

**RESEARCH INTO THE EFFECT OF ETCHING PROCESS OF POROUS
TITANIUM CURRENT COLLECTORS IN HYDROCHLORIC ACID ON THE
PERFORMANCE OF WATER ELECTROLYZERS WITH A PROTON EXCHANGE
MEMBRANE**

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Annotation. *Based on the modern methods of SEM, voltammetry, and gravimetric analysis, samples of current collectors used in electrolyzers with a solid polymer electrolyte, made of porous titanium with various degrees of etching in concentrated hydrochloric acid, were studied. A gravimetric study of the etching process of samples of various sizes from porous titanium showed that throughout the process there is a loss of mass of the sample, with the exception of two short intervals, presumably due to the formation of hydrides (60-80 sec) and oxides (4-5 min), and the samples of smaller volumes were more sensitive to weight loss and weight growth. The use of the SEM method made it possible to reveal that etching over different time intervals changes the structure of porous titanium, reducing the average particle size and increasing their porosity. In this case, the surface inhomogeneity increases due to the formation of cavities in titanium and deterioration of the contact of the current collector surface with the catalytic layer. The consequence of this is the difference in the current-voltage characteristics of electrolysis cells with different duration of etching of the current collectors: there is a decrease in the productivity of electrolysis with an increase in the duration of etching of the current collectors by ~8% for etching more than 1 minute and ~18% for etching more than 4 minutes as compared to the simultaneous immersion of the sample in acid to clean the surface.*

Keywords: *water cell with TPE, porous titanium, SEM, voltammetry, gravimetric analysis.*

Introduction

At present, traditional energy is losing its relevance due to environmental damage in the process of extraction and processing of traditional energy carriers, and its fossil resources are limited [1]. Also, the energy carriers of traditional energy are largely dependent on periodic supplies which make it difficult to use it in regions with poorly developed logistics, for example, in the conditions of the Northern regions [2]. On the other hand, fluctuations in prices for traditional fuels in some cases lead to energy crises [3]. In addition, the scale of disasters in the processes associated with the extraction and the use of traditional fuels cannot be overestimated: oil spills lead to massive and long-term damage to water areas, damage to gas pipelines leads to threats of powerful long-term fires [4-5]. Over the past few years, there have been much more frequent works devoted to the development of alternative energy sources [6] (Fig.1).

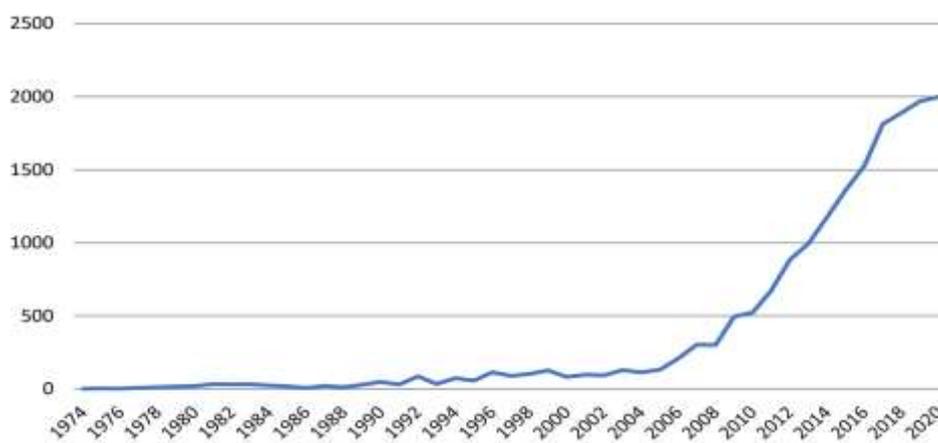


Fig. 1. Annual number of Web of Science publications mentioning RES in keywords [6].

Alternative (renewable) energy sources (RES) are the next stage in the development of energy for several reasons: an unlimited amount of natural, renewable resource in free access (wind, light, water). The production of energy using alternative sources does not involve the degree of risks that traditional energy sources face. The prevalence of the necessary resources allows not only to obtain them for free, but also resolves the issue of the logistics of such energy carriers: renewable energy sources can support a fairly wide range of generation capacity, which allows them to be used both for home use in portable technology and for local emergency power supply.

For energy consumption, processing of the primary energy source is necessary. Thus, to obtain high-purity hydrogen, it is possible to use modern, promising water electrolyzers with a proton exchange membrane (PEM). Their scientific popularity is explained as being due to the fact that they are the safest for the environment and the user, have the highest current density and the most favorable ratio of performance and weight and size characteristics of power plants on their basis and allow obtaining high-purity hydrogen from a simple electrochemical reaction without the release of foreign compounds (pure oxygen acts as a by-product of the reaction) in a fairly wide range of operating conditions, including negative temperatures [7].

However, water electrolyzers with PEM are currently not widely used, since during the practical application they face the following difficulties: the inclusion of precious metals as catalysts for electrochemical reactions (platinum, iridium) and the need to use bidistilled water together lead to an increase in the cost of hydrogen produced. Also electrolyzers can prematurely lose some of their performance and even fail due to degradation of the components of the membrane electrode assembly (MEA), which also leads to an increase in user costs [8].

To deal with the above problems, it is necessary to improve the design of the MEA water electrolyzer with PEM, which allows to reduce the effect of catalyst degradation without serious damage to the performance of the power plant. In this direction, there are already scientific works devoted to the modification of the composition of electro-catalytic materials by adding tin, molybdenum, etc. [9].

In addition to electro-catalytic materials, an important component of the MEA is the current collector, which provides a uniform distribution of reagents, removal of reaction products, and supply of electric current. Porous titanium is used as a material for current collectors. For use in a water electrolyzer, titanium is purified from impurities in the composition by etching in hydrochloric acid. On the one hand, the purification of the material from impurities makes it possible to increase the service life of titanium current collectors in the MEA composition; on the other hand, this procedure can result in significant changes in the titanium structure, subsequently leading to early damage of the material.

The purpose of this work is to determine the effect of the etching process of current collectors made of porous titanium on its structure, as well as to analyze the performance of water electrolyzers with PEM using current collectors with various degrees of etching.

