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ORIGINAL PAPER

Analysis of discrete spectra of electrochemical noise of lithium power sources

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Abstract
The Fourier, Daubechies, and Chebyshev transforms are used to analyze discrete spectra of electrochemical noise of lithium power sources under the open-circuit conditions. In the absence of trend of open-circuit voltage, all three approaches lead to similar estimates of intensity of discrete spectra of electrochemical noise of lithium power sources. A trend of open-circuit voltage has different effects on the Fourier, Daubechies, and Chebyshev spectra. The Fourier spectrum is most sensitive to a trend of open-circuit voltage; the Chebyshev spectrum is most resistant to the trend. The Daubechies spectrum occupies an intermediate position between the Fourier spectrum and the Chebyshev spectrum in the resistance to the trend of open-circuit voltage.

Keywords Lithium power sources · Electrochemical noise · Trend of open-circuit voltage · Fourier discrete noise spectra · Daubechies discrete noise spectra · Chebyshev discrete noise spectra

Introduction

All electrochemical systems are characterized by fluctuations of voltage and current, the electrochemical noise that reflects the system's state and the processes proceeding in the system. Therefore, the electrochemical systems can be studied by measuring and analyzing their noise [1–5]. The method of electrochemical noise does not require any disturbance of electrochemical system by external probing signals, even such low signals as in the impedance measurements. The noise can be measured using relatively simple and low-cost equipment.

The state of lithium power sources, primarily, a degree of discharge, can be analyzed using the electrochemical noise spectroscopy [6–12].

A specific feature of electrochemical objects, in particular, lithium power sources, is the trend of measured open-circuit voltage that distorts the noise spectrum [13–16].

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Various approaches are used to analyze the results of noise measurements. The goal of this work is to compare the Fourier, Daubechies, and Chebyshev approaches to the analysis of discrete spectra of electrochemical noise of lithium power sources. The effect of a high-level artificial trend on the discrete spectrum of electrochemical noise in the spaces of the Fourier, Daubechies, and Chebyshev orthogonal functions is analyzed. A rectangular window is used. The use of a non-rectangular window would disturb the orthogonality of the Fourier, Daubechies, and Chebyshev functions. The use of trend removal in the Fourier method would violate the correctness of the comparison of the Fourier method with the Daubechies and Chebyshev methods.

Experimental and computational procedures

The LS-14500 (SAFT, France) primary lithium thionyl chloride power sources were examined. Two lithium power sources were connected in opposite direction. The experimental setup contained a lodgement for two lithium power sources, EVAL-AD7177-2SDZ evaluation kit ("Analog Devices") based on precision 32-bit analog-to-digital converter, and a computer for recording, storage, and processing of data. The input amplifier had a gain of 100 in the bipolar mode. The input voltage range was from − 25 to + 25 mV. This measuring equipment was used for recoding the $y(t)$ time series of voltage fluctuations of two lithium power sources connected in opposite direction. The observation transient $y(t)$ contained $2^{15} = 32{,}768$ samples. The sampling frequency was 20 Hz. The time index of sample is denoted by t [$t = 0, 1, \ldots, (2^{15} - 1)$]. The time index t is the dimensionless time. Here, the time interval between two successive samples is taken to be a unit time. Below, the algorithms for estimating discrete Fourier, Daubechies, and Chebyshev spectra of random time series $y(t)$ are briefly described.

Algorithm for estimation of Fourier spectrum

In the Fourier discrete spectroscopy, the term "spectral line frequency" can be used instead of the term "spectral line number." In contrast to the Fourier complex exponents, the Daubechies functions and Chebyshev polynomials are not periodic functions. Therefore, we use a unified term "spectral line number."

