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ORIGINAL PAPER

K. Darowicki · A. Zieliński

Analysis of electrochemical noise by means of bispectral techniques

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Abstract Nonlinear processes are often encountered in the practice of electrochemical and corrosion measurements. Especially, activation-controlled processes are inherently nonlinear. Taking into account investigations of electrode reactions, linear approximation is a popular approach. In this introductory paper, the possibility of extension of electrochemical noise (EN) measurements to the nonlinear regime is presented. Natural consequence of focusing on nonlinear processes is application of higher-order spectral techniques. Utilization of bispectral representation enables analysis of stationarity and linearity properties of EN. The authors present algorithm enabling assessment of both quantities and also exemplary analysis of noise generated during cathodic polarization, which is important for corrosion protection.

Keywords Linearity · Gaussianity · Corrosion control · Bispectrum · HOS

Introduction

Nonlinearity is an important feature of majority of physical processes. In spite of its common appearance in real-world phenomena, nonlinear description is often depreciated for the benefit of linear approximation. It results from computational simplicity of the latter approach. However, conditions of correctness of such simplification should be always kept in mind. It is important to recognize the character of investigated process and to determine if linear model is appropriate in given experimental conditions. In the situation where linearization cannot yield correct results, it is necessary to utilize more sophisticated techniques. Need for analysis of nonlinear systems forced development of new analytical procedures. One of these is the higher-order statistics (HOS) technique [1–3]. It was successfully applied in the investigations of wide range of technical problems involving non-Gaussian and nonlinear processes.

Linear approximation is frequently applied in electrochemical and corrosion investigations. Linear polarization and electrochemical impedance spectroscopy (EIS) [4] are obvious examples. Design of EIS experiment is always connected with problem of compromise between preserving linearity conditions and maintaining perturbation amplitude sufficient to obtain reliable results. Suitability of linearization in the case of EIS was discussed by Darowicki and Majewska [5].

In this paper, the authors propose application of nonlinear techniques in the analysis of electrochemical experimental results. Firstly, such approach does not introduce linearity preservation demands mentioned above. The other beneficial fact is that in the conditions of activation control of a given reaction, a nonlinearity of current–potential characteristic should be observed, in contrast to diffusion control which is considered as linear. This observation is exploited in the case of harmonic analysis [6], where magnitudes of particular frequency components are used to compute the kinetic parameters of electrochemical process. In the following sections, the possibility of application of HOS to detect nonlinear behavior of electrochemical process and, thus, to reveal occurrence of activation-controlled reaction is suggested. In the authors' opinion, one of the most important aspects of the technique presented is investigation of electrochemical noise (EN) response of cathodically polarized systems, for example, protected constructions [7].

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K. Darowicki · A. Zieliński (✉)
Department of Electrochemistry,
Corrosion and Materials Engineering,
Gdańsk University of Technology,
Narutowicza Str. 11/12,
80-952 Gdańsk, Poland
e-mail: ziela@chem.pg.gda.pl
Tel.: +48-58-3471092
Fax: +48-58-3471092

Methodology

Bispectrum and bicoherence estimation

One of the fundamental tools in stochastic process analysis is autocorrelation function related to power spectrum by

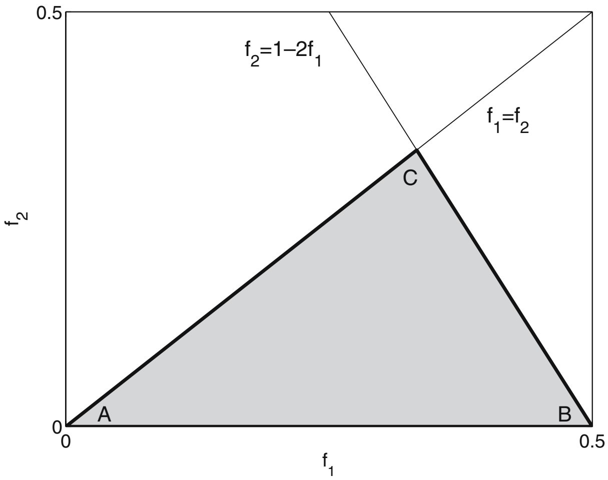


Fig. 1 Nonredundant region of bispectrum (triangle ABC) in the case of discrete time signal and assumed sampling frequency of 1 Hz

Wiener–Khintchine identity. Consequently, there is possibility of construction of spectra whose order is higher than 2 by transformations of correlation sequences known as cumulants. The third-order cumulant of stationary, zero-mean stochastic signal $x(t)$ is defined as

$$c_{3x}(t_1, t_2) = \mathrm{E}[x^*(t)x(t+t_1)x(t+t_2)] \tag{1}$$

where $E[]$ and asterisk denote averaging operator and complex conjugation, respectively [8].

