MASARYKOVA UNIVERZITA

Přírodovědecká fakulta

X. letní škola elektrochemie

X. Summer school of electrochemistry

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Úlohy pro letní školu elektrochemie

Summer electrochemical school tasks

POTENTIOMETRIC TITRATION

Determination of protonation constants of adenine

Potentiometry is a widespread electroanalytical technique, being primarily used for pH measurements in different samples and for the determination of ionic constituents in biological fluids (e. g. blood, urine), but also as a transduction mode in monitoring selective interactions in molecular sensor devices or in the course of chemical reactions. One of the major types of potentiometry, potentiometric titration is based on the monitoring of the indicating electrode potential change as a function of the reagent addition to the sample. Potentiometric methods are used to monitor of different types of titration (e.g. acid-base titrations, complexing, redox, precipitation). The result is the potentiometric titration curve of the characteristic sigmoidal shape and the titration endpoint is read out by using different mathematical methods, such as second derivative of titration points, linearization of titration curve (Gran's method), calculation of polynom (Samsonk's method)[1,2].

Potentiometric titration is a suitable method for the investigation of protonation – deprotonation equilibrium of biologicaly important compounds (purine derivatives, cytokinins, etc.) and it enables very precise determination of protonation constants $pK_{a.}$

Adenine (6-aminopurine) is one of the two most commonly occurring purines in ribonucleic (RNA) and deoxyribonucleic acid (DNA), and thus it is involved in the process of protein synthesis and transmission of genetic information. The knowledge of its protonation equilibrium is very important not only in biochemical processes and in electroanalysis, but also for the study of metal complexes in which adenine takes the role of the ligand. Adenine exhibits two dissociation constants (pK_{a1} = 4.12 and pK_{a2} = 9.83) [3]

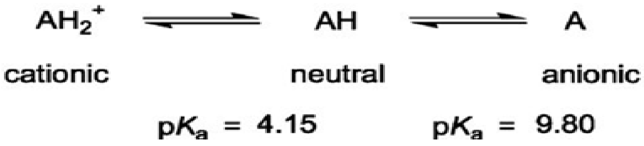

Fig.1: Protonation-deprotonation of adenine

APPARATUS, ACCESSORIES AND REAGENTS

- automatic titrator Titrando 835 (Metrohm, Switzerland), thermostat Julabo F25 – EH
- Tiamo 01/02 software (Metrohm, Switzerland)
- combined ion – selective electrode LL Ecotrode plus

- potentiometric vessel
- argon
- standardized NaOH; HCl; NaCl; milli Q water (18.2 MΩ·cm, 25 °C)
- adenine

SOLUTIONS

Stock solutions

c (NaOH) = 0.1 mol/L; c (HCl) = 0.1 mol/L; c (NaCl) = 1 mol/L; c (adenine) = $1 \cdot 10^{-3}$ mol/L

The LL Ecotrode plus electrode calibration

5 mL of HCl + 4.5 mL of NaCl + 40.5 mL of milli Q water

Sample measurement

0.5 mL of HCl (0,1mol/L) + 5 mL of adenine (mmol/L) + 4.95 mL of NaCl (1 mol/L) + 39.55 mL of milli Q water

EXPERIMENT

The LL Ecotrode plus electrode calibration

5 mL of HCl (0.1mol/L); 4.5 mL of NaCl (1mol/L) + 40.5 mL of milli Q water

Sample measurement

0.5 mL of HCl (0.1mol/L) + 5 mL of adenine (mmol/L) + 4.95 mL of NaCl (1 mol/L) +39.55 mL of milli Q water

PARAMETERS

1) *Electrode calibration*: the addition of standard titrant solution (0.1M NaOH) = 0.01 mL ; the total volume of 0.1M NaOH = 10 mL; the dosing rate is “maximal” and the titration mode is set as “optimal”. Other parameters are “0” or “off”

2) *Sample measurement:* the addition of 0.1M NaOH = 0.001 mL; the total volume of 0.1M NaOH = 1 mL; the dosing rate is “maximal” and the titration mode is set as “optimal”. Other parameters are “0” or “off”

Inert atmosphere is ensured by bubbling argon (99.999%) and stirring (magnetic stirrer, speed 3); temperature 25 °C.

MEASUREMENT

a) Start PC, open Tiamo 1.2 software (see manual below) and clean the automatic burette system with standard titrant solution (10 mL of 0.1 mol/L NaOH).

b) Prepare measured solution (for electrode calibration or sample measurement) in the vessel, put LL Ecotrode and dosing capillary into the vessel. Ensure inert atmosphere (bubbling and stirring). c) Set titration parameters in the selected method.

d) Start the measurement.

e) Record the titration curve and export data.

Note: LL Electrode plus is filled with 3M KCl, the filing hole should be opened during the measurement. After measurement don´t let the electrode in basic solution for long time, clean it and put it in stock solution (3M KCl).

POTENTIOMETRIC CURVE EVALUATION

The acidic part of calibration curve is used for the determination of the slope (q) and equilibrium potential (E^0) by linear regression. The equivalence point allows to calculate concentration of HCl. The basic part of calibration curve helps to calculate pK_w (should be for temperature 25° C about 13.78). All these values are important for calculation of pH and degree of titration *z* and subsequently of p*K*a value based on these equations:

$$pKa_1 = -\log\left[H^+\right] - \log\left(\frac{z}{1-z}\right) - \log\frac{\gamma_A}{\gamma_{HA}} \qquad pKa_2 = -\log\left[H^+\right] - \log\left(\frac{1-z}{z}\right) - \log\frac{\gamma_{A^-}}{\gamma_A}$$

$$z = \frac{\left(\dfrac{c_{NaOH}\cdot V_{ekv} - c_{NaOH}\cdot \Delta V}{V_{celk} + \Delta V} - \left[H^+\right] + \left[OH^-\right]\right)}{\left(\dfrac{c_L}{V_{celk} + \Delta V}\right)}$$

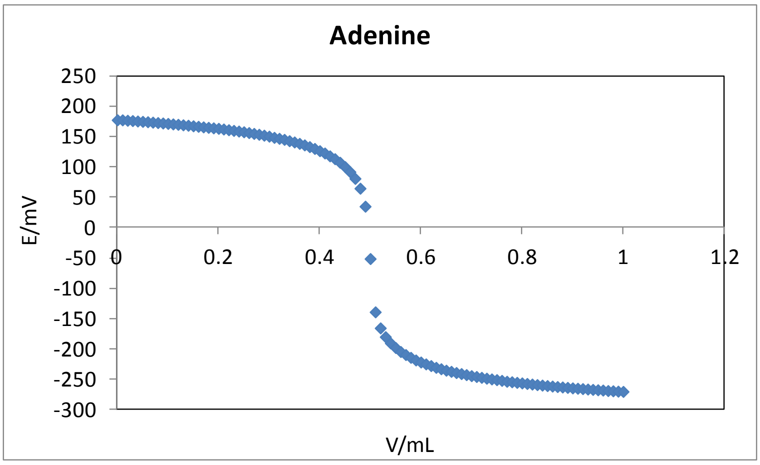

Fig.1: An example of measured data - titration curve of adenine in water

RESULTS AND REPORT

Calibration	
slope q	**E_0**

Measurement		
	pK_{a1}	**pK_{a2}**
1.		
2.		
3.		

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DISCUSSION AND REMARKS

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DISCUSSION AND REMARKS

VOLTAMMETRY ON MERCURY AND SOLID ELECTRODES

Electrochemical detection of DNA fragments on mercury and graphite electrodes

Linear sweep voltammetry (LSV) is one of the most used electrochemical methods. It requires a potentiostat and a three-electrode set, consisting of a working electrode, an auxiliary electrode, and a reference electrode [1]. The current is measured between the working and an auxiliary electrode while the potential between the working electrode and a reference electrode is swept linearly in time. The slope of the potential vs. time is called the scan rate v and the polarization process can be described by the equation: $E = E_{initial} + vt$. The oxidation or reduction processes of electro-active species are registered as current maxima (peaks I_p) providing the determination of their concentration in solutions.

$$I_p=2.99\cdot 10^5 n(\alpha n_a)^{1/2}AD^{1/2}cv^{1/2} \quad \text{(Delahay equation)}$$

Where: I_p stands for the current peak, n stands for the number of electrons participating in reaction and n_a for the number of electrons participating in a rate determining step, α is the electron transfer coefficient, A is the effective area of electrode, D is the diffusion coefficient, c is the concentration, v is the scan rate.

DNA fragments provide on mercury electrodes reduction signals of adenine and cytosine moieties, and oxidation signals of guanine moieties; on graphite electrodes (e.g., a pencil graphite electrode - PeGE) well readable oxidation signals [2-3]. Our research showed that the oxidation response of purines can be increased by using an electro-catalytical effect of monovalent copper ions. Cu(I)ions, obtained by the reduction of Cu(II) *in situ* on PeGE surface, are capable to form a Cu(I)-purine complex and this complex increases surface concentration of the purine studied. Thus, the electroanalysis of adenine, guanine or xanthine with the use of monovalent copper are based on: 1) the electrochemical reduction of Cu(II) at potential -0.1 V, 2) the formation of Cu(I)-purine complex, 3) the oxidation of complex at potentials closed to 0.5 V, 4) the oxidation of purine whose signal is higher than one without the presence of copper ions. The application of copper ions in voltammetric experiments contributes to significant decrease of the detection limit of purine [4-5].

