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The Analysis of Stationary Electrochemical Noise*

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Electrochemical noise is electrochemical technique of growing interest. In the case of random signals obtained by discussed method the power spectral density is one of the fundamental characteristic of process. However its correct estimation imposes stationarity condition on signal under analysis. In the paper the authors present technique for quantitative assessment of degree of non-stationarity for electrochemical noise data by means of the Wigner-Ville transform, which enables calculation of local power spectra.

Key words: electrochemical noise, pitting corrosion, Wigner-Ville spectrum, stationarity

The availability of novel signal processing techniques and a continuous development of equipment stimulate electrochemical investigations of various systems. For instance, the invention of electrochemical noise (EN) technique was a great progress in modern electrochemistry. According to the ASTM standard from 1994, this technique is based on the analysis of current and/or potential fluctuations of low amplitude and the frequency usually below 10 Hz. Fluctuations originates mainly from natural variations in electrode kinetics. Electrochemical noise is often considered as a random phenomenon coupled with deterministic kinetics.

The importance of electrochemical noise measurements arises from their essential from other popular electrochemical techniques. The most of analytical measurements are based on the perturbation of the system, which produces characteristic response, provided that the perturbation initially introduced to the system was well-defined. In contrast, in the electrochemical noise technique fluctuations generated spontaneously by the system allow one to determine its properties. The question is how to compare the data obtained by EN method with those obtained using other methods. Attempts to answer this question are being made since the 60. of XX century and are discussed in several literature reports [1–4]. The approach proposed by Chen and Bogaerts [5] and further developed by Mansfeld, Xiao and Lee [6,7] allows one to recognise EN phenomena in the impedance measurements. Due to the stochastic character of the studied phenomena (current and electrode potential fluctuations), it is justified to apply the theory of stochastic processes to describe them. This work is

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* Dedicated to Prof. Dr. Z. Galus on the occasion of his 70th birthday.

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focused on the characterization of the properties of electrochemical noise under stationary conditions. Stationarity is defined as the constancy of statistical description of processes in the function of absolute time of its occurrence [8].

The constancy of statistical properties of stochastic processes is very important, which becomes clear if one recalls the Wiener-Khintshin theorem. It is stated there that autocorrelation function enables one to determine the power spectral density (PSD). PSD is the most important frequency-based parameter used for the description of electrochemical system experiencing EN perturbation. According to the definition, it represents the energy distribution in stochastic process. It is successfully utilized in the determination of the reaction rate [9], investigations of the localized electrochemical corrosion [10], batteries [11] or gas evolution processes [12], provided that stationary processes are considered. For the processes the statistical properties of which are time-dependent (non-stationary processes), the PSD function fails in the precise description of energy distribution within particular frequencies and provides only averaged results.

The lack of stationarity makes the application of autocorrelation function impossible in many cases of real signals, especially in the EN, which is strongly non-stationary. For this reason, autocorrelation function was reformulated to obtain its time-dependent form, known as the function of Wigner and Ville. The applicability of this function to the quantitative analysis of stationarity was the objective of this work.

THEORETICAL BACKGROUND

Weak stationarity of the given stochastic signal, $x(t)$ is defined by the following conditions [13]:

$$\mu_x = E[x(t)] = const \tag{1a}$$

$$\gamma_x(t_1,t_2) = E[x(t_1)x^*(t_2)] = \gamma_x(t_2 - t_1) \tag{1b}$$

$$\mathrm{var}[x(t)] < \infty \tag{1c}$$

where $E[]$ stands for the expectation operator, and μ_x and γ_x denote the mean value and autocorrelation function, respectively. Asterisk denotes complex conjugate in formula (1b). It is omitted in further calculations, since only real signals were assumed. According to (1c), stochastic signal of finite variance is weakly stationary. However, its statistical properties of first (1a) and second order (1b) remain independent on the absolute time, t. The value of autocorrelation function, γ_x depends only on the relative time distance between two moments, t_1 and t_2. Noteworthy, the above definition is weaker than the assumption of strict stationarity, which implies time independence at any order. Let's assume that autocorrelation function can be redefined by introducing the weighting factor, $w(t)$ [13]. Then, a new time-dependent autocorrelation function is obtained:

$$r_x(t_1,t_2) = w\left(\frac{t_2 + t_1}{2}\right)\gamma_x(t_2 - t_1) \tag{2}$$

$w(t)$ function describes the dependence of classical autocorrelation function on the absolute time. Its argument is the arithmetical mean of two time moments, t_1 and t_2. By introducing the relative time shift, $\tau = t_2 - t_1$, equation (2) can be rewritten as:

$$r_x(t - \tau/2, t + \tau/2) = w(t)\gamma(\tau) \tag{3}$$

Applying the change of variables from equation (3), the stationary autocorrelation function, γ_x can be defined as:

$$\gamma(t_1, t_1 + \tau) = E[x(t_1)x(t_1 + \tau)] = E[x(t)x(t + \tau)] \tag{4}$$

