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METHOD OF STUDYING CORROSION PROCESSES OF METAL ELECTRODES BY SURFACE VOLTAGE FLUCTUATIONS

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Запропоновано спосіб дослідження корозійних процесів на поверхні металевого електрода за результатами спостереження флуктуацій напруги на ньому. Розроблено пристрій для обробки цих сигналів. Виявлено, що найбільш інформативним параметром при дослідженні сигналів, пов’язаних із корозійними процесами на поверхні металевого електрода, є форма розподілу ймовірностей миттєвих значень та оцінка їх інформаційної ентропії

Ключові слова: електрохімічна корозія, напруга електричного шуму, форма розподілу ймовірності миттєвих значень сигналу, інформаційна ентропія миттєвих значень сигналу

Предложен способ исследования коррозионных процессов на поверхности металлического электрода по результатам наблюдения флуктуаций напряжения на нем. Разработано устройство для обработки этих сигналов. Выявлено, что наиболее информативным параметром при исследовании сигналов, связанных с коррозионными процессами на поверхности металлического электрода, является форма распределения вероятностей мгновенных значений и оценка их информационной энтропии

Ключевые слова: электрохимическая коррозия, напряжение электрического шума, форма распределения вероятности мгновенных значений сигнала, информационная энтропия мгновенных значений сигнала

1. Introduction

Metals and alloys are important modern construction materials. Wherever metal constructions are operated, substances interacting with metals are present that destroy them gradually. During operation most metals have greater stability in oxidated state that is the result of corrosion. Iron oxides resulting from corrosion of steel constructions have substantially different mechanic properties, so metal constructions can fail to withstand mechanical stress that they are designed for.

Corrosion of metals does great harm to economic activity of enterprises. Equipment for industry collapses due to aging or corrosion. It brings not only great economic losses, but also leads to a global ecological catastrophe.

Various research methods of corrosion processes make it possible to control the electrochemical reactions associated with corrosion processes and to predict changes that arise in the metal as a result of these reactions. These methods are aimed at detection of chemical reactions that take place on the metal surface and at forecasting their impact on the mechanical properties of the metal. Research of chemical reaction types on the metal surface is based on the statement about their electrochemical nature. Thus, the course of such reactions can be controlled or explored using electrical quantities. An important prerequisite for the correctness of such studies is the correct understanding of physical and chemical processes that occur during corrosion processes of the metal surface. For constructing physical models of corrosion processes, the results of potentiostatic or heliostatic surveys, methods of impedance spectroscopy and analysis of acoustic or electrical noise occurring in the process of electrochemical reactions on the metal surface are used.

Exploring of corrosion processes of industrial equipment, pipelines, tanks, vessels is also of great interest. A peculiarity of such objects is complicated access to corroding surface and therefore limitations of methods that can be used to control corrosion processes.

2. Literature review and problem statement

Corrosion is a process that leads to deterioration of material state due to its interaction with the environment, which manifests itself in a local change or a uniform change in wide areas. Local corrosion is more dangerous. It is characterized by extensive material transformation in small areas of the equipment surface and leads to rapid loss of strength and equipment failure. Diagnostics of local corrosion is more difficult.

Corrosion of metals in aquatic environments has electrochemical nature. It is accompanied by electrochemical reactions on the surface of the metal. Processes connected to electrochemical corrosion are usually described be two reactions that occur on two surface areas. In some areas anode zone is formed where oxidation processes occur, and in other areas there is cathode zone where reduction reactions occur [1]. Such a metal surface consists of a multitude of microelectrodes short-circuited through the metal itself.

Research of corrosion processes is carried out by various methods or their combination [2]. Study of electrochemical reaction flow in various conditions is conducted using constant or alternating current. At constant current, electrochemical reaction is monitored using the potential of corroding surface or current that flows through it [3]. At alternating current, the equivalent circuit of layered electrolyte structure near the corroding surface is built for electrochemical reaction study [4] or spectral characteristics of measured signals are analyzed [5].

In production, there are widely used specimens manufactured of the same material as the equipment. The equipment state is being predicted by the state of the specimens that were under the same conditions as the equipment [6, 7]. Specimen installation requires technological mount which makes it difficult to do the research.

To identify some types of corrosion, the acoustic emission method is used, based on the analysis of acoustic noise inside of the material, whereas its surface is subject to corrosive processes [8].