APPARATUS, ACCESSORIES AND REAGENTS

- AUTOLAB PGS30 Analyzer (EcoChemie, Netherlands)
- NOVA software (Metrohm, Switzerland)
- Electrodes (working - PeGE with leads Tombow, 0.5 mm, reference – Ag/Ag Cl/3M KCl, counter electrode – Pt); voltammetric vessel
- argon
- phosphate-acetate buffer pH 5.5; c (CH_3COOH) = 0.4 mol/L, c (H_3PO_4) = 0.4 mol/L, c(NaOH) = 2 mol/L
- adenine, guanine or other purine derivative, copper sulphate; miliQ water (18.2 MΩ·cm)

SOLUTIONS

Supporting electrolyte

phosphate-acetate buffer pH 5.5; c (CH_3COOH) = 0.4 mol/L, c (H_3PO_4) = 0.4 mol/L, c($NaOH$) = 2 mol/L; $CuSO_4 = 1\cdot10^{-3}$ mol/L

Samples

DNA fragments, adenine, guanine or xanthine (stock solution = $1\cdot10^{-3}$ mol/L)

EXPERIMENT

- Voltammetric experiment of purine derivative in the absence of copper ions
  2 mL supporting electrolyte + 8 mL miliQ H_2O + 100 µL purine
- Voltammetric experiment of purine derivative in the presence of copper ions
- 2 mL supporting electrolyte + 8 mL miliQ H_2O + 100 µL of purine + 100 µL Cu(II)

PARAMETERS (CV OR LSV - CYCLIC OR LINEAR SWEEP VOLTAMMETRY)

LSV measurement

Start potential -0.1 V; stop potential -0.2 V; upper vertex potential 1.4 V; lower vertex potential -0.1 V; scan rate 200 (400, 800) mV/s; time of accumulation 120 s, room temperature

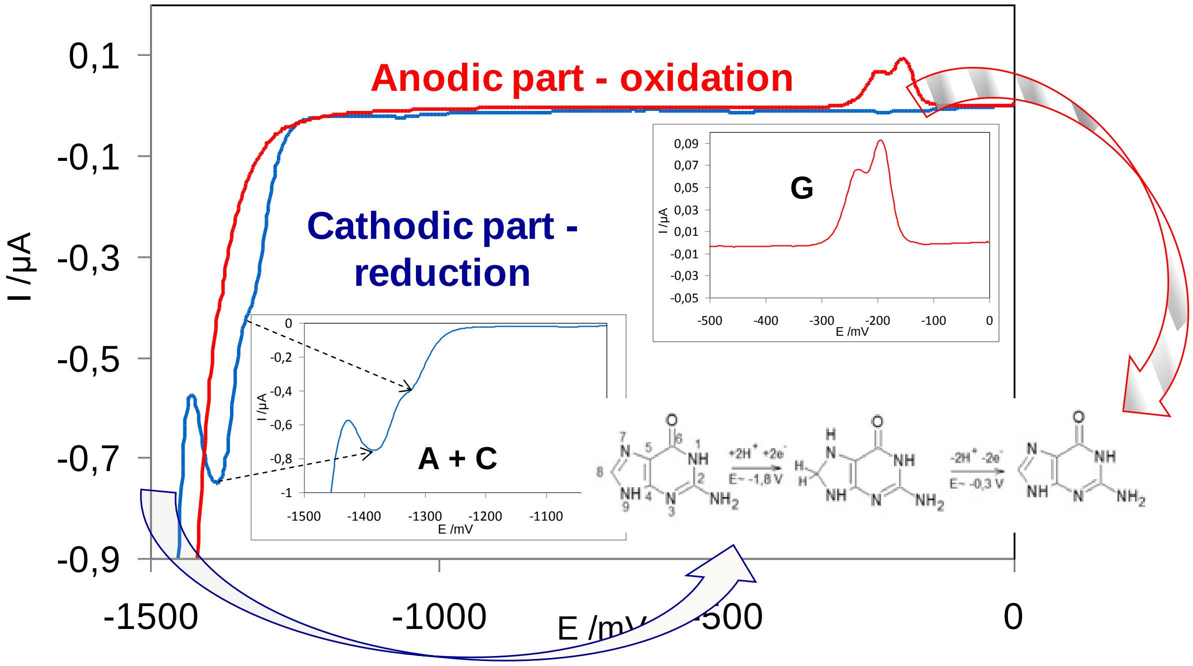
MEASUREMENT

a) Clean voltammetric vessel (diluted nitric acid, then miliQ water); add 2 mL of supporting electrolyte, 8 mL miliQ H_2O and 100 µL of Adenine or Guanine.
b) Insert working electrode into pencil and connect all electrodes.
c) Immerse three electrode set into the measuring vessel with solution of sample.
d) Record the voltammogram with the specified voltammetric parameters.
e) Smooth voltammetric curves by Savitzky-Golay filter (level 2).
f) Save the smoothed curves.
g) Add 100 µL of Cu(II) solution into solution of sample and record LSV curves with the specified parameters.
h) Smooth voltammetric curves by Savitzky-Golay filter (level 2).
i) Save the smoothed curves.
j) Load overlay total voltammograms from all experiments and compare them.

CURVE EVALUATION

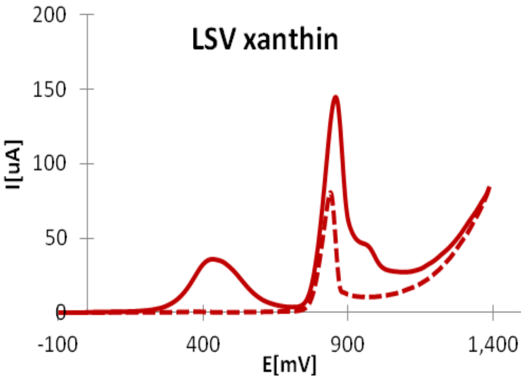
Measurements of the fragments DNA: cathodic and anodic processes on mercury electrodes

Measurements of purines: anodic processes on graphite electrodes



Voltammogram of DNA fragment.
Red line: oxidation processes
Blue line: reduction processes

Evaluate the peak potential and the peak height of the purine derivative (adenine, guanine or xanthine) in the absence and in the presence of Cu(II) ions.



Voltammogram of purine (Xan in the absence (dashed line) and in presence (full line) of Cu(II) ions

a) The evaluation of CV peak height and peak potential for both measurements (with and without Cu(II) ions) for different scan rates (from 50mV/s to 800 mV/s per 50 mV/s).
b) The assessment of the influence of scan rate and Cu(II) ions on peak height and potential.
c) The determination of rate determining step in oxidation of adenine or guanine (see Delahay equation).
d) The evaluation of oxidation process of purine derivative without Cu(I) and with Cu(I)

RESULTS

without Cu		
scan rate (mV/s)	E (V)	I(A)

with Cu		
scan rate (mV/s)	E (V)	I(A)

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DISCUSSION AND REMARKS

DISCUSSION AND REMARKS

ELIMINATION VOLTAMMETRY WITH LINEAR SCAN

The application of different elimination functions to chosen voltammetric curves

The elimination voltammetric procedure (EVP) is a mathematical processing of voltammetric data enabling achievement of better sensitivity and detection limits of studied compounds compared to voltammetric methods on which it relies. It works with elimination voltammetric functions (EVF), eliminating or conserving some chosen partial currents. EVP is based on different dependences of these partial currents on scan rate. In other words, the variable parameter is the scan rate and EVF are presented as linear combinations of total currents measured at different scan rates. In EVP must be satisfied two necessary conditions:

1) An eliminated current can be expressed as a product of two independent functions - the scan rate function and electrode potential function.

$$I_j = Y_j(E)\cdot W_j(\nu)$$

where $Y_j(E)$ is potential function and $W_j(\nu)$ is scan rate function.

2) A total voltammetric current is expressed as a sum of partial currents.

$$I = \sum_{j=1}^{n} I_j = I_d + I_c + I_k + \ldots$$

where I_d is the diffusion current, I_c the charging current and I_k the kinetic current.

Advantages of the approach consist in simplicity and availability. EVP is not time consuming procedure and it is able: (i) to provide better sensitivity, (ii) uncover of minor processes hidden in major processes, (iii) to extend potential range and (iv) to yield new information about electrode processes. The interaction of partial currents can be considered as a partial drawback. This disadvantage is sometimes reflected in an elimination signal distortion, as for example in the case of strongly adsorbed electroactive substances. Then the disadvantage is changed in the advantage because the elimination signal is much more higher and has the form (peak-counterpeak) which does not need a baseline correction [1].