Subscript x can be omitted due to the postulated independence of γ_x on the absolute time. After the Fourier transformation of both sides of eq. (3) with respect to τ, one obtains the following spectral representation of the discussed formula:

$$W_x(t, f) = w(t)\Gamma_x(f) \tag{5}$$

$W_x(t, f)$ function is referred as the Wigner-Ville spectrum of stochastic signal $x(t)$. $\Gamma_x(f)$ represents power spectral density function and was derived from eq. (3) applying the Wiener-Khintshin theorem. Due to the fact that $w(t)$ is independent on τ, it remains in the same form as in (3). From equation (5) it can be concluded that $w(t)$ factor quantifies the difference between the global power spectrum, $\Gamma_x(f)$ and the local power spectrum calculated in the particular vicinity of the absolute time moment, t. Noteworthy, for the stationary signal the time-dependent autocorrelation function (2) reduces to the form given by (1b), *i.e.* to the stationary autocorrelation function. Thus, for the stationary signal the Wigner-Ville spectrum is identical to the ordinary power spectral density. This justifies an approach to treat $w(t)$ as the measure of the local deviation of the signal from stationarity.

EXPERIMENTAL

In the measurements cylindrically shaped steel working electrodes, type 0H18N9 were used. Their active surface area (2 cm^2) was polished with abrasive paper (grade from 600 to 1000), and rinsed with ethanol prior to the immersing in the aggressive medium. Ferric (III) chloride of analytical purity was used to prepare the solution in distilled water. Platinum rod served as a counter electrode. Coupling current of the frequency of f_s = 6 Hz was applied using a PCI-DAQ-16-XE-50 card (National Instruments). Analogue signal (amplification and anti-alias filtering) was processed using the appropriate system [14] from the SCXI product line of the same manufacturer. Experimental setup was constructed according to the scheme proposed in reference [15]. It is presented in Figure 1.

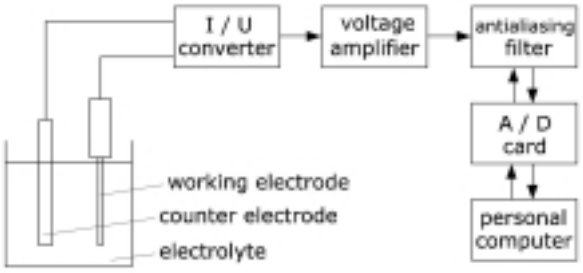

Figure 1. A scheme of the experimental setup.

RESULTS AND DISCUSSION

The objective was to develop a simple and reliable algorithm for the quantitative estimation of a degree of non-stationarity in any electrochemical response. In order to verify theoretical assumptions presented in the previous sections, the series of simulations were performed. Another aim was to convert the presented formulas into discrete forms. Discrete representations are required for discrete Wigner-Ville spectrum, in which the utilized frequency band is half as high as that determined using the Shannon-Kotielnikow sampling theorem. Specific issues concerning proper sampling in the case of WV spectra are widely discussed in the literature [16–18].

The utilized algorithms were implemented in Matlab® and in its free version GNU Octave, yielding the same numerical results. In Figure 2B the results of the application of the discussed procedure to the simplest white noise signal (WN) are presented (Fig. 2A, zero-mean, standard deviation equal to 0.99 in arbitrary units) are presented. Due to the significant scattering of the estimates of $w(t)$ function calculated using the raw Wigner-Ville spectrum (dots in Fig. 2B), one performed smoothing of the spectrum using Hann window of 1001 samples-in-length (solid line). The smoothed estimate was in agreement with theoretical assumptions, since for the stationary signal local Wigner-Ville spectra are equal to the power spectral density. Raw estimate (dots) is located randomly at both sides of $w_{SWVD}(t)$. In Figure 3 non-stationarity of stochastic signal results from its multiplication by the Gaussian-shaped function of the centre located in the middle of exemplary responses (Fig. 3A). The estimated non-stationarity of the signal (Fig. 3B) reflects the difference between global and local power spectra defined for the consecutive time moments.

