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ORIGINAL PAPER

Pitting corrosion characterization by electrochemical noise measurements on asymmetric electrodes

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Abstract Pitting corrosion of stainless steel electrodes can be detected by presence of characteristic transients in a current that flows between two short-circuited electrodes. Various methods for detection of these events are proposed in literature but still a more thorough analysis is needed. The authors present another method that preserves information about transient occurrence and their characteristic time constant. We suggest the application of the bispectrum or, even with better results, its integrated function for transient detection during metastable pitting. This method was successfully applied for noise recording at pitting corrosion of stainless steel 0H18N9 when exposed to electrolyte (1-M concentration of $FeCl_3$ in distilled water).

Keywords Pitting corrosion · Electrochemical noise · Bispectrum · Higher-order statistics

Introduction

Electrochemical noise measurements have been extensively studied for the last 30 years and reached a relatively mature state. This is true for uniform corrosion when noise resistance, defined as the standard deviation of potential divided by the standard deviation of current, is generally accepted for characterization of this corrosion type [1–3]. Then, current and voltage fluctuations are observed in a three-electrode setup [2–4]. A more complicated task is characterization of local corrosion events. The methods that are proposed in the literature utilize power spectrum [5–7], wavelet transform [8–10], skewness, and bispectrum [6, 11, 12] or estimate the intensity of characteristic transient occurrence in voltage or current records [13]. These methods have numerous drawbacks and merits that should be discussed in a more detailed way.

The power spectrum captures the frequency content of the analyzed random signal only and makes it difficult to single out which part of noise is generated by pitting events or by uniform corrosion or even by inherent noise of the used measurement setup. We can experience an analogous problem by applying a wavelet transform which additionally provides changing frequency resolution.

Another proposed parameter is skewness that is a measure of asymmetry of the probability distribution of analyzed noise. Pitting corrosion generates transients of characteristic shape (Fig. 1). The random transients, which are observed in current that flows between shortcut asymmetric electrodes, cause non-Gaussian distribution of current amplitudes. Skewness is an easily computable parameter but it does not report about the time constant that characterizes the transient shape.

Bispectrum, that is a function of two frequencies, preserves information about the transient characteristic time constant. However, a bispectrum requires intensive computing and more signal samples to restrict its random error when compared with the power spectrum [14]. Therefore, in the present exploratory study, we expand our investigations of electrochemical noise to encompass the integrated bispectrum function [15, 16]. This newly proposed function demands similar computing as a power spectrum but preserves some characteristics of the bispectrum.

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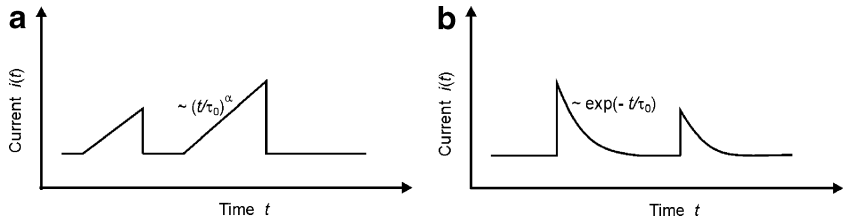

Fig. 1 Current transients at pitting corrosion versus time in: **a** stainless steel, **b** carbon steel, or aluminum; α, τ_0 are parameters that model the transients' shape

Bispectrum and its integral

A stationary stochastic signal $x(t)$ is commonly characterized by its power density spectrum $S_x(f)$, where f denotes frequency. However, an important deficiency of $S_x(f)$ is that it cannot distinguish between Gaussian and non-Gaussian signal components. Therefore, it is plausible to use other functions than $S_x(f)$ when non-Gaussian electrochemical noise generated by metastable pitting is observed. Such a separation can be accomplished by higher-order spectra [14]. The bispectrum of a stationary, zero-mean stochastic sampled signal is a function of two frequencies f_1, f_2. It is defined by

$$S_{3x}(f_1,f_2) = \sum_{\tau_1=-\infty}^{\infty}\sum_{\tau_2=-\infty}^{\infty} c_{3x}(\tau_1,\tau_2)\exp(-j2\pi(f_1\tau_1+f_2\tau_2)), \tag{1}$$

where

$$c_{3x}(\tau_1,\tau_2) = E[x(t)\cdot x(t+\tau_1)\cdot x(t+\tau_2)] \tag{2}$$

is the third-order autocorrelation function of $x(t)$, and the operator $E[..]$ denotes averaging. The main privilege of the bispectrum is that this function is zero or constant for Gaussian noise. Thus, it attenuates Gaussian noise and exposes non-Gaussian components that have asymmetric probability distribution.

