ISSN 1023-1935, Russian Journal of Electrochemistry, 2017, Vol. 53, No. 6, pp. 575–588. © Pleiades Publishing, Ltd., 2017.
Original Russian Text © A.L. Gavrilyuk, D.A. Osinkin, D.I. Bronin, 2017, published in Elektrokhimiya, 2017, Vol. 53, No. 6, pp. 651–665.

The Use of Tikhonov Regularization Method for Calculating the Distribution Function of Relaxation Times in Impedance Spectroscopy

A. L. Gavrilyuk[a, b], D. A. Osinkin[c, d, *], and D. I. Bronin[c, d]

[a] *University of Science and Technology of China, School of Mathematical Science, Anhui, 230026 PR China*
[b] *Krasovskii Institute of Mathematics and Mechanics, Ural Branch, Russian Academy of Sciences, Yekaterinburg, 620990 Russia*
[c] *Institute of High-Temperature Electrochemistry, Ural Branch, Russian Academy of Sciences, Yekaterinburg, 620137 Russia*
[d] *Ural Federal University, Yekaterinburg, 620002 Russia*
**e-mail: OsinkinDA@mail.ru*

Received August 10, 2016; accepted for publication October 19, 2016

Abstract—The state-of-the-art in realization of the method of distribution of relaxation times (DRT) as applied to the analysis of data of electrochemical impedance spectroscopy is briefly surveyed. The theoretical fundamentals of the DRT method are described, the methods of solving the Fredholm equation of the 1st order with respect to the unknown DRT function are considered as an ill-defined problem. The Tikhonov regularization method presently considered as the most suitable for solving this equation is discussed. For several numerical experiments, the high resolution of the DRT method and its stability with respect to noise in impedance spectra are demonstrated. Among the problems and limitations of the DRT methods, the choice of the optimal regularization coefficient is considered as the most significant. Particularly, it is shown that in those cases where several relaxation processes with the constant phase angle appear in the response of objects under study to ac disturbances, different regularization coefficients should be selected for each of these elements in order to obtain adequate results.

Keywords: distribution of relaxation times, DRT, impedance, Tikhonov regularization
DOI: 10.1134/S1023193517060040

INTRODUCTION

Impedance spectroscopy is used extremely widely for studying the kinetics of electrode processes, particularly, as applied to solid-oxide fuel cells.

In the first stage of the development of the electrochemical impedance method, the spectra were analyzed by the semigraphical technique [1–3]. At present, the nonlinear least square analysis (NLSA) in which the degree of impedance approximation by a certain equivalent circuit is determined by the residual errors is used almost exclusively. To analyze the impedance spectra by the NLSA method, the programs "EquivCrt" (B.A. Boukamp), "LEVM" (J.R. Macdonald), and "ZView" (Scribner Associates) are used most often.

It is relatively recently that the method of distribution of relaxation times (DRT) was introduced into the practice of certain scientific groups, few so far. The use of the DRT method as applied to electrochemical impedance spectroscopy was extended owing to the studies by the group from the Karlsruhe University. Their first publication [4] attracted attention of other scientists because of two factors: the DRT method demonstrated the higher resolution as compared with the NLSA method and did not require choosing a priori the equivalent circuit. The result of the DRT analysis of impedance spectra represents a function of distribution of relaxation times (in the further text, DRT function) which carries information on the number of relaxation processes that manifest themselves in the impedance frequency response and also on the relaxation times (frequencies) when the impedance spectrum is described by a circuit built of *RC* elements (resistance *R* and capacitance *C* switched in parallel) connected in series.

There are several mathematical approaches to calculating the DRT function [4–9]. The analysis of literature has shown that only few research groups have their own software for calculating the distribution of relaxation times of stages of electrochemical processes [4, 10–14]. Unfortunately, we do not know any software which could de facto be considered as standard and approved to be used in the DRT method.

In the present publication, we would like to describe several questions that arise during calculations of the DRT function by the Tikhonov regularization method, which is the topical subject of the recent publications. Still remaining open, these questions, which have emerged as a result of our own experience in using this method and also based on results of other authors, point to the necessity of the deeper investigation of possibilities and limitations of the Tikhonov regularization method as applied to calculations of the DTR function.

THEORY

1. Problem Statement

At present it is accepted [15–17] that admitting linearization of the tested system, its impedance $Z(\omega)$ is related to the function of distribution of relaxation times $\gamma(\tau)$ by the following equation:

$$Z(\omega) - Z(\infty) = R_{\text{pol}} \int_0^\infty \frac{\gamma(\tau)}{1 + j\omega\tau} d\tau, \qquad (1)$$

where j is the imaginary unit, ω is the angular frequency, τ is the time, $Z(\infty)$ is the ohmic resistance (frequency-independent part of impedance), R_{pol} is the total polarization resistance, $\gamma(\tau)$ is the function of distribution of relaxation times that satisfies the conditions of non-negativity and normalization:

$$\gamma(\tau) \geq 0, \quad \int_0^\infty \gamma(\tau)\, d\tau = 1. \qquad (2)$$

The necessity of non-negativity condition is associated with the fact that for the vast majority of electrochemical objects, both the total and the partial polarization resistances are positive.

In such representation, the impedance can be described as a series connection of an infinite number of RC elements with resistance $R_{\text{pol}}\gamma(\tau)d\tau$ and capacitance $\tau/R_{\text{pol}}\gamma(\tau)d\tau$ so that $R_{\text{pol}}\gamma(\tau)d\tau$ characterizes the total polarization resistance associated with the relaxation times in the interval $[\tau, \tau + d\tau]$ [4, 18].

The function of distribution of relaxation times $\gamma(\tau)$ usually represents a train of bell-shaped pulses (for examples, see Results) distributed along the time axis or close to the Dirac delta function. The positions of pulses (peaks) determine the characteristic relaxation times of the corresponding processes or stages while the areas under the peaks determine the partial polarization resistances of these processes.

Equation (1) with respect to the unknown function $\gamma(\tau)$ is called the integral equation of Fredholm of the first order with the kernel $h(\omega, \tau) = \dfrac{1}{1 + j\omega\tau}$. Thus, the DRT method consists in solving the integral equation (1) with respect to the unknown function $\gamma(\tau)$ under the assumption that its left-hand part, i.e., impedance $Z(\omega)$ is known (measured). The ohmic resistance $Z(\infty)$ can also be considered as the unknown quantity in Eq. (1) if its value cannot be found based on some other considerations or the error of its determination cannot be considered as satisfactory.

It is well known that the Fredholm equation is an incorrect (ill-staged) problem, the strict mathematical definition of which can be found in [19]. In practice, the incorrectness of the problem means that at least one of the following properties is not fulfilled:

—the equation has solution and the latter is unique,

—the solution of equation is stable with respect to small changes in the known part, i.e., the small random changes in the known part caused, e.g., by the observation noise, do not induce substantial changes in the solution.

One of the properties of this problem leading to its incorrectness is instability of the solution with respect to inevitable errors of observation, i.e., impedance measurements.

Furthermore, instead of impedance $Z(\omega)$ as a function of frequency, the practically known left-hand part of equation is presented as a set of impedance $Z(\omega_i)$ measurements on the logarithmically equidistant frequency spectrum limited by a certain bottom $\omega_{\min}$ and top $\omega_{\max}$ frequencies, where N is the number of measurements. Thus, considering, instead of the function $Z(\omega)$, a discrete finite set of its values induces an additional discretization error (i.e., the loss of information on the behavior of function $Z(\omega)$ beyond the given set of frequencies $\{\omega_i\}$).

To find solutions of ill-staged problems, several methods called regularization methods have been developed in applied mathematics, the most well-known of which is perhaps the Tikhonov method [19]. The main idea of regularization is to change the initial incorrect problem for a problem correct but dependent on the numeric parameter λ called the parameter or coefficient of regularization. For the case of concordant tendency to zero of parameter λ and errors in the observed data, the solution of the correct problem tends to the exact solution of the corresponding incorrect problem (for the formal definition of the regularizing operator, see [19]).

The application of the DRT to impedance spectroscopy was associated with using various regularization methods: entropy maximum [20–22], genetic programming [23–25], LASSO regression [26], deconvolution [4, 7, 10, 27, 28], and the Tikhonov method as such [8, 18, 26, 29, 30]; moreover, attention was focused on the latter two methods.

The below description of the regularization methods and concomitant problems does not claims for mathematical rigor or completeness of all details. Our goal was to give an idea of this mathematical apparatus

for nonspecialists and formulate certain questions that arise during its application to a particular practical problem, i.e., for calculating the DTR function in impedance spectroscopy, which in turn may be interesting for specialists in the theory of regularization.

