Electrochemistry

CHEM 5390

Hydrodynamic Methods

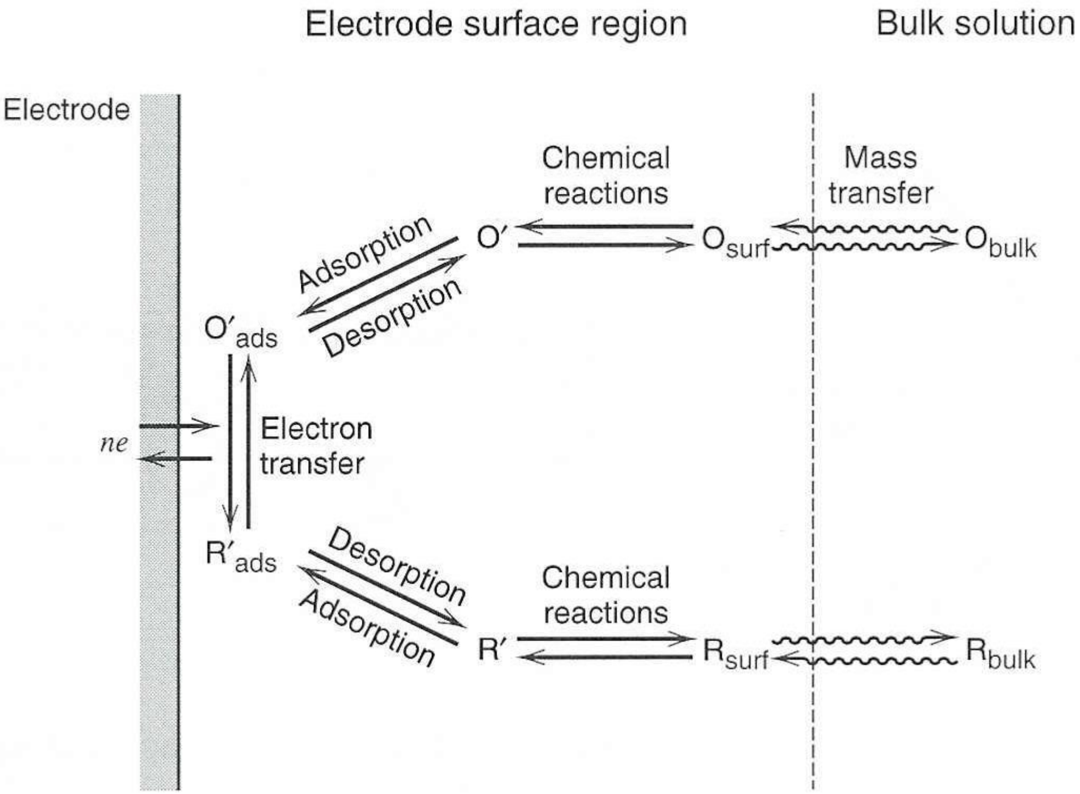


Figure 1.3.6 Pathway of a general electrode reaction.

Hydrodynamic Methods

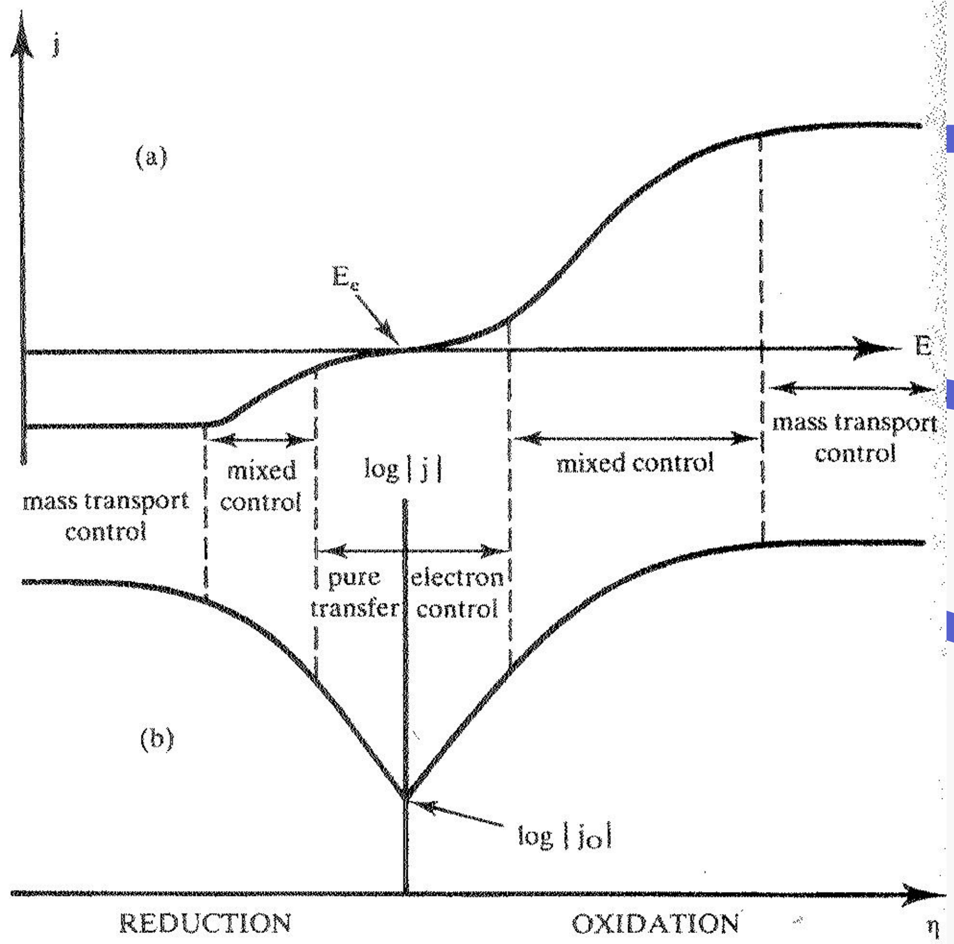


Figure 1.14 *j — E response and the corresponding log j — η curve for an irreversible electrode reaction* $O + e^- \rightleftharpoons R.\ c_R = 10c_O.$

Hydrodynamic Methods

Levich Equation

$$i_{l,c} = 0.62nFA\, D_O^{2/3}\, \omega^{1/2}\, v^{-1/6}\, C_O^*$$

C_O^* - solution concentration, mol/cm^3

i_l – limiting current, A

v – kinematic viscosity, cm^2/s

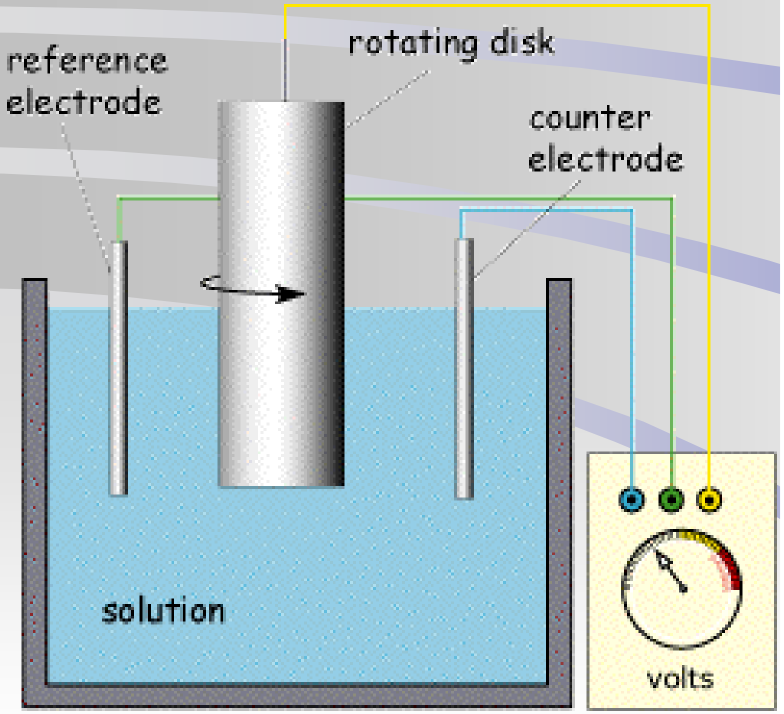
ω – angular velocity ($\omega = 2\pi f$, f- rps)

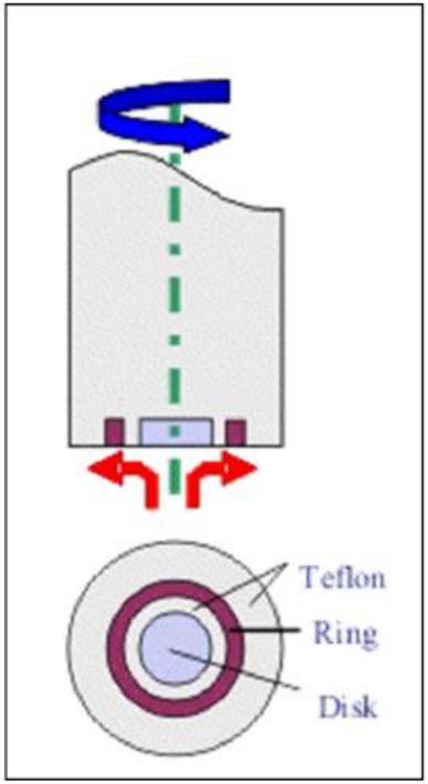
This equation applies to the mass-transfer limited condition at the RDE and predicts $i_{l,c}$ is $\propto C_O^*$ and $\omega^{1/2}$.

