Porous silicon obtained by the metallic thermal reduction of high-purity silica gel

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Abstract. The synthesis and structure of porous silicon obtained through metallothermic reduction of high-purity silica gel is described. The obtained material was a spongy formation of porous amorphous-crystalline silicon. The described reaction is cost effective, rapid, and a simple method to obtain porous silicon particles.

1. Introduction

Porous silicon is a material with unique properties such as high adsorptive activity, catalytic activity, and optical properties [1,2]. The developed surface area can dramatically increase the quantum yield of electrons from electrodes made of porous silicon in electric batteries as well as the possibility of using porous silicon as a cathode with a low electron work function [3,4]. Industrial methods for the preparation of silicon mainly consist of the carbothermic reduction of silicon dioxide [5] and purification by direct chlorination of silicon [6].

Porous silicon nanomaterials are increasingly attractive for biomedical applications, for example, as drug delivery vehicle [7] due to their promising properties such as simple and feasible fabrication procedures, tunable morphology, versatile surface modification routes, biocompatibility and biodegradability [8].

In general, high purity silicon can be produced in two steps [9]: First, a metallothermal reduction material with a high content of silica and magnesium or aluminium is chemically treated with hydrochloric and hydrofluoric acid. The by-products of the reactions are then removed. This process is summarized by the following reaction conducted in an inert argon atmosphere:

\[
SiO_2(s) + 4Mg(s) \rightarrow Si(s) + Mg_2Si(s) + 2MgO(s)
\]  (1)

To maximize the amount of silica and reduce the formation of the silicide, the optimal ratio for the reacting components is a 4.5:5.5 weight ration of Mg: SiO₂. [10]. The metallothermal reaction is highly exothermic and thus an additional material such as NaCl should be added to absorb excess heat [11]. In order to remove the Magnesium silicide and oxide from the product, HCl and HF are used to cause the following reactions:

\[
Mg_2Si(s) + 2HCl(aq) + H_2O(l) \rightarrow MgCl_2(aq) + SiH_4(g) + MgO(s)
\]  (2)
\[ MgO(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2O(l) \]  
\[ SiH_4(g) + 2O_2(g) \rightarrow SiO_2(s) + 2H_2O \]  
\[ SiO_2(s) + 4HF(aq) \rightarrow SiF_4(g) + 2H_2O(l) \]

In the process of adding HCl, the powders obtained from the thermochemical reactions (1), the silicon powder settles to the bottom of the reaction vessel and magnesium chloride goes into solution and can be removed by filtration with water. The silane (SiH\textsubscript{4}) gas combines with oxygen and ignites spontaneously to form silicon dioxide and water by reaction (4). This new mixture is then treated with concentrated hydrofluoric acid, HF, to remove the remaining silicon dioxide by producing silicon tetrafluoride (SiF\textsubscript{4}) and water (reaction (5)).

Usually, porous silicon is produced on the surface of monocrystalline silicon for the needs of electronic devices (photoluminescence) [12]. However, powdered porous silicon is not usually produced. The present work aims to address this issue and give a way to simply obtain chemically pure porous silicon powders. The synthesis of porous silicon with a high specific surface area and a nanoscale structure from high purity silica gel is presented. These powders have potential to be used as carrier particles in medicine and biotechnology [13]. In addition structure makes it a prospective material for catalysts, microelectronics, and conductive materials.

2. Experimental section

High-purity silica gel for chromatography (PURASIL TM 60Å) with grains of 63-200 microns were used as the starting silicon source. The reducing agent was chemically pure magnesium powder (Russian standard 6001-79). For comparison, instead of pure magnesium powder, waste magnesium from aircraft production was also tested (ML10, ML12, MI19 from Russian standard 2856-79 and wrought-MA8, MA8 from Russian standard 14957-76) which contain alloying elements that are readily soluble in inorganic acids. Synthesis was carried out in a steel reaction apparatus as shown in Figure 1. Argon was used as a protective inert gas at high-temperature synthesis of silicon in the working space of the reactor (Fig. 1.).

![Figure 1. Schematic of the steel reaction apparatus.](image)

1 - End cap, 2 – reaction chamber, 3 – sealing cap, 4 - nozzle for feeding in argon gas and for locking the working space of the reaction chamber, 5 – copper sealing washer.

High-purity silica was thoroughly mixed with magnesium in a ratio of 5.5:4.5 by weight. To absorb heat from the exothermic reduction reaction and to preventing sintering of the produced particles, NaCl was added in an amount of 1:1 and 1:2 by weight relative to the silica-magnesium powder. In previous works, ratios of 1:10 were used [11]. The powders were placed in the reaction apparatus, filled with argon, then placed in a preheated oven at 700 °C.
The reaction time was 1 to 2 hours; depending on the quantity of NaCl. Such a temperature is required for evaporation of the active magnesium reducing agent. The NaCl was washed out from the reduced product containing silica, magnesium silicate, and magnesium oxide by filtration with distilled water. The powders were then dried and treated with concentrated hydrochloric acid followed by thorough washing in distilled water. Finally a treatment with hydrofluoric acid was performed followed by filtration and washing.