The deconvolution method consists in transforming the original Eq. (1) into a convolution equation by extracting from it the Fourier transform of the sought function $\gamma(\tau)$, which is followed by the inverse Fourier transform with the controlled filtration of the result. This method was used for DTR calculations in [4, 7, 10, 27, 28], although its detailed analysis was given only in a recent study [28]. From our point of view, the critical drawback of this method is the fundamental impossibility of exerting control over the non-negativity condition $\gamma(\tau) \geq 0$ during the calculations, i.e., the found solution may have regions of negative values of the $\gamma(\tau)$ function, which necessitates its further processing.

In the Tikhonov method, the non-negativity condition can be taken into account. To find solution of Eq. (1), we pass from the integral equation to linear equations using the formulas of numerical integration:

$$Z'(\omega_i) - Z(\infty) = R_{\text{pol}}\int_0^\infty \gamma(\tau)\, h'(\omega_i, \tau)\, d\tau \to R_{\text{pol}}\sum_{j=1}^{M} a_j \gamma(\tau_j)\, h'(\omega_i, \tau_j), \quad (3)$$

$$Z''(\omega_i) = R_{\text{pol}}\int_0^\infty \gamma(\tau)\, h''(\omega_i, \tau)\, d\tau \to R_{\text{pol}}\sum_{j=1}^{M} a_j \gamma(\tau_j)\, h''(\omega_i, \tau_j), \quad (4)$$

where $h'(\omega,\tau)$, $h''(\omega,\tau)$ are the real and imaginary parts of the complex-valued function of the kernel $h(\omega,\tau)$, respectively; the set of coefficients $\{a_j\}$, $j = 1, ..., M$ is determined by the chosen quadrature rule (numerical integration) on a certain net of times $\{\tau_j\}$ limited by the minimum $\tau_{\min}$ and maximum $\tau_{\max}$ times.

The resulting expressions represent systems of equations linear with respect to unknown quantities $\gamma\{\tau_j\}, j = 1, ..., M$, i.e., the values of the sought function of distribution of relaxation times $\gamma(\tau)$ on the time net $\{\tau_j\}$ (note that, if necessary, the ohmic resistance $Z(\infty)$ can also be considered as an unknown quantity in these equations). Each of these systems of linear equations (with respect to imaginary and real parts) also turns out to be an ill-posed problem and the attempts to solve it by using, e.g., the least square technique, as a rule fail.

In the matrix form, any of these systems can be written as follows:

$$H\overline{\gamma} = \overline{z}, \quad (5)$$

where H is the matrix with the size $N \times M$ composed of coefficients of equations (such as $a_j h''(\omega_i, \tau_j)$), $\overline{\gamma}$ is the vector of height M which consists of unknown values $\gamma\{\tau_j\}$, $j = 1, ..., M$, $\overline{z}$ is the vector of height N, which consists of the measured impedance values.

The exact solution of Eq. (5) should satisfy the obvious equality

$$\left\|H\overline{\gamma} - \overline{z}\right\|^2 = 0, \quad (6)$$

where $\|\cdot\|^2$ means the square of the norm of vector, i.e., the sum of squares of its elements.

The classical method of Tikhonov consists of changeover of Eq. (6) for the problem of minimization in the following form:

$$\min_{\overline{\gamma}}\left\{\left\|H\overline{\gamma} - \overline{z}\right\|^2 + \lambda\left\|\overline{\gamma}\right\|^2\right\}, \quad (7)$$

where λ is a certain chosen numerical coefficient called the regularization coefficient.

The "physical meaning" of introduction of this coefficient is as follows. The exact solution of Eq. (6), i.e., $\overline{\gamma}$ demonstrates, as a rule, a wide scatter in coordinate values, being a noise-type vector. The term $\lambda\|\overline{\gamma}\|^2$ in Eq. (7) plays the role of the penalty function, because its value increases with the increase in coordinates of vector $\overline{\gamma}$. Thus, minimization of the expression in Eq. (7) is achieved on a certain vector $\overline{\gamma}$ representing the approximate solution of Eq. (6) and, at the same time, having coordinates of a "moderate" order of magnitude. The coefficient of regularization λ ensures balance between the exactness of solution (i.e., the discrepancy value $\|H\overline{\gamma} - \overline{z}\|^2$) and its "stability," i.e., the value $\|\overline{\gamma}\|^2$ (in the regularization theory, the expression $\|\overline{\gamma}\|^2$ in Eq. (7) is usually called the stabilizer). Two extreme values $\lambda = 0$ and $\lambda = \infty$ provide degenerate solutions: in the former case, the problem is reduced to the initial problem determined by Eq. (6), in the latter case, the solution represents a vector containing only zeros.

The question of the choice of the coefficient of regularization and the other aspects of using the Tikhonov method are discussed below. Here, it should be reminded that it is necessary to take into account the non-negativity of solution, i.e., the coordinates of vector $\overline{\gamma}$, which leads us to the problem

$$\min_{\overline{\gamma}:\ \overline{\gamma}\geq 0}\left\{\left\|H\overline{\gamma} - \overline{z}\right\|^2 + \lambda\left\|\overline{\gamma}\right\|^2\right\}, \quad (8)$$

which is solved by the methods of NNLS (non-negative least squares) or LDP (least distance programming), see [29, 31].

2. Certain Aspects of the Use of the Tikhonov Method

Relatively recently, in the literature, attention was shifted to the analysis of potentials and limitations of the DRT method as applied to electrochemical impedance. We believe that there are two key questions concerning the DRT method with which investigators of each particular problem are encountered:

—whether the DRT method is adequate, in principle, for analyzing the given electrochemical system;

—which calculation method should be chosen for finding the DRT function and how it should be tuned.

The first problem may be divided into several problems (see [28]): the uniqueness and accuracy of describing the impedance by the DRT function, the possibility and accuracy of determining the number of *RC* elements based on the form of this function, its behavior for the impedance generated by special elements (Warburg, Gerischer, etc.) or the impedance which cannot be generated by an equivalent circuit of a simple form.

These questions are closely associated with the second problem: how the DRT function should be calculated, i.e., how Eq. (1) should be solved, because the result of calculations depends on the chosen solution method (and, generally, even on the programmed realization of this method) and, which is most important, on its parameters. As was noted above, in the literature, attention is focused on the Tikhonov method. However, the Tikhonov method (like the other regularization methods) is only the solving instrument, which should be tuned by the investigator in each particular case. Below we describe the main problems associated with the use of the Tikhonov method.

2.1. Choice of the Coefficient of Regularization

The majority of studies devoted to regularization methods and their use in solving applied problems consider the problem of choosing the optimal values for the regularization coefficient. Indeed, the choice of λ influences the solution of Eq. (7) or Eq. (8) perhaps more strongly than all the other factors mentioned below. As was noted above, two extreme values $\lambda = 0$ and $\lambda = \infty$ produce degenerate solutions and the question on the choice of λ between these two extremes is that of the balance between the accuracy of solution and its «stability». A decrease in λ strengthens the noise of measurements in solution (and at $\lambda \to 0$, the solution tends to noise-type). An increase in λ suppressed the noise and simultaneously leads to the loss of information in solution (manifested as "blurring" of the function of distribution of relaxation times on the time scale; at $\lambda \to \infty$, the solution tends to function always equal to zero). It is natural that under the optimal coefficient of regularization one understands the value λ_{optim} at which the smallest deviation (e.g., squared discrepancy) is achieved between the theoretical function of distribution of relaxation times and the function obtained as a result of solving Eq. (7) or Eq. (8) with this λ, i.e.,

$$\lambda_{optim} = \underset{0<\lambda<\infty}{\operatorname{argmin}} \left(\sum_i \left(\gamma_{exact}(\tau_i) - \gamma_\lambda(\tau_i) \right)^2 \right), \quad (9)$$

where γ_{exact} is the theoretical distribution of relaxation times, γ_λ is the distribution of relaxation times calculated for the given λ.

Such statement of the question leads to insoluble problem because there is no algorithm of searching for the stable approximate solution of Eq. (7) based only on the data of measurements (to obtain such algorithm, the measuring error should be assessed), see [32].

Hence, from the viewpoint of theory, the attempts of scientists are directed at the quest for "quasioptimal" criteria of determination of the coefficient of regularization. Under quasioptimality, different concepts may be understood, depending on specifics of the practical problem (for instance, in probabilistic statement of the problem, the unbiasedness or efficiency of the quasioptimal assessment of the coefficient of regularization as regards its optimal value). From the viewpoint of practice, the rules of selecting the coefficient of regularization are being offered that simply work "adequately" with the concrete experimental data. Such criteria are called heuristic.

