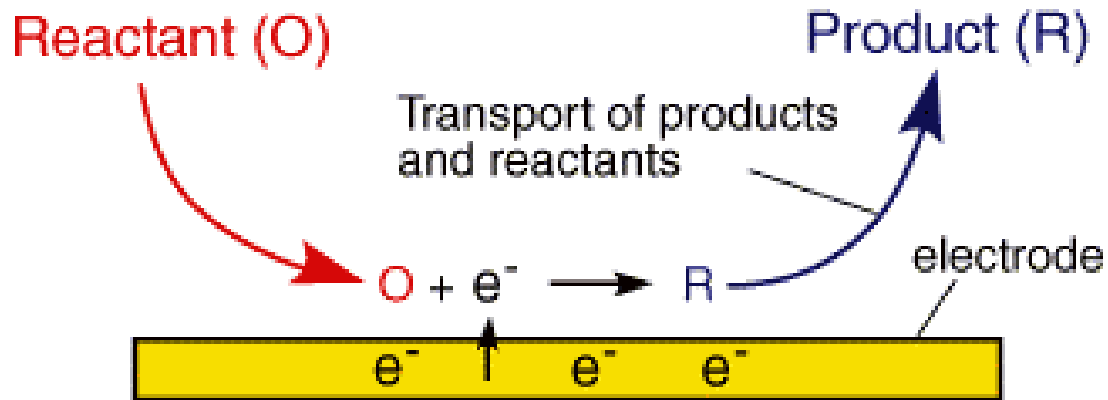


Mass transport effects in voltammetry

Lecture 14 and 15



Mass Transport in Electrochemistry

In order to react a species at an electrode it needs to be transported from bulk to surface.

Three principal mechanisms:

- **Diffusion** is the movement of molecules along a concentration gradient, from an area of high concentration to an area of low concentration.
- **Migration** is the transport of a charged species under the influence of an electric field.
- **Convection** is the transport of species by hydrodynamic transport (e.g. natural thermal motion and/or stirring).

The electrode reaction

Current flow at Electrode Surface

The current that flows from a surface electrochemical reaction can be defined as (using the example of reduction of O):

$$i = \frac{dq}{dt} \qquad i_c = -nFAk_{red} [O_{electrode}]$$

$F = N_A e = 96485 \text{ Cmol}^{-1}$ The amount of charge in C transferred for 1 mole of reactant.

Also remember:

So, in order to understand an electrochemical reaction it is necessary to have a feeling for the concentration of the reactant [O] as a function of distance from electrode *and* with respect to time as a reaction progresses.

By convention, cathodic reactions involving a reduction process have a negative current, anodic reactions involving oxidation have a positive current.

Diffusion limited electrode reactions & Fick's laws

Fick's first law quantifies the movement of a species (under diffusion control) with respect to distance x from an electrode with the flux, J .

$$J_o = -D_o \frac{\partial[O]}{\partial x} \quad \text{1st law}$$

More important is to understand how surface concentration changes as function of time:

$$\frac{\partial[O]}{\partial t} = D_o \left(\frac{\partial^2[O]}{\partial x^2} \right) \quad \text{2nd law}$$

Solving Fick's second law (for planar electrode boundary conditions), and then substituting $i_c = nFAk_{red}[O_{elect}]$ gives the Cottrell equation:

$$|i| = \frac{nFA[O] \sqrt{D}}{\sqrt{\pi} \sqrt{t}}$$

note here $[O]$ is now the *bulk* concentration of O.

Potential step Voltametry (Chronoamperometry)

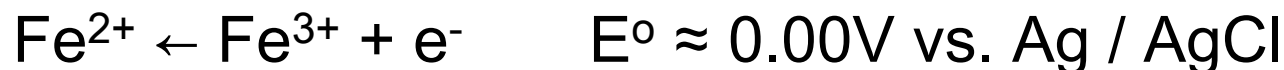
- Have seen that current is proportional to $1 / \sqrt{t}$ when reactants move under diffusion control to an electrode.

What does this mean?

Consider the equilibrium: $\text{Fe}^{2+} \rightleftharpoons \text{Fe}^{3+} + \text{e}^-$

At relatively negative voltages, equilibrium is on L.H.S.

At positive potentials equilibrium shifts to right:

