*Bulgarian Chemical Communications, Volume 50 Special Issue D (pp. 123 – 130) 2018*

# Rotating Fourier Transform - Engine for Non-Stationary Impedance Spectroscopy

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Received August 8, 2018 Revised August 18, 2018

**Explanatory Notes:** In the last year of his unwearied active scientific life Zdravko Stoynov was focused on intensive theoretical and experimental activities for effective illustration of his powerful advanced mathematical tool Rotating Fourier Transform (RFT). He would describe it as a "powerful engine for non-stationary impedance spectroscopy which opens up the exploration of the low and infra-low frequencies where many important and interesting phenomena, still hidden, can be measured precisely." He was expecting the development of a new "4th Generation" marketable impedance analyzers, applying RFT and MRFT (Multiple RFT) in the near future. In order to accelerate the coming of this "near future" and be able to see it, he was working both on the mathematical tool and on the experimental verification.

We are presenting his last manuscript, as written by him, expecting, that there will be an interest in his work on RFTs and support of his idea for the 4th Generation of impedance analyzers to fruition. We are open to collaboration for the continuation of Zdravko Stoynov's work.

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The conventional Impedance Spectroscopy is based on the original Fourier Transform (FT), which is the best estimator of periodic signals in stationary conditions. Many practical applications however require impedance measurements of typically non-stationary objects. This paper presents an advancement of the classical Fourier Transform which provides for precise measurements of sinusoidal signals in presence of non-stationary noise. The new mathematical tool was called Rotating Fourier Transform (RFT). Its architecture contains multiple integrals converting the time-domain phenomenon into its frequency domain complex image. The classical Fourier Transform is used as a kernel of the multiple integrals. The new transform filtrates orthogonally the derivatives of the drifting potential which is in this case an additive aperiodic noise. The paper reports the first practical application of the new mathematical instrument in a real laboratory experiment.

More complex is the case of measurements of impedance, which is changing with the time. In this case the changes can be defined as a multiplicative aperiodic noise. The derived analytical expressions are showing that every simple element which is changing with the time, produces methodical errors increasing with the frequency decrease. Those errors are changing the original structure of the model producing an artificial substructure, which is a product of the applied mathematical tool - the FT. When applied transform is the RFT, the artificial structure is eliminated. It was proven that the RFT filtrates orthogonally the first derivative of this noise and provides for the estimation of the proper Instantaneous Impedance. The paper presents also the first practical application of the new mathematical tool for measurement of battery impedance.

**Key words:** Non-stationary Impedance Spectroscopy, Fourier Transform, Rotating Fourier Transform, Instantaneous Impedance, Battery State of Health.

## INTRODUCTION

The Fourier Transform [1] is the kernel of the electrochemical impedance spectroscopy (EIS) - one of the most powerful methods, widely used in all fields of the electrochemical research. The EIS is based on the Transfer Function analysis developed in technical cybernetics. It is proven theoretically that under the conditions of sufficiently large frequency range, the Transfer Function is a full description of the dynamic properties of a linear system [2, 3].

Electrochemical systems are however intrinsically non-linear. In order to overcome this problem, EIS follows the theory of Friedholm - Volterra, in accordance to which the nonlinear system is measured at selected different working points of the non-linear voltage-current characteristic of the object [4]. In electrochemistry, the working point is stabilized galvanostatically (or potentiostatically) and perturbed additionally by small sinusoidal signal of a given frequency.

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The response signal measured at the output of the object - voltage (or current) is also sinusoidal, partially deformed by the object's non-linearity. This signal is periodic and contains the basic frequency and a sum of higher harmonics. When the perturbing signal is small enough the main frequency dominates the response and can be separated successfully. This operation is performed by the applied Fourier Transform. Thus the FT is used for coherent (iso-frequency) detection of the linear part of the response produced by the non-linear object. In addition, it is proven theoretically, that the Fourier Transform is the best estimator of the sinusoidal signal in the presence of Gaussian noise [3].

## THEORY

### *Aperiodic noise and Fourier Transform errors*

The Fourier Transform is efficient and best estimator (detector) of stationary periodic signal in the presence of noise. However when the signal is non-stationary or when the noise contains aperiodic component, the FT is not efficient. The analysis of the resulting errors is principally interesting and necessary for the evaluation of the acceptable low frequency limit for the application of the 4-dimensional approach.