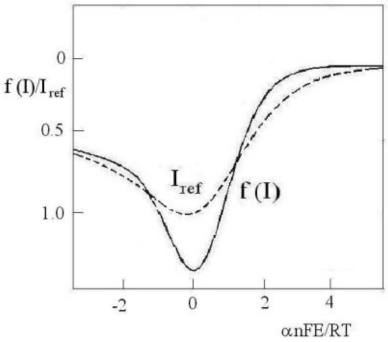

Fig.1: A substance transported to an electrode only by diffusion

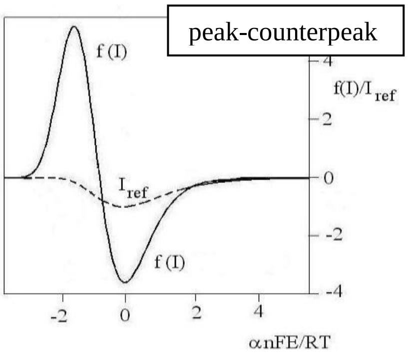

Fig.2: A totally adsorbed electroactive substances

I_{ref} – reference current, $f\,(I)$ – the aplication of the elimination function E4 ($I_k + I_c$ elimination and I_d conservation), the values on the axe x are dimensionless.

elimination function E4: $f\,(I) = a_1 I_{\,(v1/2)} + a_2 I_{\,(v)} + a_3 I_{(v2)}$

$$f(I) = -\,11.657I_{1/2} + 17.485I - 5.8284I_2$$

- Export data from NOVA 1.10 (or GPES) to Excel.
- Use elimination voltammetric procedure EPV E4 for measured data

PARAMETERS

- Scan rates with integer 2: e.g., 100, 200, 400 and 800 mV/s
- Elimination voltammetric functions with calculated coefficients

f(I)	Characteristics	EVLS equation
E1	**$I_d \neq 0$; $I_k = 0$ (I_c dist. By 1.707)**	**$f(I) = -3.4142 \cdot I_{1/2} + 3.4142 \cdot I$**
E2	**$I_d \neq 0$; $I_c = 0$ (I_k dist. By 2.414)**	**$f(I) = 4.8284 \cdot I_{1/2} - 2.4142 \cdot I$**
E3	**$I_k \neq 0$; $I_d = 0$ (I_c dist. By -0.707)**	**$f(I) = 3.4142 \cdot I_{1/2} - 2.4142 \cdot I$**
E4	**$I_d \neq 0$; $I_k = 0$; $I_c = 0$**	**$f(I) = -11.657 \cdot I_{1/2} + 17.485 \cdot I - 5.8284 \cdot I_2$**
E5	**$I_k \neq 0$; $I_d = 0$; $I_c = 0$**	**$f(I) = 6.8284 \cdot I_{1/2} - 8.2426 \cdot I + 2.4142 \cdot I_2$**
E6	**$I_c \neq 0$; $I_d = 0$; $I_k = 0$**	**$f(I) = 4.8284 \cdot I_{1/2} - 8.2426 \cdot I + 3.4142 \cdot I_2$**

CURVE EVALUATION

- Evaluate the EVP curves of the adenine in the absence and in the presence of Cu(II) ions

$$\beta_{EVP} = \frac{f\,(I)}{I}$$

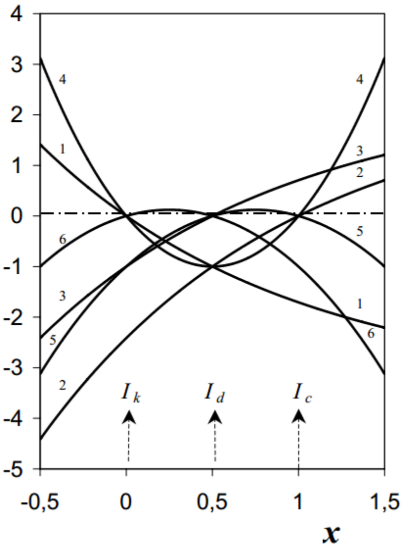

Fig. 3: Dependence of elimination current coefficient β_{EVP} on scan rate coefficient x for EVFs

RESULTS

without Cu	
method	**I(A)**
CV (LSV)	
EVP	

with Cu	
method	**I(A)**
CV (LSV)	
EVP	

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DISCUSSION AND REMARKS

DISCUSSION AND REMARKS

ELECTROCHEMICAL STUDY OF CORROSION

Determination of corrosion rate of steel samples in different environments by linear polarization assessed by Tafel equation

The simplest definition of corrosion is: It is the process of a metal returning to the material’s thermodynamic state. Most of the metal materials form oxides or sulfides, and in this chemical form mostly occur in the earth. In other words, corrosion is the gradual destruction of materials (usually metals) by reduction-oxidation reactions:

Anode: $M^o - ne \rightarrow M^{n+}$
Cathode: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ (in alkaline solutions)
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ (in acidic solutions)
$2H^+ + 2e \rightarrow H_2$

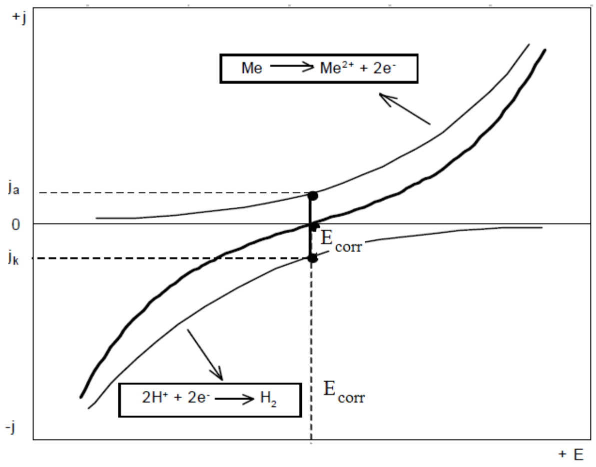

Fig. 1: The combination of anodic polarization curve with current density j_a (metal oxidation) and cathodic polarization curve with current density j_c (cation reduction and hydrogen depolarization). The bold line represents the sum of both processes.

Most corrosion phenomena are of electrochemical nature and consists of two (or more) electrode reactions on the surface of corroding material. One possible reaction is the oxidation of metal (e.g., metal or steel dissolution) refers to anodic partial reaction and the other one is the reduction reaction (e.g., reduction of oxygen) which refers to cathodic partial reaction. Non-electrochemical reaction between products of these reactions forms the final product (e.g., rust). To determine the corrosion rate, depending on kinetics of both cathodic and anodic reactions, Faraday’s law is used, where the linear relationship exists between the metal dissolution rate at some potential and the partial anodic current density for metal dissolution. If there is no external polarization, the metal spontaneously gains a certain potential (corrosion potential – E_{corr}) when in contact with an oxidizing electrolytic environment. The partial anodic current density at the E_{corr} refers to the corrosion current density i_{corr}.

$$E_{corr}=i_{corr}/nF$$

Where n is the number of electrons exchanged in dissolution reaction, F is the Faraday’s constant (F = 96 485 C/mol). The E_{corr} can be obtained between the equilibrium potentials of the anodic and cathodic partial reactions, which could be predicted by electrochemical thermodynamics [1-3].

To slow down the corrosion rate several types of inhibitors are used. Following types of inhibitors are distinguished: anodic, cathodic, mixed and volatile corrosion inhibitors (VCI). Anodic inhibitors usually form the protective oxide film on the metal surface. Cathodic inhibitors slower the cathodic reaction or selectively precipitate on the surface area and thus decrease the diffusion of reducing substances to the surface. Mixed inhibitors reduce both cathodic and anodic reactions via film forming compounds. VCI (also called Vapor Phase Inhibitors) are compounds transported in a closed environment to the site of corrosion by vaporizing from the source [4].

Steel materials are subject to corrosion and the time development can be followed by electrochemical analysis. Studied material is subjected to linear polarization (LSV - Linear Sweep Voltammetry) and LSV curves are processed using the Tafel slope analysis. This approach provides not only a corrosion rate, but also a corrosion potential, a current density and a polarization resistance. These results enable to compare corrosive properties of different materials and to evaluate the effects of corrosion accelerators or inhibitors in different environments.

Linear polarization evaluation and Tafel slope analysis are described in a greater detail in http://www.ecochemie.nl/Applications/.

CALCULATION OF CORROSION RATES

The corrosion rate depends on the kinetics of both anodic (oxidation) and cathodic (reduction) reactions. According to Faraday's law, there is a linear relationship between the metal dissolution rate or corrosion rate, R_M, and the corrosion current density i_{corr}:

$$v_{corr} = \frac{M}{nF\rho} i_{corr}$$

The relationship between current density and potential of anodic and cathodic electrode reactions under charge transfer control is given by the Butler-Volmer equation:

$$i = i_{corr} \left(e^{2.303\frac{\eta}{b_a}} - e^{2.303\frac{\eta}{b_c}} \right) \text{, where } \eta = E - E_{corr}$$

In the above equation E is the applied potential and i_{corr} the measured current density. The overpotential, η, is defined as the difference between applied potential and the corrosion potential E_{corr}. The corrosion potential, is the open circuit potential (OCP) of a corroding metal. The corrosion current (i), i_{corr}, and the Tafel constants b_a, and b_c can be measured from the experimental data.