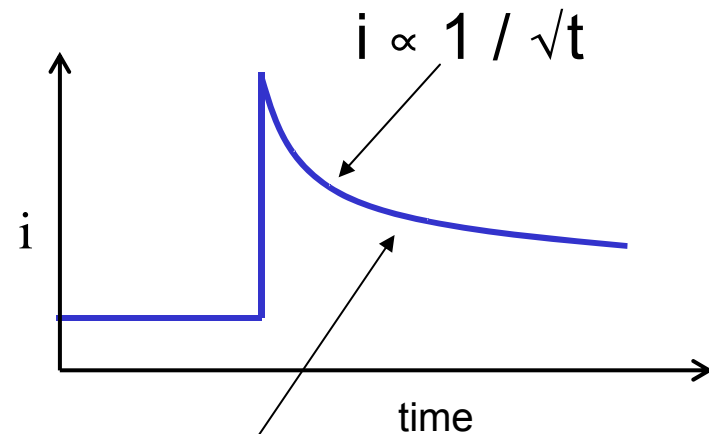
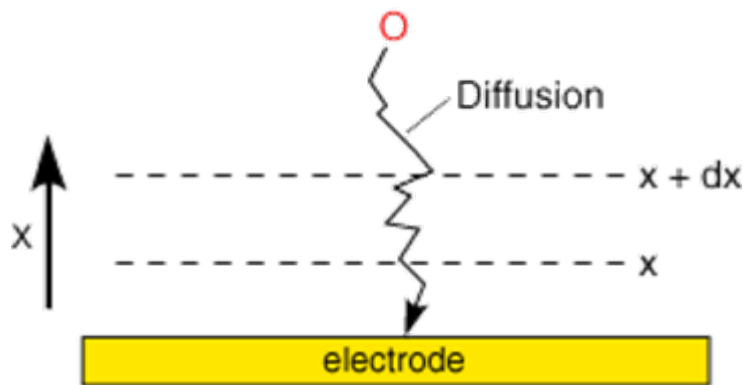


Remember, relative concentrations of Fe^{2+} and Fe^{3+} quantified by the Nernst equation:

$$E = E^\circ + \left(\frac{RT}{nF} \right) \ln \frac{[ox]}{[red]}$$

Chronoamperometry experiment

- Take a solution of e.g. Fe^{3+} at low conc. in 0.1M KCl
- Apply 0.5V (V1) then step to 0.00 V (V2).
- Measure change in current with time.



So current peaks, then decays. Note decay of current described by Cottrell equation.

$$|i| = \frac{nFA[\text{O}]_{\text{bulk}} \sqrt{D}}{\sqrt{\pi} \sqrt{t}}$$

Determination of Diffusion coefficient D from chronoamperometry

- Perform a potential step measurement.
- Ignore current before potential step.
- Linearise Cottrell equation

$$|i| = \frac{nFA[O]_{bulk} \sqrt{D}}{\sqrt{\pi} \sqrt{t}} \quad \longrightarrow \quad \frac{1}{i^2} = \frac{\pi \cdot t}{n^2 F^2 A^2 [O]_{bulk}^2 D}$$

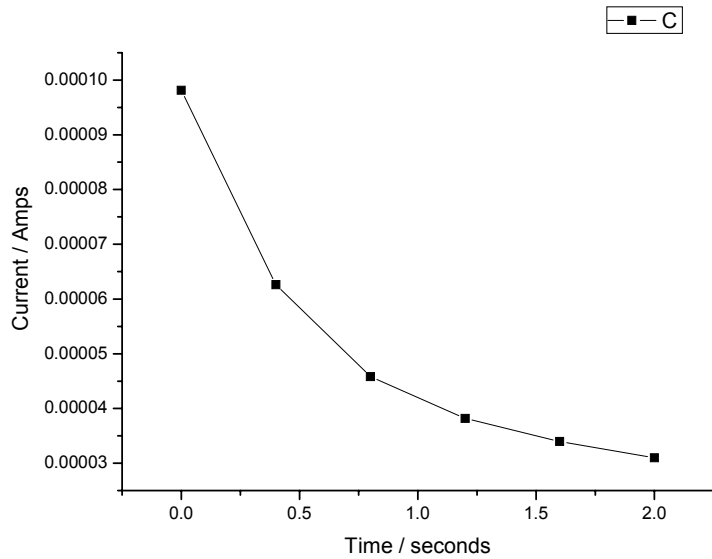
Plot $1 / i^2$ vs t

Gradient = $\pi/n^2F^2A^2[O]^2D$

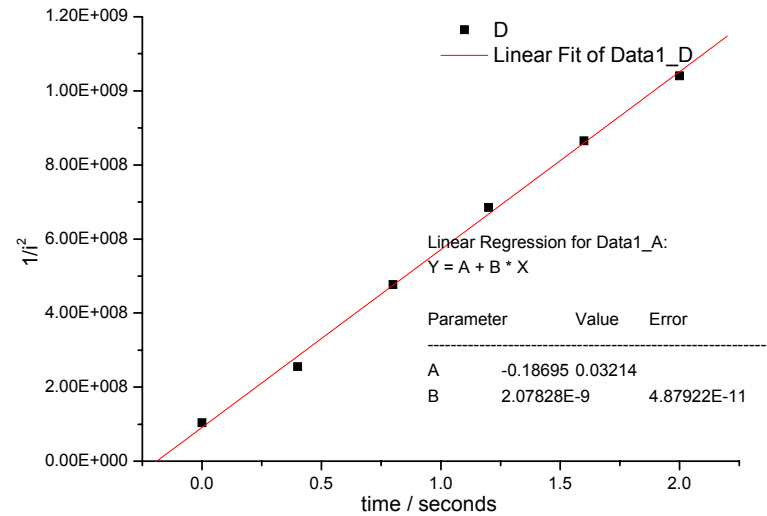
Be ultra-careful with units, especially of concentration. Best to be in mol m^{-3}