Hydrodynamic Methods

Rotating Ring Disk Electrode (RRDE)

Consist of a disk of electrode material and a ring imbedded in a rod of insulting material (usually teflon, epoxy resin or plastic).



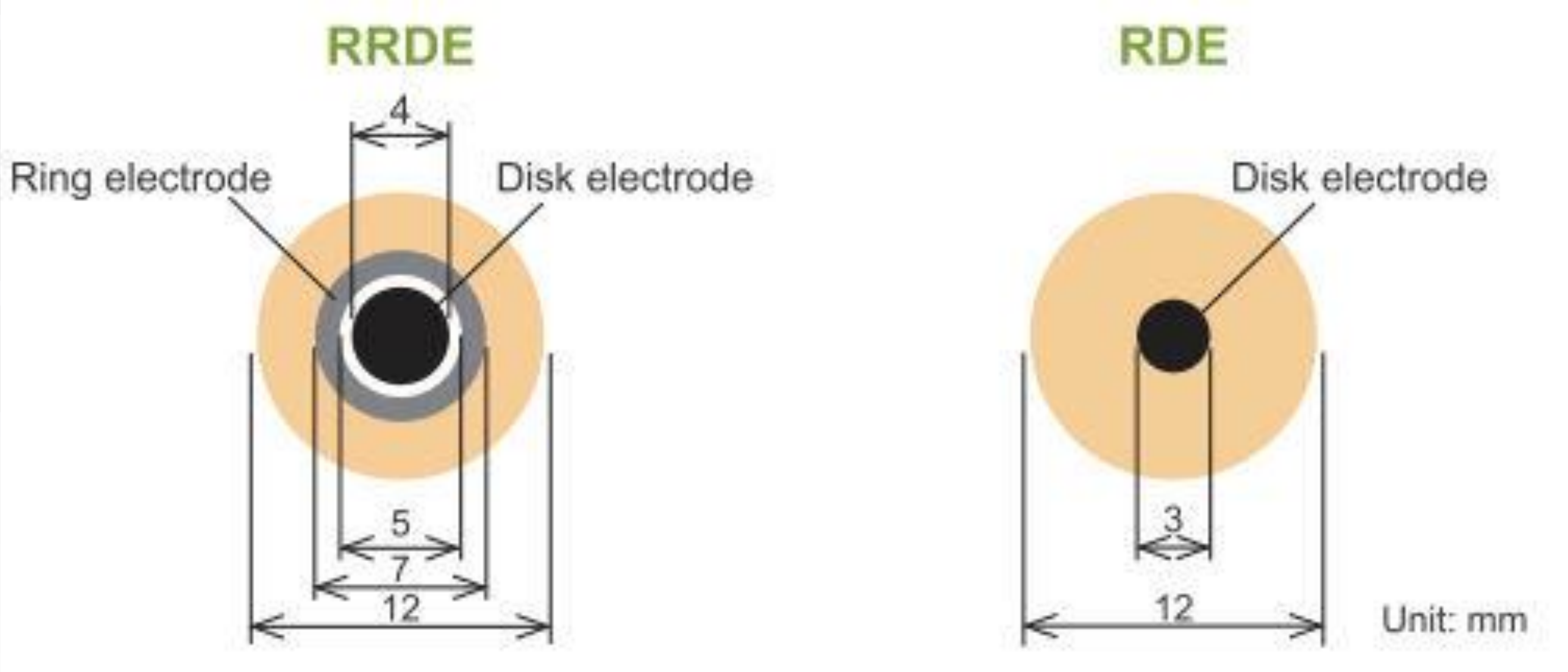


Rotating electrode assembly.

Hydrodynamic Methods

Rotating Ring Disk Electrode (RDE)

The measurements are important for the equations.



Hydrodynamic Methods

<u>Rotating Ring Disk Electrode (RRDE)</u>

A variant of the rotating-disk electrode which includes a second electrode - a concentric ring electrode.

The ring 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.

Hydrodynamic Methods

Rotating Ring Disk Electrode (RRDE)

- Convenient way to measure post-electron transfer reactions of products
- Relationship between disk current and ring current depends on rate of movement of product from the disk
- Only a fraction of disc products will reach ring

Hydrodynamic Methods

Rotating Ring Disk Electrode (RRDE)

- Since only a fraction of disc products will reach ring
- Efficiency depends on electrode geometry (radii of disk and ring)

Hydrodynamic Methods

Rotating Ring Disk Electrode (RRDE)

- Each ring-disk electrode must be calibrated with a well-behaved reversible couple to determine the collection efficiency (N)
- $N = i_R / i_D$
- Couples used - ferri/ferocyanide, quinone/hydroquinone

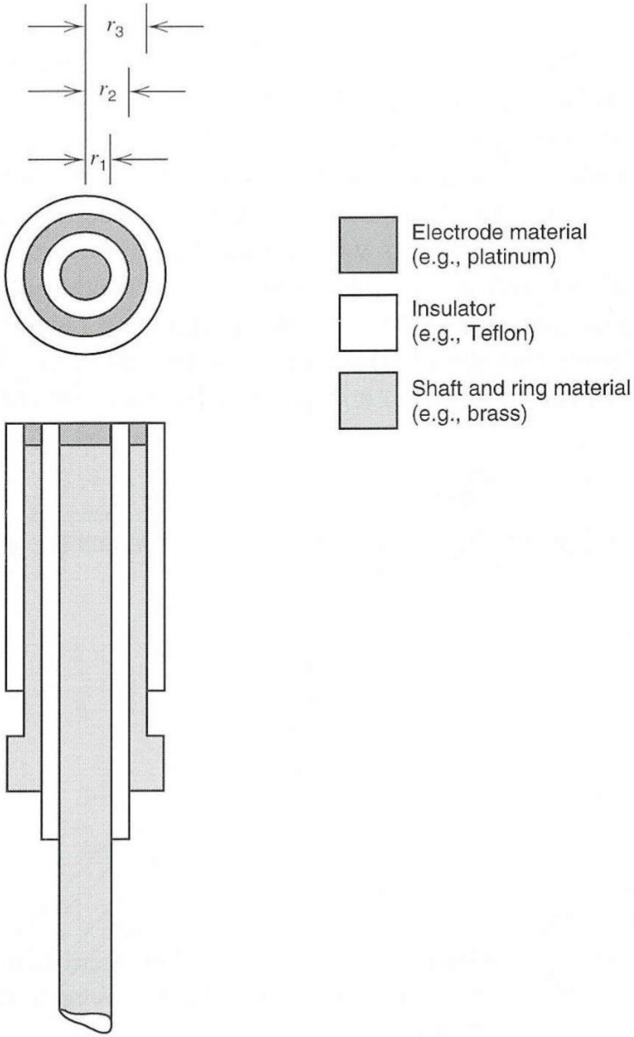
Hydrodynamic Methods

Mechanism studies

Mechanism information can be obtained in RRDE experiments,

By measuring the current at the ring electrode, some knowledge about what is occurring at the disk electrode can be obtained.

Hydrodynamic Methods



The two electrodes are electrically isolated so that different potentials can be applied to each.

Hydrodynamic Methods

Mechanism studies

For rotating ring electrode:

$i_{R,l,c} = 0.62nF\pi(r_3{}^3\text{-}r_2{}^3)^{2/3}\ D_O{}^{2/3}\ \omega^{1/2}\ v^{-1/6}\ C_O{}^*$

r_2 – inner radius

r_3 – outer radius

$A = \pi(r_3{}^2\text{-}r_2{}^2)$

$i_R = i_D\ [(r_3{}^3\text{-}r_2{}^3)^{2/3}]/r_1{}^2$

$i_R/i_D = \beta^{2/3} = (r_3{}^3/r_1{}^3 - r_2{}^3/r_1{}^3)^{2/3}$

Hydrodynamic Methods

Rotating Ring Disk Electrode (RRDE)

The current-potential characteristics of the disk are unaffected by the presence of the ring.

The RRDE experiments involve two potentials, E_D and E_R and two currents, i_D and i_R.

Use a biopotentiostat to allow separate adjustments of E_D and E_R.

Hydrodynamic Methods

Rotating Ring Disk Electrode (RRDE)

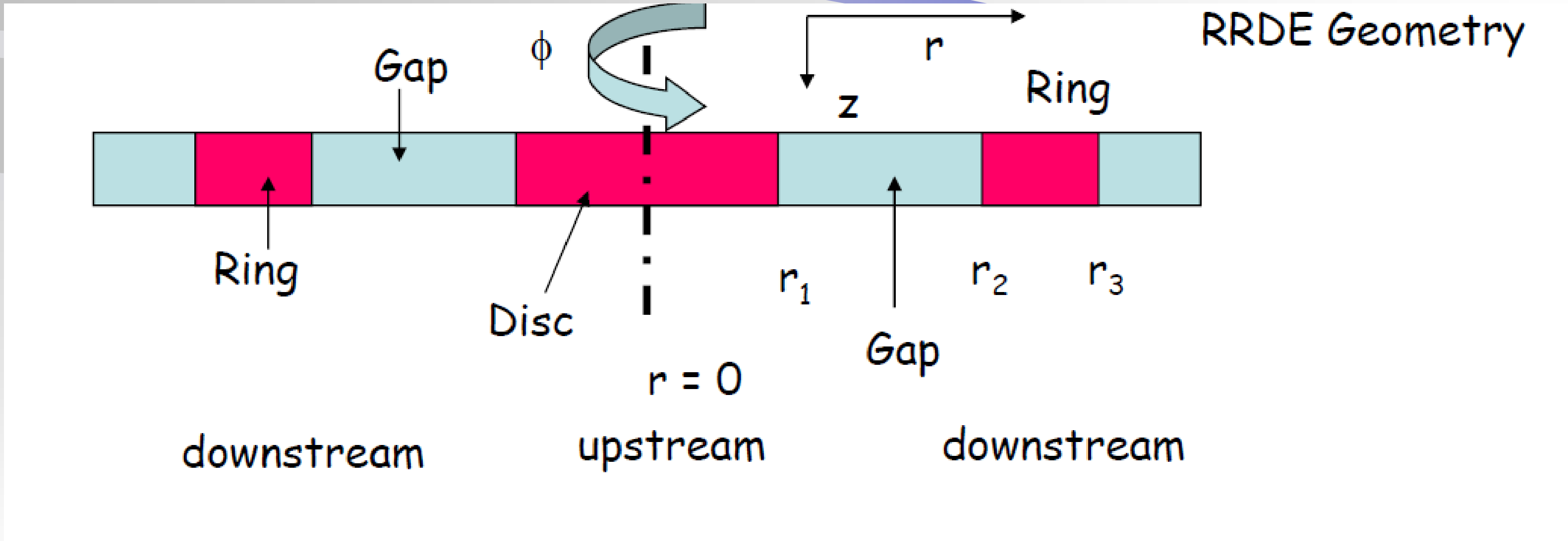
Most common experiments for RRDE are collection experiments – where disk generated species is observed at the ring

and shielding experiments, where flow of bulk electroactive species to the ring is changed by the disk reaction.

