

Micropower Composite Nanomaterials Based on Porous Silicon for Renewable Energy Sources

Alexey P. Antropov, Alexander V. Ragutkin, Nicolay A. Yashtulov

Abstract—The original controlled technology for power active nanocomposite membrane-electrode assembly engineering on the basis of porous silicon is presented. The functional nanocomposites were studied by electron microscopy and cyclic voltammetry methods. The application possibility of the obtained nanocomposites as high performance renewable energy sources for micro-power electronic devices is demonstrated.

Keywords—Cyclic voltammetry, electron microscopy, nanotechnology, platinum-palladium nanocomposites, porous silicon, power activity, renewable energy sources.

I. INTRODUCTION

ENERGY is one of the integral parts of the modern industrial society mandatory development [1]-[7]. In the face of natural resources shrinking, the actuality of the creating task and refining highly efficient electrochemical systems for storage and conversion of energy is increasing.

Renewable energy sources are the energy sources that are derived from natural sources that replenish themselves over short periods of time [1]-[3]. Most renewable energy sources include solar energy, wind, water streams, biomass, heat of the upper layers of the earth's crust and the ocean. The appropriateness and the extent renewable energy sources using are defined primarily by their economic efficiency and competitiveness with traditional energy technologies. The main advantages of renewable energy compared to energy sources for fossil fuel are the practical inexhaustibility of resources, no fuel costs, and emissions of harmful substances into the environment [2], [6]. Numerous innovations as well as its applications based on renewable energy sources are taking place. The decentralized renewable energy systems have been recognized the world over as an answer to meeting the energy demands both in the household and in the agroindustrial sector. The exhaustion of natural sources and the accelerated demand of conventional energy have forced planners and policy makers to look for alternate sources, i.e. clean renewable energy sources.

One of the main types of renewable energy sources is fuel cells (FC) [4]-[12]. An FC consists of an electrolyte medium sandwiched between two electrodes constituting an

electrochemical power source. This type of energy source belongs to the electro-chemical battery classification. In fact, an oxidation and a reduction reaction occur in the system. The particularity of the FC compared with common batteries lies in the separation of the reactant (energy-containing material or fuel) and the reactor. Thus, the system needs a fuel to operate and can work as long as fuel is provided. Both electrodes must be supplied with reactants with a hydrogen source at the anode for oxidation and the cathode being the reduction site of oxygen.

Incremental improvements in the characteristics of the micro-power current sources are supposed to use the latest achievements of nanotechnology with carbon nanotubes, graphene, porous silicon (PS), and polymer membranes [4]-[12]. The most promising power sources for electronic devices are micro-power compatible with silicon microchips cartridge hydrogen-air batteries. Compared with other power sources, they have a higher voltage, wide temperature range operation, longer shelf life, increased the magnitude of the current density, power, energy, and capacity (Fig. 1).

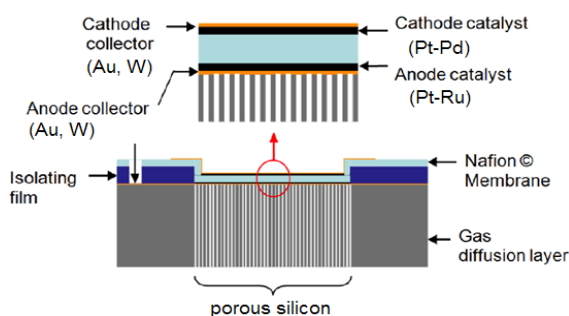


Fig. 1 Micro-power source with PS and polymer membrane-electrode assembly

The unique properties of PS allow to design mobile and micro-power FC of new generation [4], [9]-[11]. Controlled formation of nano-sized electrocatalysts in the PS matrix increases their activity and life, reduces the consumption of expensive platinum group metals. In FS based PS hydrogen or methanol, ethanol and formic acid are used as fuel, and the oxidizing agent is oxygen. The reaction products are H_2O or H_2O with CO_2 . To improve the FC performance, it is necessary to develop a catalytically active electrode for anode and cathode reactions.