$$1 \text{ mmol dm}^{-3} = 1 \text{ mol m}^{-3}$$

Using potential step results



Experiment results



Linearisation

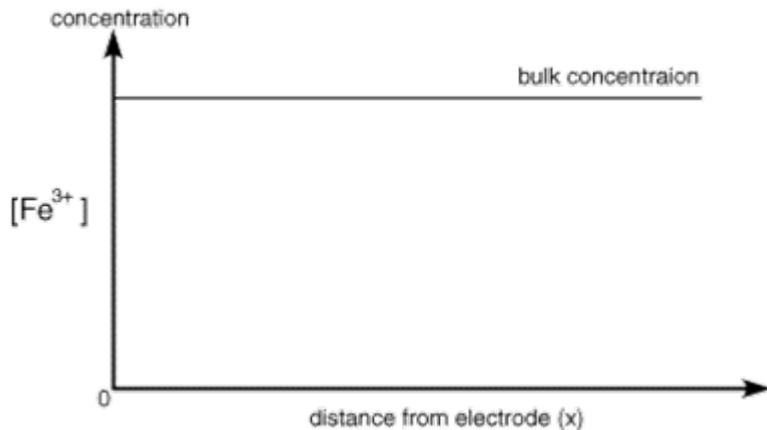
Estimation of the diffusion layer thickness

- If the diffusion coefficient of an electroactive species is known, or has been calculated, the diffusion layer thickness can be estimated using this equation:

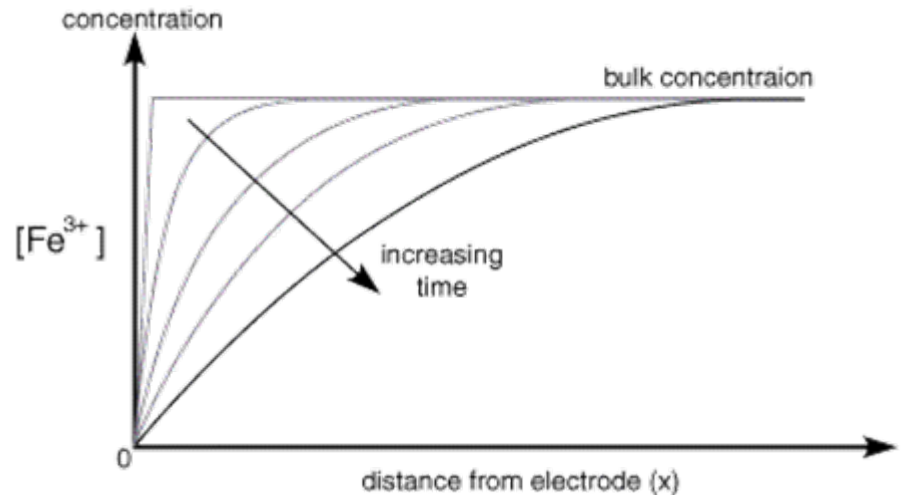
$$l = \sqrt{\pi Dt}$$

- It can clearly be seen that the diffusion layer extends into the bulk solution more and more slowly after application of a potential step. Hence for a molecule with a diffusion coefficient of $1 \times 10^{-10} \text{ m}^2\text{s}^{-1}$, the diffusion layer thickness is around $20 \text{ }\mu\text{m}$ after 1 second.
- The fraction of molecules oxidised or reduced can also be estimated by calculating the volume of a hemispherical diffusion layer around a circular electrode as a fraction of the total solution.