Hydrodynamic Methods

Generator-Collector Experiments

Generator-Collector (detector) experiments are where the intermediate/product generated at a generator electrode (disc) is detected at a collector electrode (ring).



Hydrodynamic Methods

Collection Experiments

$O + ne \rightarrow R$ at E_D giving i_D

$R \rightarrow O + ne$ at E_R giving i_R

Interested in knowing how much of disk generated R is collected at the ring, i_R

$N = -i_R/i_D$, where N – collection efficiency

N depends on r_1, r_2, r_3 but independent of other parameters, N is a constant.

N becomes larger as gap thickness (r_2-r_1) decreases and as ring size (r_3-r_2) increases.

Hydrodynamic Methods

Collection Experiments

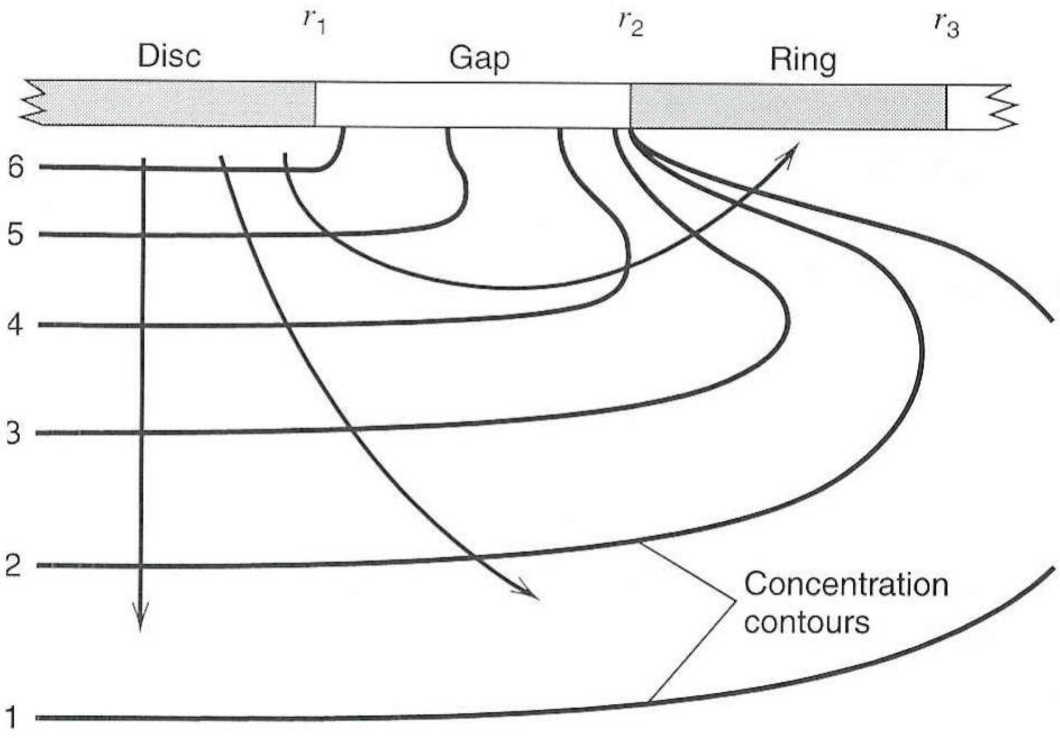


Figure 9.4.3 Concentration profiles of species R at an RRDE. Concentrations increase from curve 1 to curve 6. For the disk ($0 \leq r < r_1$), $\partial C_R/\partial r = 0$; in the gap ($r_1 \leq r < r_2$), $(\partial C_R/\partial y)_{y=0} = 0$; and at ring surface ($r_2 \leq r < r_3$), $C_R(y = 0) = 0$. [From W. J. Albery and M. L. Hitchman, "Ring-Disc Electrodes," Clarendon, Oxford, 1971, Chap. 3, by permission of Oxford University Press.]

Hydrodynamic Methods

Collection Experiments

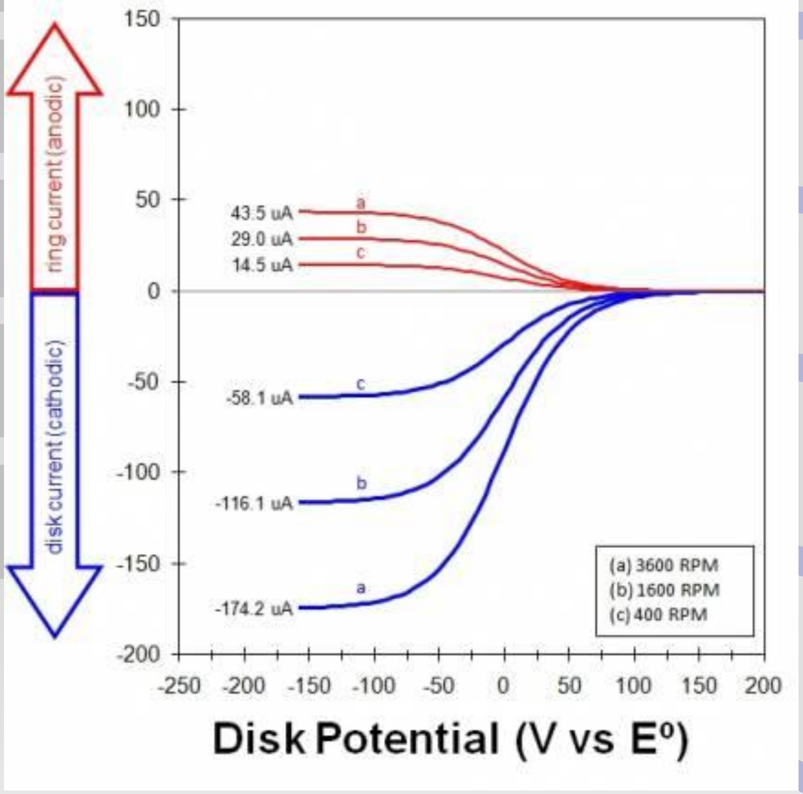
In collection experiments, i_D and i_R is plotted as a function of E_D with constant E_R.

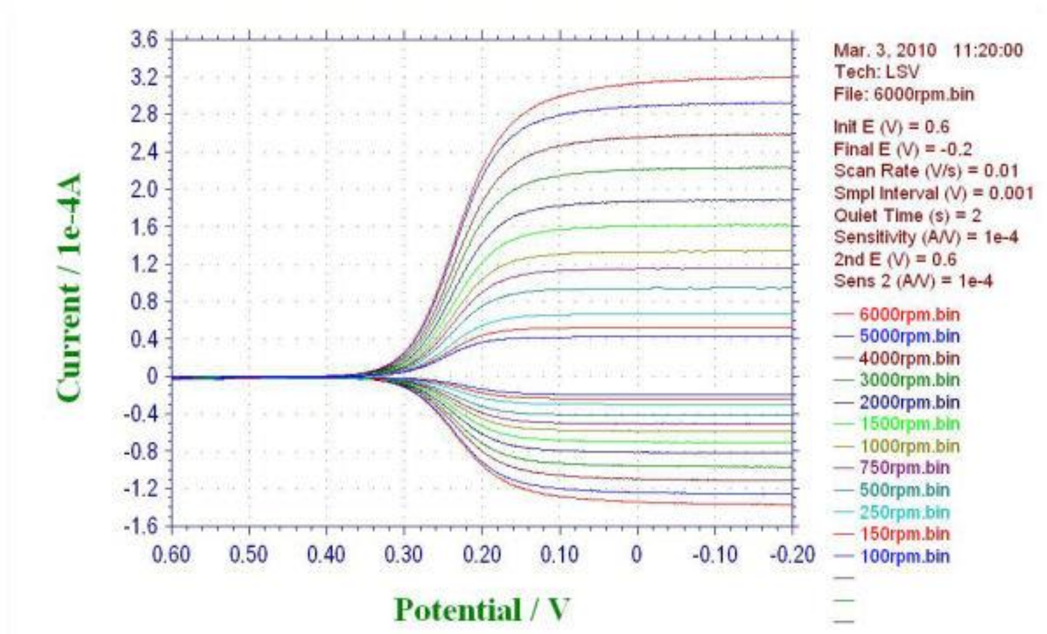
If R decomposes at a high rate and N becomes smaller, information about the rate and mechanism of decay of R is obtained.

