Amperometry &Voltammetry

•Non-equilibrium electrochemistry!

•Based on Electrolytic Cells---apply external voltage to pair of electrodes to force rxn to occur--get current flow---current α [conc]

$$E_{elect} = E^{o}_{ox/red} + \frac{0.059}{n} \log \frac{a_{ox}}{a_{red}}$$

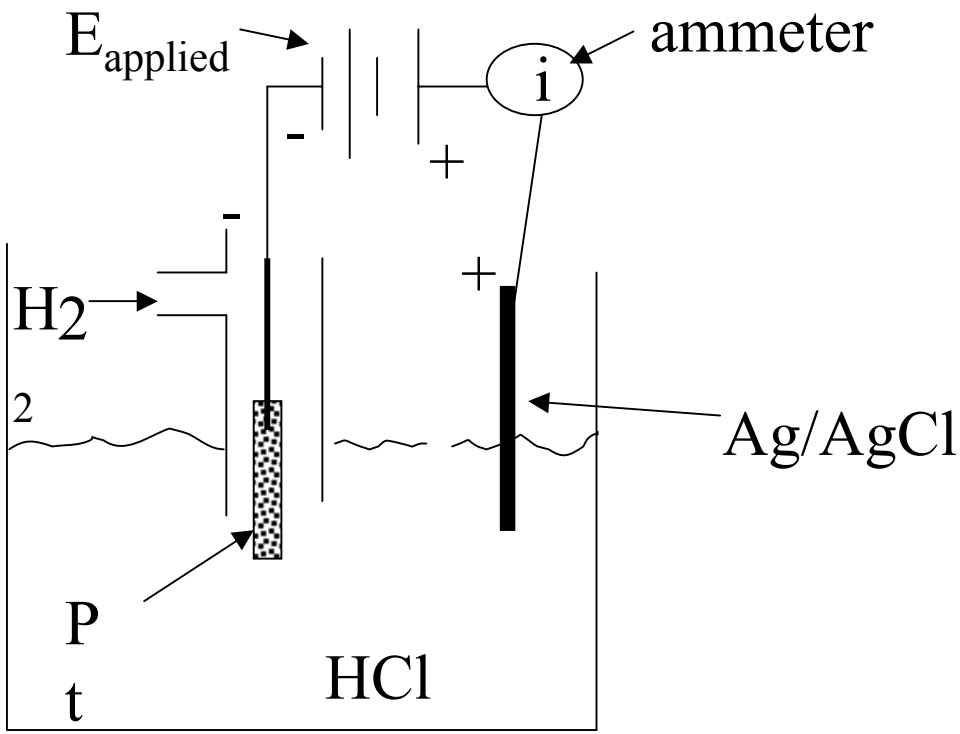
Control potential of working electrode--

a_{ox} and a_{red} must adjust and change activities based on applied potential to electrode

Lets look again at following cell:

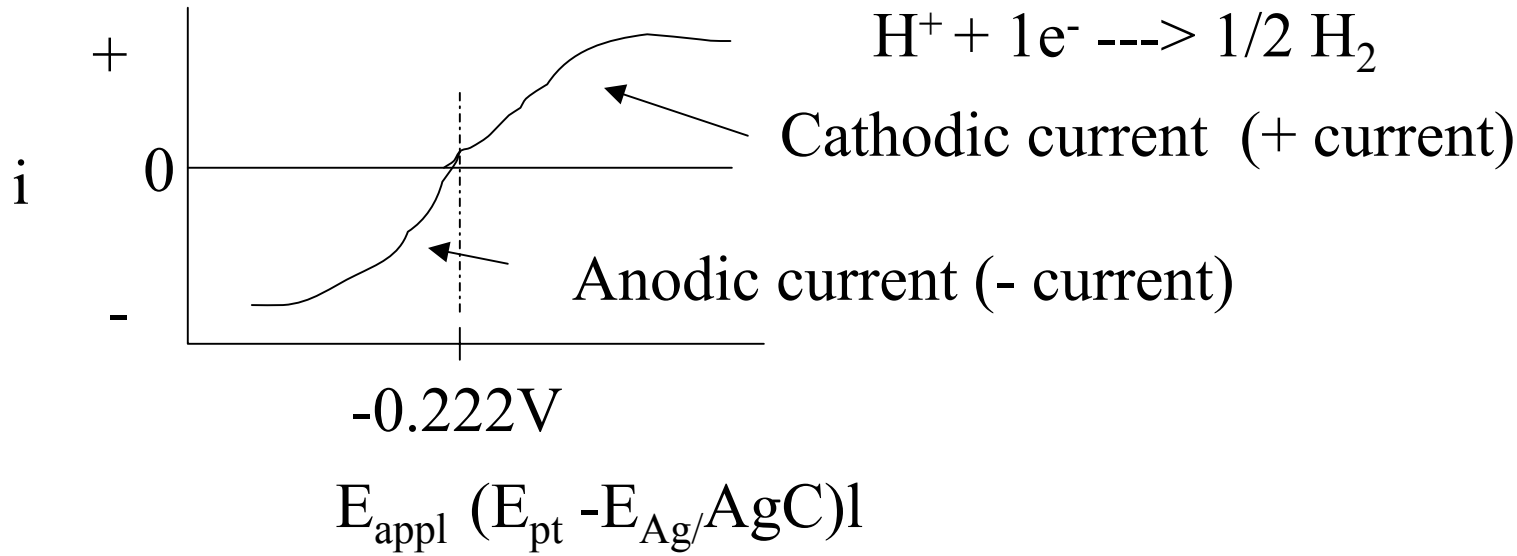
Pt/H_2 (1 atm), HCl (1M), $AgCl_{(s)}/Ag$ $\quad E_{cell} = E_{Ag/AgCl} - E_{NHE} = +0.222V$

Now let us hook up battery to cell which opposes EMF of this galvanic cell:



-if battery applies < 0.222V; then Cell will discharge as before---with Ag/AgCl electrode being cathode
-if battery applies exactly 0.222V; cell will be at equilibrium--nothing will happen--NO current---analogous to null point experiment
-if battery applies > 0.222V--we have electrolytic cell, and the cathode would be the Pt electrode--- and the anode would be the Ag/AgCl electrode

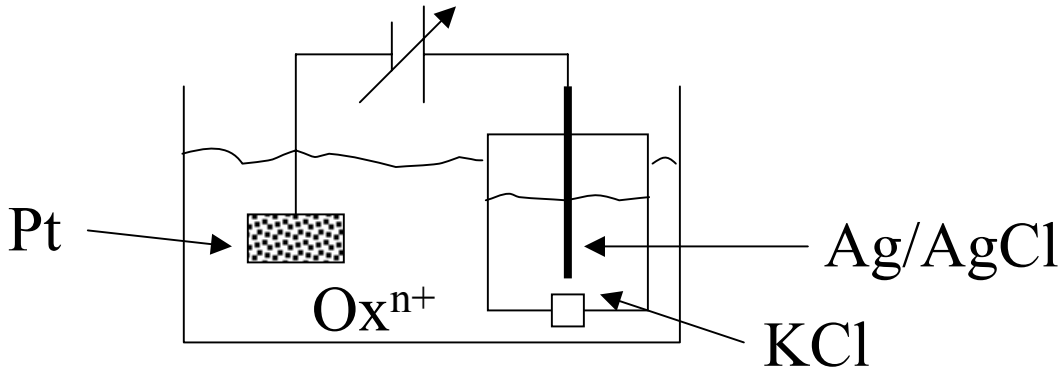
Cathode of original cell becomes anode---
Anode of orginal cell becomes cathode



For electrolytic cell: $E_{appl} = E_w - E_{ref} - iR$

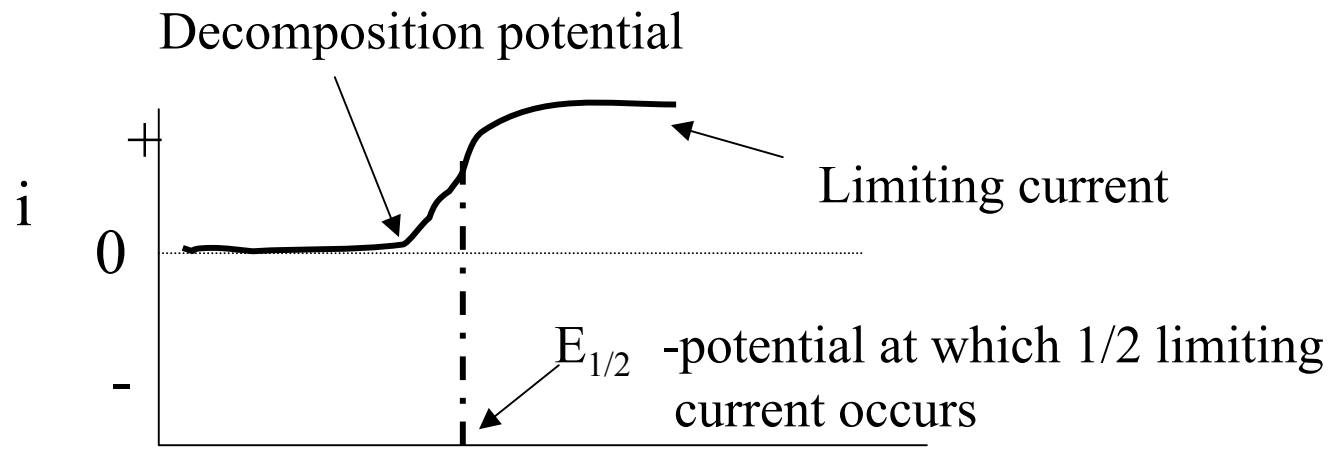
R=resistance to current flow---usually due to resistance of electrolyte solution---but also due to resistance to mass transfer of species to electrode surfaces (diffusion)!

