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APPLICATION OF GENERALIZED CATTANEO EQUATION TO MODEL SUBDIFFUSION IMPEDANCE*

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We use the hyperbolic subdiffusion equation with fractional time derivatives (the generalized Cattaneo equation) to study the transport process of electrolytes in subdiffusive media such as gels and porous media. In particular, we obtain the formula of electrochemical subdiffusive impedance of a spatially limited sample for large pulsation of electric field.

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1. Introduction

Subdiffusion occurs in systems where mobility of particles is significantly hindered due to internal structure of the medium, as in porous media, gels or amorphous semiconductors [1, 2]. The subdiffusion is characterized by the time dependence of the mean square displacement of transported particle $\left\langle \Delta x^2 \right\rangle = \frac{2D_\alpha t^\alpha}{\Gamma(1+\alpha)}$, where D_α is the subdiffusion coefficient measured in the units m^2/s^α and α is the subdiffusion parameter which obeys $0<\alpha<1$. For $\alpha=1$ one deals with the normal diffusion.

The subdiffusion has been recently extensively studied. While the phenomenon is theoretically rather well understood, there are very few experimental investigations (see for example [2]). One of the methods to study the

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diffusive or subdiffusive systems is the so–called electrochemical impedance method. The theoretical analysis was performed in the paper [3] where the parabolic subdiffusion equation with fractional time derivative was used. The method of impedance spectroscopy has been used to experimentally study porous media such as nanopore electrode [4], cement [5–7], tooth enamel [8] and gels [9].

In our paper we apply the hyperbolic Cattaneo equation with the fractional time derivative to model the subdiffusion impedance. We find an influence of τ (which is the delay time of flux with respect to the concentration gradient, see below) on a formula describing the impedance of the subdiffusive medium of finite thickness where the boundary condition for fully absorbing wall at the sample surface is assumed. Particularly, we obtain the formula of electrochemical subdiffusive impedance of a spatially limited sample in the limit of large pulsation of electric field.

2. The generalized Cattaneo equation

To describe subdiffusion one usually uses the parabolic subdiffusion equation [1, 10]

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

where D_α is the subdiffusion coefficient and $C(x,t)$ is the concentration of the diffusing substance, with the Riemann–Liouville fractional time derivative, which is defined for $\alpha > 0$ as [11]

$$\frac{\partial^\alpha f(t)}{\partial t^\alpha} = \frac{1}{\Gamma(n-\alpha)} \frac{\partial^n}{\partial t^n} \int\limits_0^t dt' \frac{f(t')}{(t-t')^{1+\alpha-n}}\,.$$

Putting $\alpha = 1$ in Eq. (1) we get the normal diffusion equation. For the initial condition $C(x,0) = \delta(x)$, where δ is the Dirac-delta function, the solution of Eq. (1) (the Green's function) has non-zero values for any x and t ($t > 0$). Thus, for extremely small time variable there exists a finite amount of the substance at very large distances from the origin, what can be interpreted as infinite propagation velocity of some diffusing particles. To avoid this 'unphysical property' Cattaneo derived the hyperbolic normal diffusion equation which Green's function achieve non-zero values for finite x. The phenomenological derivation of this equation is based on the assumption that the flux of the particles J is not generated by the concentration gradient instantaneously (as in the process described by parabolic diffusion equation), but it is delayed by time τ, what provides the relation

$$J(x,t+\tau) = -D_\alpha \frac{\partial C(x,t)}{\partial x}\,. \tag{2}$$

Expanding the left-hand side of Eq. (2) into the power series with respect to τ and assuming that the parameter τ is sufficiently small, one gets

$$J(x,t)+\tau\frac{\partial J(x,t)}{\partial t}=-D_\alpha\frac{\partial C(x,t)}{\partial x}\,. \tag{3}$$

