Electrochemistry
Lecture 2
Voltammetry

Reference Books

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 has conductivity
**Electrochemical Instrumentation**

![Electrochemical Instrumentation Diagram](image)

---

**Voltammetry**

- 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) MURCURY electrode.
- Voltammogram — The plot of the electrode current as a function of potential.

---

**Linear sweep voltammetry**

- The potential is varied linearly with time with sweep rates $v$ ranging from 10 mV/s to about 1000 V/s with conventional electrodes and up to $10^6$ V/s with ultramicroelectrodes (UMEs).
- It is customary to record the current as a function of potential, which is equivalent to recording current versus time.
- Linear sweep voltammetry, linear scan voltammetry (LSV), or linear potential sweep chronoamperometry.
Linear Diffusion to a Planar Electrode

Electrode reaction: \( A + e \rightleftharpoons A^- \) (reversible)

\( \text{at } x=0, \text{ rate constant } k^0 \text{ (cm/s)} \)

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

---

Linear Sweep/Scan Voltammetry

Peak-shaped \( i-E \) profile

For a reversible reaction, \( E^0(A/A^-) = E^0 \):

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

\( \text{DigiSim demonstration} \)
Cyclic Voltammetry (CV)

Potential: $E(t) = E_i - \nu t (V), 0 < t \leq \lambda$

$E(t) = E_i - 2\nu \lambda + \nu t (V), t > \lambda$

CV is not an ideal method for quantitative evaluation of system properties. It is powerful in qualitative and semi-quantitative reaction behavior.

Cyclic Voltammetry - \( i \) vs time

NERNSTIAN (REVERSIBLE) SYSTEMS

O + ne \( \rightleftharpoons \) R

Semi-infinite linear diffusion, only O exist initially

LSV: potential changes linearly at a sweep rate of \( v \) (V/s)

$E(t) = E_i - \nu t$

Nernst equation

$E(t) = E^0 + \frac{nF}{RT} \ln \frac{C_{o}(0,t)}{C_{a}(0,t)}$

$\therefore \frac{C_{o}(0,t)}{C_{a}(0,t)} = \exp \left[ \frac{nF}{RT} (E_i - \nu t - E^0) \right] = S(t) \theta$

$S(t) = e^{-\sigma t}, \quad \sigma = (nF / RT) v; \quad \theta = \exp \left[ (nF / RT)(E_i - E^0) \right]$
For a Nernst process:

\[ \nu_{\text{net}} = \nu_{\text{obs}} = i / nFE \rightarrow \text{flux } (J) \]

\[ \nu_{\text{net}}: \text{ net rate of electrode reaction} \]

\[ \nu_{\text{ms}}: \text{ rate of mass transfer} \]

C: current; A: area of electrode

\[ J: \text{ flux } \left( \text{mole } \text{cm}^{-2} \text{ s}^{-1} \right) \]

\[ i_{\text{net}} = i_d + i_m + i_n \]

If use short times ( < 10 s) and don’t stir (quiescent),
then \( i_{\text{net}} = i_d + i_m \)

---

Figure 4.3.1 Examples of reduction processes with different contributions of the migration current: (a) positively charged reactant, (b) negatively charged reactant, (c) uncharged reactant.

---

Nernst-Planck Equation
(governing the mass transport to an electrode)

\[ J_i(x) = -D_i \frac{\partial C_i(x)}{\partial x} - \frac{z_i F}{RT} D_i \frac{\partial \phi(x)}{\partial x} + n_i \nu(x) \]

\( J_i(x) \): flux of species \( i \) at distance \( x \) from electrode (mole cm\(^{-2}\) s\(^{-1}\))

\( D_i \): diffusion coefficient (cm\(^2\) s\(^{-1}\))

\( \partial C_i(x)/\partial x \): concentration gradient at distance \( x \) from electrode

\( \partial \phi(x)/\partial x \): potential gradient at distance \( x \) from electrode

\( \nu(x) \): velocity at which species \( i \) moves (cm/s)

\( *=^* \): flux direction opposes the concentration gradient change
If We Use High Concentration of Good Electrolyte in Quiescent Solution...

