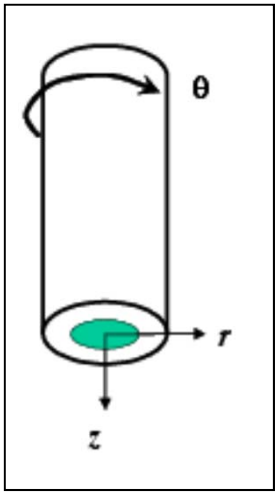
Physical & Interfacial Electrochemistry 2013.



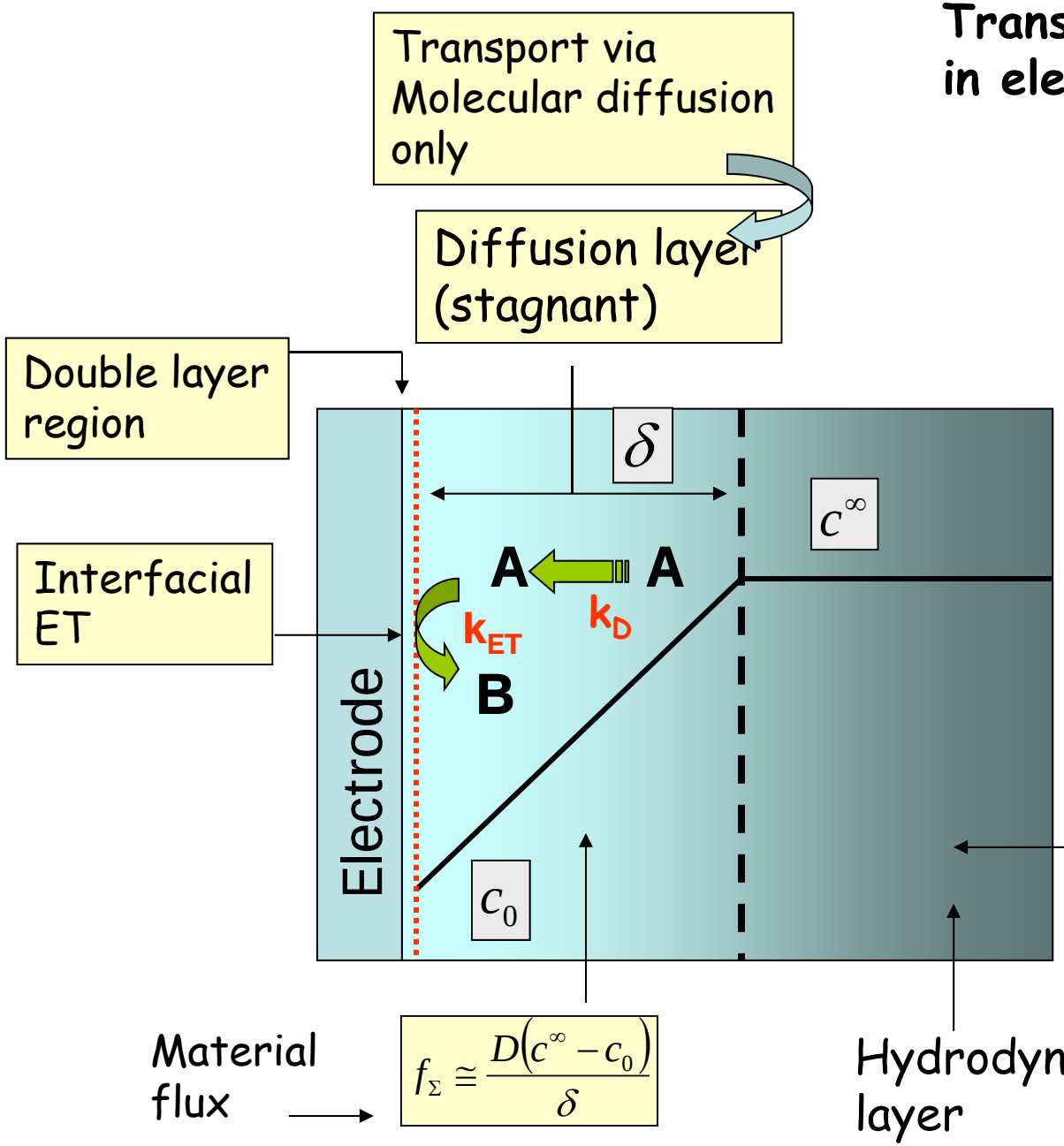
Lecture 8

Hydrodynamic Voltammetry

Hydrodynamic voltammetry

- Hydrodynamic voltammetry deals with voltammetric measurements conducted under conditions where there is controlled hydrodynamic flow of solution near the electrode.
- If convection is applied to the solution in the vicinity of the electrode then the rate of mass transport is increased which means that faster reactions may be studied.
- If the fluid flow is well defined (laminar rather than turbulent), the rate of mass transport can be controlled quantitatively by varying the solution flow rate. This is much more convenient than varying the size of the electrode. Also steady state conditions are achieved at hydrodynamic electrodes.
- Examples of hydrodynamic electrodes include the rotating disc electrode (RDE), the rotating ring disc electrode, the wall jet electrode, the tubular electrode and the channel electrode.
- The transport of reactant and product can in principle be calculated quantitatively under such circumstances by solving the mass transport equations and the relevant hydrodynamic equations either using approximate analytical methods (for particularly simple geometries) or, more often, via numerical simulation (via finite element modelling).

Transport and kinetics in electrochemical systems.



Simple diffusion layer model neglects convection effects and also simplifies analysis of Fick diffusion equations.

Transport and kinetics at electrodes.

Diffusion layer approximation used.

Current density

$$f_\Sigma = \frac{i}{nFA} = \frac{J}{nF}$$

Net flux

$$k_D = \frac{D}{\delta}$$

$$f_\Sigma = D\left(\frac{dc}{dx}\right)_0 = k_{ET}c_0 = \frac{D}{\delta}\left\{c^\infty - c_0\right\} = k_D\left\{c^\infty - c_0\right\}$$

$$c_0 = \frac{c^\infty}{1 + \frac{k_{ET}\delta}{D}}$$

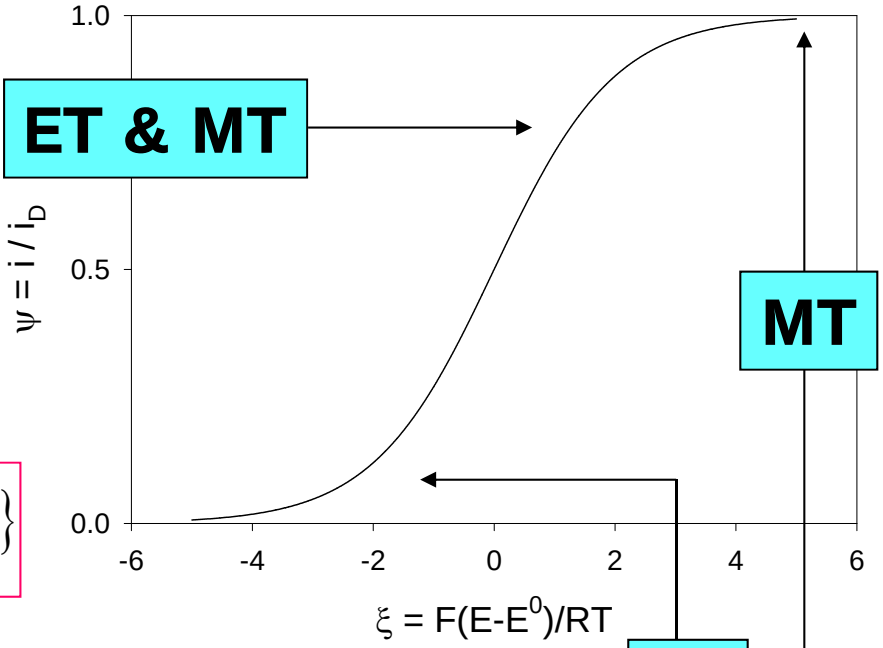
$$f_\Sigma = k_{ET}c_0$$

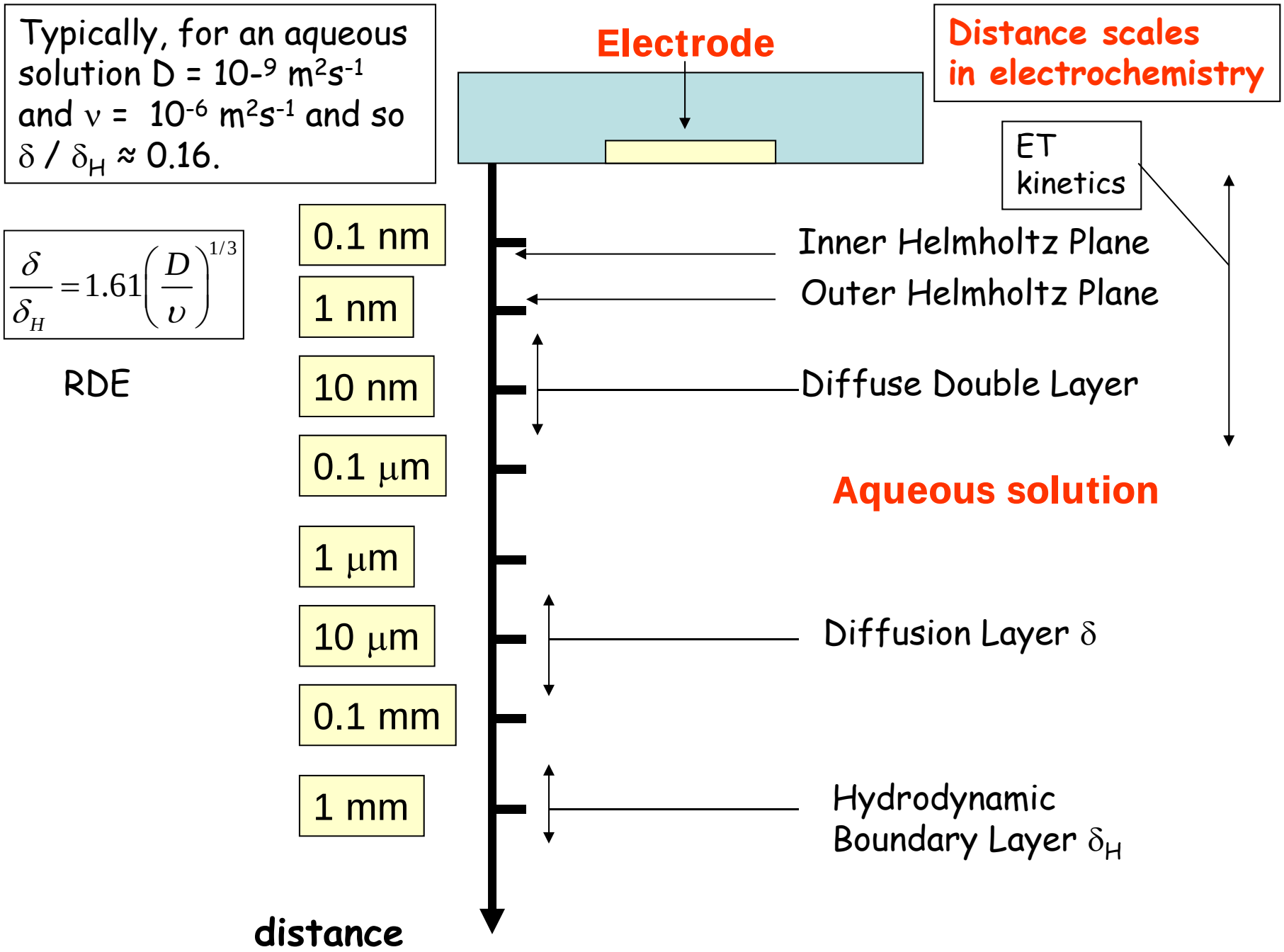
$$f_\Sigma = \frac{k_{ET}k_Dc^\infty}{k_D + k_{ET}}$$

