

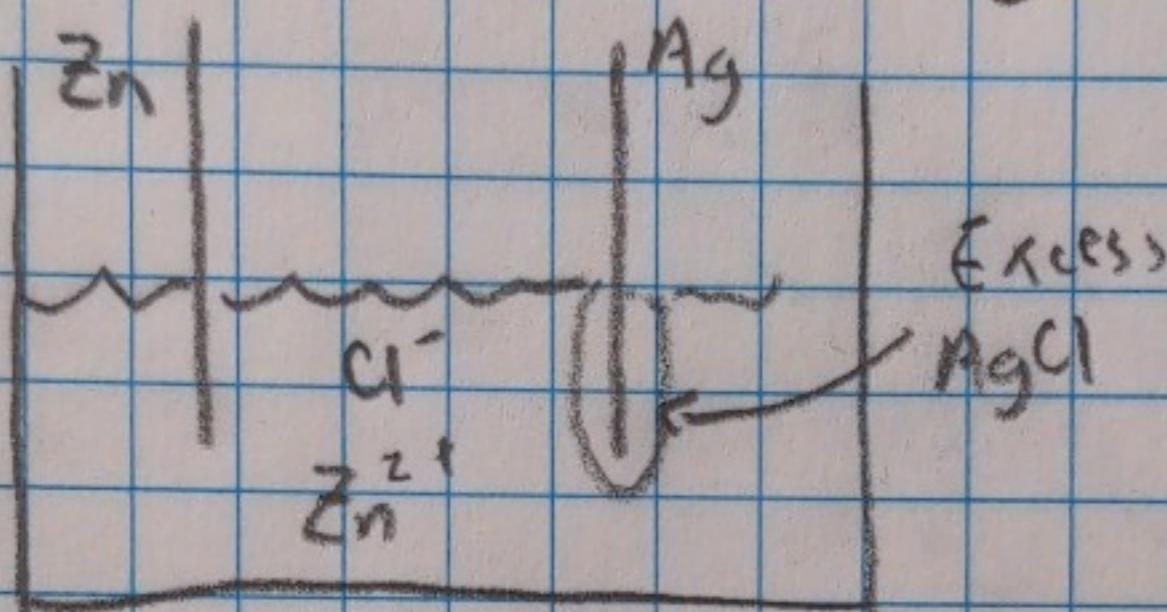
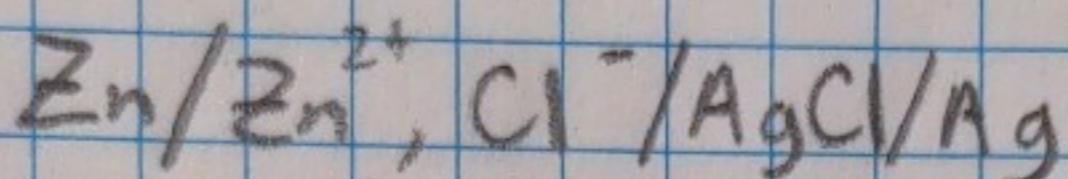
Chris Hunt

## Electrochemical Methods

$$\text{Nernst Equation: } E = E^\circ + \frac{RT}{nF} \ln \frac{a_0}{a_R}$$

In electrochemical systems - concern it with the process and factors affecting the transport of charge across interfaces b/w adjacent chemical phases.

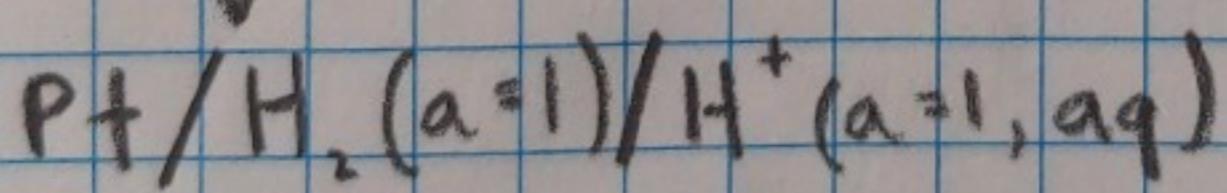
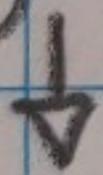
Short Hand for expressing structure of cells



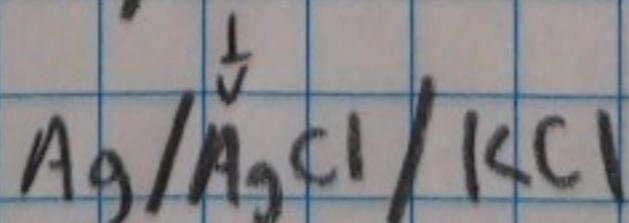
When conducting electrochemical experiments it is necessary to employ whole cells, however the behavior being analyzed is that of the working electrode

To focus on it a reference electrode is used. This electrode offers an invariant potential difference at its electrode/electrolyte boundary.