Catalysts based on Pd and Pt are the most widely spread catalysts in FC [3]-[12]. Nonetheless, if formic acid is used as a fuel, fast and substantial degradation of Pt catalysts on the anode already at the initial stages of fuel element operation is

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observed. The main reason is that platinum active centers are blocked by carbon monoxide CO which is an intermediate of the reaction of "indirect" HCOOH oxidation [8], [12]. At the same time, catalysts based on Pd provide the "direct" oxidation of carbon-containing fuels without intermediate CO production. It was demonstrated that if low-temperature fuel elements are used in the anode HCOOH oxidation reactions, Pd particles possess higher catalytic activity than similar Pt catalysts, since the oxidation reaction goes "directly" [8]. It should be noted, however, that Pd catalysts manifest lower corrosion resistance in acid media, unlike Pt. In this regard, it is promising to use Pt and Pd in combined bi- and polymetallic catalysts for HCOOH oxidation [8], [12]. It was established [8], [12] that if Pd nanoparticles are added to a platinum catalyst on a carbon carrier (soot), the activation energy of HCOOH reaction reduces, and the reaction goes mainly directly without any noticeable production of CO molecules.

In our studies, it was shown that the formation of platinum metal nanoparticles on n- and p-type of PS may be selected as the anode and cathode electrode materials for micro-power current sources in electronic engineering [4], [9]-[11]. We consider the technology of production and stabilization of catalytically active layers on the base of PS substrates as nanostructured matrices to be original. The purpose of this work is the development and investigation of nanocomposites with platinum-palladium nanoparticles on PS.

II. MATERIAL AND METHODS

Platinum-palladium nanoparticles supported on PS of n- and p-type were synthesized by chemical reduction in water organic reverse micelle solutions with NaBH_4 . Microemulsions were prepared by mixing of platinum metal aqueous solution with concentrations of 0.01 M and 0.1 M NaBH_4 solution in surfactant-hexane solution. As the surfactant, a 0.2 M solution of aerosol OT (AOT) – sodium bis(2-ethylhexyl)sulfosuccinate ($\text{C}_{20}\text{H}_{37}\text{SO}_7\text{Na}$, 99%, «Sigma Aldrich», USA) was used. The molar ratio of water/surfactant (ω) in microemulsion solutions was varied from 1 to 5. The solutions were solubilized on Ultrasonis CleanerUD150SH-6L ultrasonic disperser («Eumax», Germany) for 15 min at 25 ± 1 °C.

To obtain the PS matrices with a different porosity degree (P) (40-80 %), the anodic electrochemical etching in ethanol solutions of HF of n- or p-type silicon wafers was used. The nanoparticles deposition on PS out by sorption from micelle solution with platinum-palladium nanoparticles under the ultrasonic treatment was carried. 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 surface morphology of the nanocomposites was studied by high-resolution transmission electron microscopy (HR TEM) on the Zeiss Libra 200FE instrument («Carl Zeiss», Germany). The size, shape, and distribution of platinum metal nanoparticles were studied by atomic force microscopy (AFM) on scanning microscope NTegra Prima («NT-MDT», Russia). The electrodes catalytic activity and stability were estimated

by cyclic voltammetry (CVA) method using an IPC-PRO M instrument («Tekhnopribor», Russia). The scan rate was varied from 5 to 100 mV/s.

III. RESULTS AND DISCUSSION

The technological advantages of the proposed method include the ease of synthesis, the ability to control the number and size of platinum 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. Using this method of nanoparticles synthesis, according to HR TEM data (Fig. 2), 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. According to electron microscopy data, synthesized platinum and palladium nanoparticles which have a size in the range from 17 to 3 nm and less are characterized by a uniform distribution on the surface and in the depth of the pores.

Platinum-palladium nanoparticles obtained in reverse micelle solutions with anion surfactant as AOT, are stable for several months. Further, the agglomeration of platinum-palladium nanoparticles and deposition of sediment is observed. For the destruction of the shells of micelles in the case of anionic surfactants an intensive washing with a polar solvent does not require, which is accompanied by removal of platinum metal nanoparticles from the PS surface. Therefore, the standard procedure for treatment of the nanoparticles with ethanol and bidistilled water, followed by drying allowed almost completely to remove the remaining surfactant, organic solvent, and reducing agent.

Table I presents the results obtained by the CVA method of composites with Pt 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 is 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 (Pt/C) deposited on the soot marks XC-72 (Table I) at platinum loading 0.09 ± 0.01 mg/cm² are presented. The activity of the Pt/PS catalysts is comparable to those found in commercial samples on the soot. Commercial samples of Pt on PS are 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 platinum/PS nanocomposites obtained from solutions with $\omega = 5$ are the most effective in the electrodes formation and functional activity.