Now---replace NHE with plain Pt only electrode--- no H_2 gas; and place Ag/AgCl in separate compartment---and add Ox^{n+} (but no red)



There is no reversible redox couple at Pt electrode-would not yield stable potential if you try to measure cell potential---because Red is not present

Now if you start applying external voltage---gradually making Pt more negative:



$$E_{appl} = E_{Pt} - E_{Ag/AgCl}$$

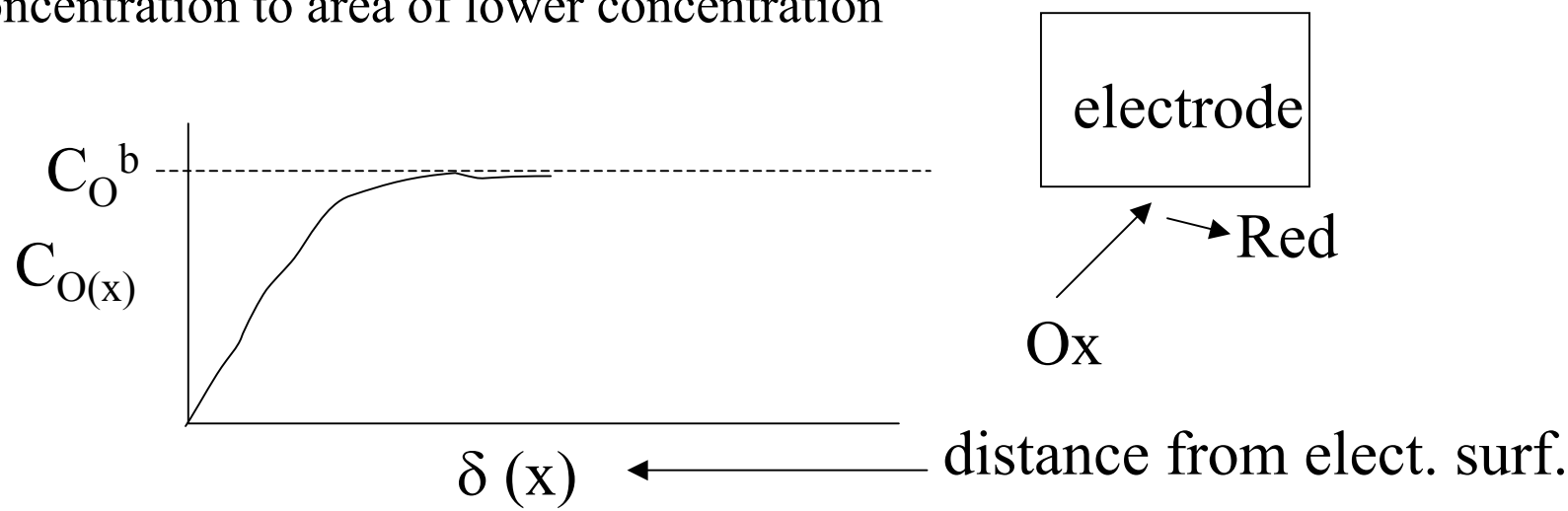
$E_{1/2}$ usually close to E^o value for ---

$Ox + ne^- <----> Red$

if this reaction is reversible at Pt working electrode surface---- however, if <u>electron transfer kinetics</u> are slow for <u>heterogeneous</u> reaction---then potential required to reduce Ox ----> Red will be more negative than E^o value---

<u>Diffusion</u>---key form of mass transport for all amperometric/voltammetric measurements--- always present, whether you have convection (stir solution) or not!

Occurs due to concentration gradient of electroactive species from area of higher concentration to area of lower concentration



$$flux = rate = D\frac{dC}{dx}$$ Fick's law of diffusion!

D= diffusion coeff.; cm^2/sec

dC/dx = concentration gradient--change in conc. of electroactive species per unit distance

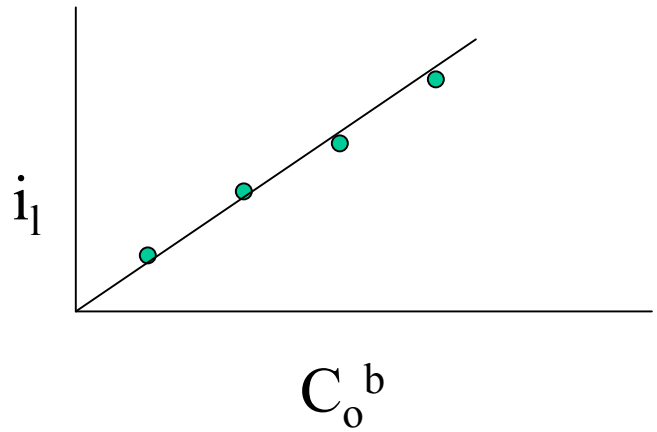
dx = δ = diffusion layer thickness

For any voltammetric/amperometric experiment--

$i = nFAm_o (C_o^b - C_o^{x=0})$

$i_l = nFAm_o C_o^b$ ----when conc. of electroactive species approaches zero near the surface----rate of electron transfer rxn at surface of electrode is limited by diffusion--how fast Ox moves up to surface!-- **$i_l = k [ox]$ ---linear relationship**

A= area of electrode (cm^2); m_o=mass transfer coeff. (D/δ)



The limiting current will be directly proportional to conc. of electroactive species!

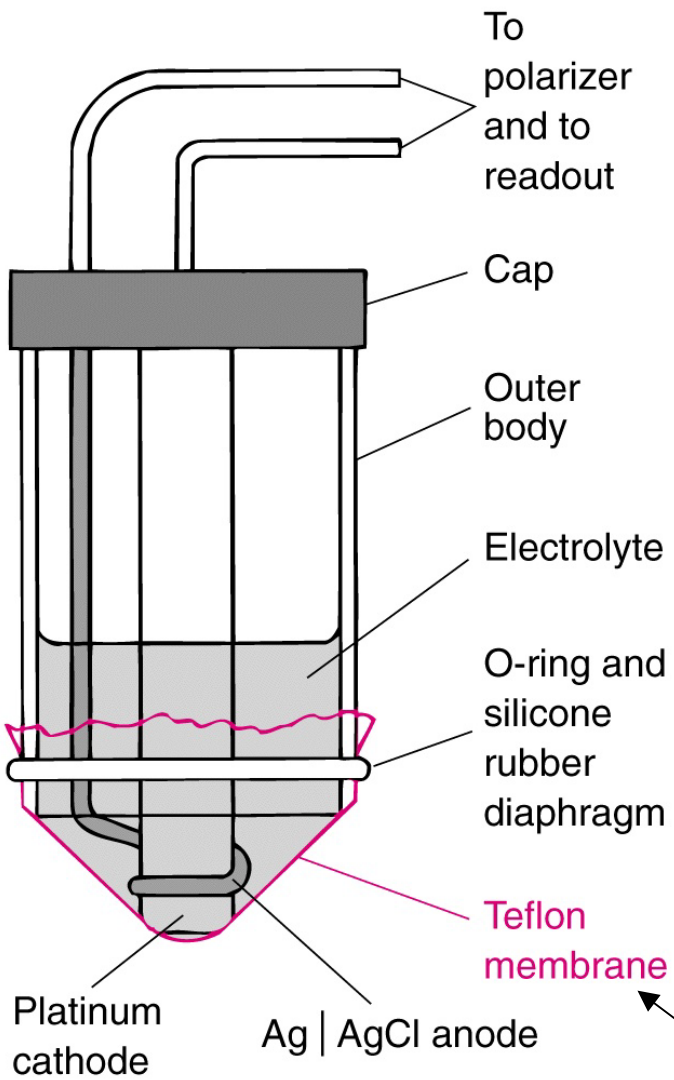
If you do amperometry---you simply apply a constant voltage to working electrode---usually at potential where limiting current will occur---and monitor current----

In voltammetry--we scan E_{appl} and record current as the voltage applied is changing!

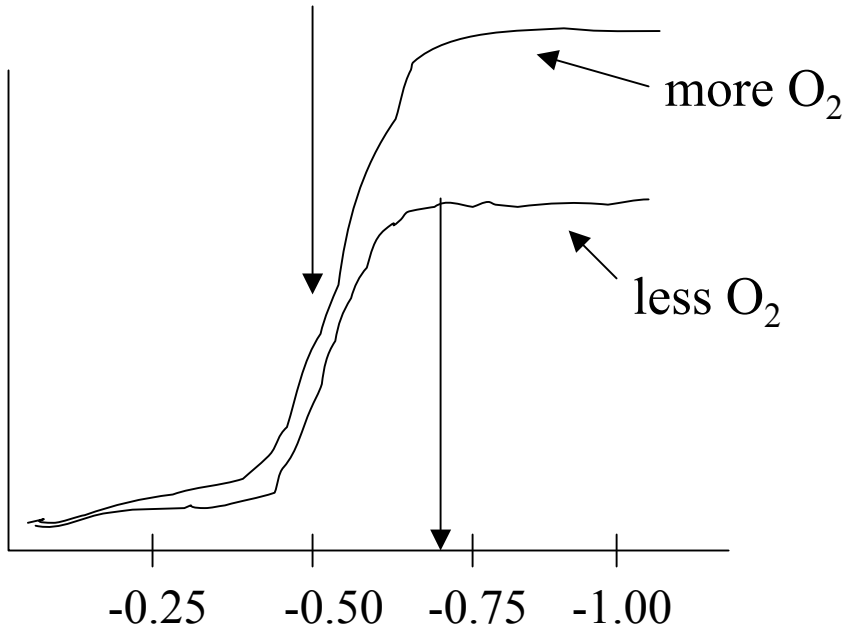
note: If Red only was present--we would need to apply + voltage to oxidize----everything is same except $i_l = k\, C_{red}$

Clark Amperometric Oxygen Sensor

$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$



(KCl)

