ELECTROCHEMICAL SPECTROSCOPY

NATIONAL CENTRE FOR CATALYSIS RESEARCH
INDIAN INSTITUTE OF TECHNOLOGY MADRAS

Electrochemistry using Cyclic Voltammetry

- Cyclic Voltammograms trace the transfer of electrons during an oxidation-reduction (redox) reaction.

- The reaction begins at a certain potential (voltage). As the potential changes, it controls the point at which the redox reaction will take place.

- Electrodes are placed in an electrolyte solution. The electrolyte contains analyte that will undergo the redox reaction.

Cycles

In CV, the current in the cell is measured as a function of potential. The potential of an electrode in solution is linearly cycled from a starting potential to the final potential and back to the starting potential. This process, in turn, cycles the redox reaction. Multiple cycles can take place.

A plot of potential versus current is then produced.

Three-Electrode Cell

• Requires a precise control of the potential at the electrode.

• Three electrodes:

– Working electrode (WE),

– Counter electrode (CE)

– Reference electrode (RE).

• No current through RE ideally.

• Use RE to provide precise control of potential at the WE, and the

forcing current from WE to CE is MEASURED

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How does C-V work?
- **The system starts off with an initial potential at which no redox can take place.**
- **At a critical potential during the forward scan, the electroactive species will begin to be reduced.**
- **After reversal of potential scan direction and depletion of the oxidized species the reverse reaction, oxidation, takes place.**

Electrodes

- Commonly used reference electrodes for cyclic voltammetry are [3]:
  – Silver/Silver Chloride Electrode
  – Calomel Electrode
- Ag/AgCl electrode is chosen for our sensor because it is possible to integrate to microdevices.
- Gold electrodes are used for WE and CE.

$$AgCl(s) + e- \rightarrow Ag(s) + Cl-(aq), E° = +0.22V$$

$$Hg2Cl2(s) + 2e- \rightarrow 2Hg(l) + 2Cl-(aq), E° = +0.27V$$
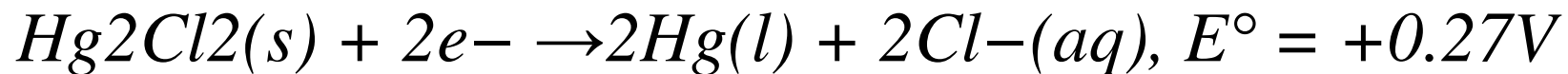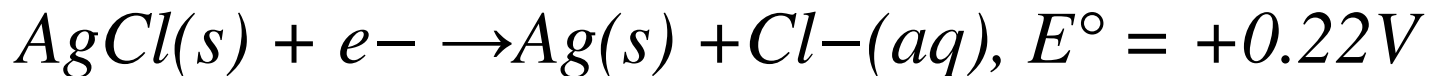
Cyclic Voltammetry

• Used for studying electrode processes.

• A triangular potential waveform is applied to the WE, resulting in a Faradic current.

• Nernst Equation equilibrium constant

equilibrium constant

$$E = -\frac{\Delta G^\circ}{nF} - \frac{RT}{nF}\ln Q = E^\circ - \frac{RT}{nF}\ln Q$$

$$E^\circ = -\frac{\Delta G^\circ}{nF} = \frac{RT}{nF}\ln K$$

f.e.m. standard

Faraday constant = 96485 C/Mol
(The charge of one electrodes mole)

Cyclic Voltammetry

• The resulting plot of current vs. potential is termed *cyclic voltammogram.*

• The current values are related to the red-ox reactions.

• Randles-Sevcik equation

Ions Concentration

$$I_n = (2.687 \times 10^5)n^{3/2}AD_0^{1/2}Cv^{1/2}$$

Diffusion coefficient   Scan rate

To study the plot of current vs. potential is useful to
understand the red-ox reactions
Diffusion coefficient Scan rate
Ions Concentration

Cyclic Voltammetry

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Ions Concentration

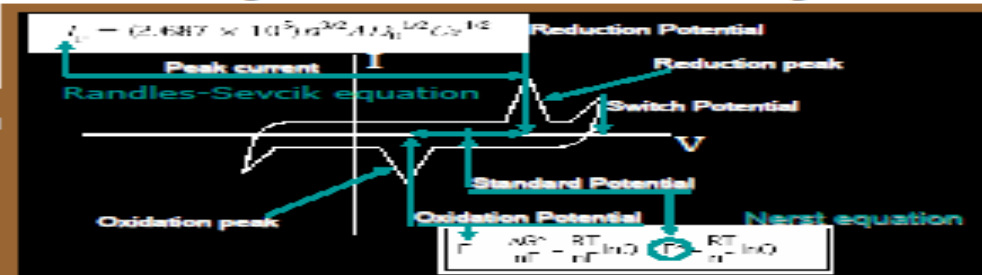$$i_p = (2.687 \times 10^5) n^{3/2} A D_0^{1/2} C_0^{1/2}$$

