Bulgarian Chemical Communications, Volume 49 Special Issue C (pp. 102 – 105) 2017

Chebyshev’s noise spectroscopy for testing electrochemical systems

B. Grafov*, A. Klyuev, A. Davydov**, V. Lukovtsev

A. N. Frumkin Institute of Physical Chemistry and Electrochemistry of Russian Academy of Sciences, Moscow, Russia

Received December 7, 2016 Revised January 11, 2017

The electrochemical noise spectroscopy based on the orthonormal Chebyshev’s polynomials of discrete variable is presented. Chebyshev’s noise spectroscopy has an important advantage. The majority of Chebyshev’s spectral lines is stable with respect to a drift of electrochemical noise. This property of Chebyshev’s noise spectroscopy is demonstrated by the examples of electrochemical corrosion noise and the noise of lithium primary power source. Chebyshev’s noise spectroscopy can be used as a technique for non-destructive testing in various field of pure and applied electrochemistry including electrochemical energetics and electrochemical corrosion.

Key words: electrochemical noise, Chebyshev’s test spectroscopy.

INTRODUCTION

The electrochemical noise spectroscopy has great advantages [1-14]. Under the conditions of electrochemical noise spectroscopy, an electrochemical system is not subjected to any external electric impact. The internal state of electrochemical system does not change in the course of noise testing. The electrochemical noise spectroscopy has many areas of application, including the electrochemical corrosion processes and electrochemical energetics.

In many cases, the analysis of noise data is complicated by a drift of electrochemical noise, which can considerably distort the noise spectra [15-20].

The aim of this work is to present the electrochemical noise spectroscopy based on orthonormal Chebyshev’s polynomials of discrete variable [21, 22]. Chebyshev’s spectroscopy has an important advantage. The majority of discrete lines of Chebyshev’s noise spectrum are stable with respect to a drift of electrochemical noise [23, 24]. The stability of discrete lines of Chebyshev’s noise spectrum is demonstrated by the examples of electrochemical corrosion noise and the noise of lithium primary power source at the open circuit.

ALGORITHM OF DISCRETE CHEBYSHEV’S NOISE SPECTROSCOPY

Let us consider a random time series $y(t)$ containing $N \cdot M$ samples. A period of discretization of electrochemical noise signal is taken as a unit time. A random series $y(t)$ can be formed, for example, by using discrete measurements of open-circuit voltage of primary power source. A random time series $y(t)$ is divided into M segments $\{y_t^{(m)}\}$. The number of segment *m* takes all integer numbers from 0 to $M-1$ inclusive. Each segment contains N samples. Index t (the sample number inside a segment) takes all integer numbers from 0 to $N-1$

Let matrix P_{kt} be a square $N \times N$ matrix based on the system of orthonormal Chebyshev’s polynomials of discrete variable t $(t = 0,1,\dots,N-1)$. The subscript k of matrix P_{kt} indicates a degree of Chebyshev’s discrete polynomial $(k = 0,1,\dots,N-1)$. The information on the properties of Chebyshev’s polynomials of discrete variable is available from [21, 22].

The matrix product of the matrix P_{kt} by a random vector $y_t^{(m)}$ forms a set of random vectors $\{P_{kt}y_t^{(m)}\}$:

$$P_{kt}y_t^{(m)} = \sum_{t=0}^{N-1} P_{kt}y_t^{(m)} \qquad (1)$$

To each segment with number *m*, its own random vector $P_{kt}y_t^{(m)}$ corresponds. To obtain a discrete Chebyshev’s spectrum $Y_k^{(2)}$, a square of random vector (1) should be averaged over the entire set of segments:

$$Y_k^{(2)} = \frac{1}{M}\sum_{m=0}^{M-1}[P_{kt}y_t^{(m)}]^2 \qquad (2)$$

The sample intensity $Y_k^{(2)}$ of any spectral line k of Chebyshev’s spectrum was calculated by equation (2). In our experiments, the total number

---

To whom all correspondence should be sent:
E-mail: *grafov.boris@yandex.ru, **alexdavydov@yandex.ru

of samples $M \cdot N$ did not exceed 2^{18} and the segment length N did not exceed 16. The choice of relatively small values of N enabled us to obtain discrete Chebyshev's spectra (2), $Y_k^{(2)}$, with a high degree of averaging.