APPARATUS, ACCESSORIES AND REAGENTS

- AUTOLAB PGSTAT101 (Metrohm Switzerland); Corrosion cell 400 ml (Metrohm, Switzerland), Thermostat F12 Julabo (Julabo, Germany)
- Software NOVA 1.10.2 (Metrohm, Switzerland)
- Electrodes (WE – sample (steel); RE – Ag/AgCl/3 M KCl; AE – Stainless steel or Pt)
- NaCl solution, $c_1(NaCl) = 0.15$ mol/L, $c_2(NaCl) = 0.6$ mol/L; mild steel sample (M_r = 55,585)
- Corrosion inhibitor: Adenine or caffeine ($1 \cdot 10^{-3}$ mol/L)

SOLUTIONS

Supporting electrolyte

0.15 M NaCl solution pH 5,75

0.6 M NaCl solution pH 5,88

Inhibitor solution: 1mM adenine or caffeine

EXPERIMENT

Measurement method: Linear sweep voltammetry (LSV), procedure in NOVA: linear polarization (with open circuit potential - OCP determination)

PARAMETERS

Measurement method: Linear sweep voltammetry (LSV)

Start potential -0.3 V, stop potential 0.3 V, scan rate 5 or 10 m V/s, temperature 25 °C

Make sure that there is no bubble at the end of the salt bridge after supporting electrolyte is poured inside the corrosion cell!

MEASUREMENT

a) There are sample of mild steel discs available. Clean them by scratching the measuring side with sandpaper 21111 2/0 then wash it in acetone.
b) Insert mild steel disc into measuring cell and connect as working electrode
c) Pour the supporting electrolyte (400 mL) into the corrosion cell and plug reference electrode and auxiliary electrode
d) Set the temperature on the thermostat to 25 °C and wait until the temperature inside the corrosion cell is stabilized.
e) Record the linear polarization voltammogram with the specified parameters. Save the voltammogram together with method parameters
f) Repeat step a) to e) with all samples.

CURVE EVALUATION

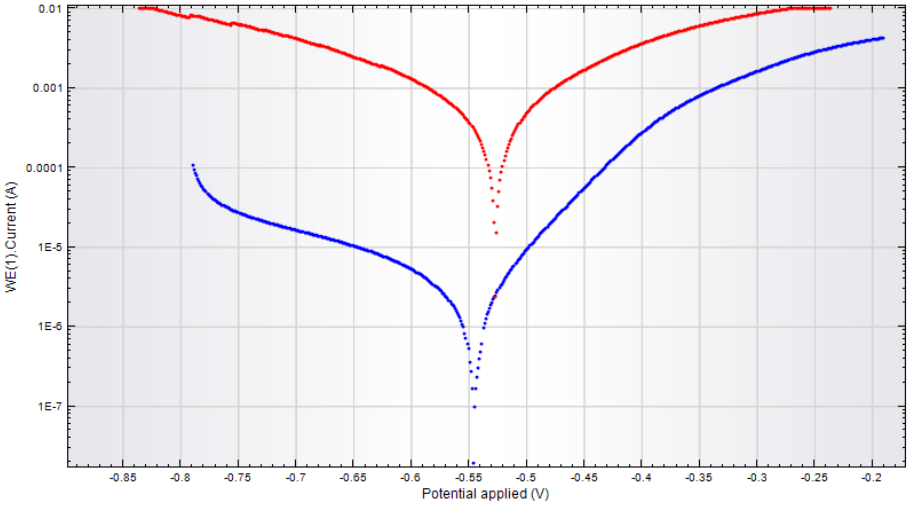

Fig. 2: Real voltammograms of mild steel samples in different environments: saline solution (blue), 0.1 M H_2SO_4 (red).

RESULTS

Solution	E_{corr} [V]	i [A]	i_{corr}[A/cm^2]	Polarization resistance R_p [Ω]	Corrosion rate v_{corr}[mm/year]
0.9 % NaCl					
3.5 % NaCl					
0.9 % NaCl + inhibitor					
3.5 % NaCl + inhibitor					
0.9 % NaCl + inhibitor					
3.5 % NaCl + inhibitor					

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DISCUSSION AND REMARKS

DISCUSSION AND REMARKS

ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY (EIS)

EIS of guanine on modified and unmodified graphite electrodes

Electrochemical Impedance Spectroscopy (EIS) is a powerful technique for the characterization of electrochemical systems. The promise of EIS is that, with a single experimental procedure encompassing a sufficiently broad range of frequencies, the influence of the governing physical and chemical phenomena may be isolated and distinguished at a given applied potential.

In recent years, EIS has found widespread applications in the field of characterization of materials. It is routinely used in the characterization of coatings, batteries, fuel cells, and corrosion phenomena. It has also been used extensively as a tool for investigating mechanisms in electro–deposition, electro–dissolution, passivity, and corrosion studies. It is gaining popularity in the investigation of diffusion of ions across membranes and in the study of semiconductor interfaces.

Principles of EIS measurements

The fundamental approach of all impedance methods is to apply a small amplitude sinusoidal excitation signal to the system under investigation and measure the response (current or voltage or another signal of interest1). In the following figure, a non-linear i-E curve for a theoretical electrochemical system is shown in Figure 1.

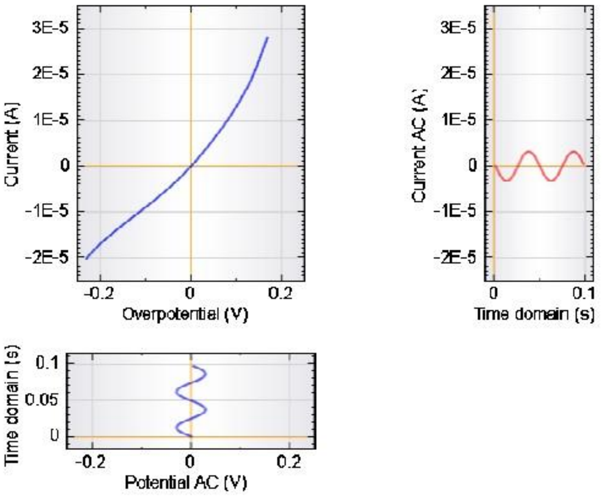


Fig. 1: Potential and current modulation recorded during an impedance measurement

A low amplitude sine-wave $\Delta E \cdot \sin(\omega t)$, of a particular frequency ω, is superimposed on the DC polarization voltage E_O. This results in a current response of a sine wave superimposed on the DC current $\Delta i \cdot \sin(\omega t+\varphi)$. The current response is shifted with respect to the applied potential (see Figure 2).

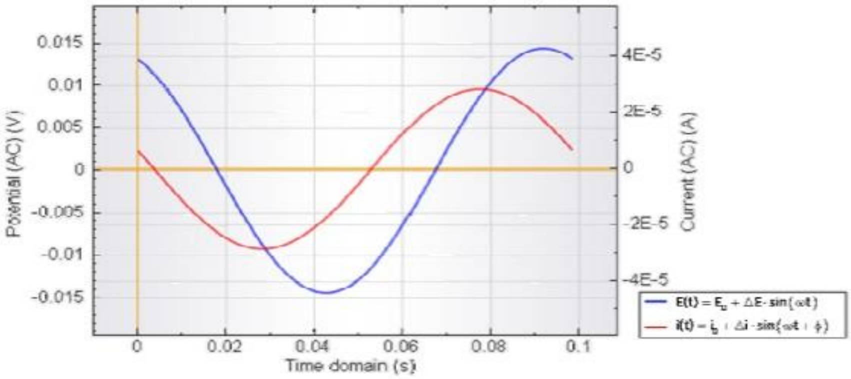


Fig. 2: Time domain plots of the low amplitude AC modulation and response

The Taylor series expansion for the current is given by:

$$\Delta i = \left(\frac{di}{dE}\right)_{E_o,i_o} \Delta E + \left(\frac{d^2 i}{dE^2}\right)_{E_o,i_o} \Delta E^2 + ...$$

If the magnitude of the perturbing signal ΔE is small, then the response can be considered linear in first approximation. The higher order terms in the Taylor series can be assumed to be negligible. The impedance of the system can then be calculated using Ohms law as:

$$Z(\omega) = \frac{E(\omega)}{i(\omega)}$$

This ratio is called impedance, Z(ω), of the system and is a complex quantity with a magnitude and a phase shift which depends on the frequency of the signal. Therefore by varying the frequency of the applied signal one can get the impedance of the system as a function of frequency. Typically in electrochemistry, a frequency range of 100 kHz – 0.1 Hz is used. The impedance Z(ω), as mentioned above is a complex quantity and can be represented in Cartesian as well as polar coordinates. In polar coordinates the impedance of the data is represented by:

$$Z(\omega) = |Z(\omega)|\, e^{\varphi\omega}$$

Where |Z(ω)| is the magnitude of the impedance and is the phase shift. In Cartesian coordinates the impedance is given by:

$$Z(\omega) = Z'(\omega) - j\, Z''(\omega)$$

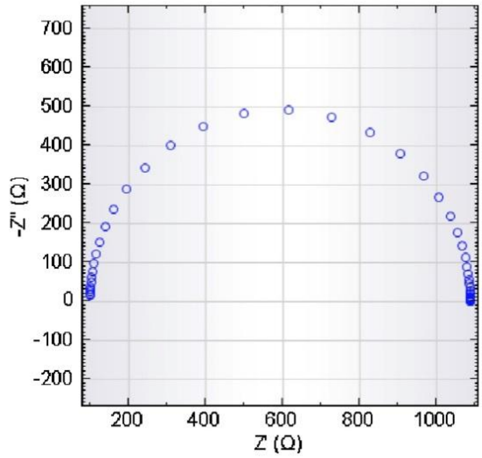
Where Z'(ω) is the real part of the impedance and Z"(ω) is the imaginary part and .

