

Chapter 17 – Electroanalytical Techniques

Homework – Due Monday, April 6

Problems 17-4, 17-9, 17-16, 17-25, 17-31

Potentiometry: No current, measure potential differences and relate to concentration of analyte (*Chapter 15*)

Techniques in Chapter 17 based on **electrolysis**: For example: apply a potential, force a redox reaction to go, measure the current.

What can you do with electrolysis-based techniques?

- Determine concentration of analytes
- Identify analytes
- Characterize redox behavior of analytes (how much voltage does it take to drive the reaction)

In theory, when no current is flowing, the potential should be stable. Ohm's Law - $E = IR$

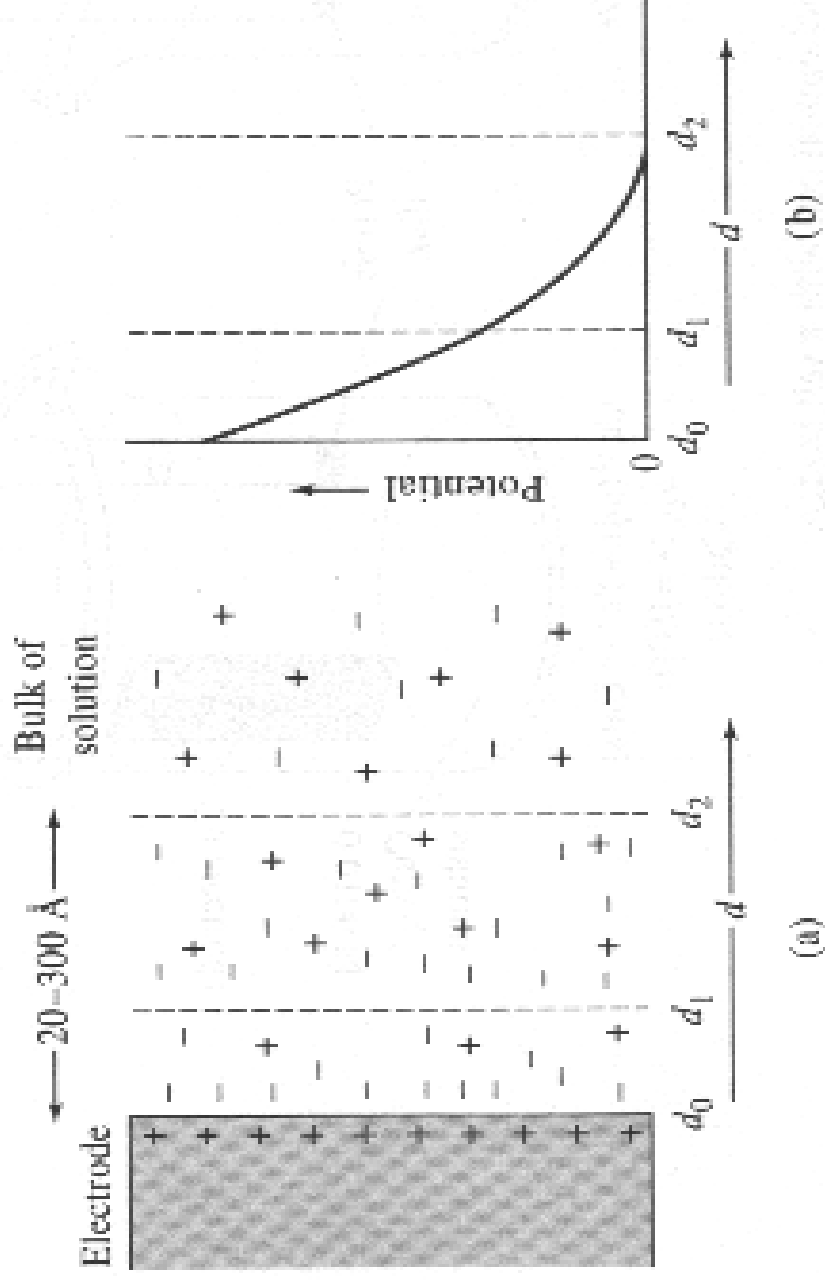
However in reality, when no current is flowing the following issues affect the potential:

- **Over potential** – the voltage needed to overcome the activation energy for a redox reaction to occur at the electrode. If you want the reaction to go fast (i.e. high current), then you apply high voltages.
- **Ohmic potential** – the voltage needed to overcome the resistance of the solution (high resistance solutions do provide easy migration of the ions).
- **Concentration polarization** – the concentration of ions at the surface of the electrode are less than they are in bulk solution.