Primary Reference Node - Normal Hydrogen Electrode (NHE)



Also common = silver/silver chloride

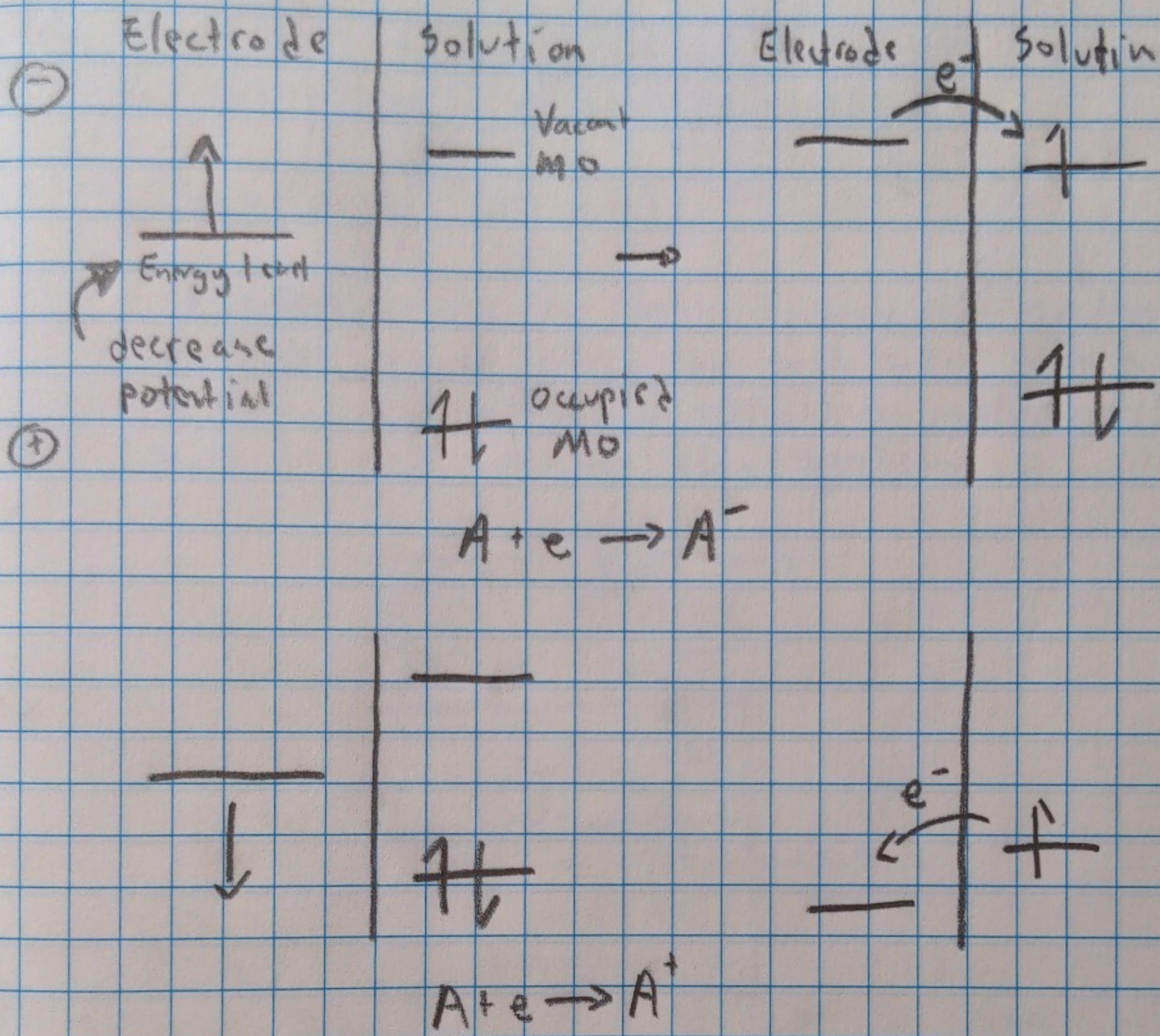


0.197 V vs. NHE

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## Electrochemical Methods

- Potential as an expression of  $E^\circ$  energy



- Current as an expression of Reaction Rate

When the potential of WE vs. RE is varied by means of an external power source, a current can flow in the external circuit because  $e^-$  cross electrode / solution as reaction occurs.

If an electrode reaction consumes or produces  $n e^-$  for each reactant, then  $n$  moles of  $e^-$  must flow through the circuit

$$Q = nF \times N \xrightarrow{\text{Faraday's Law}} i = \frac{dQ}{dt} = nF \frac{dN}{dt}$$

