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# Synthesis of composite Si@C nanopowders in a cyclic compression reactor for anodes of lithium-ion batteries

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Pyrolysis of a mixture of monosilane with light hydrocarbons in an argon atmosphere in a cyclic compression reactor was used to synthesize nanoparticles with a crystalline silicon core and a carbon shell. The resulting powders were tested as an anode material for lithium-ion batteries. It is shown that the maximum reversible electrochemical capacity is 603 and 242 mA · h/g at current densities of 0.05 and 2 A/g, respectively.

**Keywords:** composite nanopowders Si@C, chemical compression reactor, anode materials, lithium-ion batteries.

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Crystalline silicon is considered to be a promising candidate anodic material for lithium-ion batteries, since it features a high theoretical specific capacity of 3579 mA · h/g, whereas graphite anodes provide only 372 mA · h/g [1]. However, silicon expands by more than 300% in the course of charging. The structure of silicon particles is disrupted in the process, and the anodic material degrades rapidly (within the first few charge–discharge cycles [2]). Various approaches for preventing the mechanical breakdown of silicon crystalline structures have been proposed. One of them involves the application of core–shell structures with a silicon core and a carbon shell [3]. A carbon shell formed from graphene sheets does not obstruct the access of lithium ions to silicon, but keeps a silicon core from breaking down in charge–discharge cycles. The authors of [1] have produced Si@C core–shell structures with a silicon core and a carbon shell by processing crystalline silicon powder with phenolic resin in a solvent with subsequent annealing. The reported specific capacity of this anodic material of lithium-ion batteries was as high as 3092 mA · h/g in the first cycle (i.e., was close to the theoretical limit). Silicon nanoparticles were used in [3] to produce Si@C core–shell structures. A carbon shell of graphene sheets was fabricated by electrolytic exfoliation of graphite in molten LiCl, and silicon nanoparticles were then injected into the molten salt. The achieved values of electrochemical capacity were also high (about 2000 mA · h/g). However, these multistage methods for synthesis of Si@C structures are fairly costly and labor-intensive. They require the use of high-cost silicon materials and additional thermal, chemical, and electrochemical procedures.

In the present study, Si@C structures were synthesized in a cyclic compression reactor, where pyrolysis of a mixture of monosilane with light hydrocarbons was performed [4]. The reactor, which is a piston–cylinder system, has proven itself efficient in pyrolysis of monosilane and production of silicon nanoparticles [5]. Its working volume is 0.3 l, the stroke rate is 10 Hz, and the piston diameter is 40 mm. High pressure and temperature values are established within the reactor volume in the vicinity of the top dead center (TDC) piston position. The maximum pressure at TDC is 12 MPa. Pyrolysis was performed in an argon atmosphere in order to raise the adiabatic exponent (and, consequently, temperature). The pressure range in pyrolysis of monosilane with hydrocarbons was 3.5–8.5 MPa. These values are slightly higher than those corresponding to monosilane pyrolysis (2–5 MPa) [5].

The electrochemical properties of samples were examined in „button“ CR2032 cells with a lithium secondary electrode. Working electrodes were fabricated by rolling the electrode material. Samples (80 mass%), super P (10 mass%), and polyvinylidene fluoride (10 mass%) were mixed with N-methyl-2-pyrrolidone, and the prepared suspension was deposited onto copper foil 14 mm in diameter and 0.02 mm in thickness and dried at 100°C within 12 h in vacuum. A 1.0 M solution of $LiPF_6$ in an ethylene carbonate/dimethyl carbonate mixture (1:1 by volume) was used as the electrolyte. The obtained cells were tested in the galvanostatic mode at a NEWARE CT-3008 charge–discharge system within the interval from 0.01 to 2.5 V at a current density of 0.05–2 A/g.

TEM (transmission electron microscopy) images presented in Fig. 1 reveal that nanoparticles in samples Nos. 3 and 4 (Table 1) have crystalline cores and a carbon shell. Interplanar distances of 3.12 and 3.06 Å correspond to the interplanar distance of silicon ($d_{111}$), while 2.49 and 2.5 Å correspond to the Interplanar distance of silicon carbide ($d_{111}$). Purely carbon nanoparticles are also present. Raman scattering spectroscopy performed using a T64000 (Horiba Jobin Yvon) spectrometer with a micro-Raman setup based on a BX41 (Olympus, Japan) optical microscope revealed the presence of silicon peaks (500 $\text{cm}^{-1}$),

