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Modeling and Sensing of Electrochemical Processes upon Dirac Potentiostatic Excitation of Capacitive Charging/Discharging

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Modeling of the processes at the electrolyte–electrode interface by the application of electrical excitations is of great importance in electrochemistry. Straightforward and simple estimation of the parameters of double layer and charge transfer processes allows optimization, while increasing demand for the analysis of complex processes requires improvement of existing methods and establishment of new ones. In this paper a completely new technique which uses so-called Dirac pulse for investigation of electrochemical systems is introduced. Based on previous studies of electrochemical behavior of copper sulfide minerals, an electric analog is introduced and also a mathematical model is derived for potentiostatic excitation of these systems by a Dirac pulse. The obtained analytical results are compared to experimental data and to the data obtained by computer simulation. A computer system for pulse generation and the monitoring of the response is developed in the LabVIEW programming environment, and applied to real systems. High matching level between the model and the results is achieved by the proper choice of model parameters, which confirmed the proposed model and enabled possible further research within the fast and simple experiments with low number of experimental runs.

Keywords: mathematical model; computer simulation; pulse excitation; electrochemical sensing; capacitive response, chalcocite.

1. INTRODUCTION

Pulse excitation has been used in electrochemical technologies for a long time, but also in the electrochemical research process itself [1, 2]. Using the computer modeling, optimization and process control, this research area has experienced recently a large expansion [3-6]. The obtained results are used to analyze the possibilities of an increase of energy efficiency [7, 8]. During several years of research of electrochemical systems, such as supercapacitors, an equivalent electrical circuit (EEC) has been determined by the authors of the paper for copper sulfide (Figure 1) [9]. Investigations performed mainly in acid solutions [10] lead to the assumption that the metal ions from the mineral crystal lattice are transferred into the solution leaving a surface region with the higher content of sulfur. The presence of elemental sulfur on the surface of anodically treated chalcocite was confirmed by electronic microscopy [11]. That sulfur can be treated as adsorbed species giving rise to the pseudocapacitance exhibited by Cu_2S.

Mathematical analysis of the EEC and experimental results obtained using standard or modified electrochemical techniques are published earlier [9-14]. The EEC response to the potentiostatic pulse was practically the same as the response of real electrochemical systems. Similar EEC is used by some other authors [15].

Based on the determined EEC, a completely new technique for investigation of electrochemical systems is introduced. This technique uses so-called Dirac pulse. Dirac pulse is a short potentiostatic excitation of high intensity, widely used in different kinds of physical systems analysis [16].

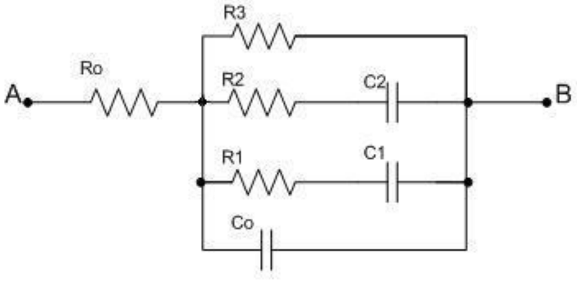


Figure 1. Equivalent electrical circuit for observed class of electrochemical systems.

The resistor R_0 fits electrically the ohmic resistance of electrolyte and electrode material (usually in order of magnitude of ohms). The capacitor C_0 (usually in order of magnitude of mF) corresponds to the capacitance of a double layer formed at the electrolyte–electrode phase boundary. The resistors R_1 and R_2 (usually in order of magnitude of tens of Ω), as well as capacitors C_1 (usually in order of magnitude of mF) andC_2 (order of magnitude of F) are related to the slow adsorption and solid-state diffusion processes, respectively (if the diffusion processes could not take place, EEC would not contain the C_2 - R_2 branch). When capacitors or batteries are charged and then left on open circuit, a certain degree of self-discharge can set in depending on the chemistry and electrochemistry of the system [17]. R_3 is the resistance of self-discharge, thus reciprocally related to the leakage current. Its value is in order from hundreds of Ω to several kΩ.

