

## 26. Determination of thermodynamical and kinetical parameters of charge transfer processes. Chronoamperometry.

### 1. Theoretical background

#### 1.1. Basic concepts of electrochemistry

At an electron conductor-ion conductor interface (at an electrode), even in the simplest case, charge separation can occur, electron, ion accumulation may occur at the boundaries of the two phases (Figure 1). The interface behaves like a capacitor and it can be characterized by its capacitance (C). If there is a substance in the ion conducting phase that is capable of giving or picking up electrons at a given interfacial potential difference, it is also possible that charge passes through the interface, charge transfer process, so called Faradaic process can take place (Figure 2). The charge transfer process can be divided into several stages (steps), kinetically (generally) complex. It is necessary to reach the surface by the reactant (mass transport, i.e., convection, migration or diffusion), possible intermediate chemical reaction can occur (e.g., protonation, deprotonation, ligand exchange, any other chemical reaction), adhesion to the electrode surface (adsorption) and after the charge transfer reaction everything can happen vice versa.

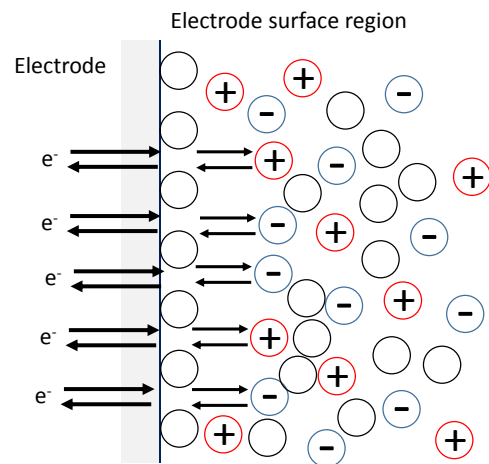


Figure 1 Ideally polarizable electrode. The empty circles represent the solvent molecules.

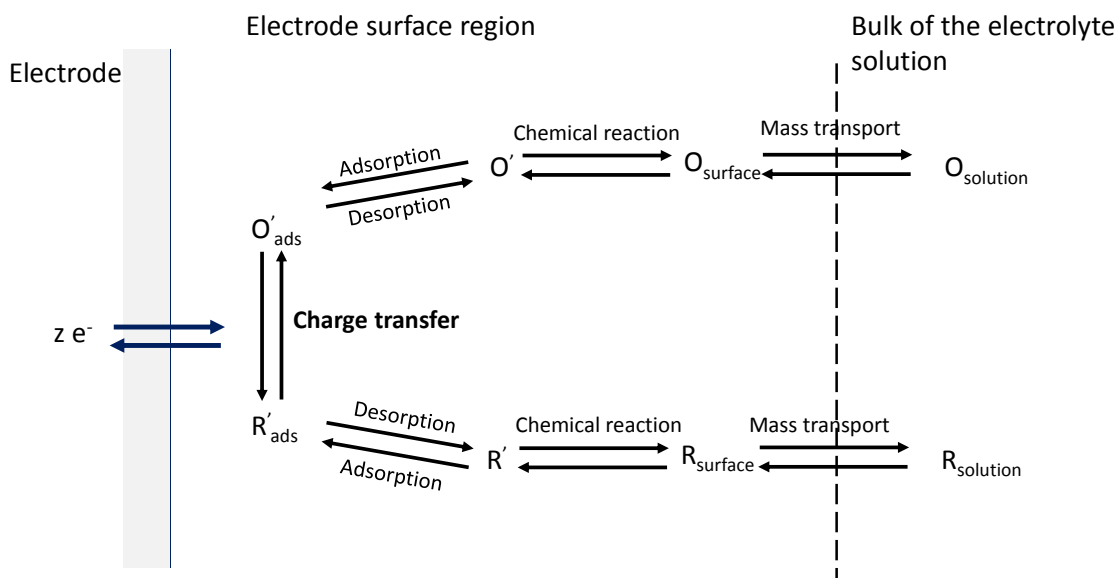
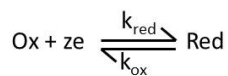


Figure 2 Possible stages (steps) of the charge transfer processes.

As with the complex heterogeneous kinetic processes, the rate of the Faradaic process will be determined by the slowest step. In the simplest case, the competition of charge transfer and mass transport may occur. Charge transport means the flux of electrical charges, i.e. current, but this can

not be greater than the flux provided by the mass transport, the two being in close contact with each other.

In a simple (elementary) redox process, e.g.



where no prior or subsequent chemical processes are to be considered, the rate of reaction ( $r$ ) can be given as

$$r = \frac{1}{A} \frac{dn}{dt} = \frac{1}{A} \frac{1}{zF} \frac{dQ}{dt} = \frac{I}{AzF} \quad 1.1.$$

where  $A$  is the surface area,  $dn/dt$  is the time derivative of the amount of substance transformed,  $z$  is the charge number change,  $F$  is the Faraday constant (molar elementary charge),  $Q$  is the amount of charge transmitted during the charge transfer procedure,  $I$  is the measurable current.

Since  $r$  and  $I$  are in direct proportion with each other and the proportionality factor is constant for a given system, therefore, in electrochemistry it is usual to express the reaction rate simply by the measured current (or with the  $I/A$ , current density). As it is common in heterogeneous kinetics, this is proportional to the amount of substances reacting, and in a simpler case, e.g.

$$I = AzF \cdot r = (AzF) \cdot k \cdot \prod_{i=1}^n c_i^{\beta_i} \quad 1.2.$$

where  $c_i$  is the concentration of the  $i$ -th substance on the surface,  $\beta_i$  is the reaction order of the  $i$ -th component,  $k$  is the rate coefficient. If the redox process is a first order reaction in both directions, then

$$r_{\text{ox}} = k_{\text{ox}} \cdot c_{\text{Red}}(0, t) = \frac{I_{\text{ox}}}{AzF} \quad 1.3.$$

$$r_{\text{red}} = k_{\text{red}} \cdot c_{\text{Ox}}(0, t) = \frac{I_{\text{red}}}{AzF} \quad 1.4.$$

where  $r_{\text{ox}}$  and  $r_{\text{red}}$  are the rate of oxidation and reduction,  $k_{\text{ox}}$  and  $k_{\text{red}}$  are the rate coefficients of the two processes,  $c_{\text{Ox}}(0, t)$  and  $c_{\text{Red}}(0, t)$  are the surface ( $x=0$ ) concentration of Ox and Red at the time  $t$ ,  $I_{\text{ox}}$  and  $I_{\text{red}}$  is the absolute value of the oxidation (anodic) and reduction (cathodic) current.

The resulting net reaction rate (and the net current,  $I$ ):

$$r_{\text{net}} = k_{\text{ox}} \cdot c_{\text{Red}}(0, t) - k_{\text{red}} \cdot c_{\text{Ox}}(0, t) = \frac{I}{AzF} \quad 1.5.$$

(By definition, oxidation is the positive current and reduction is the negative current, except in the USA!) That is,

$$I = I_{\text{ox}} - I_{\text{red}} = AzF(k_{\text{ox}} \cdot c_{\text{Red}}(0, t) - k_{\text{red}} \cdot c_{\text{Ox}}(0, t)) \quad 1.6.$$

The specificity of the electrochemical charge transfer processes is that the rate coefficient depends not only on the temperature, but also on the potential difference at the interface between the electrode and electrolyte ( $\Delta\phi$ , absolute electrode potential), i.e., on the electrode potential (a potential difference compared to another electrode being in equilibrium). This potential difference (or its change) oppositely acts on the activation energy of the oxidation and reduction processes and thus on the rate coefficients (Figure 3).

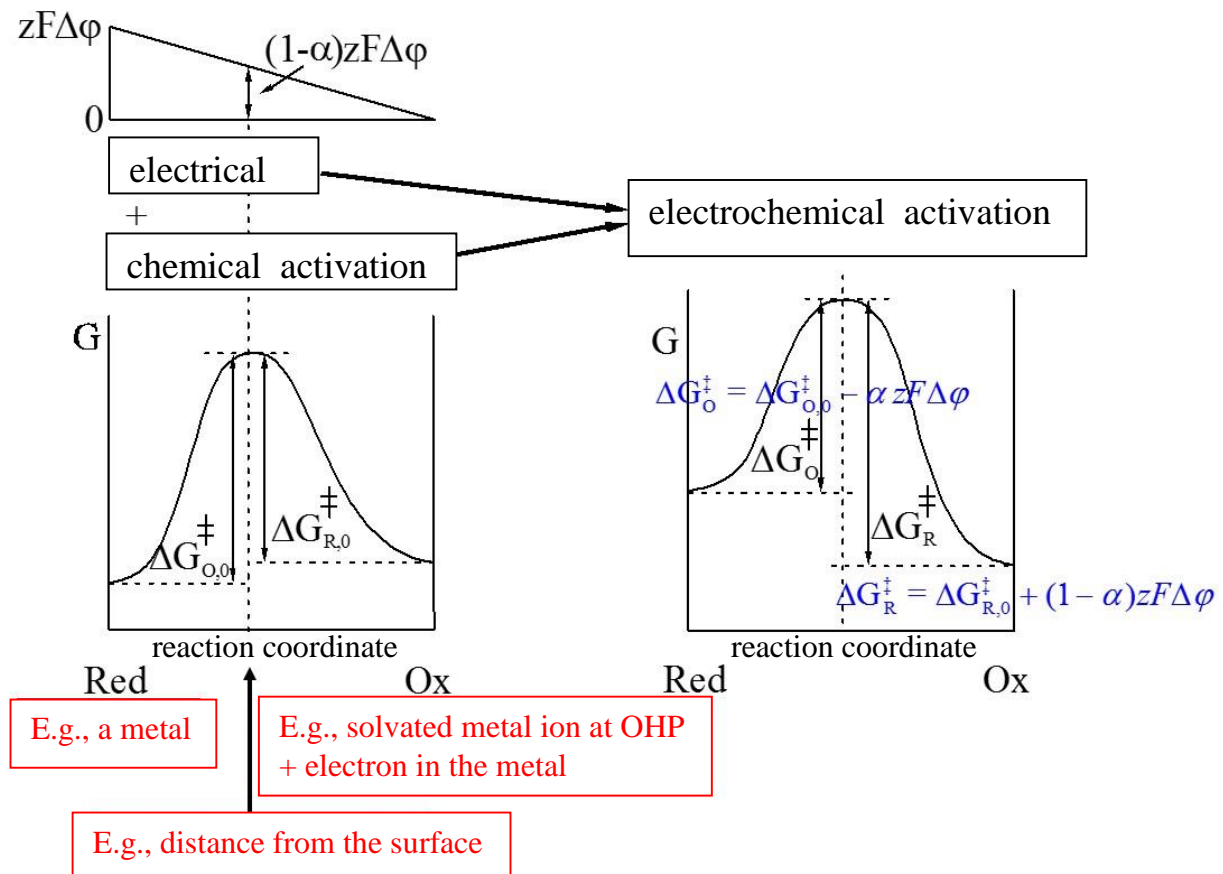


Figure 3 The combined effect of chemical and electrical activation on the activation free energy (and thus on the rate coefficient).  $zF\Delta\phi$  is the electrical energy difference for  $zF$  charge between the surface of the electrode and the Outer Helmholtz Plane (OHP),  $\Delta G_{o,0}^{\ddagger}$  is the hypothetical chemical part of the activation energy,  $\Delta G^{\ddagger}$  is the activation energy of the electrochemical process (oxidation and reduction),  $\alpha$  is the so called transfer coefficient or symmetry factor.

