Introduction to voltammetry using CV Sim

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Objectives

Understand what is performed during a voltammetry experiment.

Understand what information can be obtained on the studied electrochemical system.

Simplest case: The redox reaction (E)

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

Example: \([\text{Fe(CN)}_6]^{3-} + e^- \leftrightarrow [\text{Fe(CN)}_6]^{4-}\]

A≡O and B≡R

other reactions (EE), (EC), (CE) not presented here
1. **Study by linear voltammetry**
   1. Influence of the scan rate
      1. Reversible reaction, high $k^\circ$
      2. Irreversible reaction, low $k^\circ$
   2. The double layer capacitance and the ohmic drop

2. **Study by cyclic voltammetry**
   1. Influence of the first vertex
   2. Influence of the $k^\circ$
   3. Influence of the number of scan
   4. Influence of the scan rate
Two types of voltammetry

**Linear**

**Cyclic**

\[ E(t) \xrightarrow{} \text{Electrochemical system} \xrightarrow{} I(t) \]
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Influence of the scan rate

Experimental conditions
Only A in solution, support electrolyte, unstirred solution, no ohmic drop, negligible double layer capacitance current.
The CVSim tool in EC-Lab® is used to simulate an $I$ vs. $E$ curve corresponding to a redox reaction.
We define the peak current $I_p$ and the potential at which the peak current is reached $E_p$. $C_A \neq 0$ at $E_p$.

During the potential sweep, $C_A$ decreases and approaches 0 after $E_p$. $E^\circ = 0.2$ V
Outline

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Influence of the scan rate

**Which information can we get?**

**Limit case #1: Reversible reaction, high reaction standard constant $k^*$**

$k^*$ = 10 cm s$^{-1}$  
$A = 0.03142$ cm$^2$  
$C_A^* = 10^{-5}$ mol cm$^{-3}$

Red curve: 10 V s$^{-1}$
Green curve: 40 V s$^{-1}$
Purple curve: 160 V s$^{-1}$
Pink curve: 640 V s$^{-1}$
Blue curve: 2560 V s$^{-1}$

If the scan rate $v$ is 4 times larger, $I_p$ is $\sqrt{4}$ times larger.
For high $k^*$, $I_p$ is dependent on the scan rate but $E_p$ is not.
Influence of the scan rate

Which information can we get?

Limit case #1: Reversible reaction, high $k^o$

$I_p$ vs Scan rate

$I_p$ is proportional to the square root of the scan rate.

$I_p$ is proportional to the square root of the scan rate.
Influence of the scan rate

Which information can we get?

Limit case #1: Reversible reaction, high $k^o$

Knowing all the other parameters we can recalculate

$$ M = \frac{I_p}{AnFC_A^* \sqrt{nfvD_A}} $$

<table>
<thead>
<tr>
<th>$v$ (V/s)</th>
<th>M</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.4461</td>
</tr>
<tr>
<td>40</td>
<td>0.4458</td>
</tr>
<tr>
<td>160</td>
<td>0.4453</td>
</tr>
<tr>
<td>640</td>
<td>0.4441</td>
</tr>
<tr>
<td>2560</td>
<td>0.4420</td>
</tr>
</tbody>
</table>

As the scan rate increases, the factor M goes further away from 0.446.

The system becomes less and less reversible (more and more irreversible).

It shows that

$$ I_p = -0.446AnFC_A^* \sqrt{nfvD_A}; f = F/(RT) $$
Influence of the scan rate

Which information can we get?

Limit case #1: Reversible reaction, high $k^o$

$$E_p \text{ vs Scan rate}$$

$$E_p = E^o - \frac{1}{2nf} \ln \frac{D_A}{D_B} - \frac{1.109}{nf}$$

$$E_p = E^o - \frac{1.109}{nf}; D_A = D_B$$

$E_p$ can be used to determine the standard potential of the redox couple A/B.

