Cyclic Voltammetry
and
electrode reaction mechanism
• A technique usually used to acquire qualitative information about electrochemical reactions
• Offers a rapid location of redox potentials of the electroactive species
• Can be used to get valuable kinetic information of electrode reaction
• Electrode reaction usually involve e-transfer reaction which is influenced by electrode potential
• Mass transfer (diffusion) in some cases can control over-all electrode reaction
• Voltammetry is used to investigate electrode mechanism
• It is a technique to control electrode’s potential and measure resultant current
• Forms of voltammetry include:
  – Potential step
  – Linear sweep
  – Cyclic voltammetry
Potential step

Linear sweep

Cyclic voltammetry
• It is already known that electrode potential govern its reaction and its rate!

• Assume an electrolyte solution with one electroactive species (O) which undergoes simple 1 e and 1 step reaction

\[ O \, (aq) + e \rightleftharpoons R \, (aq) \]

where \( k_f \) and \( k_b \) are rate constants for forward and backward reactions

• electrode reaction may be reversible or irreversible
• Let us have an idea about the **electrochemical cell** first!

• an arrangement where different electrodes with specific functions are put together in an electrolyte solution that contain an electroactive species

• Working electrode

• Reference electrode

• Auxiliary electrode
• Sweep voltammetry depends on diffusion of electroactive species to electrode surface
• The mass transport of (O) as function of time and distance can be predicted by Fick’s 2nd law of diffusion

\[ \frac{\partial [O]}{\partial t} = D_o \frac{\partial^2 [O]}{\partial x^2} \]

• Potential of WE is swept from \( E_1 \) where no reaction undergo to \( E_2 \) where electron transfer is rapid (Linear sweep) and back to \( E_1 \) (Cyclic voltammetry)
• Applied potential \( (E) \) is function of sweep rate i.e. rate of potential change with time

\[
E(t) = E_1 - \nu t
\]

*Fig. 3.2* The potential sweep (a) and corresponding current response (b) for an irreversible electron transfer reaction.
• As potential is swept to from \( E_1 \) where no reaction occur (irreversible) no current passes
• As potential is swept to more reducing potential it **induces** reduction of O to R and current start to pass
• Current increases exponentially with potential or time as B-V equation suggests!
• As potential is made more negative current starts to fall off and maximum is reached
• \([O]\) at surface decreases as reaction rate increases at high negative potentials
• Diffusion of O from bulk solution is not able to balance its consumption at electrode surface at high rate
• The peak reflects a balance between the rate electron transfer reaction and rate of O diffusion towards electrode surface

• Maximum current is called peak current \((i_p)\) indicating a diffusion controlled reaction

• Thickness of diffusion layer becomes thicker and O has to cross longer distance to electrode surface
• Shape of voltammogram depends on electrode reversibility
• For irreversible reaction peak current appear at more negative potential than that of reversible reaction i.e. high over-potential

Fig. 3.3 Linear sweep voltammogram for (a) a reversible electron transfer and (b) an irreversible electrode reaction.
reversible vs. irreversible

- Peak potential $E_p$ is constant and independent of sweep rate
- $|E_p - E_{p/2}| = 2.20 \text{ RT/F}$
- Peak current is higher

$$|i_p| = 0.4663^{3/2} A F D_o^{1/2} \nu^{1/2} [O]_{bulk} \left(\frac{F}{RT}\right)^{1/2}$$

- $E_p$ shifts to more negative potentials at faster sweep rates
- $E_p$ shift by approx. 1.16 RT/$\alpha F$ for each factor of 10
- $|E_p - E_{p/2}| = 1.86 \text{ RT/ } \alpha F$

$$|i_p| = 2.99 \times 10^5 \alpha^{1/2} A D_o^{1/2} \nu^{1/2} [O]_{bulk}$$
reversible vs. irreversible, continued

- $k_a$ and $k_c$ are large near $E_{eq}$. Concentration of $O$ and $R$ at electrode surface are predicted from Nernst eq.

- Kinetics of backward reaction is negligible

For both types peak current is directly proportional to [O] and sweep rate
CV of reversible systems

- In that case potential is reversed when reaching $E_2$ and swept back to $E_1$
- this gives one cycle

Fig. 3.5 Variation of the applied potential as a function of time in a cyclic voltammetry experiment.

Fig. 3.6 Cyclic voltammogram for a reversible electron transfer reaction.
• The shape of voltammogram looks like that of linear sweep voltammetry.

• When reaching $E_2$ and reversing sweep and depending on system reversibility, R formed in forward sweep can be oxidized back to O.

• Current in reverse sweep increases initially because [R] in diffusion layer is high.