The rate coefficients can be expressed by a standard formalism such as:

$$k_{ox} = k^0 \cdot \exp\left[\alpha \frac{zF}{RT} (E - E^0)\right] \quad 1.7.$$

$$k_{red} = k^0 \cdot \exp\left[-(1-\alpha) \frac{zF}{RT} (E - E^0)\right] \quad 1.8.$$

where  $\alpha$  is the so-called transfer coefficient (or symmetry factor), showing the energetic symmetry of the transition state between the initial and the final states (activated complex) along the reaction coordinate. In a fully symmetric case  $\alpha = 1/2$ , but its normal value could be  $0.3 < \alpha < 0.7$ .  $R$  is the

molar gas constant, T is the thermodynamic temperature. E is the actual electrode potential,  $E^0$  is the so-called formal standard electrode potential, briefly formal potential. The electrode potential for a simple redox system in equilibrium could be given by the Nernst equation:

$$E_{equilibrium} = E^0 + \frac{RT}{zF} \ln \frac{a_{Ox}}{a_{Red}} \quad 1.9.$$

where  $a_{Ox}$  and  $a_{Red}$  are the activity of the oxidized and reduced form,  $E^0$  is the standard electrode potential. Instead of  $E^0$ , it is customary to use the formal potential in kinetic studies:

$$E_{equilibrium} = E^{0'} + \frac{RT}{zF} \ln \frac{c_{Ox}}{c_{Red}} \quad 1.10.$$

$$E^{0'} = E^0 + \frac{RT}{zF} \ln \frac{\gamma_{Ox}}{\gamma_{Red}} \quad 1.11.$$

where  $\gamma_{Ox}$  and  $\gamma_{Red}$  are the activity coefficients of the oxidized and reduced form. For a given system (given pH, ionic strength, etc.)  $E^{0'}$  is constant and can be used instead of  $E^0$ . (If  $\gamma_{Ox} = \gamma_{Red}$ , then they are even equal.) Another meaning of the formal potential is that at this potential when  $c_{Ox} = c_{Red}$ ,  $r_{Ox} = r_{red}$ , that is the system is in equilibrium and  $k_{ox} = k_{red} = k^0$ . Although slightly incorrectly,  $k^0$  is commonly referred to as the standard rate constant. (It would be better to call it as a rate constant at the formal potential in equilibrium, but for some reason this is not used, for example because it is too long!)

Thus

$$I = I_{ox} - I_{red} = A z F k^0 \left( c_{Red}(0,t) \cdot \exp \left[ \alpha \frac{zF}{RT} (E - E^{0'}) \right] - c_{ox}(0,t) \cdot \exp \left[ -(1-\alpha) \frac{zF}{RT} (E - E^{0'}) \right] \right) \quad 1.12.$$

This is a special form of the so-called Butler-Volmer equation, which highlights that if current flows through the system, this should cause a change in the surface concentration of Ox, Red, that is, it should cause the change in the reaction rate and thus in the current. (The snake bite into his tail!) If we ignore this and as the reference state we do not consider the formal potential, but the equilibrium electrode potential in the actual system, then

$$I = I^0 \left( \exp \left[ \alpha \frac{zF}{RT} (E - E_{equilibrium}) \right] - \exp \left[ -(1-\alpha) \frac{zF}{RT} (E - E_{equilibrium}) \right] \right) \quad 1.13.$$

(time-independent Butler-Volmer equation) where  $I^0$  is the so-called exchange current (the equal absolute value of oxidation and reduction current at the equilibrium electrode potential). It is obvious that

$$I^0 = A z F k^0 c_{ox}^\alpha c_{Red}^{1-\alpha} \quad 1.14.$$

That is,  $I^0$  is proportional to  $k^0$ , both of them can be used for the kinetic description, but the latter formalism hides the time dependence.

Another important time dependency is the mass transport of the substances to the surface or from the surface, which also changes the value of  $c_{Ox}(0,t)$  and  $c_{Red}(0,t)$ . If there is no convection (the solution is not stirred, the electrode does not move), if we do not have to consider migration (e.g., by adding a large amount of inert salt to the solution so the current is conducted (mainly) by the salt),

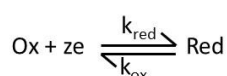
only diffusion can be considered. From a large enough space (cell) and to a large enough flat electrode, this means a one-dimensional, semi-infinite diffusion, that is:

$$\left(\frac{\partial c_{Ox}}{\partial t}\right)_x = D_{Ox} \left(\frac{\partial^2 c_{Ox}}{\partial x^2}\right)_t \quad 1.15.$$

$$\left(\frac{\partial c_{Red}}{\partial t}\right)_x = D_{Red} \left(\frac{\partial^2 c_{Red}}{\partial x^2}\right)_t \quad 1.16.$$

where  $D_{Ox}$  and  $D_{Red}$  are the Ox, Red diffusion coefficients, and  $x$  is the distance measured from the surface,  $t$  is the time.

So, to describe such a simple system as



a differential equation system is needed, and general (analytical) solution does not exist. Numerical solutions can be found for special cases, such as the large potential step, the linear sweep, or cyclic sweep techniques. Together they are called chronoamperometry, i.e., measuring the time dependency of the current.

## 1.2. Linear sweep voltammetry

In linear sweep voltammetry (the original name was linear potential sweep chronoamperometry, shortly linear sweep voltammetry (LSV)), we change the potential difference between the working electrode (the electrode to be tested) and the reference (comparison) electrode linearly with time, and measure the current between the working electrode and a counter electrode (auxiliary electrode). That is, we usually use a three-electrode system (Figure 4). A special instrument, the so-called potentiostat passes so much current through the working electrode (the electrode tested) as needed that its electrode potential compared to another electrode being in equilibrium (the reference electrode) will be what we want. The current does not flow through the reference electrode (in such a case it could not be in equilibrium), but between the working and the counter (auxiliary) electrode. As if the potential and the current measurement would occur in two separate electric circuits.

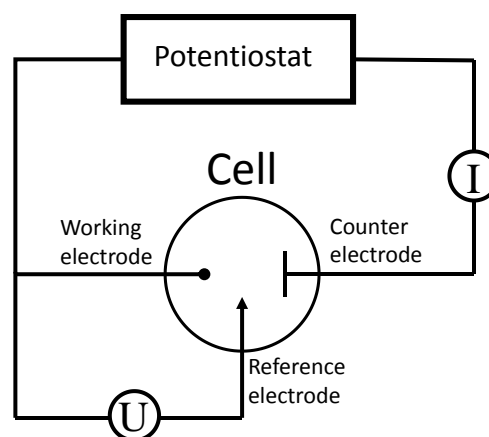


Figure 4 Schematics of a three-electrode system.

(It should be mentioned that without current the measured potential is the electrode potential of the working electrode relative to the reference electrode, but if current flows, the electrode potential and the potential difference between the working and the reference electrode may differ depending on value of the current. The deviation is caused by the current flowing through the solution between the working and the reference electrode, which causes another potential difference,  $\Delta U_{\Omega} = I \cdot R$ , the so-called ohmic potential drop, where  $R$  is the solution resistance between the working and the reference electrode. This is usually a disturbing factor, but if the solution resistance is small, e.g. using a high concentration of inert electrolyte, or the reference electrode is close enough to the

working electrode (e.g. using a so-called Luggin capillary), then  $\Delta U_{\Omega}$  is also small and the deviation of the controlled potential difference and the electrode potential is negligible.)

In LSV, the time dependence of the potential difference (exciting signal) is

$$E = E_{init} + vt \quad 1.17.$$

where  $E_{init}$  is the initial potential difference compared to the reference electrode,  $t$  is the time,  $v$  is the rate of the potential change, the so-called sweep rate (or scan rate). The current is measured as a function of time (thus the potential difference) and plotted as a function of the potential difference. (A cross section of the current-potential-time three-dimensional function.)

Since the electrode potential is not constant, even without Faradaic process, we will get a "signal", the capacitive current needed to charge the double layer (Figure 5, see also Figure 1).