The definition of the bispectrum, which is the function of two equivalent frequencies, implies a few axis symmetries (Fig. 2) [14, 17]. Thus, the bispectrum is unambiguously determined only by a segment of its frequency plane. The bispectrum function vanishes when the skewness

$$\gamma_3 = \frac{1}{\sigma_x^3}E\left[(x(t)-E[x(t)])^3\right] \tag{3}$$

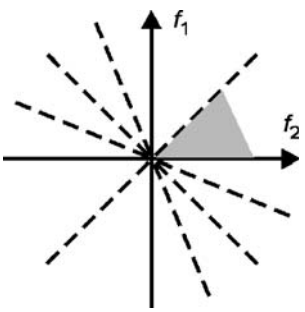

Fig. 2 Illustration of bispectrum $S_{3x}(f_1, f_2)$ axis symmetries; gray color represents nonredundant bispectrum region

of the amplitude density of the signal $x(t)$ having variance σ_x^2 is equal to that of Gaussian signals.

Equation 1 defines bispectrum as a two-dimensional Fourier transform of the third-order autocorrelation function that requires more computations when compared with the power spectrum. Moreover, for a given number of stochastic data, the power spectrum shows significantly lower variance than the bispectrum. To reduce this variance, the integrated bispectrum can be used according to [15, 16]

$$S_{3x,I}(f) = \int_{-f_s/2}^{f_s/2} S_{3x}(f,f_1)df_1 \tag{4}$$

where f_s means sampling frequency. It is interesting to note that estimation of $S_{3x,I}(f)$ does not require the determination of the bispectrum [15]. The integrated bispectrum can be calculated as cross spectra from

$$S_{3x,I}(f) = S_{x,y}(f) = \sum_{\tau=-\infty}^{\infty} E[x(t)y(t+\tau)]\exp(-j2\pi f\tau) \tag{5}$$

where the sampled time series $y(t)$ is derived from the registered noise sampled signal $x(t)$

$$y(t) = x^2(t) - E\left[x^2(t)\right] \tag{6}$$

The cross spectrum $S_{3x,I}(f)$ can be estimated by dividing the sample sequence into blocks and averaging the block-sample estimators over the blocks. This is identical to the Welch method of power spectrum density estimation [18]. Different time windows can be used for the blocks, which lead to small differences in variance of the estimated cross spectra.

It is worth underlining that the proposed integrated bispectrum reveals statistic properties of the transients abundantly observed when metastable pitting is present. At the same time, this function attenuates Gaussian components that exist in the analyzed noise. Thus, it preserves the essential characteristic of the bispectrum while radically reducing computation.

Experimental

Electrochemical current noise was observed between two identically prepared stainless steel 0H18N9 electrodes but

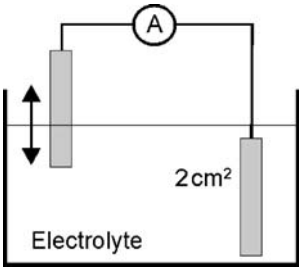

Fig. 3 An electrode setup applied for observation of current noise that flows between two short-circuited asymmetrical electrodes

having different areas exposed to the electrolyte (Fig. 3). Only one electrode was moved to change the area exposed to the electrolyte. When the difference between the corroding areas reached a factor of several times, then the observed current transients exposed pitting corrosion of the smaller electrode. This fact is visible in the registered current $i(t)$ records by asymmetric distribution of transient amplitudes (Fig. 4). Therefore, the use of bispectrum $S_{3x}(f_1, f_2)$ or its integral function $S_{3x,I}(f)$ for pitting corrosion event characterization is undoubtedly recommended. Typically, the observed transient takes a time period of ~60 s (Fig. 5) that corresponds with the characteristic frequency $f=2\pi/60\approx0.1$ Hz.

The electrolyte was prepared as a 1-M concentration of $FeCl_3$ in distilled water. As a result, the pitting corrosion processes occurred and visible pits were observed on the electrode surfaces at the end of the experiment (Fig. 6).