Fourier transform of Eq. (1) defines the third-order spectrum known as bispectrum:

$$C_{3x}(f_1, f_2) = \sum_{t_1=-\infty}^{\infty} \sum_{t_2=-\infty}^{\infty} c_{3x}(t_1, t_2) \exp(-2\pi j f_1 t_1) \exp(-2\pi j f_2 t_2) \tag{2}$$

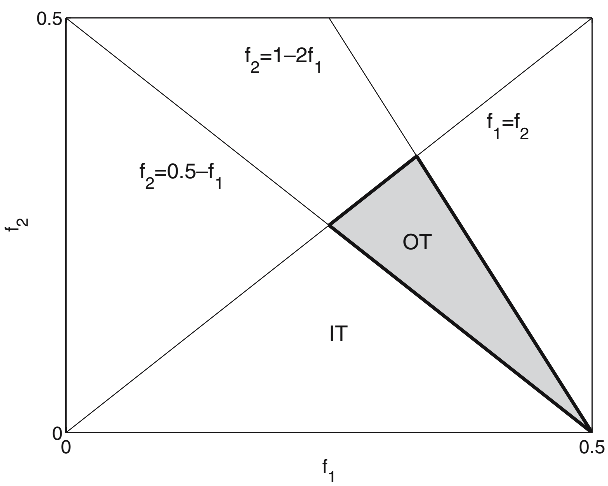


Fig. 2 Partitions of bispectrum domain considered during stationarity investigations, outer triangle (OT) and inner triangle (IT) regions. Sum of OT and IT areas is the nonredundant part of bifrequency plane. Sampling frequency assumed equals 1 Hz

and normalized function B_{3x}, called autobicoherence:

$$B_{3x}(f_1, f_2) = \frac{C_{3x}(f_1, f_2)}{\sqrt{S_{xx}(f_1 + f_2) S_{xx}(f_1) S_{xx}(f_2)}} \tag{3}$$

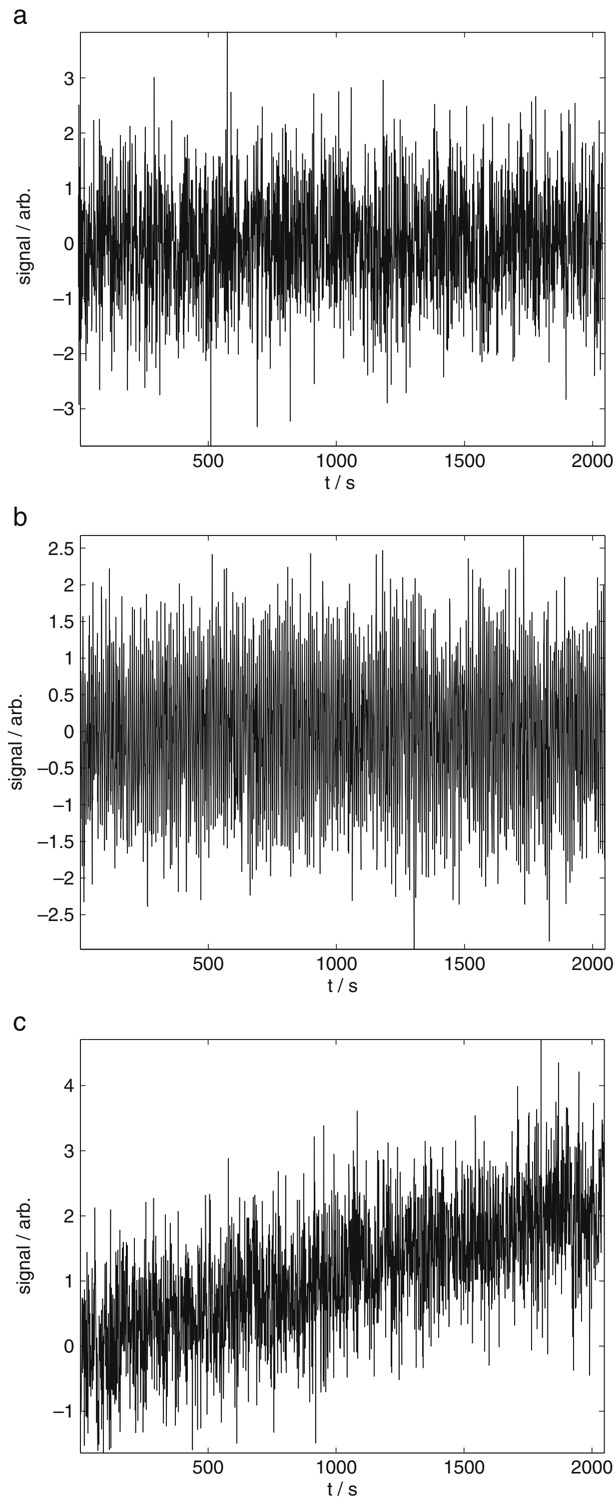


Fig. 3 Exemplary stochastic signals. **a** Gaussian white noise (0,1). **b** White noise containing sine component of unitary amplitude. **c** Sum of white noise and ramp signal

where $S_{xx}(f)$ is signal power spectrum.