Current behaviour described by Fick's 1st and 2nd laws



Concentration versus distance above the electrode before voltage step



Concentration versus distance above the electrode just after pulse

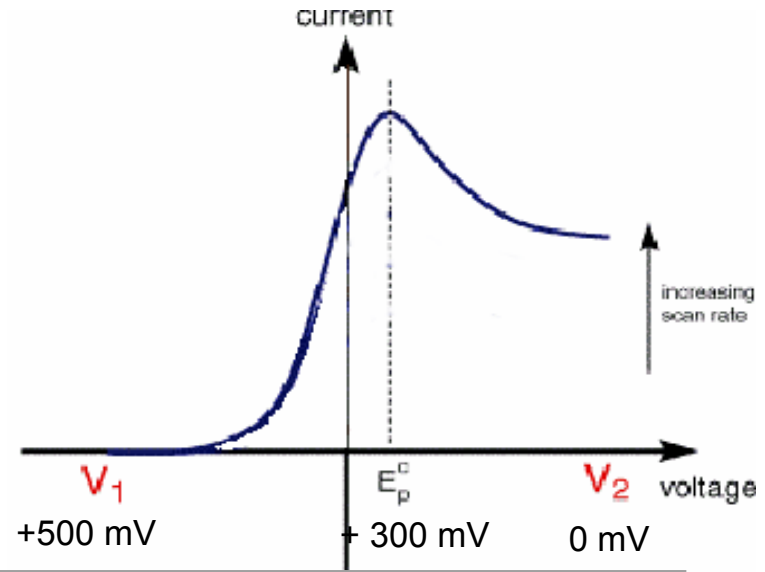
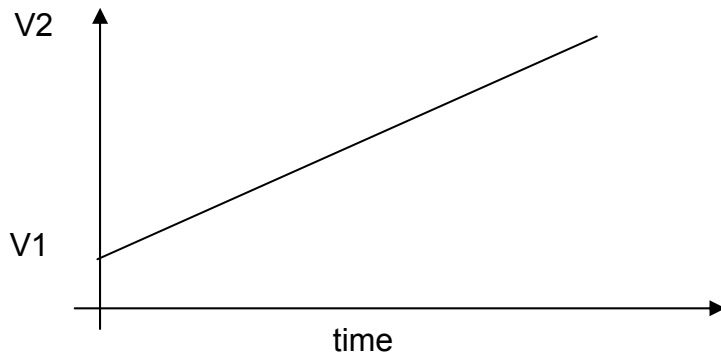


$$J_o = -D_o \frac{\partial [O]}{\partial x}$$

$$i \propto J$$

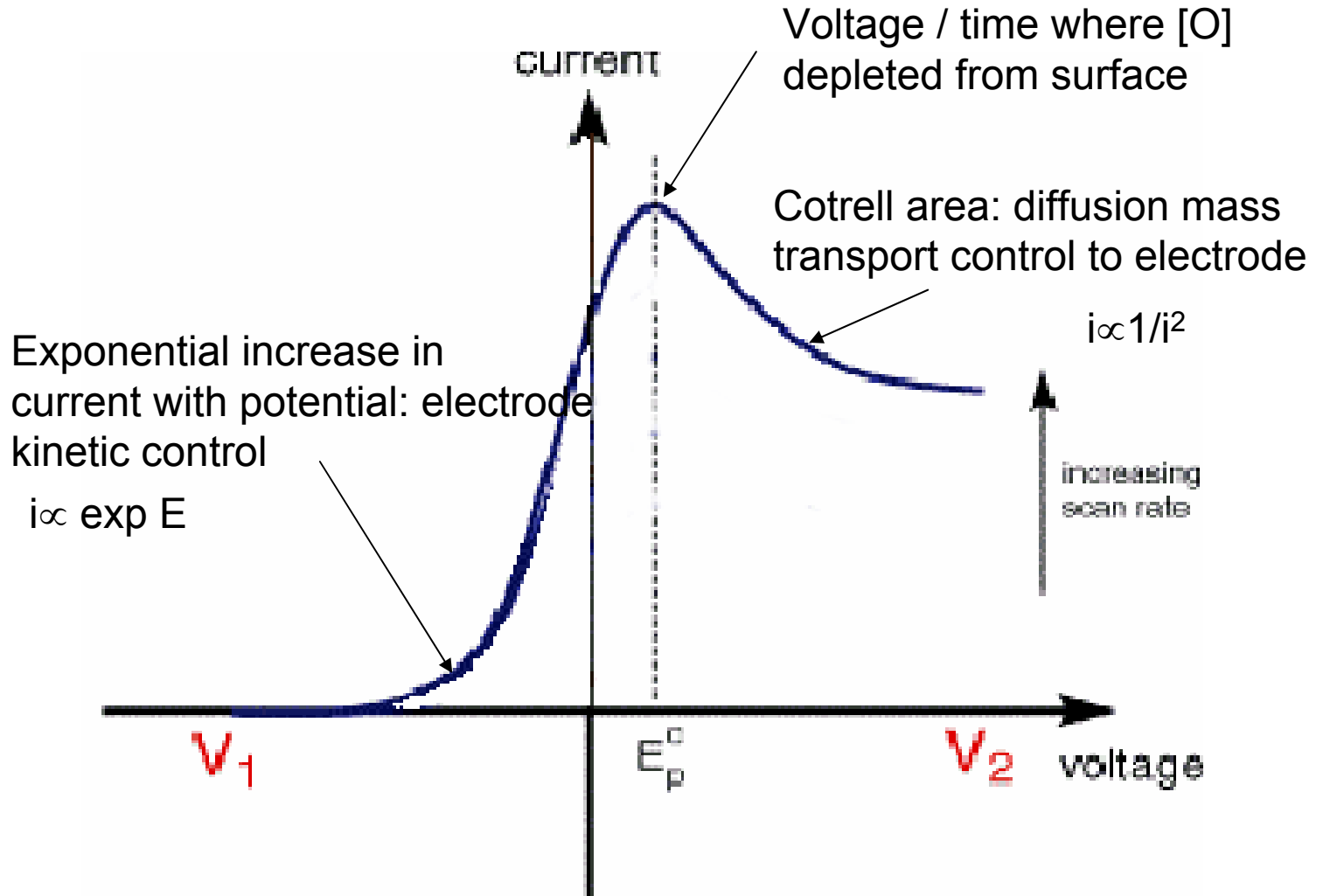
Linear Sweep Voltammetry

- Concept similar to Chronocoulometry but a voltage sweep applied instead of a pulse.



