

USE OF POWDERS AND COMPOSITES BASED ON POROUS AND CRYSTALLINE SILICON IN THE HYDROGEN POWER INDUSTRY

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Crystalline silicon powders, porous silicon (PS) fractions, and composites based on PS and Pd are studied from the viewpoint of their use as solid-state hydrogen sources. The H₂ release was initiated by H₂O:C₂H₅OH:NH₃ solutions. A comparative analysis of these materials with respect to the total yield of H₂ (i.e. total energy store) and the rate of its release (i.e. power) is performed. It is determined that the most effective material for such applications is a PS powder produced according to the electrochemical technology. It is shown that the treatment of PS and composites with gaseous H₂ insignificantly influences the release of hydrogen from these materials. The effect of the NH₃ concentration, temperature, and illumination on the kinetics of H₂ release is studied.

1. Introduction

The hydrogen power industry represents one of the promising directions of up-to-date investigations. An important problem in this field is to develop safe and mobile means for the hydrogen storage. These requirements are met by solid-state accumulators on the basis of metal hydrides or nanostructured materials [1].

Porous silicon (PS) is one of the modern materials used in the hydrogen power industry [2]. It can serve as a hydrogen source due to the presence of silane groups SiH_x, $x = 1 - 3$, on its surface arising in the course of manufacturing [3–4]. The advantages of this material are a high content of hydrogen (up to 6 mass percent), the easiness of its release, and the considerable intensity of H₂ desorption. The main drawback of PS is that it is difficult to restore the hydrogen content after one cycle of H₂ desorption, which is caused by the oxidation of silicon [4]. In order to release hydrogen from PS, one uses the following methods: heating [3–4], ultraviolet illumination [5], and reactions with water [4, 6, 7]. The drawback of two former methods lies in the possibility of the oxidation of desorbed H₂ with the formation of water, which requires to carry out the desorption in high vacuum or the inert atmosphere. That is why it is more

efficient to obtain hydrogen due to the reaction with water in the presence of a catalyst. Moreover, the hydrogen release is observed both for porous and crystalline phases of silicon [7].

Modern technologies allow one to create silicon and PS fractions with specified particle sizes, surface morphology, and fractality level [8], which is reflected in the hydrogen content in a material and the intensity of H₂ desorption [9]. In addition, there exists a possibility to increase the content of hydrogen in PS by means of the additional treatment of the material in gaseous H₂. The use of catalysts of hydrogenation reactions allows one to intensify the interaction of H₂ with a material. To such catalysts, one refers metals of the platinum group, palladium being the most efficient of them. This is related to the highest solubility of hydrogen in palladium as compared with the other metals, as well as to the dissociation of H₂ molecules into atoms under interaction with a metal surface [10–12].

The aim of this work is to determine the most effective hydrogen accumulator among silicon powders, PS fractions, or composites on the basis of PS and Pd: with respect to the total amount of H₂ (i.e. total energy store) and the rate of its release (i.e. power).

2. Preparation of Samples

We studied the following kinds of samples: crystalline silicon powders (c-Si), PS fractions with various particle sizes (prepared by the chemical etching technique), powders and free layers of mesoPS (created using the anode technology), and composites on the basis of free layers of mesoPS with Pd particles introduced into pores (1 percent or 10 mass percent).

The c-Si powders were made of silicon of p- ($\Omega\rho = 2.5 \text{ Ohm}\cdot\text{cm}$) or p⁺⁺-type ($\Omega\rho = 0.001\text{--}0.003 \text{ Ohm}\cdot\text{cm}$). Fractions with particles of various sizes were extracted by the step-by-step sedimentation of powders in water. After a certain time (2, 8, 32, and 120 min after placing a

powder in water), the generated sediment was collected and dried in air. In such a way, we created 4 fractions of Si powders. The longer the time of keeping in water, the smaller the size of their particles.