All the electrochemical current noise measurements were made in the low-frequency region and by using a current–voltage converter, which was built up by using a low-noise OPA128 operational amplifier. A low-noise voltage preamplifier, Stanford SR 560, was applied to amplify the noise voltage at the output of the current–voltage converter before sampling and registering by a data acquisition board NI 4474 controlled by LabVIEW software. The registered samples were saved as ASCII file for further analysis. The MatLab toolbox *Higher-Order Statistics* was implemented to estimate the bispectrum function and its integral from the saved samples in the ASCII file [19]. This toolbox is free of

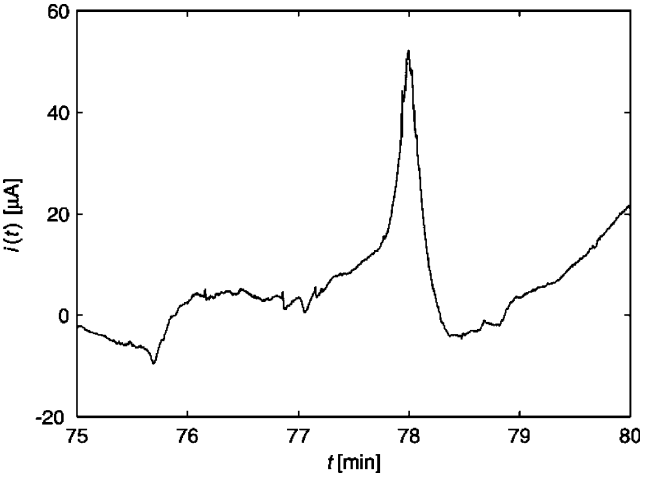

Fig. 5 A zoomed part of the electrochemical current noise $i(t)$ presented in Fig. 4

charge, available from the MathWorks company www page [20]. The bispectrum was estimated using the direct (FFT-based) method. This method applies Fourier transform to the estimated third-order cumulant $c_{3x}(\tau_1,\tau_2)$, as defined in Eq. 1. The toolbox function *bispecd* computes the bispectrum by using this method. The registered data are segmented into nonoverlapping and consecutive records. Next, the computed biperiodograms are averaged within a whole set of these records. FFT length used for computing bispectrum was 256. Then, the random error of the bispectrum was reduced by applying a window smoothing procedure. The default frequency-domain smoothing window, available in the applied *bispecd* function, was used.

The integrated bispectrum was estimated by applying MatLab function *fft* to the segmented records of noise signal $x(t)$ and the sampled time series $y(t)$ derived from $x(t)$ according to Eq. 6. The same FFT length as for the bispectrum was applied. The cross spectrum was calculated by multiplying both achieved spectra. Further, the averaging was applied within a set of cross spectra estimated independently for all the segmented data records.

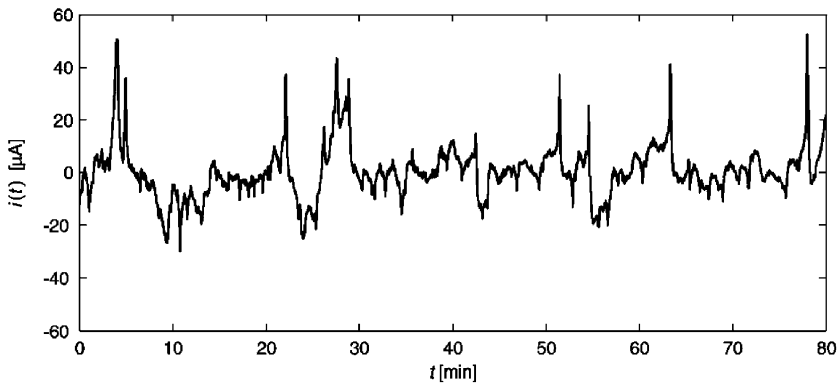

Fig. 4 Electrochemical current noise $i(t)$ that flows between two short-circuited asymmetric electrodes, made of stainless steel 0H18N9, with the ratio 1:5 of their area exposed to the electrolyte

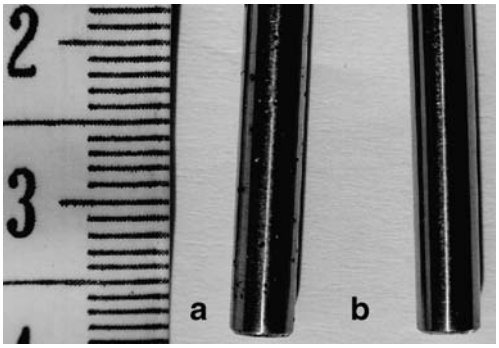

Fig. 6 Investigated electrodes made of stainless steel 0H18N9: **a** with visible pits, **b** with a clear surface before noise measurements

