Determination of kinetic parameters by electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) represents highly precise experimental technique for determination of kinetic parameters of studied systems. It is based on periodic perturbation signal, which together with its small amplitude results in small concentration changes close to the electrode surface. Wide range of applied frequencies of perturbation signal allows characterizing even systems involving more actions with different kinetics. The aim of this laboratory work is to provide basic information about EIS, experimental setup and evaluation of experimental data. The main experiment will demonstrate basic concepts of electrode-electrolyte interface boundary.

Impedance

Impedance is generally considered as a general resistance. Resistance was defined by German physicist George Simon Ohm in the form of well-known Ohm's law.

$$U = RI \tag{1}$$

where U stands for voltage on electrical resistance, I represents electric current and R is ohmic resistance.

This law is valid exclusively for conductors of the first type (electron conductors). Later, more limitations of this law were found. This is related mainly to the pass of the alternating current. It is possible to say, that Ohms law is valid only if the changes of alternating current are "sufficiently slow". Corresponding maximal speed of the changes is dependent on characteristics of the used system. In the case of the first type conductors, the main characteristics involve especially their length, geometric arrangement and shielding. In the case of existence of several types of conductors in the studied system, situation is getting more complicated rapidly. This is mainly due to the charge transfer between different phases. Description of such system is more complex. On the base of electrochemical engineering, there are three basic components describing response of the system exposed to the influence of alternating current. These are:

Ohmic resistance: (R)

Capacitance: (C)

Inductance: (L)
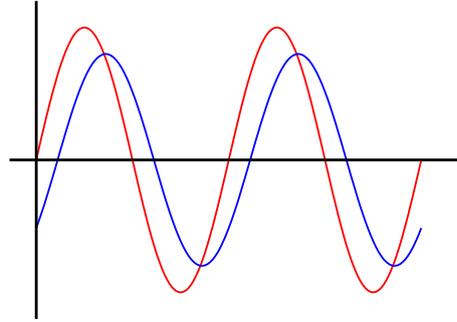
Figure 1: Time course of perturbing signal (red line) and response of the system (blue line), Cartesian plot.

While the effect of ohmic resistance is shown in magnitude of amplitude of system response on perturbing signal, in the case of the rest two elements their presence influences phase shift of the system response. This is shown in figure 1. If the perturbing signal is periodic change of the electrode potential, it is possible to express such shift mathematically using equations 2, where E_0 and I_0 stand for amplitude of perturbing signal and response of the system. ω represents angular velocity of amplitude vector rotating ($\omega = 2\pi f$) and $\Delta\varphi$ represents the phase shift. Phase shift is not experimentally available using the common measure devices (amperemeter, voltmeter,…). These devices give only the value of impedance module defined by equation 3. Therefore, for the purpose of determination of the phase angle shift, it is necessary to use specialized instrumental equipment.

$$E = E_0 \sin(\omega\tau) \tag{2A}$$

$$I = I_0 \sin(\omega\tau + \Delta\varphi) \tag{2B}$$

$$|Z| = \sqrt{Z_{real}^2 + Z_{im}^2} \tag{3}$$

In the case of systems which involve phase interfaces, the parameters described above are satisfying for description of only limited numbers of such system. This holds for those systems which features behave like ideal one. However, in the major part of systems, it is necessary to use additional elements which can describe non-ideal behaviour. This is typical especially for the electrochemical systems.