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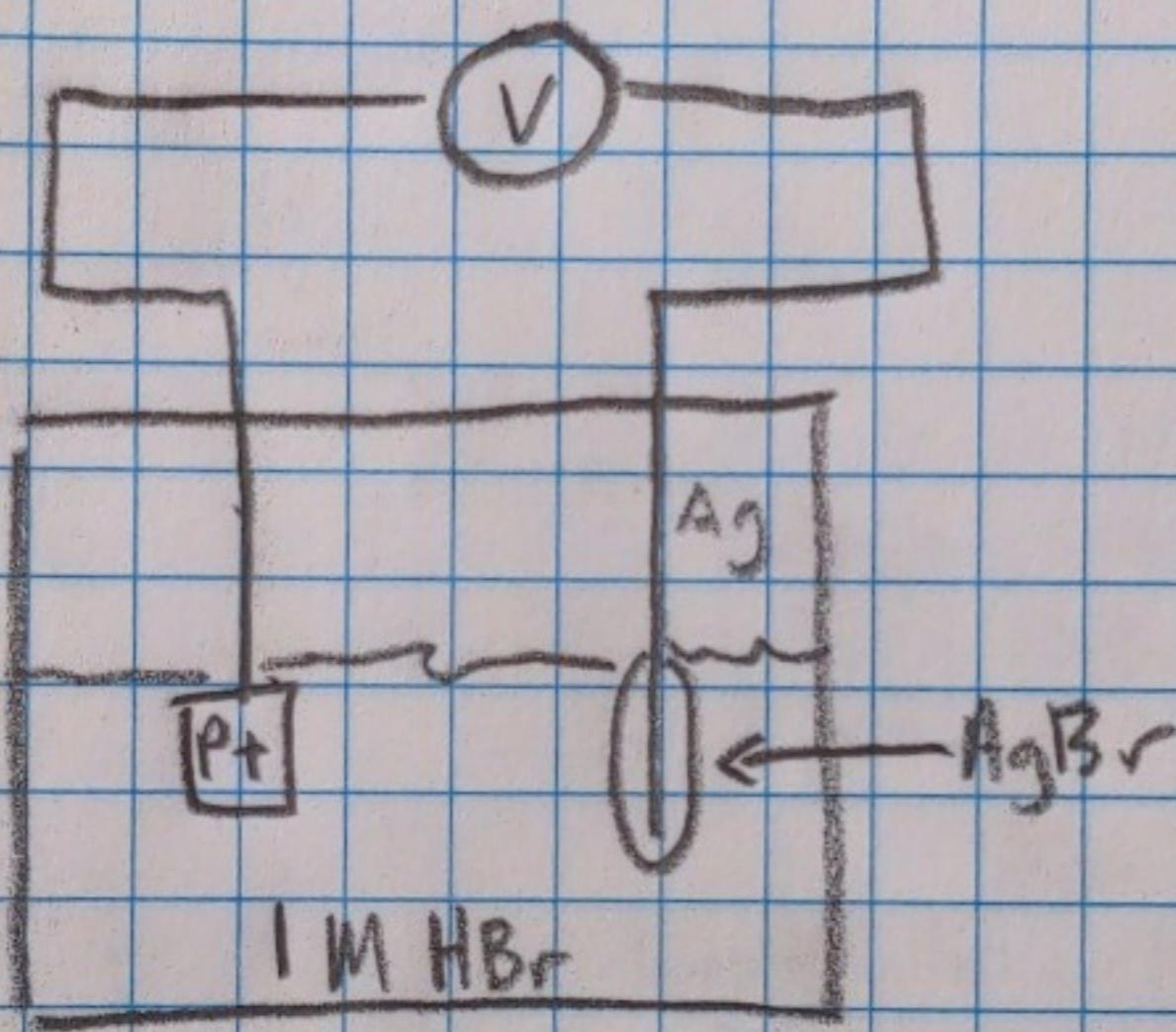
## Electrochemical Methods

## - Current - Potential Curves

A plot of the current at the working electrode vs. the potential of that electrode.

## a) Open Circuit Potential

In order to use the Nernst Equation the system must be at equilibrium on both sides. When a system cannot establish equilibrium another method must be used. Consider this system



Background  
i-E curve

Unsure...

Onset of  $\text{H}^+$   
reduction on  
Pt

Cathodic

Onset of  $\text{Br}^-$   
oxidation on Pt

Anodic

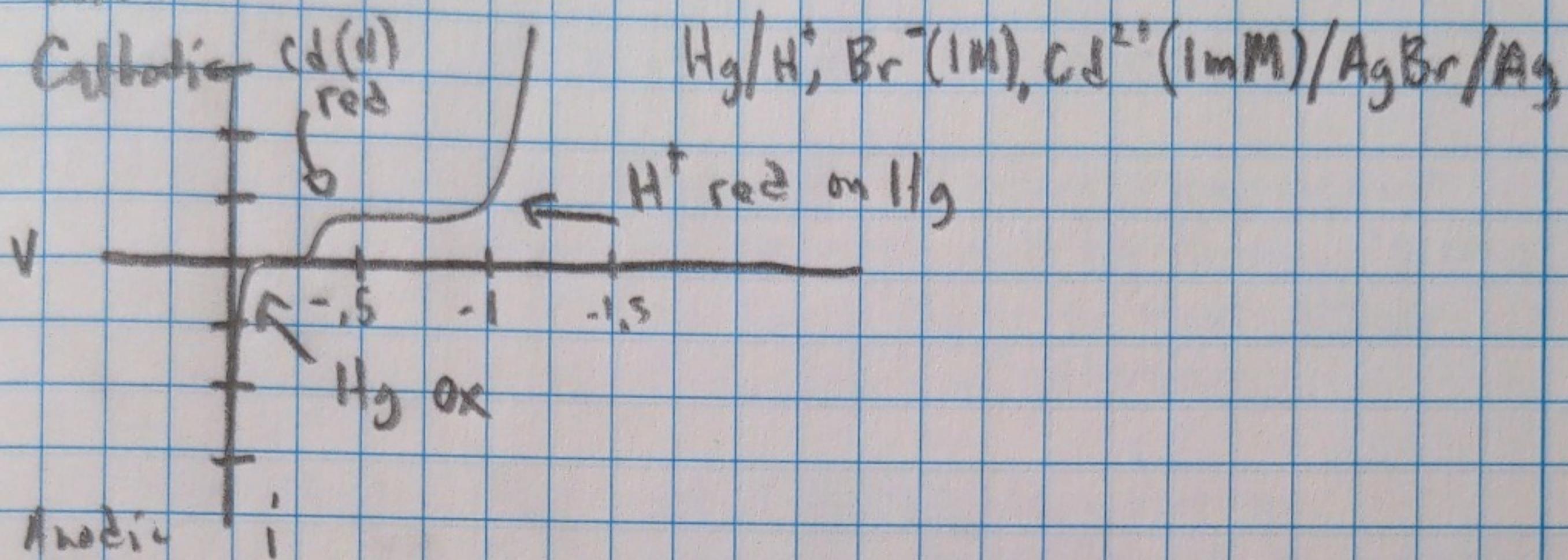
Essentially  
we see as

V is varied the  
flow of  $e^-$   
changes direction  
at specific values  
of V. This info  
tells us when  
a specific  
rxn is occurring