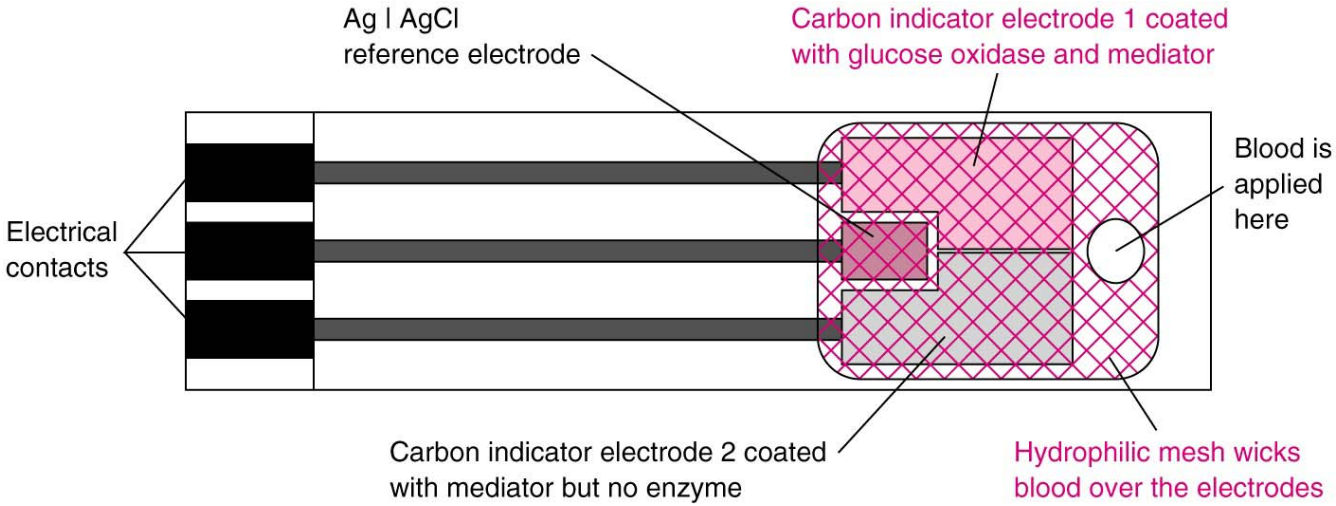


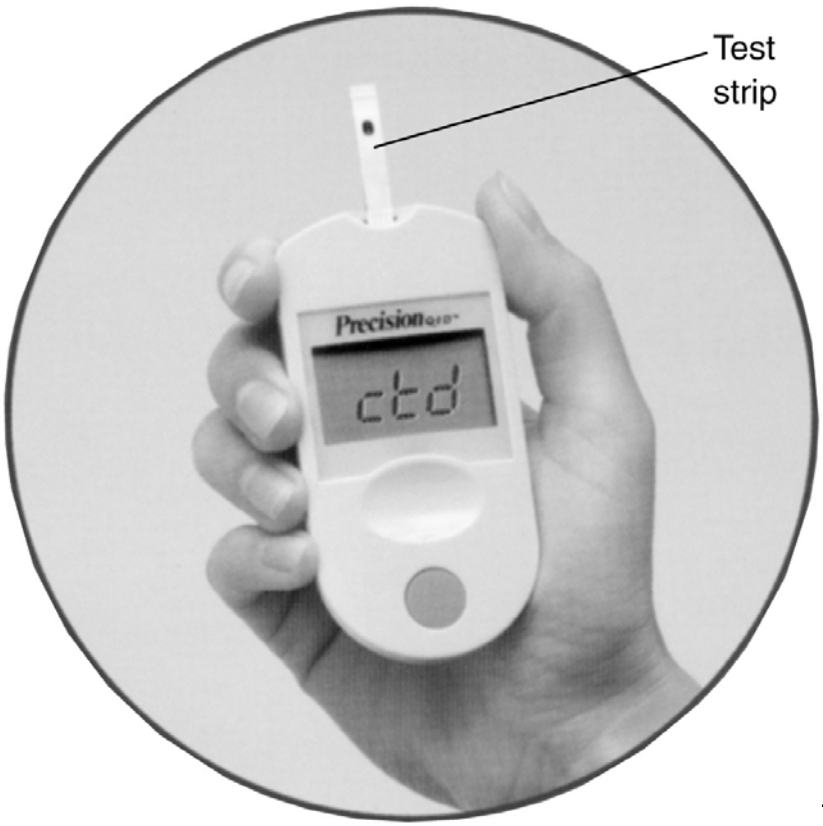
$E_{app} = E_{pt} - E_{Ag/Agcl}$

<u>At Ag/AgCl ref:</u>

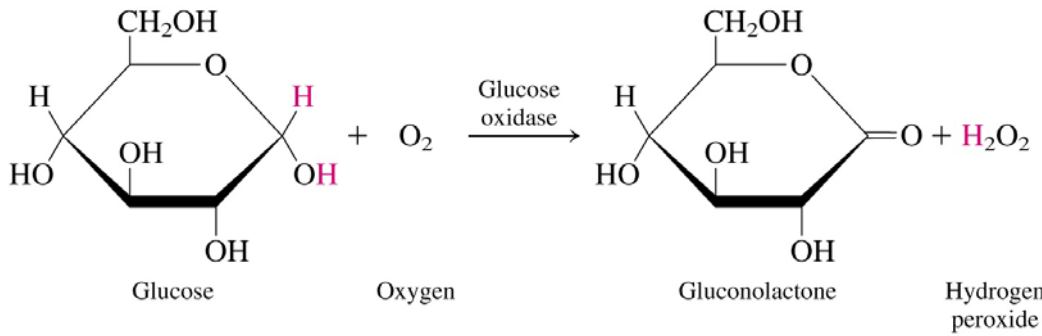
$4\ Ag + 4\ Cl^- \rightarrow 4AgCl + 4e^-$

gas permeable membrane



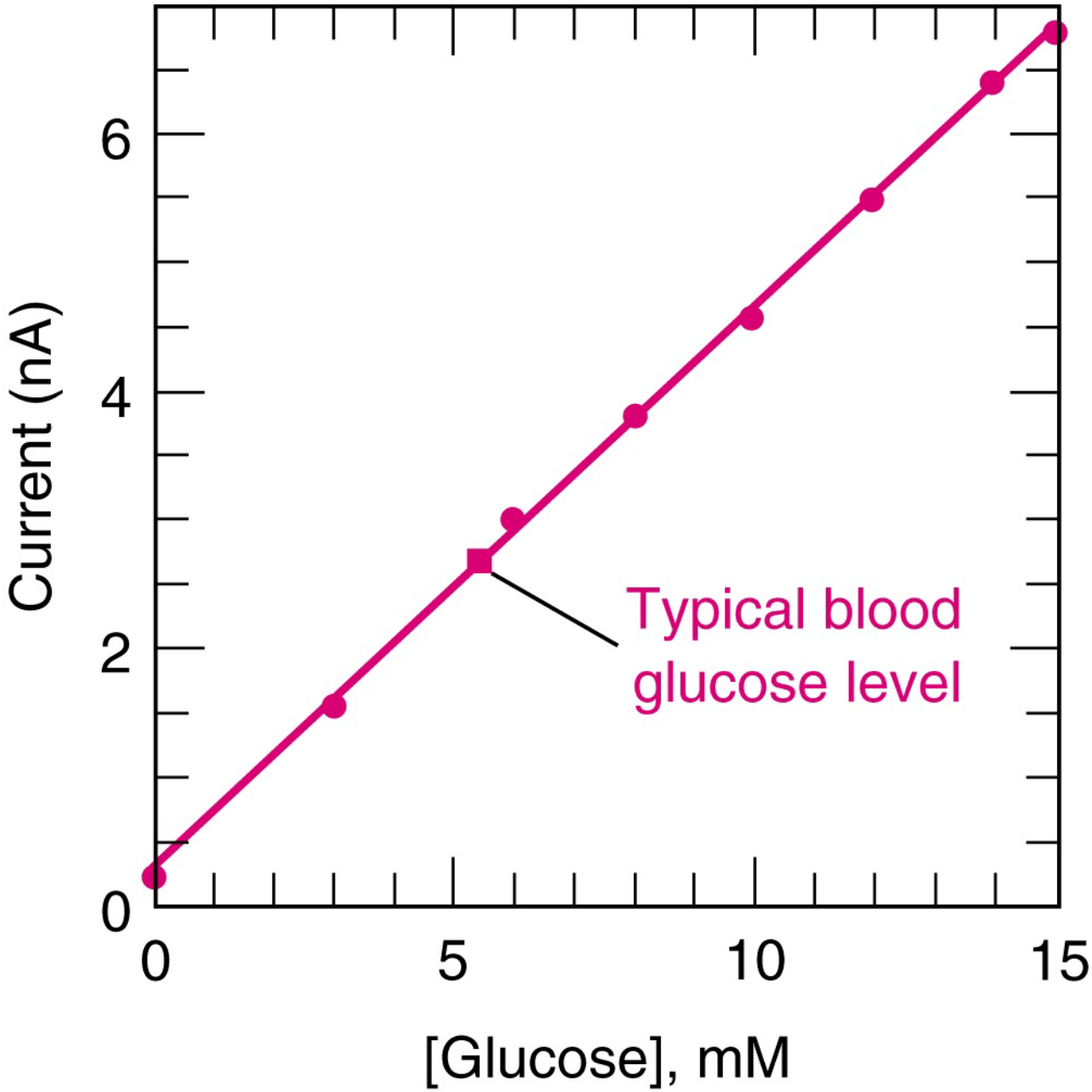


Another useful amperometric sensor---glucose sensor!

