

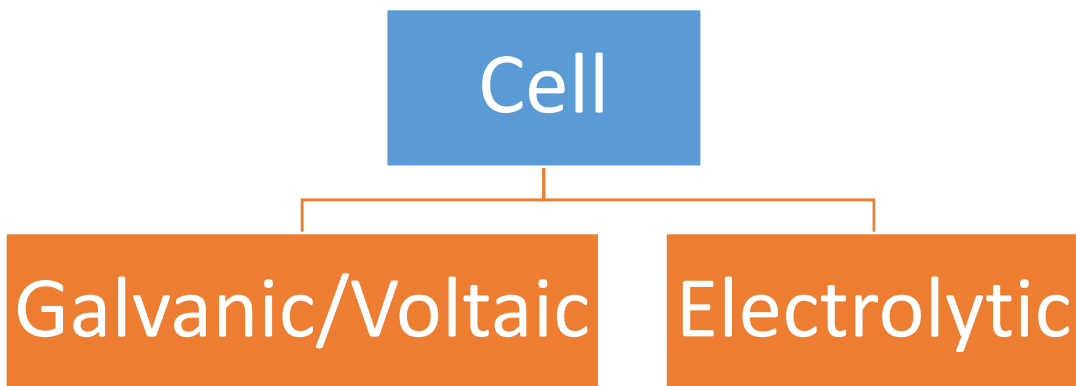
ELECTROANALYTICAL TECHNIQUES-2

Lecture 2

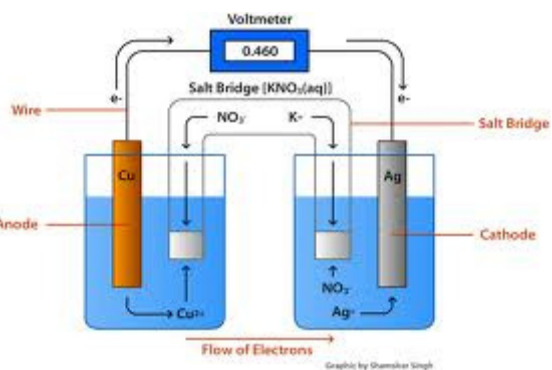
By

Dr. Shariq Syed

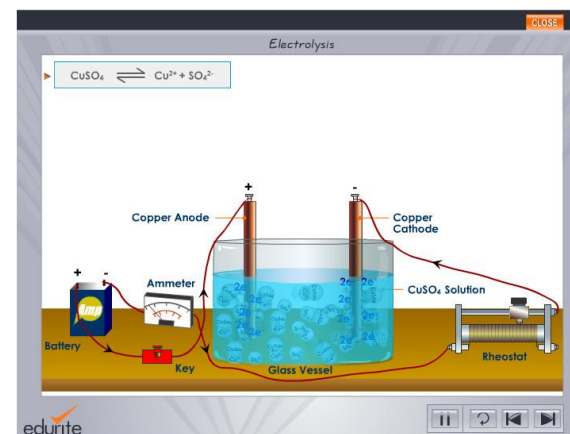
Let's Review Cell basics



- Converts Chemical to Electrical energy



- When energy is supplied from external source



Shariq
AIKC/SYB/2014

Introduction to Electro-gravimetry

Similar to gravimetry

Analyte deposited on electrode via electrolytic reaction