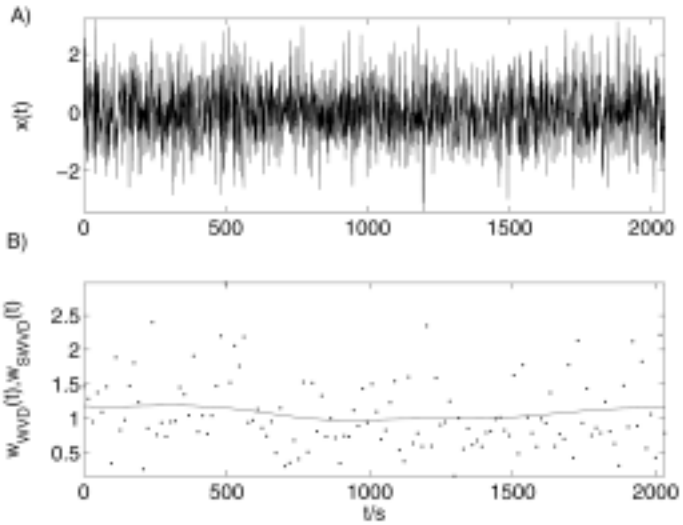

Figure 2. Non-stationarity detected in the stationary white noise of the zero-mean and standard deviation equal to 0.9935 (Fig. 2A). Estimates of $w(t)$ function were calculated on the basis of raw Wigner-Ville spectrum (dots in Fig. 2B) and averaged using Hann window of 1001 samples-in-length (solid line).

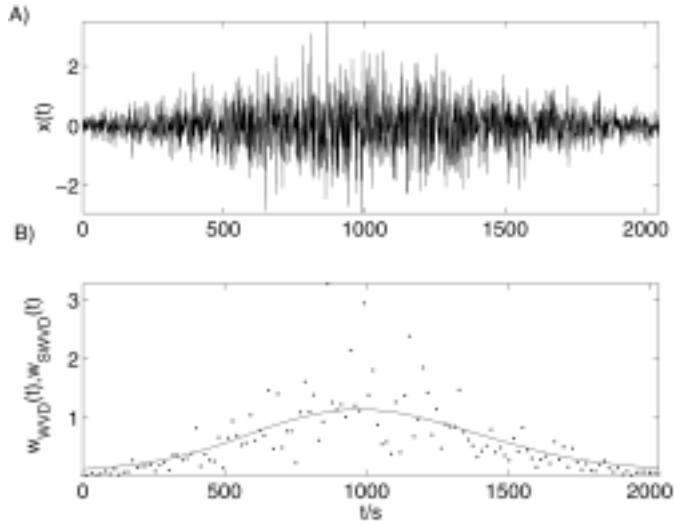

Figure 3. Non-stationarity of stochastic signal resulting from its multiplication by the Gaussian-shaped function located centrally in the responses (Fig. 3A). Non-stationarity of the signal (Fig. 3B) was calculated on the basis of raw Wigner-Ville spectrum (dots in Fig. 3B) and averaged using Hann window of 1001 samples-in-length (solid line).

In the applied algorithm an important simplification was the representation of $w(t)$ as the quotient of the local spectrum and the overall spectral density. Such a procedure does not introduce correct weighting coefficients for particular frequencies, yet utilizes the averaged energy. Despite this drawback, the analysis of the signals is still possible without changing the magnitude and the shape of local power spectrum. The signal presented in Figure 4A consists of a white noise (standard deviation 0.81), which suddenly changes its composition (in the central part of the spectrum) into the coloured noise generated as a convolution of WN using a high-pass filter (standard deviation 0.71). However, the obtained results clearly confirm the change in spectral properties of the studied signal. In Figure 4B only smoothed estimate is shown for clarity. Figures 5 and 6 illustrate the implementation of detection algorithm to the real electrochemical signals recorded during pitting corrosion experiments.

The measurement of the coupling current was performed in very aggressive medium and under conditions of anodic polarization of the working electrode in order to develop pits within relatively short time interval (several hours). In Figure 5A series of peaks corresponding to the meta-stable pitting of stainless steel in 0.5 M ferric chloride solution is presented. The variations in the Wigner-Ville spectra are indicative for the increase of non-stationarity. They correlate well with local corrosion events. The strongest deviation of the local spectra from the global power spectrum coincides with regions of the increased pitting activity, located in the initial and the final ranges of the response.

