ELECTROANALYTICAL TECHNIQUES-3

Lecture 3

By

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Voltammetry

Electrogravimetry

Analyte electrolytically deposited upon electrode

Weighed at electrode

Coulometry:

Analyte determined by quantitative reaction during electrolysis

Potentiometry:

Analyte determined by measuring electrode potential of ions compared to reference

Voltammetry:

Analyte determined by measuring current that is related to conc of analyte by application of potential

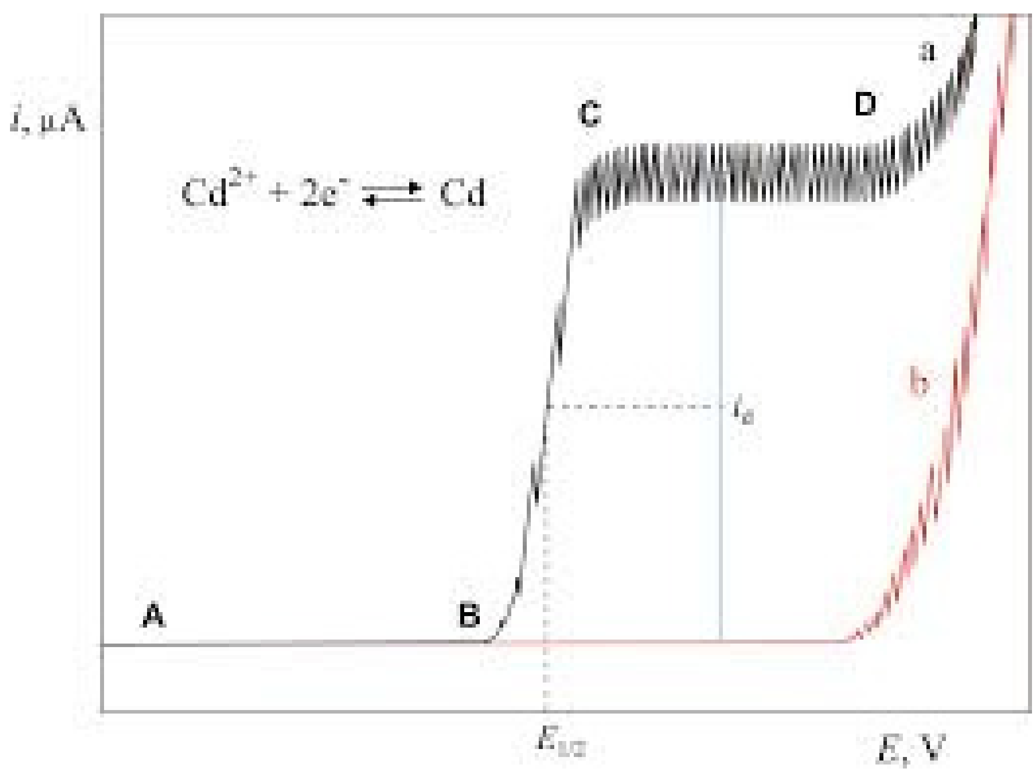
Fundamentals of Voltammetry

- Study of Voltage-current relationship during electrolysis
- Determination of substances that can be red/ox at working electrode
- Conditions of variable applied potential, current monitored
- The voltage – current graph is called voltagram
- **Polarography: Sub class of Volatammetry where working electrode is dropping mercury**

Introduction to Polarography

- Working electrode completely polarized so that current prop to conc
  - For this to happen
    - Small surface area of working electrode
    - Prevent surface contamination
- Elegant solution by Czech scientists (Heyrovsky & Shikata)
  - Apparatus that provided continuously replaceable mercury drop as working electrode
  - Voltage-current graphs called polarograms, instrument : polarograph

Theoretical Principles in Polarography

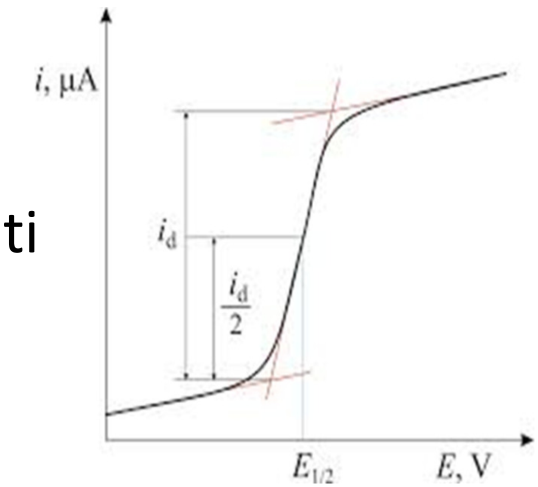


Theoretical Principles in Polarography

- Limiting current due to limiting ions reaching electrode
- Three main components to limiting current
- $i_{limit} = i_d + i_c + i_m$
- Migration current (i_m)
  - Ions move to reduce potential
  - Need to suppress, leads to erratic results for low conc analyte
  - Add supporting electrolyte (conduct current, does not get reduced, no contributions to limiting current)
  - Ex 1M HCL (typically in high conc compared to analyte)

