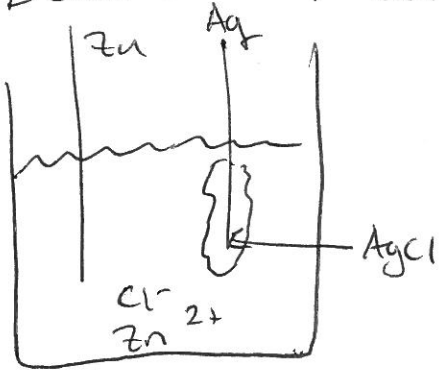
Electrochemistry – Intro

not flow of e^- → doing chemistry
enacting chemical change

A Electrochemical Cell example
(2 hrs)



→ two independent half RXNs

→ normally we are only interested in one half reaction, so we standardize the other half reaction

$Zn / Zn^{2+}, Cl^- / AgCl / Ag$

Slash = phase boundary

↓

potential – measured in Volts between electrodes
(due to different energy of e^-'s)

primary ref. electrode

Standard hydrogen electrode (SHE)
or
Normal Hydrogen Electrode (NHE)

Other reference electrodes include

$Hg / Hg_2Cl_2 / KCl$ (sat. in H_2O) 0.242 V vs NHE

$Ag / AgCl / KCl$ (sat in H_2O) 0.197 V vs NHE

Idea

- Reference has constant make up, so its potential is fixed
- control RXN / Electrode potential of interest
  "Working Electrode"

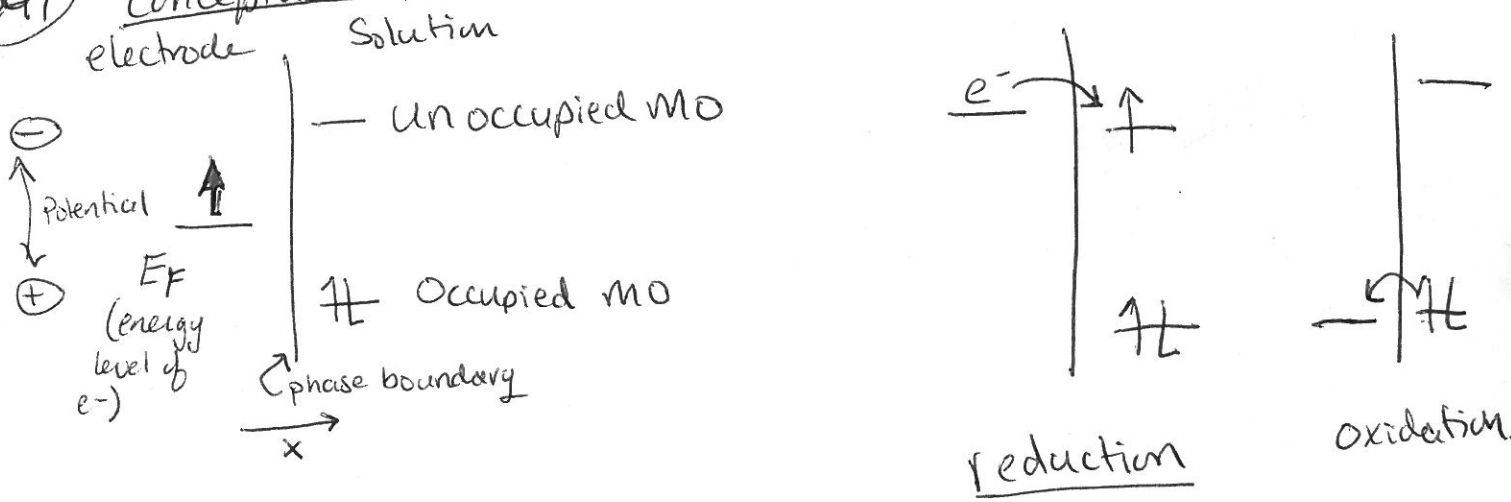
→ Electrochemistry – Intro

↑ flow of electrons ↑ chemistry

(B) Electrochemical cells and reactions

→ transport of charge across chemical phases – ie. electrode (Metal) and electrolyte (Salt solution) → redox couple → chemical species.

