cap}) decays exponentially for a constant applied potential

I (current)

t (time)

I_{cap} is high as electrode capacitive layer charges up, then drops off

Processes perturbing system can cause data to differ from Cottrell Equation

1) Capacitive Current – charging current is exponential as shown

$$I_{cap} = e^{-kt}$$

Note: Capacitive current decreases more rapidly than Faradaic current so at longer times the ratio I_{Far}/I_{cap} is larger

2) Occurrence of coupled chemical reactions e.g. $Ox + n\ e^- \rightarrow Red$

$$2\ Red \rightarrow A$$

$$A + n\ e^- \leftarrow\rightarrow B$$

Affects the shape of the current-time curve

Chronoamperometry Applications

- Can measure concentration by measuring I vs conc. at any fixed time
- Can analyze the shape of the current-time curve in order to study coupled chemical reactions
- There are better ways to do both of these with more modern techniques
- Chronoamperometry is important because it is a fundamental method on which other techniques are based

Valuable Websites

- www.PrincetonAppliedResearch.com
  - Under "Literature" choose "Application Notes"
- www.Bioanalytical.com
- www.epsilon-web.net
- www.epsilon-web.net/Ec/manual/index.html
  - Select from topics & review introductory info

  e.g., Electrodes, Electrolyte Solutions, Voltammetry, Linear Sweep Voltammetry, Chronoamperometry, Chronopotentiometry, Pulsed Voltammetry/Polarography, Stripping Voltammetry, Controlled Potential Electrolysis, etc.