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## Electrochemical Methods

Consider a case with an addition of an Electroactive Solute

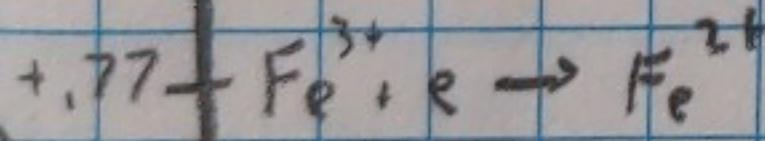
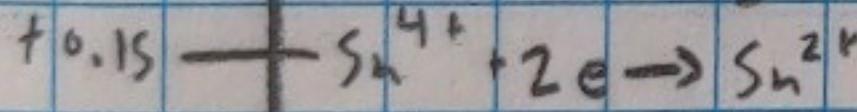
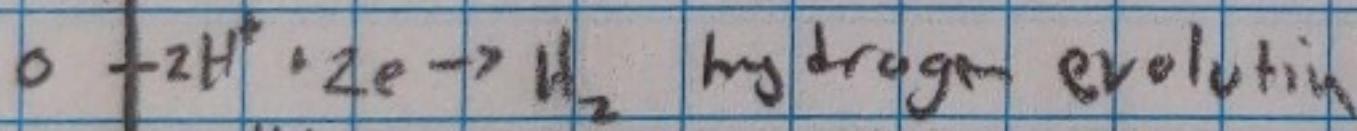


## Precedence of Electrode Rxn

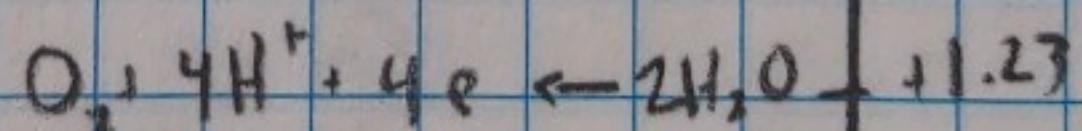
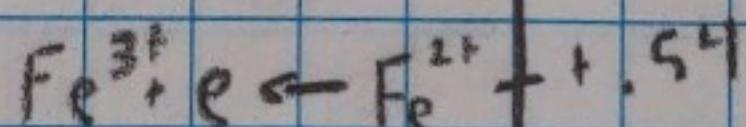
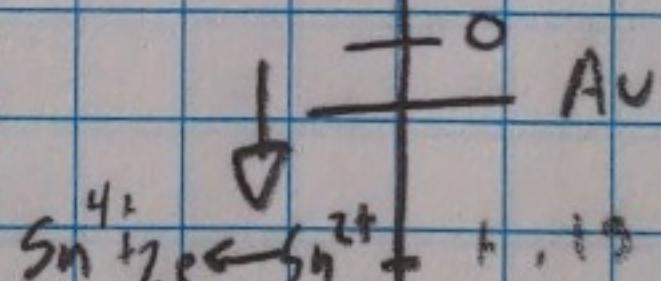
When potential of an electrode is moved from its OC value more neg the substance to red first is the one with the least neg E°

(⊖) Possible Red Rxn

(⊖) Possible Ox Rxn

 $-0.25^\circ$ 

Pt



(⊕)

You must take into consideration the electrode material each substance has different kinetic speeds

- Current and Potential Cannot Be Controlled Simultaneously unless some other variable (i.e. Temp) can change also

