POROUS SILICON NANOCOMPOSITES WITH PALLADIUM NANOPARTICLES FOR RENEWABLE ENERGY SOURCES

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Abstract- Palladium nanoparticles supported on porous silicon of n- and p- type were synthesized by chemical reduction in reverse micelles water-organic solutions with anionic surfactant – AOT. The degree of porosity, conductivity type, pore geometry of the silicon matrix, and precursor parameters affect the size, shape, and charge state of the palladium catalysts. The nanocomposites were investigated by electron microscopy and cyclic voltammetry methods. The possibility of using the obtained nanocomposites as high performance electrodes for innovative engineering technologies of renewable energy sources is demonstrated.

Keywords- Palladium Nanoparticles, Porous Silicon, Nanocomposites, Cyclic Voltammetry.

I. INTRODUCTION

The rise of portable electronic devices such as mobile phones, digital cameras and portable computers brings to the fore the crucial issue of power supplies innovative engineering technologies [1-6]. Down-scaled fuel cells can be applied as a long-lasting, low-cost and eco-friendly miniature energy source as the microelectronic industry develops. The micro fuel cell (MFC) approach is significantly influenced by two technology choices: the nature of the fuel to be used at the anode (i.e. hydrogen or an alcohol), and the fuel cell architecture. Recently, micro-fuel cells have attracted lots of attention as millimeter scale power sources due to their inherently higher energy and power densities. Most of the current research work is focused on the development of portable proton exchange membrane (PEM) fuel cells that meet the demand of portable electronic devices with 1-10 W electric power [1-6]. Millimeter scale silicon fuel cells have been explored by several groups. For example it was presented a micro-fuel cell integrated to a micro electromechanical system (MEMS) hydrogen generator, that produced a low output power [6]. A great interest to porous structures especially silicon is caused by unique properties of the porous silicon (PS) [1-5]. Electrochemical etching of silicon is attractive because of the possibility to turn the pore size from a few nanometers to a few tens of micrometers, just by choosing wafer doping level and etching conditions. Moreover, a wide range of porous layer thickness, porosities, surface areas and morphologies can be formed depending on the etching conditions.

The offer the possibility for developing electrocatalytic composites with high functional characteristics (surface area is more than 400 m^2 g^{-1}) and for preparing specific catalysts in the structure directing porous matrix with the desirable size and shape [1-5]. The micro-power electric sources of the new generation for electronics compatible with the silicon microchips are constructed on the base of catalytically active PS composites.

The catalyst layer is also an important factor, which considerably influences the fuel cell performance. The use of catalysts in the form of nanosized particles increase their efficiency and decrease their consumption, that is especially important in case of the platinum group metals [2,4,5,7,9,10]. To date nano-scale materials have received a remarkable attention due to many engineering and technological applications [1-10]. Among various nanomaterials, platinum (Pt) and palladium (Pd) nanoparticles offer well-known advantages for chemical, petrochemical, pharmaceutical and electronic industries applications [2,5]. Platinum metal nanoparticles have been widely prepared via several distinctive strategies including hydrothermal methods, sputtering methods, wet chemistry methods and electrochemical methods [7-11]. Although, nanomaterials can be synthesized using various physical or chemical methods, but synthesis of this materials in water-organic solutions is attractive especially if they are intended for large scale applications in environment science and technology [2,4].

We consider the technology of production and stabilization of catalytically active layers on the base of porous silicon substrates as nanostructured matrices to be original [2,4]. Thereby the study of physico-chemical features of highly active catalysts creating for the electrode materials creation for alternative energy sources is one of fundamental problems of environmental science and technology. The purpose of this work is the development and evaluation of palladium/porous silicon nanocomposites catalytic activity, obtained by the chemical reduction method in the reverse microemulsions with anionic surface-active substance – AOT.

II. DETAILS EXPERIMENTAL

Materials and Procedures

Palladium nanoparticles supported on porous silicon of n- and p-type were synthesized by chemical reduction in water organic solutions of reverse micelles with $NaBH_4$ as reductant. Microemulsions were prepared by mixing of palladium aqueous solution with concentration of 0.01 M and 0.1 M $NaBH_4$ solution in surfactant-isooctane. As the surfactant it was used a 0.2 M solution of aerosol OT – AOT – sodium bis(2-ethylhexyl)sulfosuccinate ($C_{20}H_{37}SO_7Na$, 99%, «Sigma Aldrich», USA). The molar ratio of water/surfactant (ω) in microemulsion solutions was 3 and 5. The solutions were solubilized on Ultrasonis CleanerUD150SH-6L ultrasonic disperser («Eumax», Germany) for 15 min at 25 $\pm$ 1°C.

To obtain the PS matrices with a different porosity degree (P) (40-80%) it was used anodic electrochemical etching in ethanol solutions of HF of n- or p-type silicon wafers. By a galvanostatic regime of anodization, the current density varied from 20 to 100 mA cm^{-2}. As a result, the thickness of porous layers was equal to 1 µm, the diameter of channels of PS pores for p-type amounted to 5-20 nm, and for n-type it was 15-40 nm [2,4]. As the electrolyte we used a 25% alcoholic solution of HF. The nanoparticles deposition on PS was carried out by sorption from micelle solution with palladium nanoparticles under the ultrasonic treatment. To remove residual solvent and surfactant the obtained samples of PS with nanoparticles were treated by n-heptane and ethanol and washed with distilled water.

