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Electrochemical Noise Diagnostics: Analysis of Algorithm of Orthogonal Expansions[1]

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Abstract—The algorithm of orthogonal expansions is applied to the problem of extraction of diagnostic information from random noise. It is shown that the spectral analysis of electrochemical noise can be performed by a unified algorithm regardless of the type of orthogonal expansion used. A multi-channel indicator of color of electrochemical noise can be constructed on the basis of the orthogonal expansions. It is concluded that the algorithm of orthogonal expansions is an advantageous tool for noise monitoring and noise diagnostics of practically important electrochemical devices, including the devices of electrochemical energetics and systems of protection against corrosion.

Keywords: electrochemical noise, electrochemical energetics, electrochemical systems of protection against corrosion, electrochemical noise monitoring, electrochemical noise diagnostics

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INRODUCTION

The fluctuations in the electrochemical systems have a pronounced effect on the rate of all electrochemical processes [1]. The internal heat fluctuations determine the emergence of random fluctuations of electrical voltage and electrical current. Both fluctuations can be recorded with a sensitive device as the electrochemical noise. The electrochemical noise is caused by random (in the microscopic sense) electrochemical processes and carriers the information about the internal state of the electrochemical system. This fact is used in the noise methods of investigation of electrochemical systems and in the technologies of noise diagnostics of objects and devices of electrochemical energetics.

The main principle of electrochemical noise diagnostics can be explained by the following simple example. Assume that we have the results of long-term observations of fluctuations of electrical double layer charge, which were obtained by recording equilibrium fluctuations of electrode potential. Determining dispersion $\sigma^2(Q)$ of heat fluctuations of charge Q on the capacitance C of electrical double layer from the noise measurements and using equation (1) of Gibbs statistical thermodynamics

$$C = \frac{\sigma^2(Q)}{k_B T} \quad (1)$$

(where k_B is the Boltzmann constant and T is the temperature), the noise electrical double layer capacitance C can be estimated.

In this case, if two electrodes (an electrode, which operated for a long time, and a new electrode) are available, these electrodes can be distinguished by the noise electrical double layer capacitance and, thus, the electrochemical noise diagnostics of the electrodes can be performed.

In contrast to many other electrochemical diagnostic methods, the electrochemical noise diagnostics does not require the application of perturbations in the form of electric current or voltage onto the test system. This is the advantage of electrochemical noise diagnostics. Its drawbacks are very high requirements on the measuring instruments, the necessity of large number of experimental data, and rather complicated algorithms of diagnostic information extraction.

In this work, the attention focusses on the algorithm of spectral analysis, which is based on the theory of orthogonal expansions. Far from complete list of literature [1–19] reflects the interdisciplinary character

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of the methods of information extraction from random time series and electrochemical noise.

Below, the Chebyshev spectroscopy [2, 16, 18], the Schuster spectroscopy based on the Fourier transform [7] and the broad outlines of application of a system of discrete orthogonal functions [2–4, 6, 13–15] in the electrochemical noise diagnostics are briefly considered.

1. CHEBYSHEV NOISE SPECTROSCOPY

1.1. Chebyshev Expansion

The development of Chebyshev noise spectroscopy was induced by the necessity of eliminating linear trend and also high-order polynomial trend. A researcher deals with the digitized signal; therefore, the discrete Chebyshev polynomials are used in the Chebyshev noise spectroscopy.

The main specific feature of discrete Chebyshev polynomials is associated with their orthogonality. Let there be a set of N discrete Chebyshev polynomials $\{C_k(t,N),\ [k=0,1,2,\dots,N-1]\}$. Each polynomial is determined in N time points of discrete time interval $[t=0,1,2,\dots,N-1]$. The orthogonality property is expressed by the following equation:

$$\sum_{t=0}^{N-1} C_k(t,N)C_n(t,N)=0,\quad [n\neq k]. \tag{2}$$

Various normalizations of Chebyshev polynomials are available from the literature. Two of them are given below:

$$\sum_{t=0}^{N-1} C_k(t,N)C_k(t,N)=1, \tag{3}$$

$$\sum_{t=0}^{N-1} C_k(t,N)C_k(t,N)=\frac{(N+k)!}{(2k+1)(N-k-1)!}. \tag{4}$$

If normalization (3) is used, the system of Chebyshev polynomials $\{C_k(t,N)\}$ is designated as orthonormal.

Regardless of the type of normalization, any discrete realization of electrochemical noise $x(t,N)$ of duration N can be presented by a finite Chebyshev series:

$$x(t,N)=\sum_{k=0}^{N-1} X_k C_k(t,N), \tag{5}$$

where the expansion coefficients X_k are random values.

