

Introduction to voltammetry using CV Sim

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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)



other reactions (EE), (EC), (CE) not presented here

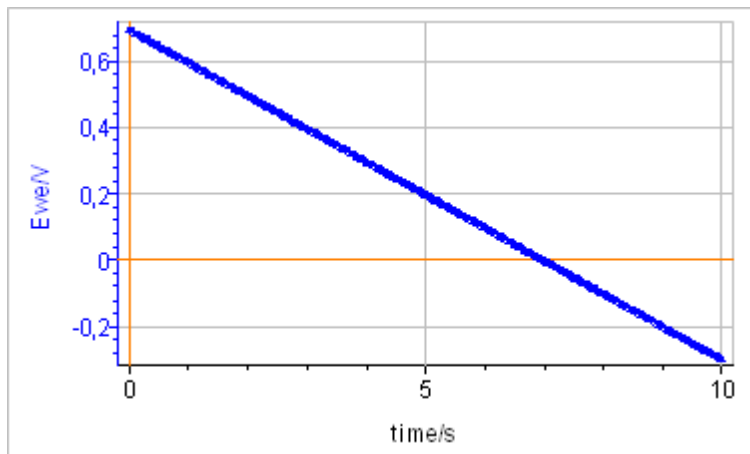
1. Study by linear voltammetry

1. Influence of the scan rate
 1. Reversible reaction, high k°
 2. Irreversible reaction, low k°
2. The double layer capacitance and the ohmic drop

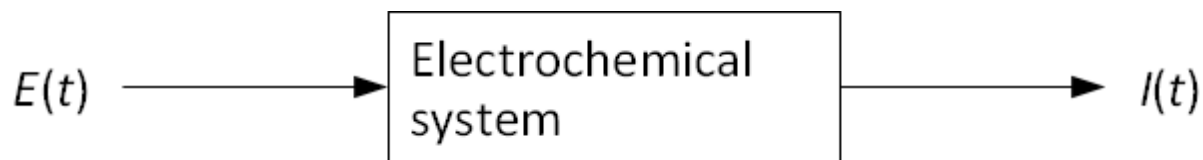
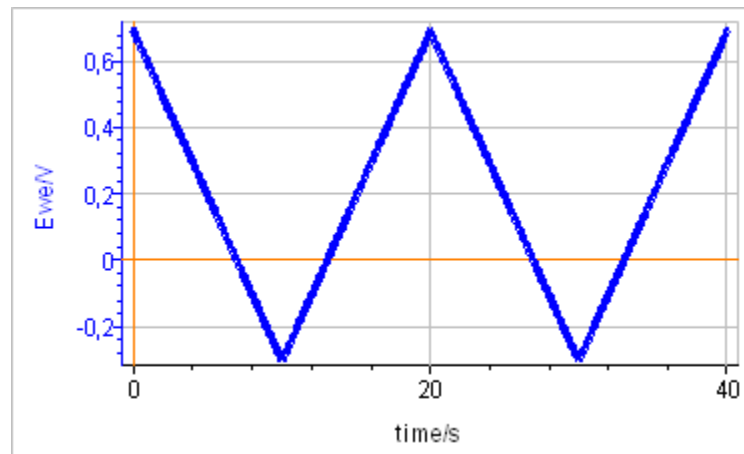
2. Study by cyclic voltammetry

1. Influence of the first vertex
2. Influence of the k°
3. Influence of the number of scan
4. Influence of the scan rate

Linear



Cyclic



1. Study by linear voltammetry

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2. Study by cyclic voltammetry

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4. 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.

CV Sim

Example

Mechanism E

E Setup

Reaction

Reduction $A + z e \leftrightarrow B$

z 1

E^0 0,2 V

k^0 0,001 cm/s

αf 0,5

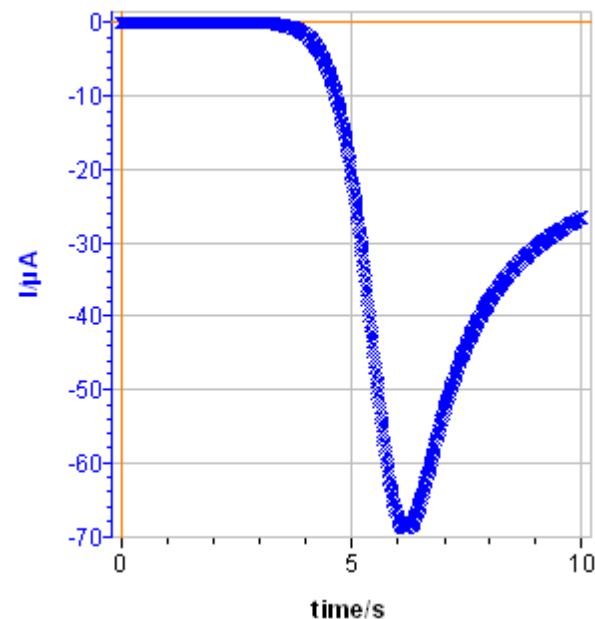
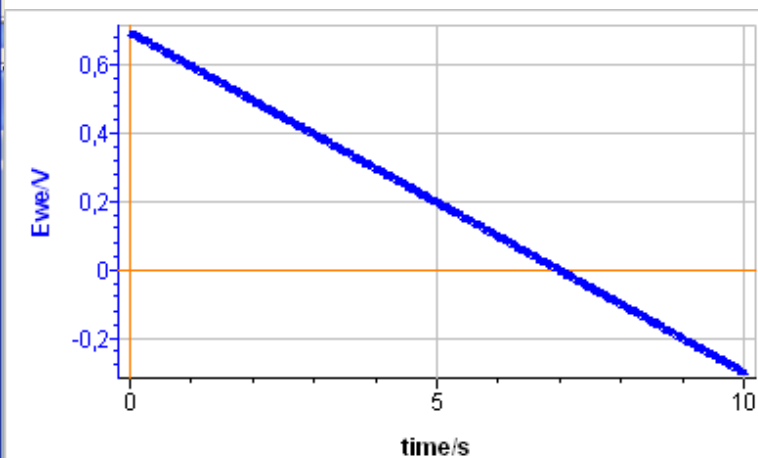
Species

C_A initial 1e-2 mol/L

C_B initial 0 mol/L

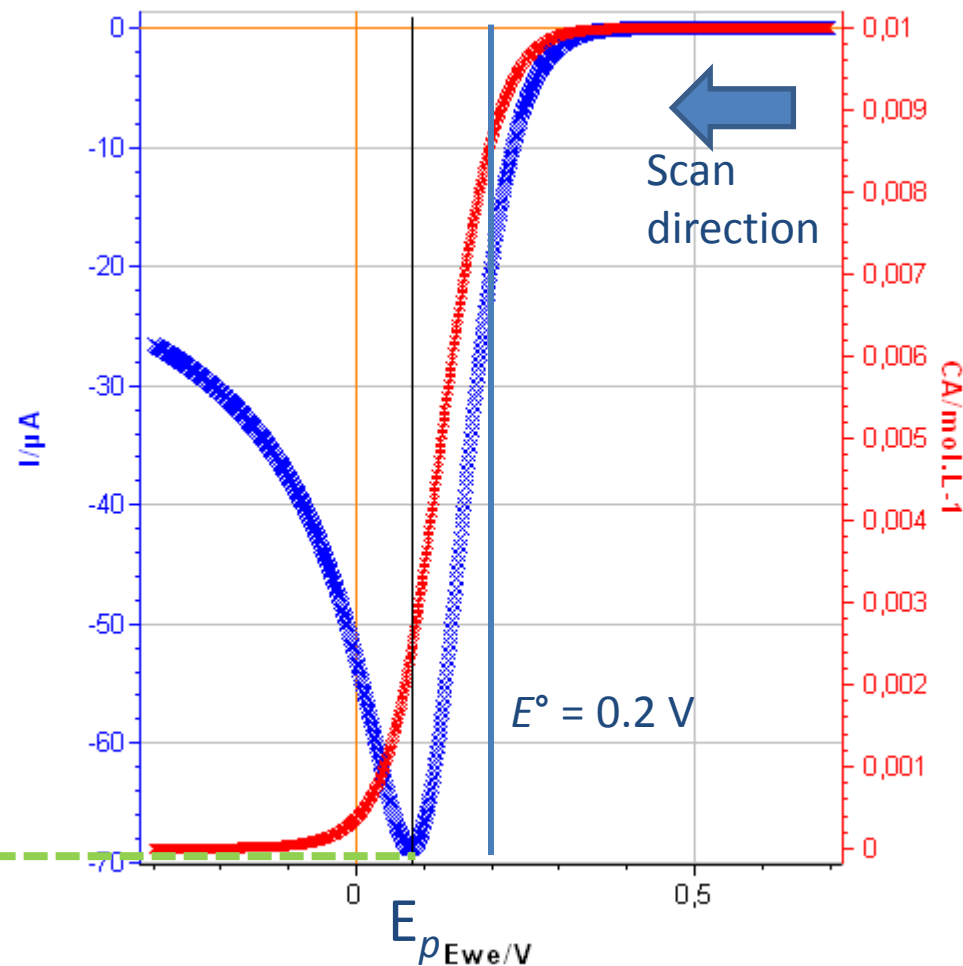
D_A 1e-5 cm²/s

D_B 5e-6 cm²/s



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 .

Peak current: I_p



During the potential sweep, C_A decreases and approaches 0 after E_p .

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Which information can we get ?