Fig. 1 shows the discrete Chebyshev's polynomial of the 15th degree, when $N = 16$. It is seen that the discrete Chebyshev's polynomials serve as a window [25, 26]. A modulus of the Chebyshev's polynomial in the center of segment has the largest value.

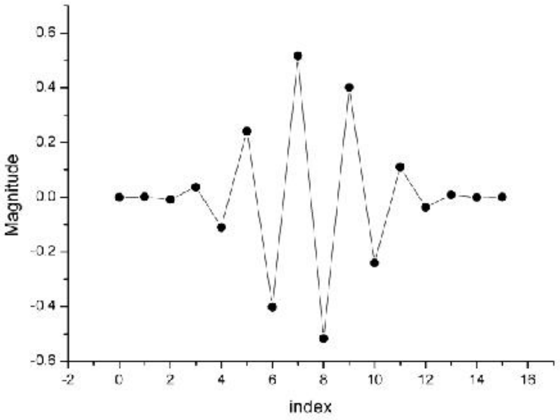

Fig. 1. Discrete Chebyshev's polynomial of 15th degree (N = 16).

STABILITY OF DISCRETE CHEBYSHEV'S SPECTRUM WITH RESPECT TO A DRIFT OF CORROSION NOISE

Figure 2 (curve A) shows a discrete realization of electrochemical corrosion noise. The discretization frequency was 45.5 Hz. The noise signal was measured with an IPC-Pro MF potentiostat (Russia). The realization $y_C(t)$ of electrochemical corrosion noise contained 2^{15} samples.

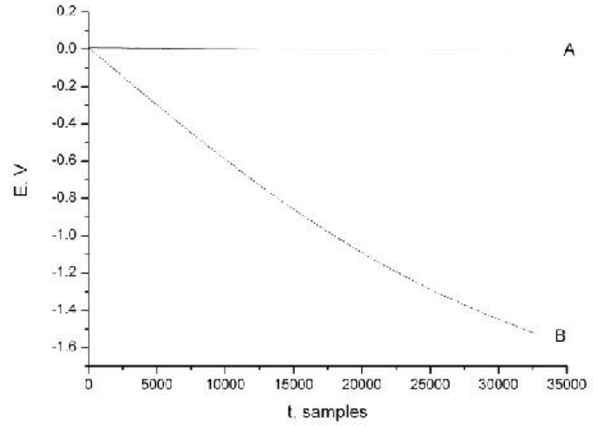

Fig. 2. (A) Electrochemical corrosion noise of a couple of identical NiMo16Cr15W electrodes $y_c(t)$ and (B) the same noise with added artificial drift $y_c(t) + y_c^{(d)}(t)$.

To check the stability of intensity of Chebyshev's spectral lines with respect to a drift of electrochemical noise, an artificial drift signal $y_C^{(d)}(t)$ was added to the realization $y_C(t)$:

$$y_C^{(d)}(t) = b_C \cdot \tanh(t / \tau_C), \qquad (3)$$

where b_C = -2 V and $\tau_C = 2^{15}$. Figure 2 (curve B) shows the total signal $y_C(t) + y_C^{(d)}(t)$, (the realization plus an artificial drift).

Figure 3 (A) shows the discrete Chebyshev's spectrum $Y_k^{(2)}$ of corrosion noise signal $y_C(t)$ calculated by equation (2) ($N = 8$). Curve B (Fig. 3) shows the discrete Chebyshev's spectrum of the total signal $y_C(t) + y_C^{(d)}(t)$. It is seen that the dependences A and B (Fig. 3) almost coincide at all spectral lines except for lines $k = 0$ and $k = 1$. When an artificial trend (3) is added, the intensity of the first spectral line of Chebyshev's spectrum increased by 35 times. It is seen that the intensity of high spectral lines starting from the line $k = 2$ of Chebyshev's spectrum is stable with respect to a drift of electrochemical corrosion noise.