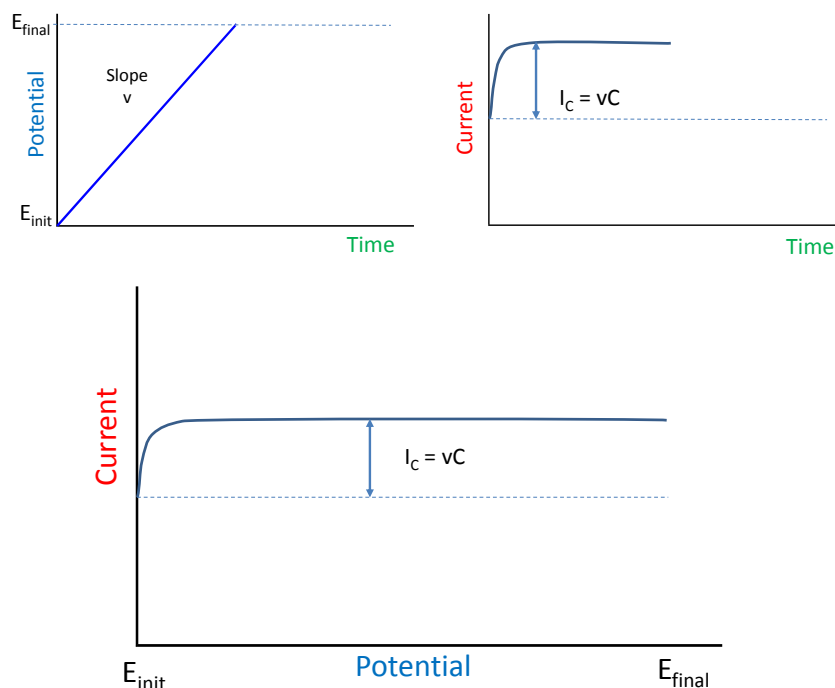


Figure 5 LSV response of an ideally polarizable electrode

If the capacitance does not depend on the electrode potential:

$$C = \frac{dQ}{dE} = \frac{\frac{dQ}{dt}}{\frac{dE}{dt}} = \frac{I_c}{v} \quad 1.18.$$

where  $C$  is the differential capacitance of the double layer,  $dQ$  is the change in the excess surface charge,  $dE$  is the variation of the electrode potential (and thus the interfacial potential difference),  $t$  is the time,  $I_c$  is the capacitive current,  $v$  is the rate of the potential change (sweep rate, scan rate).

That is  $I_c = vC$  (at least after a short, transient time).

If there is a Faradaic process in the potential range examined, the resulting current will be  $I_c + I_F$ .

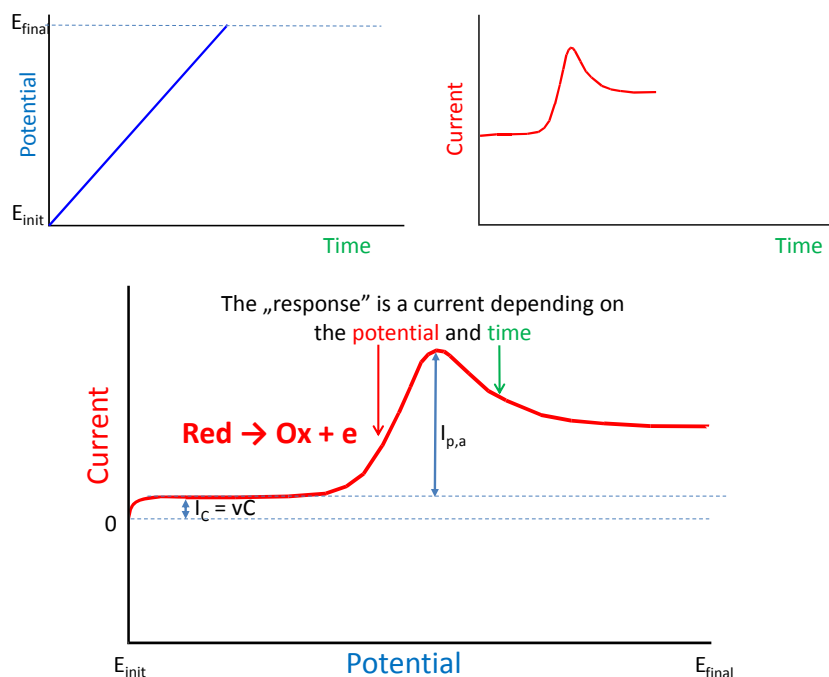


Figure 6 Typical LSV curve for a Red  $\rightarrow$  Ox transformation

One of the characteristic parameters of voltammogram is the background current. If we start from a system that initially contains only Red with  $c_{\text{Red}}$  concentration and start the scan far from the possible equilibrium electrode potential, i.e., there is no Faradaic process, only capacitive current can flow, which is proportional to the sweep rate ( $I_c = vC$ ). From the dependence of the background current on the sweep rate, the capacitance of the double layer can be estimated (see also Figure 5).

From a given electrode potential, a Faradaic current is added to the capacitive current, and its value depends on the electrode potential and on the time (Figure 6).

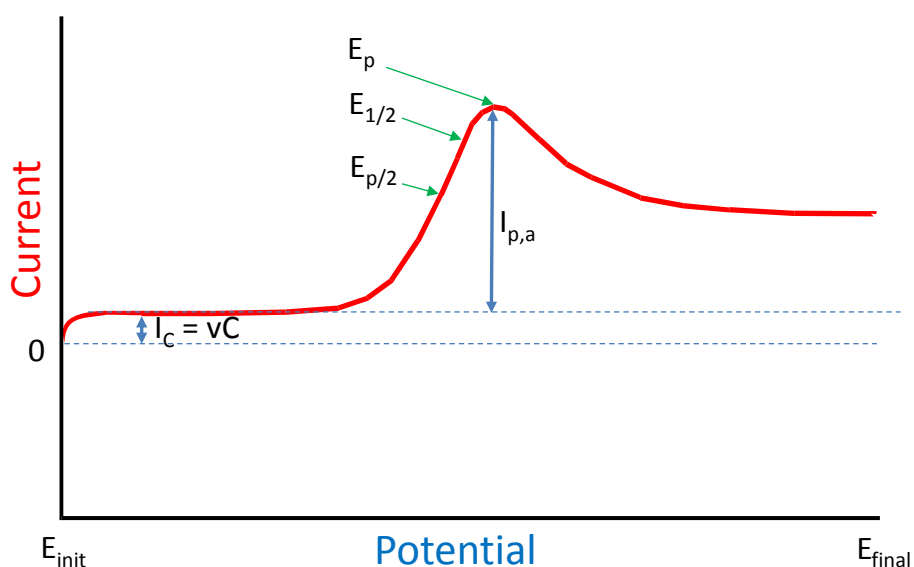


Figure 7 Parameters of a voltammogram

Characteristic parameters of the voltammogram are the (background current corrected) peak current,  $I_{p,a}$ , the peak potential,  $E_p$ , the potential where the current is the half of the peak current, so-called

half-peak potential,  $E_{p/2}$ , and the so-called half-wave potential  $E_{1/2}$ . (The latter one is a term from an old electroanalytical method, from polarography (using dropping mercury electrode). In polarography there is no current peak but a current step (wave) is measured for a Faradaic process and the potential at the half of the current step was  $E_{1/2}$ ) In today's use:

$$E_{1/2} = E^{0'} + \frac{RT}{zF} \ln \left( \frac{D_{Ox}}{D_{Red}} \right)^{1/2} \quad 1.19.$$

That is, it is given by the formal potential and the ratio of the diffusion coefficients.

If  $D_{Ox} = D_{Red}$ ,  $E_{1/2} = E^{0'}$ .

In electrochemistry, the charge transfer processes are divided into three categories according to the nature of voltammograms.

### 1.2.1. Reversible charge transfer process

The Nernst equation applies at any given moment to the relation between the electrode potential and the surface concentrations, i.e.

$$E = E^{0'} + \frac{RT}{zF} \ln \frac{c_{Ox}(0, t)}{c_{Red}(0, t)} \quad 1.20.$$

Strangely, the electrochemical reversibility (a thermodynamical phrase) is kinetically defined, since the above equation can only be true if the rate of the charge transfer process is infinite. ( $k^0$  is infinite, so-called ideally non-polarizable electrodes. The usual reference electrodes approach this condition thus they can be always in (nearly) equilibrium.) Of course, there are no such real systems, but in some cases  $k^0$  is large enough that the diffusion can provide orders of magnitude less rate, completely the diffusion will be the rate determining process. In a reversible case, the numerical solution of the kinetic and diffusional equation system gives for (the background corrected) current:

$$I_p = 0,4463 \left( \frac{F^3}{RT} \right)^{1/2} z^{3/2} A D_{Red}^{1/2} c_{Red} v^{1/2} \quad 1.21.$$

(Randles-Sevcik equation). The value of the multiplier is valid, if the current ( $I$ ) is given in Amperes, the surface area ( $A$ ) in  $cm^2$ , the diffusion coefficient ( $D$ ) in  $cm^2/s$ , the concentration ( $c$ ) in  $mol/cm^3$ , the sweep rate ( $v$ ) in  $V/s$ . The equation shows that the peak current changes linearly with the square root of the sweep rate and that the slope of the  $I_p - v^{1/2}$  function is proportional to  $D^{1/2}$  and to  $c$ . Whichever is known, the other can be determined.

$E_p$  is not dependent on the sweep rate and

$$E_p - E_{p/2} = 2,20 \frac{RT}{zF} \quad 1.22.$$

which can be used to determine the change in charge number ( $z$ ),

$$\frac{1}{2} (E_p + E_{p/2}) = E_{1/2} + 0,05 \frac{RT}{zF} \quad 1.23.$$

if  $D_{Ox} = D_{Red}$ ,  $E_{1/2} = E^{0'}$ , see Eq. 1.19.



### 1.2.2. Quasi reversible charge transfer process

The rate of the charge transfer process is comparable to the rate of diffusion and a mixed kinetics is established. It is characterized that the peak current does not change linearly with the square root of the sweep rate and the peak potential is not constant. Because the peak current is not a linear function of the square root of the sweep rate, this method is not suitable for determining the diffusion coefficient.