$$\frac{1}{f_\Sigma} = \frac{1}{k_{ET}c^\infty} + \frac{1}{k_Dc^\infty}$$

$$k_{ET} = k^0 \exp\left[\pm \beta \xi\right]$$

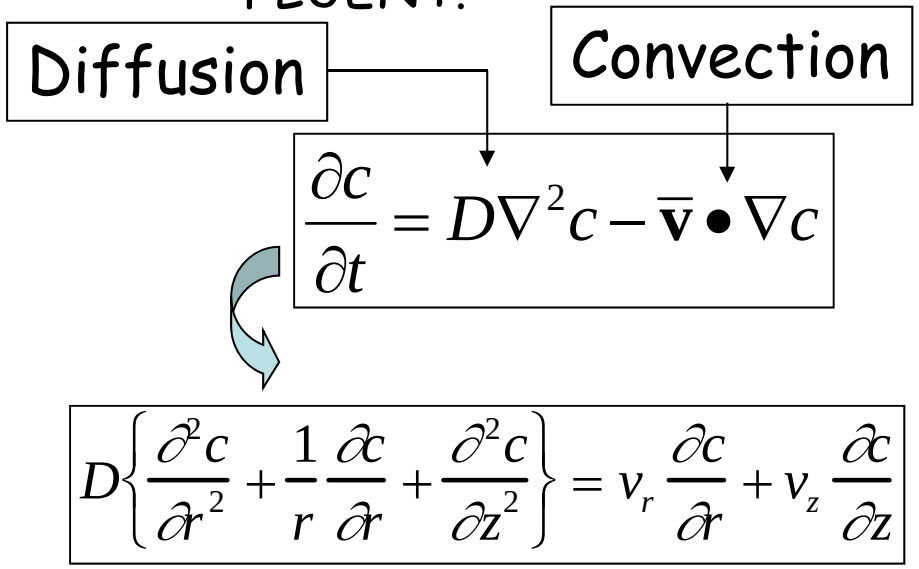
Normalised potential




Typically, for an aqueous solution D = 10-9 m2s-1 and ν = 10-6 m2s-1 and so δ / δH ≈ 0.16.
$\frac{\delta}{\delta_H} = 1.61\left(\frac{D}{\upsilon}\right)^{1/3}$
RDE
Electrode
Distance scales in electrochemistry
ET kinetics
0.1 nm
1 nm
10 nm
0.1 μm
1 μm
10 μm
0.1 mm
1 mm
Inner Helmholtz Plane
Outer Helmholtz Plane
Diffuse Double Layer
Aqueous solution
Diffusion Layer δ
Hydrodynamic Boundary Layer δH
distance

Convective diffusion equation.

- Material flux near an electrode surface computed by solving the convective diffusion equation (this neglects electromigration effects).
- To do this the velocity profile in the fluid must be evaluated using the Navier Stokes equation of hydrodynamics, which is non linear and therefore difficult to solve analytically.
- The convective diffusion equation admits analytical solutions for only a few problems in electrochemistry such as the rotating disc electrode.
- In most cases a numerical approach has to be adopted.
- Commercial software packages utilising finite element and finite difference methods are available to solve the convective diffusion and Navier Stokes equations. These include FEMLAB and FLUENT.



RDE CV eqn.

$$v_r \frac{\partial c}{\partial r} + v_z \frac{\partial c}{\partial z} = D \frac{\partial^2 c}{\partial z^2}$$

$$v_r = Crz$$

$$v_z = -Cz^2$$

$$C = 0.51\omega^{3/2}\upsilon^{-1/2}$$

Normal diffusion

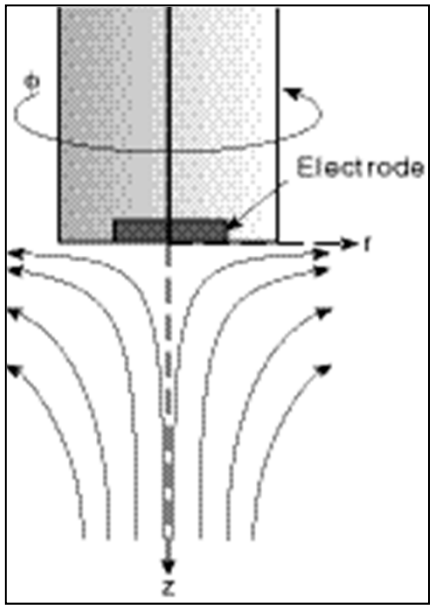
$$D \frac{\partial^2 c}{\partial z^2} = -Cz^2 \frac{\partial c}{\partial z} + Crz \frac{\partial c}{\partial r}$$

Normal convection

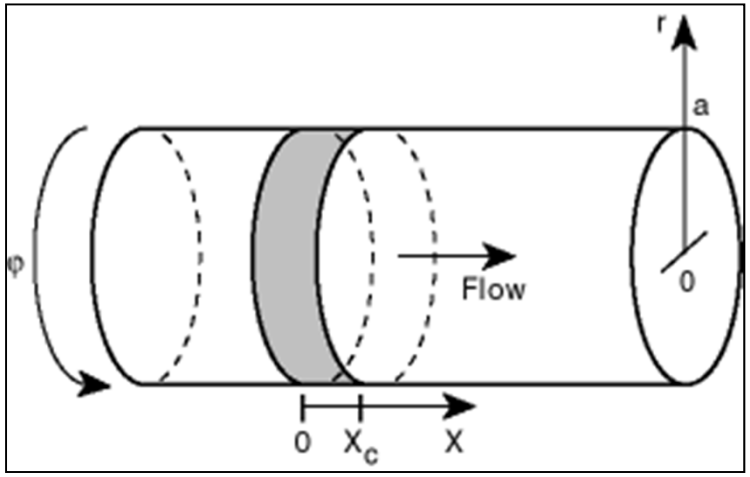
Radial convection

Either of these equations may be solved analytically for a
Number of well defined geometries such as RDE, RRDE, ChE TE etc.

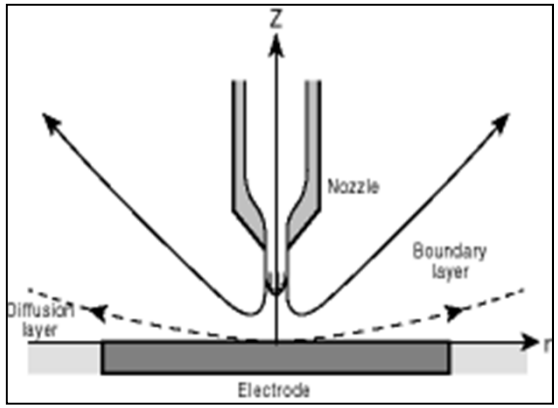
http://physchem.ox.ac.uk/~rgc/john/Thesis/1/1.html



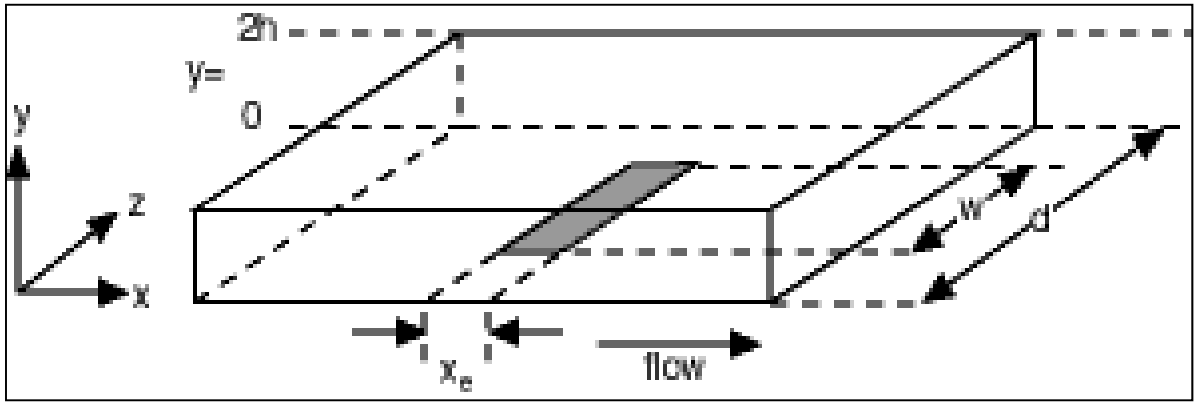
Rotating disc electrode (RDE)



