SOLID MATTER

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PROBLEMS OF APPLICATION OF POROUS SILICON TO CHEMICAL AND PHOTOCATALYTIC PRODUCTION OF HYDROGEN

Advantages of the use of silicon and porous silicon (PS) for the chemical production of hydrogen have been analyzed and compared with other fuels. An analytic expression is derived for the dependence of the volume of hydrogen produced at the PS interaction with water on the material porosity, as well as for the corresponding energy yield, when the produced gas is used in the power sources of electronic systems. It is found that the silicon porosity growth results in a reduction of the total volume of hydrogen released in the reaction with water, as compared with the amount of H_2 obtained from the initial quantity of raw silicon. This effect is explained by significant losses of a material at PS formation. The ratio between the accumulation of hydrogen in the PS material and silicon losses in the etchant is determined to be optimal for the silicon porosity in the interval of 60–70%. When applying the produced hydrogen in fuel cells, the etching of silicon provides a growth of the output power, but reduces the total amount of the produced energy. Those mechanisms are analyzed to demonstrate the inexpediency of using the composites on the basis of pure nano-PS for the photocatalytic water dissociation.

K e y w o r d s: porous silicon, water dissociation, hydrogen.

1. Introduction

Hydrogen is an important raw material for the chemical industry, as well as a promising energy carrier [1]. There are a lot of methods of H_2 production, such as methane conversion, biomass decomposition, water dissociation, and others [1–3]. A considerable attention is paid by researchers to the reduction of minerals consumption and the application of regeneration resources to the hydrogen production.

Water is one of the main renewable resources. The major industrial technology for the generation of H_2 from water is electrolysis [1,2]. The efficiency of modern electrolyzers reaches 80% and even more. However, the rationality of this way to transform the electric power is doubtful. This is the more so, if the

matter concerns the further application of H_2 in fuel cells. For example, the theoretical efficiency for the scheme "electric power $\rightarrow$ hydrogen $\rightarrow$ mechanical energy" used in transport vehicles powered by fuel cells amounts to 25% [4]. The corresponding value for electromobiles with storage batteries reaches 69%. In addition, in many cases, the electric power is obtained by burning an organic fuel, the consumption of which should be confined.

Therefore, the alternative ways of water dissociation such as thermal, chemical, and photocatalytic ones are actively studied. The corresponding technologies that are based on thermochemical cycles are promising, if the heat generated at nuclear reactors or solar stations is used to support the reactions [1]. The chemical methods allow a high level of H_2 extraction to be achieved, but they are accompanied by irre-

versible expenses of reacting substances [5, 6]. The photocatalytic methods make it possible to decompose water using the energy of absorbed photons, but they have a low efficiency in the visible spectral range [1, 7].

The development of alternative hydrogen sources is closely associated with researches of semiconductors. The careful selection of a material substantially improves the efficiency of the H_2 production technology. Silicon and porous silicon (PS) can be applied to the chemical or photocatalytic dissociation of water [8–10]. However, there is no definite answer to the question till now: Is it beneficial to use silicon composites for the hydrogen production?

2. Hydrogen Production at Interaction of Silicon with Water

The application of silicon for the chemical production of hydrogen is based on the reactions of this substance with water or alkali. The corresponding reactions are described by the equations [8, 9]

$$Si + 2H_2O = SiO_2 + 2H_2 \uparrow, \tag{1}$$

$$Si + 4H_2O = Si(OH)_4 + 2H_2 \uparrow, \tag{2}$$

$$Si + 2NaOH + H_2O = Na_2SiO_3 + 2H_2 \uparrow. \tag{3}$$
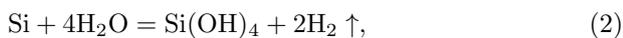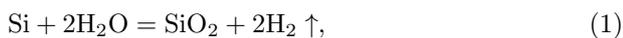
For those reactions to run quickly, the heating to a temperature within the interval from 50 °C to the solution boiling point, the application of alkalies, and the mixing of reagents are required.