Research of electrical noise of electrochemical reactions that accompany corrosive processes is also promising. Electrochemical noise has been investigated since 1968. Studies have shown that electrochemical noise parameters provide valuable information about complex electrochemical reactions that occur in corroding systems.

Using a voltmeter with high input impedance and low zero offset and an auxiliary electrode of platinum foil such materials as magnesium, aluminum, iron, low carbon steel, and zinc were investigated [9]. It was shown that each detected voltage fluctuation in the metal with its frequency and amplitude corresponds to a certain electrochemical process and should be studied. Voltage fluctuations on electrodes made of pure aluminum, aluminum alloys and magnesium usually have amplitudes of 100μV and are faster than on electrodes made of cast iron, steel and zinc. Voltage fluctuations on electrodes made of cast iron, steel and zinc are less than 50μV. As long as after addition of a corrosion inhibitor oscillations disappeared, fluctuations were explained by corrosion processes.

During the experimental study of electrochemical reactions, a potentiostate and electrochemical cell with three electrodes immersed into electrolyte are often used. The electrode for which its interaction with given electrolyte is studied is called working electrode (WE). The electrode which acts as a reference for measuring potential is called research electrode (RE). Auxiliary electrode that acts as a receiver of electrons (or a source of electrons) for the reactions that occur on WE surface is marked as AE [10]. WE potential is measured relative to RE at constant current density J between WE and AE electrodes. In operation conditions, the installation of three-electrode system is not always possible, so two electrodes are used for studying polarization resistance of electrochemical reaction or electrical noise between electrodes.

Noise is a random process. To describe the electrochemical noise, different estimates of random signals can be used, such as variance or standard deviation in the time domain. In addition, the signal is converted from the time domain to the frequency domain, and then spectral components of the signal are studied [11]. The technique of wavelet analysis can also be used, which is based on a set of wavelets of varying amplitude and duration, and wavelet coefficients are calculated in such a way that linear combination of wavelets reproduces the measured signal [12, 13].

In the study of electrochemical reaction associated with electrochemical corrosion, electrode systems are used that have mutual electrolytic connection. Consequently, the system with all-around access to the surface and electrolyte presence is needed. There is a large number of existing industrial objects that are subject to corrosion processes and whose structure and placement does not allow easy electrode system installation. Electrolyte is present stationary on electrodes. Such objects include various pipelines, vessels, tanks. For example, during gas pumping through gas-main pipelines temperature and pressure changes cause water-containing condensate formation from gas mixture that accumulates inside the pipe and creates conditions for electrochemical reaction flow.

While corrosion processes control on the outer wall of these objects is well mastered and performed regularly, control of corrosion processes on the inner walls can be made only during the large-scale intrapipe survey or when installing additional equipment into the pipe, thus causing considerable difficulties.

It is important to identify and classify electrochemical reactions accompanying corrosion processes that occur inside the pipe as long as electrolyte formed by water-containing condensate favors local corrosion that is much more dangerous.

Galvanic microelectric pairs are known to emerge during electrochemical reactions on the surface of the heterogeneous electrode in the presence of electrolyte. Electrons move between these pairs through the electrolyte and metal. Some of the electrons are redistributed in the thickness of the electrode and potential change emerges in this area. Potential change is chaotic and depends also on the presence and intensity of galvanic microelectric pairs. By measuring the change in potential, namely electrochemical noise, on the electrode surface, changes related to the flow of electrochemical reactions can be indirectly detected. Thus, by measuring electrochemical noise on the outside surface of the pipe, corrosion processes within the pipe can be detected and classified.

3. Purpose and objectives of research

The purpose of the research is to establish the possibility of detecting electrochemical reactions on the surface of the metal electrode by analysis of potential difference on its surface.

To achieve this, it is necessary to solve the following tasks:

– developing a structural diagram of the device for processing the voltage electrical noise signal on the surface of the metal electrode and producing a device for conversion of electrical noise voltage on the surface of the metal electrode into the signal suitable for further digital processing using a computer;

– analysis of the results of electrical noise voltage measurement on the surface of the metal electrode;

– determination of an estimation parameter that enables to identify the presence of electrochemical reaction on the surface of the metal electrode.