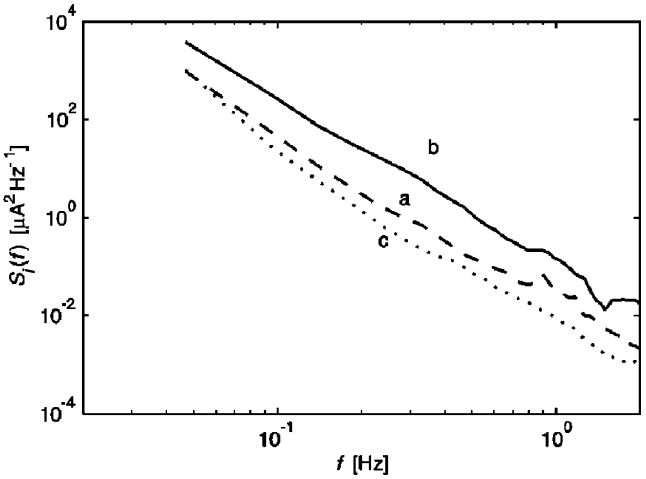

Fig. 7 Power spectrum $S_i(f)$ of the observed electrochemical current noise $i(t)$; the quotient of the electrodes area exposed to the electrolyte was equal to: *a* 1:3, *b* 1:6, *c* 1:9

Noise was registered at a sampling frequency of f_s= 6 Hz within a period of a few hours for each record. A nonstationary trend was observed in the current. The algorithm proposed by Donoho was applied to remove this nonstationary component using MatLab software (function *wden* of the wavelet toolbox) [21]. The current noise after trend removal was assumed to be a stationary random signal. All current noise measurements were made at a few chosen quotients of the electrode area exposed to the electrolyte.

Results and discussion

The proposed methods of electrochemical noise analysis were applied for the analysis of the registered current fluctuations to recognize which of the methods is the most appropriate for pitting corrosion detection and its intensity estimation. We measured and considered current noise only because it was proportional to the charge participating in electrochemical corrosion reactions which occurred during metastable pitting.

The observed noise consisted of two components:

- Gaussian noise caused by uniform corrosion and inherent noise of electronic components being part of the measurement setup,
- Non-Gaussian noise having asymmetric probability distribution and caused by metastable pitting events; its asymmetry depended on the quotient of the electrode area exposed to the electrolyte and intensity of transients presence at the same time.

The power spectrum gives us information about the intensity of fluctuations generated by corrosion reactions that took place on surfaces of both electrodes exposed to the electrolyte. This function depended on frequency as $1/f^m$, where parameter $m \approx 2$ (Fig. 7). The power spectrum intensity was an individual feature of the investigated electrode pair despite the fact that all electrodes were prepared nominally in the same way.

The bispectrum, estimated for the same data as the previously discussed power spectrum, reveals new facts about the strength of local corrosion events. Figure 8 presents only the nonredundant region of the estimated bispectrum when the rest of this function exhibited theoretically predicted axial symmetries. The bispectrum was more intensive when the electrode area quotient was 1:9 than at 1:3. The power spectra behave in an opposite way when the same quotients are considered. This exploratory study confirms that the bispectrum uncovers new details about pitting corrosion, whereas the power spectrum is dominated by other noise sources, being Gaussian noise and caused by uniform corrosion processes or internal noise of the measurement setup. Therefore, the proposed idea can be applied in practice for characterization of local corrosion processes.

The bispectra should exhibit maxima in the vicinity of a frequency inversely proportional to the time constant that is characteristic for the observed transients. All the estimated bispectra displayed a sharp bend below 0.1 Hz, which is contrary to the power spectra exposing a $1/f^m$ type dependence on frequency only. The frequency of the mentioned bends responds to the roughly calculated, and mentioned earlier, value $f \approx 0.1$ Hz that replies to the time constant of the observed transients (Fig. 1).

The integrated bispectrum (Fig. 9) uncovers the same information as the bispectrum function but does not require such intensive computations. Therefore, we suggest applying the integrated bispectrum to detect and characterize events of pitting corrosion.

The applied bispectrum and its integrated version reveal existence of non-Gaussian component in the registered

