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Mathematical modeling of subdiffusion impedance in multilayer nanostructures

Kostrobij P. P.[1], Grygorchak I. I.[1], Ivaschyshyn F. O.[1], Markovych B. M.[1], Viznovych O. V.[1], Tokarchuk M. V.[1,2]

[1] *Lviv Polytechnic National University*
12 S. Bandera str., 79013, Lviv, Ukraine
[2] *Institute for Condensed Matter Physics*
of the National Academy of Sciences of Ukraine
1 Svientsitskii str., 79011, Lviv, Ukraine

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The model of impedance subdiffusion based on the Cattaneo equation in fractional derivatives in applications to multilayer nanostructures is considered. Nyquist diagrams with changes of the parameter τ (time for which the flow is delayed with respect to the concentration gradient) and the subdiffusion coefficient D_α are calculated.

Keywords: *fractional derivative, Cattaneo equation, Nyquist diagram, impedance*
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The current stage of the development of physics of photoelectrode, electrode processes stimulates theoretical investigations and mathematical modeling of reactionary-electrodiffusion processes in electrolytic systems. The research of photocatalysis kinetics in semiconductor systems is important from the point of deeper understanding the processes at accumulation of solar energy into electricity at solar batteries. As one of the most important technological problems in modern accumulate batteries is prolonging the life and stability of electrodes (metallic, amorphous carbon, etc.) during their operation. In this direction, the researches of electrochemical and impedance electrodiffusion transport processes for lithium battery are carried out [1–9].

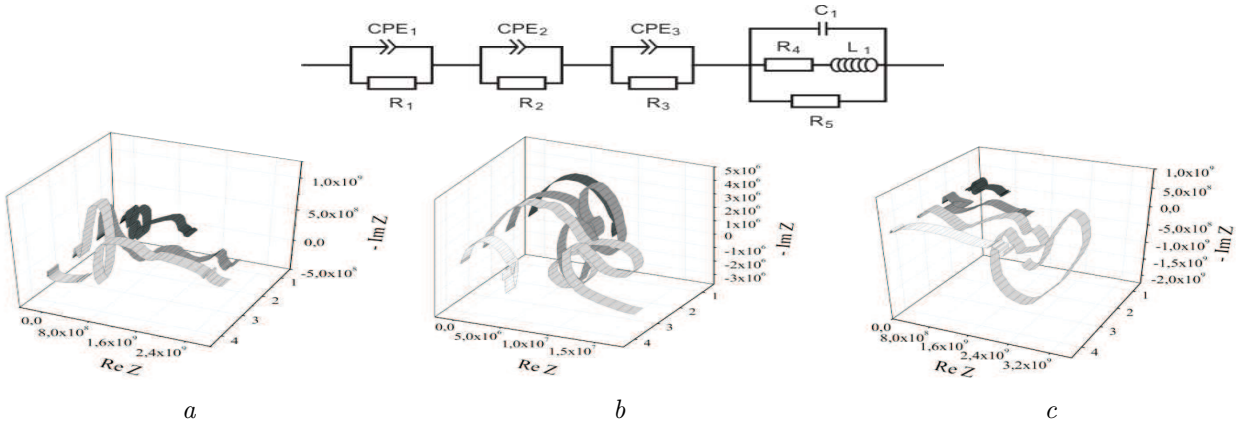

Fig. 1. Nyquist diagrams constructed for the direction normal to the layers of an extended matrix of GaSe with incapsulated β–CD in an amount of 6–(2), 10–(3) and 20–(4) mol% for 293 K in the dark (a), in the light (b), and in magnetic field (c). (1) is the extended crystalline matrix. In the inset, the equivalent circuit diagram is represented.

In particular, in Refs. [10,11] there were obtained Nyquist diagrams constructed for the direction normal to the layers of extended matrix of GaSe with incapsulated β–CD in an amount of 6–(2), 10–(3), and 20–(20) mol% for 293 K in the dark (a), in the light (b), and in magnetic field (c). Analyzing constructed impedance locus (Fig. 1), one should pay attention to the fact that the Nyquist diagram of gallium selenide unexpanded sample looks like a half-circle that reflects the capacitive response of localized states. After the expansion (without β-cyclodextrin), it is transformed into three-arc form (Fig. 1a), which indicates the formation of the energy relief for current carriers with three periods of the relaxation and the explicit system of levels of adhesion, which cause the transition of midrange interval to IV ("inductive") quadrant of complex impedance plane. The transformation of the equivalent electrical circuit from the parallel RC-interval to the form shown in the inset to Fig. 1a, corresponds to this. Here a fixed element of the CPE phase, which the impedance in the complex plane is expressed as follows [3]:

$$Z_{CPE} = K^{-1}(i\omega)^{-\gamma}, \tag{1}$$

where K is the coefficient of proportionality, γ is the exponent of power that indicates the phase deviation, it reflects the capacitance distribution for each relaxation process. After the introduction of β-cyclodextrin, the frequency genesis of Nyquist diagram is complicated significantly displaying the energy barriers for current rate through layers of β-cyclodextrin and interface of matrix || cavitand content. The data of investigations testify the peculiarity of fractalled guest system. Thus, on the basis of the practical purpose (use for high-Q capacitors of radio frequency ranges), for analysis of data there were taken into account the data, which correspond to the value of the tangent δ of the angle of electrical losses being less than unity. The frequency interval ($1 \div 10^6$ Hz) corresponds to this condition. Uppermost, we should note that the first introduction of β-CD changes the frequency dispersion $\operatorname{tg}\delta$ of extended matrix, while the increase in the organic content up to 10 mol.% causes its reduction along the investigated ω-axis. The β-cyclodextrin amount of 20 mol.% reverses this change probably due to the growth of the concentration of current carriers. Dielectric permittivity along the crystallographic axis is changed the most significantly after reaching β-cyclodextrin content of 10 mol.%. In this case, in the range of the high-frequency $\varepsilon(\omega)$ the growth of dielectric permittivity with the increase in frequency assumes an expressive oscillation nature demonstrating anomalous frequency dispersion. It can be caused by the emergence of additional polarization in jumped charge transfer along localized states near the Fermi level. Frequency impedance behavior (1) and dielectric permittivity [10,11] point to a complex nonlinear, oscillation nature of charge transfer processes in such a system. The behavior (1) testifies the impedance processes anomality. Their research is topical both from the experimental and theoretical point of view. Subdiffusion is reffered to anomalies phenomena in electrolytic process.

For the mathematical modeling of these processes we have applied the Riemann-Liouville equation of subdiffusion with fractional derivative with respect to time. In general, subdiffusion processes occur in systems where the movement of particles is complicated significantly by the internal structure of the medium, such as a porous medium, helium, amorphous semiconductors, etc. [12–25]. Subdiffusion is characterized by the dependence of the particle displacement mean square on time:

$$\langle \Delta x^2 \rangle = 2D_\alpha t^\alpha / \Gamma(1+\alpha),$$

where D_α is the subdiffusion coefficient measured in m^2/c^α units and α is the subdiffusion parameter with the values in the range $0 < \alpha < 1$. For $\alpha = 1$, we have the usual diffusion. Subdiffusion impedance theoretical analysis was presented in Ref. [2] using Riemann-Liouville equations of subdiffusion with fractional derivative with respect to time. In Ref. [23] to describe the subdiffusion processes, the Cattaneo equation [12] was suggested:

$$\tau \frac{\partial^2 c(x,t)}{\partial t^2} + \frac{\partial c(x,t)}{\partial t} = D_\alpha \frac{\partial^{1-\alpha}}{\partial t^{1-\alpha}} \frac{\partial^2 c(x,t)}{\partial x^2}, \tag{2}$$

where the parameters D_α and τ (period, for which the current is delayed relatively to the concentration gradient $c(x,t)$) are considered as independent from each other. On the basis of the equation (2), we shall investigate the frequency dependence of the $Z(i\omega)$nanostructured system impedance, which is determined from the correlation:

$$Z(i\omega) = R_W \frac{\hat{c}(0,i\omega)}{\hat{j}(0,i\omega)},$$

where R_W is the Warburg resistance, $\hat{j}(0,i\omega)$ is the flow of charge, ω is the frequency. Further we assume that the process of charge transfer in the system is described by the generalized Cattaneo equation (2) with the following initial boundary conditions (on the boundary L): $c(x,0) = \frac{\partial}{\partial t}c(x,t)_{|t=0} = 0$, $a_j j(L,t+\tau) + b_L c(L,t) = 0$ [23]. On the basis of the solutions of the Cattaneo equation, we have calculated Nyquist diagrams with variation in the frequency in the range $\omega \in (10^{-1}, 10^5)$, with $R_W = 1$, $L = 1$, the results of which are presented in Fig. 2–7.