Practical part

Preparation and etching of current collectors

Titanium sheets of commercial grade VT 1-0 with a porosity of 41–44% and a thickness of about 0.8–1 mm were selected for the study; sets of current collectors in the form of a circle with an area of 7 cm² and 20 cm² were cut out of titanium sheets. After cutting and grinding, the current collectors must be washed and degreased by boiling in isopropyl alcohol; at the end of the process, titanium must be dried in a drying cabinet at a temperature of 60 °C for about 1 hour.

The etching procedure was carried out as follows: the cleaned and dried current collectors were weighed on a scale with an accuracy of 10⁻⁴ g; the geometric parameters of the samples were measured using a caliper and a micrometer. Chemically pure hydrochloric acid with a measured volume of 100 ml, taken in a beaker with a wide bottom (volume of about 300-500 ml), was heated on a hot plate with temperature control using an alcohol thermometer placed in a solution fixed on a tripod until a temperature of 55 °C was reached with accuracy up to 0.5 °C. This temperature is used to ensure maximum diffusion and is the boundary for hydrochloric acid, since when 58-60 °C is reached, the acid with a concentration of 36% gradually begins to boil.

After the required conditions were reached, the current collector was placed into the solution with stainless steel tweezers, while a stopwatch was started to record the etching time. A few seconds before the end of the required period, titanium was fixed with tweezers and simultaneously with the end of the period was removed from hydrochloric acid and placed in a previously prepared beaker with bidistilled water taken in an amount of 500 ml to stop the reaction, after which a similar sample rinsing procedure was repeated twice. Next, the sample is subject to boiling in the same amount of bidistilled water; after boiling, the water is renewed, and the rinsing is performed three times in cold bidistilled water. The described procedure of boiling and rinsing was repeated three times; at the end of the whole, the sample was dried in a drying cabinet at a temperature of 60°C for 2 hours. The dried and cooled sample is subject to re-weighing and measurement of geometric parameters.

Study of the structure and surface of titanium by SEM

In order to determine the effect of etching in hydrochloric acid on the structure and morphology of the titanium surface, the surfaces of samples with a surface area of 20 cm² were studied using scanning electron microscopy (SEM). Analysis of the results of the method makes it possible to determine the size distribution of particles and pores, qualitatively evaluate the effect of etching on the structure over time, and determine and consider inclusions of foreign elements in the composition of the sample.

Synthesis of catalytic materials

Electro-catalytic materials used in commercial samples of PEM electrolyzers manufactured at the National Research Center "Kurchatov Institute" were chosen for the study: a platinum catalyst on carbon black of the Vulcan trademark with a mass fraction of platinum of 40% for the cathode and an iridium catalyst for the anode.

The platinum catalyst was synthesized from chloroplatinic acid (hydrogen hexachloroplatinate H₂[PtCl₆], hereinafter referred to as platonic acid) and an aqueous dispersion of Vulcan carbon black. The iridium catalyst is synthesized in a similar way from chloroiridic acid (hydrogen hexachloroiridate H₂[IrCl₆], hereinafter referred to as iridic acid) and sodium borohydride.

MEA preparation

The resulting current collectors and catalyst are used as a part of the MEA of experimental laboratory cells with a working surface area of 7 cm^2 , a set of grids; a rubber gasket and a Nafion 117 membrane are being prepared.

The anode and cathode are prepared by spraying the necessary catalyst onto the current collectors, while an iridium catalyst was applied to the anode with a load of 2 mg/cm^2 , the cathode load for platinum was 1 mg/cm^2 , and in both cases *Nafion* conductive varnish was added to the sprayed dispersion in an amount of 5 % by mass fraction. The catalyst loading was controlled by weighing with an accuracy of 0.00001 g.

The laboratory cell with the finished MEA was placed on a stand prepared for testing cells of electrolyzers. The cell is connected to the flasks for hydrogen and oxygen, respectively, along the inner contour of the cell and along the outer contour with a thermostat. Electrically, the cell is connected in series to a current source through an ammeter and in parallel to a voltmeter.

VAC study

Measurements of the volt-ampere characteristics (VAC) of the cells were carried out in terms of temperature control of the samples at temperatures of 40, 60 and $80 \text{ }^\circ\text{C}$. The cells were tested in manual mode, the VAC measurements were carried out in line with the following algorithm: the voltage was recorded according to the voltmeter readings, the adjustment was carried out manually on the current source in the range from 1.5 to 2 V; with a step of 0.5 V, the ammeter readings were recorded with an accuracy of 0.01 A in terms of complete stabilization of the readings on both devices.

Results and discussion

Visual observation of the titanium etching reaction in hydrochloric acid makes it possible to specify the key points of the study: 75 s and 5 min. At the junction of these time intervals, a sharp change in the reaction conditions is observed: an increase in temperature, a change in color, and an intense outgassing.

At the first point $t = 75 \text{ s}$, a change in the color of the solution to blue is observed; over time, the color saturation changes from the presence of a blue tint in transparent water up to a thick dark one. Together with intense gassing and temperature increase at a given time, these signs are explained as being due to the onset of the titanium hydride formation reaction - the titanium delta phase.

At the second point $t = 5 \text{ min}$, it becomes difficult to observe a change in the color of the solution, however, when hydrochloric acid is poured into water after etching for more than 5 min, a pink tint appears, the saturation of which increases with the duration of the etching process. Along with this, intense gas evolution and an increase in temperature at this moment indirectly confirm the onset of the titanium oxidation process.

After a qualitative observation of the reaction for 30 min and the determination of the key points of the reaction, 12 points of the duration of the entire study were established, differing in the duration of the etching process when other conditions were fixed: the temperature of the medium, the concentration and volume of the acid, and the dimensions of the titanium samples (for each series). A point was also added, denoted later in the work as $t = 0 \text{ min}$, indicating a short-term effect of acid on the sample, carried out as follows: upon reaching the necessary environmental conditions, the sample was immersed entirely in the acid solution using tweezers, after complete immersion, the sample was immediately removed and placed in a glass of bidistilled water to stop the reaction. The set of points is given in Tab.1.

Tab.1. A set of conditions for studying the titanium etching process.