Limit case #1: Reversible reaction, high reaction standard constant k^0

$$k^0 = 10 \text{ cm s}^{-1}$$

$$A = 0.03142 \text{ cm}^2$$

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

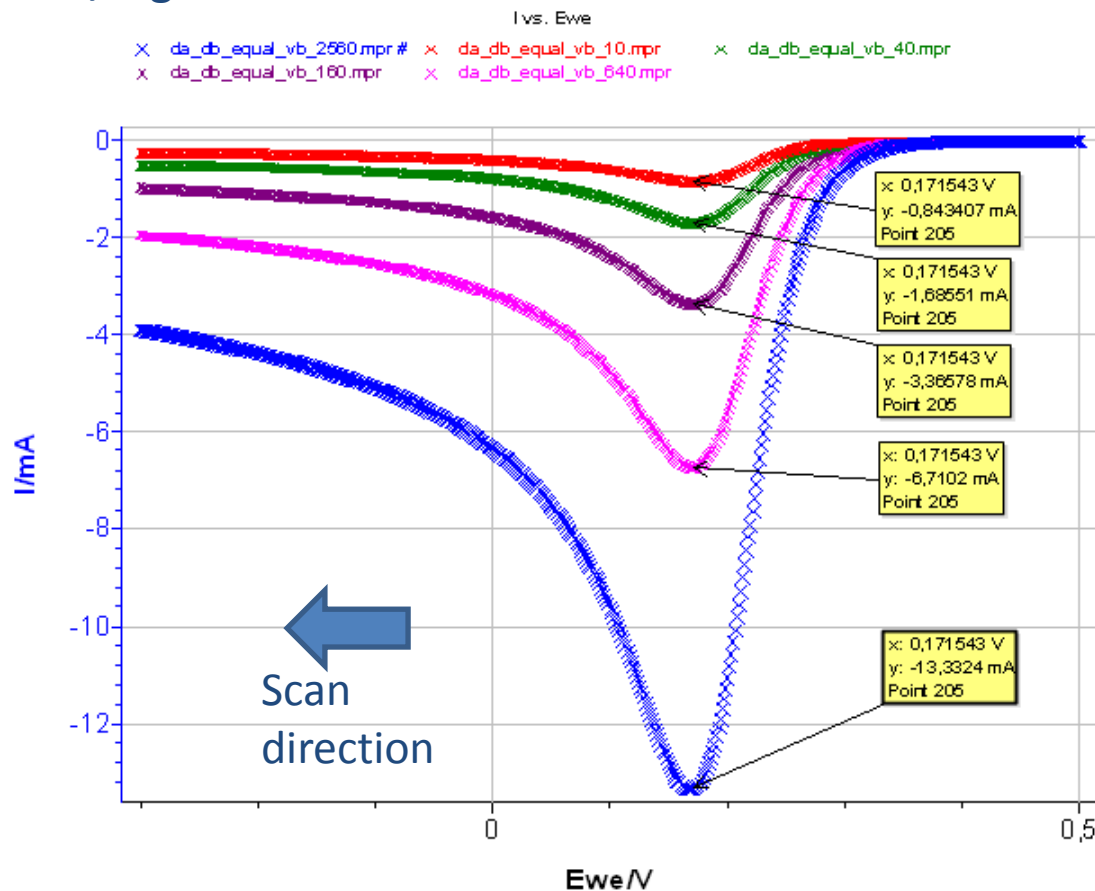
Red curve : 10 V s^{-1}

Green curve : 40 V s^{-1}

Purple curve : 160 V s^{-1}

Pink curve : 640 V s^{-1}

Blue curve : 2560 V s^{-1}



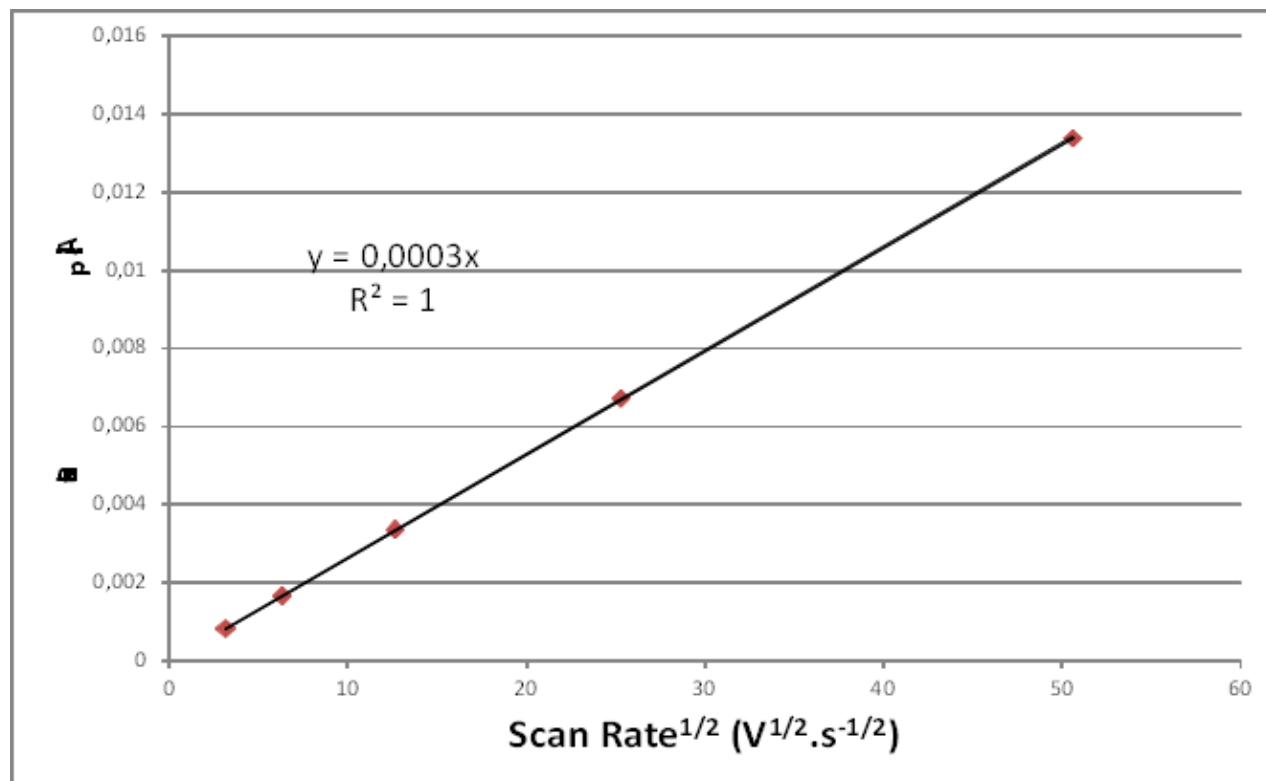
If the scan rate ν is 4 times larger, I_p is $\sqrt{4}$ times larger.
 For high k^0 , I_p is dependent on the scan rate but E_p is not.

Which information can we get ?

Limit case #1: Reversible reaction, high k^0

I_p vs Scan rate

I_p (A)



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

Which information can we get ?

Limit case #1: Reversible reaction, high k^0

Knowing all the other parameters we can recalculate

$$M = \frac{I_p}{AnFC_A^* \sqrt{nf\nu D_A}}$$

ν (V/s) M

10 0.4461

40 0.4458

160 0.4453

640 0.4441

2560 0.4420

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 $I_p = -0.446AnFC_A^* \sqrt{nf\nu D_A}; f = F/(RT)$

Which information can we get ?

Limit case #1: Reversible reaction, high k°

E_p vs Scan rate

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

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

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° cannot be determined.

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Which information can we get ?

Limit case #1: Irreversible reaction, low k^0

$$k^0 = 10^{-3} \text{ cm s}^{-1}$$

$$A = 0.03142 \text{ cm}^2$$

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

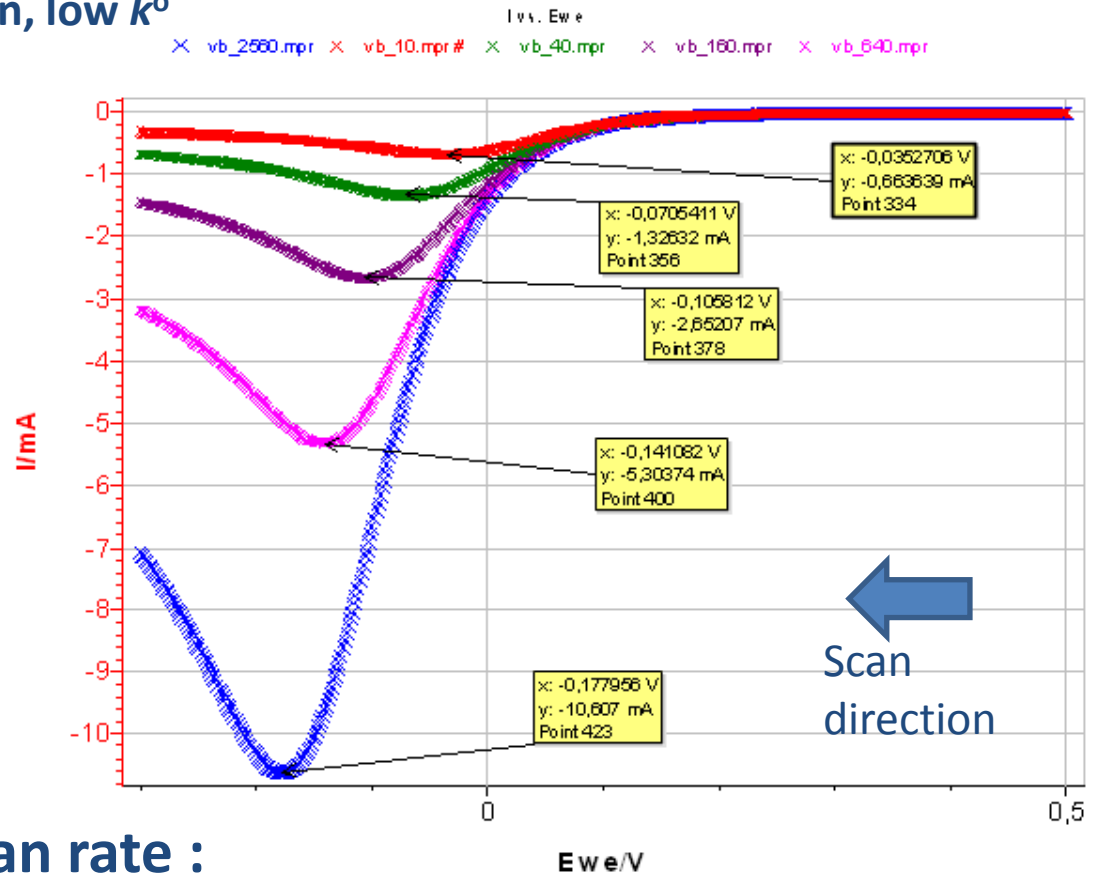
Red curve : 10 V/s

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I_p and E_p depend on the scan rate :