(A1) Conceptual representation of e⁻ transfer (redox)



Critical potentials for flow of charge related to Standard potential, E^o

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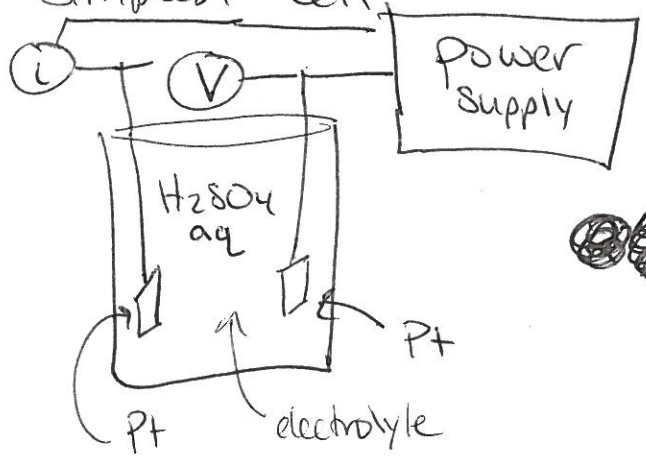
to measure these processes, and to control (ie. current)

potentials we are typically use a potentiostat

Example of Electrochemical process – 2 electrode vs. (power supply) 3 electrode

– water electrolysis

Simplest cell



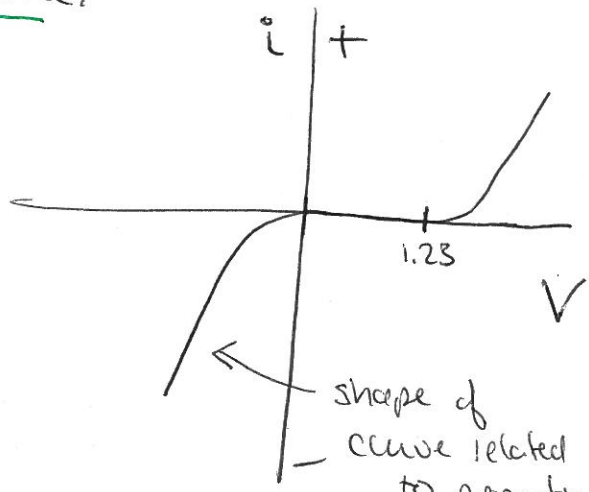
$2H^+ + 2e^- \rightarrow H_2$ $E^\circ_{red} = \emptyset V$ vs SHE

$E^\circ_{red} = 1.23V$ vs SHE

$H_2O \rightarrow 1/2\, O_2 + 2H^+ + 2e^-$

$2OH^- \rightarrow 1/2\, O_2 + H_2O + 2e^-$ (base)

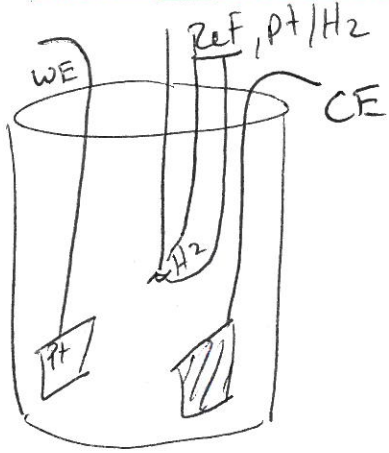
2-electrode:



V (applied between two pt electrodes)

shape of curve related to properties of both electrodes!

3-electrode w/ potentiostat:

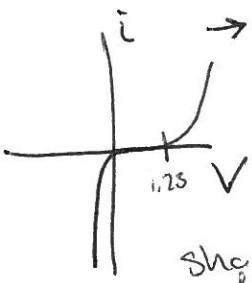


What potentiostat does (See chapter 15 for details) Bard

→ Control WE potential versus RE

pass current to the CE

(apply as much pot. between WE and CE to ~~make~~ set WE vs RE



V vs Ref (SHE)

shape of curve now only a function of process taking place at one electrode.