The sizes, shape, and distribution of palladium nanoparticles were studied by atomic force microscopy (AFM) on NTegra Prima scanning microscope («NT MDT», Russia). The nanocomposite catalytic activity and stability were estimated by cyclic voltammetry (CVA) method using an IPC-PRO MF instrument («Tekhnopribor», Russia). The scan rate was varied from 5 to 100 mV/s.

III. RESULTS AND DISCUSSION

In previous publications we demonstrated the possibility of palladium metals nanoparticles obtaining using the method of radiation-chemical reduction with anionic surfactant (AOT) [2,4]. In the formation of palladium nanoparticles in solution formed nanoparticles are mainly elliptical shape. For aqueous-organic solutions of palladium at $\omega = 1.5$ the average size of the particles was 2-5 nm, and for solutions c $\omega = 5 – 8$-11 nm. During the formation of the nanoparticles, the proportion of low and large size fractions is approximately the same [2,4].

Despite the advantages of the method of synthesis of platinum metals nanoparticles in reverse micelle solutions with anionic surfactant (AOT) by radiation-chemical reduction, it also presents certain disadvantages. The main disadvantages include the following. First, the need for special installation of certified gamma-radiation source. Secondly, the duration of the experiment, high radiation dose, specialized techniques. Thirdly, with increased dose there is an intensive generation of reactive radicals in aqueous-organic solutions.

The technological advantages of the proposed method include the ease of synthesis, the ability to control the number and size of palladium metal nanoparticles on the PS due to varying characteristics of precursors: the metal ions concentration, the aqueous phase content, the solubilization degree ω, the time of solution contact with the PS, the intensity of ultrasonic influence. According to atomic force microscopy (AFM) (fig. 1) data synthesized palladium nanoparticles have a size in the range from 15 to 3 nm and less, are characterized by a uniform distribution on the surface and in the depth of the pores. Using this method of nanoparticles synthesis there is a simultaneous reduction of metal ions in reverse micelles and their deposition not only on the surface but also in the pores of the silicon matrix.
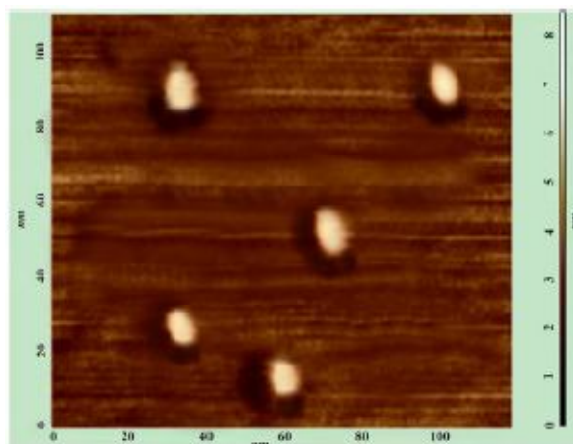

Fig. 1. AFM image of Pd nanoparticles at $\omega = 5$.

Palladium nanoparticles obtained in reverse micelle solutions with anionic surfactant as AOT, are stable for a several month [2,4]. In further the nanoparticles agglomeration and deposition of residue is observed. For the destruction of the shells of micelles in the case of anionic surfactants an intensive washing with a polar solvent does is required.

We would attribute the activation of the silicon matrix surface under the action of molecular hydrogen released by the hydrolysis of sodium tetraborate in the process of the simultaneous reduction of platinum metal ions and the sorption of the formed nanoparticles on PS [2,4]. The fact is that, when PS samples come into contact both with an aqueous-organic solution and air oxygen, the surface silicon atoms form oxide-hydroxide fragments, which

block active silicon centers when nanoparticles are sorbed on them. As a result, palladium nanoparticles do not fix at the PS surface; their agglomeration occurs and a sediment is formed. The action of hydrogen reduces silicon ions from oxide–hydroxide surface compounds. The appearance of an additional number of active centers at the PS surface facilitates the formation of palladium/PS nanocomposites.

Thus, under these conditions, a simultaneous reduction of metal ions in reverse micelles occurs and their precipitation takes place not only at the surface (fig. 1), but also in the pores of the silicon matrix. According to the AFM data (fig. 1), the synthesized palladium nanoparticles possess sizes in the range from 13 to 3 nm and smaller and are characterized by a homogeneous distribution at the surface and in the bulk of pores. The nanoporous structure of silicon limits the agglomeration of Pd nanoparticles in agreement with the size of nanopores, fulfilling the function of a stabilizer and facilitating a homogeneous distribution of nanoparticles over the surface. Further studies by the cyclic voltammetry (CVA) have shown that an increase in the catalytic activity of Pd nanoparticles on PS is associated just with the increased content of catalyst nanoparticles with sizes smaller than 10 nm due to the stabilization in the porous PS matrix.