In order to cover the surface of the particles by SiH_x groups, the powders were held in a $\text{H}_2\text{O}:\text{HF}:\text{HNO}_3$ solution (with the ratio 20:4:1) at a temperature of 40–60 °C for 10–60 min. In the process of etching, a layer of porous silicon on the surface of particles was formed. The hydrogen content grew in correspondence with increase in the specific surface of particles [9].

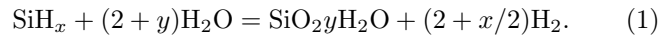
Free mesoPS layers (porosity 55 %, thickness 300 μm) were obtained by means of the electrochemical etching (100 mA/cm^2) of a silicon plate (p^{++} , orientation (100), $\Omega = 0.001 \text{ Ohm}\cdot\text{cm}$) in a mixture of 48% HF with ethanol (taken in the volume ratio 1:1) during 2 h. After the end of the anodization, the PS film was separated from the base with an intense current pulse (1 A/cm^2 , 5 s).

In order to introduce metallic Pd into free PS layers, they were treated by solutions of palladium acetate ($\text{Pd}(\text{CH}_3\text{CO}_2)_2$) in acetonitrile. This procedure was accompanied by the processes of Pd reduction on the PS surface. In order to remove the oxide layer, the initial PS samples were washed immediately before the treatment with the $\text{HF}(48\%):\text{ethanol}(1:9)$ mixture during 5 min and then with pure ethanol. After that, the PS samples were dried in air and placed into acetonitrile solutions of palladium acetate with the ultrasound mixing for 1 h. Then they were washed with acetonitrile and dried in air. The volume of the $\text{Pd}(\text{CH}_3\text{CO}_2)_2$ solutions was equal to 1 ml of the solution per 10 mg of PS. The concentration amounted to 0.001 moles/l and 0.01 moles/l for obtaining samples with the 1-% and 10-% mass contents of Pd, respectively. The decoloration of the solutions initially having yellow color after the end of the treatment and an increase of the mass of the samples testify to the complete deposition of palladium.

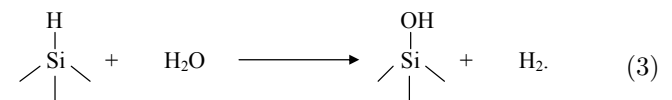
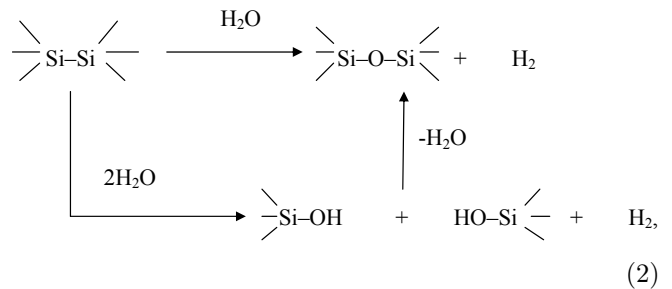
3. Experiment

The release of hydrogen from the samples was initiated by the $\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH}:\text{NH}_3(10\%)$ solution with the volume ratio 5:1:1 (usually 0.2 ml of the solution per 1 mg of the sample). As the molar number of ammonia is much less than that of silicon, it represents a catalyst rather than a reagent. Ethanol favors a better wettability of the samples. In this way, we realized a reaction of the samples with water, whose final products were molecular hydrogen and hydrated silicon oxide (silicic

acid), which can be illustrated by the general scheme:



The interaction of water with the PS surface includes two main processes: the reaction with silicon bonds and the reaction with silane groups:



With the help of a tube, the vessel with a sample in the solution was brought to a measuring cylinder with water sealed from above and immersed into a glass. The gas release was accompanied by a decrease of the level of the water column in the cylinder that determined the volume of H_2 . Systematic errors arising due to the excess pressure of displaced water, the evaporation of a solution, and the solubility of H_2 in water are inessential (< 10%) and were not taken into account.

The samples were treated with molecular H_2 with the help of a hydrogen generator “Gradient-M1”. The steady-state partial pressure of hydrogen equal to 50 kPa was maintained during 15 min. The air was not preliminarily pumped out. The hydrogen capture from the gas phase by the samples was controlled, by measuring the capacity and the resistance of the structure.

