Development of Advanced Electrode Materials on Porous Silicon for Micropower Formic Acid-Oxygen Fuel Cells

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DOI: 10.5185/amlett.2019.9912
www.vbripress.com/aml

Abstract

In this work, in order to create electrode materials for electrochemical energy converters, composites on porous silicon modified by palladium have been obtained. The functional characteristics of the electrodes have been studied by scanning electron microscopy, X-ray phase analysis, ex-situ and in-situ cyclic voltammetry. The electrode materials based on porous silicon had demonstrated high catalytic activity and specific characteristics in fuel cells with direct oxidation of formic acid. The fuel cell prototype with low palladium content showed the maximum specific power of about 30 mW/cm^2 at a current density of 95-100 mA/cm^2. Copyright © VBRI Press.

Keywords: Porous silicon, palladium electrocatalysts, watt-ampere characteristics, formic acid, current density, specific power.

Introduction

To date, there is an increased interest in semiconductor materials containing micro- and nanoscale structures which exhibit significantly higher properties compared to conventional materials [**1-15**]. Among such semiconductor structures a special place is occupied by porous silicon (PS). There are many works devoted to development of light-emitting structures, photovoltaic solar energy converters, chemical sensors and other semiconductor devices based on porous silicon layers.

The main difficulty to the wide commercialization of porous silicon for the semiconductor devices production is the instability of its functional characteristics, in particular, fluorescent and electrophysical [**2-7**] parameters. At the same time, porous silicon has a number of unique properties, which makes this material promising for use. Especially it should also be stated that PS is usually used in microelectromechanical systems (MEMS) designing [**8, 11, 12**]. It depends on special PS parameters (porosity, thickness of the porous layer, resistance to chemical reagents, high active surface area). These properties affect specific characteristics of the current source created on the basis of PS electrodes.

It is worth noting that among the powerful current sources for electronic equipment fuel cells (FC) with formic acid are of great interest. The advantages of formic acid in comparison with traditional fuels (hydrogen and methanol) are: the possibility of direct supply of the reagent to anode space without special purification stages, low values of the crossover effect, the possibility of highly concentrated solutions (more than 10 M) using [**15, 16**], high values of the thermodynamic efficiency. Special attention is paid to composite materials, which are most active in the formic acid oxidation reaction (FAOR). This is due to decrease in the probability of carbon monoxide formation that is typical catalytic poison for platinum metals. Catalysts based on Pd and Pt are the most widely spread catalysts in fuel elements [**15-18**]. 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 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 [**15-18**]. 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” [**17, 18**]. It should be noted, however, that Pd catalysts manifest lower corrosion resistance in acid media, unlike Pt.

In previous publications authors had proposed new advanced PS electrodes development technology in water-organic solutions in the presence of surfactants [**2, 6, 9, 10, 16**]. Synthesis of electrocatalytic layers of platinum metals on PS in microemulsions solutions in the presence of nonionic (Triton X-100) and anionic (AOT)surfactants was considered. The evaluation of the electrocatalytic activity and stability of porous silicon-platinum (PS/Pt) nanocomposites had demonstrated the prospects of received electrodes in hydrogen-oxygen low-temperature fuel cells.

In this paper, the models of formic acid-oxygen fuel cells on the basis of porous silicon-palladium composite electrodes had been tested. Creation of nanocomposites on the basis of PS-palladium with a wide range of structural parameters was possible due to advanced formation methods of porous structures [**2, 6, 9, 10, 16**]. The principal novelty of this work consists in the following – for the first time: 1) composite electrodes, obtained by chemical reduction (using nonionic surfactant – Triton X-100) of palladium ions on porous silicon support have been formed; 2) a study of catalytic activity and power characteristics of PS-palladium composites in formic acid-oxygen FC with a low metal content have been carried out. In scientific publications devoted to formic acid fuel cells based on porous silicon investigations, an increased content of palladium at the anode (more than 2 mg/cm^2) have been used [**19,20**]. Proposed in present work advanced technology allows to save the expensive platinum catalysts with increasing of fuel cell power parameters.