Nernst-Planck Equation reduces to...

Fick's First Law

- Flux of substance is proportional to its concentration gradient:

\[-J_i(x,t) = D \frac{\partial C_x (x,t)}{\partial x} = \frac{-i}{nFA}\]

i.e., flux \( \propto \) concentration gradient

---

LSV Reversible System

After the Laplace transformation and a series of mathematical treatments of the diffusion equations:

\[i = nFAC_o^{k}(\pi D_O\sigma)^{1/2} \chi(\sigma t)\]

\[(\sigma = (nF/RT)\nu)\]

where \( \chi(\sigma t) \) is a pure number at any given point and can be solved numerically.

\( \chi \) ("kai")

---

Excel Calculation of \( \chi(\sigma t) \)

<table>
<thead>
<tr>
<th>( x, ) cm</th>
<th>( y, ) cm</th>
<th>( z, ) cm</th>
<th>( w, ) cm</th>
<th>( u, ) cm</th>
<th>( v, ) cm</th>
<th>( w, ) cm</th>
<th>( u, ) cm</th>
<th>( v, ) cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.446295</td>
<td>My Excel calculation</td>
<td>0.446295</td>
<td>0.446295</td>
<td>0.446295</td>
<td>0.446295</td>
<td>0.446295</td>
<td>0.446295</td>
<td>0.446295</td>
</tr>
</tbody>
</table>

*To calculate the current:

1. \( i = \alpha \beta \gamma \delta \) (electrical calculation).
2. \( i = \alpha \beta \gamma \delta \) (electrical calculation).
3. \( i = \alpha \beta \gamma \delta \) (electrical calculation).

*\( \sigma = (nF/RT)\nu \) with \( n, F, R, T, \) and \( \nu \) at 25°C.
Reversible system

\( \langle \sqrt{\pi} \chi(\sigma) \rangle_{\text{max}} = 0.4463 \) when \( n(E - E^\circ) = 28.5 \text{mV} \)

Peak current and potential

- **Peak current** \( i_p \)
  \[ i_p = 0.4463 \frac{E^1}{RT} \frac{1}{1^2} n^{1/2} AC_i^{1/2} D_i^{1/2} V^{1/2} \]
  \[ = (2.69 \times 10^3) n^{1/2} AC_i^{1/2} D_i^{1/2} V^{1/2} \text{ at } 25^\circ \text{C}. \]
  Units: Amperes, \( \text{cm}^2, \text{cm}^2/\text{s}, \text{mol}/\text{cm}^3, \text{V/s} \)

- **Peak potential** \( E_p \)
  \[ E_p = E_{1/2} - 28.5 / n \text{ (mV) at } 25^\circ \text{C} \]
  \[ E_{1/2} = E^\circ + \frac{(RT/nF) \ln(D_x/D_o)^{1/2}}{1/2} \]
  \( \rightarrow E_p \) is independent of scan rate.
Current (A) vs. Potential (E mV, vs. ref electrode)

$E_n = E_{ref} - 1.109RT/nF = 28.5/n$ mV @ 25 °C

$E_{ox} = E_{ref} + 1.109RT/nF = E_{ox} + 28.5/n$ mV @ 25 °C

$E_{red} = E^* + \frac{RT}{nF} \ln \left( \frac{D_{ox}}{D_{red}} \right)^{1/2} \approx E^*$

$|E_p - E_{p/2}| = 2.22RT/nF = 57.0/n$ mV @ 25 °C

$E_p \neq f(v)$

$i_p = f(v^{1/2})$

Cyclic Voltammograms

Cyclic Voltammetry

Cyclic Voltammetry for a Reversible Reaction

- $i_{pa}/i_{pc} = 1.0$
- $\Delta(E_{pc} - E_{pa}) = 2(1.109) \frac{RT}{nF}$
  
  $= 57$ mV/n at 25 °C

  (independent of the scan rate)

- $E^* = (E_{pc} + E_{pa})/2$

- $i_p = \text{constant} \times n^{3/2} AD_0^{1/2} C^* v^{1/2}$

  (at 25 °C, constant = $2.69 \times 10^5$)
Peak separation potentials, although close to 57 mV, are slightly a function of switching potentials.