Information about the reversibility of a reaction can be obtained by plotting i_R versus E_R at a constant E_D.

Hydrodynamic Methods

Collection Experiments





Mar. 3, 2010 11:20:00
Tech: LSV
File: 6000rpm.bin

Init E (V) = 0.6
Final E (V) = -0.2
Scan Rate (V/s) = 0.01
Smpl Interval (V) = 0.001
Quiet Time (s) = 2
Sensitivity (A/V) = 1e-4
2nd E (V) = 0.6
Sens 2 (A/V) = 1e-4

Figure 5. Current-potential curves of potassium ferricyanide solution

Hydrodynamic Methods

Collection Experiments

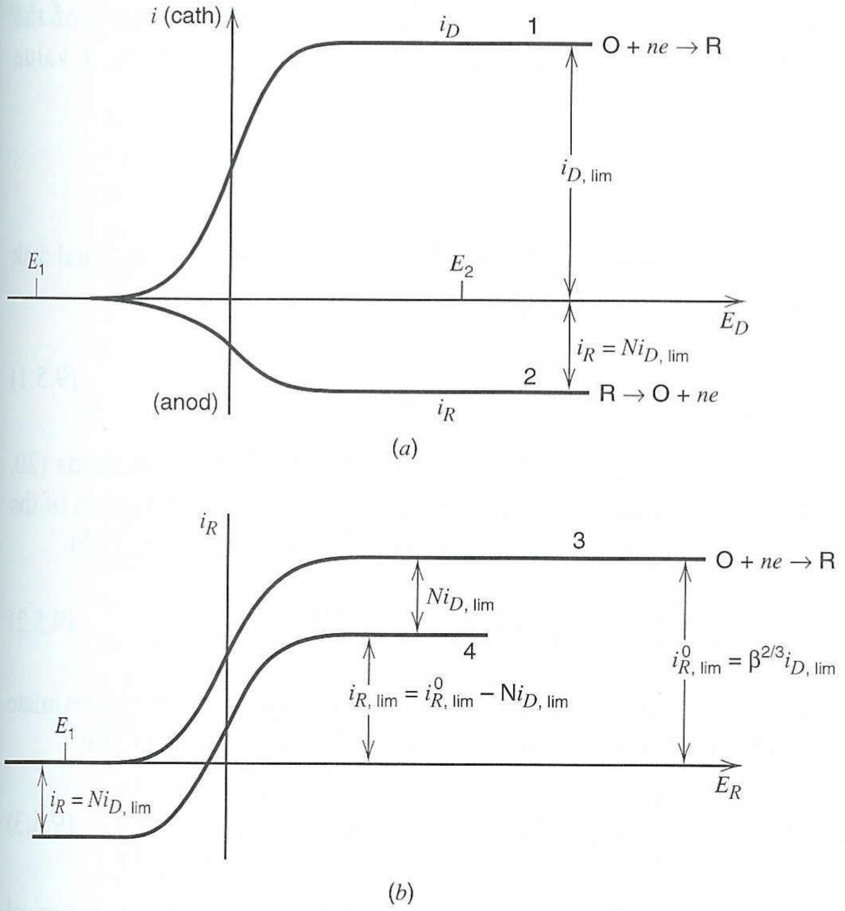


Figure 9.4.4 (*a*) Disk voltammogram. (*1*) i_D *vs.* E_D and (*2*) i_R *vs.* E_D with $E_R = E_1$. (*b*) Ring voltammograms. (*3*) i_R *vs.* E_R, $i_D = 0$ ($E_D = E_1$) and (*4*) i_R *vs.* E_R, $i_D = i_{D,l,c}$ ($E_D = E_2$).

Hydrodynamic Methods

Shielding Experiment

Measure O + ne → R at ring when disk is at OCP ($i_D = 0$).

If disk current is applied, flux of O to ring will decrease.

$$i_{R,l} = i^o_{R,l} - Ni_D$$

$$i_{R,l} = i^o_{R,l}\,(1\text{-}N\beta^{-2/3})$$

$(1\text{-}N\beta^{-2/3})$ – called the shielding factor

Hydrodynamic Methods

RDE Examples

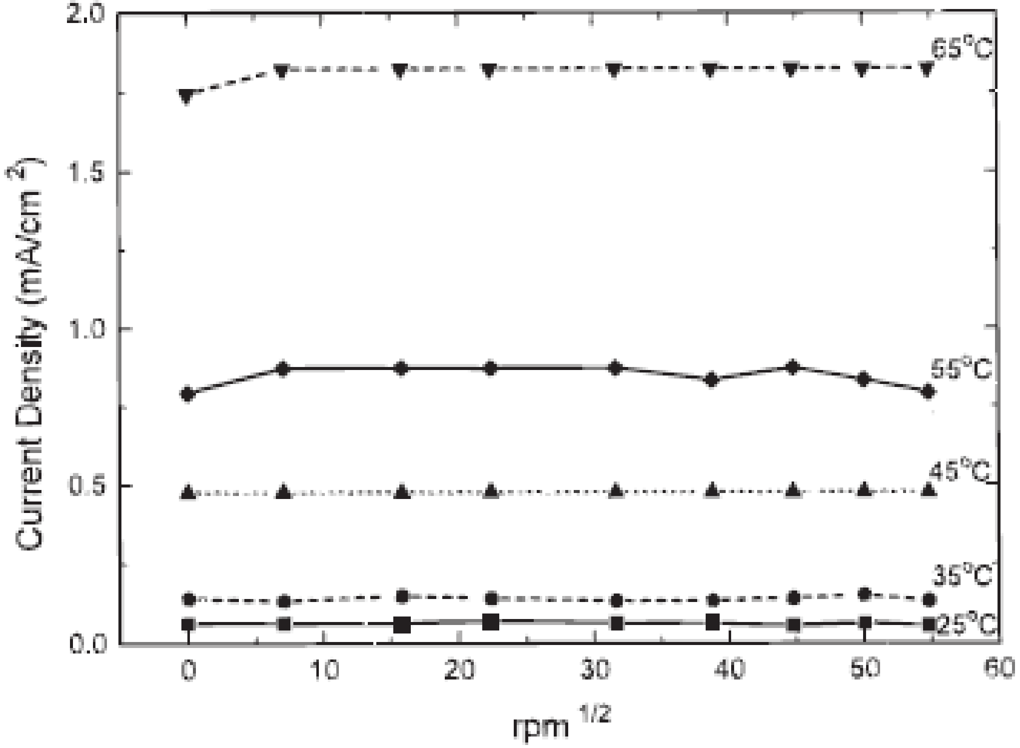


Figure 2. Levich plots for a 10 μm Cu_2O film deposited at −0.45 V.

Hydrodynamic Methods

RDE Examples

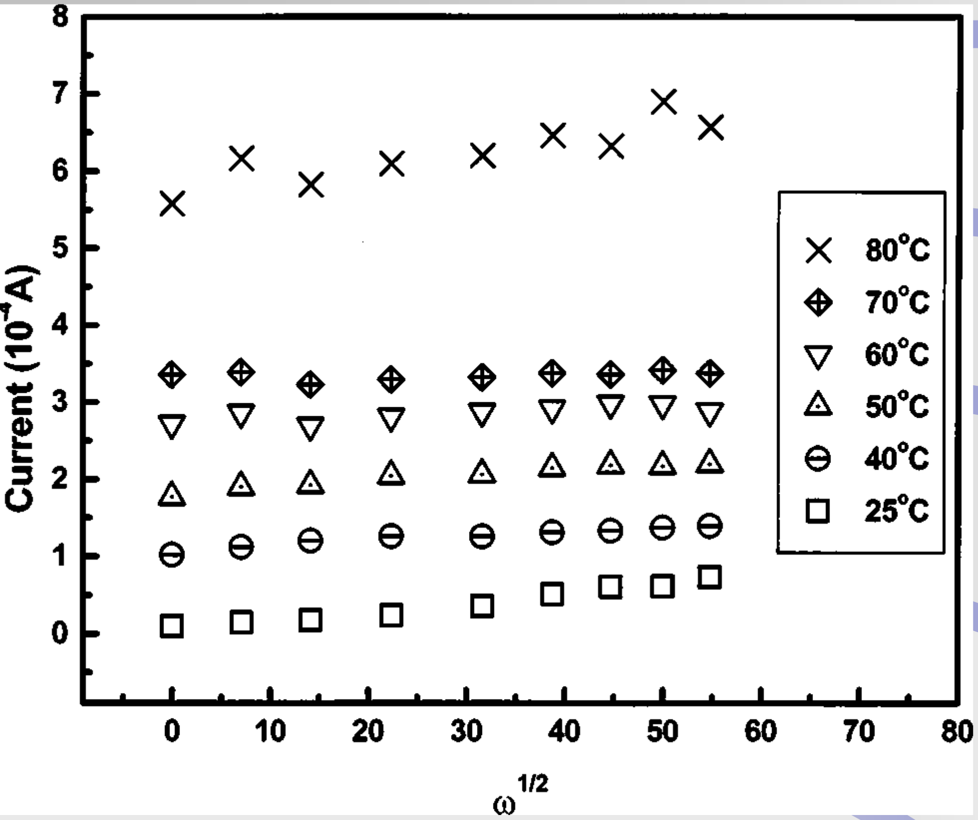


Figure 6. Levich plots for CeIII/CeIV oxidation at temperatures of 25, 40, 50, 60, 70, and 80°C at rotation rates from 0 to 3000 rpm.