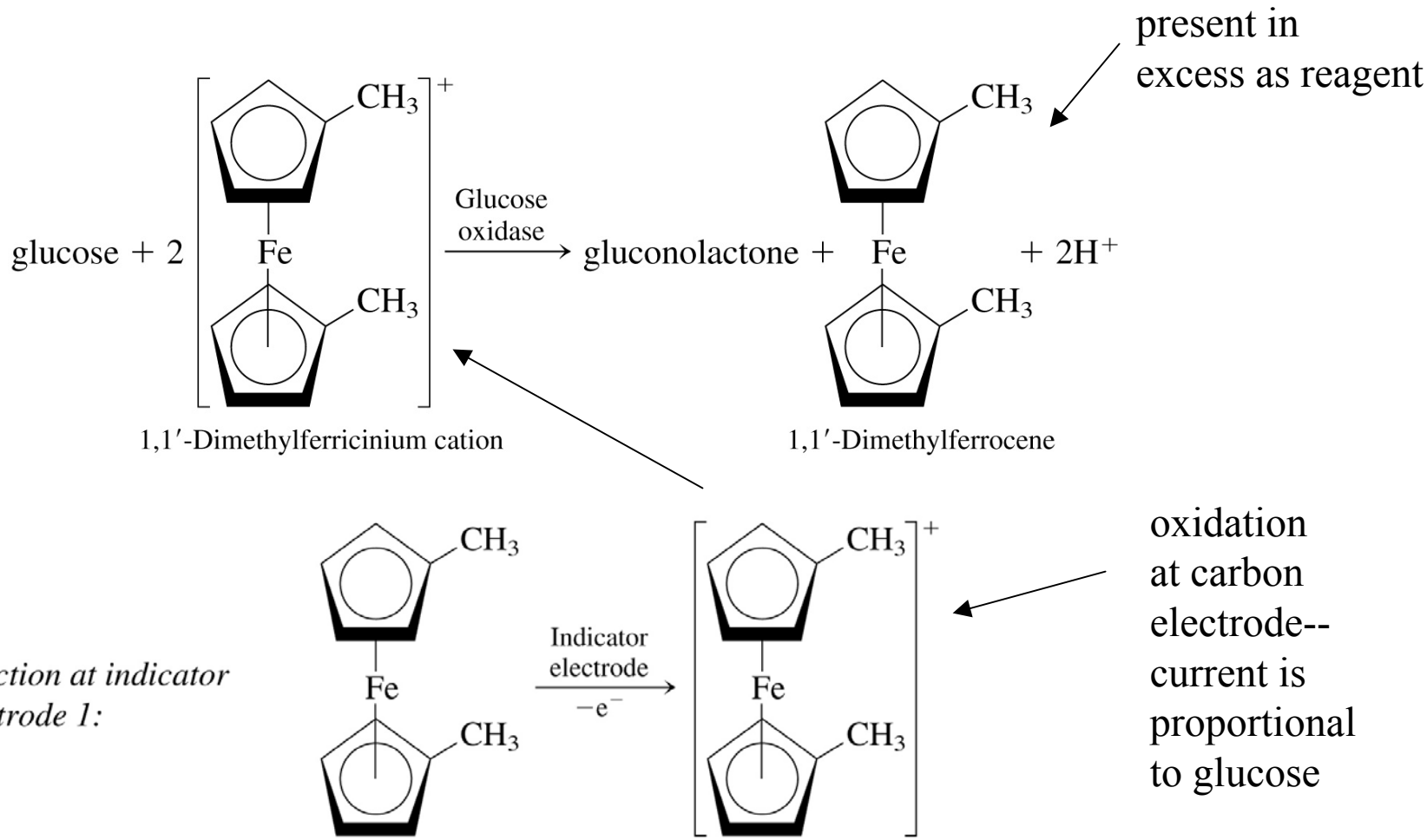


H_2O_2 -----> $O_2 + 2H^+ + 2e^-$

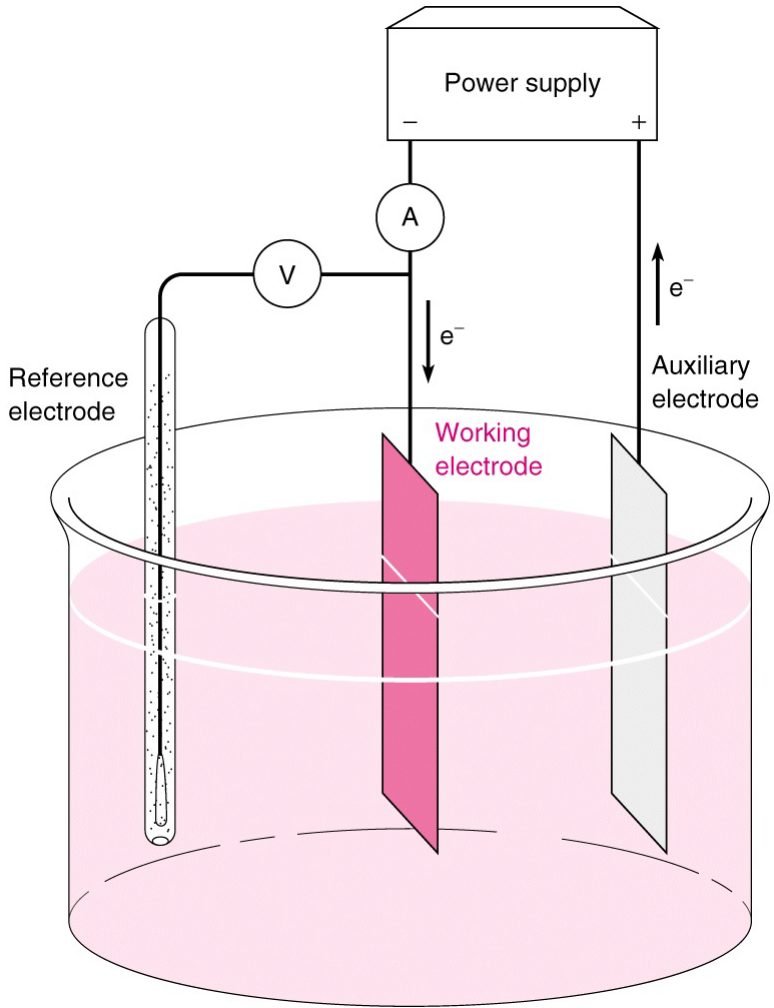
oxidation at carbon electrode---apply +0.6V vs. Ag/AgCl


Current (nA)
6
4
2
0
0
5
10
15
[Glucose], mM
Typical blood
glucose level

Problem with measuring peroxide---amperometrically----
reaction to generate H_2O_2 from glucose is limited by amount of oxygen present in blood sample----
<u>To avoid oxygen dependence</u>----use different electron acceptor---
Ferrocenium derivative!

