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Study of deposition of heterogeneous structures on ion-exchange membranes

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Abstract. The process of a heterogeneous catalytic coating formation on the ion-exchange membranes surface was studied in this work. It is determined that the use of the chemical deposition method results in a highly porous coating, but with low strength and durability. A combined method for obtaining a heterogeneous catalytic coating is proposed, which includes the formation of adsorption centers by thermal vacuum spraying and the growth of the bulk of the catalyst by chemical deposition.

Keywords: heterogeneous structure, ion-exchange membrane, electrolysis, hydrogen production, catalyst, deposition

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Исследование нанесения гетерогенных структур на ионообменные мембраны

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Аннотация. В работе исследован процесс формирования гетерогенного каталитического покрытия на поверхности ионообменных мембран. Определено, что использование способа химического осаждения приводит к получению высокопористого покрытия, однако обладающего малой прочностью и долговечностью. Предложен комбинированный способ получения гетерогенного каталитического покрытия, включающий в себя формирование адсорбционных центров методом термического вакуумного напыления и выращивание основной массы катализатора методом химического осаждения.

Ключевые слова: гетерогенная структура, ионообменная мембрана, электролиз, получение водорода, катализатор, осаждение

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Introduction

Polymer Electrolytic Membrane (PEM), despite more than 50 years of research and development history, still finds new applications and potential for performance enhancement, which provides researchers and manufacturers with a field for research and development.

One of the areas where PEM has found wide application is the production of chemically pure substances by electrolysis, for example, the production of hydrogen of especially high purity. However, when using PEM in its original form, the process productivity is low, which requires the use of a catalyst. The degree of the electrolytic process intensification, in turn, significantly depends on its properties and structure. It was shown in [1, 2] that the implementation of the catalyst in the form of nanosized particles on the surface of a PEM is the most efficient.

Materials and Methods

An ion-exchange membrane Nafion 324 (DuPont) was used in the experiments.

Table 1

Lists the specifications for the used membrane

Parameter name	Value
Thickness, nm	0.15
Equivalent mass, g/mol	1100
Moisture capacity, %	15.1
Ionic group	Sulfo group (SO_3H)
Ionic form – counterion	H^+
Inert binder	Polytetrafluoroethylene
Reinforcement fabric	Kevlar

Metals such as platinum and palladium were used as a catalyst.

The membrane with the applied catalyst for performance evaluation is installed in the electrolytic cell. The cell is mounted on a test bench, with the help of which the initial substance - water - is fed into the cell, current is supplied and the output of hydrogen is recorded.

The objects under study are catalytic coatings obtained on the membrane surface by the combined method. At the first stage, adsorption centers are formed by the method of thermal vacuum spraying of platinum canopies with the use of the UVN-71P-3 installation. At the second stage, the bulk of the catalyst was increased by chemical deposition of platinum from H2PtCl6 solution.

Results and Discussion

The study of membranes obtained by the combined method showed that the catalytic layer has a porous structure that does not prevent the protons transport to the membrane surface. Fig. 1 and 2 show the results of energy dispersive analysis on PEM. According to the obtained total spectrum of X-ray energy dispersive analysis (Fig. 1), there are pronounced peaks of both platinum of the active catalyst layer and fluorine of the ion-exchange membrane with a minimum amount of impurities. Therefore, it can be concluded that the catalytic nanostructured coating did not completely cover the membrane structure and fully retained the characteristics and functions performed by it.