### 1.2.3. Irreversible charge transfer process

This is the case if the rate of the charge transfer process is very small compared to diffusion, or if the charge transfer process is chemically irreversible, i.e., e.g. oxidation is possible within the given potential range but the reduction is not. Then the peak current is proportional again to the square root of the sweep rate, but the proportionality factor is different from the reversible case and the peak current depends on the symmetry factor, as well.

$$I_p = 0,4967 \left( \frac{F^3}{RT} \right)^{1/2} \alpha^{1/2} z A D_{\text{Red}}^{1/2} c_{\text{Red}} v^{1/2} \quad 1.24.$$

The peak potential changes logarithmically with the sweep rate:

$$E_p = E^{0'} + \frac{RT}{\alpha F} \left[ 0,780 + \ln \left( \frac{D_{\text{Red}}^{1/2}}{k^0} \right) + \ln \left( \frac{\alpha F v}{RT} \right)^{1/2} \right] \quad 1.25.$$

That is

$$E_p = \left\{ E^{0'} + \frac{RT}{\alpha F} \left[ 0,780 + \ln \left( \frac{D_{\text{Red}}^{1/2}}{k^0} \right) + \frac{1}{2} \ln \left( \frac{\alpha F}{RT} \right) \right] \right\} + \frac{RT}{2 \cdot \alpha F} \ln v$$

The following connection can be given between peak current and peak potential:

$$I_p = 0,227 \cdot z F A c_{\text{Red}} k^0 \exp \left[ \alpha \frac{F}{RT} (E_p - E^{0'}) \right] \quad 1.26.$$

The logarithm of the peak current gives a straight line as the function of  $(E_p - E^{0'})$ , from whose slope  $\alpha$ , from its intercept  $k^0$  can be calculated.

$$\ln I_p = \ln(0,227 \cdot z F A c_{\text{Red}} k^0) + \frac{\alpha F}{RT} (E_p - E^{0'})$$

$\alpha$  could be determined from the following relation, as well:

$$E_p - E_{p/2} = 1,857 \frac{RT}{\alpha F} \quad 1.27.$$

where  $E_{p/2}$  is the potential where the current is the half of the peak current, so-called half-peak potential.

## 1.3. Cyclic voltammetry

In cyclic voltammetry (CV, the full original name is cyclic potential sweep chronoamperometry) the beginning is the same as in linear sweep voltammetry but at reaching an  $E_\lambda$  limiting potential difference, the sweep rate becomes opposite, i.e. the potential scan reversed.

$$E = E_{init} + vt \quad (0 < t \leq \lambda) \quad 1.28.$$

$$E = E_{init} + 2v\lambda - vt \quad (t > \lambda) \quad 1.29.$$

Here again, the current is plotted as a function of the potential difference of the working and reference electrodes (i.e., as a function of time). (A cutoff of the three-dimensional function of the current-potential-time is represented but now as a result of a cyclic potential change.) The cycle is repeatable, and in a chemically reversible process, after a few cycles, a stationary state (a voltammogram that does not change in time) can develop.

Since the potential of the working electrode during these measurements is not constant, there is a "signal", i.e. measurable current, without a charge transfer process. This is the result of a change in the double layer of the working electrode (charge accumulation or depletion) (see Figure 1, Figure 5), the capacitive current of charging and discharging the double layer. That is,  $I_C = vC$  (at least after a short, transient time) and in the other half of the cycle  $I_C = -vC$ .

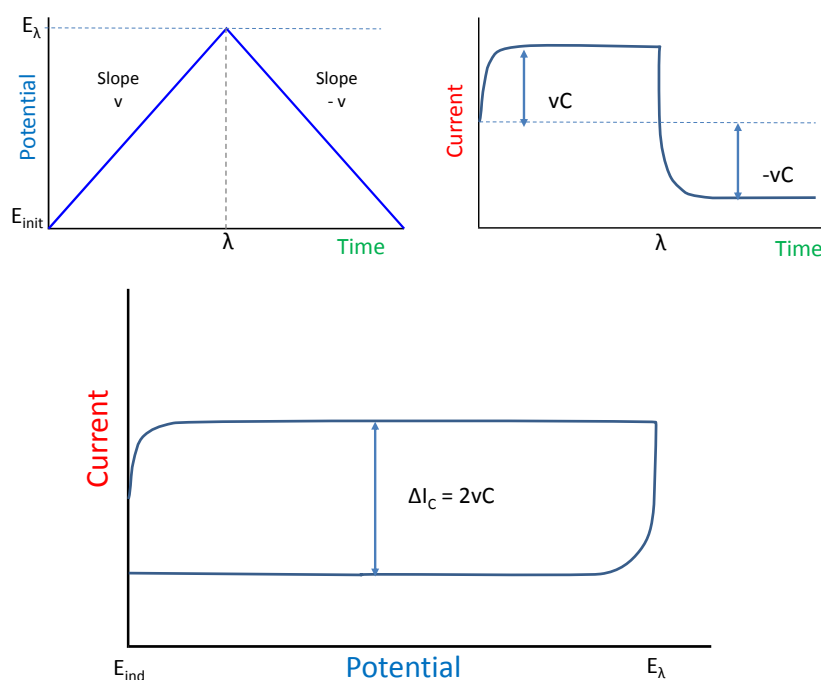


Figure 8 Cyclic voltammogram for an ideally polarizable electrode if the double layer capacitance does not depend on the electrode potential

So-called capacitive loop appears whose value is directly proportional to the sweep rate, and provides a simple way to determine the double layer capacitance.

$$\frac{\Delta I_c}{2v} = C \quad 1.30.$$

If a Faradaic process can occur on the surface in a given potential range, as well, the resulting current will be the sum of capacitive and Faradaic current ( $I = I_c + I_f$ ).

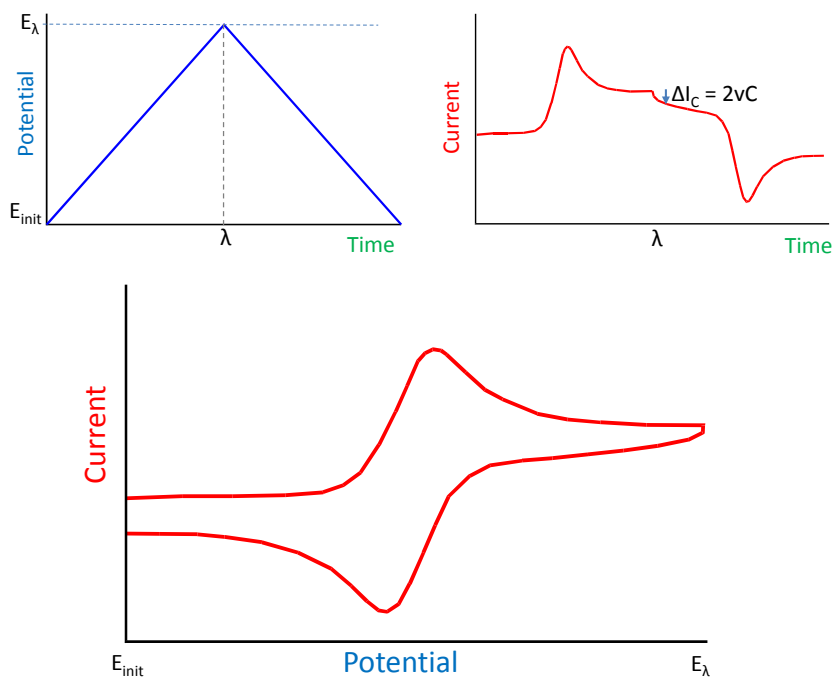


Figure 9 Cyclic voltammogram when a charge transfer process also occurs on the electrode surface.

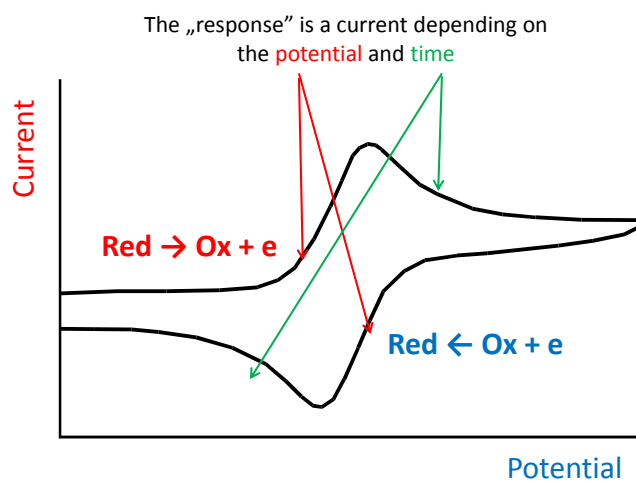


Figure 10 Interpretation of certain regions of the voltammogram.

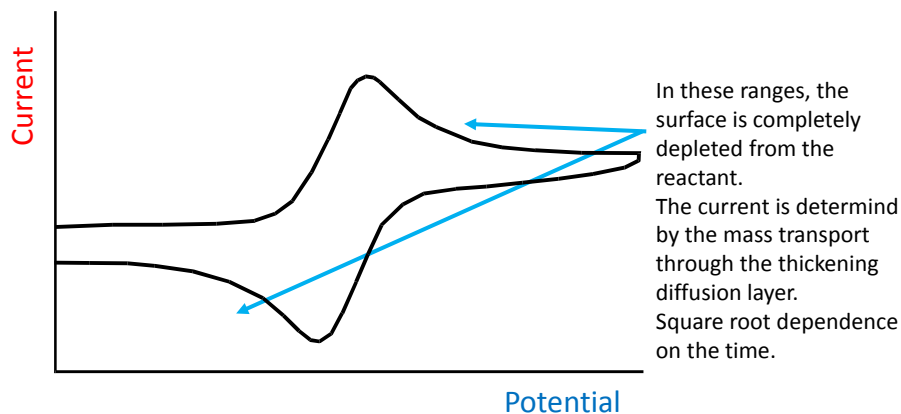
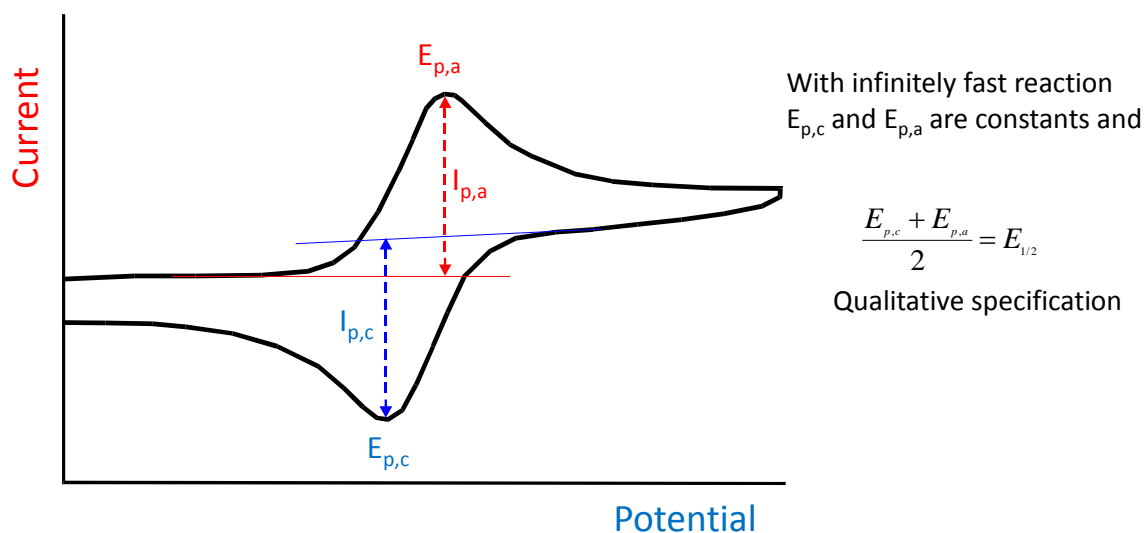


