B+F chap.

5. Basic Potential Step Experiments

5.2 Cottrell Equation:

$$i(t) = i_d(t) = \frac{nFAD_0^{1/2}C_0^*}{\pi^{1/2}t^{1/2}}$$

current dies off at a rate of $\underline{1/t^{1/2}}$ ~~or~~

- typical signature of a diffusion-limited process.

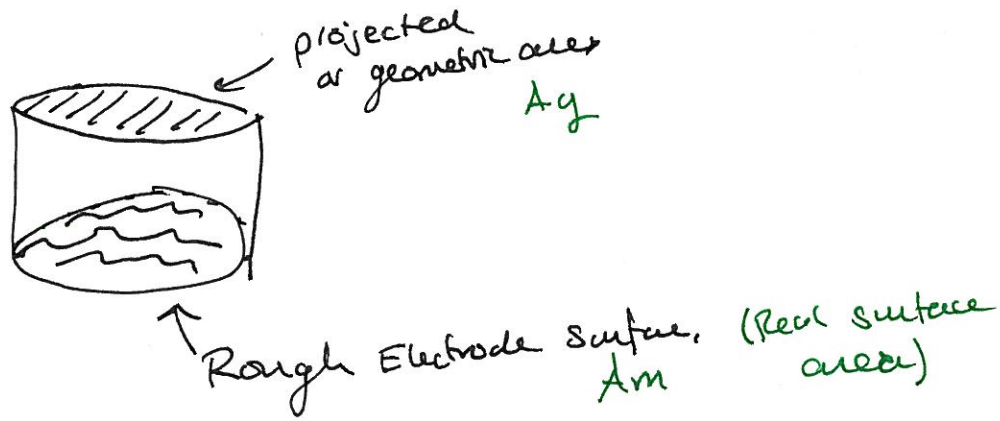
notice also dependence on $\underline{D_0^{1/2} \text{ and } A}$.

a. So if you know A and C_0^*, you can extract $\underline{\underline{D_0}}$; the diffusion coefficient.

b. if you know $D_0^{1/2}$ and C_0^*, you can extract $\underline{\underline{A}}$.

5.2.3

Microscopic vs. Geometric Areas (projected area)



