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Nonlinearity of electrochemical noise caused by pitting corrosion

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Abstract

Measurements of statistical quantities other than spectrum or amplitude distribution can provide additional information about mechanisms of electrochemical noise generation. The third-order cumulant and bispectrum are used to determine whether the nonlinear components exist in the observed noise. The electrochemical current noise, recorded under conditions when pitting corrosion dominated, is analyzed. Transients, characteristic for metastable pitting, are observed. The recognized nonlinear components in the recorded current fluctuations characterize processes of the electrode film repassivation during metastable pitting. It is suggested that the intensity and form of the nonlinear components are related to the intensity of metal dissolution into the electrolyte.

Keywords: Corrosion; Noise; Nonlinearity; Bispectrum

1. Introduction

Electrochemical noise measurements (ENM), particularly useful for corrosion-monitoring methods, have been extensively studied for the last 30 years. The methods based on ENM do not need any externally imposed perturbation of the electrochemical system that could change its specific properties. The other advantage of methods based on ENM is their ability to distinguish different types of corrosion. This is very important in the case of localized corrosion when other electrochemical methods are substantially less effective. Typically, current and voltage fluctuations in a three-electrode setup have been observed [1–4]. In the last decade, the ENM techniques have been applied in the laboratory for the evaluation of corrosion protection by organic coat-ing and inhibitors [5,6], and also in industry [7,8].

Different methods of electrochemical noise analysis can be implemented, but even now some of the proposed noise parameters are debatable and can lead to ambiguous results. When uniform corrosion prevails, the methods of noise analysis are quite well established, but even then some serious concerns have to be taken into account [9]. Much more sophisticated cases are the processes of local corrosion. The recorded current noise is only a fractional part of the currents that come from reactions involved in pit creation on both working electrodes [10]. Nevertheless, the measured current fluctuations can be applied for characterization of pitting corrosion processes.

When pitting corrosion is dominant, different methods are proposed [11–14]. The most synonymous seem to be methods that detect the presence of transients, characteristic for processes of metastable pitting, because the probability of metastable pitting is directly proportional to the probability of stable pitting [15].

None of the methods suggested differentiates between linear and nonlinear mechanisms of noise generation. The detection of nonlinear mechanisms is particularly interesting for a study of localized corrosion where a sudden change of instantaneous noise values followed by an exponential recovery are recorded. The observed changes of $I(t)$ and $U(t)$ are caused by a breakdown in the surface-protecting film of the electrode followed by its slow partial repassivation. The process of electrode repassivation during metastable pitting is controlled by

dynamically changeable conditions that exist within the pit area. It is highly probable that the process of film repair is nonlinear and can be characterized by nonlinear components present in the observed noise. For instance, there are some suggestions that a nonlinear feedback mechanism in the local passive current of the electrode film may initiate pitting [16].

The observed fluctuations of $I(t)$ and $U(t)$ can be treated as an output signal of the physical system that consists in a set of three electrodes immersed in an electrolyte. The system characteristics can be recognized only by statistical analysis of the recorded noise. A similar approach was assumed in developing stochastic models of pitting corrosion that were validated only by current–time series analysis [15]. Measurements of spectrum and amplitude distribution of noise generated by the system are unable to determine whether nonlinear effects are significant. Even the observed Gaussian distribution of noise in different physical systems is possible for both linear and nonlinear processes [17].

The aim of this work is to characterize the nonlinear components of the observed fluctuations by applying the third-order cumulant and its Fourier transform called the bispectrum [18,19]. The above-mentioned functions characterize the statistical behavior of transients observed in the recorded noise. Moreover, the presence of any relationship between the consecutive transients observed in a time series will be also detected.

The proposed method of analysis is limited to the current noise, because it is connected to the transport of charge (leakage of mass) from the electrodes into the electrolyte and because the current noise measurements are less sensitive to outside sources of distortion than the voltage measurements. This last remark has a very important practical meaning in corrosion-monitoring systems and their application in industry, where intensive sources of distortion are commonly present. The above-mentioned parameters of nonlinearity in time series are described and the results obtained are discussed in detail.