One can see that, according to reactions (1)–(3), one mole of silicon is required to produce two moles of molecular hydrogen. The maximum specific reaction yield amounts to 1600 l of H_2 per 1 kg of Si. The energy that is released at the burning of this quantity of hydrogen equals 17.2 MJ. For comparison, the corresponding value equals 5.7 MJ for iron and 13.3 MJ for aluminum [8]. Those numbers illustrate the advantages of silicon over the competing inorganic sources of hydrogen.

The combustion heat of peat amounts to 10.5–14.5 MJ/kg, coal to 27 MJ/kg, and natural gas to 41–49 MJ/kg [11]. Those values are of the same order of magnitude as the combustion heat of hydrogen produced in reactions (1)–(3).

However, there arises a question: Is such an application of silicon reasonable? The main application of Si as a material for semiconductor devices demands

labor-consuming procedures aimed at purifying raw materials from impurities [12]. There are plenty of cheap versions of the material, such as crude metallurgical silicon, "black" silicon, and polysilicon. Each of them does not satisfy the requirements of semiconductor electronics. Moreover, silicon industry produces a lot of waste. It is this silicon raw material that can be used for the chemical production of hydrogen.

3. Hydrogen Production by Hydrolysis of Porous Silicon

Porous silicon is formed by treating the raw material in the solutions of fluoric acid and alcohol. The main technologies of PS fabrication are chemical and electrochemical etchings [13].

During the etching, a porous material is formed. Its surface is densely covered with SiH_x ($x = 1, 2, 3$) complexes. At present, specimens with the hydrogen content reaching 60 mmol per 1 g of PS (6 wt.%) are obtained, which corresponds to the atomic ratio $H : Si \approx 1.8$ [14].

When PS interacts with water, hydrogen is released both from the destroyed SiH_x groups and owing to the dissociation of H_2O in accordance with reactions (1) and (2). Both mechanisms can be generalized by the following reaction equation:

$$SiH_x + (2 + y)H_2O = SiO_2\, yH_2O + (2 + x/2)H_2. \tag{4}$$
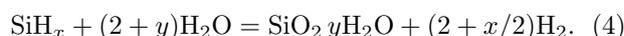
The maximum level of hydrogen accumulation in PS corresponds to the continuous coating of the material by SiH_2 complexes. In this case, the H_2 release is described by the following equation, which can be obtained from Eq. (4) by putting $x = 2$:

$$SiH_2 + (2 + y)H_2O = SiO_2\, yH_2O + 3H_2. \tag{5}$$
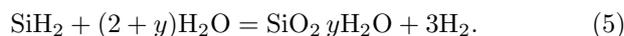
Hence, the reaction of one mole of PS with water produces about three moles of molecular hydrogen, i.e. the hydrogen yield is one and a half times larger than at the interaction between crystalline Si and water. The corresponding specific yield amounts to 2240 l of H_2 per 1 kg of a PS powder. The oxidation of this volume of hydrogen generates an energy of 24.19 MJ, which is comparable with 27 MJ of heat obtained at the combustion of 1 kg of coal.

The intensity of reactions (4) and (5) can be controlled by adding a catalyst, heating, or subjecting to the illumination. If the reaction with water runs in

the presence of a catalyst, the rate of H_2 release from PS is by more than an order of magnitude higher than the rate of hydrogen generation at a similar reaction with crystalline silicon [6].

It should be noted that the factors indicated above are not mandatory for the reaction to run. For instance, PS-based ecological sources of hydrogen are created, which are activated by pure water under normal conditions and without additional requirements [15].

4. Problem of Effective Application of Porous Silicon to Chemical Production of Hydrogen

As was mentioned above, the interaction of PS with water allows the yield of H_2 to be made 1.5 times larger and the corresponding reaction rate an order of magnitude higher in comparison with the relevant parameters for crystalline Si, even without heating or mixing the reagents. At first sight, this is an evident advantage. However, a question arises: Does the increment in the hydrogen release cover the expenses for the PS fabrication?

There are two basic mechanisms of losses. These are the dissolution of the silicon raw material in the course of PS etching and the expense for reactants and electric power. Below, only the former mechanism will be considered, because it dominates. The economic analysis of the prices for electric power and reactants that are required to transform silicon into a porous material will be left beyond the scope of this work.