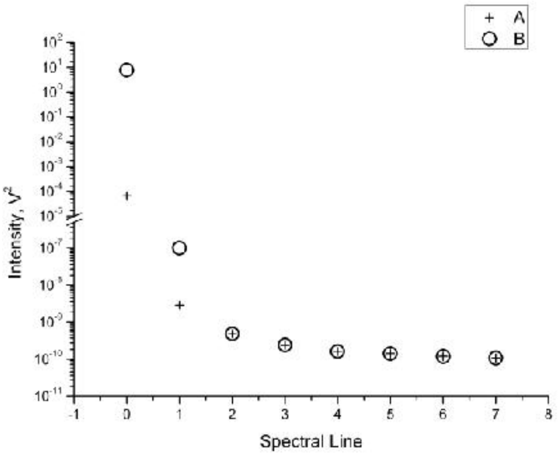

Fig. 3. Discrete Chebyshev's spectra of (A) electrochemical corrosion noise of a couple of identical NiMo16Cr15W electrodes $y_c(t)$ and (B) the same noise with added artificial drift $y_c(t) + y_c^{(d)}(t)$.

STABILITY OF DISCRETE CHEBYSHEV'S SPECTRUM WITH RESPECT TO A DRIFT OF CORROSION NOISE OF LITHIUM PRIMARY POWER SOURCE

The fluctuating voltage $y_L(t)$ (Fig. 4, curve A) of uncharged lithium primary power source LS-33600 (Saft) (17 A h) was recorded with a spectrometer of electrochemical noises (Frumkin Institute of Physical Chemistry and Electrochemistry, RAS). The discretization frequency of noise signal was 25 Hz. The noise signal realization contained 2^{13} samples. To demonstrate the stability of Chebyshev's spectrum with respect to a drift of electrochemical noise, an artificial drift signal $y_L^{(d)}(t)$ was added to the curve A (Fig. 4):

$$y_L^{(d)}(t) = b_L \cdot \tanh(t / \tau_L) \qquad (4)$$

where $b_L = 0.2$ V and $\tau_L = 2^{13}$.

The total signal $y_L(t) + y_L^{(d)}(t)$ is shown on Fig. 4, curve B.

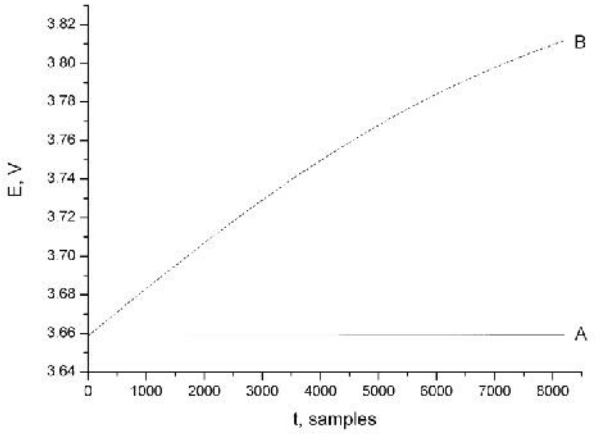

Fig. 4. (A) Noise of lithium primary power source LS-33600 $y_L(t)$ and (B) the same noise with added artificial drift $y_L(t) + y_L^{(d)}(t)$.

Figure 5 gives the Chebyshev's spectra ($N = 8$) for noise signal $y_L(t)$ of lithium primary power source (A) and for the total noise signal a $y_L(t) + y_L^{(d)}(t)$ (B). The Chebyshev's spectra were calculated by equation (2).