Figure 6A corresponds to the situation of stable pitting corrosion observed for the same type of steel in more concentrated solution (1 M). Metal dissolution in stable pits does not cause an appearance of high current peaks; however, some small peaks

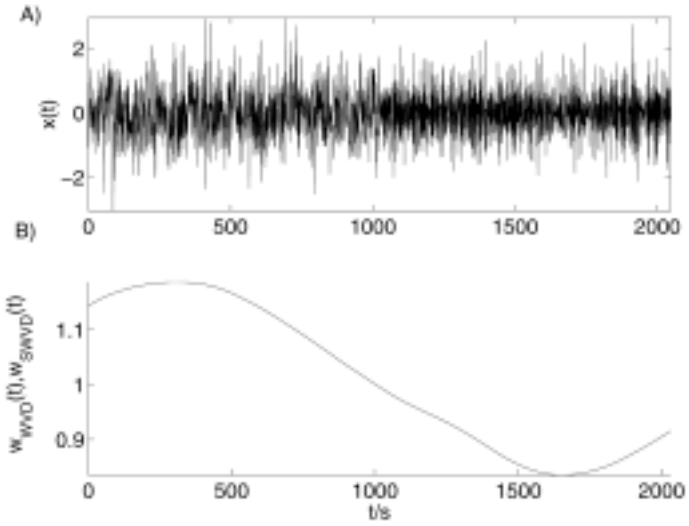

Figure 4. Exemplary white noise signal (Fig. 4A) (standard deviation 0.81), which changing its composition (central part of the response) and becomes coloured noise, generated by convolution of WN using a high-pass filter (standard deviation 0.71). Non-stationarity (Fig. 4B) was calculated using raw Wigner-Ville spectrum averaged with Hann window of 1001 samples-in-length (solid line).

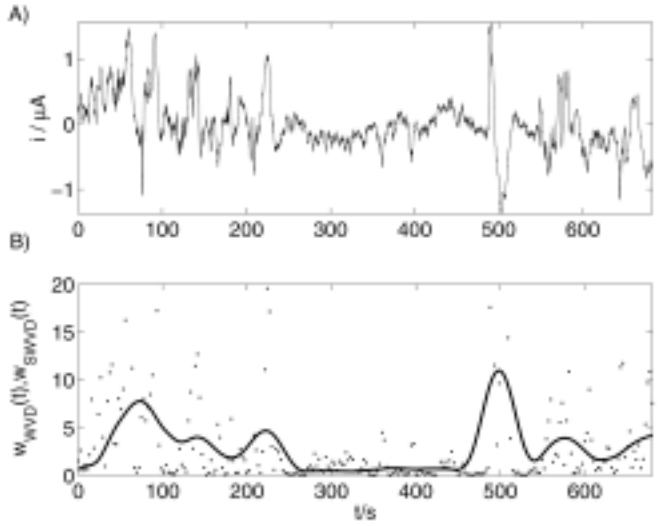

Figure 5. A series of peaks corresponding to meta-stable pitting of stainless steel in 0.5 M ferric chloride solution (Fig. 5A). Non-stationarity (Fig. 5B) was calculated using raw Wigner-Ville spectrum (dots in Fig. 5B) and averaged with Hann window.

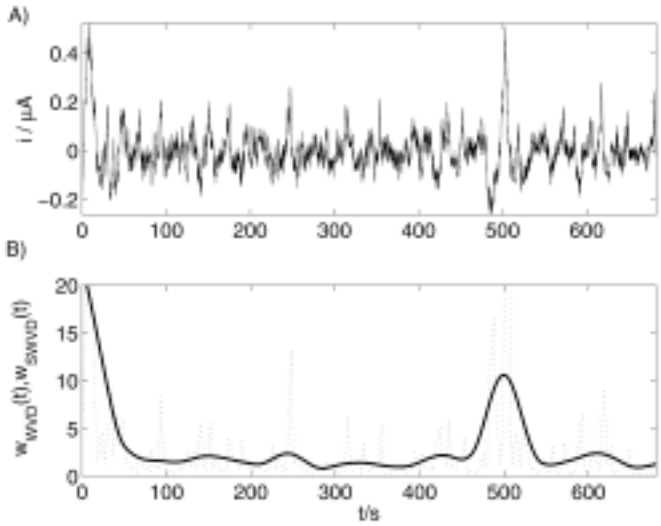

Figure 6. Stable pitting corrosion observed for the same type of steel in more concentrated solution (1 M) (Fig. 6A). Non-stationarity (Fig. 6B) was calculated using raw Wigner-Ville spectrum (dotted line) and averaged with Hann window (solid line).

(one order of magnitude less intense) are noticeable. It should be mentioned that in certain cases the non-smoothed estimated (dotted line) better illustrates the changes in spectral properties, since is more time-selective. Thus, depending on the expected behaviour of a given electrochemical system, the proposed detection procedure can be appropriately adapted.

CONCLUSIONS

In most of the cases, spectral composition of electrochemical noise is not uniform. This fact makes the reliability of the EN experimental data doubtful. Thus, estimation of a degree of non-stationarity of the noise signal is of fundamental importance. For this purpose, a new method utilizing the difference between power spectral density and local Wigner-Ville spectra was developed and described in this paper.

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