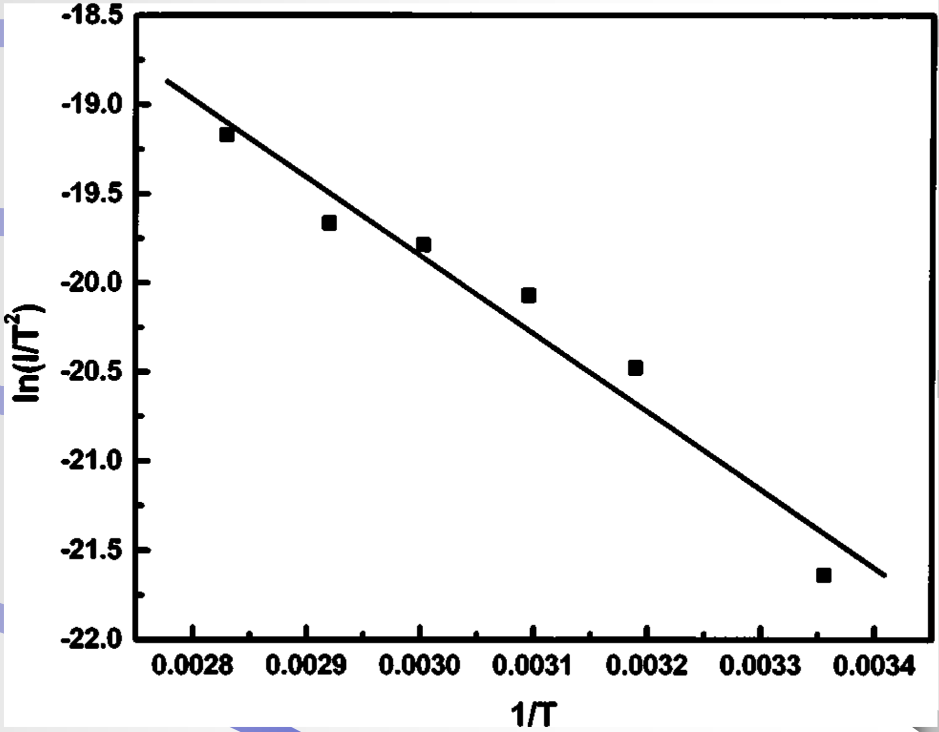


Figure 7. Activation plot from LSV data at a rotation rate of 1000 rpm. From the slope of the plot of Fig. 7, the barrier height for the cerium oxide/solution interface is 0.30 eV.

Hydrodynamic Methods

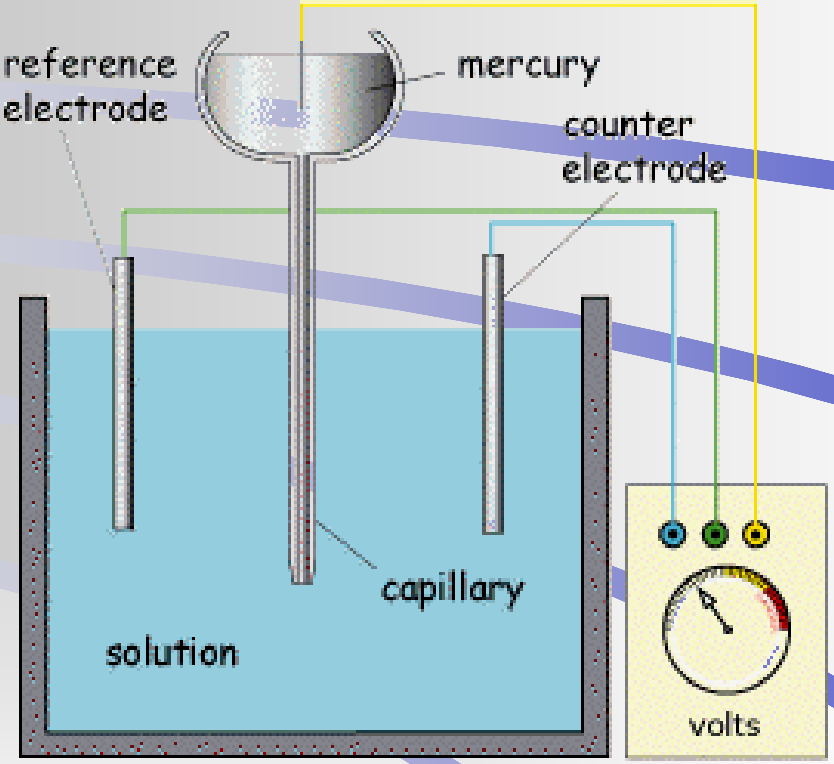
Flowing hydrodynamics

The first hydrodynamic techniques developed was the Dropping Mercury Electrode (DME). In this arrangement a fine capillary is connected to a reservoir of mercury. The cell is designed so that mercury is allowed to flow down the capillary at a controlled rate and out into the solution.

Polarography is a subclass of voltammetry where the working electrode is dropping mercury.

Hydrodynamic Methods

Flowing hydrodynamics



Heyrovsky (1922) (Nobel prize 1959)

Hydrodynamic Methods

Flowing hydrodynamics

Electrical contact to the mercury is made in the reservoir and a reference and counter electrode are sited in the electrolyte solution.

This technique proved very popular due to the ability to continually refresh the electrode surface during the experiment and wide cathodic range.

Hydrodynamic Methods

Flowing hydrodynamics

The excitation signal is a linearly increasing potential ramp. Current vs potential is measured.

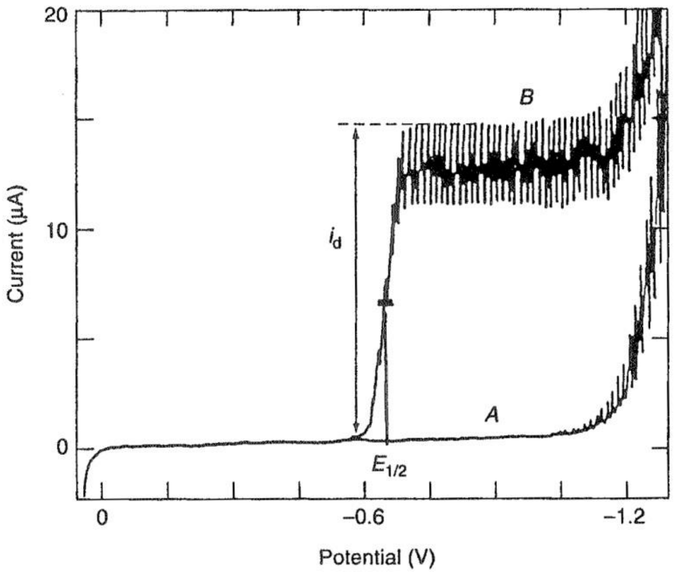


Figure 3.3 Polarograms for 1 M hydrochloric acid (A) and 4×10^{-4} M Cd^{2+} in 1 M hydrochloric acid (B); i_d represents the limiting current, while $E_{1/2}$ is the half-wave potential.

Hydrodynamic Methods

Flowing hydrodynamics

The equation used for DME experiments is the Ilkovic equation:

$$i_d = 708\, n\, D^{1/2}\, m^{2/3}\, t^{1/6}\, C$$

where

i_d – limiting diffusion current (A)
D – diffusion rate (cm^2/s)
m – mass flow rate of mercury (g/s)
t – drop time of mercury (sec)
C – concentration (mol/cm^3)

(this equation represents the current at the end of the drop life)

Hydrodynamic Methods

Flowing hydrodynamics

The equation used for DME experiments is the Ilkovic equation:

$$i_d = 607\, n\, D^{1/2}\, m^{2/3}\, t^{1/6}\, C$$

(this equation represents the average current over the drop life and obtained by integrating the current with time)

Hydrodynamic Methods

Flowing hydrodynamics

The potential where the current is one-half of its limiting value is called the half-wave potential, $E_{1/2}$. The half-wave potential is related to the formal potential, E^o, of the electroactive species.

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

Hydrodynamic Methods

Flowing hydrodynamics

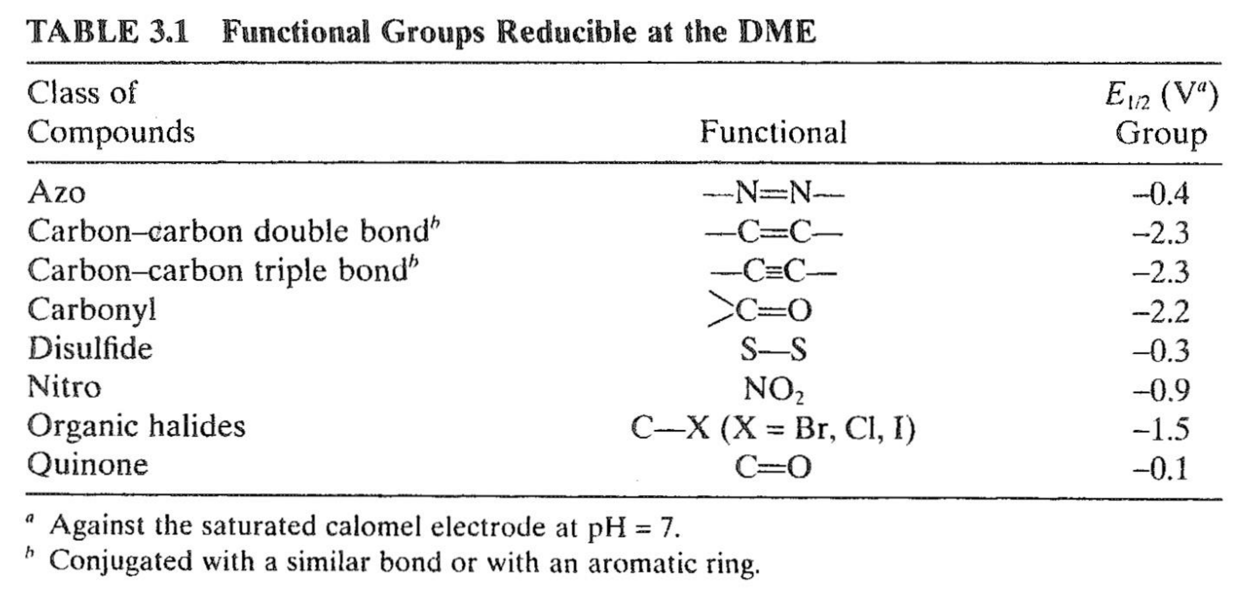


TABLE 3.1 Functional Groups Reducible at the DME

Class of Compounds	Functional	$E_{1/2}$ (V[a]) Group
Azo	—N=N—	–0.4
Carbon–carbon double bond[b]	—C=C—	–2.3
Carbon–carbon triple bond[b]	—C≡C—	–2.3
Carbonyl	$>C{=}O$	–2.2
Disulfide	S—S	–0.3
Nitro	NO_2	–0.9
Organic halides	C—X (X = Br, Cl, I)	–1.5
Quinone	C=O	–0.1

[a] Against the saturated calomel electrode at pH = 7.