The aim of this work is formation of composite electrodes based on porous silicon with palladium electrocatalysts and functional specific characteristics evaluation during formic acid-oxygen fuel cells operation.

Experimental

Nanoparticles synthesis and nanocomposites formation

In this paper, porous silicon of n- and p-type with different porosity degree (P) (40-80%) was formed by anodic electrochemical etching of silicon wafers. A water-alcohol solution of hydrofluoric acid HF with mass content of 25% was used as electrolyte. Anodizing process was carried out in galvanostatic mode with varying of etching current density from 20 to 60 mA/cm^2 [**2, 6, 9, 10, 16**]. As a result, the channels diameter of n-type PS was of 10-40 nm, p-type PS – 5-20 nm when samples porosity degree was 64 ± 2% and 46 ± 2%, respectively [**2, 5, 8, 9, 15**]. After the anodizing process, the samples were washed in ethanol and dried in a muffle furnace at temperature of 150-200°C for 1 hour. To create nanocomposite materials, the sorption process of micellar solutions with palladium nanoparticles on the PS under ultrasonic treatment influence was carried out. In order to remove solvent and surfactant residues from the samples surface, a thorough washing with solutions of isooctane, ethanol and distilled water was carried out.

Palladium nanoparticles were synthesized by chemical reduction in reverse microemulsions with sodium tetrahydroborate $NaBH_4$ (98%, Merck, Germany), using nonionic surfactant – Triton X-100. The method of solution preparation was as follows: a water-organic solution of palladium $[Pd(NH_3)_2]Cl_2$ (Sigma Aldrich, USA) was prepared. To form a microemulsion medium, 0.15 M solution of Triton X-100 (Sigma Aldrich, USA) and propanol-2 was used. Then, a microemulsion of the similar composition, contained 0.1 M aqueous solution of the reducing agent – $NaBH_4$, was added to this solution under ultrasonic action for 2-3 min. The molar water/surfactant ratio (ω) while making the experiments was changed from 1.5 to 8. In order to prevent the sunlight destruction of nanoparticles, the solutions of microemulsions were stored in darkness at room temperature.

Characterizations

The surface morphology of electrode materials based on porous silicon was studied by scanning electron microscopy (SEM) using JSM-7401F (JEOL, Japan) with the INCA analyzer (Oxford Instruments, England). The phase composition of Pd nanocomposites with PS was studied on a powder X-ray D8 FOCUS diffractometer (Bruker AXS, Germany). Filtered CuKα radiation in the step mode with a pulse collection time of 5 s and a step size of 0.5o was used. Evaluation of electrodes catalytic activity and stability was carried out by cyclic voltammetry (CVA) on IPC PRO M device (Technopribor, Russia). Measurements were carried out at room temperature in a three-electrode cell, the formic acid water solution served as electrolyte. The reference electrode was silver chloride electrode, the auxiliary electrode was platinum. Scanning speed was 10 mV/s [**21-23**]. The error in measuring the current density did not exceed 2-3%. To obtain the volt- and watt-ampere characteristics of the formed electrode materials based on porous silicon, a certified unit for testing fuel cells Fuel Cell Test System 850C (Scribner Associates Inc., USA) was used.

Results and discussion

Through the simultaneous reduction of palladium ions and deposition of nanoparticles on porous silicon plates porous silicon/palladium (PS/Pd) nanocomposites were formed [**2, 6, 9, 10, 16**]. As a result, the process of palladium nanoparticles deposition on the surface as well as in the pores of the porous silicon matrix [**2, 6, 9, 10, 16**] was observed. In order to prevent aggregates formation of palladium nanoparticles on the surface and in porous silicon volume ultrasonic treatment was used.

Fig. 1 shows an example of SEM photomicrographs of the porous n-type surface, modified with palladium nanoparticles obtained in reverse microemulsion solutions when the molar ratio water/surfactant (ω) was 1.5. In previous publications of the author's team it was found that the molar ratio ω affects the size of the forming nanoparticles [**2, 6, 9, 10, 16, 21**]. Previously, it was found that application of anionic surfactant (AOT) during synthesis promoted nanoparticles aggregation inside the micelle water pools. When using nonionic surfactants such as Triton X-100 nanoparticles are formed at the interface of the water pool, which contributes to the formation of small particles [**16**]. According to SEM data, it may be concluded that the average size of Pd nanoparticles is from 9 to 2 nm or less.