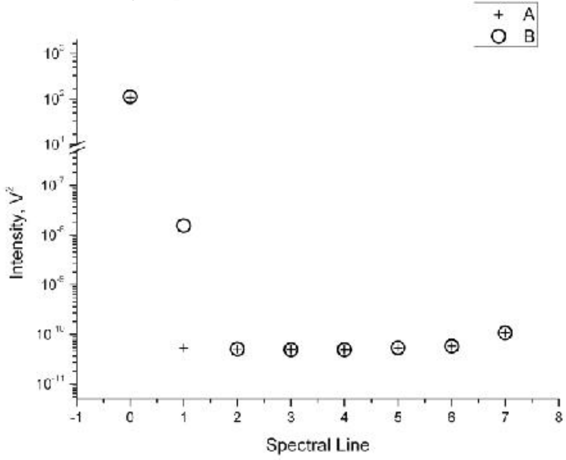

Fig. 5. Discrete Chebyshev's spectra of (A) noise of lithium primary power source LS-33600 $y_L(t)$ and (B) the same noise with added artificial drift $y_L(t) + y_L^{(d)}(t)$.

Figure 5 shows that the intensities of spectral lines $k = 2,3,4,5,6,7$ for dependences A and B virtually coincide. The Chebyshev's spectra are stable to a drift of electrochemical noise. The exceptions are the spectral lines $k = 0$ and $k = 1$. The intensities of these lines are rather sensitive to the drift of electrochemical noise. When an artificial trend (4) was added, the intensity of the first spectral line ($k = 1$) of Chebyshev's spectrum increased by 291 times.

CONCLUSIONS

The electrochemical Chebyshev's noise spectroscopy is a powerful tool for gaining the information on the internal state of electrochemical systems without imposing an external electrical signal. The intensities of spectral lines, starting from the second spectral line of Chebyshev's spectrum, are stable against a drift of electrochemical noise.

Sustainability of discrete Chebyshev spectrum to a strong drift of electrochemical noise is the basis for reliable noise monitoring of electrochemical systems. Moreover, the sustainability of discrete Chebyshev spectrum allows one to investigate the structure of electrochemical noise. The structural description of noise of electrochemical systems can be used for their monitoring.

We can perform the discrete spectrum analysis of electrochemical noise with a strong drift by using the transformations of other type. The transformations include the discrete wavelet transformation [9] and the discrete Fourier transformation with special windows [25-26]. We believe that the Stoynov rotating transformation [27] can be useful for spectral analysis of electrochemical noise with a strong drift. A comparison between the spectral properties of discrete Chebyshev transformation and the spectral properties of the discrete transformations outlined above is outside the scope of the present paper. The authors hope to discuss this topic elsewhere.

The Chebyshev's noise spectroscopy is appropriate for soft testing of electrochemical systems. The soft testing, i.e. testing without imposing an external electrical signal, is especially important for the devices and systems of electrochemical energetics and the electrochemical corrosion systems.

Acknowledgements. *We are grateful to Daria Vladikova, Visnja Horvat-Radosevic, and Tamas Pajkossy for their kind invitation to present a paper for a special issue of the journal Bulgarian Chemical Communications devised by the*

Bulgarian Electrrochemical Society to honor Prof. Zdravko Stoynov.

This work was supported by the Russian Foundation for Basic Research, project no. 16-29-09375.