Normally distributed stochastic process is completely described by the spectrum of second order (power spectrum); thus, all spectra of order higher than 2 are by definition zero. Nonzero value of the modulus of bicoherence can be treated as indication of non-Gaussianity of stochastic process [9]. Further, nonzero but constant bicoherence modulus is characteristic for non-Gaussian linear process [10], while its variability suggests non-linearity of a given process [8].

Investigation of higher-order spectra of finite, discrete time sequences requires calculation of appropriate estimators. To solve the problem, a direct method described by Proakis et al. [8] was used. In the first stage, discrete data course $x[k]$ is segmented into M subrecords consisting of K samples each, with optional truncating or padding data fulfilling the fast Fourier transformation requirements. For

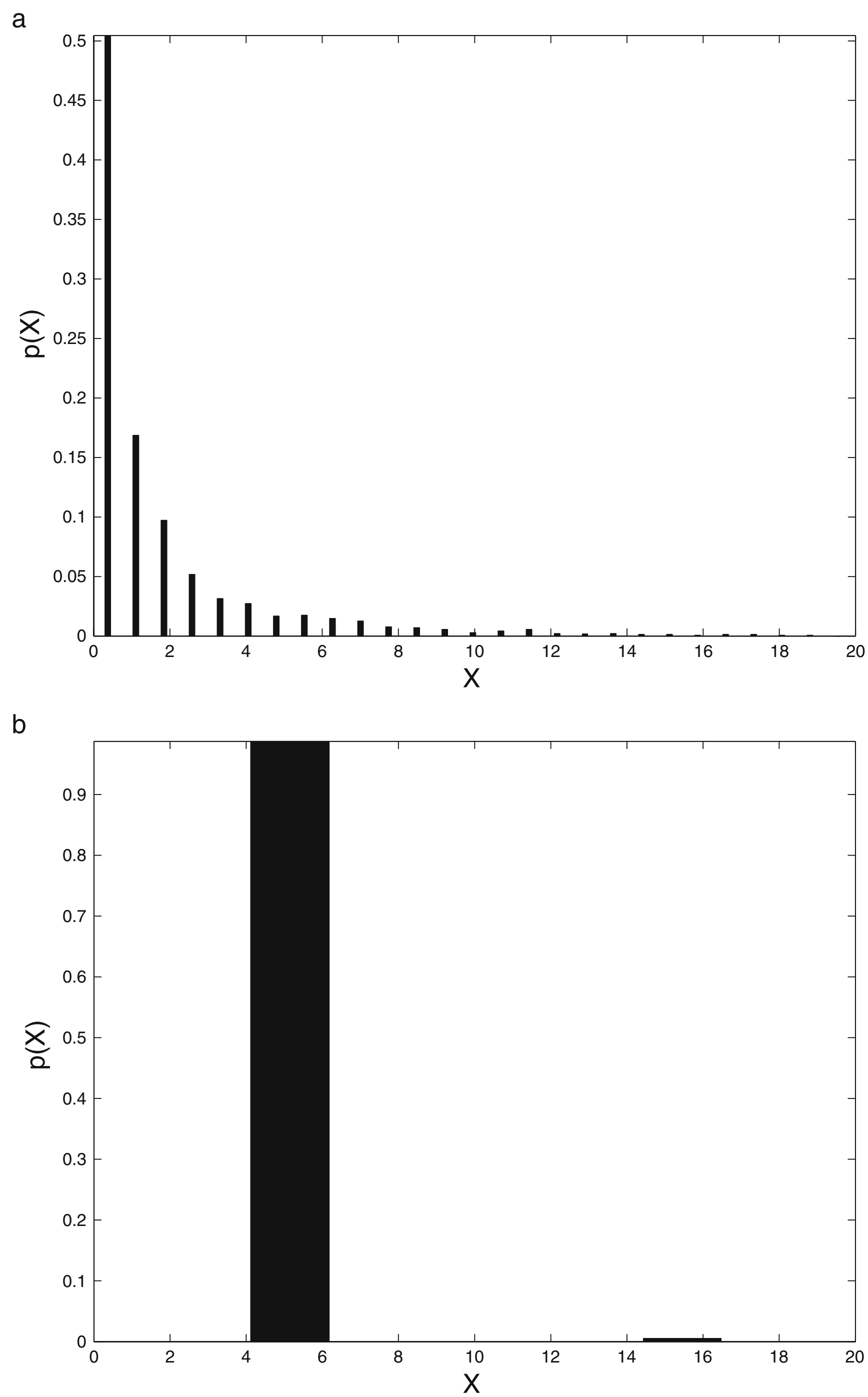
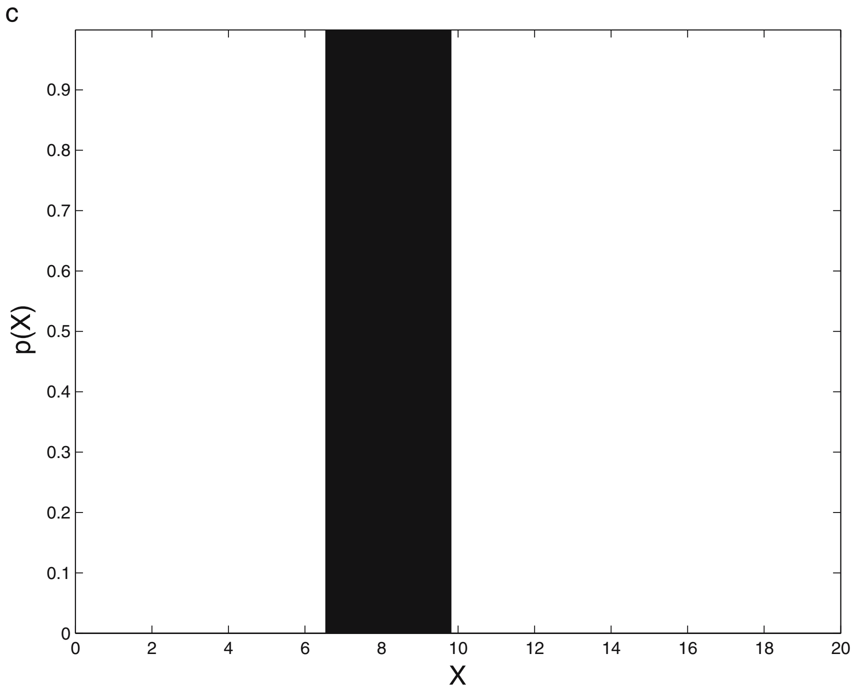