Data presentation

The plot of the real part of impedance against the imaginary part gives a Nyquist plot, as shown in Figure 3. The advantage of Nyquist representation is that it gives a quick overview of the data and one can make some qualitative interpretations. While plotting data in the

Nyquist format the real axis must be equal to the imaginary axis so as not to distort the shape of the curve. The shape of the curve is important in making qualitative interpretations of the data. The disadvantage of the Nyquist representation is that one loses the frequency dimension of the data. One way of overcoming this problem is by labeling the frequencies on the curve.

The absolute value of impedance and the phase shifts are plotted as a function of frequency in two different plots giving a Bode plot in Figure 4. This is the more complete way of presenting the data.



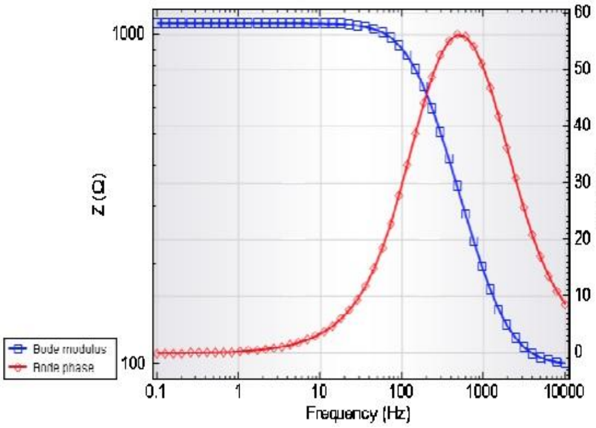


Fig. 3: A typical Nyquist plot

Fig.4: A typical Bode plot

A third data presentation mode involving a 3D plot, is available. In this presentation mode the real and imaginary components are plotted on the X and Y axis, respectively and the logarithm of the frequency is plotted on the Z axis (see Figure 5).

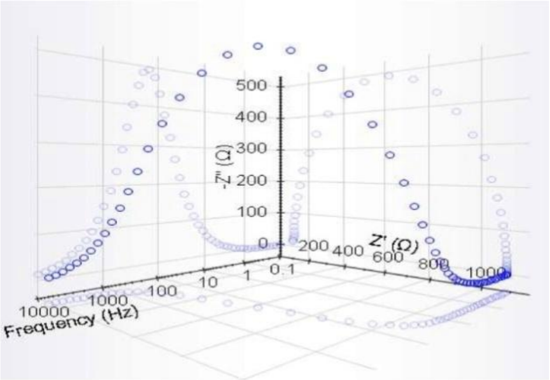


Fig.5: 3D plot

The relationship between the two ways of representing the data is given by:

$$|Z|^2 = (Z')^2 + (-Z'')^2 \qquad tg(\varphi) = \frac{-Z''}{Z'}$$

Alternatively, the real and imaginary components can be obtained from:

$$Z' = |Z|\cos\varphi \quad \text{and} \quad -Z'' = -|Z|\sin\varphi$$

APPARATUS, ACCESSORIES AND REAGENTS

- AUTOLAB PGSTAT20 Analyzer (Metrohm AUTOLAB, Netherlands)
- NOVA software 1.10
- Electrodes (working - PeGE with leads Tombow, 0.5 mm, reference – Ag/Ag Cl/3M KCl, counter electrode – Pt); voltammetric vessel
- argon
- phosphate-acetate buffer pH 5.5; c (CH_3COOH) =0.4 mol/L, c (H_3PO_4)=0.4 mol/L, c(NaOH)=2 mol/L
- adenine; copper sulphate; miliQ water (18.2 MΩ·cm)

SOLUTIONS

Supporting electrolyte

phosphate-acetate buffer pH 5.5; c (CH_3COOH) =0.4 mol/L, c (H_3PO_4)=0.4 mol/L, c(NaOH)=2 mol/L, c($CuSO_4$)=$1\cdot10^{-3}$ mol/L

Samples

adenine = $1\cdot10^{-3}$ mol/L; (or guanine)

EXPERIMENT

- EIS experiment for adenine in the absence of copper ions – 2 mL supporting electrolyte + 8 mL miliQ H_2O + 100 µL adenine (guanine)

PARAMETERS

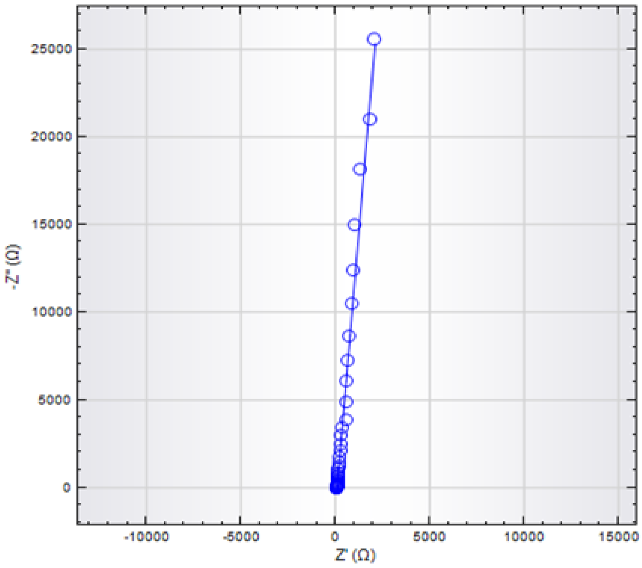
- Mesurement method potentiometric electrochemical impedance spectroscopy
- Start 0.1 V, End potential 1.2V, logarithmic step 0.2V
- Frequency 10 000- 0.1 Hz, 50 steps (logarithmic)
- RPM 0.1V

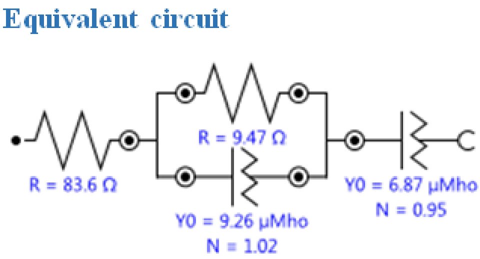
MEASUREMENT

a) Clean voltammetric vessel (diluted nitric acid, than miliQ water). Than we added in the vessel 2 mL of supporting electrolyte, 8 mL miliQ H_2O and 100 µL of adenine (guanine)
b) Insert working electrode into pencil and connect all electrodes.
c) Start potentiometric EIS
d) Save data
e) Data analysis, Fit and Simulation
f) Insert equivalent circuit and Fit data
g) Export results

Measured data

Equivalent circuit





Results

Element	Parameter	Value
R1	R	83.613
R2	R	9.4724
Q1	Y0	9.2585E-06
	N	1.0198
Q2	Y0	6.8726E-06
	N	0.94971
	χ^2	0.033201

REFERENCES

[1] Metrohm Autolab, *Application note EIS01*

[2] Barsoukov E., Macdonald J. R.: *Impedance spectroscopy. Theory, Experiment, and Applications*. J. Wiley, New Jersey 2005.

DISCUSSION AND REMARKS

DISCUSSION AND REMARKS

ROTATION DISC ELECTRODE (RDE)

Cyclic voltammetry with rotating disc electrode

Cyclic voltammetry, CV is the most widely used electrochemical technique, which evolved from polarography. In CV, the tested solution is subjected to potential imposed onto the electrodes in a following way: it is linearly increased from the initial to vertex potential, which is the so-called forward scan and then decreased to final potencial in reverse scan; the initial potential is usually equal to final potential, forward and reverse scans make up one CV cycle. Where appropriate, one or more than one CV cycle can be made, if the experiment is limited into a half-cycle, the technique is denoted as linear sweep voltammetry (LSV). The rate of the potential change (scan rate) determines the time window of the experiment.

