

## Detrending and Other Features of Data Processing in the Measurements of Electrochemical Noise

E. A. Astafev<sup>a,\*</sup>, A. E. Ukshe<sup>a</sup>, L. S. Leonova<sup>a</sup>, R. A. Manzhos<sup>a</sup>, and Yu. A. Dobrovolsky<sup>a</sup>

<sup>a</sup>*Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, Moscow oblast, 142432 Russia*

\**e-mail: tdsipch@list.ru*

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**Abstract**—Measurements of electrochemical noise in solid-state electrochemical cells with a heteropoly-compound-based electrolyte are carried out. The noise power spectral density is calculated using various detrending methods. The impedance real component is calculated by means of the Nyquist formula. The results of the calculations are compared with the data obtained by the electrochemical impedance classical method.

**Keywords:** electrochemical noise, detrending, power spectral density, impedance real component, chemical power sources

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### INTRODUCTION

The electrochemical noise measurement method was used in the studying of chemical power sources long ago, in the mid-twenty century [1]. Since then, many researchers actively developed the method in their attempts of its using both for practical applications and in the constructing of theoretical models. In our opinion, Tyagai works [2, 3] stand out against a background of other experimental studies; those of Grafov [4, 5], among theoretical ones. In these works their authors made use of different approaches to the subtraction of the electrochemical system constant potential drift. It is to be noted that the drift correct subtraction is decisive in the interpretation of the electrochemical noise.

In his analysis of experimental data, Tyagai used the Nyquist formula for thermal noise [6] in the calculating of the real component of the impedance. For the liquid-electrolyte-based cells close fit of the data calculated from the electrochemical noise and those obtained by the electrochemical impedance method was obtained. Importantly, in these measurements noise signal was subjected to analog hardware preprocessing. In particular, in all works the analog filtering of the constant component was performed; in what follows, signal with the frequency exceeding several Hertz was analyzed using analog instruments [7]. Actually, in this case no additional data processing, such as the constant potential drift subtraction, was required.

Different approach was suggested by Grafov in his recent works. In the analysis of experimental data, he used the Chebyshev polynomials [8, 9]. The method

of Chebyshev orthogonal polynomial expansion was shown [10] to give more accurate mathematical restoration of the noise signal than the Fourier-transform-based method of the power spectral densities. The method's indubitable advantage is that it does not require additional stage of detrending (that is, the constant potential component drift elimination) because the trend information appears being implicated in lower polynomials and hence it purely is thrown away. However, to our view, a decisive restriction for the Chebyshev-polynomial-based approach is the absence of their explicit referencing to physical phenomena occurring in electrochemical systems under study. The same disadvantage is also inherent in wavelet transform actively used by numerous researchers in their mathematical description of the electrochemical noise [11, 12].

The above-mentioned approach to the electrochemical noise analysis using the power spectral density calculation has a prime advantage. In this case, spectra are calculated, that is, one obtains a frequency dependence that can be referenced to physical phenomena by using the fluctuation-dissipative theorem [13]. This allows, in its turn, calculating the impedance real component in the absence of direct current by using the Nyquist formula for thermal noise [6]:

$$\langle V^2 \rangle = 4k_B T R \Delta f, \quad (1)$$

where  $\langle V^2 \rangle$  is the noise root-mean-square amplitude,  $k_B$  is the Boltzmann constant,  $T$  is the absolute temperature,  $R$  is the resistance, and  $\Delta f$  is the frequency interval.

The impedance spectra analysis (the analysis of frequency dependences of the electrochemical impedance) is widely used in the studying of electrochemical systems, in particular, the chemical power sources. However, the current methods for the measuring of the electrochemical impedance require the using of external disturbing signal. This external signal (of sine or more complex form) should have minimal possible amplitude both for a nonlinear electrochemical system response linearization and for the system remaining unchanged by the external signal during the measurements, the more so, at lower frequencies. On the other hand, the using of small-amplitude signals requires the response filtering at a background of the system's intrinsic noise, which lowers the measurements' accuracy. In this situation, more perspective would be the obtaining of the impedance spectra without using any external signal, that is, by the analyzing of the electrochemical noise frequency dependence. In this case, it is the ever present exchange current thermal oscillation that plays the role of an inner signal with the minimal possible amplitude.

