CYCLIC VOLTAMMETRY

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Controlled Potential

Potential Sweep Methods

(1) Potential sweep methods: Cyclic Voltammetry (CV) and linear sweep voltammetry (LSV).

(2) Cyclic voltammetry is a very popular technique for electrochemical studies, useful for obtaining information about fairly complicated electrode reactions.

(3) Signal ↔ Response
UNDERSTANDING CYCLIC VOLTAMMETRY BEHAVIOR
Cyclic voltammetry

Cyclic potential sweep

(initial potential and switching potential)

Resulting cyclic voltammogram
Equilibrium for Reaction

The Nernst equation:

$$E_{\text{cell}} = E^0 - \frac{RT}{nF} \ln \left( \frac{c_R^*}{c_o^*} \right)$$

- $E_{\text{cell}}$ is related directly to $[O]$ and $[R]$.

- **Limitations**: Applies only when there is no net current flow through the electrode. The activity of ions at the electrode surface changes when there is current flow, and there are additional over potential and resistive loss terms which contribute to the measured potential.
Concentration-Distance profiles

At various stages of Cyclic Voltammogram

Solid Lines correspond to reducing species and dotted lines the oxidizing species.
Close-up of CV experiment

- **$C_0$** is the concentration of the electrode active species at the electrode surface.
- **$C$** is the concentration in the bulk solution.

There is no stirring in CV. So, the thickness of the diffusion layer increases as the experiment unfolds. ($C$ will have further to diffuse from the Bulk).
- The shorter the diffusion layer, the greater the current.
- The faster the scan rate, the shorter the diffusion layer.
Cyclic Voltammetry
Understanding Response

- At a potential well positive of $E^0$, only nonfaradaic currents flow for awhile.
- When the potential reaches the vicinity of $E^0$, the reduction begins and current starts to flow.
- As the potential continues to grow more negative, the surface concentration of the reactant must drop, hence the flux to the surface and the current increase.
- As the potential moves past, the surface concentration drops to near zero and mass transfer of reactant to the surface reaches a maximum rate.
- Then it declines as the depletion effect sets in.
The current is first observed to peak at $E_{p_c}$ (with value $i_{p_c}$) indicating reduction of species and then drops due to depletion of the reducing species from the diffusion layer.

b: onset potential
d,j: Peak Potential
F: Switching Potential
Cyclic Voltammetry

- \( E^0 = \frac{(E_{pa} + E_{pc})}{2} \).
- Separation of peaks for a reversible couple is 0.059V/n volts.
- A one electron transfer fast reaction thus gives 59mV separation.
- Half-peak potential \( E_{p/2} = E_{1/2} + 0.028/n \)
- This potential is attained in the interval in which the rate of the charge-transfer process, and hence the current, increase monotonically with time.
Cyclic Voltammetry

Effect of Scan Rate

- In a slow voltage scan rate the diffusion layer will grow much farther from the electrode in comparison to a fast scan.

- Flux to the electrode is smaller at slow scan rates vs. faster rates.

- The current is proportional to flux towards the electrode.
Randles-Sevcik equation

Reversible systems (Effect of scan rate on peak current)

\[ i_p = 0.4463nFAC\left(\frac{nFvD}{RT}\right)^{1/2} \]

- \( n \) = Number of electrons
- \( F \) = Faraday’s Constant 96,485 C/mole
- \( A \) = Electrode Area cm\(^2\)
- \( D \) = Analyte Diffusion Coefficient cm\(^2\) s\(^{-1}\)

The ratio of \( i_{pa} \) to \( i_{pc} \) should be close to one, but vary with chemical reactions coupled to electrode process.
If the plot of peak height vs. the square root of the scan rate produces a linear plot, the diffusion coefficient can be obtained from the slope of the plot.
UNDERSTANDING REACTION MECHANISMS
Factors affecting electrode reaction rate

In general, the electrode reaction rate is governed by rates of processes such as:

(1) Mass transfer (e.g., from the bulk solution to the electrode surface).
(2) Electron transfer at the electrode surface.
(3) Chemical reactions preceding or following the electron transfer.
(4) Other surface reactions.

◆ The magnitude of this current is often limited by the inherent sluggishness of one or more reactions called rate-determining steps.
Electrode reactions with coupled homogeneous chemical reactions

- If $E$ represents an electron transfer at the electrode surface, and $C$ represents a homogeneous chemical reaction.
- Classification of reactions: $CE$ reaction, $EC$ reaction, Catalytic ($EC'$) reaction, $ECE$ reaction.
EC mechanism

- In the KP region, $E_p$ is given by

$$E_p = E_{1/2} - \frac{RT}{nF} 0.780 + \frac{RT}{2nF} \ln \lambda$$

$$\lambda = \frac{knF}{RT\nu}$$

- $k_f$: heterogeneous rate constant for oxidation
- $k_b$: heterogeneous rate constant for reduction
- $K$: equilibrium constant
- $\lambda$: dimensionless homogeneous kinetic parameter, specific to mechanism
- DP: diffusion zone
- KP: pure kinetic region
EC mechanism

- At small values of “λ”, reversible behavior is found.
- For large “λ” no current is observed on scan reversal and shape of the curve is similar to that of a totally irreversible charge transfer.
Types of EC mechanisms

1. $E_rC_i$ mechanism
2. $E_rC_r$ mechanism
3. $E_rC_i'$ mechanism
4. $E_rC_iE_r$ mechanism

