

## ABSTRACT

**Validity of research.** Electrochemical noise is the result of the flow of a complex of stationary and non-stationary spontaneous electrochemical reactions, the result of compensation of which due to differences between electrodes is measured in the external electric circuit as oscillations of an electric current in a wide frequency range. Until now, there is no single theoretical basis methods to reduce electrochemical noise, nor specific practical recommendations for achieving such a result. In most cases, such problems are solved by the method of empirical selection of materials and technical solutions, taking into account general recommendations on the thermodynamic and corrosion compatibility of electrode materials and electrolyte solutions. To reduce noise in the finished electro-electric systems, one simply expects a long time for the so-called "aging" - the achievement of the state of the state of the whole complex of spontaneous processes. Titanium is a widespread electrode material due to a complex of chemical, electrochemical, physical and mechanical properties. The master's thesis is devoted to the actual problem of reducing the level of electrochemical noise of titanium electrodes of chemotronic devices without reducing the basic functional characteristics of these electrodes.

**Link with scientific programs, plans, themes.** The work was carried out within the framework of the scientific and technical problem of nano- and microsizing structuring of semiconductor layers on the surface of valve metals in order to improve the electrode materials of chemotronic equipment, especially electrochemical sensors. The work was carried out at the Department of Electrochemical Productions Technology of the National Technical University of Ukraine "Igor Sikorsky Kyiv Polytechnic Institute" within the framework of fundamental research works of the State Fund for Fundamental Research of the

Ministry of Science and Education of Ukraine № 2614-ф «Scientific fundamentals of corrosion of micro- and nanostructured materials in electrochemical Systems of sensors and supercapacitors» (completed in 2015, state registration number of technical specification – 0113U001595) and № 2920-f «Scientific fundamentals and with the dimensionality of the electrochemical processes for the formation of ordered nanoscale and micro-level chemotronic materials» (state registration number of the terms of reference – 0116U003761) in accordance with the coordination plan of the Ministry of Education and Science of Ukraine in the direction 6.4 «Investigation of adsorption, catalytic and corrosion phenomena on the surface of solids for the purpose of developing resource-saving technologies».

Surface images of prototypes are made by scanning electron microscopy on the technical base and with the assistance of the Faculty of Physical Engineering of the National Technical University of Ukraine "Igor Sikorsky Kyiv Polytechnic Institute".

**Purpose and objective of the study.** The purpose of the study is to develop a method for processing titanium electrodes of finished electrochemical systems, in which the reduction of their electrochemical noise is achieved without reducing the target technical characteristics. In the case of amperometric sensors, the background signal is reduced without a noticeable decrease in the sensor conversion factor. To achieve this goal, it is necessary to solve the following tasks::

- determine the methods for studying the corrosion resistance of polished compact titanium under conditions of its high corrosion resistance (mainly in neutral, acidic and weakly acid chloride solutions);
- to investigate the influence of the impulse-reverse mode on the corrosion resistance of polished compact titanium;

- select the method and regimes of modifying the corrosion resistance of porous titanium and determine its correlation with the target electrochemical characteristics of the electrodes under study.;
- establish the mechanism of inhibition of electrochemical noise under unchanged quality criteria for the theoretical justification of the reliability of the proposed method;
- an original technique for labeling fresh metatitanic acid, invisible in secondary SEM electrons against a background of  $\text{TiO}_2$ , is proposed by introducing heavy metal ions into it from stable complexes with polyhexamethylene guanidine hydrochloride under pulsed polarization.

**Objective of the study** – A complex of unauthorized (including corrosive) processes caused by external polarization in the "titanium-aqueous electrolyte solution" system (mainly alkali metal chlorides), accompanied by qualitative and structural changes in semiconductor oxide layers at the interface.

**Subject of study** – mechanism, kinetics and steric distribution factors of electrochemical processes that cause the appearance and reduction of electrochemical noise of the "titanium-semiconductor oxide-aqueous solution" system without significant influence on its target characteristics.