All criteria of selecting the coefficient of regularization can be divided into two groups: the criteria that use certain available information on the observation noise, i.e., its approximate level or some model (for instance, the assumption on normality of noise), and the criteria that use exclusively the available data of measurements.

Probably, in view of specifics of the considered problem of applying the regularization methods to calculating the DRT function in impedance spectroscopy, only the second-group methods were considered. Below we mention certain results obtained by the other authors in this direction.

The first study in this direction was probably [33] in which the criterion of choosing the coefficient of regularization, called the SC (self-consistency) rule was proposed and compared (in numerical experiments) with two other criteria known in the regularization theory: the rule of discrepancy (known also as the Morozov criterion) and the PMSE rule (minimization of the least-square deviation of measured values from those predicted by the model, i.e., by Eq. (1)). All three criteria are general, i.e., ignore the specifics of the problem under consideration, e.g., the fact that Eq. (1) may be interpreted as two equations (with respect to imaginary and real parts of impedance). For solving the integral equations of Fredholm, i.e., Eq. (1), by the Tikhonov regularization method, the author of [8] developed also the FTIKREG program which was used later (or was rewritten with the use of

modern software) by other authors [34] in the field of impedance spectroscopy.

The subsequent studies we know [26, 31] were published relatively recently. In [26], two criteria based on the specifics of the considered problem were proposed. The first criterion, called Re-Im discrepancy test, suggests to compare the functions of distribution of relaxation times calculated as a result of solving two equations such as Eq. (8) with respect to different impedance components

$$\mathrm{ReImDisc}(\lambda) = \left\| \overline{\gamma'_\lambda} - \overline{\gamma''_\lambda} \right\|^2, \qquad (10)$$

where $\overline{\gamma'_\lambda}$, $\overline{\gamma''_\lambda}$ are the solutions of Eq. (8) with respect to the imaginary and real components of impedance, respectively, for the given λ. As the quasioptimal value of coefficient of regularization, the λ value that minimizes ReImDisc(λ) is chosen, i.e., such that the solutions obtained with respect to different impedance components are the closest to one another.

The second criterion, called Re-Im cross-validation test, is based on the cross-validation of the solution quality, i.e., the quality of solution found by the method of regularization of Eq. (8) with respect to the imaginary/real component is checked by the following substitution into Eq. (10) with respect to the real/imaginary component:

$$\mathrm{ReImCV}(\lambda) = \left\| H' \overline{\gamma''_\lambda} - \overline{z'} \right\|^2 + \left\| H'' \overline{\gamma'_\lambda} - \overline{z''} \right\|^2. \qquad (11)$$

Similarly, for the quasioptimal value of the coefficient of regularization, we choose the λ value that minimizes ReImCV(λ), i.e., for which the solutions obtained with respect to different impedance components give the minimum error in the cross-tests.

It cannot be ruled out that the authors of [26] in their description of proposed criteria could omit certain details, because, on our opinion, the terms in the expression of ReImCV(λ) function are usually of the different orders of magnitude; hence, to obtain concrete results, one probably needs to weigh the errors of cross-tests.

The proposed criteria were studied in a series of numerical experiments with synthesized impedances (of the simplest model, i.e., involving elements of one type) and certain experimental data. Based on these results, the authors concluded in favor of the Re-Im cross-validation test criterion.

In [31], among other results, two criteria are proposed and compared for selecting the coefficient of regularization when solving Eq. (8). These criteria are also well-known in the theory of regularization: the *L*-curve criterion and the criterion of residual periodogram. Based on numerical experiments with synthesized impedances (of sufficiently simple model involving two *RQ* elements), the authors concluded in favor of the criterion of residual periodogram.

Thus, on our opinion, so far no thorough analysis was carried out (as in [35]) for choosing the criteria of regularization coefficients for the cases where the Tikhonov method was used for calculating the DRT function.

Moreover, in section Results of this publication, we show an example of synthesized impedance for which no coefficient of regularization can be selected that would provide any adequate result. The optimal value surely exists in the form of Eq. (9); however, this value and any other one give the picture strongly differing from the result we would like to obtain in our analysis. In connection with this, of special interest is the recent study [36] in which it was proposed to use the vector of regularization coefficients (instead of one coefficient) each of which corresponds to its own time. Hypothetically this makes it possible to distinguish the processes with considerably differing characteristics, which could allow us to solve this example.

2.2. Choice of Stabilizer

In Eq. (7), the quantity $\|\overline{\gamma}\|^2$ which is the function of coordinates of vector $\overline{\gamma}$ that penalizes Eq. (7) for the increase in coordinates of vector $\overline{\gamma}$ is called the stabilizer. The stabilizer can also represent more complex functions which place more complex constraints on the possible vectors-solutions $\overline{\gamma}$, particularly:

1. Tikhonov stabilizers of the *p*-th order [19], which have the form

$$\Omega(\gamma) = \int \sum_{n=0}^{p} q_n(\tau) \left(\frac{d^n \gamma}{d\tau^n} \right)^2 d\tau, \qquad (12)$$

i.e., the sum of weighed squared norms of derivatives of the *p*-th order ($n = 0, 1, ..., p$) of function $\gamma(\tau)$, where $q_n(\tau)$ is the preset non-negative weighting functions (constants, in the simplest case). In numerical calculations, such stabilizer is changed for its finite-difference analogue.

The Tikhonov stabilizer of the *p*-th order penalizes not only for the increase in the absolute values of solution $\gamma(\tau)$ (or vector $\overline{\gamma}$), but also for the increase in the values of *p*-th order ($n = 0, 1, ..., p$) derivatives of this function (or finite-difference analogue of the derivative of vector $\overline{\gamma}$ for the numerical solution), which thus imposes constraints on the smoothness of function (measured as the norms of its derivatives).

2. LASSO stabilizer (or L_1 norm) in the form of $\Omega(\overline{\gamma}) = \|\overline{\gamma}\|_1$, where $\| - \|_1$ is the sum of absolute magnitudes of vector coordinates. Such stabilizer penalizes for non-zero values of vector coordinates.

Among Tikhonov stabilizers as applied to the problem of DRT calculation, it is the finite-difference ana-

logues of first- and second-order derivatives [31] or simply the classical stabilizer $\|\overline{\gamma}\|^2$ that are used most often. The only comparison of these stabilizers we could find in the literature was carried out in [31]. This comparison was based on numerical experiments which analyzed the synthetic impedances of a single model representing a combination of *RQ* elements with various parameters. It deserves mention that the distribution function of relaxation times of *RQ* elements is smooth and differentiable, which may justify the use of stabilizers of the 1st and 2nd order. However, its limiting value, i.e., the Dirac delta function that corresponds to the *RC* element is not such. In connection with this, the question of applicability of high-order stabilizers to the analysis of impedances involving responses of elements close to those of ideal *RC* elements is still open.

Among the other results, the comparison of the Tikhonov stabilizer of the 1st order and LASSO regression was carried out in [26] for some examples of different nature. Its authors formulated no conclusion in favor of one or another stabilizer because it is evident that the higher-quality solution can be obtained with a stabilizer that emphasizes the properties of solution (which, however, is unknown a priory): for smooth time-distributed DRT functions, the 1st- or 2nd-order stabilizers are preferable for distributions close to discrete, namely, the classical Tikhonov stabilizer or LASSO.

2.3. The Choice of the Analyzed Impedance Part (Imaginary, Real)

The separate consideration of the imaginary and real impedance parts in Eq. (1) gives two Fredholm equations of the 1st order with different kernels, which represent the imaginary and real components of the original kernel, respectively. It is well-known that the imaginary and real impedance components of the linear time-invariant system satisfy the Kramers–Kronig relationships and, the more so, it is shown [37] that the impedance described by Eq. (1) also satisfies these relationships. In other words, two Fredholm equations corresponding to different impedance components are theoretically equivalent to one another.

In practice, it should be taken into account that the measurement noises for imaginary and real components are, generally speaking, different (as regards both the level and, probably, the nature). Hence, the joint consideration of two Fredholm equations (or the system of equations such as system (5)) may improve hypothetically the solution quality. This was noted, in particular, in [31, 38], although this conclusion was made based only on comparing the condition numbers of matrices of coefficients (i.e., a certain cumulative index of correctness of the equation) for the corresponding systems of equations rather than solutions themselves found from the different equations.