By definition, the impedance is the ratio between the voltage and current, defined in the complex frequency space:

$$Z\ (\mathrm{i}\omega) = Z'(\omega) + \mathrm{i}\, Z''\ (\omega) = \{a_{\mathrm{u}}(\omega) + \mathrm{i} b_{\mathrm{u}}(\omega)\ .\ \{a_{\mathrm{I}}\omega + \mathrm{i} b_{\mathrm{I}}(\omega)\}^{-1}, \quad (1)$$

where $Z'$ and $Z''$ are the real and the imaginary impedance components, $a_{\mathrm{u}}$, $b_{\mathrm{u}}$, $a_{\mathrm{I}}$ and $b_{\mathrm{I}}$ are the real and the imaginary components of the object's voltage and current correspondingly. The voltage and the current are measured by the instrument as functions of the time and the acquired data are converted into the frequency space by the FT:

$$a_{\mathrm{u}}\ (\omega)\ +\ \mathrm{i} b_{\mathrm{u}}(\omega) = \boldsymbol{FT}\, \{u(t)\}, \quad (2a)$$

$$a_{\mathrm{I}}\ (\omega)\ +\ \mathrm{i} b_{\mathrm{I}}(\omega) = \boldsymbol{FT}\, \{\mathrm{i}(t)\}, \quad (2b)$$

where $\boldsymbol{FT}$ is a symbolic notation for Fourier Transform operator. In accordance with the classical FT definition [1, 2] the coefficients *a* and *b* are calculated by the Euler equations:

$$a = w \int_0^{NT} x(t)\, sin(\omega t) dt, \quad (3a)$$

$$b = w \int_0^{NT} x(t)\, cos(\ \omega t) dt, \quad (3b)$$

where *w* is the weighting normalizing factor, *N* is the number of periods *T* of integration and *x(t)* is the input function (measured voltage or current). In order to keep the ortho-normality of the Fourier spectra, the weighting coefficient should have the value $w = 2\ (NT)^{-1}$.

Performing these operations the instrument is changing the selected frequency step by step, under given program. The full programmed range of frequencies is covered and the produced set of data forms a linearized (quasi-linear) impedance function, characterizing the object dynamics in the vicinity of the selected working point. In order to enlarge the observation of the object, the same set of measurements should be performed at others working points. It is worth to state here, that the available frequency range is never enough wide to observe the entire variety of processes taking place in the electrochemical objects. Thus the EIS can give only partial and local description of the object dynamics.

As a matter of fact the impedance analyzer performs the FT over both voltage and current signals. Assuming galvanostatic mode and perfect operation of the galvanostat, the full calculation at a given frequency $\omega$ is:

$$Z\ (i\omega) = [FT\ \{U_{DC} + u(t) + n(t)\}]\ .$$

$$[\ FT\ \{I_{DC} +\ I_{AC}\ (t)\}]^{-1}, \quad (4)$$

where $Z\ (\mathrm{i}\omega)$ is the measured impedance, *t* is the time, $U_{\mathrm{DC}}$ and $I_{\mathrm{DC}}$ are constant values characterizing the selected working point, $I_{\mathrm{AC}}$ is the perturbating small galvanostatic sinusoidal current, $u(t)$ is the object response and $n(t)$ is a noise, which could be present. This noise can contain components of different origin, nature and structure. In the general case

$$n\ (t) = n_{uobj} + n_{k\omega} +\ n_{ss} + n_{instr}, \quad (5)$$

where $n_{\mathrm{uobj}}$ is the noise produced by the object voltage, $n_{\mathrm{k}\omega}$ is the cumulative noise of the frequency harmonics produced by the object's non-linearity, $n_{\mathrm{ss}}$ is a typical statistically sufficient noise and $n_{\mathrm{instr}}$ is a noise related to the power supply frequency and to other instrumental imperfections. As far as the FT is a linear operator [2], the components of the errors caused by the different noise components in Eq. 5 can be studied separately.

The errors produced by the statistical noise are very small – the FT is filtering this kind of noise very efficiently. The errors produced by $n_{\mathrm{k}\omega}$ depend on the relative nonlinearity - for small signal perturbation those errors are also small. They are separated by FT very efficiently and some instruments are evaluating those errors in a range of higher harmonics. The instrumental errors depend to a large degree on the construction of the instrument and on its environment. Their evaluation however is out of the scope of this paper.

