Voltammetry (stirred)

- Stationary electrode
- Stirred = mass transport by convection
- Vary potential linearly with time
- Measure current vs time

Theory

- Assume \( \text{Ox} + n \text{e}^- \leftrightarrow \text{Red} \)
  - Both Ox and Red are soluble
  - Reversible reaction (electrochemically)
  - Potential varies
Define - Limiting Current as steady state current when \([\text{Ox}] = 0\) at electrode surface i.e., applied potential is sufficiently cathodic such that all Ox is reduced at electrode.

\[
I = \frac{nFADC_{\text{bulk}}}{\delta}
\]

Gives quantitative information

\[
E = E^o - \frac{RT}{nF} \ln \frac{[\text{Red}]}{[\text{Ox}]}
\]
Linear-scan voltammogram for stirred solution

Limiting current

Quantitative information

Qualitative information

Current, $\mu$A

$E_{\text{appl}}$ (vs. SCE)

$E_{1/2}$

$i_1$

$i_1/2$
Linear Scan Voltammetry (stirred)

$\text{Ox} + e^- \rightarrow \text{Red}$

$I_C =$ Capacitive current
$I_L =$ Limiting current
$E_{1/2} =$ Half wave potential

$I_C =$ Capacitive current
$I_L =$ Limiting current
$E_{1/2} =$ Half wave potential
Linear Scan Voltammetry (stirred)

Ox + e⁻ → Red

Half wave potential (E½)
is E when I = I_L/2
Linear Scan Voltammetry (stirred)

Ox + e⁻ → Red

I is proportional to [Red], $I_L$ represents the situation where Red is maximum and Ox is zero.
Linear Scan Voltammetry (stirred)

When $I = I_L/2$, then

$[\text{Red}] = [\text{Ox}]$ and

$E = E_{\frac{1}{2}}$

$$E = E_{\frac{1}{2}} - \frac{RT}{nF} \ln \left( \frac{I_L - I}{I} \right)$$
Linear Scan Voltammetry (stirred)

Can assign rate constants ($k$) for irreversible processes
Linear Scan Voltammetry (stirred)

For two reversible processes reducing at different potentials

\[ I \quad E \quad E_{\frac{1}{2}} \quad I_L \quad E_{\frac{1}{2}} \]
Linear Scan Voltammetry (stirred)

- Normally use Pt or C (graphite) electrodes
- Better to use rotating electrode than stir bar
- LSV can be used for quantitative analysis
- Can measure many metal ions & organics
- Fairly sensitive due to convective mass transport, i.e., $I_F$ is large
- The output signal in the form of a wave is considered a drawback
  - can be difficult to perform data analysis
  - multiple components gives stacked waves
Linear Scan Voltammetry (stirred)

For a two component system it is difficult to measure the second species in the presence of a large concentration of the first species. The second \( I_L \) becomes small since the range is set by the first species.

This problem is inherent for techniques that produce waves.
Voltammetry (unstirred)

- Stationary electrode
- Unstirred solution = mass transfer by diffusion
- Vary potential linearly with time
- Measure current vs time

Theory

\[ \text{assume } \text{Ox } + \ n \ e^- \leftrightarrow \text{Red} \]

- both Ox and Red are soluble
- reversible reaction (electrochemically)
- potential varies
Linear Scan Voltammetry (unstirred)

$L_{p}$

Largely Nernstian controlled region of the curve

Primarily diffusion controlled region from Cottrell Eq.

$I_{p}$ = Peak current

$E_{p}$ = Peak potential

Irreversible

Reversible
Voltammetry (unstirred) - Theory

\[ I_P = 0.452 \frac{n^{3/2} F^{3/2}}{R^{1/2} T^{1/2} A D^{1/2} C_{\text{bulk}} V^{1/2}} \]

New term \( V = \) scan rate

Increase scan rate & \( I_P \) increases, however, \( I_C \) is directly proportional to \( V \)

Ratio \( I_F/I_C \) is greatest at slow scan rates

\[ E_P = E^{1/2} - 1.1 \frac{R T}{n F} \]
Linear Scan Voltammetry (unstirred)

More than one component

Can be difficult to determine baseline for second peak

I

E

I_p?
Applied Signal for Linear Scan Voltammetry

Slope = scan rate in mV/sec

time
Convention for plotting current & potential

$I_{\text{cathodic}}$
\begin{align*}
\text{Current due to reduction}
\end{align*}

$E_{\text{anodic}}$
\begin{align*}
\text{oxidizing potentials}
\end{align*}

$E_{\text{cathodic}}$
\begin{align*}
\text{reducing potentials}
\end{align*}

$\text{Red} - e^- \rightarrow \text{Ox}$

$\text{Ox} + e^- \rightarrow \text{Red}$

$I_{\text{anodic}}$
\begin{align*}
\text{Current due to oxidation}
\end{align*}
Applied Signal for Linear Scan Voltammetry

Slope = scan rate in mV/sec
Cyclic Voltammetry
Going from A to B to C to D is the same as for LSV in an unstirred solution scanning in one direction.

Convention for plotting current & potential

\[ \text{Ox} + e^- \rightarrow \text{Red} \]

\[ \text{Red} - e^- \rightarrow \text{Ox} \]
Convention for plotting current & potential

Going from D to E there is a sharp decrease due to the change in sign of the capacitive current.
Convention for plotting current & potential

Going from E to F the current decreases slowly due to capacitive current building (opposite in sign)
Convention for plotting current & potential

Going from F to G the anodic current increases rapidly due to Nernstian control of the system.
Convention for plotting current & potential

Going from H to I to J the current becomes diffusion controlled again as mentioned previously.
<table>
<thead>
<tr>
<th>CV Diagnostics</th>
<th>$I_p/V^{1/2}$</th>
<th>$I_{\text{anodic}}/I_{\text{cathodic}}$</th>
<th>$\Delta E_p/2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reversible Charge Transfer</td>
<td>Constant with $V$</td>
<td>1</td>
<td>Constant with $V$</td>
</tr>
<tr>
<td>Irreversible Charge Transfer</td>
<td>Not constant with $V$</td>
<td>$&lt; 1$</td>
<td>$\Delta E_p/2$ increase with $V$</td>
</tr>
</tbody>
</table>

The diagram shows a cyclic voltammetry (CV) curve with anodic and cathodic peaks. The table summarizes the behavior of different charge transfer processes with respect to $V$. The graph illustrates the relationship between the anodic and cathodic currents ($I_{\text{anodic}}$, $I_{\text{cathodic}}$) and the applied potential ($E$). The curvature of the graph indicates the change in $\Delta E_p/2$ with respect to $V$. The table indicates that for reversible processes, $I_p/V^{1/2}$ is constant with $V$, while for irreversible processes, $I_{\text{anodic}}/I_{\text{cathodic}}$ decreases with $V$.
Cyclic Voltammetry of Complex Systems

- $\text{Ox} + e^- \rightarrow \text{Red}$
- $\text{Red} \leftrightarrow \text{A}
- \text{A} - e^- \rightarrow \text{B}$
- $\text{Red} - e^- \rightarrow \text{Ox}$
Cyclic Voltammetry

- Powerful technique for elucidating mechanisms of oxidation & reduction
- Good for studying electrode kinetics
- [http://www-biol.paisley.ac.uk/marco/Enzyme_Electrode/Chapter1/Cyclic_Voltammetry1.htm](http://www-biol.paisley.ac.uk/marco/Enzyme_Electrode/Chapter1/Cyclic_Voltammetry1.htm)