Combining Eq. (3) with the continuity equation

$$\frac{\partial C(x,t)}{\partial t}=-\frac{\partial J(x,t)}{\partial x}\,, \tag{4}$$

one obtains the hyperbolic normal diffusion equation

$$\tau\frac{\partial^2 C(x,t)}{\partial t^2}+\frac{\partial C(x,t)}{\partial t}=D_\alpha\frac{\partial^2 C(x,t)}{\partial x^2}\,. \tag{5}$$

The parabolic subdiffusion equation can be derived form Continuous Time Random Walk formalism or by using the phenomenological approach [1,10]. In the latter case one sets the Riemann–Liouville fractional time derivative of the order $1-\alpha$ in the right-hand side of Eq. (2) (with $\tau=0$) or replaces the time derivative of the first order in Eq. (4) to Caputo fractional time derivative of order α. In similar way one can obtain hyperbolic subdiffusion equation. In the paper [12] three possible generalizations of the Cattaneo equation (5) were proposed and each of them leads to the one with the fractional time derivative, each one supported by a different scheme. In each of them the fractional time derivative replaces the one of natural order in Eqs. (2) or (4), or it is putting in the right-hand side of Eq. (2). The schemes provide the different hyperbolic subdiffusion equations which are not equivalent of each other. To derive the hyperbolic subdiffusion equation, we use the last scheme, which is the most natural in our opinion.

For many ‘typical systems’ (as the membrane one) it is hard to observe the difference between the solutions of parabolic and hyperbolic subdiffusion equations even for relatively large values of τ [13]. However, in some processes the non-zero parameter τ plays crucial role. The example is the diffusion in a system where boundary conditions are given by functions quickly changing in time. Such a situation occurs in the electrochemical system with (sub)diffusion impedance, where for large values of ω the concentration at the sample surface oscillates with high frequency. As far as we know, till now the Cattaneo equation was used to study electrochemical impedance only for system where normal diffusion occurs [14].

As we mention above, in our paper we use the generalized Cattaneo equation derived from continuity equation (4) and delayed flux-force relation, which reads

$$J(x,t+\tau)=-D_\alpha\frac{\partial^{1-\alpha}}{\partial t^{1-\alpha}}\frac{\partial C(x,t)}{\partial x}\,. \tag{6}$$

Equation (6) ensures that changes of the flux due to the concentration gradient are delayed by the time τ. Assuming that τ is small and keeping linear terms with respect to τ in the series expansion of l.h.s. of Eq. (6), we get

$$J(x,t)+\tau\frac{\partial J(x,t)}{\partial t}=-D_\alpha\frac{\partial^{1-\alpha}}{\partial t^{1-\alpha}}\frac{\partial C(x,t)}{\partial x}\,. \qquad (7)$$

Combining Eq. (7) with the continuity equation (4), we obtain the generalized Cattaneo equation

$$\tau\frac{\partial^2 C(x,t)}{\partial t^2}+\frac{\partial C(x,t)}{\partial t}=D_\alpha\frac{\partial^{1-\alpha}}{\partial t^{1-\alpha}}\frac{\partial^2 C(x,t)}{\partial x^2}\,. \qquad (8)$$

3. Subdiffusion impedance

The impedance of electrochemical system $Z(i\omega)$ can be defined by the response to a voltage or current perturbation from a steady-state situation as [15]

$$Z(i\omega)=\frac{\hat{\eta}(i\omega)}{\hat{I}(i\omega)}\,, \qquad (9)$$

where $\hat{\eta}(i\omega)$ and $\hat{I}(i\omega)$ are the Laplace transforms of the overvoltage and current perturbation; ω is the angular frequency of the ac-voltage related to the frequency f by the relation $\omega=2\pi f$. A parametric plot of the real and imaginary parts of the impedance in the complex plane $(\mathrm{Re}\,Z,-\mathrm{Im}\,Z)$, where ω is treated as a parameter, is called the Nyquist plot.