The transmission spectra were registered using a Fourier spectrometer Perkin Elmer Spectrum BXII in the range 7800–400 cm^{-1} . For this purpose, we prepared tablets by means of compressing the mixture of the sample powder and KBr. The masses of the sample material and KBr in the mixture related as 1:25.

4. Results and Discussion

4.1. Release of hydrogen from silicon fractions

The hydrogen release intensity in a solution is determined by a part of the porous silicon phase in samples. H_2 is most fast released in mesoPS fabricated according

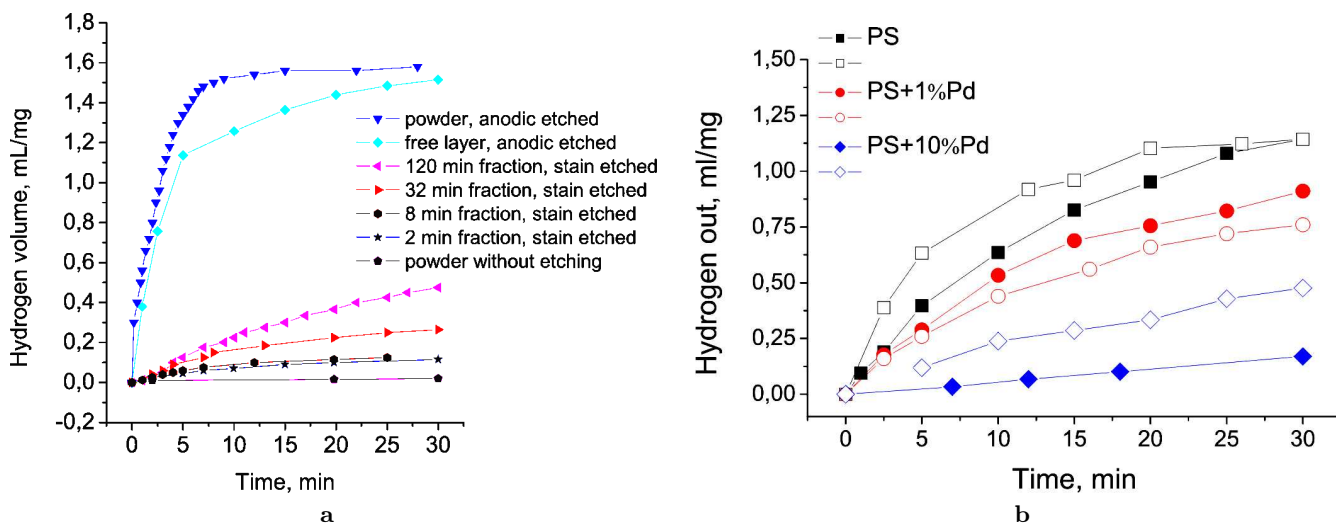


Fig. 1. Kinetics of the hydrogen release during 30 first minutes of the reaction in dark: (a) from various silicon fractions at a temperature of 50 °C; (b) in free PS layers with various content of Pd at 20 °C (solid dots – hydrogen-treated samples, hollow dots – reference samples)

to the anode technology (powder and free layer) (Fig. 1, a). Chemically etched powders (treated with the $\text{H}_2\text{O}:\text{HF}:\text{HNO}_3$ solution) are characterized by the slower rates of H_2 formation which decrease with increase in the size of particles in the fraction. The lowest intensities of the reaction are registered in nonetched silicon powders. It is worth noting that a noticeable reaction of the solution with crystalline Si is initiated at a temperature not lower than 50 °C. At the same time, PS reacts already at room temperature.

The most intense release of hydrogen from PS is observed during the first minutes of the reaction, while the kinetics of gas release has a nonlinear character. Such a behavior of the curve is determined by the immediate breakage of Si–H₃ and Si–H₂ groups. The developed PS surface also considerably intensifies the reactions of Si–Si and Si–H bonds with water. The latter effect makes a noticeable contribution to the rate of H_2 release, as silicon is less resistant to the oxidation as compared with Si–H groups, which is explained by the lower energy of the Si–Si chemical bond as compared with the Si–H one [6].