The target of this investigation is the study of the errors, produced by the object's voltage. In the cases when this voltage is constant (the object is stationary) the Fourier Transform is filtering this constant orthogonally (unconditionally) and the precision of this operation depends only on the limited precision of the calculations. The application of the ABC (Automatic Bias Correction) by the modern impedance analyzers supports the perfection of this noise filtration. In the opposite case - when the object's voltage changes with time, the FT produces methodical errors [6]. The analysis is based on the presentation of the voltage-time dependence as a typical aperiodic signal, which could be approximated by a Taylor's series expansion:

$$U_{\mathrm{obj}}(t) = U_{\mathrm{DC}} + \alpha t + k_2 \beta t_2 + k_3 y t_3 + \cdots, \quad (6)$$

where $U_{DC}$ is a constant, $k_n = (n!)^{-1}$ are the Taylor's series coefficients, and $\alpha, \beta, \chi, \ldots$ are the derivatives of $U_{obj}(t)$ for $t = 0$. All these derivatives form the Taylor Spectrum [7], the shape of which could play an important role in the analyses. When the noise corresponds to the presentation of Eq. 6 it can be called aperiodic noise.

As far as the FT is a linear operator, the errors produced by the individual terms of Eq. 6 can be studied separately. The analytical solution of FT (Eq. 3) of the linear aperiodic term given with Eq. 6 is a direct one [5] and it gives $a = -2\alpha\omega^{-1}$ and $b = 0$. As it can be seen, the error is present only in the real component (defined by Eq. 3) and is absent in the imaginary one. Thus the linear aperiodic noise corrupts the orthogonality between the real and imaginary impedance components. For high frequencies the error is small and could be neglected. For low frequencies however, this error could be large and increases quickly with the decrease of the frequency. This phenomenon can corrupt significantly the shape of the measured impedance.

Fig. 1 and Fig. 2 illustrate the significance of those errors on very simple examples of electrochemical impedances.

The analytical derivation of the errors caused by the second Taylor term shows that they are in both the real and imaginary components: $a = -2\pi\beta N\omega^{-2}$ and $b = 2\beta N\omega^{-2}$ [7]. The analytically derived expressions for the errors from the higher Taylor's terms of Eq. 6 are more complicated. They are with increasing complexity and show interesting properties of conversion after the fifth term under given conditions [8].

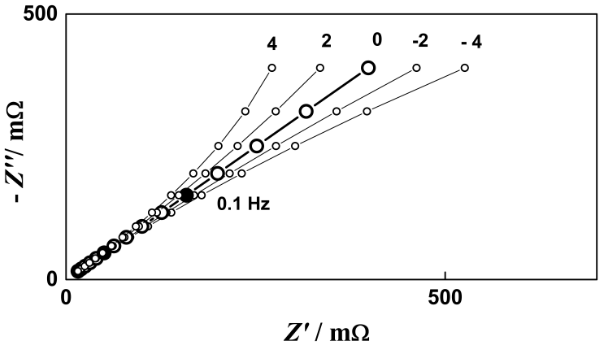


**Fig. 1.** Deformations of an ideal Warburg-type impedance diagrams from the errors of the Fourier Transform, caused by linear drift of the cell potential. Frequency range 10 Hz - 0.01 Hz, 5 points/decade, linear aperiodic noise with derivative values $\alpha$ = -4, -2, 0, 2, 4 mVsec$^{-1}$.

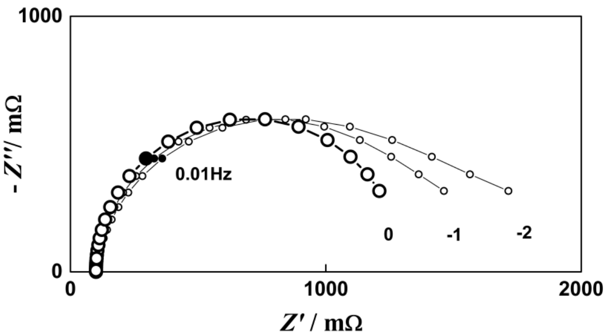


**Fig. 2.** Deformations of an ideal impedance diagram of Polarisable electrode from the errors of the Fourier Transform, caused by linear drift of the cell potential. Frequency range 100 Hz - 1.25 mHz, 5 points/decade, linear noise with derivative values $\alpha$ = -2, -1, 0 mVsec$^{-1}$.