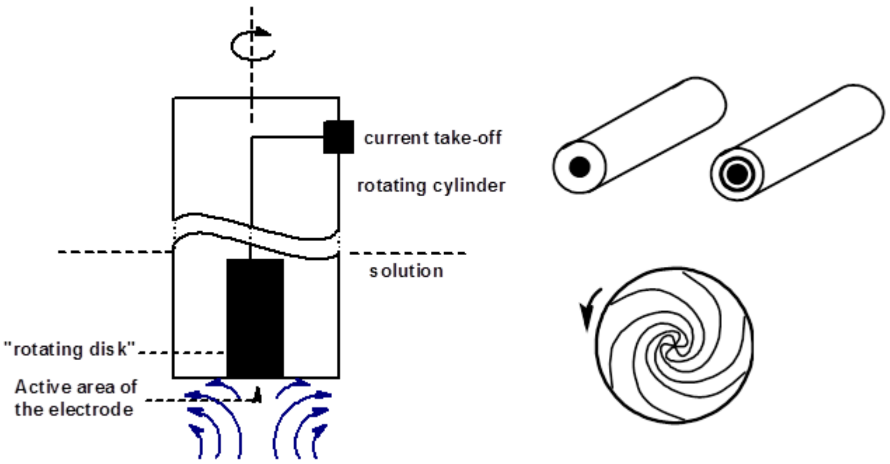
The result of the CV experiment is the plot of current flowing through the system in dependence on applied voltage - ie., a voltammogram. Modern instruments for measuring voltamograms (potentiostats) use three-electrode circuit. Therefore, following three electrodes are necessary to perform the experiment:

- working – e.g. glassy carbon, carbon paste, carbon fiber, Pt, Au, Hg, (drop or film) etc.
- reference – calomel or argentochloride electrode
- auxiliary – Pt wire or foil

The potentiostat forces to pass between the working and counter electrodes current of such magnitude, so that the required potential program is kept between the working and reference electrode. In addition to the tested compound a solution suitable for voltammetric study shall contain an excess of supporting (indifferent) electrolyte. Typically, a suitable salt is added - KCl, KNO_3, buffer when working in an aqueous medium or a quaternary ammonium salt (e.g. tetramethylammonium perchlorate or hexachlorophosphate) for nonaqueous solution. The concentration of supporting electrolyte should be chosen in a way that the ionic strength of the tested substance should amount maximum 3 % of the total ionic strength of the solution. When working with solid electrodes it is usually necessary to polish the electrode using a suitable procedure, hand polishing with alumina slurry or diamond paste is a common electrode way of the electrode handling. In certain cases it is sufficient to polarize the electrode by sufficiently high potential, causing desorption of the material contaminating the electrode (electrochemical electrode cleansing).

In addition to CV, many other voltammetric techniques exist, mutually differing in the program according to which the potentiostat changes the potential of the working electrode during the experiment. In some techniques, gradually increasing or decreasing potential is applied while other techniques use sudden change of potential or complex sequence of pulses. Further division distinguishes whether the solution during analysis is quiescent or moves relative to the working electrode. In most cases, the solution does not move, but there are also many hydrodynamic techniques in which the solution moves in a defined manner. The voltammetry with rotating disk electrode is an example hydrodynamic method.

Working electrode rotates at relatively high speed. The rotational movement ensures a defined flow of the solution to the electrode disk, similar to the vortex dragging the tested to the electrode (Fig. 1).



The resulting voltammogram has the shape of the sigmoidal wave, the height of which represents the analytical signal. To understand the processes taking place in the RDE experiment a notion of the layer of solution immediately adjacent the electrode, which moves alongwith it, is important. Through this layer the transport of the test compound proceeds by diffusion. From the electrode point of view this layer is stationary (stagnant layer).

The stagnant layer is continued by Prandtl (boundary) hydrodynamic layer in which each additional layer of molecules is moving more slowly than the previous layer, from a certain distance from the electrode, the solution is at rest. By increasing the rotational speed - the thickness of the diffusion layer can be controlled - reduced. The analyte molecule, as shown in the figure (Fig. 1), experiences the two types of transport before reaching the electrode surface. First, the analyte molecules move as they are dragged by vortex perpendicular to the electrode surface until they reach the outer edge of the diffusion layer.

Then molecules diffuse to the electrode surface (This is crucial for understanding the RDE - convection movement first attracts the depolarizer molecule in the direction towards the electrode, then the electrode rotation "throws the molecule to the side." If the diffusion did not work at the same time with the convection movement, the molecule would never reach the surface of the electrode. The narrower the diffusion layer, the faster the molecule reaches the electrode surface. Therefore, at higher speeds higher current values are recorded in the RDE experiment. Unlike CV with stationary electrode, the limiting current can be reached in RDE CV experiment after certain potential, i.e. the current that is controlled only by the speed of transport of the substance being tested to the electrode (Fig. 1).

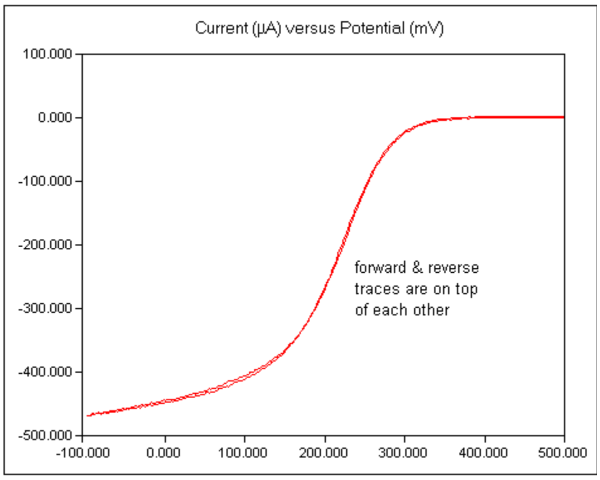


Figure 1: Model hydrodynamic voltammogram of ferricyanide

The magnitude of the limiting current I_L is given both by diffusion as well as by convection contribution; mathematical analysis of the problem leads to the so-called Levich equation:

$$I_L = (0.620)\cdot n\cdot F\cdot A\cdot D^{2/3}\cdot\omega^{1/2}\cdot\nu^{-1/6}\cdot c,$$

where ω is angular speed of the electrode rotation (rad·s^{-1}), ν is the solution kinematic viscosity (cm^2·s^{-1}), c is the concentration of the electroactive species (mol/cm^3), D its diffusion coefficient (cm^2·s^{-1}). Kinematic viscosity is the ratio between the solution viscosity and its density. For pure water, the value is: $\nu = 0.0100$ cm^2·s^{-1}, for 1.0 mol·dm^{-3} KNO_3 the is $\nu = 0.00916$ cm^2·s^{-1} (for 20°C).

APPARATUS, ACCESSORIES AND REAGENTS

- Potentiostat (Metrohm Autolab)
- RDE assembly
- Electrodes (working – Pt or Au, reference – Ag/Ag Cl/3M KCl, counter electrode – Pt); voltammetric vessel
- 1 mmol/L $K_3[Fe(CN)_6]$ diluted in 1 mol/L KNO_3
- miliQ water (18.2 MΩ·cm)

PARAMETERS

- Potential range: from 500 to -100 mV
- Rotation range: 25, 50, 100, 200, 400, 800 and 1000 rpm

EVALUATION

1. Familiarize yourself with the potentiostat operation, ways to clean the electrodes etc.
2. Record the CV $K_3[Fe(CN)_6]$ on the RDE in quiescent solution (i.e., without rotation) in the range from 500 to -100 mV vs. Ag/AgCl, 10 $mV.s^{-1}$. Calculate the product $A \cdot D^{1/2}$ using Randles – Ševčík equation.
3. Then record CV at ten different electrode rotation speeds within the capability of the device. Allow ten seconds to establish hydrodynamic equilibrium in the electrode cell.
4. Determine the limiting currents for individual CV experiments, evaluate the of I_L vs. ω dependence (don’t forget to transform r.p.m. values into radians per seconds).
5. Make the nonlinear estimation analysis and find $A \cdot D^{2/3}$ product.
6. Obtain the electrode area and difusion coefficient of $Fe(CN)_6^{3-}$.

RESULTS

Rotation [rpm]	[rad/s]	I_L[A]	$D^{2/3}$	D [cm^2/s]

DISCUSSION AND REMARKS

DISCUSSION AND REMARKS

ELECTROCHEMICAL QUARTZ CRYSTAL MICROBALANCE (EQCM)

Deposition and stripping of copper on gold

The quartz crystal microbalance (QCM) is capable to sensitively measure the mass of thin films adhering to the surface of quartz crystal. The technique is based on the monitoring the changes in the frequency of quartz crystal resonant oscillations. The term quartz crystal used in QCM represents a thin (fraction of millimeter) plate cut from the quartz crystal in certain crystallographic orientation (AT-cut quartz wafer). The plate, usually a circle approx. 1 cm in diameter, is equipped with two metal contacts which are used to establish an electric field across the crystal. Driven by appropriate electronics, the crystal is made to oscillate at its resonant frequency, typically used are crystals resonating in the range from 5 to 30 MHz. The measured frequency is dependent on the thickness of the quartz wafer, metal electrodes, and material deposited on the quartz crystal microbalance surface. Because the resonance is very sharp, high precision frequency measurements allow the detection of minute amounts of deposited material, as small as 100 picograms per square centimeter, corresponding to submonolayer coverage. In the combination of QCM with electrochemistry i.e., EQCM, one of the metal contacts on the crystal serves as a working electrode and is a part of the common thre-electrode electrochemical cell. In EQCM, the typical technique is cyclic voltammetry with simultaneous recording of frequency change of QCM oscillations. Depositing material onto working electrode results in decrease in the frequency of oscillations while stripping the deposit from the electrode is accompanied with an increase in the frequency. The frequency change occuring in the event of a mass change on the QCM surface is governed by Sauerbrey equation:

$$\Delta f = \frac{2 f_0^2}{A\sqrt{\rho_q \mu_q}} \Delta m,$$

where f_0 is the resonant frequency (Hz), Δf is frequency change (Hz), Δm is mass change (g), A piezoelectrically active crystal area (Area between electrodes in $\mathrm{cm^2}$), ρ_q is density of quartz (2.643 $\mathrm{g/cm^3}$) and μ_q is the shear modulus of quartz for AT-cut crystal ($2.947\mathrm{x}10^{11}$ $\mathrm{g{\cdot}cm^{-1}{\cdot}s^{-2}}$). Sauerbrey's equation only applies to systems in which the following three conditions are met: the deposited mass must be rigid, the deposited mass must be distributed evenly and the frequency change $\Delta f < 0.02$.