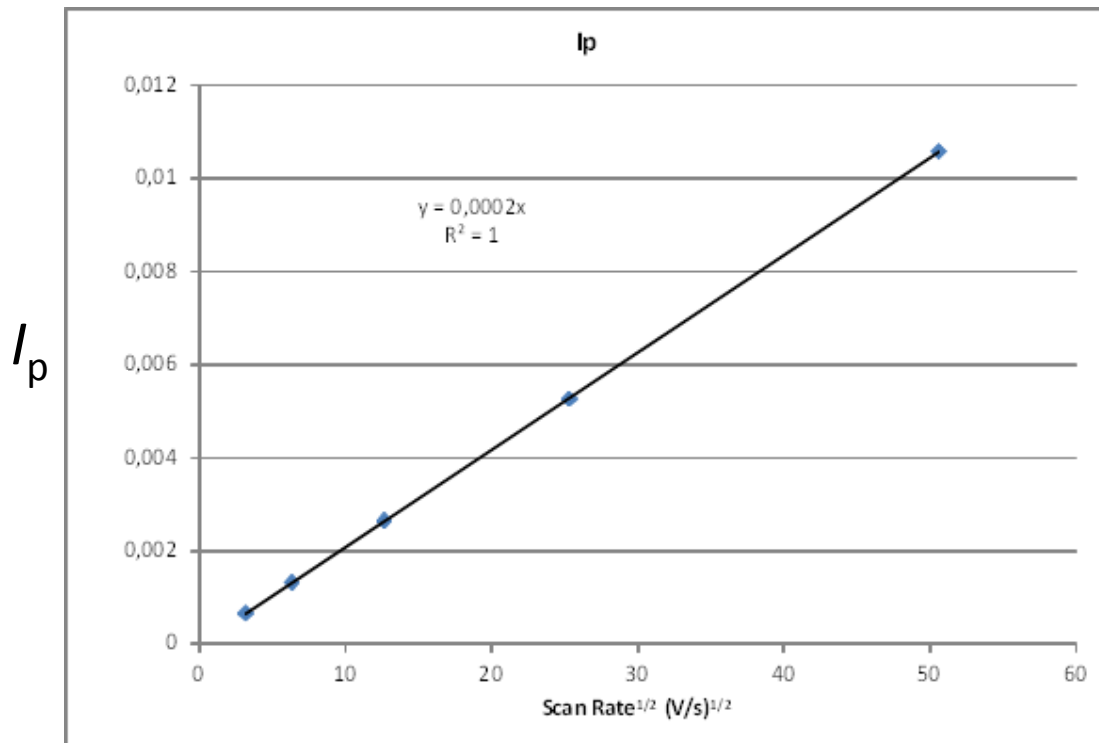
the higher the scan rate, the higher $|I_p|$ and the lower E_p .

What can we measure from this dependence ?

Which information can we get ?

Limit case #1: Irreversible reaction, low k^0

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

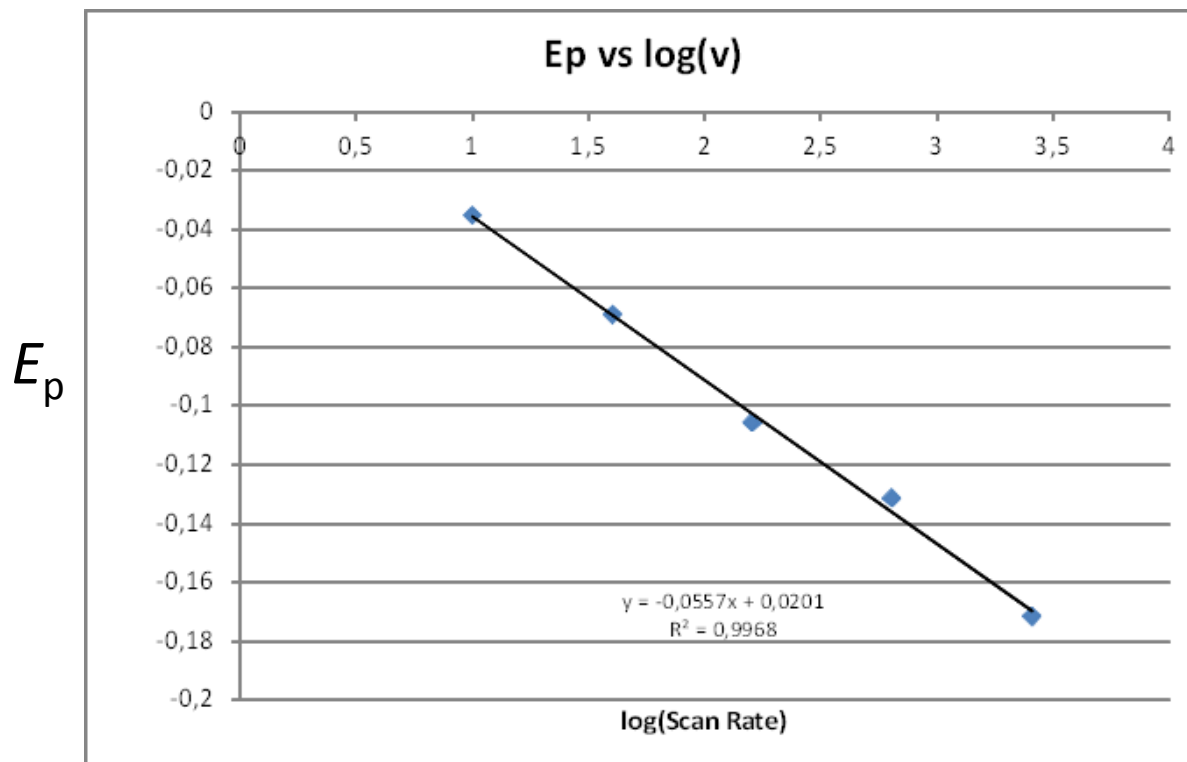


$$I_p = -0.496AnFC_A^* \sqrt{\alpha_r n f v D_A}; f = F/(RT)$$

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

Which information can we get ?

Limit case #1: Irreversible reaction, low k°



$$E_p = E^\circ + \frac{1}{\alpha_r n f} - \left(0,78 + \ln \frac{k^\circ}{\sqrt{\alpha_r} n f v D_A} \right)$$

The dependence of E_p with v can be used to determine α_r and k° .

To investigate a redox system in the standard condition, one can make several CV's with different scan rates ν :

- if E_p is invariant and I_p is proportional to $\nu^{1/2}$ → reversible behaviour (high k^0). Possible measurements : diffusion coefficient D_A and the standard potential E^0 of the reaction.
- if E_p varies with $\log(\nu)$ and I_p is proportional to $\nu^{1/2}$ → irreversible behaviour (low k^0).

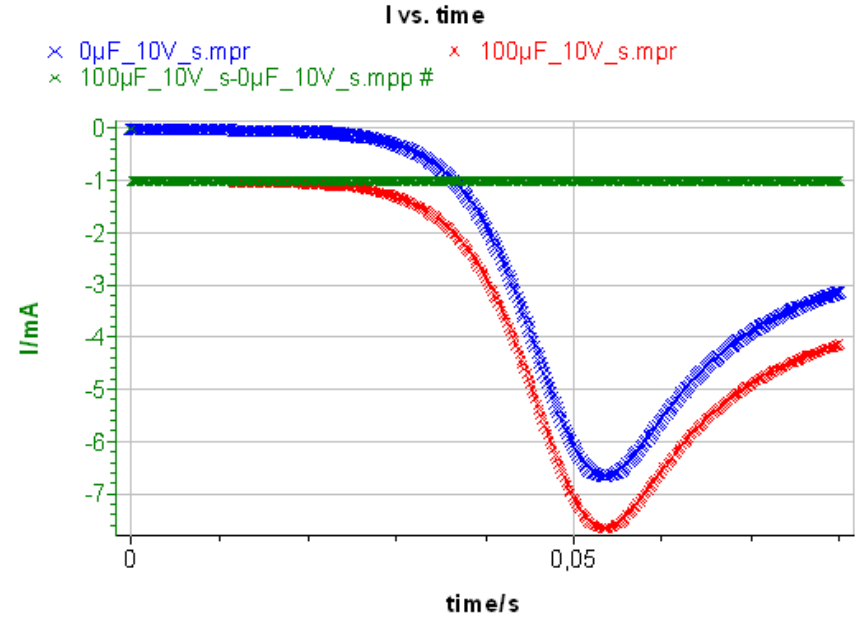
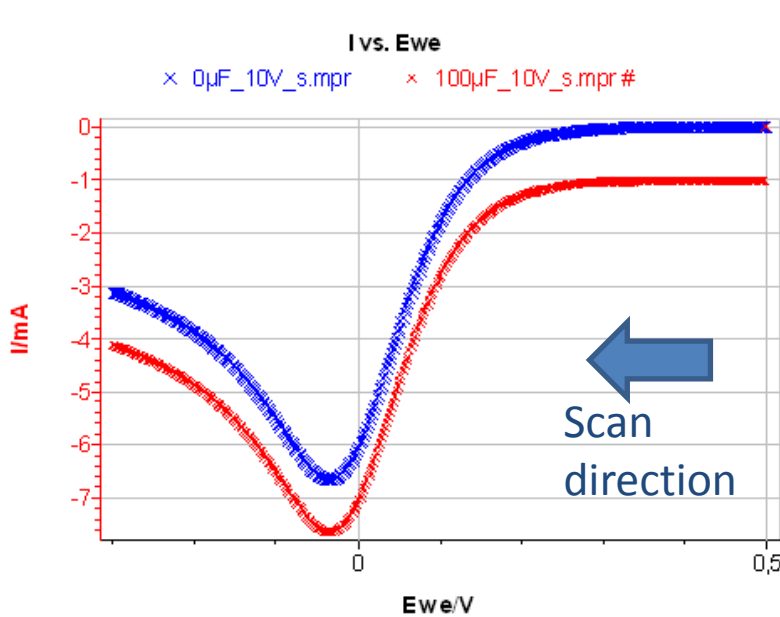
Possible measurements : the symmetry factor α_r and the standard constant k^0 of the reaction.