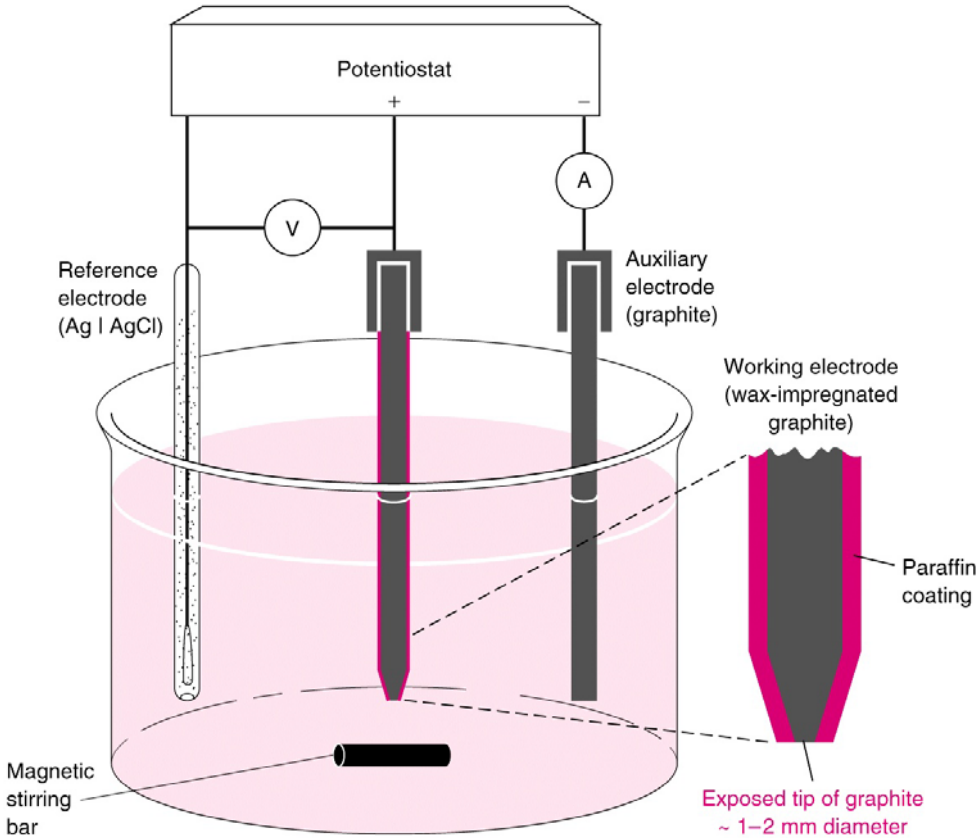


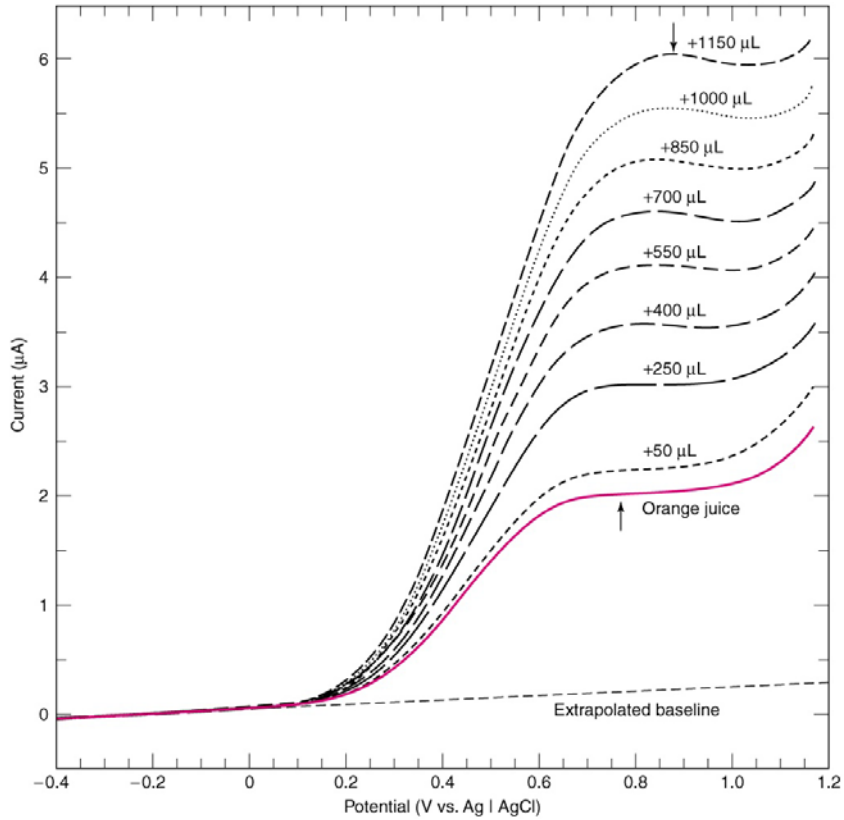
Three electrode amperometric/voltammetric cells!--used when current flowing through reference electrode would change potential of the reference electrode--by changing the surface concentration of the species that controls the potential (e.g., Ag/AgCl : $AgCl + e^- \rightarrow Ag + Cl^-$)



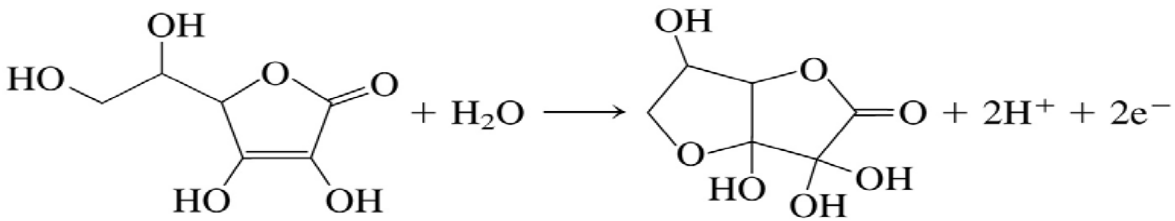
$[Cl^-]$ controls $E_{Ag/AgCl}$ value--
if reduction occurs
then [Cl] increases
near surface of elect-
$E_{Ag/Cl}$ --decreases

in 3-electrode config---
no current passes through
reference electrode---current
passes through working elect.
and auxiliary (counter)electrode!





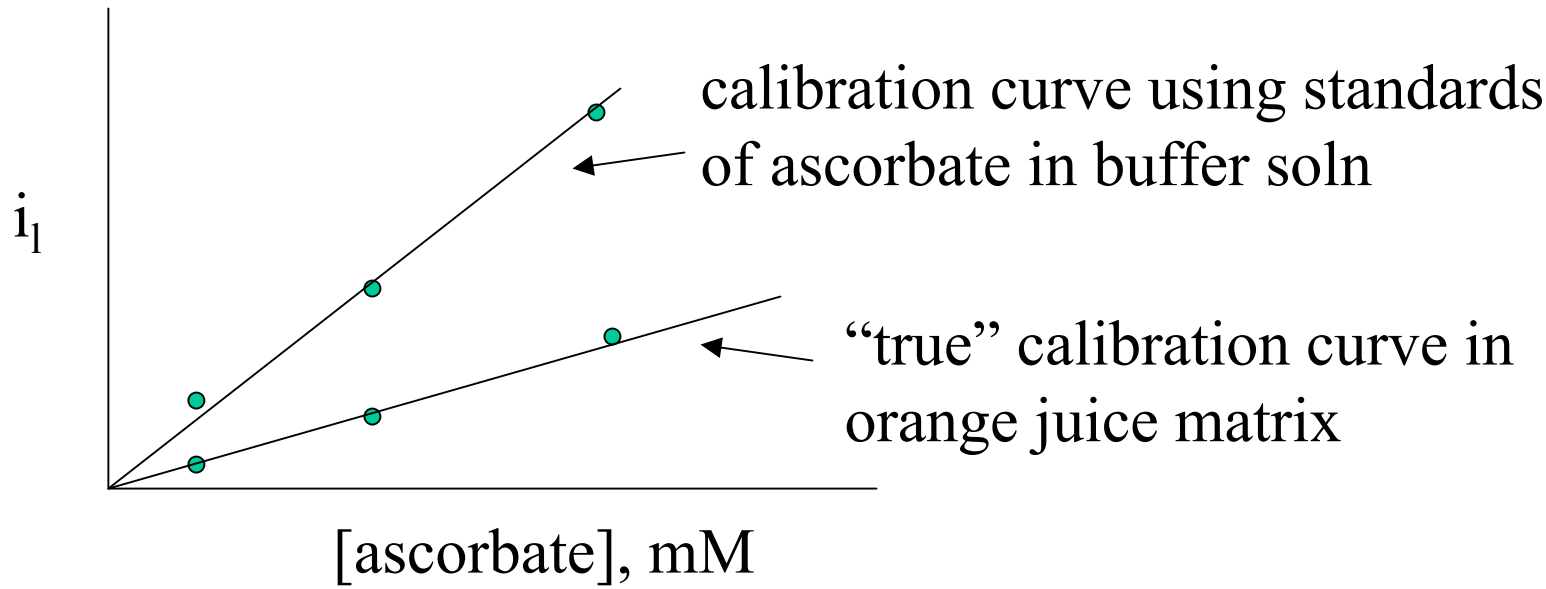
Working electrode:



Ascorbic acid (vitamin C)

Dehydroascorbic acid

In amperometric or voltammetric techniques---we often use method of Standard Addition technique---to obtain more accurate analytical results! Can't use calibration method--because slope--e.g., sensitivity toward analyte are different in the presence of sample matrix---then in matrix used to prepare standards!!--(**called Matrix Effect!!)**



In voltammtric/amperometric techniques---when bare electrode are used----can often get matrix effect---(e.g. difference in mass transport of analyte to surface of electrode in presence of sample components (viscosity); also adsorption of species blocks sites on elect. for e^- transfer to occur (appears like less area of electrode).

For standard addition method you do following:

-obtain signal from sample directly---I_x

-spike sample with known amount of standard analyte x, to change concentration, and obtain a new signal --I_{x+s}

-sometimes we make multiple standard additions (we shall see), and record the new signal each time

In effect, we are calibrating *in situ*---in the presence of the sample matrix---determining the sensitivity (slope) toward the analyte!

For single standard addition, we can use equation:

$$\frac{[x]_i}{[x]_f + [s]_f} = \frac{I_x}{I_{x+s}}$$

where: $[x]_f = [x]_i \frac{V_o}{V_f}$

$$[s]_f = [s]_i \frac{V_s}{V_f}$$

then solve for $[x]_i$

V_f = final vol. V_s = vol. of std. added; V_o = initial vol. sample

$[x]_f$ = final conc. of analyte from sam.; $[x]_I$ = unknown conc.

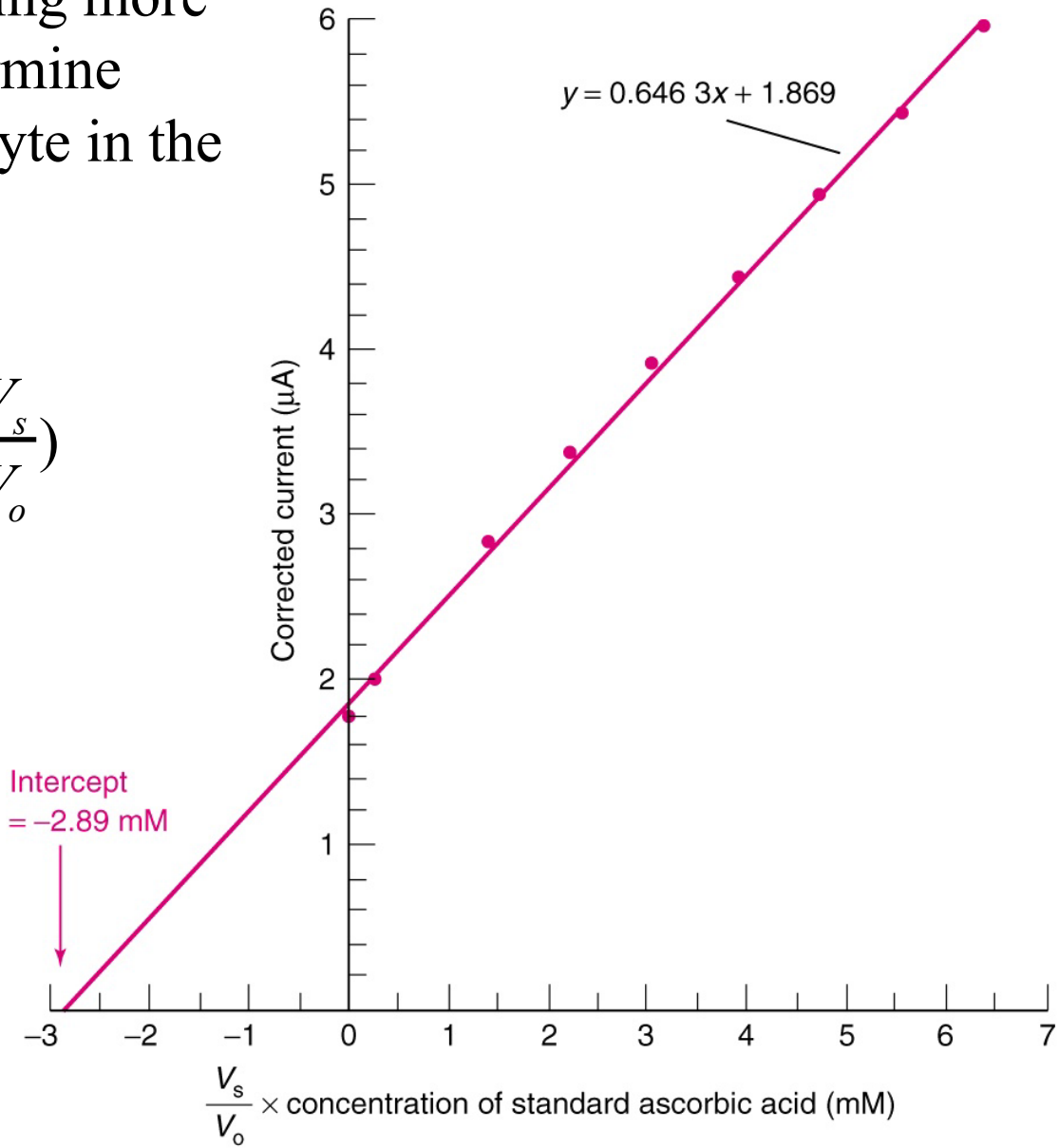
Multiple Standard Addition--
better since you are using more concentrations to determine sensitivity toward analyte in the given matrix!