If $E_p$ does not change with $v$, it means it is a reversible redox reaction, then $k^o$ cannot be determined.
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Influence of the scan rate

Which information can we get?

Limit case #1: Irreversible reaction, low $k^o$

$k^o = 10^{-3}$ cm s$^{-1}$

$A = 0.03142$ cm$^2$

$C_A^* = 10^{-5}$ mol cm$^{-3}$

Red curve: 10 V/s
Green curve: 40 V/s
Purple curve: 160 V/s
Pink curve: 640 V/s
Blue curve: 2560 V/s

$I_p$ and $E_p$ depend on the scan rate:
the higher the scan rate, the higher $|I_p|$ and the lower $E_p$.

What can we measure from this dependence?
Influence of the scan rate

Which information can we get?

Limit case #1: Irreversible reaction, low $k^o$

The peak current $I_p$ is proportional to the square root of the scan rate.

$$I_p = -0.496AnFC_A^*\sqrt{\alpha_rnfvD_A}; f = F/(RT)$$

The slope above can be used to determine the diffusion coefficient $D_A$ or the symmetry factor $\alpha_r$. 

Linear Voltammetry
Influence of the scan rate

Which information can we get?

Limit case #1: Irreversible reaction, low $k^\circ$

The dependence of $E_p$ with $v$ can be used to determine $\alpha_r$ and $k^\circ$. 

$$E_p = E^\circ + \frac{1}{\alpha_r n f} - (0.78 + \ln \frac{k^\circ}{\sqrt{\alpha_r n f v D_A}})$$

Graph showing the relationship between $E_p$ and $\log(v)$ with the equation $y = -0.0557x + 0.0201$, $R^2 = 0.9968$. 

Linear Voltammetry
To investigate a redox system in the standard condition, one can make several CV's with different scan rates \( v \) :

- if \( E_p \) is invariant and \( I_p \) is proportional to \( v^{1/2} \) → reversible behaviour (high \( k^o \)). Possible measurements: diffusion coefficient \( D_A \) and the standard potential \( E^o \) of the reaction.
- if \( E_p \) varies with \( \log(v) \) and \( I_p \) is proportional to \( v^{1/2} \) → irreversible behaviour (low \( k^o \)).

Possible measurements: the symmetry factor \( \alpha_r \) and the standard constant \( k^o \) of the reaction.

Whichever the value of \( k^o \), it is possible to shift from an reversible to a irreversible behaviour by increasing the potential scan rate.

In reality there is an ohmic drop and the double layer capacitance current is not negligible. They must be taken into account, which is possible with CVSim.
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For a « random » \( k^\circ, \nu = 10 \text{ V/s} \)

\[
I_{\text{total}} = I_c + I_f
\]

(with CV Sim the two contributions can be separated)

\[
I_c = C_{dl} \frac{dE(t)}{dt} = -C_{dl} \nu
\]

For a constant scan rate the capacitive current is also constant.
For a « random » \( k^\circ \), \( \nu = 1000 \text{ V/s} \)

\[ I_{\text{total}} = I_c + I_f \]

\[ I_c = C_{\text{dl}} \left( \frac{dE(t)}{dt} \right) = -C_{\text{dl}} \nu \]

For a high scan rate, the value of the capacitive current \( I_c \) can be higher than the faradaic current \( I_f \) and cannot be neglected.
The actual potential seen by the electrode is not linear. 
\( E(t) = vt + RI(t) \). The ohmic drop leads to a shift of \( I_p \) and \( E_p \).
The potential shift is due to the term \(-RI\).
For a « random » $k^\circ$, $\nu = 10$ V/s

\[ I_c(t) = C_{dl}(dE(t)/dt) \]

Because of the ohmic drop $dE(t)/dt = \nu - R_\Omega dl(t)/dt$, $I_c(t)$ is not constant even if the scan rate is constant.