Study No.	1	2	3	4	5	6	7	8	9	10	11	12
Etching	0	1	1.33	2	3	4	5	7.5	10	15	20	30

duration, min												
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When exposed to hydrochloric acid for more than 5 minutes, titanium samples begin to change their color, gradually losing their metallic luster and acquiring a dark shade. This also indicates the beginning of oxidative processes, gradually leading to irreversible damage to porous titanium. The dynamics of the appearance of the samples is shown in Fig. 2.



Fig. 2. Appearance of samples from left to right: No. 1, No. 6 and No. 12.

Samples No. 1 - 5, etched for up to 3 minutes, do not clearly change their appearance; however, starting from No. 6, changes in appearance become visually distinguishable. At the same time, titanium enters an oxidation reaction with the formation of a pink tint in an acid solution, which also confirms the onset of oxidative processes with titanium degradation.

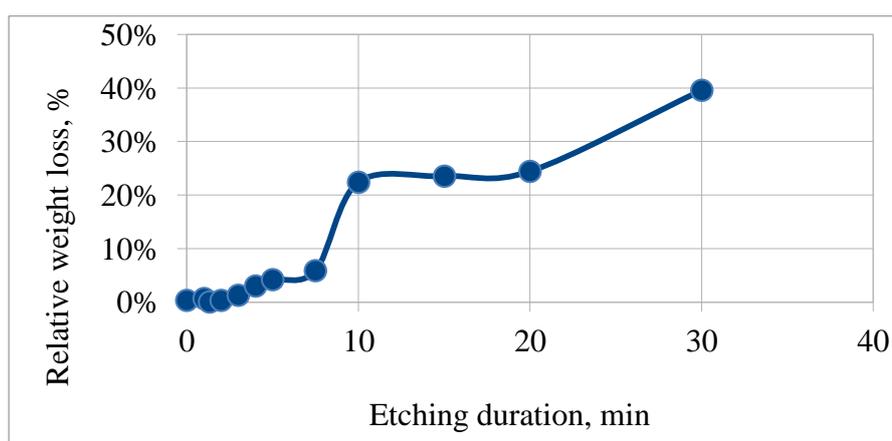


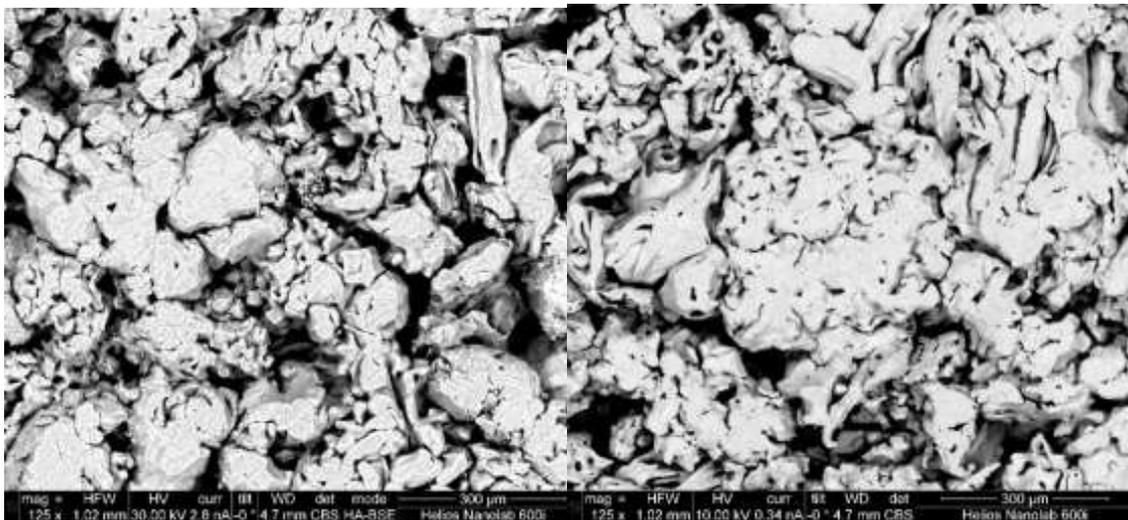
Fig. 3. Graph of the dependence of the mass loss, normalized to the initial mass, of samples No. 1 - 12 with a surface area of 20 cm² on the duration of etching.

The results of weighing samples having been normalized to the initial mass also confirm the above statements. A graph of the change in the mass of each sample is shown in Fig. 3. The results

of weighing samples with different degrees of etching before and after the implementation of the process indirectly confirm the described processes in the form of inflections and the formation of a plateau in the graph of the normalized weight loss of the sample depending on the duration of etching.

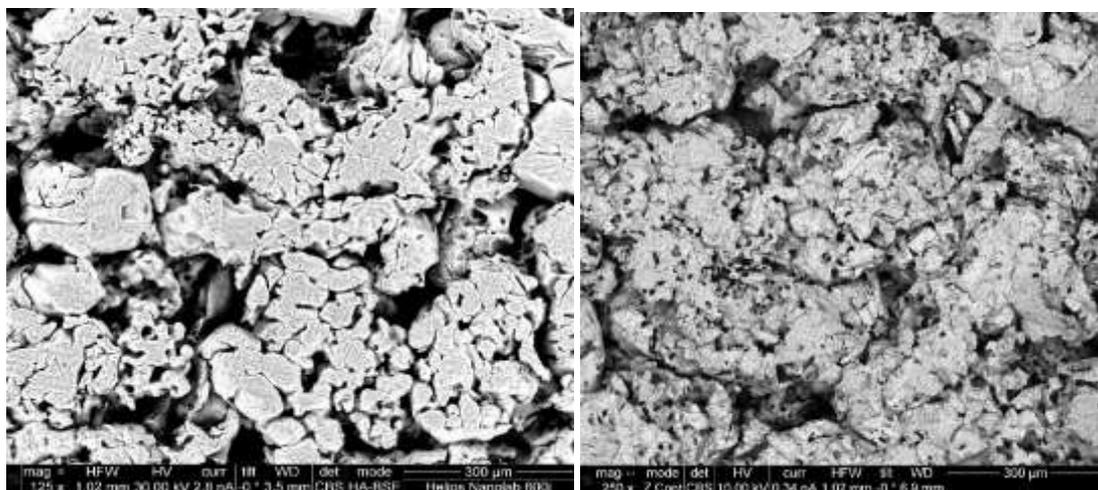
Also, from Fig. 3, a sharp loss of mass is noticeable in the samples, starting from No. 7, at fixed sample sizes. This confirms the beginning of the process of titanium degradation in the composition of the sample, leading to a loss of strength and a decrease in the volume of titanium involved in the electrochemical reaction.