APPARATUS, ACCESSORIES AND REAGENTS

- AUTOLAB PGSTAT100 (Metrohm, Switzerland)
- NOVA software
- EQCM cell and crystals
- Reference nad auxiliary electrodes
- 1 mM copper sulphate solution in 0.1 M H_2SO_4
- 0.1 M H_2SO_4
- 1 mM lead nitrate solution in 0.1 M $HClO_4$
- 0.1 M $HClO_4$

EXPERIMENT

The purpose of the experiment is to find a calibration factor for the crystal using the copper electrodeposition method. By the use of the known calibration factor, molar mass of the „unknown“ electrodeposited species (lead) will be estimated. Finally, the total mass of the deposited lead determined from EQCM frequency change is compared with the total mass of the deposited lead evaluated from Faraday Law.

MEASUREMENTS

The crystal electroactive area is determined using the ferro-ferricyanide electrochemistry. For this purpose, the cyclic voltammogram of ferricyanide is measured from +500 mV vs. Ag/AgCl (initial potential) to -100 mV vs. Ag/AgCl (vertex potential) using lower value of scan rate (20-50 mVs^{-1}).

EQCM experiment is performed for copper deposition (scan limits are: +200 mV vs. Ag/AgCl (initial potential) to -700 mV vs. Ag/AgCl (vertex potential), scan rate (20 mVs^{-1}) and lead deposition (scan limits are: +200 mV vs. Ag/AgCl (initial potential) to -800 mV vs. Ag/AgCl (vertex potential), scan rate (20 mVs^{-1}) for overpotential deposition, if the vertex potential is set to -400 mVs^{-1}, underpotential deposition of lead can be observed.

EVALUATION

The electroactive area of the crystal is calculated from peak current using Randles-Ševčík equation:

$$I_{p_a} = I_{p_c} = 2.69 \cdot 10^5 \, A n^{3/2} D^{1/2} c v^{1/2},$$

where $I_{p_a} = I_{p_c}$ is anodic resp. cathodic peak current, A is electrode area in cm^2, n is a number of exchanged electrons, D diffusion coefficient in cm^2s^{-1}, c is concentration in $mol \cdot cm^{-3}$ (note unusual unit!), v is scan rate in Vs^{-1}.

The slope of Δf vs. charge curve is obtained by fitting the data using linear regression. The calibration factor for the crystal is then calculated according to the equation:

$$C_f = \frac{slope \cdot FAn}{M_{Cu} \cdot 10^6},$$

where F is the Faraday Constant, A is the electroactive area, M_{Cu} is the molar mass of Cu, and n is the number of electrons. The 10^6 is used to convert from grams to micrograms.

To determine molar mass of lead, the measured Δf data are expressed as change in mass (Δm). Then, Δm versus charge plot is constructed. The molar mass is calculated from the slope of the aforementioned plot:

$$M = \frac{|slope| Fn}{10^6}.$$

Finally, compare the total mass of the deposited lead determined from EQCM frequency change with mass evaluated from Faraday Law.

RESULTS

Theoretical value of calibration factor for copper is 226 Hz cm^2/µg, the determined value should be close to this value.

DISCUSSION AND REMARKS

DISCUSSION AND REMARKS

SPECTROELECTROCHEMISTRY

Spectroelectrochemical investigation of the ferro-ferri redox system

Spectroelectrochemistry is a hybrid technique that enables to measure UV-vis spectra of the analyte that is exposed to a given potential. The technique therefore provides the volt-ampere characteristics together with the information about the absorption spectra of generated intermediates. In the classical mode, cyclic voltammetry is coupled with the UV-vis spectrometry, but other methods like chronoamperometry or linear sweep voltammetry can be used as well. The technique provides much deeper insight into redox processes in comparison to classical electrochemical methods and therefore becomes very popular in recent years. [1] The main drawback of this technique is a need of special equipment, a diode-array UV-vis spectrometer with a suitable cuvette space and the spectroelectrochemical cell. The construction and performance of different types of spectroelectrochemical cells can significantly differ and the commercially available types are usually very costly.

The OTTLE cell (optically transparent thin layer electrochemical cell) depicted in Figure 1 is one of the most advanced commercially available cells. The set of three electrodes is placed in a thin measuring window. The working electrode (WE, Fig. 1, right part) is usually fully transparent (ITO electrode) or is a semitransparent grid from a thin wire. The pseudoreference electrode is a thin wire pointing towards WE. The auxiliary electrode (AUX) is located at the opposite side of the measurement window. The electrode set is fixed into the plastic spacer which determines the thickness of the measurement window and therefore the length of the optical pathway. The whole setup is covered with the optically transparent crystal (SiO_2, CaF_2, KCl, Fig. 1, left part) and fitted into a gas-tight housing.

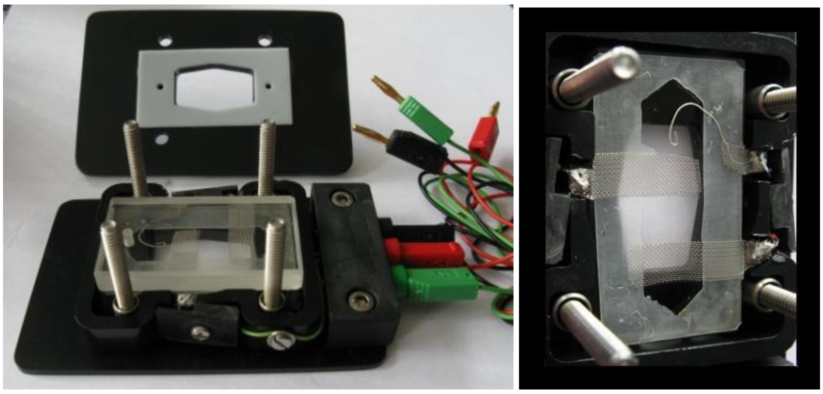


Fig 1: OTTLE spectroelectrochemical cell
(https://www.reading.ac.uk/web/FILES/chemistry/SEC_Products.pdf)

Since the electrochemical process in the cell must occur fast and quantitatively, the volume of the measurement window is usually very small (~100 μL). The optical pathway is also very short (0.1 mm) which results in a need of usage of higher concentrations of the analyte (~ 1 mM) in comparison to the UV-vis spectrometry (~ 10 μM).

The ferro-ferri system is a standard reversible water-based redox system commonly used in electrochemistry as a benchmark. It is based on the redox interconversion of potassium ferrocyanide ($K_4[Fe(CN)_6]$) to potassium ferricyanide ($K_3[Fe(CN)_6]$) and vice versa. The ferrocyanide ion in aqueous solution is not stable and gets oxidized by oxygen dissolved in the solution. Therefore the more stable ferricyanide is used as a stock solution and the Fe(II) species are generated electrochemically *in situ* by a pretratment. [2]

APPARATUS, ACCESSORIES AND REAGENTS

- AUTOLAB PGSTAT101 Analyzer (EcoChemie, Netherlands)
- NOVA software (Metrohm, Switzerland)
- OTTLE spectroelectrochemical cell (prof. Hartl, University of Reading, UK), electrodes (working – platinum grid, pseudoreference – Ag wire, counter electrode – Pt grid); optical pathway 0.1 mm
- Agilent 8453 (Agilent, CA, USA)
- potassium ferricyanide stock solution: $c(K_3[Fe(CN)_6]) = 0.02$ mol/L; $c(KCl) = 0.1$ mol/L
- deionized water
- argon
- degassing sealed vial with septum

- balloon with a needle
- acetone

SOLUTIONS

Supporting electrolyte

potassium chloride solution: c = 0.1 mol/L

Samples

potassium ferricyanide stock solution: c($K_3[Fe(CN)_6]$) = 0.02 mol/L; c(KCl) = 0.1 mol/L

EXPERIMENT

- Blank measurement of degassed KCl solution
- Electrochemical pretreatment
- Estimation of the maximal scan rate
- Measurement of the sample of $K_3[Fe(CN)_6]$
- Data analysis, comparison of electrochemical and spectral result

PARAMETERS (CV OR LSV - CYCLIC OR LINEAR SWEEP VOLTAMMETRY, SPECTROSCOPY)

Blank measurement

Start potential -0.1 V, stop potential -0.1 V, upper vertex potential 1.0 V, lower vertex potential -1.0 V, scan rate 100 mV/s, number of cycles 3

Electrochemical pretreatment

Start potential -0.1 V, waiting time 60 s, spectroscopic measurement – interval time 1 s, wavelengths followed 230 nm, 303 nm, 410 nm

Estimation of the maximal scan rate

Start potential -0.1 V, scan rate 200 mV/s (100, 20, 10 mV/s), stop potential 0.6 V, spectroscopic measurement – interval time 1 s, wavelengths followed 230 nm, 303 nm, 410 nm

Sample measurement

Start potential -0.1 V, determined pretreatment wait time, determined scan rate, stop potential 0.6 V, spectroscopic measurement – interval time 1 s, wavelengths followed 230 nm, 303 nm, 410 nm

MEASUREMENT

k) Clean the OTTLE cell (acetone, distilled water).
l) Degass the blank solution in a vial sealed by a septum by bubbling with nitrogen for 10 minutes
m) Fill the blank solution into the OTTLE cell
n) Measure the CV scan of the blank solution
o) Degass the sample solution
p) Fill the OTTLE cell with the sample solution
q) Perform the electrochemical pretreatment, determine the time needed for quantitative reduction of the sample
r) Refill the OTTLE cell with the fresh degassed solution of the sample
s) Measure the sample at different scan rates, estimate the maximum suitable scan rate
t) Refill the OTTLE cell with the fresh degassed solution of the sample
u) Measure the sample with the appropriate pretreatment and the determined scan rate
v) Determine the redox potential of the ferro-ferri system based on the UV-vis spectra and voltammogram analysis

RESULTS AND DISCUSSION

The typical voltammogram of the ferro-ferri system is shown in Figure 2. The oxidation from ferrocyanide to ferricyanide occurs at approximately +0.24 V vs SCE.