4. Method of studying corrosion processes by analysis of electrical noise of electrochemical reactions

4. 1. Device for measuring electrical noise voltage on working electrode

For studying voltage fluctuations on the surface of the metal electrode emerging during corrosion processes, a device has been developed for measuring the voltage on the surface of the metal electrode. Block diagram of the device is shown in Fig. 1.

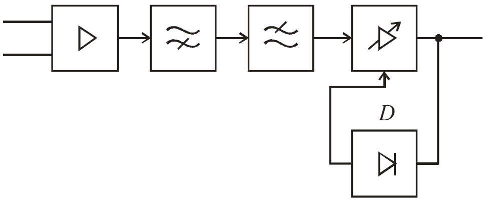

Fig. 1. Block diagram of the device for studying voltage fluctuations on the electrode surface

The frequency range of the noise measuring device is from several Hertz to several hundreds of Hertz. Narrowing the bandwidth increases noise immunity measurements. High-frequency signals that accompany pitting corrosion are of pulse type and due to the wide frequency range fall within a working frequency band of the developed device.

There is a differential amplifier A_1 on the input of the device that provides input symmetry. The amplifier has a frequency-dependent transfer coefficient. This eliminates the effect of DC components, such as the natural potential of electrochemical reactions and various external polarization sources. Without limiting DC gain, the output signal of the differential stage can go into saturation.

The next two stages are a high-pass filter F_1 and a low-pass filter F_2. Using high-pass filter in the first stage is due to the need to eliminate the influence of the bias voltage of the differential output of the previous stage.

At the output of the low-pass filter F_2, there is the amplifying stage A_2 with variable gain for automatic adjustment of the output level. The RMS converter D controls the gain. In order to optimize the number of used processing stages and to provide high gain, each of these stages is tuned for high gain and AC processing only.

According to the proposed block diagram, a circuit diagram of the electrochemical noise measuring device has been developed. The circuit is made on a separate board. To reduce the influence of extraneous noise, the board is fixed in a metal casing that acts as an electromagnetic screen. The device is powered from a separate autonomous supply that is also contained in the package. Laboratory studies were conducted using this device.

4. 2. Method of experiment

For testing of the developed device, the experimental setup has been made (see the block diagram in Fig. 2).

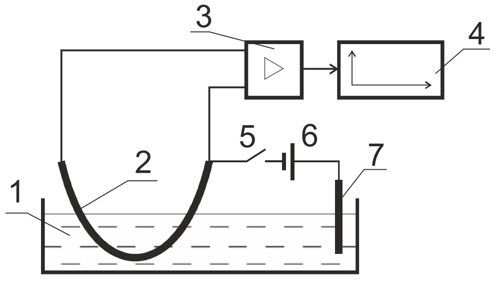

Fig. 2. Block diagram of the experimental setup:
1 — electrolyte bath, 2 — metal electrode, 3 — amplifying and filtering block, 4 — processing and display block, 5 — commutator, 6 — current source, 7 — auxiliary electrode.

The setup consists of a bath of electrolyte. Water or 10 % solutions of NaCl, Na_2CO_3, H_2SO_4 are used as electrolytes. The metal electrode is made of steel St3 of size 20×70×1 mm. The developed device performs filtering and amplification tasks. Processing and display of measurement results are performed on the computer. An accumulator is used as a current source. Auxiliary electrode is made of pressed coal. Experiments are conducted at 20 °C.

Voltage fluctuations on the surface of the metal electrode can be caused by various sources. Among them are thermal noises, the noise of the contact pair in place of joining conductors to metallic electrodes, electromagnetic interference and so on.

5. Results of studying electrical noise voltage caused by electrochemical reactions on the surface of metal electrode

For determining the level of noise components that are not associated with electrochemical reactions, the device input has been connected to the tested metal electrode without electrolyte. The signal formed on the output of the developed device was recorded for further processing and analysis.

Measured signal contains the main component at 50 Hz and random noise component. The maximum amplitude of the output signal of developed device is within the 3 mV range. Signal form for dry metal electrode is shown in Fig. 3.

