Bulgarian Chemical Communications, Volume 44, Number 4 (pp. 383 – 388) 2012

Selected problems of the analysis of impedance and transfer function spectra: a revue paper

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Received February 20, 2012, accepted February 20, 2012

Experimental impedance spectrum (IS), or, more generally, a transfer functions spectrum (TFS) of a system, and especially sets of spectra measured at various values of the system variables provides a wealth of information about the system and the processes taking place there. However, the knowledge of this information in concepts of physical chemistry requires the application of special procedures in the spectra analysis.

In this paper, selected major issues associated with the reliability of TFSs and of their analysis procedures, mainly based on personal experience of the author of this article, are reminded. Mainly, these issues are: problems arising from the fact that actual systems imperfectly meet the requirements for the measurement of TFS (e.g. linearity), the initial visual analysis of TFS, the principles of modelling and the discussion of different types of models (the latter for ISs), and know-how of the fitting of a selected model to the given TFS and criteria of the fit goodness.

Key words: Impedance spectra, Transfer function spectra, Spectra quality, Modeling,Fittings

INTRODUCTION

The transfer functions (TFs), *H*'s, are ratios of a chosen response of a linear system being close to steady state to the perturbing signal (more generally, ratio of generalised force and resulting displacement) or vice versa, or else ratios of two chosen responses of such a system. *H*'s are vector quantities, and they are dependent on the frequency of the signal [1–3]. In a frequency range, H_k is described by its spectrum (TFS), which can be presented as a 3-column matrix where in the first and next columns the successive frequencies and quantities describing the corresponding vector (e.g. in rectangular coordinates, its real and imaginary components) are given, respectively.

H_k is immittance, X_k, in a specific case when: 1/ the signal and response are electric potential, *E*, and current, *I*, and 2/ the system is one-port. Main forms of *X* are impedance, *Z*, and admittance, *Y*, defined as follows, respectively:

$$Z = \delta E / \delta I \tag{1}$$

$$Y = Z^{-1} = \delta I / \delta E \tag{2}$$

where δ denotes small-amplitude function; its presence in these definition is necessary for the general case of nonlinear systems, in order to allow their linearization. For simplicity, below it will be assumed that δ *E* is the signal. In such a case:

$$\delta E = \Delta E \sin(\omega t) \tag{3}$$

$$\delta I = \Delta I \sin(\omega t + \varphi) \tag{4}$$

where Δ, *ω*, *t* and *φ* denote amplitude functions, angular frequency ($\omega = 2\pi f$, *f* being frequency in Hz), time and phase shift (angular delay of the response), respectively. In the above equations, Δ's are real functions.

The last two equations can be presented in a more convenient notation:

$$\delta E = \Delta E \exp(st) \tag{5}$$

$$\delta I = \Delta I \exp(st) \tag{6}$$

where ΔE and ΔI are complex quantities, and *s* denotes imaginary angular frequency ($s = i\omega$, i being the imaginary unit: $i = \sqrt{-1}$). For instance, from Eqs. 1, 5 and 6 it follows that:

$$Z = \frac{\Delta E}{\Delta I} \tag{7}$$

Formally, it is unimportant whether IS is measured under control of *E* or *I*. However, from the physico-chemical point of view it can be of real importance. For instance, for passivating metal electrodes the dependence of *I* on *E* is univocal, but the opposite dependence is multi-valued (in fact, the passive state is not a steady state in the thermodynamic sense). However, the most important argument for using the *E* signals is that, in general, *E* directly controls the chemical potentials of main reactants.

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An experimental immittance spectrum (IS), and especially a set of ISs measured at various values of system variables (e.g. composition of specimen or surroundings, *E*, temperature etc.), can provide a wealth of information on the system under study and the processes taking place there [4, 5]. However, the knowledge of this information in physico-chemical concepts requires the application in spectra analysis of special procedures [6]. The above applies to TFSs, too.

Recently, several monographs on immittance spectroscopy (traditionally called "impedance spectroscopy"), including to some extend also the transfer function spectroscopy, have been published [7–9]. However, the practical problems of applying this method and the know-know of the spectra analysis are treated there a little cursorily.