$\text{Fe}^{3+} + \text{e}^- \rightleftharpoons \text{Fe}^{2+}$	V1
$\text{Fe}^{3+} + \text{e}^- \rightleftharpoons \text{Fe}^{2+}$	$\sim E_p$
$\text{Fe}^{3+} + \text{e}^- \rightleftharpoons \text{Fe}^{2+}$	
$\text{Fe}^{3+} + \text{e}^- \longrightarrow \text{Fe}^{2+}$	V2

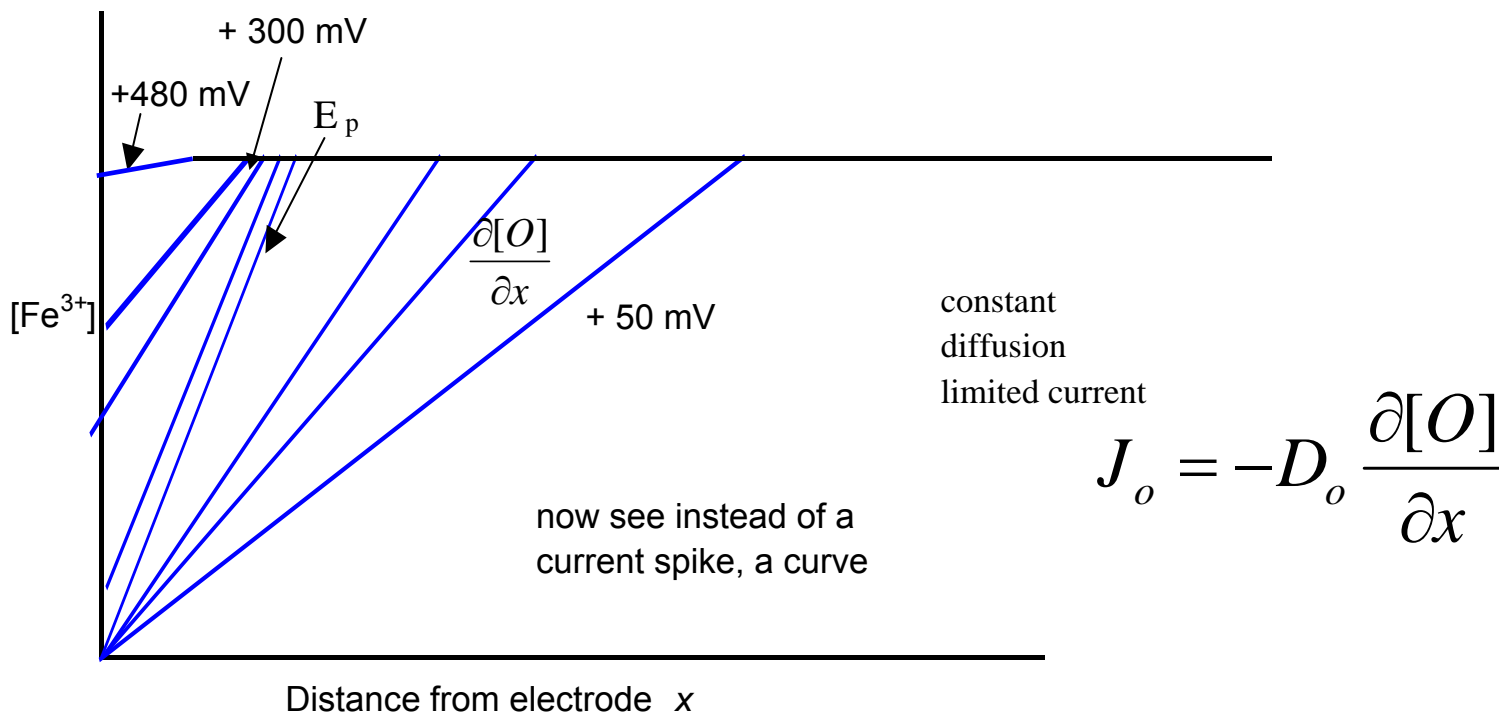
LSV result



Interpretation of LSV results

It is very important to remember when interpreting such data, that since the voltage is being swept at a constant rate, then the voltage axis in the current – voltage curve is **also** a time axis.