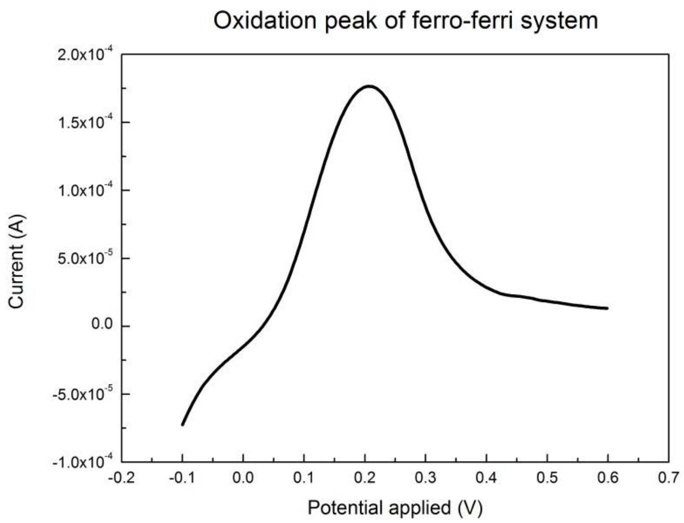


Fig 2: Voltammogram of the ferro-ferri system

The absorption spectrum of $K_3[Fe(CN)_6]$ is shown in the Figure 3.

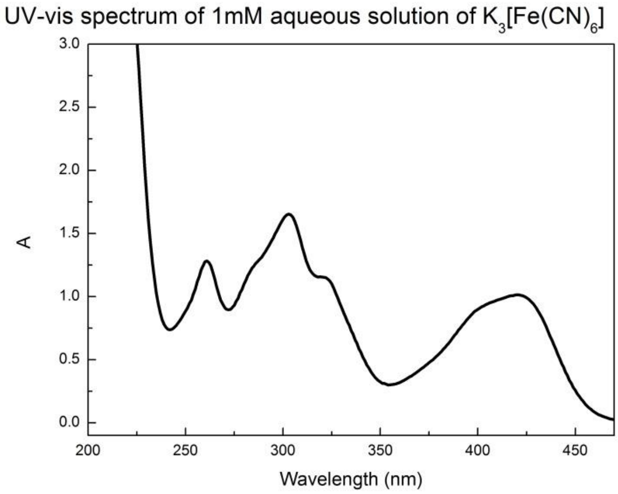


Fig 3: Absorption spectrum of $K_3[Fe(CN)_6]$

Stacked spectra of ferro-ferri system at varying potential are depicted in Figure 4. The blue curve corresponds to the ferricyanide ion, the red spectrum is the initial ferrocyanide.

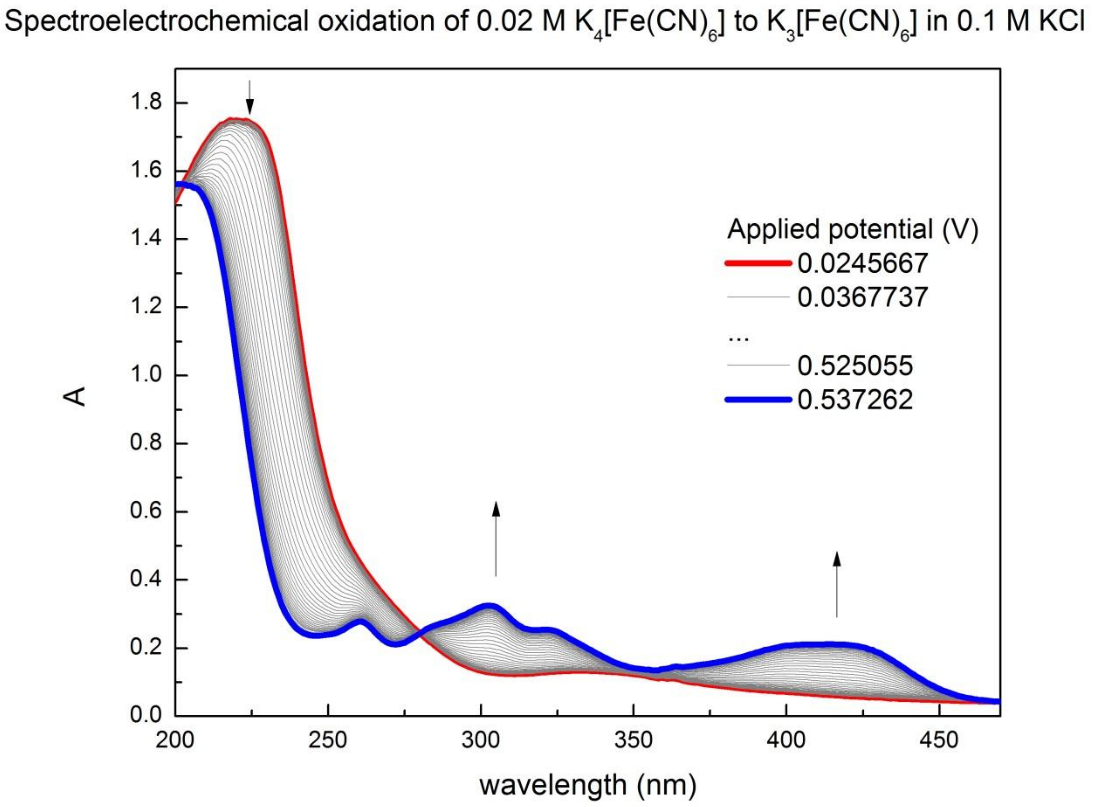


Fig 4: Stacked absorption spectra of ferro-ferri system at different potentials

The distribution digram of ferrocyanide and ferricyanide determined from different wavelengths (ferrocyanide: 230 nm, ferricyanide: 303 nm, 410 nm; normalized from 0 to 1) at varying potential is shown in Figure 5.

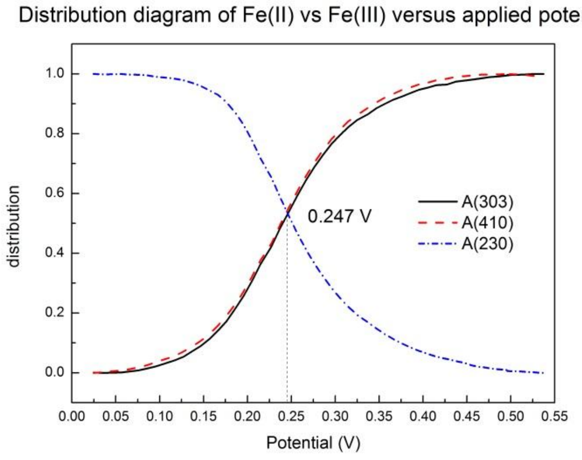


Fig 5: Dependence of the distribution of forms of ferrocyanide and ferricyanide at different potential

RESULTS

Pretreatment time [s]	

Scan rate determination (absorbance at 0.6 V)			
Scan rate (mV/s)	A^{230}	A^{303}	A^{410}
10			
20			
100			
200			

Determined potential	A^{230}	A^{303}	A^{410}
spectroscopical			
electrochemical			

REFERENCES

[1] Kaim W., Fiedler J. *Chem. Soc. Rev.*, **2009**, *38*, 3373-3382.
[2] Huang T. H., Salter G., Kahn S. L., Gindt Y. M. *J. Chem. Educ.*, **2007**, *84*, 1461-1463.

DISCUSSION AND REMARKS

DISCUSSION AND REMARKS

ACKNOWLEDGEMENT

- Project MUNI/A/1500/2015
- Project KONTAKT II (LH13053) of the Ministry of Education, Youth and Sports of the Czech Republic

Metrohm
Autolab B.V.

- Founded in 1986
- Based in Utrecht, The Netherlands
- Since 1999 part of the Metrohm Group
- Introduced the first computer controlled potentiostat/galvanostat
- Develops and produces the high quality Autolab range of products
- Strong background in electrochemistry
- Supported by the worldwide Metrohm distribution network
- Three years factory warranty on all instruments
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