The aim of the present paper is to remind some important issues related with the reliability of experimental TFSs and procedures of their analysis, mainly basing on the personal experience of the author of the paper. That will be performed for the most part on the example of ISs, as being best recognised.

PROBLEMS RELATED WITH THE LINEARITY AND NUMBER OF PORTS OF AN ACTUAL SYSTEM

As *X* is a quantity characterising a linear system, the ratio of the two Δ functions in Eqs. 3 and 4 cannot depend on Δ of the signal. Otherwise, the measured IS will be distorted by systematic errors [6]. Obviously, for TFS a similar requirement is in force.

In electrodics, typically the 3-electrode measurement cell is used. In such a case, the system under study consists of the working electrode (WE) plus the counter and reference electrodes, and electrolytic solution in between; hence, actually it is not a one-port system. In order to fulfil the respective requirement, the cell must be designed in a way allowing for ascribing the measured *X* only to WE itself. Otherwise, the measured IS will be distorted by systematic errors [6].

INITIAL INSPECTION OF INDIVIDUAL EXPERIMENTAL IMMITTANCE SPECTRA

Prior to beginning the first step of analysis of an experimental IS, i.e. a trial of modelling of the system characterized by this IS, the so-called „wild points", where at individual *f*'s IS is contaminated by exceptionally large noise, should be eliminated. These points can be noticed when IS in question is inspected simultaneously in plots of several different coordinates, e.g. *Z* and *ωZ* (so-called elastance) complex planes (–Im(X_k) vs. Re(X_k)), Bode coordinates (log |*Z*| and *φ* vs. log *f*) etc., because particular coordinates are characterised by differentiated sensitivity or zooming in various frequency ranges. For instance, *Z* and *ωZ* complex planes are especially sensitive in the low (lf) and high frequency (hf) regions, respectively (see Fig. 1). In some coordinates, the wild points will be visible as points breaking the smoothness of the experimental IS curve [4, 6]. By the way, any plot of IS should not be confused with IS itself. For TFS an analogous approach is advisable.

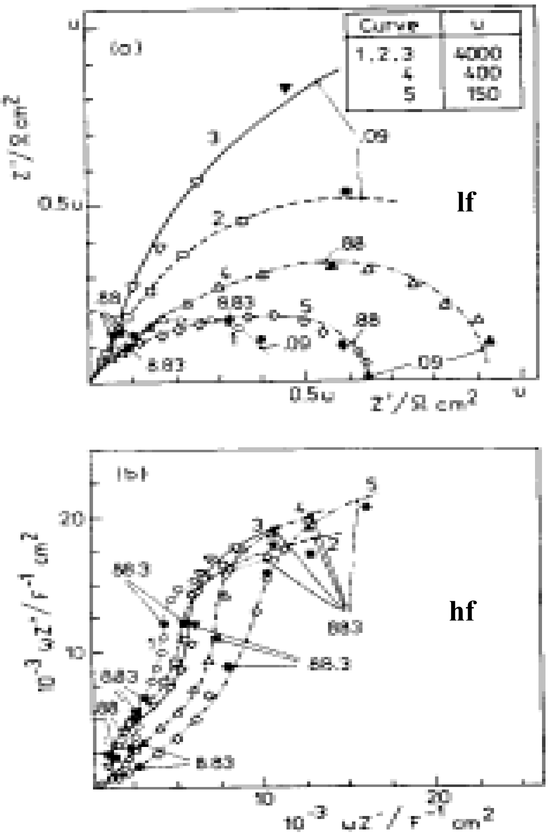


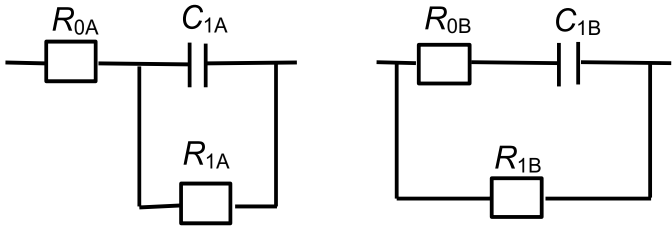
Fig. 1. Example of plots of a set of immittance spectra measured for the same system at several values of some system variable, in various coordinates: (a) and (b) in *Z* and *ωZ* complex plane, respectively. Values close to solid points indicate the respective frequencies in Hz, and lf and hf denote low and high frequency regions, respectively [4]

The visual inspection of IS in various plots can help also in the elimination of the frequency range where the given IS seems to be obviously unreliable [4].