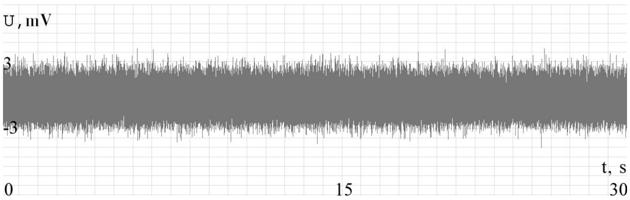

Fig. 3. Signal form on dry metal electrode during 1 minute

The next experiment was conducted with metal electrode immersed into the bath with electrolyte. It was found that when metal electrode is immersed in the electrolyte the signal amplitude at its ends increases. At the beginning of the experiment, the maximum amplitude of the signal increased to approximately 15 mV. Within 30 minutes, the maximum amplitude gradually decreased to the steady value (about 6 mV). Then the maximum amplitude of the signal did not change significantly. After a long exposure time, signal level got stabilized. The form of noise signal at the beginning of the experiment is shown in Fig. 4.

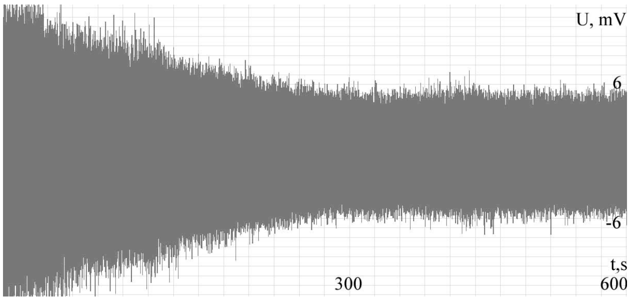

Fig. 4. Noise signal on the metal electrode immersed into electrolyte during 30 minutes

Decreasing of noise signal amplitude can be explained by the forming of oxide film on the electrode surface that makes electrochemical reactions impossible. In the beginning of the experiment, there is no oxide film, so the processes are more intensive and noise signal with greater amplitude can be detected, and after some time amplitude reduces to the steady level.

In order to change the parameters of the flow of electrochemical reactions, the metal electrode was polarized by external DC source. Within 10 minutes, external source current of 10 mA flew from the metal electrode through the electrolyte to the carbon electrode. After polarization, the external current source was disconnected and electrical noise voltage was recorded. Voltage amplitude compared to the previous experiment did practically not change and was about 6 mV.

6. Result discussion

Results of voltage measurements were recorded and processed using a PC. Sample rate 8 kHz and 16-bit analog-to-digital conversion were used. Processing included calculation of spectral components of the signal values, moving standard deviation, variance, information entropy and probability distribution of instantaneous values of the signal.

Analysis of spectral components of the signal in various experiments has not given a reliable estimation parameter. After several series of external current source polarization of the metal electrode and several polarity changes, it was found that fluctuation of spectral signal components at frequencies between 10 and 12 Hz is present. The spectra of two signals are shown in Fig. 5.

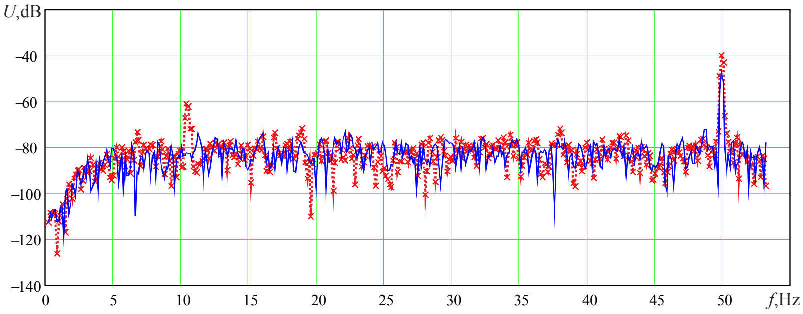

Fig. 5. Results of spectral analysis of signal on the metal electrode immersed into electrolyte

Two moments were selected for result displaying. The spectrum of the signal with a temporary 10.5 Hz component is marked red. The signal without this fluctuation is marked blue. Periodic fluctuation appearance at these frequencies can be associated with a periodic impulse electrochemical process that occurs on the surface of the electrode. But this process seems to be nonstationary.

Standard deviation and variance calculated using sliding window for the time of the experiment have not provided reliable differentiation of signals obtained in various experiments.