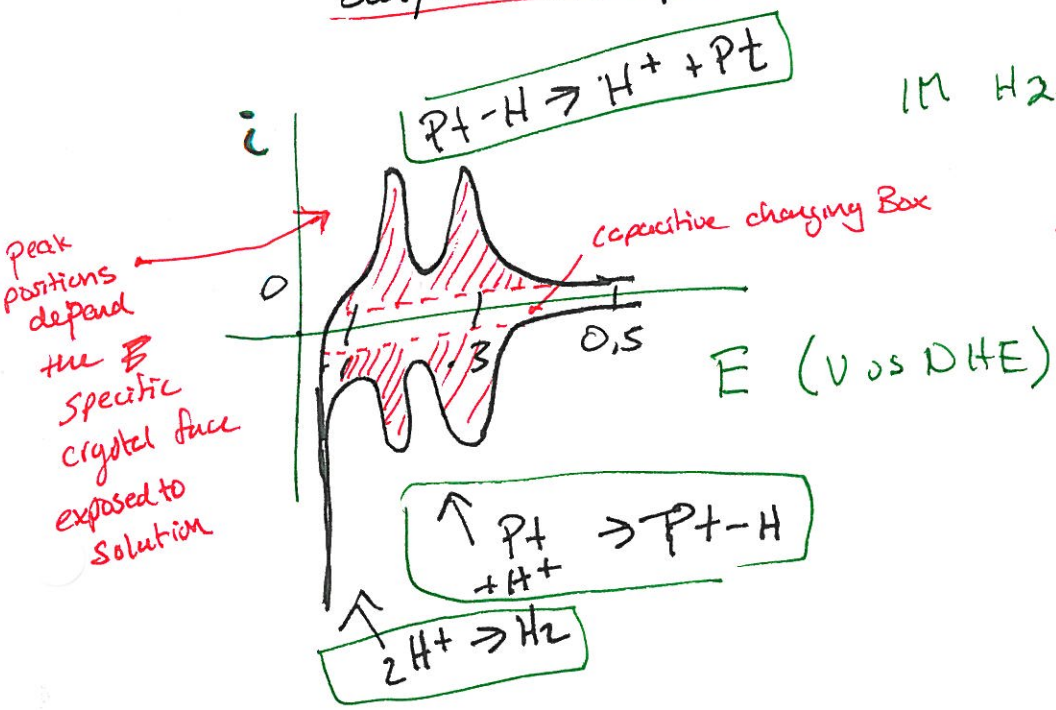
roughness factor = A_m / A_g

→ 2-3 for polished electrode (mirror)

→ >1.5 single crystal surface

mercury pool electrodes assumed atomically smooth

How do you measure the real surface area of an electrode?

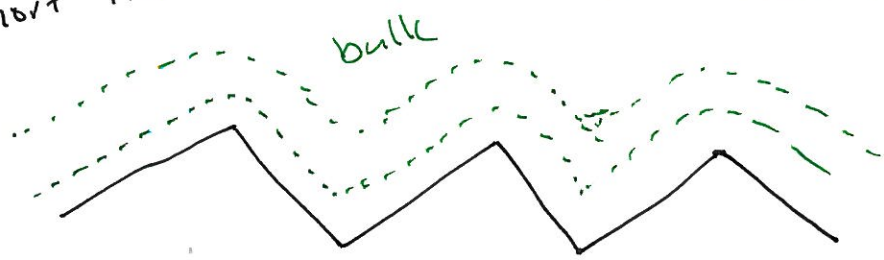


→ integrate peaks to get Q, which is related to the number of exposed surface Pt sites.

in Cottrell potential step experiment, with freely diffusing redox species, which is the correct area to use?

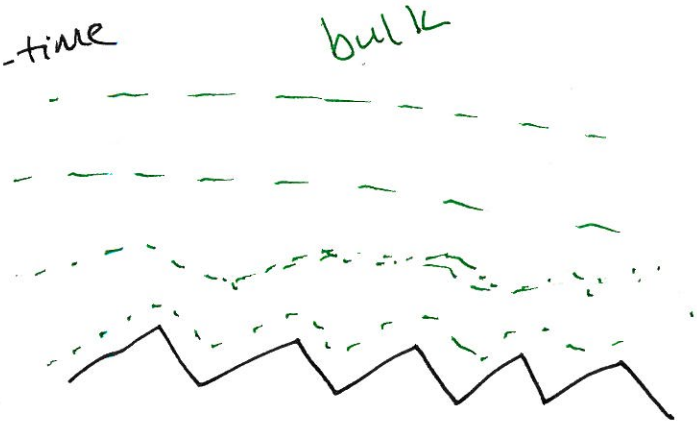
Depends on the time scale!

Short time



Diffusion field → does the ~~diffusion~~ concentration gradient that drives diffusion follow the surface ~~contours~~ contours?

long-time



← far from the electrode, surface looks "flat"

i.e. active species is consumed in the regions close to the rough electrode.

Remember from "Drunken Sailor" walk

$\bar{\Delta} = \sqrt{2Dt}$ (root mean square displacement)

$D \sim 10^{-5}\ cm^2/s$ so in $1\ \mu s$

$\bar{\Delta} = \sim 5 \times 10^{-6}\ cm = 50\ nm$ → (can't record this fast (RC time constant))