MODELS AND THEIR FEATURES

The simplest goal of modelling of an experimental IS is its synthetic description in the whole range of frequencies where it is supposed to be reliable. In other words, the model should provide a computed (theoretical) IS as close to the modelled experimental one as possible, both qualitatively and quantitatively. The model should be possibly simple and of minimal number of parameters, these being independent of frequency. Finally, it should be of a form suitable for estimation of kinetics of processes taking place in the system under study, in further steps of analysis, e.g. a simultaneous analysis of a set of ISs measured at several values of a system variable.

The starting information for formulating a hypothetical model of a selected experimental IS should be drown out from the inspection of its plots in various coordinates. For instance, the plots presented in Fig. 1a (probably two overlapped semicircles in the 1st quadrant a conventional complex plane, i.e. $-\mathrm{Im}H_k$ vs. $\mathrm{Re}H_k$) suggest that in the system in question two RC time constants (τ's) are involved, whilst, in turn, these in Fig. 1b suggest a larger number of time constants, the hf τ resulting from a presence of a constant phase element (CPE) (at hf's apparently straight-line section of a none-zero slope) [4]. It is noteworthy that in ωZ or Y/ω complex planes the curve shapes are richer than in the Z or Y planes, as in the former cases an apparently straight-line section supplements the semicircles or shorter arc sections characteristic for RC electrical circuits (please notice the hf section in Fig. 1b).



(a) (b)

Fig. 2. One time constant RC electrical equivalent circuits used in modelling of an IS characterised in Z conventional complex plane by a one semicircle in the first quadrant.

As models, the so-called electrical equivalent circuits are most frequently used. If in the Z complex plane a given IS is represented by a simple semicircle in the first quadrant, one of the circuits presented in Fig. 2, differing by their topology, can by alternatively applied, as both of them result in an identical IS under condition of proper recalculations of their elements [6,10]. If the system under study is an electrode||electrolytic solution interface, in the case of choice of circuit of Fig. 2a its elements R_{0A}, C_{1A}, and R_{1A} will model the ohmic resistance (mainly of the solution), the interfacial double layer capacitance and the resistance of a simple redox reaction (e.g. $Fe^{+2} \leftrightarrow Fe^{+3} + e$). However, if one will tray to apply this circuit as subcircuit modelling only a Faradaic process with ad-/desorption (e.g. $H_2 \leftrightarrow 2H_{ad} \leftrightarrow 2H^+ + 2e$) taking place at this interface, the physical meaning of its elements will be not so simple [5, 10, 11].

Hence, if the system under study is considered as a "black box" and one know solely its IS, there is no criterion for making the choice of the circuit topology. Accordingly, the topological ambiguity is one of the features of the equivalent circuit models. It results from the fact that the X functions of both above circuits can be transformed to an identical mathematical formula (for further details see below).

Similarly, if in the Z complex plane a given IS is represented by two simple semicircles in the first quadrant, for instance any of the circuits presented in Fig. 3, all of them involving two RC τ's, can be applied, as all of them result in an identical IS under condition of proper recalculations of their elements [4, 6, 10].

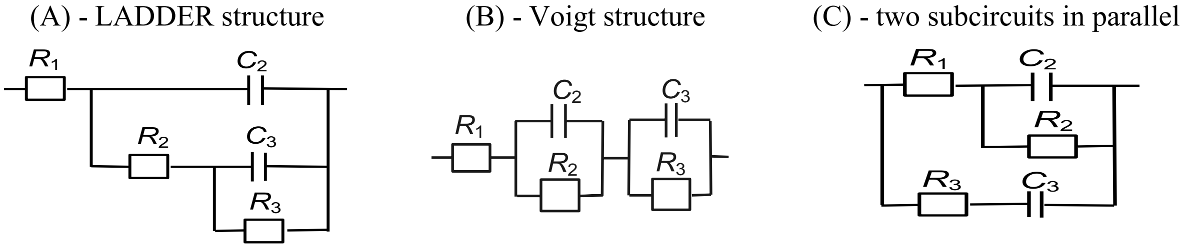
The topological ambiguity results from the fact that all equations in Fig. 3 can be transformed to a common formula (for Y it would be quite similar) [4, 6, 8]:

$$Z = \frac{s^2 a_2 + s a_1 + a_0}{s^2 + s b_1 + b_0} \tag{11}$$

where only the definitions of coefficients in particular terms depend on the circuit topology.