\[ I_{\text{total}} = I_c + I_f \]
For a negligible faradaic current i.e. at short times, the system is equivalent to an $R+C$ electrical circuit.

\[ I_c = -C_{dl} \nu \quad \text{(for } t > 0.01 \text{ s)} \]

\[ \tau = R_\Omega C_{dl} \]

A time constant, $R_\Omega C_{dl}$ can be measured at short times.
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Cyclic Voltammetry

$E$ vs. $t$

$E_{\text{init}}$

Vertex 1

Vertex 2
Cyclic Voltammetry

$E_{p \text{ox}}, I_{p \text{ox}}$

$E_{p \text{red}}, I_{p \text{red}}$

$E_{\text{init}}$

Oxidation

Reduction

Vertex 1

Vertex 2

CVsim.mpr
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Influence of the first vertex

Vertices: -0.3 V  0 V  0.1 V

Reversible system ($k^\circ = 10 \text{ cm}^2 \text{s}^{-1}$)

$I_{p,ox}$ and to a smaller extent $E_{p,ox}$ depend on the value of the Vertex 1. The correct vertex value is the one after which $I_{p,ox}$ and $E_{p,ox}$ do not vary.
For a vertex 1 of -0.3 V, the difference $\Delta E_p$ is equal to 57.7 mV. It was calculated that for a vertex 1 of $-\infty$, this difference is 57 mV. It can be considered that -0.3 V is a sufficiently low vertex 1 potential.

1. A. J. Bard, L. R. Faulkner, Electrochemical Methods, Wiley, p. 242
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Influence of $k^o$

$k^o = 10 \text{ cm/s}$

$k^o = 0.001 \text{ cm/s}$

The peak difference increases as the value of $k^o$ decreases. The red curve is characteristic of an irreversible system.
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When the scan number increases, reduction $|I_p|$ decreases and oxidation $|I_p|$ increases to reach a limit value. It is due to the fact that after one scan the initial conditions are not recovered: there is less A and more B.
Influence of the number of scan

**Reversible system** \((k^\circ = 10 \text{ cm}^2 \text{s}^{-1})\)

For each cycle (1 reduction and 1 oxidation scans) there are more A species reduced into B than produced by the oxidation of B. The integral function available in EC-Lab allows to calculate the charge involved in the reduction scan and the oxidation scan.

-6.2 µC

( obtained using Peak Analysis and integral calculation in EC-Lab®)

3.5 µC and increasing
If vertex 2 is more positive (0.7 V compared to 0.5 V), more B are oxidized in A and the value $I_{p,ox}$ shows little variation from one scan to another.
Influence of the number of scan

Reversible system \((k^\circ = 10 \text{ cm}^2 \text{s}^{-1})\)

The evolution of the interfacial concentration \(C_A\) does not vary from one cycle to another because the chosen reaction constant is characteristic of a Nernstian system. Consequently:

\[
E(t) = E^\circ + \frac{RT}{F} \ln \frac{A(0,t)}{B(0,t)}
\]

with \(D_A = D_B, A(0,t) + B(0,t) = A^*\)

Whatever the cycle number, to any \(E(t)\) corresponds one ratio \(A(0,t)/B(0,t)\) and \(E(t)\) does not vary from one cycle to another.
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Increasing the scan rate leads to an increase of $I_p$ and $E_p$ but all scans intersect at a specific point.

If all the curves were divided by $(v)^{\frac{1}{2}}$, they would all look the same.
• The magnitude of the oxidation peak depends on the value of the potential of the first vertex.

• The difference between the two peak potentials depends on the potential of first vertex and also on the value of $k^\circ$ of the reaction.

• As the number of scans increases, the oxidation peak current decreases due to the fact that the reverse reaction is less complete than the forward reaction.

• Choosing a sufficiently high potential of second vertex makes the reverse reaction more complete.

• Increasing the scan rate has the same effect as with a linear scan. All the curves intersect at $I=0$ on the reverse scan.
To be continued...