[b] Conjugated with a similar bond or with an aromatic ring.

Hydrodynamic Methods

Flowing hydrodynamics

Another way to control mass transport through convection is to fix the electrode and allow solution to flow over the surface by an applied force such as pressure.

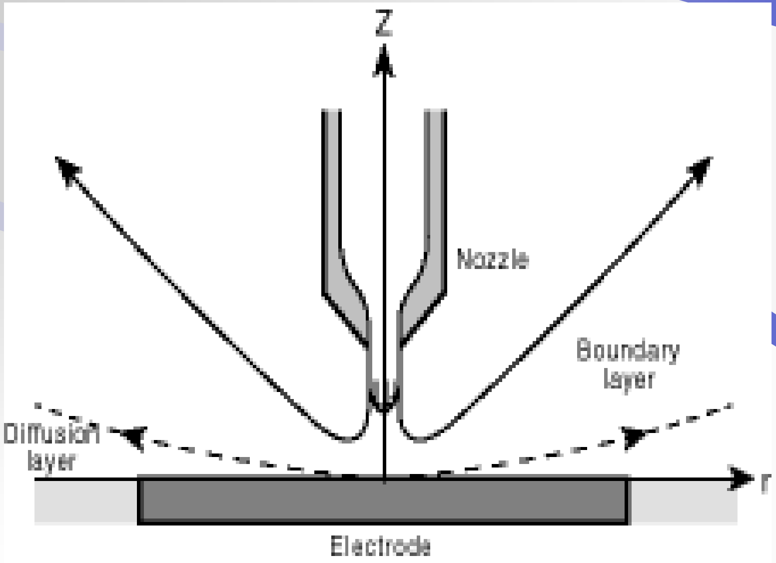
Examples: wall jet electrode, channel electrode

Hydrodynamic Methods

Flowing hydrodynamics

Wall jet electrode

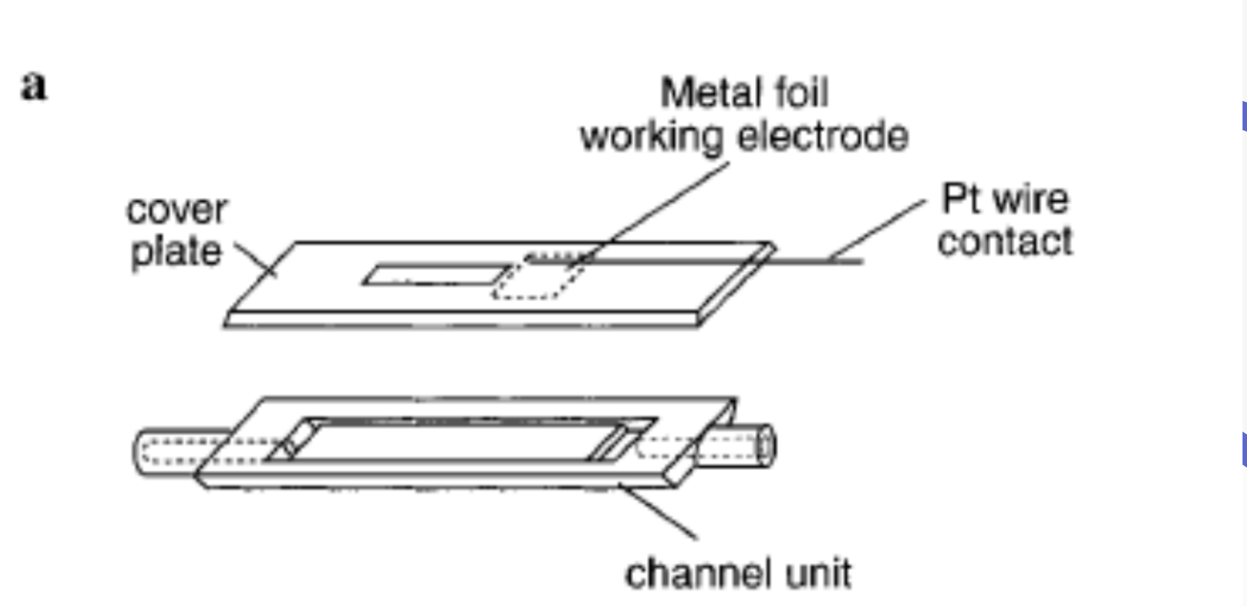
A fine nozzel is sited within a large container of electrolyte and positioned directly above a disc working electrode. Solution is pumped through the nozzel (under laminar flow conditions) and impinges on the surface containing the electrode. The reagent then flows from the surface creating a complex but predictable flow pattern.



Hydrodynamic Methods

Channel Electrode (ChE)

The channel electrode (ChE) consists of an electrode embedded in one wall of a rectangular duct down which solution flows.



Hydrodynamic Methods

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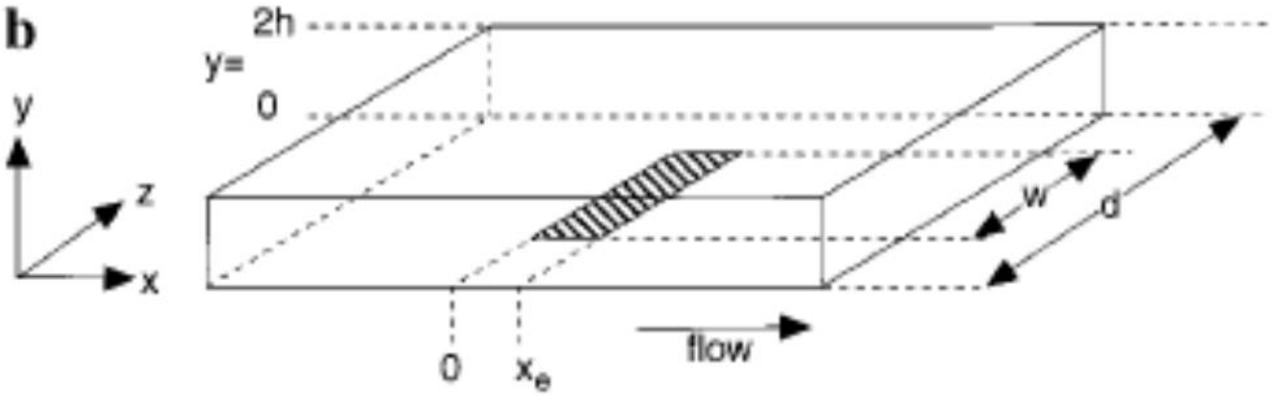


Figure 1. (a) Practical channel flow cell for mechanistic electrochemical studies. (b) Schematic diagram which defines the coordinate system adopted in the text.

Hydrodynamic Methods

Channel Electrode (ChE)

Advantages include:

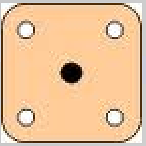
- Flow through facilitates continuous monitoring in analytical applications following chromatographic separation.
- Well defined hydrodynamics permits rigorous mechanistic investigation of reactions via voltammetric techniques.
- Channel geometry can be readily used in spectroelectrochemistry (IR, UV/VIS,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