Concentration Polarization

- Arises because of differing analyte concentrations in solution when a reaction is initiated
- An electrical layer is created at the electrode surface
- This layer resists the flow of electrical charge unless fresh ions are brought to the electrode

- Stirring
- Diffusion



How do you overcome or compensate for these issues?

Overpotential – choose an electrode material that minimizes the overpotential (like the evolution of H_2 at Pt has a smaller overpotential compared to evolution of H_2 at Hg).

Ohmic potential – add an electrolyte to increase the ionic strength of the solution which improves the conductivity of the solution (decreases the resistance). Higher conductivity means the ions are more mobile.

Concentration polarization – use methods to minimize the depletion of analyte concentration at the electrode surface (convection, flow cells, etc.).

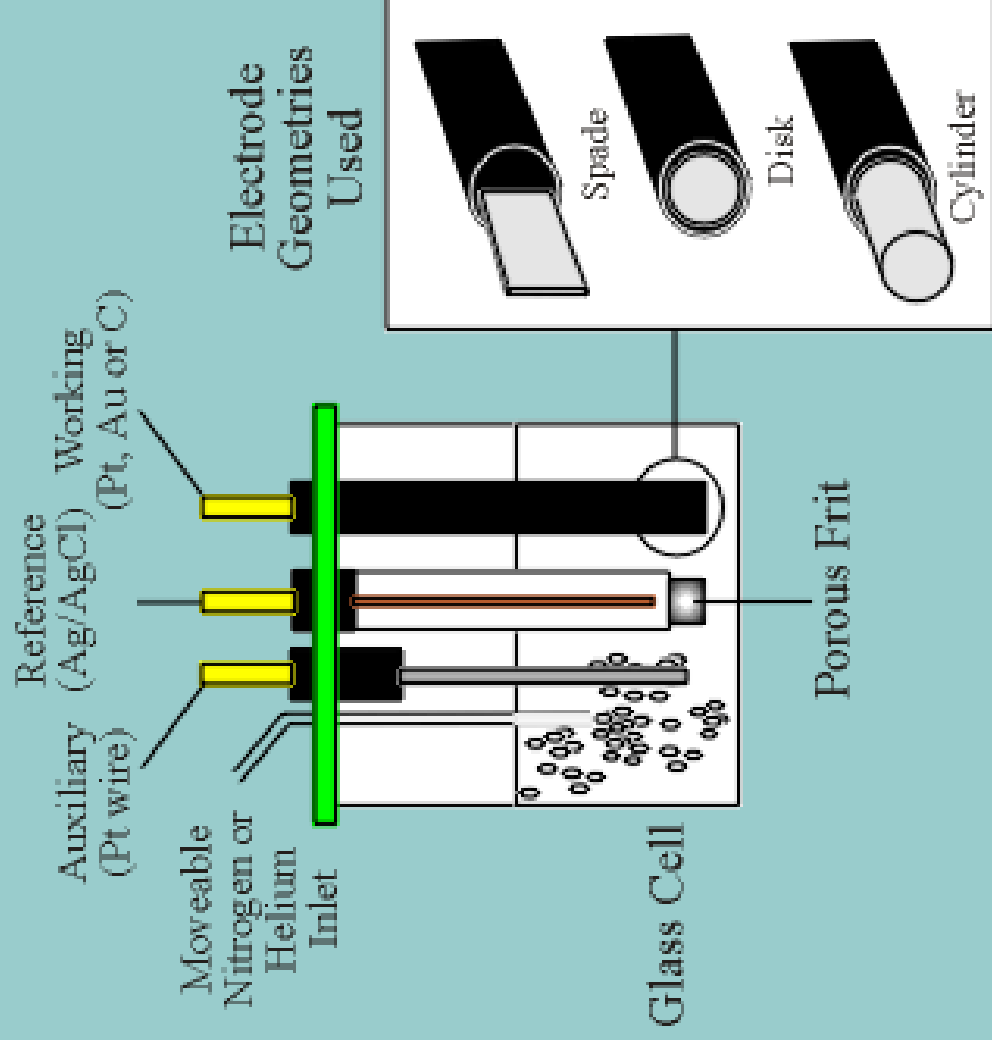
Three-Electrode System

