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RESEARCH ARTICLE

# Behaviour of the electrochemical intrgrator on the basis of solid electrolyte in galvanoharmonic charging mode

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**Abstract:** Behaviour of the Electrochemical integrator on the basis of Solid Electrolyte is studied in the galvanoharmonic charging mode. The possibility of application of simpler and more graphic calculation technigue and separation of impedance of electrochemical systems into active and reactive components is shown. The plotting of the dependences of the active and reactive impedance components on ac freguency was used to find the values of parameters of the studied equivalent electric cuircuits.

**Keywords:** electrochemical integrator, solid electrolyte, operational impedance, galvanoharmonic charging mode

## 1 Introduction

The investigation of the electrochemical behavior of the integrator was performed by operation impedance method which is based on the Laplas transformation and Ohms low between current, voltage and complex resistance (impedance). And what is more in this article was performed the new method of separating of the impedance into active and reactive components.

The basic constructive element of the electrochemical integrator on the basis of solid electrolyte is the electrolytic cell which contains the reversible silver electrode and the inert coal or graphite electrode. The solid electrolyte $Ag_4RbI_5$ is placed between two electrodes.

The electrochemical integrator may be represented schematically in the next form

$$( - )\ \mathrm{Ag}|Ag_4RbI_5|C\ \ (+) \tag{1}$$

Equivalent electric circuit of a cell with the blocked electrode- solid electrolyte interface C / $Ag_4RbI_5$ can be presented in the form of (Figure 1) where $R_e$ is the resistance of solid electrolyte; $C_2$ is the adsorbtion desorbtion capacitance; $Z_{W2}$ diffusion impedance of Warburg related to the sublattice defects of the solid electrolyte.


**Figure 1.** Equivalent electric circuit of the electrochemical integrator (ionix) on the basis of solid electrolyte $Ag_4RbI_5$

In this work we study the behavior of the electrochemical integrator (ionix) in the mode of galvanoharmonic charging of the electrode solid electrolyte interface.

## 2 Thoretical analysis

In the course of ionix charging on the silver electrode cathode the electrodeposition takes place according to equation $Ag^+ + e = Ag$.

On the graphite electrode the charging of double electric layer process takes place. Owing to a small electronic conductivity of the solid electrolyte $Ag_4RbI_5$ $(\tau_e)$= $10^-11$ohm$^-1\cdot$ cm$^-1$[1] the double layer capacity $C_2$ is retained without change.

Operational impedance of a cell shown in Figure 1 can be presented in the form of

$$Z(p) = R_e + \frac{W_2}{\sqrt{p}} + \frac{1}{pC_2} \tag{2}$$

where $W_2$ is diffusion impedance of Warburg connected with the diffusion of the sublattice defects of the solid electrolyte; $C_2$ is the capacitance of double electric layer; $R_e$ is active or Ohmic resistance.

So far as the current is applyd in the galvanoharmonic mode $I(p) = I_o\frac{\omega}{p^2+\omega^2}$ the operational voltage can be presented in galvanoharmonic mode also, as

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$$E(p) = I_o \frac{\omega}{p^{2+\omega^2}} \left[ R_\varepsilon + \frac{W_2}{\sqrt{p}} + \frac{1}{pC_2} \right] \quad (3)$$

where $I_0$ is the amplitude of the wave current; is the angular frequency. To obtain the primitive function of *E(t)* one has to carry out term- by- term transformation of expression (3) into the original function space. Let us designate the transformation operation as $\ll \stackrel{\cdots}{\longrightarrow} \gg$. Herewith, it is obvious that[2–4]

$$R_e I_o \frac{\omega}{p^2 + \omega^2} \stackrel{\cdots}{\longrightarrow} I_o R_e \sin \omega t \quad (4)$$

The other terms in expression (3) can be transformed using the convolution technique,[5] whereby one can write the following relationships;[6]

$$I_o \frac{\omega}{p^2 + \omega^2} \cdot \frac{1}{C_{2P}} \stackrel{\cdots}{\longrightarrow} \int_o^{t-\infty} \frac{I_o}{C_2} \sin \tau d\tau = -\frac{I_o}{\omega C_2} \cos \omega t \quad (5)$$

$$I_o \frac{\omega}{p^2 + \omega^2} \cdot \frac{W_2}{\sqrt{p}} \stackrel{\cdots}{\longrightarrow} \int_o^{t\to\infty} I_o W_2 (t-\tau)^{-\frac{1}{2}} \sin \tau d\tau = \frac{I_o W_2}{\sqrt{\omega}} \Gamma(\frac{1}{2}) \sin \frac{1}{2} \pi \frac{1}{2} = \frac{I_o W_2}{\sqrt{\omega}} \Gamma(\frac{1}{2}) \sin \frac{\pi}{4} \quad (6)$$

where $\Gamma(\frac{1}{2}) = \sqrt{\pi}$- is the gamma function.