The Fourier spectrum of random time series is obtained using a discrete complex exponential transformation [17–19]. The following algorithm is used for estimating a discrete spectrum of electrochemical noise realization $y(t)$. Any statistical analysis implies averaging. The higher is the averaging depth, the more reliable is the sample mean. A realization containing 2^{15} samples is divided into 2^{12} non-overlapping sequential segments. Then, each segment contains 8 sequential samples. In each segment, the discrete Fourier transformation is performed using a set of 8 complex exponential functions. We obtain 8 Fourier transforms. In each segment, the module of Fourier transform is squared yielding the Schuster periodogram [20]. Then, following [21], the Schuster periodogram is averaged over 2^{12} segments. As a result, we obtain the discrete Fourier spectrum of electrochemical noise at a transformation depth of 8 and an averaging depth of 2^{12}. A segment of eight points provides reliable averaging of Schuster periodogram by the Burtlett method. The use of segments with a larger length leads to a decrease of the averaging depth.

The algorithm used can be presented in the analytical form. The kth complex exponent determined on the segment containing 8 points is denoted by $Fk8(\tau)$. The values of electrochemical noise within a segment with number m are denoted by $y(m + \tau)$, where $\tau = 0, \ldots, 7$ and $m = 0, \ldots, (2^{12} - 1)$. The operation of averaging over all 2^{12} segments is denoted by angle brackets ‹…›. Then, the intensity of the kth spectral line of Fourier spectrum ($FSk8$) can be written as follows:

$$FSk8 = \left\langle \left| \sum_{\tau=0}^{7} y(m+\tau)\cdot Fk8(\tau) \right|^2 \right\rangle \quad [\tau = 0, \ldots, 7; m = 0, \ldots, (2^{12}-1)] \qquad (1)$$

Here, the term in angle brackets is the Schuster periodogram,

$$Fk8(\tau) = \frac{1}{2\sqrt{2}} \exp\left(-2\pi j \frac{k\tau}{8}\right) \quad [k = 0, \ldots, 7] \qquad (2)$$

where $j = \sqrt{-1}$ is imaginary unit.

Algorithm for estimation of Daubechies spectrum

The algorithm for estimating the Daubechies spectrum is similar to that of the Fourier spectrum (1). Here, we use the realization of electrochemical noise with a zero mean. To pass from Eq. (1) to Eq. (3) for the Daubechies spectrum, 8 complex exponents $Fk8(\tau)$ should be replaced by 8 discrete Daubechies functions $Dk8(\tau)$ [$k = 0, \ldots, 7$]. Each Daubechies function $Dk8(\tau)$ can be presented as a vector $\vec{D}k8 = [Dk8(0), Dk8(1), \ldots, Dk8(7)]$ in the 8-dimensional space. Similarly, the 8-dimensional vector $\vec{y}8(m) = [y(m), y(m+1), \ldots, y(m+7)]$ is the realization of electrochemical noise within the segment with number m. Introducing a scalar product $\left(\vec{y}8(m), \vec{D}k8\right)$ of two 8-dimensional vectors $\vec{y}8(m)$ and $\vec{D}k8$, we obtain Eq. (3) for

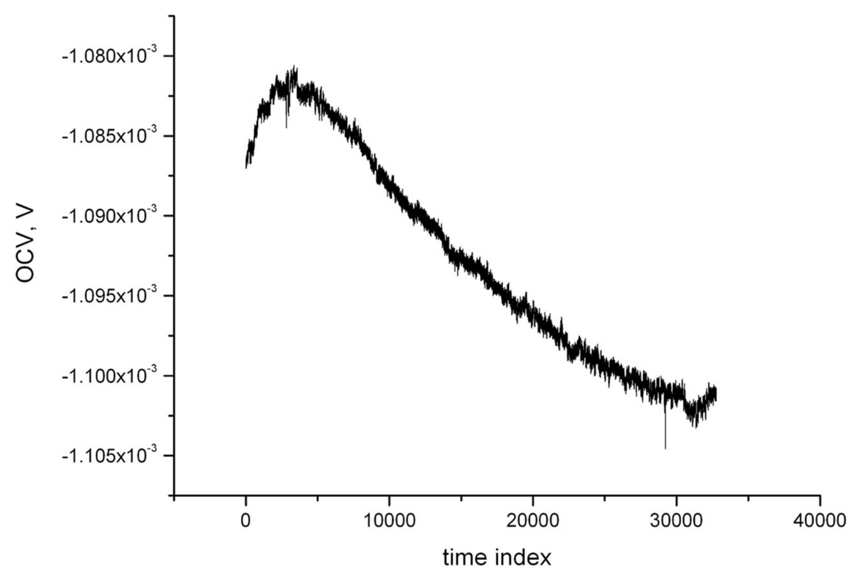

Fig. 1 Realization $y(t)$ of electrochemical noise of open-circuit voltage of two lithium power sources connected in opposite direction as a function of discrete time index t

