ABSTRACT
of the dissertation work on the topic:
«Development and research of technological bases for obtaining silicon–based anodes for practical use in the field of electronics in order to reduce the environmental burden on the environment»,
submitted for the degree of Doctor of Philosophy (PhD)
in the specialty 6D074000 – «Nanomaterials and nanotechnology» by
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Relevance of the topic

The ever-increasing demands on modern lithium-ion batteries strongly stimulated the search for reliable electrodes with high areal capacity. The production of electrodes from high-performance active material would maximize this parameter.

Creating a reliable silicon anode with high performance properties and a long battery life is an urgent task.

Electric battery storage is the key to the future of personal electronics, electric vehicles (EVS), and more efficient power systems. But to date, commercial lithium-ion batteries do not provide fast enough power supply. Therefore, it is relevant to search for new materials that can either increase the energy intensity, or replace the currently used expensive cathodes, anodes and electrolytes that make up the lithium-ion battery.

Of particular interest is the replacement of graphite carbon of the negative electrode (anode) with silicon. When the lithium-ion battery is charged, lithium ions move between the layers of carbon atoms in the graphite anode during the intercalation process. Today, batteries use a special kind of layered graphite, limited in the amount of lithium that they can absorb. Silicon can provide an economical alternative.

The usual solution to this problem is to add a polymer carbon binder, which creates a structure containing silicon.

Over the past two decades, lithium-ion batteries (LIA) have revolutionized portable electronic devices and have a major impact on vehicle electrification. Despite their outstanding potential, modern lithium-ion batteries (such as $LiCoO_2$/graphite batteries) have not been able to meet the ever-increasing need for vehicle electrification, which requires high energy density and high power density, as well as a long life cycle at the same time. In this context, silicon is one of the most promising anode candidates for next-generation lithium-ion batteries. This is due to its low voltage profile and high theoretical capacity (4140 mAh/g for the $Li_{15}Si_4$ phase at room temperature), which is more than ten times more than that of carbonaceous materials, including graphite, pyrolytic carbon and mesophase resin (about 372 mAh/g).

In addition, silicon is the second most common element in the earth's crust. Hence, mass production of silicon with low cost is not a problem.

Analysis of literature and patent information sources has shown that in modern portable electronic devices, mono-, polycrystalline or amorphous silicon, as well as thin-film structures based on silicon, are used as a negative anode based on silicon. The use of aspiration material in the production of silicon has not been studied.

The purpose of the dissertation research: research and development of technology for producing anodes based on nanosized silicon powders for practical application in the field of electronics, reducing the environmental impact on the environment and increasing the discharge capacity of lithium-ion batteries obtained using silicon nanostructures.

Research objectives

To achieve these goals, the following tasks were set:

1. To analyze the production of metallurgical silicon and methods for its purification to high-purity technical quality. Conduct a literature search for obtaining nanoscale silicon, the use of its various modifications in lithium-ion batteries.

2. To improve the existing methods of purification of metallurgical silicon from impurities by slag refining and acid leaching and obtain nanosized powders (UMG-Si, Si-dust).

3. Develop technological bases for the production of lithium-ion battery electrodes from silicon-containing nanopowders and create a new technology for manufacturing battery anodes with a nanosilicon anode by laser printing.

4. Determination of the discharge capacity of the obtained silicon anodes (UMG-Si, Si-dust, mc-Si).

Research methods

As part of the dissertation work, the following methods were used: critical analysis of literary sources and patent research, planning and conducting an experiment on the development of a silicon-based anode and the creation of a lithium-ion battery unit, statistical analysis methods**.**

The main provisions submitted for protection

The following provisions are submitted for the defense of the dissertation work:

1. Slag refining with mixtures consisting of quicklime, silicon dioxide, fluorspar, alumina, burnt magnesia leads to a silicon yield of 75-85%. Subsequent acid leaching, grinding to nano-sized powders (5-100 nm) of metallurgical silicon makes it possible to obtain modernized UMG-Si silicon with a purity of 93.15-99.98% for impurities such as Ca, Al, Fe, B and P.

2. The obtained modifications of powdered nanosilicon in the form of silicon dust Si-dust, upgraded silicon UMG-Si and nanofilm structures of single-crystal silicon mc-Si showed high electrochemical characteristics: the discharge capacity of negative electrodes for Si-dust is 950 mAh/g; UMG-Si - 2250 mAh/g; mc-Si - 2800 - 3400 mAh/g.

3. Laser printing of a block of lithium-ion batteries (nSi + Mx-“C” + Mx-“N”) allows the formation of films consisting of silicon nanolayers with a high adhesive ability of a silicon-containing nanopowder with an optimal percentage of a binder in the electrode active mass - 10 % and the content of active silicon electrode mass - 85%.

