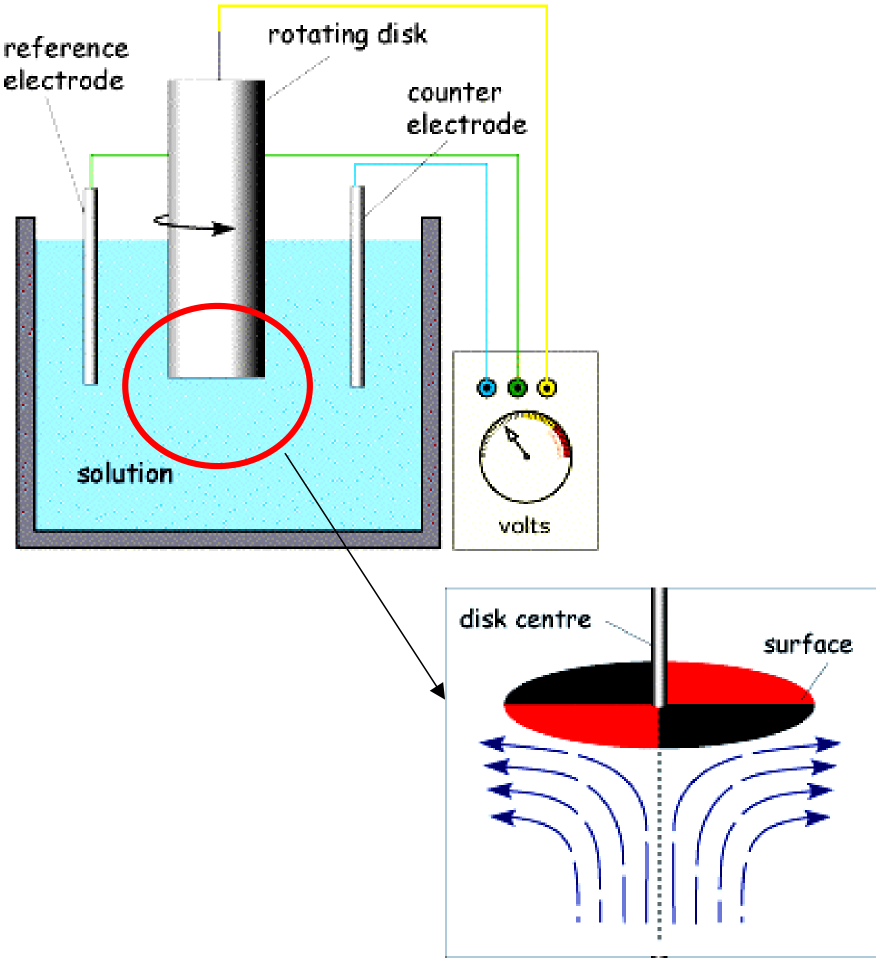
CHEM465/865, 2006-3, Lecture 23+24, Oct. 27, 2006

Rotating Disc Electrode (RDE)

- **most widely used hydrodynamic electrode**
- **efficient mass transport**
- **highly reproducible**

RDE: cylindrical metal rod embedded into bottom face of insulating cylindrical plastic holder (e.g. Teflon).



Constant angular velocity $\omega = 2\pi f$.

Rotation drags solution to electrode surface, resulting in a vortex. Due to this drag and the steady laminar flow to the electrode surface, solution is continuously replaced.