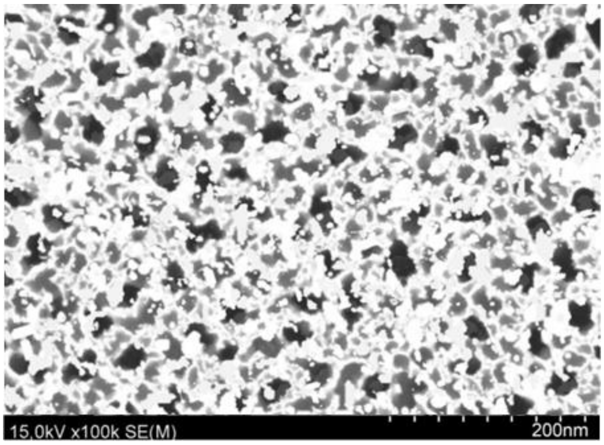

Fig. 1. SEM of the n-type PS surface modified by palladium nanoparticles obtained at ω = 1.5.

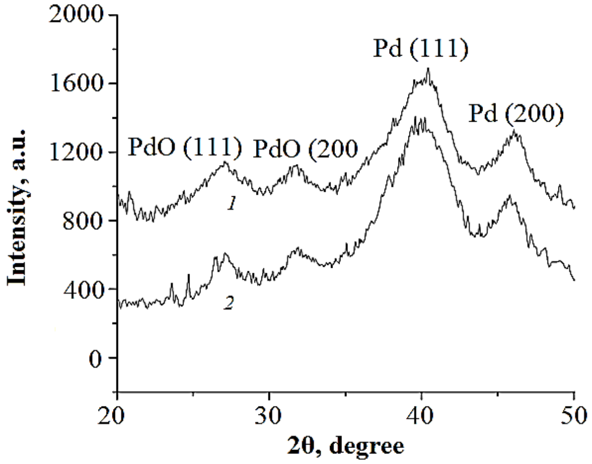

Fig. 2. Diffractogram of Pd composites on PS of: *1* – n-type, *2* – p-type.

X-ray phase analysis of PS composites with Pd confirmed the formation of metal and oxide forms of nanoparticles (see **Fig. 2**). PS composites with Pd have the same phase composition for both PS of n- and p-types. The positions of Pd peaks in PS composites correspond to crystal phases PdO (111), PdO (200), Pd (111) and Pd (200) with angles 2θ = 27.4; 31.6; 39.1 and 45.5, respectively. Reflexes, which could be attributed to the formation of palladium silicides, were not found, probably, because of their X-ray amorphousness.

In order to study the electrochemical characteristics of the formed electrode materials based on porous silicon, the method of cyclic voltammetry (CVA) was used. The current density (j) on voltammograms was estimated from the area of hydrogen oxidation peak. The parameters of the electrocatalytic surface active area (ECSA) was determined according to standard methods according to catalyst loading and the scan rate [**2,6,9,10,16, 21-24**].

In this paper, the electrocatalytic activity of palladium nanocomposites in the formic acid oxidation reaction was evaluated. For fuel cells with direct oxidation of formic acid, the total reaction at the anode is recorded as:

$$HCOOH \rightarrow CO_2 + 2H^+ + 2\bar{e} \quad (1)$$

According to the literature data, the HCOOH electrooxidation reaction proceeds via two mechanisms [**8, 15-17**]. The first way (direct oxidation of formic acid without the formation of carbon monoxide (CO)) is typical only for electrocatalysts based on palladium:

$$HCOOH \rightarrow COOH + H^+ + \bar{e} \rightarrow CO_2 + 2H^+ + 2\bar{e} \quad (2)$$

The second mechanism is indirect oxidation with the formation of adsorbed CO:

$$HCOOH \rightarrow CO_{ads} + H_2O \rightarrow CO_2 + 2H^+ + 2\bar{e}. \quad (3)$$

This mechanism is typical for other platinum metals, in particular, platinum [**9, 21**]. Direct mechanism of the oxidation reaction of formic acid (reaction 2) explains the palladium choice as the electrocatalyst metal in this work. It is known that platinum group metals are typical electrocatalysts in hydrogen-containing fuels oxidation reactions in chemical current sources [**9, 21**]. Platinum shows the highest electrocatalytic activity. However, platinum application as a catalyst in the formic acid oxidation reaction is hampered by the formation of Pt-CO intermediates (reaction 3) on the electrode surface, which leads to catalyst degradation and reduces the service life of FC [**9, 21**].