In addition, in the carrying out of classic impedance measurements, that is, upon the implying of external harmonic signal, hence, passing of alternating current able to change the electrochemical system, an additional method of controlling the measurements' correctness is required. Currently, only one such method is known, namely, the Boukamp method [14] for the controlling of the system's linearity and invariance during the measurements. The principle of the method consists in the checking-up of fulfillment of the Kramers–Kronig relations for the impedance measured. Thus, the determination of the impedance real component by the analyzing of the electrochemical noise spectral characteristics in a system under study can be used in the novel method for the controlling of the impedance spectra measurements' correctness.

On the other hand, the comparison with the results of the impedance measurements also can be used in the analyzing of the measured electrochemical noise. Electrochemical noise can comprise both thermal component (the Nyquist noise of the impedance real component) and some excessive noise related to long-term processes of the studied system evolution. To analyze the nature of this excessive noise basing on the measured data, the thermal noise should be subtracted. The latter can be obtained from the measured impedance real component by using formula (1).

One of the most important features of the method of power spectral densities is the using of the Fourier analysis that is deeply sensitive to the drift of the measured signal constant component. The drift somehow or other is practically always observed in the electrochemical system noise measurements. It is well known that wrong subtraction of the initial noise signal drift, called the detrending, can distort frequency spectrum

drastically [15, 16]. Its effect is particularly noticeable at lower frequencies. The most often used detrending methods are: linear and polynomial approximation, moving average method, and analog and digital filtration [15–18]. Some authors [15] draw attention to the necessity of the using of window function, different from a rectangle one, immediately prior to the performing of the Fourier analysis.

It is concluded in numerous works [15, 18, 19] on the successive applying of the polynomial-based detrending. This fact has no explanation, however. To our view, the using of polynomials with order exceeding unity cannot be substantiated because they do not describe any of the physical or other type processes occurring in any electrochemical system. The main advantage of the first-order-polynomial, that is, linear approximation is that it can be related to the certain physical phenomenon, i.e., increase in the voltage at a capacitor plates (for example, in electrical double layer) during its charging with constant current. This occurs in galvanostatic regime or under the action of the leakage current in the measuring instrument (the potentiostat) during the potential measuring. The absence of referencing of some or other mathematical operation carrying out during the noise data processing to any physical phenomenon in a system under study can have unpredictable consequences and, as a result, lead to ambiguous and irreproducible impairment of computational result. Occurrence of periodical splashes (artifacts) resulting from the Runge phenomenon is also possible [20]. Such effects have been reported in literature [21].

One of the simplest and intuitively understandable detrending methods is the moving average method. Its apparent advantage is ease of application and moderate requirements to the calculation power. Moreover, the method has no referencing to physical features of systems under study; and yet, the potential successfulness of its application might be explained by the same prerequisites as for any other statistical approach, for example, the calculation of root-mean-square deviation of potential or current noise, with subsequent resistance determination thereof.

Different types of analog and digital filters often lead to close results. The choice of the best filter to be used in a particular case mainly depends on the instrumental organization of the measurements. It should be noted that the analog filtration method often appears physically necessary due to design philosophy of the measurement instrumentation. For example, electrochemical noise of unit sample of a chemical power source cannot be measured at an adequate accuracy or resolution without the subtraction of the constant component. So, in numerous works in the field the measurements were mainly carried out using capacitor filters [22–24], as well as transformer ones [25]. Therefore, to our view, these detrending methods cannot be ruled out, but one must be aware of the possible

consequences of their application and be able using the methods adequately in low-frequency region where time constants can be as long as tens of minutes. In the latter case, it is important to pay due attention to the finishing of transients in the filter, as it took place in the Tyagai works [2, 3, 26–28], where bare time was added prior to the measurements, which exceeded the time constant of the filter significantly [2, 3].