According to reactions (4) and (5), the pore formation is accompanied by the transition of silicon into the etching solution in the form of SiF_4 compound followed by the formation of H_2SiF_6 acid. After PS has been fabricated, this solution, which includes the remnants of acids and the reaction products, goes to waste. As a result, the amount of obtained PS is determined by the amount of silicon, which was not dissolved in HF.

The major characteristic of the produced material is its porosity [16]

$$P = \frac{m_{\mathrm{Si}} - m_{\mathrm{PS}}}{m_{\mathrm{Si}}}, \tag{6}$$

where m_{Si} and m_{PS} are the masses of the silicon raw material and the produced PS, respectively.

The hydrogen content is known to be higher in PS with higher porosity (Fig. 1, *a*) [17]. By calculating the ratio between the amount of bound hydrogen and the volume of H_2 released at the oxidation of a PS matrix by water following Eqs. (1) and (2), we obtain a dependence shown in Fig. 1, *b*. One can see that, at a higher porosity, the contribution of SiH_x groups to the total H_2 yield substantially increases. The fraction of hydrogen chemically bound in nano-PS with a porosity exceeding 95% reaches a record 50% of the total amount of gas released according to reaction (5).

However, the porosity also determines how much silicon was lost at the fabrication of PS. For example, a porosity of 0.95, which corresponds to PS nanopowders with the maximum hydrogen content, indicates that 95% of initial silicon raw material was lost at the etching.

To solve the problem, it is necessary to compare the volume of hydrogen released from PS and its volume formed at the reaction of the initial silicon raw material with water.

Let the interaction between crystalline silicon of the mass m_{Si} and water result in the production of molecular hydrogen of the volume $V_{\mathrm{Si}}^{\mathrm{H}_2}$:

$$m_{\mathrm{Si}} \to V_{\mathrm{Si}}^{\mathrm{H}_2}. \tag{7}$$

At reactions (1)–(3), one mole of Si is required to obtain two moles of H_2. Therefore, the volume of the obtained gas can be calculated by the formula

$$V_{\mathrm{Si}}^{\mathrm{H}_2} = 2\frac{m_{\mathrm{Si}}}{\mu_{\mathrm{Si}}}V_m, \tag{8}$$

where μ_{Si} is the molar mass of silicon, and V_m the molar volume of the gas.

If a decision is made to increase the amount of hydrogen in the material by the etching, some fraction of silicon will be lost in the HF solution. The mass m_{PS} of produced PS will be less than m_{Si} by a factor equal to the porosity value. During the etching, the silicon surface becomes hydrogenated. Accordingly, the PS mass will consist of the silicon matrix mass, m_{matrix}, and the mass of hydrogen bound on the surface, m_{SiH_x}:

$$m_{\mathrm{PS}} = m_{\mathrm{matrix}} + m_{\mathrm{SiH}_x} = (1 - P)m_{\mathrm{Si}}. \tag{9}$$

Therefore, at the interaction between PS and water, the total amount of H_2 will consist of the products of
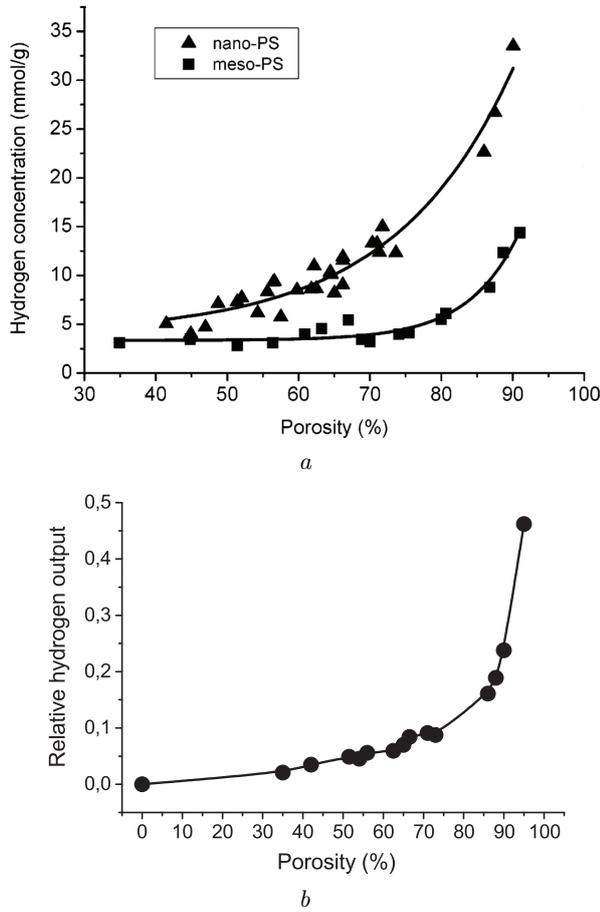
Fig. 1. Specific amount of atomic hydrogen bound in SiH_x groups as a function of the PS porosity for PS of various porosity groups [17] (*a*). Volume ratio for the hydrogen released from SiH_x groups of nano-PS and the hydrogen generated at the oxidation of a PS matrix by water (*b*)