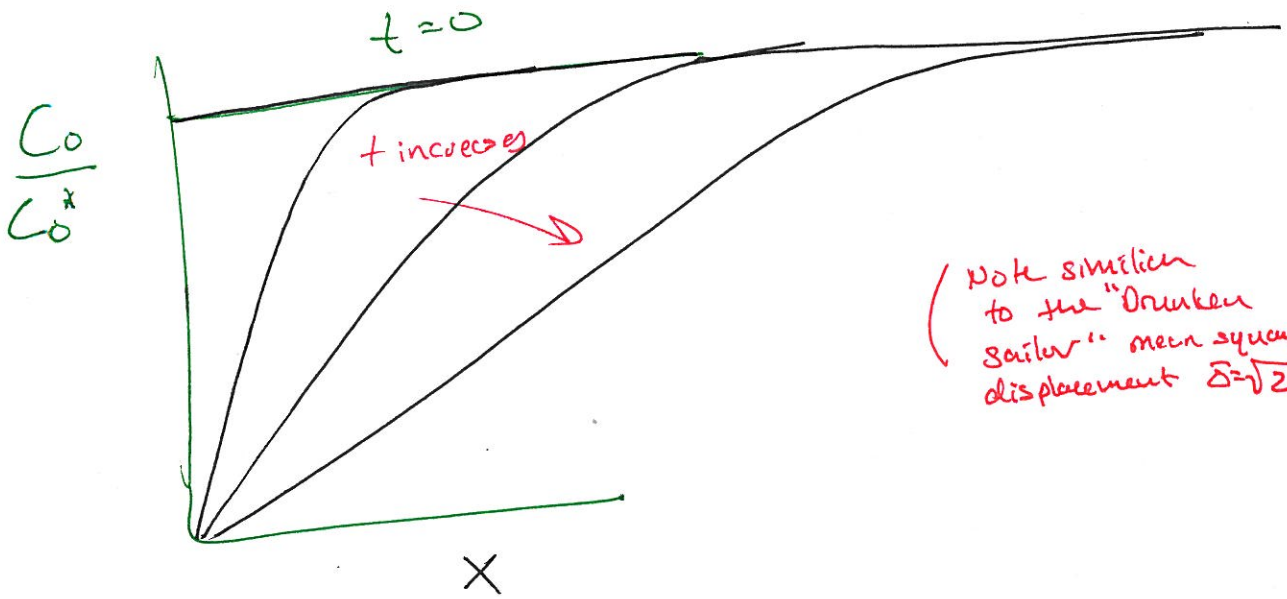
in $1\ ms$ $\bar{\Delta} = 50\ \mu m$ → surface roughness "invisible"

Skip see next page.

More rigorously

$$\boxed{C_o(x,t) = C_o^* \, \mathrm{erf}\left[\frac{x}{\underbrace{2(D_o t)^{1/2}}_{\text{Diffusion length}}}\right]}$$

$$\boxed{\mathrm{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2}\, dt}$$



(Note similiar to the "Drunken sailor" mean square displacement $\bar{\delta} = \sqrt{2Dt}$)

if $x = 2(D_o t)^{1/2}$ then $\boxed{\mathrm{erf}(1) = 0.84}$

so at distance of $2(D_o t)^{1/2}$, concentration is 84% of the bulk concentration.