Fig. 4 Probability density function for three exemplary cases of signals. **a** Stationary signal (Fig. 3a). **b** Signal containing sine component (Fig. 3b). **c** Signal of increasing mean value (Fig. 2b)

Fig. 4 (continued)



every segment, discrete Fourier transform (DFT_m) is computed:

$$DFT_m(f) = \sum_{k=0}^{K-1} x[k] \exp\left(-j\frac{2\pi kf}{K}\right) \quad (4)$$

Then the bispectrum estimator for each segment numbered by m=0…M is obtained,

$$C_{3x}^{(m)}(f_1,f_2) = \frac{1}{\Delta_N^2} DFT_m(f_1) DFT_m(f_2) DFT_m{}^*(f_1+f_2) \quad (5)$$

where $\Delta_N = f_s/N$, N is the number of DFT_m frequency points, and f_s is the sampling frequency. Set of M bispectra is then averaged to obtain the C_{3x} estimator.

Bicoherence estimator is calculated according to Eq. (3) using power spectrum of signal. Both bicoherence and bispectrum are functions of two frequencies, f_1 and f_2. Thus, they are defined in two-dimensional domain referred as bifrequency plane. Exemplary bispectrum domain for discrete signal is depicted in Fig. 1. Important question is redundancy of the bispectrum estimate obtained. For stationary, real-valued signal, cumulants have symmetry property, which is inhered by corresponding polyspectrum. This relation is obvious for the second-order spectrum, which is always even. In the bispectrum case, the symmetry relations can be described by the following formulas:

$$\begin{aligned} C_{3x}(f_1,f_2) &= C_{3x}(f_2,f_1) = C_{3x}(f_1,-f_1-f_2) \\ &= C_{3x}(f_2,-f_1-f_2) = C_{3x}(f_1-f_2,-f_2) \\ &= C_{3x}(f_1-f_2,-f_1) = C_{3x}^*(-f_1,-f_2) \\ &= C_3^*x(-f_2,-f_1) \end{aligned} \quad (6)$$

which determine borders of nonredundant region of bifrequency plane. Assuming discrete time signal sampled at rate of 1 Hz, the nonredundant area of bispectrum domain is presented in Fig. 1 (triangle ABC). For such situation, it is sufficient to investigate bispectrum only in the domain defined by the triangle of vertices A(0,0), B (0,1/2), and C(1/3,1/3).

Assessment of signal stationarity on the basis of signal bispectrum

The bispectrum, whose estimation procedure was described in the preceding section, can be used as the criterion for determining whether the signal under investigation is stationary. Due to the fact that the stationarity is crucial for correctness of further signal analysis presented in the following sections, the possibility of stationarity assessment by means of higher-order spectra is worthy to be discussed here. Hinich [11] observed that for properly sampled stationary stochastic process, bispectrum should be zero in the subregion of the earlier defined domain presented in Fig. 1.