oxidation of Si–Si bonds in the silicon matrix, $V_{matrix}^{H_2}$, and the hydrogen released from SiH_x groups, $V_{SiH_x}^{H_2}$:

$$m_{PS} \rightarrow V_{PS}^{H_2} = V_{matrix}^{H_2} + V_{SiH_x}^{H_2}. \qquad (10)$$

The value of $V_{SiH_x}^{H_2}$ can be calculated from the experimental dependence of the specific amount of atomic hydrogen bound in PS, v_H, on the material porosity P (see Fig. 1, *a*). Taking into account that the mole number of molecular hydrogen (H_2) is half as large as the mole number of atomic hydrogen (H), the contribution of SiH_x groups to the total gas yield is determined as follows:

$$V_{SiH_x}^{H_2} = \frac{1}{2} \nu_H(P) m_{PS} V_m. \qquad (11)$$

The quantity $V_{matrix}^{H_2}$ can be determined using formulas (8) and (9):

$$V_{matrix}^{H_2} = 2 \frac{m_{matrix}}{\mu_{Si}} V_m = 2 \frac{m_{PS} - m_{SiH_x}}{\mu_{Si}} V_m. \qquad (12)$$

The mass of hydrogen in SiH_x groups, m_{SiH_x}, is expressed in terms of the PS mass m_{PS}, the specific amount of the material $\nu_H(P)$, and the molar mass of atomic hydrogen μ_H by the formula

$$m_{SiH_x} = \mu_H \nu_H(P) m_{PS}. \qquad (13)$$

Substituting this expression into Eq. (12), we obtain

$$V_{matrix}^{H_2} = 2 \frac{1 - \mu_H \nu_H(P)}{\mu_{Si}} m_{PS} V_m. \qquad (14)$$

As a result, on the basis of formulas (8), (11), and (14) and the porosity definition, the ratio between the hydrogen volumes obtained at the reaction of water with either PS or the initial silicon raw material looks like

$$\frac{V_{PS}^{H_2}}{V_{Si}^{H_2}} = (1 - P) \left[1 + \left(\frac{1}{4} \mu_{Si} - \mu_H \right) \nu_H(P) \right]. \qquad (15)$$

The obtained dependence is plotted in Fig. 2, *a*. One can see that the growth of the silicon porosity results in the reduction of the total H_2 yield if the initial raw material reacts with water or alkali. The dependence decreases almost linearly as $1 - P$.

The contribution of SiH_x groups of PS to the relative hydrogen volume is determined by the formula

$$\frac{V_{SiH_x}^{H_2}}{V_{Si}^{H_2}} = \frac{1}{4} \mu_{Si} (1 - P) \nu_H(P). \qquad (16)$$

The values of this ratio calculated for various porosities are illustrated in Fig. 2, *b*. The analyzed dependence has a nonlinear character, which is unnoticeable in Fig. 2, *a* because of a large scale. One can see that, even at the maximum concentration of SiH_x groups, their contribution to the volume of released H_2 amounts to only 2–3% of the hydrogen formed at the reaction of the initial silicon raw material with water.

The optimum relation between the hydrogen accumulation in SiH_x groups and the silicon losses in the etching solution is obtained at a porosity of 60–70%. In this case, the contribution of bound hydrogen

to the relative yield of H_2, which can be obtained with the use of PS, with respect to the yield obtained, by using the non-etched silicon raw material is maximum.

