

Electroreduction of silicon from the NaI–KI–K₂SiF₆ melt for lithium-ion power sources

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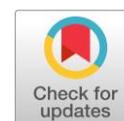
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This paper belongs to a Regular Issue.

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Abstract

Silicon and silicon-based materials are increasingly used in microelectronics, metallurgy and power generation. To date, the active study aimed at the development of silicon materials to be used in devices for solar energy conversion, accumulation and storage is underway. In addition, silicon is a promising anode material for lithium-ion fuel cells. In the present paper, a possibility of silicon electroreduction from the NaI–KI–K₂SiF₆ melt in the argon atmosphere was studied. With this aim in view, the electrolysis of the NaI–KI–K₂SiF₆ melt with glassy carbon cathode was performed under galvanostatic and potentiostatic regimes at the temperatures from 650 to 750 °C. The morphology, phase and elemental analyses of the obtained silicon deposits were performed after their separation from the electrolytes by the ICP, SEM-EDX, XRD and Raman spectroscopy methods. Fiber and thread-like silicon samples of 60 to 320 nm in diameter with admixture concentrations (mainly oxygen) from 1.2 to 4.6 wt.% were synthesized. The obtained samples were tested as possible Si/C composite anodes for lithium-ion power sources. The discharge capacity of such power sources after 30 cycles of lithiation-delithiation ranged from 440 to 565 mAh·g⁻¹, and the coulombic efficiency ranged from 89 to 91%.

Keywords

silicon
nanofibers
electroreduction
melt
lithium-ion power source
cycling

Received: 21.10.22

Revised: 01.12.22

Accepted: 01.12.22

Available online: 06.12.22

Key findings

- The possibility of electrodeposition of silicon deposits with a developed surface from the NaI–KI–K₂SiF₆ melt at a temperature from 650 to 750 °C was shown for the first time.
- The energy characteristics of the obtained silicon in the anode material of a lithium-ion current source during cycling were determined.

1. Introduction

Silicon and silicon-based materials are becoming widely used in microelectronics, metallurgy and power generation [1]. Silicon materials to be used in devices for solar energy conversion, accumulation and storage are being actively developed [2–4]. Silicon is a promising anode material for lithium-ion power sources because its specific lithium-adsorption capacity (4200 mAh·g⁻¹) is by an order of magnitude higher than those of graphite-containing anode materials (372 mAh·g⁻¹) [5–7]. However, high silicon anode lithium-adsorption capacity implies a significant volume expansion (up to 300%) that may result either in destruction of the power source or in the contact fault between the anode material and the substrate (current collector).

Application of composite materials based on nano-size or submicron silicon particles is one of the possible ways to solve this problem [8, 9].

The methods of carbothermal reduction of quartz followed by refining the obtained silicon from admixtures via chlorination and hydration [10] were implemented in the industrial scale, but thus-obtained silicon has a form of crystals of several tens of μm in size. To obtain nano-size silicon crystals, relatively complex and expensive methods of laser ablation, plasma chemical synthesis, laser-induced dissociation, etc. [11], are known. These methods are unsuitable for industrial silicon production.

Methods of silicon electroreduction from molten salts for producing the nano- and micro-sized silicon with

controlled morphology are industrially promising, relatively simple and inexpensive.

Fluoride mixtures of KF–NaF–LiF, LiF–NaF, LiF–CaF₂ and similar compositions were suggested as first possible electrolytes for silicon production at the process temperatures ranging from 500 to 1500 °C [12–14]. However, their main drawback was the difficulty of separating the fluoride residues from the cathode deposits because of their low solubility in water and high boiling temperatures. High chemical aggressiveness to the reactor materials is the main disadvantage of fluoride melts, which limits the possible range of their application and leads to the complication of the reactor construction as well as to the silicon contamination by the corrosion products.

The KCl–KF system with KF concentration up to 66 mol.% was suggested as a water-soluble electrolyte that is a good solvent for both K₂SiF₆ and SiO₂ [15–17]. A relative aggressiveness of KF to the reactor materials and a required decontamination of KF from H₂O and HF during the molten KCl–KF mixture preparation are the disadvantages of the method of electrolytic silicon production. All mentioned factors may cause the melt composition instability and appearance of the admixtures in the obtained silicon.