Faradaic and Nonfaradaic Processes

ie. → what happens when you apply a potential (voltage) to an electrode?

(1) Faradaic → charges transfer across interface (i.e. metal-solution boundary)

(2) non-Faradaic process → structure of electrode/solution interface changes w/o transfer of charge

- absorption-desorption of ions

→ always have non-faradaic processes!

Nonfaradaic Processes → ideal polarizable electrode

→ no current flow as potential of electrode is changed (ie. no redox couple in electrolyte to accept charge)

- no e^- flow as V changed → electrolyte | electrode interface analogous to * a capacitor

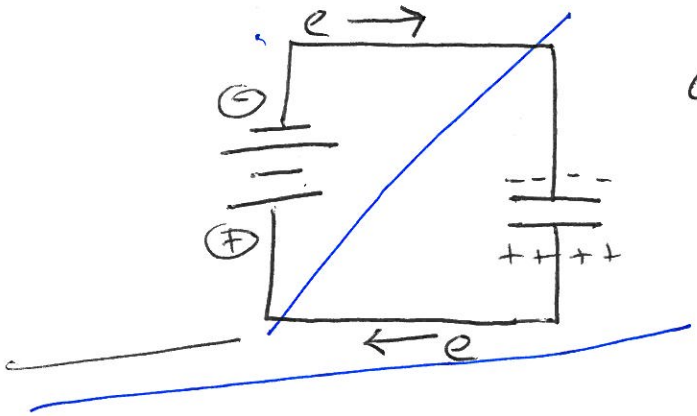
$$C_d = \frac{q}{E}$$

q ← charge, in coulombs

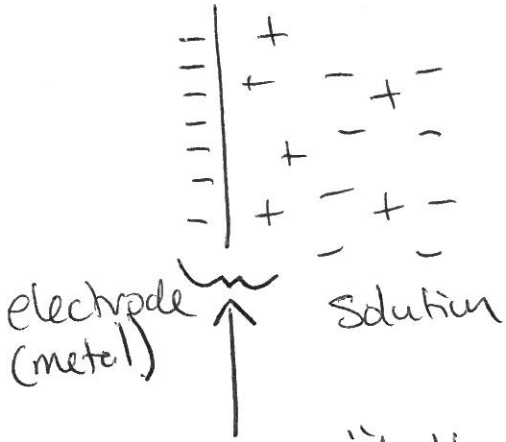
E ← potential across capacitor (in V)

C_d ↑ capacitance (in Farads)

Skip



charging a capacitor



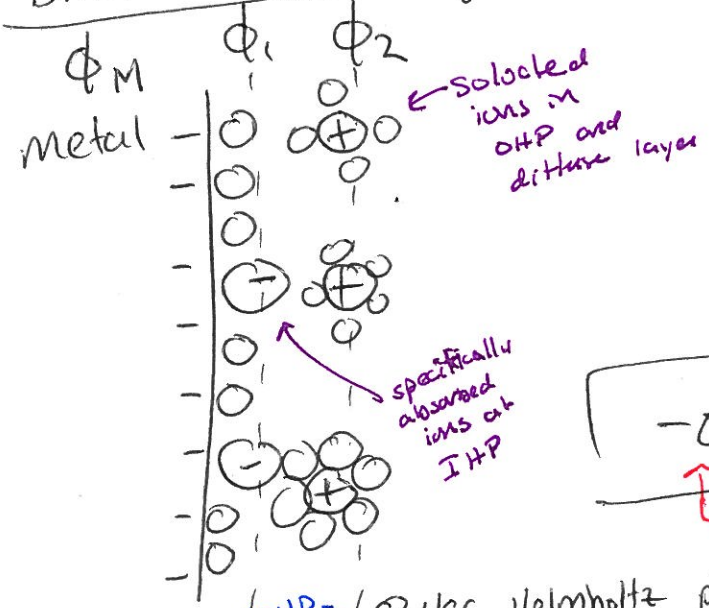
termed "double layer"
ie. two "planes" of charge

