# The investigation of the porous silicon powder formed by the Pd-assisted chemical etching with different temperatures

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**I.Introduction.** Hydrogen fuel cells are one of the most promising resources and energy-saving technologies as of now. One possible implementation is the generation of electricity by means of the oxidation of alcohol directly in a fuel cell [1-3]. Among the potential benefits of using porous silicon for this purpose can be noted several factors, in particular, high specific surface area and surface chemical reactivity, the possibility of modifying the surface morphology of the porous layers at the nano- and micro levels [7, 8]. The use of porous Si powder in this regard ensures the increasing specific surface area due to the extensive pore network [9] and higher cost-effectiveness because of the low cost metallurgical Si powder.

**II.Sample preparation.** Si powder was treated in a mixture of 0.5 g/L $PdCl_2$ and 0.65 M HC1 aqueous solutions for 30 min at 25 °C. Etching of Si/Pd powder was carried out in a mixture of 40 % aqueous HF solution, 30 % aqueous $H_2O_2$ solution, and deionised water in a volume ratio of 25:10:4 at 25, 50, and 75 °C without thermal stabilization. Etching duration was 30-120 minutes (fig. 1).

**III. Results and discussions.** Etching duration is known to be an essential parameter for the formation of porous materials, especially when etching the powder mainly due to problems such as flotation and possible overetching. Figure 2 shows the micrographs of Si powder etched in $HF/H_2O_2/H_2O$ at 25 °C with the varying duration of the etching.