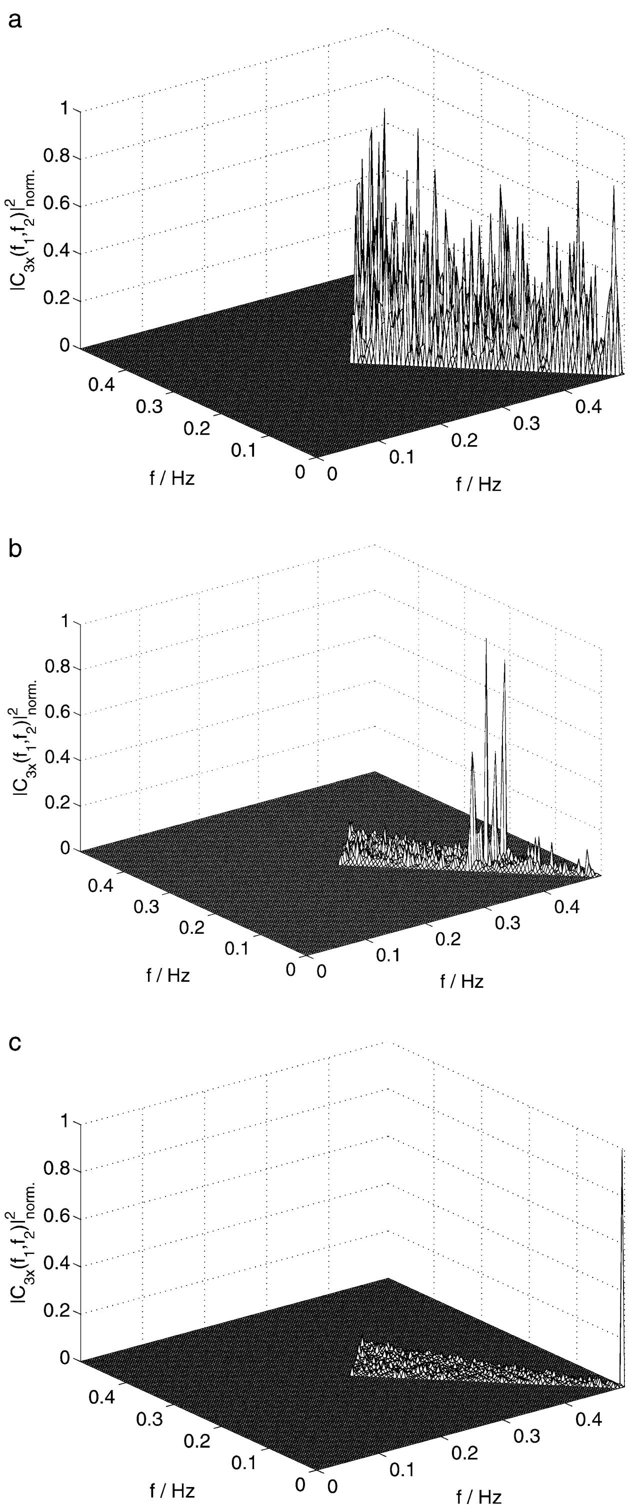


Fig. 5 Normalized bispectra for three exemplary signals presented in Fig. 3. **a** White noise. **b** Sine + white noise. **c** Ramp + white noise

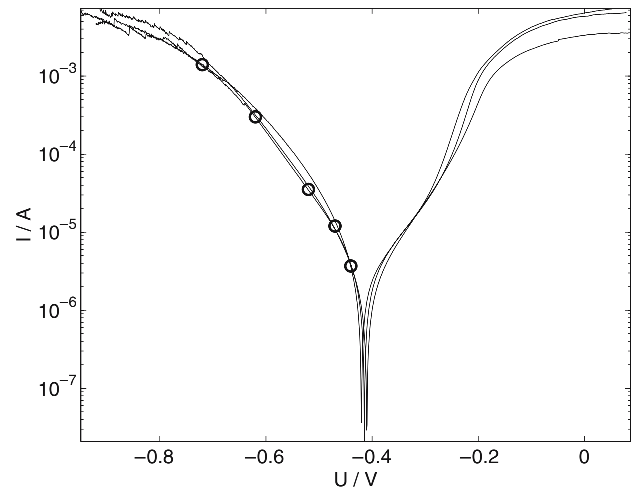


Fig. 6 Polarization curves of iron in the solution of 5% hydrochloric acid. Potentials expressed vs Ag/AgCl reference electrode. Scan rate: 1 mV/s

The discussed area, referred as the outer triangle (OT), is depicted in Fig. 2 and described by the following relation (under the assumption f_s=1):

$$OT = \{f_1, f_2 : f_2 \leq f_1, 0.5 \leq f_1 + f_2 \leq 1 - f_1\} \tag{7}$$

According to earlier statements, samples of bispectrum taken from the OT region should be characterized by zero mean even if the investigated noise is not Gaussian. In such situation, the following statistics,

$$X(f_1, f_2) = 2N\Delta_N |C_{3x}(f_1, f_2)|^2 / V \tag{8}$$

where N is number of analyzed frequency samples, Δ_N is bispectrum bandwidth, and V is energy of analyzing