Time constants, as the products of capacitance and corresponding resistance, are of different orders of magnitude. As a consequence, discharging follows a double exponential function. So, the discharging curve exhibits two regions, first one where current changing have to be observed in a time of the order of magnitude of seconds, and the second one, where changing have to be monitored in a much longer time. Taking into account the magnitudes of capacitances C_0, C_1 and C_2, the EEC can be simplified by omitting the C_0 branch that is almost opened as the system approaches the steady state of discharging process.

2. SYSTEM ANALYSIS

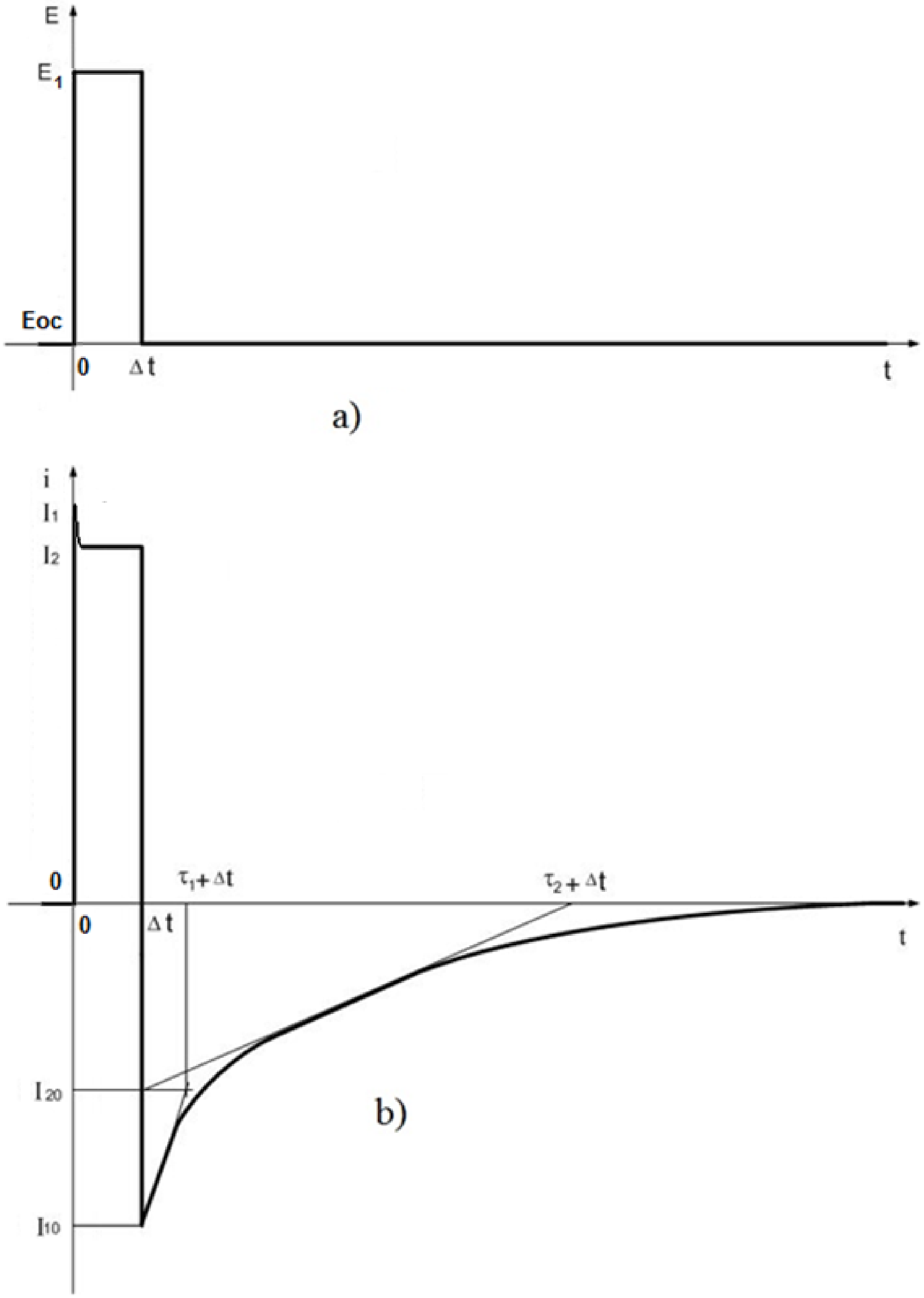


Figure 2. Excitation (a) and corresponding response of the EEC (b)

System excitation by voltage short pulses (Fig. 2a) is called the Dirac excitation. For the EEC of the electrochemical system presented in Fig. 1, a short potentiostatic pulse (usually far from equilibrium) and subsequent forced relaxation toward previously registered open-circuit potential, the theoretical response of the system (in this case current) is as shown in Figure 2b.