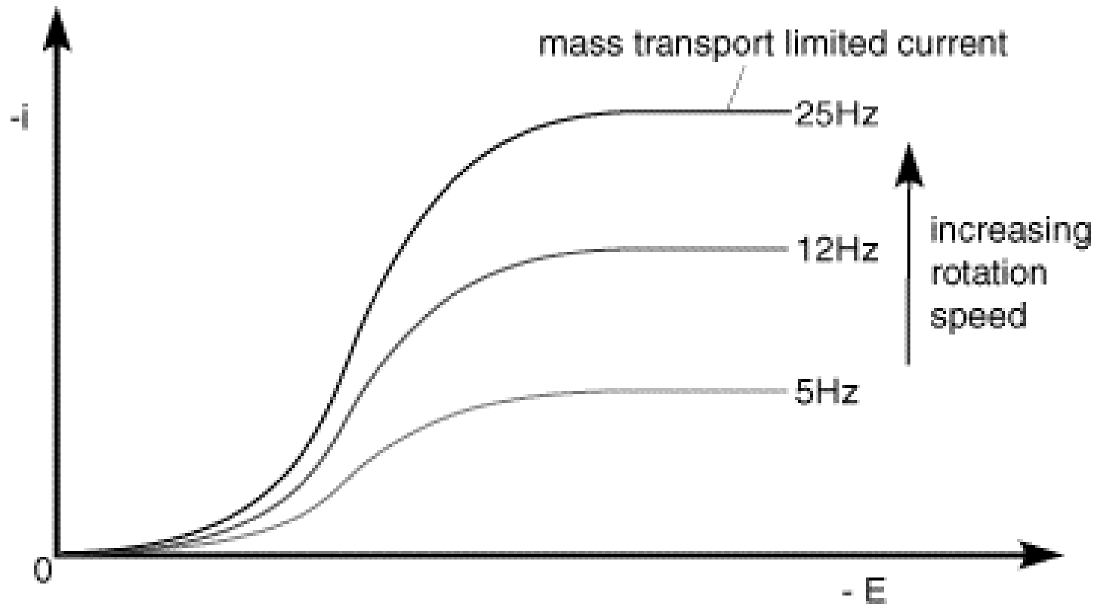
RDE: electrode can be operated at steady state

Small angular velocities $\omega < \omega_c$**: laminar flow profile**

Electrode disc small compared to surface of insulating rod: uniform conditions at electrode surface.

Figure: potential sweep voltammograms

cathodic reaction: $j < 0$**, negative** $E < E^{eq}$**, various** ω



Current in the mass transfer limited region (large $|E|$): independent of time – controlled by rotation speed.

In order to understand this behaviour, we have to return to the concept of the diffusion layer.

What controls the thickness of the diffusion layer?

Transport equations: modified form of Fick's equations

molar flux: $J = \vec{v}c_{\mathrm{ox}} - D\nabla c_{\mathrm{ox}}$

t-variation: $\dfrac{\partial c_{\mathrm{ox}}}{\partial t} = -\vec{v}\nabla c_{\mathrm{ox}}^{\mathrm{b}} + D\Delta c_{\mathrm{ox}}$

convection + diffusion

Results from linear sweep voltammetry indicate, that δ is now controlled by convection and not by diffusion! Stationary operation is possible.

Theory for RDE: Levich theory!

Details of this theoretical solution will be skipped here. They can be found for instance in the book: *Electrochemistry – Principles, Methods and Applications*, C.M.A. Brett, A.M.O. Brett, Oxford University Press, Oxford, 1993, section 5.9).

Consider steady state limiting current density for $\frac{\partial c_{\mathrm{ox}}}{\partial t} = 0$

Thickness of the diffusion layer is given by:

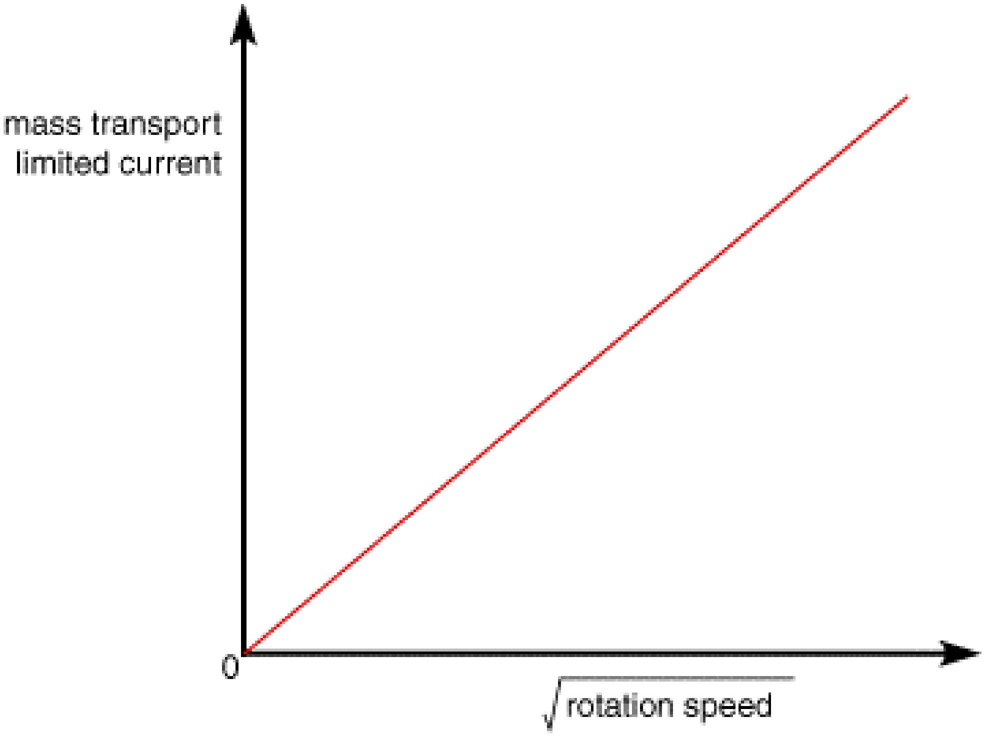
$$\delta = 1.61 D^{1/3} \nu^{1/6} \omega^{-1/2}$$

