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METHOD OF ELECTROCHEMICAL NOISE MEASUREMENTS FOR CHARACTERIZATION OF LOCAL CORROSION PROCESSES

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Abstract − The new method of electrochemical noise (current and voltage fluctuations) measurements is presented. The proposed method can characterise local corrosion events while the other electrochemical methods are much less effective than electrochemical noise measurements. The new measurement setup is proposed. The system can identify metal surface where local corrosion events take place. The realized measurement system is described in detail. All the practical problems of noise measurements and methods of outside distortion reduction are presented. The preliminary measurement results are also discussed.

Keywords: electrochemical noise, local corrosion

1. INTRODUCTION

Electrochemical noise is a well-known phenomenon, applied for corrosion processes characterisation in laboratory and industry practice [1-3]. It is particularly useful for local corrosion processes for the other electrochemical techniques have quite limited application [3]. The standard measurement system consists of a three-electrode set (Fig. 1) [4,5]. The current and voltage fluctuations are observed and analysed for corrosion evaluation. The reliable results are obtained for characterization of rate of uniform corrosion processes.

When the localized corrosion attack takes place, the characteristic transients in current and voltage fluctuations are observed (Fig. 2) [6-8].

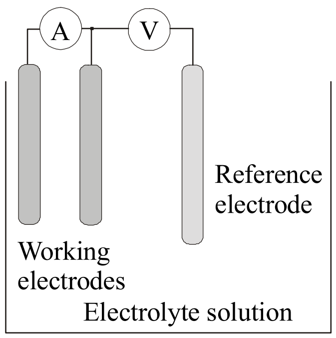

Fig. 1. The circuit for observation of electrochemical noise (current and voltage fluctuations)

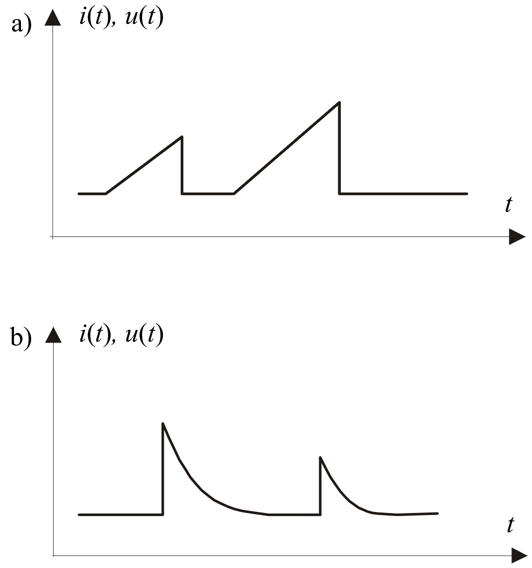

Fig. 2. The oserved characteristic transients of current $i(t)$ and voltage $u(t)$ noise for local corrosion events in materials: (a) stainless steel, (b) carbon steel and aluminum alloy

The shape of transients depends on corroding material. The transients of triangle shape (Fig. 2a) are observed for stainless steel [3]. The transients, characterized by sudden change of an instantaneous noise value and an exponential return to a previous state, are observed in carbon steel or aluminium alloy and are caused by local breakdown in a surface-protecting film of electrode followed by a slow partial repassivation [6]. Corrosion processes are slow, so the described transients take place at least a few seconds or are even significantly longer.

The mentioned system of the three-electrode set (Fig. 1) does not enable to determine a working electrode and area where the local corrosion event happens.

It is proposed a new method of noise measurements and the measurement system that makes possible to point to an electrode where the local corrosion event occurred [9]. Determination of the electrode area where the local corrosion events take place more frequently can evaluate whether only a few places on metal surface are under corrosion attack (e. g. single, separate pits are in progress) or breakdowns in a surface-protecting film of electrode are more uniformly distributed. The main idea of the new method consists in applying a set of N working electrodes and an additional electrode of area substantially greater than the area of each working electrode. The current or voltage fluctuations between each working electrode and the additional electrode can be observed and analysed. Detection of characteristic transients and their statistical distribution between the *N* working electrodes give information about a distribution of corrosion events occurrence on the investigated metal surface – total surface of *N* working electrodes. The intensity of the characteristic transients occurrence is directly connected with creation and size of pits on metal surface [10].

The initial experimental results are also presented and discussed.

2. MEASUREMENT METHOD

The method applies a set of *N* working electrodes and an additional electrode of area 10-times greater than the area of each working electrode. The electrodes are made of the same metal, using the identical method of their surface preparation.

Voltage fluctuations between each working electrode and the additional electrode can be observed separately (Fig. 3). When current fluctuations between each working electrode and the additional electrode are observed, the same multi-channel voltage amplifier and current/voltage converters, attached to the each channel input, can be applied.

The proposed solutions of the voltage or current noise measurement system limits a number *N* of working electrodes to the number of the amplifier channels. Another method does not have such limitation, it requires only two channels but additional hardware is necessary (Fig. 4). The electrodes are connected to the nodes of the serial circuit of resistors having resistance *R* each. The additional electrode has also significantly greater area (10 times) than the working electrodes. The resistance between the additional electrode and electrolyte is a factor of about 10 times lower than between each of the working electrodes and electrolyte. The value of $R \in (0{,}1 \div 1)\ \Omega$ is much lower than a standard resistance between working electrode and electrolyte [2].