Whichever the value of k^0 , 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° , $v = 10 \text{ V/s}$



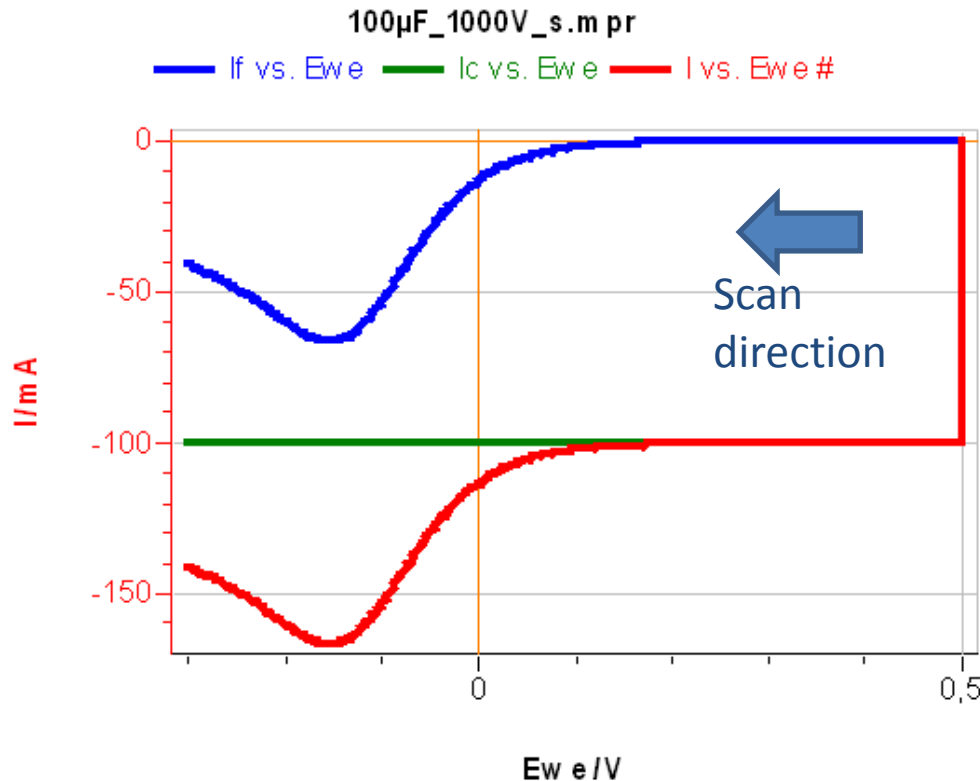
$$I_{\text{total}} = I_c + I_f$$

(with CV Sim the two contributions can be separated)

$$I_c = C_{dl}(dE(t)/dt) = -C_{dl}v$$

For a constant scan rate the capacitive current is also constant.

For a « random » k° , $v = 1000$ V/s



$$I_{total} = I_c + I_f$$

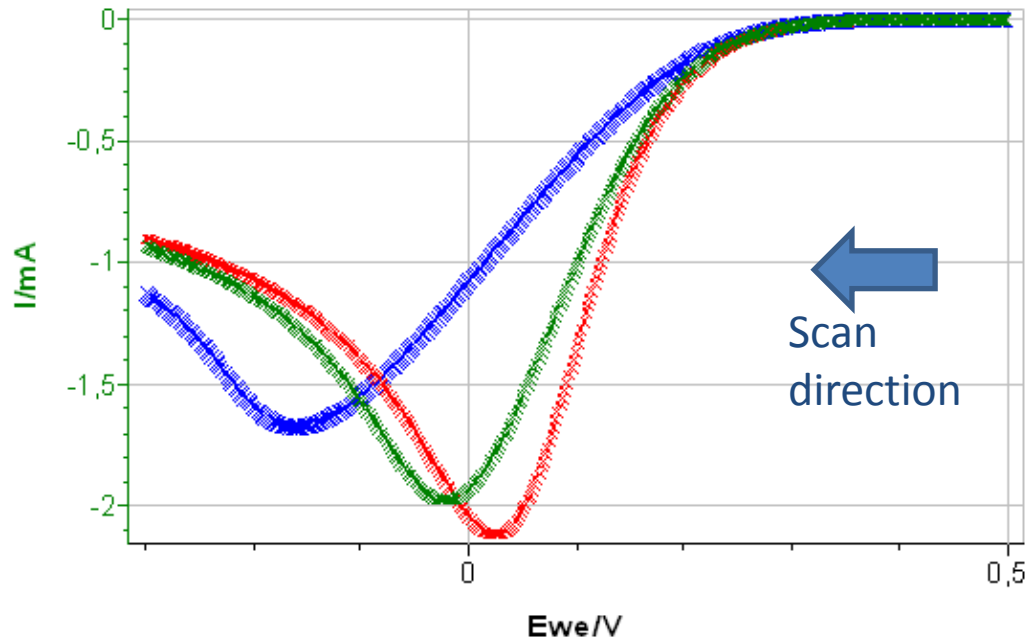
$$I_c = C_{dl}(dE(t)/dt) = -C_{dl}v$$

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.

For a « random » k° , $v = 1 \text{ V/s}$

I vs. Ewe

× 100ohm_1V_s.mpr × 0ohm_1V_s.mpr × 20ohm_1V_s.mpr#



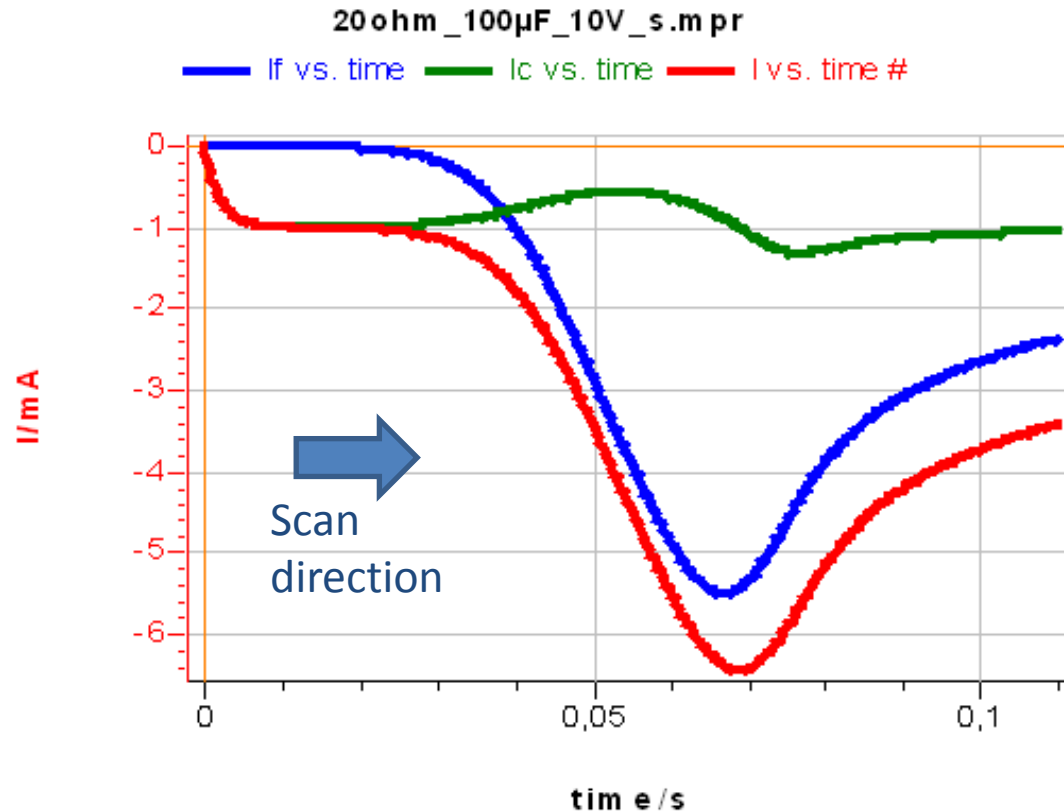
$$R_{\Omega} = 0 \Omega, R_{\Omega} = 20 \Omega, R_{\Omega} = 100 \Omega$$