Curves in Figure 2 can be described by the following:

$I_1 = \frac{E_1}{R_0}$ - instant charging current (1)

$I_2 = \frac{E_1}{R_0 + R_{123}}$ - quasi-stationary charging current (current plateau on the curve for extremely short pulse duration) (2)

$I_{10} = \frac{-U_{C_{10}}}{R_1 + R_{023}}$ - instant discharging current, (3)

where:

$R_{123} = \frac{R_1 R_2 R_3}{R_1 R_2 + R_1 R_3 + R_2 R_3}$ - equivalent resistance of R_1, R_2 and R_3 in parallel connection (4)

$R_{023} = \frac{R_0 R_2 R_3}{R_0 R_2 + R_0 R_3 + R_2 R_3}$ - equivalent resistance of R_0, R_2 and R_3 in parallel connection (5)

$U_{C_{10}} = \frac{I_2 \cdot \Delta t}{C_1} \frac{R_2}{R_1 + R_2}$ - initial discharging voltage of capacitor C_1 (6)

$I_{20} = \frac{-U_{C_{20}}}{R_2 + R_{03}}$ - quasi-stationary discharging current (7)

$R_{03} = \frac{R_0 R_3}{R_0 + R_3}$ - equivalent resistance of R_0 and R3 in parallel connection (8)

$U_{C_{20}} = \frac{I_2 \Delta t}{C_2} \frac{R_1}{R_1 + R_2}$ - initial discharging voltage of capacitor C_2 (9)

$\tau_1 = (R_1 + R_{023}) \cdot C_1$ - time constant of the first discharging phase (10)

$\tau_2 = (R_2 + R_{03}) \cdot C_2$ - time constant of the second discharging phase (11)

In Eq. 3 R_1 is in series with equivalent resistance of R_0, R_2 and R_3 in parallel connection, defined with Eq. 5, because Eq. 3 describes the system immediately after switching off if the Dirac pulse.

Based on these expressions, EEC parameters can be easily calculated as follows:

$$R_0 = \frac{E_1}{I_1} \qquad (12)$$

From Fig. 2b the values of I_1, I_2, I_{10}, I_{20}, τ_1 and τ_2 can be read easily to solve the following system of equations:

$$I_{10} = \frac{-I_2 \Delta t}{(R_1 + R_{023})C_1} \frac{R_2}{R_1 + R_2} \tag{13}$$

$$I_{20} = \frac{-I_2 \Delta t}{(R_2 + R_{03})C_2} \frac{R_1}{R_1 + R_2} \tag{14}$$