2. Bispectrum and third-order cumulant

The different measures of nonlinearity in time series can be found in Refs. [19–21]. We propose to use a third-order cumulant that detects nonlinearities and intermodulations between different components of the current noise $I(t)$ analyzed [18].

$$C_{3i}(\tau_1, \tau_2) = E[I(t)I(t+\tau_1)I(t+\tau_2)] \tag{1}$$

where $E[I(t)I(t+\tau_1)I(t+\tau_2)]$ denotes an average.

The parameter $C_{3i}(\tau_1,\tau_2)$, that can be transformed by Fourier transform, leads to the definition of the bispectrum function:

$$S_{3i}(f_1,f_2) = \sum_{\tau_1=-\infty}^{\infty} \sum_{\tau_2=-\infty}^{\infty} C_{3i}(\tau_1,\tau_2)\, \mathrm{e}^{-\mathrm{j}2\pi f_1 \tau_1}\, \mathrm{e}^{-\mathrm{j}2\pi f_2 \tau_2} \tag{2}$$

where the function $C_{3i}(\tau_1,\tau_2)$ is obtained for a discrete time signal $I(t)$ determined at instants $t = 0, \Delta t, 2\Delta t, \ldots$; Δt —the interval between consecutive noise samples.

Both functions defined can be applied equivalently due to their unambiguous relationship by Fourier transform. The bispectrum function $S_{3i}(f_1,f_2)$ is equal to zero, when the process $I(t)$ is Gaussian and linear. It is constant if the process $I(t)$ is non-Gaussian and linear. It is not equal to zero and changes, when $I(t)$ is a nonlinear process. The process $I(t)$ is linear in the case when it is represented by the following equation [22]:

$$I(t) = \sum_{k=0}^{\infty} h(k)w(n-k) \tag{3}$$

where $h(0) = 1$, $\Sigma_{k=0}^{\infty} h^2(k) < \infty$, and $w(n)$ is a white-noise process. The set $\{h(k)\}$ is an adequate impulse response of the system that determines its frequency characteristic unambiguously. If Eq. (3) cannot describe a process $I(t)$, then the process is nonlinear.

The above-mentioned feature of the bispectrum function means that all Gaussian and linear components of the analyzed noise will become zero and only nonlinear components will be visualized. The spectrum or autocorrelation function, commonly used for random signal characterization, does not give any evidence of nonlinearity in the random signal analyzed [20–22].

A pitting corrosion process manifests its presence in a time series as randomly distributed typical transients, characterized by a sudden drop of an instantaneous noise value $I(t)$ and an exponential return to the previous state ($I(t) \sim \mathrm{e}^{-t/\tau}$) [10]. The presence of the described transients in recording noise causes a plateau on its power spectral density around the frequency $f = 1/2\pi\tau$. Any disturbances of an electrode repassivation process that is modeled as an exponential return of the $I(t)$ value should influence the plateau. Moreover, the proposed functions should detect whether any correlation between the consecutive transients exists.

The function $S_{3i}(f_1,f_2)$ is estimated from a real noise recording that is limited to N signal samples. The variance of the estimated bispectrum function is inversely proportional to N for large values [22,23].

3. Experimental

ENM were performed in a three-electrode measurement system (Fig. 1) [24]. The identically prepared steel electrode sets were made of CrNi18-9 steel in a cylinder shape each of mass about 2 g. The surfaces of the electrodes were mechanically polished with different grade sandpapers up to 1000 and degreased with