Molten electrolytes based on CaCl₂–CaO, where SiO₂ is a source of silicon, were extensively studied for the electrolytic silicon production [18–20]. The advantages of these electrolytes include high CaCl₂ solubility in water that allows separating deposits from the electrolyte residues after the electrolysis and lower chemical aggressiveness, as compared with fluorite salts, to the reactor materials. Among the disadvantages of this method, we should mention a relatively high temperature, unstable composition of electroactive ions in the molten electrolyte and presence of oxide admixtures, which causes inevitable appearance of oxygen in the silicon deposit bulk.

To decrease the electrolysis temperature, stabilize the composition of the silicon-containing electroactive particles and to control the morphology of silicon deposits, the melts containing iodides may be used. In particular, the KCl–KF–KI–K₂SiF₆ system containing KI up to 75 mol.% [21] is assumed to eliminate the presence of water traces in the reactor and, therefore, the requirements to the preparation of the molten electrolytes and equipment used increase.

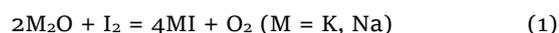
Electrodeposition of silicon and silicon-based materials from low-temperature ionic liquids and organic electrolytes is also a promising direction [22–26]. However, the productivity of such methods seems to be relatively low, and the organization of feeding the electrolyzer with SiCl₄ is more complex and requires additional equipment.

In this work, we studied the possibility of electrodeposition of fibrous silicon deposits from the NaI–KI–K₂SiF₆ melt as well as the cycle ability of the obtained silicon deposits in the lithium-ion current sources with silicon-based anodes. The selected melt is promising for silicon electrodeposition, since it has a relatively wide range of compositions with a liquidus temperature below 700 °C [27].

2. Experimental

2.1. Electrolyte preparation

Electrolytes for silicon electroreduction were prepared in a glassy carbon crucible from commercial chemically pure individual NaI and KI salts (Reakhim, Russia) and commercial reagent grade K₂SiF₆ (Reakhim, Russia), which was preliminary subjected to hydrofluorination by stepwise heating to 450 °C in the mixture with NH₄F [28]. The salt mixture of (wt.%) 56NaI–44KI was purified from oxygen and other admixtures immediately prior to the experiments. The salts were mixed with elemental iodine, heated stepwise to 400 °C and exposed for 3–4 h. The evaporating iodine interacted with oxides according to reaction (1) [21]:



After this, the mixture was heated to the working temperature, and the obtained melt was additionally subjected to the galvanostatic electrolysis at the cathode current density of 0.02 A·cm⁻² during 2–4 h. A graphite cathode and an insoluble glassy-carbon anode (crucible) were used. The electrolysis durability was determined empirically by the moment of shifting the electrode potential to the potential of alkali metal electroreduction. During the electrolysis, electropositive admixtures (Fe, Ni and etc.) were deposited on the cathode and removed from the reactor with a cathode.

2.2. Reactor for the silicon synthesis

The experiments on the silicon electroreduction were performed at the temperatures from 650 to 750 °C in a hermetically sealed quartz reactor with the pure argon atmosphere. A glassy carbon container with a molten electrolyte was located at the bottom of the reactor. The walls of the reactor were screened with nickel foil to protect them from possible salt vapors. The electrodes and the control thermocouple were assembled to the fluoroplastic cover of the reactor. Cylindrical graphite bars of the MPG8 grade (TechnoCarb company, Chelyabinsk, Russia) were preliminary rinsed in acidic water solution and dried under vacuum. These bars served as working electrodes. Monocrystalline silicon (99.9999 wt.%) was used as a counter electrode and a quasi-reference electrode.

The silicon electroreduction from the NaI–KI melt with the addition of 7 wt.% of K₂SiF₆ was performed under the potentiostatic regime at the cathode overpotential of 0.2 V and under galvanostatic regime at the cathode current density ranging from 1 to 5 mA·cm⁻². The parameters of the electrolysis were determined during the process of silicon electroreduction in halide melts in the temperature range of 700–750 °C [15–17, 29]. The electrolysis was performed using a PGSTAT AutoLAB device with the Nova 1.12 software (Metrohm, Netherlands). When the electrolysis was terminated, the deposits were lifted from the melt, cooled down to room temperature and then removed from the reactor.