the intensity of the kth spectral line $DSk8$ of Daubechies spectrum:

$$DSk8 = \left\langle \left(\overrightarrow{y}8(m), \overrightarrow{D}k8 \right)^2 \right\rangle \quad [k = 0, \ldots, 7; m = 0, \ldots, (2^{12}-1)] \quad (3)$$

A set of vector Daubechies functions $\overrightarrow{D}k8$ ($k = 0, \ldots, 7$) can be written via the Daubechies coefficients $h0$, $h1$, $h2$, $h3$, $h4$, $h5$, $h6$, $h7$ as follows [22]:

$$\begin{aligned}
4\sqrt{2}\overrightarrow{D}08 &= (h0, h1, h2, h3, h4, h5, h6, h7),\\
4\sqrt{2}\overrightarrow{D}18 &= (h6, h7, h0, h1, h2, h3, h4, h5),\\
4\sqrt{2}\overrightarrow{D}28 &= (h4, h5, h6, h7, h0, h1, h2, h3),\\
4\sqrt{2}\overrightarrow{D}38 &= (h2, h3, h4, h5, h6, h7, h0, h1),\\
4\sqrt{2}\overrightarrow{D}48 &= (h1, -h0, h3, -h2, h5, -h4, h7, -h6),\\
4\sqrt{2}\overrightarrow{D}58 &= (h7, -h6, h1, -h0, h3, -h2, h5, -h4),\\
4\sqrt{2}\overrightarrow{D}68 &= (h5, -h4, h7, -h6, h1, -h0, h3, -h2),\\
4\sqrt{2}\overrightarrow{D}78 &= (h3, -h2, h5, -h4, h7, -h6, h1, -h0)
\end{aligned}$$

Below, the Daubechies coefficients $h0$, $h1$, $h2$, $h3$, $h4$, $h5$, $h6$, $h7$ are written to three decimal places [22]:

$h0 = 0.230$, $h1 = 0.714$, $h2 = 0.630$, $h3 = -0.027$, $h4 = -0.187$, $h5 = 030$, $h6 = 032$, $h7 = -0.010$

Algorithm for estimation of Chebyshev spectrum

The Chebyshev polynomials of discrete variable are well described in the literature [23, 24]. The equations for estimating the 8-dimensional Chebyshev spectrum $CSk8$ of electrochemical noise can be obtained from Eq. (3) by replacing the Daubechies discrete functions $\overrightarrow{D}k8$ with the discrete Chebyshev polynomials $\overrightarrow{C}k8$ [25–28]:

$$CSk8 = \left\langle \left(\overrightarrow{y}8(m), \overrightarrow{C}k8 \right)^2 \right\rangle \quad [k = 0, \ldots, 7; m = 0, \ldots, (2^{12}-1)] \quad (4)$$

The discrete Chebyshev polynomials in the 8-dimensional space are as follows:

$$\begin{aligned}
\sqrt{8}\,\overrightarrow{C}08 &= (1, 1, 1, 1, 1, 1, 1, 1),\\
\sqrt{168}\,\overrightarrow{C}18 &= (-7, -5, -3, -1, 1, 3, 5, 7),\\
\sqrt{168}\,\overrightarrow{C}28 &= (7, 1, -3, -5, -5, -3, 1, 7),\\
\sqrt{264}\,\overrightarrow{C}38 &= (-7, 5, 7, 3, -3, -7, -5, 7),\\
\sqrt{616}\,\overrightarrow{C}48 &= (7, -13, -3, 9, 9, -3, -13, 7),\\
\sqrt{2184}\,\overrightarrow{C}58 &= (-7, 23, -17, -15, 15, 17, -23, 7),\\
\sqrt{264}\,\overrightarrow{C}68 &= (1, -5, 9, -5, -5, 9, -5, 1),\\
\sqrt{3432}\,\overrightarrow{C}78 &= (-1, 7, -21, 35, -35, 21, -7, 1)
\end{aligned}$$