Diffusion coefficient

Scan rate

To study the plot of current vs. potential is useful to understand the red-ox reactions

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Cyclic Voltammetry

$$i_p = (2.687 \times 10^5) n^{3/2} A D_0^{1/2} C_0^{1/2}$$

Reduction Potential

Peak current

Reduction peak

Randles-Sevcik equation

Switch Potential

Standard Potential

Oxidation peak

**Oxidation Potential**

**Nerst equation**

Impedance Spectroscopy

(Or, how a sinusoidal varying voltage is used
to probe multiple electrical properties of materials)
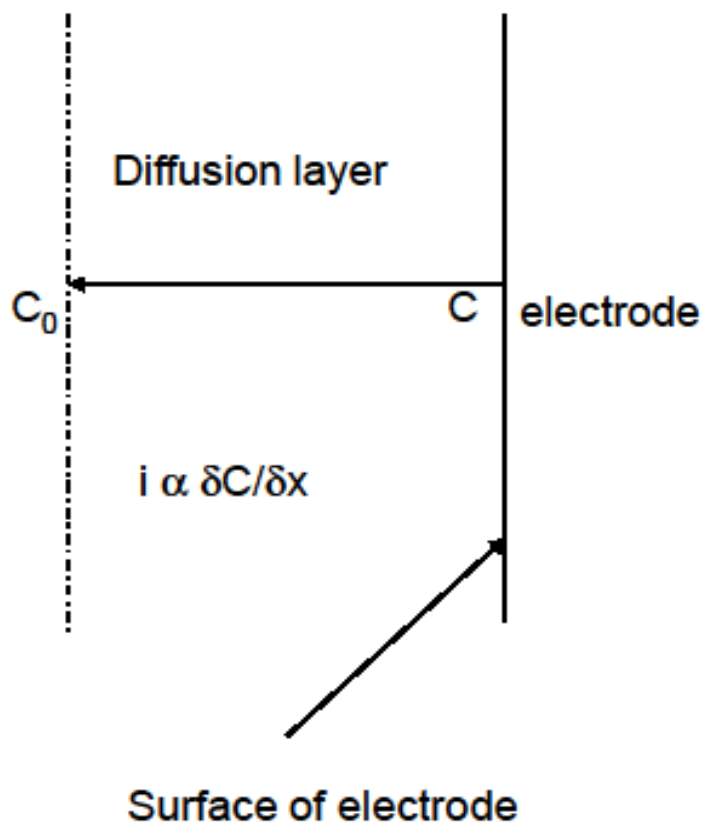
Cyclic Voltammetry

- three electrode system; working, reference and counter electrodes
- Ramp the voltage between the working and reference electrodes at a constant rate from V_1 to V_2 and back to V_1.
- Measure the current between the working and counter electrodes.
- No stirring, diffusion controlled