Despite the fact that a great deal of works on the detrending during the electrochemical noise processing has been published, their main part is focused on corrosion measurements. Only some of them contain rigorous logically completed analysis of systems under study, resulting in quantitative characteristics that can be impartially compared with results obtained by using other well-known electrochemical methods, in particular, electrochemical impedance spectroscopy and dc measurements. Unfortunately, no choice of a definite detrending is possible if a result obtained thereby cannot be compared with an a fortiori known and reliably determined characteristic of the studied system. Otherwise, the comparing of results assignable by different detrending methods is largely subjective.

The systematic studies of Tyagai [2, 3, 26–28] are an absolute exclusion. However, they are many decades old and were carried out using analog instruments. Moreover, they do not touch upon such features of the modern digital signal processing like the detrending, Fourier analysis, and other methods of the mathematical data processing. While discussing the detrending methods it should be noted that in the above-mentioned works, the constant component was removed by using analog *RC*-filters.

Authors of some works on electrochemical corrosion (see, e.g., [29]) attempted determining the polarization resistance by analyzing current and potential noise registered simultaneously (by calculating the ratio of standard deviations of the current and potential noise at lower frequencies), aiming at an obtaining of objectively measured quantities. However, these calculations were carried out in the absence of any model of electrochemical system; therefore, they are potentially restricted because the connection between the behavior of the observed noise and the state of the system under study lies beyond the bounds of understanding.

The above-discussed and other methods of the electrochemical-noise statistical data manipulation, not connected with physical processes in electrochemical systems, are most concisely analyzed in several review-articles [30, 31].

Based on the above discussion, in this work we aimed at studying of rather simple and well predictable electrochemical objects by the electrochemical noise method, with the using of some routine methods of detrending and varying of the window function. This analysis allows choosing the most adequate set of pro-

cedures for the signal pre-processing, which potentially can be used in the studying of excessive noise in more complicated systems and the systems' state. An important task is validation of the author's instrumentation and the measuring unit, as well as the choosing and checking-up of applicability of all mathematical procedures used in the calculating of the spectral power density of the electrochemical noise.

Besides, of great basic interest is the answering of the question whether it is possible to measure the impedance real component reliably in the region of diffusion impedance in the absence of external source of ac excitation. Indeed, in the case of the using of classic electrochemical impedance spectroscopy the object under study is disturbed from equilibrium condition, and diffusion flows occur therein. While in the case of the electrochemical noise potentiometric measurements the object under study is not disturbed by alternating current and actually remains in its steady state.

One more critical goal of this work is the comparison of the results obtained from electrochemical noise with true data of electrochemical impedance spectroscopy, a well-developed electrochemical method.

To execute the above-listed goals, we performed measurements in two electrochemical cells. The impedance real component was calculated by the Nyquist formula (1) from the power spectral density of measured electrochemical noise. The spectrum of the impedance real component thus obtained was compared with the data obtained from impedance measurements. Prior to the noise power spectral density calculations, different methods of detrending were applied; the calculated resistances were compared with the impedance real component.

## EXPERIMENTAL

### *The Experimental Setup*

We used a home-developed NM-4 instrument [32] for the measuring of electrochemical noise, jointly made with the Electrochemical Instruments Company (Russia). It is based on an analog-to-digital converter with large resolution and a low-noise high-resistance preamplifier. The preamplifier gain coefficient was equal to 100. The analog to digital converter actual resolution exceeded 24 bit. At the chosen gain coefficient the input voltage measurement range was  $-24$  to  $+24$  mV; discreteness, less than 3 nV, that is, no more than  $2 \Omega$  being recalculated into thermal resistance noise in the maximal frequency band of 250 Hz.