Table 1. Electrocatalytic parameters evaluation for PS/Pd electrodes in the formic acid oxidation reaction (palladium loading m_s = 1.5 mg/cm^2).

ω	PS type, (P), %	ECSA, m^2/g	j, mA/cm^2	d, nm
1.5	n(64)	124	201	4.0
5		131	210	3.8
8		116	195	4.3
1.5	p(64)	101	174	5.0
5		119	187	4.2
8		95	166	5.3
1.5	n(42)	82	153	6.1
5		90	161	5.6
8		76	140	6.6
1.5	p(42)	66	124	7.6
5		72	138	6.9
8		59	117	8.5

Table 1 presents the results of the electrocatalytic activity evaluation (current density, electrocatalytic surface area, palladium content) of the PS/palladium nanocomposites obtained by the CVA method in the formic acid oxidation reaction. The calculated interval of nanoparticle sizes (d) in concordance with CVA data [**19, 25**] was from 3.5 to 8.5 nm. The results of nanoparticles size estimating obtained by the CVA method are in good consistent with the SEM data.

According to previously obtained data [**16**] the nanoparticles are formed and stabilized both in the surface layer and deep in the pores of n-type porous silicon. For PS of p-type nanoparticles are mainly formed in the surface layer. As it was established [**16**] the pore size in PS with the n-type conductivity (10-30 nm) exceeds that in PS of p-type (5-15 nm). Thus, the probability of stabilization of synthesized Pd nanoparticles with a size of 2-9 nm in the pore volume of PS matrix of n-type is higher than for PS matrix of p-type. It can be assumed that the difference in the catalytic activity of palladium nanoparticles is caused by a higher degree of nanoparticle aggregation on the surface of the silicon matrix with conductivity of p-type than that of n-type. To ensure a given palladium load (1.5 mg/cm^2) formed at a minimum solubilization degree ω a multiple layer-by-layer deposition of the catalyst to the substrate is required, resulting in increased probability of nanoparticles aggregation in contrast to the catalysts formed atω = 5 [**16**]. When increasing ω to 8, there is a strong decrease in activity due to the large particle size [**16, 21**]. So, analyzing the values in **Table 1** it may be concluded that the electrodes formed on the n-type PS with a porosity degree of 64%, modified by palladium nanoparticles and synthesized at the solubilization coefficient ω = 5, have increased activity in the formic acid oxidation reaction.

To study the specific characteristics of PS/Pd composite electrodes the models of formic-oxygen fuel cells were developed [**19, 20, 25, 26**]. Platinum electrodes based on PS served as cathodes in the oxygen reduction reaction [**2**]. PS/palladium electrodes with variable metal loading were used as anodes in the formic acid oxidation reaction.

To investigate the efficiency of selected fuel, volt-ampere characteristics of the fuel cell with different formic acid concentrations (2 M, 5 M and 10 M) were obtained. The models were prepared by hot pressing of membrane-electrode units using a Nafion solution for increasing the area of contact of electrodes with a proton-conducting membrane [**6**]. The membrane-electrode unit consisted of Nafion-115 membrane pressed between the composite anode and cathode based on PS. PS with Pd nanoparticles when metal loading (m_s) was 1.5 mg/cm^2 served as anode, PS with Pt nanoparticles when metal loading (m_s) was 0.5 mg/cm^2 served as cathode, the process temperature was 25° C, the electrodes porosity degree (P) was 64%.