Tubular electrode (TE)

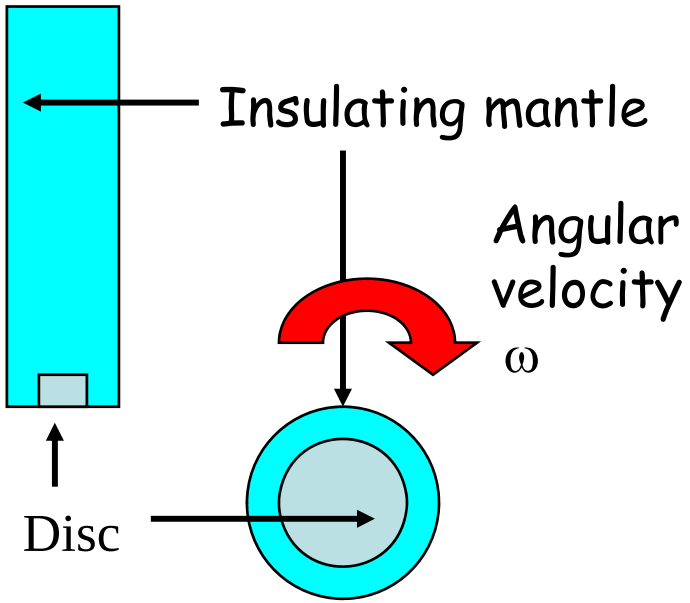


Wall Jet electrode (WJE)



Channel electrode (CE)

The Rotating Disc Electrode .



$$k_D = \frac{D}{\delta}$$

$$\delta = 0.643 D^{1/3} \upsilon^{1/6} \omega^{-1/2}$$

k_D= diffusive rate constant (cms^{-1})
D = substrate diffusion coefficient
δ = Nernst diffusion layer thickness

- RDE has well defined hydrodynamic flow to electrode surface .
- Fluid velocity profile near disc well defined .
- Transport of reactant to surface obeys steady state Convective diffusion equation which may be rigorously solved .
- Rate of material transport depends in a well defined manner on the rotation speed of the electrode .

ν = kinematic viscosity
ω = rotation speed (Hz)

Rotating disc electrode (RDE)

The RDE is constructed from a disk of electrode material (e.g. gold, glassy

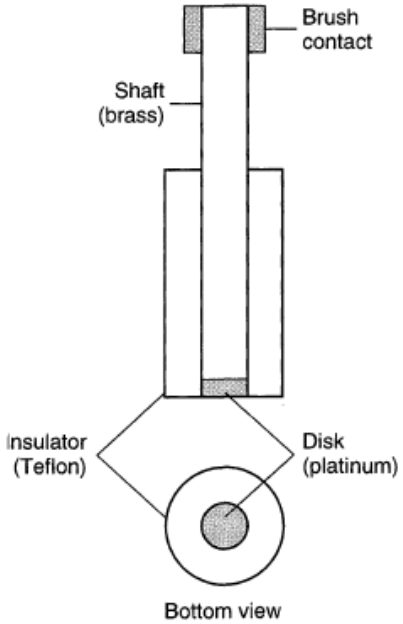
carbon or platinum) imbedded in a rod of insulating material (e.g. Teflon).

The electrode is attached to a motor and rotated at a certain frequency.

The movement of rotation leads to a very well defined solution flow pattern.

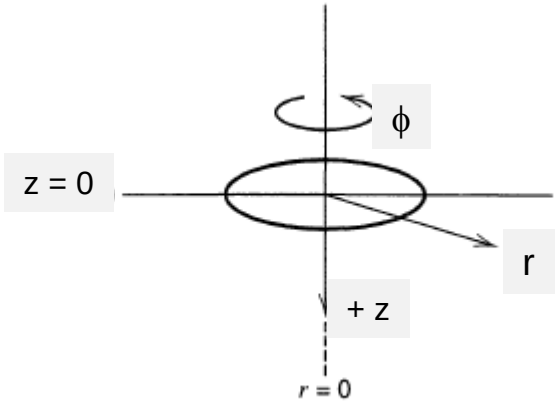
The rotating device acts as a pump, pulling the solution upward and then

throwing it outward.



RDE Configuration

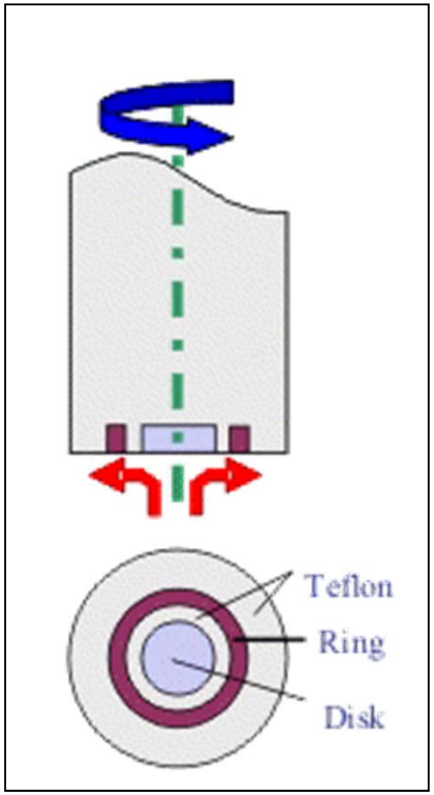
The reactant is conveyed to the electrode surface by a combination of two types of transport : convection and diffusion.
Vortex flow in the bulk solution continuously brings fresh reactant to the outer edge of the stagnant diffusion layer.
The reactant diffuses across stagnant layer. The thinner the stagnant layer, the faster the reactant can diffuse across it and reach the electrode surface.
Faster electrode rotation makes the stagnant layer thinner. Higher rotation rates permit the reactant to diffuse to the electrode faster, resulting in a higher current being measured at the electrode.



Cylinderical polar co-ordinate system

Rotating-ring-disk electrode (RRDE).

RRDE is a variant of the rotating-disk electrode which includes a second electrode -a concentric ring electrode – that is placed outside the disk and used to analyze the species generated on the disk. The ring is electrically insulated from the disk so that their potentials can be controlled independently. Abbreviated as RRDE



RRDE is a convenient way to measure post-electron transfer reactions of products. The relationship between disk current and ring current depends on rate of movement of product from the disk and is quantified in terms of the Collection Efficiency which can Be computed analytically and depends only on the geometry of the RRDE.

Rotating electrode assembly.

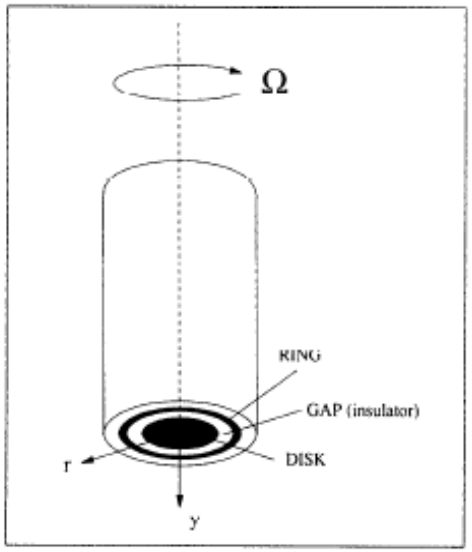
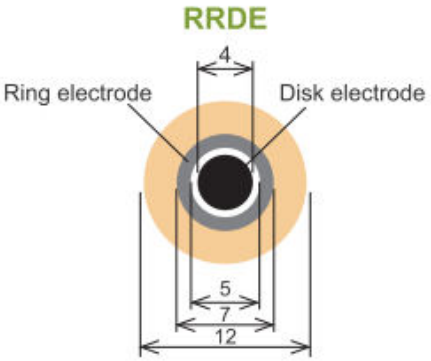
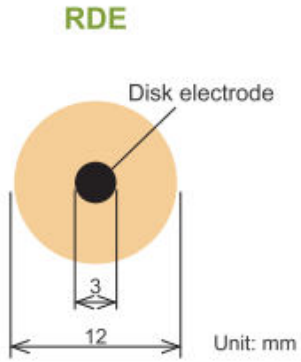


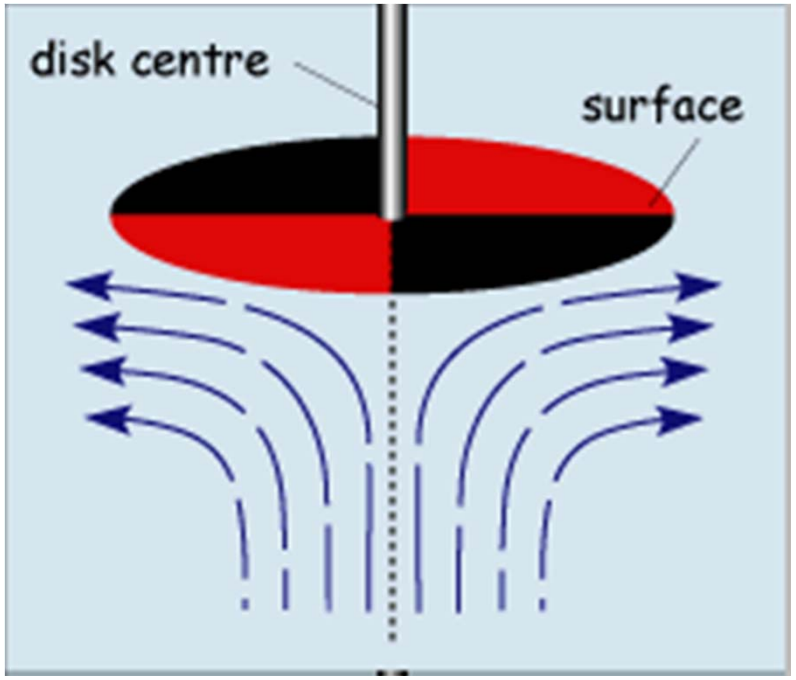
Figure 1. Rotating ring-disk electrode (RRDE).
The ring electrode is kept at open circuit potential.