PS etched according to the anode technology contains the largest amount of the porous phase and, therefore, the higher number of Si–H_x groups with $x \geq 2$ [9]. The chemically etched Si powders have a less developed surface and, respectively, a smaller number of silane groups and larger dimensions of crystalline Si cores. Moreover, such a worsening of the properties becomes more pronounced with increase in the size of particles. These

considerations explain the effect of a decrease of the H_2 release rate with increase in the size of particles in Si fractions (see Fig. 1, a). Nonetched silicon powders do not contain the porous phase and have practically no surface Si–H_x groups. In addition, the surface of nonetched silicon is partially oxidized. This results in the low intensity of H_2 release and the absence of the reaction with water at room temperature. The heating of a solution causes a rise of the penetrability of oxide layers and, therefore, stimulates the reaction.

Considerations of such a kind are confirmed by the corresponding changes of the IR transmission spectra (Fig. 2). Silane Si–H_x ($x = 1, 2, 3$) groups manifest themselves as the absorption zone of valence vibrations (2080–2140 cm^{-1}) and bands of deformation ones (621–663, 906–909 cm^{-1}). After 30 first minutes of the reaction, there remains the only absorption band of a lower intensity with a minimum at 2085–2100 cm^{-1} . The end of the reaction at room temperature is characterized by the complete breakage of Si–H_x bonds, as follows from the disappearance of the corresponding absorption zones in the spectra.

A significant activity of silicon bonds under interaction with water is confirmed by the intense formation of O_3SiH surface fragments at the beginning of the reaction, as one can see from the presence of the absorption bands of valence (2256–2264 cm^{-1}) and deformation (879–882 cm^{-1}) vibrations of the Si–H bond in this fragment. The further reaction results in the breakage of O_3SiH bonds and a considerable decrease of the ab-

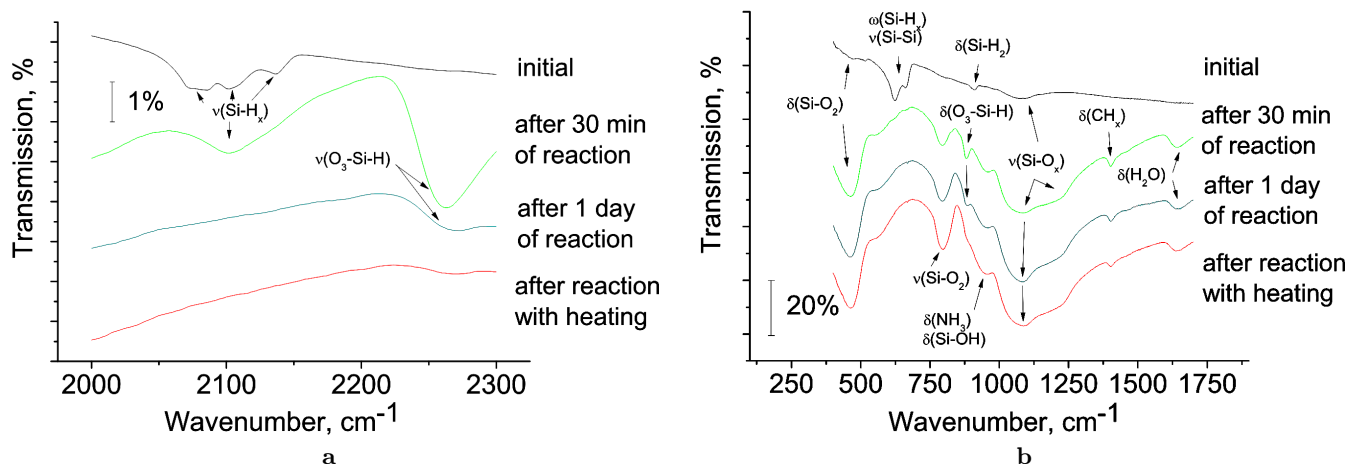


Fig. 2. IR transmission spectra of tablets of free PS layers in various stages of the reaction

sorption in this zone that completely disappears after the heating of the solution to 60–70 °C.