From (2), it follows that any polynomial $P_n(t,N)$ of degree n is orthogonal to the Chebyshev polynomial $C_k(t,N)$, if $n<k$. Therefore, if a trend is polynomial of order n, the higher coefficients of expansion of discrete noise signal X_k, starting from $k>n$, are free of the effect of trend.

1.2. Chebyshev Spectrum

Assume that the realization of noise signal consists of M sequentially arranged segments; each segment contains N points. Then, a set of expansion coefficients $\{X_k(m,M)\}$ containing M elements (one element per a segment) can be determined. Hereafter, we assume that the sample mean of noise signal analyzed is zero. This can be always achieved by simply subtracting the sample mean corresponding to the initial noise signal. By definition, the Chebyshev sample spectrum $X_k^{(2)}$ is equal to the sample mean of the squares of expansion coefficients $\{X_k(m,M)\}$:

$$X_k^{(2)}=\frac{1}{M}\sum_{m=0}^{M-1}[X_k(m,M)]^2. \tag{6}$$

In (6), the averaging is performed over the nonoverlapping segments. The recommendations on the application of also the overlapping segments are available from the literature.

The chief merit of Chebyshev spectroscopy is its ability to eliminate a polynomial trend of any order. The main drawback of Chebyshev spectroscopy is that the Chebyshev polynomials lack the scaling property: a Chebyshev polynomial of a certain order cannot be converted into a Chebyshev polynomial of another order by changing the internal scale, as it takes place, for example, in the Schuster spectroscopy with respect to the harmonic functions.

2. SCHUSTER SPECTROSCOPY

2.1. Schuster Periodogram (Expansion by Harmonic Orthogonal Functions) [7]

From the mathematical viewpoint, the method of Schuster periodograms is very close to the Chebyshev method. The matter is that both methods are based on the expansion of noise signal in terms of orthogonal system of functions. In the case of Schuster periodograms, a system of complex harmonic orthogonal functions $\{F_k(t,N)\}$ is used:

$$F_k(t,N)=\frac{1}{N^{1/2}}\exp(-j2\pi kt/N),\quad [t=0,1,2,\dots,N-1],\quad [k=0,1,2,\dots,N-1] \tag{7}$$

(j denotes imaginary unity).

The orthogonality property for functions $F_k(t,N)$ can be written as follows:

$$\sum_{t=0}^{N-1} F_n(t,N)F_k^*(t,N)=0\quad (k\neq n), \tag{8}$$

where $F_k^*(t,N)$ is the complex-conjugate function with respect to $F_k(t,N)$:

$$F_k^*(t,N) = \frac{1}{N^{1/2}}\exp(j2\pi kt/N),$$
$$(t = 0,1,2,\ldots,N-1),\quad (k = 0,1,2,\ldots,N-1). \tag{9}$$

The system of functions $\{F_k(t,N)\}$,which was determined in (7), is orthonormal:

$$\sum_{t=0}^{N-1} F_k(t,N)F_k^*(t,N) = 1. \tag{10}$$

At the same time, a system of orthogonal functions without a normalizing factor at the exponent is frequently used:

$$F_k(t,N) = \exp(-j2\pi kt/N),$$
$$(t = 0,1,2,\ldots,N-1),\quad (k = 0,1,2,\ldots,N-1). \tag{11}$$

In this case, in the right-hand side of normalizing equation, unity is replaced by N:

$$\sum_{t=0}^{N-1} F_k(t,N)F_k^*(t,N) = N. \tag{12}$$

2.2. Fourier Series

To distinguish clearly the Schuster spectra and the Chebyshev spectra, hereafter, the electrochemical noise realization is designated by $y(t,N)$ instead of $x(t,N)$. The Fourier series for the Schuster periodogram is written as a finite sum:

$$y(t,N) = \sum_{k=0}^{N-1} Y_k F_k(t,N). \tag{13}$$

2.3. Schuster Spectra

The expansion coefficients Y_k are random complex values. As before, assume that the complete realization of electrochemical noise contains M sequentially arranged segments, and each segment contains N points. In each segment numbered m, expansion (13) can be performed and its expansion coefficient $Y_k \equiv Y_k(m,M)$ can be obtained. Then, a Schuster spectral line of order k can be determined as a sample mean of the square of expansion coefficient Y_k modulus from (13):

$$Y_k^{(2)} = \frac{1}{M}\sum_{m=0}^{M-1} |Y_k(m,M)|^2. \tag{14}$$

As well as in the case of Chebyshev noise spectroscopy, in (14), the averaging can be performed over nonoverlapping or overlapping segments. We choose the nonoverlapping segments.

The main advantage of Schuster spectroscopy is its ideological affinity to the method of electrochemical impedance. The main drawback of Schuster spectroscopy is associated with the difficulties in eliminating the polynomial trend.