The study of samples by SEM allows us to make some key conclusions regarding the effect of etching in hydrochloric acid on the structure and surface of porous titanium. One of them is the reduction in particle size due to the dissolution of bonds of large particles in hydrochloric acid and the complete dissolution of small grains. A characteristic feature is a strong change in the average particle diameter, starting from sample 3, when a visually observed onset of an intense process occurs. Before the beginning of the process, the particles have a distribution in the size range up to 30 μm ; after the start of the intensive stage of etching, the distribution changes to 2–3 μm . Such a sharp drop in particle size can lead to a decrease in the surface area of the particles involved in the electrolysis of water. The structure dynamics of porous titanium and particle distribution are shown in Figs. 4 and 5, respectively.



a)

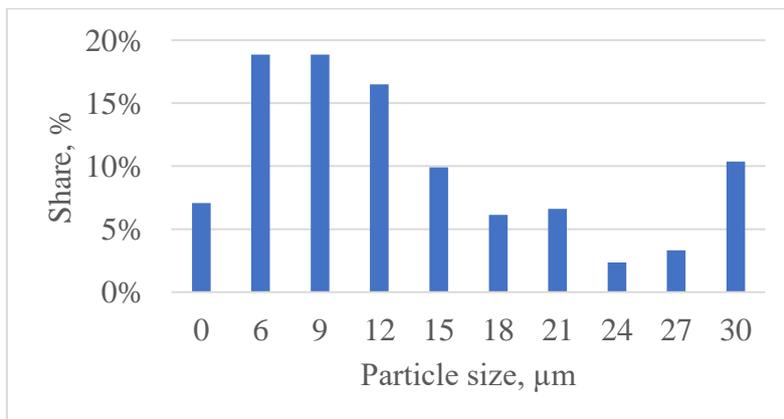
b)



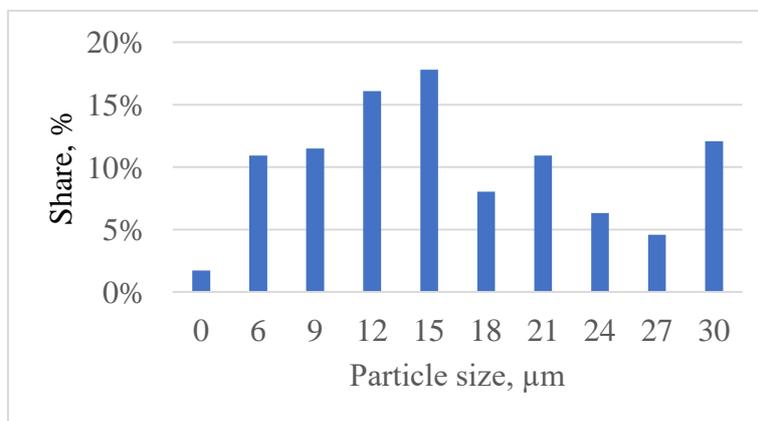
c)

d)

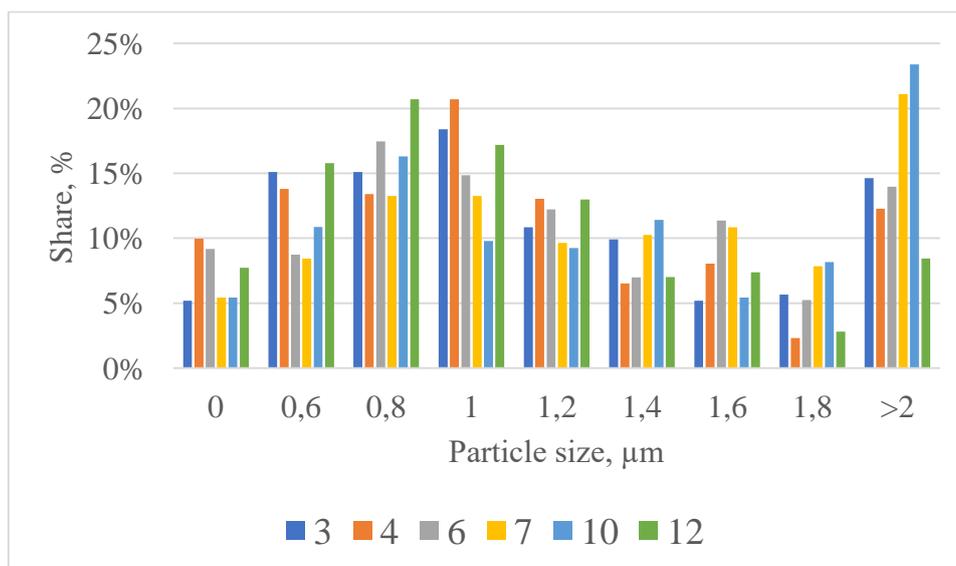
Fig. 4. SEM images of surfaces of porous titanium samples on a large scale: a - No. 1, b - No. 2, c - No. 6, d - No. 12.



a)



b)



c)

Fig.5. Particle distributions in samples with predominantly large (a and b) and small (c) particles for samples with different etching durations.

Also, when considering the samples on a small scale in Fig. 6 reveals an increase in the specific number of pores on the surface of titanium particles, as well as an increase in their diameter. It can be assumed that this is due to the presence of gas pores in the titanium structure caused by the presence of air at the time of casting the titanium sheet. As the degree of etching of titanium increases, more and more such pores open, and the diameter of the existing ones increases. The distribution of pores is shown in Fig. 7.