• Kinetics of $R \rightarrow O + e$ reaction becomes faster as potential is swept in positive direction.
• R in diffusion layer is converted to O and its concentration drops to zero
• Current peak appear in reverse sweep indicating reversibility of O/R system
• The concentration profile of O and R at electrode surface under non-steady state diffusion is shown in the following figure
Change of O and R concentration with distance of electrode surface during the backward sweep and specific potentials before and after peak.
Fig. 6.5 – Cyclic voltammograms for a reversible process, \( O + e^- \rightleftharpoons R \) when only \( O \) is initially present in solution. The potential sweep rates are (a) \( \nu \), (b) \( 10\nu \), (c) \( 50\nu \), and (d) \( 100\nu \).
Diagnostic test for reversibility

- $\Delta E_p = E_p^a - E_p^c = 59/n \text{ mV}$
- $|E_p - E_{p/2}| = 59/n \text{ mV}$
- $|I_p^a / I_p^c| = 1$
- $I_p \propto \nu^{1/2}$
- $E_p$ is independent of $\nu$
CV of irreversible systems

• In case of irreversible electrode reaction, the rate of electron transfer is insufficient to maintain the Nernstian equilibrium

• Shape of CV in that case is different from that for reversible system

• At low sweep rate system behaves reversibly because rate of ET is higher than MT and reversible CV is obtained

• As sweep rate increased rate of MT ≈ ET and peak separation becomes noticable
• In case of totally irreversible reaction, reverse peak is absent in reverse sweep

Fig. 6.6 — Simulated cyclic voltammograms for reaction $O + e^{-} \rightleftharpoons R$ when $D = 10^{-5}$ cm s$^{-1}$ and $\kappa^{\Theta} = 10^{-2}$ cm s$^{-1}$. Only O initially present in solution. Potential sweep rates (a) 0.13 V s$^{-1}$, (b) 1.3 V s$^{-1}$, (c) 4 V s$^{-1}$, (d) 13 V s$^{-1}$. 
• Change of electrode reaction behavior from reversible to irreversible at higher sweep rates can be seen in the plot of $I_p$ vs. $\sqrt{\nu}$
Diagnostic test for irreversibility

- No reverse peak
- $I^c_p \propto \nu^{1/2}$
- $E^c_p$ shifts by $-30/\alpha_c n_\alpha$ mV for each decade increase in $\nu$
- $|E_p - E_{p/2}| = 48/\alpha_c n_\alpha$ mV
Adsorption

• Formation of some type of bond between adsorbate and electrode surface

• Interaction may be due to:
  – Electrostatic interaction, where cations or anions are attracted to surface with opposite charge
  – Charge dipole interaction like adsorption of amines, thiourea
  – Or due to covalent bond formation
• According to type of adsorption, variation in bond strength, reversibility of adsorption may be seen

• Adsorption affect to great extent electrode’s reaction as it assumed that intermediate(s) formed in reaction is adsorbed on surface

• Extent of adsorption is measured by surface coverage ($\theta$)

• $\theta$ is the fraction of surface covered by adsorbate
• Many factors control the value of $\theta$ such as solvent type, electrolyte, adsorbate structure and concentration

• Nature of electrode surface is an important factor in adsorption

• Electrode potential plays an important role as it controls surface charge where some adsorbate may be adsorbed
• Coverage of surface is quantitatively described by an isotherm.

• The simplest isotherm is Langmuir isotherm which assume that:
  – the free energy of adsorption is independent of coverage
  – No lateral interactions between adsorbates
  – Active sites on surface are equal

\[
\frac{\theta}{1-\theta} = C \exp\left(-\frac{\Delta G^o_{ads}}{RT}\right)
\]
• An excellent example to show the importance of adsorption is the reduction of protons on Pt electrode

• CV of Pt in sulfuric acid solution shows two pairs of peaks on the forward and backward sweeps correlated to adsorption and desorption of H at different sites on surface.

• The two peaks are for strong and weak adsorptions

• Adsorption and desorption processes result in current (non-faradic current)
Fig. 6.22 – Cyclic voltammogram for a Pt electrode in 1 mol dm$^{-3}$ H$_2$SO$_4$ at a potential sweep rate of 42 Vs$^{-1}$ showing the hydrogen adsorption and desorption peaks.
Hydrogen evolution reaction (HER)

• Historically important reactions
  – HOR for PEM FC
  – HOR in water electrolysis, chlor-alkali cell, anodic electrosynthesis
  – HER and HOR wanted or not wanted, that depends on the application!
  – The surface where the reaction takes place plays the main role (electro-catalysis)
HER in acid medium