The instrument was shielded carefully. To this purpose, a printed-circuit board with electronic components was placed into molded aluminum box with 2 mm-thick walls. Another aluminum box was screw-attached to the first one; and an electrochemical sample under study was placed therein. The boxes had common wall with an opening that ensured all cables

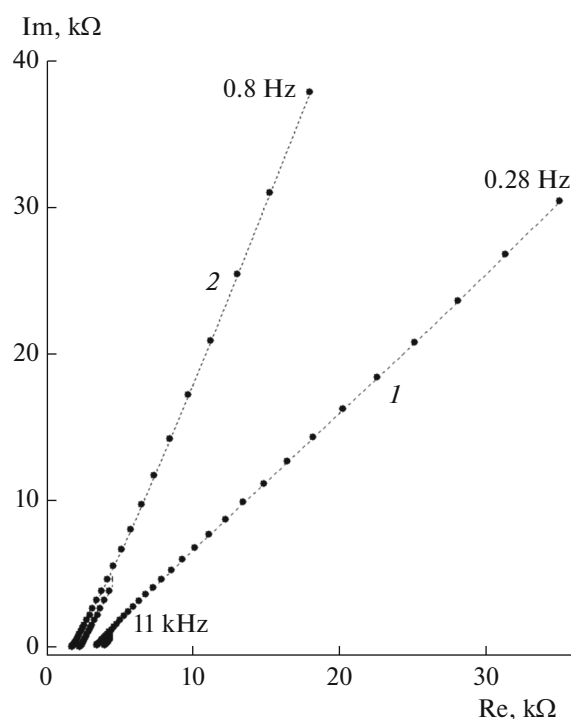


Fig. 1. Impedance diagrams of electrochemical cells I (1) and II (2).

and components remaining strictly inside the measuring boxes. The entire assembly was locked in a steel housing (a screen) with 1 mm-thick walls. Internal screens were mechanically damped by technical foam rubber, to diminish vibration. The measuring instrument and all components of the metal screens were earthed carefully. For the instrument-to-PC connec-

tion, a USB-bus was used. The data processing was carried out using specialized software jointly developed with the Electrochemical Instruments Company.

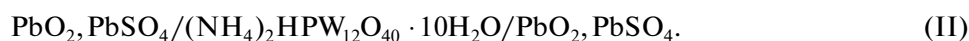
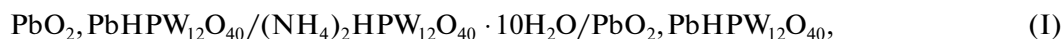
Prior to each experiment, the setup operating capacity checking-up and its zero calibration was performed as follows. At first, short-circuit input noise was measured. The measurement was carried out for the same time and at the same data rate as in the subsequent experiments. Then a constant resistor with a rating of 10 kΩ was connected to the input. We used a low-noise (with low noise factor) thin-film precision Yageo MFP-12BTC52 resistor accurate to 0.1%. The data obtained for the resistor were processed in the same way as for electrochemical cells; the calculated spectra were plotted on the same diagrams, to demonstrate the experiment purity. The setup intrinsic noise was subtracted upon the calculations of the power spectral density.

The electrochemical impedance was measured using an Elins P-40X potentiostat with a FRA-24M frequency analyzer (Electrochemical Instruments, Russia). The frequency operation range was 11 kHz to 0.1 Hz; the ac signal amplitude, 20 mV. All measurements were carried out at a temperature of 24°C.

#### Objects and Materials under Study

In this work, we used solid-state electrochemical cells, primarily, in order to simplify the studied objects' behavior and make it maximally predictable. In particular, we tried to exclude convective fluxes of all kinds, which potentially could be the sources of dynamic noise [33].

The following symmetrical electrochemical cells were the objects of the studies:



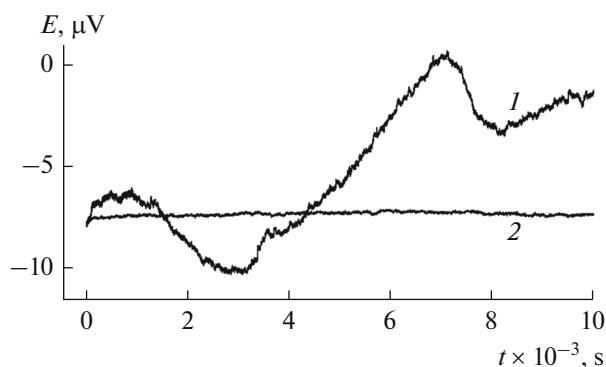
They were prepared from powders of the corresponding materials by sequential pressing under the pressure of 2 t/cm<sup>2</sup> in a Teflon cylinder (5 mm in diameter). The current collectors passed through titanium dies, with lead-outs through encapsulating stainless-steel sleeve, with a spring ensuring a permanent tightening in the course of the measurements.