The electrolyte residues were removed from the deposits by the high-temperature distillation under the argon flow at 950 °C for 6–8 h. During this procedure, cathode sediments with the salt residues were heated in argon to a temperature of 950 °C. In these conditions, the component with the highest vapor pressure (salts) evaporated and crystallized in the cold part of the distillation device [30]. The conventional method (washing out electrolyte residues in water-acid solutions) is less effective in the case of fibrous deposits, since it leads to silicon oxidation and its significant losses.

2.3. Analysis of the melts and deposits

The concentration of silicon in the melt before and after the electrochemical measurements and electrolysis was determined using the atomic-emission method by an iCAP 6300 Duo spectrometer (Thermo Scientific, USA). The morphology of the obtained deposits was studied using a scanning electron microscope Tescan Vega 4 (Tescan, Czech Republic) with an Xplore 30 EDS attachment (Oxford, Great Britain). The phase composition and the presence of Si–Si and Si–O bounds were determined by the XRD and Raman spectroscopy methods using a “Leica DMLM” microscope and “Renishaw U1000” spectroscope (Great Britain) equipped with a notch-filter and CCD camera (solid state laser produced by Cobolt Samba company (Sweden) of the 50 mW capacity).

2.4. Electrochemical characteristics of silicon

The electrochemical characteristics of the obtained silicon powders at lithiation/delithiation were tested in the composition of the composite anode of the lithium-ion power source containing (wt.%): 80 – silicon, 10 – carbon, 10 – bounding polyvinylidene difluoride dissolved in N-methyl-2-pyrrolidone. The samples of lithium-ion power sources were assembled in a hermetically sealed argon box with the concentration of admixtures (O₂, H₂O) not exceeding 0.1 ppm. The anode material was spreaded on the steel net, a lithium foil served both as a counter electrode and as a reference electrode. All electrodes were separated from each other by two separator layers. A solution of LiPF₆ in the mixture of ethylene carbonate/dimethyl carbonate/diethyl carbonate was used as the electrolyte. The purity of all elements used was 99.99 wt.% (Sigma-Aldrich, Germany). The measurements were performed by the galvanostatic cycling using a multichannel potentiostat Wonatech WBCS-3000 M2 (WonATech Co., Ltd., Korea).

3. Results ana Discussion

3.1. Silicon electroreduction

The parameters and results of the silicon electroreduction are illustrated in Table 1. Depending on temperature, electrolysis regime and parameters, fiber and thread-like silicon deposits of 50 to 320 nm in diameter and up to 20 μm in length were primarily obtained on the graphite cathode. The microphotographs of the typical deposits are presented in Figures 1 and 2. According to the EDS analysis, the

concentration of admixtures in the obtained silicon varied from 1.2 to 4.6 wt.%. Oxygen was the main admixture. We have not been able yet to determine whether it is a surface oxide or a bulk one. However, we assume that this is surface oxygen and oxidated Si, since the methods and devices used allow the electrodeposition to be carried out as cleanly as possible.

Figures 3 and 4 provide the X-ray diffraction pattern and Raman spectra of the obtained silicon deposit. It is seen that the sample has the form of polycrystalline silicon with SiO₂ admixtures. Only a Si–Si bond is observed, which testifies that there is no interaction between the deposited silicon and the carbon substrate under the experiment conditions.

3.2. Electrochemical characteristics of silicon

Figure 5 provides potential dependencies of Si/C composite anodes, fabricated from the fiber (sample 1) and thread-like (sample 2) silicon deposits, in the composition of the experimental lithium-ion power sources, during their first lithiation/delithiation cycle (forming cycling). It is seen that the anode is subjected to charging and discharging, which proves the possibility of application of such anodes in lithium-ion power sources.

Table 1 Parameters and results of silicon electroreduction from the NaI-KI melt with addition of 7 wt.% of K₂SiF₆.