Electrochemical Impedance Spectroscopy (EIS)

All electrochemical processes are heterogeneous due to the charge transfer over the phase interface. It means that these processes are always connected with transfer actions on electrode-electrolyte boundary and with limitations due to their kinetic, respectively. This complicates description of the whole system, when compared to electrical circuits. This is because of non-linear equations describing such system. This gives the first import limitation. Amplitude of the perturbing signal has to be small enough in order to ensure that the dependence of current on potential in such range is linear. From this reason, it is recommended to do not exceed perturbing signal amplitude of 10 mV. This puts significant requirements on instrumental equipment. Another potential obstacle represents separation of electrodes effects, which are not subject of interest. One way how to deal with these obstacles is to use three-electrode arrangement, which eliminates influence of counter-electrode on system response (deeper explanation is in lab work cyclic voltammetry). If the aim of the study is behaviour of liquid or polymer electrolyte, it is recommended to use four-electrode arrangement. Both of the current loaded electrodes are not use in measurement and two sensing electrodes are typically placed in this case between them and serve for reading of the response of the electrolyte.

The main measurement is taken in the wide range of frequencies of perturbing signal. This allows efficiently separate single mechanisms of the charge transfer, and thus gives information about their share on overall kinetics parameters. Exact approach to solution is in design of kinetic model and optimization of its parameters using experimental data. This is, unfortunately, not possible for majority of real systems due to the complexity of the equations, which describe such systems and which are not resolvable without accepting too big simplifications. In practice, the physical model approach in the form of equivalent electrical circuit is thus preferred. This approach is based on description of the system using electrical circuit with electrical elements standing for the processes ongoing on electrode-electrolyte phase interface and/or between sensing electrodes. Using appropriate software equipment it is possible to set the values of each single element in circuit to fit with experimentally measured data. The most difficult is in this case definition of physical reason for each single element and its design with respect to achieve the lowest number of free parameters.

It is obvious that for description of electrochemical systems is not possible to use only basic electrochemical elements. As a typical example the resistance of the system associated with diffusion is possible to illustrate. These elements, however, are out of the frame of this work.
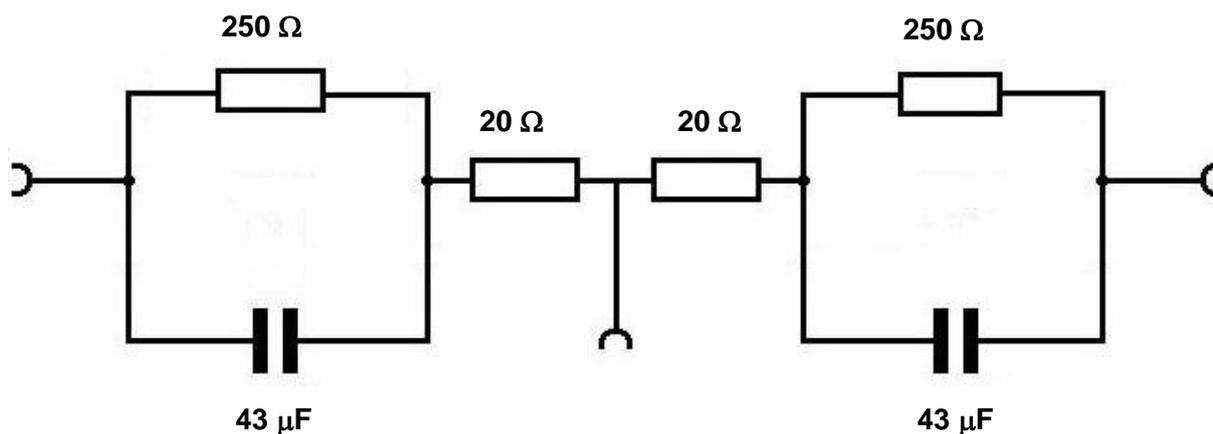
Electrode double layer

Electrode-electrolyte boundary represents from the electrochemical point of view the most interesting part of the whole system, because the main electrochemical process occurred here. This is the reason why even in the early stage of EIS the description of this boundary was point of interest. As a base and the easiest model of this boundary the Helmholz model is used. This model is shown in figure. 2.