Table 6.5.1 Variation of $\Delta E_p$ with $E_a$ for a Nernstian System at 25°C (3)

<table>
<thead>
<tr>
<th>$n(E_{pc} - E_a)$ (mV)</th>
<th>$n(E_{pa} - E_{pc})$ (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>71.5</td>
<td>60.5</td>
</tr>
<tr>
<td>121.5</td>
<td>59.2</td>
</tr>
<tr>
<td>171.5</td>
<td>58.3</td>
</tr>
<tr>
<td>271.5</td>
<td>57.8</td>
</tr>
<tr>
<td>$\infty$</td>
<td>57.0</td>
</tr>
</tbody>
</table>

Reversibility of Electrochemical System Can be Changed via the Change of Scan Rate

Reversible (nernstian) $\Lambda > 15, \phi^{0} \geq 0.3 \text{V}^{1/2}$ cm/s
Quasireversible $15 \geq \Lambda = 10^{-2} \text{V}^{1/2}, 0.3 \text{V}^{1/2} \geq \phi^{0} \geq 2 \times 10^{-5} \text{V}^{1/2}$ cm/s
Totally irreversible $\Lambda = 10^{-2} \text{V}^{1/2}, \phi^{0} \geq 2 \times 10^{-5} \text{V}^{1/2}$ cm/s

$\Lambda = \frac{\phi^{0}}{(D_{0}^{1/2} + \phi_{0}^{1/2})^{1/2}}$

$\Lambda = \frac{\phi^{0}}{(D_{0}^{1/2})^{1/2}}$

$f = nF/RT$

At small $v$ (or long times), systems may yield reversible waves, while at large $v$ (or short times), irreversible behavior is observed.
Electron Transfer Rate $k^0$

$$k^0 \rightarrow \Delta E_{p} \rightarrow i_p$$

**Figure 16-13** Examples of reversible, quasi-reversible and irreversible cyclic voltammograms. Data used: $F = 96,480 \ A \cdot \text{mol}^{-1} \cdot \text{V}^{-1} \cdot \text{cm}^{-2}$, $z' = 1.0 \ \text{mM}$, $D_e = 1.0 \ \text{mM}$, $n = 0.5$, $E_r = -200 \ \text{mV}$, $E_{red} = -200 \ \text{mV}$, $v = 200 \ \text{mV} \cdot \text{s}^{-1}$, and $k^0 = 10^6$, $10^8$, $10^{-8} \ \text{m} \cdot \text{s}^{-1}$.

---

**Totally Irreversible System**

(NO Reversal Peak)

**Figure 2.** Main panel: Cyclic voltammograms of 15.2 mmol L$^{-1}$ 4-diazo-tert-butylamine in acetate buffer solution, pH 4.6 recorded at different potential sweep rates. Potential sweep rates from lower to upper are 15, 25, 50, 100 and 500 mV s$^{-1}$. Inset: The dependency of anodic peak current on the square root of potential sweep rate in a wide range of 15-500 mV s$^{-1}$.

---

**CV Applications in Diagnosing Chemical Reaction Mechanisms**

**EC Reaction** (Electron Transfer followed by a Chemical Reaction)

$$RO + e \rightarrow E + CR$$

Increasing $k_{oc}$

$$k_{oc}$$

Products

**Figure**

---

30
EC Reaction: Scan Rate Dependent

(a) At Fast Scan Rate  
(b) At Slow Scan Rate

ECE Process

(a) S is more difficult to reduce than O (i.e., \(E_{0S}' < E_{0O}'\))
(b) S is easier to reduce than O (i.e., \(E_{0S}' > E_{0O}'\))

Multi-step Systems

- \(O + n_e \rightarrow R_1 (E_0^1)\)
- \(R_1 + n_e \rightarrow R_2 (E_0^2)\)
- \(\Delta E^0 = E_0^2 - E_0^1\)

\(\Delta E^0 = -(2RT/F)\ln(2) = 36mV\)

The CV looks the same as one electron-transfer process.