Hence, the silicon etching results in a reduction of the H_2 yield, if the chemical technology is applied. Accordingly, the transformation of silicon into PS turns out inexpedient for the commercial hydrogen production. However, a high level of hydrogen accumulation and high rates of hydrogen release from PS, as well as simple conditions required for the material to react with water, comprise an essential advantage in the case where this method is applied to small autonomous systems.

For the generated hydrogen to be used in power sources of electronic systems, the reactor, which contains PS immersed into the solution, is combined with a low-temperature fuel cell. The energy produced by this system can be calculated by the formula

$$W = \eta Q_{H_2} V_{PS}^{H_2}, \qquad (17)$$

where $Q_{H_2} = 10.8$ MJ/m^3 is the specific heat of hydrogen oxidation, and η the efficiency of a fuel cell (50% for membrane devices). In other words, the power source energy is proportional to the volume of consumed hydrogen.

The direct proportionality between the capacity of a power source and the rate of H_2 generation can be found in a similar way. The intensity of reaction (4) increases with the PS porosity [6]. Hence, according to formulas (15) and (17), the silicon etching increases the power of an energy source, but diminishes its capacity.

5. Problems of Porous Silicon Application to Photocatalytic Dissociation of Water

The application of semiconductors as photocatalytic materials is associated with their ability to generate an electron-hole pair after absorbing a light quantum. Holes provide the splitting of water molecules into oxygen and hydrogen ions. Electrons reduce hydrogen ions to the molecular state. Those processes are described by the formula [7]

$$H_2O \xrightarrow{h\nu} H_2 + \frac{1}{2}O_2. \qquad (18)$$

The potential corresponding to the theoretical minimum required for the splitting of a water molecule
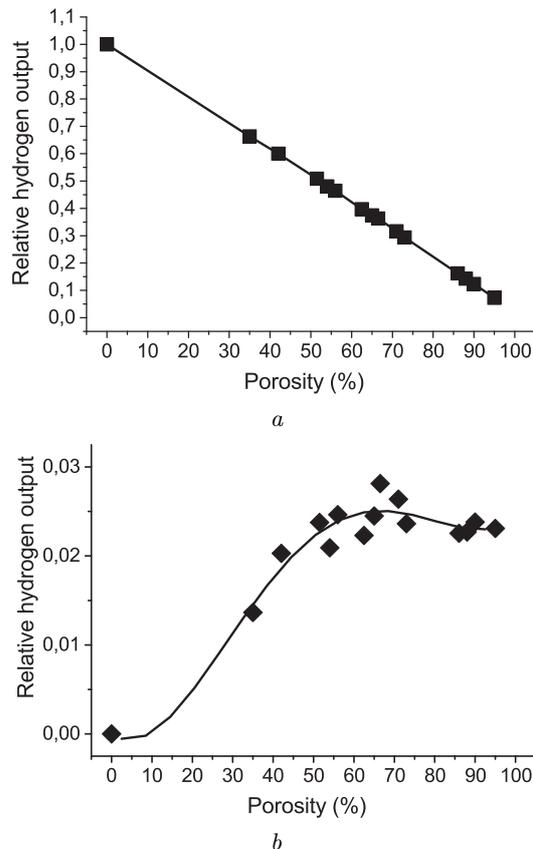

Fig. 2. Volume ratio for the hydrogen released at the reaction of PS with water and hydrogen released from the initial raw material according to reaction (15) (*a*) and reaction (16) (*b*)

amounts to 1.23 eV. The real value of energy gap width in the photocatalyst with the activation in the visible spectral range should amount to 2.0–2.2 eV [1, 7].

Silicon is a basic material for manufacturing solar cells [18, 19]. However, the energy gap in crystalline Si does not allow this semiconductor to be used for the photocatalytic dissociation of water. Two ways were proposed to solve this problem. First, the reduction of Si crystallite sizes to nanodimensions gives rise to a growth of the energy gap width in this material. Technologies of nano-PS etching make it possible to reach the required values of dissociation potential [10]. Second, the application of catalytic coatings diminishes the reaction activation barrier. For this purpose, metals of the platinum group are used, as a rule. They are deposited on the walls of pores in silicon [20–22].