The survey of publications shows that, in practice, the majority of scientists use the equation with respect to the imaginary impedance component, which probably is explained by the richer visual information it provides as compared with the frequency dependence of the real component.

2.4. Choice of the Time Net

When Eq. (1) is solved by numerical methods based on the Tikhonov regularization (this is also true for deconvolution methods [10]), the sought DRT function $\gamma(\tau)$ is represented in the form of a set (vector) of its values $\gamma\{\tau_j\}, j = 1, ..., M$ in points of a finite time net of moments $\{\tau_j\}$ restricted by the minimum τ_{min} and maximum τ_{max} times. In view of the inverse dependence between the frequency and time, it seems natural to choose the time net inversely proportional to the frequency net in which the impedance is measured, i.e., $\tau_j = 2\pi/\omega_j$. The authors of [31] provided a certain evidence in favor of this choice (based on comparing the condition numbers of matrices of coefficients of systems of equations such as (5) for various time nets).

Thus, equations such as Eq. (5) which are considered separately for imaginary and real impedance parts consist of N linear equations with respect to N unknown quantities such as $\gamma\{\tau_j\}, j = 1, ..., N$, where N is the size of the frequency net on which the impedance is measured. The joint consideration of two systems gives the system of equations with respect to the same N unknowns. As noted in [31, 38], this makes it possible to double the time resolution by increasing the number of unknowns also to $2N$ (in this case, the time net becomes denser than the frequency net). However, whether this increase in time resolution results in the higher-quality solutions is not evident for us (at least, the same comparison of the condition numbers of matrices of coefficients of the corresponding systems of equations was not in favor of this choice, see [31, 38]).

2.5. Choice of the Method of Numeric Integration

The substitution of a finite sum for the integral in Eq. (1) brings up the problem of choosing formulas for numerical integration. Note that integration in the initial Eq. (1) is carried out with respect to the "linear-scale" time variable, whereas the time net $\{\tau_j\}$ on which the DRT function values $\gamma\{\tau_j\}$ are determined is equidistant on the logarithmic scale (and the latter scale cannot be changed, because otherwise the number of unknowns $\gamma\{\tau_j\}$ will exceed by several orders the number of equations in system (5) determined by the size of the frequency net of impedance measurements). Probably, this was the reason for the follow-

ing substitution for the integration variable proposed in [29]:

$$\int_0^\infty \frac{\gamma(\tau)}{1+j\omega\tau}d\tau = \int_{-\infty}^{\infty} \frac{e^s\gamma\left(e^s\right)}{1+j\omega e^s}ds = \int_{-\infty}^{\infty} \frac{G(s)}{1+j\omega e^s}ds, \quad (13)$$

where $s = \ln\tau$ is the new integration variable, $G(s) = \tau\gamma(\tau) = e^s\gamma(e^s)$ is the modified distribution function of relaxation times dependent on the "linear-scale" variable s.

This substitution of variable became de facto a standard transformation; thus, in the majority of publications, the function $G(s)$ is written in place of function $\gamma(\tau)$. It was mentioned [31] that function $G(s)$ is more informative visually as compared with function $\gamma(\tau)$. It was also demonstrated on several examples that the change of variables had a positive effect on the condition number of the matrix formed by coefficients of the corresponding system of equations such as system (5) and even when the simple trapezium rule was used, the error of numerical integration with respect to the new variable s was smaller by several orders of magnitude than the error of numerical integration with respect to τ.

Yet another sort of errors associated with integration which arise upon the transition from Eq. (1) to Eq. (5) lies in constriction of integration limits: the lower limit equal to 0 is changed for τ_{min}, and the upper limit equal to ∞ is changed for τ_{max}. Mathematical analysis of this type of errors can be found in [31, 38].

We would like to complete our discussion on realization of numerical integration by mentioning the study [30] in which an interesting approach was proposed based on expanding the sought function $G(s)$ in terms of a certain basis of radial (smooth bell-shaped) functions:

$$G(s) = \sum_{j=1}^{M} g_j\varphi_j(s), \quad (14)$$

where $\{g_i\}$ are the expansion coefficients of $G(s)$ in terms of the chosen basis of radial functions $\{\varphi_j(s)\}$.

Substituting Eq. (14) to the initial Eq. (1) with account for Eq. (13) leads to the equation with respect to unknown expansion coefficients $\{g_i\}$, which also can be solved by a regularization method. Further, the sought function $G(s)$ is recovered by substituting the found coefficients into Eq. (14). It was noted [30] that for calculating DRT functions smooth and distributed along the time scale, preference may be given to this approach. The results of numerical experiments with the synthetic impedance corresponding to the *RQ*-element model, exemplified in [30], demonstrated that DTR functions obtained based on expansion (14) even with the smaller number of points per decade (*ppd*, see below) described the theoretical dependence better as regards the weighted squared discrepancy. Unfortunately, this effect was totally leveled by the addition of artificial observation noise to the synthesized data.

On the whole, it can be assumed that after the aforementioned changeover of variables, the error of numerical integration can be neglected, because even when the simplest rule of rectangles is used, this error is negligibly small as compared with the errors in experimental data, i.e., measurements, see [8].

2.6. The Effect of the Frequency Net Density (Number of Points per Frequency Decade)

Intuition suggests that the smaller the frequency step between $Z(\omega)$ measurements, i.e., the denser the frequency net, the better DRT function one can expect to obtain in calculations. To decrease the time consumed in carrying out the experimental study, the reverse problem may be of interest: what minimum number of points per frequency decade (*ppd*) can provide a reasonable result (particularly, for distinguishing the relaxation times of two closest processes). On the other hand, because of our limited possibilities in changing the *ppd*, the question of the point resolution in the DRT method (the minimum distinguishable difference in relaxation times) at the given *ppd* seems to be more correct. Such study was carried out in [18] for synthesized impedances corresponding to two *RQ* elements connected in series, or two Warburg elements, or two Gerischer elements, respectively. On our opinion, it is difficult to make practical recommendations based on this study (except for the obvious conclusion that the increase in *ppd* increases the resolution of this method), because, for example, several numerical experiments as regards the resolution were carried out at the fixed regularization coefficient $\lambda = 1$ and in the absence of observation noise. We believe that this question requires further studying.

2.7. Numerical Experiments

Aimed at understanding deeper the interaction between different aspects of using the Tikhonov method described above (the criteria of choice of regularization coefficient, stabilizer, analyzed impedance part, frequency net density, and the model itself for the processes observed) it is of interest to carry out numerical experiments with the synthesized impedances corresponding to various models. We believe that when carrying out detailed studies, the following questions deserve attention.

1. Model of observation noise (error of measurements). To bring the conditions of numerical experiment closer to real ones, the artificial noise is added to the synthesized impedance. The mathematical model of noise (its description as a random process or a combination of random values) and its level (expressed most often as a dispersion) apparently have the crucial effect on the results obtained. Surveying the literature

showed that the majority of authors use one of the following noise models

(i) $\tilde{Z}(\omega) = \bar{Z}(\omega) + (\eta' + j\eta'')$, see [31],

(ii) $\tilde{Z}(\omega) = Z(\omega) + |Z(\omega)|(\eta' + j\eta'')$, see [26],

(iii) $\tilde{Z}(\omega) = Z(\omega) + (Z'(\omega)\eta' + jZ''(\omega)\eta'')$, see [38],

where η', η'' are independent values (for each ω) distributed according to the normal law (with zero mathematical expectation and the dispersion determining the noise level).

To our regret, in the literature devoted to the use of DRT method in impedance spectroscopy, we encountered no mention of any studies based on one or another noise model.

2. Assessing the solution quality. For the chosen model of synthesized impedance, it is natural to carry out a comparison of different conditions associated with the use of the Tikhonov method (the criterion of choice of the regularization coefficient, stabilizer, etc.) by comparing the corresponding calculated distributions of relaxation times (i.e., functions $\gamma(\tau)$ or $G(s)$ or their values on the chosen time net) with the known theoretical distribution corresponding to the given model. Conventionally, this comparison is carried out by using the squared discrepancy of the following form:

$$\sum_i (\gamma_{\text{exact}}(\tau_i) - \gamma_{\text{test}}(\tau_i))^2, \qquad (15)$$

where γ_{exact} is the theoretical distribution of relaxation times, γ_{test} is the distribution of relaxation times calculated for the definite parameters of using the regularization method. However, it should be borne in mind that, first, the calculation error of the DRT function may depend on time (i.e., the terms corresponding to different times may introduce contributions of different level to the squared discrepancy) and, second, this form of comparison function matches better the smooth DRT functions distributed over the time interval and is less suitable for DRT functions with distributions close to discrete.