The impedance of the diffusion layer is called the Warburg impedance. For the layer of the infinite thickness the impedance is defined as [3]

$$Z(i\omega)=\frac{R}{\sqrt{i\omega}}=\frac{R}{\sqrt{2\omega}}(1-i)\,, \qquad (10)$$

where R is the diffusion resistance. On the Nyquist plot the Warburg impedance is presented by the straight half line with the slop angle $\pi/4$ passing through the origin of coordinates. In real systems the diffusion layer has a finite thickness. Let the diffusion layer be limited by the planes localized at $x=0$ and $x=L$. The perturbation of the voltage is applied on $x=0$. The characteristic angular frequency is defined as [3]

$$\omega_d\equiv\frac{D}{L^2}\,, \qquad (11)$$

where D is the diffusion coefficient. The frequency (11) is the inverse of the average time of passing of transported ion through the sample. When $\omega\gg\omega_d$ the size of the sample plays no role and the impedance is the

Warburg impedance (10). However, for a small frequency the ions can be absorbed by the opposite wall before end of the period.

The oscillating overvoltage $\eta(t) = E_0 \sin(\omega t + \varphi)$ cause the oscillation of the concentration on the surface layer according to the formula [3]

$$\eta|_{x=0}(t) = \left(\frac{d\eta}{dC}\right)_{\text{eq}} C(0,t)\,, \tag{12}$$

where 'eq' denotes a derivative computed in the local equilibrium. The conduction current $I(t)$ at $x = 0$ corresponds to the flux of diffusing particles $J(0,t)$

$$I(t) = qAJ(0,t)\,, \tag{13}$$

where q is the charge of diffusing particle and A is the area of the sample surface. From Eqs. (9), (12) and (13) one obtains the relation [3]

$$Z(i\omega) = R_{\text{W}} \frac{\hat{C}(0,i\omega)}{\hat{J}(0,i\omega)}, \tag{14}$$

where $R_{\text{W}} = \frac{1}{qA}\left(\frac{d\eta}{dC}\right)_{\text{eq}}$.

Let us assume that at $x = 0$ there is the oscillating concentration of diffusing particles and at $x = L$ there is a fully absorbing wall (Fig. 1). Consequently,

$$C(0,t) = C_0 \sin(\omega t + \varphi)\,, \tag{15}$$

where $C_0 = R_{\text{W}} qAE_0$, and

$$C(L,t) = 0\,. \tag{16}$$

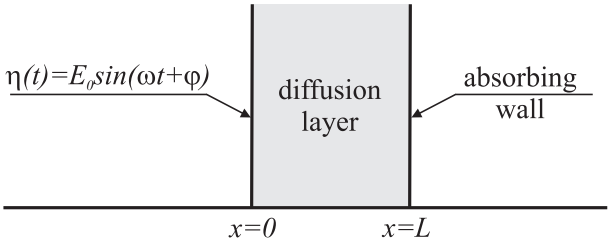

Fig. 1. The system under considerations, η denotes the overvoltage, E_0 — its amplitude, ω is the angular frequency.

We assume that the transport process is described by the Cattaneo equation (8) with the following initial conditions

$$C(x,0) = \left.\frac{\partial C(x,t)}{\partial t}\right|_{t=0} = 0\,. \tag{17}$$

The Laplace transform of (8) for the initial conditions (17) is

$$\tau s^2\hat{C}(x,s)+s\hat{C}(x,s)=D_\alpha s^{1-\alpha}\frac{d^2\hat{C}(x,s)}{dx^2}\,. \tag{18}$$

The solution of Eq. (18) is

$$\hat{C}(x,s)=B_1\exp\left[\gamma(s)x\right]+B_2\exp\left[-\gamma(s)x\right]\,, \tag{19}$$

where

$$\gamma(s)=\frac{s^{\alpha/2}}{\sqrt{D_\alpha}}\sqrt{1+\tau s}\,. \tag{20}$$

The Laplace transform of the flux reads

$$\hat{J}(x,s)=-D_\alpha\frac{s^{1-\alpha}}{1+\tau s}\frac{d\hat{C}(x,s)}{dx}\,. \tag{21}$$

Combining Eqs. (14)–(16) and (19)–(21) we obtain

$$Z(s)=-R_{\rm W}\frac{1}{\lambda(s)}\tanh\left[\gamma(s)L\right]\,, \tag{22}$$

where

$$\lambda(s)=s^{1-\alpha/2}\sqrt{\frac{D_\alpha}{1+\tau s}}\,. \tag{23}$$

We add that for subdiffusive systems the relation (11) should be changed as $\omega_d\equiv(D_\alpha/L^2)^{1/\alpha}$ (see also [3]).