$r$: Reversible  $I$: Irreversible
1. E\textsubscript{r}C\textsubscript{i} mechanism

E\textsubscript{r} : Ox + ne\textsuperscript{−} \rightleftharpoons Red

C\textsubscript{i} : Red \xrightarrow{k_c} Z

- **Z** : Electrochemically inactive in the scanned potential range, no equilibrium exists.
- Slow scan rates enough time elapse between initiation of “Ox” reduction and its reoxidation.
- Complete conversion to Z.
2. $E_rC_r$ mechanism

$E_r : \text{Ox} + ne^- \leftrightarrow \text{Red}$

$C_r : \text{Red} \leftrightarrow Z$

- Equilibrium maintained in the chemical step.
- “Red” conc. in vicinity of electrode is small as its converted back to Ox.
- Very slow scan rates, the peak current ratio is 1.0.
- Fast scan rate, peak current decreases.
3. $E_r C_i'$ Mechanism

In presence of catalyst

$E_r : \text{Ox} + n\text{e}^- \leftrightarrow \text{Red}$

$C_i' : \text{Red} + Z \xrightarrow{k_c} \text{Ox} + Y$

- Z is present in large
- If $k_c$ is small vs. “$\nu$”, the voltammetry appears reversible and peak current ratios approach unity.
- As $k_c$ increases, so does catalytically revived “Ox”.
With increasing scan rate the shape transition between diffusion control and steady state behavior.
C_rE_r mechanism

\[ C_r : Z \rightleftharpoons_{k_f}^{k_r} Ox \]

\[ E_r : Ox + ne^- \rightleftharpoons Red \]

- For small rates “Ox” is less.
- “Red” reaches electrode due to diffusion.
- For faster scan rates a reversible behavior is noted as only initial “Ox” contributes to current.
4. \(E_rC_iE_r\) Mechanism

Increasing scan rates fixed \(k_c\)

- \(E_r : \text{Ox} + ne^- \leftrightarrow \text{Red} \quad E_1^0\)
- \(C_i : \text{Red} \xrightarrow{k_c} \text{A}\)
- \(E_r : \text{A} + ne^- \leftrightarrow \text{B} \quad E_2^0 < E_1^0\)

- Cathodic peak increases with \(k_c\).

- Peak w.r.t oxidation of Red to Ox diminishes relative to A formed.

- Shown is a 2e\(^-\) transfer process, with oxidation of B to A following Red to Ox.
4. $E_{rC_iE_r}$ Mechanism

As $E_2^o < E_1^o$ any A produced in $C_i$ step following reduction of Ox is immediately reduced to B.

$E^0$ values for 2e$^-$ transfer is well separated.
The Legendary Butler-Volmer Equation
Butler-Volmer Equation

- Describes how the electrical current on an electrode depends on the electrode potential, considering that both a cathodic and an anodic reaction occur on the same electrode.

\[
I = A \times i_0 \times \left\{ \exp \left[ \frac{(1-\alpha) \times n \times F}{R \times T} \times (E-E_{eq}) \right] - \exp \frac{\alpha \times n \times F}{R \times T} \times (E-E_{eq}) \right\}
\]
Butler-Volmer Equation

Limitations

(a) \[ i_a^* = i_0 \exp \left[ \frac{(1 - \alpha)nF\eta_a}{RT} \right] \]

at high anodic overpotential

(b) \[ i_c^* = i_0 \exp \left[ -\frac{\alpha nF\eta_c}{RT} \right] \]

at high cathodic overpotential

\[ i_a \text{ and } i_c \text{ are the exchange current densities for the anodic and cathodic reactions} \]
At high overpotential the Butler-Volmer equation simplifies to the Tafel equation:

\[ E - E_{eq} = a - b \log(i_c) \]

for a cathodic reaction

\[ E - E_{eq} = a + b \log(i_a) \]

for an anodic reaction

where \( a \) and \( b \) are constants (for a given reaction and temperature) called Tafel equation constants.

At low over potential the Stern Geary equation applies.

Valid when the electrode reaction is controlled by electrical charge transfer at the electrode and not by the mass transfer.
(a) Tafel Equations – high $\eta$

- Relates the rate of an electrochemical reaction to the over potential. Plots of $\ln i$ vs. $\eta$ are called Tafel plots, can calculate $\alpha$ from slope and $I_o$ from y-intercept.

- Cathodic: $\ln I = \ln I_o + (-\alpha C n F / RT) \eta$

\[
\eta = \frac{RT}{\alpha n F} \ln(\frac{i}{i_0}) \text{ or } \eta = b \ln(\frac{i}{i_0})
\]

where

\[
b = \frac{2.303 RT}{\alpha n F} = \text{the Tafel slope}
\]

\[
\ln i = 2.303 \log i
\]
In real systems often there is large negative deviations from linearity at high $\eta$ due to mass transfer limitations.
(b) Stern Geary Equation - low $\eta$

- Applicable in the linear region of the Butler Volmer Equation at low over-potentials

\[ i_{\text{corr}} = \frac{B}{R_p} \]

$B$ = the Tafel constant

$R_p$ = the measured polarisation resistance

= $\Delta E/\Delta i$
Synopsis

- Nernst equation
- Randles-Sevcik equation
- Electrode reactions with coupled homogeneous chemical reactions
  - Butler Volmer Equation
  - Tafel Behavior
- Stern Geary Equation
THANK YOU