Chapter 25. Voltammetry

- Excitation Signal in Voltammetry
- Voltammetric Instrumentation
- Hydrodynamic Voltammetry
- Cyclic Voltammetry
- Pulse Voltammetry
- High-Frequency and High-Speed Voltammetry
- Application of Voltammetry
- Stripping Methods
- Voltammetry with Microelectrodes

Voltammetry

- Voltammetry: measurement of current (I) as a function of applied potential (E). Under condition with polarization (η). Negligible consumption of analyte
  - Amperometry: measure I at a fixed E
  - Potentiometry: measure E when I → 0, no polarization
  - Coulometry: measure C, polarization is compensated, all analyte is consumed
- Polarography: voltammetry at the dropping mercury electrode (DME)
  - DA: Hg (poison), apparatus (cumbersome), better techniques
- Application:
  - Oxidation and reduction process
  - Adsorption processes on surfaces
  - Electron transfer mechanism

Jaroslav Heyrovsky
1890-1967
Excitation Signals and Instrumentation

- **WE:** E (relative to RE); **RE:** constant E; **CE:** Pt wire (current)
- Supporting electrolyte: a salt added in excess to the analyte solution, like alkali metal salt
  - No reaction at the E region
  - Reduce effect of migration
  - Lower R of the solution

Supporting electrolyte

A salt added in excess to the analyte solution, like alkali metal salt—No reaction at the E region—Reduce effect of migration—Lower R of the solution

Voltammetric Working Electrode

- **Disk electrode:** A small flat disk in a rod of an inert material like Teflon, glass or Kel-F.
- **HMDE:** Hanging mercury drop electrode
  - Large negative E, fresh metallic surface, reversible reaction
- **UME:** Microelectrode, r: < 25 µm, wire in glass, tip polished
- **Flow cell WE:** in flowing stream, PEEK (polyetheretherketone)
- **E_{min}**: reduction of water (H₂), **E_{max}**: oxidation of water (O₂)
Modified Electrode

- **Chemical modification:**
  - Irreversibly adsorbing substances:
    - Oxidation of electrode (metal or C) surface (O- or –OH)
    - Electrodeposition
  - Covalent bonding of components:
    - Like SAM of thiols with amine or carboxyl group on the other end
    - Organosilanes or amines
  - Coating of polymer films
    - Dip coating, spin coating

- **Application:**
  - Electrocatalysis
  - Smart window: electrode changes color upon reaction
  - Analytical sensor

Circuit Model of a Working Electrode

A. Randles circuit:
   - \( R_\Omega \), solution resistance
   - \( C_d \), double layer capacity
   - \( Z_f \), faradaic impedance \( \rightarrow f \) dependence

B. Faradaic impedance:
   - \( R_s \), electron transfer resistance
   - \( C_s \), pseudocapacitance, mass transfer

C. Faradaic impedance:
   - \( R_{ct} \), charge transfer resistance
   - \( Z_w \), Warburg impedance
Concentration Profile in Unstirred Solution

- Reaction: \( A + e^- \rightarrow P \) reversible and rapid
- Mass transfer: 1. Migration: electric field; Supporting electrolyte (100×) 2. Diffusion: concentration gradient 3. Convection: mechanical
- Potential vs. surface concentration:
  \[
  E_{\text{app}} = E_A^0 - \frac{0.0592}{n} \log \frac{c_P}{c_A^0} - E_{\text{ref}}
  \]
- Current:
  \[
  i = nFAD \frac{\partial c_A}{\partial x}
  \]
  where:
  - \( n \): #electron
  - \( F \): Faraday constant
  - \( A \): surface area, cm\(^2\)
  - \( D \): diffusion coefficient, cm\(^2\)/s

Hydrodynamic Voltammetry

- the analyte solution is kept in continuous motion
  - stir the solution,
  - flow solution, like in HPLC

Flow pattern in a flow stream

- Laminar flow region
- Turbulent flow region (bulk solution)
- Convection

Flow pattern near an electrode

- Nonsoluble layer
- Convective
- Diffusion
**Voltammograms**

- Voltammetric wave: an \( \int \)-shaped wave of I-E
- Limiting current, \( i_l \): the current plateau observed at the top, \( \propto c_A \)
  - \( c_A = 0 \) at electrode surface
  - maximum mass transfer rate
- Current in American way:
  - Reduction current +
  - Oxidation current -
- Half-wave potential:
  - \( E_{1/2} \) at \( i = i_l/2 \), \( \neq E^0 \)
  - Relative to \( E^0 \)
  - Identification