Cyclic Voltammetry Potential Waveform

$FeIII(CN)_6^{3-} + e- \leftrightarrow FeII(CN)_6^{4-}$
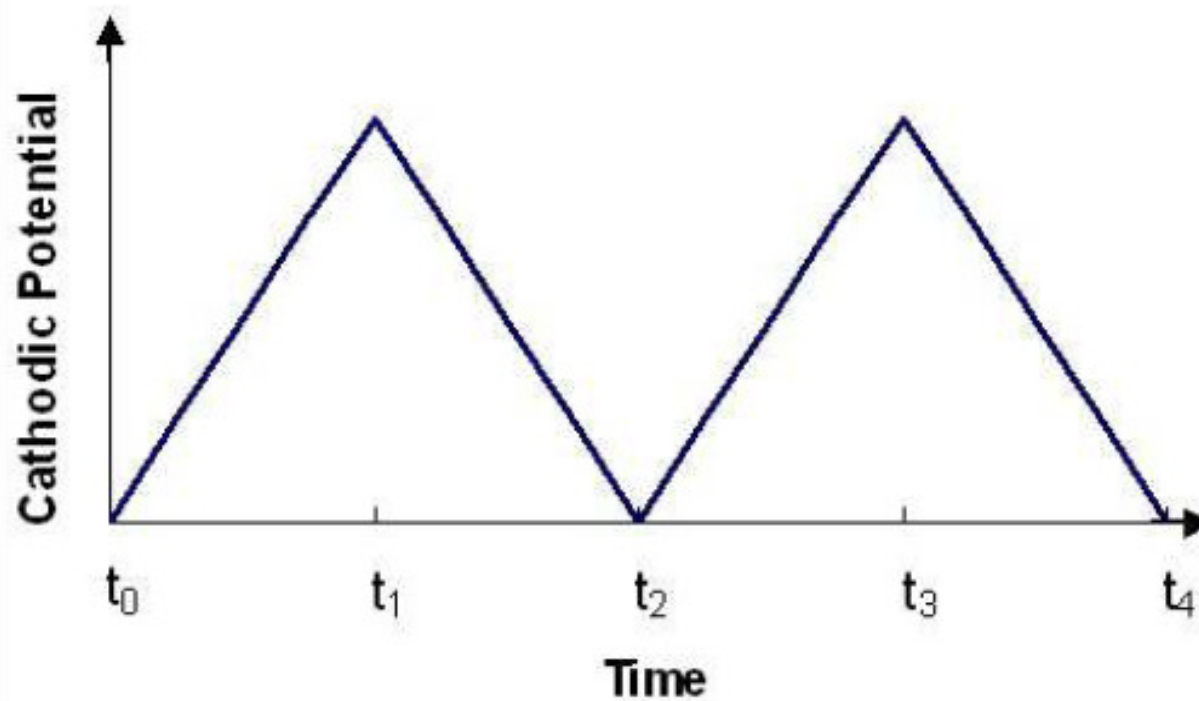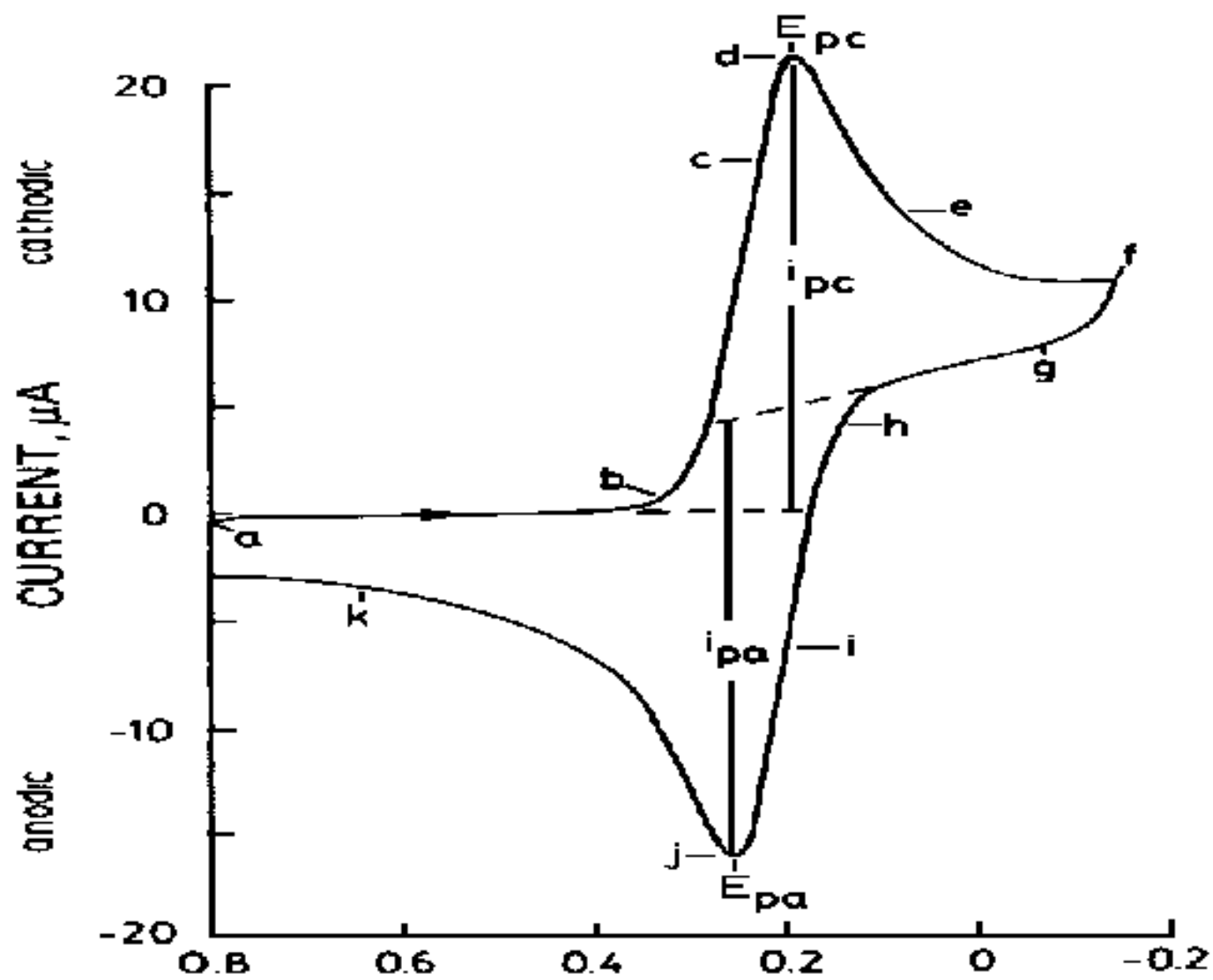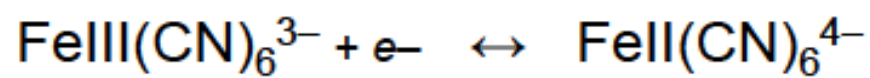
A Close-up view of the CV experiment

Diffusion layer

C_0 C | electrode

$i \; \alpha \; \delta C / \delta x$

Surface of electrode

C is the concentration of
the electrode active species
At the electrode surface

C_0 is the concentration
in the bulk solution.