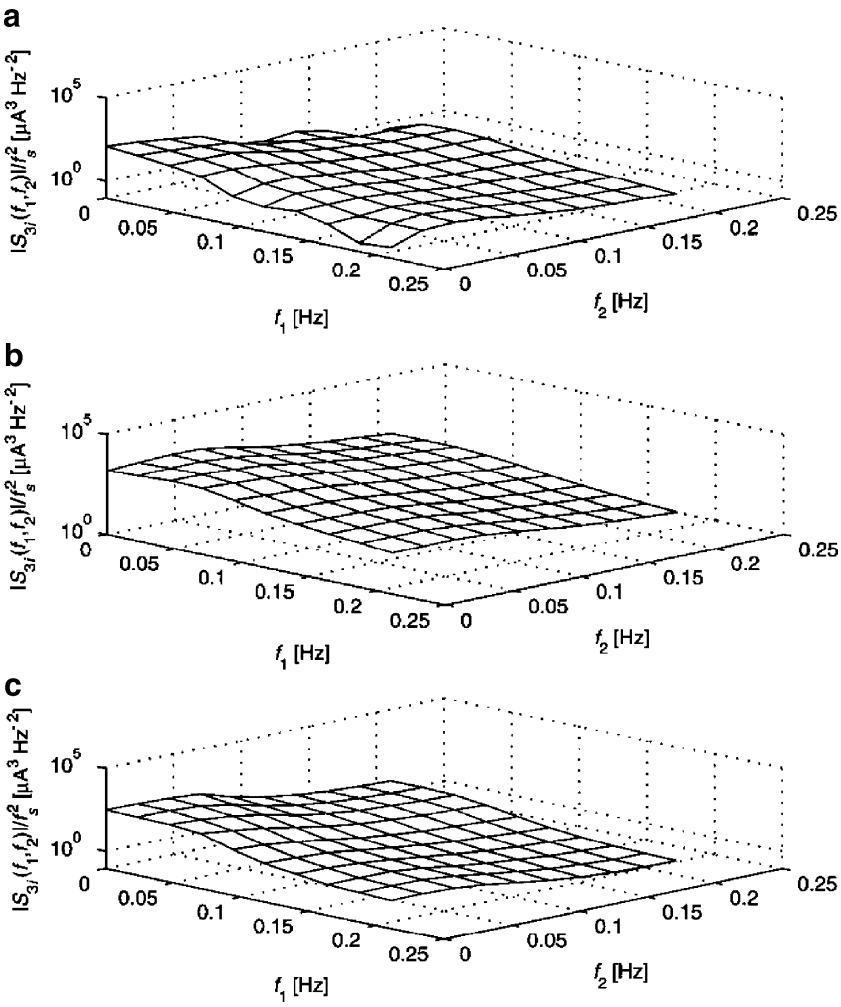

Fig. 8 Module of the bispectrum $|S_{3i}(f_1,f_2)|$ of the observed electrochemical current noise $i(t)$; the quotient of the electrodes area exposed to the electrolyte was equal to: **a** 1:3, **b** 1:6, **c** 1:9

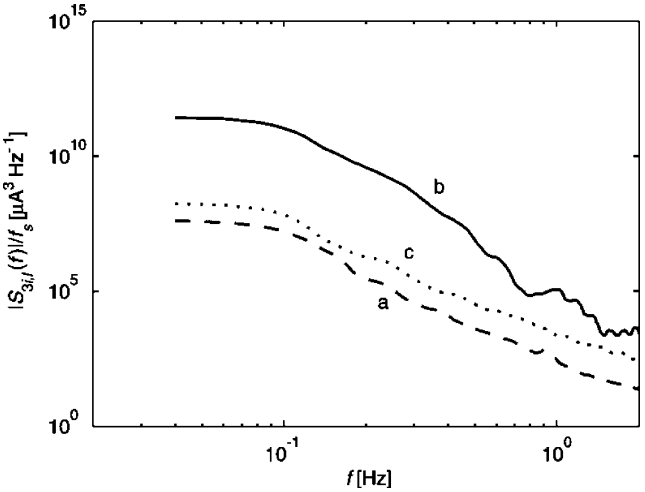

Fig. 9 Integrated bispectrum $S_{3i,I}(f)$ of the observed electrochemical current noise $i(t)$; the quotient of the electrode area exposed to the electrolyte was equal to: *a* 1:3, *b* 1:6, *c* 1:9

current noise. This component is caused by nonlinear processes of metastable pitting that manifest their presence as current transients with characteristic shape (Fig. 5). We can suppose that the registered fluctuations can be modeled by nonlinear system (e.g., Volterra system [19]) to shed light on electrochemical processes responsible for the observed phenomena. This issue would be worthy of a more thorough investigation but this is out of the scope of this paper that focuses only on new measures of pitting corrosion events occurrence.

Conclusions

In this exploratory study, we propose the application of the bispectrum or its integrated version for characterization of pitting corrosion events. The presented results confirmed that the observed electrochemical current noise in stainless steel could be analyzed in the proposed way. Transients,

which are characteristic for metastable pitting, were detected by both proposed functions. The time constant that characterizes the observed current transients can be identified by these functions. Moreover, a way of estimating integrated bispectrum needs almost the same amount of computations as when the power spectrum is calculated. Thus, we suggest that the current noise analysis be limited to the integrated bispectrum exclusively.

The results of the bispectrum and its integral were compared with the power spectrum which in general reveals the energy distribution of the observed current noise versus frequency. Both proposed functions reveal new information that is lost when the power spectrum only is considered.

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