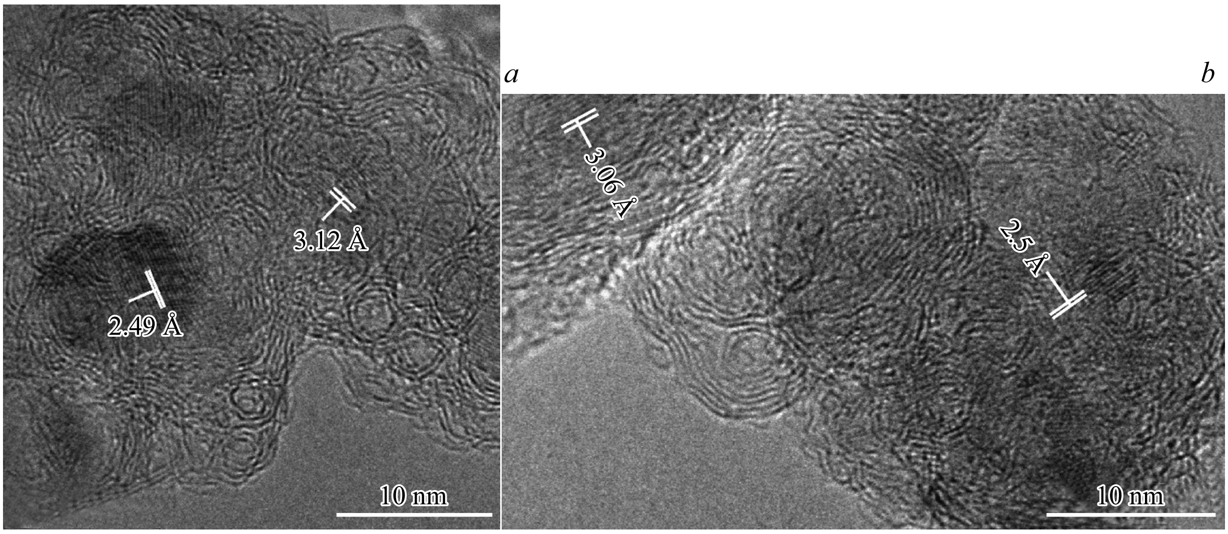

**Figure 1.** TEM images of nanoparticles with nanoscale Si and SiC crystallites coated with graphene layers. *a* — sample No. 4, *b* — sample No. 3.

**Table 1.** Conditions of synthesis of silicon–carbon nanopowders

| Sample number | Gas mixture composition | Pressure at TDC, MPa |
|---|---|---|
| 1 | $SiH_4$ — 5%, $C_2H_4$ — 5%, Ar — 90% | 3.5–4.0 |
| 2 | $SiH_4$ — 5%, $C_2H_4$ — 5%, Ar — 90% | 5.0–5.5 |
| 3 | $SiH_4$ — 5%, $C_2H_4$ — 5%, Ar — 90% | 8.0–8.5 |
| 4 | $SiH_4$ — 8%, $C_3H_8$ — 17%, Ar — 75% | 7.0 |

silicon carbide peaks ($920\,\mathrm{cm}^{-1}$), and the so-called $D$ ($1340\,\mathrm{cm}^{-1}$) and $G$ ($1590\,\mathrm{cm}^{-1}$) peaks, which correspond principally to $sp^2$-hybridized carbon. X-ray diffraction analysis (XRD) was carried out with an automatic Philips PW 1830/1710 diffractometer (Cu$K_\alpha$ radiation, graphite monochromator) and revealed crystalline Si and SiC (Table 2).

Figures 2, $a, b$ present the charge–discharge curves in the first three cycles. It is evident that the curves of samples Nos. 1 and 2 are similar in shape and the curve corresponding to the first lithiation cycle is irreproducible (apparently, this is attributable to the formation of a solid electrolyte interface, SEI) [6]. Two plateaus (at 0.75 and 0.35 V) were found in the process of lithiation. Three plateaus (at 1.3, 0.7, and 0.35 V) were observed in the first delithiation cycle for both samples.

The results of electrochemical cycling of samples at different current densities (Fig. 3) revealed that sample No. 3 has the lowest capacity. This may be attributed to the abundance of silicon carbide, which does not interact with lithium, in the material of this sample.

Samples Nos. 1 and 2 demonstrate similar specific capacities at a current density of 0.05 A/g, since the percentages of silicon in them are also close. The capacity of both samples becomes reproducible following the formation of a SEI within the first five cycles. However, the capacity of sample No. 1 at high current densities was $242\,\mathrm{mA\cdot h/g}$, while sample No. 2 had only $111\,\mathrm{mA\cdot h/g}$. This two-fold capacity variation is indicative of differences in the structure parameters of the carbon phase, which supports the accumulation of lithium both via intercalation and sorption/desorption of lithium at defects.

Thus, varying the synthesis parameters, one may affect the processes of interaction with lithium by altering the composition and defect structure of the Si/SiC/C material. It was found in the process of electrochemical testing of the obtained materials in a lithium-ion cell that materials produced at higher pressures and temperatures degrade rapidly during cycling. This may be associated with the formation of a hard graphite shell and silicon carbide. Significant capacity losses due to irreversible lithium sorption were noted in the material with a high percentage of SiC.