Two possible mechanisms are considered with H as an adsorbed intermediate

(I)

\[ \text{M} + \text{H}^+ + \text{e} \rightarrow \text{M-H} \quad (A) \]
\[ 2\text{M-H} \rightarrow \text{H}_2 + 2\text{M} \quad (B) \]

(II)

\[ \text{M} + \text{H}^+ + \text{e} \rightarrow \text{M-H} \quad (A) \]
\[ \text{M-H} + \text{H}^+ + \text{e} \rightarrow \text{H}_2 + 2\text{M} \quad (C) \]
- HER has different rates on different metals

<table>
<thead>
<tr>
<th>Metal</th>
<th>Log $i_o$, mA cm$^{-2}$</th>
<th>Tafel slope, mV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>-3.4</td>
<td>120</td>
</tr>
<tr>
<td>Au</td>
<td>-2.7</td>
<td>120</td>
</tr>
<tr>
<td>Cd</td>
<td>-9.0</td>
<td>120</td>
</tr>
<tr>
<td>Pb</td>
<td>-9.6</td>
<td>120</td>
</tr>
<tr>
<td>Pd</td>
<td>+0.6</td>
<td>40</td>
</tr>
<tr>
<td>Pt</td>
<td>-0.3</td>
<td>30</td>
</tr>
<tr>
<td>Rh</td>
<td>+0.5</td>
<td>60</td>
</tr>
<tr>
<td>W</td>
<td>-3.4</td>
<td>60</td>
</tr>
</tbody>
</table>
• $H_{ads}$ which is the intermediate has important role in the kinetics and mechanism of HER
• Due to H adsorption the free energy of e-transfer change by an amount equal to bond energy between H atom and surface
• CV can be used to detect H adsorption on different metals, where difference can be seen
• One of the steps in previous mechanism is the rate determining step (RDS)
• Adsorption and desorption can be seen to take place in the mechanism
• Surface concentration of H depending on $\Delta G^o_{ads}$
• Correlation between $I_o$ and $\Delta G^o_{ads}$ was observed known as “volcano plot”
• One example is shown for HER
• The enhancement of HER is called “electro-catalysis”
Fig. 2. Experimental “volcano”-shaped curve for hydrogen generation on metals. From ref. 54, by permission of Elsevier Sequoia.
Kinetic parameters obtained from Tafel equation for HER at 25°C

<table>
<thead>
<tr>
<th>Cathode</th>
<th>Electrolyte</th>
<th>Tafel line parameters (V)</th>
<th>RDS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>a</td>
<td>b</td>
</tr>
<tr>
<td>Hg</td>
<td>0.1M HCl</td>
<td>1.41 (6.64x10^{-12})</td>
<td>0.115 (.51)</td>
</tr>
<tr>
<td>Pt</td>
<td>1 M HCl</td>
<td>0.09 (1.15x10^{-4})</td>
<td>0.03 (0.5)</td>
</tr>
</tbody>
</table>
Table 5.5 Constants \(a\) and \(b\) of the Tafel equation and the probable mechanism of the hydrogen evolution reaction at various electrodes with \(\text{H}_2\text{O}^+\) as electroactive species \((a_{\text{H}_2\text{O}^+} = 1)\). (According to L. I. Krishtalik)