\(\Delta E^0\): (a) -180 mV, (b) -90 mV, (c) 0 mV, (d) 180 mV.
**Ohmic Potential, IR Drop**

- Potential change (drop) due to electrochemical solution resistance
- \( E_p = IR \)
  - \( I \) — current of the electrochemical cell,
  - \( R \) — resistance of the electrolyte solution.
- \( E_{cell} = E_{cathode} - E_{anode} - IR \)

- Question: In electrochemical study, an inert electrolyte is always added to the analyte solution. Why?

---

**Faradaic and Nonfaradaic Processes**

**Faradaic**

- Charges or electrons are transferred across the electrode|electrolyte interface as a result of electrochemical reactions
- Governed by Faraday's law

\[
Q = nF N_a \quad \text{where } n = \# \text{ of } e \text{ transferred}
\]

- \( F \) = Faraday constant (96,485 C/mol)
- \( N_a = \# \text{ of moles of electroactive species} \)

\[
\frac{dQ}{dt} = nF \frac{dN_a}{dt}
\]

---

\[
A + e^- \rightarrow B
\]

\[ R = 0 \]
\[ \Delta E_p = 58 \text{ mV} \]
\[ R = 10 \text{ Ohm} \]
\[ \Delta E_p = 100 \text{ mV} \]

\[ c_A = 1 \text{ mM} \]
\[ 50 \text{ mV/s} \]
\[ \text{Area} = 1 \text{ cm}^2 \]
Nonfaradaic Process

- Charges associated with movement of electrolyte ions, reorientation of solvent dipoles, adsorption/desorption of species, etc. at the electrode|electrolyte interface.
- Changes with changing potential and solution composition
- Charges do not cross the interface but external currents can still flow
- Regarded as "background current"

Nonfaradaic Processes and the nature of electrode|electrolyte interface: the Double layer

- Electrons transferred at electrode surface by redox reactions occur at liquid/solid interface (heterogeneous)
- (1) A compact inner layer (d₀ → d₁)
- (2) A diffuse layer (d₁ - d₂)

Charging current $i_c$

$$\frac{q}{E} = C$$

10-40 $\mu$F/cm²

Potential dependent

Figure 1.2.2 The metal-solution interface as a capacitor with a charge on the metal, $\phi^0$, (a) negative and (b) positive.

Figure 1.2.1 (a) A capacitor, (b) Charging a capacitor with a battery.
Equivalent Circuits of Electrochemical Cell

\[ C_{\text{SCE}} >> C_d \]

\[ C_{\text{out}} = \frac{1}{C_1} + \frac{1}{C_2} + \ldots + \frac{1}{C_n} \]

*Figure 12.5* Left: Two-electrode cell with an ideal polarized mercury drop-electrode and a SCE. Right: Representation of the cell in terms of linear circuit elements.

1 Actually, the capacitance of the SCE, \( C_{\text{SCE}} \), should also be included. However, the series capacitance of \( C_1 \) and \( C_{\text{SCE}} \) in \( C_{\text{out}} = C_{\text{SCE}} + C_1 + \ldots + C_n \) and normally \( C_{\text{SCE}} >> C_1 \) so that \( C_1 = 0 \). Thus, \( C_{\text{SCE}} \) can be neglected in the circuit.

---

RC Circuit-Voltage Ramp (Potential Sweep)

\[ E = vt = E_R + E_i \]

\[ vt = R (dq/dt) + q / C_d \]

if \( q = 0 \) at \( t = 0 \)

\[ i = vC_d[1 - \exp(-t / RC)] \]

*Figure 12.6* Current component potentially generated from the reference electrode and potential applied to q.