The electrolyte material was mainly chosen because it has been thoroughly studied by us [34]; also, it is of great practical interest in connection with the designing of electrochemical devices, gas sensors, in particular [35]. One of the sensor's principal characteristics is its sensitivity that must be limited in practice, in particular, by the electrochemical noise. Therefore, it is quite reasonable to investigate electrochemical cells on the base of this material with the objective to study their excessive noise.

## RESULTS AND DISCUSSION

#### Electrochemical Impedance Measurements

We started our experiment with the measuring of the electrochemical impedance, in order to determine, knowing the instrumentation resolving power, whether the studied object's thermal noise appears measurable over the accessible frequency range. We see from Fig. 1 that it is possible to do by using the NM-4 instrument in the studied cells with the heteropolycompound-based electrolyte because the impedance under study is of the order of to units or tens of kΩs. The impedance was measured down to rather low frequency that still allows the comparing of the obtained data with that calculated from the electrochemical noise whose measurements by using our instrument are limited by the frequency of 250 Hz.



**Fig. 2.** The cell I electrochemical noise (1) and the instrument noise (2). Low-frequency measurements at data rate of 20 points per second.

### The Measurements of Electrochemical Noise

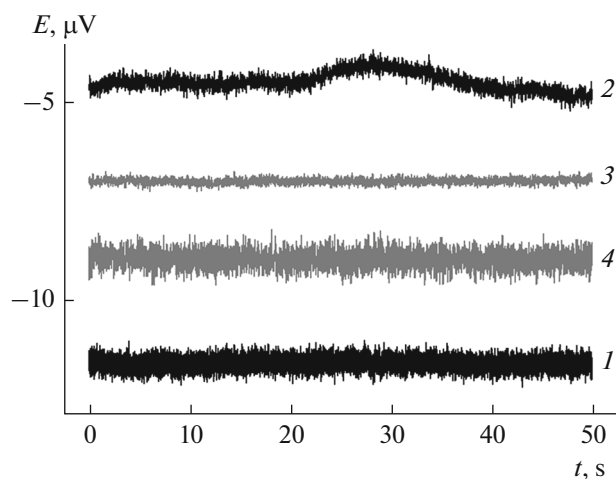
The electrochemical noise of the heteropoly-compound-based cells was measured in two steps. The first (high-frequency) step was performed at a maximal data rate of 500 points per second. Here the net body of data came to 250000 points. The second measurement was performed at a data rate of 20 points per second, in order to cover the low-frequency region as widely as possible. The number of registered points came to 200000. In Fig. 2 we give the initial data (a periodogram, that is, the voltage change in time), prior to the detrending, for one of the cells, along with the instrument's intrinsic noise.

We see from Fig. 2 that the electrochemical cell noise measured at a registration rate of 20 points per second not only has a higher amplitude but also shows a better pronounced trend as compared with the instrument's intrinsic noise in the low-frequency region.

In Fig. 3 we show a high-frequency periodogram. In this frequency range, the trend is less pronounced than for the low-frequency measurements, which is likely to weaken the effect of the detrending procedure. For the sample II some more strongly pronounced trend is observed than for the sample I, therefore, further calculations in the high-frequency region are performed just for this sample.

### Detrending and the Thermal Noise Calculations

Prior to the power spectral density calculations, we performed the detrending of the entire processed body of data. In this work we tested several methods: the moving average method (over 1000 points), polynomial approximation of 10th order, recursive filter of 1st order with the cutoff frequency by 1000 times lower than the quantization frequency [36], and convolution-product-based digital filter [36] with the cutoff frequency by 1000 times lower than the quantization frequency. We have chosen the filters' cutoff frequen-



**Fig. 3.** Noise data for different samples: (1) cell I, (2) cell II, (3) the instrument intrinsic noise, (4) a 10 kΩ-resistor. High-frequency measurements at a rate of 500 points per second.

cies rather low, in order to fall closer to the instrument analog input filter frequency in the case of low-frequency measurements and to cover as low frequency band as possible. In addition to traditional detrending methods, a rarely used local linear approximation was also examined.