$$R_{123} = \frac{E}{I_2} - R_0 \tag{15}$$

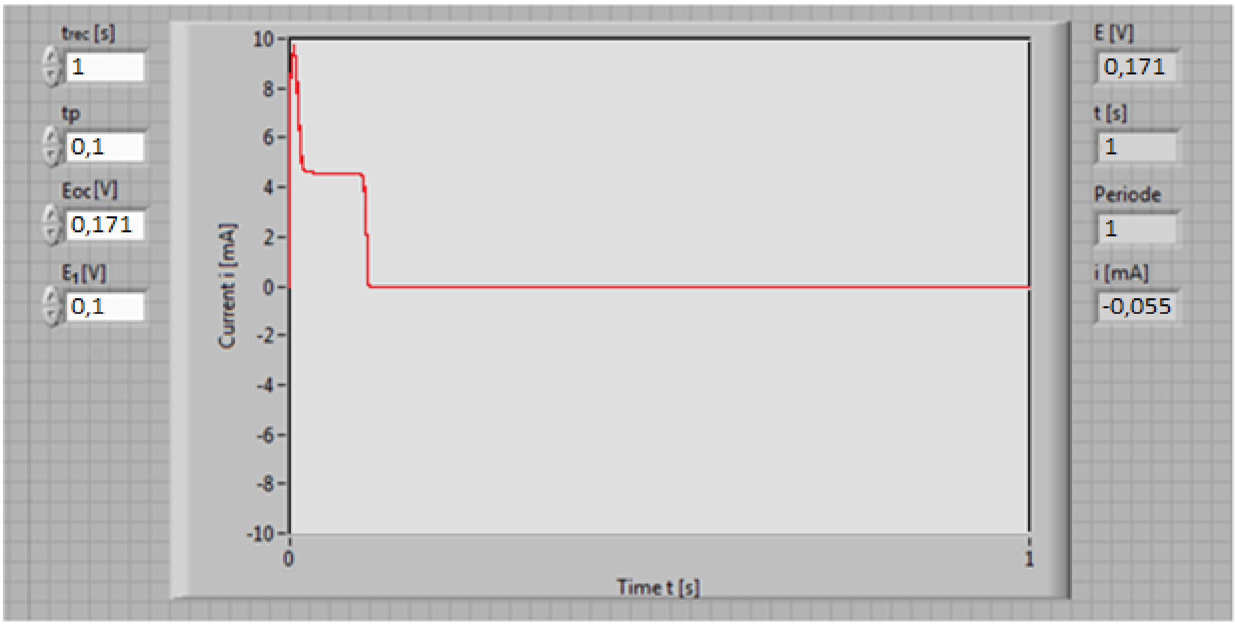
$$\tau_1 = (R_1 + R_{023})C_1 \tag*{\textbf{(16)}}$$

$$\tau_2 = (R_2 + R_{03})C_2 \tag{17}$$

Based on the given analysis, the parameters of the electric circuit can be determined, and consequently the physical parameters of the process [10-13, 18-21], which are essential for the understanding and the control of electrochemical reactions in the analyzed systems.

3. EXPERIMENTAL

Several experiments have been performed with this method and it was found applicable for the rapid characterization of electrochemical systems. The experiments are performed using an electrochemical test system supported by PC and LabVIEW software package [22]. Interface and application software have been developed by authors [23]. A specimen of natural mineral chalcocite from Bor copper mine (Serbia) was used as working electrode in a standard three electrode electrochemical cell. Saturated calomel electrode served as reference, and a platinum sheet used as a counter electrode.



trec [s] 1

tp 0,1

Eoc [V] 0,171

E_1 [V] 0,1

E [V] 0,171

t [s] 1

Periode 1

i [mA] -0,055

Figure 3. Dirac potentiostatic excitation control panel with typical pulse and relaxation response.

All experiments are performed at room temperature. Sulfide minerals, are usually semiconductors, but their conductivity can reach in some cases that of metals. It makes them suitable for electrochemical techniques of analysis. In spite of being natural, used specimen of mineral chalcocite was of very high purity and it was proved by X-ray analysis [11]. Chalcocite attracted much attention after discovering that it exhibits plausable capacitive characteristics. Those characteristics depend on the electrolyte. Our previous investigations [11,12], pointed out that the best capacitance performance can be obtained in solution of $1MH_2SO_4 + 0.01MCuSO_4$.

Figure 3. shows a panel with controls for setting the intensity (E_1) and duration of the voltage pulse (tp), previously determined open-circuit potential (Eoc) and total time (trec), as well as the indicators of actual values (E, t, Periode and i), with an real-time graphical representation of $i = f(t)$.

Figure 4. shows a diagram of the application software in G language of LabVIEW.