The oxide phase is manifested in the absorption bands corresponding to the valence (1070–1086 cm^{-1}) and the deformation (455–470 cm^{-1} , 798–800 cm^{-1}) vibrations of SiO_2 (Si–O–Si) (Fig. 1, b). We also note the presence of longitudinal SiO_x modes (1152–1220 cm^{-1}) usually observed in SiO_2 films on a silicon substrate in the case of the oblique incidence of p -polarized light [13]. The condition for the appearance of longitudinal modes in tablets is satisfied automatically. The absorption in the spectral bands of oxides considerably grows after the first 30 min of the reaction and, after that, goes on increasing gradually. The band of valence vibrations of Si–O–Si (1070–1086 cm^{-1}) broadens, while its minimum slightly shifts by 3–5 cm^{-1} toward larger wave numbers. This phenomenon is especially pronounced when heating the solution. In other words, the oxide layer becomes wider and denser in the course of the reaction getting closer to the stoichiometric one [13].

The formations related to residuals of the solution in pores of the material and the adsorption of the corresponding molecules also manifest themselves in the spectra. The absorption band in the region of valence vibrations of OH (2600–3780 cm^{-1}) and the peak of deformation vibrations of H_2O (1637–1645 cm^{-1}) are well pronounced in all the stages of the reaction. These regions do not significantly change after the beginning of the reaction. The absorption peak at 952–959 cm^{-1} corresponds to the deformation symmetric vibrations of ammonia. The accompanying peaks of the valence (3334 cm^{-1}) and deformation (1625 cm^{-1}) flexural vibrations of NH_3 must be present in the intense absorption bands

of water [14]. Residuals of ethanol in the structure are manifested as the absorption peaks of the valence symmetric (2852–2860 cm^{-1}), asymmetric (2922–2928 cm^{-1}), and deformation (1398–1410, 1430–1460 cm^{-1}) vibrations of CH_x [15]. The absorption bands of water, alcohol, and ammonia remain intense after the third stage, even in the case of keeping during 3–4 days after the reaction.

The regularities of variation of the IR spectra of Si powders are similar to those of the PS spectra with regard for the lower absorption intensity in the SiH_x region and the higher one – in the Si–O–Si bands.

Continuous observations of the hydrogen release confirm the peculiarities marked out when analyzing the initial moments of the reaction of samples in the solution (see Table). The release of H_2 from PS at room temperature does not last longer than 24 h, and, at the end of the process, the material converts into hydrated oxide. Crystalline silicon in a heated solution (50–70 °C) reacts during a long time (at least several days). Thus, in the samples under study, the breakage of the PS layer comes first and is followed by the interaction of crystalline Si cores with water (under the condition of the heating of the solution that causes an increase of the penetrability of the oxide layer). Moreover, the crystalline phase of silicon is converted into the oxide not completely, which testifies to the possibility to increase the H_2 yield from such structures. The latter statement is confirmed by the following considerations. Comparing the schemes of reactions (3) and (5), that correspond to the cases of crystalline Si and high-quality PS, one can see that the contribution of $\text{SiH}_{1,2}$ groups to the total amount of released hydrogen does not exceed 1/3. The maximum

Hydrogen yield from the samples after a long period and the intensity of its release (V_{H_2} , ν_{H_2} are the hydrogen volume and the release rate, respectively)