- When current is flowing, the potential is changing.
- We want to affect the current/potential at the working electrode (where our redox reaction of interest is occurring).
- However, we want the reference electrode to stay stable.
- With only 2 electrodes (working and reference), there will be current flowing making the reference unstable.

Overcome instability in reference electrode under electrolysis conditions by introducing a 3rd electrode.

- Auxiliary (or counter) electrode
- Purpose of 3rd electrode is to allow current to flow between working and auxiliary electrodes but measure potential between working and reference electrodes.

Electrodes

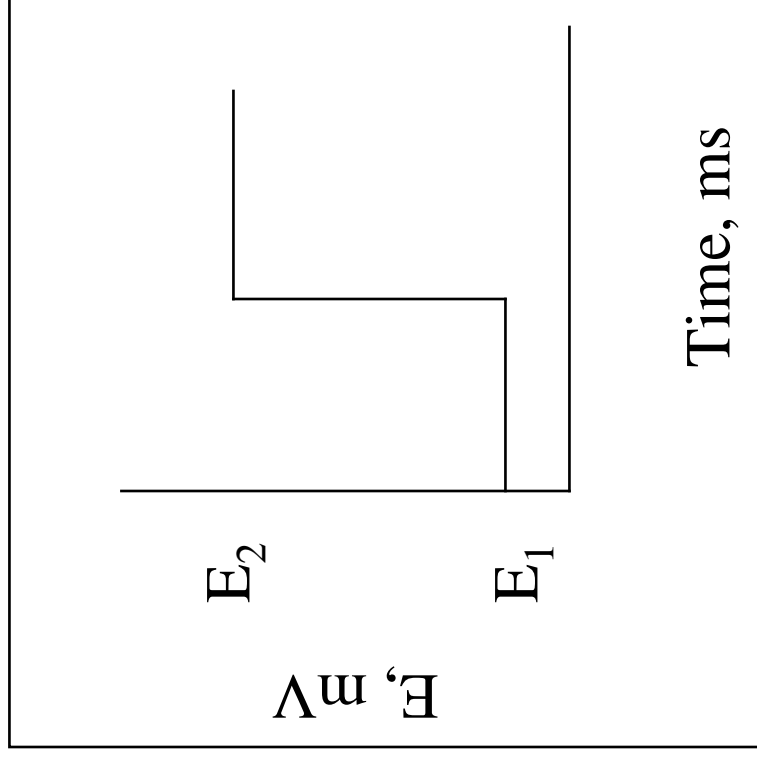


Electroanalytical techniques are categorized by:

- the excitation waveform - 2 kinds:
 - Variation in Applied Potential (E)
 - Step
 - Ramp
 - Variation in Applied Current (I)
(we will NOT cover these types of techniques)
- the response waveform
 - Voltammetry (I vs. E)