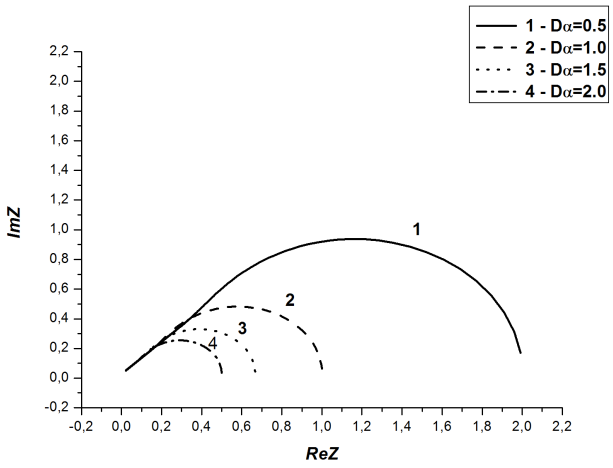

Fig. 2. Nyquist diagram for $\tau = 0$.

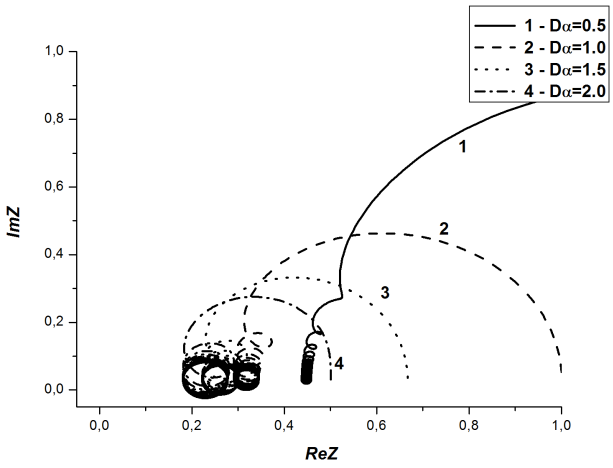

Fig. 3. Nyquist diagram for $\tau = 0.1$.

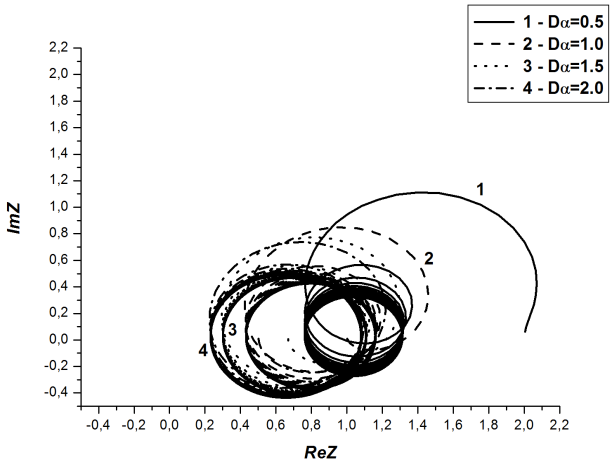

Fig. 4. Nyquist diagram for $\tau = 0.5$.

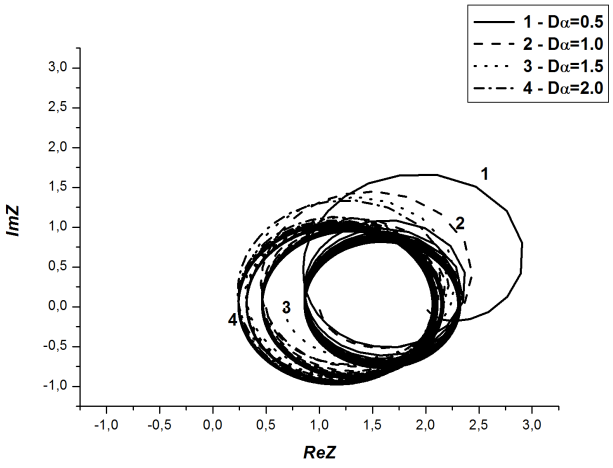

Fig. 5. Nyquist diagram for $\tau = 1.0$.

