Analysis of a nanometer catalyst layer using various methods of spraying an active catalytic coating of an ion-exchange polymer membrane embedded in an electrolytic hydrogen cell

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Abstract. Today, the industrial production of hydrogen by traditional methods (high-temperature conversion of hydrocarbons, steam-water conversion of natural gas) against the background of a reduction in natural resources does not allow achieving the necessary purity of the produced gas and imposes serious economic and environmental restrictions. As a result, the solution of the task of developing technologies providing the improvement, high specific and operational characteristics of new methods for producing hydrogen is extremely urgent.

1. Introduction

Progress in various fields of energy, chemical, electronic, medical, pharmaceutical and other areas of industry has led to the widespread use of hydrogen in systems where it serves as an energy carrier [1-2]. Particular interest in the development of hydrogen energy 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 [3-4]. This paper presents an analysis of existing technologies for obtaining such structures and identifies their operational shortcomings, as well as provides a cost-effective and technologically optimal method for their production.

2. Modeling

To ensure high resource and current-voltage characteristics for ion-exchange membranes, the following basic requirements were formulated:
- high proton conductivity;
- long-term mechanical strength in the presence of water;
- long-term chemical stability;
- lack of electronic conductivity;
- low permeability of gas reagents [5].

The main functional characteristics of the membranes according to the stated requirements require comprehensive modernization not only in their production process, but also during testing directly in flow reactors. However, despite all the numerous requirements for membranes, the intensity of degradation processes in them is often determined by the quality of the active catalyst layers (ACL) coating. The degradation of the catalyst in the active layers is manifested due to the platinum dissolution, leading to the membrane reprecipitation, enlarging the structure as a whole and reducing the electrochemical activity of the layer surface, as well as due to sintering migration, increasing and shifting the curve maximums distribution of catalytic particles to the region of larger particles. The problems of ACL degradation are also associated with methods of their deposition on the ion-exchange membrane [6]. The synthesis technology of the catalytic layer determines the adhesion ACL properties to the ion-exchange membrane, the ACL purity associated with possible contaminants in the production process, clogging of pores involved in electrochemical reactions, the applied material, etc [7].

One of the first methods for the ACL formation was the use of a phosphoric acid electrolyte with an impregnation procedure that expanded the region of the three-phase boundary of already sintered active
electrode layers, which did not fully ensure the structure uniformity and did not allow efficient use of the platinum introduced into the active layers [8]. This structure is shown in figure 1.

Figure 1. Structure of the «classical» ACL electrode of a phosphoric acid element with sintered PTFE particles.

The use of «Nafion» film as a binder of thin-film technology, as well as an upgraded method using a colloidal design, as shown in Figure 2, increased the platinum use efficiency. However, the «clogging» of the membrane pores due to the large thickness of the deposited layer, the heterogeneity of the coating, which does not allow activation of the entire membrane area, the complexity of the process preparation and the purity of the reagents involved in the process, did not allow the full use of this technology [9].

Figure 2. Thin-Film electrode with «Nafion».
The ACL production is possible by vacuum deposition, as well as the deposition of organometallic precursors from solutions in supercritical media, followed by the precursor conversion to metal (MOCVD) and the direct current magnetron sputtering method of ultrapure platinum targets in an inert argon working gas. Such application methods provide a high degree of homogeneity, as a result, platinum loading is significantly reduced without loss of productivity, improving the adhesion of the active catalyst layer to the polymer electrolyte and the purity of the process. «Dry» methods of obtaining a catalyst are convenient for obtaining multi-layer or gradient active layers, which further increases the efficiency of the injected catalyst. [1, 2, 11-12].

One of the most promising methods for ACL producing is electrochemical (galvanic) metal deposition. In subsequent work of OIE the catalyst efficiency also remains high, which reduces the loading of platinum; however, the structures fabricated by this method had an unsatisfactory adhesion degree to the surface, which is a critical factor when applied to movable flexible substrates [13-14].

The palladium-based ACL structures did not meet the required characteristics, the «cell» structure of the ion-exchange membrane was absent and completely «overgrown», which is shown in figure 3, and when they were built into the electrolytic hydrogen cell were inoperative. The accumulated spectrum shown in figure 4, obtained by X-ray energy dispersive SEM analysis, also did not show the presence of ion-exchange membrane materials, in which only palladium and technological materials are observed.

![Figure 3. Image of the catalytic layer made using X-ray energy dispersive SEM analysis.](image3)

![Figure 4. X-ray energy dispersive analysis of an ion-exchange membrane with ACL based on palladium.](image4)

Works on obtaining a high-quality structure using a nanostructured coating only due to thermal vacuum evaporation also did not lead to positive results. To the changed properties on the membrane due to thermal damage, clogging of the pores by the catalyst material was detected, which led to an ionic...
conductivity violation through the membrane. Sprayed by this technology with pronounced thermal damage, the ion-exchange polymer membrane is shown in Figure 5.

![Image of an ion-exchange polymer membrane with ACL.](image)

**Figure 5.** Image of an ion-exchange polymer membrane with ACL.

To date, the improvement of the characteristics of ion-exchange polymer membranes with a catalytic layer is associated with the development of «breakthrough technologies» with the widespread use of nanostructured materials. To achieve the required quality of the ACL coating and the operating conditions of the membranes in flow hydrogenation reactors, the researchers implemented a combined technology for creating a nanostructured catalyst. «Dry» vacuum methods for obtaining ACL allow obtaining low-dimensional nanostructured thin films with good adhesion properties and purity. Such application methods methods for obtaining MOCVD catalytic coating and magnetron sputtering are limited to the use of complex and expensive equipment. The implementation of the magnetron method is complicated by the acquisition of a platinum target, which has a high cost and low efficiency of use, since the material is sprayed only in the zone of «erosion», and possible contamination from working gases, the purity of which is often insufficient for the tasks set. Nanoscale thin films of satisfactory quality can be obtained by thermal vacuum sublimation of the initial components of platinum. The implementation of thermal evaporation in a vacuum does not require the acquisition of such an expensive target as in the case of magnetron sputtering and is limited to the use of «attachments» of platinum in several hundred milligrams. The use of a rotating mechanism and technological equipment for spraying allows for group manufacturing technology. Platinum films of several tens of nm completely repeat the structure of the ion-exchange membrane, settling in the places of the three-phase boundary organization, do not clog the pores, thereby absolutely do not change the properties of the membrane. The nanoscale thickness of the layer makes it resistant to deformations and sufficiently porous, and the high adhesion to the ion exchange membrane and the growth of the film at the three-phase boundary allow the structure to be used as activation centers for further structured electrochemical deposition. As a result, the combined method of ACL coupling allows obtaining the necessary nanostructured coating with good adhesion mechanical characteristics that do not affect the functional features of the membrane, as well as the specified electrophysical parameters [1, 3].

### 3. Conclusion

As a result of the analysis, the most technologically advanced and economically feasible method for producing an active catalytic coating of an ion-exchange polymer membrane embedded in a hydrogen electrolytic cell in hydrogenation flow reactors, consisting in a combined method of thermal evaporation in vacuum, creating a nanostructured activation surface with high adhesion for subsequent electrochemical deposition is presented.

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