The influence of star-like palladium nanocrystallites on the gas transport parameters of modified palladium-containing membranes

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Abstract. Methods to modify the surface of Pd-23% Ag alloy films were developed in order to increase the velocity of hydrogen transmission; we obtained palladium coating of “nanostars” and “nanopores” type. Modification of Pd-Ag films surface, obtained by nanostars palladium coating makes it possible to achieve a hydrogen flow density of 0.76 mmol / (s*m2), which is 1.6 times greater in comparison with modification by “nanopores” coating under low temperature (<90 ° C) and pressure (<0.6 MPa) conditions.

1. Introduction

Every year for the needs of alternative energy requires more and more high-purity hydrogen. The most common method to obtain it is reforming of organic raw materials with gas mixture formation and subsequent release of high-purity hydrogen, with the help of various types of metal membrane filters [1-4]. As a basis for creation of these membrane filters palladium and its alloys are used as they have unique properties in relation to the hydrogen transmission [5-7].

The operating temperature range of such membrane filters is in the range of 500-600°C, which creates some limitations and disadvantages in use. First, the energy loss in the process of hydrogen production. Secondly, the pollution of diffused hydrogen by impurities released from the structural materials of the equipment for diffusion purification of hydrogen. These aspects limit the use of palladium membranes and prevent their mass adoption in the industry. The situation would be different if there were membranes capable of transporting hydrogen in the temperature range up to 200°C with sufficient mass transfer rate. Ideally, they should be operational at ambient temperatures.

Some of the few studies affecting the temperature range up to 200°C have shown a critical drop in hydrogen permeability up to instability of the results [8-10], however, studies showing stable reproducible results of hydrogen permeability of low-temperature palladium-containing membranes with any significant density of hydrogen flow. At the time of this writing, the authors are not known.

The absence of such membranes hinders the development of processes and devices in which they could be implemented. Such devices could be a low-temperature hydrogen diffusion electrode and devices based on it: an electrochemical hydrogen pump (compressor) that can be used in devices for the economical separation of hydrogen isotopes, and a low-temperature hydrogen fuel cell [11,12].
In addition, these membranes are integrated into methanol steam reformers, which allows creating compact membrane reformers that are effective for in situ hydrogen production [13-15]. Also, their use is relevant for the separation of hydrogen isotopes, for example, membrane production of water with a modified isotopic composition [16-18].

The aim of the work was to obtain resistant to long-term use of palladium-containing films capable of passing hydrogen at low temperatures. For this, two types of surface modifiers were synthesized for membranes made of Pd-23% Ag alloy and their effect on the kinetic characteristics of hydrogen transfer was studied.

The formation of nanostructured palladium layer capable for chemisorbing of hydrogen on the surface of membrane increases the actual operating surface, which leads to increase of chemisorption centers quantity, which role is most often played by crystallites angles and facets. Moreover in case of sufficiently small Pd crystal size the majority of octahedral interstices belong to the surface, that facilitates the transmission of hydrogen and reduces the probability of hydrogen atom capture by various kinds of surface defects. This modification may be effective in case of limiting the process of hydrogen transfer through the membrane by dissociative-associative absorption-elimination processes at the boundaries.

2. Methods and materials

Two methods were used for the deposition of finely dispersed palladium onto the surface of thin Pd–Ag alloy films.

(1) Magnetron sputtering of alloy films with subse- quent diffusion annealing and etching. Zinc was used as the active component of the Raney palladium alloy for sputtering, since the sputtering current strength for Zn (50 A) is close that for Pd (30 A). The alloy with 50% Zn was chosen for modifying the palladium–silver surface. Diffusion annealing in an inert argon (99.99%) environment was the next processing stage. The volume flow rate was set to 2 L/min to establish firm adhesion between the Raney alloy and the substrate material and secure attachment of finely dispersed platinoid grains after etching of the active component (zinc). Zinc (soluble component) leaching in a 6M NaOH solution was the last phase of the process.

(2) The surface of a Pd–23%Ag film secured in a holder was rinsed with 96% ethanol, degreased by boiling for 30 min in a 6M NaOH solution, and immersed in a 60% HNO3 solution for etching (30 s). Immediately after etching, the film was introduced into a vessel with flowing distilled water and held there for 10 min. The film on an inert holder made of 99.99% pure silver was then transferred to an electrolytic cell for coating. The holder served as the cathode current lead; contact was established by a silver wire. The palladium–silver alloy film was then transferred to a cell with 0.1M HCl and polarized anodically at a current density of 10–20 mA/cm² using a P-2501 potentiostat/galvanostat, was rinsed again with bidis- tilled water, and polarized cathodically in 0.05 M H₂SO₄ at a current density of 10–20 mA/cm². After rinsing with bidistilled water, the cell was filled with a solution of the following composition: 2% H₃PdCl₄, 0.1M tetrabutylammonium bromide (surfactant). Palladium black precipitated for 30 min at 2–6 mA/cm².

3. Results and discussion

To obtain thin palladium-silver films the magnetron sputtering method was used. Plates of silver and palladium with different ratio of its areas were used as a target for the magnetron [19, 20]. Magnetron sputtering was performed on the Quorum Q150TS / E / ES device. The chemical composition of the obtained films was studied by method of micro-X-ray spectral analysis on INCA (Oxford) semiconductor energy dispersive add-on device with JEOL JSM-7500F scanning electron microscope. To obtain a film with silver content of 23%, which is optimal for hydrogen permeability and mechanical properties [21, 22], a target with an areas ratio S (Ag) / S (Pd) = 20.8 / 79.2 was used.

In the course of this study, two types of surface modification of hydrogen permeable membranes were developed: “nanostars” and “nanopores”. The microphotographs of the films surface obtained by JEOL JSM-7500F scanning electron microscope are shown in figure 1. In figure 2 the data is shown
on the measurement of hydrogen permeability for a palladium-silver alloy modified by coating of “nanostars” type (a) and coating of “nanopores” type (b).

![Figure 1](image1.png)

**Figure 1.** Microphotographs of palladium-silver films surface with modified surface, obtained by the method of “nanostars” (a), and by the method of “nanopores” (b).

![Figure 2](image2.png)

**Figure 2.** Dependence of the rate of fluence (the ratio of hydrogen flow to the area of a sample) on the excess pressure of hydrogen on the outer face of the membrane for the method “nanostars” (a) and the method of “nanopores” (b).

From figure 2 it is obvious that the dependence of the flow density on hydrogen overpressure on the input side of the membrane with modified surface is well approximated by a line of the 1st order, which indicates according to [23] that hydrogen penetration velocity is limited by dissociation of hydrogen on the surface.

Thus it has been experimentally confirmed that the velocity of hydrogen transmission under conditions of low temperature (<90°C) and pressure (<0.6 MPa) through sufficiently thin palladium membranes (<10 μm), is limited by dissociative-associative processes at the boundaries, and can be significantly increased (up to order of magnitude) due to acceleration of the limiting stage by applying a superficial modifying palladium coating. Modification of membranes with “nanostars” type of
coating allows achieving hydrogen flow density up to 0.76 mmol / (s*m²) that is 1.6 times greater than with modified by “nanopores” type of coating.

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