From figure 2 is clearly visible, that the boundary can be represent as an electric capacitor (capacity) C_p. From real observations is clear that this imagination is not complete, because in this arrangement the direct current could not pass through the system. Thus, it is completed by ohmic

Figure 2 : Helmholz model of the electrode double layer and development of potentials in it.

resistance R_p in parallel arrangement with capacitor. Whereas the meaning of the capacitor is quite clear (electric capacity of the electrode-electrolyte phase interface), explanation of the ohmic resistance is more difficult. Basically R_p represents polarization resistance to the electrode reaction. Physical meaning of this resistance is slope of polarization curve of electrode reaction. Thus, its value is function of the electrode potential. With increasing overpotential of the electrode reaction, and thus related accelerating of charge transfer kinetic, the value of R_p decreases. The parallel combination is finally completed with ohmic resistance R_s in serial arrangement. Its physical meaning is simulation of resistance of electrolyte between sensing electrodes. Equivalent circuit for electrode-electrolyte phase boundary is shown in figure 3.

Figure 3 : Equivalent electrical circuit with description of construction parameters of electronic elements.

It is obvious that this equivalent circuit called Randles is valid only for ideal cases of charge transfer kinetic controlled processes. It means that no mass transfer, sorption, desorption and so on processes are involved. Under real conditions, however, the number of such systems is limited.

Aim of the work

The aim of this work is to characterize equivalent Randles circuit schematically shown in figure 3 by EIS, evaluate values of single elements, make and discuss comparison of measured data with known values. The second part of this work is to characterize electrochemical system and discuss its relation to equivalent circuit.

Plan of the work

Solution preparation

In the frame of this work are the electrochemical systems represented by $K_4[Fe(CN)_6]$, $K_3[Fe(CN)_6]$ solutions (Ferro/Ferri system) with equal concentration of $2.5*10^{-3}$ mol/dm^3 and with different concentration of supporting electrolyte (KNO_3) equal to 1, 0.1 and 0.01 mol/dm^3. Volume of tested electrolytes is 0.25 dm^3.

Molar masses:

|	
$K_4[Fe(CN)_6]$	368.34 g/mol
$K_3[Fe(CN)_6]$	329.25 g/mol
KNO_3	101.1 g/mol

Equivalent circuit characterization

Characterization of Randles circuit will be done by frequency response analyser Solartron 1250 and electrochemical interface Solartron SI 1287 in three electrode arrangement. Real parameters of Randles circuit are shown in figure 3. To control potentiostat and to data evaluation the commercial software ZPlot and ZView respectively is used. The conditions of experiment are:

Frequencies   65535 Hz – 0.1 Hz

Amplitude   10 mV

Experimental setting is also possible to see in figure 4.
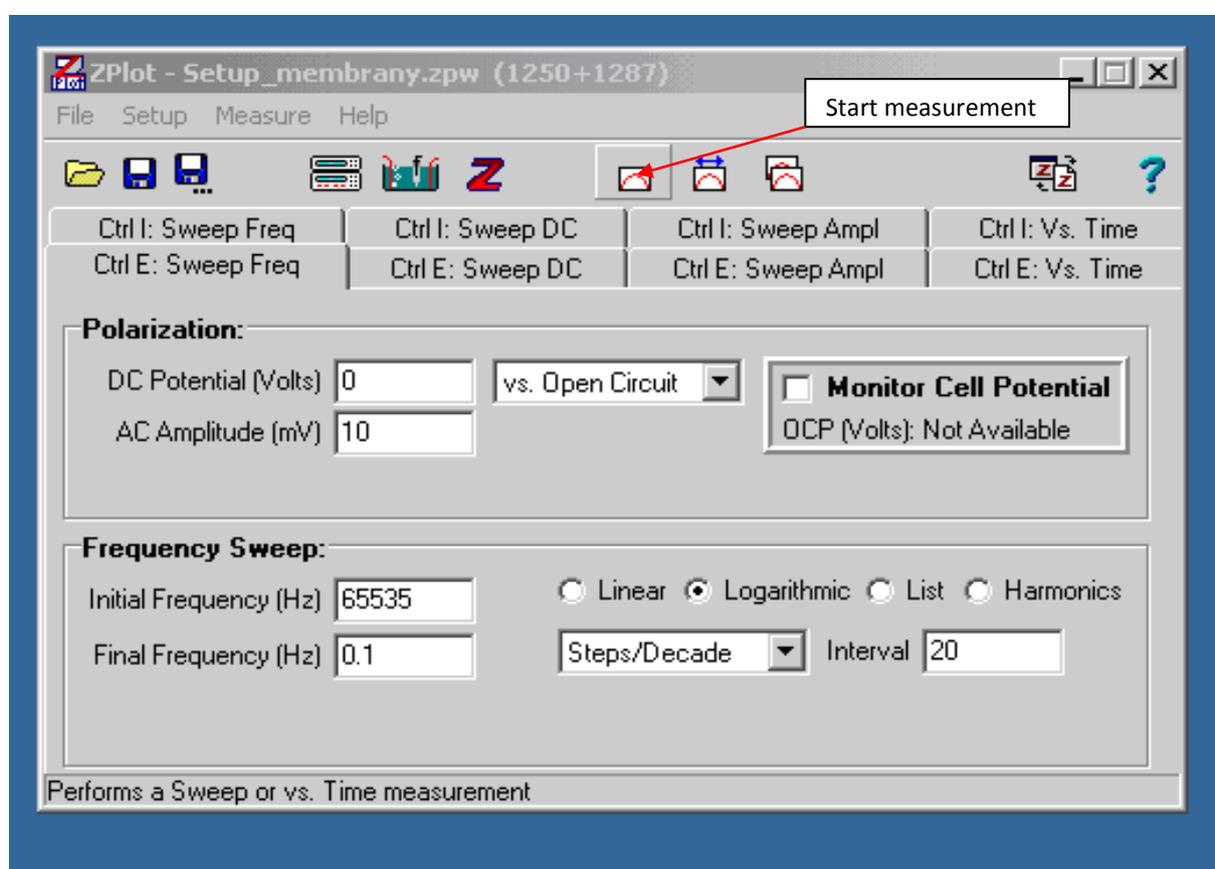
Figure 4: Control software ZPlot and conditions of experiment