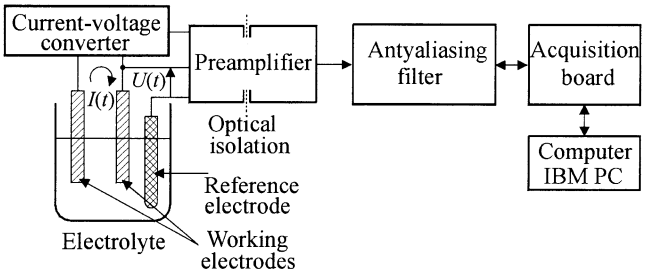

Fig. 1. Measurement system.

acetone. The electrodes were immersed in a 1 M aqueous solution of $FeCl_3$ at room temperature. The noise measurements started 1/2 h after electrode immersion. The current noise samples were collected at a sampling frequency $f_s = 9$ Hz through the same time period of 18 h for each set of electrodes. The total mass change of each pair of electrodes during noise recording was also measured. The measuring error of the mass change did not exceed 5% of its maximal recognized value.

Transients, typical for pitting corrosion, were observed (Fig. 2). The number of visible transients in data records was stable within the time of data recording. The observed electrochemical noise was treated as a stationary random signal. The electrode surface showed evident pits, different in size and depth. Each working electrode of area about 3.5 cm^2 had on its surface more than a dozen or so, visible and separate pits of depth up to about 1 mm and size not greater than 1–3 mm^2. Fig. 3 displays the power spectral density of the registered current noise. The function $S_i(f)$ obtained for all the electrode sets had a visible roll-off around a frequency of $f \sim 10^{-2}$ Hz that is relevant to the presence of transients in the recorded noise. The power spectral densities were calculated using Welsh's averaged method from noise records, each about 6×10^5 noise samples long [26]. The single spectrum was calculated from 2^{14} samples using Hanning windowing. Such large numbers of samples for each spectrum enabled estimation of the power spectral density at very low frequencies down to

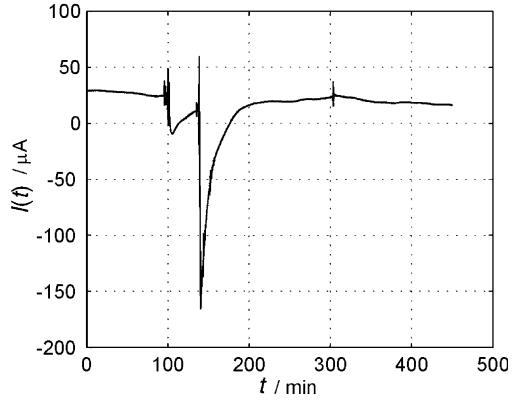

Fig. 2. The transient in the observed current noise caused by pitting corrosion.

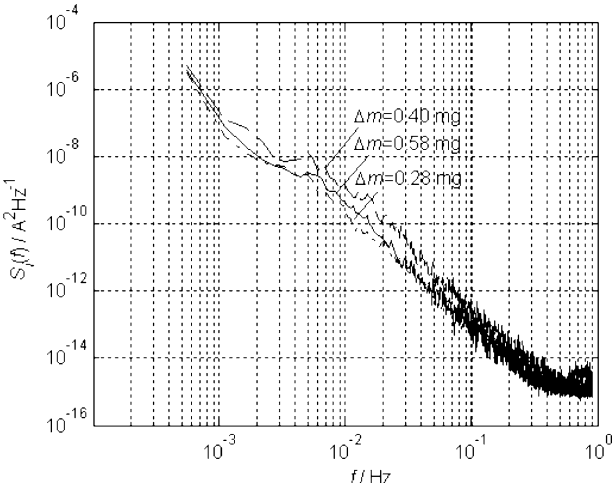

Fig. 3. Power spectral density $S_i(f)$ of the recorded current noise for the three identically prepared electrode sets; Δm —loss of mass of the electrode set during time of noise observation.

singular milliHertz. The power spectral densities from Fig. 3 were averaged over the number $L = 36$ of spectra. The random error of the calculated power spectral density was inversely proportional to the square root of number L which was adequate to 16% [26]. The values of the summarized loss of mass, Δm, for the working electrodes are also given in Fig. 3.