**Methods of research.** The work used electrochemical methods: chronopotenzimetry, coulometry and potentiostatic polarization measurements. The state of the surface of titanium samples was studied by interferometry and scanning electron microscopy in secondary (with determination of the chemical composition of near-surface layers) and reflected electrons. The transient characteristics of electrochemical cells in chlorine reduction reaction from the gas phase and the conversion factor of chlorine concentration into the current signal was determined by standard methods, standard of the technique developed at the Department of Electrochemical Productions Technology of The National Technical University of

Ukraine "Igor Sikorsky Kyiv Polytechnic Institute" using a certified coulometric chlorine dispenser and a dynamic dosing system for Chlorine air mixture. The data was recorded using video recording, and their processing - using Microsoft Office Excel spreadsheets.

**Scientific novelty of the results:**

- for the first time, a method was proposed for reducing electrochemical noise of finished electrochemical systems with titanium electrodes without significantly reducing the target characteristics by pulse-reverse polarization in the intrinsic solution of its system;
- the method is developed in the sequential alternation of cathode (-0.05 V) and anode (0.3 V) pulses of duration  $1 \cdot 10^{-5}$  s for 2 s with obligatory termination at the anode impulse;
- it is established that in the solutions of alkali metal chlorides using the developed method promotes the formation of thin and dense films of semiconductor  $\text{TiO}_2$  with numerous breakdowns that are immediately filled with metatitanic acid, the subsequent dehydration of which forms zones with increased conductivity within 24;
- it is shown that the electrochemical noise caused by the reduction of oxygen and water and the oxidation of titanium flows over the entire surface of the titanium, and the rate of the target processes (for example, reduction of chlorine) correlates with the presence on the surface of microbursts (of the order of 1  $\mu\text{m}$  in size) of the semiconductor film that are infected with metatitanic acid;
- it has been shown that the almost complete restoration of the target catalytic properties of a porous titanium electrode after a pulse-reverse treatment takes place during one day as a result of dehydration and a decrease in the volume of metatitanic acid in the pores of microbursts;

- the method of pulse-reverse processing is developed with increasing its duration to 1 min and irrespective of the polarity of the current at the termination of polarization contributes to the growth of the polarization resistance of titanium and increases its resistance to oxidation during anodic polarization. It suggests the development of a method for increasing the corrosion resistance of titanium products without changing their functional properties and appearance.

**The practical significance of the results obtained.** A method has been developed to reduce the electrochemical noise of both individual titanium electrodes and electrodes in finished electrochemical systems, and does not change their target characteristics. The developed method can be used to increase the corrosion resistance of titanium products without changing their other characteristics, incl. appearance. It is possible to improve the method for corrosion protection of other metals and alloys prone to passivation.

**Personal contribution of the applicant.** The searcher performed a complex of studies of the effect of pulse-reverse treatment on chemical noise and the conversion coefficient of titanium electrodes in the chlorine reduction reaction from the gas phase, performed the initial processing of the results obtained, prepared samples for scanning electron microscopy and participated in obtaining the corresponding CEM images. The effect of updating the properties of porous titanium electrodes a day after treatment has been discovered. Processed literary and experimental data and formalized the results of the work in the form of abstracts and papers.

**Approbation of the thesis results.** Main results for participation in international conferences: VIII International scientific and technical conference of students, postgraduates and young scientists "Chemistry and modern technologies"; All-Ukrainian scientific conference "Actual problems of chemistry: research and prospects"; VIII International scientific and technical conference "Chemistry and

modern technologies"; 2nd ISE Satellite Student Regional Symposium on Electrochemistry "Promising Materials and Processes in Applied Electrochemistry"

**Publications.** According to the results of the thesis an article is published in a collective monograph under the aegis of the International Electrochemical Society and the thesis of three reports.