Figure 11 The diffusion limited current

When we start from a state that initially only Red was present in the solution, the first half of the cycle produces Ox on the surface and in the second half of the cycle this Ox is reduced back to Red in the appropriate potential range.

The characteristic parameters of the voltammogram are the (corrected) anodic and cathodic peak current,  $I_{p,a}$  and  $I_{p,c}$ , the anodic and cathodic peak potential,  $E_{p,a}$  and  $E_{p,c}$  and the difference between the peak potential  $\Delta E_p$ .



$$I_{p,a} = I_{p,c} = 0,4463 \left( \frac{F^3}{RT} \right)^{1/2} z^{1/2} A D^{1/2} c v^{1/2} \quad \text{Quantitative specification}$$

Figure 12. The characteristic parameters of a cyclic voltammogram.

The determination of the peak current is a little tricky because it is not the absolute value of the current at the peak, but the difference between the "background current" (capacitive current and the decreasing diffusion limiting current) and the actual peak current (see Figure 12). This separates the actual oxidation and reduction processes from the other processes.

In electrochemistry it is customary to classify charge transfer processes, according to the appearance of cyclic voltammograms, into three categories.

### 1.3.1. Reversible charge transfer process

In a reversible case, the numerical solution of the kinetic equation system yields:

$$\left| \frac{I_{p,a}}{I_{p,c}} \right| = 1 \quad 1.31.$$

$$\frac{1}{2}(E_{p,a} + E_{p,c}) = E_{1/2} \quad 1.32.$$

if  $D_{Ox} = D_{Red}$ ,  $E_{1/2} = E^0$ , see Eq. 1.19.

$E_{p,a}$  and  $E_{p,c}$  are independent of the sweep rate and

$$\Delta E_p = 2,3 \frac{RT}{zF} \quad 1.33.$$

This can be used to determine the change in charge number,  $z$ .

$$I_p = 0,4463 \left( \frac{F^3}{RT} \right)^{1/2} z^{3/2} A D^{1/2} c v^{1/2} \quad 1.34.$$

(Randles-Sevcik equation if the diffusion coefficients of Ox and Red are equal,  $D$ ). The value of the multiplier is valid, if the current ( $I$ ) is given in Amperes, the surface area ( $A$ ) in  $\text{cm}^2$ , the diffusion coefficient ( $D$ ) in  $\text{cm}^2/\text{s}$ , the concentration ( $c$ ) in  $\text{mol}/\text{cm}^3$ , the sweep rate ( $v$ ) in  $\text{V}/\text{s}$ . The equation shows that the peak currents change linearly with the square root of the sweep rate and that the slope of the  $I_p - v^{1/2}$  function is proportional to  $D^{1/2}$  and to  $c$ . Whichever is known, the other can be determined.

### 1.3.2. Quasi reversible charge transfer process

In this case the rate of the charge transfer process is comparable to the rate of diffusion and a mixed kinetics is formed. Typically, the ratio of the peak currents is not necessarily one, they do not change with the square root of the sweep rate, and the peak potentials are not constant,  $\Delta E_p$  is dependent on the sweep rate. Because the peak current is not a linear function of the square root of rate of the potential change, this dependence is not suitable for determining the diffusion coefficient. Another experimental method is required to determine the diffusion coefficient. However, if the diffusion coefficient is known then the kinetics of the charge transfer process can be characterized.

The so-called Nicholson parameter ( $\Psi$ ) gives the ratio of the rate of charge transfer process to the rate of the diffusion process.

$$\Psi = \frac{\left( \frac{D_{Red}}{D_{Ox}} \right)^{\alpha/2} k^0}{\left( \pi D_{Red} \frac{zF}{RT} v \right)^{1/2}} \quad \text{or if } D_{Ox} = D_{Red} = D$$

$$\Psi = \frac{k^0}{\left( \pi D \frac{zF}{RT} v \right)^{1/2}} \quad 1.35.$$

Its value is determined by the peak separation ( $\Delta E_p$ ), and by numerical methods the relationship between the two:

| $\psi$ | $\Delta E_p/mV$ |
|--------|-----------------|
| 20     | 61              |
| 7      | 63              |
| 6      | 64              |
| 5      | 65              |
| 4      | 66              |
| 3      | 68              |
| 2      | 72              |
| 1      | 84              |
| 0.75   | 92              |
| 0.5    | 105             |
| 0.35   | 121             |
| 0.25   | 141             |
| 0.1    | 212             |

Table 1 The Nicholson parameter as a function of peak separation

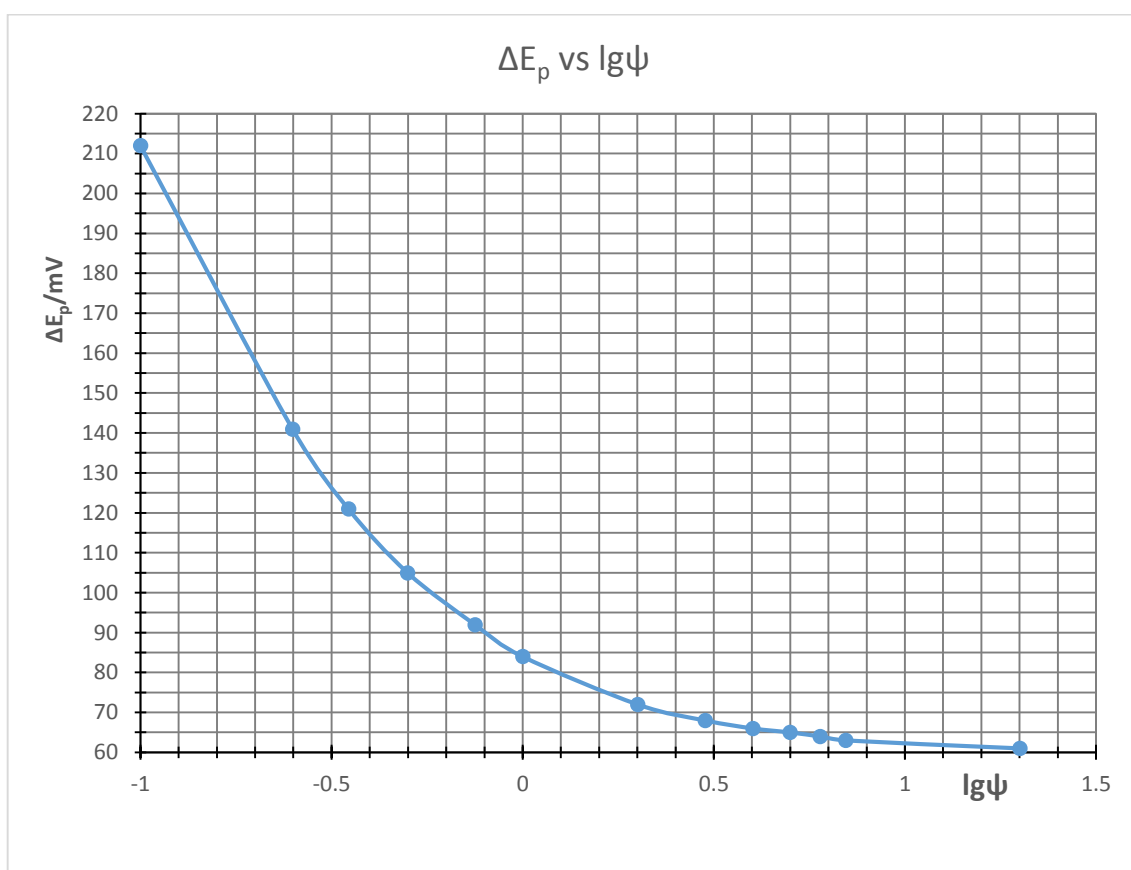


Figure 13 Peak separation as the function of the logarithm of the Nicholson parameter.

This gives an opportunity to determine  $\psi$  by measuring the peak potential difference and thus to determine  $k^0$  if the other parameters are known.

### 1.3.3. Irreversible charge transfer process

If the value of the Nicholson parameter is very small, the charge transfer rate is very small compared to the diffusion rate or if the charge transfer process is chemically irreversible, i.e., e.g. oxidation is possible within the given potential range but the reduction is not possible. Then, what is written for the LSV is valid, the other half of the cycle has no information.