REFERENCES

1. V. A. Tyagai, *Elektrokhimiya*, **3**, 1331 (1967).
2. W. P. Iverson, *J. Electrochem. Soc.*, **58**, 617 (1968).
3. B. M. Grafov, V. G. Levich, Soviet *Journal of Experimental and Theoretical Physics*, **27**, 507 (1968).
4. M. Fleischmann, J, W. Oldfield, *J. Electroanalyt. Chem.*, **27**, 207 (1970).
5. G. C. Barker, *J. Electroanalyt. Chem.*, **39**, 484 (1972).
6. I. Epelboin, C. Gabrielli, M. Keddam, L. Raillon, *J. Electroanalyt. Chem.*, **105**, 389 (1979).
7. P. C. Searson, J. L. Dawson, *J. Electrochem. Soc.*, **135**, 1908 (1988).
8. S. Martinet, R. Durand, P. Ozil, P. Leblanc, P. Blanchard, J. *Power Sources*, **83**, 93 (1999).
9. A. Aballe, M. Bethencourt, F. J. Botana, M. Marcos, *Electrochim. Acta*, **44**, 4805 (1999).
10. A. Hassibi, R. Navid, R. W. Dutton, T. H. Lee, *J. Appl. Phys.*, **96**, 1074 (2004).
11. R. A. Cottis, *Russ. J. Electrochem.*, 42, 497 (2006).
12. S. F. Timashev, Y. S. Polyakov, *Fluct. Noise Lett.*, **7**, R15 (2007).
13. C. A. Loto, I*nt. J. Electrochem. Sci.*, **7**, 9248 (2012).
14. P. S. Singh, S. G. Lemay, *Anal. Chem.*, **88**, 5017 (2016)
15. F. Mansfeld, Z. Sun, C. H. Hsu, A. Nagiub, *Corr. Sci.*, **43**, 341 (2001).
16. U. Bertocci, R. P. Nogueira, P. Rousseau, *Corrosion*, **58**, 337 (2002).
17. H. Ashassi-Sorkhabi, D. Seifzadeh, *J. Appl. Electrochem*., **38**, 1545 (2008).
18. M. Ohanian, V. Martinez-Luaces, V. Diaz, J. *Corros. Sci. Eng.*, **13**, 52 (2010).
19. A. M. Homborg, T. Tinga, X. Zhang, E. P. M. van Westing, P. J. Oonincx, J. H. W. de Wit, *Electrochim. Acta*, **70**, 199 (2012).
20. S. S. Jamali, D. J. Mills, *Prog. Org. Coat.*, **95**, 25 (2016).
21. A. V. Nikiforov, S. K. Suslov, V. B. Uvarov, Classical Orthogonal Polynomials of a Discrete Variable, Springer-Verlag, Berlin, Heidelberg, 1991.
22. N. Gogin, M. Hirvensalo, On the Generating Function of Discrete Chebyshev Polynomials, TUCS Technical Report No.819, TUCS, Turku, 2007.
23. M. G. Astaf'ev, L. S. Kanevskii, B. M. Grafov, Russ. *J. Electrochem.*, **43**, 17 (2007).
24. B. M. Grafov, Yu. A. Dobrovol'skii, A. D. Davydov, A. E. Ukshe, A. L. Klyuev, E. A. Astaf'ev, *Russ. J. Electrochem.*, **51**, 503 (2015).
25. J. Harris, *Proc. IEEE*, **66**, 172 (1978).
26. D. J. Thomson, *Proc. IEEE*, **70**, 1055 (1982).
27. Z. Stoynov, Fourier analysis in the presence of nonstationary aperiodic noise, Diss. Techn. Wiss. ETH Zürich, Nr. 7839, 1985.

СПЕКТРОСКОПИЯ НА ШУМ НА ЧЕБИШЕВ ЗА ТЕСТВАНЕ НА ЕЛЕКТРОХИМИЧНИ СИСТЕМИ

Б. Графов*, А. Клюев, А. Давидов**, Б. Луковцев

А. Н. Фрумкин Институт по физикохимия и електрохимия на Руската академия на науките, Москва, Русия

Постъпила на 7 декември 2016 г.; коригирана на 11 януари 2017 г.

(Резюме)

Представена е спектроскопия на основата на електрохимичен шум, която се базира на ортонормални полиноми на Чебишев с дискретна променлива. Спектроскопията на Чебишев има едно важно предимство - по-голяма част от спектралните линии на Чебишев са стабилни по отношение на дрейфа на електрохимичния шум. Това свойство на спектроскопията на Чебишев е демонстрирано с примери на електрохимичен шум при корозия, както и при шум в литиев първичен елемент. Шумовата спектроскопия на Чебишев може да се използва като техника за безразрушително тестване в различни области на чистата и приложна електрохимия, включително в електрохимичната енергетика и електрохимичната корозия.