We are particularly interested in the case of large ω, since then a substantial influence of τ is expected. In the limit $\omega\to\infty$ we obtain from Eqs. (22) and (23)

- For $\tau\neq 0$

$$Z(i\omega)=\frac{R_{\rm W}\sqrt{\tau}}{\sqrt{D_\alpha}\omega^{(1-\alpha)/2}}\left[\cos\left(\pi\frac{1-\alpha}{4}\right)-i\sin\left(\pi\frac{1-\alpha}{4}\right)\right]\,, \tag{24}$$

  thus, the Nyquist plot of the impedance is a linear function passing through the origin of coordinates with the angle slope given by

$$\tan\varphi=\tan\left(\pi\frac{1-\alpha}{4}\right)\,, \tag{25}$$

  $0<\alpha<1$, $\varphi\in(0,\pi/4)$.

- For $\tau = 0$

$$Z(i\omega) = \frac{R_{\mathrm{W}}}{\sqrt{D_\alpha}\omega^{1-\alpha/2}}\left[\cos\left(\pi\frac{1-\alpha/2}{2}\right) - i\sin\left(\pi\frac{1-\alpha/2}{2}\right)\right] , \quad (26)$$

where

$$\tan\varphi = \tan\left(\pi\frac{1-\alpha/2}{2}\right) , \quad (27)$$

$\varphi \in (\pi/4, \pi/2)$.

Let us illustrate our considerations by four plots performed for different values of the parameters α and τ. Calculating Re Z and Im Z from (22) for $s = i\omega$ we obtain the Nyquist plots (Figs. 2–5), where for larger values of ω the points on the plots are laid nearer the origin. In our calculations we take $\omega \in (10^{-1}, 10^5)$, $R_{\mathrm{W}} = 1$, $L = 1$ and $D_\alpha = 1$ (all quantities are given in arbitrary units).

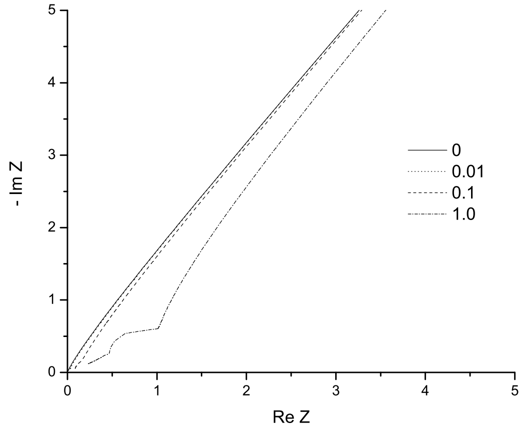

Fig. 2. The Nyquist plots for $\alpha = 0.4$ and for τ given in the legend. The curves for $\tau = 0$ and $\tau = 0.01$ are practically undistinguishable.

In Figs. 2 and 3 the plots for $\tau = 0$ and $\tau = 0.01$ are practically undistinguishable, but for larger values of the subdiffusion parameter α these plots differ from each other for large ω (see Figs. 4 and 5). Let us note that for relatively large τ the Nyquist plots show 'chaotic' behavior, which is stronger when α and τ increase. So, in presented cases there is no reason to consider values of τ larger than the one presenting on the plots. The plots suggest that the curves for different values of parameter τ aim to one curve for very small values of ω.