With account for relationship (4) (6), expression (3) for voltage assumes the form of

$$E(t) = I_o R_e \sin \omega t - \frac{I_o}{C_2 \omega} \cos \omega t + \frac{I_o W_2}{\sqrt{\omega}} \Gamma(\frac{1}{2}) \sin \frac{\pi}{4} = E_O \sin(\omega t - \theta) \quad (7)$$

where $E_o$ is the ac voltage amplitude; $\theta$ is the current voltage phase angle.

Equation (7) follows from the theory of linear ac circuit,[4] according to which imposing sine wave current on the cell results in the sine wave voltage response in the circuit with similar angular frequency $\theta$ in the steady state mode.

Equation (7) must be correct at any time $t$. In particular, $\omega t = 0$ and $\omega t = \frac{\pi}{2}$, the two following relationships can be obtained on the basis of expression (7)

$$-\frac{I_o}{\omega C_2} + \frac{I_o W_2}{\sqrt{\omega}} \sqrt{\pi} \frac{\sqrt{2}}{2} = -E_o \sin \theta \quad (8)$$

$$I_o R_e + \frac{I_o W_2}{\sqrt{\omega}} \sqrt{\pi} \frac{\sqrt{2}}{2} = E_o \cos \theta \quad (9)$$

$$\begin{cases} \frac{I_O}{\omega C_2} - \frac{I_O W_2}{\sqrt{\omega}} \sqrt{\pi} \frac{\sqrt{2}}{2} = E_o \sin \theta \\ I_O R_e + \frac{I_o W_2}{\sqrt{\omega}} \sqrt{\pi} \frac{\sqrt{2}}{2} = E_o \cos \theta \end{cases} \quad (8a, 9a)$$

As seen in the vector diagram (Figure 2), any sine wave voltage can be formally sepated into an active and reactive components[6] corresponding to:

$$E_o \sin \theta = E_{react}$$

$$E_o \cos \theta = E_{act}$$

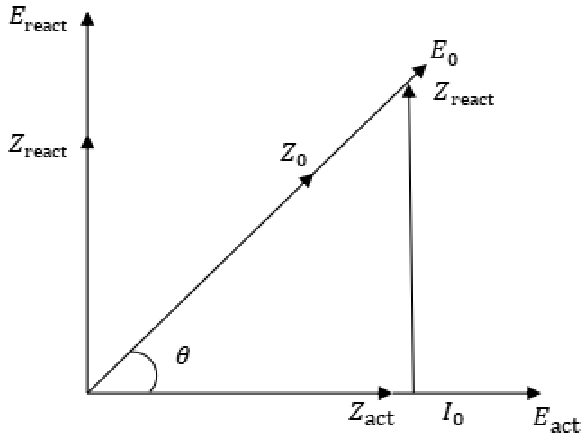


**Figure 2.** Vector diagram showing the relationship between the voltage triangle and resistance triangle

Division of relationship (8) and (9) by current $I_o$ allows passing from the voltage triangle to the resistance triangle in which reactive $E_{react}$ and active $E_{act}$ impedance components are:

$$Z_{react} = \frac{1}{\omega C_2} - \frac{W_2}{\sqrt{\omega}} \sqrt{\pi} \frac{\sqrt{2}}{2} \quad (10)$$

$$Z_{act} = R_e + \frac{W_2}{\sqrt{\omega}} \sqrt{\pi} \frac{\sqrt{2}}{2} \quad (11)$$

Division of relationship (10) by relationship (11) yields the expression for the slope of the electrode impedance phase angle:

$$tg\theta = \frac{Z_{react}}{Z_{act}} \quad (12)$$

Figure 4 shows the impedance complex plane plot of the electrochemical integrator calculated according to expression (10) and (11) at the following values of the equivalent electric circuit parameters: $R_e = 4\ Ohm \cdot cm^2$; $C_2 = 13,3 \cdot 10^{-6}\ F/cm^2$; $W_2 = 50\ Ohm \cdot cm^2 \cdot s^{-1/2}$

The phase angle of electrode impedance tends to at a decrease in the ac frequency and tends to $90^0$ at increase in the ac frequency and tends to $0^0$ at increase in the ac frequency (Figure 3).