It should also be taken into account that in the presence of observation noise, the result of a single numerical experiment becomes a random event; hence, the reliable comparison of different conditions of application of regularization methods requires the use of the Monte Carlo method, i.e., performance of a series of numerical experiments (with different realization of the random noise of observation) followed by statistical analysis of results. The same recommendation can be applied to the analysis of experimental data, provided the impedance measurements can be repeated.

RESULTS

In this section, we show the results of certain numerical experiments. To begin with, we demonstrate the resolution power of the DRT method. This material is meant for scientists who is unfamiliar with this method, being aimed at demonstrating its advantages over the NLSA method.

In the second part of this section, we discuss the evaluation of the distribution function of relaxation times for the *RQ*-model impedance. Numerical experiments have shown that the optimal value of the regularization coefficient for calculating the DRT function by the Tikhonov method depends on the parameters *R*, *Q*. This means that for the impedance corresponding the model of two or more *RQ* elements with substantially different parameters, no acceptable regularization coefficient can be chosen.

With the use of MATLAB software, the algorithm of solving Eq. (8) was realized. As the stabilizer, the classical Tikhonov stabilizer (zeroth order) was chosen. As the analyzed impedance part, one of its components was considered, either imaginary or real (the chosen component is specified below in each case, if necessary). The calculations were carried out on the time net inverse with respect to the frequency net. The numerical integration in Eq. (1) was carried out by the simple method of rectangles with preliminary substitution of variable $\tau \to s = \ln\tau$; thus, below in figures, the function $G(s)$ appears. The number of points per decade *ppd* varies depending on the experiment. In numerical experiments concerning the resolution power of the DRT method, the observation noise corresponding to the (ii) model was added to the synthesized impedances (see above).

1. Resolution Power of the DRT Method

To demonstrate the resolution power of the DRT method realized here, we synthesized five impedance spectra for a circuit containing five *RC* elements connected in series: $(R_1C_1)(R_2C_2)(R_3C_3)(R_4C_4)(R_5C_5)$ in the Boukamp notation. The resistances in this circuit were the same in all five cases: $R_1 = 0.4\ \Omega$, $R_2 = 1.1\ \Omega$, $R_3 = 0.7\ \Omega$, $R_4 = 0.8\ \Omega$, $R_5 = 0.5\ \Omega$**.** The capacitances were preset in such a way that the characteristic frequencies (relaxation frequencies) were in the frequency intervals of different width: from five orders (case 1) to one order (case 5), see Table 1.

Figure 1 shows the synthesized spectra with five well distinguishable arcs for cases 1 and 2, whereas in cases 3–5 the spectra are vague due to closeness of characteristics frequencies. The analysis of spectra by the NLSA method with the use of the "EquivCrt" software has shown that for spectra *1–3*, all five relaxation processes and their parameters (resistances and relaxation times) can be easily identified. Spectra *4* and *5* resist the analysis without knowledge of the true equivalent circuit. Figure 2 shows the results of pro-

Table 1. Preset values of characteristic frequency for five synthesized circuits of the $(R_1C_1)(R_2C_2)(R_3C_3)(R_4C_4)(R_5C_5)$ form

Spectrum no.	Interval of characteristic frequencies, Hz	Characteristic frequencies, Hz
1	10^0–10^5	$10^5/6.1\times10^3/354/22/1$
2	10^1–10^5	$10^5/1.06\times10^4/1.05\times10^3/118/10$
3	10^2–10^5	$10^5/1.79\times10^4/3.3\times10^3/632/100$
4	10^3–10^5	$10^5/3.06\times10^4/10^4/3.4\times10^3/10^3$
5	10^4–10^5	$10^5/5.36\times10^4/3.01\times10^4/1.76\times10^4/10^4$

cessing the synthesized spectra by the DRT method. It can be seen that its use allows correct results to be obtained for cases 1–4 but not for case 5 in which all characteristic relaxation frequencies lie in the range from 10^4 to 10^5 Hz. As the evidence of the high "sensitivity" of the DRT method for case 4 which cannot be analyzed correctly by the NLSA method, Table 2 shows the preset and calculated parameters of the corresponding circuit. The maximum error exceeded 3.6% as regards determination of characteristic relaxation times and 2.4% as regards the resistance values. Thus, it can be suggested that in the absence of information on the number of relaxation processes, the DRT method has the higher resolution power as compared with the NLSA method.

To demonstrate how the *ppd* affects the results of calculations of the DRT function, we considered the example from [39]. Figure 3 shows the results of our calculations for the equivalent circuit $(R_1Q_1)(R_2Q_2)$, where $R_1 = R_2 = 0.1\ \Omega$, $Q_1 = 1s^{0.8}$ S, $Q_1 = 5s^{0.8}$ S. Whereas the authors of [39] failed to reveal two relaxation processes by processing the spectrum with ten points per decade of frequency, our realization of this method clearly revealed both relaxation processes for *ppd* 10 and higher (this may be associated with peculiarities of software realization).

Now we consider the effect of observation noise in impedance spectra on the results of their analysis by the DRT method by the example of spectrum *3* (see Fig. 1) in which the characteristic frequencies of five relaxation processes lie in the frequency range from 10^2 to 10^5 Hz. Figure 4 shows the form of synthesized impedance spectrum and also of spectra with 2% and 5% of added noise. Note that both the initial spectrum and the spectrum noised by 2% could be analyzed by the NLSA method. However, for the spec-

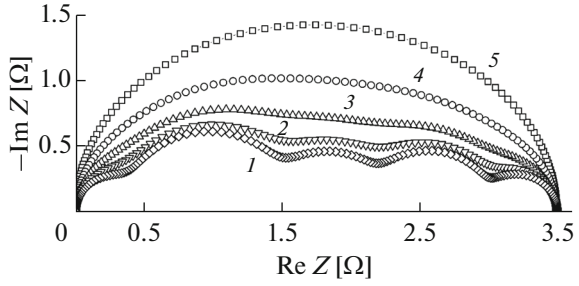

Fig. 1. Impedance spectra of five synthesized circuits $(R_1C_1)(R_2C_2)(R_3C_3)(R_4C_4)(R_5C_5)$ with characteristic relaxation times lying in the intervals from five (spectrum *1*) to one (spectrum *5*) orders of magnitude.

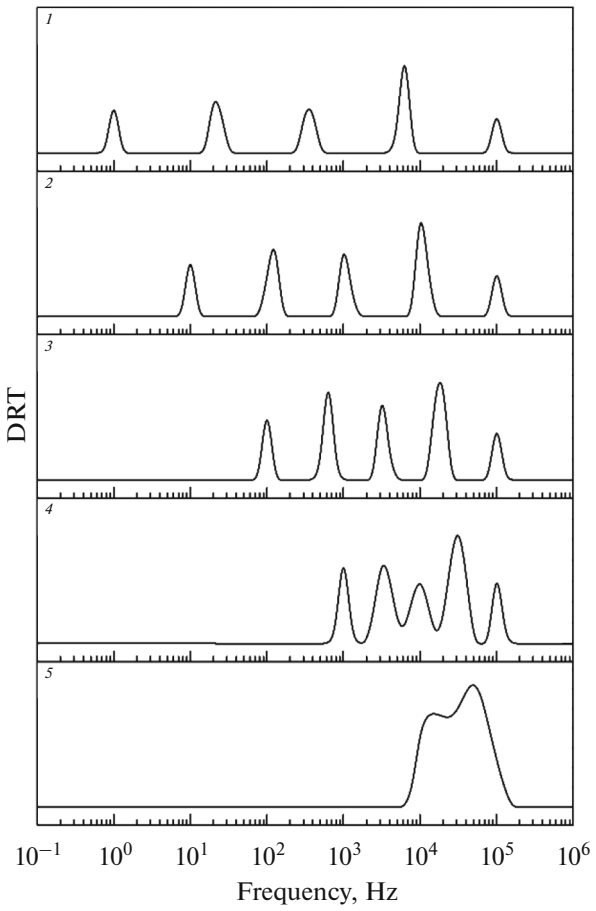

Fig. 2. Distribution of relaxation frequencies of five synthesized circuits $(R_1C_1)(R_2C_2)(R_3C_3)(R_4C_4)(R_5C_5)$ with relaxation times lying in intervals with the length from five (spectrum *1*) to one (spectrum *5*) orders of magnitude.