4. Results and discussion

The measures of nonlinearity presented were calculated for the recorded noise. The results obtained for $C_{3i}(\tau,2\tau)$ and $S_{3i}(f_1,f_2)$ values are displayed in Figs. 4 and 5. The bispectrum was calculated using fast Fourier transform of signal segments of length 2^{10} samples and averaged over number $L = 6 \times 10^5/2^{10} \approx 580$ times. The random error of the estimated bispectrum at each point (f_1,f_2) does not exceed a value of $2/\sqrt{580} \approx 8\%$ [23]. A

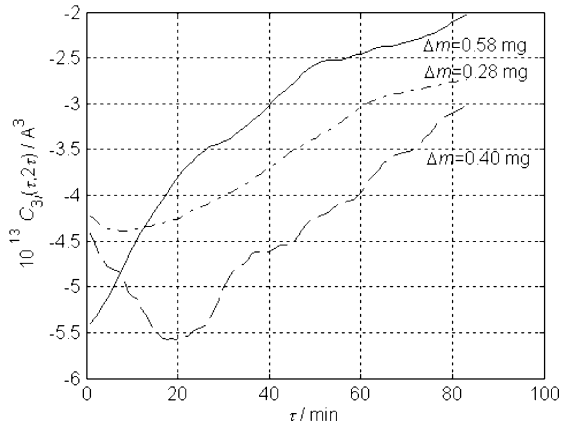

Fig. 4. Third-order cumulant $C_{3i}(\tau,2\tau)$ calculated for the recorded current noise; Δm —loss of mass during the same time of noise observation for each of the three identically prepared electrode sets.

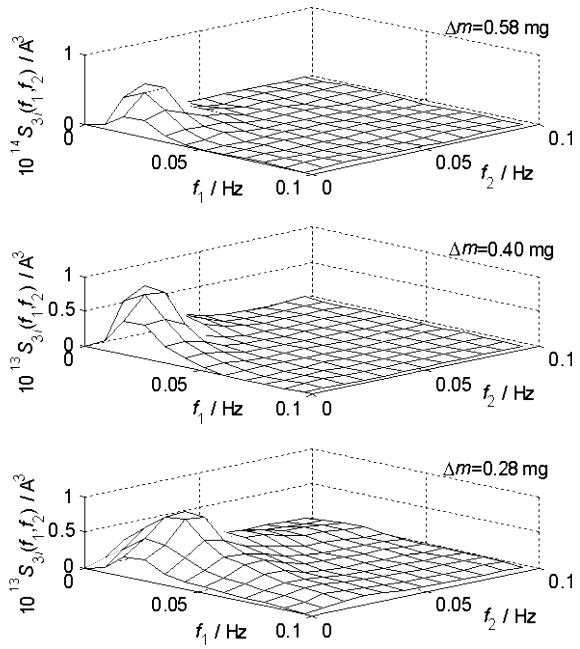

Fig. 5. Bispectrum function $S_{3i}(f_1,f_2)$ calculated for the recorded current noise for the three identically prepared electrode sets having different mass losses, Δm, at the same time of noise observation.

similar value of the random error can be assumed for the estimated third-order cumulant [21]. The necessary computations were carried out in MATLAB software, using scripts prepared by us and also functions from the higher-order spectral analysis toolbox [21].

All the estimated functions have a different course for each of the recorded noise. The differences observed are significantly greater than the values accepted due to the error of their estimation. This evidently confirms the existence of some differences in the mechanisms of noise generation in the steel electrode sets investigated, though nominally their methods of preparation were identical. Also, the measured total loss of mass during the time of noise recording was different between samples by a factor of 2, which repeatedly exceeded the measuring error. The estimated power spectral density of the current noise showed a plateau around $f \sim 10^{-2}$ Hz, caused by the transients observed in noise records. There is a clear relationship between the intensity of the power spectral density and the measured loss of mass (Fig. 3).