Sample	V_{H_2} after 30 min, ml/mg	V_{H_2} at the 30 min, $10^3 \cdot \text{ml/mg} \cdot \text{min}$	V_{H_2} after 18 h, ml/mg	V_{H_2} at the 18th h, $10^3 \cdot \text{ml/mg} \cdot \text{min}$
Reaction at 50 °C				
Nonetched Si powder, 32-min fraction	0,02	0.5	0.13	0.05
Si powder etched with HF, 2-min fraction	0.115	1	0.3	0.07
Si powder etched with HF, 8-min fraction	0.135	1.5	0.45	0.07
Si powder etched with HF, 32-min fraction	0.265	3.3	0.77	0.21
Si powder electrochemically etched with HF	1.58	2	1.6	0
Free PS layer	1.5	6	1.55	0
Reaction at 20 °C				
Free PS layer,	1.14	5	1.3	0
Free PS layer treated with H_2	1.14	14	1.37	0
Free PS layer + 1% Pd	0,76	8	1,14	0
Free PS layer + 1% Pd treated with H_2	0.91	18	1.27	0
Free PS layer + 10% Pd	0,47	10	0,52	0
Free PS layer + 10% Pd treated with H_2	0.16	7	0.17	0

theoretically possible yield of H_2 from crystalline Si is equal to 1.6 l/g and from SiH_2 groups – to 2.24 l/g. In other words, the presence of the crystalline Si phase results in the complication and the slowing-down of the process of hydrogen production as compared with PS rather than in a decrease of the total amount of H_2 that can be released.

4.2. Effect of Pd and hydrogen treatment on the reaction yield

The samples with Pd contain much more the oxide phase and less silane groups as compared with pure PS (Fig. 3, *a, b*), which is explained by the oxidation of Si–Si and Si– H_x bonds at the Pd reduction on the PS surface due to the presence of water admixtures in acetonitrile.

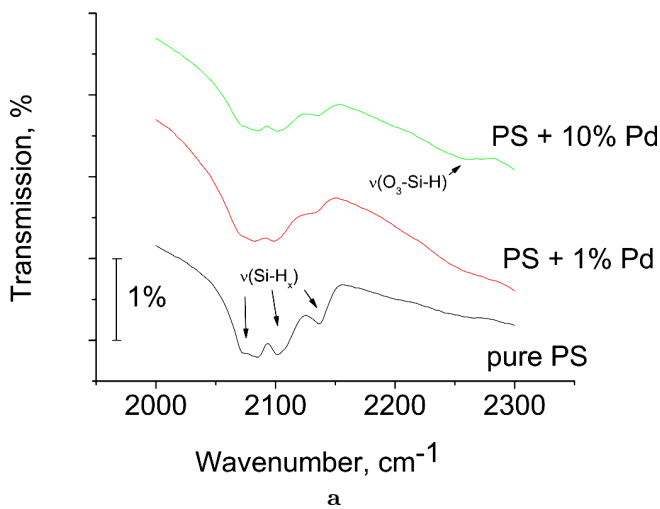
This results in the slowing-down of hydrogen desorption, larger linearity of the kinetic curve (Fig. 1, *b*), and decrease of the total volume of the released gas (see Table). The regularities of the variation of the IR spectra during the reaction are similar to those typical of PS. It is worth noting the retarded breakage of Si– H_x bonds during the reaction with increase in the Pd content in samples (Fig. 3, *c*). This phenomenon is due to the preventing of the penetration of the solution inside the structure by metal particles, as well as the presence of a large initial layer of silicon oxide playing a protecting role.

The pretreatment of samples with molecular H_2 does not considerably influence the kinetics of the reaction (see Fig. 1, *b*). The obtained increment in the hydrogen yield is small as compared with the spread of its initial