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## Electrochemical Methods

## Faradaic and Nonfaradaic Processes

Two distinct processes occur at electrodes

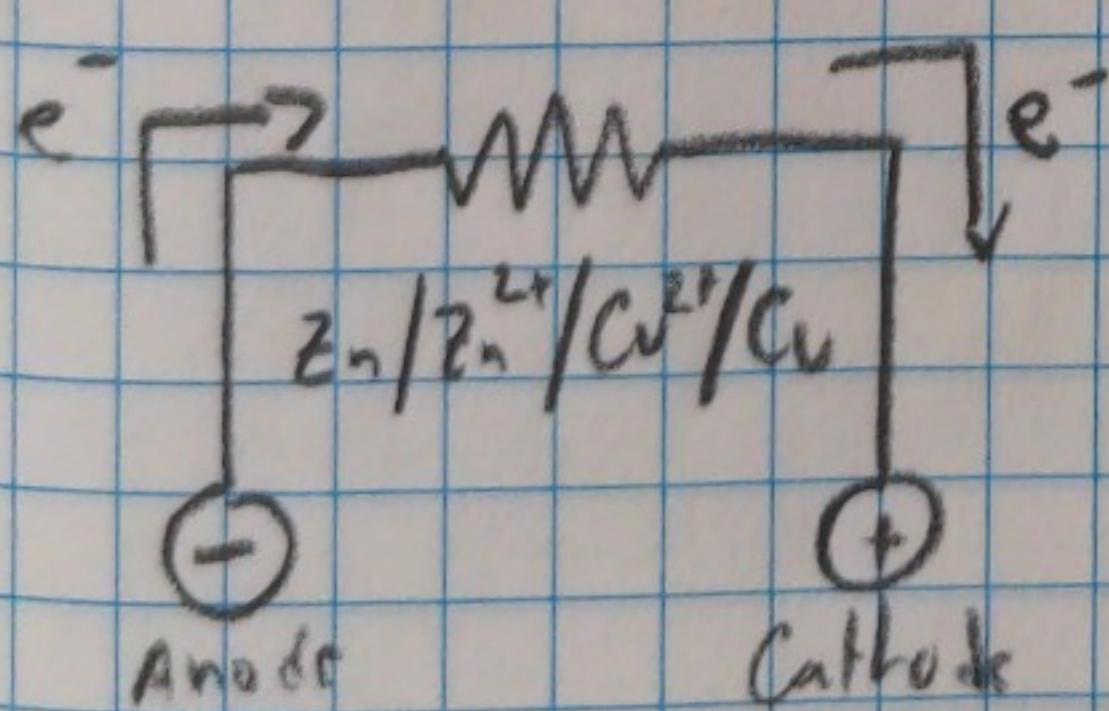
- Faradaic: The case when Redox rxn occur  
These can be explained by Faraday's Laws  
These rxn cause charge to move across the electrode/solution interface.
- Non Faradaic: A range of potentials where no charge-transfer takes place, however the distribution of ions does change with changing potential or solution comp.

Electrochemical Cells, in which Faradaic currents are flowing are classified as Galvanic or electrolytic cells  
Galvanic - Rxn spontaneously occur at the electrodes when connected externally by a conductor

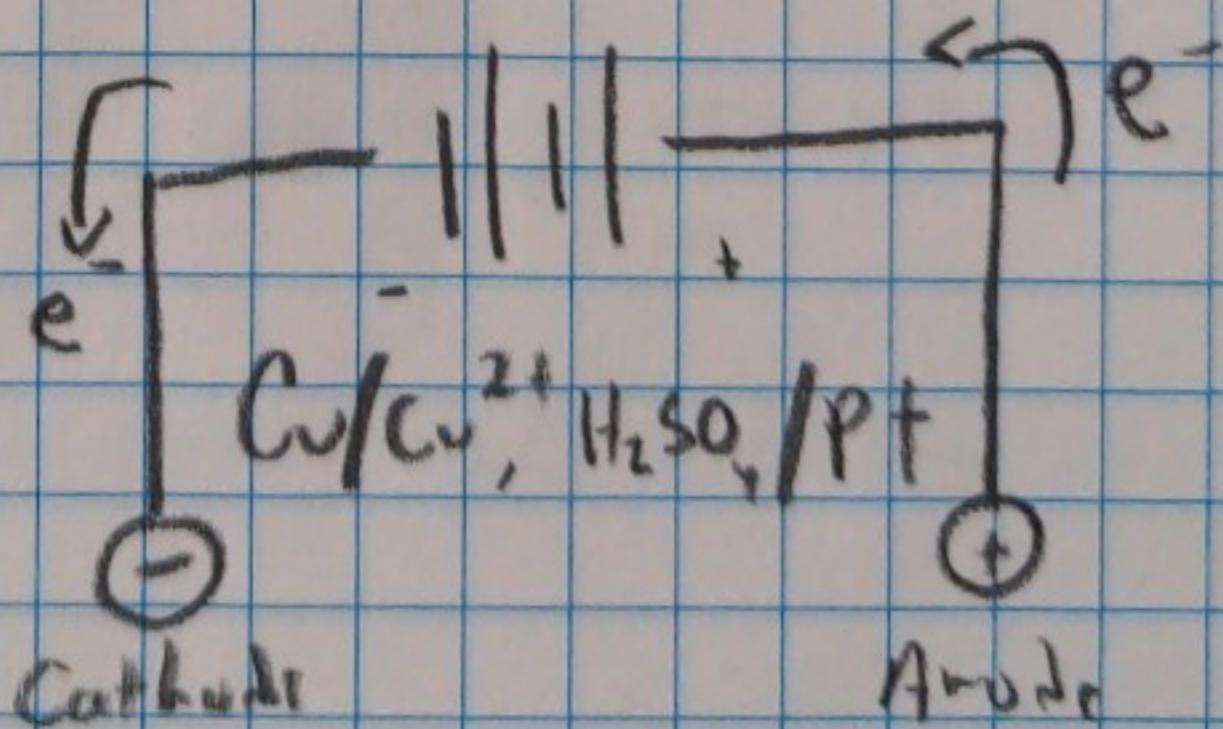
Ex. - Zn - MnO<sub>2</sub> cell, Pb-PbO<sub>2</sub> or Li-ion, H<sub>2</sub>-O<sub>2</sub> cell

Electrolytic - Rxn do not occur spontaneously - driven by an external voltage greater than the open-circuit potential of the cell