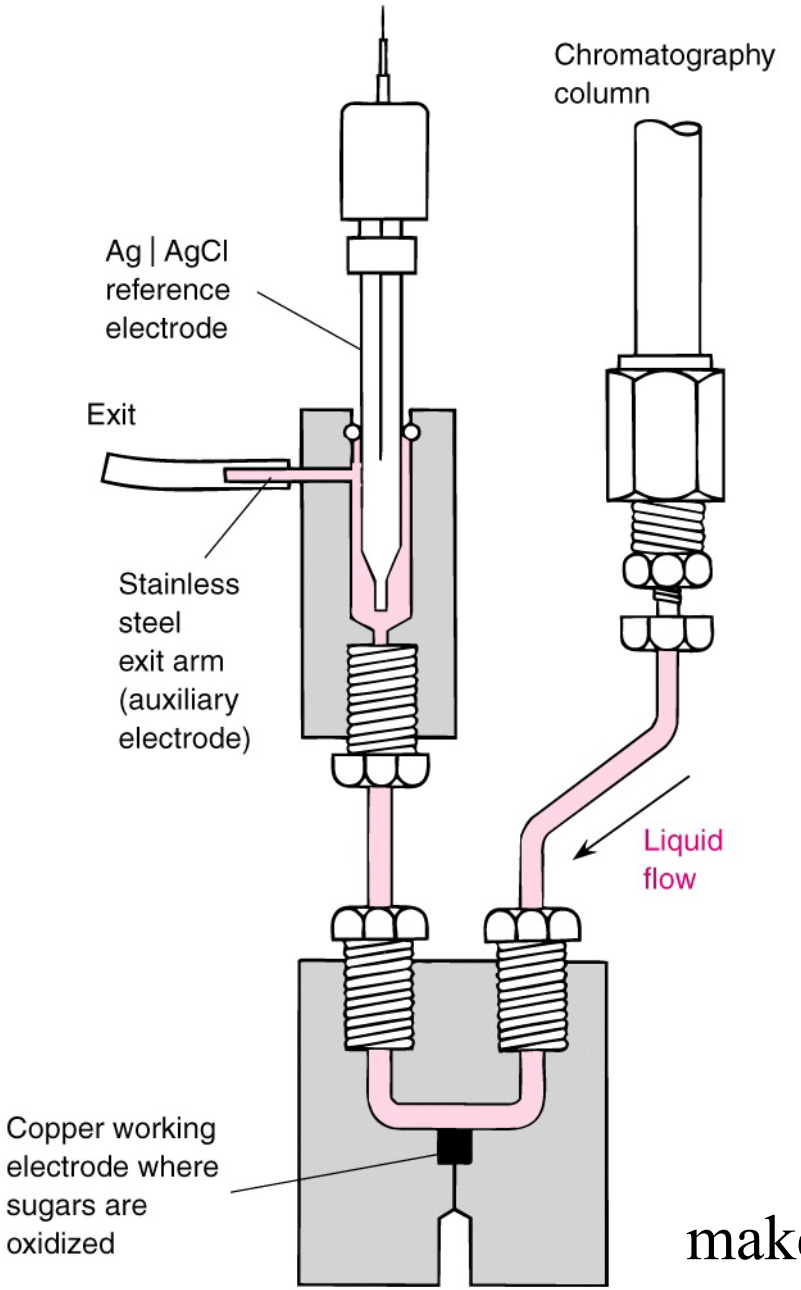
$$I_{x+s}\frac{V_f}{V_o} = I_x + \frac{I_x}{[x]_i}[s]_i\left(\frac{V_s}{V_o}\right)$$

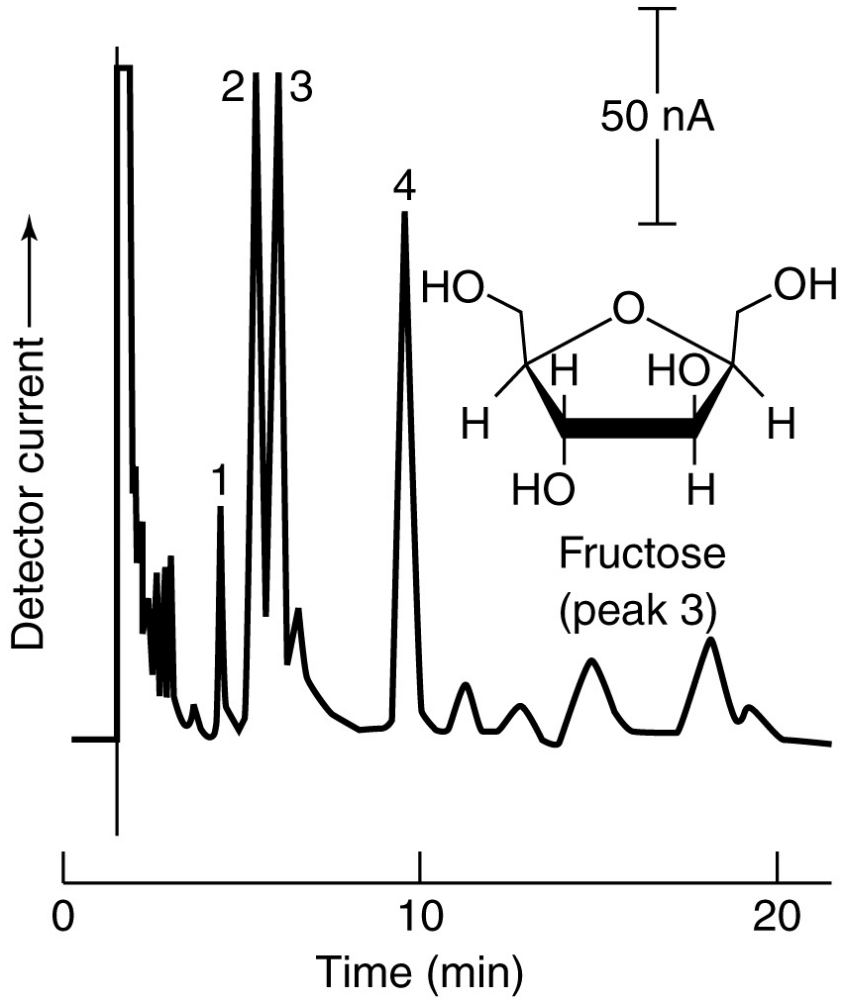
$$y = b + mx$$

when y = 0;