A substantial growth of hydrogen production in electrochemical cells with photocathodes fabricated on the basis of PS with respect to the case with crystalline Si cathodes was demonstrated experimentally [10]. Moreover, the water decomposition without the application of an external potential was registered in cells with an electrode on the basis of Pd-doped PS [22].

However, the PS application of this type has a considerable shortcoming, which is related to the chemical interaction between this material and water (see the discussion in Sections 2 and 3). Reaction (4) can run even at room temperature and in the absence of a catalyst. This means that, if the photocathodes fabricated from PS are immersed in water, the generation of H_2 will be accompanied by the oxidation of the material. As a result, hydrated silicon oxide with closed pores will be formed, and it cannot be used as a photocatalyst.

The influence of light on the hydrogen release intensity in the course of reaction (4) was detected experimentally [6]. The total H_2 yield increases if the blue or ultra-violet illumination is applied. This fact can be explained by the photocatalytic effect. However, after the oxidation, the PS material becomes inapplicable for generating H_2.

The deposition of Pd nanoparticles into silicon pores does not change the situation. An island-like coating does not protect the material from its interaction with water. If the specimens are immersed in an aqueous solution, reaction (4) accompanied by the irreversible oxidation of silicon runs as well [23]. The problem can be solved by covering the PS surface with a continuous Pd film, but this method faces considerable technological difficulties.

Hence, the application of composites on the basis of pure PS for the photocatalytic dissociation of water turns out inexpedient. The passivation of the silicon surface by halogens may be a way to solve this problem.

6. Conclusions

The chemical reaction of silicon with water or alkali is an effective method of hydrogen production, in which cheap raw materials and wastes can be used. The specific yield of H_2 in this reaction exceeds the corresponding parameters for aluminum and iron. Porous silicon allows one to obtain the H_2 yield 1.5 times larger and the reaction rate by an order of magnitude higher in comparison with the case where crystalline Si is used. Moreover, the reagents do not require the heating or mixing.

It is analytically shown that the growth of silicon porosity gives rise to a reduction in the total amount of hydrogen released at the PS reaction with water, in comparison with the corresponding parameter for the initial silicon raw material. This fact is explained by substantial losses of the material at the etching owing to the dissolution of Si in HF. The law of hydrogen mass fraction growth is not violated, as the specimen porosity increases. However, the accumulation of hydrogen in the SiH_x groups of PS does not compensate the losses of a raw material in the etching solution. The calculated amount of bound hydrogen at the porosity maximum amounts to only 2–3% of the gas volume that is formed in the reaction with initial silicon.

From the viewpoint of using the produced hydrogen in fuel cells to feed electronic systems, the silicon etching gives rise to a growth of the electric source power, but decreases its total energy capacity. The optimal value of silicon porosity for such applications was calculated to equal 60–70%.

The application of composites on the basis of pure nano-PS for the photocatalytic dissociation of water is inexpedient. This conclusion is associated with the chemical interaction between water and the PS material, which results in the silicon oxidation and the pore closure. As a result, the processing of silicon into PS is inexpedient for the commercial hydrogen production. However, a high level of hydrogen accumulation in PS and high rates of hydrogen release from it, together with simple conditions required for the reaction of this material with water to run, are an indisputable advantage of its application in power sources of small autonomous systems.

1. L.M. Gandía, G. Arzamendi, P.M. Diéguez, *Renewable Hydrogen Technologies: Production, Purification, Storage, Applications and Safety* (Elsevier, Amsterdam, 2013).
2. A.V. Stepanov, *Production of Hydrogen and Hydrogen-Containing Gases* (Kyiv, Naukova Dumka, 1982) (in Russian).
3. A.A. Tsygankov, Ross. Khim. Zh. **6**, 25 (2006).
4. U. Bossel, Proc. IEEE **94**, 1826 (2006).
5. A.E. Sheindlin and A.Z. Zhuk, Ross. Khim. Zh. **6**, 105 (2006).
6. A.I. Manilov, S.V. Litvinenko, S.A. Alekseev, G.V. Kuznetsov, and V.A. Skryshevsky, Ukr. J. Phys. **55**, 928 (2010).

