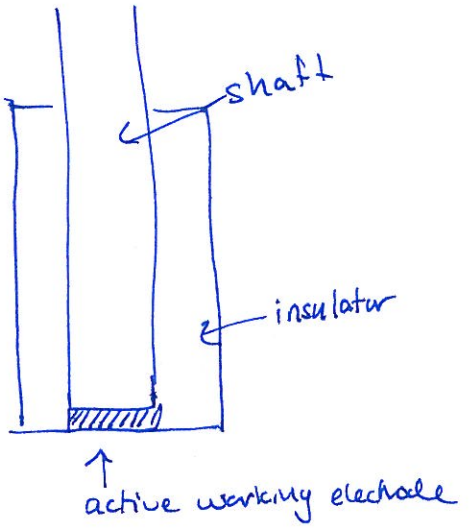
Rotating Disk Voltammetry / Electrode (B+F chapter 9)

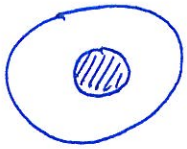
Hydrodynamic methods → involve the forced convection (movement) of solution.

→ many methods to do this, one is called the R.D.E.

advantages

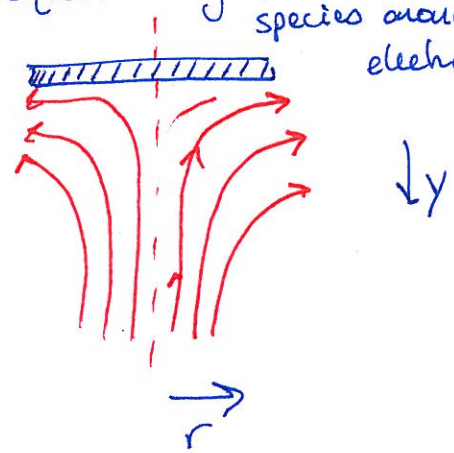
1. steady-state attained quickly
2. rates of mass-transfer typically larger than rate of diffusion alone
   → less effect of mass transport on i-E curves
3. ability to control the delivery of species to the electrode surface by controlling the rotation velocity.

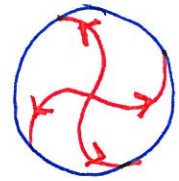




Bottom view

solution of hydrodynamic equations gives the flow of species around the electrode:





Bottom view of solution flow

→ now need to solve the "convective-diffusion" equation. – Difficult but details are in Bard & Faulkner

$$i_c = 0.62\, n F A D_o^{2/3} \omega^{1/2} \nu^{-1/6} \left[C_o^* - C_o(y=0) \right]$$

Bulk Concentration

concentration at the electrode surface

or

$$\boxed{i_{l,c} = 0.62\, n F A D_o^{2/3} \omega^{1/2} \nu^{-1/6} C_o^*}$$

* Levich Equation

→ limiting current, (associated w/ delivery of species to the electrode surface via convection/diffusion)

i_a and $i_{l,c}$ can be written similarly

so for a reversible couple (Nernst equation defines the surface concentration of species)

need to show more steps next time through

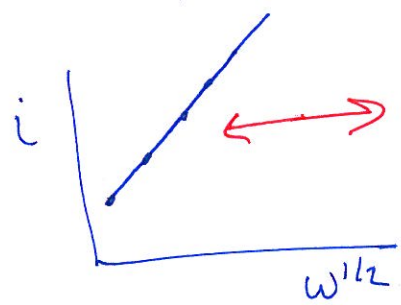
$$E = E_{1/2} + \frac{RT}{nF} \ln \left(\frac{i_{l,c} - i}{i - i_{l,a}} \right)$$

$$E_{1/2} = E^o + \frac{RT}{nF} \ln \left(\frac{D_R}{D_O} \right)^{2/3}$$

Note: very similar to equations derived in chapter 1, assuming linear diffusion across the stagnant layer

thus, for a reversible reaction, the shape of the curve is independent of ω, the rotation frequency. but

$$i \propto \omega^{1/2}$$



• deviation from linearity indication that kinetics are important.

i.e. as you increase $\omega^{1/2}$ you don't get linear increase in current.

For example, for a totally irreversible (i.e. reverse reaction negligible) reaction:

$$i = FA\,k_f(E)\,C_o(y=0) \quad \text{where } k_f(E) = k^o \exp(-\alpha f(E-E^o))$$

9.3.31

$$C_o(y=0) = \left(\frac{i}{i_{l,c}} - 1\right) C_o^* \; (-1)$$

re-arranged

$$i = i_{l,c}\left[\frac{C_o^* - C_o(y=0)}{C_o^*}\right]$$

so

$$i = FA\,k_f(E)\,C_o^*\left(1 - \frac{i}{i_{l,c}}\right) = i_K\left(1 - \frac{i}{i_{l,c}}\right)$$

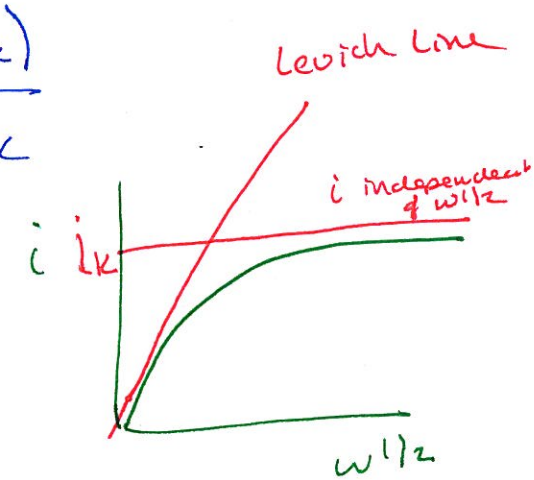
where $\boxed{i_K = FA\,k_f(E)\,C_o^*}$

↳ kinetic current

$$i = i_k\left(1 - \frac{i}{i_{l,c}}\right) = i_k - \frac{i\,(i_k)}{i_{l,c}}$$

$$i\left(1 + \frac{i_k}{i_{l,c}}\right) = i_k$$

$$i = \frac{i_k}{1 + \frac{i_k}{i_{l,c}}} = \frac{1}{\frac{1}{i_k} + \frac{1}{i_{l,c}}}$$