$b/m = -x = [x]_i$

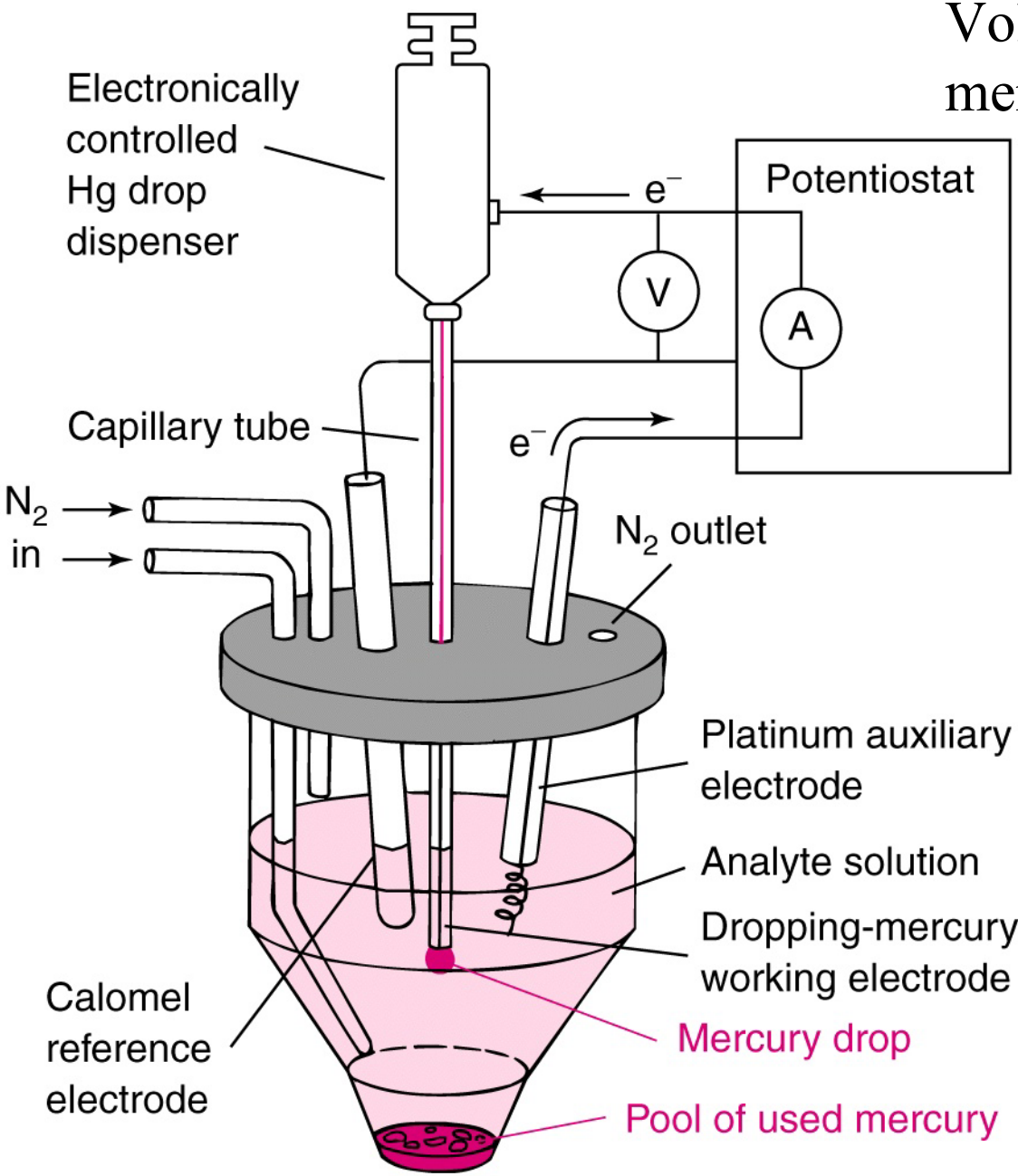




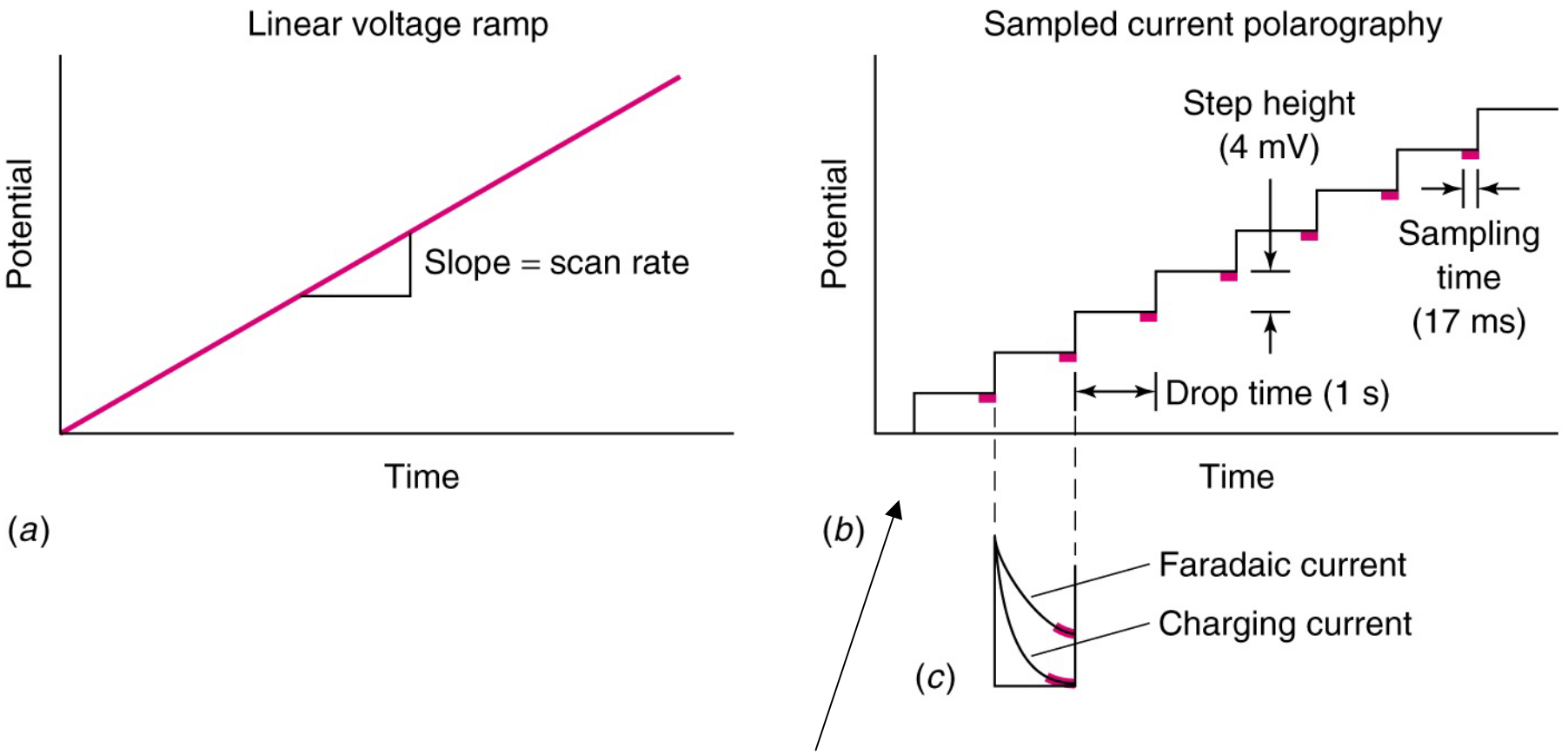


make E_{appl} to working electrode--positive enough to oxidize all the sugars as they elute!

Polarography--special case of Voltammetry----uses dropping mercury electrode (DME)--