for $D_o = 1 \times 10^{-5}\ cm^2 s^{-1}$

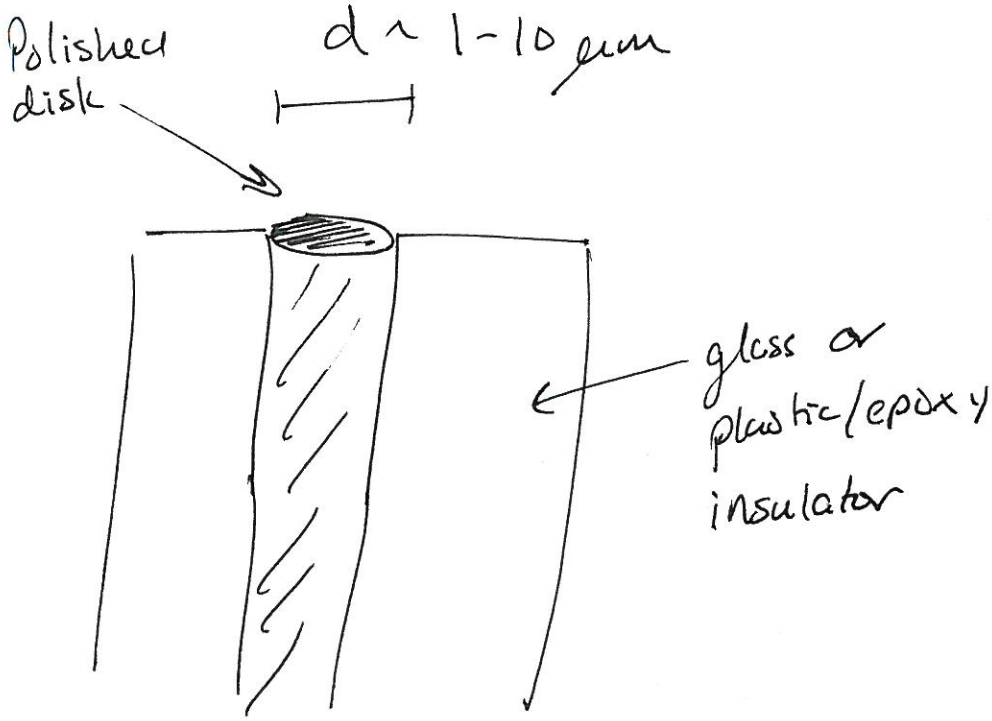
	$t = 1\,\mu s$	1 ms	1 s
$2(D_o t)^{1/2} =$	60 nm	2 μm	60 μm

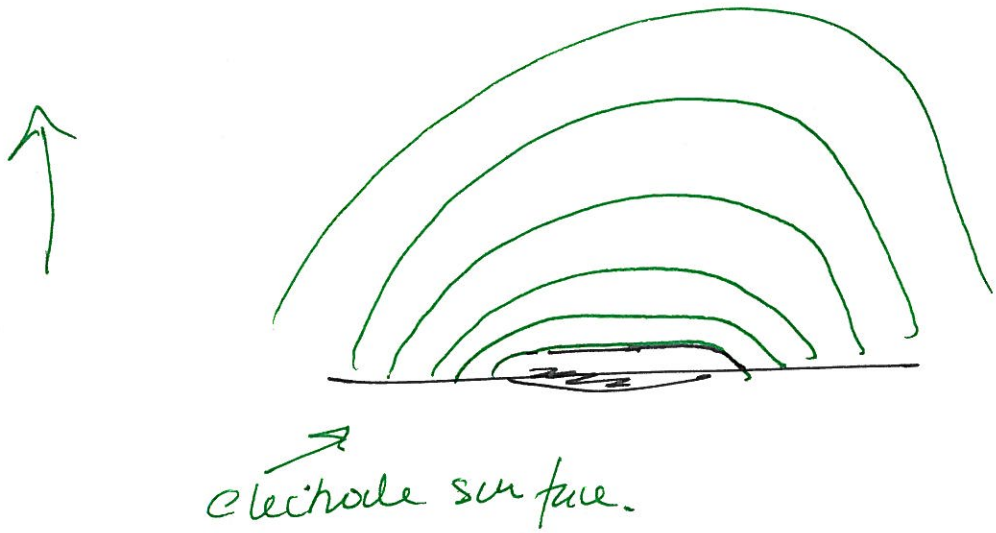
So, surface roughness only comes into play when "diffusion" fields of surface features do not overlap.

5.3.1

Ultra micro electrodes and Semi-infinite Spherical Diffusion

Q: What happens if the diffusion field is much larger than the size of the electrode





look far enough away, everything appears to be like a point...