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° , $v = 10$ V/s

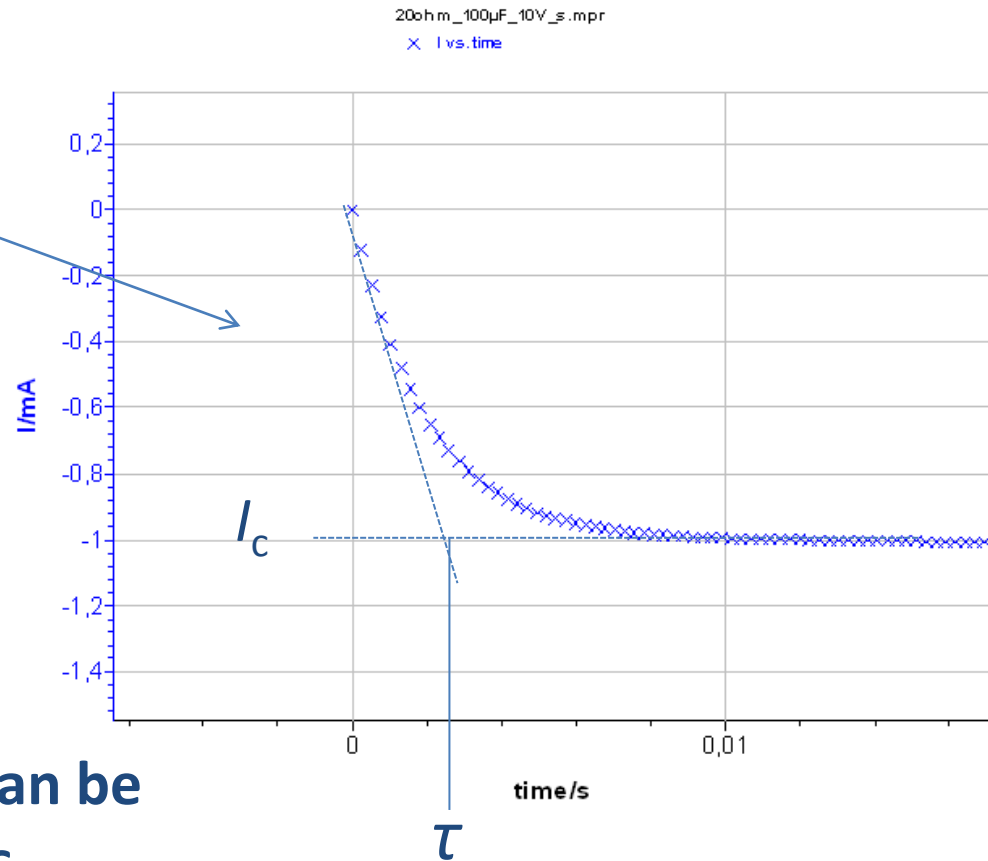
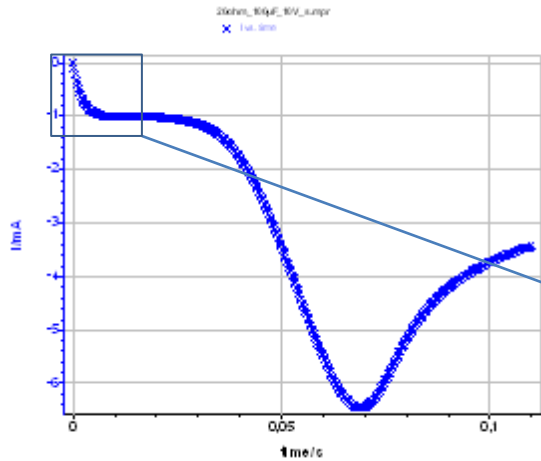


$$I_c(t) = C_{dl}(dE(t)/dt)$$

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

$$I_{total} = I_c + I_f$$

For a negligible faradaic current i.e. at short times, the system is equivalent to an $R+C$ electrical circuit.



$$I_c = -C_{dl} V \text{ (for } t > 0.01 \text{ s)}$$

$$\tau = R_{\Omega} C_{dl}$$

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

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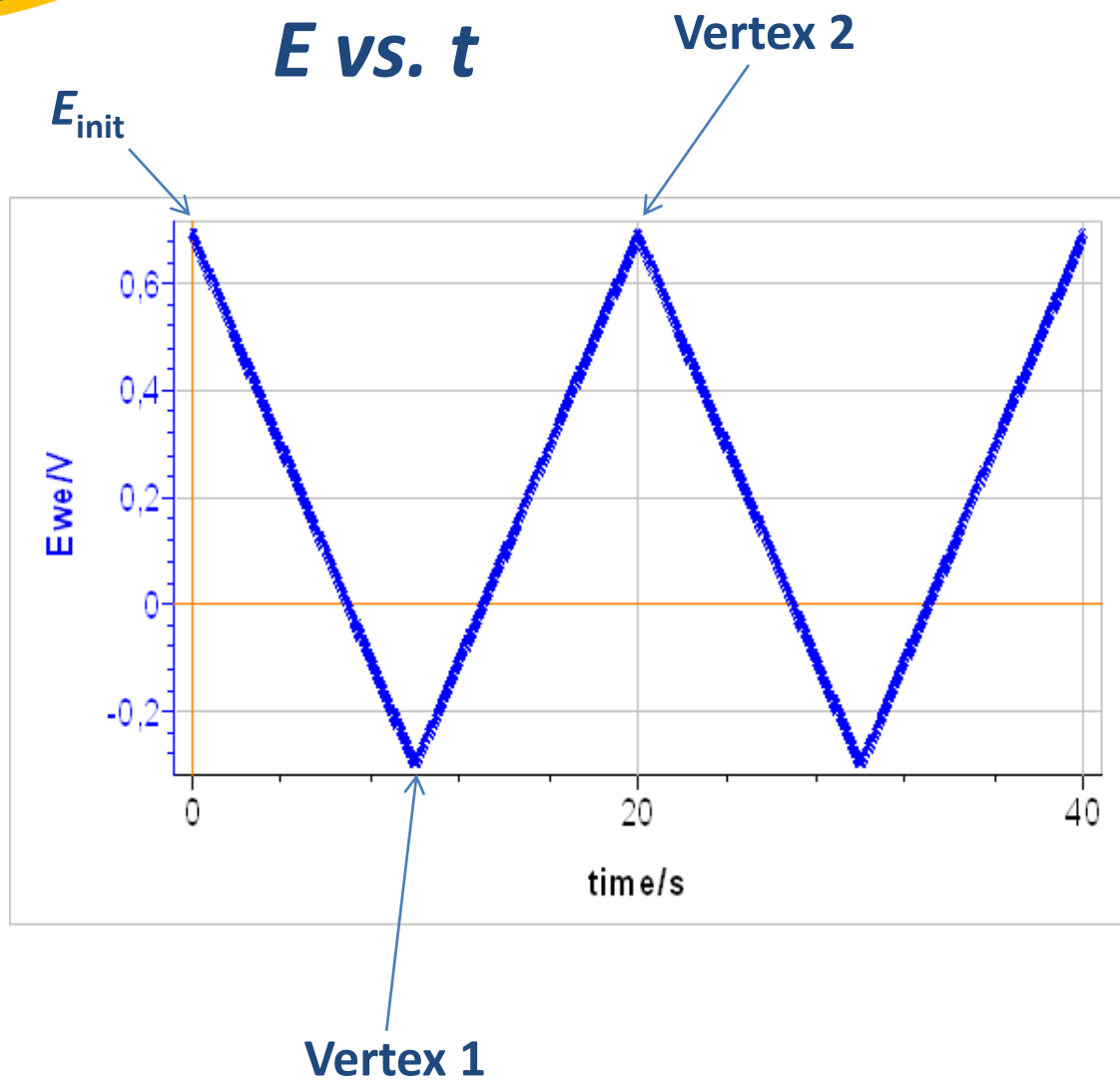
2. Study by cyclic voltammetry