Occurs due to application of applied potential

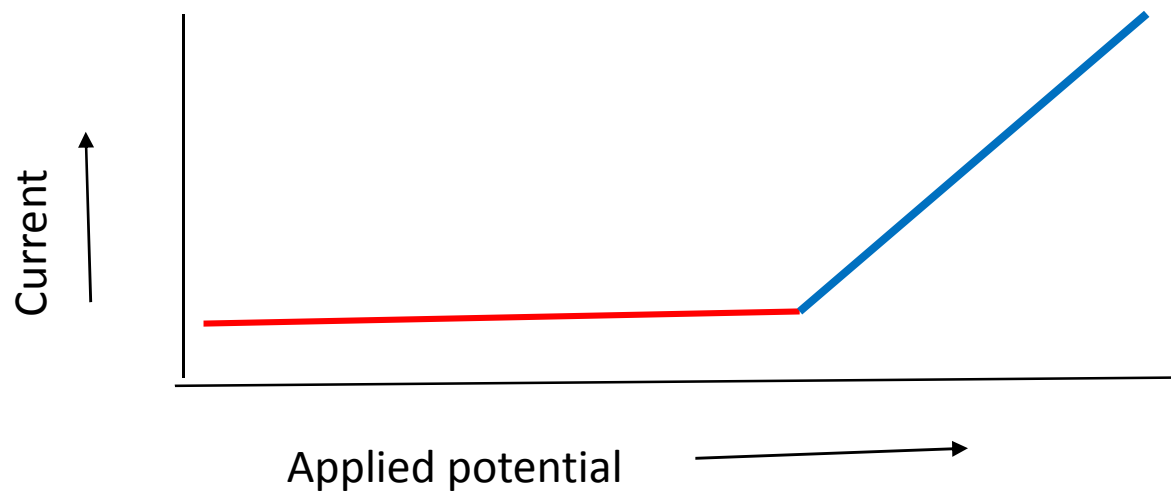
Hence ELECTRO- gravimetry

Electro-gravimetry Theory

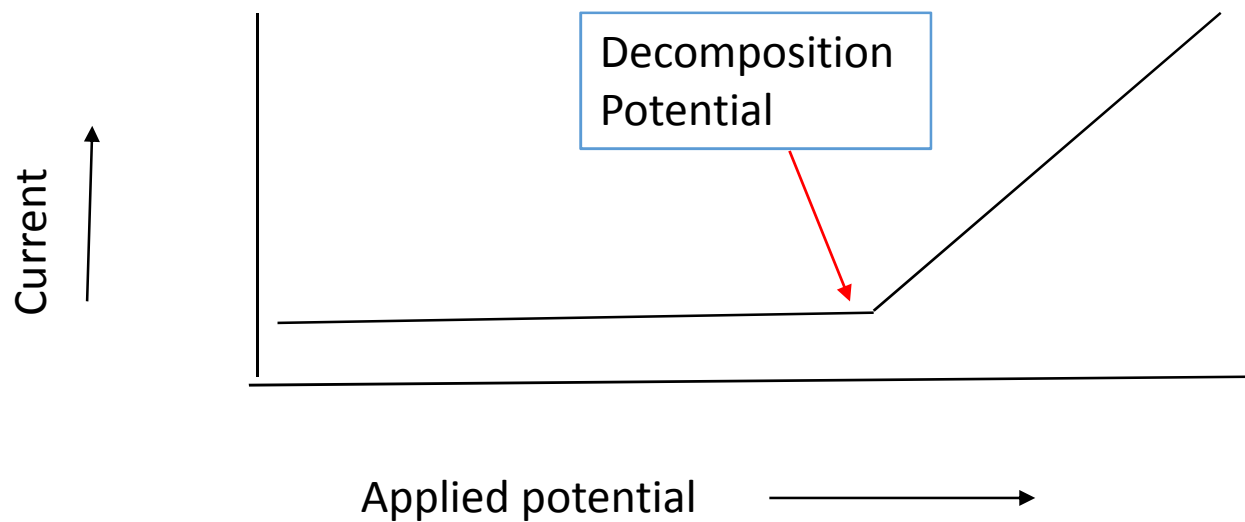
Consider a simple case

Two or more Pt electrodes in dilute CuSO_4 soln

Source of potential applied



Electro-gravimetry Theory



Decomposition Potential : Applied voltage which is just sufficient to overcome back emf and also brings about electrolysis of electrolyte without any hindrance