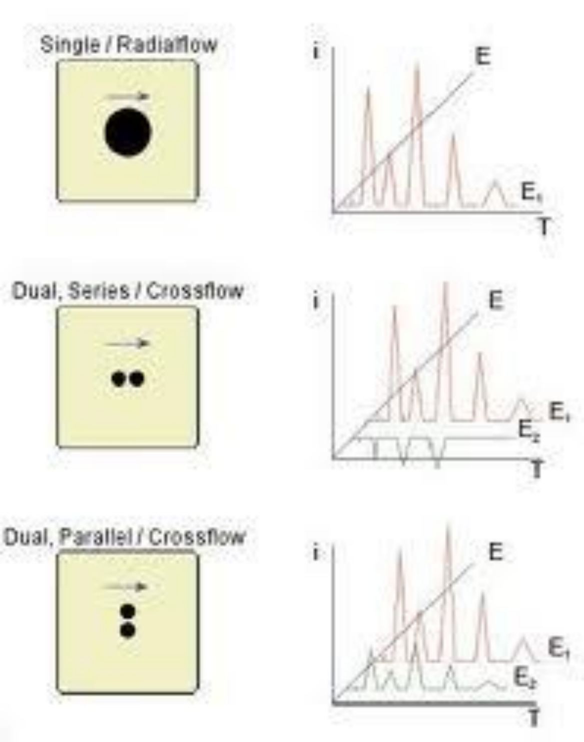
Hydrodynamic Methods

Flowing hydrodynamics

Radial Flow electrode

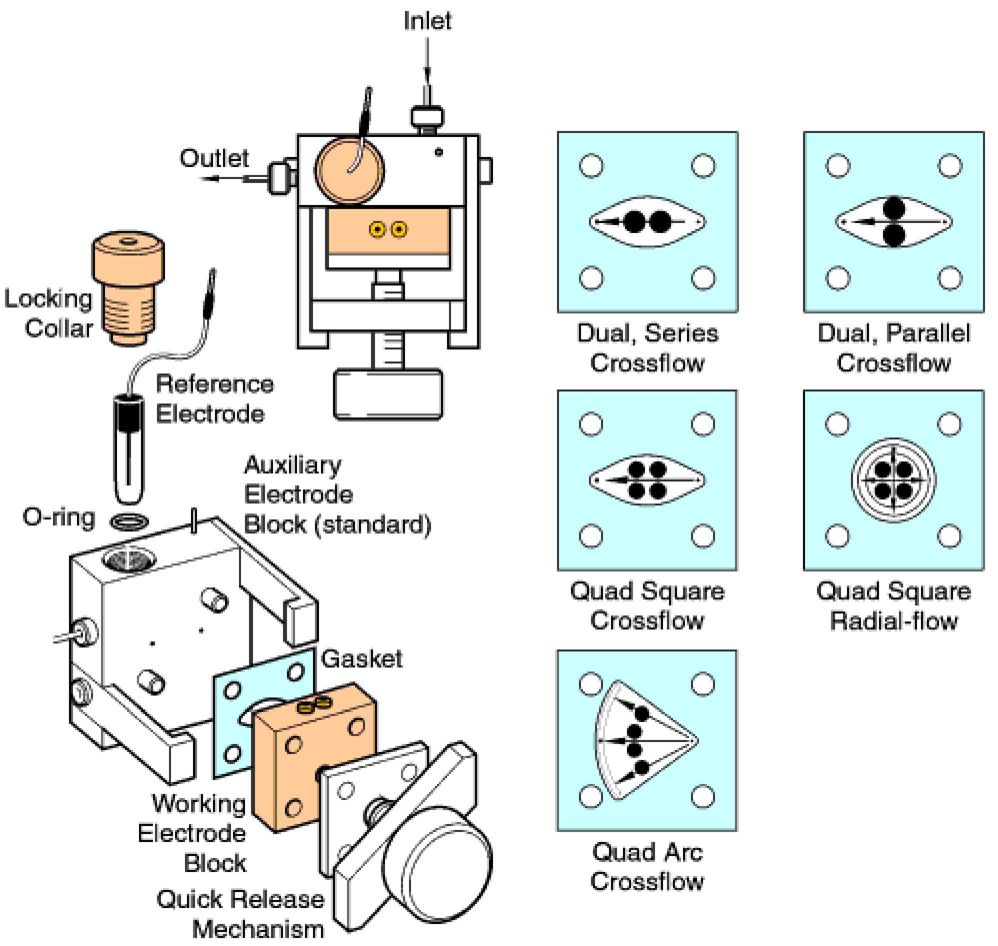
Marketed by BAS for flow injection and LC techniques.





Hydrodynamic Methods

Flowing hydrodynamics



Hydrodynamic Methods

Flowing hydrodynamics examples

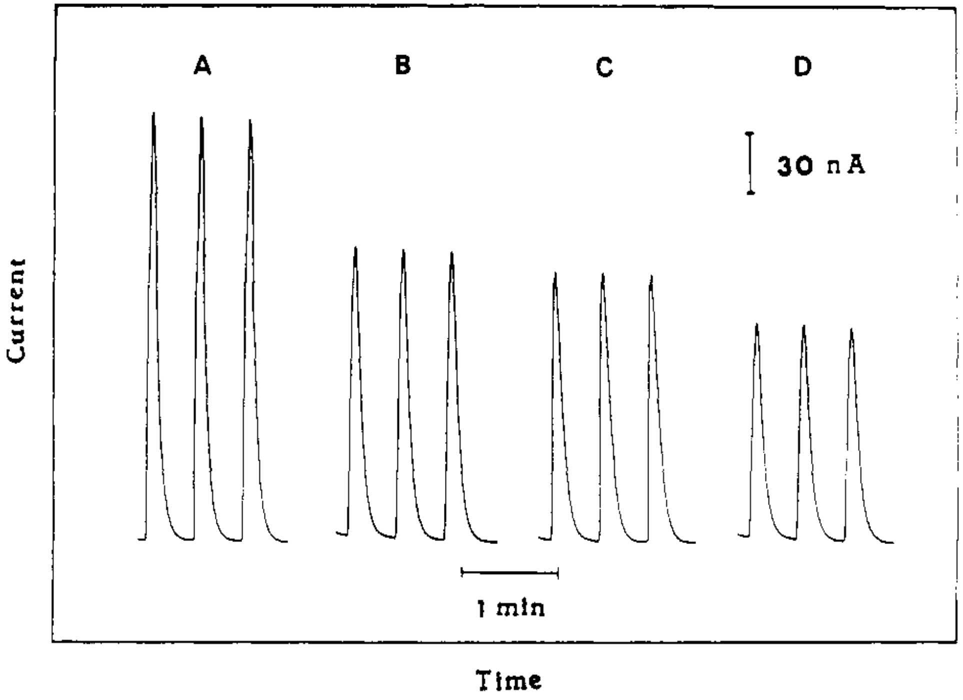


Figure 1. Flow injection detection peaks for 1×10^{-5} M acetaminophen using the bare (A) and PVP-coated (B-D) glassy carbon electrodes. Electrodes were modified with 5 (B), 10 (C), and 15 (D) μL of PVP solution. Flow rate 1.0mL/min; applied potential, +0.90V. Electrolyte and carrier, 0.05M phosphase buffer (pH 5.5).

Hydrodynamic Methods

Flowing hydrodynamics examples

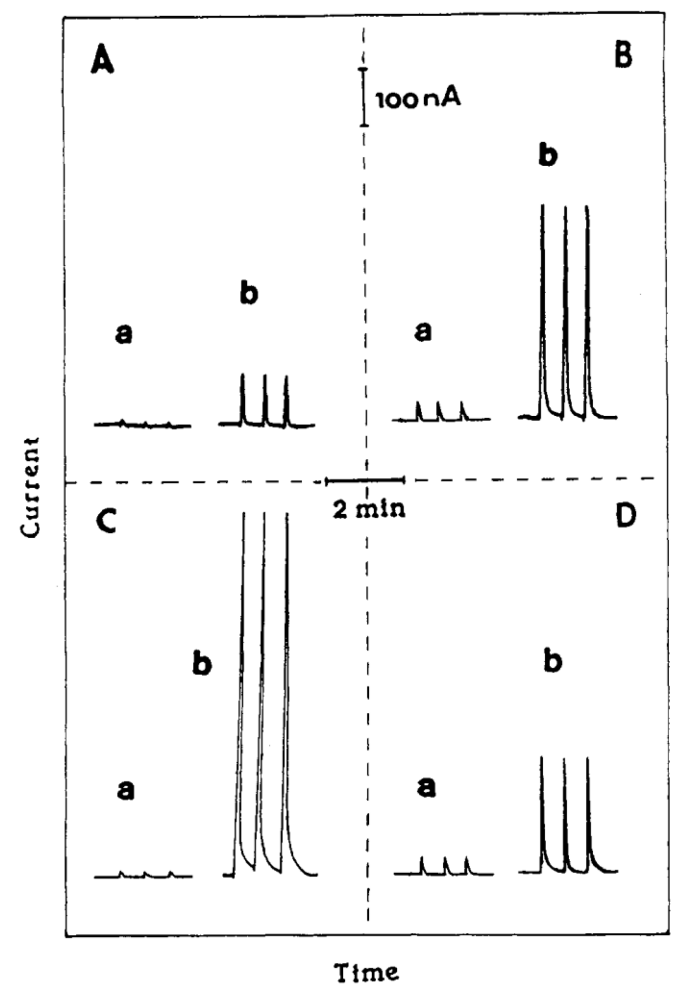
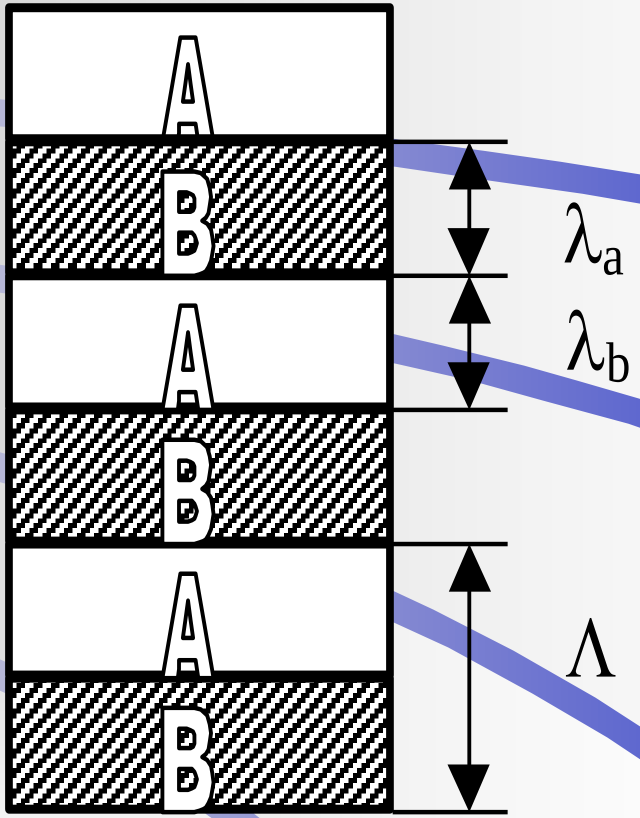


Figure 5. Flow injection peaks for 2×10^{-4} M hydrazine (A), 2×10^{-4} M L-cysteine (B), 1×10^{-4} M oxalic acid (C), and 2×10^{-4} M penicillamine (D) for unmodified (a) and CoPC-modified (b) graphite epoxy electrodes. Conditions: applied potential, +0.40 (A, B, D) and +0.75 (C) V; flow rate, 1.0 mL/min; carrier solution, 0.05 M phosphate buffer of pH 5.9 (A, B, D) and 3.1 (C).