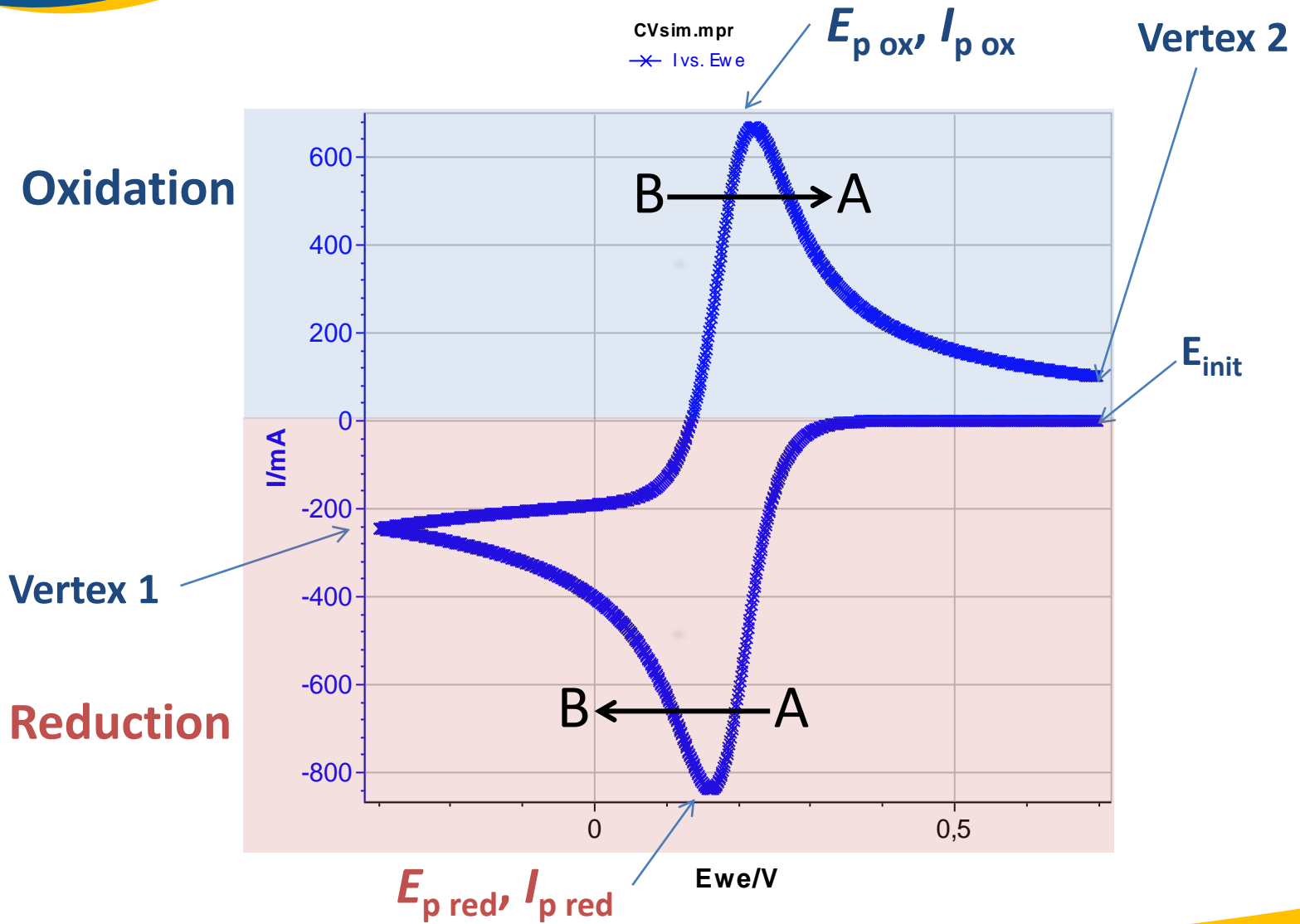
1. Influence of the first vertex

2. Influence of the k°

3. Influence of the number of scan

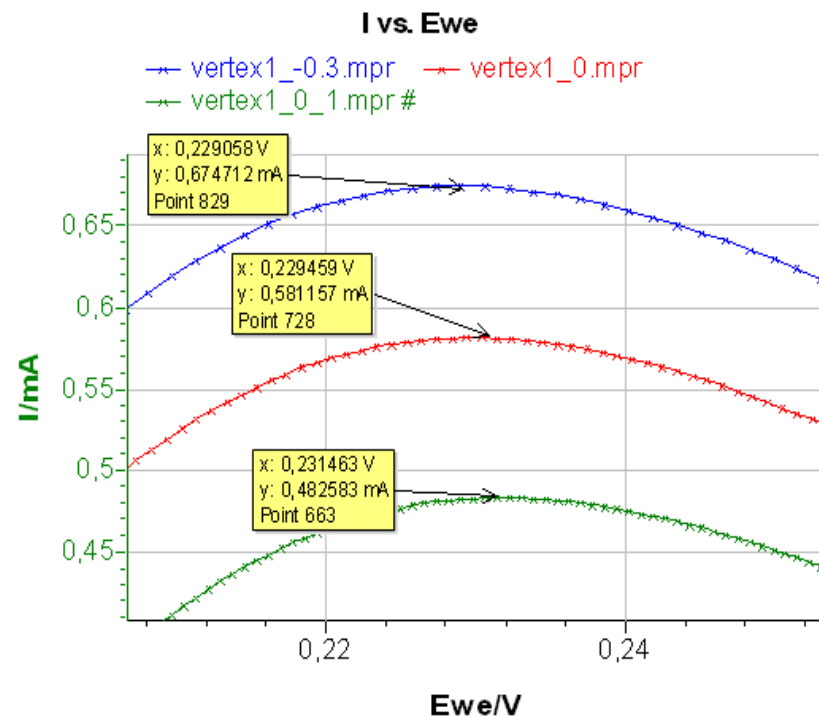
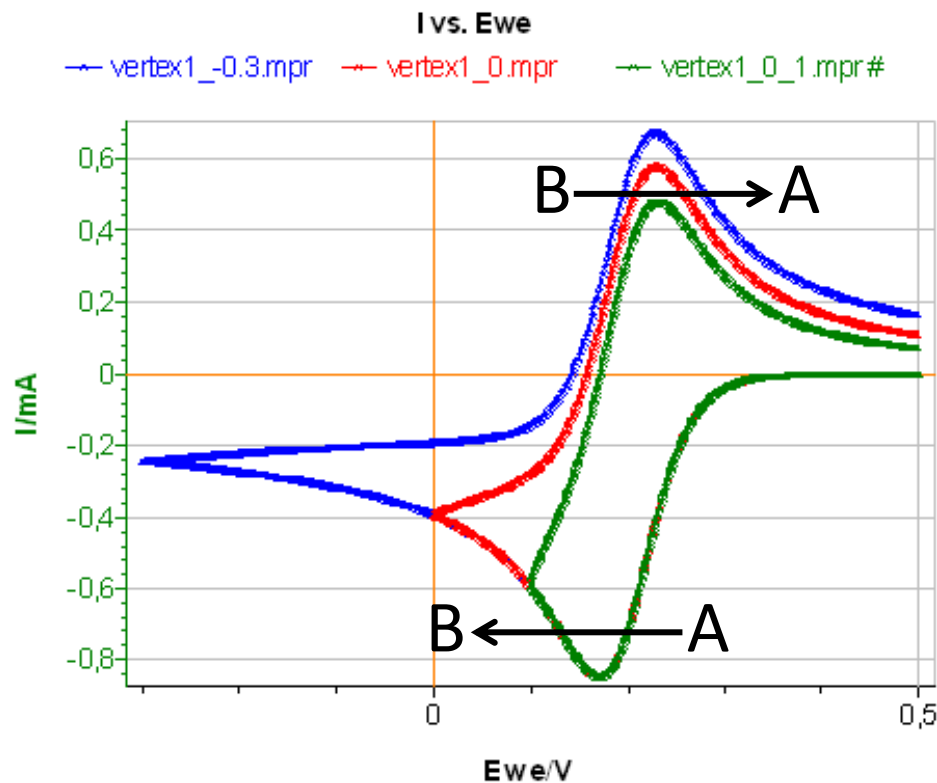
4. Influence of the scan rate





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Vertices : **-0,3 V** **0 V** **0,1 V**
Reversible system ($k^\circ = 10 \text{ cm}^2 \text{ s}^{-1}$)

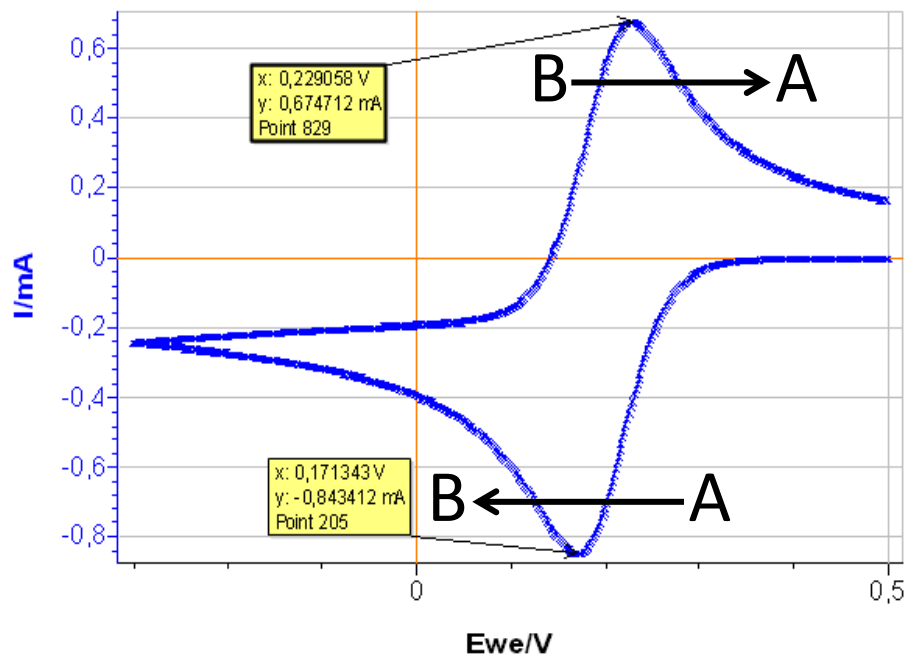


$I_{p,ox}$ and to a smaller extent $E_{p,ox}$ depend on the value of the Vertex 1.
The correct vertex value is the one after which $I_{p,ox}$ and $E_{p,ox}$ do not vary.