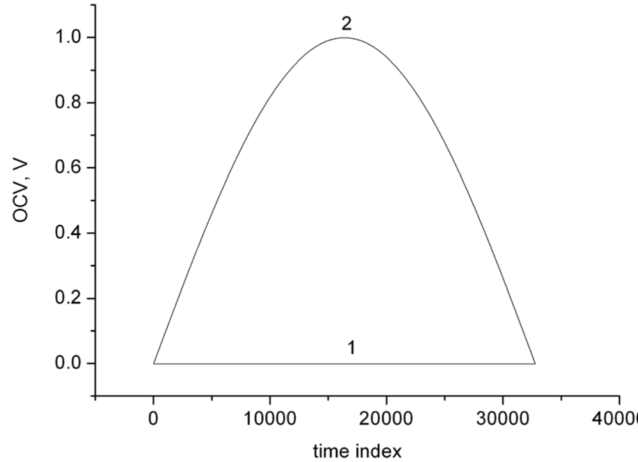

Fig. 2 (1) Realization $y(t)$ of electrochemical noise of open-circuit voltage of two lithium power sources connected in opposite direction and (2) the same realization with added strong artificial trend $[y(t) + TR(t)]$

The normalizing factor at each Chebyshev polynomial $\overrightarrow{C}k8$ provides the orthonormality of the system of discrete Chebyshev polynomials.

Results and discussion

Figure 1 shows a sample realization $y(t)$ of open-circuit voltage of two lithium power sources connected in opposite direction. A trend of electrochemical noise with a slope of order 10^{-8} V/s is clearly seen. In the noise measurements, a trend of realization $y(t)$ is almost always observed.

To attain the aim of the work, the effect of strong trend on the spectrum of electrochemical noise of two lithium power

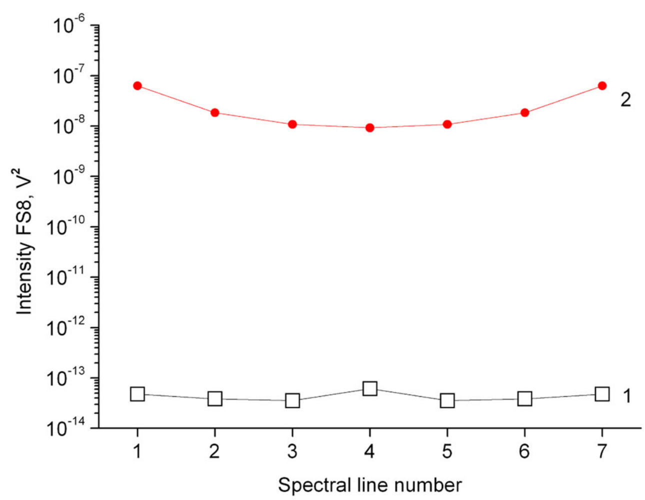

Fig. 3 Effect of artificial trend on the Fourier spectrum of electrochemical noise of two lithium power sources connected in opposite direction: (1) spectrum of electrochemical noise $y(t)$ and (2) spectrum of electrochemical noise with added artificial trend $[y(t) + TR(t)]$

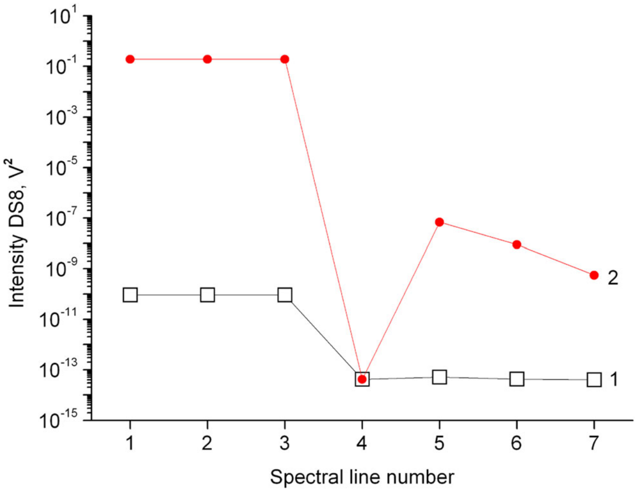

Fig. 4 Effect of artificial trend on the Daubechies spectrum of electrochemical noise of two lithium power sources connected in opposite direction: (1) spectrum of electrochemical noise $y(t)$ and (2) spectrum of electrochemical noise with added artificial trend $[y(t) + TR(t)]$

