Formation technology of effective electrode materials based porous silicon with platinum metal nanoparticles for autonomous energy systems

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Abstract. In this work the effective electrode materials for autonomous energy sources based on porous silicon modified by platinum nanoparticles have been obtained. The functional characteristics of the electrodes have been studied by transmission electron microscopy and voltammetry methods. The electrode materials based on porous silicon had demonstrated high catalytic activity in fuel cells with hydrogen oxidation.

1. Introduction

One of the promising ways to miniaturize the autonomous power sources such as fuel cells (FC) is to use standard microfabrication techniques that have been developed for decades for microelectronics applications. These techniques enable mass fabrication at low cost (very large number of devices on a very small area), which could lead to a reduction in the global cost of miniature fuel cells. As a consequence, a large part of the hydrogen micro-fuel-cell prototypes reviewed from the literature involves silicon [1-12].

In recent decades, porous silicon has been regarded as a means to further increase the functionality of autonomous and portable energy technology. It was found that silicon porosification is a simple and cheap way of nanostructuring and bestowing to silicon properties, which are markedly different from the bulk material properties. In this regard, increased interest in porous silicon appeared in various fields, including microelectronics, photonics, medicine, chemical sensing and bioengineering [1-12]. Especially it should also be stated that PS is usually used in microelectromechanical systems (MEMS) designing [1, 3, 9, 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.

We used in a number of our studies porous silicon (PS) as one of the most promising kinds of support matrices for autonomous micropower current sources compatible with microchips for electronics. We suggested a process for preparing and stabilizing catalytically active layers of platinum metals on PS, polymer and carbon supports in water-organic solutions in the presence of surfactants [2, 5, 10].
The aim of this work is formation of composite electrodes based on porous silicon with platinum electrocatalysts and functional specific characteristics evaluation in hydrogen oxidation reaction during model fuel cells operation.

2. Experimental

2.1. Platinum nanoparticles synthesis
Platinum nanoparticles were synthesized by chemical reduction in reverse microemulsions with sodium tetrahydroborate NaBH₄ (98%, Merck, Germany), using nonionic surfactant – Triton X-100. The method of solution preparation was as follows: a water-organic solution of platinum K₂PtCl₄ (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 water solution of the reducing agent – NaBH₄, 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.

2.2. Porous silicon formation
In this work, porous silicon of n- and p-type with different porosity degree (P) (40-80%) was prepared by anodic electrochemical etching of silicon wafers [2, 5]. Anodic etching of monocrystalline silicon had been carried out in water-alcoholic solutions of hydrofluoric acid in a cell, which is a fluoroplastic cylinder without a bottom, mounted on a silicon plate (figure 1). In this case, the silicon plate is clamped between the cylinder and the aluminum anode. A platinum electrode is used as the cathode and reference electrode. The cylinder is filled with an electrolyte solution containing hydrofluoric acid, deionized water and isopropyl alcohol (IPA) in the ratio HF:H₂O:IPA = 1:3:1. Anodizing process was carried out in galvanostatic mode with varying of etching current density from 20 to 60 mA/cm² [2, 5]. 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.

2.3. Instrumentation
The morphology of the nano composite surface was studied by high-resolution transmission electron microscopy (HRTEM) on a Zeiss Libra 200FE device (Carl Zeiss, Germany). The catalytic activity and stability of the electrodes were estimated using cyclic voltammetry (CV) on an IPC PRO M device (Tekhnopribor, Russia). The scanning rate was varied from 10 to 100 mV/s. The CV data were fixed after the stabilization of the parameters of voltamperograms.

3. Results and discussions

3.1. Features of porous silicon production
The electrophysical properties of porous silicon are strongly affected by microimpurities present in it. With the introduction of small amounts of impurities of other elements the intrinsic semiconductor can be converted to an impurity, and depending on the type of impurity a semiconductor with a hole (p-type) or electronic (n-type) conductivity can be produced. During the
formation of a porous layer on single-crystal silicon plates, an important factor is the effect of illumination on the sample. This effect allows to generate an additional number of electron-hole pairs, increasing the concentration of holes on the surface of monocrystalline silicon. The illumination has a special effect on the n-type samples, allowing to increase the concentration of "holes" involved in the pore formation on the surface of the plate. However, the increased concentration of "holes" in the etching area leads to a sharp increase in the pore diameter of the sample, allowing to obtain layers of macroporous silicon. To obtain the layers of mesoporous n-type silicon in this work, we chose the values of the current density is higher than for samples p-type, at the same time the impact of current on the plate was reduced. The process of pore formation on the surface of a single-crystal silicon plate can be described by the following scheme (figure 2) [1, 3]:

As a result, the channels diameter of n-type PS was of 15-45 nm, p-type PS – 10-25 nm when samples porosity degree was 65±2% and 47±2%, respectively (table 1).