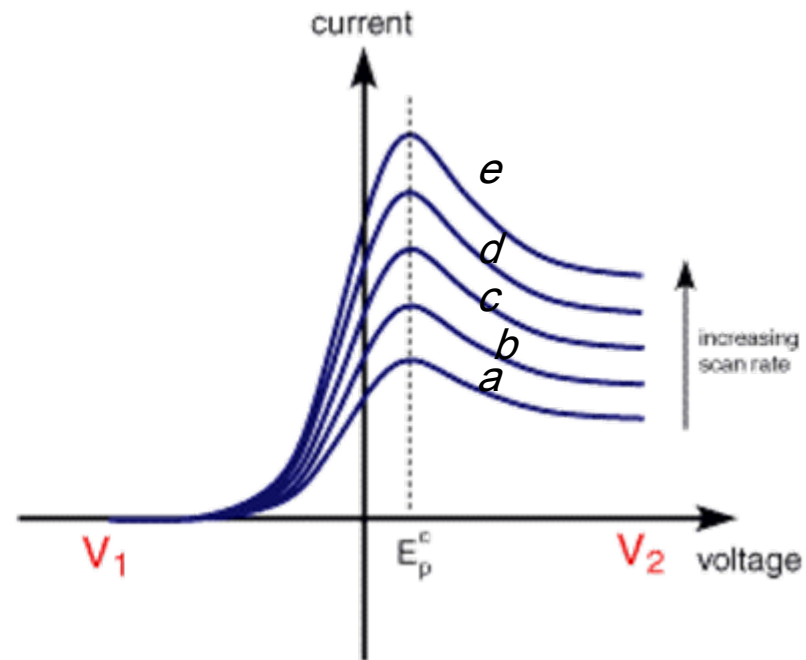
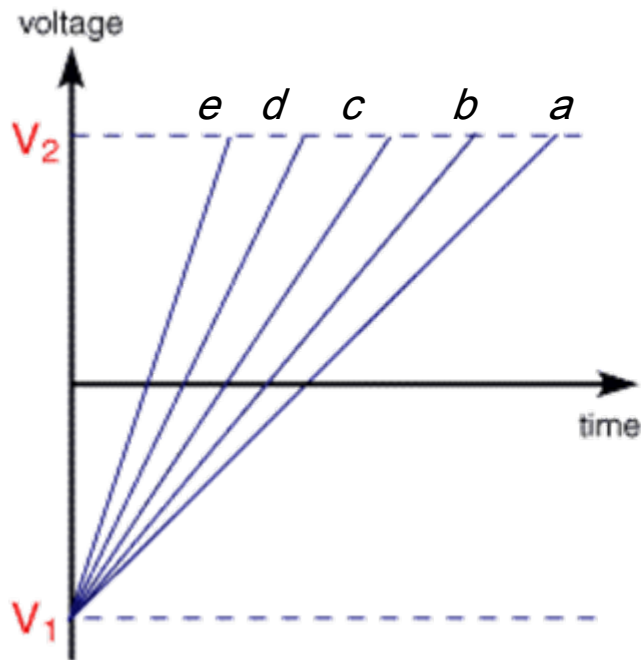
- Why does the current not just rise with applied voltage? / Why is a current peak observed?
- Can be understood in terms of the mass transport of reactants to the electrode in the same way as for chronoamperometry.



Effect of scan rate

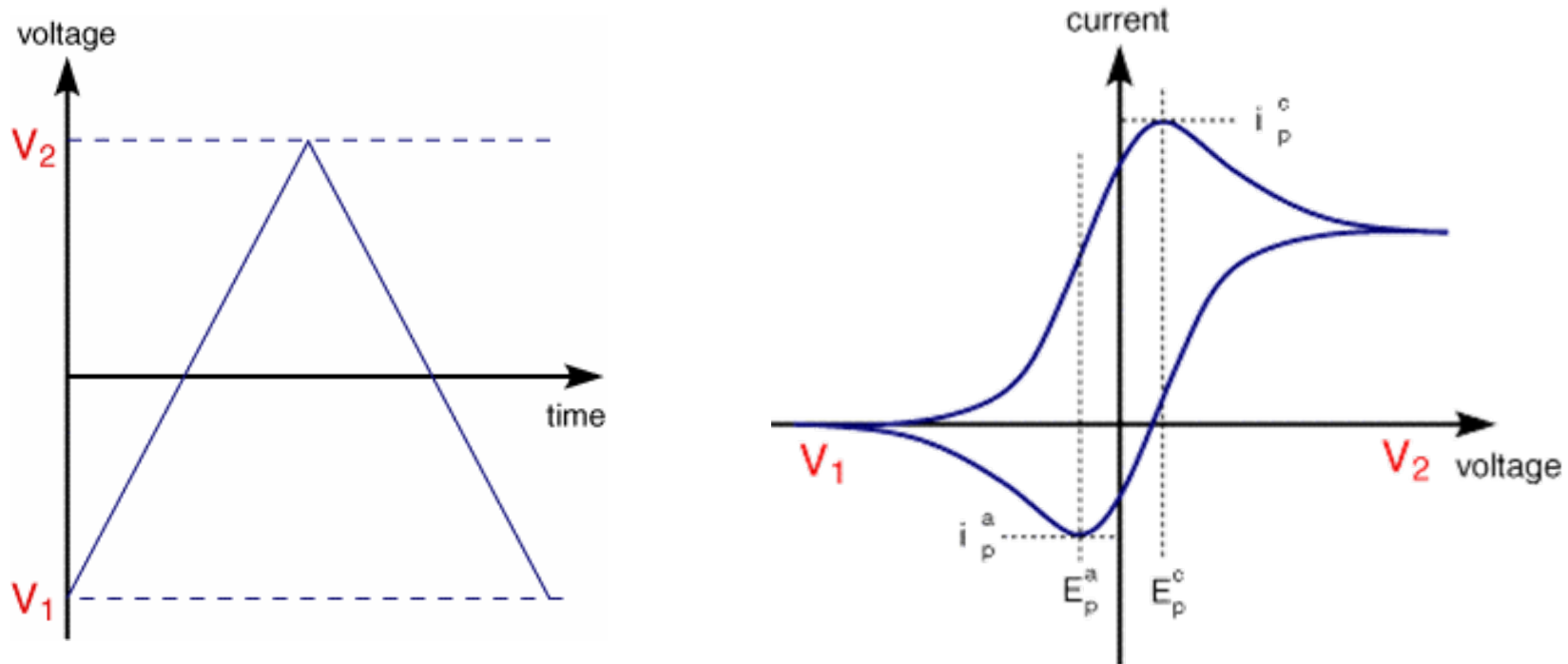
Since current is proportional to flux, and flux is proportional to the concentration gradient between surface and bulk it should be evident that a higher scan rate will give a higher current.