3. UNIFIED ALGORITHM OF ORTHOGONAL EXPANSIONS

3.1. Systems of Discrete Orthogonal Functions

For spectral treatment of electrochemical noise, one or another orthogonal system of functions can be chosen. The Chebyshev polynomials belong to the classical orthogonal polynomials of discrete variable. The orthogonal Hahn polynomials and orthogonal Kravchuk polynomials can be placed in the same group. In addition, it is known that the discrete derivatives of Chebyshev polynomials, Hahn polynomials, and Kravchuk polynomials also form the systems of discrete orthogonal functions [2]. Lastly, a large class of discrete orthogonal functions can be formed on the basis of the orthogonal wavelets [3, 4, 13]. This causes us to analyze a general computational scheme for the spectral treatment of electrochemical noise, without specifying a type of discrete orthogonal function system.

3.2. Orthonormal System of Functions of Discrete Variable

Let there be a system $\{G_k(t,N)\}$ of N orthonormal functions of discrete variable t [$t = 0, 1, 2, \ldots, N-1$]. The property of orthonormality is given by the matrix equation:

$$\sum_{t=0}^{N-1} G_k(t,N)G_n^*(t,N) = \delta_{kn},$$
$$[k = 0,1,2,\ldots,N-1];\quad [n = 0,1,2,\ldots,N-1], \tag{15}$$

where δ_{kn} is the Kronecker delta. In addition to equation (15), the orthonormality of the system of functions $\{G_k(t,N)\}$ means that one more matrix equation is fulfilled:

$$\sum_{k=0}^{N-1} G_k(t,N)G_k^*(\tau,N) = \delta_{t\tau}. \tag{16}$$

In equation (16), the summing is performed by the number of orthogonal function.

3.3. Orthogonal Expansion

Let there be a realization of electrochemical noise $r(t)$, which consists of M sequentially arranged segments. Each m^{th} [$m = 0, 1, 2, \ldots, M-1$] segment contains N reference points.

Let us present the realization of electrochemical noise $r(t,m)$ on the m^{th} segment as the expansion in terms of orthogonal system of functions $\{G_k(t,N)\}$:

$$r(t,m) = N^{1/2}\sum_{k=0}^{N-1} R_k(m)G_k(t,N). \quad (17)$$

The expansion coefficients $R_k(m)$ are random values. They can be determined by the following equation:

$$R_k(m) = \frac{1}{N^{1/2}}\sum_{t=0}^{N-1} r(t,m)G_k(t,m). \quad (18)$$

As earlier, assume that the realization of electrochemical noise is reduced to zero mean value:

$$\frac{1}{MN}\sum_{m=0}^{M-1}\sum_{t=0}^{N-1} r(t,m) = 0. \quad (19)$$

3.4. Spectrum of Electrochemical Noise

Let the orthogonal expansion spectrum be determined as the sample mean of the square of expansion coefficients $R_k(m)$:

$$R_k^{(2)} = \frac{1}{M}\sum_{m=0}^{M-1} (R_k(m))^2. \quad (20)$$

Let (20) be related to the sample value of electrochemical noise dispersion $\sigma^2(r(t))$. From (15)–(20), a very important equation (the Plancherel equation) is obtained:

$$\sigma^2(r(t)) = \sum_{m=0}^{M-1} R_k^{(2)}. \quad (21)$$

It is seen that the sample dispersion of electrochemical noise realization is equal to the sum of all intensities $R_k^{(2)}$ of orthogonal expansion spectrum. It should be emphasized that equation (21) is of exact character.

3.5. Estimation of Color of Electrochemical Noise

In the case of white noise, the intensities of all noise spectrum lines are identical:

$$R_k^{(2)} = \frac{\sigma^2(r(t))}{N}. \quad (22)$$

Therefore, the application of noise spectra of different orthogonal systems can form the basis of multi-channel system for recognizing the color of electrochemical noise.

CONCLUSIONS

(1) The spectral analysis of random time series provides a powerful tool for the nondestructive control of internal state of devices of electrochemical energetics and various technically important electrochemical systems [5, 8–11, 17].

(2) The spectral analysis of electrochemical noise can be performed by a unified algorithm regardless of the type of used discrete orthogonal expansion, including the Fourier expansion (Schuster periodogram), Chebyshev expansion, Hahn expansion, Kravchuk expansion, or wavelet expansion.

(3) The orthogonal discrete expansions can be used simultaneously in the multi-channel system of spectral analysis.

(4) For white noise, the spectra of orthogonal discrete expansions are identical. Therefore, a multichannel indicator of color of electrochemical noise can be developed.

(5) The Chebyshev orthogonal discrete expansion allows one to eliminate polynomial trend of any order.

(6) The drawbacks of electrochemical noise spectroscopy are (a) the necessity of highly sensitive measuring instruments and (b) rather complicated methods of extraction of diagnostic information from the electrochemical noise data, including the methods of processing, which are based on the orthogonal discrete expansions of noise signal.

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