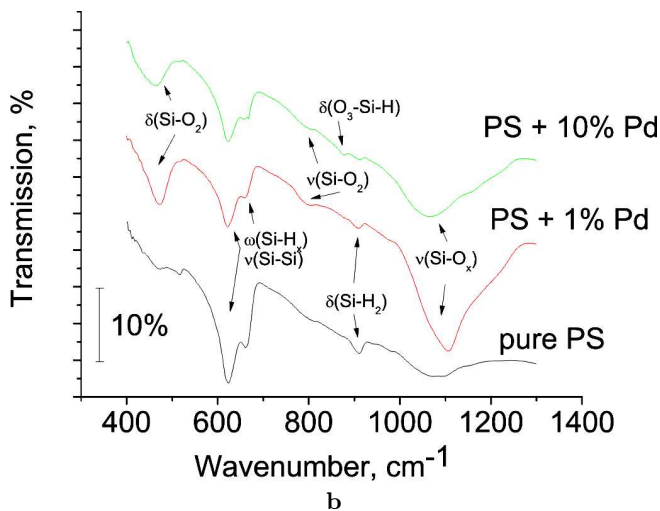
content. Moreover, it is valid both for pure PS and in the presence of Pd. The latter fact is explained by the following reasons. First, composites of PS with Pd include the oxide and palladium silicide phases passive with respect to hydrogen. Second, the presence of oxygen and hydroxyl groups adsorbed at Pd results in their interaction with some part of hydrogen. Third, deposited metal particles are present only in the surface region of the structure (according to the results of studying the side cleavage of the samples with the help of an optical microscope). That is why the expected dissociation and adsorption of hydrogen molecules take place only from the top of a sample rather than over the whole disordered PS surface. Thus, the penetration inside the lattice and to the surface levels due to the splitting into H atoms is stimulated only in the places of the direct Pd–Si contact. In the whole other (deeper) part of the structure, the accumulation of hydrogen takes place in the same way as that for common PS. In this case, the Pd layer impedes the process, as it keeps a part of hydrogen from penetrating inside pores. The direct accumulation of hydrogen in Pd must not considerably influence the reaction yield because of the small amount of the deposited metal.

4.3. Effect of external factors (catalyst concentration, temperature, and illumination) on the kinetics of hydrogen release

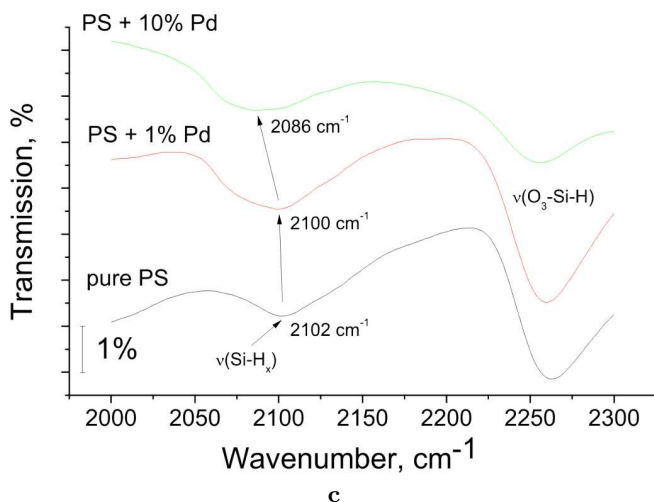
The hydrogen release intensity also depends on a number of external factors such as the catalyst concentration in the solution, temperature, and illumination.



a



b



c

Fig. 3. IR transmission spectra of tablets of samples with various contents of Pd

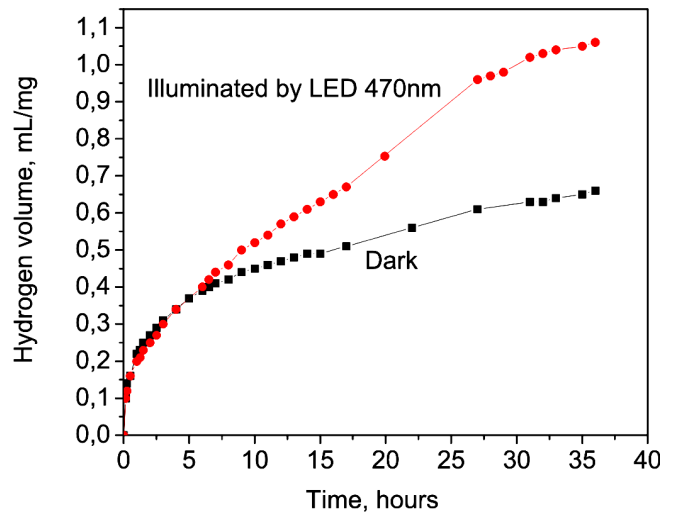


Fig. 4. Kinetics of the hydrogen effusion from the PS fraction (32 min) in the solution under illumination with a light-emitting diode (470 nm) and in dark

The increase in the ammonia concentration in the solution results in the intensification of the reaction. We registered the rise of the H_2 release rate by 5–10% due to the twofold increase in the ammonia concentration. Moreover, no effect of the ammonia percentage on the total hydrogen yield was observed, which confirms the catalytic role of NH_3 .