The power spectral density was calculated using a Fourier analysis. At that, each processed experimental array of data (250000 or 200000 points) was divided into segments. In high-frequency measurements, the segments were 500 points long; in low-frequency ones, 100 points long. Further, the noise power spectral density was calculated for each segment, after which the results for all segments were averaged over the processed array of data. The averaging made the concept of spectrum for a random signal mathematically sensible.

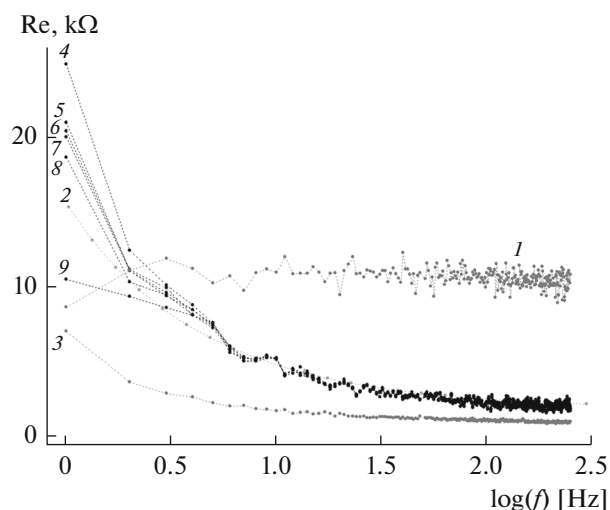
Thereafter the noise equivalent resistance was calculated from the electrochemical noise power spectral density by the Nyquist formula (1).

The calculations were carried out for a control resistor and the instrument's intrinsic noise at each data rate. Then, the obtained spectrum of the instrument's noise resistance was subtracted from the resistance spectrum for each electrochemical sample and the control resistor:

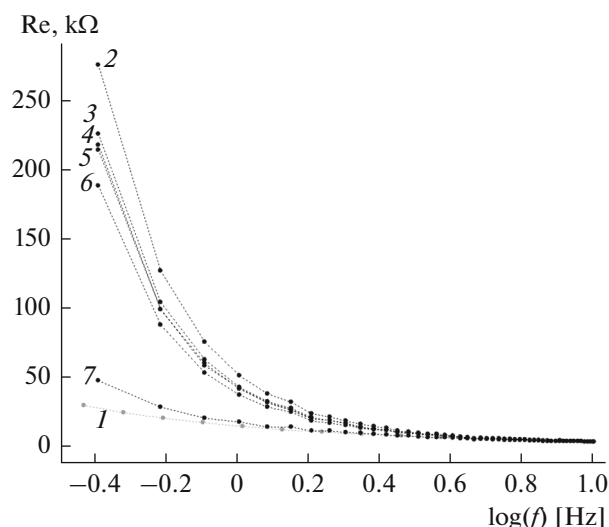
$$S_X = S_M - S_I, \quad (2)$$

where  $S_X$  is the noise power spectral density for an object under study,  $S_M$  is the measured power spectral density,  $S_I$  is the noise power spectral density for the instrument.

When the local linear approximation was used as a detrending procedure, no detrending of the entire array of data was carried out; instead, the linear trend was subtracted for each segment, into which the array



**Fig. 4.** Frequency dependences of impedance real component for different samples: (1) a 10 k $\Omega$ -resistor, (2) cell II, electrochemical impedance method, (3) the instrument noise recalculated into thermal noise resistance. Frequency dependences of the impedance real component for cell II, calculated from noise data with the using of different detrending procedures: (4) no detrending, (5) the moving average method, (6) polynomial of 10th order, (7) recursive filter of 1st order, (8) convolution-product-based digital filter, (9) local linear approximation. High-frequency measurements at a data rate of 500 points per second.



**Fig. 5.** Frequency dependences of the impedance real component for cell II, calculated by electrochemical impedance method (1). Frequency dependences of the impedance real component calculated from noise data with the using of different detrending procedures: (2) no detrending, (3) the moving average method, (4) polynomial of 10th degree, (5) recursive filter of 1st degree, (6) convolution-product-based digital filter, (7) local linear approximation. Low-frequency measurements at a data rate of 20 points per second.

of data was divided for the carrying out the Fourier analysis.