### *Phase definite Fourier Transform*

The initial phase of integration in Eq. 3 could not be zero. In the early definition of Eq. 3, Euler has used for initial limit of integration also $\pi$ and $\pi/2$. As far as we are analyzing measurement of impedance which is defined as the ratio between two Fourier Transforms we can select any desired initial phase applied for both Transforms. Thus an additional definition the Fourier Transform can be constructed [8]. It was called Phase definite Fourier Transform and can be denoted by the symbol ***pFT*:**

$$a = w \int_{t_0}^{t_0+NT} x(t)\sin(\omega t)\mathrm{d}t, \tag{7a}$$

$$b = w \int_{t_0}^{t_0+NT} x(t)\cos(\omega t)\,\mathrm{d}t, \tag{7b}$$

where the only difference from the classical definition is the presence of one additional parameter - the initial time of integration, which corresponds to an initial phase $\varphi = t_0 T^{-1}$. In respect to stationary periodic signals the pFT is equivalent to the classical FT. However in respect to aperiodic noise pFT has different properties. The error produced by a linear noise term is a function of the initial phase $\varphi$. One remarkable property of this dependence is the equality of the errors correspondent to initial phase $\varphi$=0 and phase $\varphi$=2$\pi$. It corresponds to the analytical property of the space of the errors as functions of the initial phase. However the shape of the error produced by the second – quadratic term of the Taylor Spectrum of Eq. 6 is more complicated. This function is also complex, but it is non-linear and the correspondent space is not analytical.

### *Rotating Fourier Transform*

On the base of the described analysis a novel transform was created. Using the analytical property of the pFT, the new transform has the following form [8]:

$$a = w_1 w_0 \int_{\Psi}^{\Psi+2\pi N_1} \int_{t_0}^{t_0+N_0T} x(t)\, sin(\omega t) dt\, d\varphi \tag{8a}$$

$$b = w_1 w_0 \int_{\Psi}^{\Psi+2\pi N_1} \int_{t_0}^{t_0+N_0T} x(t)\, cos(\,\omega t) dt\, d\varphi \tag{8b}$$

where the first (internal) integration is the classical phase definite Fourier Transform with initial phase $\varphi = t_0 T^{-1}$, the second (external) integration is in respect to this phase. It starts from the external initial phase $\psi$ and is a full circulation. The coefficients $w_1$ and $w_0$ are normalizing coefficients, dependent on the numbers of the periods of integration $N_1$ and $N_0$ and on *T*. As far as the last integration is with respect to the phase $\varphi$, which symbolizes a rotation, the new transform can be called Rotating Fourier Transform (RFT). The operator symbol ***RFT*** has a number of parameters:

$$RFT\{x(t) \mid \omega, \varphi, \Psi, N_0 \; and \; N_1 \mid\}, \tag{9}$$

where *x(t)* is the input signal, which is defined in the time domain and has to be converted into the frequency domain.

The kernel of this double integration is the classical Fourier Transform - as a result the RFT keeps the properties of the FT in respect to periodic signals and constant bias (zero term of the noise Taylor spectrum). The difference is with respect to the linear and higher terms of this spectrum - the RFT is orthogonal to the linear term (RFT filtrates it totally) and is suboptimal to the higher terms of the noise Taylor spectrum. This property is in correspondence with the classical FT, which is orthogonal to the zero term (constant bias) of the same Taylor spectrum. Thus the RFT is in continuity of the FT. This property of RFT was proved theoretically [8]. Fig. 3 is showing the described orthogonal property which keeps the precision of the FT.

### *Multiple Rotating Fourier Transform*

The described continuity can be enlarged further. A second order and higher orders Rotating Fourier Transforms can be constructed also.

The general Multiple Rotating Fourier Transform (***MRFT***) of order $\nu$ has the form:

$$a = W_\nu \int_{\Psi_\nu}^{\Psi_\nu+2\pi N_\nu} \dots \int_{\Psi_1}^{\Psi_1+2\pi N_1} \int_{t_0}^{t_0+N_0T} x(t)\sin(\omega t)\mathrm{d}t\mathrm{d}\varphi\mathrm{d}\Psi_1 \dots \mathrm{d}\Psi_{\nu-1} \tag{10a}$$

$$b = W_\nu \int_{\Psi_\nu}^{\Psi_\nu+2\pi N_\nu} \dots \int_{\Psi_1}^{\Psi_\nu+2\pi N_1} \int_{t_0}^{t_0+N_0T} x(t)\cos(\omega t)\mathrm{d}t\mathrm{d}\varphi\mathrm{d}\Psi_1 \dots \mathrm{d}\Psi_{\nu-1} \tag{10b}$$

where the initial phase of the first integration is $\varphi = t_0 T^{-1}$, the normalizing coefficient $W_\nu$ is the product of all individual normalizing coefficients.

The MRFT keeps the property of the classical FT in respect to periodic signals. The MRFT of order $\nu$ is orthogonal to all $\nu$ terms of the noise Taylor spectrum - the MRFT filtrates unconditionally all ν derivatives of this noise (voltage drift).

Thus the RFT and MRFT are natural generalization of the Fourier Transform. They are keeping the continuity of its properties [9].

## EXPERIMENTAL

The theory derived above was proven by multiple simulation studies as well as by real experimental measurements of battery under charge and discharge.