There is no stirring in CV. So, the
thickness of the diffusion layer
increases as the experiment unfolds
(C will have further to diffuse from the
Bulk).
The shorter the diffusion layer,
the greater the current.
The faster the scan rate,
the shorter the diffusion layer

$$FeIII(CN)_6^{3-} + e- \leftrightarrow FeII(CN)_6^{4-}$$
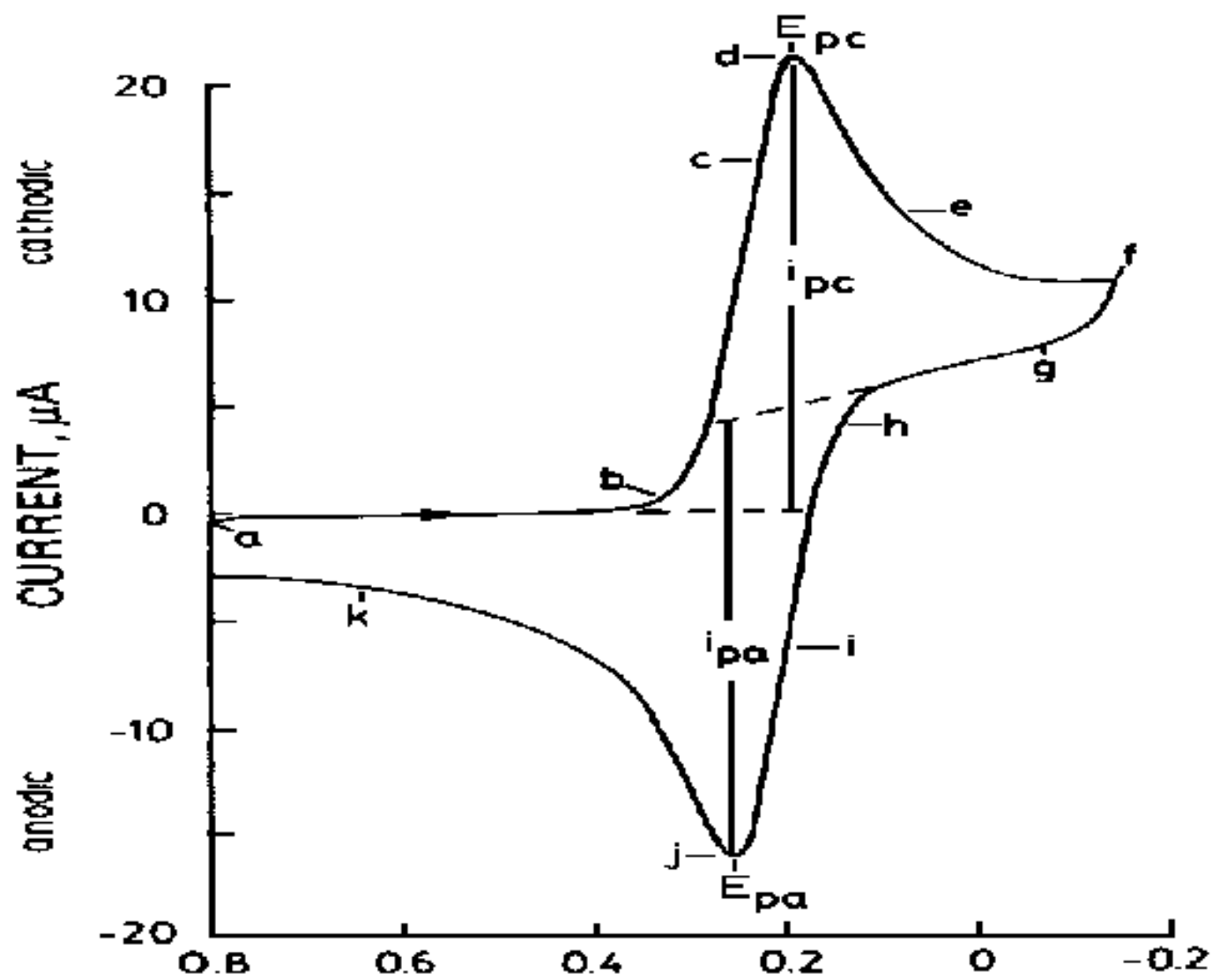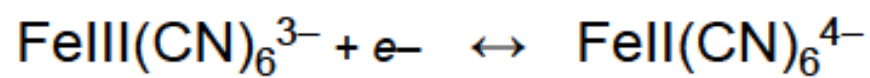
The Working Electrode

The most important electrode in CV is the working electrode. It can be made from a variety of materials including: platinum, gold, silver, glassy carbon, nickel and palladium.

