The study on effects of mass variation of fine-dispersed catalytic plating to a potential of the hydrogen electrode used in electrochemical Harned cells

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Abstract. This work is devoted to the study on effects of mass variation of fine-dispersed catalytic plating to a potential of the hydrogen electrode, as well as, establishment of the optimal electrochemical plating time of the catalytic coating of the measuring electrodes used in the Russian State Primary Standard of pH in aqueous solutions GET 54-2011. The experiments were carried out by a measuring system of precision measuring devices, using a silver chloride sensor as a reference electrode, to establish the change of the potential difference. The necessary time for the plating of the hydrogen electrode was determined. It is in the range of 7 to 8 minutes with 45 mA current.

1. Introduction

Measurement of the hydrogen index (pH) is by far the most common method for controlling liquid environments and water solutions. Controlling of the state of water objects and standardized indexes at the production stages of entire industries (production of medical preparations, foodstuffs, agricultural products, chemical reagents) is carried out by direct measurement of pH. Also, it is important to measure pH in determining the characteristics of water objects of fish farms, the control of high-purity materials and water treatment. The most of analytical and research laboratories in Russia are provided with various types of devices for pH measurement - pH meters, and the final conclusions about the properties of samples or materials depend on the quality of specific measurements. The pH unit of the comparative method is transferred from the State Primary Standard pH of GET 54-2011 to buffer solutions.

The composition of the State Primary Standard pH GET 54-2011 includes hydrogen electrodes, which must be coated with a finely dispersed catalytic layer – niello of precious metals (hereinafter referred to as "niello") before measurements, for increase the area of active catalytic centers on the surface of the electrode and for ensure sufficient contact with hydrogen gas. It should be noted that the finely dispersed catalyst layer adsorbs very well various substances, especially when working with solutions containing traces of sulfur and arsenic [1], therefore, before each measurement it is necessary...
to replace the old niello with a new niello, which makes the process of measuring pH on the primary standard very long and laborious. This circumstance led to the need to study a method for reducing the sedimentation time and the amount of niello on the electrode surface, without changing the value of the potential of the standard hydrogen electrode (activity).

2. Method of experiments

2.1. The method of deposition platinum niello to electrodes
For the deposition of platinum niello to the electrodes, an installation was assembled which included a power supply unit, a milliampermeter and a U-shaped cell.

For the deposition of platinum niello on electrodes, an electrolyte which consisted of 5 g. of chloroplatinic acid which was dissolved in 110 g of distilled water was prepared, and there were added 5.5 grams of lead acetate for better adhesion of platinum to the electrode [2]. Two electrodes were placed in this electrolyte (the first one was an accessory electrode, the second electrode was an electrode covered with platinum niello) and one of them was connected to the minus terminal "-", and to the other electrode was connected to the plus terminal "+", from the power supply unit. To start the platinum plating, the installation was switched on; using the "on" button on the power supply and a current of 45 mA was switched. Platinum plating time was detected by a timer with duration of 3, 6, 9 and 12 minutes, respectively. At the end of the required time, the power supply was switched off with the "off" button and the electrode covered with platinum niello was taken out from the electrolyte solution. Then it was carefully washed with distilled water to prevent damage to the platinum niello. The electrodes were kept in a glass beaker with distilled water.

2.2. Method of preparation of buffer solution
For carry out basic experiments on the effect of the mass of deposited platinum niello on the efficiency of setting the hydrogen electrode potential, a solution possessing a buffer property was required. The choice was made in favor of a phosphate buffer solution with a pH value of pH 7.00. The buffer solution was prepared according to the classical method given in [3] from a mixture of sodium hydrogen phosphate Na$_2$HPO$_4$ (Purity > 99.5%), potassium dihydrogen phosphate KH$_2$PO$_4$ (Purity > 99.5%) and deionized water. For prepare the solution, weighed the sample of Na$_2$HPO$_4$ salt in an amount of 4.25062 ± 0.00015 grams and the sample of KH$_2$PO$_4$ salt in the amount of 2.90062 ± 0.00015 grams per liter of water. For determine the weight of samples, we used the scale, which belong to the 1st special class of accuracy using an internal alignment system. After the samples of salts were weighed, they were transferred to a 1 liter container and dissolved in deionized water by a weight method. Dissolution of the salt mixture was carried out in warm deionized water with previously removed carbon dioxide gas by boiling.

The prepared solution was packaged in clean bottles made of high-purity plastic, 0.5 liter in volume with tightly screwed lids and kept in a difficult place for light.

3. Results of experiment behavior

3.1. Preliminary experiments
All the main experiments were carried out on the installation shown in figure 1. The installation consists of a set of high-precision measuring instruments in analogy with the state primary standard: precision thermostat, high-precision hydrogen supply, a set of Harned cells, a precision multimeter, a personal computer, a high-precision thermometer complete with a «Pt 100» sensor.

Before the beginning of a series of basic experiments on the study of the potentials of the hydrogen electrode, there was a preliminary experiment to determine the amount of time when the installation would reach a stationary mode. The experiment was carried out at $T = 25^\circ$ C, within one hour. The values of the potential difference of the electrodes in three Harned cells were obtained, which show that the values become constant after 40 minutes. However, in order to ensure the maximum saturation
of the hydrogen electrode, it was decided to consider that the achievement by installation a stationary mode by time was one hour.