Galvanic Cell



Electrolytic Cell



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Electrochemical Methods

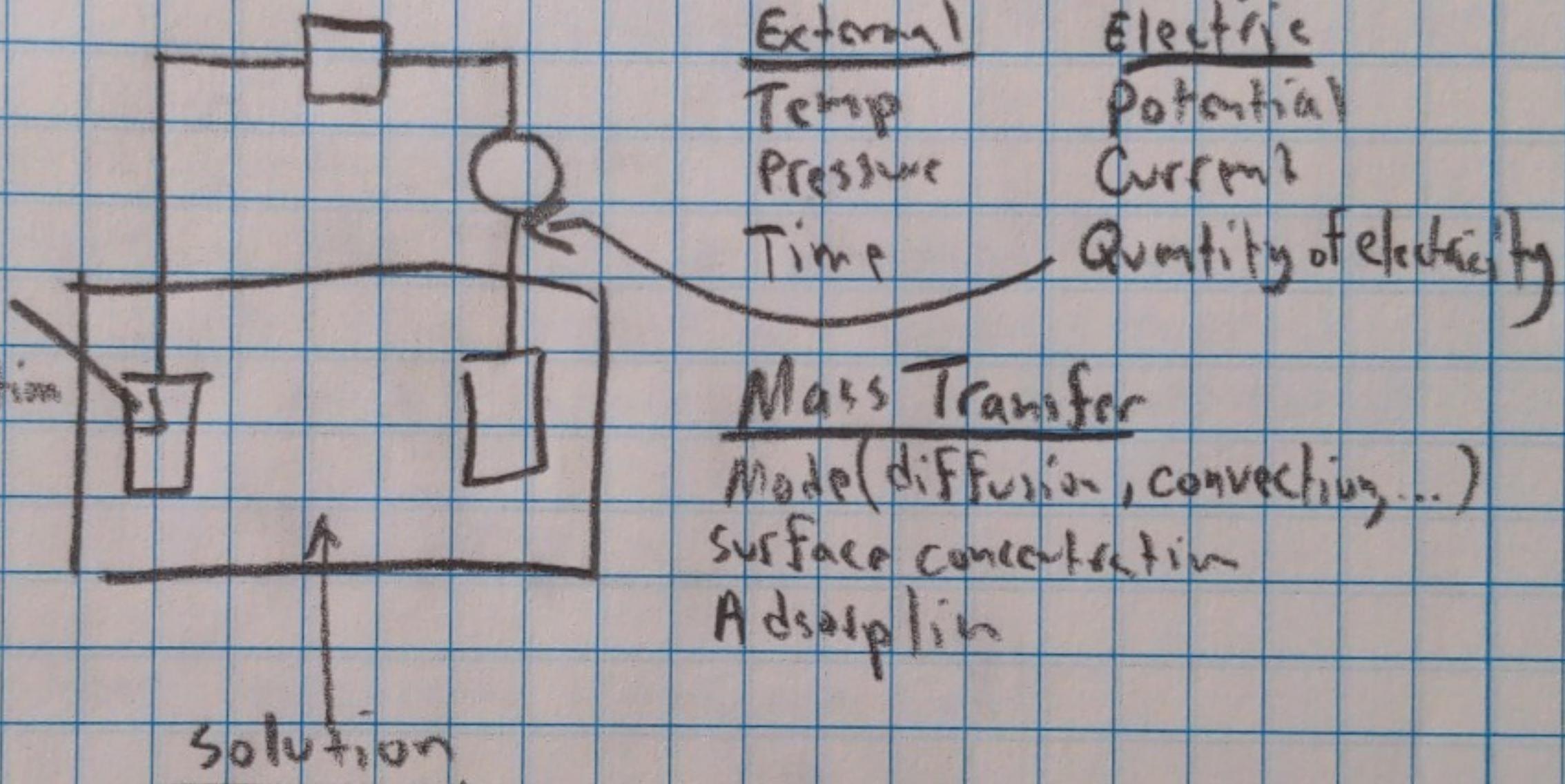
Electrolysis - Chemical changes accompanying Faradaic rxn at electrodes in contact with electrolytes

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The electrochemical experiment and Variables

An experimental investigation of electrochemical behavior consists of controlling certain variables of a cell (usually current, potential, or concentration)

- Electrode
- Material
- Surface Area
- Geometry
- Surface condition



Bulk Concentration of electroactive species  
Concentration of other species  
Solvant

Potentiometry:  $i = 0$ ,  $E$  is determined as a function of concentration  
no net Faradaic rxn occurs b/c no current  
 $E$  is governed by thermodynamic properties

Voltammetry: The potential ( $E$ ) is controlled, resulting current is measured

Galvanostatic: The current is controlled, potential is measured

Coulometry: The potential is constant, current is integrated to find total charge passed.