Redox of the analyte takes place here.

The Auxiliary Electrode

**The auxiliary electrode is also known as the counter electrode.
Its purpose is to conduct electricity from the signal source into the solution, maintaining the correct current**

The Reference Electrode

The reference electrode is usually made from silver/silver chloride (Ag/AgCl) or saturated calomel (SCE). This electrode's potential is known and constant.
The potential that is cycled is the potential difference between the working electrode and the reference electrode.
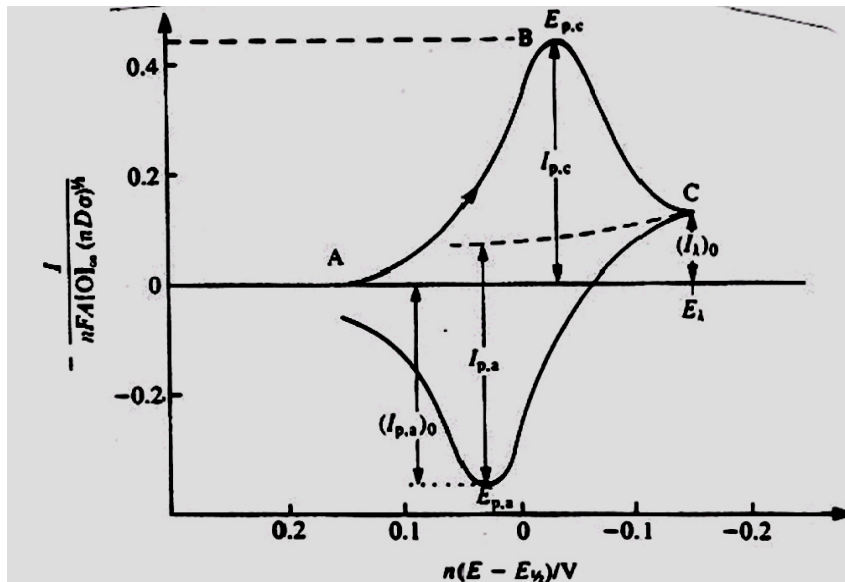
CV

$$E° = (E_{pa} + E_{pc})/2$$

$$|E_{p,c} - E_{p/2,c}| = 2.2RT/nF = 56.6/n \text{ mV}$$

$$|I_{p,a}/I_{p,c}| = (I_{p,a})_0/I_{p,c} + 0.485(I_\lambda)_0/I_{p,c} + 0.086$$

$$\Delta E_p = E_{pa} - E_{pc} = 59mV/n$$
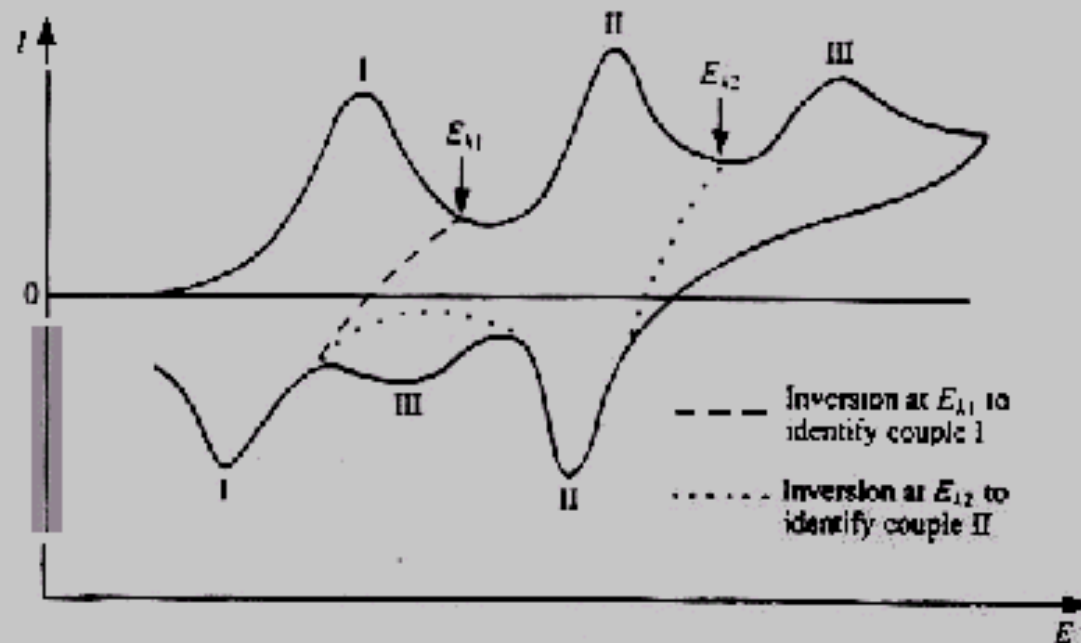
More than one component?

