Development and research of a technology for producing a low-dimensional porous platinum-based catalyst by thermal evaporation in vacuum on an ion-exchange polymer membrane of a hydrogen generator electrolytic cell

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Abstract. The use of hydrogen structures as a universal energy carrier led to its application in various fields of industry. Currently used production methodologies make it possible to produce systems with high reliability and a long service life. However, at the moment, the creation of such structures is limited by the lack of natural origin materials necessary for the production of such structures, which leads to the search for alternative and most universal manufacturing methods against the background of increasing needs.

1. Introduction
Particular interest in the hydrogen energy development is based on the wide possibilities of energy storage, highly efficient production of chemical compounds based on pure hydrogen, the ecological situation improvement, as well as limited reserves of organic resources [1-2]. Under such conditions, multifunctional electrolytic cells of a hydrogen generator are capable of fulfilling the assigned tasks in electric energy storage systems, microelectronics and recovery [3-5]. In this paper, we consider a phased technology for the manufacture of such assemblies using completely different from the traditional methods of structure growth, as well as an analysis of the created structures that are not inferior in their characteristics to existing analogues.

2. Modeling
Currently, perfluorinated ion-exchange membranes «Nafion» developed by «DuPont» are the most popular membranes for electrolytic hydrogen cells in flowing hydrogenation reactors. The membrane «Nafion» is a copolymer of tetrafluoroethylene and comonomer having perfluorinated vinyl ether side chains ending in sulfo groups, as shown in Figure 1 [6-8].

Due to the fact that the membranes in flowing hydrogenation reactors are exposed to high pressure from the side of the reagent, to its unsteady effect during the exit to the regime, we used reinforced membranes «Nafion» N 324 with a thickness of 150 μm to increase the resource [9].

One of the most important aspects of platinum deposition technology on an ion-exchange polymer membrane using the thermal vacuum method is surface preparation, which cleans the membrane surface from various organic and inorganic contaminants, as well as surface modification to increase the adhesive and adsorption activity of the surface relative to the coating [10-12].

At the liquid cleaning stage, the membrane surface is cleaned from organic and inorganic contaminants, molecular organic and chemically related contaminants are removed, and then residual ionic and atomic. During physical liquid cleaning, desorption of surface-adsorbed contaminants occurs without changing their composition, i.e., without chemical reactions, by simple dissolution [13-14].

At the stage of plasma-chemical cleaning, more thorough cleaning from organic contaminants and surface modification takes place. Plasma-chemical cleaning of the substrates surface occurs due to the chemical interaction of contaminants with ions and radicals of active gases with the formation of volatile compounds. Ions and active radicals arise in a gas discharge plasma during the dissociation of gas molecules. In plasma-chemical cleaning plants, plasma of active gas is usually formed as a result of an
electrodeless high-frequency discharge. The main components of the gas mixture for cleaning the substrates surface from organic contaminants is oxygen with small (up to 1% by volume) additives of nitrogen or helium, and argon from inorganic contaminants [15].

![Nafion structure](image)

**Figure 1.** «Nafion» structure.

The liquid cleaning stage consisted of boiling the ion-exchange polymer membranes in isopropyl alcohol for 30 minutes. Then, ion-exchange polymer membranes were placed in a barbator and purified for 15 minutes in isopropyl alcohol vapors, because when boiling in isopropyl alcohol, the resulting contaminants during dissolution can be localized on the surface and in the pores of the membranes. After purification in isopropyl alcohol and its vapors, the membranes were aged in a vacuum oven for 4 hours at a temperature of (40..50) ° C.

The next stage of preparing the surface of ion-exchange membranes was low-temperature plasma-chemical cleaning in a mixture of argon and oxygen gases in a ratio of 1: 1 for 12 minutes. The source power was set to 180-200 W, the temperature did not exceed 45 ° C. After cleaning, the membranes were placed in a moisture-proof fume hood in a Petri dish with silica gel. The time to the spraying process did not exceed 30 minutes. The transportation of containers with membranes prior to the installation of vacuum deposition was carried out in a special container where a Petri dish with silica gel was placed.

To minimize the thermal effects of the evaporation process, a special volume holder of ion-exchange membranes was developed and manufactured with the aim of more heat removal from the substrates, shown in figure 2. Additionally, to avoid overheating, the deposition was carried out on a rotating tooling in order to remove the membrane from the zone of constant deposition. As a heating element, a tungsten evaporator, consisting of several wires stacked in a row with copper tips was used. The holder consists of a massive plate that increases the heat sink from the substrates, and a frame connected to the plate with fixing screws. The membrane is placed on the plate and is drawn in by the frame. To increase the contact area with the heat sink plate during the assembly, the membrane is rolled with a special fluoroplastic roller. The holder is made of stainless steel. Before spraying, the holder is thoroughly washed and annealed.

As a weighed sample, approximately 500 mg of 99.9% pure platinum, which was placed on an evaporator preliminarily annealed by a spraying method without a sample, was used. The equipment rotation began when the pressure in the chamber reached the values (3-5) $10^{-6}$ mm Hg and a gradual increase in current to values of 430-450 A. The shutter was opened after the sample was melted. To prevent platinum spraying, the evaporator current was reduced by 10-15 A. The deposition duration was about 5-7 minutes.

Because of the remnants of platinum material on the evaporator, leading to current shunting, the second side was sprayed in the same way, except for a peak current value of 500 A. The duration of spraying on the second side was 8-10 minutes.
After spraying, ion-exchange membranes were given for visual inspection, control of surface resistance and electrical insulation. The surface resistance of the active catalyst layer (ACL) on the membrane ranged from 20 to 50 MOmh. Insulation resistance showed more than 100 GOmh. Figure 3 shows the images of the two sides of the ion-exchange membranes with ACL performed on an optical microscope at fifty times increase. In the obtained structures, the “cellular” structure of the ion-exchange membrane with platinum islands without the presence of thermal damage is clearly traced.

An increase in the ion-exchange membrane with a nanostructured ACL layer obtained by thermal evaporation in vacuum, using SEM indicates a clearly traceable porous («island») structure of the catalytic coating, which is the activation centers for subsequent electrochemical deposition at the three-phase boundary, as shown in figure 4.
Figure 4. SEM image of an ion exchange membrane with a nanostructured layer of ACL obtained by thermal evaporation in a vacuum.

The total accumulated spectrum using X-ray energy dispersive SEM analysis is shown in Figure 5.

Figure 5. X-ray energy dispersive analysis of the ion-exchange membrane with ACL obtained by thermal evaporation in vacuum.

3. Conclusion
According to the obtained total spectrum of X-ray energy dispersive analysis, shown in Figure 5, pronounced peaks of platinum of the active catalyst layer, as well as fluorine ion exchange membrane with a minimum amount of impurities are visible. Therefore, we can conclude that the catalytic nanostructured coating did not completely cover the membrane structure and fully preserved the characteristics and functions performed by it. In this case, the simulation results confirm the technical feasibility of manufacturing prototypes of such structures.

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