- when potential E of electrode is changed charge flows until Eqn. satisfied. (q)

- C_d typically 10 to 40 $\mu F\ cm^{-2}$
- C_d is often a F(V)

Brief Description of Electrical Double Layer

other names for inner absorbed ion layer: Compact, Inner Helmholtz, Stern



Note: Hermann von. Helmholtz 1853
- acoustics and aesthetics
- ophthalmic optics
- age of earth / origin of solar system

$$-\sigma^M = \sigma^i + \sigma^d = \sigma^s$$

total charge on the metal

total charge in solution

OHP = Outer Helmholtz plane (σ^d) diffuse double layer, extends from OHP into solution

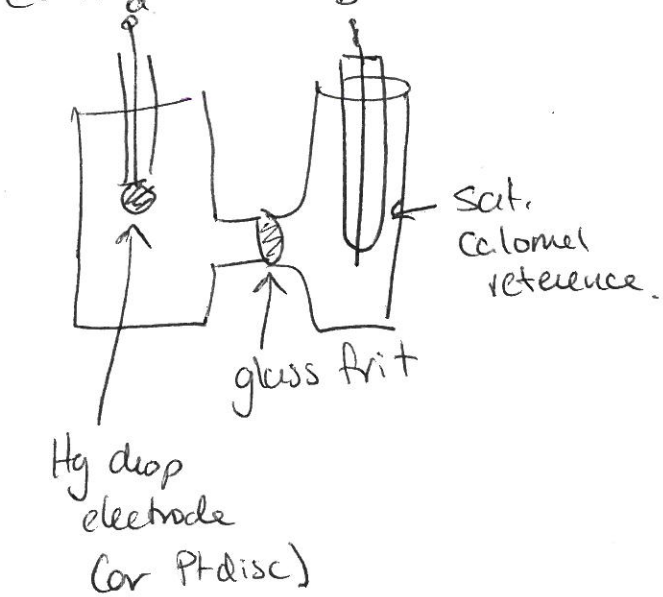
IHP = Inner Helmholtz plane (σ^i) (C/cm^2)

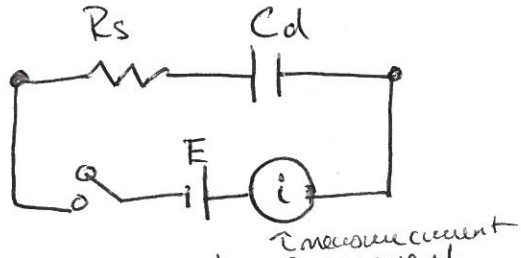
Double-layer Capacitance and Charging

→ quantitative description of non-faradaic response

R_s = series cell resistance
C_d = capacitance of double layer

consider cell





(A) potential step experiment

What is the current response?

$$q = C_d E_c$$

total charge on capacitor as function of potential across capacitor.

$$E = E_R + E_c$$

total

$$= iR_s + \frac{q}{C_d}$$

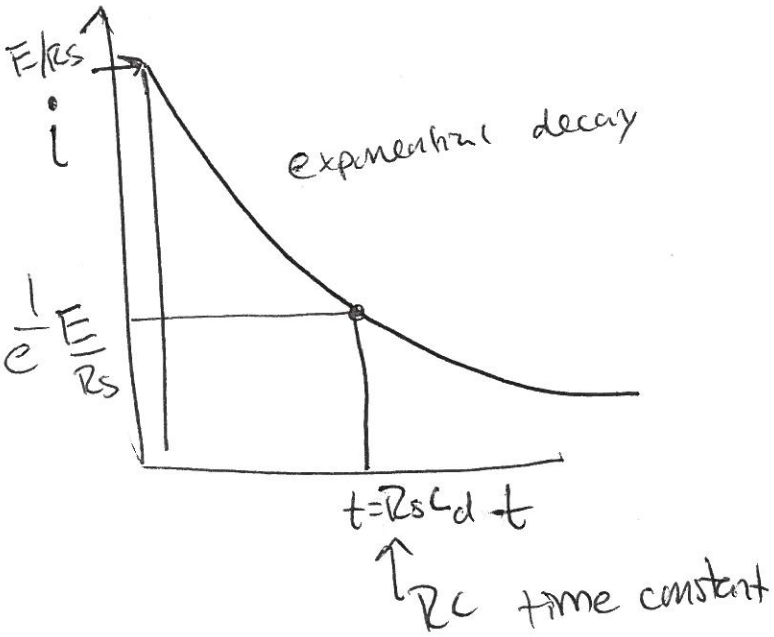
$$\boxed{i = \frac{\partial q}{\partial t}}$$ (definition)

