Voltammetry and Polarography

- Electrochemistry techniques based on current ($i$) measurement as function of voltage ($E_{app}$)
- Voltammetry—Usually when the working electrode is solid, e.g., Pt, Au, GC.
- Polarograph—A special term used for the voltammetry carried out with a (liquid) MERCURY electrode.
- Voltammogram—The plot of the electrode current as a function of potential.

“Polarographic curves”-- Voltammograms

Typical polarographic curves (dependence of current $I$ on the voltage $E$ applied to the electrodes; lower curve - the supporting solution of ammonium chloride and hydroxide containing small amounts of cadmium, zinc and manganese, upper curve - the same after addition of small amount of thallium.
Electrochemical Cell

- **Working electrode**: place where redox occurs, surface area few mm² to limit current flow.
- **Reference electrode**: constant potential reference
- **Counter (Auxiliary) electrode**: inert material, plays no part in redox but completes circuit
- **Supporting electrolyte**: alkali metal salt does not react with electrodes but can reduce the effect of migration and lower the resistance of the solution.

2-Electrode vs. 3-Electrode Cell

- 2-electrode cell is OK in potentiometry—very small i
- Now in voltammetry, measuring (big) i vs. applied E, but
  1. Potential drops when current is taken from electrode due to solution resistance (IR drop): The actual \( E_{WE} \) is smaller than \( E_{Appl} \) (vs \( E_{Ref. E} \))
  2. Large i passes the ref. electrode → instability of the reference potential (not constant)

\[
E_{Appl} = E_{WE} + iR + E_{Ref.E} \\
E_{Appl} - E_{Ref.E} = E_{WE} + iR \\
\text{or } E_{Appl} \text{(vs } E_{Ref.E}) = E_{WE} + iR \\
E_{WE} = E_{Appl} \text{(vs } E_{Ref.E}) - iR
\]

Advantages of 3-over 2-electrode Cell System

Remember: In 3-electrode cell system, electrochemical cell current passes between WE and Counter electrode

3-electrode system
1. Provides great flexibility in location of the reference and the working electrodes and minimizes the effect of solution IR drop.
2. Virtually has no current passing through the reference electrode.
### Potentiostat

- **Voltage (E)** source that drives the cell
- Supplies whatever $E$ needed between WE and CE to maintain specific $E$ between WE and Ref. electrode
- Very high impedance (so that $i$ passes through the ref. electrode is minimized)

### Working Electrodes

- Mercury electrodes (liquid)—dropping mercury electrode, hanging mercury drop electrode…
- Solid electrodes: mm in diameters, Pt, Au, GC.
- Micro(Ultramicro) electrodes: $\mu$m in diameter: Pt, Au, carbon fiber.
- Solid/liquid electrode: Mercury film electrodes, carbon paste electrode.
- Chemically modified electrodes
- ITO electrode (Transparent glass coated with In-SnO$_2$)
- Screen printing electrodes
Electrode material vs. Potential Window

Potential window varies with material/solution due to \textit{overpotentials}.

Potential Excitations vs Voltammogram at a Solid Electrode

- Linear Sweep/San Voltammetry (LSV)
- Cyclic Voltammetry (CV)
- Potential Step Voltammetry
- Differential Pulse Voltammetry (DPV)
Mass Transfer/Transport

Three Transport Modes: migration, diffusion and convection

- Migration: occurs in response to a gradient of electrical potential or concentration pressure.
- Diffusion: occurs in response to a concentration gradient.
- Convection: occurs due to a pressure gradient.