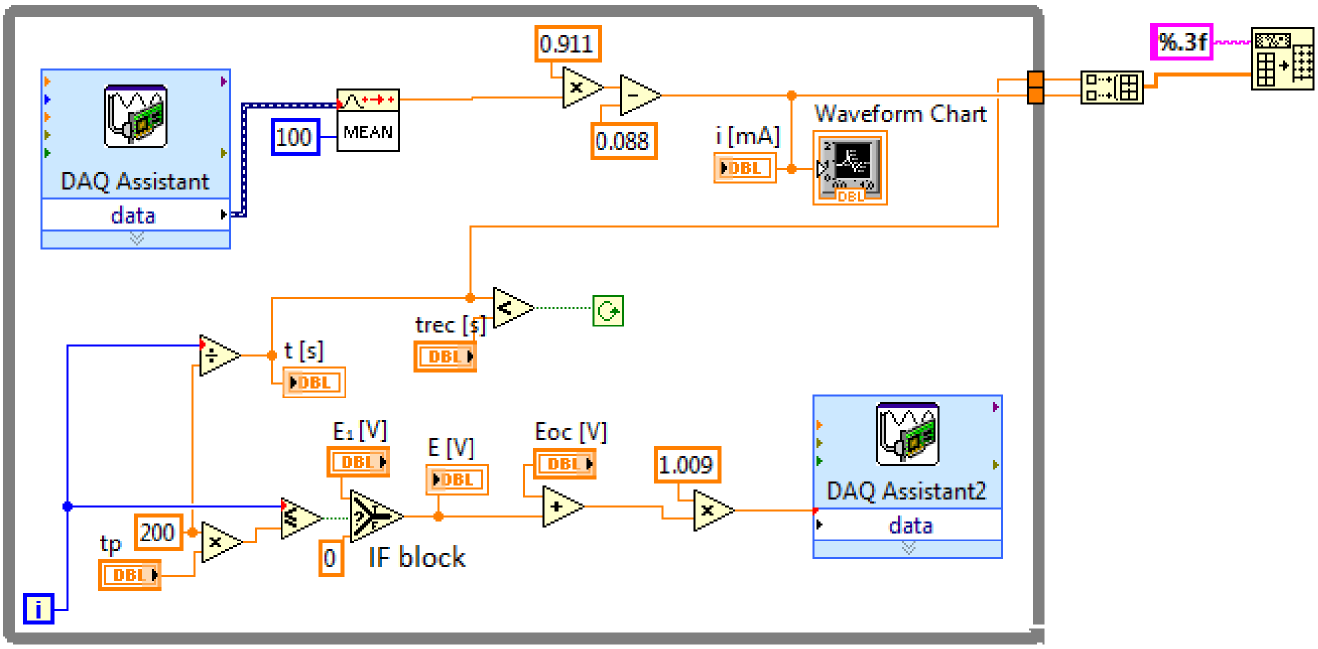
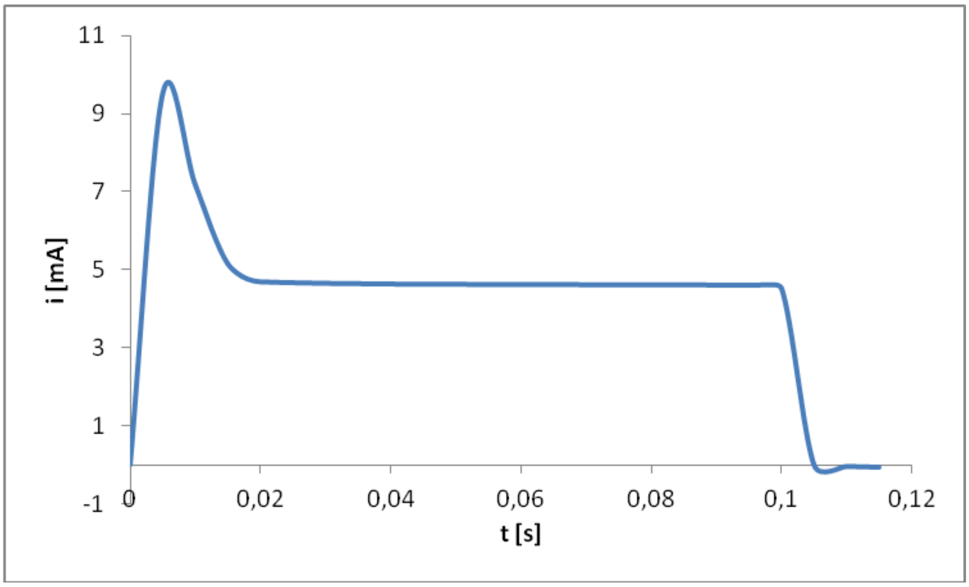