Fig. 9.9. Cyclic voltammetry in the investigation of systems of more than one component, showing the importance of the inversion potential in the identification of the peaks on the inverse scan.

Irreversible

For irreversible processes peaks are reduced in size and widely separated. Totally irreversible systems are characterized by a shift of the peak potential with the scan rate:

$$E_p = E° - (RT/\alpha n_a F)[0.78 - \ln(k°/(D)^{1/2}) + \ln (\alpha n_a Fn/RT)^{1/2}]$$

where α is the transfer coefficient and n_a is the number of electrons involved in the charge-transfer step. Thus, E_p occurs at potentials higher than E°, with the overpotential related to k° and a.
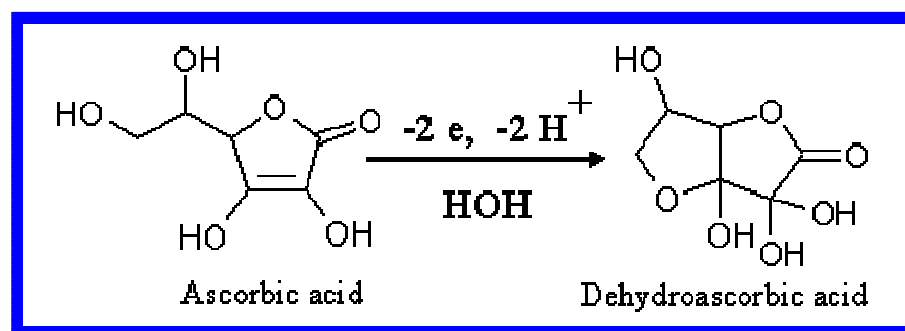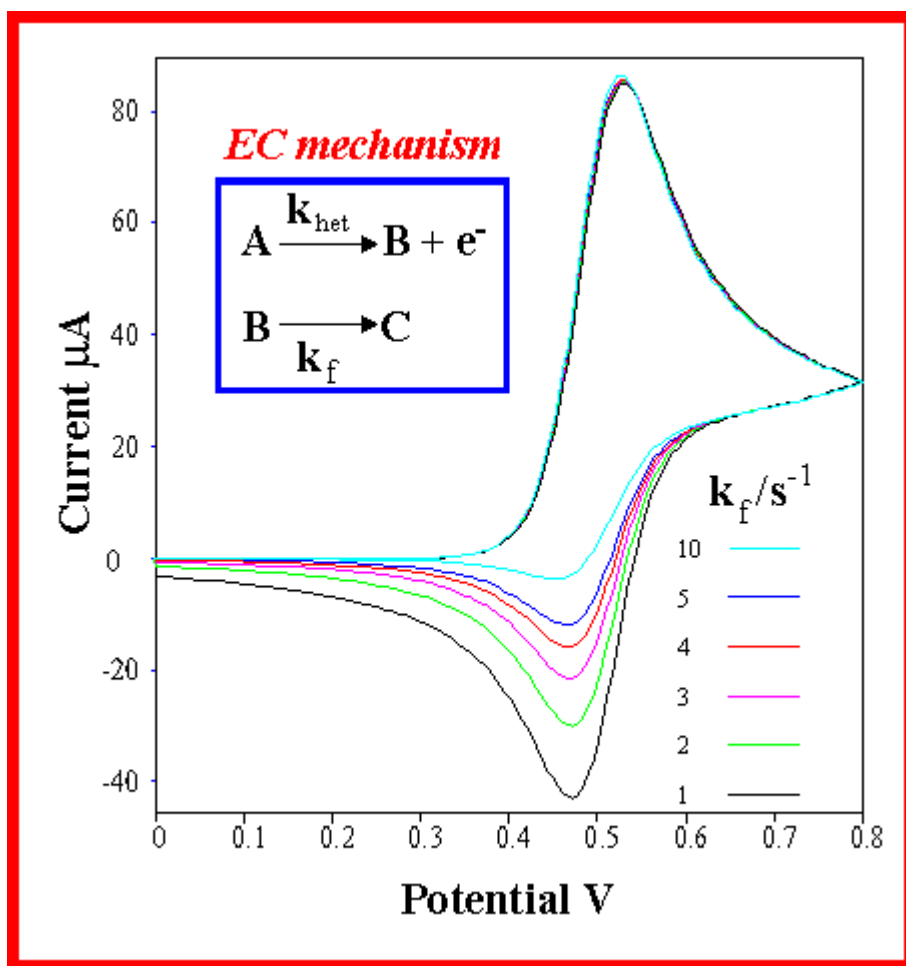
The peak current, given by:

$$\boldsymbol{i}_p = (2.99 \times 10^5)\boldsymbol{n}(\alpha n_a)^{1/2}ACD^{1/2}n^{1/2}$$