Probability distribution of instantaneous signal samples turned to be more informative. Probability distribution shape allows identifying of extraneous processes on the metal surface. However, to provide an acceptable resolution when analyzing the distribution shape it is necessary to process large amounts of data. In particular, results shown in Fig. 6 show how the shape of the probability distribution changes with the amount of processed data. Signal 1 is for experiment without wetting the electrode. Signal 2 is obtained after a long staying of the metal electrode in electrolyte. Signal 3 is obtained after a long staying of electrode in electrolyte and forced polarization by external DC source.

For a small number of observations, fluctuations of noise signal increase. Obviously, shape analysis isn't effective in this case.

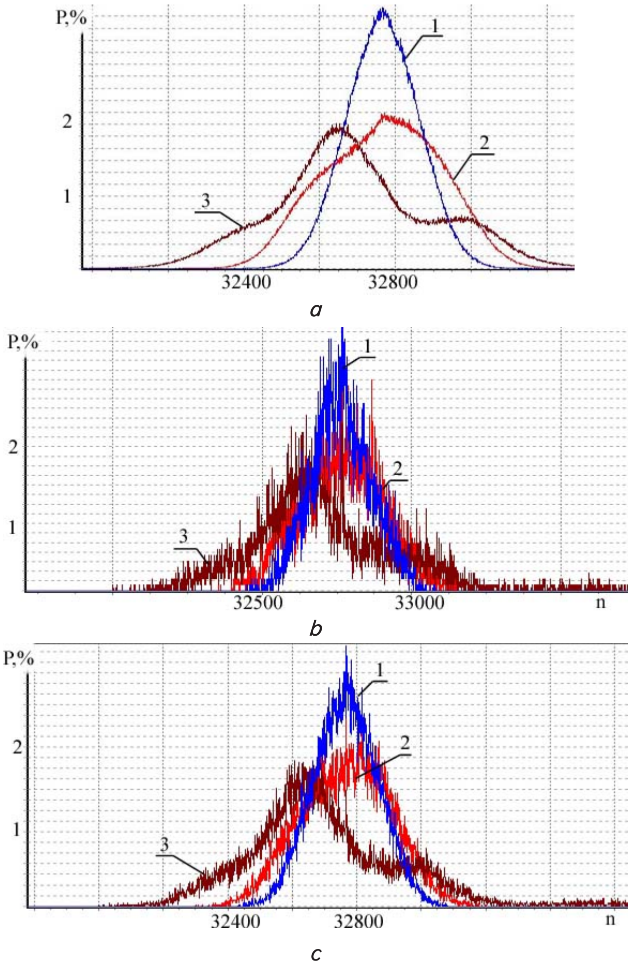

Fig. 6. Probability distribution of noise signal measurement results for various sample number: *a* – 300000 samples, *b* – 8192 samples, *c* – 32768 samples

One way of preliminary detecting the presence of corrosion process by noise method is using estimates of statistical characteristics, particularly of informational entropy. A similar approach was proposed for the processing of measuring and diagnostic signals [14].

Estimation of informational entropy of successive fixed-length fragments was done. Shannon informational entropy as a function of code probability is defined by the formula [15]

$$H_S = -\sum_{i=0}^{N-1} p_i \cdot \log_2(p_i).$$

Using this formula, sliding dependence of information entropy on sample offset was calculated for signals obtained during different experiments and for different length of sliding window. After that a probability distribution of information entropy was built in the case of dry electrode – 1, wet electrode – 2 and wet electrode after polarization – 3 (Fig. 7).

These results show that small length of the window causes overlay of information entropy estimates for experiment 1 and 2, which may lead to false identification of the presence of external sources of noise signal on the electrode surface.

From the results of experimental studies and modeling in numerical experiment, it was found that the use of information entropy estimation provides an acceptable resolution of signals when the sample number is 2048 and more.