Consider a spherical diffusion field:

(from a spherical electrode)

Ficks Second law

$$\frac{\partial C_O(r,t)}{\partial t} = D_O \left\{ \frac{\partial^2 C_O(r,t)}{\partial r^2} + \frac{2}{r} \frac{\partial C_O(r,t)}{\partial r} \right\}$$

Note: this comes from form of the Laplacian operator in spherical coordinates.

$$\nabla^2 = \frac{\partial^2}{\partial r} + \frac{2}{r}\frac{\partial}{\partial r}$$

The boundary conditions are:

initial condition $C_O(r,0) = C_O^*$ ($r > r_0$, the radius)

semi infinite condition $\lim_{r \to \infty} C_O(r,t) = C_O^*$

surface condition, $C_O(r_0,t) = 0$ $t > 0$

$$i_d(t) = nFAD_oC_o^* \left[\frac{1}{(\pi D_o t)^{1/2}} + \frac{1}{r_o} \right]$$

which can be re-written as

$$i_{spherical} = i_d(t) = \underbrace{i_d(\text{linear})}_{\text{Cottrell part}} + \underbrace{\frac{nFAD_oC_o^*}{r_o}}_{\text{constant part}}$$

so at $\lim t \to \infty$, $i_{spherical} \to \frac{nFAD_oC_o^*}{r_o}$

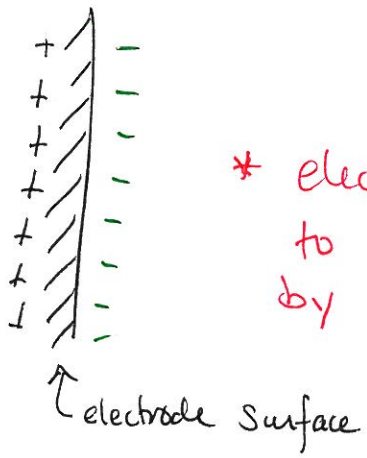
Diffusion Field able to draw current from ~~for~~ continually increasing in size regions of the cell.

if

- For large (ie $r_o \sim 1mm$) electrodes can't see this due to convection from vibrations, ΔT, or $\Delta \rho$.
- for microelectrodes, very easy to see this → diffusion layer $\sim \sqrt{Dt}$ needs to be on order of thickness as r_o (analogy to planet Earth.

Applications of Micro electrodes

Consider how a potentiostat works



* electrode potential relative to the solution is adjusted by changing double-layer charge.

What determines how long it takes to change the potential?

double layer capacitance

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

potential step

$\tau = R_s C_d$ = cell time constant.

- for $t \ll \tau$ $q = \emptyset$!
- for $t \gg \tau$ $q = E C_d$

So the time constant for the cell $(R_a C_d)$ determines how fast one can change the electrode potential.

The size of the working electrode controls the time response.

capacitance per unit area.

$$\boxed{C_d = \pi r_0^2 C_d^0}$$

↑ radius

$$\boxed{C_d^0 = 10\text{-}50\ \mu F\ cm^{-2}}$$

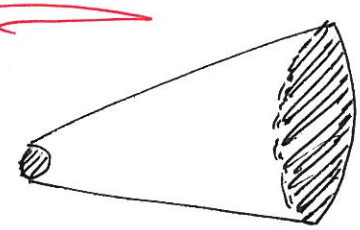
but the series resistance, R_u, also depends on the electrode area.

$$R_u = \frac{1}{4\pi K r_0}\left(\frac{x}{x + r_0}\right)$$

$x \gg r_0$

$$\boxed{= \frac{1}{4\pi K r_0}}$$

solution conductivity



So $$R_u C_d = \frac{\cancel{\pi} r_0^{\cancel{2}} C_d^0}{4\cancel{\pi} K \cancel{r_0}} = \boxed{\frac{C_d^0 r_0}{4K}}$$

So cell time constant is linear function of r_0 → can make $R_u C_d = \tau$ as small as you want.