The study of the catalytic activity of the synthesized Pd/PS composites was carried out under standard model operation conditions for a low-temperature air-hydrogen cell using the method of cyclic voltammetry (CVA). The potentiodynamic curves were taken at room temperature in a three-electrode cell in an aqueous solution of sulfuric acid after blowing with argon. A plate of platinum foil was the auxiliary electrode, while the reference electrode was silver chloride. The catalytic activity of nanocomposites is determined by two factors: the electrocatalytic active region (ESA) and the current density (j). The current density j, which is proportional to the rate of the electrochemical reaction, was calculated according to the following expression: $j = I/S$ (A/m^2), where I is the maximum value of the current strength calculated by the peak of hydrogen oxidation and S is the area of the electrode's surface. The electrocatalytically active region is the index of the general amount of electricity generated in the process of fuel (hydrogen) oxidation. The value of ESA is determined on the basis of the standard method used to estimate the parameters of CVA with account for catalyst loading and the potential scanning.

Table 1 presents the results obtained by the CVA method of composites with Pd on PS that showed the maximum functional activity (current density, electrocatalytic surface area, the metal content, resource) in the oxygen reduction and hydrogen oxidation reactions. The analysis of the results allows to conclude that the increased activity of the electrodes, characterized by: first, n-type conductivity of PS, secondly, the porosity degree of 64%, thirdly, synthesized by chemical reduction method with ultrasonic treatment solution at $\omega = 5$, and, fourthly, the minimum size of the nanoparticles.

For comparison the data for the evaluation of the electrocatalytic activity of standard commercial catalyst E-TEK (Pd/C) deposited on the soot marks XC-72 (tabl. 1) are presented. The activity of the Pd/PS catalysts are comparable to those found in commercial samples on the soot. Commercial samples of Pd on PS is not currently available. Demonstrated results in the formation of nanoporous composites generated using the original technology, seem undeniable success in the development of a new type electrodes.

Thus, it was found that the most effective as in the formation of the electrodes, and life tests of functional activity, manifest themselves the samples of nanocomposites palladium/PS obtained from solutions with $\omega = 3$.

Table 1. Characteristics of the Pd/PS nanocomposites according to CVA data

PS type	P, %	ω	m_s, mg/cm^2	ESA, m^2/g	j, A/m^2	d, nm
n	64	5	0.08	141	88	3.5
n	64	3	0.08	163	95	3.1
p	64	5	0.08	108	61	4.6
p	64	3	0.08	125	82	3.9
n	46	5	0.08	64	50	7.8
n	46	3	0.08	81	59	6.2
Pd/C commer. (XC-72)			0.10	150	75	3.2

For the Pd nanocomposites, greater catalytic activity is observed on the samples of n-type conductivity of PS than for those with p-type by 20-30%. Based on the method used to estimate the sizes of nanoparticles according to the CVA data [11,12], the range of palladium nanoparticles (d) amounts from 1.5 to 7 nm. This result is in a satisfactory agreement with the AFM data (fig. 1). As can be seen from the Table 1 data, when the diameter of nanoparticles decreases, the catalytic activity of nanocomposites increases.

Multiple electrochemical tests of Pd/PS nanocomposite electrodes were carried out using the CVA method for 90 h and more in the range of potentials from 0 to 1100 mV. A comparison of the results presented in Table 1 shows the substantial lowering of the catalytic activity of practically all the samples of the electrodes by multiple potentiodynamic testing. For example, the current density and electrocatalytically active region decrease for the time of testing to 22% and more. An exception

is the samples of PS composites of n-type formed by a degree of porosity of 64% and ω = 3, which exhibit the maximum stability by multiple testing. In this case, the sizes of nanoparticles grow both according to the data of CVA (Table 1) and the data of AFM. Hence, the lowering in the activity of the electrodes may be associated with an increase in the agglomeration of palladium nanoparticles. An increase in the sizes palladium nanoparticles results in the reduction of the number of most active reactionable centers, which leads to a decrease in the electrocatalytically active region and current density.

The presented results concerning the estimation of the functional characteristics of the electrode samples based on palladium/PS nanocomposites are comparable to the commercial samples based on carbon materials (E-TEK, Pd/C-XC-72) both on the catalytic activity and platinum metal content (less than 0.1 mg/cm^2). We note that the commercial Pd samples based on PS are absent at present. A further improvement in the technology of the formation of Pd/PS nanocomposites will probably improve the functional characteristics of the electrode materials with a lowered content of platinum metals for micropower fuel elements innovative engineering technologies.

CONCLUSIONS

An advanced chemical method of synthesis is proposed and the optimal conditions are established for the formation of catalytically active Pd-containing electrode materials based on PS. The technological advantages of the method include the simplicity of synthesis; the possibility to save platinum metals; and control over the amount and sizes of nanoparticles on PS, the concentration of platinum metal ions and the reductant, and the duration of the contact of the solution with PS and the intensity of ultrasonic treatment. The results confirm the possibility of the highly efficient and stable platinum metal nanocatalysts formation on the porous silicon substrates of n-type conductivity, obtained by chemical reduction of metal ions to construct a membrane-electrode assemblies of renewable energy sources.

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