#### 1.4. Potential step method, chronoamperometry

Since, in a quasi-reversible case, the peak current is not a linear function of the square root of the scan rate, it is not suitable for determining the diffusion coefficient. A much simpler method is the potential jump technique instead of linear (or cyclic) voltammetry. (Large potential step chronoamperometry)

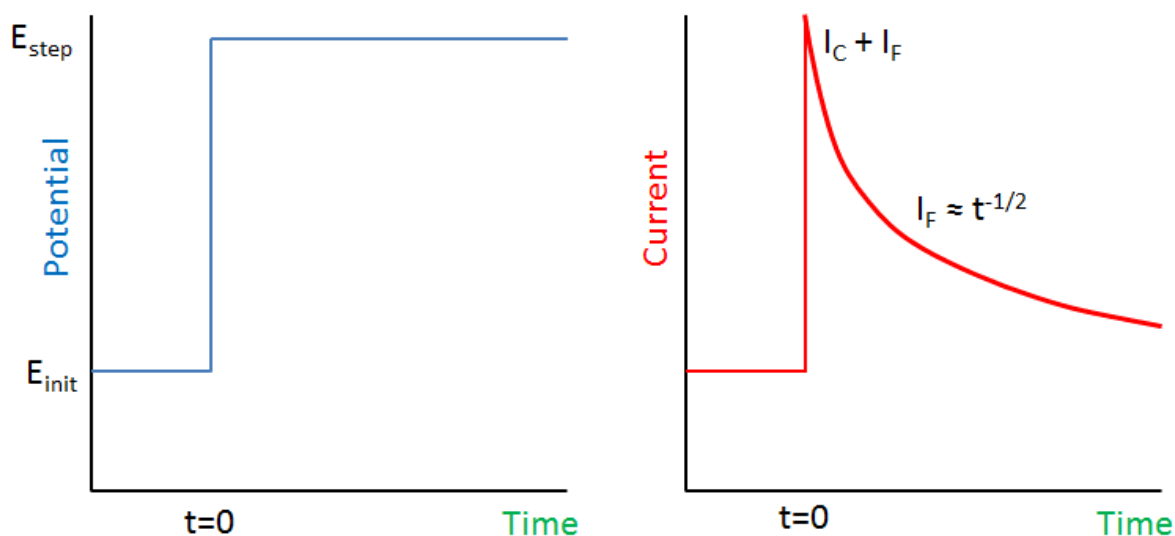


Figure 14 The large potential step method.

From an (ideally) Faradaic process free electrode potential ( $E_{init}$ ), we “jump” so much with the electrode potential that the charge transfer rate would be very high so that the surface concentration of the reactant substance becomes virtually zero immediately. The rate of further charge transfer is thus completely determined by the mass transport, the diffusion, which at this time means an increasingly slowing process through a thickening diffusion layer. If in the starting state only Red is present in  $C_{Red}$  concentration, the so-called Cottrell equation shows the time dependence of the diffusion limited current.

$$I = \frac{zFAD_{Red}^{1/2}C_{Red}}{\pi^{1/2}t^{1/2}} \quad 1.36.$$

That is, the current changes linearly with the reciprocal of the square root of the time, and from the slope, if the other parameters are known,  $D$  can be calculated. It should be noted that after the potential jump, for a short time, the current is the sum of a capacitive current and a Faradaic current, since it is also necessary to charge the electrochemical double layer to the potential change. The capacitive current, however, decreases exponentially in time, drops rapidly, and the square root time dependence is then clearly measurable. Not too long, until the convection, possibly vibration of the system, does not interfere with the measurement.

#### 1.5. Potential step method, chronocoulometry

Frequently, current measurement is "noisy", it contains components that are not related to the Faradaic process. For example, due to the high potential jump, the potentiostat is overloaded, and coming back to the normal operation takes time. For electrical measurements, the environment is also a source of noise. Anyone who goes by near to the measuring system causes "noise". It is therefore normal to use the smoother charge-time function instead of the current-time function (chronocoulometry). By integrating the Cottrell equation:

$$Q = \int_0^t Id\tau = \int_0^t \frac{zFAD_{Red}^{1/2}c_{Red}}{\pi^{1/2}\tau^{1/2}} = \frac{2zFAD_{Red}^{1/2}c_{Red}}{\pi^{1/2}}t^{1/2} + Q_0 \quad 1.37.$$

That is, the charge of the diffusion limited Faradaic process varies proportionally with the square root of time. The additive part is the integral of the capacitive current coming from the charging of the double layer and from the possible charge needed to transform substances adsorbed on the surface before the potential jump.

$$Q_0 = Q_{\text{double layer}} + zFA\Gamma \quad 1.38.$$

where  $\Gamma$  is the excess amount of substance on the surface (an excess of adsorbed material compared to the concentration in the solution). In today's practice, we do not measure the charge directly, but the current, and by its numerical integration the charge can be determined.

### 1.6. Computer-controlled potentiostats

Most of today's potentiostats (unless they have a special accessory) do not work with continuous signals, but are digitally controlled. A computer set up for regulation and data collection sends the control signals via digital-to-analogue (DA) converter and collects the measured data via an analog-to-digital (AD) converter (see Figure 15).

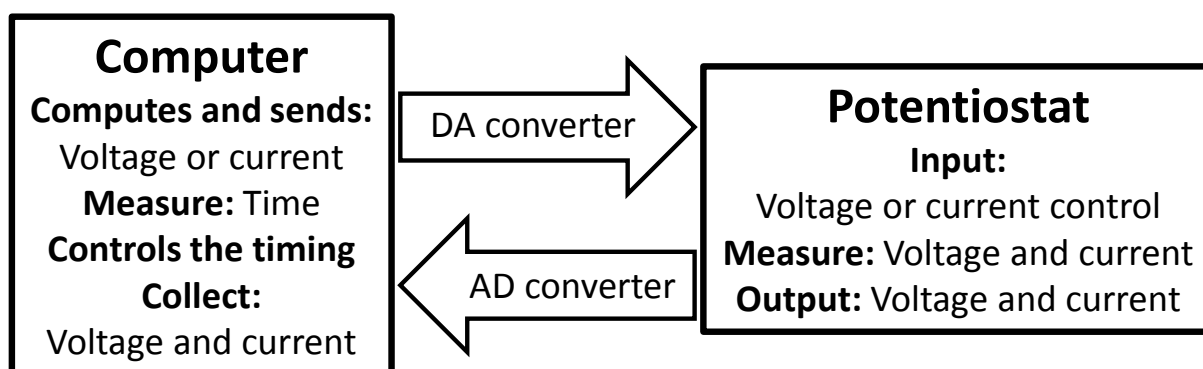


Figure 15 Schematics of digital control and data collection

All this means technically that in linear, or cyclic voltammetric measurements the potential - time dependence differs from analogue instruments. The computer schedules the potential differences at the DA converter and reads the current and potential values in the AD converter. That is, the actual potential - time function represents a "staircase" compared to the linear dependence (see Figure 16). The value of the time step ( $\Delta t$ ) could not be less than the sum of the time of the transmission and the collection of the data, so the potential step ( $\Delta E$ ) could not be any value at a given sweep rate ( $v$ ). It should be minimally  $v \cdot \Delta t$ . In "staircase" voltammetry, measuring the current is also not continuous, but certain "sampling" takes place at a certain stage of the potential step (see Figure 17), usually several, and their values are averaged to reduce the noise level of the signal, which is transferred to



the computer. Obviously, the smaller and more frequent the stairs, the closer you approach the measurement of linear voltammetry. However, this method of measurement distorts the shape and values of the voltammograms described in the theoretical introduction. This method can be used if the distortion is not significant, as in this chronoamperometric practice.