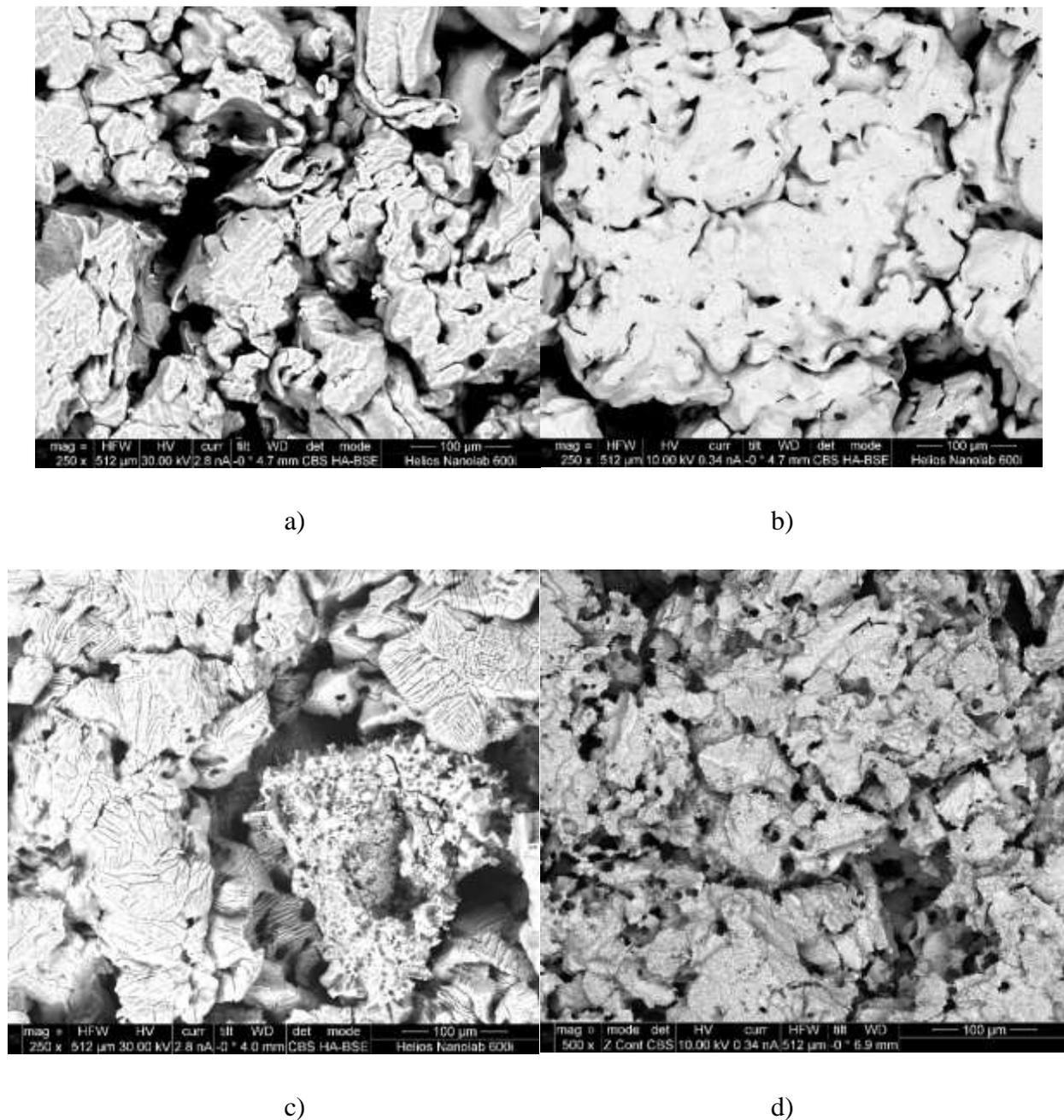


Fig. 6. SEM images of the surfaces of porous titanium samples on a small scale and the corresponding pore size distributions: a - No. 1, b - No. 2, c - No. 8, d - No. 12.