Data evaluation

Measured impedance spectra are evaluated by previously mentioned ZView software, using pre-defined Randles equivalent circuit. Interface of the ZView software is shown in figure 5. Obtained values for prepared electric circuit will be compared with real values shown in figure 3.
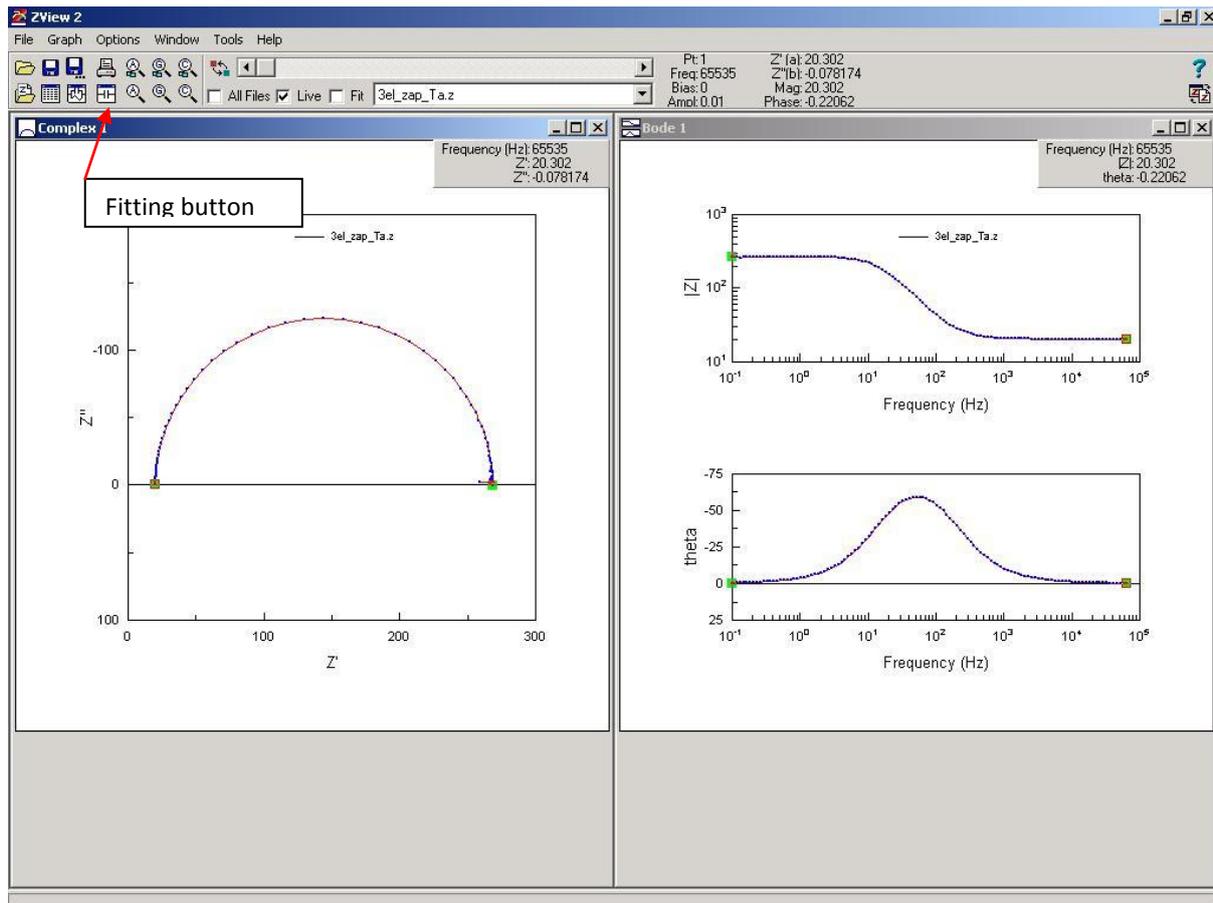
Figure: Record of impedance spectra measured for the case of equivalent Randles circuit.

Electrochemical system characterization

Characterization of the electrochemical systems will be done with the same instrumental equipment and under the same conditions as in the case of Randles equivalent circuit measurement. For the measurement Pt electrodes will be used.

Data evaluation 2

Evaluation of data measured for electrochemical system will be done by ZView software. Differences in spectra for three different systems will be discussed.

Used solutions:

1) $c(K_4[Fe(CM)_6]) = c(K_3[Fe(CN)_6]) = 2,5*10^{-3}$ mol/dm^3, $c(KNO_3) = 0,01$ mol/dm^3

2) $c(K_4[Fe(CM)_6]) = c(K_3[Fe(CN)_6]) = 2,5*10^{-3}$ mol/dm^3, $c(KNO_3) = 0,1$ mol/dm^3

3) $c(K_4[Fe(CM)_6]) = c(K_3[Fe(CN)_6]) = 2,5*10^{-3}$ mol/dm^3, $c(KNO_3) = 1$ mol/dm^3

Exam questions:

1.) Name the basic elements which describe response of the system, which is exposed to alternating current. How these elements change the perturbing signal?

2.) What is the physical meaning of single electronic elements in Randles equivalent circuit?

3.) How the different mechanisms taking part in electrochemical reaction can be separated using EIS?

4.) In which frequencies of perturbing signal is possible to expect mass transfer resistance?

Others:

It is necessary to use laboratory coat for the whole time of laboratory work. It is recommended to have calculator, pen and some paper or work notebook for notes and memory stick.