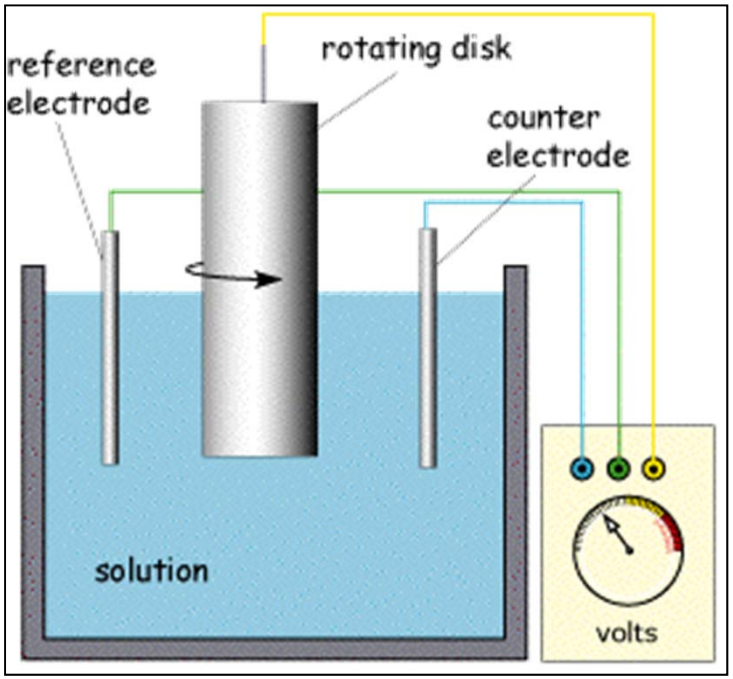
RDE Configuration

RRDE Configuration









Rotating disk electrode (RDE) can be used in the same stand

The whole disc acts as a pump, sucking solution towards it, spinning the solution around and then flinging it out sideways.

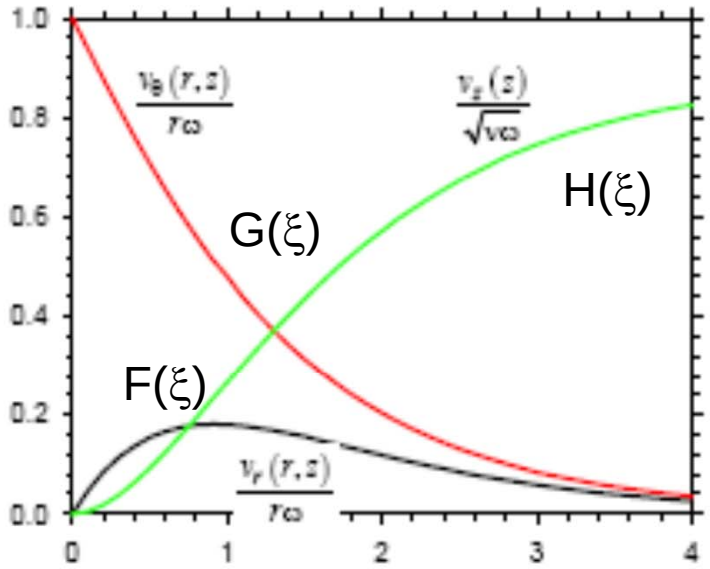
Hydrodynamics of Rotating Disk

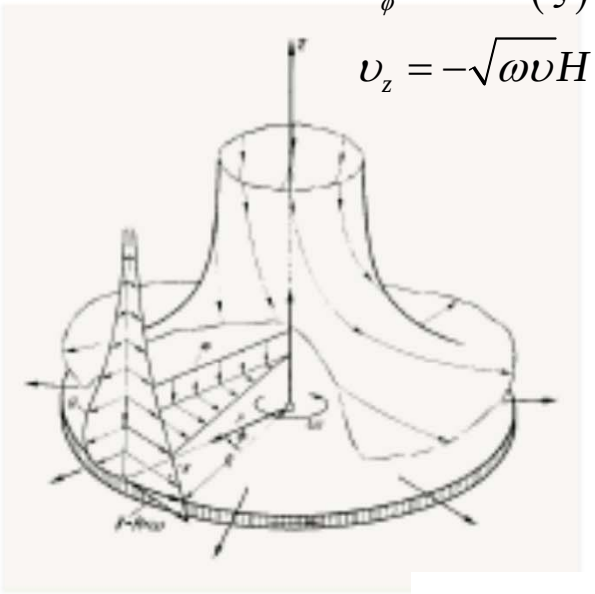
Th. von Kármán (1921) and W.G. Cochran (1934)

$$\upsilon_r = r\omega F(\xi)$$ Radial

$$\upsilon_\phi = r\omega G(\xi)$$ Angular

$$\upsilon_z = -\sqrt{\omega\upsilon}\,H(\xi)$$ Normal





$$\xi = \frac{z}{\delta_H} = \sqrt{\frac{\omega}{\upsilon}}\,z$$

$$\gamma = \left(\frac{\omega}{\nu}\right)^{1/2} x$$

$2R = 25$ mm $\qquad \sqrt{\nu/\omega} = 2$ mm for $\omega = 1000$ rpm $\qquad \kappa^{-1} = 30$ nm for 0.1 mM

Velocity profiles near RDE Surface.

$$v_z = -a\xi^2\sqrt{\omega\upsilon} = -0.51\omega^{3/2}\upsilon^{-1/2}z^2 = -Cz^2$$

$$v_r = a\xi r\omega = 0.51\omega^{3/2}\upsilon^{-1/2}rz = Crz$$

Convective diffusion equation : Rotating disc electrode (RDE)

Neglect radial Diffusion & Convection.

Fluid velocity profile (approximate)

Steady state time independent equation.

$$D\frac{\partial^2 c}{\partial z^2} = -Cz^2\frac{\partial c}{\partial z}$$

$$C = 0.51\omega^{3/2}\upsilon^{-1/2}$$

Convective diffusion equation expressed in cylinderical polar co-ordinates (r,z,ϕ)

radial

normal

angular

Rotation frequency (Hz)

$\omega = 2\pi f$

Angular velocity (rad/s)

$$r \to \infty \quad c \to c^{\infty}$$

$$r \to 0 \quad \frac{\partial c}{\partial r} \to 0$$

$$z \to \infty \quad c \to c^{\infty}$$

$$z \to 0 \quad f_{\Sigma} = D\left(\frac{\partial c}{\partial z}\right)_{z=0} = k_{ET}c_0$$

Normalised distance

$$\chi = zC^{1/3}D^{-1/3}$$

$$x = r\cos\phi \quad y = r\sin\phi \quad z = z$$

$$r \geq 0 \quad 0 \leq \phi \leq 2\pi \quad -\infty \leq z \leq \infty$$

$$r = \sqrt{x^2 + y^2} \quad \phi = \tan^{-1}\left\{\frac{y}{x}\right\}$$

$$c(\chi) = c_0 + \frac{c^{\infty} - c_0}{\delta}\int_0^{\chi}\exp\left[-\frac{\chi^3}{3}\right]d\chi$$

Reactant concentration profile near RDE

C = convective constant

$$\left(\frac{\partial c}{\partial z}\right)_{z=0} = \frac{c^{\infty} - c_0}{KC^{-1/3}D^{1/3}} = \frac{c^{\infty} - c_0}{1.288 \times 1.25\,\upsilon^{1/6}\omega^{-1/2}D^{1/3}}$$

$$= \frac{c^{\infty} - c_0}{1.61\,\upsilon^{1/6}D^{1/3}\omega^{-1/2}}$$

K = $3^{1/3}\,\Gamma(4/3) = 1.288$.

Nernst diffusion layer Approximation.

$$\left(\frac{\partial c}{\partial z}\right)_{z=0} = \frac{c^{\infty} - c_0}{\delta}$$

Diffusion layer thickness for RDE (Levich)

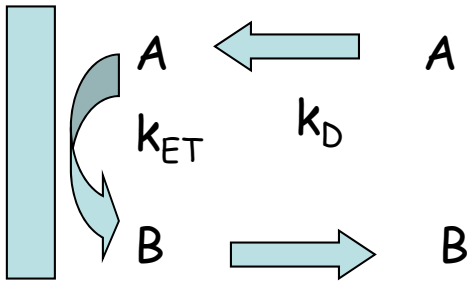
$$\delta = KC^{-1/3}D^{1/3} = 1.61D^{1/3}\upsilon^{1/6}\omega^{-1/2}$$

Levich equation Diffusion limited Current.

$$i_L = 2\pi nFD\int_0^a \left(\frac{\partial c}{\partial z}\right)_{z=0} dr$$

$$= 0.62nF\pi a^2 D^{2/3}\upsilon^{-1/6}c^{\infty}\omega^{1/2}$$

Transport and kinetics at electrodes.



$$f_\Sigma = \frac{i}{nFA} = k_{ET} c_0 = \frac{k_{ET} k_D c^\infty}{k_{ET} + k_D}$$

$$\frac{c^\infty}{f_\Sigma} = \frac{1}{k_{ET}} + \frac{1}{k_D}$$

Linear Plot:

$$f_\Sigma^{-1} \; vs \; \omega^{-1/2}$$

Kinetic info (k_{ET},k^0) got from intercept
Diffusion coefficient got from slope.

$$k_{ET} = k^0 \exp[\pm \beta \xi]$$

$$k_D = \frac{D}{\delta}$$

$$\delta = 0.643 D^{1/3} \upsilon^{1/6} \omega^{-1/2}$$

k_D can be computed accurately provided Convective-diffusion equation can be solved.

Specific result for RDE, RRDE geometry.

$$k_D = \frac{D}{Z_D} = 0.62 D^{2/3} \upsilon^{-1/6} \omega^{1/2} = 1.55 D^{2/3} \upsilon^{-1/6} W^{1/2}$$

Rad s^{-1} Hz

Levich equation.

