

DECREASE OF ELECTROCHEMICAL NOISE OF TITANIUM ELECTRODE

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The electrochemical noise at the phase interface "electrode – electrolyte" has been insufficiently studied. It is a significant problem for the measurement systems based on electrochemical cells. This noise determines the resolution for electrochemical sensors. The corrosive nature of a significant part of the electrochemical noise has long been known. The problem of reducing electrochemical noise became relevant after the emergence of the need to increase the resolution of sensors and reducing the time between manufacture and delivery to the customer. Today the sensors were subjected to aging for reduce the electrochemical noise. That demanded time from several days up to several weeks. Artificial accelerated aging at elevated temperature should be carried out in "climatic chambers" and is not always safe for sensors. A method for rapid reduction of electrochemical noise (background current) for titanium electrodes of amperometric sensors after their manufacture was developed, which requires no special equipment and does not affect other specifications of the electrodes. The method is based on the amplification of surface protection of titanium against corrosion by conducting pulse-reverse polarization with an anode pulses +0.60 V (duration $1 \cdot 10^{-5}$ s) and a cathodic pulses -0.1 V (duration $1 \cdot 10^{-5}$ s) for 5 min. This treatment forms the oxide as a film that is thin (the thickness variation does not register interferometry in the optical range) and dense (low zero-current). This oxide film have low ohmic resistance (does not reduce significantly the analytical signal in the reaction of cathode reduction of chlorine).

The electrochemical noise at the phase interface "electrode – electrolyte" has been insufficiently studied. It is a significant problem for the measurement systems based on electrochemical cells. This noise determines the resolution for electrochemical sensors. It's possible to increases resolution using the increase of conversion ratio of concentration in the analytical signal. This method is limited by laws that define the speed function of electrochemical process from its driving force. So, the electrochemical noise is simply ignored in this case or it's

possible to think that is stable and it can be removed from the measured signal mathematically or hardware. This approach is used to mask a large noise signal that occurs in the oxygen sensor with a lead anode in acidic and alkaline electrolytes. This noise signal is called the zero-current. It is possible to predict and even calculate quantitatively with known polarization curves of hydrogen evolution on noble metals at the corrosion potential of lead in the same solution. However, there are some components of electrochemical noise which value can not be estimated a priori.

The well-known study of electrochemical noise refers only to its high-frequency components [1-3]. The assumptions regarding the corrosion origin of this current were expressed long ago [1,2]. However, specific proposals on reduction of such electrochemical noise have not been developed. The problem of reducing electrochemical noise came after the spread of amperometric sensors in industrial gas analyzer. It was always believed that it is necessary to reduce the electrochemical noise under stationary conditions of functioning of the electrochemical sensor.

Today there is another challenge is connected with reducing electrochemical noise. This task is aimed at solving the problem of reducing the time from receipt of specifications for the manufacture of a particular sensor until it is delivered to the customer in full compliance with the specifications. The cause of this problem is the occurrence of unacceptably high zero-current of amperometric sensor immediately after its production. This increased background current may persist from days to a month or more. In the case of the use of complex composite electrodes, the decrease in too high background current to acceptable values is explained by the aging of the active mass of the catalysts in the system with the selected electrolyte solution. Artificial accelerated aging at elevated temperature should be carried out in climatic chambers, that is requires special equipment. For many sensory systems of the aging at elevated temperatures may cause reduced lifetime if they are based on systems with non-equilibrium mass-exchange between the electrolyte and the process media (non-aqueous solutions in sensors for operation in air with natural humidity; aqueous solutions with the electrolyte that is a source of volatile expenditure components or mediators), or comprising metastable supplies. Therefore, the development of alternative methods for the reduction of non-stationary electrochemical noise is an actual problem.

The increased zero-current after manufacture is also typical for electrodes made of pure titanium. For its reduction and stabilization of the zero-current requires from one day to one week while all other technical characteristics of a sensor fully complies with the specifications after manufacture. The problem of increased zero-current of titanium

electrodes should be primarily given the corrosive nature and the thermodynamic characteristics of titanium in the system with oxygen-water environment. Therefore, the approaches to its solution should be based on the peculiarities of the passivation of the surface of Titan.