Theoretical Principles in Polarography

- $i_{limit} = i_d + i_c + i_m$
- <u>Convection current (i_c)</u>
  - Current due to artificial movement of ions
  - Traditional polarography conducted in unstirred soluti
- <u>Diffusion current (i_d)</u>
  - Current due to normal diffusion of ions
  - Rate of diffusion of ion $dc/dt = D. d^2c/dx^2$
  - As convection & migration current negligible, limiting current is mostly due to diffusion current

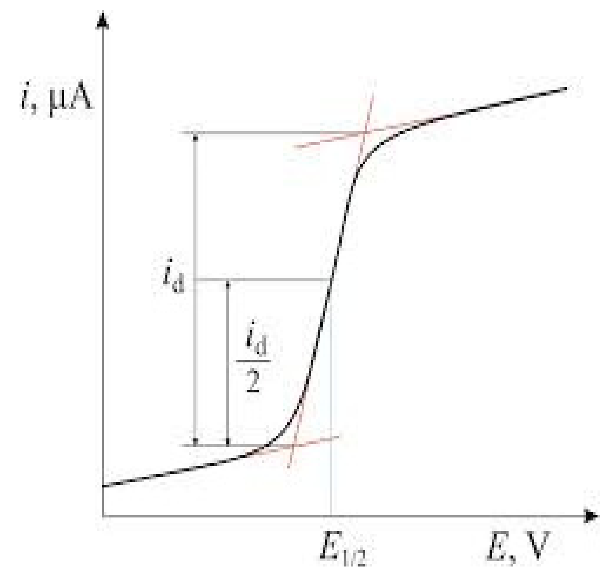


Theoretical Principles in Polarography

- Diffusion current (i_d)
  - i_d is directly prop to conc of ions in sol
  - Ilkovich examined all factors that governed diffusion current
  -
  - $i_d = 607nD^{1/2}Cm^{2/3}t^{1/6}$
- Where
  - n = num of faradays of electricity required/mole of analyte
  - D = diffusion coefficient
  - C = conc of analyte
  - m = mass of mercury drop/sec
  - t = dropping time (sec)
  - For more accurate calculations a correction factor of 1.05-1.15 is applied

Theoretical Principles in Polarography

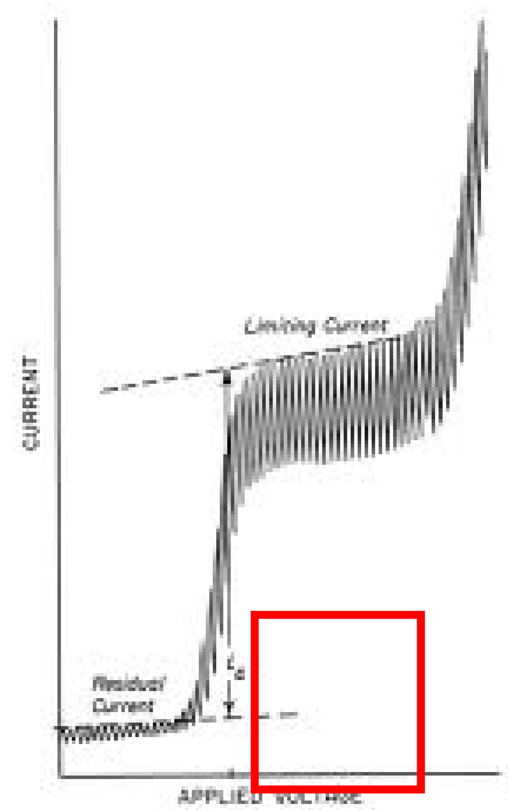
- <u>Half-wave potential ($E_{1/2}$)</u>
  - Half-wave potential ($E_{1/2}$) is a potential at which polarographic wave current is equal to one half of diffusion current
  - Potential at polarized electrode obeys Nernst equation and conc of electrolytic species is directly related to diffusion current:
  - $E = E_{1/2} + RT/nF \ln (I_d\text{-}I/I)$
  - $E = E_{1/2} + 0.0591/n \ln (I_d\text{-}I/I)$
  - When $I = I_d/2$, $E = E_{1/2}$