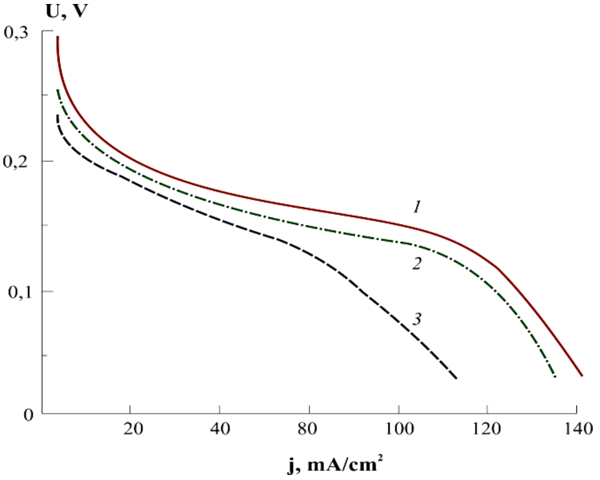

Fig. 3. Volt-ampere characteristics of the formic-oxygen fuel cell with different HCOOH concentrations: *1* – 5 M, *2* – 10 M, *3* – 2 M.

Fig. 3 shows that the voltage U on the fuel cell current collector begins to decrease with formic acid concentration increasing of more than 5 M. Such decrease can be caused by fuel penetration increasing through the membrane (crossover effect) [**19**]. Thus, the optimal concentration of formic acid (5 M) was chosen for further fuel cells testing.

While fuel cells models testing the process, temperature was 25±0.1 °C, the oxidizer was air oxygen. Four typical models based on n-type PS with palladium nanoparticles with increased electrocatalytic activity according to the **Table 1** were formed. All the models had the following parameters: nanoparticle diameter of 3.5-6 nm, different catalyst loading and PS porosity degree:

Model 1: palladium catalyst content (m_s) was 1.5 mg/cm^2, the n-type silicon porosity degree (P) was 64%;
Model 2: palladium catalyst content (m_s) was 0.8 mg/cm^2, the n-type silicon porosity degree (P) was 64%;
Model 3: palladium catalyst content (m_s) was 1.5 mg/cm^2, the n-type silicon porosity degree (P) was 42%;
Model 4: palladium catalyst content (m_s) was 0.8 mg/cm^2, the n-type silicon porosity degree (P) was 42%;

Fig. 4 demonstrates examples of volt-ampere characteristics (U-j) of membrane-electrode assembly with *models № 1-4*. In accordance with **Fig. 4**, it may be concluded that with current density increasing the voltage falling for all kinds of models. This dependence occurs due to polarization losses in the membrane-electrode assembly of the fuel cell [**2, 5**]. The highest specific characteristics are obtained for electrodes based on porous silicon of n-type with a porosity degree of 64%. The maximum current density was 100 to 105 mA/cm^2 at the operating voltage of 0.25-0.35 V. This process accompanied with agglomeration of particles on the electrodes surface during the fuel cells operation.

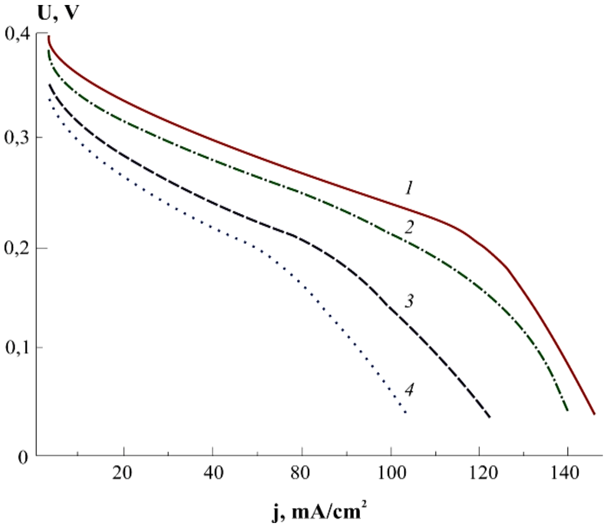

Fig. 4. Volt-ampere characteristics of *models № 1-4* based on porous silicon electrodes modified with palladium: *1* – model № 1, *2* – model № 2, *3* – model № 3, *4* – model № 4.