Table 2. Preset values of characteristic relaxation frequencies and resistances in synthesized circuit $(R_1C_1)(R_2C_2)(R_3C_3)(R_4C_4)(R_5C_5)$ for case 4 and their values determined by the DRT

Preset relaxation frequency, Hz	Calculated relaxation frequency, Hz	Preset resistance, Ω	Calculated resistance, Ω
100000	100051	0.4	0.38
30628	30215	1.1	1.12
10035	10005	0.7	0.69
3417	3313	0.8	0.80
1000	1001	0.5	0.49

trum noised by 5%, no reasonable result could be obtained without the a priori knowledge of the correct equivalent circuit.

Figure 5 shows that in all three cases, the DRT method in our realization reveals all five relaxation processes; and, moreover, all characteristic frequencies of three processed spectra are sufficiently close to one another. Thus, we can assume that the DRT method is more stable to the presence of observation noise in impedance spectra as compared with the NLSA method.

2. Specific Features of Evaluation of the DTR Function for RQ Elements

Now we consider the synthesized impedance corresponding to a simple model of a single *RQ* element described by the equation

$$Z(\omega) = R_\infty + \frac{R}{1 + (i\omega\tau_0)^n}, \quad (16)$$

where R_∞ is the ohmic resistance, n is the power index in the frequency dependence of the constant phase element (CPE), τ_0 is the relaxation time of the circuit involving CPE and resistance R connected in parallel.

Let the spectrum be synthesized on the logarithmically equidistant frequency net in the range from 10^{-3} to 10^6 Hz with equal steps of 20 points per frequency decade. No noise was added to the synthesized spectrum. The theoretical DRT function (taking into account the change of integration variable $\tau \to s = \ln\tau$) corresponding to this spectrum is described by the following equation [11, 17]:

$$G(s) = \frac{R}{2\pi} \frac{\sin((1-n)\pi)}{\cosh(n(s-\ln\tau_0)) - \cos((1-n)\pi)}. \quad (17)$$

In evaluating the DRT function by a regularization method, the following effect is observed. At the high values of regularization coefficient λ, the resulting DRT function is too smoothed, as λ decreases gradually the DRT curve approaches its theoretical form, the further decrease in λ gives rise to false peaks (even in the absence of observation noise). The nature of these false peaks is explained below. Thus, there is a certain optimal value of regularization coefficient λ_{optim}

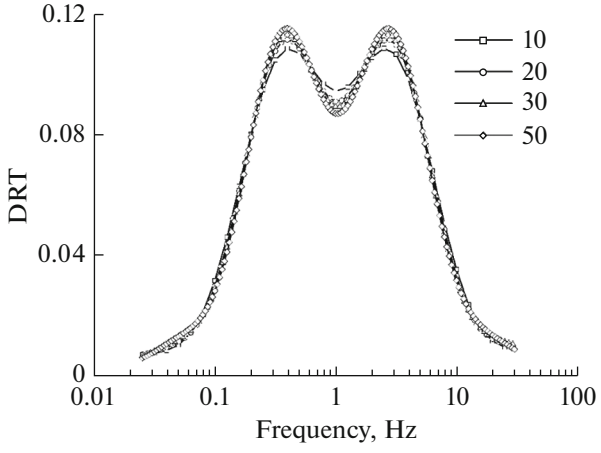

Fig. 3. Results of calculating the distribution of relaxation times for equivalent circuit $(R_1Q_1)(R_2Q_2)$, where $R_1 = R_2 = 0.1$ Ω, $Q_1 = 1s^{0.8}$ S, $Q_1 = 5s^{0.8}$ S as a function of the number of points per frequency decade.

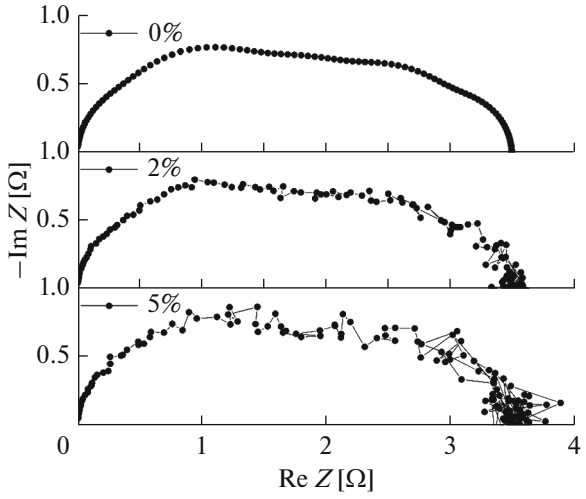

Fig. 4. Synthesized impedance spectrum corresponding to spectrum *3* in Fig. 1 in the absence of noise and upon superposition of 2 and 5% noise.

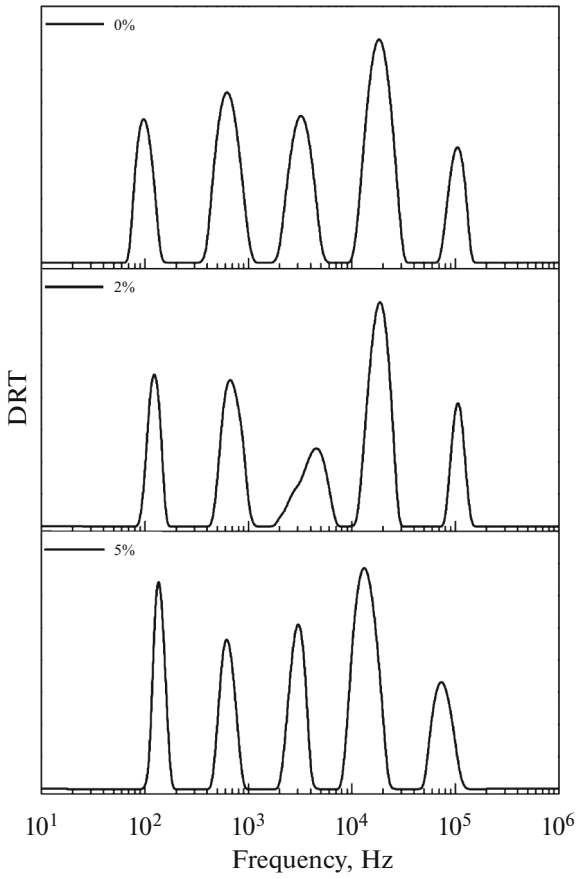

Fig. 5. Distribution of relaxation times of impedance spectra shown in Fig. 4.

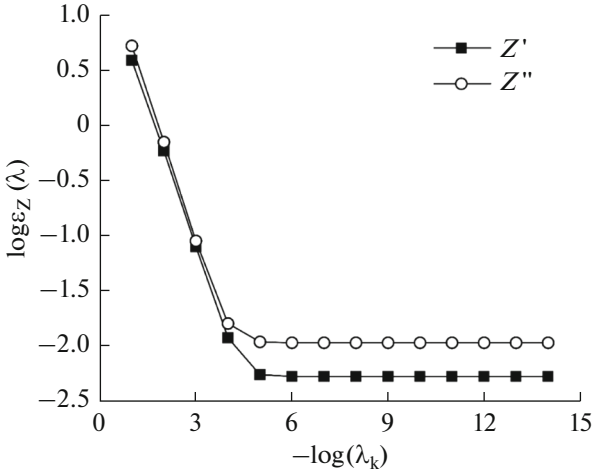

Fig. 6. Time dependences of $\varepsilon_{Im}(\lambda)$ and $\varepsilon_{Re}(\lambda)$ for $n = 0.7$ and $\tau_0 = 10^{-2}$ s.

for which the calculated DRT function is the closest to the theoretical dependence.

The problem is that the optimal value of the regularization coefficient depends substantially on the *RQ* element parameters themselves, i.e., n and τ_0. The aim of this section is to demonstrate this dependence. Thus, for the impedance corresponding to a combination of two or more *RQ* elements with different parameters (and, correspondingly, with different optimal values $\lambda_{optim,1}$, $\lambda_{optim,2}$, ...), there may exist no optimal value of regularization coefficient providing the satisfactory result.

Insofar as the theoretical DRT function corresponding to the model of the *RQ* element is a smooth function (in the studied range of frequencies), the squared discrepancy can be taken as the criterion of the quality of calculations of the DRT function:

$$\Delta(\lambda) = \sum_i \left(G(s_i) - G_\lambda(s_i)\right)^2, \qquad (18)$$

where $G(\tau_i)$ is the theoretical DRT function determined by Eq. (17) and calculated in point $s_i = \ln\tau_i$ of the time net, $G_\lambda(s_i)$ is the value of DRT function in the same point s_i calculated by solving Eq. (8) by the Tikhonov regularization method with regularization coefficient λ. In this calculation experiment, we study the DRT functions denoted as $G'_\lambda(s)$ and $G''_\lambda(s)$, calculated independently for real and imaginary impedance components, respectively.