All the bispectrum functions had a non-zero component around frequencies $f_1, f_2 \sim 10^{-2}$ Hz. Its presence is caused by the observed transients in data records. Similar behavior of the bispectrum function, as obtained for the analysis of noise recorded during the experiment, was recognized also for computer-generated noise. The simulated random signal consisted of white-noise and randomly distributed transients, characterized by a sudden drop of an instantaneous noise value and an exponential return to the previous state for a given constant τ-value. The amplitude of the simulated transients was constant but instants of transient occurrence were random. The bispectra, calculated for the computer-generated noise, had one maximum around a frequency point f_1, $f_2 \approx 1/2\pi\tau$. The maximum moved when the τ-value was changed in the prepared noise generator. The observed shape of the bispectrum having a single maximum for the noise analyzed around $f_1, f_2 \approx 1/2\pi\tau$ could be predicted also from the other practical examples that can be found in Ref. [21].

For the data record when the loss of electrode mass $\Delta m = 0.28$ mg was a minimum, the non-zero values of the bispectrum (Fig. 5) extend to much higher frequencies than for the other data analyzed. We suggest that the observed result may be explained by the stochastic nature of the electrode repassivation processes that are responsible for the shape of the observed transient (exponential return of current to the previous value before transient occurrence). In the case analyzed, when $\Delta m = 0.28$ mg, the time constant, τ, being a slightly fluctuating random value, tends towards lower values that are equivalent to faster values on an average electrode film recovery. This means that the maximum of the bispectrum function is moved into higher frequencies and can be non-zero in a broader frequency band due to the increased variance of the τ-values. The statistically faster processes of the electrode film recovery during metastable pitting (shorter recovery time, characterized by smaller τ) cause the lower probability of stable pitting that is responsible for the decrease of the metal mass. This suggested explanation is supported by the theoretical models of pitting corrosion processes proposed by Williams et al. [16] and Shibata [25]. The longer time of repassivation (lower repassivation rate) is in accord with an increase in the probability of macropit formation [25].

The proposed explanation does not assume any detailed reasons why the repassivation processes are faster or slower in the electrode sets examined but many different suggestions can be quoted, e.g. the influence of heterogeneous steel admixtures that can differ slightly between the electrode sets examined, local surface tension effects or different hydrodynamical conditions [24]. The clarification presented explains only the observed behavior of the bispectrum function and justifies its usefulness for the estimation of pitting corrosion presence and intensity. The detailed mechanisms of the electrochemical reactions on metal surfaces are beyond the scope of this work.

All the data investigated showed a global maximum of the bispectrum and its continuous drop outside of the maximum. The position of the maximum is presumably determined by the averaged τ-value. The existence of only one maximum means that consecutive transients are uncorrelated (their occurrence in noise is independent) and the observed current noise can be recognized as a Poisson process [22,23].

5. Conclusions

The chosen measures of nonlinearity in random signals are calculated for recorded electrochemical current noise samples. Differences between the calculated nonlinear quantities, at least a few times greater than their errors of estimation, are observed. The results suggest that some differences in the noise generation mechanisms between the electrode sets investigated are present when pitting corrosion prevails. The observed different shapes of the bispectrum functions can be explained by the effectiveness of the electrode repassivation processes. The measured different mass changes of the working electrodes are reflected by different positions of the maximum of bispectrum function. This suggests that the bispectrum can be treated as a potentially sensitive measure of pitting corrosion processes. We would like to underline that no independent evidence exists to confirm the explanation presented but the proposed reasoning explains the behavior of the calculated bispectrum functions and is supported by theoretical models of pitting corrosion proposed in Refs. [15,25]. The other published results of application of the bispectrum function confirm that the bispectrum appears to indicate the structure in the noise data investigated (presence of transients) [4].

The proposed measures of nonlinearity in current noise records give additional information about the nature of the observed corrosion process. The suggested explanation of the bispectrum course connects its behavior with the processes of repassivation at the metastable pitting events.

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