Table 1. Conditions of PS layers formation during anodic etching.

| Conductivity type and porosity | Anodizing time, Sec | Current density, mA/cm² | Specific internal surface area Sᵥ, m²/cm³ |
|-------------------------------|---------------------|--------------------------|------------------------------------------|
| n-type, 48                    | 44                  | 25                       | 154,2                                    |
| n-type, 66                    | 32                  | 53                       | 171,4                                    |
| p-type, 66                    | 62                  | 22                       | 287,6                                    |

The specific area of the PS inner surface (Sᵥ, table 1) has been determined with oxidative gravimetry method [3]. The method has a high accuracy and allows to characterize samples with a large specific surface area. The method is based on thermal oxidation of the inner surface of the pores and measurement of the mass and thickness of the formed oxide layer. PS samples were weighed before and after oxidation, and the thickness of the porous layer was determined by the SEM method on the sample cleavage. Next, the Sᵥ value was calculated by the formula [3]:

\[
Sᵥ = \frac{4S}{\pi D^2 t}
\]  

\[
S = 1.88 \frac{m_{ox} - m_0}{\rho_{SiO_2} t} - 2 \left( \frac{M}{\rho_{Si} L} - \frac{\pi D^2}{4} \right)
\]

In the future, the PS nanopore sizes were controlled by scanning electron microscopy and transmission electron microscopy methods.
3.2. Composites investigation

To create nanocomposite materials, the sorption process of micellar solutions with platinum 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. The application of ultrasonic treatment while the formation of platinum–PS nanocomposites allows us, first, to initiate the decomposition of the associates of the reverse micelles and facilitate the destruction of micellar shells of nanoparticles. Second, localizing the PS samples in the zone of the formation of the platinum nanoparticles free from the micellar shells stimulates the localization of small nanoparticles on active PS centers and using an ultrasonic treatment prevents the agglomeration of nanoparticles both at the surface and in the pores of the matrix according to the HRTEM (figure 3) data.

![Microphotograph HRTEM of Pt nanoparticles in the depth of n-type PS pores.](image)

According to the HRTEM data (figure 3), the synthesized platinum nanoparticles possess sizes in the range from 7 to 2 nm and smaller and are characterized by a homogeneous distribution at the surface and in the bulk of pores.

The catalytic activity of the synthesized Pt/PS composites was evaluated by cyclic voltammetry (CVA). The electrocatalytically active surface area (ECSA) was determined by the standard procedure of evaluation of CVA parameters, taking into account the catalyst content and the potential scanning rate. Figure 4 shows the potentiodynamic curves (CVA) for Pt nanocomposites on n- and p-type porous silicon, taken at the solubilization coefficient \( \omega = 1.5 \) and metal content \( m_s(Pt) = 0.08 \text{ mg cm}^{-2} \). Characteristic peaks corresponding to hydrogen adsorption/desorption (0-0.3 V) and oxygen reduction (>0.6 V) can be seen in the curves. At the Pt content lower than 0.03 mg cm\(^{-2}\), these peaks are weakly pronounced. This is associated with relatively low platinum content of the samples.

![Potentiodynamic curves of Pt nanocomposites on (1) n- and (2) p-type porous silicon at \( \omega = 1.5 \) and metal content \( m_s(Pt) = 0.08 \text{ mg cm}^{-2} \)](image)

Table 2 shows the parameters of the catalytic activity (current density, ECSA, stability) of platinum/PS nanocomposite samples containing 0.08 mg cm\(^{-2}\) Pt, prepared at solubilization coefficients \( \omega \) of 1.5 and 5. These parameters were determined by CVA in reactions of oxygen electroreduction and hydrogen oxidation. Comparison of the results given in Table 2 shows that enhanced activity is exhibited by electrodes characterized by n-type of PS conductivity, 66% porosity, and minimal nanoparticle size and synthesized from water-organic solutions with \( \omega = 1.5 \). The nanoparticle size (d) range calculated from the CVA data \([2, 5]\) is 1-4 nm. The CVA data agree with the HRTEM data (figure 3).
Table 2. Characteristics of Pt/PS nanocomposites with the metal content of 0.08 mg cm\(^{-2}\), according to CVA data

| № | PS type | Porosity degree, \(\omega\), % | ECSA, \(\sigma\), m\(^2\)/g | \(j\), A/m\(^2\) | \(d\), nm |
|---|---------|-------------------------------|--------------------------|-------------|------|
| 1 | n       | 66                            | 1.5                      | 214         | 121  | 1.3 |
| 2 | n       | 66                            | 5                        | 202         | 117  | 1.4 |
| 3 | p       | 66                            | 1.5                      | 188         | 110  | 1.5 |
| 4 | p       | 66                            | 5                        | 165         | 105  | 1.7 |
| 5 | n       | 48                            | 1.5                      | 119         | 82   | 2.4 |
| 6 | n       | 48                            | 5                        | 104         | 76   | 2.7 |
| 7 | p       | 48                            | 1.5                      | 91          | 70   | 3.1 |
| 8 | p       | 48                            | 5                        | 84          | 67   | 3.3 |

4. Conclusion

Effective electrode materials based on porous silicon with platinum nanoparticles had been prepared. Received nanocomposites exhibit high catalytic activity in hydrogen oxidation and oxygen reduction. The enhanced activity showed the PS electrodes with n-type conductivity, porosity of 66% and with minimal nanoparticle size synthesized from water-organic solutions with \(\omega = 1.5\). These materials are of great interest in the autonomous energy sources constructing with high specific characteristics.

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