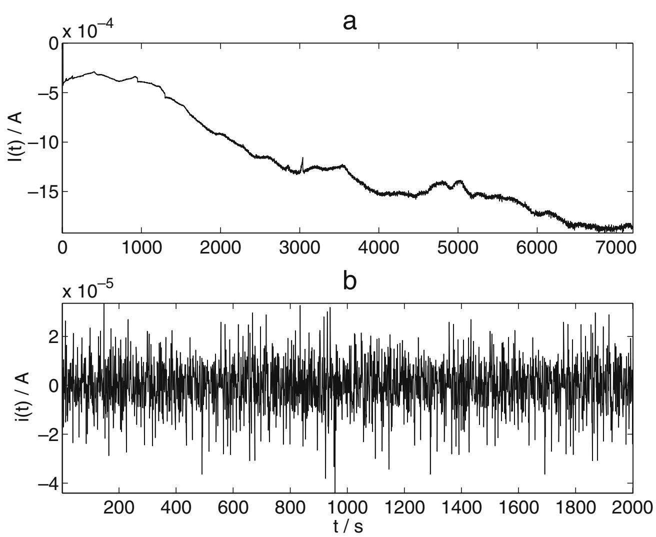


Fig. 7 Exemplary course of the current recorded in potentiostatic measurement (**a**) and extracted fragment of stationary electrochemical noise (**b**)

window (in the discussed case, $V\equiv1$), should be approximately χ^2-distributed with two degrees of freedom [10].

In Fig. 4, the results of bispectral analysis for simulated stationary (Fig. 3a) and nonstationary (Fig. 3b,c) signals are presented in the form of statistics (Eq. 8) histograms in the OT region. It is visible that only for the case of noise not containing deterministic component can the shape of probability density function (pdf) be approximated by χ^2 distribution, while for two nonstationary signals, significant difference is observed. Additionally, one can note that mean value of χ^2 random variable should be equal to the number of degrees of freedom, namely, α=2 in the discussed case. Comparison of value of $\alpha_{\text{estimated}}$ obtained as a result of averaging of statistics (Eq. 8) in the OT range of bifrequency domain with the expected value of α=2 provides information concerning the degree of signal nonstationarity. In the case of stationary signal (Fig. 4a), value of $\alpha_{\text{estimated}}$=1.97 confirms good fit of its bispectrum distribution to the assumed one. In the two remaining cases, shapes of pdf are sharply peaked, which can be justified by form of signal bispectra in the OT region. Normalized values of squared bispectra are presented in Fig. 5 (subplots a, b, and c refer to corresponding cases in Fig. 3). In the case of noise modulated by sine signal (Fig. 5b), increase of bispectrum is visible for particular frequencies. Similarly, in the case of increasing signal (Fig. 5c), intense peak located near bifrequency (0,0.5) Hz can be noticed.

Such procedure enables diversification between stationary and nonstationary EN records depending on statistical distribution of their bispectra in the OT of bifrequency domain. The following part of the paper will be devoted to the bispectral analysis of experimental EN data.