However, in spite of the topological ambiguity, in the case of two (or n, $n \geq 2$) RC τ 's circuits another ambiguity appears. It is the solution ambiguity. Namely, for the circuit of a given topology there are n sets of values of its elements resulting in an identical IS [4, 10, 11].

The solution ambiguity results from the fact that, in contrast to the transformation of any formula of the type presented in Fig. 3 (simple reduction to a common denominator) to Eq. 11, the opposite transformation needs the solution of a set of five equations, one of them being a square one. It is similar as the case of solution of a typical square equation, $x^2a + xb + c = 0$. The sole exception is for the circuit of LADDER structure (Fig. 3A), because it corresponds to the case of square equation when the two solutions are identical. In turn, in the case



$$Z_{(A)} = R_1 + \cfrac{1}{sC_2 + \cfrac{1}{R_2 + \cfrac{1}{sC_3 + \cfrac{1}{R_3}}}} \tag{8}$$

$$Z_{(B)} = R_1 + \frac{1}{\frac{1}{R_2} + sC_2} + \frac{1}{\frac{1}{R_3} + sC_3} \tag{9}$$

$$Z_{(C)} = \cfrac{1}{\cfrac{1}{R_1 + \cfrac{1}{sC_2 + \cfrac{1}{R_2}}} + \cfrac{1}{R_3 + \cfrac{1}{sC_3}}} \tag{10}$$

Fig. 3. Two time constant RC electrical equivalent circuits used in modelling of ISs characterised in *Z* complex plane by two semicircles in the first quadrant, and the respective equations for *Z* in forms closest related with these circuits topology ($Z_R = R$, $Y_C = sC$) [4, 6, 11]

of Voigt structure the two solutions differ only by the subscripts of the two R_jC_j couples in parallel. However, but the case of circuits of LADDER or Voigt structure, the two solutions can result in sets of drastically different values for particular circuit elements [4].

Both above types of ambiguities are important disadvantages of equivalent circuit models. In the literature the topological ambiguity is seldom taken into consideration, whilst the solution ambiguity is quite neglected, in spite that its existence is crucial for the conclusions on the system under study in physico-chemical terms [4, 5, 10, 11].

Free of the above disadvantage is "the generalised mathematical model", formulated by extension of Eq. 11 for modelling the systems characterised by n τ's and generalised from Z to X [10]:

$$X = \frac{\sum_{k=n}^{0} s^k a_k}{s^n + \sum_{k=n-1}^{0} s^k b_k} \tag{12}$$

where k's are integers. Obviously, a_k and b_k coefficients depend also on the detailed meaning of X (Z or Y) [7].

When for the system under study also a CPE should be taken into account (in contrast to e.g. R and C elements, CPE has two parameters), a model similar to Eq. 12 can be used. However, in such a case both in the numerator and denominator additional terms of s at fractional powers (fractal values of k) appear, what results in constrains between some coefficients; hence, not all of them are independent [10].

In the general case of H's, i.e. when signals and responses are not restricted to electrical quantities, and the system is not restricted to one-port, relatively simple models, similar to the discussed above for X, find no application. Instead, just from the beginning of modelling much more detailed models, taking into account also the system variables, must be used. For instance, one of the various possible TFs of transport of hydrogen (H) throughout a large thin single-phase elastic metal (M) membrane (one-dimensional transport, along the z coordinate, $0 < z < L$) in response to a small amplitude H concentration, c, signal at the $z = 0$ surface, $\delta c_{z=0}$, close to equilibrium ($c_{0 \leq z < L} \approx c_{\mathrm{eq}}$) is the ratio of small-amplitude hydrogen flux, δJ, responses at the $z = L$ and $z = 0$ surfaces of the specimen. Under assumptions that 1/ this transport takes place in a self-stressed (as, typically, H atoms expand the original M lattice) M, and 2/ hindrances of the surface processes can be neglected, the following model has been proposed [1]:

$$H_{L/0} = \frac{\Delta J_{z=L}}{\Delta J_{z=0}} \tag{13}$$

$$= \frac{(1 + \mathrm{A}\mathrm{c}_{eq})\mathrm{q}\sinh^{-1}(\mathrm{qL}) - \mathrm{c}_{eq}\frac{12\mathrm{A}}{\mathrm{q}^2\mathrm{L}^3}\left[\left(\frac{\mathrm{qL}}{2}\right)\coth\left(\frac{\mathrm{qL}}{2}\right) - 1\right]}{(1 + \mathrm{A}\mathrm{c}_{eq})\mathrm{q}\coth(\mathrm{qL}) - \mathrm{c}_{eq}\frac{12\mathrm{A}}{\mathrm{q}^2\mathrm{L}^3}\left[\left(\frac{\mathrm{qL}}{2}\right)\coth\left(\frac{\mathrm{qL}}{2}\right) - 1\right]}$$

where $$A = \frac{2V^2\overline{Y}}{3RT} \tag{14}$$

$$q = \sqrt{\frac{s}{D\left(1 + Ac_{\mathrm{eq}}\right)}} \tag{15}$$

and V and $\overline{Y}$ denote partial molar volume of H in M (its not-zero value causes self-stress in M lattice) and bulk elastic modulus of the M-H solid solution, respectively, R and T gas constant and temperature, and D diffusion constant of H in the M-H solid.

The main criterion of correctness, or rather usefulness of the chosen hypothetical model for a given TFS is the qualitative and quantitative similarity of its theoretical computed spectrum to the modelled, i.e. experimental TFS. The qualitative similarity is determined by the selected model, while the quantitative similarity is improved in the procedure of fitting of this model by a gradual change of its parameters, i.e. fitting of its theoretical spectrum to the modelled experimental one [6].

ADVICES RELATED TO THE FITTING OF A SELECTED MODEL TO TFS

Typically, the fitting of a selected model to a given experimental TFS is performed by Complex Non-linear Least Squares method (CNLS), by minimising in an iterative procedure the weighted χ^2 function, defined as follows [6]:

$$\chi^2 = \sum_{k=1}^{l} \left\lfloor w_k^{'} \left(H_{k_{\mathrm{ex}}}^{'} - H_{k_{\mathrm{th}}}^{'}\right)^2 + w_k^{''} \left(H_{k_{\mathrm{ex}}}^{''} - H_{k_{\mathrm{th}}}^{''}\right)^2 \right\rfloor \tag{14}$$

where k denotes sequence number of successive experimental points (usually from the highest to the lowest f) up to l ($0 \le k \le l$), H' and H'' are real and imaginary components of H_k, respectively, and the subscripts th and ex denote the theoretical (computed from the model) and experimental quantities, while w' and w'' are respective statistical weights.

As all least squares (NLS) methods, CNLS is based on the assumption that the experimental TFS is contaminated only by random errors, Gaussian in character. Hence, the presence of errors of any other character in the given modelled TFS reduces the reliability of the fitting results.

At a proper convergence of the iterative procedure, χ^2 should gradually decrease down to its so-called "global minimum" value, where the model parameters free (i.e. not fixed at an assumed value) in the given fitting computation attain their so-called "best-fit" estimates. The smaller the value of χ^2, the better is the (statistical) goodness of the fit.

With respect to the choice of weighting system, the assumption that $w' = w'' = 1$ (so-called "unit weights") is worst. If there is no specific premises, the so-called "modulus weights" should be advised [6, 13]:

$$w_k^{'} = w_k^{''} = \frac{1}{\left|H_{k_{\mathrm{ex}}}\right|^2} \tag{15}$$

The number of experimental points in the fitted spectrum should be possibly large. On the other hand, the model should be not over-flexible, i.e. the number of its parameters should be possibly small. Both above aspects are taken into account if as the measure of fit goodness, instead of χ^2, the standard deviation of the given fit is considered [6]:

$$\sigma_{\mathrm{fit}} = \sqrt{\frac{\chi^2}{l - nfp}} \tag{16}$$

where nfp denotes the number of model parameters being free in the given fitting. Hence, σ_{fit} can be considered as χ^2 normalised on ($l - nfp$). Another advantage of σ_{fit}, in comparison with χ^2, is that at the advised weighting system (Eq. 15) it is dimensionless.

