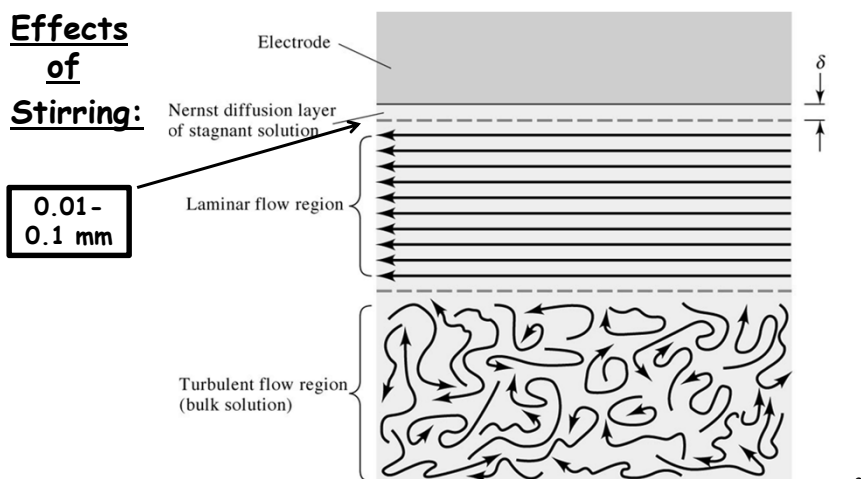


February 6, 2012

- **EChem**: Problem Set Solutions now posted
- **Intro to Optical Spectroscopy**:
 - Readings Posted
 - Problem Set Posted
- **EXAM #1 Info Page**
 - Now online
 - Will update as week progresses
 - Alternate times must be requested by Friday

Hydrodynamic Voltammetry



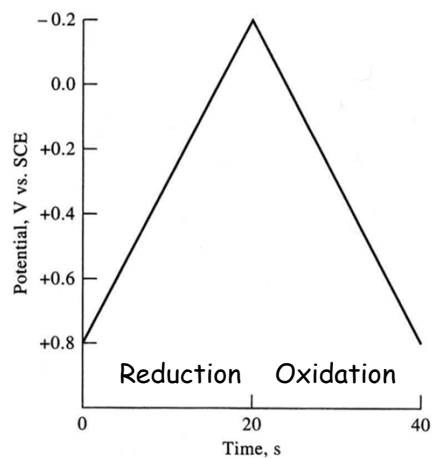
Other Working Electrodes

- ✓ Hanging Hg Drop Electrode (HMDE)
- ✓ Hg Thin Film Electrode
- ✓ Platinum
- ✓ Gold
- ✓ Carbon
- ✓ Rotating Disc Electrode (RDE)
- ✓ Microelectrodes

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Cyclic Voltammetry

- Unstirred solution
- Apply both an *anodic* and a *cathodic* sweep:



4

A Cyclic Voltammogram

System is *reversible* if:

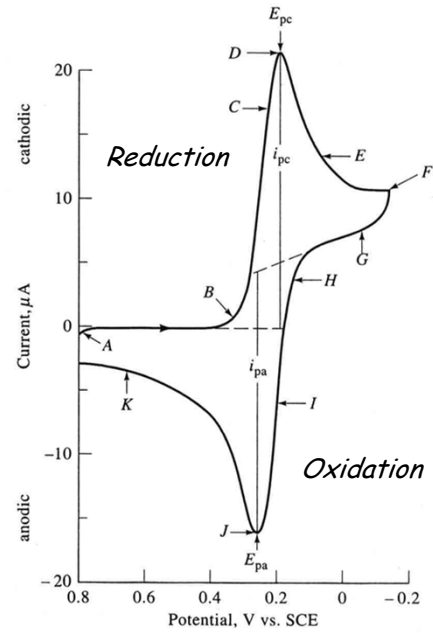
$$\Delta E = 0.0592/n$$

and

$$i_{pc} = i_{pa}$$

Note: $E_{pc} \neq E^{\circ}$

$$E_{pc} = E^{\circ} - 1.1[RT/nF]$$



Stripping Methods: The Ultimate in Detectability

■ Concept:

- *Pre-concentrate* analyte species onto electrode (electrolysis)
- *Strip* reduced species off of electrode and measure current (voltammetry)

■ Requirement:

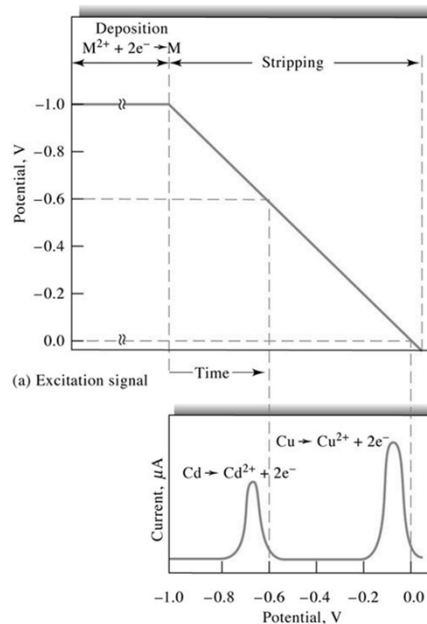
Reduced analyte must form an *amalgam* with electrode

Anodic Stripping Voltammetry (ASV)

- Use a HMDE or Hg Thin Film Electrode
- Stir solution and apply potential ~ 200 mV more negative than E° of analyte
 - Allow reduction to proceed for 5 - 60 minutes
 - Stop electrolysis and stop stirring solution
- ➔ Apply a *slow ANODIC* potential ramp (or differential pulse measurement)
- ➔ Measure current due to *oxidation of reduced analyte species*

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ASV: Example



(b) Voltammogram
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DPP-ASV: Multi-Component Ultra-Trace Analysis

-all components must
be able to form an
amalgam with Hg
(about 15 - 20
elements can)

-Detection limits can
be as low as $10^{-9} M$