<table>
<thead>
<tr>
<th>Cathode material</th>
<th>(-a)</th>
<th>(b)</th>
<th>Mechanism</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>1.52-1.56</td>
<td>0.11-0.12</td>
<td>I(s),III</td>
</tr>
<tr>
<td>Tl</td>
<td>1.55</td>
<td>0.14</td>
<td>I(s),III</td>
</tr>
<tr>
<td>Hg</td>
<td>1.415</td>
<td>0.116</td>
<td>I(s),III</td>
</tr>
<tr>
<td>Cd</td>
<td>1.40-1.45</td>
<td>0.12-0.13</td>
<td>I(s),III</td>
</tr>
<tr>
<td>In</td>
<td>1.33-1.36</td>
<td>0.12-0.14</td>
<td>I(s),III</td>
</tr>
<tr>
<td>Sn</td>
<td>1.25</td>
<td>0.12</td>
<td>I(s),III</td>
</tr>
<tr>
<td>Zn</td>
<td>1.24</td>
<td>1.12</td>
<td>I(s),III</td>
</tr>
<tr>
<td>Bi</td>
<td>1.1</td>
<td>0.11</td>
<td>I(s),III</td>
</tr>
<tr>
<td>Ga (l)</td>
<td>1.05</td>
<td>0.11</td>
<td>I(s),III</td>
</tr>
<tr>
<td></td>
<td>(s)</td>
<td>0.90</td>
<td>I(s),III</td>
</tr>
<tr>
<td>Ag</td>
<td>0.95</td>
<td>0.12</td>
<td>I(s),III</td>
</tr>
<tr>
<td>Au</td>
<td>0.65-0.71</td>
<td>0.10-0.14</td>
<td>I(s),III</td>
</tr>
<tr>
<td>Cu</td>
<td>0.77-0.82</td>
<td>0.10-0.12</td>
<td>I(s),III</td>
</tr>
<tr>
<td>Fe</td>
<td>0.66-0.72</td>
<td>0.12-0.13</td>
<td>I(s),III</td>
</tr>
<tr>
<td>Co</td>
<td>0.67</td>
<td>0.15</td>
<td>I(s),III</td>
</tr>
<tr>
<td>Ni</td>
<td>0.55-0.72</td>
<td>0.10-0.14</td>
<td>I(s),III</td>
</tr>
<tr>
<td>Pt (anodically activated)</td>
<td>0.05-0.10</td>
<td>0.03</td>
<td>I,II(s)</td>
</tr>
<tr>
<td>(large (j))</td>
<td>0.25-0.35</td>
<td>0.10-0.14</td>
<td>I,III(s)</td>
</tr>
<tr>
<td>(poisoned)</td>
<td>0.47-0.72</td>
<td>0.12-0.13</td>
<td>I(s),?</td>
</tr>
<tr>
<td>Rh (anodically activated)</td>
<td>0.05-0.10</td>
<td>0.03</td>
<td>I,II(s)</td>
</tr>
<tr>
<td>Ir (anodically activated)</td>
<td>0.05-0.10</td>
<td>0.03</td>
<td>I,II(s)</td>
</tr>
<tr>
<td>Re</td>
<td>0.15-0.21</td>
<td>0.03-0.04</td>
<td>I,II(s)</td>
</tr>
<tr>
<td>W</td>
<td>0.58-0.70</td>
<td>0.10-0.12</td>
<td>I,III(s)</td>
</tr>
<tr>
<td>Mo</td>
<td>0.58-0.68</td>
<td>0.10</td>
<td>I,III(s)</td>
</tr>
<tr>
<td>Nb (unsaturated with H)</td>
<td>0.92</td>
<td>0.11</td>
<td>I,III(s)</td>
</tr>
<tr>
<td>(saturated with H)</td>
<td>0.78</td>
<td>0.11</td>
<td>I,III(s)</td>
</tr>
<tr>
<td>Ta (unsaturated with H)</td>
<td>1.2</td>
<td>0.19</td>
<td>I,III(s)</td>
</tr>
<tr>
<td>(saturated with H)</td>
<td>1.04</td>
<td>0.15</td>
<td>I,III(s)</td>
</tr>
<tr>
<td>Ti</td>
<td>0.82-1.01</td>
<td>0.12-0.018</td>
<td>I,III(s)</td>
</tr>
</tbody>
</table>

I indicates the Volmer mechanism (Eq. 5.7.1), II the Tafel mechanism (Eq. 5.7.2) and III the Heyrovský mechanism (Eq. 5.7.3). The slowest step of the overall process is denoted (s).
6.5: o-dianisidine is oxidized in a 2 e nernstian reaction. If the solution contain 2.27 mM of the compound in 2M sulfuric acid at carbon paste electrode with an area of 2.73 mm², then calculate the diffusion coefficient if $i_p$ was 8.19 uA at sweep rate of 0.5V/s
What would be $i_p$ at sweep rate of 0.1V/s?
Can you suggest what is the product after oxidation?
6.9: Azotoluene is reduced in two steps with 2 e involved. The following table shows the data obtained from cyclic voltammetry for the two peaks. Use the data to discuss the reversibility of the two steps in reduction reaction and the stability of products.

Draw the cyclic voltammogram of the first peak as data in table suggest.

<table>
<thead>
<tr>
<th>Scan rate(mV/s)</th>
<th>First wave</th>
<th></th>
<th>Second wave</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$I_{pc}$ (μA)</td>
<td>$I_{pa}$ (μA)</td>
<td>$-E_{pc}$ (V vs. SCE)</td>
</tr>
<tr>
<td>430</td>
<td>8.0</td>
<td>8.0</td>
<td>1.42</td>
</tr>
<tr>
<td>298</td>
<td>6.7</td>
<td>6.7</td>
<td>1.42</td>
</tr>
<tr>
<td>203</td>
<td>5.2</td>
<td>5.2</td>
<td>1.42</td>
</tr>
<tr>
<td>91</td>
<td>3.4</td>
<td>3.4</td>
<td>1.42</td>
</tr>
<tr>
<td>73</td>
<td>3.0</td>
<td>2.9</td>
<td>1.42</td>
</tr>
</tbody>
</table>