Veniamin Grigorievich (Benjamin) Levich.

$$i_L = 2\pi nFD\int_0^a \left(\frac{\partial c}{\partial z}\right)_{z=0} dr$$

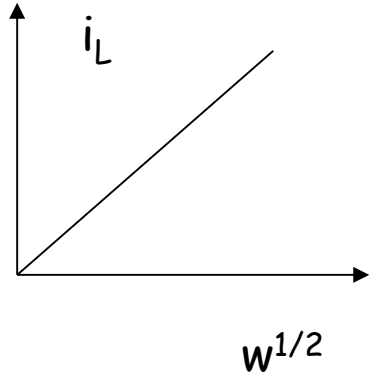
$$= 0.62nF\pi a^2 D^{2/3}\upsilon^{-1/6}c^{\infty}\omega^{1/2}$$

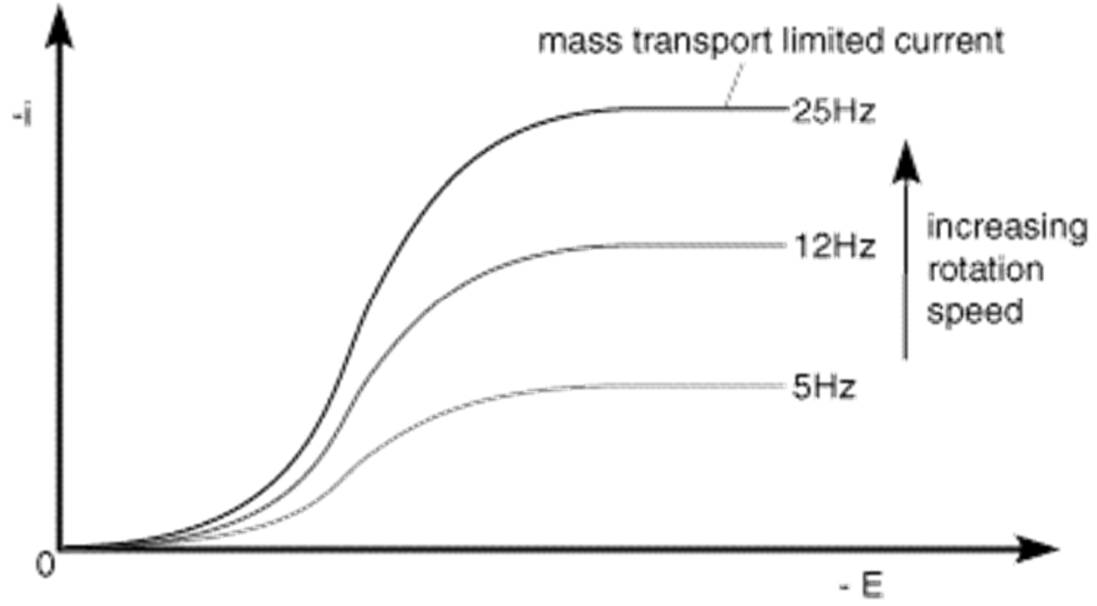
Levich equation

$$i_L = S_L\omega^{1/2}$$

Levich slope

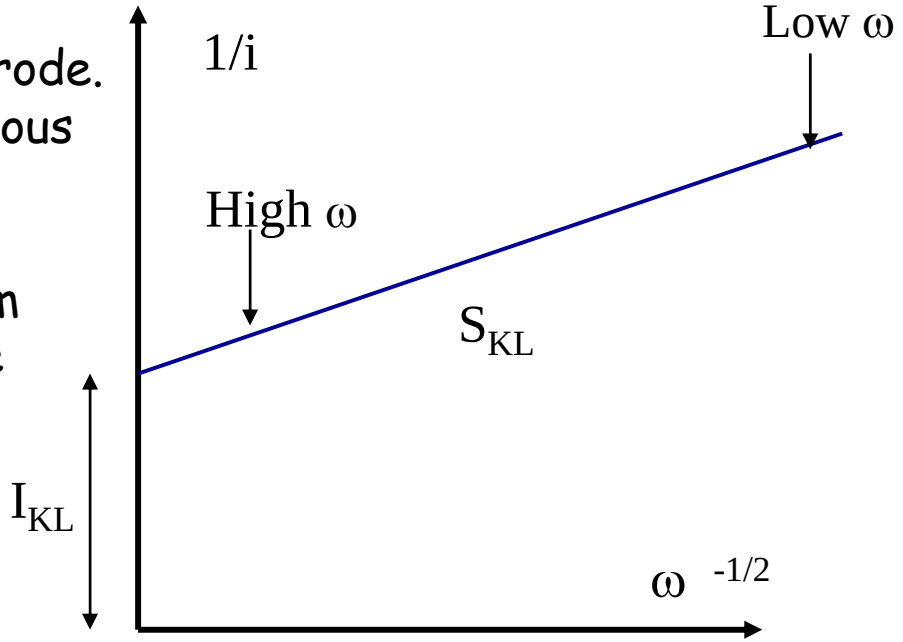
$S_L = 0.62nF\pi a^2 D^{2/3} c^{\infty} \nu^{-1/6}$





Data Analysis using the RDE.

- Apply constant potential to electrode.
- Measure limiting current i at various rotation speeds ω .
- Plot 1/i versus $\omega^{-1/2}$.
- Kinetic information obtained from intercept corresponding to infinite rotation speed .
- Transport information obtained from slope .



$$\frac{nFAc^{\infty}}{i_L} = S_{KL}\omega^{-1/2} + I_{KL}$$

$$I_{KL} = \frac{1}{k_{ET}}$$

$$S_{KL} = B^{-1}$$

$$B = \text{Levich constant} = 1.55\text{D}^{2/3}\upsilon^{-1/6}$$

Koutecky-Levich Plot .

Diffusion coefficient calculated from slope, ET rate constant calculated from intercept.

Tube Electrode (TE)

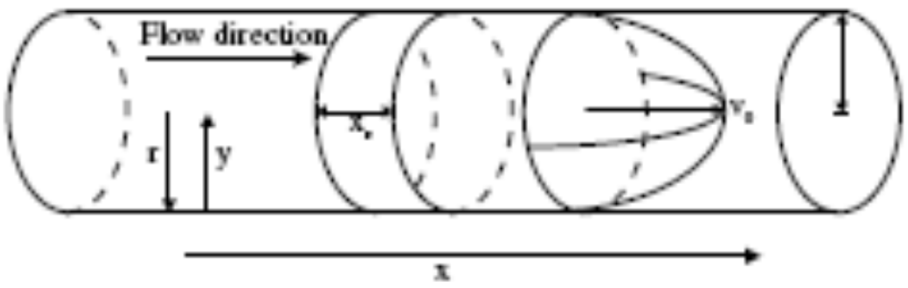


Fig. 1. The tubular electrode setup showing the coordinate system and laminar flow pattern.

The TE system consists of an annular electrode that is inserted into the length of a cylinderical tube down which the solution under study flows.
The volume flow rate V_f is chosen to ensure laminar flow of solution in the tube.
Because of friction with the tube walls, the velocity of liquid v in the tube varies in a parabolic manner with the distance r from the tube centre.

Velocity at tube centre

$$v_x = v_0\left(1 - \frac{r^2}{\rho^2}\right)$$

Tube radius

Since the flow is laminar
The diffusion layer thickness
Increases with the
Distance x downstream
From the upstream edge of the
Tube electrode and $\delta \sim x^{1/3}$.
The mass transport controlled flux varies as $x^{-1/3}$ across the electrode surface and so the TE is not uniformly accessible.

Transport to the TE is given by the convective diffusion equation written in terms of axial (x) and radial (r) coordinates.

Levich assumed that the fluid flow pattern is linear close to the electrode surface and v_x is given by the **Leveque approximation**.

If axial and radial diffusion effects are neglected then the CD equation can be solved to obtain a well defined expression for the limiting current which will be valid when the diffusion layer is sufficiently thin in comparison with the tube radius.

The Levich equation is derived by assuming that fluid flow is sufficiently fast such that diffusion in the direction of convective flow can be neglected, and that convection is sufficient to ensure that the concentration gradient of reactive species near the electrode surface can be linearised.

Note that limiting current does not depend on radius of tube ρ or on the solvent viscosity.

Slow flow or long electrode conditions produces a more simple expression for the limiting current.

Complete expression for TE response for all values of V_f only obtained numerically.

$$\frac{\partial c}{\partial t} = D\left(\frac{\partial^2 c}{\partial r^2} + \frac{1}{r}\frac{\partial c}{\partial r} + \frac{\partial^2 c}{\partial x^2}\right) - v_x \frac{\partial c}{\partial x},$$

Leveque approximation

$$v_x = \frac{2v_0 y}{\rho},$$

TE Levich equation

$$i_L = 5.43nF(D\,x_E)^{2/3}V_f^{1/3}c^{\infty}$$

x_E: Electrode length

TE slow flow limit

$$i_L = nFV_f c^{\infty}$$

TE geometry used in Electrochemical ESR Measurements.

http://physchem.ox.ac.uk/~rgc/john/Thesis/1/1.html

Method	**Variable Parameter**	**Controls**
Steady-state voltammetry	Potential	Rate of electrochemical kinetics
Linear-sweep/cyclic voltammetry	Potential and time	Rate of electrochemical kinetics and mass transport
Potential-step chronoamperometry[†]	Time	Rate of mass transport
Transport-limited current: wall-jet	Jet velocity	Rate of mass transport
Transport-limited current: channel flow cell	Flow rate, (electrode length)	Rate of mass transport
Transport-limited current: microdisc electrode	Radius	Rate of mass transport
Transport-limited current: RDE	Rotation speed	Rate of mass transport

Object of most voltammetric experiments is to record current flowing as a function of rate of mass transport and/or electrochemical kinetics (which have an associated time scale).

Channel Electrode (ChE)

The channel electrode (ChE) is closely related to the Tube electrode.
It consists of an electrode embedded in one wall of a rectangular duct down which solution flows.
Advantages include:

- flow through facilitates continuous monitoring in analytical applications following chromatographic separation.
- Well defined hydrodynamics permits rigorous mechanistic investigation of reactions via Voltammetric techniques.
- Channel geometry can be readily used in spectroelectrochemistry (IR, UV/VIS, ESR, fluorescence).
- Double electrode collector/generator experiments readily done.