Hydrodynamic Methods

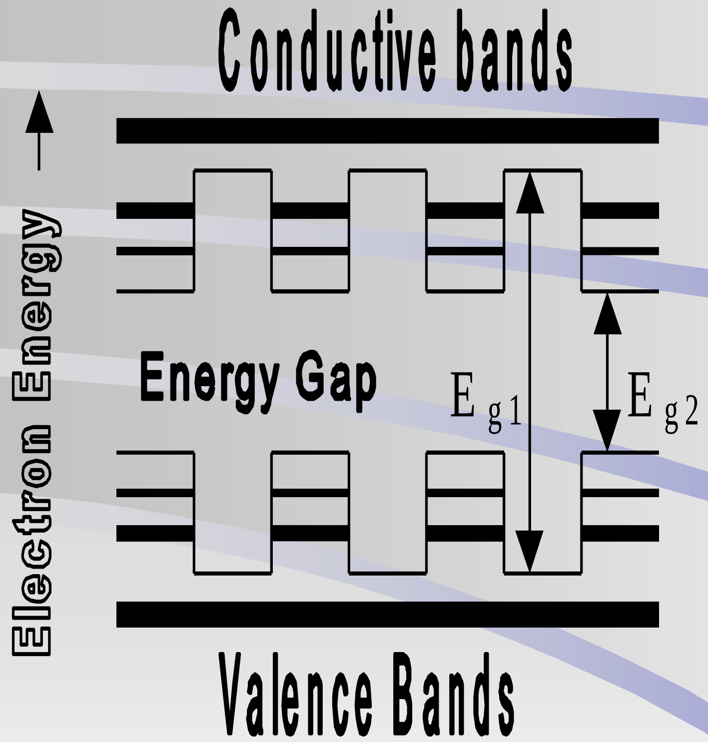
Flowing hydrodynamics

Multilayers



Hydrodynamic Methods

Flowing hydrodynamics

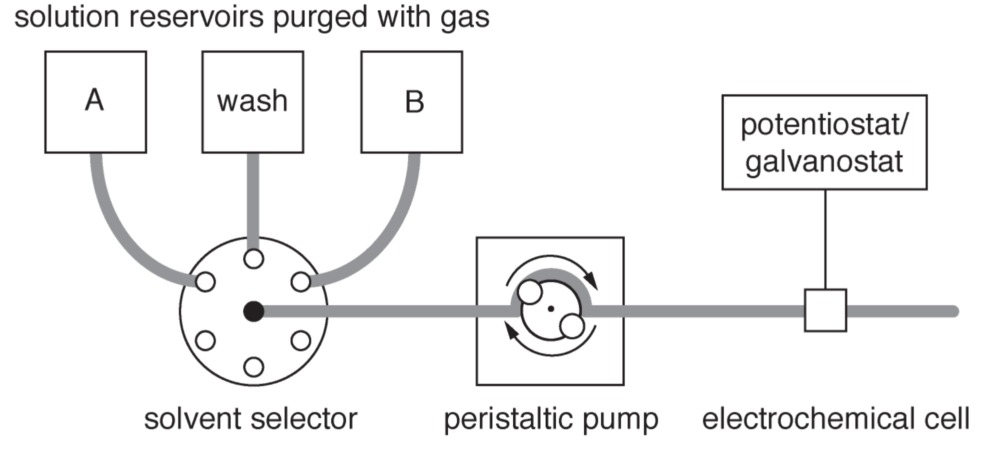


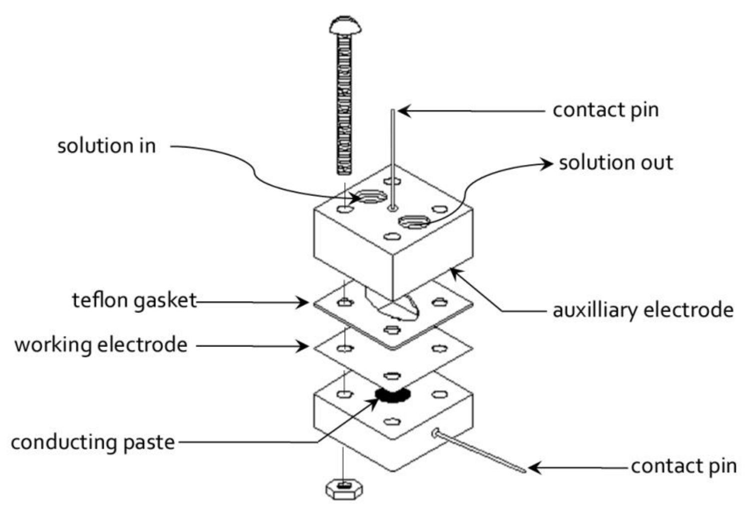
Properties associated with multilayers mainly due to deformation of energy gaps.

- Increased tensile strength
- Increased electronic properties
  - conductive
  - magnetic

Hydrodynamic Methods

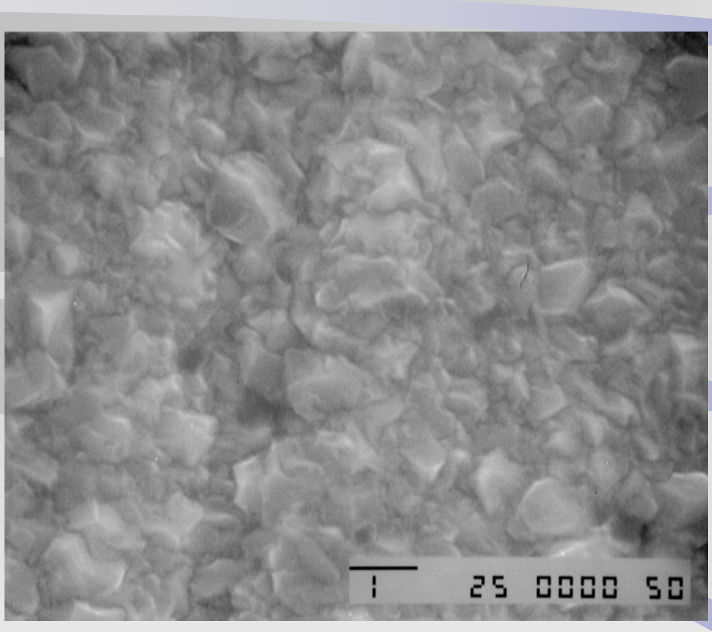
Flowing hydrodynamics

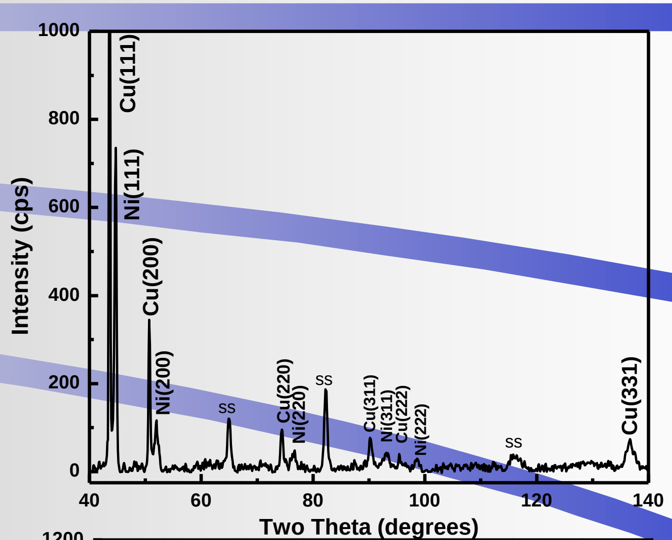


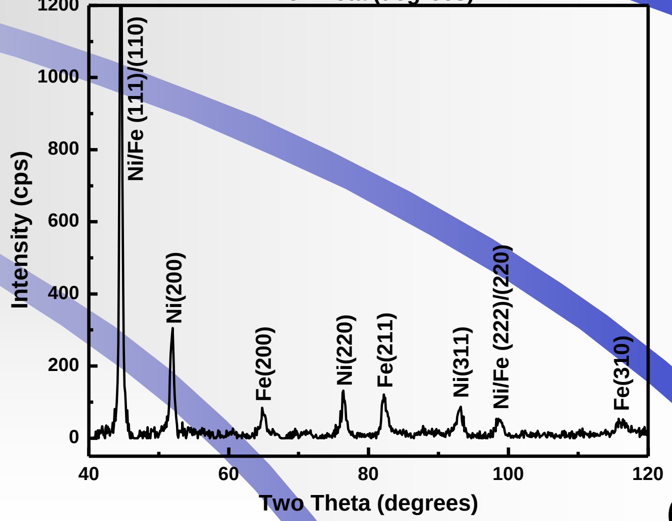


Hydrodynamic Methods

Flowing hydrodynamics







Class Assignment

- Read Chapter 9 – Bard and Faulkner