is still proportional to the bulk concentration, but will be lower in height (depending upon the value of α). Assuming $\alpha = 0.5$, the ratio of the reversible-to-irreversible current peaks is 1.27
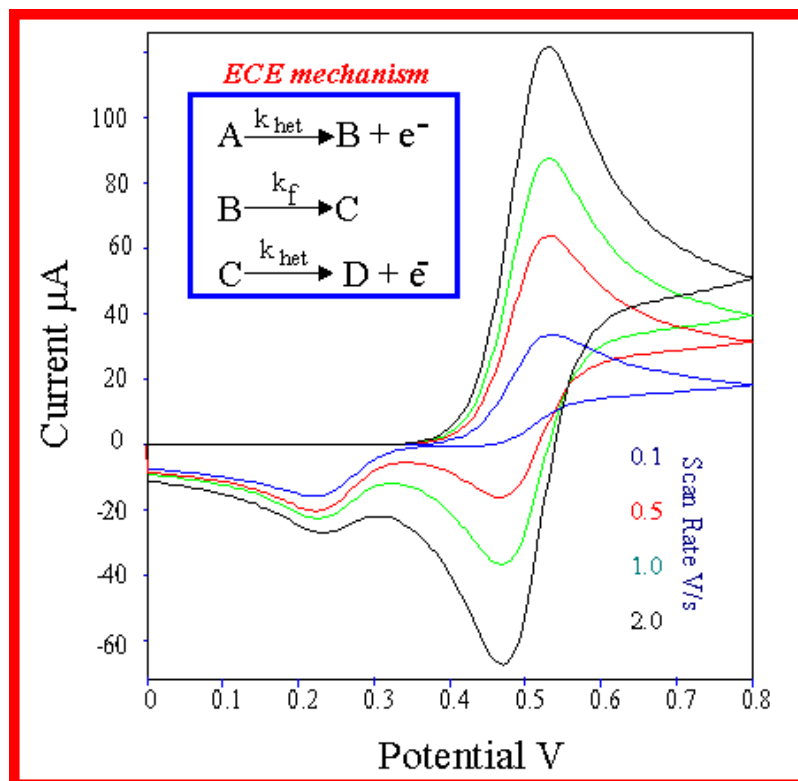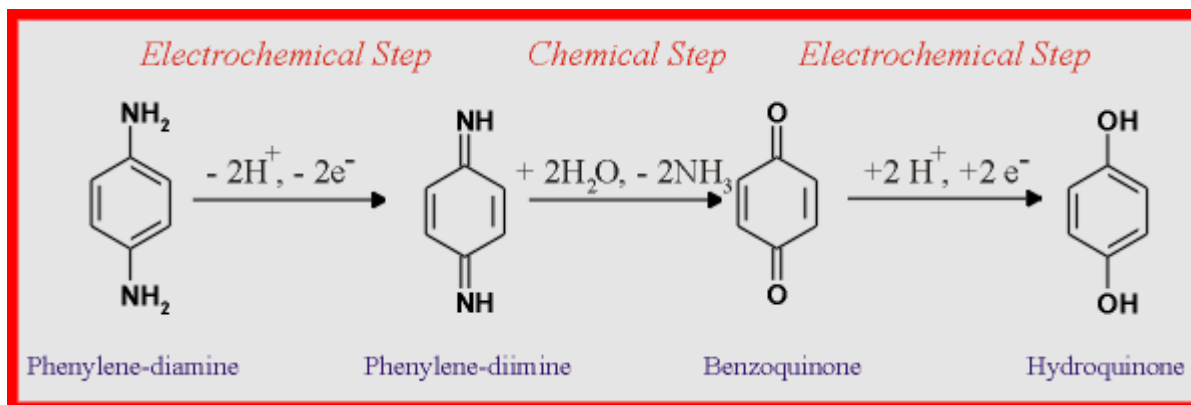
Quasi-reversible