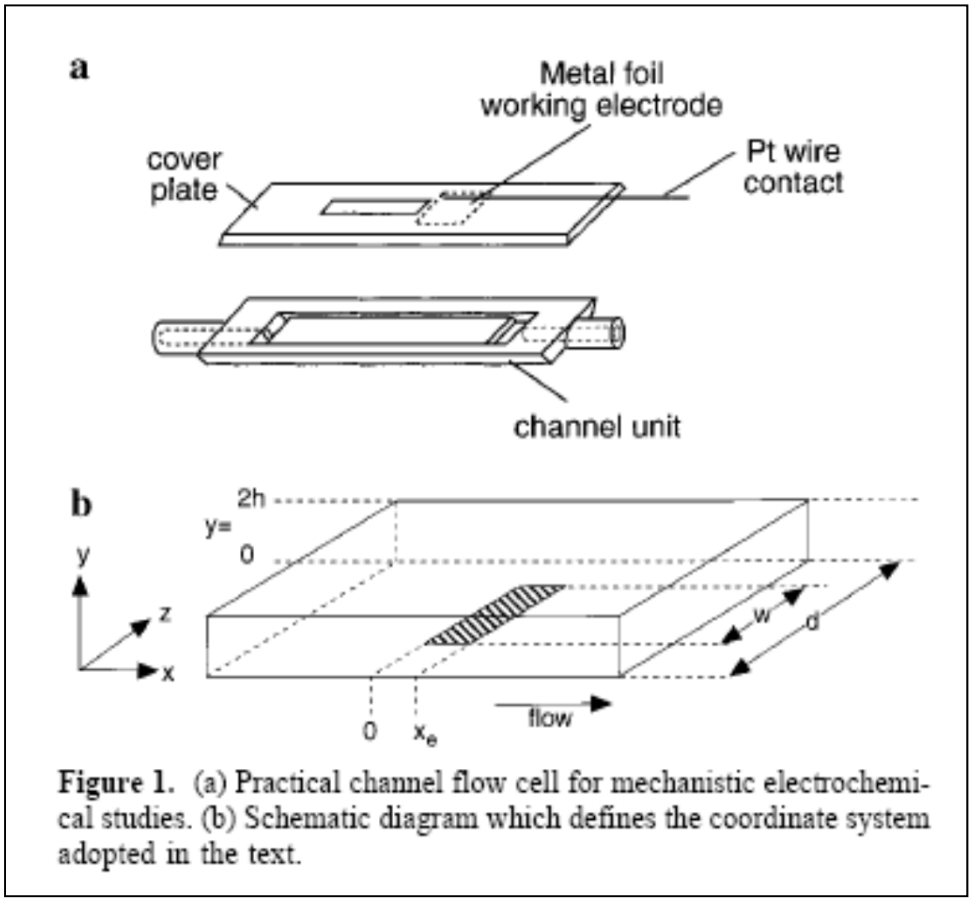


Figure 1. (a) Practical channel flow cell for mechanistic electrochemical studies. (b) Schematic diagram which defines the coordinate system adopted in the text.

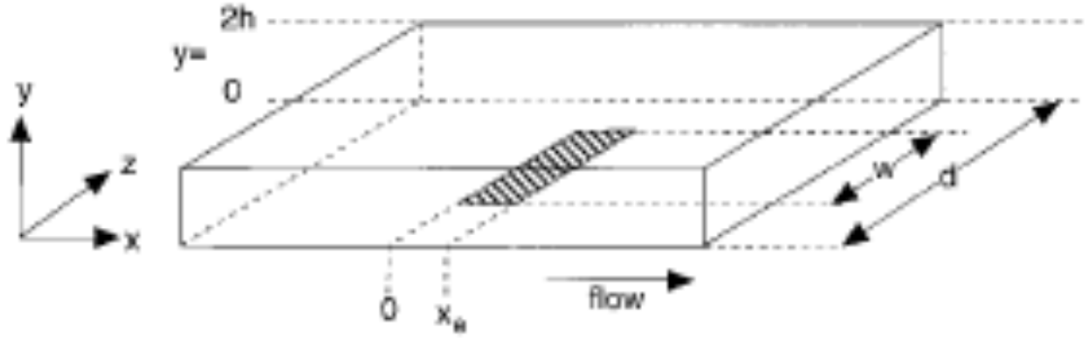


Fig. 1. A typical channel flow cell, with the conventional x, y and z-directions marked.

Cooper, Compton

Electroanalysis **1998**, 10, No. 3

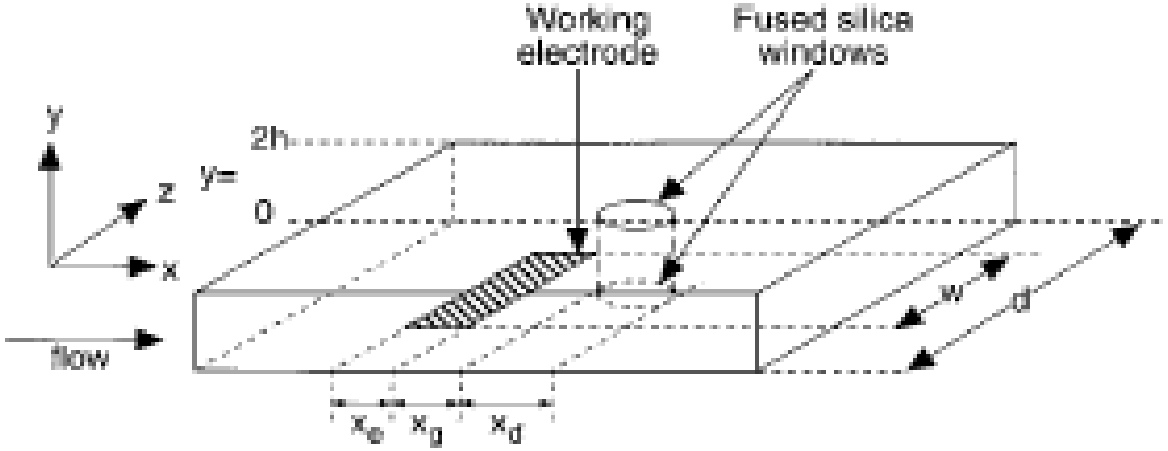


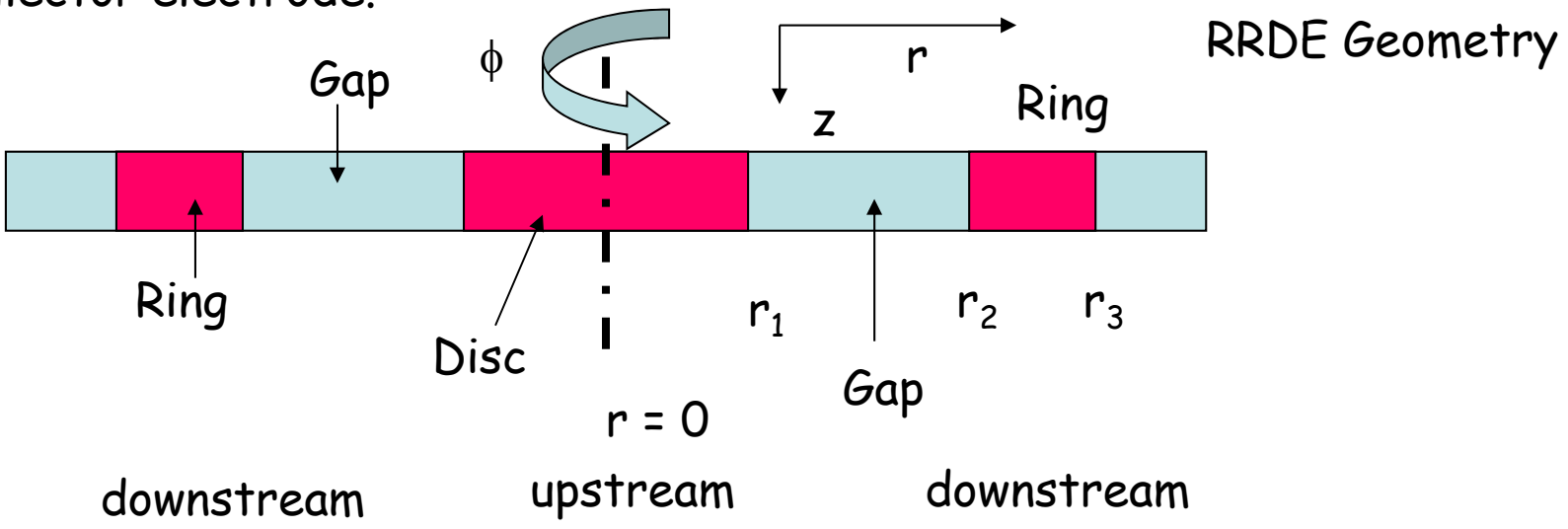
Fig. 3. A modified channel flow cell for in situ UV/vis spectroscopy. The marked lengths represent the electrode length, the distance between the electrode and the window and the radius of the window itself.

'Levich' type equations for various types of hydrodynamic electrodes.

Geometry	Limiting Current
RDE[47]	$I_{lim} = 0.621 nFA[C]_{bulk} \frac{D^{2/3}\sqrt{\omega}}{\nu^{1/6}}$
WJE[28]	$I_{lim} = 1.590 nF[C]_{bulk} \frac{k_c D^{2/3} v_f^{3/4} r_e^{3/4}}{\nu^{5/12} r_{jet}^{1/2}}$
MJE[48,49]	$I_{lim} = 1.923 nF[C]_{bulk} \frac{D^{2/3} v_f^{1/2} r_e^2}{\nu^{1/6} r_{jet}^{3/2}} \left[\frac{z_{jet}}{r_{jet}}\right]^{-0.054}$
ChE[50,51]	$I_{lim} = 0.925 nF[C]_{bulk} w. \frac{D^{2/3} x_e^{2/3} v_f^{1/3}}{d^{1/3} h^{2/3}}$

Double hydrodynamic electrodes : Generator-Collector Experiments.

Hydrodynamic electrode systems useful for Generator-Collector (detector) experiments where the intermediate/product generated at an upstream generator electrode is detected at a downstream collector electrode.



Generator : $A + n_1e^- \rightarrow B$
Collector : $B + n_2e^- \rightarrow P$

Fraction of B which reaches collector/ detector electrode is always less than unity,
since some B is lost to bulk solution in transit from generator to collector electrode.