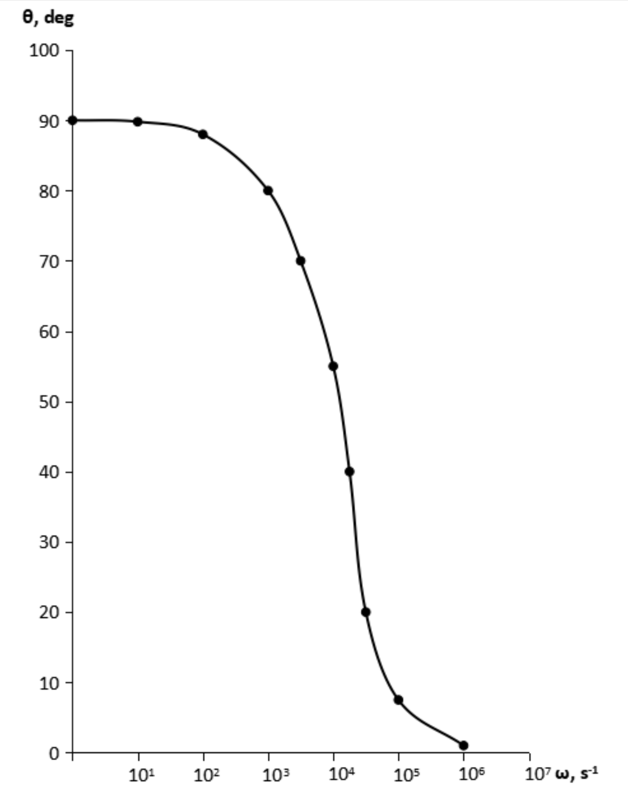


**Figure 3.** Frequency dependence of the impedance phase angle of a electrochemical integrator

As seen in Figure 4 the slope of the impedance complex plane plot to the active resistance axis is decreased at increasing of ac frequency.

The absolute impedance of the electrochemical integrator calculated according to relationship (13)

$$|Z| = \sqrt{Z_{act}^2 + Z_{react}^2} \tag{13}$$

can be presented in the form of the following expression

$$Z = \left\{ R_e^2 + \frac{W_2^2\pi}{\omega} + \frac{W_2\sqrt{\pi}}{\sqrt{\omega}2}(2R_e - \frac{2}{c_2\omega}) + \frac{1}{c_2^2\omega^2} \right\}^{\frac{1}{2}} \tag{14}$$

The dependence of the absolute impedance on the ac frequency is shown in Figure 5. According to relationship (14), the absolute impedance tends at an increase in a frequency to a constant value equal to resistance $R_e$ of the solid electrolyte.

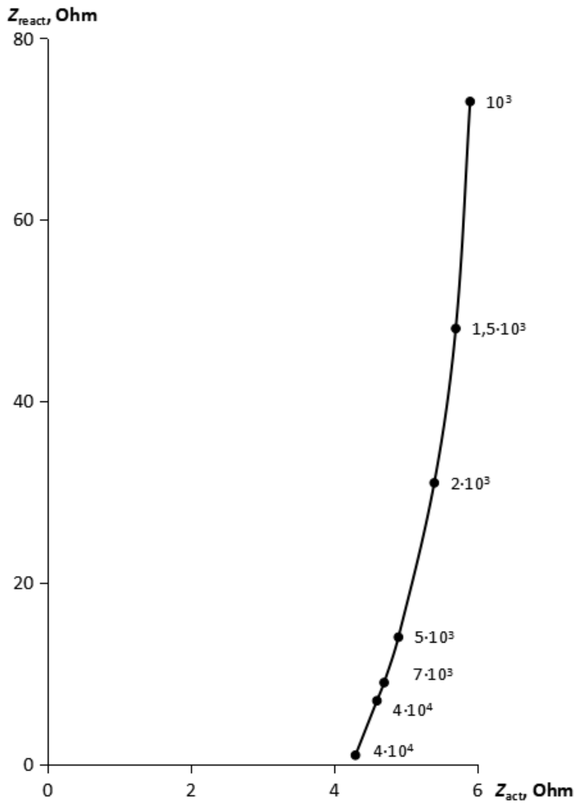


**Figure 4.** Impedance complex plane plot of electrochemical integrator. Numbers near the points correspond to the angular frequency values in Hz.