---

General Equivalent Circuit

\[ E: \text{Potential applied to WE} \]

\[ C_d^o: \text{Double layer capacitance} \]

\[ Z_F: \text{Impedance (Faradaic reaction)} \]

\[ i_c: \text{Charging current ("noise")} \]

\[ i_F: \text{Faradaic current ("signal")} \]

\[ i: \text{Total measured current} \]

Overall current \( i = i_c + i_F \)

Signal-to-noise ratio (SNR) = \( \frac{i_c}{i} \)

SNR ↑, limit of detection (LOD) ↓
How do we eliminate the charging current so that electrochemical techniques could be used in quantifying low concentrations of redox species?

(Pulse Voltammetry)
A is reduced to A\textsuperscript{-} at potential $E_2$

This kind of experiment is called chronoamperometry, because current is recorded as a function of time.

Cottrell Equation

$$i = \frac{nFA}{\sqrt{\pi Dt}} = \frac{D_o (\Delta c_o)}{\sqrt{\pi Dt}}$$

$$i = nFA \frac{D_o c^*}{\sqrt{\pi Dt}} = \frac{nFAD_o^{1/2} c^*}{\pi^{1/2} t^{1/2}}$$

Curves 1, 2, 3, $C_o(0, t)$ not 0

-not diffusion controlled

(electrode reaction-controlled)

Sampled Current Voltammetry

Steps to different potentials

Current-time curves

Sampled current voltammogram
Sampled Current Voltammetry
(Normal Pulse Voltammetry)

Eliminating \(i_c\): Potential Step/Pulse Voltammetry

Staircase Voltammetry
When applying \(\Delta E\):
\[i = \frac{\Delta E}{R} \exp(-t/RC) \rightarrow i \propto e^{-t}
\]
\[i(t) = \frac{nFADc_i}{\sqrt{2t}} \rightarrow i \propto t^{-1/2}
\]
at \(t, i_c \rightarrow 0\), so SNR ↑
(LOD~10^{-8} M)

Additive Cyclic Square Wave Voltammetry (ACSWV)

Total additive \(i_c\)
\[i_c = i_c^F + i_c^R = 0
\]

\(i_c^F\): forward anodic \(i_c\)
\(i_c^R\): forward cathodic \(i_c\)
\(i_c^{aF}\): reverse anodic \(i_c\)
\(i_c^{aR}\): reverse cathodic \(i_c\)
Pulse Voltammetric Techniques

- All pulse techniques are based on the difference in the rate of the decay of the charging and the faradaic currents following a potential step (or "pulse").

\[ i_{cl} = \frac{\Delta F}{R} \exp\left(-\frac{t}{R\mathcal{C}_{dl}}\right); i_{fr} = \frac{nFE\mathcal{C}_{dl}}{\sqrt{2\pi}} \] (Cottrell Eq)

- The rate of decay: \( i_{cl} \) much faster than \( i_{fr} \), is negligible at a time of \( 5R\mathcal{C}_{dl} \) (time constant, \( \sim \)μs to ms) after the potential step.

- The sampled \( i \) consists solely of the faradaic current.

Important parameters

- **Pulse amplitude**: the height of the potential pulse. This may or may not be constant depending upon the technique.

- **Pulse width**: the duration of the potential pulse.

- **Sample period**: the time at the end of the pulse during which the current is measured.
Digital potentiostats use a staircase wave form as an approximation to a linear wave form. This approximation is only valid when $\Delta E$ is small ($<0.26 \text{ mV}$) and analog current integration filtering is used.
Differential Pulse Voltammetry (DPV)

Figure 3.6  Excitation signal for differential-pulse voltammetry.

\[ \Delta i = i(t_2) - i(t_1) \]
Square Wave Voltammetry (SWV)

Peak Current: 

\[ i_p = \frac{nFAD^{1/2}C}{\sqrt{\pi d_m}} \left( \frac{1-\sigma}{1+\sigma} \right) \]

where \( \sigma = \exp[(nF/RT)(\Delta E/2)] \) (\( \Delta E \) is the pulse amplitude)