Research methodology. Study of passivation of titanium was performed on the electrodes made of titanium foil brand VT1-00. The change in the thickness of the oxide coating was evaluated by comparison of the digital photographs obtained under a constant angle in identical lighting. The influence of the selected mode on the plate porous titanium electrodes was evaluated by with the three-electrode scheme with the separation of the cathodic and anodic spaces in the cell shown in Fig. 1. The working electrode 1 (diameter of 18 mm and thickness of 2 mm pressed from a titanium powder) was immersed in the solution to a depth of 20 mm for carrying out passivation. The electrode 1 is raised to the surface of the solution, as shown in Fig. 1, to study the effect of passivation on cathodic reduction of chlorine. The measurements were performed in neutral and acidic solutions of alkali metal halides. Determination of the activity of the electrode in the reaction of the oxidizing gas reduction was carried out under flow of chlorine-air mixture (concentration 10 ppm) from electrochemical chlorine generator. All potentials are given relative to the normal hydrogen electrode.

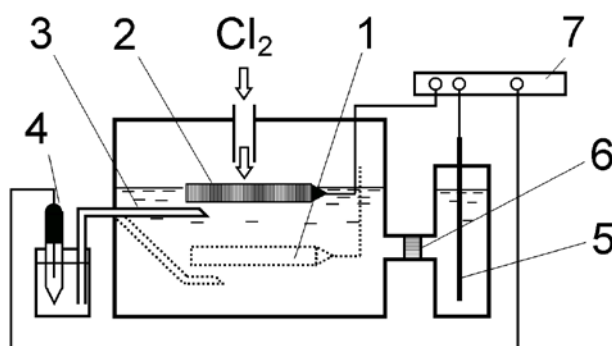


Fig. 1. The scheme of testing and electrochemical treatment of porous titanium electrodes in the solution 1 M KCl:

1 – working electrode in the position for treatment; 2 – working electrode in the position for chlorine reduction; 3 – Lugin's capillary; 4 – Ag/AgCl reference electrode; 5 – Ag-electrode; 6 – diaphragm; 7 – potentiostat.

Results and Discussion. Titanium electrodes treated to obtain the mechanical damage of protective oxide films. Titanium foil before experience were cleaned with emery paper to simulate the mechanical damage during the manufacture of the electrode. After that, the potential of titanium electrode increases with time and stabiliziruemost during the time from 10 h (titanium foil), 50 h (porous titanium electrode) (Fig. 2).

The background current of titanium electrode at a potential of +0.20 V (elected according to previous studies for optimal recovery of chlorine, its imposed from the potentiostat) is reduced and becomes stable three times faster and it has an anode polarity. A temperature increase accelerates this process. This behavior of the titanium electrodes is consistent with the assumption of the electrochemical mechanism of the growth of the oxide film on the damaged surface.

The obvious recommendation is to accelerate the reduction in background current by polarization of the titanium electrode at a potential of +0.20 V or higher at elevated temperature. However, this requires "a climatic chamber" that can maintain a constant relative humidity. It is necessary to develop a method to accelerate the corrosion rate of titanium, that not increases the resistance of new oxide films and does not affect the magnitude of the current signal of the titanium electrode in the reaction, for example, of the chlorine reduction.

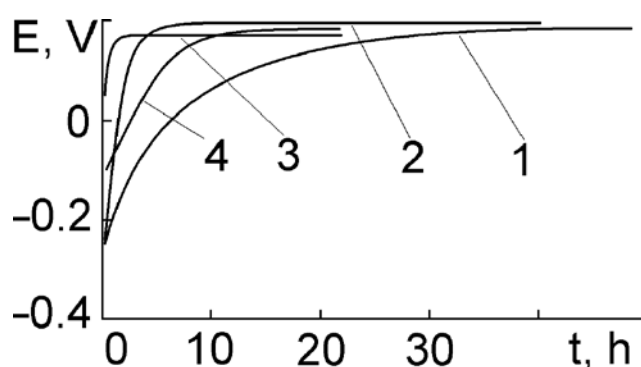


Fig. 2. Stabilization of titanium electrode's potential without electrical current at the temperature of 10 °C (1-3) and 30±3 °C (4) after machining (1,2,4) and after the special pulse-reverse treatment (3): 1,3,4 – porous titanium; 2 – titanium foil.