As the optimal value of the regularization coefficient λ_{optim}, we take the λ value for which function $\Delta(\lambda)$ reaches the minimum. To find the dependence of the optimal regularization coefficient λ_{optim} on parameters of the *RQ* element, we synthesize the spectrum determined by Eq. (17) for each pair of parameters

$$n \in \{0.5, 0.6, 0.7, 0.8, 0.9\}$$
$$\text{and} \quad \tau_0 \in \left\{10, 1, 10^{-1}, 10^{-2}, 10^{-3}, 10^{-4}\right\}.$$

Next, for each synthesized spectrum, we determine the DRT functions $G'_\lambda(s)$ and $G''_\lambda(s)$ for different values of regularization coefficient $\lambda_k = 10^{-k}$, $k = 1, 2, 3, ..., 14$, and also the corresponding values of discrepancy $\Delta(\lambda_k)$.

We begin the discussion of results of numerical experiments with considering the squared discrepancy of impedance description, i.e., the error of impedance $Z_\lambda(\omega)$ description based on Eq. (1) performed after substitution of the found DRT function $G_\lambda(s)$ with respect to the exact synthesized impedance $Z(\omega)$:

$$\varepsilon_Z(\lambda) = \sum_i \left(Z(\omega_i) - Z_\lambda(\omega_i)\right)^2. \qquad (19)$$

In the studied variation range of the regularization coefficient, the quantity $\varepsilon_Z(\lambda)$ first decreases rapidly with the decrease in λ and then stabilizes (see Fig. 6). Moreover, the quality of the DRT function $G_\lambda(s)$ as regards its closeness to the theoretical DRT function varies nonmonotonously (see Fig. 7 illustrating this effect). Thus, for the given impedance corresponding

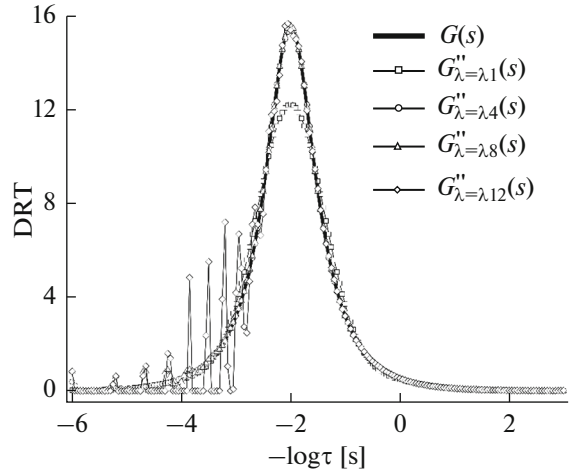

Fig. 7. Time dependences of $G'_\lambda(s)$ for $n = 0.7$ and $\tau_0 = 10^{-2}$ s and different λ_k.

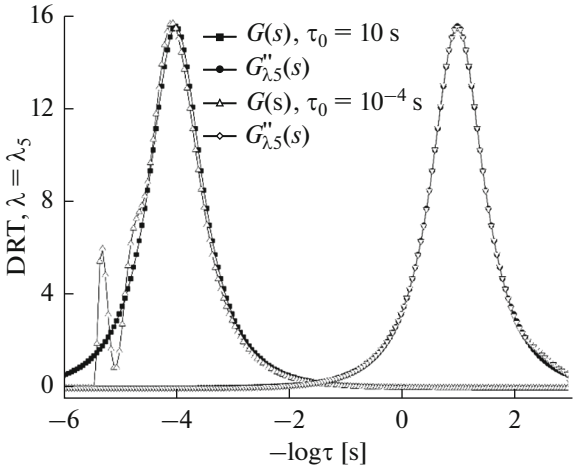

Fig. 8. Time dependences of $G''_{\lambda_k}(s)$ for $n = 0.7$, $\lambda_k = \lambda_5$, and different τ_0.

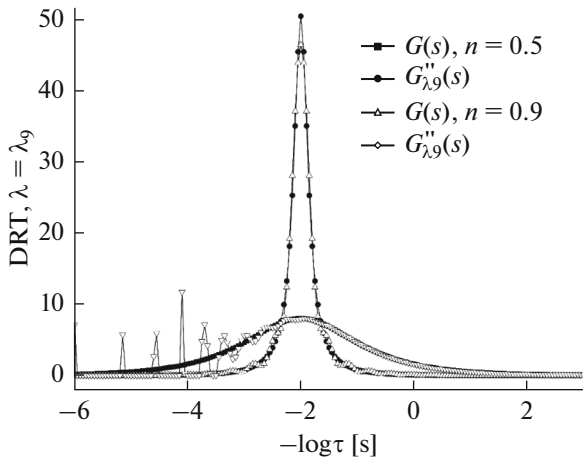

Fig. 9. Time dependences of $G''_{\lambda_k}(s)$ for $\tau_0 = 10^{-2}$ s, $\lambda_k = \lambda_9$, and different n.

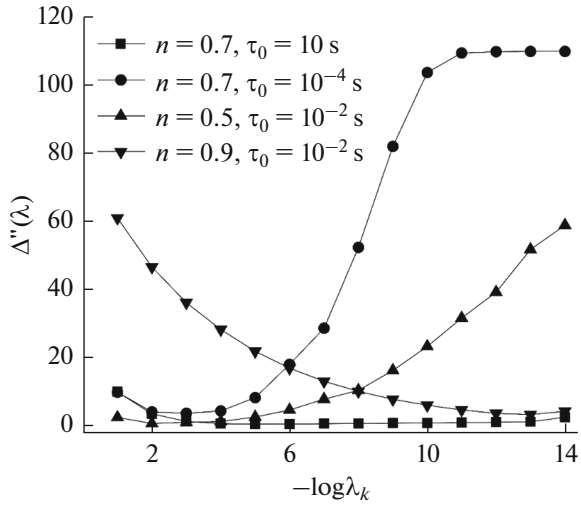

Fig. 10. Dependences of $\Delta(\lambda_k)$ on λ_k at different n and τ_0 for $G''_{\lambda_k}(s)$.

to the model of a single *RQ* element, these is the optimal value for which the calculated *RQ* function best describes the theoretical dependence.

Figure 8 shows that by fixing one parameter of the *RQ* element model, i.e., n (or τ_0), and varying the second parameter, we obtain the impedances which should be analyzed with different optimal values of regularization coefficients. For instance, for $n = 0.7$ and $\tau_0 = 10$, the optimal (or close to optimal) value is regularization coefficient λ_s. However, as follows Fig. 8, for $n = 0.7$ and $\tau_0 = 10^{-4}$, the value of regularization coefficient is lower than the optimal value, because false peaks appear in the left-hand part of DTR function. Figure 9 illustrates the analogous effect for fixed $\tau_0 = 10^{-2}$ and varied n.

The curves of the discrepancy $\Delta(\lambda_k)$ between the calculated and theoretical DRT function at different *RQ* element parameters n and τ_0 (see Fig. 10) demonstrate that the optimal values of regularization coefficient λ may substantially depend on both parameters.

Table 3 shows the results of determination of the optimal values of regularization coefficient as a function of *RQ* element parameters n and τ_0 (in the studied spectrum of values).

3. Interpretation of Results of Calculation Experiment

First of all, we explain the existence of the optimal value of regularization coefficient for calculating the

Table 3. Optimal coefficients of regularization as a function of n and τ_0

$k = -\log\lambda_k$	$n = 0.5$	$n = 0.6$	$n = 0.7$	$n = 0.8$	$n = 0.9$
$\tau_0 = 10$ s	4	3	5	10	13
$\tau_0 = 1$ s	4	4	6	11	13
$\tau_0 = 10^{-1}$ s	3	4	6	10	13
$\tau_0 = 10^{-2}$ s	2	3	5	8	13
$\tau_0 = 10^{-3}$ s	2	2	4	6	10
$\tau_0 = 10^{-4}$ s	1	2	3	5	8

DRT function based on the impedance spectrum corresponding to the *RQ* element model.

On the one hand, for the high value of the regularization coefficient, the DRT function is too smoothed as compared with theoretical one, which follows from the regularization principle itself. On the other hand, as the regularization coefficient decreases, the effect of noise increases. Moreover, despite the fact that no observation noise was added to the synthesized spectrum, it should be borne in mind that Eq. (8) to be solved has been obtained:

(1) as a result of discretization of integral Eq. (1) which entails the presence of errors of numerical integration and constricts the integration limits,

(2) as a result of impedance measurements in a finite set of frequencies, which often gives rise to discretization errors, because, strictly speaking, the behavior of function $Z(\omega)$ beyond the measured points is not known.