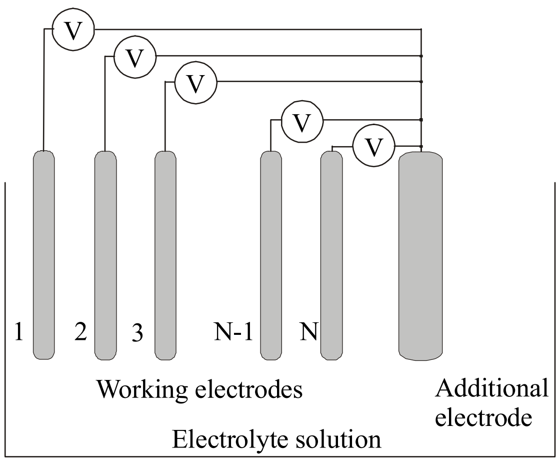

Fig. 3. The circuit for characterisation of local corrosion events on metal surface by electrochemical voltage noise measurements

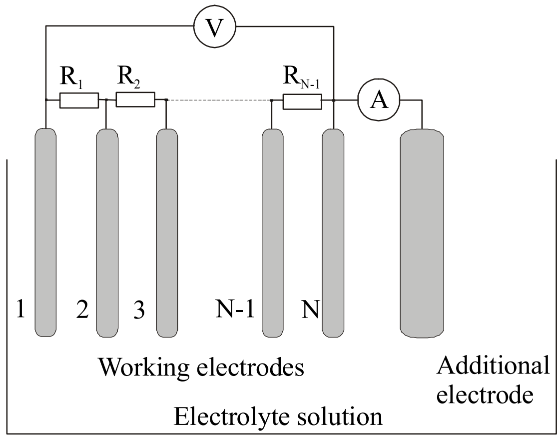

Fig. 4. The circuit for characterisation of local corrosion processes by electrochemical current noise measurements

The given low values of *R* is necessary to assure short circuit between each of the working electrodes and the additional electrode.

The mentioned conditions cause that during a breakdown of a surface protecting film of the *k*-th working electrode, the measured current fluctuation $i(t)$ flows mainly between the additional electrode and the *k*-th working electrode. The measured fluctuation of voltage drop $u(t)$ simultaneously (Fig. 4) is caused by current flow only through resistors R_k, $R_{k+1},\ldots,R_{N-1}$:

$$R = R_k + R_{k+1} + \ldots + R_{N-1} \cong \frac{u(t)}{i(t)} \qquad (1)$$

The attached relation is valid only at instants when current transients, characteristic for local corrosion processes, occurs. The measurements of current and voltage fluctuations at instant when transient is detected enable an identification by (1) which working electrode was attacked by local corrosion. The detection of transient can be performed automatically by different algorithm [7,8]. One of these algorithms, based on joined time-frequency analysis, presents Fig. 5 [8].

The all described methods allow a research of the localized corrosion events distribution between the working electrodes. It enables continuous monitoring of chemical environment (e.g. prediction of the maximal depth of pit on the surface of industrial construction [10]), where the electrodes are placed, and efficiency of the existing electrodes protection films in laboratories.

3. MEASUREMENT SYSTEM

The proposed method of voltage fluctuations measurements (Fig. 3) can be prepared by applying a multi-channel voltage amplifier and data acquisition board, controlled by computer. At least a few reasonable ready products are offered [11]. Only special precautions have to be undertaken to avoid ground looping and transmission of distortion to input of the amplifier, mainly from the

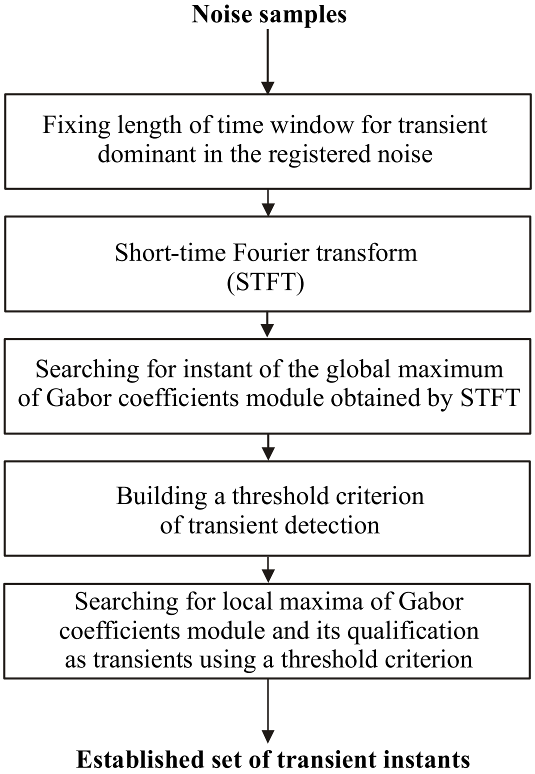

Fig. 5. The algorithm proposed for detection of transients characteristic for local corrosion events [8]

computer [12,13]. The effective method of outside distortion reduction is an application of galvanic isolated multi-channel amplifier. Galvanic isolation can be obtained by applying optocoupler or isolation amplifier that transmit signal digitally across differential capacitive barrier (modulation-demodulation technique) [14].