This is observed experimentally:



Cyclic Voltammetry

Cyclic voltammetry is very similar to LSV except a triangular waveform is applied:



A fully reversible reaction where just electron exchange takes place under diffusion mass transport control and labile electron kinetics has a CV with specific properties:

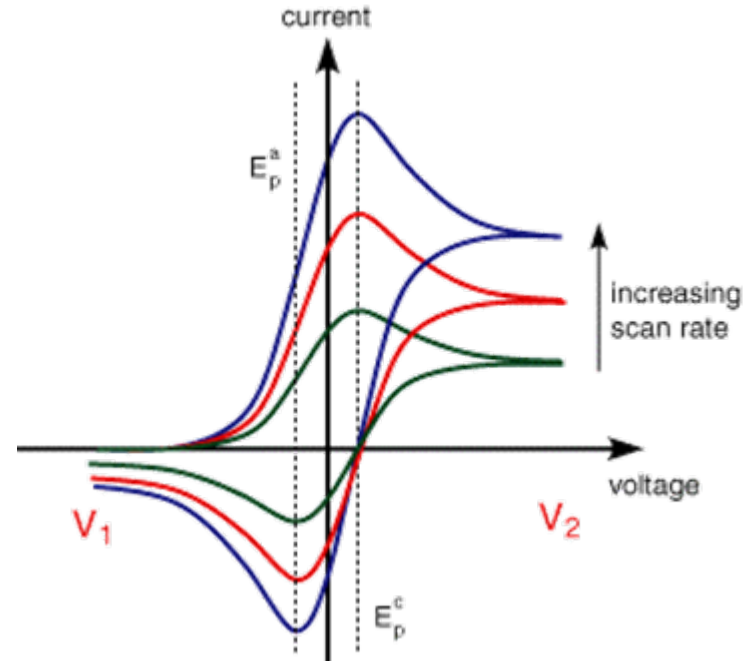
Diagnosics of fully reversible electrode reaction

- I) The voltage separation between the current peaks is $59/n$ mV.
 - II) The positions of peak voltage do not alter as a function of voltage scan rate.
 - III) The ratio of the anodic and cathodic peak currents is equal to one
 - IV) The peak currents are proportional to the square root of the scan rate
- The influence of the voltage scan rate on the current for a reversible electron transfer can be seen below:

$$\left| \frac{i_p^a}{i_p^c} \right| = 1 \quad i_p^a \text{ and } i_p^c \propto \sqrt{\nu}$$

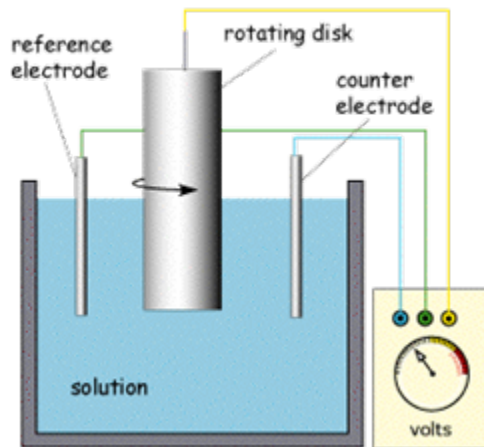
$$\Delta E = E_p^a - E_p^c = \frac{59}{n} \text{ mV}$$