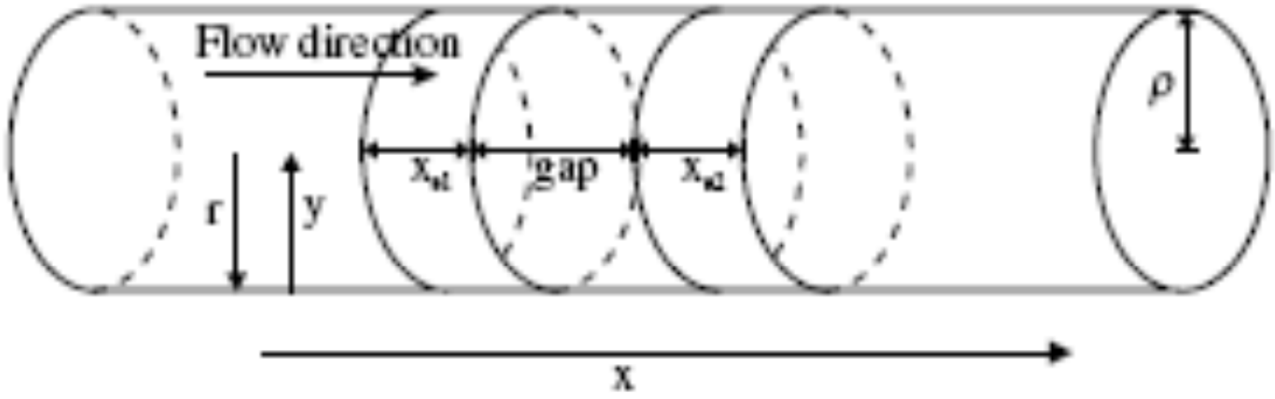


Fig. 1. A schematic of the double tubular electrode, showing coordinate system and dimension labels.

$$\frac{\partial c}{\partial t} = D\left(\frac{\partial^2 c}{\partial r^2} + \frac{1}{r}\frac{\partial c}{\partial r} + \frac{\partial^2 c}{\partial x^2}\right) - v_x \frac{\partial c}{\partial x}$$

$$v_x = v_0\left(1 - \frac{r^2}{\rho^2}\right)$$

$$i_{\text{lim}} = 5.24 \times 10^5 nF[A]_{\text{bulk}} x_e^{\frac{2}{3}} D_A^{\frac{2}{3}} V_f^{\frac{1}{3}},$$

R.G. Compton, G.M. Stearn.

J. Chem. Soc., Faraday Trans. 1, 1988, **84**(12), 4359–4367

Other double hydrodynamic electrode systems.

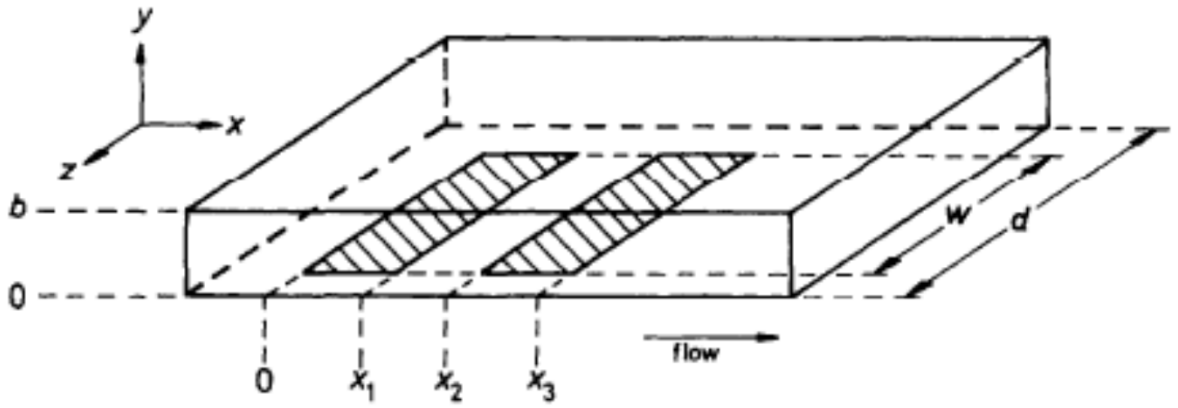


Fig. 1. Double-channel electrode geometry.

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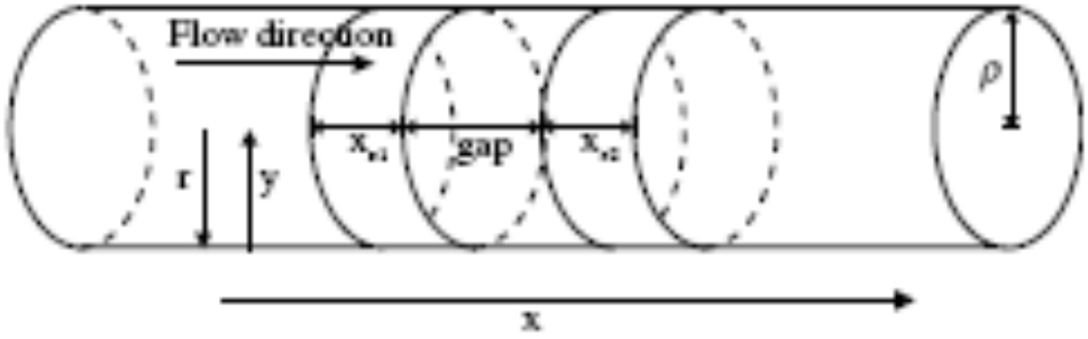


Fig. 1. A schematic of the double tubular electrode, showing coordinate system and dimension labels.

Double Hydrodynamic Electrode Collection efficiency.

$$N_0 = \left|\frac{n_1 I_D}{n_2 I_G}\right| = 1 - F\left(\frac{\alpha}{\beta}\right) + \beta^{2/3}\left\{1 - F(\alpha)\right\} - (1+\alpha+\beta)^{2/3}\left\{1 - F\left[\left(\frac{\alpha}{\beta}\right)(1+\alpha+\beta)\right]\right\}$$

$$F(\theta) = \frac{3^{1/2}}{4\pi}\ln\left\{\frac{\left(1+\theta^{1/3}\right)^3}{1+\theta}\right\} + \frac{3}{2\pi}\tan^{-1}\left\{\frac{2\theta^{1/3}-1}{3^{1/2}}\right\} + \frac{1}{4}$$

α,β are functions only of electrode geometry and are independent of mass transport and electrode kinetics.

RRDE, WTRDE

$$\alpha = \left(\frac{r_2}{r_1}\right)^3 - 1 \qquad \beta = \left(\frac{r_3}{r_1}\right)^3 - \left(\frac{r_2}{r_1}\right)^3$$

WJRDE

$$\alpha = \left(\frac{r_2}{r_1}\right)^{9/8} - 1 \qquad \beta = \left(\frac{r_3}{r_1}\right)^{9/8} - \left(\frac{r_2}{r_1}\right)^{9/8}$$

TDE, CDE

$$\alpha = \frac{\ell_2}{\ell_1} - 1 \qquad \beta = \left(\frac{\ell_3}{\ell_1}\right) - \left(\frac{\ell_2}{\ell_1}\right)$$

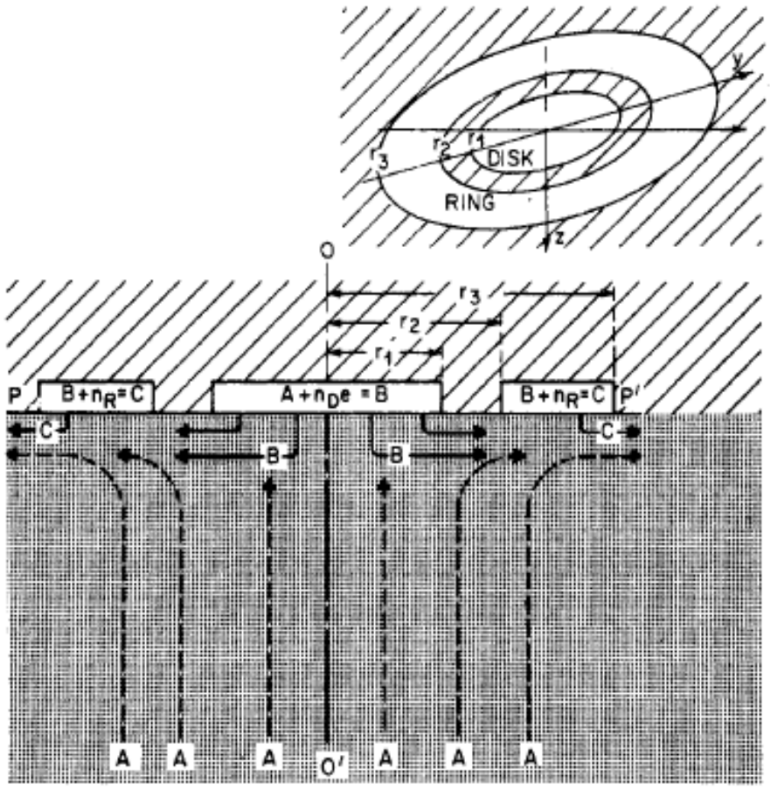


Figure 1. Rotating electrode geometry and flow patterns.

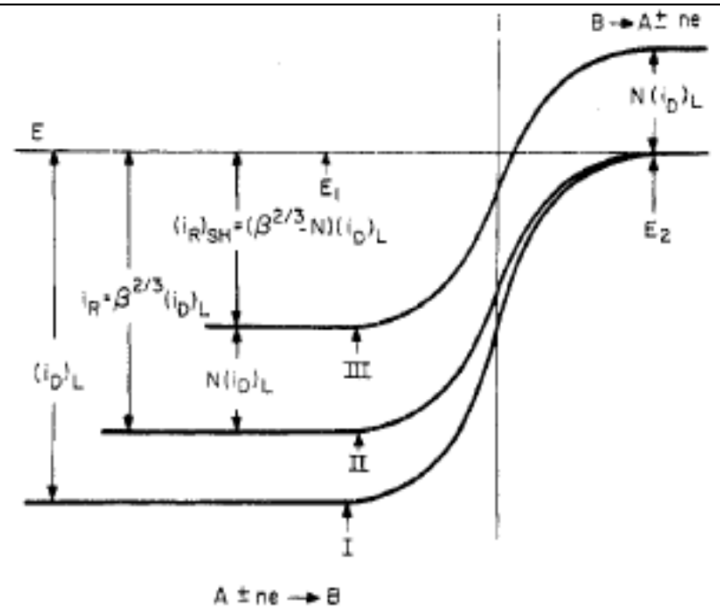


Figure 2. Ring and disk current–potential curves in solution of A. (I) Isolated disk; (II) isolated ring; (III) ring and disk. $\beta^{2/3} < 1$.