Potential Step Methods

Apply voltage then measure current or charge before and after voltage applied



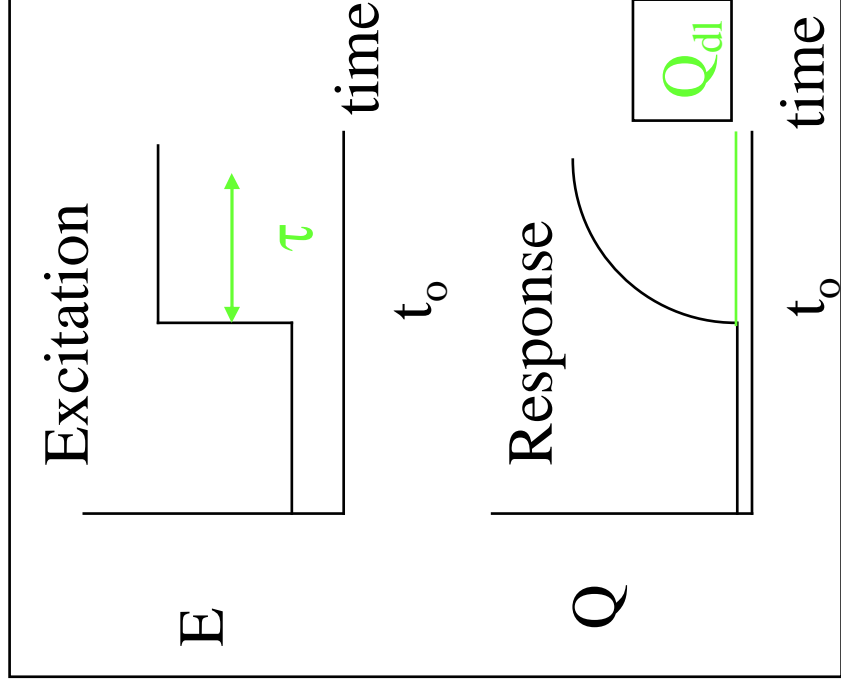
- Chronoamperometry (CA)
 - Response: i vs. t
- Chronocoulometry (CC)
 - Response: Q vs. t

All in unstirred solution.