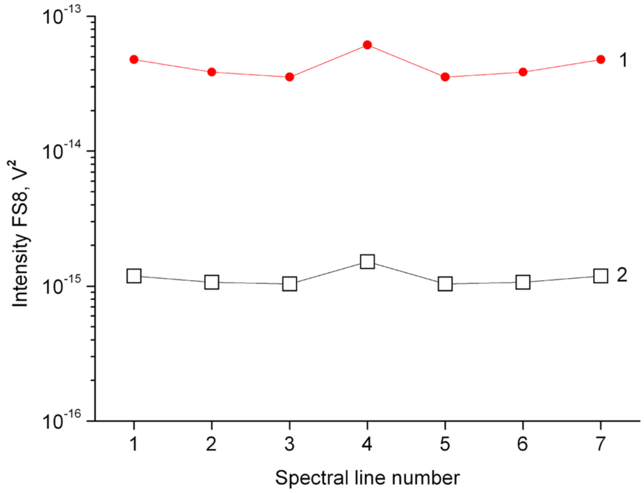

Fig. 6 Discrete Fourier spectra for (1) the electrochemical noise $y(t)$ and (2) the intrinsic noise of measuring setup in the short-circuit mode

sources connected in opposite direction should be studied. Therefore, an artificial trend $TR(t)$ in the form of a half of period of sinusoid (5) with amplitude $A = 1$ V was considered.

$$TR(t) = \sin\left(\frac{\pi t}{2^{15}}\right) \quad \left[t = 0, 1, \ldots, \left(2^{15}-1\right)\right] \tag{5}$$

Figure 2 shows the realization of open-circuit voltage of two lithium power sources connected in opposite direction with added strong artificial trend (5).

Figures 3, 4, and 5 show the effect of added artificial trend on the 8-dimensional Fourier, Daubechies, and Chebyshev spectra, respectively, of two lithium power sources connected in opposite direction. In all three transformations, zero spectral line in the plots is omitted, because this line is weakly resistant to the electrochemical noise trend and DC component of signal. It is seen that, under the conditions of weak trend (i.e., without adding a strong artificial trend), in principle, any of the spectra (Fourier, Daubechies, or Chebyshev spectra) can be used as the spectral characteristic of electrochemical noise of two lithium power sources connected in opposite direction

However, Figs. 3, 4, and 5 also show that a strong trend considerably distorts the spectra of electrochemical noise of lithium power sources. The Fourier spectrum undergoes the most serious distortions (Fig. 3). The Daubechies spectrum (Fig. 4) also suffers severely from a strong trend, except for the fourth spectral line *DS*48: its intensity appears to be resistant to a strong trend of electrochemical noise. In the

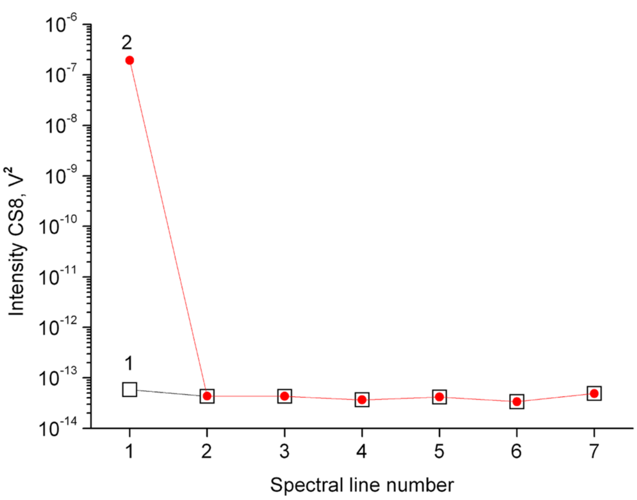

Fig. 5 Effect of artificial trend on the Chebyshev spectra of electrochemical noise of two lithium power sources connected in opposite direction: (1) spectrum of electrochemical noise $y(t)$ and (2) spectrum of electrochemical noise with added artificial trend $[y(t) + TR(t)]$