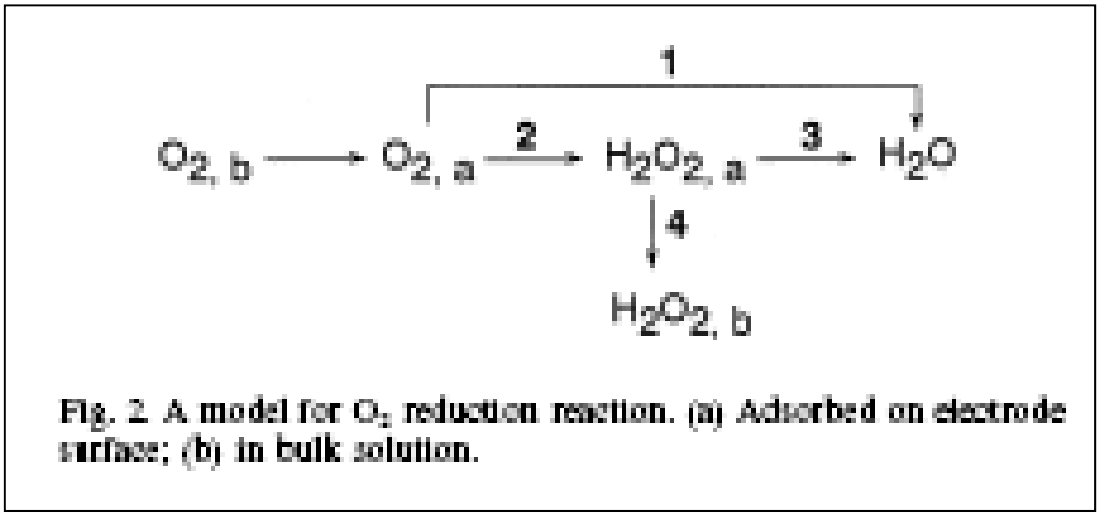
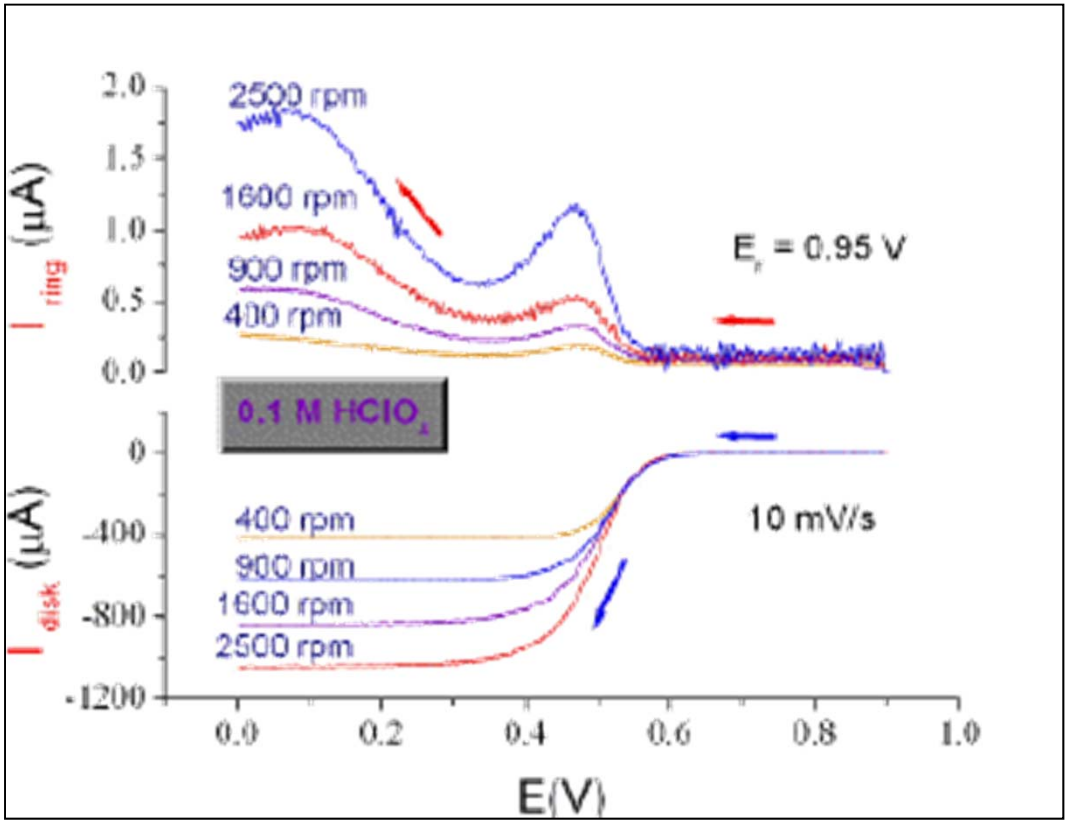


Fig. 2. A model for O_2 reduction reaction. (a) Adsorbed on electrode surface; (b) in bulk solution.

(a) Ring currents recorded with the Pt ring being potentiostated at 0.95 V, at which the H_2O_2 could be oxidized to O_2 if it is generated at the disk.

(b) Potentiodynamic oxygen reduction current recorded ot ploycrystalline Pt disk in 0.1 M $HClO_4$ in a RRDE assembly.



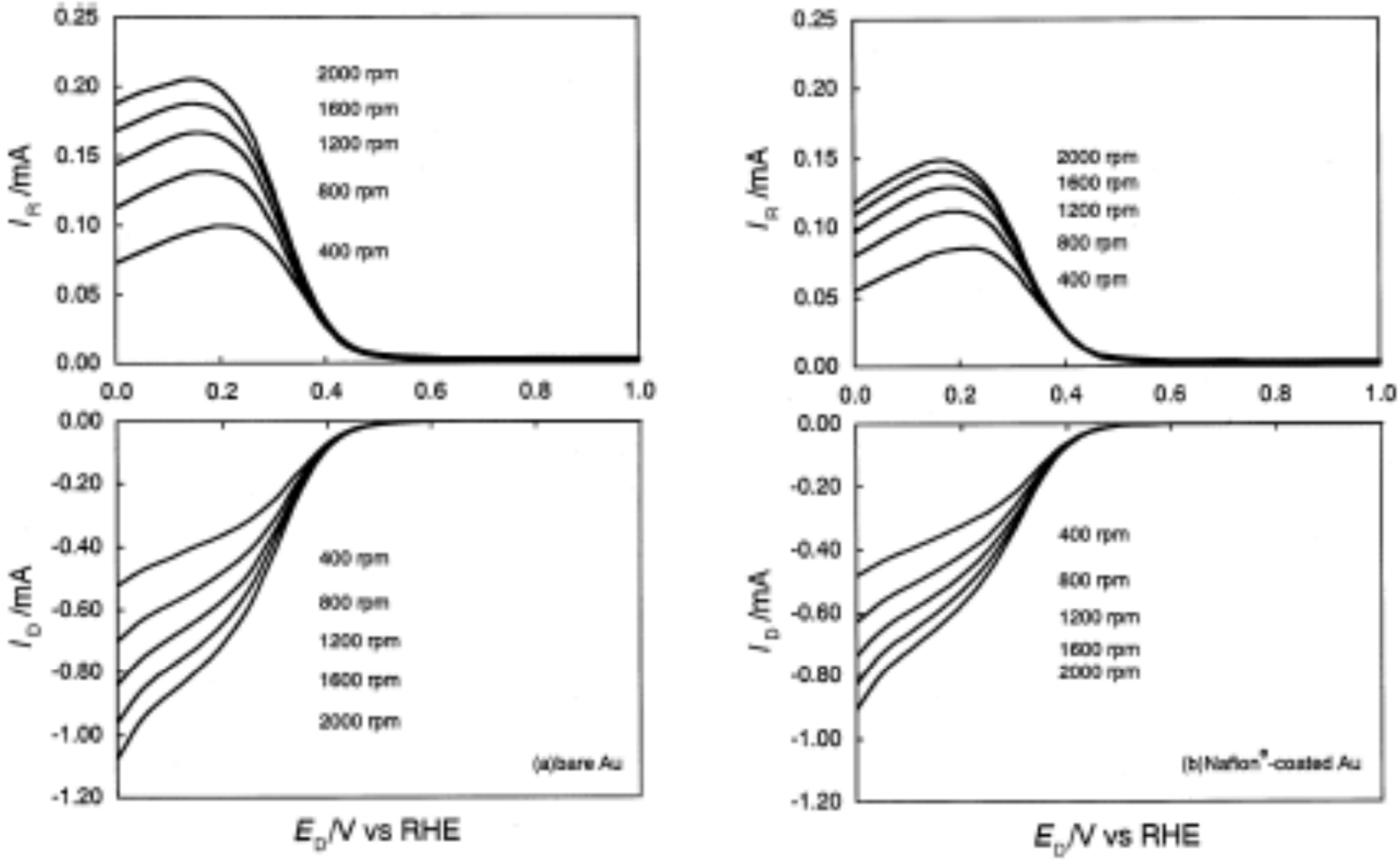


Fig. 3. Hydrodynamic voltammograms for the O_2 reduction reaction and H_2O_2 oxidation at (a) a rotating bare Au–Pt ring electrode and (b) a rotating Nafion®-coated ($\delta_f = 1.5$ μm) Au–Pt ring electrode in 0.5 M H_2SO_4 under an O_2 atmosphere. Scan rate of disk potential, 10 mV s^{-1}. Ring potential, 1.4 V.