where ν is the **kinematic viscosity** [cm^2 s^{-1}].

Mass transport limited current density as a function of **rotation speed**

$$j_{\mathrm{L}} = nFD \frac{c_{\mathrm{ox}}^{\mathrm{b}}}{\delta}$$
$$= 0.62 nF c_{\mathrm{ox}}^{\mathrm{b}} D^{2/3} \nu^{-1/6} \omega^{1/2}$$

Plot of j_{L} vs. $\omega^{1/2}$: straight line



Slope of the straight line depends on

- **bulk concentration of reactant**
- **diffusion coefficient**
- **kinematic viscosity**

$$slope = 0.62nFc_{ox}^{b}D^{2/3}\nu^{-1/6}\ .$$

Some notes on using RDE:

- **laminar flow profile:** ω **should be small enough.**

  ⇒ **Reynolds number Re, a characteristic of the flow profile, has to be smaller than a critical value.**

  Reynolds number is defined by

$$\boxed{\mathrm{Re} = \frac{\mathbf{v}l}{\nu}}$$

v: characteristic velocity (fluid vs. electrode surface)

***l*: characteristic length of the electrode**

ν **: kinematic viscosity (inner friction within fluid)**

For RDE:

- v is linear velocity at outer edge of the disc electrode, i.e. $\mathrm{v} = \omega \cdot r$
- $l = r$ is disc radius
- critical Reynolds-Number: $\mathrm{Re}_{\mathrm{crit}} = 10^5$

Criterion for laminar flow:

$$\mathrm{Re} = \frac{\omega r \cdot r}{\nu} = \frac{\omega A_{\mathrm{disc}}}{\pi \nu} << 10^5$$

Kinematic viscosities for dilute aqueous solutions: typically in the range $\nu = 10^{-2}\,\mathrm{cm^2 s^{-1}}$ and thus

$$\omega A_{\mathrm{disc}} << 3 \cdot 10^3\,\mathrm{cm^2 s^{-1}}$$

Consider for example the following disc areas and corresponding upper limits on angular velocity:

$$A_{\mathrm{disc}} = 1\ \mathrm{cm^2} \;\Rightarrow\; \omega << 3 \cdot 10^3\,\mathrm{s^{-1}},$$

$$A_{\mathrm{disc}} = 1\ \mathrm{mm^2} \;\Rightarrow\; \omega << 3 \cdot 10^5\,\mathrm{s^{-1}}$$

Smaller electrode surface area – operation at larger angular velocities possible

- On the other hand: ω controls thickness of the diffusion layer (see expression for δ in Levich theory), which controls the limiting current density due to diffusion.

Larger ω $\Rightarrow$ smaller δ $\Rightarrow$ larger j_L

$\Rightarrow$ ω should not be too small

Typical frequency range for RDE with 0.3 cm radius:

$$10\ \mathrm{s}^{-1} \ll \omega \ll 3 \cdot 10^{3}\ \mathrm{s}^{-1}$$

- Electrode and rod need to be perfect cylinders to avoid wobbling around the axis. This is not a problem for mm sized electrodes. It could be a problem for smaller electrodes.