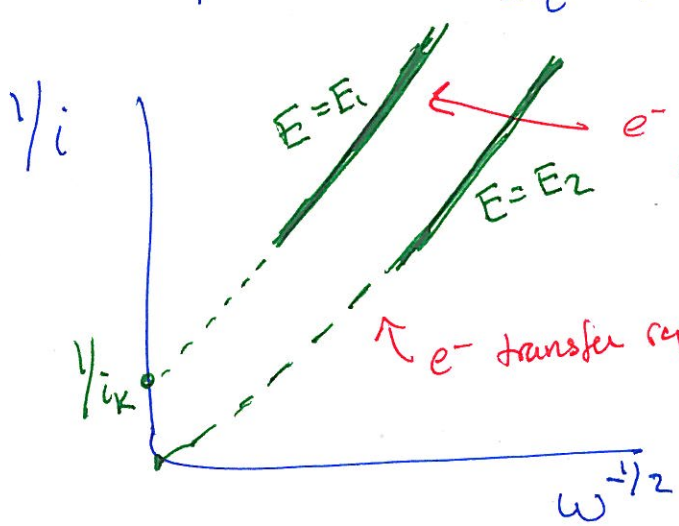
$$\boxed{\frac{1}{i} = \frac{1}{i_k} + \frac{1}{i_{l,c}}}$$

tells you something about mass transfer

tells you something about kinetics

Koutecky-Levich Equation $\quad i_{l,c} \propto \omega^{1/2}$

K-L Plot →



e^- transfer slower, i_k smaller.

e^- transfer rapid ($\frac{1}{i_k}$ negligible)

Determination of i_K at different values of the electrode potential allow for determination of k^o and α!

So RDE is good for kinetic studies.

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since $i_K = \underbrace{FAC_o^*}_{\text{known}} \; k^o \exp\left(-\alpha \underbrace{f(E-E^o)}_{\text{known}}\right)$

two parameters

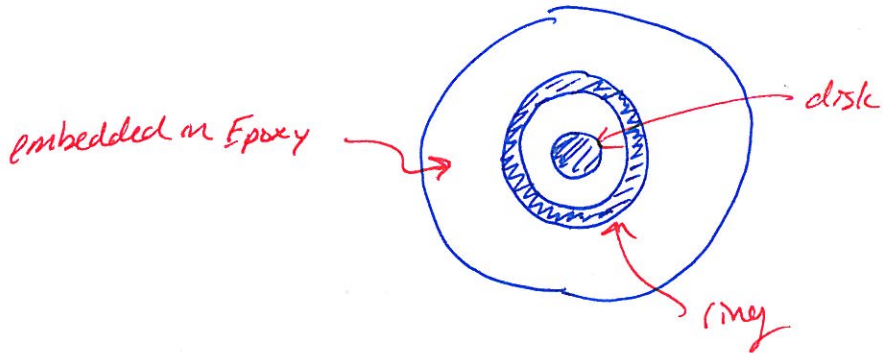
linearize and fit, so that we have expressions for slope and intercept, that give k^o and α.

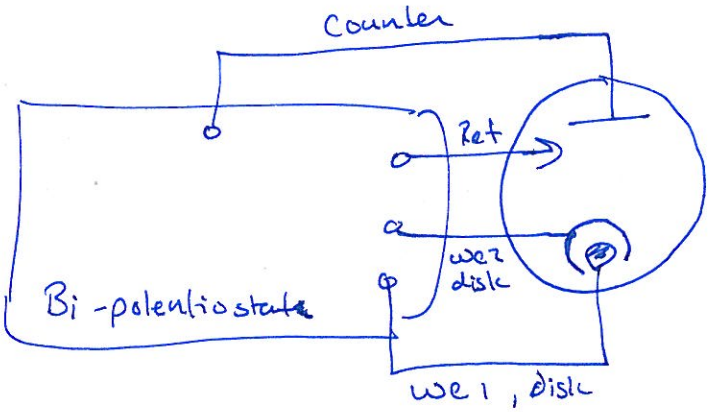
Very common approach for studying the kinetics of electrode reactions.

* Ring-Disk Electrodes → RRDE

rotating ring disk electrode

Similar design, except that





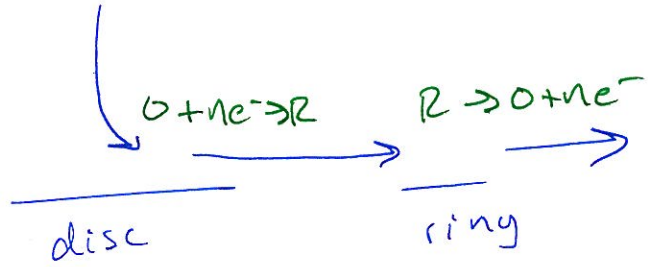
* Bipotentiostat can control the two working electrode potentials independently!

Commonly used for

(a) collection

(b) shielding experiments

Collection experiment



observe what you generate in the disc, by oxidizing it in the ring.

example → generate O_2 at disc,

ask question, does all current go to make O_2 or are there other competing processes?

Answer by reducing water (to i.e. peroxide) at the disk.

Compare current to that expected based on the collection efficiency of the RRDE system.