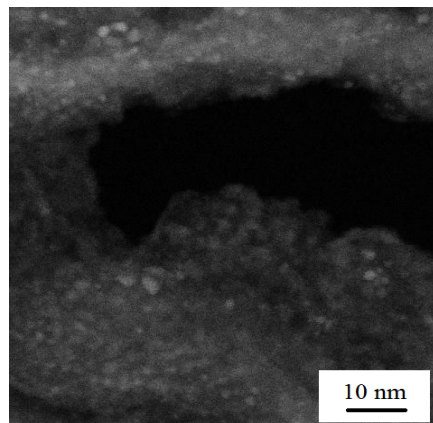


Fig. 2 HR TEM micrograph of Pt-Pd nanoparticles in the pores depth of the n-type PS

An important indicator of nanocatalysts efficiency in fuel elements is their stabilization on the substrate matrix preventing agglomeration upon operation as part of membrane-electrode units [4], [9]-[11]. The stability resource of catalytic activity was tested for the synthesized Pt-Pd/PS (3:1) and Pd/PS samples in the course of an amperochronometric analysis of time evolution of the current density at a fixed oxidation potential (Fig. 3). It was discovered that Pt-Pd/PS (3:1) nanocatalysts manifest noticeably higher stability than the Pd/PS sample without platinum. The current density (j) decreases during 4 h of testing for the Pt-Pd/PS (3:1) sample by 8% and for the Pd/PS sample by 14%. Such results can be connected with different charge state and morphology of Pd and Pt-Pd nanoparticles on PS substrate [10]. Pt-Pd/PS of n type (3:1) nanocomposites manifest higher corrosion stability than nanocomposites with pure palladium. At the same time, Pt-Pd/PS of n type (3:1) nanocomposites demonstrate the growth of catalytic activity in the reaction of formic acid oxidation when compared to nanoparticles with increased platinum content (for example, Pt:Pd = 1:1) on PS. These results prove the possibility of forming high-efficiency stable platinum-palladium nanocatalysts on substrates of PS with conductivity of n-type obtained by metal ion reduction in solutions of reverse microemulsions with anionic surfactant for the reaction of formic acid oxidation.

TABLE I

CHARACTERISTICS OF THE PS/PT NANOCOMPOSITES ACCORDING TO CVA
DATA AT PLATINUM LOADING 0.09 MG/CM²

PS type	Porosity, P, %	ω	ESA, m ² /g	j , A/m ²	d, nm
n	64	5	186	108	1.5
n	64	8	128	102	2.2
n	42	5	67	58	4.2
n	42	8	52	56	5.4
p	64	5	145	98	1.9
p	64	8	91	87	3.1
Pt/C commercial. (XC-72)			206	104	1.4

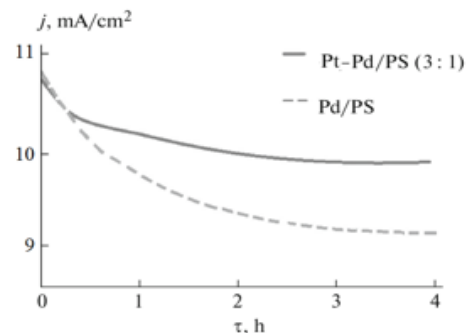


Fig. 3 Variation of catalytic activity Pt-Pd/PS (3:1) and Pd/PS nanocatalysts in the reaction of HCOOH oxidation

The hydrogen-air fuel cell testing on the basis of the obtained composite electrodes by in-situ voltammetry was carried out. The experimental model was made by hot pressing of membrane electrode assemblies using solution of Nafion to increase the contact surface of the electrodes with proton conducting membrane. The gas diffusion layer consisted of membrane Nafion-117 compressed between the composite anode and cathode based on PS. To avoid destruction of the silicon during pressing the temperature was chosen equal to 115 °C, pressing time 3 minutes. For the diffusion layer formation in PS composites additional operations of photolithography and plasmochemical etching was carried out. As the result the network of through pores with a diameter of 5 micrometers was formed, through which the pre-prepared hydrogen and oxygen was supplied.

As the standard samples, the commercial membrane-electrode assemblies on the basis of membrane Nafion-112 and carbon electrode E-TEK with a platinum loading 0.5 mg/cm² were used.

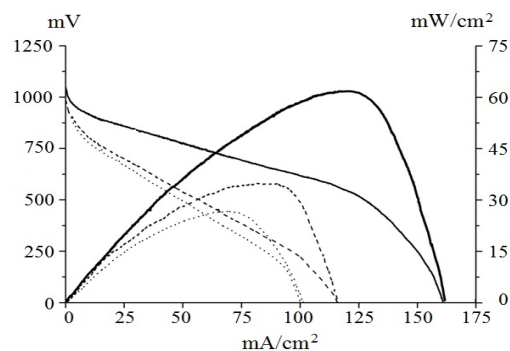


Fig. 4 Volt-Ampere and Watt-Ampere characteristics of hydrogen-air FC: solid line – the anode and the cathode, E-TEK (platinum loading 0.5 mg/cm²), the membrane Nafion-112; dashed line – anode n-PS/Pt, cathode p-PS/Pt; point line – anode n-PS/Pt-Pd, cathode p-PS/Pt (platinum metals loading 0.3 mg/cm²). Conditions: T = 298 K, humidity – 60%

The Volt-Ampere and Watt-Ampere characteristics of hydrogen-air FC based PS (see Fig. 4) were obtained. The scanning speed is 5 mV/s, the pressure of fuel and oxidant is 1 bar, cell temperature is 25 °C, relative gas humidity is 60%.