Capabilities of RDEs:

- **Diffusion limited regime (large $|\eta|$):**

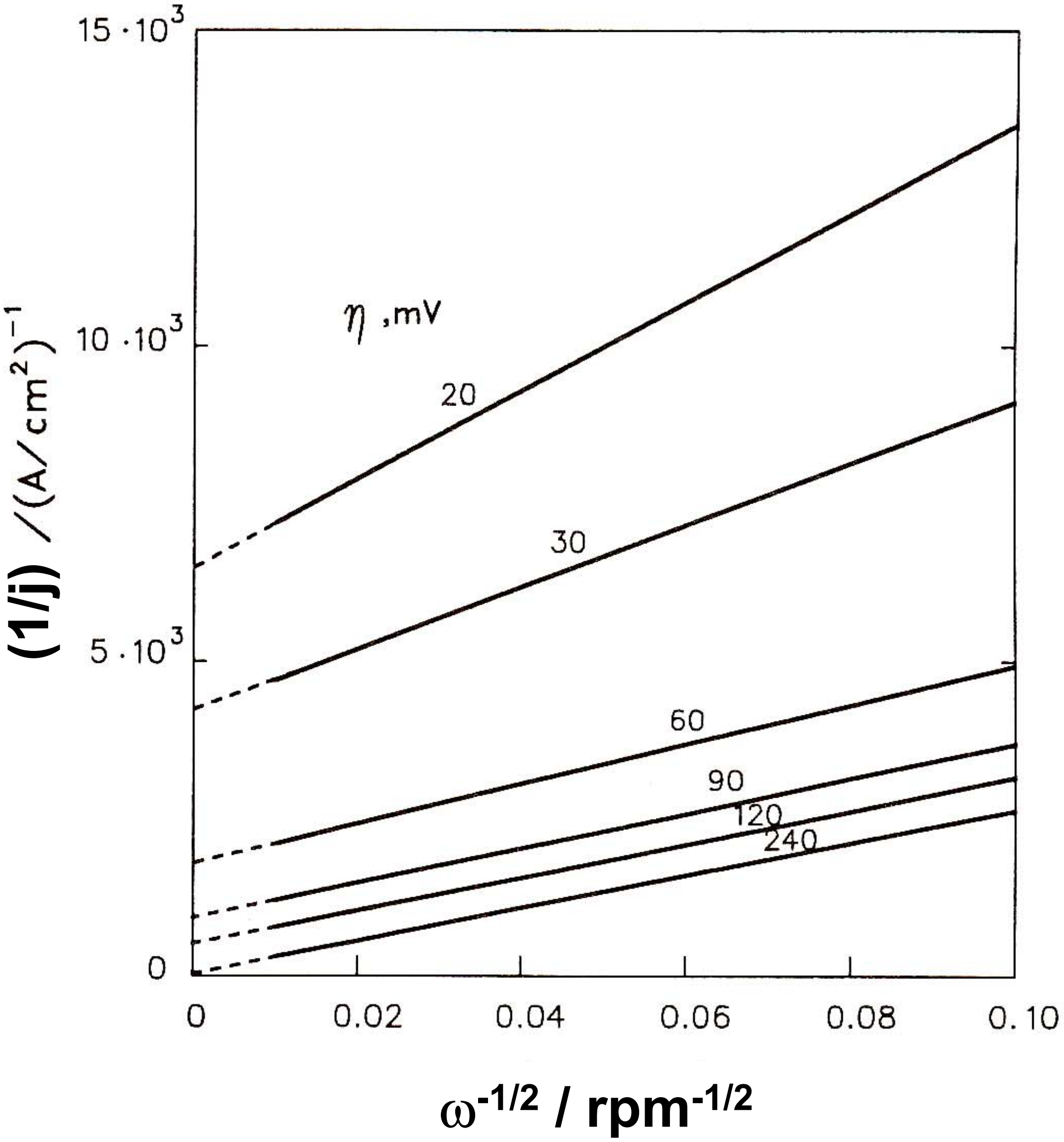
  Plot j_L vs. $\omega^{1/2}$ – determine diffusion coefficient of reactant in solution or concentration of reactant