### *Simulation studies*

The theoretically derived equations for FT and pFT errors, as well as the construction of RFT and MRFT were checked by series of simulations with varying structures and amplitudes of the additive aperiodic noise and varying periods of integrations. The influence on the final results of the calculations precision was also evaluated. The next examples are showing some of these simulation studies.

The property of the RFT for filtration of linear drift (orthogonality to the linear term of the noise Taylor spectrum) is shown in Fig. 3. The figure contains the equation used for synthesis of the input signal, having sinusoidal component and additive linear noise (drift). The resulting values of the produced transform into the frequency domain, together with the ratio signal to noise (S/N) are also given. It is clear that the RFT filtrates efficiently the linear noise.

The next Fig. 4 and Fig. 5 illustrate the property of the MRFT of second order for filtration of more complex additive noise. In this case the noise contains linear and quadratic terms. In Fig. 5 the amplitude of the sinusoidal signal is extremely low and un-visible. Nevertheless the final results are excellent.

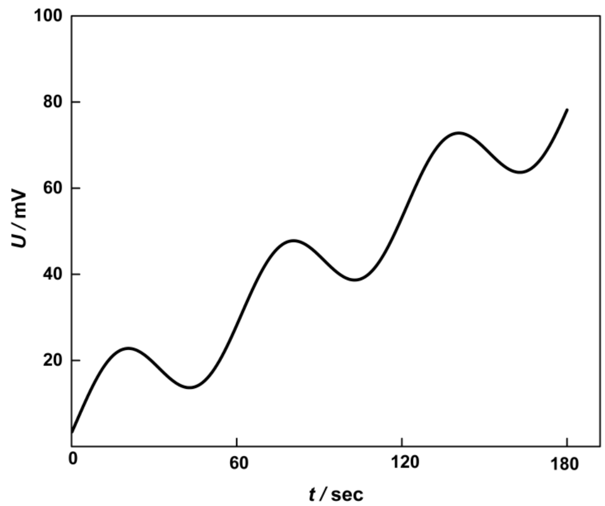


**Fig. 3.** Detection of sinusoidal signal in presence of linear aperiodic noise. Frequency 0.0156 Hz, A.C. amplitude 10 mV, derivative of the trend: $\alpha = 0.4$ mVsec$^{-1}$. Input signal $x(t) = 10.01 \sin(\omega t) + 5 + 0.4t$ [mV], signal to noise ratio S/N = 0.1. RFT estimate: $10.01001 \sin(\omega t) + 3.52.10^{-6} \cos(\omega t)$.

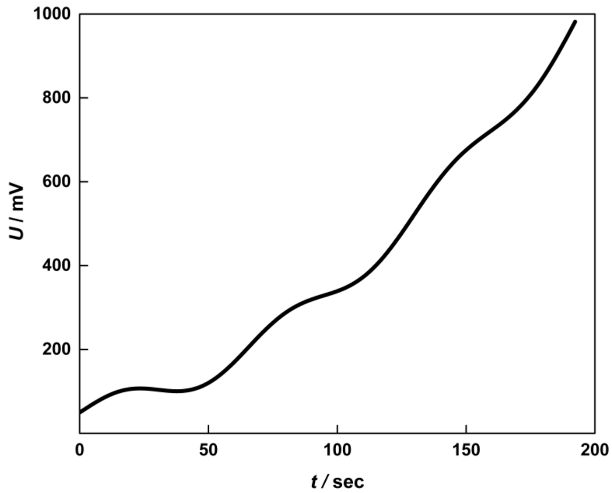


**Fig. 4.** Detection of sinusoidal signal in presence of complex aperiodic noise. Frequency 0.0156 Hz, A.C. amplitude 30 mV, derivatives of the noise: $\alpha = 1$ mVsec$^{-1}$, $\beta = 0.02$ mVsec$^{-2}$. Input signal $x(t) = 30.01 \sin(\omega t) + 50 + t + 0.02 t^2$ [mV]. Signal to noise ratio S/N = 0.06. $R^2$FT estimate: $30.01002 \sin(\omega t) – 6.78.10^{-6} \cos(\omega t)$.