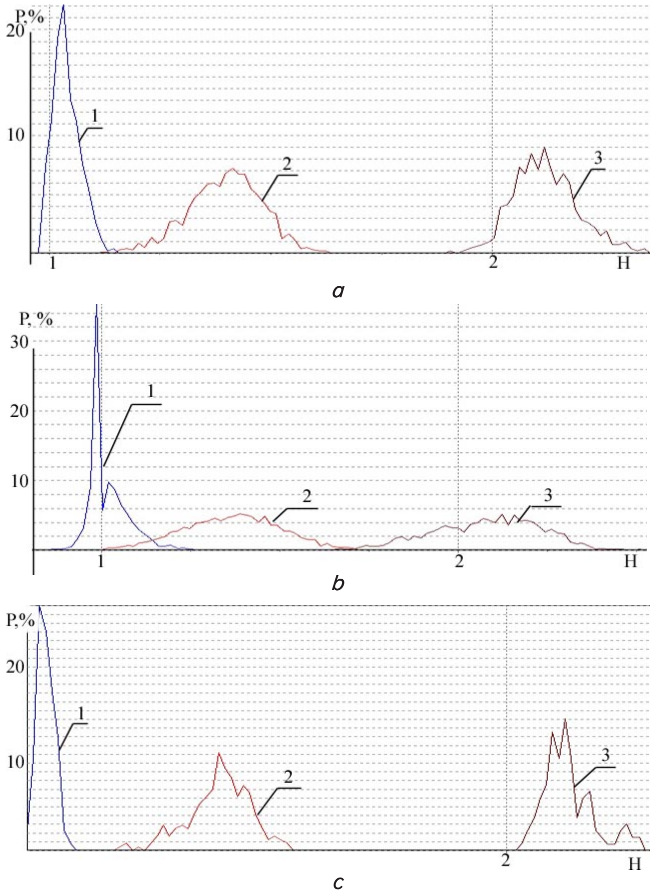

Fig. 7. The probability distribution of information entropy of noise signal for different length of sliding window: *a* – window length of 2048 points, *b* – window length of 512 points and *c* – window length of 8192 points

The proposed method allows to determine the presence of electrochemical reactions on the surface of the metal electrode. The danger of corrosion damage to industrial equipment with difficult access to internal and periodically wettable surfaces can be thus detected and estimated quantitatively. The disadvantage of this method is the difficulty of detection of signals associated with the flow of local electrochemical reactions on the surface of large size.

By such research method, the corrosion processes that take place on the inner surface of metal pipes or tanks without interference in their work can be conducted.

However, objects under consideration are working in the environment with increased levels of electromagnetic fields and under the influence of electrical currents. Therefore, further research should be aimed at finding ways to detect signals related to local corrosion processes.

7. Conclusions

1. The structural diagram of the device for studying noise voltage of electrochemical reactions that take place on the surface of the metal electrode was developed. The developed device comprises a differential amplifier, bandpass filters and an amplifier with controlled gain. Processing and recording of electrical noise voltage signal were carried out using a PC. Using a differential amplifier allows using sym-

metrical input signal, dependent only on the potential difference in the electrode connection. Bandpass filter is used to separate the constant component of the signal, which can be associated with the voltage sink caused by external sources in the investigated area of he electrode. Voltage sink also has some information, but the purpose of development was to investigate the noise components and the impact of the constant component can overload the amplifier stage. To prevent overloading, an amplifier with controlled gain was used.

2. With the developed device in the course of experiments, recording and further processing of signals were performed. When processing, spectral signal components ranging from 0 to 4 kHz were determined. Signal fluctuations were detected in spectral components in the range of 10 to 12 Hz that could explain how reactions associated with pitting corrosion. The result was non-stationary, so analysis of voltage spectral components of electric noise cannot provide an accurate assessment of corrosion processes on the electrode surface. The probability distribution of instantaneous values of electrical noise voltage signal was drawn. The analysis of a shape of the distribution made it possible to identify several sources of external signals on the electrode surface and in a sufficiently large amount of data we can obtain the existence of electrochemical reactions on the surface. A moving evaluation of information entropy instantaneous values of recorded signals was found, the use of it allowed to distinguish between the results of several experiments obtained at different intensities electrochemical reactions on the surface of the investigated electrode.

3. Analysis of the processing results showed the dependence of the shape of the probability distribution of instantaneous values of the signal on the electrochemical processes that flowed on the surface of the investigated electrode. The main source of the signal at the dry electrode surface was thermal noise, which has a distribution law is similar to normal. Changing the shape of this distribution with the introduction of additional local maximum indicates the impact of third-party input sources, which can be an electrochemical reaction. The signals containing components associated with corrosion processes were split by assessing the information entropy of instantaneous values of electrical noise voltage. Using the received during the experiment data with 2,048 samples allowed to distinguish these experiments with a probability of 99 %. Thus, when a small amount of processed data, with information entropy change of instantaneous values, we can get a conclusion about changing the properties of the electrical signals sources on the investigated electrode surface.

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