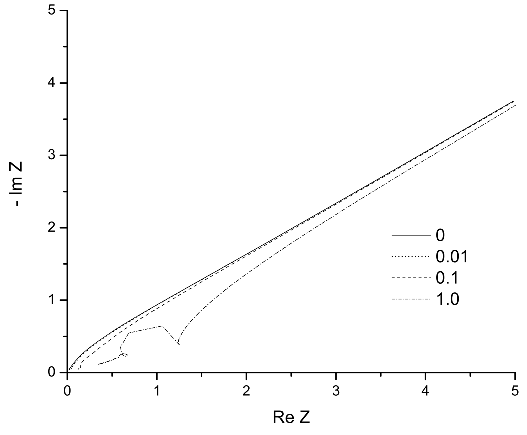

Fig. 3. The Nyquist plots for $\alpha = 0.6$. Similar as in Fig. 2, the curves for $\tau = 0$ and $\tau = 0.01$ are practically undistinguishable.

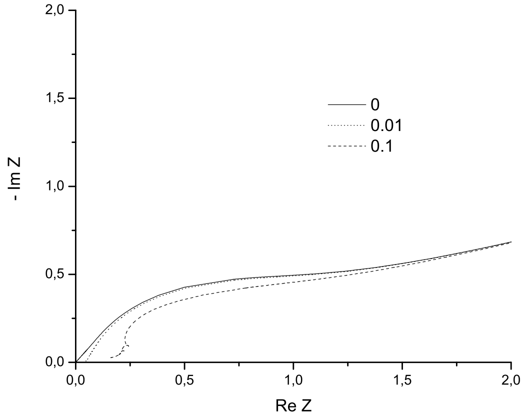

Fig. 4. The Nyquist plots for $\alpha = 0.8$.

The plot for $\alpha = 1$ and $\tau = 0$ for small ω is approximated by a part of circle. This is characteristic for normal diffusion [15] and subdiffusion [3] for the system with fully absorbing wall located at $x = L$ with $\tau = 0$. More detailed analysis (especially for large ω) will be presented elsewhere [13]. Here we note that:

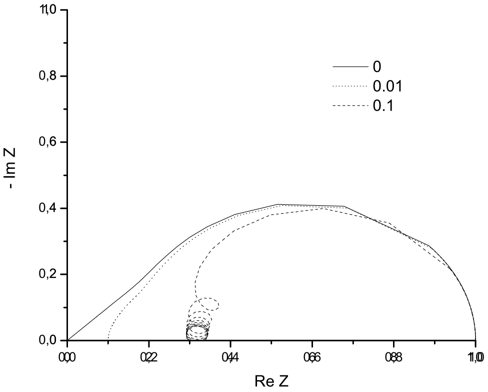

Fig. 5. The Nyquist plots for $\alpha = 1.0$.

- For $\omega \to 0$ and for given α the plots are not dependent on τ and they are going to the one curve.
- For $\omega \to \infty$ the slope of the plot gradually decreases as τ increases. When $\alpha = 1$ and $\tau \neq 0$ the plots going to the point for which $-\mathrm{Im}\, Z$ is very closed to zero whereas $\mathrm{Re}\, Z$ is finite. We suppose that in the following it goes to the origin with zero slope (according to the formula (25)).

4. Final remarks

The main result of our paper is Eq. (22) with the asymptotic formulas (24)–(27). These functions and Figs. 2–5 show the following

- For $\omega \to \infty$ the Nyquist plot is the linear function passing through the origin of coordinates with the slop angle given by Eq. (24) and (26).
- For non-zero τ, φ does not dependent on τ.
- It is possible to determine the values of parameters of the system from experimental data. For example, measuring the slop angle for large ω, one can extract the subdiffusion parameter α.

Let us note that for the layer with infinite thickness ($L \to \infty$) the impedance (22) takes the form

$$Z(i\omega) = R_{\mathrm{W}} \frac{\sqrt{1 + \tau i\omega}}{\sqrt{D_\alpha}(i\omega)^{1-\alpha/2}}\,, \tag{28}$$

which for $\tau = 0$ and $\alpha = 1$ corresponds to the classical Warburg impedance.

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