No.	t , °C	i , mA cm ⁻²	Over-potential, V	Time, min	Deposit
1	650	1	–	60	Fibers, Ø 60–160 nm
2	700	–	0.2	40	Threads, Ø 130–200 nm
3	750	5	–	25	Fibers, Ø 90–320 nm

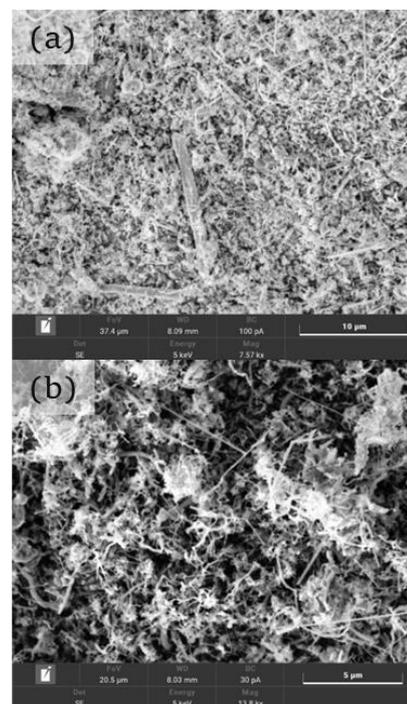


Figure 1 Microphotographs of a typical fiber silicon deposit obtained by the electrolysis of the NaI-KI-K₂SiF₆ melt at a cathode current density of 5 mA cm⁻² and 750 °C before (a) and after (b) the electrolyte residues removal.

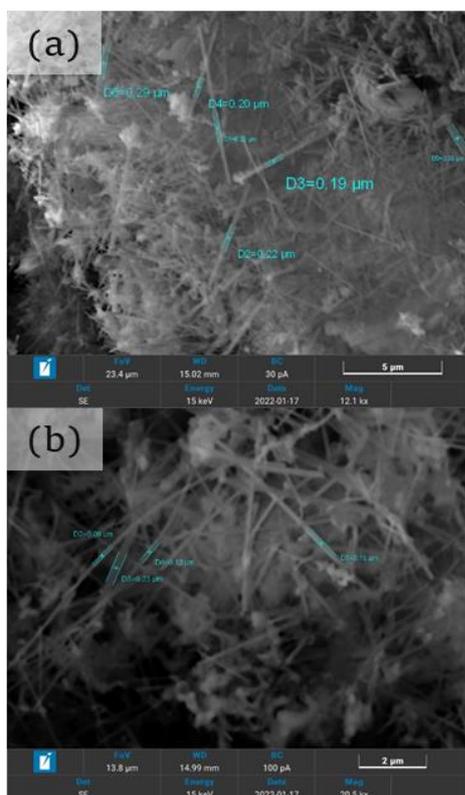


Figure 2 Microphotographs of a typical thread-like silicon deposit obtained by the electrolysis of the NaI-KI-K₂SiF₆ melt at 700 °C and cathode overpotential of 0.2 V after the electrolyte residues removal.

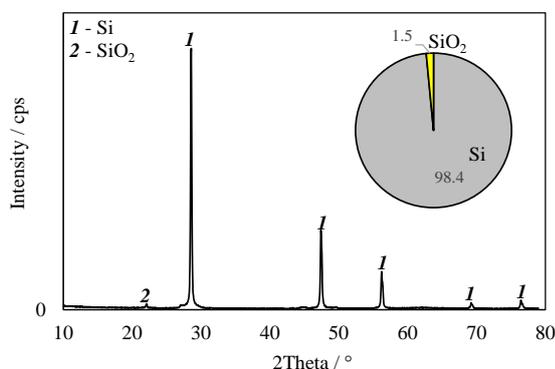


Figure 3 X-ray diffraction of the silicon deposit, obtained by the electrolysis of the NaI-KI-K₂SiF₆ melt at a cathode current density of 5 mA cm⁻² and 750 °C after the electrolyte residues removal.