**Structure and scope of the dissertation.** The thesis consists of an introduction, six chapters, conclusion, a list of used sources and applications. The total volume of 102 pages, including 29 illustrations and 3 applications. The list of sources used includes 35 references.

**Literary Review.** Electrochemical noise occurs in various types of electrodes. The most detailed investigation was made of electrodes made of metallic materials that are capable of passivation. At the the last quarter of a twentieth century, more reviews were given to the thermodynamic justification and experimental high-frequency (more than 100 Hz) noise. Only in the tenth years of the twenty first century, attention was drawn to low-frequency noise associated with the vibrational distribution of the current yield between several parallel and coupled electrode reactions. Such a complex of reactions is especially characteristic for technical metals and alloys, especially in the case of their propensity to passivate and the formation of non-stoichiometric oxides.

Electrochemical high-frequency noise occurs even on electrodes from high-purity noble metals. In this case, the proportionality of the noise amplitude to the area of the electrode obviously follows from the functional relationship of the potential with the current density. But the inverse dependence of the amplitude of the potential fluctuations on the area of the electrode indicates the course of individual processes on sections of the surface with a certain area. And this area is measured not by square microns, but much more. As a result of averaging the

electroneutrality and equipotentiality of the electrode, rinse 10 mm<sup>2</sup> is much more effective than the electrode in 2 mm<sup>2</sup>.

The whole complex of causes that cause electrochemical noise is integrated in amperometric sensors in the so-called background current. According to the research of the Department of Electrochemical Productions Technology, in addition to the above phenomena, among which corrosion should be particularly emphasized, it also includes nonstationary processes. It is the nonstationary processes that often cause the noise to exceed the permissible limits. The simplest solution to this problem has always been the expectation of establishing a stationary state, in which noise is significantly reduced. It is obviously possible to accelerate this process by raising the temperature. However, for open systems, which are amperometric sensors, this leads to accelerated mass exchange with the environment, accelerated corrosion and self-discharge of active masses. As a result, part of the working resource of the elements of the electrochemical system is lost and the service life is shortened. Therefore, the acceleration of stabilization and reduction of the background current is an urgent task.

**Technique of experiments.** The studies were carried out on a polished titanium foil of grade VT1-00, since high-purity titanium is the basis for a large part of the electrodes of chemotronic devices and sensors, among others. Since corrosion plays a leading role in the formation of the background current, it was decided to modify and compact the oxide film to reduce its velocity on the titanium. It was decided to select a certain pulse-reverse processing mode, in which the cathode pulse promotes loosening of the oxide film, and the high amplitude anode pulse contributes to the formation of a new fine-crystalline phase of the oxide. Since a significant number of sensors use solutions of alkaline halides, the experiments began in a common and cheap model solution of 3% NaCl. The main studies were

performed in 6 m LiCl, in which the behavior of porous titanium electrodes made by pressing from titanium of the PTES grade was studied.

Polarization of the electrodes was carried out using the PI-50-1.1 potentiostat, complete with a PR-8 programmer for three- and two-electrode circuits. Porous electrodes were treated with a tri-electrode scheme with silver chloride auxiliary and comparative electrodes. Two-electrode porous cells were treated similarly, and tested in glass adapters with a chloropovitrene mixture through special fittings. After mounting such cells in plastic cases, a special plastic adapter with an axial supply of a chlorine air mixture was used. Chlorine air mixture was supplied from a certified coulometric batcher according to the dynamic scheme.

The introduction of heavy metal ions into the surface layers of fresh metatitanic acid was carried out from their complexes with polyhexamethylene guanidine (PGMG), which, due to their strength, allowed the yield of ions in pulsed cathodic polarization only when the complex interacted with metatitanic acid. In this way, contrasting for SEM with the substance of the site of exit to the surface of fresh titanium corrosion products in the zones of microprojections of  $\text{TiO}_2$  semiconductor layers was marked. Polarization resistance of polished titanium electrodes was studied on the polarization resistance indicator, developed at the Department of Electrochemical Productions Technology.