All use potential step excitation

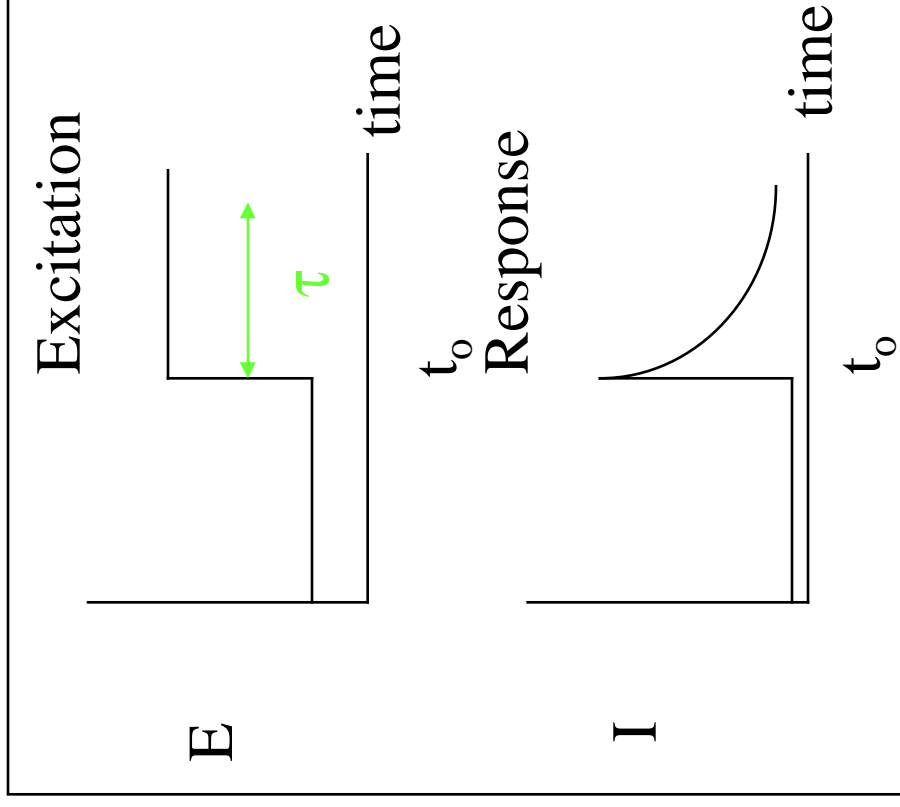
charge vs. time

chronocoulometry



current vs. time

chronoamperometry

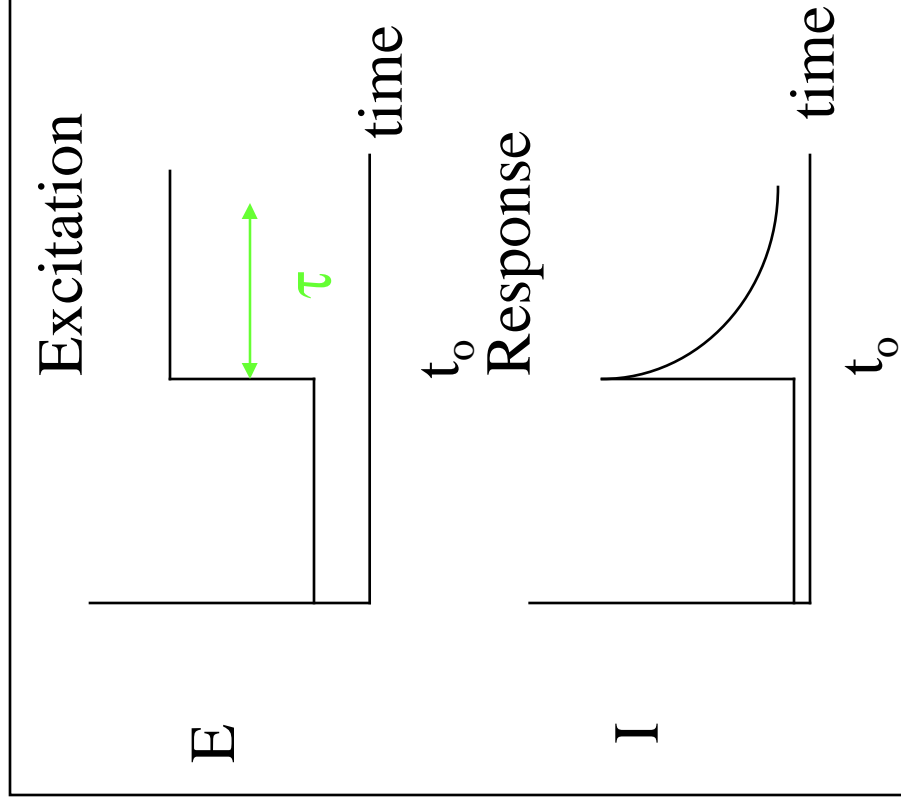


Chronoamperometry (CA)

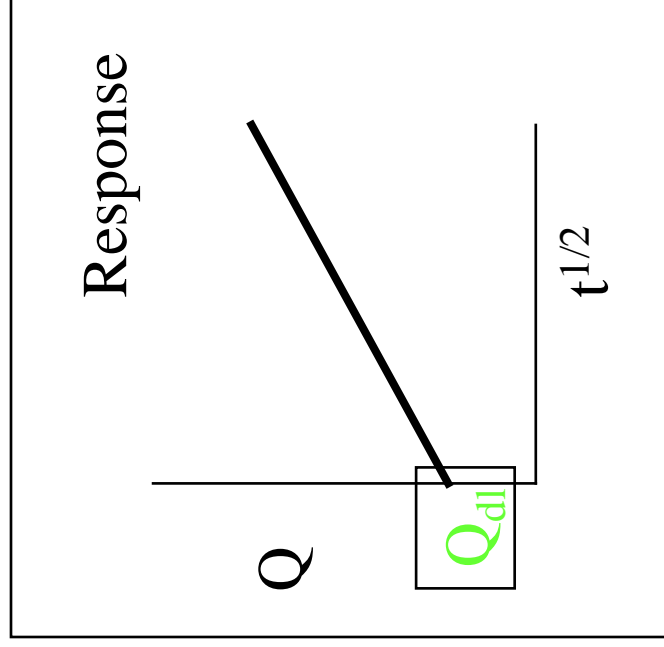
- Solution: Cottrell equation

$$i(t) = \frac{nFA D_o^{1/2} C_o^*}{\pi^{1/2} t^{1/2}}$$

- E_1 - no redox activity
- $E_2 : |E| > E^0$
- $n = \#$ of e^- ,
- A = area of electrode
- D_o = diffusion of ions
- C_o = initial concentration
- $t \equiv$ time