The final powders were analysed using energy dispersive X-ray fluorescence analysis (EDX), X-ray diffraction (XRD), surface area analysis, Fourier transform infrared spectrometry (FTIR), and scanning electron microscopy. EDX and SEM were performed on a SEM JEOL 6510 LV (accelerating voltage 30 kV, a resolution of 3 nm). XRD was performed on a D8 ADVANCE Bruker, Germany (CuKα radiation with a wavelength of 0.15418 nm). Determination of the specific surface area was performed on a "Sorbie-M", Novosibirsk, Russia. FTIR was performed on a Shimadzu-8300 at a resolution of 4 cm⁻¹ with 200 scans.

3. Results and Discussion

XRD analysis of the synthesized powders before any post-process treatments is shown in Figure 2. The analysis revealed the presence of crystalline Si, MgO, MgSiO₃, and an amorphous component amounting to about 56.2 wt% of the sample. It was interesting and unexpected that no Mg₂Si was formed and instead the magnesium silicate MgSiO₃ was formed. It appeared that when the powder was treated with HCl no combustion was observed and thus it is likely that the reaction

\[
MgSiO₃(s) + HCl(aq) \rightarrow MgCl₂(aq) + SiO₂(s) + H₂O(l)
\]  

occurred as SiH₄ did not form through equation (2). Thus, the formation of MgSiO₃ instead of Mg₂Si makes the synthesis safer.
Figure 3. IR spectrum of the silicon powder obtained from the silica gel before treatment.

The IR spectrum of the synthesized powder before any treatments is shown in Figure 3 to investigate possible components of the amorphous phase. Hydrides of silicon were found (possibly with magnesium) around the 2100 cm⁻¹ band. Silica was present in the sample as evidenced by the bands at 480, 875, and 1080 cm⁻¹. Silica was also identified by the SiOH group at 3742 cm⁻¹. The amount of silica is low, since the intensity of the 3742 cm⁻¹ bands are significantly lower compared with the hydrides and it is well-known that the extinction coefficients of SiH bands are significantly lower compared to SiOH bands.

To determine the proportion of silicon oxide and silicon metal in a sample was not possible as the bands used to identify silicon at 562 and 620 cm⁻¹ likely to belong to the defect structure of silicon metal and the defects for different silicon samples can vary greatly. However, if this is not taken into account, it can be estimated that silica makes up only 1-2wt% of the amorphous component. It follows that most of the synthesized was in the amorphous state.

Figure 4. SEM images of the final silicon powder after treatment with HCl and HF which were synthesized with a)Mg powders and b) magnesium alloy chips.

SEM images of synthesized and treated silicon powders are shown in Figure 4; from two different magnesium sources. It is shown that the powders have a spongy structure and the final appearance did not change significantly between them. Other analyses did not show significant differences and so waste magnesium alloys can also be used to reduce the cost of the synthesis.

The high porosity and open structure of the silica gel used in this synthesis reduced the synthesis time required to produce porous silicon powders compared to previous reports such as in [9] which used sand as the starting material. When the reactant,NaCl ratio was 1:1, the specific surface area for the
The specific surface of the synthesized silica was lower compared to the specific surface of the silica gel (250-350 m²/g) [14]. It is expected that the main cause of porosity for the resultant silicon is a retention of the structure of the silica gel which is thermally stable to 900 °C. Some silicon may have been released from the starting structure during the synthesis and treatment processes and later re-condensed onto the silica/silicon and NaCl – resulting in some decrease of the surface area. With higher NaCl content, the released silicon may have condensed onto NaCl (m.p. ~ 800 °C) more than the porous silica/silicon and formed denser structures which reduced the overall surface area of the sample.

TEM analysis results show that silicon is stood out in the form of a porous, the pore size of less than 10 nm and above (Figure 5). Moreover, silicon is linked together in the form of crossed fibers with a diameter of about 10 nm. Such a structure is particularly important for making electrodes with high surface area, which enhances electron emission.

Figure 5. TEM images of the final silicon powder after treatment with HCl and HF which were synthesized with Mg powders:

a – x12000, (b, c) - x50000, d - x150000.
Elemental analysis EDX (Figure 6) showed only silicon and oxygen. Some oxidation may have occurred after removal of the reacted powders from the argon environment and treatment process. Thus oxidation may be hindered if the treatments are performed in a reducing (CO, H₂) or inert (N₂, Ag) atmosphere. Additionally, it was observed that less oxidation was present in the samples produced from waste magnesium trimmings. Further studies will be required to investigate the effects of the alloying elements in the waste magnesium trimmings on the synthesis process.

![Figure 6](image)

**Figure 6.** a) SEM image of obtained porous silicon. b) EDX analysis of the porous silicon powder.

### 4. Conclusion

The synthesis process of porous silicon powders were demonstrated. The synthesis utilizes silica gel heated to 700 °C with magnesium and NaCl. It was shown that waste magnesium trimmings can be used instead of pure magnesium powders which can further reduce the synthesis costs. Further, the synthesis times were short at about 1-2 hours. Post treatment processes involve washing the synthesized powders with HCl and HF. The resultant silicon had a spongy, mainly amorphous structure and had specific surface areas between 160-200 m²/g.

### 5. Acknowledgments

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