The effect of relative humidity drops on the nonstationary component of electrochemical noise was studied by rapid displacement of cells between two hygrometers, the relative humidity of the air in which was given by saturated solutions of salts with a certain osmotic coefficient.

#### **Impulse-reverse modifying the surface of compact polished titanium.**

Optical properties in NaCl. An evaluation of the increase in corrosion resistance of the titanium surface was carried out using visual inspection. Experiments have shown that the stationary anodic polarization of the clean polished titanium surface



causes a thickening of the oxide film at 2.0 V, which becomes noticeable as the appearance of a yellow color as a result of interference and corresponds to an oxide thickness of about 100 nm. Several series of experiments were able to select the processing mode by the sequence of anode (1.0 V) and cathode (-0.10 V) impulses of duration  $1 \cdot 10^{-5}$  s for 1 min, after which the titanium sustains a stationary polarization of more than 3.0 V without yellowing.

Optical properties in LiCl. The developed mode of pulse-reverse polarization was tested in a solution with a high osmotic coefficient of 6 m LiCl. A significant increase in chloride concentration as a depassivator caused a leveling effect on a possible range of treatment regimes, and a noticeable thickening of the oxide layers is achieved with higher anodic polarization.

Polarization resistance is a good criterion of corrosion resistance and an indicator of changes in the kinetics of electrode processes. The dependence of the polarization resistance on the stationary potential of processing electrodes from titanium foil says that if it is necessary to obtain a uniform oxidized surface, it is not worthwhile to set the cathodic polarization below -0.1 V. The alternation of pulses of low amplitude less than 100 mV forms too thin passive films. Pulses of 0.6 V already contribute to the formation of very dense films, which dominate the results of a similar stationary polarization. The optimum for the solution of the problem is anodic pulses + 0.6 ... + 0.3 V and cathode pulses -0.05 ... -0.1 V.

SEM photos showed that titanium oxide on a titanium background gives a low contrast picture. The surface changes very much during the scanning process. It is likely that heating in a vacuum causes intense loss of bound water and the destruction of surface layers. However, it can be argued that a short 2 s treatment gives the same oxide structure as after a few minutes. However, after 2 s, the oxide film is much thinner, as indicated by more breakdowns of the oxide film. The fact that in the breakdowns crystallized the electrolyte indicates an increased sorption of its solution

in these places. Probably, in the breakdowns, a gelled metatitanic acid is first formed, which subsequently crystallizes into  $\text{TiO}_2$ .

The appearance of metatitanic acid due to the intense corrosion-induced breakdown of breakdowns is possible due to its ability to form metatitanates of heavy polyvalent metals. Metals such as lead and iron are good contrast agents for SEM. Electrochemical dosing lead in metatitanic acid decided its complex with PGMG. It follows from the experiments at the Department of Electrochemical Productions Technology that the strength of the complex will not allow the lead to electronically be emitted on the entire surface of the titanium in the pulsed regime. Its release will occur only in places where additional energy will be provided by interaction with metatitanic acid.

SEM photographs with chemical analysis showed that the places of the breakdown are filled with a substance that is close in composition to the surface of the titanium (after special drying), which occupies a larger volume than the time and contains a noticeable amount of iron and lead. Obviously, iron (III) fell into the metatitan as a result of the first washing of samples with tap water. This also confirms the formation in the pores of special hydrated structures, possibly should contribute to a better expression of the valve properties of titanium. In the future, it is necessary to ensure the formation of thin oxide films with a large number of breakdowns.