E_p difference

CVsim.mpr

→ I vs. Ewe

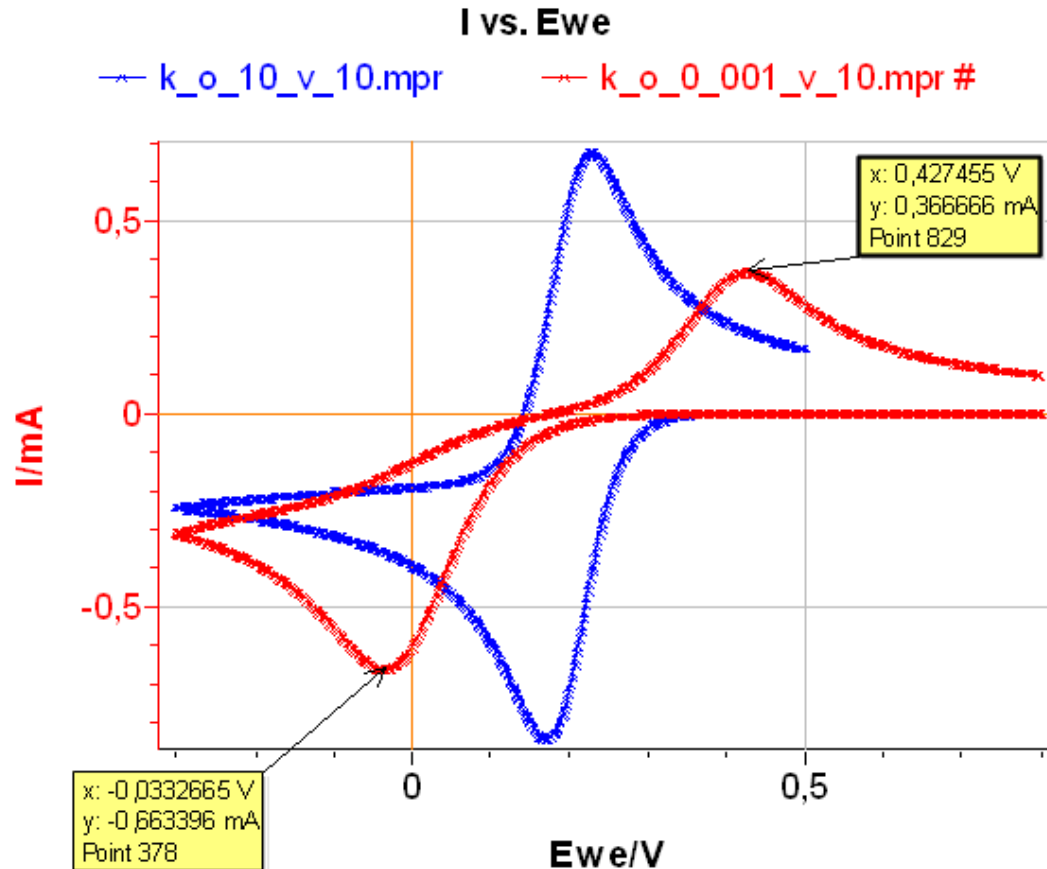


For a vertex 1 of $-0,3$ V, the difference ΔE_p is equal to $57,7$ mV. It was calculated¹ that for a vertex 1 of $-\infty$, this difference is 57 mV. It can be considered that $-0,3$ V is a sufficiently low vertex 1 potential.

1. A. J. Bard, L. R. Faulkner, Electrochemical Methods, Wiley, p. 242

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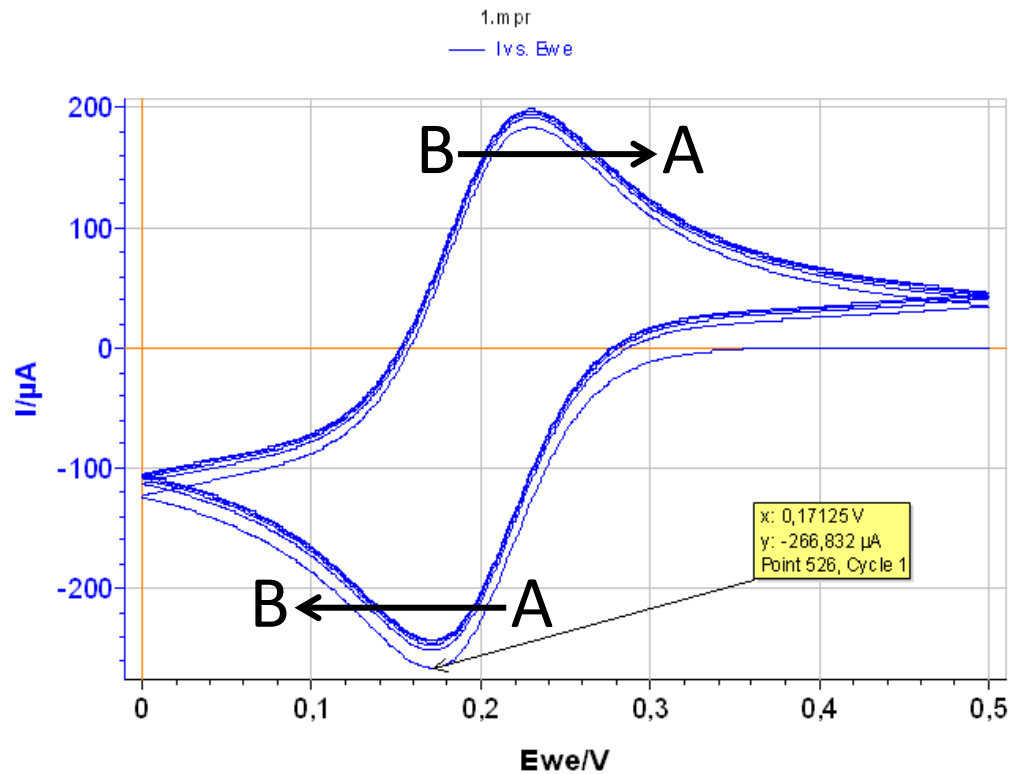
$k^\circ = 10 \text{ cm/s}$
 $k^\circ = 0.001 \text{ cm/s}$



The peak difference increases as the value of k° decreases.
The red curve is characteristic of an irreversible system.

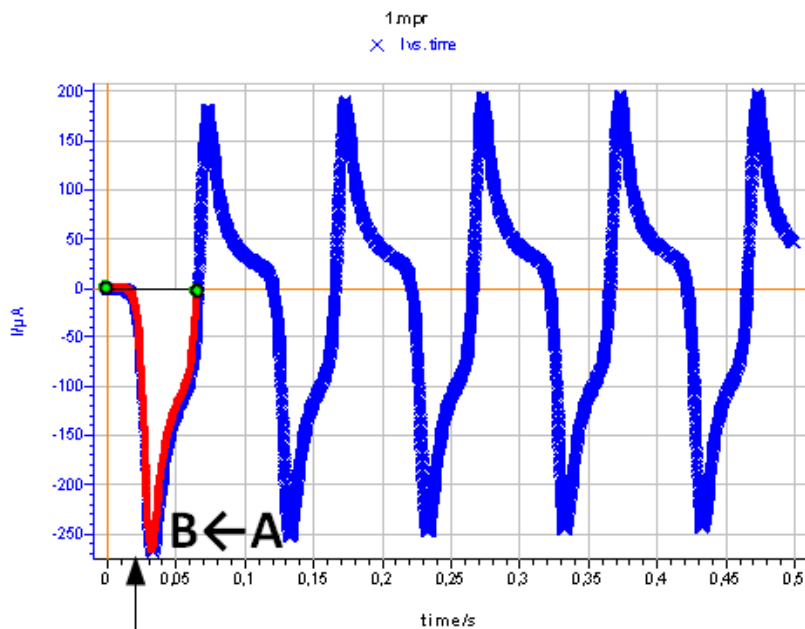
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Reversible system ($k^\circ = 10 \text{ cm}^2 \text{ s}^{-1}$)



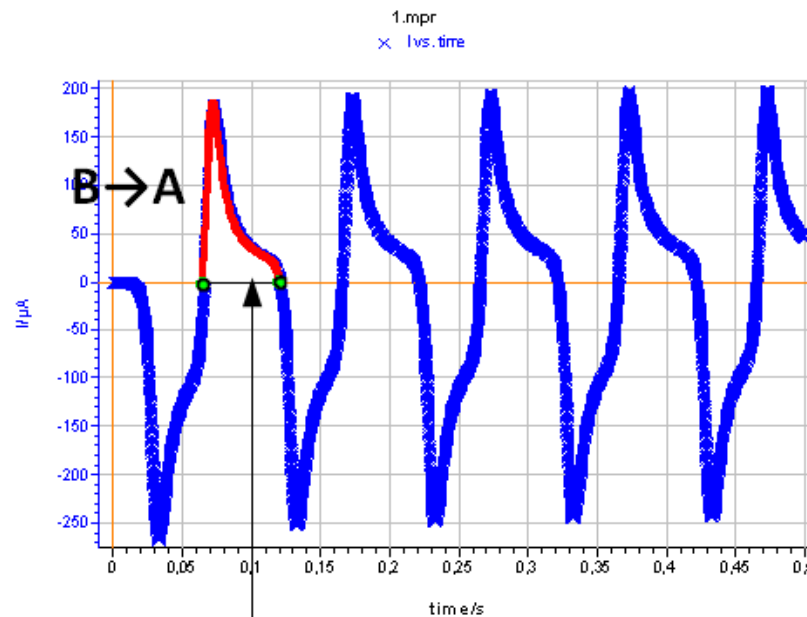
When the scan number increases, reduction $|I_p|$ decreases and oxidation $|I_p|$ increases to reach a limit value. It is due to the fact that after one scan the initial conditions are not recovered : there is less A and more B.