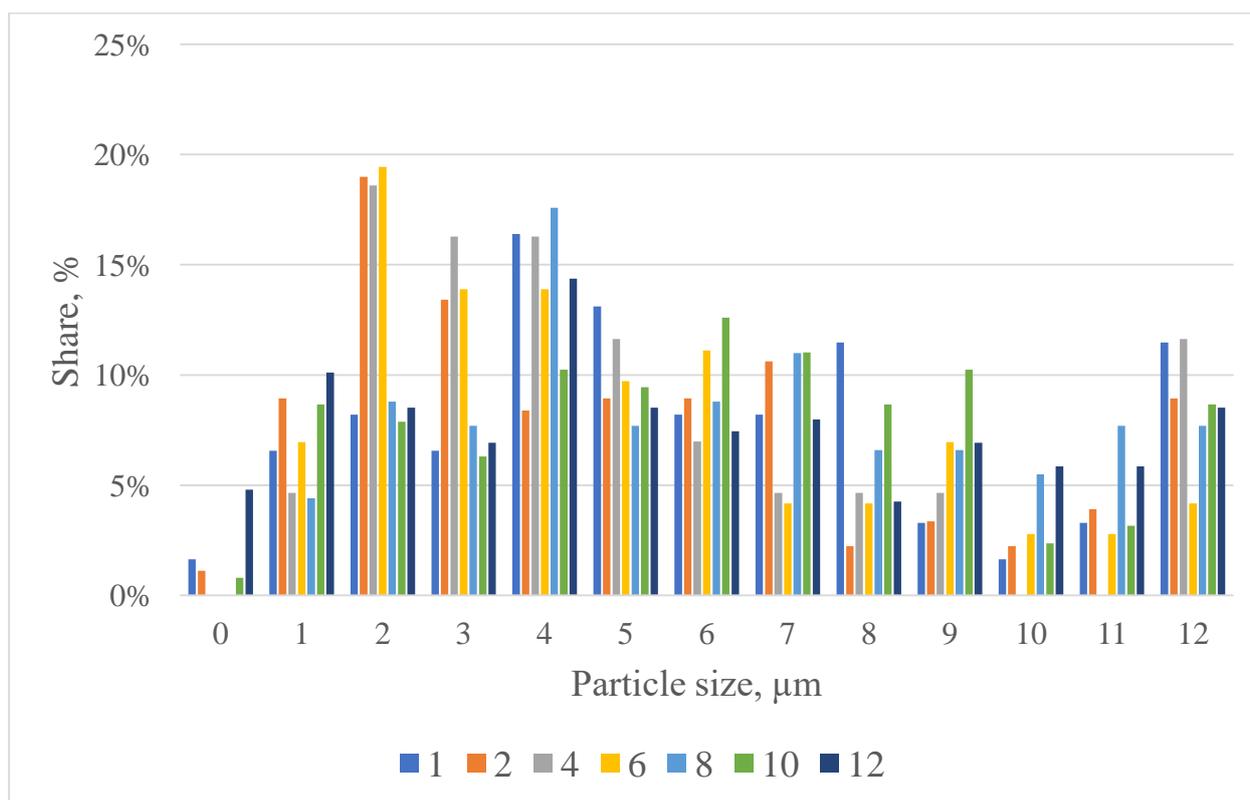
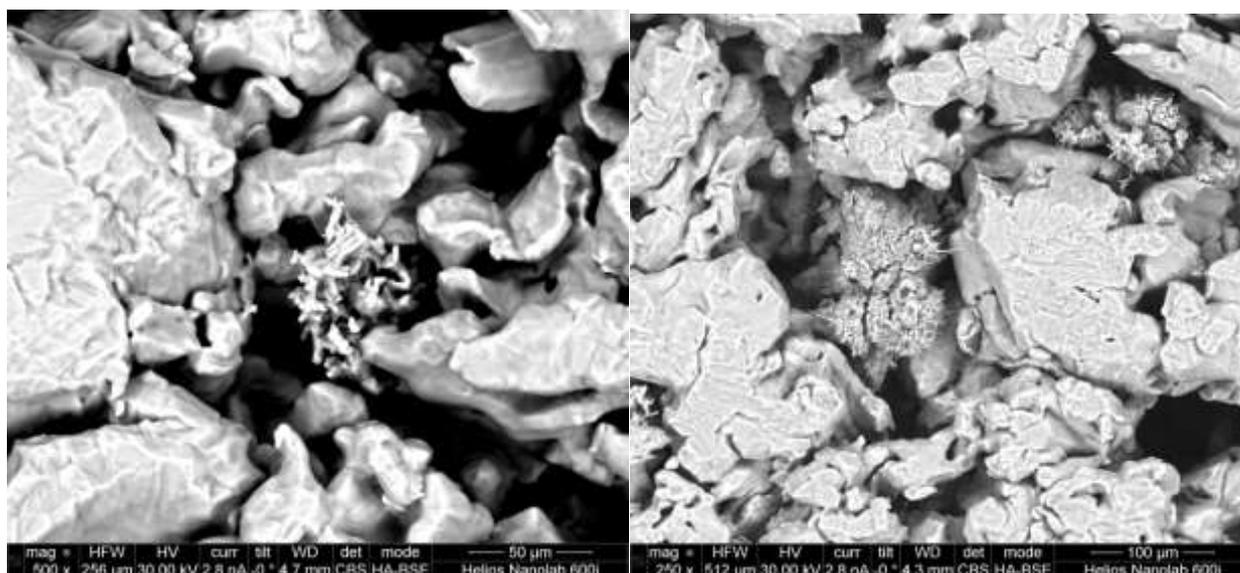


Fig. 7. Pore distributions on the surface of particles in samples with different etching durations.

An increase in the etching time leads to an increase in the number and a decrease in the characteristic size of particles in the images of samples on an average scale, shown in Fig. 6. It can be assumed that such changes in the structure of the current collectors can affect the performance of the cell. The formation of pores with a diameter outside the range of mesopores (macro- and micropores) can lead to incorrect distribution of the catalyst over the surface of the current collector [10].

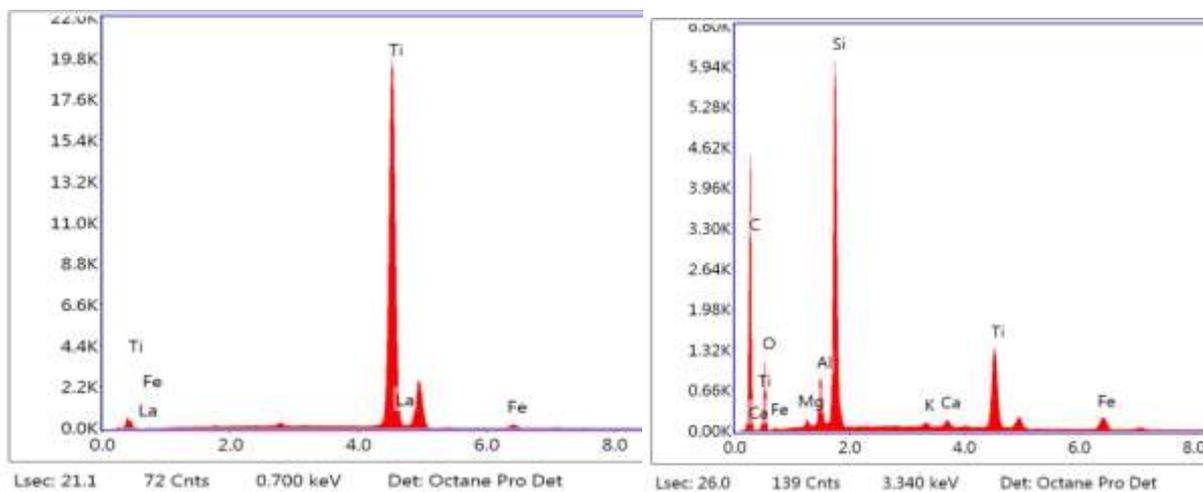
The study of the composition of the samples by the SEM method, shown in fig. 8 shows the presence of foreign intermetallic compounds among the titanium particles. It can be assumed that such compounds inevitably enter the composition of titanium sheets in greater or lesser quantities, which must be considered in the manufacture of current collectors.

In consideration of the above features of the titanium etching process with a duration of more than 5 min, namely, the onset of oxidation, loss of strength and structure, and titanium degradation, it was decided to take only the first 6 samples with an etching duration of up to 4 min for study in the MEA composition.



a)

b)



c)

d)

Fig. 8. The results of the study of the composition of porous titanium samples, images and the distributions corresponding to them: a-c and b-d, respectively.

When preparing samples for testing as part of the MEA, it was noted that samples with smaller dimensions $S = 7 \text{ cm}^2$ are more sensitive to the etching process at the same material thickness, which indicates an inverse relationship between the size of the sample and the depth of penetration of hydrochloric acid into the sample. The data are presented in Fig. 9. On this scale, the effect is insignificant; however, in the manufacture of large current collectors, the data presented may differ greatly from those indicated for the experimental samples of the cells of the electrolyzer, and the degree of etching may be different.