Proposed method of pulse-reverse polarization of titanium, which corresponds to the following beliefs about the relevant processes: anodic pulse with a high amplitude contributes to the formation of many germs of a new oxide phase, low duration pulse does not allow it to become a significant transportation limitations, the following short-term cathodic pulse "breaks" of the oxide phase, all this contributes to the formation of thin and dense oxide layer which stops corrosion of titanium and stabilize the zero-current and not follow to have a high ohmic resistance of the oxide film.

It was established experimentally that any polarization with a duration period of more than $1 \cdot 10^{-3}$ s cause a significant lengthening of transients or to cover electrode with oxide film as 100 nm as thick (according to interferometry). This oxide film makes the electrode

inactive to the reduction reaction of chlorine. So, the electrode loses its ability to be a working electrode of the sensor.

The necessary effect of the formation of a thin oxide film of a stable composition is achieved by alternating polarisation: anodic (+1.0 V) and cathode (-0.10 V) polarization pulses of equal duration $1 \cdot 10^{-5}$ s for 5 min. The potential of thus prepared electrodes gets stable on the value of about +0.20 V in duration for 15 min, and the background current gets stable for 5 minutes. In Fig. 2 the result of stabilization of the potential are shown taking into account the preparation and conduct of pulse-reverse polarization of the electrode.

The titanium foil electrode was processed by a pulse-reverse mode (anodic pulse of +1.0 V, cathodic pulse -0.10 V) holds stationary polarization to +3.0 V without thickening of the passive film (change in thickness is determined either visually nor interferometry in the optical range). For comparison, the electrode after surface mechanical treatment gets covered with an yellow oxide film after a fixed polarization at a potential of +2.0 V. That is the proposed mode of treatment forms a thin and dense oxide film on the surface of Titan.

The mode of treatment of porous titanium electrodes is proposed considering the results obtained: to apply in duration of 5 min the anodic pulse (less than +1.0 V) and cathodic pulses (-0.1 V) of equal duration $1 \cdot 10^{-5}$ s. The decrease in the amplitude of anode pulses should contribute to the formation of thin oxide films. A series of experiments showed that 5 min of processing of anode pulses of +0.6 V and cathodic pulses of -0.1 V with a total duration of period $2 \cdot 10^{-5}$ s allows to achieve stabilization of the background current of the porous titanium electrode at a potential of +0.20 V after 10 min from the manufacturing (including the duration of preparatory operations and pulse processing). As shown in Fig. 3, the activity of processed of the titanium electrode is not significantly decreased.

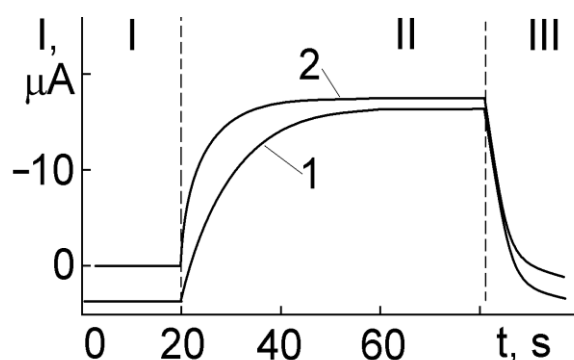


Fig. 3. The variation of the current signal (zone II) and zero-current (zone I) of the porous titanium electrode after machining (1) and special pulse-reverse treatment (2) in a solution of 1 M KCl: I,III – air; II – air-chlorine mixture with 10 ppm Cl₂.

Conclusions. A method was developed for rapid reduction of electrochemical noise (background current) of titanium electrodes for amperometric sensors after their manufacture, which requires no special equipment and does not affect other specifications of the electrodes. The method is based on the amplification of surface protection of titanium against corrosion by conducting pulse-reverse polarization of the anode pulses +0.60 V and cathodic pulses -0.1 V of equal duration $1 \cdot 10^{-5}$ s for 5 min. When this mode is used, a thin (the thickness variation does not register interferometry in the optical range) and dense (slow background current of a corrosive nature) oxide film with low ohmic resistance (does not reduce significantly the analytical signal in the reaction of cathode reduction of chlorine) is formed.

References

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