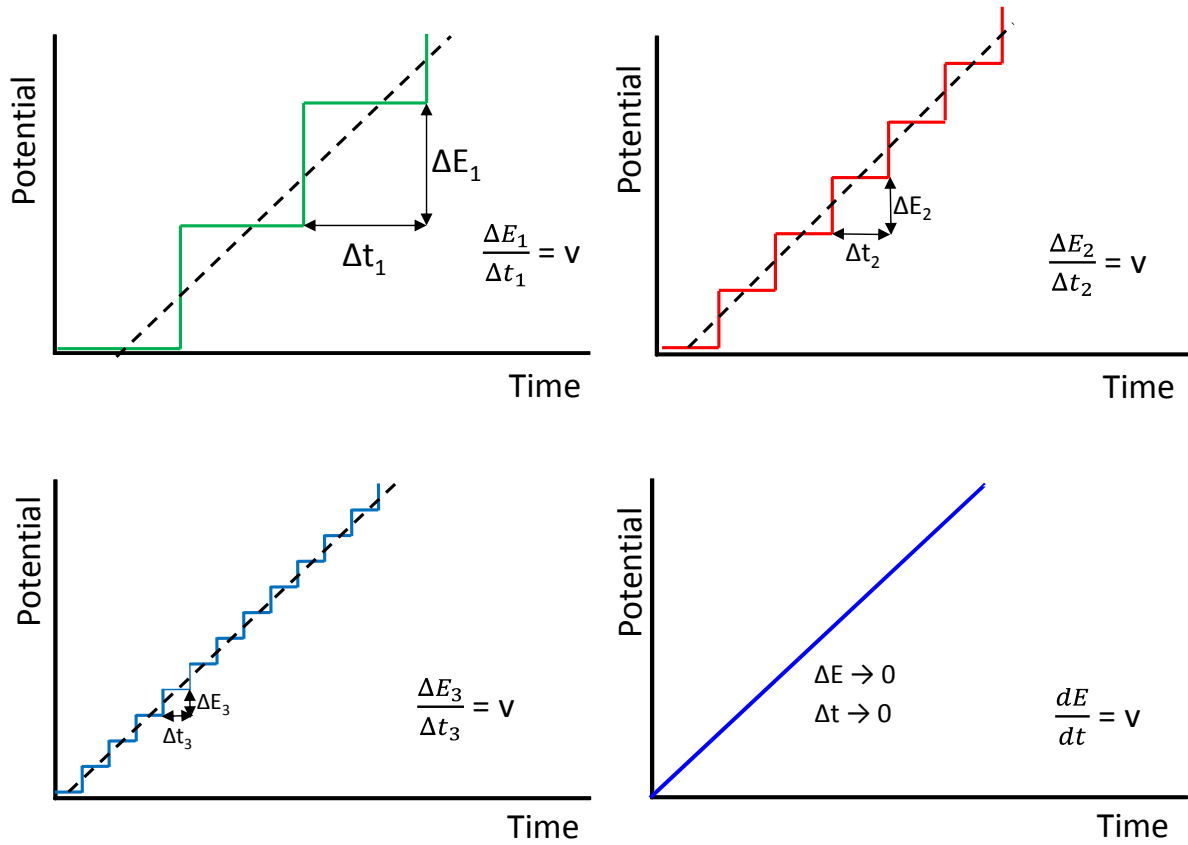


Figure 16 Staircase voltammetry

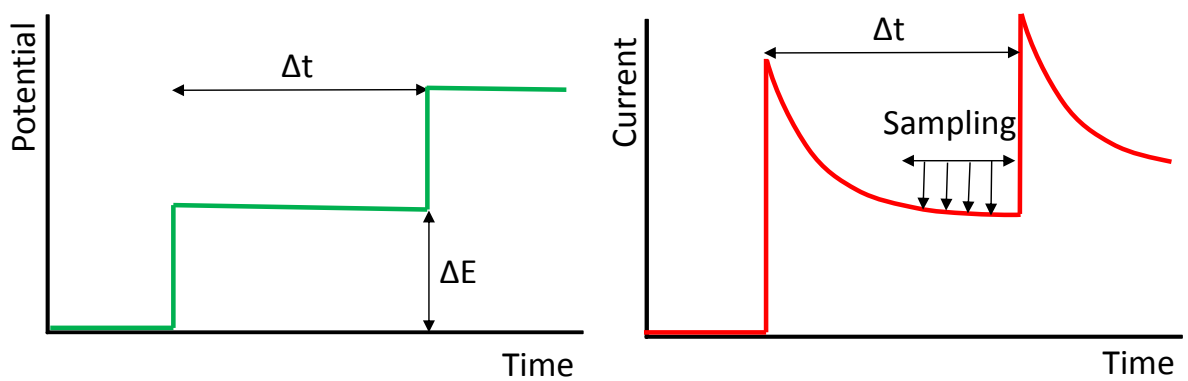


Figure 17 Potential stair, current response and current "sampling" in a staircase voltammetry.

## 2. Measurements

### 2.1. Preparation of the electrodes

The gold (Au) and glassy carbon (GC) electrodes of 3 mm diameter are sealed in a Teflon rod. Before the measurements the electrode surfaces have to be polished. For polishing, use  $\gamma$ -alumina powder on a polishing velvet, slightly moistened with distilled water (make a slurry). Hold the electrode vertically, move it circularly and in a rosette shape, to avoid deformation and distortion on the flat surface (see Figure 18)

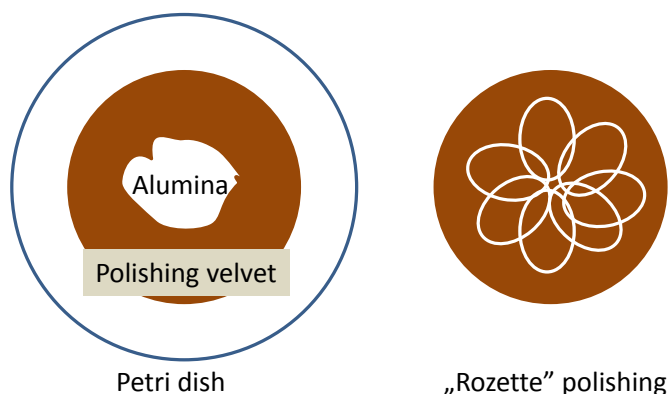


Figure 18 Polishing

After polishing (about 5 minutes with each electrode), clean the electrodes in an ultrasound bath to remove the polishing powder (twice for 1 minute in clean distilled water) and finally rinse with distilled water!

### 2.2. Assembling the cell

Use a low 50 ml beaker! Place the working electrode in the center of the beaker, next or above the counter electrode (Pt) and place the Luggin capillary or the reference electrode itself on the other side. If using Luggin capillary, fit the reference electrode in the capillary and use a syringe to suck the electrolyte solution through the side stem to the reference electrode. Make sure that the rubber seal of the reference electrode is properly placed and tight and the solution does not flow out during the measurement. If the contact with the cell breaks, the system may be damaged. Connect the three electrodes to the appropriate terminals of the potentiostat.

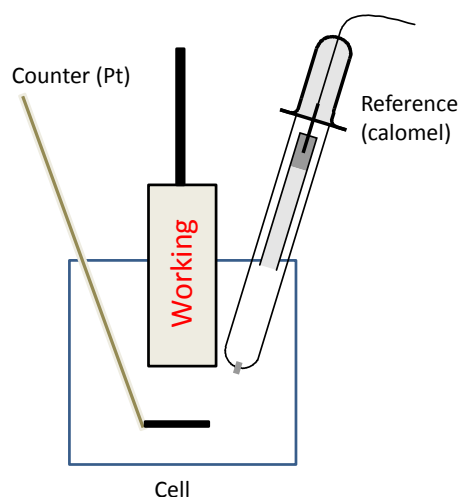


Figure 19 Arrangement of the electrodes

As a reference electrode, use a calomel electrode with 1 M KCl solution. (Normal Calomel Electrode, NCE, i.e.  $\text{Hg} | \text{Hg}_2\text{Cl}_2 (s) | \text{cc. Hg}_2\text{Cl}_2 (aq) + 1 \text{ M KCl}$ )

The manual (description) of the potentiostat can be found among the exercise equipments.

### 2.3. Electrochemically reversible system

If the instructor does not specify anything else, prepare 50 cm<sup>3</sup>, 5 mmol/dm<sup>3</sup> K<sub>4</sub>[Fe(CN)<sub>6</sub>] (HCF) solution containing 1mol / dm<sup>3</sup> KCl.

If the instructor does not specify anything else, take the cyclic voltammograms at Au electrode in 5 mM K<sub>4</sub>[Fe(CN)<sub>6</sub>] solution within the electrode potential range of -50 mV to +450 mV with 320, 160, 80, 40, 20, 10, 5 mV/s sweep rates. One cycle is enough, the current range should be  $\pm 200 \mu\text{A}$  (or in NOVA program with Autolab potentiostat it is automatic). The potential steps are 1 mV in each scan. After each measurement, homogenize the solution around the electrode by mixing and wait for

approx. one minute until the solution is standstill. (If you use the Autolab potentiostat with NOVA controller program, the parameters are set in the appropriate "Procedure", ONLY the sweep rate has to be specified before each measurement!)

Also do a potential step measurement from -50 mV to jump to +450 mV potential! The pre-polarization is 60 s and the stair (step) time is 10 s. The current range is  $\pm 200 \mu\text{A}$  (or automatic). (If you use the Autolab potentiostat with NOVA controller, the parameters are set in the appropriate "Procedure".)

#### **2.4 Electrochemically quasi-reversible system**

If the instructor does not specify anything else, use the previous assembly and solution, only replace the working electrode! If the instructor does not specify anything else, take the cyclic voltammograms at the GC electrode within the potential change rates of -50 mV to +450 mV with 320, 160, 80, 40, 20, 10, 5 mV/s sweep rates. 1 cycle is enough, the current range should be  $\pm 200 \mu\text{A}$  (or automatic). The potential steps are 1 mV in each scan. After each measurement, homogenize the solution around the electrode by mixing and wait for approx. one minute until the solution is standstill. (If you use the Autolab potentiostat with NOVA controller program, the parameters are set in the appropriate "Procedure", ONLY the sweep rate has to be specified before each measurement!)

#### **2.5. Irreversible system**

If the instructor does not specify anything else, prepare an L-ascorbic acid solution of 50  $\text{cm}^3$ , in 5  $\text{mmol}/\text{dm}^3$  concentration which contains 1  $\text{mol}/\text{dm}^3$  KCl.

Take the cyclic voltammograms at the Au electrode in a potential range from -100 to +500 mV with 160, 80, 40, 20, 10, 5 mV/s sweep rates. 1 cycle is enough, the current range should be  $\pm 200 \mu\text{A}$  (or automatic). The potential steps are 1 mV in each scan. After each measurement, homogenize the solution around the electrode by mixing and wait for approx. one minute until the solution is standstill. (If you use the Autolab potentiostat with the NOVA controller, the parameters are set in the appropriate "Procedure", ONLY the sweep rates have to be specified before each measurement!)

#### **The electrode must be re-polished before the measurement.**

Also make a potential step measurement from -100 mV to +500 mV potential! The pre-polarization is 60 s and the stair (step) time is 10 s. The current range is  $\pm 200 \mu\text{A}$  (or automatic). (If you use the Autolab potentiostat with the NOVA controller, the parameters are set in the appropriate "Procedure".)

### 3. Evaluation

#### 3.1. Electrochemically reversible system

3.1.1. Plot the voltammograms in one diagram.

To do this, you can use the NOVA measuring program, but it can also be done after exporting data to Excel. We recommend this because of further data processing! For details of data transfer, see Measurement Evaluation in Annex.

3.1.2. Make a summary table to evaluate the cyclic voltammograms of the Au /  $K_4[Fe(CN)_6]$  system!

| v[V/s] | $I_{p,a,meas}$ [A] | $I_{p,c,meas}$ [A] | $I_{p,a,backg}$ [A] | $I_{p,c,backg}$ [A] | $I_{p,a}$ [A] | $I_{p,c}$ [A] | $E_{p,a}$ [V] | $E_{p,c}$ [V] | $\Delta E_p$ [V] |
|--------|--------------------|--------------------|---------------------|---------------------|---------------|---------------|---------------|---------------|------------------|
|        |                    |                    |                     |                     |               |               |               |               |                  |

To determine the background currents ( $I_{p,backg}$ ) at the peak potentials, fit straight lines as shown in Figure 12 to the start and to the turning of the cycle when using Excel or import the requested parameters from the NOVA "Peak search" analysis command. Then, of course, convert (modify) the table appropriately. E.g.,

| v[V/s] | $I_{p,a}$ [A] | $I_{p,c}$ [A] | $E_{p,a}$ [V] | $E_{p,c}$ [V] | $\Delta E_p$ [V] |
|--------|---------------|---------------|---------------|---------------|------------------|
|        |               |               |               |               |                  |

3.1.3. Based on the difference in the peak potentials of cyclic voltammograms with small sweep rates ( $\Delta E_p$ ), estimate the charge number change ( $z$ ) for  $K_4[Fe(CN)_6]$  according to Eq. 1.33.

