Hydrogen permeability and catalytic characteristics of a palladium-silver membrane with a modified surface

I Petriev¹,²
¹Department of Physics, Kuban State University, Krasnodar, 350040, Russia
²Laboratory of problems of stable isotope spreading in living systems, Southern Scientific Centre of the RAS, Rostov-on-Don, 344000, Russia
petriev_iliya@mail.ru

Abstract. Thin films of Pd-23% Ag modified with nanostructured highly dispersed palladium by the method of electrolytic deposition have been obtained by magnetron sputtering. Electrochemical studies have demonstrated that the modified Pd-23% Ag film shows a high peak current (up to 2.15 µA cm⁻²) and excellent electrocatalytic activity in relation to the methanol oxidation reaction. The stability of the developed modified film is confirmed by the results of multi-scanning. Comparison of the hydrogen permeability has been demonstrated a significant increase in the hydrogen permeability of the modified membrane compared to the smooth one at an overpressure of 0.3 MPa. According to the approximation of the results obtained by a first-order line and calculations of the activation energy, which was 30.6 kJ mol⁻¹, it can be concluded that the transport of hydrogen is limited by surface effects, namely chemisorption.

1. Introduction
Palladium and its alloys are an attractive material for manufacturing hydrogen-permeable membranes based on them [1-5], since palladium is able to absorb and desorb hydrogen under relatively flexible environmental conditions. The metal has a low tendency to dilatation, so the palladium crystal lattice is slightly deformed and the properties of the metal remain practically unchanged even after a long stay in the hydrogen atmosphere.

The reactivity of palladium can be regulated by doping by transition metals [4]. Silver is considered the most applicable in membrane applications [6-8]. Such alloys are mechanically stable, which makes it possible to obtain sufficiently thin films [9] and demonstrate sufficiently high rates of hydrogen permeability at the same time.

The materials can be used in alcohol (ethanol, methanol) and oxygen-hydrogen fuel cells as all-metal gas diffusion electrodes operating in the low temperature range (< 100°C), as well as in the processes of membrane separation of hydrogen isotopes [10,11].

A common feature of metal – hydrogen systems is kinetic inhibition of reaching equilibrium at temperatures below 200°C, which is caused by slowing down the transition of hydrogen through the metal surface [12]. Powdered hydrogen-absorbing substances (for example, Fe, Co, Ni, Cu, platinum metals) in contact with compact Pd samples can significantly accelerate the dissolution of hydrogen at room temperature or make this dissolution possible at all [13-15].

Based on the above, the aim of this article has been a synthesis of a nanostructured highly dispersed functional layer on the surface of Pd-23% Ag membranes and a study of the catalytic and kinetic characteristics of the process of hydrogen transport through the developed all-metal membranes.

2. Methods and materials
2.1. Method of manufacturing self-supporting membranes
The most optimal Pd-23% Ag alloy films in terms of mechanical properties and hydrogen permeability have been obtained by magnetron sputtering. Silver and palladium plates with different ratios of their areas have been used as a composite target for the magnetron [16,17]. Magnetron sputtering has been performed on a Quorum Q150TS/E/ES device.

In the process of modifying the surface of the Pd-23% Ag alloy film, it has been fixed in a holder, washed in 96% ethanol, and degreased by boiling for 30 minutes in a concentrated 6 M NaOH solution. Next, the films have been transferred for etching in a 60% HNO₃ solution for 30 seconds, after which they have been immediately transferred to a vessel with running distilled water for 10 minutes. Then the film on an inert holder has been transferred to an electrolytic cell for coating, and the mass of the holder made of 99.99% pure silver has been used as the cathode current supply. The contact has been made with silver wire. Then the palladium-silver alloy film has been transferred to a cell with 0.1 M HCl and anodically polarized at a current density of 10-20 mA cm⁻², using a potentiostat-galvanostat P-250I, washed, cathodically polarized in 0.05 M H₂SO₄ at a current density of 10-20 mA cm⁻², then filled with a 2% solution of H₂PdCl₄. Pd black deposition has been performed at a current density of 5-6 mA cm⁻² for 30 minutes, after which it has been washed with bidistillate and cathodically polarized in 0.05 M H₂SO₄.