The convergence of the CNLS procedure and aptitude for finding the global minimum depends on many factors. For instance, the procedure may stop at a so-called "local minimum", characterised by a large χ^2. In such a case, a change of the staring value of some model's parameter and/or an instantaneous change of its character from free to fixed can be helpful. Both the convergence of procedure and its sensitivity to the starting estimates of parameters is very sensitive to the applied detailed type of model. For instance, the application of the selected equivalent circuit model in its Y form to the given IS recalculated from its Z to Y form may allow for attaining the global minimum, what before those recalculations was not possible. However, the generalised mathematical models (Eq. 12) seem to be by very far the best [12]. Probably, the smaller the degree of nonlinearity of the model with respect to its parameters, the smaller the sensitivity on the aptness of starting estimates and the higher the convergence of the fitting procedure are [6, 12]. On the other hand, the generalised mathematical models are cumbersome to use because the starting estimates of their parameters cannot be proposed directly from the plots of ISs.

Additional important criteria of the choice of optimal model for the given TFS and its fit goodness are the computed relative confidence limits of the best-fit parameter estimates (or individual standard deviations), and magnitude of correlation coefficients of pairs of the best-fit estimates. Very broad confidence limits of a parameter suggest that it is probably redundant in the model. In turn, the magnitude of correlation coefficients of two estimates approaching ± 1 indicates that the respective couple is poorly independent. However, one should bear in mind that, as in all NLSs, those quantities are computed under the assumption that close to the fitting minimum the model is linear [4, 6].

CONCLUSIONS

Experimental transfer function spectra (TFS) can be considered as reliable only if they were measured at steady state of the system and under experimental conditions assuring its linearity.

An initial inspection of an experimental TFS in plots of various coordinates is necessary, mainly for elimination of “wild points”, elimination of the frequency range where the TFS in question seems to be unreliable, and the preliminary estimation of the character and complexity of the system under study.

The character and complexity of the primary proposed hypothetical model for a given TFS should result from the initial inspection of the latter. Its poor fit goodness should result in modification of the previously applied model.

In the case of looking for equivalent electrical circuit models for an immittance spectrum (IS) one should take into account their possible ambiguities: topological and solution.

Free of ambiguities are the generalised mathematical models. Their additional advantages are 1/ high convergence ability in the fitting procedure, and 2/ exceptionally small sensitivity to the selection of staring estimates of the model parameters.

Acknowledgements: *The author would like to express his gratitude to Prof. V. Horvat-Radošević for organising the 9th Internat. Microsymposium on Electrochemical Impedance Analysis at St. Andrew Island in Croatia and encouraging him to give a lecture there, what has finally resulted in the preparation of this article.*

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ИЗБРАНИ ПРОБЛЕМИ НА АНАЛИЗА НА СПЕКТРИТЕ НА ИМПЕДАНСА И ПРЕХОДНАТА ФУНКЦИЯ: ОБЗОР

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Постъпила на 20 февруари 2012 г.р приета на 20 февруари 2012 г.

(Резюме)

Експерименталният импедансен спектър (IS), или по-общо, спектърът на преходната функция (TFS) на дадена система и особено множество спектри, снети при различни стойности на системните променливи, дават обилна информация за системата и протичащите в нея процеси. Изразяването на тази информация в термините на физикохимията, обаче, изисква прилагането на специални процедури при анализа на спектрите.

В тази работа се припомнят избрани въпроси, свързани с надеждността на TFS и на процедурите за техния анализ, основани главно на личния опит на автора. Тези въпроси са преди всичко: проблеми, произтичащи от факта, че действителните системи не изпълняват напълно изискванията за измерването на TFS (напр. линейност), първоначалният визуален анализ на TFS, принципите на моделиране и дискусията на различни видове модели (последното за IS), както и ноу-хау за напасването на избрания модел към даден TFS и критерии за качеството на това напасване.