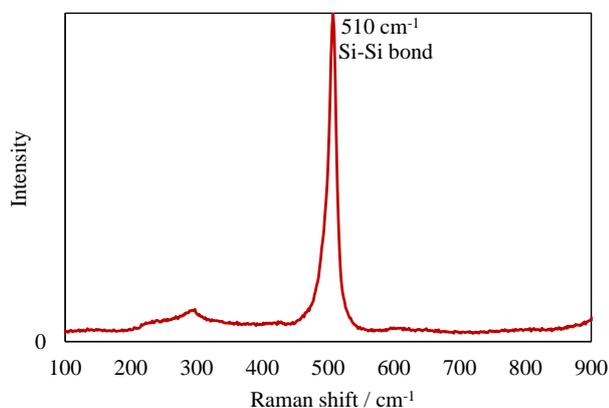
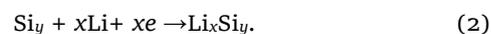


Figure 4 Raman spectra of the silicon deposit, obtained by the electrolysis of the NaI-KI-K₂SiF₆ melt at a cathode current density of 5 mA cm⁻² and 750 °C after the electrolyte residues removal.

The inclined regions at the potentials of 0.2–1.25 V for the sample 2 and at the potentials of 0.2 and 1.2 V for the sample 1 correspond to the process of electrode/electrolyte interphase boundary formation (SEI). On the charge curves (left part) there is a region where the potential stabilizes at 0.18 V. The characteristic plateau in the region of 0.1–0.2 V corresponds to the process of lithium intercalation into silicon according to reaction [31]:



The discharge (right part) curves illustrate an abrupt potential jump up to 1.4 V, which corresponds to the process of silicon deintercalation. During the first (forming) cycling the coulombic efficiency of the charge/discharge process was 60%.

To estimate the reversibility of the anode material, CVs of samples 1 and 2 were also obtained after its cycling (see Figure 6). From them, we can draw a preliminary conclusion about the presence of reversibility (the presence of peaks in the cathode and anode regions) of the samples, as well as the closeness of the lithium reduction/oxidation potentials to the charge/discharge potentials from the dependences shown in Figure 5.

To determine the discharge capacity and coulombic efficiency (the ratio of the charge capacity to the discharge one) a galvanostatic cycling of the experimentally obtained samples was charged at the current of 200 mA·g⁻¹. We performed 30 cycles. Figure 7 presents the dependencies of discharge capacity and coulombic efficiency of the samples during cycling. After 30 charge/discharge cycles, the discharge capacity of the anode samples composed of fiber and thread-like silicon decreased from 1390 and 1610 to 440 and 565 mAh·g⁻¹, and the coulombic efficiency was 89 and 91%, respectively. An irreversible capacity may be explained by the presence of SiO₂ admixture that transforms into lithium silicate during the lithiation, by the interaction of the substrate components with silicon and lithium, and by the destruction of silicon fibers and the contact fault with the substrate [32]. Further research is needed to determine the reasons for such behavior.

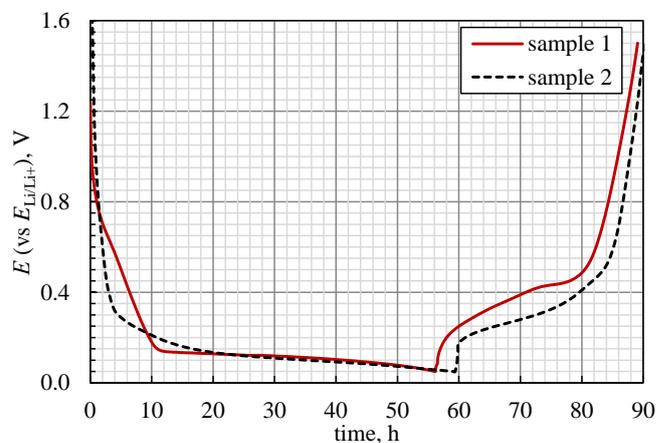


Figure 5 First charge/discharge cycle of half-elements with silicon-based composite anodes.