$$i_p = -n^{3/2} F A D^{1/2} [O] \nu^{1/2}$$

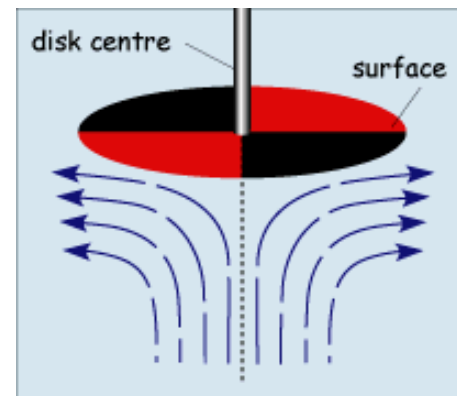


Systems with diffusion and convection control: Rotating Disc Electrode

- So, far the situation where diffusion is the rate limiting mass transport step in an electrode reaction has been considered. However, it is also possible to control the movement of material to the electrode via convection.
- This can be achieved by encasing the electrode in a Teflon outer layer and rotating in a controlled fashion.



Experimental setup



Laminar flow at electrode centre

The RDE

- The rotating electrode draws electrolyte from the bulk onto its surface. Within certain limits, the rotation rate is directly related to the rate of transport to the surface.
- In fact, in the mass transport taking place in such systems is dependent both on diffusion and convection. So one can write:

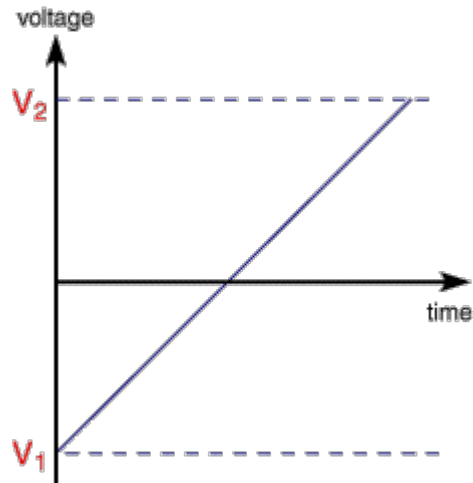
$$\frac{\partial[O]}{\partial t} = D_o \frac{\partial^2 [O]}{\partial x^2} + v_x \frac{\partial[O]}{\partial x}$$

- which is like Fick's 2nd law, but has an additional term, $v_x \frac{\partial[C]}{\partial x}$

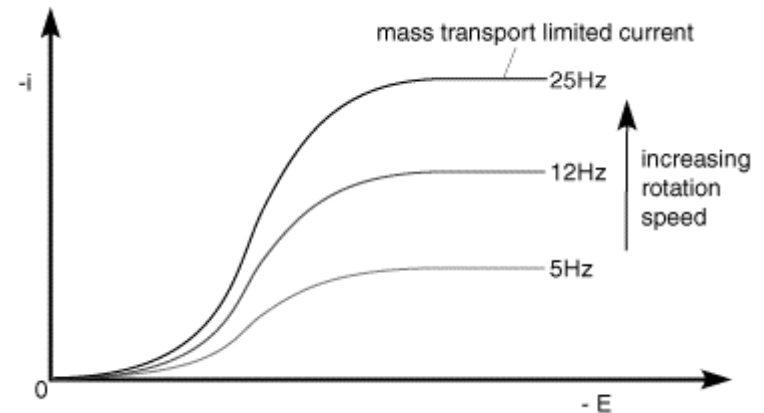
that relates to the convection component is the velocity of the flow at some distance x normal to the electrode surface.

Experimental results

- The experimental manifestation of this convection effect can be seen if one ramps a voltage on an electrode.
- The effect of applying a linear voltage sweep to an electrode can be seen in the above diagrams:



Linear applied voltage



Current voltage curve as a function of rotation rate

Note, that unlike systems under just diffusion control, there is no current peak. This time the rate of reaction – that is the limiting current is influenced by how fast one can transport material to the electrode by rotation.

Using RDE results to calculate D

- Quantitatively, the above diffusion equations can be solved and the following equation obtained:

$$i_L = 0.692nFA[O]_{bulk} D^{2/3} \nu^{-1/6} \omega^{1/2}$$

The Levich equation:

- where i_L is the limiting current, $[O]_{bulk}$ the bulk concentration of species to be reduced (or oxidised), D the diffusion constant, A electrode area, ν a kinematic viscosity of the solution and $\omega = 2\pi f$, where f is the rotation rate.
- So, by plotting i_L vs. $\omega^{1/2}$ for different rotation rates, and knowing (looking up n), it is possible to obtain the diffusion constant of the electroactive species.
- Note:** be careful about units! For example, when switching between concentration in mol dm^{-3} to diffusion constant D in $\text{m}^2 \text{s}^{-1}$.

What can be learnt from voltammetry?

- Mechanism of electrode reaction.
- Concentration of oxidative or reductive species: useful for making a sensor.
- Determination of Diffusion coefficient of electroactive species, D .