**Impulse-reverse modifying electrodes from porous titanium.** Subsequently, experiments in LiCl with the selected treatment regimes were carried out on porous electrodes pressed from powdered titanium. The behavior of the surface of titanium damaged by mechanical treatment was also imitated on the electrode from titanium foil immediately after their grinding with finely dispersed emery paper. Pulsed-reverse processing and other studies were carried out at full immersion, and if necessary to determine the resistance of the formed oxide film in

external electrochemical processes, the electrode was fixed above the electrolyte mirror and a stream of chlorine air mixture was fed to its surface.

Chronopotentiometry of establishing the steady-state potential has shown that on the damaged surface of both porous and flat electrodes the potential grows and stabilizes in full accordance with the notions of passivation. The expected result is a significant acceleration of stabilization with temperature. Pulse-reverse processing dramatically reduces the duration of transient processes. Slower stabilization of the potential of porous electrodes suggests an important role of the concentration polarization of corrosion processes. This is an important result, indicating the need to dramatically shorten the pulse duration for pulsed-reverse processing of porous electrodes or to reduce their amplitude.

Stationary polarization of porous electrodes at the potential of a chlorine-silver reference electrode allows the reduction of gaseous chlorine in the pores of the titanium electrode. Electrodes after pulse-reverse processing are more quickly distinguished by low electrochemical noise and somewhat slower reduction of chlorine, due to the inclusion of higher electrical resistance of passive films in the electrical circuit. The slowing down of the transition process and the reduction in the rate of reduction of chlorine require more detailed study.

**Amperometric studies of two-electrode cells with porous titanium electrodes.** Further studies required more accuracy in measuring amperometric current currents, could not be achieved by using worn PI-50-1.1. Therefore, we switched to using more expensive two-electrode cells but with a well-planned experiment. Electrochemical treatment of amperometric cells was carried out according to the trielectrode scheme in a solution of LiCl identical to their own electrolyte. The reference electrode was their auxiliary chlorine-silver electrode, and an auxiliary wire was a silver wire

Analysis of the transition characteristics of the reduction of gaseous chlorine indicates a slight decrease in the conversion factor of working electrodes after special processing. However, the problem of slowing down the transient processes was solved using a low amplitude of pulses, processing time of only 2 s and its completion necessarily at the anode pulse.

Evaluation of the influence of various electrochemical treatment options in selected ranges of amplitudes and durations allowed to confirm the optimal regime:  $E_1 = -0.05 \text{ V } 10^{-5} \text{ s}$   $E_1 = +0.3 \text{ V } 10^{-5} \text{ s}$ . Also, taking into account the results of SEM, it is established that a slight decrease in the conversion coefficient immediately after the pulse-reverse treatment occurs due to the release of "caps" of metatitanic acid from breakdowns at the time filled with the electrolyte solution. Such hydrophilization promotes the flooding of the pores with a solution, as a result of which the area of the current generating surface of the electrode is reduced. However, after a day, the metatitanic acid loses water, recrystallizes, decreases in volume. Therefore, the magnitude of the current generating surface increases like the conversion coefficient. According to the research of the Department of Electrochemical Productions Technology, such an effect should contribute to the stabilization of the conversion coefficient, and some of its decrease will be imperceptible, since diffuse supports are installed in the sensors and should determine the value of the conversion coefficient. In this case, a thin and dense oxide film on the entire surface of the electrode will help reduce electrochemical noise, regardless of the use of diffuse impedances or filters.

The last test of the effectiveness of measures to reduce electrochemical noise is of a non-stationary nature was carried out with the installation of cells in the case with subsequent investigation into hygrometers.

Subsequently, experiments in LiCl with the selected treatment regimes were carried out on porous electrodes pressed from powdered titanium. The behavior of

the surface of titanium damaged by mechanical treatment was also imitated on the electrode from titanium foil immediately after their grinding with finely dispersed emery paper. Pulsed-reverse processing and other studies were carried out at full immersion, and if necessary to determine the resistance of the formed oxide film in external electrochemical processes, the electrode was fixed above the electrolyte mirror and a stream of chlorine air mixture was fed to its surface.