Electro-gravimetry Theory

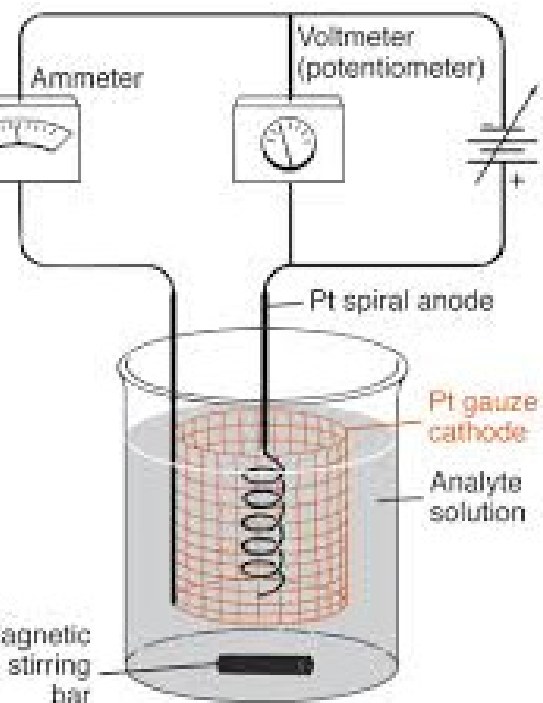
Decomposition Potential $E_d = E_s + E_b + E_v$

System or resistance Potential E_s = Potential required to overcome resistance of the system (Ohm's Law $E = I \cdot R$)

Back Potential E_b = Potential that would be produced if the cell was behaving as a galvanic cell; $E_b = E_{\text{anode}} - E_{\text{cathode}}$

Over Voltage E_v = Additional voltage in addition to $E_s + E_b$ to reach decomposition potential

Electro-gravimetry Apparatus



Electrodes:

- Generally made of Platinum (offers several benefits), but some metals cause damage

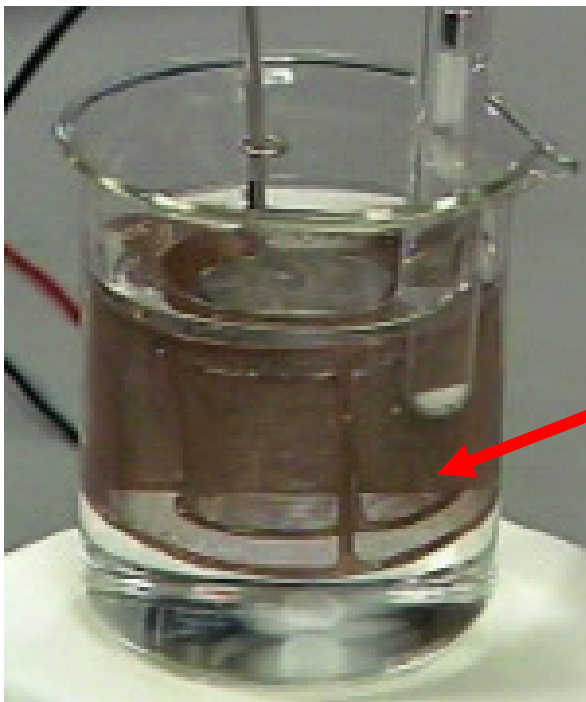
Cathode :

- Shape of gauze cylinders (2-3 cm diam, 6 cm length)
- Gauze prevents polarization due to rapid mixing

Anode :

- Can shape of gauze cylinders , but need to fit in cathode
- In small cells- shape of heavy wire or paddle