The current fluctuations, that require only two-channel amplifier, can be realized by the measurement system presented at Fig. 6. The voltage fluctuations observed between terminals of the resistors R_1 and R_{N-1} are gained about 50 times by voltage amplifier made of operational amplifier AD797, that is ultra-low noise amplifier, designed for signal sources of low resistance. The voltage signal is gained again 500 times by voltage amplifier made of low noise operational amplifier LM357. The current fluctuations are converted into voltage fluctuations by current-voltage converter made of a low noise operational amplifier OPA128. The both described signals are attached to the inputs of the multichannel voltage amplifier SCXI1121, produced by National Instruments through the isolation amplifiers ISO122 with unit voltage gain. The described technical solution assures that the both circuits for current and voltage fluctuations are galvanicly separated. All the applied operational amplifiers are power supplied by DC/DC converters to assure isolation between circuits. It prevents penetration of outside distortion through voltage supply circuits. The mentioned precautions reduced intensity of distortion caused by power supply lines at least 20dB at frequency 50 Hz.

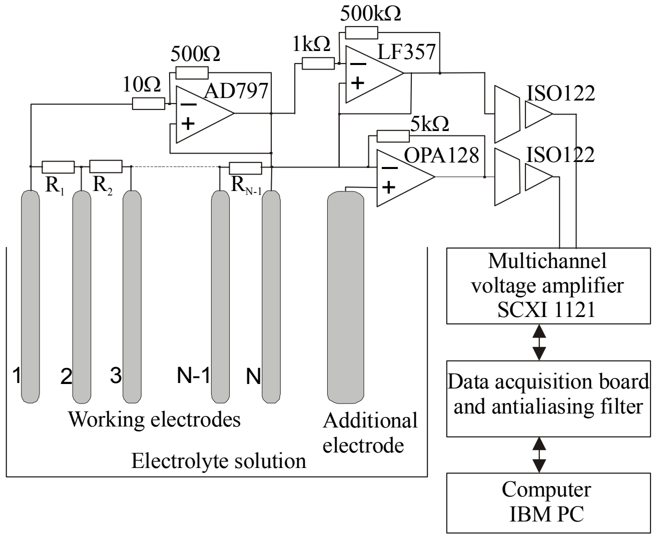

Fig. 6. The realized measurement system for characterisation of local corrosion processes by electrochemical noise measurements

The preliminary obtained measurement results confirm that the prepared system, presented at Fig. 6, can measure voltage fluctuations with power spectral density above 10^{-16} V^2/Hz and current fluctuations above 10^{-15} A^2/Hz within the frequency range 0.08÷40 Hz. For the mentioned results, the prepared measurement system enables identification of local corrosion events within a set of $N \leq 10$ working electrodes by applying only two-channel amplifier.

Usually, multi-channel amplifiers available in the market have four or eight separate channels [11]. The inputs of not in use channels can be also attached to the outputs of amplifiers ISO 122 (Fig. 6) in a parallel way. It enable parallel measurements of the same instantaneous noise values at different voltage gains for each channel. The parallel voltage measurements and an adequate virtual instrumentation that switch off between channels can increase a range of the measured voltage values and resolution of the applied A/D converter. The last remark has significant practical meaning when random signals having normal distribution (like electrochemical noise) are observed for it is always nonzero probability that its instantaneous value exceeds a voltage range of the A/D converter.

4. CONCLUSIONS

The proposed method enables better than in typically applied three-electrode system characterization of the localized corrosion events by electrochemical noise observation. The working electrode, where the breakdown of its protection film occurred, can be identified. The adequate distribution of local corrosion events within the electrode set can be established. All the proposed measurement circuits can be applied for it.

The preliminary obtained results of local corrosion events distribution for a set of N=8 carbon steel working electrodes confirm a presence of differences of factor ten in number of the detected transients between the electrodes during one day measurements.

The presented method of local corrosion events measurements give more detailed information about the nature of the mechanisms that control these events. Such information is significantly crucial when we have to monitor corrosion in changing environmental condition.

The preliminary obtained measurement results suggest that the realized measurement system (Fig. 6), based on commercially available electronic components, enables measurements of very low voltage drops. The observed instantaneous voltage values do not exceed a few μV within frequency range 0.08÷40 Hz.

The registered noise data in the presented multi-channel measurement system can be gathered and saved for the further analysis or can be performed on-time. The mentioned algorithm of transient detection can be performed by a virtual instrument, that controls the process of data acquisition.

The proposed measurement method is more adequate for local corrosion events characterisation than the ordinary used. The method can be used not only for transients detection and for evaluation of its distribution. The other methods of local corrosion events characterisation can be also applied [15].

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