7. M. Matsuoka, M. Kitano, M. Takeuchi, K. Tsujimaru, M. Anpo, and J.M. Thomas, Catalysis Today **122**, 51 (2007).

8. N. Auner, Deutsche Bank Res. **11**, 1 (2004).

9. S. Litvinenko, S. Alekseev, S. Litvinenko, S. Alekseev, V. Lysenko, A. Venturello, F. Geobaldo, L. Gulina, G. Kuznetsov, V. Tolstoy, V. Skryshevsky, E. Garrone, and D. Barbier, Int. J. Hydrogen Energy **35**, 6773 (2010).

10. N.R. Mathews, P.J. Sebastian, X. Mathew, and V. Agarwal, Int. J. Hydrogen Energy **28**, 629 (2003).

11. E.V. Ametistov, *Fundamentals of Modern Power Engineering* (MEI, Moscow, 2004) (in Russian).

12. E.S. Falkevich, E.O. Pulner, I.F. Chervonnyi et al., *Technology of Semiconductor Silicium* (Metallurgiya, Moscow, 1992) (in Russian).

13. G. Korotcenkov and B.K. Cho, Crit. Rev. Solid State Mater. Sci. **35**, 153 (2010).

14. A.I. Manilov and V.A. Skryshevsky, Mater. Sci. Eng. B **178**, 942 (2013).

15. A.I. Manilov, V.A. Skryshevsky, S.V. Litvinenko, and G.V. Kuznetsov, Patent of Ukraine No. 100084, Bull. No. 21 (2012).

16. V. Parkhutik, Solid-State Electron. **43**, 1121 (1999).

17. V. Lysenko, F. Bidault, S. Alekseev, V. Zaitsev, D. Barbier, Ch. Turpin, F. Geobaldo, P. Rivolo, and E. Garrone, J. Phys. Chem. B **109**, 19711 (2005).

18. L. Fraas and L. Partain, *Solar Cells and Their Applications* (Wiley, Hoboken, 2010).

19. O.V. Kozynets and S.V. Litvinenko, Ukr. J. Phys. **57**, 1234 (2012).

20. G.V. Kuznetsov, V.A. Skryshevsky, T.A. Vdovenkova, A.I. Tsyganova, P. Gorostiza, and F. Sanz, J. Electrochem. Soc. **148**, 528 (2001).

21. V.G. Litovchenko, T.I. Gorbanyuk, V.S. Solntsev, and A.A. Evtukh, Appl. Surf. Sci. **234**, 262 (2004).

22. V.E. Primachenko, B.M. Bulach, S.I. Kirilova, V.A. Chernobai, and E.F. Venger, Ukr. J. Phys. **52**, 236 (2007).

23. A.I. Manilov, S.A. Alekseev, V.A. Skryshevsky, S.V. Litvinenko, G.V. Kuznetsov, and V. Lysenko, J. Alloys Comp. **492**, 466 (2010).

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ПРОБЛЕМИ ЗАСТОСУВАННЯ
ПОРУВАТОГО КРЕМНІЮ ДЛЯ ХІМІЧНОГО
ТА ФОТОКАТАЛІТИЧНОГО ВИРОБНИЦТВА ВОДНЮ

Р е з ю м е

Проаналізовано переваги кремнію і поруватого кремнію (ПК) як хімічних джерел водню, порівняно з іншими видами палива. В аналітичному вигляді отримано залежність об'єму водню, виробленого при взаємодії з водою, від поруватості матеріалу та відповідний енергетичний вихід при застосуванні газу у джерелах живлення електронних систем. Розраховано, що зростання поруватості кремнію супроводжується спаданням загального об'єму водню, виділеного при реакції з водою, порівняно до рівня видобутку H_2 з вихідної кремнієвої сировини. Закономірність пояснюється суттєвими втратами матеріалу протягом виготовлення ПК. Визначено, що оптимальне співвідношення між накопиченням водню у матеріалі і втратами кремнію у травнику відповідає поруватості 60–70%. При застосуванні утвореного водню у паливних елементах, травлення кремнію забезпечує ріст потужності джерела живлення, але зменшує його загальний енергоресурс. На основі зазначених механізмів показано недоцільність застосовування композитів на основі чистого наноПК для фотокаталітичної дисоціації води.