Figure 1. The scheme of the experimental installation.
1 - cylinder with hydrogen, 2 - high-precision hydrogen supply system, 3 - precision thermostat, 4 - Harned's cell, 5 - test electrode, 6 - saturator, 7 - reference electrode, 8 - high-precision thermometer complete with «Pt 100» sensor, 9 - precision multimeter, 10 - personal computer, 11 - barometer, 12 - thermometer.

3.2. The results of the basic experiments to determine the potential difference of hydrogen electrodes with different masses of platinum niello deposited.
The final stage of the work was experiments to determine the potential difference using electrodes with different masses of platinum niello deposited. The amount of platinum deposited over time was calculated according to Faraday's law and determined experimentally with the help of microbalances, referring to 1-st class of accuracy. Platinum plating was carried out by supplying a direct current with a current strength of 45 mA. The results of calculations and experimental data are presented in table 1.

Table 1. Mass of platinum niello deposited to the electrode as a function of time.

| τ, min | 0   | 3   | 6   | 9   | 12  |
|-------|-----|-----|-----|-----|-----|
| m theor., g | 0.013069 | 0.026139 | 0.039208 | 0.052278 |
| m exp., g  | 0.012942 | 0.026049 | 0.039107 | 0.052077 |

During the experiments, it was noted that the amount of platinum deposited on the electrode is less than the theoretical value. In our opinion, this is due to the fact that, due to the presence of electrode polarization, the current output did not reach 100%, but was slightly less. However, if we take into account that the difference in mass appears only in the 4th mark, then this influence can be neglected.

In the first preliminary experiments in order to save the resources of silver chloride electrodes, a platinum-palladium system was chosen as the reference electrodes. As a reference electrode, a platinum substrate with palladium niello deposited was taken. The experiments were carried out at the installation shown in figure 1. The temperature of the experiment was T = 25 ° C. The results of the experiments are shown in figure 2.
Figure 2. Results of experiments of electrodes coated with platinum niello with a reference electrode coated with palladium niello.

As can be seen from the figure, no couple of electrodes has not reached stationary mode in the form of stabilization of the potential difference. This is due to the fact that the palladium electrode very sorbs hydrogen from the working space of the hydrogen electrode, which comes to it due to the presence of diffusion and electrical forces. The speed of hydrogen supply to the palladium electrode is much less than the speed of irrigation of the hydrogen electrode, so the graph shows a slow saturation of the palladium electrode, which does not allow reaching the limiting potential difference between the electrodes. Therefore, it was decided to use as reference electrode chlorine silver, which practically does not absorb hydrogen.

For test the need for deposition of niello, a preliminary experiment was carried out using an electrode with a smooth surface without the deposition of niello. This experiment showed that electrode stabilization occurs 50 minutes after the start of the experiment. The value of the potential difference was $E = 0.55873442\ \text{V}$. For comparison of the obtained potential difference, experiments with electrodes coated with niello were carrying out. The results are presented in table 2.

It shows that the maximum jump in the potential level is observed at the time of platinum plating equal to 3 minutes, which is shown in figure 3. With an increase in time to 6 to 12 minutes, the difference between the potential levels can be traced in the 4th mark. Thus, it can be argued that the optimal platinum time is in the range of 7 to 8 minutes.

Table 2. Results of experiments to determine the potential of the hydrogen electrode as a function of the mass of platinum deposited (platinum-silver chloride system) $T = 25\ ^\circ\text{C}$.

| Platinum plating time | mass of niello Pt, g | meaning of potential, V |
|-----------------------|----------------------|-------------------------|
| 0                     | 0                    | 0.55873442              |
| 3                     | 0.012942             | 0.88913912              |
| 6                     | 0.026049             | 0.89689976              |
| 9                     | 0.039107             | 0.89695933              |
| 12                    | 0.052077             | 0.89694176              |
Figure 3. Comparison of the stabilization of the electrode covered with niello for 3 minutes and the electrode without the niello

4. Conclusions
Thus, an advanced technology for making hydrogen electrodes based on [2] is proposed. This technique has been improved taking into account the requirements for minimizing the amount of platinum niello deposited.

The optimum time necessary for carrying out the process of electrochemical deposited of platinum niello, which lies in the range of 7 to 8 minutes, is determined. A further increase in time does not lead to a change in the potential of the hydrogen electrode relative to the silver chloride electrode.

At present, the time of sedimentation of a finely dispersed catalytic layer is 9 minutes on the current primary State pH standard [2]. Taking into account the work of the standard for 1 year (including international comparisons) and the number of hydrogen electrodes used, decrease the time for sedimentation a finely dispersed catalytic layer from 9 to 7 minutes, will allow to decrease the time of preparation of the primary standard to high-precision measurements by more than 20%.

Based on the results of the work, it is planned to produce a batch of hydrogen electrodes using the improved technology and carry out measurements on the primary State Standard pH of GET 54 - 2011 with the aim of confirming the stability of the metrological characteristics of the produced electrodes.

5. References
[1] Newman J. 1977 Electrochemical systems (World, since 456)
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