In the performing of the Fourier analysis, the frequencies to be calculated were chosen in such a way as to obtain an integer number of periods in the analyzed data segment.

In Figs. 4 and 5 we show spectra of the impedance real component for the sample II obtained by the classic electrochemical impedance method, as well as those calculated from the noise. We see that for both high-frequency and low-frequency measurements at higher frequencies the detrending procedure exerted practically no effect onto the result. The differences are observed only in the low-frequency parts of the spectra, and this is quite logical a result. The choice of some or other detrending method affects only one property: how low are the frequencies that can be correctly calculated by using the method.

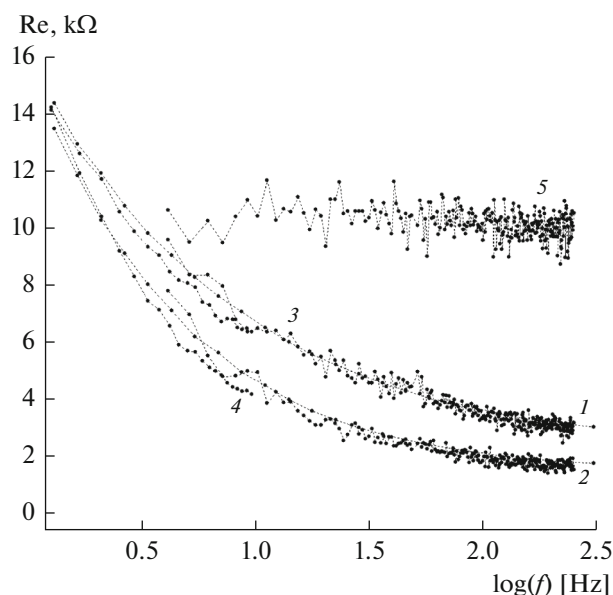
From Fig. 4 we do not see any basic difference between the applying of the detrending methods in high-frequency measurements with less pronounced trend (Fig. 3). However, we note the local linear approximation because it gives the smallest, as compared with other detrending procedures, deviation from the actual spectrum of the impedance real component (excluding the point at 1 Hz, the lowest frequency we used), the convolution-product-based digital filter appeared to be closest to this method. Other

detrending methods demonstrated well similar behavior. However, the worst result was obtained with detrending-free calculations (an expectable a result).

We see from Fig. 4 that the resistance of the standard resistor is determined accurate within no less than 10%, which is quite acceptable for the studies of this kind. Moreover, the obtained frequency dependences do not show any excessive noise, resonances, or pickups. This justifies the working capacity of our measuring setup and its suitability for more complicated measurements of electrochemical noise. At frequencies above 30 Hz, the setup's intrinsic noise came to about 4 nV/Hz<sup>1/2</sup>, or less than 1 k $\Omega$  when converted into thermal resistance.

More interesting situation was observed for low-frequency measurements where the trend is better pronounced (Fig. 2). It is this case where the detrending method affects the results significantly. As with the high-frequency measurements, the local linear approximation showed the best result. This method allowed obtaining results down to as low frequency as 0.8 Hz where the error of calculations is about 10%, whereas the rest of detrending methods showed higher deviations (by 3 times or more). In other words, all methods other than the local linear approximation are absolutely inapplicable to the processing of data obtained at low frequencies. Actually, the detrending methods appeared efficient only at frequencies above 5 Hz, that is, an order of magnitude higher than the