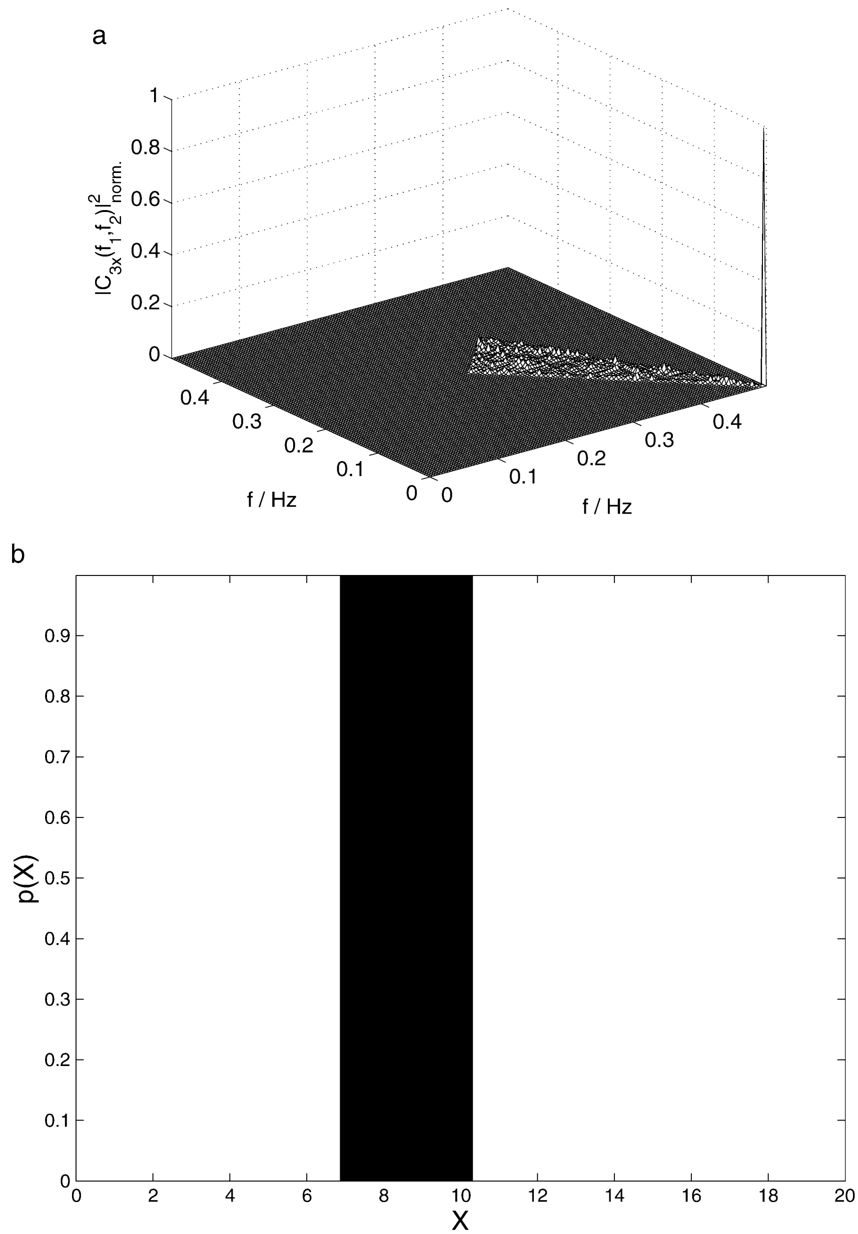


Fig. 8 Bispectral analysis of "raw" potentiostatic noise (Fig. 7a). **a** Corresponding normalized bispectrum. **b** Probability density function of statistics (Eq. 8)

Experimental

Electrochemical noise measurements were conducted in potentiostatic regime to obtain appropriate cathodic polarization of investigated system. Samples of 99.9% pure ARMCO iron of area of 0.2 mm^2 were embedded in the epoxy resin. Prior to measurements, the surface of each electrode was polished with sandpaper up to grade 1,000, degreased with methanol, and rinsed with distilled water. As electrolyte, 5% hydrochloric acid of p.f.a. class was used. Measurements were carried out in typical three-electrode setup with platinum mesh counter and silver/silver chloride reference electrode, respectively. Potential was controlled by Autolab PGSTAT30 device equipped with GPES 4.9.004 software.

Results and discussion

Potentiostatic current noise measurements were performed for five points taken from cathodic region of iron potentiodynamic curve (Fig. 6) obtained at voltage change rate of 1 mV/s. Measurements were performed at noncontrolled ambient temperature. For the specimens investigated, high reproducibility of the current–potential characteristic was observed; thus, a group of electrodes was subjected to the potentiostatic measurement at different potentials.

On the other hand, each particular current record obtained in potentiostatic experiment was highly nonstationary (Fig. 7a), which was additionally confirmed by application of algorithm described earlier.

