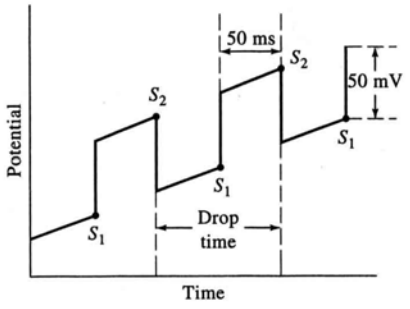
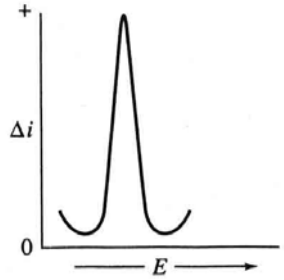
February 11, 2005

- **Exam #1:** Wed Feb 16th – See Info page!
- **Review Session:**
  - Sunday, Feb 13th, 7 pm
  - B203 Angell
  - Come with questions!
- **Office Hours:**
  - Modified for today: 3:30 – 4:30 (300 Waterman)

Differential Pulse Polarography: Peaks!

- Make a *differential* current measurement to change the shape of the polarogram:

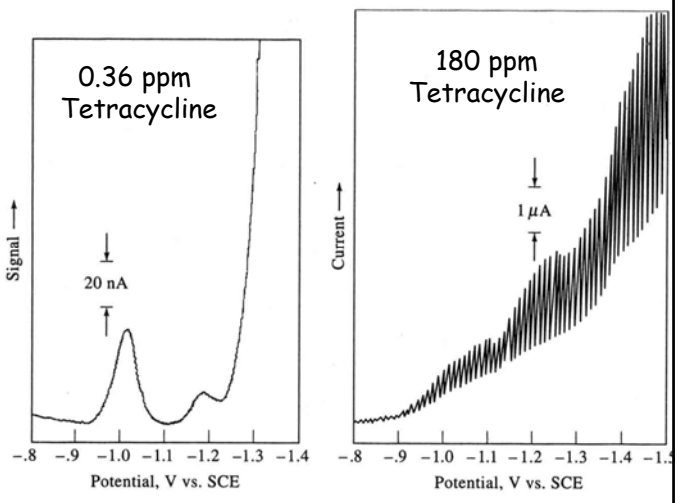




- $\Delta i = S_2 - S_1$
- Plot Δi versus E_{appl}

Benefits of DPP

- ✓ **Resolution:**
  $\Delta E \approx 50$ mV
- ✓ **Det. Limits:**
  ~10^{-8} M

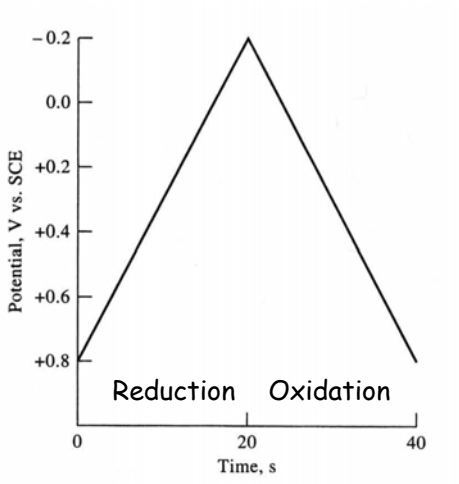


Other EChem Methods

- **ac Polarography**
  - -superimpose ±5 mV ac (10 - 50 Hz) potential onto linear sweep
  - -only measure *ac component* of current
  - -get a peak for any *reversible* analyte reaction
- **Square-Wave Polarography**
  - -apply an *increasing* square wave potential ramp
  - -use on a *single Hg drop*
  - -*rapid* sweep (scan 1 volt in <1 second)
  - -differential current measurement (get a *peak*)

Cyclic Voltammetry

- On a single Hg drop (HMDE), apply both an *anodic* and a *cathodic* sweep:



A Cyclic Voltammogram

System is *reversible* if:

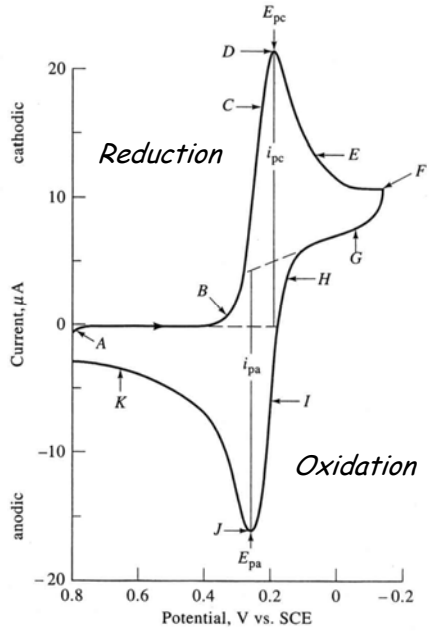
$$\Delta E = 0.0592/n$$

and

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

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

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



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 Hg electrode

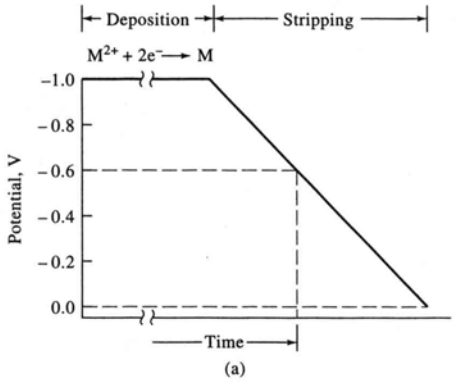
Anodic Stripping Voltammetry (ASV)

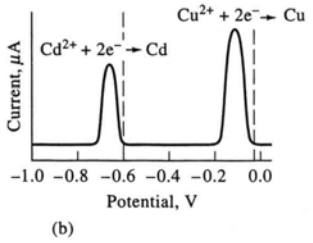
- Use a HMDE
- Stir solution and apply potential ~200 mV more negative than E^o of analyte
  - Allow reduction to proceed for *5 - 60 minutes*
  - Stop electrolysis and stop stirring solution

➲ Apply a *slow* ANODIC potential ramp (or DPP)
➲ Measure current due to *oxidation of reduced analyte species*

ASV: *Example*

Can you find the mistake?





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***