The best energy characteristics were obtained for electrodes based n-type PS on the anode with platinum- and p-type PS at the cathode: the maximum power was equal to (34 ± 2) mW/cm². The layout test with n-type PS with Pt-Pd as the anode also showed good results (23 ± 2) mW/cm².

The electrodes made by the proposed technique of nanocomposites showed high stability: with the resource of more than 1000 hours decrease in current density was not more than 15% for Pt-Pd/PS nanocomposites.

The results of a long endurance test of hydrogen-oxygen FC confirmed the effectiveness of the developed nanocomposite electrodes forming method based PS and showed high activity and stability of composite cathodes and anodes.

IV.CONCLUSION

It was established that formic acid oxidation in the presence of palladium–platinum–PS nanocomposites with excessive palladium content goes mainly via direct oxidation by dehydrogenization. Platinum-palladium nanoparticles smaller than 10 nm obtained by the deposition of water-organic solutions of reverse microemulsions on the PS surface with n-type conductivity manifest maximum catalytic activity. The results confirm the possibility of the highly efficient and stable platinum metal nanocatalysts formation on the PS substrates of n-type conductivity, obtained by chemical reduction of metal ions to construct a membrane-electrode assembly of renewable micropower energy sources.

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REFERENCES

- [1] Antropov A.P., Batenin V.M., Zaichenko V.M. New technologies for distributed energetics // *High Temperature*. 2015. V. 53. № 1. P. 124-129.
- [2] Bhatia S.C. *Advanced renewable energy sources*. – Woodhead Publishing India Pvt Ltd, 2014 – 760 p.
- [3] Gandia L.M., Arzamedi G. *Renewable hydrogen technologies: production, purification, storage, applications and safety*. – Elsevier. 2013. – 472 p.
- [4] Gautier G., Kouassi S., 2014. Integration of porous silicon in microfuel cells: a review // *Int. J. Energy Res*. 2014. V. 39. P. 1-25.
- [5] Leung D. Y.C., Xuan J. *Micro & Nano-Engineering of Fuel Cells*. – CRC Press, 2015. – 338 p.
- [6] Popel O.S., Reutov B.F., Antropov A.P. Prospective lines of using renewable energy sources in centralized and independent power systems // *Thermal Engineering*. 2010. V. 57. № 11. P. 909-918
- [7] Stolten D., Emonts B. *Fuel cell science and engineering: materials, processes, systems and technology*. – Wiley-VCH Verlag GmbH & Co KGaA, 2012. V. 1-2. – 1268 p.
- [8] Winjobi O., Zhang Z., Liang C., Li W. Carbon nanotube supported platinum-palladium nanoparticles for formic acid oxidation // *Electrochim. Acta*. 2010. V. 55. № 13. P. 4217-4221.
- [9] Yashtulov N.A., Patrikeev L.N., Zenchenko V.O., Smirnov S.E., Lebedeva M.V., Flid V.R. Formation and catalytic properties of materials based on porous silicon with platinum nanoparticles // *Nanotechnologies in Russia*. 2015. V. 10. № 11–12. P. 910-916.
- [10] Yashtulov N.A., Patrikeev L.N., Zenchenko V.O., Lebedeva M.V., Zaitsev N.K., Flid V.R. Palladium-platinum-porous silicon nanocatalysts for fuel cells with direct formic acid oxidation // *Nanotechnologies in Russia*. 2016. V. 11. № 9–10. P. 562-568.
- [11] Yashtulov N.A., Lebedeva M.V., Kuleshov N.V. Porous silicon nanocomposites with palladium nanoparticles for renewable energy sources // *International Journal of Advances in Mechanical and Civil Engineering*. 2016. V. 3. № 4. P. 81-84.
- [12] Zhou Z.M., Shao Z.G., Qin X.P., Chen X.G., Wei Z.D., Yi B.L. Durability study of Pt-Pd/C as PEMFC cathode catalyst // *Int. J. Hydr. Energy*. 2010. V. 35. № 4. P. 1719-1726.