Linear Diffusion to a Planar Electrode

At \( x = 0 \) (electrode surface) heterogeneous electron transfer rate constant \( k^o \) (cm/s)

Electrode Reaction: \( A + e^+ \rightleftharpoons A^+ \) (Reversible)

\[ E = E^o + \frac{RT}{nF} \ln \left( \frac{[A]_{x=0}}{[A^+]_{x=\infty}} \right) \]

In solution: \( A_{x=0} \rightarrow A_{x=\infty} \) by diffusion

Square Wave Voltammetry (SWV)
Potential Step at a Planar Electrode

Cottrell Equation

\[ i_t = \frac{nFA}{\sqrt{\pi D_0 t}} = \frac{nFAD_0^{1/2} C_o^{*}}{\pi^{1/2} t^{1/2}} \]

\( A \): Area of electrode
\( D_0 \): Diffusion Coefficient
\( C_o^{*} \): Bulk concentration

Linear Sweep/Scan Voltammetry

For \( A + e = A^- \) reversible reaction, \( E(A/A^-) = E^0 \)

1. \( E \gg E^0 \), \( i \approx 0 \)
2. \( E = E^0 + \delta E, i \gg 0 \), increases
3. \( E = E^0, i \gg 0, [A] = [A^-] = [A^{*}] = 1/2 \)
4. \( E = E^0 - 28.5 \text{ mV}, i \rightarrow \text{maximum, } [A^{*}] = 0.25[A] \)
5. \( E < E^0, i \gg 0 \), decreases, as the depletion effect

\[ \text{At } 25 \text{ C, } (2.69 \times 10^6)n^{1/2}D_0^{1/2}v^{1/2} \text{ at } 25 \text{ C. (v: scan rate)} \]

DigiSim simulations
Cyclic Voltammetry (CV)

e.g.: Fe$^{II}(CN)_{6}^{3-} + e \rightleftharpoons Fe^{III}(CN)_{6}^{4-}$

Fc$^{-} + e \rightleftharpoons$ Fc (Fc: ferrocene)

DigiSim simulations

Cyclic Voltammograms for a Reversible Reaction

- $I_{pc}/I_{pa} \approx 1.0$
- $\Delta(E_{pa} - E_{pc}) = 2(1.109 \frac{RT}{nF})$
  $= 57$ mV/n at 25°C
  (independent of the scan rate)
- $E^{o} = (E_{pa} + E_{pc}) / 2$
- $i_{p} = \text{constant} \times n^{3/2}AD_{o}^{1/2}c_{o}^{1/2}$
  (at 25°C, constant $= 2.69 \times 10^{5}$)

Diffusion Controlled Reversible Process
Hydrodynamic Voltammetry

- Voltammetry in which analyte solution is kept in continuous motion.
- Two ways: Stirring the solution, and rotating the electrode.

Flow patterns and regions of interest near the working electrode in hydrodynamic voltammetry

Disk (a) and ring (b) $i$ for reduction of $O_2$ at a RRDE. Studies of reaction mechanisms (intermediates).
**Chapter 23 Summary**

- Voltammetry, polarography, voltammogram
- Potentiosat, electrochemical cell, 2 vs 3-electrode, types of working electrodes
- Voltammetric signals: excitation vs response
- Processes at the surfaces of working electrodes, mass transfer/transport
- Pulse/linear/cyclic/stripping/hydrodynamic voltammetry

**Important Equations**

- At electrode: $A + e \rightleftharpoons A^*$ (Reversible)
  \[
  E = E^o + \frac{RT}{nF} \ln \frac{[A]}{[A^*]}
  \]

- For potential step: Cottrell Equation
  \[
  i = \frac{nFA_Dc^o}{4\pi D_i \tau} \frac{nFAD_i^2 c^o}{\pi^{3/2}}
  \]

- For linear/cyclic voltammetry:
  \[
  i_p = (2.69 \times 10^5) n^{3/2} A c^o D_i^{1/2} \tau^{1/2} \text{ at } 25^\circ C
  \]
  \[
  \frac{i_p}{i_p} = 1.0, \Delta(E_m^o - E_m) = 57 \text{ mV/n at } 25^\circ C
  \]
  \[
  E'' = (E_m + E_m^o) / 2
  \]