$$E = \frac{\partial q}{\partial t} R_s + \frac{1}{C_d} q$$

$$\frac{\partial q}{\partial t} = \frac{-q}{R_s C_d} + \frac{E}{R_s}$$

voltage step size

constants



Solution:

$$q = E C_d \left[1 - e^{-t/R_s C_d}\right]$$

or

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

Supplement 6a - Solve differential Equation

$$\frac{dq}{dt} = \frac{-q}{R_s C_d} + \frac{E}{R_s} \cdot \frac{C_d}{C_d}$$

$$\frac{\partial q}{\partial t} = \frac{-q + EC_d}{R_s C_d}$$

$$\int \frac{1}{-q+EC_d}\, dq = \int \frac{1}{R_s C_d}\, dt$$ ← separate variables and integrate

$$-\ln(-q + EC_d) = \frac{t}{R_s C_d} + C$$ ← constant of integration

use "Initial" boundary conditions to solve for C

at $t = \emptyset$, $q = \emptyset$ (no charge on the capacitor)

$$\boxed{-\ln EC_d = C}$$

rewrite expression:

$$-\ln(-q + EC_d) = t/R_s C_d - \ln(EC_d)$$

$$\ln(-q + EC_d) = \ln(EC_d) - t/R_s C_d$$

$$-q + EC_d = \exp\left[\ln(EC_d) - t/R_s C_d\right]$$

$$-q + EC_d = EC_d\, e^{-t/R_s C_d}$$

$$q = EC_d\left(1 - e^{-t/R_s C_d}\right)$$

time constant for decay ... aside

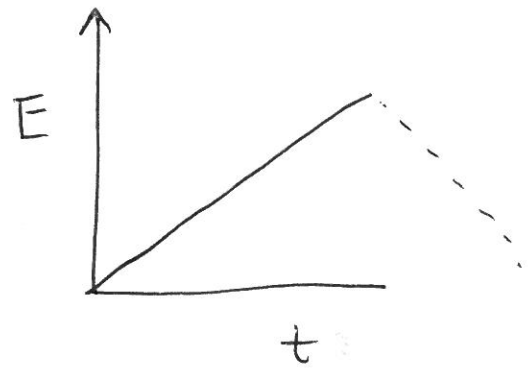
this gives way to measure cell resistance

Sweeping potential → as you do in cyclic voltametry

↳ which we will discuss later

$$E = vt$$

↑ sweep rate in $(V s^{-1})$

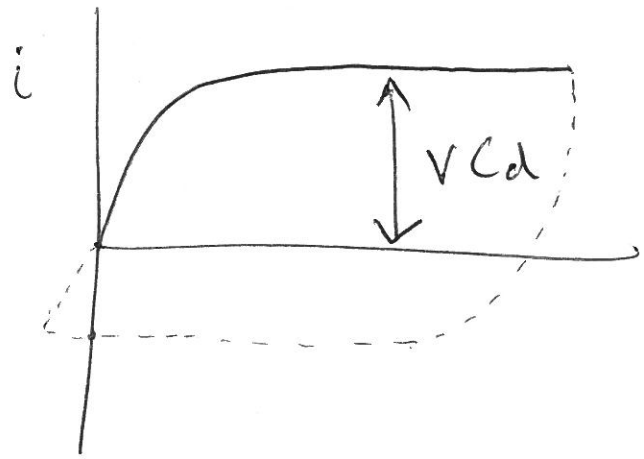


again $\underline{\underline{E}} = E_R + E_c = iR_s + \frac{q}{C_d}$

$$\underline{\underline{vt}} = iR_s + \frac{q}{C_d}$$

Solution to this as

$$i = vC_d[1 - \exp(-t/R_sC_d)]$$



key point → magnitude of <u>charging current</u> depends on sweep rate and capacitance.