The silicon–carbon composite material produced under mild synthesis conditions with a maximum pressure of 3.5–4.0 MPa demonstrates a stable cyclable capacity of 603 and $242\,\mathrm{mA\cdot h/g}$ at a current density of 0.05 and 2 A/g, thus exceeding considerably the capabilities of graphite anodic materials. In our view, significant differences between the measured capacities and theoretical values are attributable to the presence of a greater percentage of purely

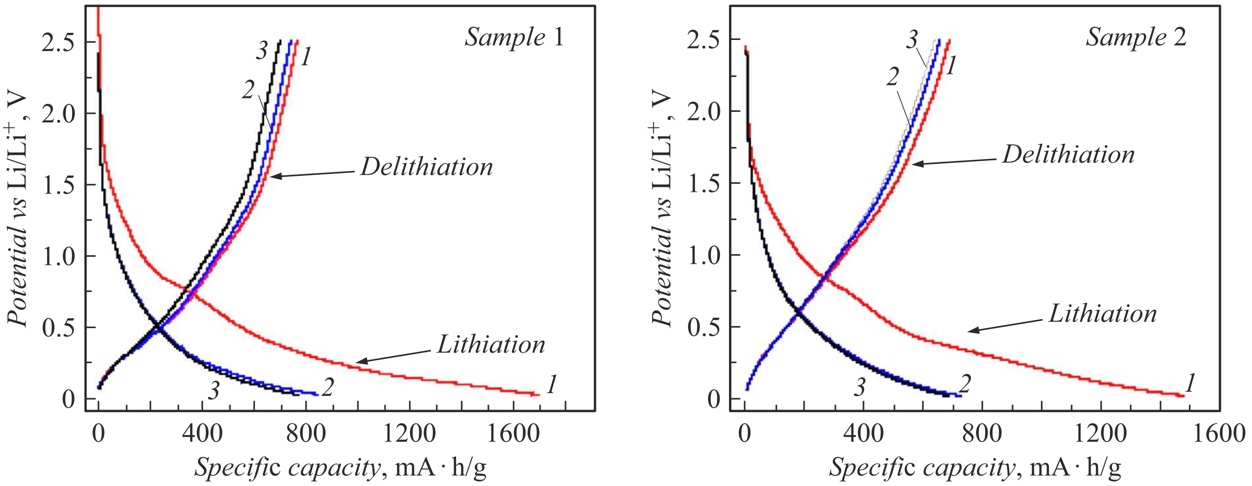

**Figure 2.** Charge–discharge curves in the first three cycles at a current density of 0.05 A/g for samples Nos. 1 and 2. The numbers next to curves correspond to the numbers of cycles.

**Table 2.** Percentage of silicon and silicon carbide determined by XRD and electrochemical properties of samples

| Sample number | Si, % | SiC, % | Specific capacity, mA · h/g | |
|---|---|---|---|---|
| | | | at a current of 0.05 A/g | at a current of 2 A/g |
| 1 | 55 | 45 | 603 | 242 |
| 2 | 44 | 56 | 552 | 111 |
| 3 | 24 | 76 | 90 | 3 |

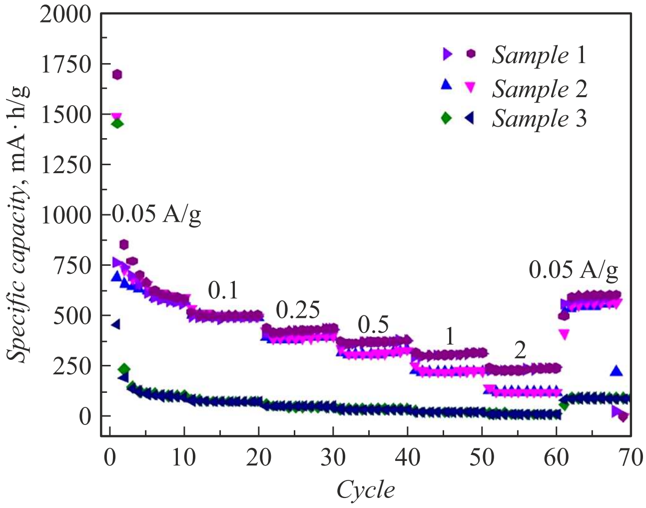

**Figure 3.** Dependence of the specific capacity on the charge–discharge cycle number at current densities of 0.05–2 A/g for samples Nos. 1–3.

carbon and SiC-containing phases. The characteristics of obtained anodic materials may be improved substantially by optimizing the synthesis parameters (including pressure and stoichiometric composition of the gas mixture). Separation, purification, and enrichment of the synthesized product (with the use of, e.g., gravimetric methods) should allow one to produce an anodic material with electrochemical parameters close to the theoretical limits.

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## Conflict of interest

The authors declare that they have no conflict of interest.

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