For quasi-reversible systems (with $10^{-1} > k° > 10^{-5}$ cm/s) the current is controlled by both the charge transfer and mass transport. The shape of the cyclic voltammogram is a function of the ratio $k°/(\pi \nu nFD/RT)^{1/2}$. As the ratio increases, the process approaches the reversible case. For small values of it, the system exhibits an irreversible behavior. Overall, the voltammograms of a quasi-reversible system are more drawn out and exhibit a larger separation in peak potentials compared to a reversible system.
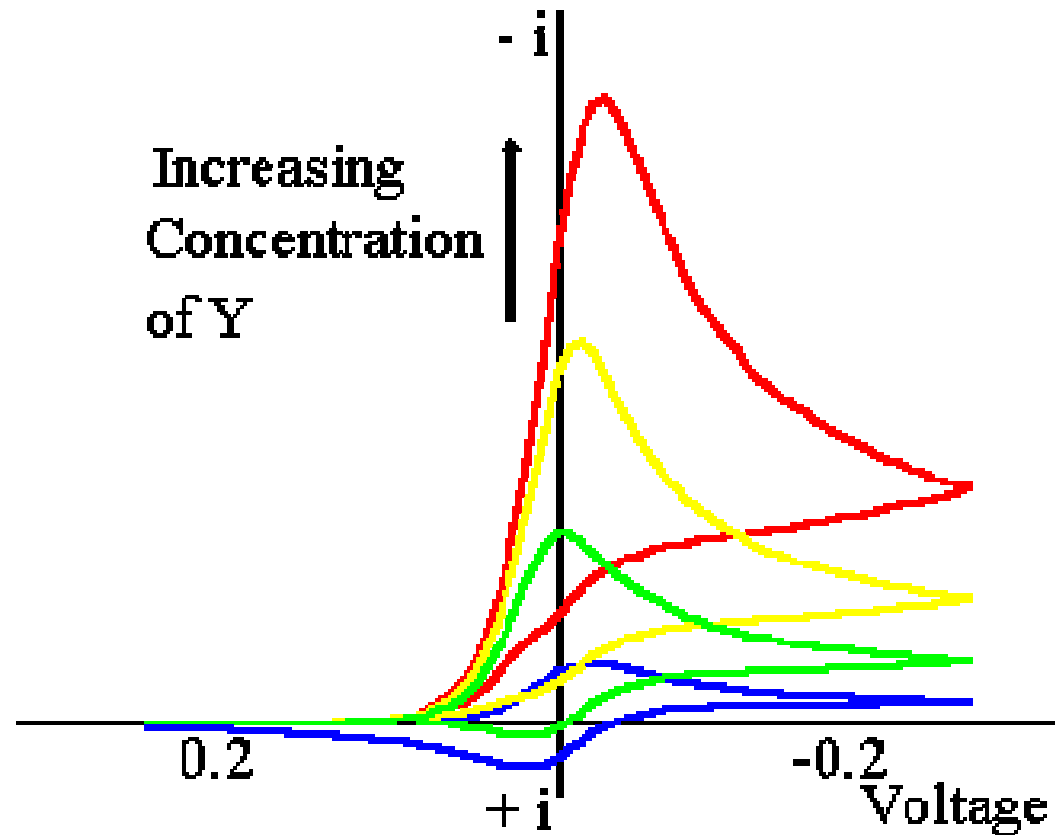
Mechanistic complications part 1: The EC mechanism

The ECE mechanism

Electrochemical Step — Chemical Step — Electrochemical Step

Phenylene-diamine $\xrightarrow{- 2H^+, - 2e^-}$ Phenylene-diimine $\xrightarrow{+ 2H_2O, - 2NH_3}$ Benzoquinone $\xrightarrow{+2 H^+, +2 e^-}$ Hydroquinone

ECE mechanism

$A \xrightarrow{k_{het}} B + e^-$

$B \xrightarrow{k_f} C$

$C \xrightarrow{k_{het}} D + e^-$

Scan Rate V/s
0.1
0.5
1.0
2.0

Catalytic

$$E \quad O \; + \; e \; \rightleftharpoons \; R$$

$$C` \quad R + Y \xrightarrow{k_{EC`}} O \; + \; Products$$

Cottrell equation

$i_p = (2.69 \times 10^5)n^{3/2} A\, D^{1/2}\, C\, v^{1/2}$

where

i_p is the peak current (i_{pa} anodic and i_{pc} cathodic)

n is the electron stoichiometry

A is the electrode area (cm^2)

D is the diffusion current

C is the concentration (mol/cm^3)

v is the scan rate (V/s)

Cottrell equation

$ip = (2.69 \times 10^5)n^{3/2} A D^{1/2} C_0 v^{1/2}$

where

ip is proportional to C_0

Ip is proportional to scan rate
   concentration gradient (dC/dx)
   between surface of electrode and
   bulk

Cottrell equation can be used to find the diffusion coefficient

Applications

- Quantitative
  - C is proportional to concentration of analyte
  - Cottrell equation:

    relates peak current to concentration
- Qualitative
  - Reversibility: $\Delta Ep = E_{pa}-E_{pc} = 59$ mV/n, independent of scan rate

    $E^0 = (E_{pa}+E_{pc})/2$
  - Mechanism: $i = kv^{1/2}$ for pure redox process
  - Kinetics: ΔEp as a function of scan rate
    - Ipa/Iac

Reaction Mechanisms and Kinetics

- EC reaction

  E_1 $A + e- \leftrightarrow B$

  C_1 $B + C \rightarrow D$ k_c
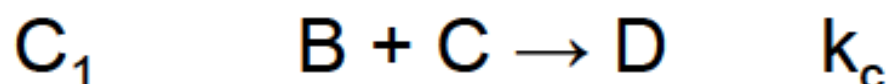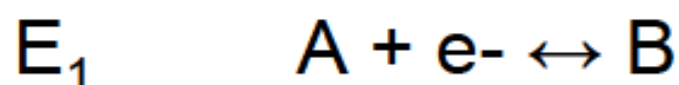
- One can determine k_c by measuring i_{pa}/i_{pc} as a function of scan rate can