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## Electrochemical Methods

The aim of experimentation is to obtain info (thermodynamic, kinetic, analytical, ...) from observations of excitation and response functions

"What is  $j$ ?" = "What is the rate of rxn?"

$$j = \frac{dQ}{dt} = nF \frac{dN}{dt}$$

↓  
 e<sup>-</sup> transferred  
 Faraday's  
 law

Charge of Mols  
 with respect to time

The departure of the electrode potential from the equilibrium value upon passage of Faradaic current is "polarization" which is measured by overpotential,  $\eta$

$$\eta = E - E_{eq}$$

Current = electrode reaction rate

When there is a steady state current, the rates of all reaction steps in a mechanistic series are the same

The magnitude of this current is often limited by the sluggishness of one or more steps

- rate-determining step

Each value of current is driven by a certain  $\eta$

$\eta_m$  (mass-transfer),  $\eta_c$  (charge-transfer)

$\eta_{rxn}$  (reacting rxn)

Mass Transfer: Modes - Migration - movement of a charged body under influence of an E field

Diffusion - movement of a species under the influence of a gradient of chemical potential

Convection - stirring or hydrodynamic transport  
Fluid flow occurs b/c of natural convection

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## Electrochemical Methods

Mass Transfer to an electrode surface is governed by the Nernst-Planck equation

$$\overline{J}_j(x) = -D_j \frac{\partial C_j(x)}{\partial x} - \frac{z_j F}{RT} D_j C_j(x) \frac{\partial \phi(x)}{\partial x} + C_j(x) v(x)$$

$\overline{J}_j(x)$  : Flux of species ; Net rate a species crosses a unit area  
mol/cm<sup>2</sup> at  $x$

$D_j$  : Diffusion coefficient (cm<sup>2</sup>/s)

$\frac{\partial C_j}{\partial x}$  : Concentration gradient     $\frac{\partial \phi}{\partial x}$  : Potential gradient

$z_j$  : Charge     $C_j$  : Concentration

If  $J$  is neg  $\rightarrow$  species  $j$  is moving into the area  
If  $J$  is pos  $\rightarrow$  species  $j$  is moving away

Neg  $J$  can be understood as the rate at which species  $j$  is consumed by electrolysis

Pos  $J$  is the rate at which species  $J$  is produced by the electrode reaction

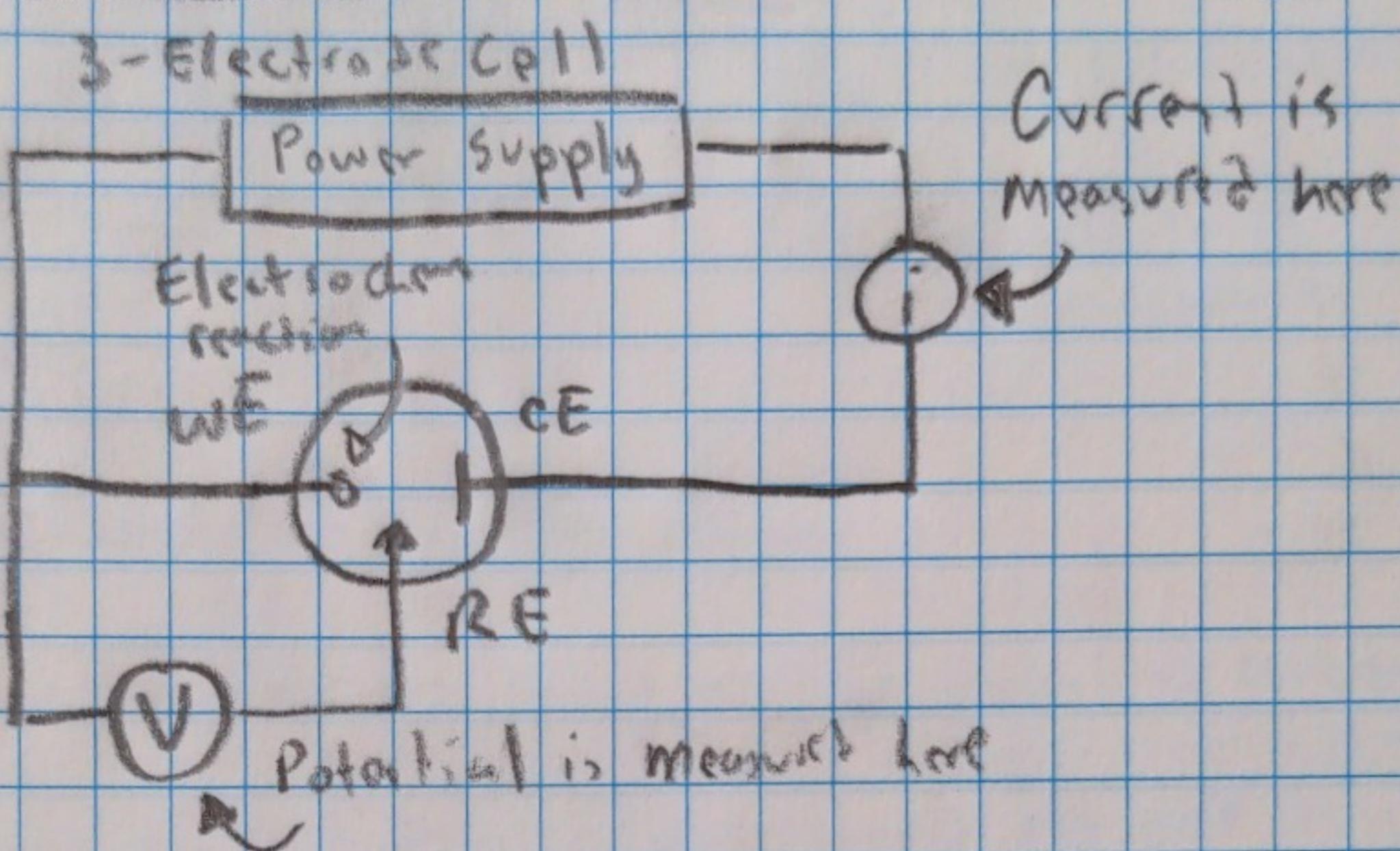
Nernstian Diffusion Layer : As electrolysis begins between the electrode/electrolyte a concentration profile develops from the electrode surface to the bulk ( $\delta_0$  is the width of this layer)