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



-6,2 μC

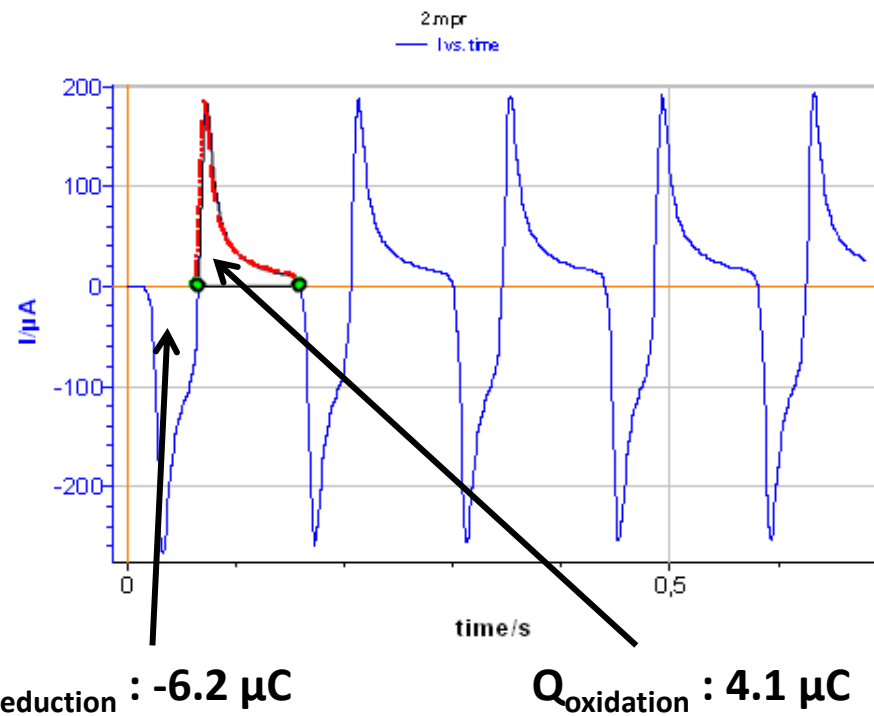
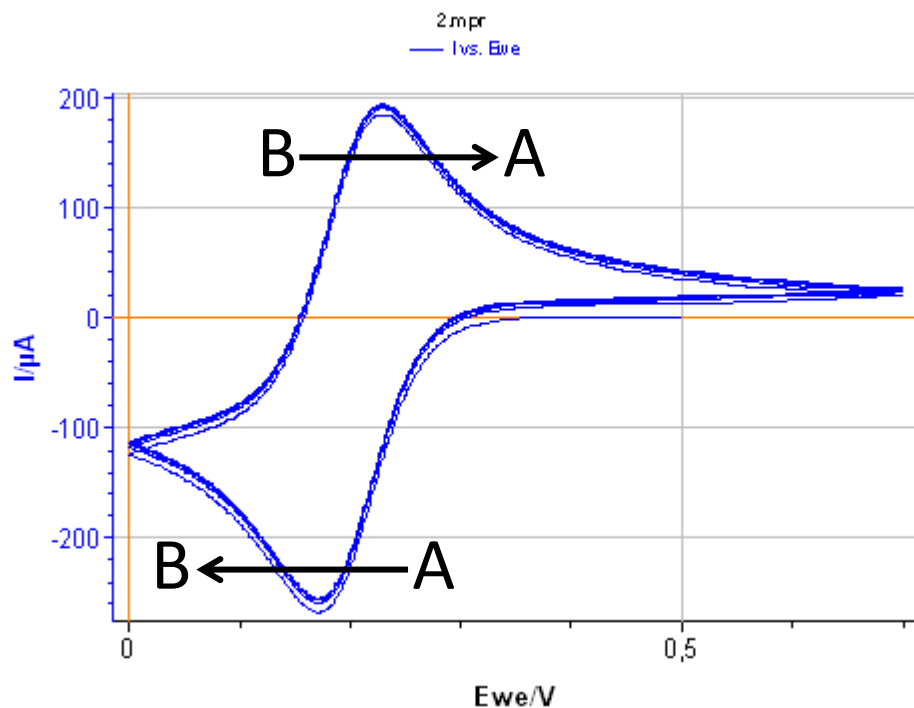
(obtained using Peak Analysis and integral calculation in EC-Lab®)



3,5 μC and increasing

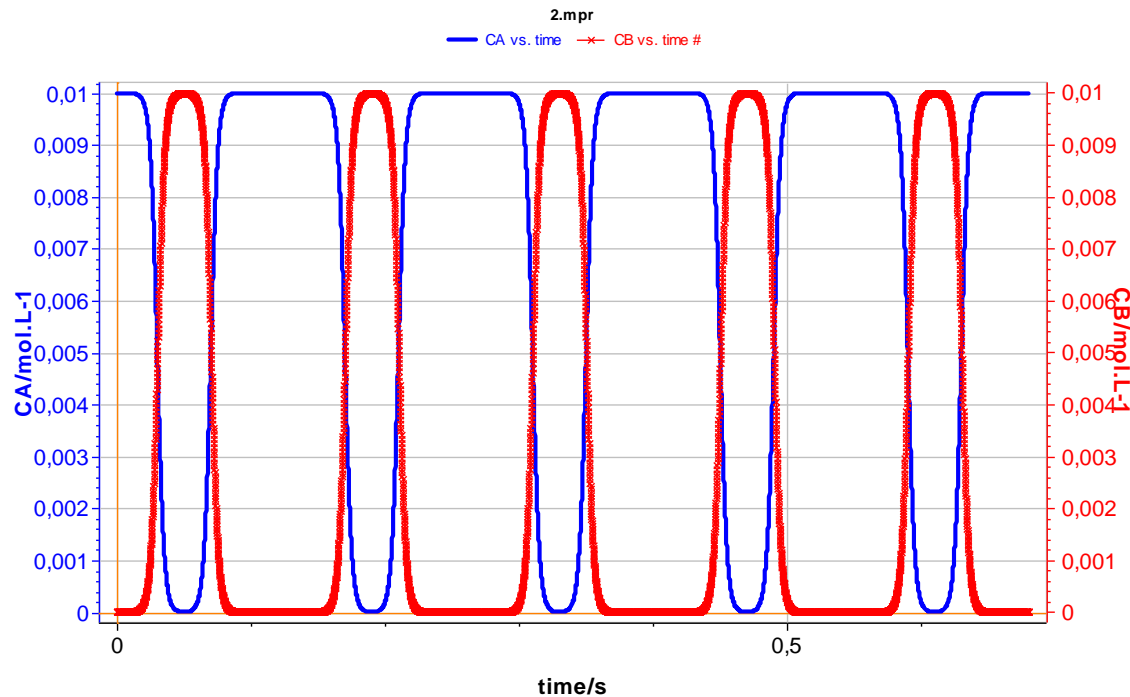
For each cycle (1 reduction and 1 oxidation scans) there are more A species reduced into B than produced by the oxidation of B. The integral function available in EC-Lab allows to calculate the charge involved in the reduction scan and the oxidation scan.

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



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

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 :

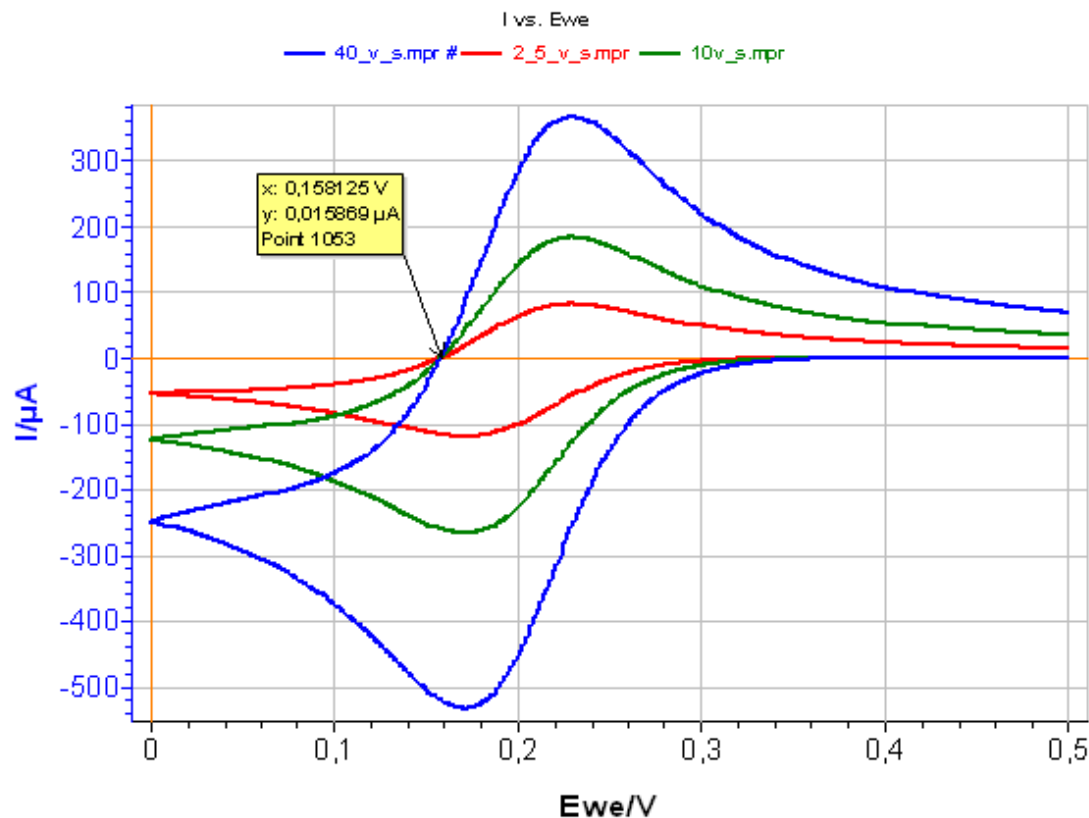
$$E(t) = E^\circ + \frac{RT}{F} \ln \frac{A(0,t)}{B(0,t)} \quad \text{with } D_A = D_B, A(0,t) + B(0,t) = A^*$$

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

2.5 V/s
10 V/s
40 V/s



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 $(\nu)^{1/2}$, 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° 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...