In Figs. 2–5 the results of the investigations of the frequency dependence of the impedance for the given values of the parameter τ with the change of subdiffusion coefficient of the diffusion are shown. When $\tau = 0$, we have a standard Nyquist diagram, in which with the increase of values of time for which the flow is delayed with respect to the concentration gradient, the nature of the Nyquist diagram

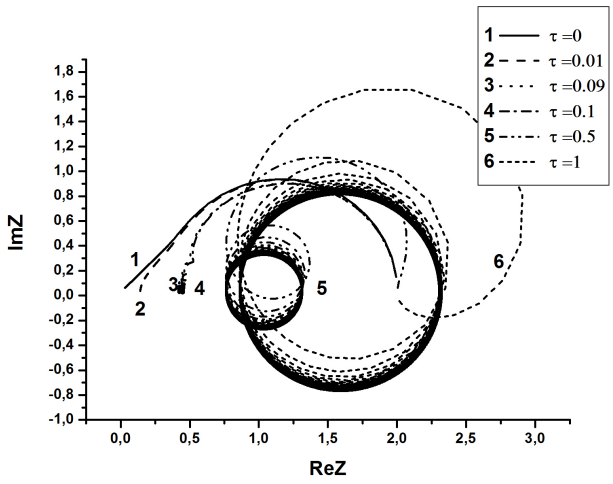

Fig. 6. Nyquist diagram for $D_\alpha = 0,5$.

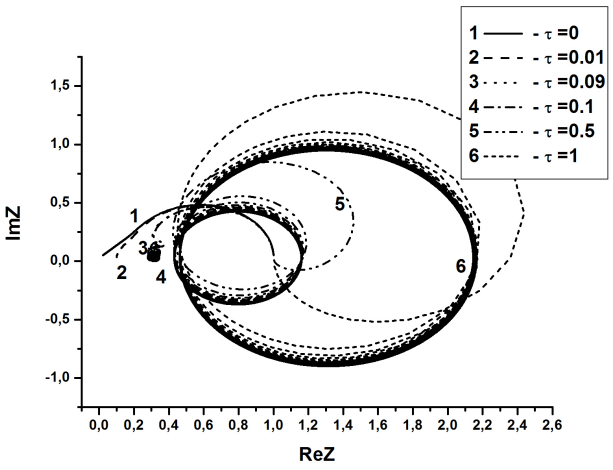

Fig. 7. Nyquist diagram for для $D_\alpha = 1$.

with the change of the diffusion coefficient changes significantly and assumes an oscillation character. Obviously, both changes of the diffusion coefficient and a flow depend on the mechanisms of electron transfer, changes of the system structure, the influence of a magnetic or electromagnetic field in a certain direction. Figs. 6 and 7 represent Nyquist diagrams when the values of the diffusion coefficients are fixed but the time for which the flow is delayed with respect to the concentration gradient changes. As we can see, when $\tau = 0$ and small $\tau = 0,01$ we have Warburg resistance, at $\tau = 0,09$ and $\tau = 0,1$ the behaviour of the frequency dependence of the impedance is drastically changed and further at $\tau = 0,5$ and $\tau = 1$ it assumes an oscillation character. In Ref. [23] it was shown that the parameter τ influences the process of transferring less (difficulties in movement of charges increase) when α is small.

Thus, we have considered the model of subdiffusion impedance based on the Cattaneo equation in fractional derivatives in applications to multilayer nanostructures. The calculated Nyquist diagrams with change of the parameter τ and D_α testify to the complicated transport processes that occur in the system and which are characteristic for the experimental data in Fig. 1. For the interpretation of such behavior of the parameters τ and D_α their influence on the impedance dependences, the development of microscopic theory of transfer processes, which would take into account the nature of the interaction between electrons in multilayer nanostructures under the action of external fields (magnetic, electromagnetic), is necessary.

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Математичне моделювання субдифузійного імпедансу в мультишарових наноструктурах

Костробій П. П.[1], Григорчак І. І.[1], Іващишин Ф. О.[1], Маркович Б. М.[1], Візнович О. В.[1], Токарчук М. В.[1,2]

[1] *Національний університет «Львівська політехніка»*
вул. С. Бандери, 12, Львів, 79013
[2] *Інститут фізики конденсованих систем НАН України*
вул. Свенціцького, 1, Львів, 79011

Розглянуто модель субдифузійного імпедансу на основі рівняння Кеттано у дробових похідних у застосуванні до мультишарових наноструктур. Розраховано діаграми Найквіста із зміною параметрів τ (час, на який потік затримується відносно градієнта концентрації) та субдифузійного коефіцієнта D_α.

Ключові слова: *дробова похідна, рівняння Кеттано, діаграма Найквіста, імпеданс*

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