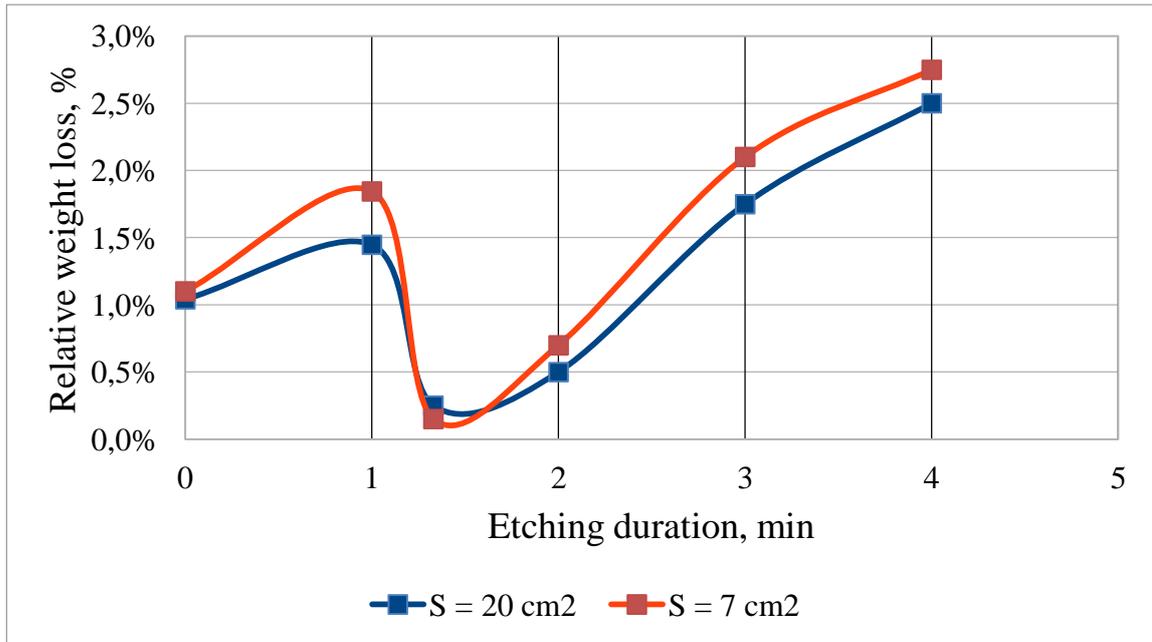


Fig. 9. Graph of the dependence of the sample mass loss, normalized to the initial mass, on the etching duration for samples of the same thickness and surface area $S = 7 \text{ cm}^2$ and $S = 20 \text{ cm}^2$.

To determine the experimental error in measuring the VAC during testing of cells of water electrolyzers with PEM, a study of the VAC was carried out with a set of current collectors prepared in accordance with the method of etching in a 10% hydrochloric acid solution used in a number of works carried out at the National Research Center "Kurchatov Institute", 2 h at room temperature. To study the error, 4 sets of current collectors were prepared. The test results are shown in Fig. 10. Thus, the relative error in current density is approximately 0.9%.

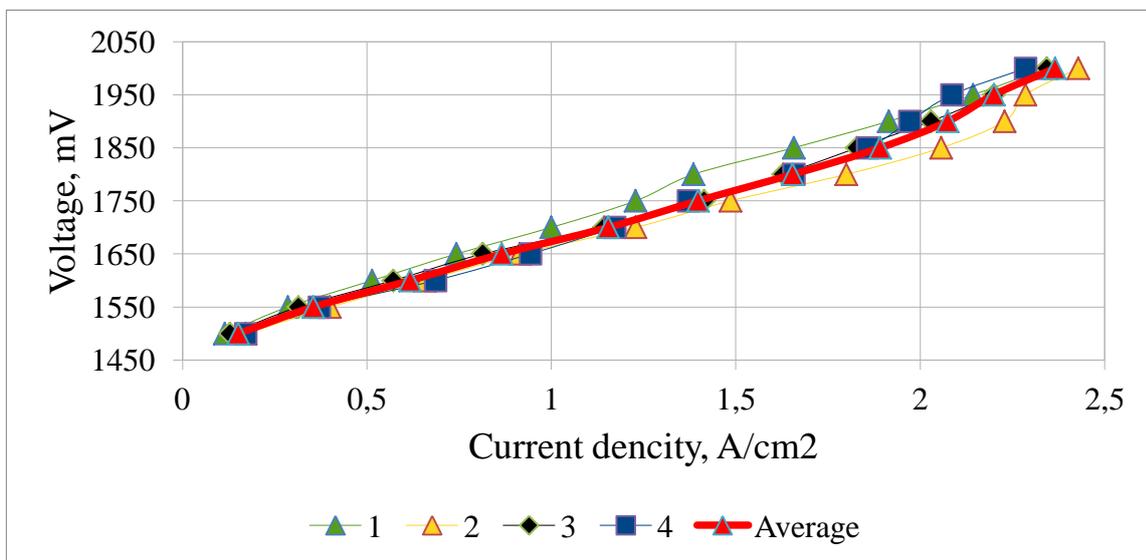


Fig. 10. The results of the study of the VAC of cells with standard etching of current collectors.

Considering the measurements carried out on the assembled stand for testing electrolysis cells, tests of experimental cells with etching under the same conditions were also carried out. The anode and cathode collectors in the same MEA were etched under completely identical conditions.

For comparison, the averaged results of measuring the VAC were selected from the experiment to determine the measurement error of the VAC. Thus, the study involved MEAs with traditionally accepted etching of current collectors and with experimental etching, respectively, samples No. 1 - 6 from Tab. 1. Test results are shown in Fig. 11.