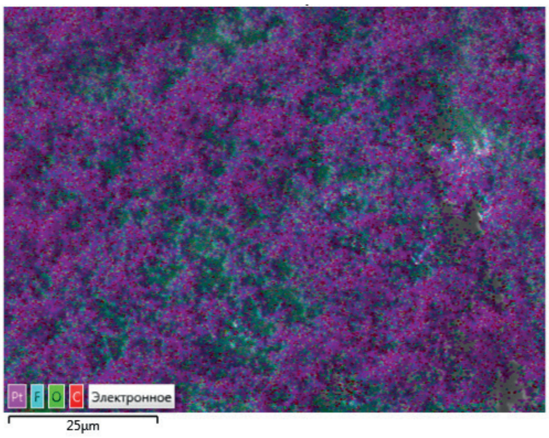

Fig. 1. Multilayer spectral map

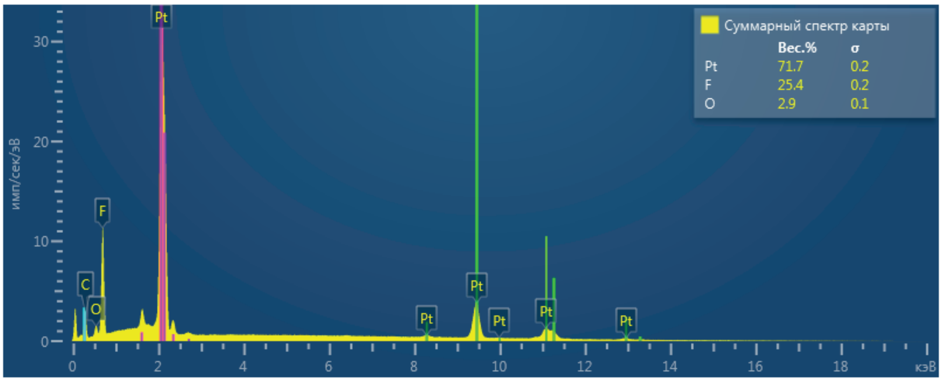

Fig. 2. X-ray energy dispersive analysis of an ion-exchange membrane with a catalyst obtained by thermal evaporation in vacuum followed by chemical precipitation

Fig. 3 shows the performance curves of the pure hydrogen production process when using:

- membranes in their original form;
- membranes obtained by thermal vacuum evaporation in gentle modes;
- membranes obtained by combined technology.

The study of catalytic coatings of ion-exchange membranes coated only by chemical precipitation based on reduction from solutions of H_2PtCl_6 or $PdCl_2$ showed its failure due to low adhesion and washability of the applied coating with a fairly light effect of the supplied substance flow. This is due to the use of fluorine compounds as the basis of the membrane, which practically do not create stable bonds with the catalyst material.

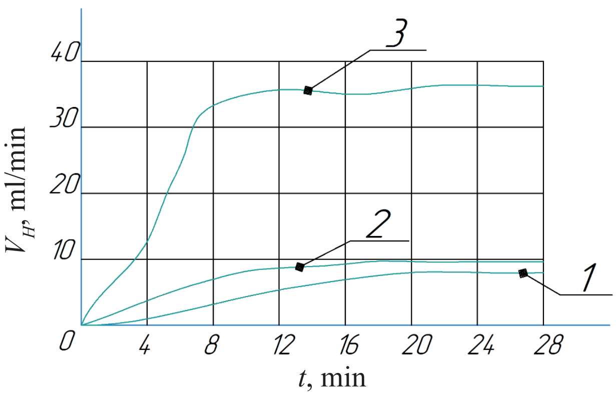

Fig. 3. Performance curves of hydrogen yield in an electrolytic cell with membranes with different coatings. (*1* – original structure of the membrane; *2* – coating in a vacuum evaporator at modes: I = 400 A, T = 300 seconds; *3* – combined coating)

Analyzing the curves in Fig. 3, it can be estimated that the membrane with the catalytic layer formed under gentle conditions in vacuum evaporators increased the hydrogen generation productivity by only 20% compared to the original membrane structure. The stated assumption is confirmed by a significant increase in the hydrogen yield of about 5 times compared with the coating obtained in gentle modes by the vacuum evaporation method.

Conclusion

The parameters of the catalytic heterogeneous coating, at which a high efficiency, which is expressed in an increase in the maximum current strength in the circuit up to 5 A at a voltage of 4 V were revealed. This is a higher indicator compared to competitive technologies [3–5].

The study of membranes with a heterogeneous coating formed by a combined method showed the effectiveness of using a coating obtained by thermal vacuum evaporation as the first fundamental layer. The structure of the first layer makes it possible to form the prerequisites for creating a multilayer catalytic coating with a high specific area, a developed tree structure, and high porosity. Such a heterogeneous coating provides an intensification of the water electrolysis process and an increase in the productivity of hydrogen production by 4–5 times compared to the process in which PEM is used in its original form. There is also an increase in the strength of the heterogeneous coating, and, accordingly, the service life of the membrane compared to membranes coated with a platinum-carbon dispersed catalyst.

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