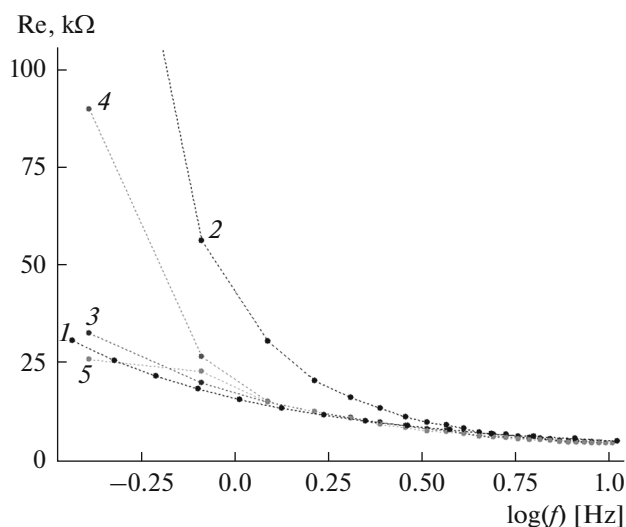




**Fig. 6.** Frequency dependences of the impedance real component for cell I (1, 3) and cell II (2, 4), obtained by electrochemical impedance method (1, 2) and calculated from electrochemical noise data (3, 4). The calculations are carried out by the high-frequency and low-frequency measurements, the detrending is carried out by the local linear approximation method. Frequency dependence of the impedance real component for a 10 kΩ-resistor (5) is given for comparison.

frequency suitable for the local linear approximation method. Nonetheless, the comparing of these detrending methods showed the priority of the convolution-product-based digital filter, whereas the moving average method demonstrated the worst result, just as in the case of high-frequency measurements. It should be noted that there is no distinction of kind between these detrending methods, which is not important since the local linear approximation method allows obtaining much more accurate results.

Basing on the above-given comparison of different detrending methods one can conclude that the local linear approximation gives the best results. In what follows, this method could be improved by the using of any above-discussed detrending method (from the polynomial approximation method to digital-filter one) instead the linear approximation at the data segment. However, this approach is hardly efficient because it is the linear approximation at the unit segments that shows the least effect on the lower frequencies of all above-discussed filters. This is due to the using of a lowest (other than zero) order polynomial, which allowed determining and subtracting the constant component and the slope with high accuracy. At that, the using of higher order (2nd and higher) polynomials not only is physically meaningless but also



**Fig. 7.** Comparison of frequency dependences of the impedance real component obtained with using different procedures of data processing: (1) electrochemical impedance method, (2) no detrending, rectangular window function, (3) local linear approximation, rectangular window function, (4) no detrending, Hann window function, (5) local linear approximation, Hann window function.

leads to excessive suppressing of lower frequencies which evidently impairs the obtained frequency characteristics.

In Fig. 6 we give results of the processing of noise data for the studied electrochemical cells I and II. The detrending was carried out using the local linear approximation method. In the figure we show low-frequency and high-frequency dependences of the active resistance in comparison with the spectrum of the impedance real component obtained from impedance measurements. We see that with the using of the electrochemical noise method and the Nyquist formula (1), without applying of an external ac current excitation, quite true data concerning the impedance real component for electrochemical objects can be obtained in the frequency region where diffusion impedance is observed.

In Fig. 7 we compare results obtained using the Hann window function or rectangular window function. We see that the using of special window function does not exert positive influence on the result. Moreover, it even impairs the situation during the electrochemical noise measurements. The using of the local linear approximation with rectangular window gives much better result in this case as well.

We successively tested the above-discussed method of the trend elimination, based on the linear approximation of local segments, by example of the electrochemical noise studying in air-hydrogen fuel cell [37, 38].

## CONCLUSIONS

Electrochemical noise of electrochemical cells with heteropolycompound-based solid electrolyte is measured.

The equivalent noise resistance spectra were calculated using Nyquist formula. The results of the calculations are in good compliance with the electrochemical impedance real component over a frequency range encompassing more than two orders of magnitude.

The using of electrochemical noise method is shown to allow measuring the impedance real component with no external ac current excitation, the more so, in the frequency range where diffusion processes contribute predominantly.

Different detrending methods are compared in the course of the analyzing of the electrochemical system electrochemical noise. The local linear approximation method is shown to give much better results as compared with the polynomial approximation and moving average methods.

The applying of window function other than the rectangular one is shown to give no improvement of the calculated result when using Fourier-analysis calculated frequencies with integer number of periods over a processed data segment. Equally, the using of window functions by no means can be substituted for the detrending procedure when studying electrochemical objects.

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