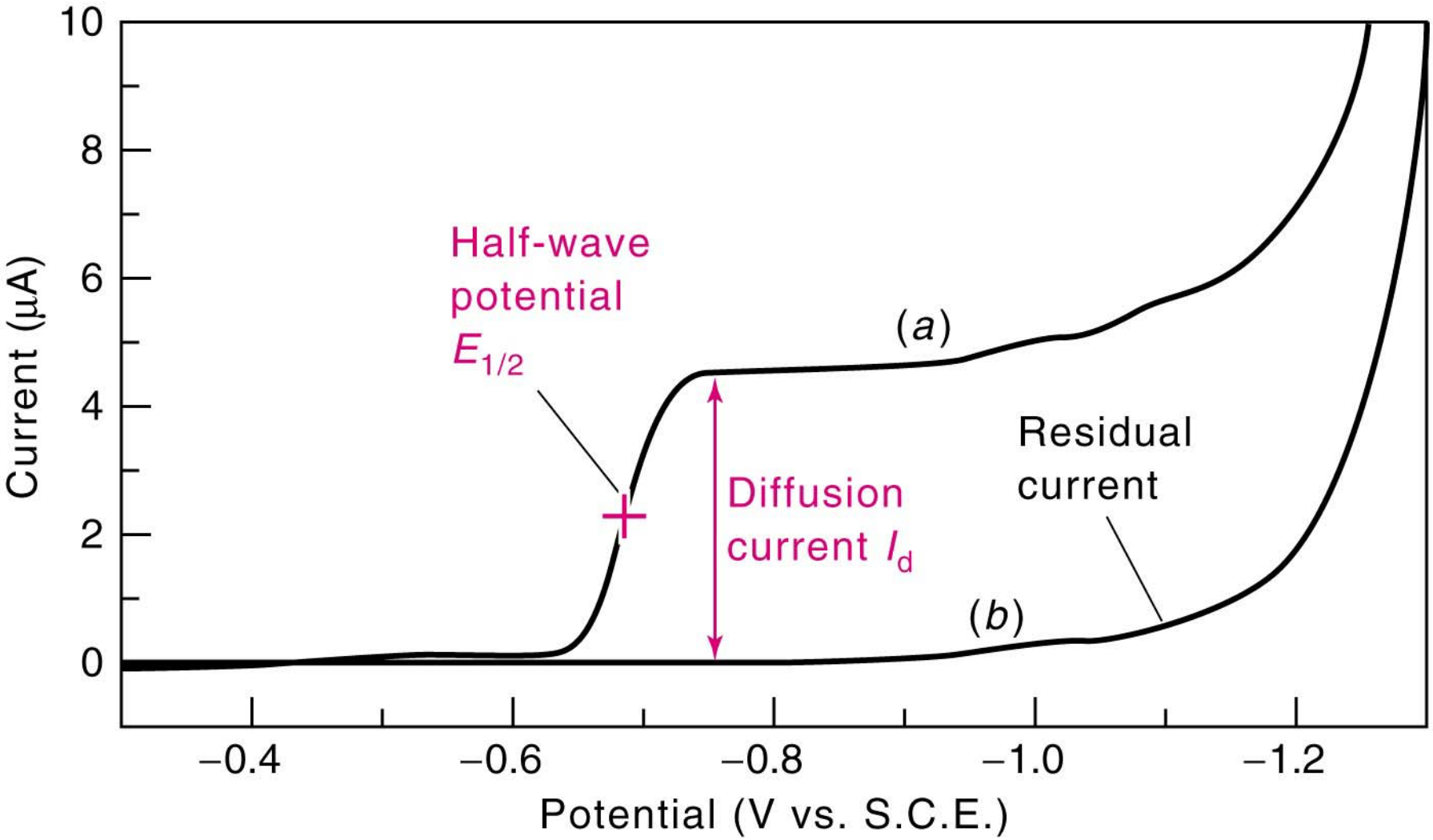


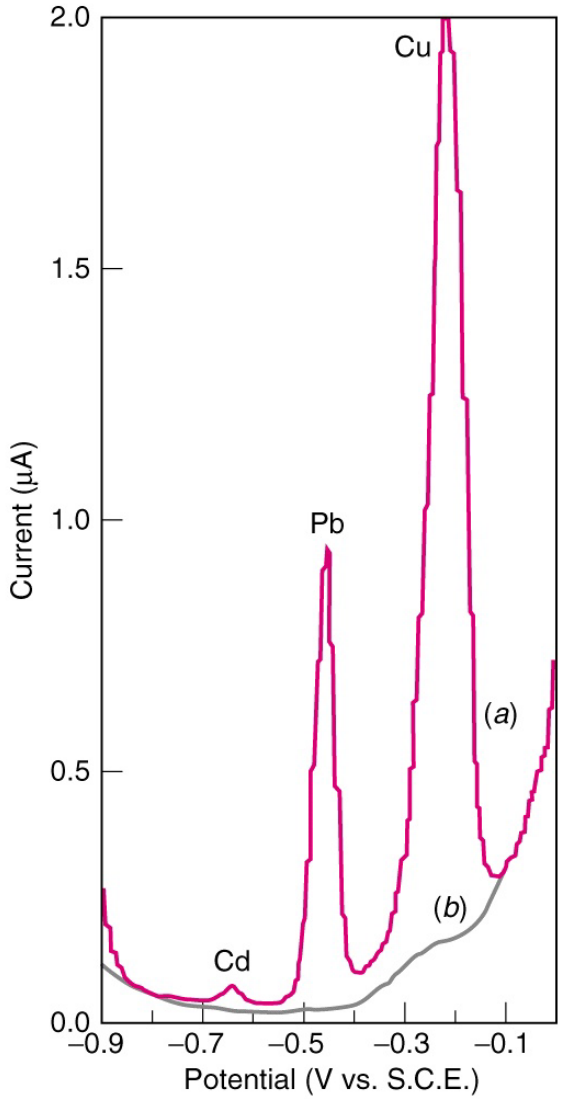
DME give fresh electrode surface all the time---no fouling of electrode by adsorption of species in sample!



more sensitive for measuring Ox

Can't use polarography to measure Red---since at high + E_{appl}, Hg -->Hg^{+2} + 2 e^-


10
8
6
4
2
0
Current (μA)
Half-wave
potential
$E_{1/2}$
(a)
Residual
current
Diffusion
current I_d
(b)
−0.4
−0.6
−0.8
−1.0
−1.2
Potential (V vs. S.C.E.)



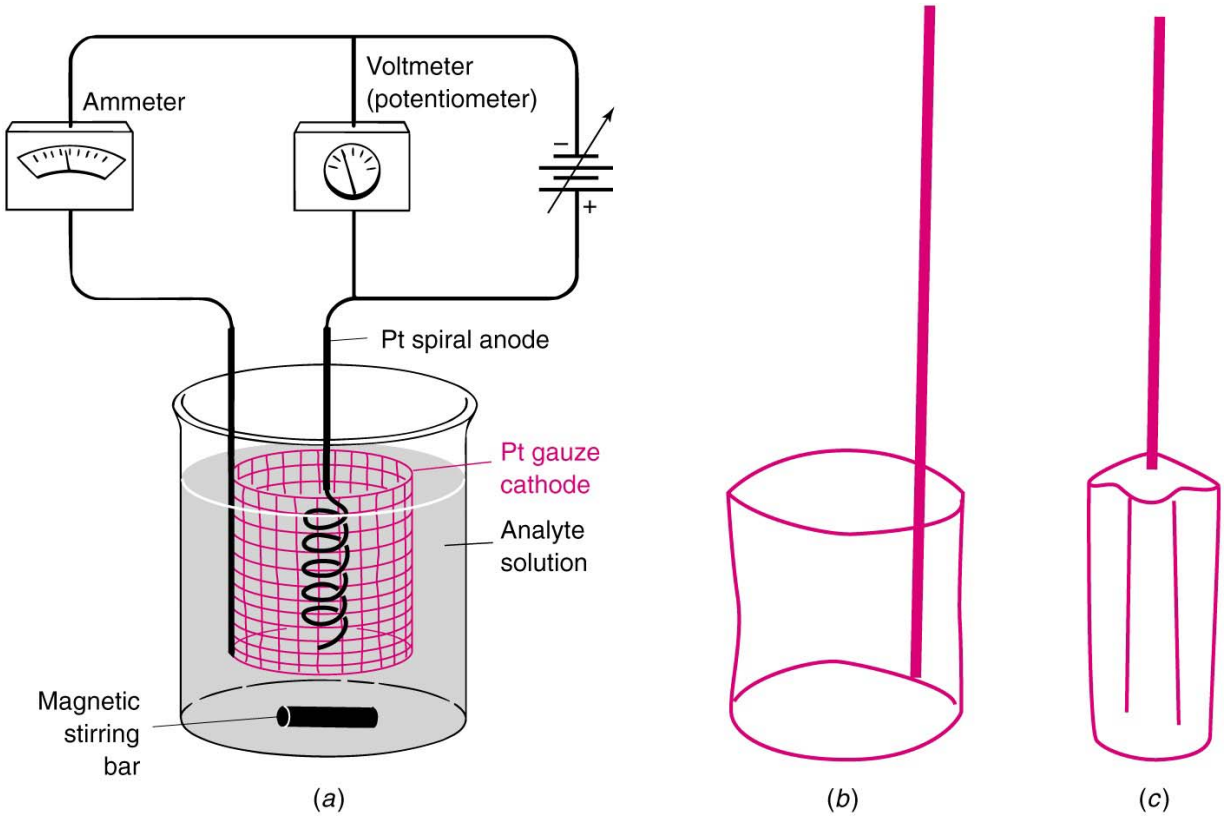
can detect down to 10^{-10} M metal ion in original sample!

Stripping Analysis---most sensitive of all voltammetric techniques---used to simultaneously detect metal ions----based on different E^0 values!

Usually use Hg film electrode---thin layer of liquid Hg on carbon electrode;

first step---apply very negative voltage to Hg film---and stir solution---to plate reduce all metal ions as $M^o(Hg)$ into Hg electrode.---$M^{+n}+ne^-$ --->M^{0-} longer you do this---more sensitive since you plate all metal ions out!

Then scan potential more positive and monitor current-due to oxidation $M^O(Hg)$ --> $M^{n+} + ne^-$

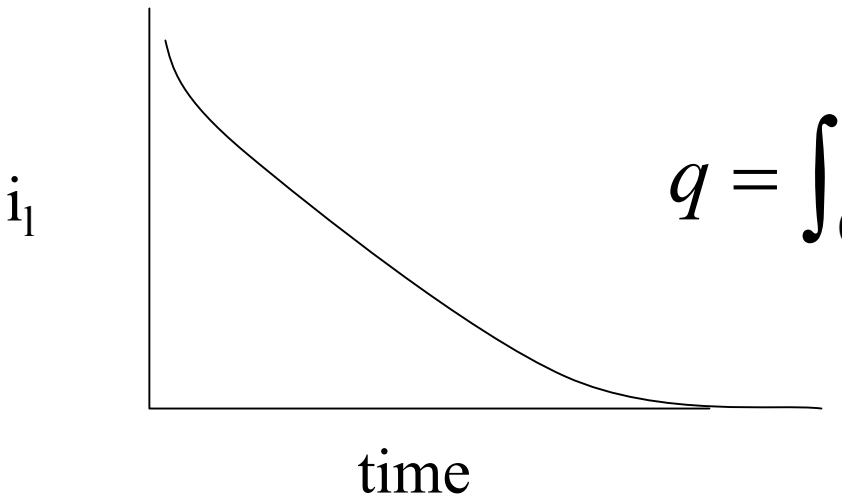


Techniques based on exhaustive electrolysis of sample---use large area electrode, and stir sample, so that can electrolyze all of Ox or Red analyte----

Electrogravimetry-----We talked about already---based on plating metal out---and weighing electrode!

coulometry---two methods;

-integrate total current flow over time---for given redox reaction at large area electrode; As analyte is consumed, and its conc. decreases, limiting current also decreases----



$$q = \int_0^t i dt$$

q= nF(moles electrolyzed)

moles = q/nF

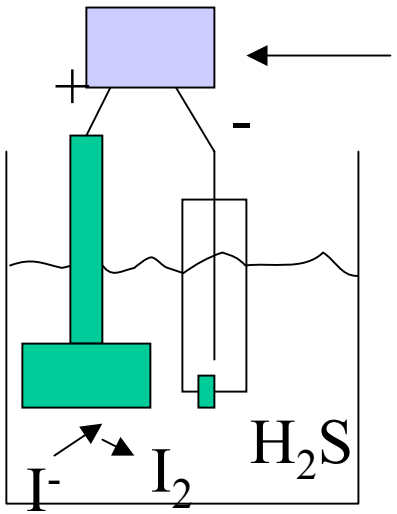
Must have 100% current efficiency---which means current measured as function of time can only come from analyte----must choose applied potential to electrode carefully to make sure other species (including solvent) are not being electrolyzed at that applied potential!

coulometric titrations: Use constant current supply--to generate titrant at known rate (based on constant current)

e.g., coulometric titration of H_2S ----

analytical reaction is : $I_2 + H_2S \text{ -----> } S_{(s)} + 2H^+ + 2\ I^-$

need to generate I_2 coulometrically at large area electrode---that is anode in cell; apply constant current through electrodes----
Add excess NaI to sample-----: $2\ I^- \text{ -----> } I_2 + 2\ e^-$ at anode



constant current source

current x time = coulombs (q)

q /nF = moles of I_2 generated to get to endpoint

Detect endpoint in this case by adding starch to solution---gives blue color with excess I_2

Another famous coulometric titration:

Determination of cyclohexene---by coulometric titration with Br_2

Br_2 + cyclohexene ------> dibromocyclohexane

(bromine adds across double bond!)

Use excess NaBr as reagent---and large electrode with constant current source to generate Br_2---

Use another pair of electrodes (Pt) electrodes as indicator electrodes to signal the first excess of Br_2 in the sample---
apply small voltage between two electrodes----(0.2 V or so)---can only get current flow if there is both Ox and Red in solution (red= Br^-; Ox = Br_2) ---so first appearance of current signals the endpoint!
(total of 4 electrodes are used---two to generate the Br_2 and two to detect the presence of excess Br_2)