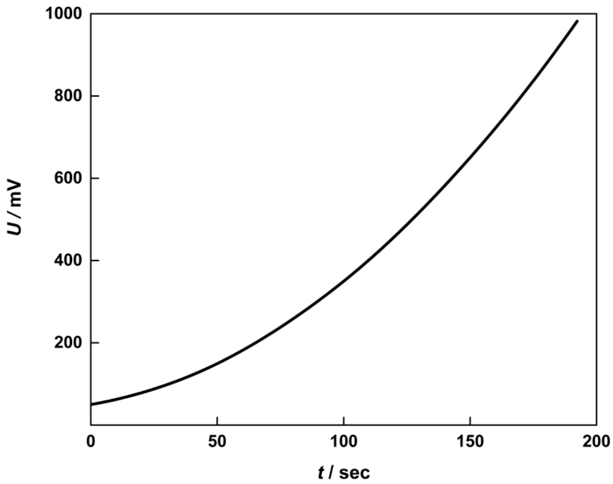


**Fig. 5.** Detection of very small (un-visible) sinusoidal signal in presence of complex aperiodic noise. Frequency 0.0156 Hz, A.C. amplitude 0.5 mV, derivatives of the noise: $\alpha = 1$ mVsec$^{-1}$, $\beta = 0.02$ mVsec$^{-2}$. Input signal $x(t) = 0.505 \sin(\omega t) + 50 + t + 0.02 t^2$ [mV], signal to noise ratio S/N = 0.001. $R^2$FT estimate: $0.505015 \sin(\omega t) – 9.83.10^{-6} \cos(\omega t)$.

### *Experimental measurements*

In order to verify the theory, a series of real experimental measurements were recently carried out. The impedance measurements of a battery during charge, performed by a classical impedance analyzer and by the new mathematical instrument are compared.

The first measurement was conventional. It was performed in the frequency range 1 kHz down to 1 mHz during the charge of a battery (Li-ion, NiCo - type, 2000 mAh) using Solartron 1260 impedance analyzer, controlled by an external computer. Fig. 6 shows the produced impedance diagram. As it is seen in the frequency range down to approximately 1 Hz the diagram is smooth and regular. However below 0.4 Hz irregularities appear and down to 1 mHz the diagram contains mainly increasing errors. In this range the measurements are totally non-usable.

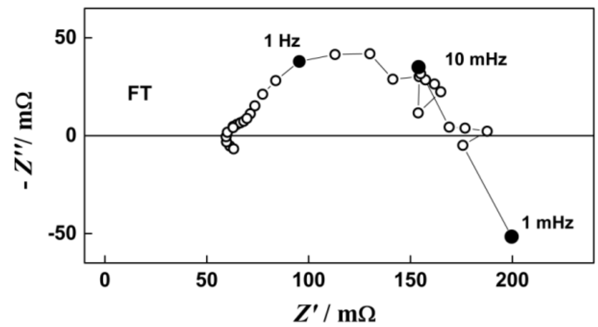


**Fig. 6.** Impedance diagrams of Li-ion battery 2000 mAh during charge with 100 mA produced by conventional Impedance Analyzer (Solartron 1260) using Fourier Transform. Frequency range 1 kHz – 1 mHz, 5 points/decade, A.C. current amplitude 11 mA.

The second series of impedance measurements are produced by using the Rotating Fourier Transforms. For this purpose a special laboratory set-up was assembled. In the frequency range 0.01 down to 0.001 Hz, the Solartron instrument is used only as a generator of the necessary frequencies with given amplitudes. This signal is mixed with the selected D.C. current via laboratory made galvanostat, connected to the measured battery. The current and the battery voltage are measured by two parallel AD converters (17 bits) with selectivity 0.002 mV and controllable acquisition time. The data are stored in the computer memory for post-experimental processing.

Fig. 7 shows the data record from the last decade (0.01 - 0.001 Hz) during the charge of the battery, measured immediately after the conventional measurements. The current signal shows a stationary DC component and a sinusoidal AC component with varying frequency and stationary amplitude (~ 10%). The battery response - the voltage signal, contains also sinusoidal components, however they are naturally mixed with the voltage drift during the battery charge.

The acquired data records are processed post-experimentally by FT, RFT and MRFT of second order. As it could be expected, the FT gives unreliable results with errors, which are frequency and phase dependent. The RFT and MRFT are producing similar estimates with very small differences - obviously the drift contains mainly linear term (un-known in advance). The RFT - produced diagram for the last decade of the measurement is given in Fig. 8. The impedance diagram is smooth, reliable and shows the real impedance of the battery in this very low frequency range, where the most interesting properties of the cathode intercalation are taking place.

The estimation of the impedance by using consecutive periods of the last frequency is showing the independence on time, which leads to the conclusion that the impedance is stationary during this measurement. This example shows again the property of RFT to filter efficiently a linear drift of the object voltage and confirms the applicability of the theory in real conditions.