Chronocoulometry (CC)



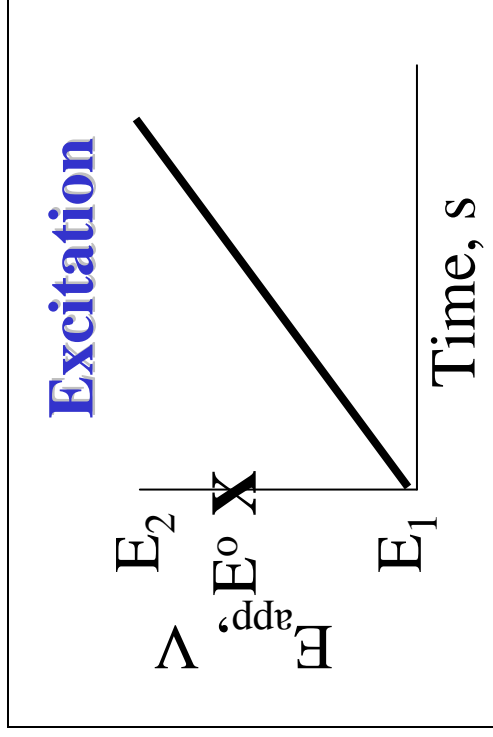
$$Q = \frac{2nFA D_o^{1/2} C_o^*}{\pi} t^{1/2} + Q_{dl} + Q_{ads}$$

- Anson Plots
 - Q vs. $t^{1/2}$
 - Intercept: Q_{dl}
 - Slope: $2nFAD_o^{1/2}C_o^*/\pi^{1/2}$(Q_{dl} = charging of double layer
 Q_{ads} = charging associated with adsorption of analyte)

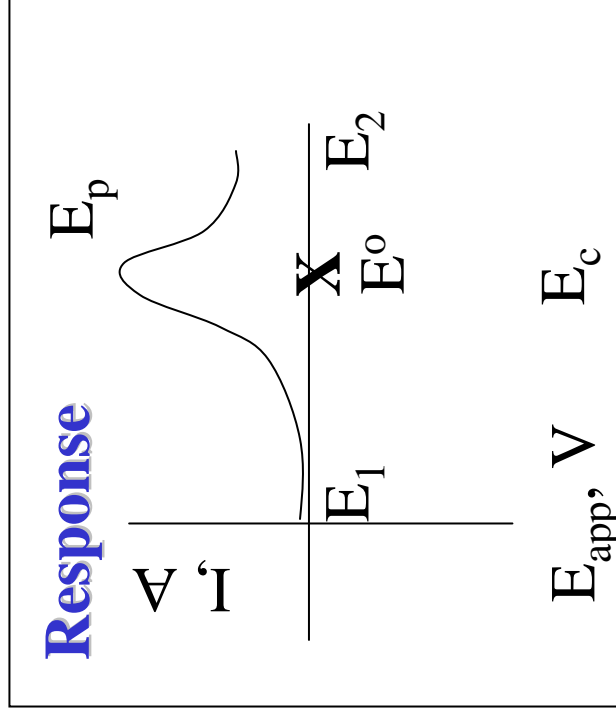
Why would you use chronoamperometry or chronocoulometry???