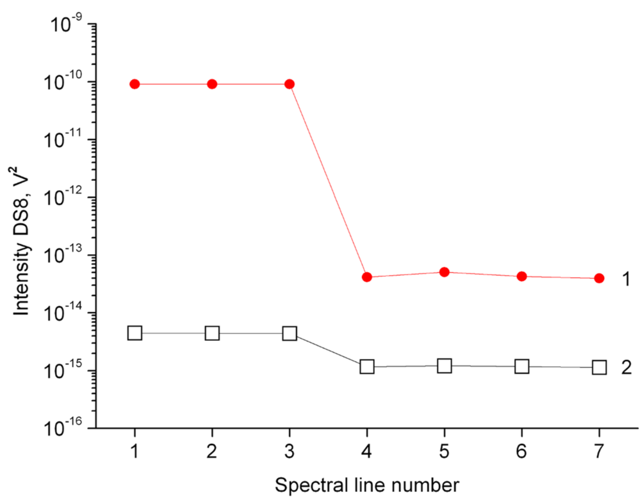

Fig. 7 Discrete Daubechies spectra for (1) the electrochemical noise $y(t)$ and (2) the intrinsic noise of measuring setup in the short-circuit mode

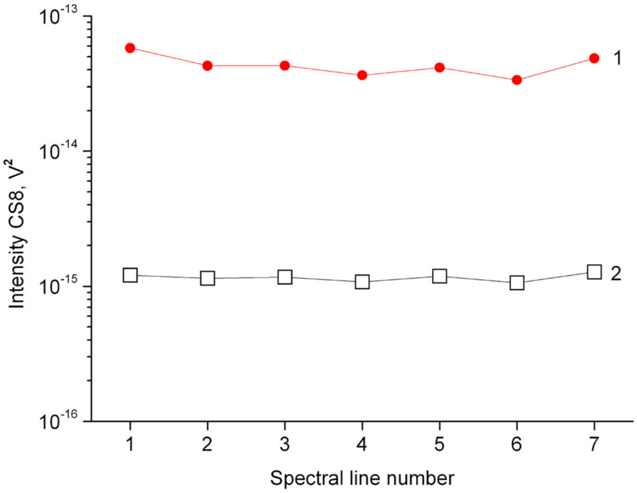

Fig. 8 Discrete Chebyshev spectra for (1) the electrochemical noise $y(t)$ and (2) the intrinsic noise of measuring setup in the short-circuit mode

Chebyshev spectrum (Fig. 5), 6 of 8 spectral lines (*CS*28–*CS*78) are resistant to a strong trend of electrochemical noise.

Figures 6, 7, and 8 show that the level of the Fourier, Daubechies, and Chebyshev discrete spectra of electrochemical noise is considerably higher than that of intrinsic noise of measuring setup in the short-circuit mode.

The experimental results show that the realization of fluctuations of open-circuit voltage of lithium power sources contain a trend. Using the method of artificial trend, it is found that all spectral lines of discrete Chebyshev spectrum (except for zero and first spectral lines) are resistant to the trend of electrochemical noise. The discrete Daubechies spectrum contains only one spectral line resistant to the trend of electrochemical noise. The discrete Fourier spectrum, which is based on the Schuster periodogram, contains no spectral lines resistant to the trend of electrochemical noise.

Conclusions

It is found that the discrete Fourier spectrum is most sensitive to the trend of electrochemical noise. The method of discrete Fourier spectra needs an additional operation of detrending of electrochemical noise.

The discrete Chebyshev spectrum is most resistant to the trend of electrochemical noise. The method of discrete Chebyshev spectra needs no additional operation of detrending of electrochemical noise.

The Daubechies spectrum occupies an intermediate position between the Fourier spectrum and the Chebyshev spectrum in the resistance to the trend of electrochemical noise.

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