2.2. Electrochemical measurements
Studies of catalytic characteristics in methanol oxidation reactions have been performed using a cyclic voltammetric (CV) method at room temperature (25°C) using a three-electrode cell on an automated potentiostat-galvanostat device (Elins P-40X). Modified Pd-23% Ag films have been used as working electrodes, silver chloride electrode has been used as a reference electrode, and smooth Pd-23% Ag foil has been used as an anti-electrode. CV scanning has been performed in the operating potential range from -0.9 V to +0.5 V with a scanning speed of 50 mV s⁻¹ in 1.0 M aqueous NaOH solution with 0.5 M methanol. The currents are normalized to the geometric area of the electrodes, and all potentials are reported relative to the silver chloride electrode.

2.3. Measurement of hydrogen permeability
The measurement of hydrogen permeability has been carried out using a device developed at Kuban state University based on the microgazolumetric method [15].

3. Results and discussion
In the course of the study, a method has been developed for the synthesis of a nanostructured functional layer on the surface of Pd-23% Ag. Micrographs of the surface of films modified by electrochemical deposition are shown in the Figure 1.

![Figure 1. Microphotographs of the surface of palladium-silver films with a modified surface.](image-url)
Cyclic voltammetry of the developed modified high-dispersed coating Pd-23% Ag film and smooth Pd-23% Ag film that are resistant to the methanol oxidation reaction (MOR) are shown in Figure 2. The large distinct peak of methanol oxidation at 2.15 µA cm⁻², which is shifted to the negative region during direct (laser) scanning, indicates good catalytic properties of the developed modified electrode in the MOR reaction. The appearance of peaks during reverse (cathodic) scanning is associated with the removal of chemisorbed CO and the resumption of methanol oxidation. The values of the current density indicators normalized by area prove that the modified nanostructured highly dispersed Pd-23% Ag film demonstrates enhanced electrocatalytic activity compared to the smooth Pd-23% Ag film, which allows the former to be used in alcohol fuel cells.

![Figure 2. CV of steady-state cycles for a modified and smooth Pd-23%Ag film in the reaction of alkaline methanol oxidation at room temperature.](image)

Figure 2. CV of steady-state cycles for a modified and smooth Pd-23%Ag film in the reaction of alkaline methanol oxidation at room temperature.

The stability of the developed modified Pd-Ag 23% film has been investigated by multi-scanning, shown in Figure 3. The highest value of the area-normalized current density is registered on the 30th cycle, after which it begins to decrease and by the 100th cycle it decreases by 9.4 %.

![Figure 3. MultiScan CV modified Pd-23%Ag film in the reaction of alkaline oxidation of methanol at room temperature.](image)

Figure 3. MultiScan CV modified Pd-23%Ag film in the reaction of alkaline oxidation of methanol at room temperature.

Measurements of hydrogen permeability for the three samples of membranes: pure palladium, smooth Pd-23%Ag alloy uncoated and surface-modified are presented in Table 1 and Figure 4.
Table 1. Measurement of hydrogen permeability.

| Δp, MPa | V, ml | v, 10^{-6} mol | F, 10^{-9} mol s^{-1} | J, 10^{-5} mol s^{-1} m^{-2} | P, 10^{11} mol s^{-1} m^{-2} sm^{-1} Pa^{0.5} |
|---------|-------|----------------|------------------------|-----------------------------|---------------------------------|
|         |       |                |                       |                             |                                 |
| Pure palladium                               |
| 0.1-0.3 | 0     | 0              | 0                      | 0                           | 0                               |
| 0.4     | 0.03  | 1.13           | 1.87                   | 2.39                        | 1.21                            |
| 0.5     | 0.06  | 2.62           | 4.38                   | 5.57                        | 2.41                            |
| 0.6     | 0.11  | 4.50           | 7.50                   | 9.54                        | 3.64                            |
| Alloy (Pd-Ag 23 %) with smooth surface       |
| 0.1-0.3 | 0     | 0              | 0                      | 0                           | 0                               |
| 0.4     | 0.02  | 0.75           | 1.25                   | 1.59                        | 0.81                            |
| 0.5     | 0.05  | 2.06           | 3.44                   | 4.38                        | 1.89                            |
| 0.6     | 0.08  | 3.38           | 5.62                   | 7.17                        | 2.73                            |
| Alloy (Pd-Ag 23 %) with modified surface     |
| 0.1     | 0.01  | 0.38           | 0.62                   | 0.79                        | 1.21                            |
| 0.15    | 0.03  | 1.31           | 2.18                   | 2.79                        | 3.01                            |
| 0.2     | 0.06  | 2.25           | 3.75                   | 4.77                        | 4.10                            |
| 0.3     | 0.12  | 4.87           | 8.13                   | 10.36                       | 6.50                            |
| 0.4     | 0.18  | 7.50           | 12.48                  | 15.87                       | 8.09                            |
| 0.5     | 0.27  | 10.91          | 18.16                  | 23.11                       | 10                              |
| 0.6     | 0.35  | 14.22          | 23.76                  | 30.28                       | 11.56                           |