The hydrogen release intensifies due to the growth of the solution temperature. This fact is explained by a higher intensity of the interaction of water with silicon, as well as an increase in the penetrability of the silicon oxide layer. In addition, the only phase participating in the reaction at room temperature is the porous silicon phase, whereas the heating of the solution to 50 °C activates the reaction of water with the crystalline phase. Respectively, the total yield of hydrogen from PS also increases due to the heating (see Table), as c-Si residuals in the structure also get involved into the reaction. In such a way, one can separate the contributions of the crystalline and porous Si phases to the total hydrogen yield controlling the temperature of the solution.

The illumination of PS favors an increase of the hydrogen yield in the reaction, but has some peculiarities. The illumination by a red light-emitting diode had no effect on the kinetics of H_2 release. At the same time, a blue light-emitting diode (470 nm) resulted in a significant effect (Fig. 4). In this case, the temperature of the solution was stabilized in order to eliminate its influence on the kinetics. Similar results in the case of the ultraviolet illumination were obtained in [16]. It is

worth noting that a relative increase of the H₂ release at the illumination (470 nm) manifests itself after a certain time of the reaction (1–5 h). At the initial moments, the kinetics of illuminated samples is similar to that of unilluminated ones.

5. Conclusions

The most effective hydrogen source is PS prepared by the electrochemical etching technology both with respect to the total content of hydrogen (due to the considerable coating of the surface by SiH_x groups) and the intensity of its release (due to the stimulation of the reaction with water caused by the developed surface of the structure). Pure c-Si powders have the worst characteristics of the H₂ release and require the heating of the solution in order to maintain the reaction. The smaller the particles of silicon fractions and the larger the portion of the porous phase in them, the better they interact with water. The addition of Pd results in a decrease of the hydrogen content in the samples due to the partial oxidation of silicon.

The H₂ release intensity in the reaction of PS with water and a catalyst can be controlled, by changing the ammonia concentration, temperature, and illumination.

The pretreatment of the samples by molecular H₂ results in an insignificant increase of the hydrogen content and does not considerably influence the reaction kinetics. The obtained increment in the hydrogen yield is small as compared with the spread of its initial content. Moreover, it is valid both for pure PS and in the presence of Pd. This phenomenon can be explained by (a) the existence of the silicon oxide and palladium silicide phases which are passive with respect to hydrogen; (b) the presence of oxygen and hydroxyl groups adsorbed at Pd and Si; (c) the presence of Pd particles only in the surface layer of the structure.

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ВИКОРИСТАННЯ У ВОДНЕВІЙ ЕНЕРГЕТИЦІ ПОРОШКІВ І КОМПЗИТІВ НА ОСНОВІ ПОРУВАТОГО ТА КРИСТАЛІЧНОГО КРЕМНІЮ

A.I. Manilov, S.V. Litvinenko, S.O. Alekseev, G.V. Kuznetsov, V.A. Skryshevskiy

Резюме

Досліджено порошки кристалічного кремнію, фракції поруватого кремнію (ПК) та композити на основі ПК і Pd з точки зору їх застосування як твердотільних джерел водню. Виділення H₂ ініціювалось розчинами H₂O:C₂H₅OH:NH₃. Проведено порів-

няльний аналіз цих матеріалів по загальному виходу H_2 (тобто за загальним запасом енергії) і за швидкістю його виділення (тобто за потужністю). Визначено, що найбільш ефективним матеріалом для таких застосувань є порошок ПК, виготовле-

ний за електрохімічною технологією. Показано, що обробка ПК і композитів газоподібним H_2 має незначний вплив на виділення водню цими матеріалами. Досліджено вплив концентрації NH_3 , температури та освітлення на кінетику виділення H_2 .