↑ you can estimate electrode area from this

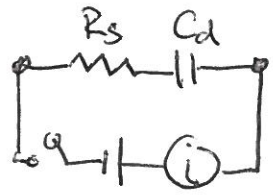
$$C_d \sim 10 - 40 \mu C\ cm^{-2}$$

Note: you will measure this "charging" box in any typical CV experiment in the lab. You can tell if your electrolyte is clean if this charging box is devoid of any peak features

linear scan rate dependence ~~as~~ shows capacitive effect.

on resistance:

go back to simple cell model



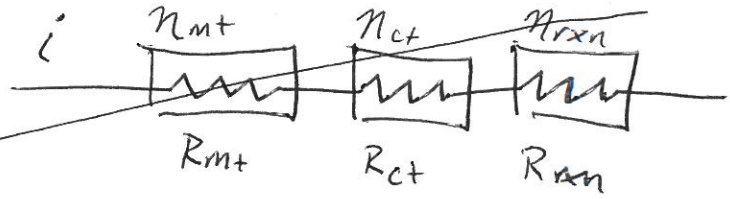
what about Rs

↓

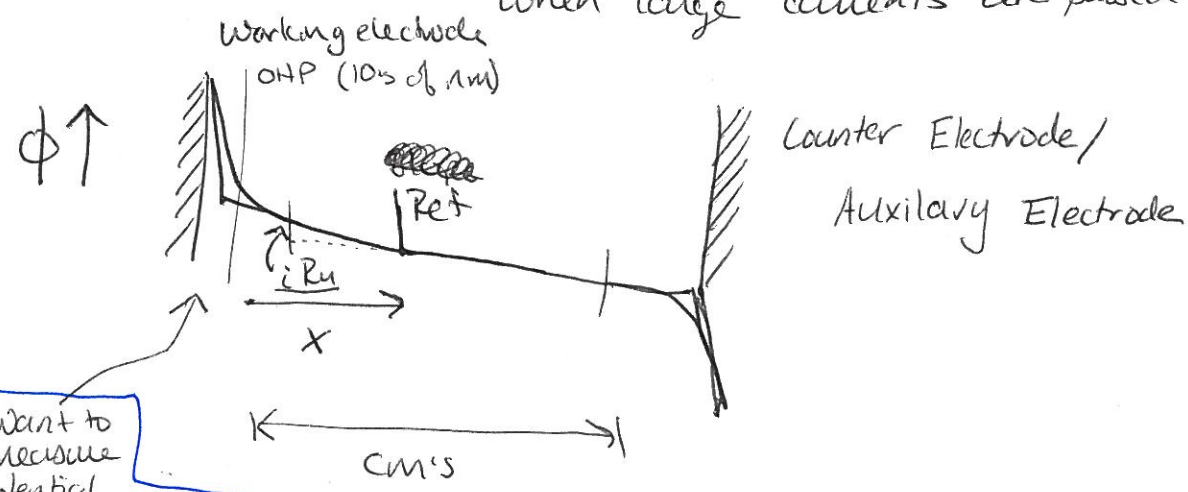
→ Series Resistance

→ in any electrochemical cell

also ~~chemical~~ electrode processes related to resistance →



Cell resistance → minimize uncompensated resistance very important when large currents are passed (> ~ 1 mA)



want to measure potential drop at electrode surface (where chemistry takes place)

→ for small currents (< 1 mA) and in highly conductive electrolytes (ie. 1 M aq. solution) these iR_u is negligible.

→ for larger currents this becomes very important ... can measure and correct for the uncompensated resistance.

a. use transient i response to E step

b. use AC impedance – to discuss later.