- Determination of:
 - n (# of electrons)
 - A (surface area of electrode)
 - D_o (diffusion coefficient of analyte)
- Kinetics/reaction mechanism
- Double potential step
 - Generate species, probe fate

Linear Sweep Voltammetry (LSV)



- Excitation: potential ramp/sweep at constant rate
 - scan rate, $v = dE/dt$
 - 5 mV - 10 V/s
- Response: voltammogram, I vs. E

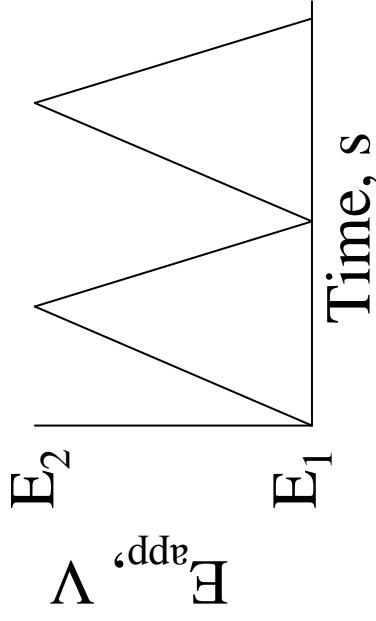


Applications of Linear Sweep Voltammetry

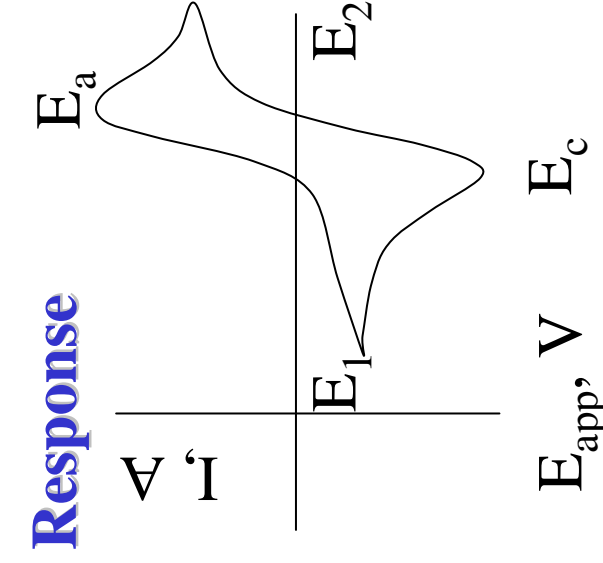
- Determination of:
 - n , A , (D_o , C_o^*)
- Study of kinetics
- Study of adsorption
- Characterization of new materials

Potential Sweep Methods

Excitation



- Cyclic Voltammetry (CV)



- Excitation: E_1 to E_2 and back to E_1
- Response: I vs. E
- Linear sweep voltammetry (LSV)
 - Excitation: E_1 to E_2