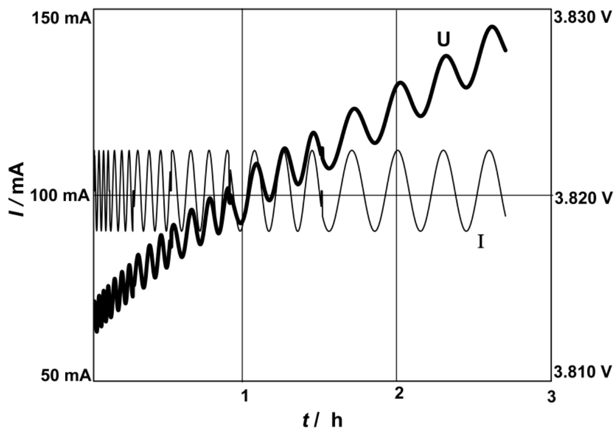


**Fig. 7.** Record of the current and voltage signals during the measurement of Li-ion battery 2000 mAh at charge with 100 mA. Frequency range 10 – 1 mHz, 5 points/decade, A.C. current amplitude 11 mA.

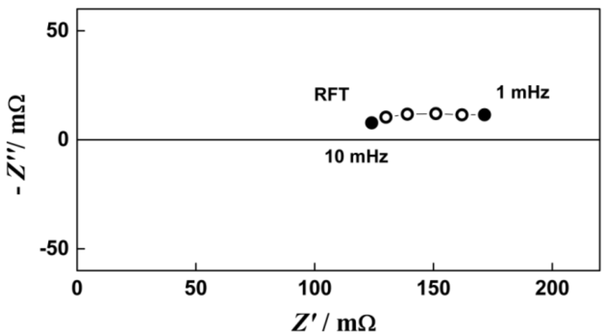


**Fig. 8.** Impedance diagrams produced by Rotating Fourier Transform of the data from Fig. 7. Frequency range 10 mHz to 1 mHz, 5 points/decade.

## DISCUSSION

New types of Fourier Transforms are developed. The classical Fourier Transform, the Rotating Fourier Transform and the Multiple Rotating Fourier Transforms form a consistent and full set of transforms of evolving in the time domain phenomena into the frequency domain. The general conclusion which can be derived is that the projection of time evolving phenomena into the frequency domain depends on the applied transform, which can have specific properties.

The RFT and MRFT keep the property of the classical FT in respect to periodic signals. The MRFT of order $\nu$ is orthogonal to all $n$ terms ($n = \nu$) of the aperiodic noise Taylor spectrum - the MRFT filtrates unconditionally all $n$ derivatives of this noise (voltage drift). Thus the RFT and MRFT are natural generalization of the Fourier Transform. They are keeping the continuity of its properties [10].

The newly developed transforms together with the classical FT are unidirectional operators. As the FT, the RFTs are filtrating unconditionally the zero term of the time-domain Taylor spectrum (constant value) of the signal under operation. The application of the back transforms can not restore the filtrated initial constant value and its time - derivatives. Other mathematical tools should be applied for that. The multiple integrals (8, 10) are of a specific type - every next integration is a circulation with respect to the parameter (initial phase) of the previous one, which is not conventional.

The first real experimental application of RFT, reported in this paper, shows the applicability of the new mathematical instrumentation and its robustness. The variations of the initial phase of the RFT of a single frequency record, produce impedance results with a very small phase differences ($\Delta < 0.25^o$), which confirms this robustness. The comparison between the estimates produced by RFT and MRFT ($\nu$=2) shows the quasi-linear nature of the present aperiodic noise.

From practical point of view the RFT operators could be used in many scientific and applied areas. The typical example is the measurement of the battery impedance during its operation (charge or discharge), when large parts of the active materials volumes participate in the studied processes. However many electrochemical fields like corrosion, passivation, AC polarography and others can successfully apply the RFT for improvement of their precision and for enlargement of their applicability. Other scientific fields in physics, geophysics and material science could also gain from this novel mathematical tool. Areas of a special interest are the studies of non-stationary impedances - the situations when the impedance of the object is changing during the period of the single frequency measurements. In this case a multiplicative aperiodic noise can be defined [8]. In general, the amplitude and the phase can be also functions of time:

$$Z(\omega, t) = A_0 (1 + \alpha t + \beta t^2 + \cdots) e^{\{-i\omega t + \varphi(t)\}}, \tag{11}$$

where the terms $\alpha, \beta, \ldots$ form again a Taylor spectrum and can be treated by the RFT tools. Preliminary studies carried out on this subject have shown that the RFT filtrates orthogonally the linear multiplicative term. Thus the RFT can estimate the real Instantaneous Impedance for every point inside a single frequency period [9 - 11, 13]. This is a significant progress of the notion of Instantaneous Impedance, given by Harkevich [12], where it is defined as the limit of the mean value of the impedances of series of periods, when their number tends to 1; or that defined by the 4-D method where single period measurements are used [14, 15]. This subject however is out of the frame of this paper and will be discussed elsewhere.