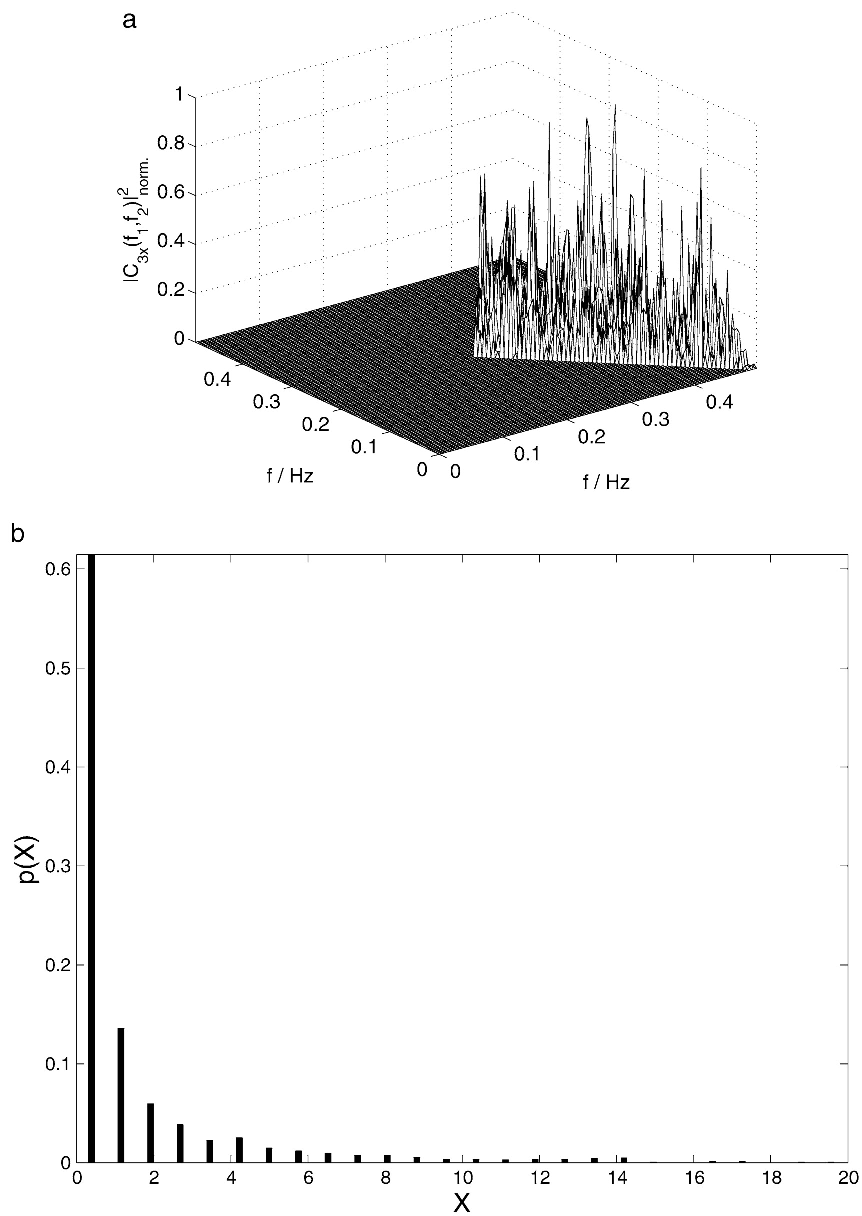


Fig. 9 Bispectral analysis of stationary fragment of potentiostatic noise (Fig. 7b). **a** Corresponding normalized bispectrum. **b** Probability density function of statistics (Eq. 8)

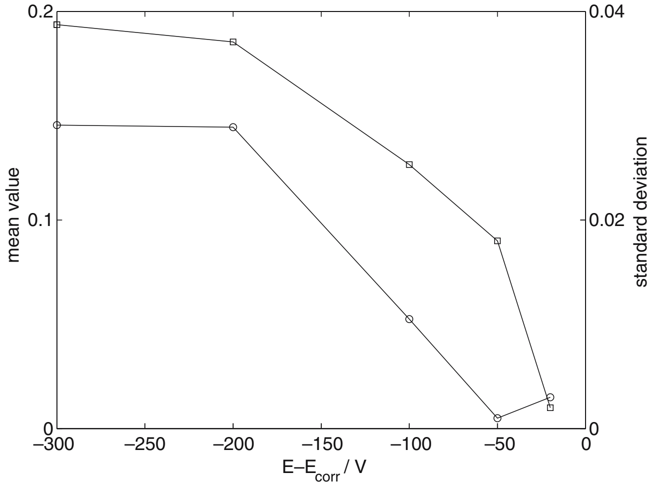


Fig. 10 Results of estimation of mean value and standard deviation of modulus of bicoherence for potentiostatic noise records acquired at selected cathodic polarizations

In Fig. 8, corresponding normalized bispectrum (a) and probability density function of statistics (Eq. 8) are presented (b). Strong peak similar with the simulated case of "ramp + noise" signal is visible, which is in accordance with the shape of time course presented in Fig. 7a (significant change of mean value).

For each potentiostatic record, wavelet trend removal was applied. Then the segment of 2,000 samples from the terminal part of each one was selected for further investigations (Fig. 7b). After such operations, stationary signal was obtained. Results of its stationarity analysis are visualized in Fig. 9.

Substantial change in shape of bispectrum (Fig. 9a) and distribution of squared bispectrum modulus statistics (Eq. 8) in the OT (Fig. 9b) confirms stationarity of processed noise. Due to the strong demand regarding stationarity, initial trend removal turned out to be necessary for proper calculation of parameters related to linearity of signals investigated.

For each potential investigated, computations of current noise bicoherence were performed by means of algorithm based on Eqs. (3, 4, and 5). For the nonredundant region of bifrequency domain, values of mean and standard deviation were obtained.

It is visible that with the growth of cathodic polarization (lower potential values), increase of bicoherence modulus mean is observed. The same tendency can be noted for its standard deviation. According to the theory of activation-controlled electrochemical processes, region of current–potential curve corresponding to cathodic polarizations of more than 100 mV can be treated as Tafel range [12]. This conclusion can be easily verified by looking at Fig. 10, where linear dependence between potential and current logarithm is visible. Behavior of statistical parameters (mean and standard deviation) of bicoherence modulus reveals growth of both of them in the Tafel region of cathodic branch. Taking into account the relation between bicoherence and linearity and Gaussianity of a given random process, it can be concluded that EN measurements confirm nonlinear character of Tafel curve. This feature can be easily detected by other electrochemical techniques, for example, harmonic analysis [13]; however, fundamental advantage of EN is lack of high-amplitude perturbation significantly changing the electrochemistry of electrode. Such conclusion has special meaning in the case of external polarization, which in practice is typical for cathodic protection.

Conclusions

Results of bispectral analysis of current noise response of electrochemical corrosion process were presented. Usability of higher-order spectral technique in the detection of nonstationary and nonlinear EN was confirmed. The possibility of selection of nonlinear regions of a given process is undoubtedly an important element in the research of electrochemical systems. Additionally, on the basis of specific regions of bispectrum, stationarity and linearity assessment can be performed in one analytical run. Further work on problem discussed in the paper is continued in order to apply HOS technique to industrial measurements.

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