Thus, the developed method of pulse-reverse processing allows to reduce the electrochemical noise of a titanium electrode caused mainly by corrosion interaction with oxygen and water and does not affect the catalytic activity of the electrode in other target processes. However, this method is most widely used to improve the corrosion resistance of titanium products.

### **Conclusions**

The effect of pulse-reverse polarization on the state and properties of the titanium surface in a system with aqueous solutions of alkali metal chlorides has been studied. It has been established that under conditions of alternating cathodic polarization pulses up to  $-0.1$  V and anodic polarization of  $1.0$  V equal to the duration of the reduction of the period to  $2 \cdot 10^{-5}$  s over the total processing time of 2 s or more, an increase in the corrosion resistance of titanium without visible changes in the optical properties of the surface is observed, Which indicates the formation of passive  $\text{TiO}_2$  films thinner than 90 nm.

An increase in corrosion resistance is confirmed by an increase in the polarization resistance of the titanium electrode and an increase in the resistance to anodic polarization-the surface of the titanium withstands stationary anodic polarization without the formation of films with a yellow interference color (thicker than 100 nm) by 1 ... 2 V higher than without pulse- , The amplitude of the anode impulses of which by 1 ... 2 V below the named stationary polarization. Decrease in chloride concentration leads to differentiation of the results of treatment regimes,

and in concentrated solutions (6 m LiCl) stabilization of the surface state provides only the above-named regime.

The proposed pulse-reverse treatment of titanium electrodes sharply reduces their electrochemical noise, provided that it is terminated by an anode impulse. The rate of cathodic reduction of chlorine at such an electrode in concentrated chloride solutions can decrease two to three times immediately after treatment. Reducing the duration of treatment to 2 seconds contributes to such a reduction of a maximum of one and a half to two times.

The decrease in the polarization of the corresponding pulses to -0.05 and +0.30 V (the termination of processing at the anode pulse) with a duration of every  $1 \cdot 10^{-5}$  s for a total processing time of 2 s ensures suppression of electrochemical noise when the cathodic reduction of chlorine is slowed down by not more than one and a half times. It was established that the catalytic activity of the electrode is resumed almost completely on the day after the treatment, and the electrochemical noise does not increase. The sensitivity of the electrode to the cause of electrochemical noise such as relative humidity drop is also reduced - complete stabilization of the background current with a change in the relative humidity by ~20% is achieved in 100 ... 600 s against 1000 ... 6000 s on untreated electrodes.

Deterioration of the target characteristics of titanium electrodes while simultaneously suppressing electrochemical noise immediately after pulsed-reverse processing is explained by the formation of passive films with numerous microbursts that are immediately filled with volumetric metatitanic acid of corrosive origin, increases the hydrophilization of the pores of the titanium electrode and causes their flooding, which worsens mass exchange conditions, Surface and velocity, for example, the cathodic reduction of chlorine from the gas phase. On the second day, the ability of the electrode to conduct the cathodic reduction of chlorine resumes almost completely, since metatitanic acid loses water and significantly decreases in

volume, which helps to reduce flooding of electrode pores with an aqueous solution. The ability of the electrode to carry out the reduction of chlorine is proportional to the number of microprotrusions according to SEM, and their amount is inversely proportional to the duration of pulse-reverse processing and the amplitude of the pulses, while electrochemical noise does not depend on the number of microprotrusions.

An original technique for labeling fresh metatitanic acid, invisible in secondary SEM electrons against a background of  $\text{TiO}_2$ , is proposed by introducing heavy metal ions into it, incl. From stable complexes with polyhexamethylene guanidine under pulsed polarization.

ELECTROCHEMICAL NOISE, REDUCTION, TITANIUM ELECTRODE,  
IMPULSE-REVERSE TREATMENT, CORROSION PROTECTION,  
METHATHYTENIC ACID, MARKING BY CONTRAST SUBSTANCE,  
ELECTRONIC MICROSCOPY