Having these properties, the RFT mathematical instrumentation can serve as a powerful engine for non-stationary impedance spectroscopy. The implementation of this new transform tool opens the exploration of the low and infra-low frequencies in impedance spectroscopy. Many interesting phenomena, specially in Li-ion batteries, can be measured precisely, supporting the understanding of the processes under investigation. The acquired results will booster the further improvement of those objects. The efficient implantation of the RFT into the 4-Dimentional technology will provide for intensive application of this methodology for battery studies, State of Charge and State of Health diagnostics.

An important feature of the proposed new mathematical instrumentation is the possibility for separation of the real time data recording from the post-experimental data processing. In this second stage different algorithms can be applied, resulting in a set of frequency domain images. The comparison of the results produced by FT, RFT and high levels MRFTs can provide for precise impedance measurements and in addition can supply objective information about the structure and values of the noises, present in the analyzed signals.

The fine details concerning the robustness, noise immunity and other properties of the RFTs as well as the optimal design of MRFT are targets of next investigations. In any case the development of marketable impedance analyzers from a new "4-Generation" (applying RFT and MRFT) can be expected in the near future. They will perform the standard FT and also RFTs (as option), and could be of open architecture type, providing the recorded data sets to the user for customized processing.

## REFERENCES

1. J. Fourier, Sur la propagation de la shaleure (1805 draft), Bibliotheque Nationale, Paris, MFF25252.
2. A. Papoulis, The Fourier Integral and its Applications, McGrow Hill Book Co. 1962.
3. R. B. Randall, Frequency Analysis, Bruel Kjaer, Naerum, 1977.
4. A. Oppenheim, Application of Digital Signal Processing, MIT, Mass.02139.
5. I. Gradshtein, I. Rizik, Tables of Integrals, Series and Products, ed. PM, Moskau, 1962.
6. Z. Stoynov, B. Savova-Stoynov, *J. Electroan. Chem.* **157**, 112 (1980).
7. Z. Stoynov, B. Savova-Stoynov, *J. Electroan. Chem.* **133.**183 (1985).
8. Z. Stoynov, Dissertation No7839, ETH Zurich, 1985.
9. B. Grafov, Z. Stoynov, V. Elkin, Electrochemistry, Moskau **25**, 1427(1989).
10. Z. Stoynov, B. Grafov, B. Savova-Stoynov, V. Elkin, Electrochemical Impedance, ed. Science, Moskau, 1991.
11. Z. Stoynov, Electrochimica Acta **37**, 2357 (1992).
12. A. Harkevich, Spectra and Analysis, ed. TTL, Moskau, 1957, 236.
13. Z. Stoynov, Electrochemistry, Moskau **29.1**, 43 (1993).
14. C.Julien, Z. Stoynov, Materials for Lithium-Ion Batteries, Kluver Academic Publishers, 1999.
15. Z. Stoynov, D. Vladikova, “Impedance Spectroscopy of Electrochemical Power Sources”, Encyclopedia of Electrochemical Power Sources, ed. Juergen Garche, Elsevier Ltd., UK, 2008.


## Ротираща Фурие трансформация - двигател на нестационарната импеданснa спектроскопия


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**Обяснителни бележки:** През последната година от своя активен научен живот Здравко Стойнов работи интензивно както теоретично, така и експериментално, за да демонстрира нагледно мощния си математически инструмент "Ротираща Фурие Трансформация" (РФТ). Той го описваше като "мощен двигател за нестационарна импедансна спектроскопия, който осигурява нови информационни възможности в диапазона на ниските и свръх-ниски честоти, където много значими и интересни явления, все още неоткрити, могат да бъдат прецизно измерени". Той очакваше в близко бъдеще появата на ново, "четвърто поколение" импедансни анализатори, използващи РФТ и МРФТ (Многократна РФТ). За да ускори идването на това "близко бъдеще", което да може да види, той работеше както по математическия инструмент, така и по експерименталната му проверка.

Представяме последния му ръкопис, така както е написан от него. Очакваме, че работата му по РФТ ще предизвика интерес и неговата идея за 4-то поколение импедансни анализатори ще срещне необходимата за реализирането й подкрепа. Отворени сме за сътрудничество, което да продължи работата на Здравко Стойнов.

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