Figure 4. LabVIEW application diagram

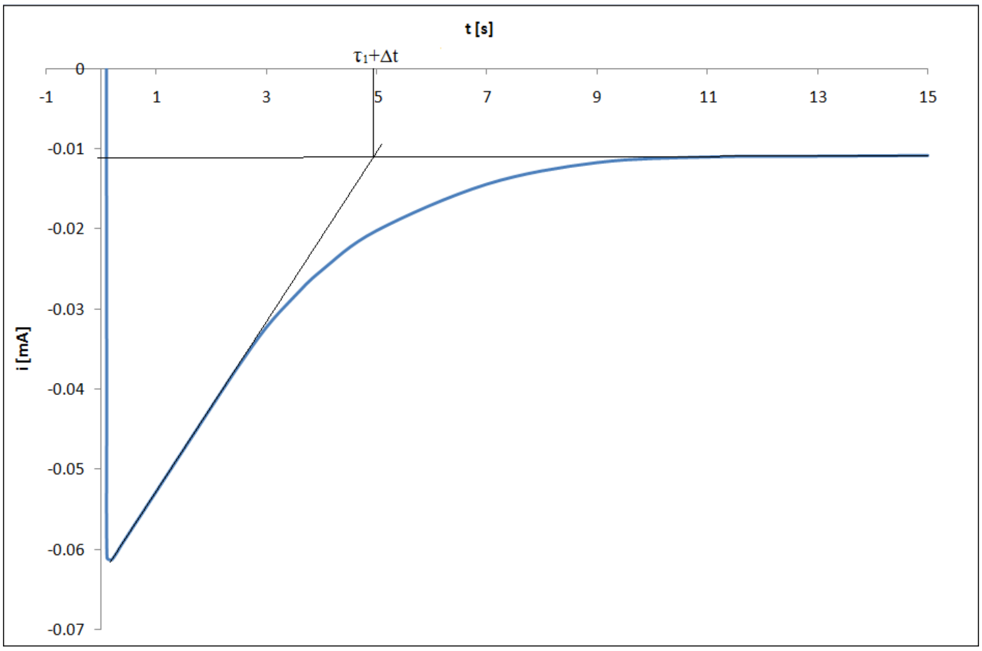
The WHILE loop (gray-framed) defines the excitation signal (Dirac pulse at the output of DAQ Assistant2) and at the same time acquires current response data (DAQ Assistant). In one iteration of WHILE loop the value of the current is measured 100 times repeatedly, and then the mean value of the measurements is calculated by the block MEAN (discrete *i*–*t* pair). Software correction of the gain (multiplication constant of 0.911) and offset (subtraction constant 0.088) are incorporated to compensate real parameters of the interface. The resulting mean current value is displayed on the front panel (indicator i[mA] and the diagram on the Waveform Chart) and simultaneously that value is written in the current column of the ASCII table of measured values. The time populates the first column of the table with a resolution of typically 5ms (duration of one WHILE loop cycle, can be set in DAQ Assistant). This means that the instant time in the loop is obtained by dividing counter variable by 200. Execution of the WHILE loop is repeated until the recording set time (trec) is reached.

The pulse duration is set by the LabVIEW control, tp. Meanwhile, the intensity of the potential pulse, E_1, is set at the output of the IF block. It is superimposed to the previously measured open circuit potential value, E_{0C}, multiplied by the correction gain 1.009 and led to the output via DAQ Assistant2. As t_p is spent, the output of the IF block is set to 0V and the open circuit potential value, E_{0C}, is at the interface output, during trec period.

