Structural, morphological and catalytic characteristics of nanostructured palladium catalysts

P D Pushankina, I S Lutsenko, I S Glazkova, T I Malkov and M A Mukhanov
Department of Physics, Kuban State University, Krasnodar, 350040, Russia

polina_pushankina@mail.ru

Abstract. A new method for the highly active palladium catalyst synthesis on the surface of a Pd-23%Ag film has been developed to increase the material activity with respect to reactions involving hydrogen. Comparison of the electrochemical experiments data of classical palladium black and a new developed nanocatalyst demonstrated a significant increase in catalytic activity in the methanol oxidation reaction (up to 17.09 μA cm⁻²) for electrodes modified with the latter catalyst. The reason for that is an increase in the number of localized potentially more active surface regions due to the creation of a larger number of active sites in comparison with spherical particles. Estimation of resistance to CO poisoning showed high efficiency of nanocatalysts. Chronoamperometric experiment established the long-term stability and activity of the developed catalyst and confirmed the possibility of its practical use.

1. Introduction
Nanoparticles based on noble metals are of great interest for many branches of modern science and industry [1-6]. Particular attention is drawn to the potential of using palladium-based functional nanomaterials as catalysts for hydrogen separation and purification [6-12]. Such a catalyst must be active, stable, with low overvoltage, which requires effective catalytic properties, such as high electronic conductivity and a large number of active sites [13]. Since the reactions catalyzed by Pd exhibit structural sensitivity, the activity and selectivity depend on the control of the shape and size of metal nanoparticles and the arrangement of atoms on the surface. Therefore, the key to the development of highly efficient nanoscale systems is to understand the effect of nanoparticle morphology (facets with high or low Miller index, defects, bends, adatoms, etc.) on their physicochemical and catalytic properties.

At the moment, various methods for the synthesis of nanostructures have been developed, which made it possible to obtain particles of various shapes, structural organizations, monometallic or bearing synergistic effects from secondary metals [14, 15]. The most advanced of these are particles with one or more fifth-order axes [16-18]. However, these particles have a regular geometric shape (icosahedron, decahedron) close to spherical and therefore have low activity.

Therefore, the aim of the article was to synthesize new types of highly efficient nanostructured palladium-based catalysts that increase the adsorption / desorption activity of the material with respect to reactions involving hydrogen and to investigate their catalytic characteristics.
2. Methods and materials

2.1. Synthesis of nanostructured catalysts

The substrate of a Pd-23% Ag film was prepared by washing in ethyl alcohol (96%) and boiling for 20 minutes to degrease before deposition. Then the film was washed in running distilled water for 5-10 minutes. After that, the prepared film was fixed in the working cell as an anode, the cathode from which the deposition was carried out was fixed parallel to anode. Then the substrate was polarized in sulfuric acid (0.05 M) at a current density of 10 mA/cm², after which it was washed with bidistillate. In order to start deposition the electrolytic cell was filled with a palladium chloride solution (2%). Depending on the type of the obtained coating, a surfactant (tetrabutylammonium bromide) in various concentrations was added to the growth solution. The coating deposition on the substrate was carried out at a current density varying for different coatings from 5 to 6 mA/cm² for 20 minutes. The highly dispersed palladium coating electrolytic deposition was carried out on a potentiostat-galvanostat (Elins) R-40X. At the end of the process, the film was washed with bidistillate.

2.2. Electrochemical measurements

Electrochemical experiments were carried out using a potentiostat-galvanostat "Elins" P-40X. The experiment was carried out in a standard three-electrode cell filled with a solution of NaOH (1 M) and methanol (0.5 M) and consisting of a working electrode, a counter electrode, and a reference electrode. The working electrode was a sample of palladium-silver films modified with various types of palladium coatings. The counter electrode was a platinum foil comparable in size to the working electrode. A silver chloride (Ag/AgCl) electrode was used as a reference electrode. Before measurements, all electrodes were washed and the platinum counter electrode was degreased.

Measurements of the samples electrocatalytic characteristics were carried out by the method of cyclic voltammetry (CV). The multiscanning was carried out in the operating potential range from -0.9 V to +0.5 V at a scan rate of 50 mV s⁻¹. The currents were normalized to the geometric area of the working electrodes. All potentials were reported with respect to the reference electrode.

Chronoamperometric (CA) measurements of the samples stability were carried out at a constant potential of -0.3 V for 2400 s.

3. Results and discussion

Modified films samples of two series were synthesized by the electrolytic deposition method with variation of some parameters. The synthesis of the first sample series was carried out without surfactant at the current density during deposition of 6 mA cm⁻². The synthesis of the second sample series was carried out with tetrabutylammonium bromide as a surfactant at a concentration of 0.005 M at the current density during deposition of 5 mA cm⁻².

Modified palladium-silver films surface microphotographs were taken using SEM. The resulting images shown in figure 1 made it possible to study the morphology of the synthesized Pd nanocatalysts. SEM images of the first sample series (classical palladium black) (figure 1a) demonstrate a spherical structure of particles with a characteristic size in the range of 90-100 nm. SEM images of the second sample series (figure 1b) demonstrate a filamentary structure of particles with pointed tips. Probably, the obtained particles morphology was influenced by a change in such synthesis parameters as a rate of the particles deposition on a substrate and a change in the composition of the growth solution by increasing the concentration of surfactant, which also affected the halide ions ratio (Cl⁻ and Br⁻) in the growth solution. The characteristic size of the particles synthesized on the surface of the Pd-Ag film was 100-150 nm.