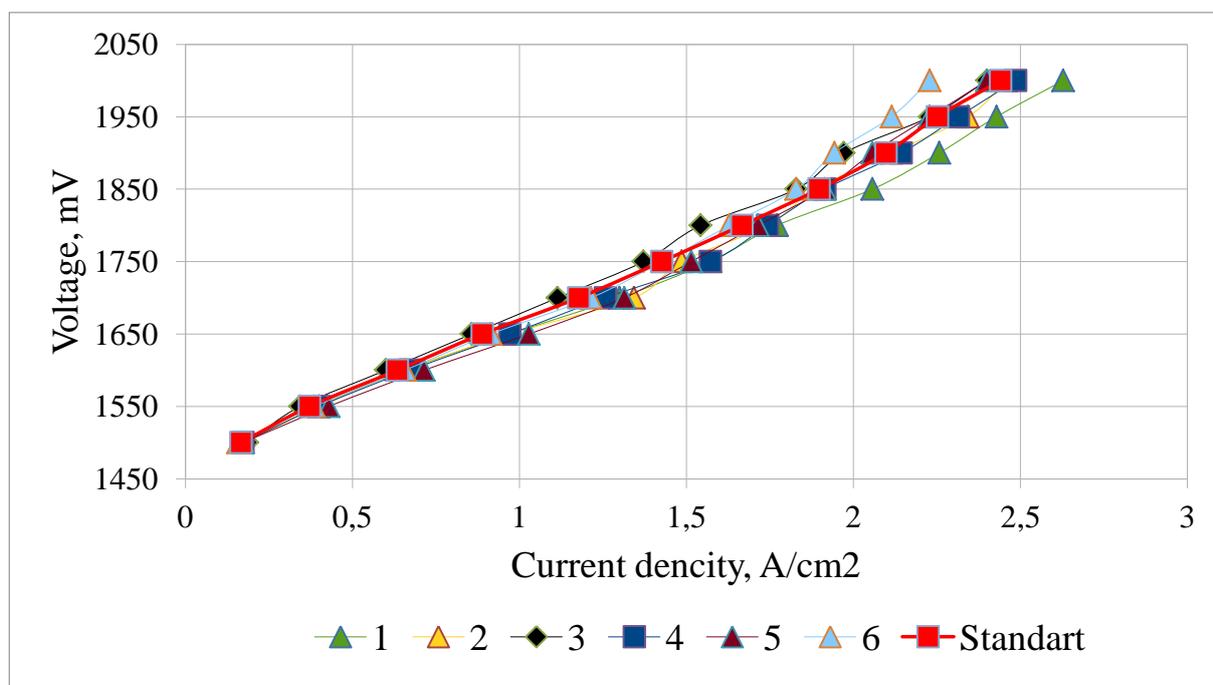


Fig. 11. The results of the study of the VAC of cells with different durations of etching current collectors.

The data of a comparative study of VAC indicate that with an increase in the duration of etching of current collectors in hydrochloric acid, the performance of electrolysis cells with PEM decreases, and samples No. 1 and No. 6 are out of the general picture, and samples No. 2-5 are barely visible as compared to the traditional etching of current collectors. As for the case of “single-stage” etching No. 1, the VAC measurements have a difference with the standard etching at the end of the graph for electrolysis with a voltage of 2 V by 7.8% in favor of sample No. 1. The sample with the longest etching from set No. 6, etched for 4 min, showed a decrease in performance during electrolysis with a voltage of 2 V by 9.9%.

In total, the obtained research data may indicate that as the degree of etching increases, the structure of titanium undergoes significant changes associated with a decrease in the proportion of “useful titanium”: the appearance of pores on the particles and a general decrease in the number of large titanium particles leads to an increase in the number of cavities. The ingress of particles of catalytic materials during the preparation of electrodes into these cavities leads to the isolation of a certain portion of the catalyst from the current collector surface. In turn, this leads to a decrease in electrochemically active surface and a drop in the performance of electrolytic cells with PEM. Moreover, starting from a certain moment (more than 4–5 min), etching has a negative effect on the mechanical parameters of current collectors, leading to titanium embrittlement. Along with this, etching leads to an increase in the geometric inhomogeneity of the surface (formation of “craters”) and deterioration of the contact of the current collector with the catalyst particles of the catalytic layer. At that, the conducted studies show that the initial porosity of the current collectors at the

level of 41-44% allows them to be effectively used in the electrolysis process at current densities up to several A/cm². For higher current densities, it is advisable to increase the porosity not by etching the current collectors, but by introducing a pore agent into titanium powder during current collector sintering and using titanium particles with sizes in the range of 4 – 10 μm to increase the geometric uniformity of the surface.

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ИССЛЕДОВАНИЕ ВЛИЯНИЯ ПРОЦЕССА ТРАВЛЕНИЯ КОЛЛЕКТОРОВ ТОКА ИЗ ПОРИСТОГО ТИТАНА В СОЛЯНОЙ КИСЛОТЕ НА ПРОИЗВОДИТЕЛЬНОСТЬ ЭЛЕКТРОЛИЗЕРОВ ВОДЫ С ТВЕРДЫМ ПОЛИМЕРНЫМ ЭЛЕКТРОЛИТОМ

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Аннотация. С помощью современных методов СЭМ, вольтамперометрии и гравиметрического анализа были исследованы образцы коллекторов тока, используемые в электролизерах с твердым полимерным электролитом, из пористого титана с различной степенью травления в концентрированной соляной кислоте. Гравиметрическое исследование процесса травления образцов различного размера из пористого титана показало, что на протяжении всего процесса происходит потеря массы образца за исключением двух коротких интервалов, предположительно, по причине образования гидридов (60-80 сек) и оксидов (4-5 мин), причем образцы меньшего объема оказались более чувствительными к потере и росту массы. Применение метода СЭМ позволило обнаружить, что травление на протяжении различных по длительности интервалов времени меняет структуру пористого титана, уменьшая средний размер частиц и увеличивая их пористость. При этом растет неоднородность поверхности, в том числе за счет образования углублений из-за вытравленного титана и ухудшения контакта поверхности коллектора тока с каталитическим слоем. Следствием этого является различие вольтамперных характеристик электролизных ячеек с различной длительностью травления коллекторов тока: наблюдается снижение производительности электролиза с ростом длительности травления коллекторов тока на ~8% для травления более 1 минуты и ~18% для травления более 4 минут по сравнению с одномоментным погружением образца в кислоту для очистки поверхности.

Ключевые слова: электролизер воды с ТПЭ, пористый титан, СЭМ, вольтамперометрия, гравиметрический анализ