3.1.4. Knowing  $z$ , determine the diffusion coefficient of  $K_4[Fe(CN)_6]$  under the given conditions from the potential step measurement (Cottrell equation, linear fitting where applicable, or linear fitting of the integrated equation where applicable, Eq. 1.36, Eq. 1.37)! Integration can also be done with the NOVA "Integrate" command, and then you can import the data to Excel for plotting and evaluation.

3.1.5. Prepare the (corrected) peak current - square root (sweep rate),  $I_p$  vs  $v^{1/2}$  diagram and determine the diffusion coefficient (Eq. 1.34) from the slope of the linear range.

3.1.6. Calculate the formal potential (Eq. 1.32) from the values of  $E_{p,a}$  and  $E_{p,c}$ . Compare to the value of the standard redox potential of  $[Fe(CN)_6]^{4-} / [Fe(CN)_6]^{3-}$  system which can be found in the literature, and explain the difference.

3.1.7. If  $\Delta E_p$  is not less, equal to 60-65 mV (i.e. quasi-reversible behavior), estimate the  $k^0$  value from the Nicholson parameter (Eq. 1.35, Table 1, Figure 13).

#### 3.2. Electrochemically quasi-reversible system

3.2.1. Plot the voltammograms in one diagram.

To do this, you can use the NOVA measuring program, but it can also be done after exporting data to Excel. We recommend this because of further data processing! For details of data transfer, see Measurement Evaluation in Annex.

3.2.2. Make a summary table to evaluate the cyclic voltammograms of the GC /  $K_4[Fe(CN)_6]$  system!

| v[V/s] | $I_{p,a,meas}$ [A] | $I_{p,c,meas}$ [A] | $I_{p,a,backg}$ [A] | $I_{p,c,backg}$ [A] | $I_{p,a}$ [A] | $I_{p,c}$ [A] | $E_{p,a}$ [V] | $E_{p,c}$ [V] | $\Delta E_p$ [V] |
|--------|--------------------|--------------------|---------------------|---------------------|---------------|---------------|---------------|---------------|------------------|
|        |                    |                    |                     |                     |               |               |               |               |                  |

To determine the background currents ( $I_{p,backg}$ ) at the peak potentials, fit straight lines as shown in Figure 12 to the start and to the turning of the cycle when using Excel or import the requested

parameters from the NOVA "Peak search" analysis command. Then, of course, convert (modify) the table appropriately. E.g.,

| v[V/s] | I <sub>p,a</sub> [A] | I <sub>p,c</sub> [A] | E <sub>p,a</sub> [V] | E <sub>p,c</sub> [V] | ΔE <sub>p</sub> [V] |
|--------|----------------------|----------------------|----------------------|----------------------|---------------------|
|        |                      |                      |                      |                      |                     |

3.2.3. Prepare the (corrected) peak current - square root (sweep rate), I<sub>p</sub> vs v<sup>1/2</sup> diagram and the peak potentials - square root (sweep rate), E<sub>p</sub> vs v<sup>1/2</sup> diagram and the ΔE<sub>p</sub> vs v<sup>1/2</sup> diagram! In what sweep rate range is the electrochemical reversibility satisfied?

3.2.4. Where it is not, knowing z and D (previously defined values), determine k<sup>0</sup> according to Nicholson's method! Explain the deviations from the Au electrode!

### 3.3. Irreversible system

3.3.1. Plot the voltammograms in one diagram.

3.3.2. Estimate the capacitive currents from the currents of the Faradaic process free part of the voltammograms. For this, in the -100 mV - 0 mV electrode potential range (where oxidation of L-ascorbic acid has apparently not yet started and no other Faradaic process could be observed, i.e. the voltammograms are approximately straight lines), read the values of anodic and cathodic currents. (If the signals are noisy, average) Plot ΔI<sub>C</sub> = I<sub>C,a</sub> - I<sub>C,c</sub> as a function of the sweep rate (v)! As Figure 8 shows determine the electrode's capacitance from the slope of the line. Explain the capacitance value according to literature's data that a completely smooth, inert electrode has a typical capacitance of 20 μF/cm<sup>2</sup>! What is the ratio of the actual surface area of the electrode tested to the geometric surface (what is the so-called roughness factor)?

3.3.3. Make a summary table for the Au / L-ascorbic acid system!

| v[V/s] | I <sub>p,a,meas</sub> [A] | I <sub>p,a,backg</sub> [A] | I <sub>p,a</sub> [A] | E <sub>p,a</sub> [V] | E <sub>p/2</sub> [V] |
|--------|---------------------------|----------------------------|----------------------|----------------------|----------------------|
|        |                           |                            |                      |                      |                      |

Values can be obtained from Excel or NOVA program. In the latter case, convert the table. E.g.

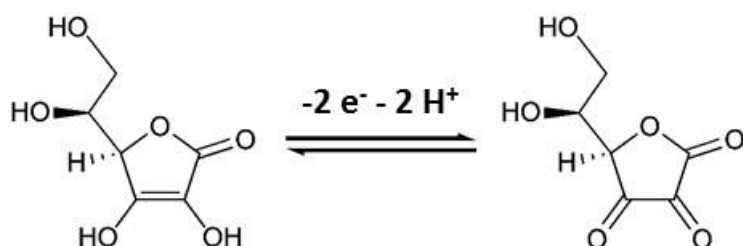
| v[V/s] | I <sub>p</sub> [A] | E <sub>p</sub> [V] | E <sub>p/2</sub> [V] |
|--------|--------------------|--------------------|----------------------|
|        |                    |                    |                      |

Determine the value of the symmetry factor from the average of (E<sub>p</sub> - E<sub>p/2</sub>) values (Eq. 1.27).

3.3.4.

Determine the diffusion coefficient of L-ascorbic acid] under the given conditions from the potential step measurement (Cottrell equation, linear fitting where applicable, or linear fitting of the integrated equation where applicable, Eq. 1.36, Eq. 1.37)! Integration can also be done with the NOVA "Integrate" command, and then you can import the data to Excel for plotting and evaluation.

To this, it is to be known that the oxidation of L-ascorbic acid in the given conditions results in dehydro-L-ascorbic acid:



That is, the gross electron number change is two. This data can not be determined from the measurements. The process is therefore a complex, not an elementary charge transfer process, but an Electrochemical-Chemical-Electrochemical-Chemical (ECEC) mechanism. See Figure 2. The relationships of the elementary charge transfer processes can be used only because the first step is the slowest, the rate determining.

3.3.5. Plot  $I_p$  vs  $v^{1/2}$  and determine the diffusion coefficient (Eq. 1.24) from the linear range with knowing  $\alpha$  and  $z$ . Explain the deviation or identity to the result of 3.3.4.

3.3.6. Plot the  $E_p - \ln v$  relationship and determine the symmetry factor from the slope (Eq. 1.25) as well. Explain the deviation or identity to the result of 3.3.3.

3.3.7. Plot the  $\ln I_p - (E_p - E^0)$  function and determine the  $k^0$  value from its intercept (Eq. 1.26). For this, it is necessary to know that in the given conditions (ionic strength, pH, and reference electrode) the formal potential is 0.210 V. From these measurements this value can not be determined!

#### 4. Summary

Make a summary table of your results!

| Results                            | System studied                          |   |                    |
|------------------------------------|---|---|--------------------|
|                                    | Au/[Fe(CN) <sub>6</sub> ] <sup>4-</sup> | GC/[Fe(CN) <sub>6</sub> ] <sup>4-</sup> | Au/L-ascorbic acid |
| $z$                                |   |   |                    |
| $E^0$ (V)                          |   |   |                    |
| $k^0$ (cm/s)                       |   |   |                    |
| $D$ (average) (cm <sup>2</sup> /s) |   |   |                    |
| $\alpha$ (average)                 |   |   |                    |
| $C$ ( $\mu$ F)                     |   |   |                    |
| Roughness factor                   |   |   |                    |

Literature: Allen J. Bard, Larry R. Faulkner, ELECTROCHEMICAL METHODS Fundamentals and Applications; JOHN WILEY & SONS, INC., 2001

### **Control questions (Week 1)**

1. What is the electrode potential, the standard electrode potential and the formal potential?
2. What are the ideally polarizable and ideally non-polarizable electrodes?
3. What sub-processes should be considered in the kinetics of a charge transfer process?
4. How is the reaction rate of heterogeneous reactions defined?
5. How can the rate of the electrochemical charge transfer processes be expressed with the measurable current?
6. How does the rate of charge transfer processes change with the electrode potential?
7. Write the Nernst equation for an elementary Red-Ox transformation.
8. What are the characteristic parameters of a linear voltammogram?
9. What are the characteristic parameters of a cyclic voltammogram?
10. What is the essence of potential step technique and what data can be derived from the measurements?
11. What does it mean: electrochemically reversible, quasi-reversible and irreversible system?

### **Control questions (Week 2)**

1. What is the symmetry factor and what is the standard rate coefficient?
2. In an electrochemically reversible process how would you determine the formal potential, the symmetry factor, and the standard rate coefficient?
3. In an electrochemically quasi-reversible process how would you determine the formal potential, the symmetry factor, and the standard rate coefficient?
4. In an electrochemically irreversible process how would you determine the formal potential, the symmetry factor, and the standard rate coefficient?
5. How can you determine the diffusion coefficients of electroactive substances?
6. How does the formal potential change with the composition of the solution and why?
7. In an electrochemically reversible process, how does the peak current change with the sweep rate? What is the condition of reversibility?
8. In an electrochemically irreversible process, how does the peak current change with the sweep rate? What is the condition of irreversibility?
9. What is the electrode capacitance and how can you estimate its value?
10. Is the reaction rate of the charge transfer process dependent on the geometric or the actual surface area? What's the difference between the two?
11. Why is oxidation of L-ascorbic acid irreversible?