- **Kinetic or mixed regime (small to medium $|\eta|$):**

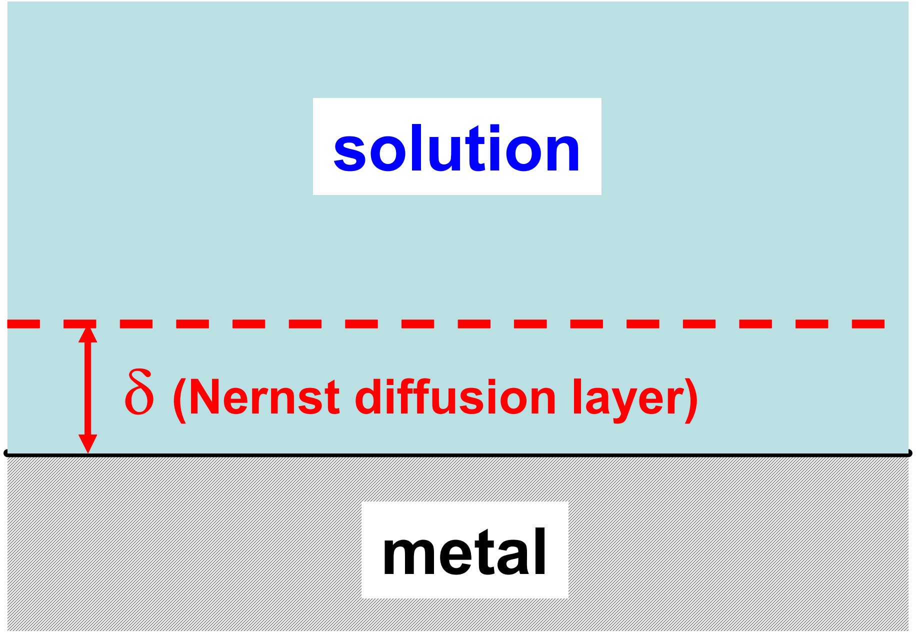
  Total current density j – determined by activation controlled current density j_{ac} and diffusion-limited current density j_{diff}

$$\boxed{\frac{1}{j}=\frac{1}{j_{ac}}+\frac{1}{j_{diff}}=\frac{1}{j_{ac}}+\frac{1}{B\omega^{1/2}}}$$

  - ❑ **Series equivalent circuit of mass transport and activation barrier that electroactive species have to overcome in order to react**
  - ❑ **Right hand side: frequency dependence of diffusion limited current**
  - ❑ **Plot $1/j$ over $\omega^{-1/2}$ (at fixed potential): straight line, intercept with ordinate, i.e. the $\omega \to \infty$ limit give j_{ac}, as shown below**



So far, we have always been considering (semi-)infinite systems! What does this mean?



- electrode surface is planar
- solution: infinite reservoir of electroactive species
- far away from electrode/solution interface: constant concentrations (bulk concentration)

In this situation:

one relevant length scale in the system →

thickness δ of the Nernst diffusion layer, adjacent to electrode, concentrations deviate significantly from bulk concentrations

Essentially, always the same basic competition

rate of the electrode reaction vs. rate of mass transport to the surface

k^0

$$k_{\text{diff}} = \frac{D}{\delta}$$

Want to understand how a certain electrochemical system would perform in an experiment? Start by having a look at the two relevant constants, k^0 and k_{diff}!!! This will tell you which process is the most important one.

- Rate of reaction k^0: fixed (electrode material, crystallographic surface structure, solution, redox couple); range of variation: 10 cm/s to 10^{-14} cm/s!!.
- Diffusion coefficients: also fixed system; vary in narrow range, ~ 10^{-5} cm^2/s (aqueous solutions)
- Only parameter that you can somehow control: thickness of the diffusion layer, δ

Hydrodynamic devices: control δ

Microelectrodes: another critical length scale, the **radius of the electrode**

If you …

- understand these principles,
- know how to describe the corresponding phenomena (Butler-Volmer equation, diffusion-equation, convection, ...)
- know how to apply this to real systems (e.g. DME, RDE)
- know how to circumvent problems with mass transfer (control δ)

... then you have already a good understanding of some of the main topics in electrochemistry!

What is a microelectrode