When studying diffusion it is critical to reduce effects of migration (by adding a supporting electrolyte) and convective convection (by stirring bulk solution) This leaves the concentration of  $C_0$  and  $C_p$  at the electrode dependent on the electrode potential. The largest rate of mass transfer of O occurs when  $C_0(x=0)$  is driven to zero. The value of the current under these conditions is called the limiting current,  $i_L \rightarrow i_L = nFA_m C_0^*/A$  At  $i_L$  the electrode process is occurring at the max rate

## Christoff

## Electrochemical Methods

The concentration of species O at the electrode surface is linearly related to the current and varies from  $C_0$  when  $i=0$  to a negligible value when  $i=i_L$



Capacitance and Charge at an electrode:

Since charge cannot cross the IPE interface when the potential is changed, the behavior of the electrode/solution interface is analogous to a capacitor

$$C = \frac{q}{E}$$

The whole array of charged species and oriented dipoles existing at the electrode/solution interface is called the electrical double layer

inner layer - contains solvent molecules and sometimes other species that are said to be specifically absorbed. AKA Helmholtz layer  
The locus of the electrical control of specifically absorbed ions

outer layer - Outer Helmholtz plane - Solvated ions that cannot approach metal electrode as closely - involves only long-range electrostatic forces - nonspecifically adsorbed

Distributed in the diffuse layer

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## Electrochemical Methods

## Double Layer Capacitance and Charging Current:

- Potential (or Voltage) step - Similar to an RC circuit

$$i = \frac{E}{R_s} e^{-t/R_s C_d}$$

 $R_s$  - solution resistance $C_d$  - Double layer capacitance

- Linear Potential sweep (Voltage ramp)

Scan Rate = V/s the slope of the potential sweep

A charging current must flow through the cell  
and a potential drop occurs in solution

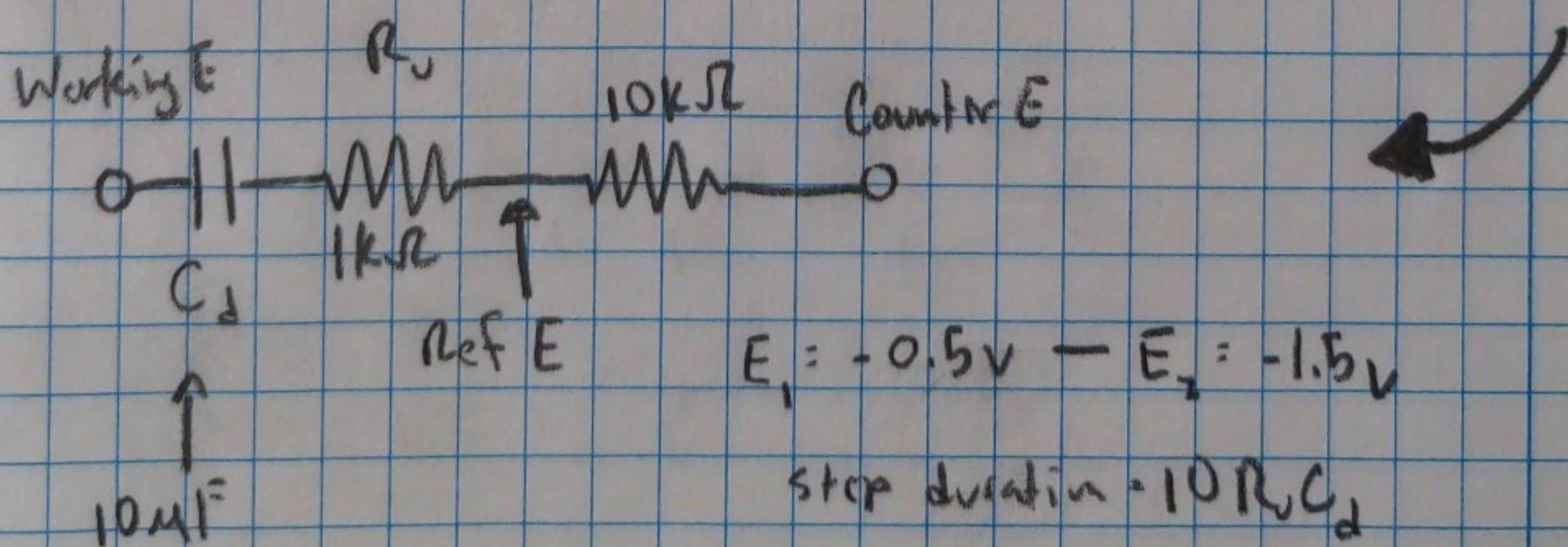
$$\bar{E} = E_i - vt + iR_v \quad V = \text{scan rate}$$

$$i = \pm v C_d (1 - e^{-t/(R_s C_d)})$$

Use LT

Common Potentiostats can place  $\pm 13 - 19$  V across the cell and can furnish  $\pm 100$  mA of current

SPICE  
To simulate  
Section 1.9.3



Consider Doing Problem Sets..