Thus, in the problem the observation noise is always present in the implicit form, inducing the appearance of false peaks. The false peaks begin to appear in the region of short times (in the left part of the DRT function) because the latter region corresponds to the high frequencies for which the step between $Z(\omega)$ measurements increases exponentially bringing about the discretization error. This explains the U-shaped curve of discrepancy $\Delta(\lambda_k)$ and the existence of the optimal regularization coefficient.

The effect of the aforementioned noises of observation depends on the form of impedance spectrum, i.e., on the parameters n and τ_0, which entails the dependence of the optimal regularization coefficient λ_{optim} on these parameters.

CONCLUSIONS

In numerical experiments, the DRT method demonstrates extremely high resolution power and resistance to noises. However, it should be borne in mind that when dealing with real experimental data, the choice of the regularization coefficient is an acute problem. Its unsuitable value may lead to incorrect results. Thus, the further investigation of the DRT method as such is required, particularly, the analysis of heuristic criteria for the choice of regularization coefficients. Attention is attracted to the development of the Tikhonov method, e.g., as in [36] or by taking account of additional a priori limitations to the form of DRT function (see [40]).

In addition to its undeniable advantages (the high resolution power, stability to noise, no need of choosing the equivalent circuit), the DRT method has substantial limitations, particularly, the aforementioned necessity of choosing different values of regularization coefficient in cases where the studied object is described by several CPE. It was shown [41] that, the DRT method can nonetheless be successfully used but not as an independent method but as an additional tool for preliminary identification of the number of relaxation processes and the values of partial polarization resistances. For this purpose, the measured impedance spectrum is transformed into the DRT frequency dependence which serves as the basis for selecting the initial values of parameters of fitting to a particular equivalent circuit by the NLSA method. The results of fitting in the form of calculated impedance spectrum are transformed again to the frequency dependence of DRT. Comparing two DRT dependences makes it possible to conclude on the adequacy of the model in the form of an equivalent circuit. We believe that this approach is of interest and requires further studying.

ACKNOWLENDGMENTS

We are grateful to B.L. Kuzin for initiating this study and also to A.L. Ageev for valuable remarks. The study was carried out with the partial support by the Russian Foundation for Basic Research (grant 16-03-00434) and the Program 211 of the Government of the Russian Federation (contract no. 02.A03.21.0006).

REFERENCES

1. Grafov, B.M. and Ukshe, E.A., *Elektrokhimicheskie tsepi peremennogo toka* (Electrochemical Alternating-Current Circuits), Moscow: Nauka, 1973.
2. Ukshe, E.A. and Bukun, N.G., *Tverdye elektrolity* (Solid Electrolytes), Moscow: Nauka, 1977.
3. Boukamp, B.A., *Solid State Ionics,* 2004, vol. 169, p. 65.
4. Schichlein, H., Muller, A.C., Voigts, M., Krugel, A., and Ivers-Tiffee, E., *J. Appl. Electrochem.,* 2002, vol. 32, p. 875.
5. Macdonald, J.R. and Brachman, M.K., *Rev. Mod. Phys.,* 1956, vol. 28, p. 393.
6. Colonomos, P. and Gordon, R.G., *J. Chem. Phys.,* 1979, vol. 71, p. 1159.
7. Franklin, A.D. and de Bruin, H.J., *Phys. Status Solidi A,* 1983, vol. 75, pp. 647–656.
8. Weese, J., *Comput. Phys. Commun.,* 1992, vol. 69, p. 99.

9. Liedermann, K., *J. Non-Cryst. Solids,* 1994, vol. 175, p. 21.
10. Smirnova, A.L., Ellwood, K.R., and Crosbie, G.M., *J. Electrochem. Soc.,* 2001, vol. 148, p. A610.
11. Dion, F. and Lasia, A., *J. Electroanal. Chem.,* 1999, vol. 475, pp. 28–37.
12. Prilezhaeva, I.N., Solov'ev, N.P., and Khramushin, N.I., *Russ. J. Electrochem.,* 2004, vol. 40, p. 1223.
13. Ramos, T., Thyden, K., and Mogensen, M., *ECS Trans.,* 2010, vol. 28, p. 123.
14. Kazlauskas, S., Kežionis, A., Šalkus, T., and Orliukas, A.F., *Solid State Ionics,* 2013, vol. 231, p. 37.
15. Fuoss, R.M. and Kirkwood, J.G., *J. Am. Chem. Soc.,* 1941, vol. 63, p. 385.
16. Macdonald, J.R. and Brachman, M.K., *Rev. Mod. Phys.,* 1956, vol. 28, p. 393.
17. *Impedance Spectroscopy. Theory, Experiment, and Applications,* Barsoukov, E. and Macdonald, J.R., Eds., Hoboken, New Jersey: John Wiley and Sons, Inc., 2005, 2nd Ed.
18. Zhang, Y., Chen, Y., Yan, M., and Chen, F., *J. Power Sources,* 2015, vol. 283, p. 464.
19. Tikhonov, A.N. and Arsenin, V.Ya., *Metody resheniya nekorrektnykh zadach,* (Methods of Solving Ill-Posed Problems), Moscow: Nauka, 1979, 2nd. Ed.
20. Hörlin, T., *Solid State Ionics,* 1993, vol. 67, p. 85.
21. Hörlin, T., *Solid State Ionics,* 1998, vol. 107, p. 241.
22. Noot, T.J.V., *J. Electroanal. Chem.,* 1995, vol. 386, p. 57.
23. Tesler, A., Lewin, D., Baltianski, S., and Tsur, Y., *J. Electroceram.*, 2010, vol. 24, p. 245.
24. Hershkovitz, S., Baltianski, S., and Tsur, Y., *Solid State Ionics,* 2011, vol. 104.
25. Hershkovitz, S., Tomer, S., Baltianski, S., and Tsur, Y., *ECS Trans.,* 2011, vol. 33, p. 67.
26. Saccoccio, M., Wan, T.H., Chen, C., and Ciucci, F., *Electrochim. Acta,* 2014, vol. 147, p. 470.
27. Schmidt, J., Berg, P., Schönleber, M., Weber, A., and Ivers-Tiffée, E., *J. Power Sources,* 2013, vol. 221, p. 70.
28. Boukamp, B.A., *Electrochim. Acta,* 2015, vol. 154, p. 35.
29. Macutkevic, J., Banys, J., and Matulis, A., *Nonlinear Analysis: Modeling and Control*, 2004, vol. 9, p. 75.
30. Wan, T.H., Saccoccio, M., Chen, C., and Ciucci, F., *Electrochim. Acta*, 2015, vol. 184, p. 483.
31. Hansen, J.K., Hogue, J.D., Sander, G.K., Renaut, R.A., and Popat, S.C., *J. Comput. Appl. Math.*, 2015, vol. 278, p. 52.
32. Tikhonov, A.N., *Dokl. Akad. Nauk SSSR*, 1985, vol. 280, p. 559.
33. Honerkamp, J. and Weese, J., *Continuum Mech. Thermodyn.,*1990, vol. 2, p. 17.
34. Leonide, A., *PhD Thesis*, Karlsruher Inst. Technologie, 2010.
35. Bauer, F. and Lukas, M.A., *Math. Comput. Simulation*, 2001, vol. 81, p. 1795.
36. Zhang, Y., Chen, Y., Li, M., Yan, M., Ni, M., and Xia, C., *J. Power Sources,* 2016, vol. 308, p. 1.
37. Brachman, M.K. and Macdonald, J.R., *Physica,* 1954, vol. 20, p. 1266.
38. Renaut, R.A., Baker, R., Horst, M., Johnson, C., and Nasir, D., *Inverse Problems,* 2013, vol. 29, no. 24, p. 045006.
39. Zhang, Y., Chen, Y., Yan, M., and Chen, F., *J. Power Sources,* 2015, vol. 283, p. 464.
40. Vasin, V.V. and Ageev, A.L., *Nekorrektnye zadachi s apriornoi informatsiei* (Ill-posed Problems with a priory Information), Yekaterinburg: UIF Nauka, 1993.
41. Klotz, D., Schmidt, J.P., Kromp, A., Weber, A., and Ivers-Tiffée, E., *ECS Trans.,* 2012, vol. 41, p. 25.

Translated by T. Safonova