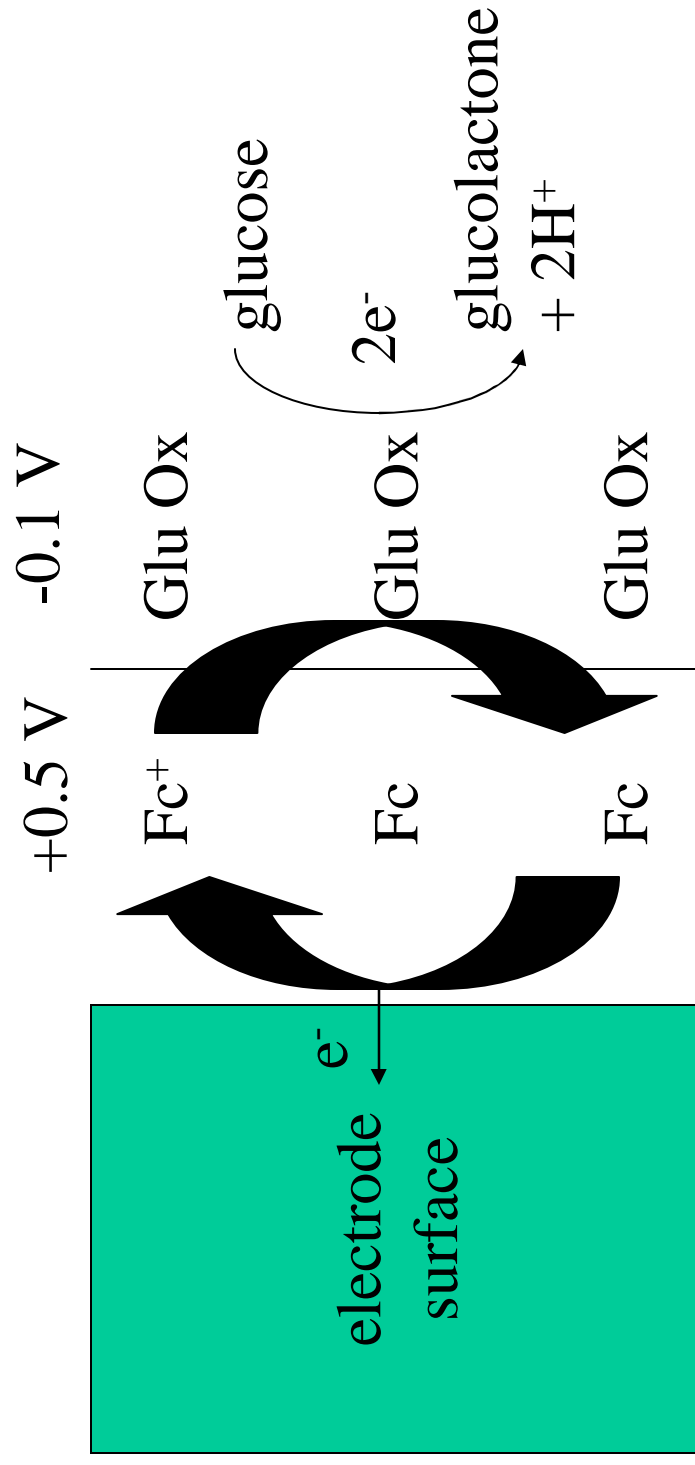
All in unstirred solution

$$\frac{dE}{dt} = v, \text{ scan_rate}$$

Bioelectrochemistry: The ExacTech

Glucose Electrode

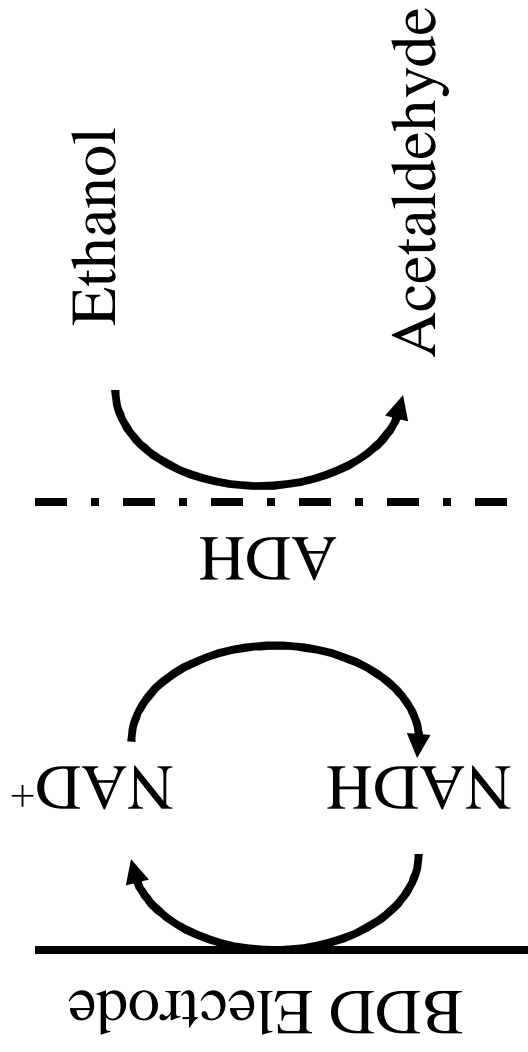
- Amperometric Biosensor:
Mediated electron transfer



Idea: measure current which is correlated with [Glucose]

Enzyme Electrodes

- Amperometric ethanol sensor



Rao, T.N.; Yagi, I.; Miwa, T.; Tryk, D.A.; Fujishima *Anal. Chem.* **1999**, *71*, 2506-11.

Electroanalytical Methods:

So much to choose from!!