The temperature dependence shows that the values of the hydrogen permeability index at room temperature demonstrated by the modified Pd-23% Ag membrane significantly exceed the values of this indicator for a smooth Pd-23% Ag membrane, which makes it possible to use the former as a solid anode of an oxygen-hydrogen fuel cell.

**Figure 4.** The dependence of the hydrogen flux for membranes of pure palladium (a), smooth Pd-23% Ag alloy without coating (b) and with a modified surface (c) on the high pressure on the input side of the membrane at a temperature of 25°C.
When considering the process of hydrogen transport through the membrane, three main processes must be taken into account [18]:

- a chemisorption process in which hydrogen molecules in the gas phase dissociate on a solid surface, forming adsorbed atoms that can diffuse into the solid;
- the process of desorption in which the adsorbed hydrogen atoms recombine and are released in the form of molecules;
- diffusion phenomena in which hydrogen atoms move through the membrane.

The first and the second processes are known as "surface effects", and under certain conditions they can completely control the rate of penetration (surface-limited permeability), whereas under other conditions, diffusion through a solid is the rate-limiting factor (diffusion-limited permeability).

The graph of the dependence of the hydrogen flux on the high-pressure shown in Figure 5 demonstrates that the dependence of the flux for a Pd-Ag 23% membrane with a modified surface is well approximated by a first-order line, which according to [20,21] indicates that the rate of hydrogen permeation is limited by hydrogen dissociation on the surface.

![Figure 5](image1.png)

**Figure 5.** The dependence of the flux on the excess pressure of hydrogen on the input side of a modified Pd-Ag 23% membrane at a temperature of 25°C.

![Figure 6](image2.png)

**Figure 6.** Temperature dependence of the hydrogen flux through a modified Pd-Ag 23% membrane.

Data on measuring the rate of hydrogen transport through the developed modified Pd-Ag 23% membrane in the temperature range of 25-100°C are shown in Table 2 and Figure 6.

**Table 2.** The results of measuring the temperature dependence of the hydrogen permeability of a palladium-silver membrane.

| T, °C | T, K | V, ml | v, 103 ml s⁻¹ m⁻² | J, s⁻¹ m⁻² | k, s⁻¹ |
|------|------|-------|-----------------|-----------|--------|
| 25.0 | 298.15 | 0.06  | 0.30            | 0.01      | 0.10   |
| 30.0 | 303.15 | 0.07  | 0.40            | 0.02      | 0.14   |
| 40.0 | 313.15 | 0.14  | 0.76            | 0.03      | 0.26   |
| 50.0 | 323.15 | 0.26  | 1.43            | 0.05      | 0.48   |
| 60.0 | 333.15 | 0.41  | 2.29            | 0.08      | 0.76   |
| 70.0 | 343.15 | 0.72  | 3.97            | 0.14      | 1.33   |
| 80.0 | 353.15 | 1.15  | 6.37            | 0.22      | 2.13   |
| 90.0 | 363.15 | 1.65  | 9.17            | 0.31      | 3.06   |
The activation energy of the process has been calculated using the Arrhenius equation:

\[ k = A \exp\left(-\frac{E_A}{RT}\right), \]

\[ -RT \ln(k) = \frac{1}{A_T} - R \ln(A). \]

Figure 7 shows the dependence of Rln(k) on 1/T. As it has been mentioned earlier, the hydrogen transport process consists of several stages and the resulting activation energy value of 30.6 kJ mol\(^{-1}\) exceeds the value of this indicator for the process of hydrogen diffusion through palladium, which is 22-25 kJ mol\(^{-1}\). The obtained value is a function of the activation energies of individual stages and confirms that the limiting stage of the hydrogen transfer process is chemisorption.

![Figure 7](image.png)

**Figure 7.** The dependence of Rln(k) on 1/T for the process of hydrogen transfer through a Pd-Ag 23% membrane.

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