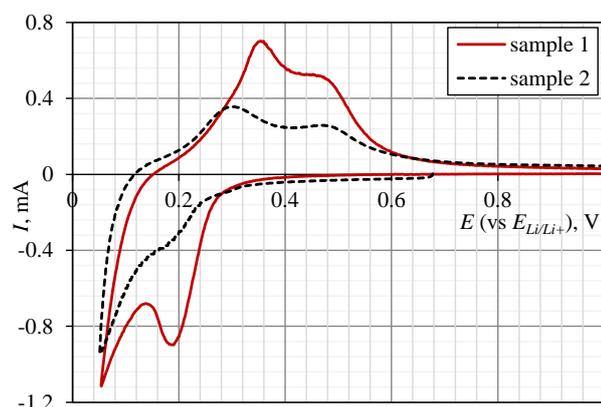


Figure 6 CVs for samples of silicon-based composite anodes after cycling. Sweep rate of 0.1 mV s^{-1} .

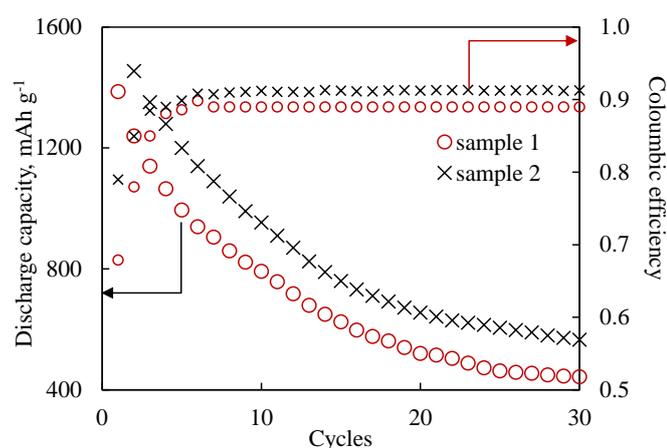


Figure 7 Change in the discharge capacity and coulombic efficiency of the charge/discharge process of the samples during cycling.

4. Conclusions

The possibility of using silicon fibers electrolytically produced from the NaI-KI-K₂SiF₆ melt at 650–750 °C in composite Si/C anodes of lithium-ion power sources was studied. The silicon electroreduction was performed under the galvanostatic regime at the cathode current density ranging from 1 to 5 mA cm⁻², as well as under the potentiostatic regime and the cathode overpotential of 0.2 V. The electrolysis was found to result in the formation of fiber and thread-like silicon deposits with the average diameter from 60 to 320 nm and length up to 20 μm. According to the analyses, the concentration of admixtures, primarily oxygen, in the obtained deposits varied from 1.2 to 4.6 wt.%.

The energy characteristics of the obtained silicon samples were determined during their lithiation-delithiation in the composition of the lithium-ion power source. After 30 cycles, the discharge capacity of the anode samples of fiber and thread-like silicon decreased from 1390 and 1610 to 440 and 565 mAh·g⁻¹, and the coulombic efficiency was 89% and 91%, respectively. We assume that the irreversible capacity of the samples may be associated with the presence of SiO₂ admixture; it also may be caused by the interaction of the substrate components with silicon and lithium as well as by the destruction of silicon fibers and contact fault between silicon and the substrate.

Supplementary materials

No supplementary materials are available.

Funding

The work was performed within the Agreement No. 075-03-2022-011 dated 14.01.2022 (theme number FEUZ-2020-0037).

Acknowledgments

The facilities of the Composition of Compounds the Shared Access Center of Institute of High-Temperature Electrochemistry UB RAS were used in this work.

Author contributions

Conceptualization: A.V.S.
 Data curation: R.K.A., A.V.S.
 Formal Analysis: R.K.A., N.M.L., A.M.L.
 Funding acquisition: A.V.S.
 Investigation: R.K.A., M.V.L., N.M.L., A.M.L.
 Methodology: R.K.A., A.S.S., N.M.L., A.M.L.
 Project administration: A.V.S.
 Resources: R.K.A., M.V.L., N.M.L., A.M.L.
 Supervision: A.S.S., A.V.S.
 Validation: N.M.L., A.M.L., A.V.S.
 Visualization: R.K.A., A.V.S.
 Writing – original draft: R.K.A., N.M.L., A.M.L.
 Writing – review & editing: A.V.S.

Conflict of interest

The authors declare no conflict of interest.

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