**Linear-sweep voltammogram at slow scan rate**

**Volumetric Currents**

- A planar electrode: Nernst diffusion layer \( \delta \) control

\[
A + ne \rightarrow P \quad i = nFAD_A \frac{\partial c_A}{\partial x} = \frac{nFAD_A}{\delta} (c_A - c_A^0) = \frac{nFAD_A}{\delta} c_A = k_A c_A^0
\]

- Limiting current: \( c_A^0 \) at the electrode surface = 0.

\[
i_l = \frac{nFAD_A}{\delta} c_A = k_A c_A^0
\]

- Reverse current: \( c_P \) in the bulk solution = 0.

\[
i = \frac{nFAD_P}{\delta} (c_P - c_P^0) = \frac{nFAD_P}{\delta} c_P^0 = k_P c_P^0
\]

- Half-wave potential, \( E_{1/2} \): \( i = i_l/2 \)

\[
E_{\text{appl}} = E_A^0 - 0.0592 \frac{n}{k_A} \log \frac{k_A}{k_P} - 0.0592 \frac{n}{k_l} \log \left( \frac{i}{i_l} - 1 \right) - E_{\text{ref}}
\]

\[
E_{1/2} = E_A^0 - 0.0592 \frac{n}{k_A} \log \frac{k_A}{k_P} - E_{\text{ref}} = E_A^0 - E_{\text{ref}}
\]
Voltammetric I-E

- Based on the kinetics of the reaction:
  - Reversible systems: obey Nernst equation
  - Totally irreversible system: either the cathodic or anodic reaction is too slow to be negligible
  - Partially reversible system: the reaction in one direction is much slower than the other one.
  - Like organic system, \( i = kc, E = f(v, c, il) \)
- Voltammogram for mixture:
  - \( \Delta E \geq 0.1 \text{ V} \)
- Anodic/Cathodic Voltammogram:
  - A: oxidation current –
  - B: both reaction
  - C: reduction current +

Oxygen Wave and Sensors

- Oxygen wave:
  - \( I \) is proportional to \( n \)
  - Sparging: deaerate the solution with inert gas, \( N_2, Ne \) and \( He \)
  - Highly depends on the pH of the solution
- Clark electrode: volumetric sensor
  - Cathodic Pt electrode: \( O_2 + 4H^+ + 4e^- \leftrightarrow 2H_2O \)
  - Anodic Ag electrode: \( Ag + Cl^- \leftrightarrow AgCl (s) + e^- \)
  - Diffusion across membrane (\( \sim 10 \text{ } \mu\text{m} \))
  - Diffusion across the thin electrolyte solution (\( \sim 10 \text{ } \mu\text{m} \))
  - Steady-state current \( \Rightarrow \) \( I \) is dependent on electrochemical equilibrium, \( [O_2] \rightarrow 10 \sim 20 \text{ s} \) and \( d_{m+s} < 20 \text{ } \mu\text{m} \)
Enzyme-based Sensors

- Glucose detection: largest selling chemical instruments
  - A polycarbonate film (glucose permeable, not for protein and other blood constitutes): diffuse through
  - An immobilized enzyme layer (glucose oxidase): glucose reduction $\rightarrow$ H$_2$O$_2$
  - A cellulose membrane layer for H$_2$O$_2$ diffusion: H$_2$O$_2$ oxidation $\rightarrow$ O$_2$
    - Amperometric detection (I $\propto$ c) or volumetric detection (E $\propto$ c) of sucrose, lactose, ethanol and L-Lactate

Amperometric Titration

- At least one species is electrochemical active
- A WE (rotating Pt) + RE: confined to product either a precipitate or a stable complex.
  - Ag$^+$ for X$^-$; Pb$^{2+}$ for SO$_4^{2-}$
  - Exception: Br$_2$ (BrO$_3^-$) titration of organics
- Two WEs:
  - simple instrument, determination of a single specie
  - Karl fisher titration for determining water

$$BrO_3^- + 5Br^- + 6H^+ \rightarrow 3Br_2 + 3H_2O$$
Rotating Electrodes

- Rotating electrode:
  - RDE: rotating disk electrode, affiliate mass transfer
  - RRDE: rotating ring disk electrode, intermediate detection
- Levich equation:
  \[ i_l = 0.620nFAD_\omega^{1/2}v^{-1/6}c \]
  - \( n \): electron / analyte
  - \( D \): diffusion coefficient, \( cm^2/s \)
  - \( \omega \): angular velocity, radians/s
  - \( v \): kinematic viscosity, \( cm^2/s \)
  - \( c \): mol/cm\(^3\)