Theoretical Principles in Polarography

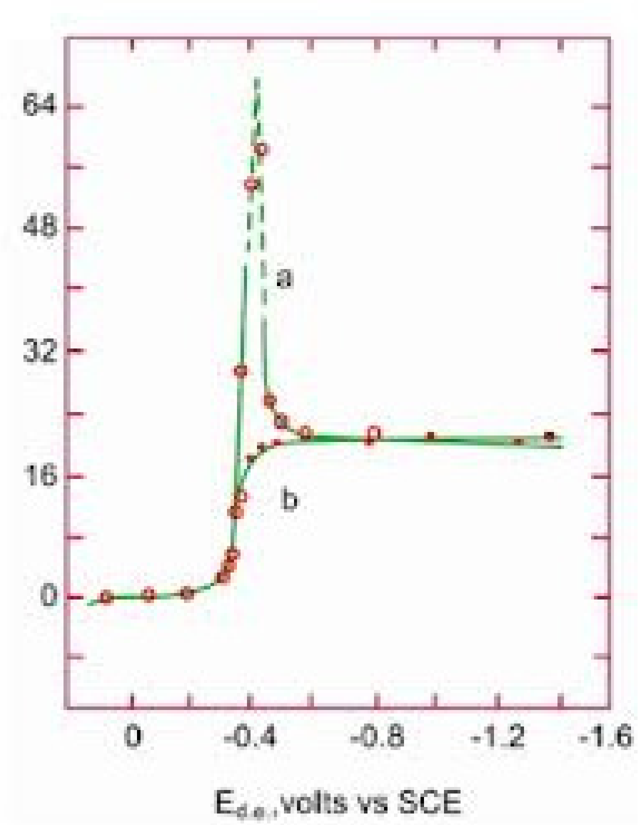
- <u>Residual current (i_d)</u>

- Solutions of ONLY supporting electrolyte also display small current at voltage above -0.4V
- Negative charge surround electrode leading to non-faradaic current
- Increases linearly with applied potential & also on size of mercury drop
- Net current = Faradaic + Non-faradaic
- At low conc, Non-faradaic predominates, limits how low we can go (10^{-5}M)

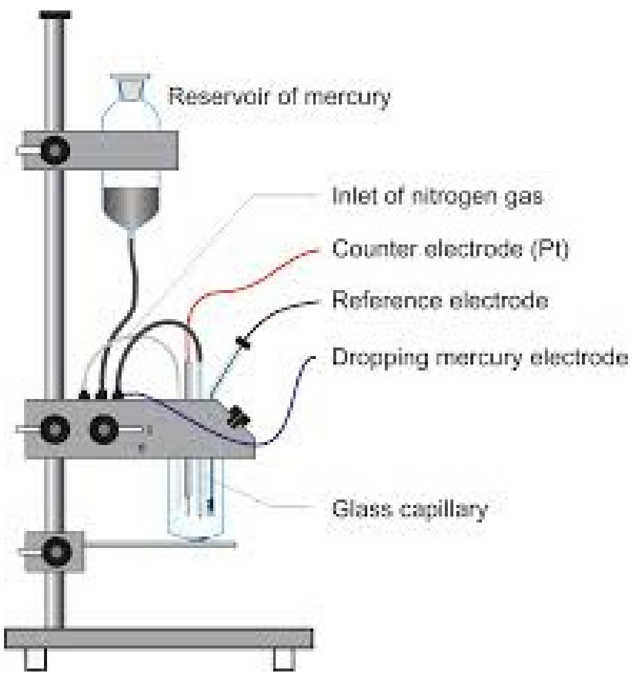


Theoretical Principles in Polarography

- <u>Polarographic Maxima</u>
  - Occasionally hump/peak seen
  - Reasons not clearly known
  - To measure true diffusion current, this hump/peak must be suppressed
  - Add colloids (gelatin, dyestuff) or detergent (Triton X-100)
  - Adsorb at interface, form layer, prevent migration of ions



Construction of Polarographic apparatus



Advantages/Disadvantages of DME

- **Advantages:**
- Fresh, reproducible drop at regular intervals, limits contamination
- Many metals reversibly reduced to amalgams at the surface
- Hydrogen has high overvoltage, allows reduction of many metals without interference
- Surface area can be calculated from weight of drop
- **Disadvantages:**
- Size of mercury drop changes with & this complicates electrochemistry