CV of two series samples were carried out in the potential range from -0.9 V to +0.5 V at a scan rate of 50 mV s⁻¹ at room temperature (25 °C). The choice of the potential range is due to the presence of deep hydrogen evolution below the negative threshold and oxygen evolution above the positive threshold. The current peaks observed in the methanol oxidation reaction (MOR) on palladium (figure 2) are caused by the occurrence of competing processes of electrochemical adsorption of
methanol and water on the catalytic palladium surface. Electrochemical methanol adsorption occurs with the formation of Pd – C bonds. MOR is a multi-stage process, the result of which is the formation of carbon monoxide tightly bound to the Pd surface. The MOR process limiting stages on Pd are the oxygen chemisorption stage and / or the chemisorbed CO removal stage.

Figure 1. SEM images of the first (a) and second (b) series samples surfaces of Pd-Ag films.

A distinct peak recorded during direct scanning on the anode branch in the potential range from -0.3 V to -0.05 V for all samples is due to processes of electrochemical methanol adsorption on Pd, water adsorption and removal of carbon monoxide bound to the palladium surface. A negative potential peak bias indicates good catalytic performance with respect to MOR. Second series sample had the highest value of the current density peak, and, consequently, the highest activity - 17.09 mA cm⁻². Next, the current density peak decrease can be explained by the electrochemical methanol adsorption rate decrease, caused by the modified surface sample blocking by the products of the electrochemical adsorption of water. At higher anodic potentials (over 0.3 V), methanol oxidation proceeds in a parallel reaction with weakly bounded to the surface active particles participation.

A lower intensity peak with the reverse potential sweep in the cathodic direction was observed in the potential range from -0.33 V to -0.4 V, it is due to the methanol oxidation resumption. The oxidation reaction becomes possible when the catalyst surface is reduced. In this case, adsorbate-free palladium atoms are formed, which can participate in the electrochemical methanol adsorption process.

Figure 2. CV of steady-state cycles of the first (a) and second (b) series samples in the alkaline methanol oxidation reaction.

Figure 3. Chronoamperometry of the first (a) and second (b) series of samples in alkaline methanol oxidation.
The catalysts resistance to CO poisoning was assessed through the current peaks \( i_F / i_B \) ratio [19, 20]. Low values of the ratio indicate an excessive residual forms of carbonaceous products accumulation on the catalyst surface, while higher values indicate effective CO desorption on the studied catalyst. So the entire studied sample series demonstrated a fairly high carbon monoxide poisoning resistance, however, the highest \( i_F / i_B \) values were achieved for the first sample series, which amounted to 3.83 in numerical equivalent.

The stability of two series of samples was investigated by CV-multiscanning of 100 cycles. The highest current density values were achieved by the samples on average by the 30th cycle, after which a moderate current decrease was observed. Based on the obtained experimental data, the second sample series had the most long-term stability, for which the current density decrease by the 100th cycle was 11.99%.

Further activity and stability assessment of the obtained sample series was carried out by the CA method in MOR (figure 3). According to the experiment results, the second sample series showed the highest stabilized current density value - 0.099 mA cm\(^{-2}\) compared to the rest of the samples.

Along with the presented above indicators, the electrochemically active surface area (ECSA) and the roughness factor (RF) are also quite important in the catalyst quality assessing. The values of these indicators were calculated by equation (1):

\[
ECSA = \frac{C_{DL}}{C_s},
\]

where \( C_{DL} \) is the double layer capacity, \( C_s \) is the specific sample capacity or the capacity of an atomically smooth flat surface of the material per unit area under identical electrolyte conditions.

The roughness factor (RF) was calculated by dividing the calculated ECSA value by the geometric area of the electrode as in equation (2):

\[
RF = \frac{ECSA}{S}.
\]

The obtained data are presented in table 1. It is shown that the second sample series had the highest ECSA and the highest RF values, which indicates an increased active sites number in comparison with the of the first sample series.

### Table 1. Characteristics of the synthesized catalysts.

| Sample characteristics | Types of coatings |
|------------------------|-------------------|
|                        | I series | II series |
| **Electrolytic deposition conditions** |          |          |
| Deposition time, min   | 20.0     | 20.0     |
| Current density, mA cm\(^{-2}\) | 6.0     | 5.0     |
| Surfactant concentration, M | –       | 0.005    |
| **Size characteristics** |          |          |
| Average particle size, nm | 90-100 | 100-150 |
| Layer thickness, μm    | 2.102    | 2.224    |
| **Electrocatalytic characteristics** |          |          |
| ECSA, cm\(^2\)         | 0.031    | 0.19     |
| RF                      | 0.62     | 3.8      |
| **Peak potentials**     |          |          |
| \( E_F \), V            | -0.13    | -0.012   |
| \( E_B \), V            | -0.37    | -0.33    |
| **Current density peaks** |          |          |
| \( i_F \), mA cm\(^{-2}\) | 5.6     | 17.09   |
| \( i_B \), mA cm\(^{-2}\) | 1.45    | 6.93    |
| \( i_F / i_B \)        | 3.86     | 2.47     |
The study was demonstrated a new approach to solving the problem of creating a highly efficient nanostructured palladium-based catalysts. These catalysts increase the material adsorption/desorption activity with respect to reactions involving hydrogen. High catalytic activity indicators (up to 17.09 mA cm$^{-2}$), long-term stability and CO oxidation resistance for the second sample series with a completely new catalyst is due to an increase not only in the surface roughness, but also in the reactive active sites number, compared with classical palladium black.

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