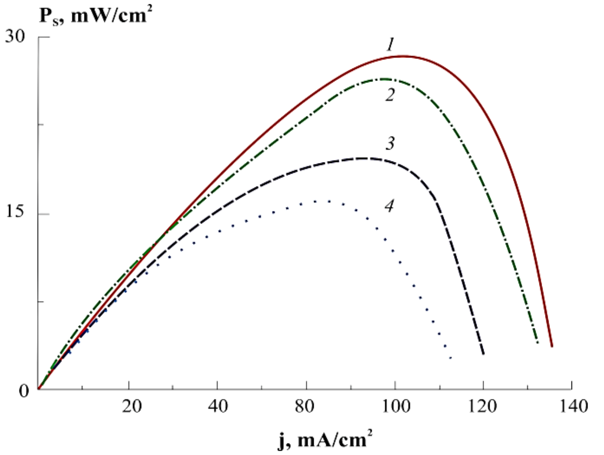

Fig. 5. Watt-ampere characteristics of *models № 1-4* based on porous silicon electrodes modified with palladium: *1* – model № 1, *2* – model № 2, *3* – model № 3, *4* – model № 4.

On **Fig. 5** the watt-ampere characteristics of the power dependence on the current density (P – j) for *models № 1-4* based on palladium electrodes with particle sizes of 3.5-6 nm on n-type porous silicon are presented.

Analysis of the data presented in **Fig. 5**, allows to conclude that with current density increasing, the specific power passes through the maximum for all four models of fuel cells. With a further increase in the current density, the specific power decreases due to a significant increase in polarization losses characteristic of all types of reducing fuels [**2, 5, 26**]. The best energy characteristics were obtained with the following parameters: n-type PS electrodes with a porosity degree of 64%, temperature of 25° C and electrocatalyst loading of 1.5 mg/cm^2. The maximum specific power was 31 ± 0.5 mW/cm^2 with a current density of 95 ± 10 mA/cm^2. The results obtained in this paper correspond to the maximum values for similar systems based on porous silicon presented to date [**1, 20, 26**] in terms of specific values of power and current density. The benefits generated samples of electrodes for energy sources should be attributed to advanced porous silicon/palladium (PS/Pd) composites, and lower palladium electrocatalyst loading in comparison with the known fuel cells prototypes [**19, 10, 26**].

To compare the obtained power characteristics with analogous systems the **Table 2** is presented. As it can be seen the formed composites have high specific power both under similar conditions of FC investigation (3-5 M HCOOH) with other works, and at the reduced palladium content at the anode (1.5 mg/cm^2) in comparison with other data [**19, 20**], which confirms the advantages of the created materials.

Table 2. Summary of the performance of formic-acid fuel cells (at room temperature) available in the literature as well as the PS/Pd of this work.

Ref.	Palladium content, mg/cm^2	Power density, mW/cm^2	Conc. of HCOOH, M
[**19**]	4	15	5
[**20**]	4	40	5
This work	1.5	30	5
This work	2	42	5
[**26**]	2	22	3
This work	1.5	26	3
This work	2	35	3

Conclusion

Advanced formation methods of composite porous silicon/palladium electrodes with increased activity in formic acid electrooxidation reaction have been proposed. Investigation of membrane-electrode assemblies models of formic acid-oxygen fuel elements were carried out. The optimal characteristics of structural materials used in fuel cell models are established. The study of the properties of the developed electrode materials based on porous silicon modified by palladium is carried out, and the prospects of using porous silicon as a structural material for micro-power current sources in electronic engineering are shown. It is determined that the maximum specific power of the fuel cell prototype is about 30 mW/cm^2 at a current density of 95-100 mA/cm^2 and a reduced palladium content in the silicon matrix in comparison with existing analogues.

Acknowledgements

This work is supported by State Assignment of the Russian Federation (project № 13.3140.2017/PCh).

Author’s contributions

Conceived the plan: nay, avr, mvl; Performed the expeirments: nay, mvl; Data analysis: nay, mvl; Wrote the paper: nay, avr, mvl. Authors have no competing financial interests.

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