\( \left( \frac{1-\sigma}{1+\sigma} \right) = 1 \) for large pulse amplitudes

The peak potential \( (E_p) \) can be used to identify the species.

\[ E_p = E_{1/2} - \Delta E/2 \]

Charging current (smaller more than an order of magnitude than that of NPV) with LOD 10 nM.
Square Wave Voltammetry (SWV)

Figure 7.3.3 Waveform and measurement scheme for square wave voltammetry. Shown in bold is the actual potential waveform applied to the working electrode. The light intervening lines indicate the underlying staircase onto which the square wave can be regarded as having been superimposed. In each cycle, a forward current sample is taken at the time indicated by the solid dot, and a reverse current sample is taken at the time marked by the shaded dot.

\[ E_m = E_i - \left[ \text{Int} \left( \frac{m+1}{2} \right) - 1 \right] \Delta E_a + (-1)^m \Delta E_p \quad \text{(for } m \geq 1) \]
SWV Response

\[ \Delta i_p = \frac{nFAD_{D^{2+}}^{O=}}{\pi^{1/2}A^{1/2}D^{1/2}} \Delta \phi_p \]

**TABLE 7.3.2.** Dimensionless Peak Current (\(i_p\)) vs. SWV Operating Parameters

<table>
<thead>
<tr>
<th>(n\Delta E_p/\text{mV})</th>
<th>1</th>
<th>5</th>
<th>10</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td>0º</td>
<td>0.0053</td>
<td>0.0238</td>
<td>0.0437</td>
<td>0.0774</td>
</tr>
<tr>
<td>10</td>
<td>0.2376</td>
<td>0.2549</td>
<td>0.2726</td>
<td>0.2998</td>
</tr>
<tr>
<td>20</td>
<td>0.4531</td>
<td>0.4686</td>
<td>0.4845</td>
<td>0.5077</td>
</tr>
<tr>
<td>50</td>
<td>0.9098</td>
<td>0.9186</td>
<td>0.9281</td>
<td>0.9432</td>
</tr>
<tr>
<td>100</td>
<td>1.1619</td>
<td>1.1643</td>
<td>1.1675</td>
<td>1.1745</td>
</tr>
</tbody>
</table>

*Data from reference 50.

\(\Delta E_p = 0\) corresponds to staircase voltammetry.
Comparison between SWV and CV

**SWV Strengths**
- Low electrochemical background.
- Much low detection limit.
- Much less distortion of voltammogram—easy to fit theoretical data.
- Better for evaluating quantitative parameters.

**CV Strengths**
- More intuitively in chemical terms for most practitioners.
- Reversal of CV covers a large span of $E$—more readily highlights linkages b/w processes occurring at widely separated potentials.
- Wider range of time scales.

Applications of Voltammetry

- Dopamine detection in mice brains
- ……
- Au or Si NPs redox behavior
- ……

Anodic Stripping Voltammetry (ASV)

Principle of anodic stripping. (a) Preelectrolysis at $E_d$; stirred solution, (b) Rest period; stirrer off. (c) Anodic scan.
ASV-Electrode Dependence

Sensitivity and Limit Detection

![Diagram showing ASV-Electrode Dependence]

<table>
<thead>
<tr>
<th>preconcentration</th>
<th>stripping</th>
<th>sensitivity</th>
<th>symbols</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASV: $M \rightarrow M^6$</td>
<td>$M^6 \rightarrow M$</td>
<td>$0.1 \text{ nM}$</td>
<td>![Symbol]</td>
</tr>
<tr>
<td>ACSV: $M \rightarrow ML \rightarrow ML_a$</td>
<td>$ML_a \rightarrow e^{-}$</td>
<td>$p\text{M}$</td>
<td>![Symbols]</td>
</tr>
</tbody>
</table>

**FIGURE 3.19** Elements measured by conventional ASV and adsorptive stripping schemes with reduction of the element in the complex $\square$, reduction of the ligand $\square$, or catalytic process $\square$. (Reproduced with permission from reference 40.)