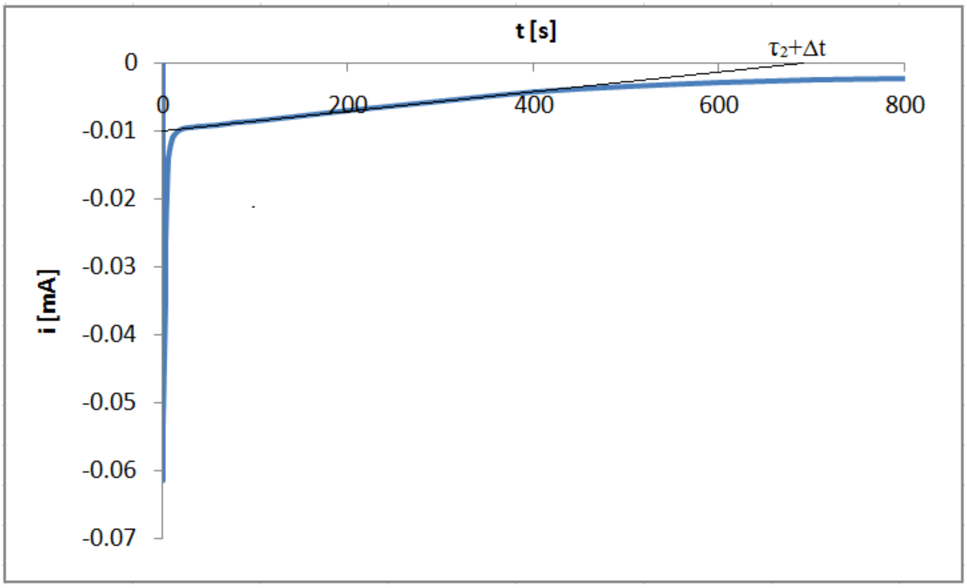
As an example, Figure 5 shows the response at Dirac pulse of 100 mV for the working electrode of copper sulfide, *i.e.*, mineral chalcocite (Cu_2S), in a solution of $1MH_2SO_4+0.01MCuSO_4$ with 0.1 s of excitation duration.



a)



b)



c)

Figure 5. System response at Dirac voltage pulse: charging phase (a), first discharging region (b) and second discharging region (c).

In order to read values reliably, diagram for short time (charging phase) is shown in Fig.5a and diagrams for longer times (first and second discharging region) are shown separately in Fig. 5b and 5c, respectively.

Using the described method, following parameters of the equivalent circuit are obtained:

R_0=10.5□□□R_1=17.1□□□R_2=33.1□□□R_3=153.5□□□$C_□$□□□□F, $C_□$□□□□□F.

In order to compare EEC parameters obtained using the Dirac potentiostatic excitation with the results obtained using other traditional electrochemical methods, these parameters are presented in Table 1 altogether. It has to be emphasized that Dirac pulse excitation is the only electrochemical method which enables simple and reliable measurement of the parameter R_0.

Table 1. Parameters of the equivalent circuit obtained using different measurement methods

Method	R_0 [Ω]	R_1 [Ω]	R_2 [Ω]	R_3 [Ω]	C_1 [F]	C_2 [F]
Dirac excitation	10.5	17.1	33.1	153.5	□□□	□□□□
Galvanostatic method	-	17,3	31,2	210	0,23	33,1
Potentiostatic method	-	17,1	30,8	206	0,22	31,8
Cyclic Voltametry	-	-	32,1	-	-	32,2
Linear sweep current excitation	-	-	30,9	201	-	33,4

These results are in accordance with the values that have been registered on the same system using other methods which would require a much longer time of excitation [14]. Therefore, the main advantage of the method based on the Dirac voltage excitation is very short period of pulse duration, and thus a negligible degradation of the electrode material.

4. CONCLUSIONS

Analyzing the electrochemical system analog circuit upon Dirac potentiostatic excitation and comparing the calculated results with the experimental ones, the possibility of determination of the process parameters by described method is presented. Definition of the parameters of equivalent electrical circuit allows the analysis of the electrochemical behavior of the system. Dirac potentiostatic excitation allows to obtain these parameters by a fast and reliable experimental procedure. Even more, ohmic resistance can be also obtained directly, which otherwise requires dynamic excitation of the system. Experimental results obtained by testing an extensively investigated system proved that the parameters obtained by Dirac potentiostatic pulse method and those gained by other more complex, expensive and rather long-term methods (for example EIS) do match. Also, there is a possibility to calculate the equivalent circuit parameters from system response at Dirac potentiostatic excitation by using adequate software application in LabVIEW.

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