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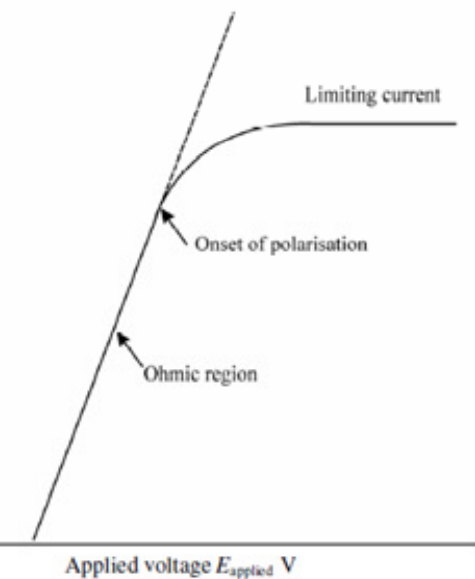
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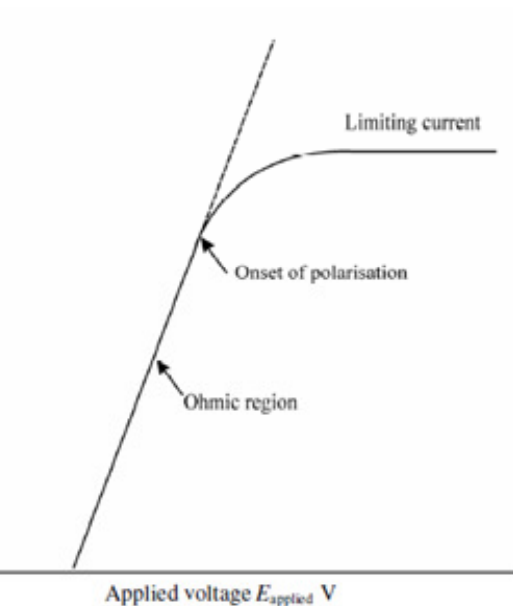
Polarisation Concepts

- Divided in 2 kinds
- Concentration Polarisation:



- Ions get discharged, deposited on electrode
- Conc gradient created if ions do not rapidly migrate towards cathode
- This gradient leads to resistance
- This resistance due to changes in concentration of the electrolyte around the electrode is known as concentration polarisation.
- occurs when the ions do not arrive at the cathode or the product species do not leave the anode fast enough to maintain the desired current
- vigorous stirring and heating are important in electrodeposition to minimize the concentration polarisation

Polarisation Concepts



- Kinetic or chemical Polarisation:
 - Polarisation cause due to electro-deposition of another metal or because of the coating of the electrode along with a layer of gas like as hydrogen or oxygen
 - Pronounced in electrode processes that yield gaseous products

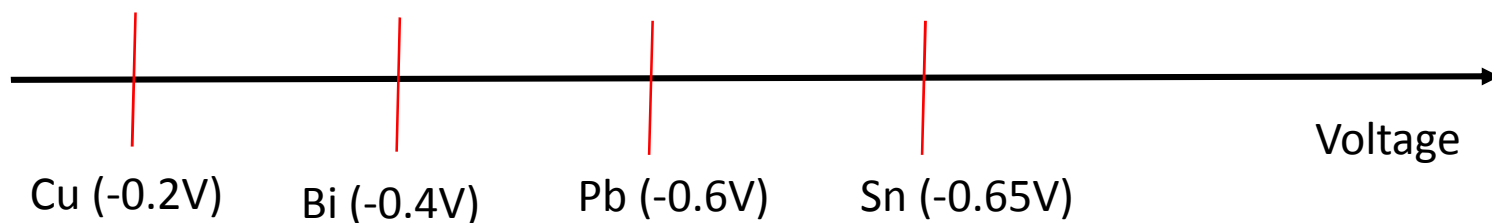
Applications of Electro-gravimetry

Constant Current Method:

- Crude method, lacks specificity, applied voltage is not controlled
- Used in situations where only single analyte
- If mixture then some pre-workup needed
- Useful in cases of easily reduced ions

Controlled Electrode potential Method:

- Analysis of mixture can be done
- By selectively controlling the potential



Analyte
mixture of
Cu, Bi, Pb,
Sn)