Description of the main results of the study

1) An analysis was made of obtaining metallurgical silicon and methods for its purification to high-purity technical quality. Modern silicon nanoparticles for the electronics industry are obtained by silane methods, which are environmentally unsafe and consume a large amount of electricity. It was found that in order to obtain silicon nanoparticles for the electronics industry in order to reduce the environmental impact on the environment, it is necessary to carry out the following silicon purification measures: slag refining, acid leaching, crystal growth from the melt.

2) The methods of purification of metallurgical silicon by slag refining and acid leaching to obtain nanosized silicon are substantiated. In the course of carrying out activities for the purification of metallurgical silicon for the subsequent manufacture of electrodes from nanosized silicon dust and metallurgical silicon after a 2-stage cleaning were:

- optimal compositions of slag mixtures were selected;
- the purity of silicon was achieved in terms of the main impurities (Ca, Al, Fe) of 93.15-99.98%, the yield of silicon in the melt reached 75-85%;
- a technical solution was proposed - a device for burning a hole in order to prevent part of the slag with impurities from entering the metal.

3) Technological foundations for the production of lithium-ion battery electrodes from silicon-containing nanopowders have been developed:

- a method for laser printing of a block of lithium-ion batteries is proposed and the assembly of a block of lithium-ion batteries (nSi+Mx-"C"+Mx-"N") is justified;
- the optimal percentage of the binder in the electrode active mass was established - 10% and the content of the active electrode mass based on silicon - 85% using cheap materials as an electrically conductive additive and a binder material (polymethyl methacrylate, polyaniline, polyvinylidene fluoride, citric acid).

4) The discharge capacities of the proposed anodes of lithium-ion batteries from silicon nanostructures were determined (silicon dust - 950 mAh/g, 2-stage-purified silicon - 2250 mAh/g, silicon films - 3000-3400 mAh/g). For the first time, the proposed silicon nanostructures have shown their effectiveness over 170 cycles of a lithium-ion battery.

As a result of a comprehensive study of the physicochemical features of the interaction of lithium with single-crystal and thin-film silicon, as well as silicon-containing nanopowder, it can be argued that silicon-based negative electrodes can be used to create flexible thin-film lithium-ion batteries.

Substantiation of the novelty and importance of the results obtained

The rationale for the need for this research work is the relevance of research in the creation of a lithium-ion battery unit, the replacement of a graphite anode with a silicon one, which provides a sharp increase in the theoretical charging capacity.

The novelty of the work lies in the improvement of the technology of production and production of silicon products, namely lithium-ion battery anodes, the development of innovative methods for applying a mixture of powder and silicon nanopowder to create hybrid silicon-containing anodes. The resulting silicon anodes were assembled into a lithium-ion battery unit. As a result of the study, the importance of the obtained results was substantiated:

- for the first time, methods of using metallurgical silicon, as well as its waste, namely the aspiration material of metallurgical silicon, in the production of silicon-based anodes are proposed;
- the assembly of a block of lithium-ion batteries consisting of prismatic cells, including an anode, a cathode, separated by a separator, and electrically contacting through a lithium-containing electrolyte is justified;
- an innovative method of laser printing of anode cells is proposed;
- a technical solution is proposed – a device for burning a pilot hole in order to prevent a part of the slag with impurities from entering the metal.
- the use of cheap materials as an electrically conductive additive and binder is justified - organic glass, citric acid.

Compliance with the directions of science development or state programs

According to the State Program of Industrial and innovative development of the Republic of Kazakhstan for 2020-2025, it is necessary to create a competitive manufacturing industry of the Republic of Kazakhstan in the domestic and foreign markets. Therefore, the research and development of technological bases for the production of silicon-based anodes for practical use in the field of electronics, starting from the stage of production of metallurgical silicon to the use of high-purity silicon of solar quality, will expand the range of processed goods in demand in domestic and foreign markets.

The development of the market for the purification of metallurgical silicon and the use of waste (aspiration material) as an anode material will also contribute to reducing the environmental burden on the environment.

The creation of new cyclically stable negative LIA electrodes contributes to a smooth transition from Industry 4.0 to Industry 5.0.

Personal contribution of a doctoral student to the preparation of publications

The author's personal contribution consists in planning and conducting experiments, performing theoretical and experimental studies, discussing and summarizing the results. According to the results of the dissertation work, 8 scientific papers have been published, including 1 article in a journal included in the Scopus database, 4 publications (including 2 patents) in publications included in the list recommended by the CCSON, 2 in materials in international scientific conferences.