Polarography

- WE: DME, diffusion control, no convection
- Residue current: current observed in the absence of an electroactive specie
- Diffusion current: limiting current which is limited by the diffusion
- A: DL \( \sim 10^{-5} \) M, Faster equilibrium + new electrode surface \( \rightarrow \) reproducible current; High \( \eta \) for H\(_2\) evolution \( \rightarrow \) low \( E \) window
- DA: new surface \( \rightarrow \) large charging current

\[ (i_d)_{max} = 708nD^{1/2}m^{2/3}l^{1/6}c \]

\[ a = \text{electron / analyte} \]
\[ D = \text{diffusion coefficient, cm}^2/s \]
\[ m = \text{mass of Hg through the capillary, mg} \]
\[ c = \text{mol/cm}^3 \]
\[ l = \text{length of capillary, cm} \]

The ripples are caused by the constant forming and dropping of the mercury electrode.
Cyclic Voltammetry

- CV: forward scan, switching potential, reverse scan
- Application of CV:
  - Study of redox reaction
  - Detection of reaction intermediates
  - Observation of follow-up reactions
- Reaction:
  - A: H₂O oxidation → O₂
  - B-H: reduction
  - B-D: cₐ₀ → 0
  - D-F: cₐ₀ = 0, δ↑
  - F-H: reduction
  - H-K: oxidation

Irreversible or rapid removal of Red
(reduction)

CV- Fundamental Studies

- Peak potential: Ecı and Eırpa
  - Reversible: \( \Delta E_p = \frac{0.0592}{n} \)
  - Irreversible: \( \Delta E_p > \frac{0.0592}{n} \)
- Peak current:

\[
i_p = 2.686 \times 10^5 n^{3/2} A D^{1/2} v^{1/2} c\]

- Qualitative information in organic and inorganic chemistry
  - first choice
  - reaction intermediate

\[
A: \phi N O_2 + 4e^- + 4H^+ \rightarrow \phi N H O H + H_2O
\]

\[
B: \phi N H O H \rightarrow \phi N O + 2H^+ + 2e^-\]

\[
C: \phi N O + 2H^+ + 2e^- \rightarrow \phi N H O H
\]

Parathion in 0.5 M acetate buffer in 50% ethanol, pH = 5
CV of Modified electrode

- Reversible surface redox couple → no mass transfer effect → symmetrical peaks + same peak height

Digital Simulation of CV

- Digital simulation: DigiSim, DigiElk
  - Fast implicit finite difference methods
  - 1st or 2nd order homogeneous chemical reaction
  - Generate dynamic concentration profiles
  - The exact current may be offset as the nonfaradaic current is not easily simulated
Differential Pulse Polarography

- **DPP**: increasing sensitivity
  - Lower DL: $\sim 10^{-7}$ to $10^{-8}$ M ($2 \sim 3$ order lower than CV)
  - Enhancing faradic current: diffusion current ($i_d$) + Nernst contribution due to $\Delta E$, several times larger than $i_d$, $\Delta t$ is small enough
  - Decrease in nonfaradic current: charging current decays exponentially with time, is small at the late lifetime of the drop, $\Delta t$ is large enough
  - Trace heavy metal detection

Square-wave Polarography

- **SWP**: increasing sensitivity
  - Great speed: step $< 10$ ms, signal average is possible
  - Lower DL: $\sim 10^{-7}$ to $10^{-8}$ M
  - Enhancing faradic current + Decrease in nonfaradic current
  - $\Delta I = I_f - I_r$, the current difference is plotted
Stripping Methods

- Stripping methods:
  - Anodic stripping methods: $C \rightarrow A$ for metal
  - Cathodic stripping methods: $A \rightarrow C$ for halides

- Electrodeposition step:
  - Stirring the solution: mass transfer
  - Only a fraction of analyte is deposited: accumulation process
  - Depends on $c$, stir rate, deposition time, electrode surface and potential
  - $t < 1$ min. for $c \sim 10^{-7}$ M
  - $t > 30$ min. for $c \sim 10^{-9}$ M, (higher sensitivity)
  - HMDE or noble metal (Pt, Au, Ag and C)

Microelectrodes

- Microelectrode: $r \sim 1$ to 20 µm
  - $r >> \delta$, normal electrode, short time
  - $\delta >> r$, UME, long time, steady state

- Advantage:
  - Small current ($I \sim pA$ to nA) $\rightarrow$ small IR drop $\rightarrow$ no RE
  - Capacitor charging current ($I_{cd} \propto A$) $\rightarrow$ $I_{cd} \downarrow$ faster scan
  - Faradaic current ($I \propto A/r$) $\rightarrow$ bigger contribution from $I_f$ $\rightarrow$ lower DL
  - Rate of mass transport increases $\rightarrow$ steady state is established within $\mu$s $\rightarrow$ faster kinetic study, higher S/N ration
  - Little disturbance to the system under study
  - Small sample volume
  - Small current $\rightarrow$ system with low dielectric constants, like toluene
Homework

- 25-2 (a, b, c, e), 25-5