*Fig.1.*

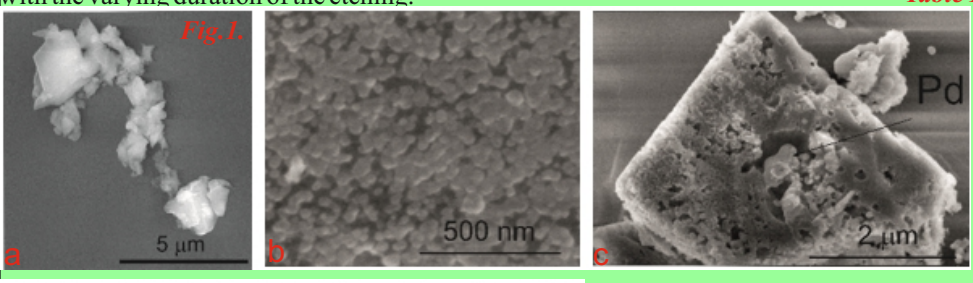


*Fig.2.*

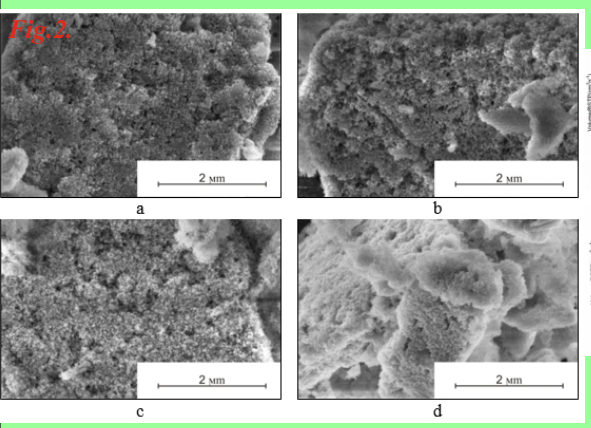


*Fig. 4.*

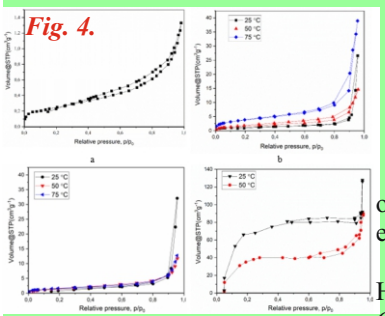

*Fig. 3.*

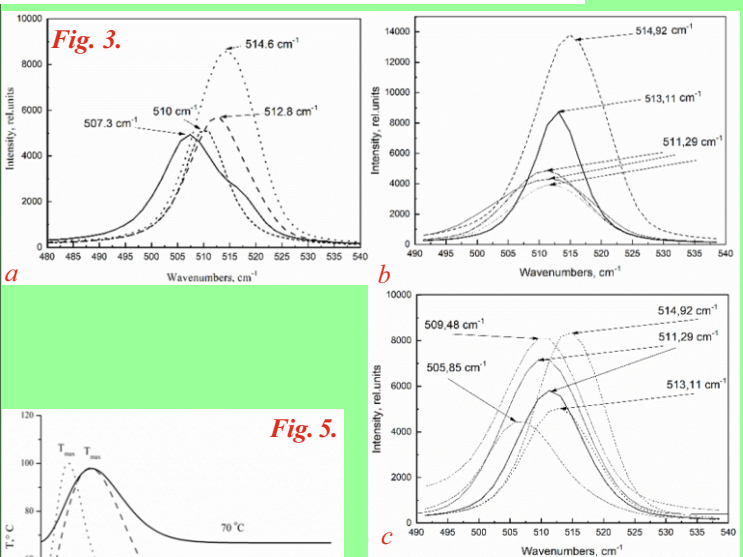


*Fig. 5.*




*Table 1.*

| T, C | t, min | S, $m^2/g$ | V, $\cdot 10^{-3}$ cc/g | d, nm | V, $\cdot 10^{-4}$ cc/g | N, |
|---|---|---|---|---|---|---|
| 25 | 30 | 5.44 | 43 | 41.6 | 19.3 | 5,1227E+13 |
| | 60 | 7.57 | 52 | 41.7 | 18.4 | 4,84+13 |
| | 90 | 19.7 | 196 | 21<br>27<br>32 | 160<br>250<br>1300 | 3,30129E+15<br>2,427E+15<br>7,5808E+15 |
| 50 | 30 | 6 | 22 | 3.67<br>24 | 12.3<br>5.2 | 4,75476E+16<br>7,18772E+13 |
| | 60 | 4.97 | 18 | 3.65<br>31.1 | 11<br>3.82 | 4,32251E+16<br>2,42663E+13 |
| | 90 | 25.9 | 45 | 11<br>28 | 40<br>80 | 5,74253E+15<br>6,96366E+14 |
| 75 | 30 | 13.6 | 60 | 3.7<br>15.8 | 19.1<br>18.8 | 3,88556E+16<br>9,15613E+14 |
| | 60 | 4.67 | 19 | 3.66<br>31.7 | 6.52<br>4.92 | 2,67031E+16<br>2,95127E+13 |
| | 90 | 0 | 0 | - | - | - |

## Description:

***Fig.1.*** SEM images of Si powder (a), Pd nanoparticles on silicon powder (b), porous silicon powder after 120 min etching.

***Fig.2.*** SEM images of Si powder etched in $HF/H_2O_2/H_2O$ (25/10/4) at 25 °C with the duration of 30 (a), 60 (b), 90 (c) and 120 min (d).

***Fig. 3.*** Raman spectra obtained for Si powder etched in $HF/H_2O_2/H_2O$ with 60 min etching at 25 °C (a), 50 °C (b), 75 °C (c).

***Fig. 4.*** Isotherm of $N_2$ adsorption-desorption at 77 K for Si powders before etching (a), after etching at 25 (a), 50 and 75 °C during 30, 60 and 90 min (b).

***Fig. 5.*** Temperature-time dependencies for solutions during the Si powder etching process at different initial temperatures.

***Table 1***. Results of analysis of SEM images and Adsorption-desorption Isotherms of $N_2$ at 77K for Si powder

***Table 2.*** Crystal size of porous Si powder formed by MACE without thermal stabilization at different temperatures of the solution 25/10/4.

*Table 2.*

| Etching duration ($t$), min | Crystal size ($D$), nm $T$ = 25 °C | $T$ = 50 °C | T = 75 °C |
|---|---|---|---|
| 30 | 2-7 | 2 | 2 |
| 60 | 2-4 | 2 | 2 |
| 90 | 2-3 | 2 | full etching |
| 120 | 2-5 | 2 | full etching |

**Conclusions.** We prepared porous Si powder by Pd-assisted chemical etching powders in solutions containing hydrofluoric acid and hydrogen peroxide. In order to develop an approach for controllable synthesis by this simple and cost-effective method, we have investigated the effect of some crucial parameters on the etching process, such as etchant composition, temperature, duration, and powder/etchant ratio. According to the results obtained, the increase of the HF concentration in the etchant leads to the increasing porosity of porous Si powder and the etchant $HF/H_2O_2/H_2O$ with volumetric proportions of components 25/10/4 provides the formation of high porosity silicon powder. Also, we have found the non-linear dependence of the etching rate on the powder/etchant ratio. The specific volume of micropores decreases with increasing etching temperature because of the dissolution of the pore walls and decreasing porosity. That is, overetching occurs. Moreover, Si powder completely dissolves at 75 °C and the etching duration of more than 90 min irrespective of the powder/etchant ratio. We have experimentally shown the necessity of thermal stabilization (cooling) and control of the duration to prevent the overetching of Si powder particles. ***Acknowledgments.*** This investigation was supported by the Russian Science Foundation (project № 19-79-00205). **References.**[1] S. Lazarouk, A. Dolbik, P. Jaguiro, V. Labunov and V. Borisenko. 2005 *Semiconductors* **39** 881.[2] S. Siwal, S. Thakur, Q. Zhang, V. Thakur, 2019 *Materials Today Chemistry* **14** 100182.[3] N. Shrivastava ,T. Harris. 2017 *Encyclopedia of Sustainable Technologies* (Elsevier) Pp. 343-357.[4] T. Dzhafarov and S. Yuksel . 2011 *Alternative Fuel* (Granada: University of Granada press) Pp. 309 – 334.[5] G. Gautier 2014 *Handbook of Porous Silicon* ed. L. Canham (Cham: Springer International Publishing) Pp 957-964.[6] T. Dzhafarov, S. Yuksel. 2011 *J. Nanosci Nanotechnol.* **11** 9012.[7] Z. Huang, N. Geyer, P. Werner, J. De Boor, U. Gösele. 2011 *Advanced Mater.* **23** 285.[8] N. Sing, M. Sahoo, P. Kale. 2018 *Journal of Crystal Growth* **496** 10.[9] K. Kolasinski, B. Unger, A. Ernst, M. Aindow 2019 *Frontiers in Chemistry* **6** 651.