For plotting the experimental results it is convenient to reduce expression (10) to the form of

$$Z_{react}\omega = \frac{1}{c_2} - \frac{w_2\sqrt{2\pi}}{2}\sqrt{\pi} \tag{10a}$$

The plot corresponding to relationship (10a) is shown in Figure 6, it can be used to estimate the value of parameters $C_2$ and $W_2$.

The dependence of active impedance component $Z_{act}$ on the frequency according to equation (11) is shown in Figure 7.

The plot of function $Z_{act} - f\left(\frac{1}{\sqrt{\omega}}\right)\ at\ \omega \to \infty$ approaches the constant value equal to $R_e$.

## 3 Results and conclusion

In this article we were obtained frequency dependances of impedance, frequency dependence of the impedance phase angle, of the absolute impedance and the frequency dependances of the active and reactive

 

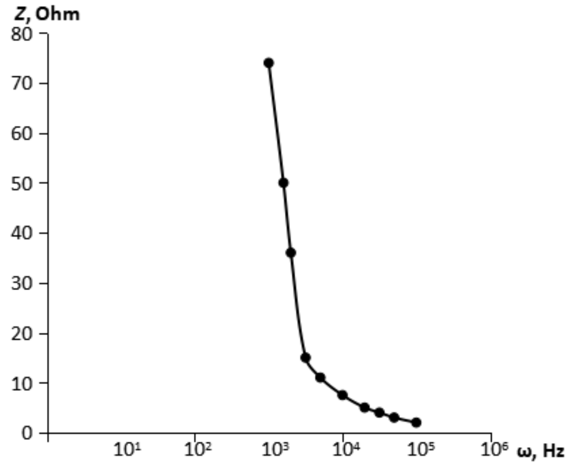


**Figure 5.** Dependance of absolute impedance of electrochemical integrator on ac frequency

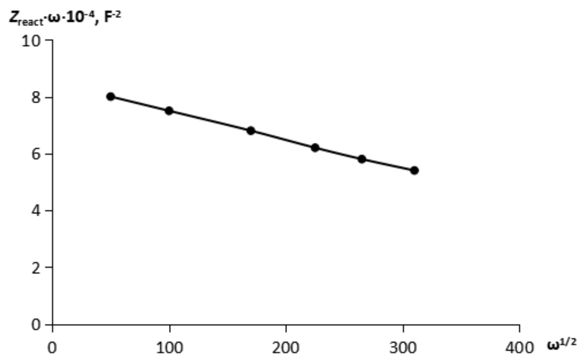


**Figure 6.** Determination of $C_2$ and $W_2$ according to equation (10a)

components of the impedance of the electrochemical integrator on the basis of the solid electrolyte. This work uses a new method based on the results of the throry of linear ac circuits for calculation and factori zation of impedance into active and reactive components. Conclusion. One should note that the method of calculation and separation of impedance into components used in this work is simple and graphic, which in our opinion, makes the operational methods especially attractive for analysis of properties of ac circuits.

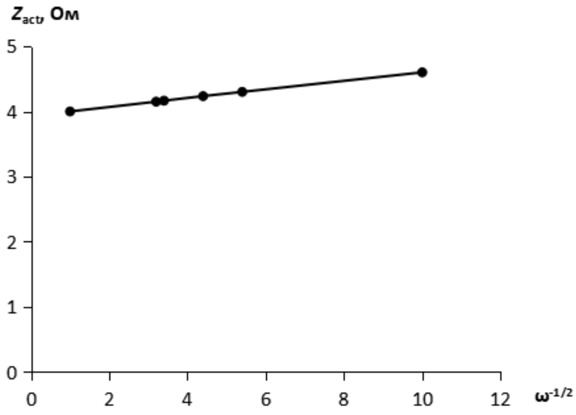


**Figure 7.** Determination $R_\varepsilon$ in according to equation (11)

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