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USE OF Si-COMPOSITE ASPIRATION DUSTS PRODUCTION IN THE CREATION OF THIN-FILM ANODES

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Preliminary Note – Prethodno priopćenje

The present time is marked by the progress of technology related to energy storage. One of the promising priority energy storage devices is lithium-ion batteries (LIB), which have a high energy density and a low self-discharge level. To increase the charging capacity and general characteristics of LIB, researchers think about replacing one of the electrodes, in particular the anode, with more promising and cheaper materials. Of all the possible materials on the market, silicon (Si) is one of the most effective, promising, cheap, and widespread materials. In contrast to pure Si, composites based on it are becoming more widespread and are actively used as a material for LIB.

Keywords: lithium-ion batteries, silicon-based anode, dust, energy storage, X-Ray research

INTRODUCTION

The development of electronic technology does not stand still, so there is a need to develop stable, powerful, and durable batteries. Currently, scientists are increasingly resorting to the study of metallic silicon, the development of technology for creating batteries and its use in portable devices, and increasing the charging capacity of the structures used.

Lithium-ion batteries (LIB) are one of the most common and used types of energy storage in modern electronic devices on the market. LIB consists of two electrodes, one of which is negatively charged (anode), and the other is positively charged (cathode).It is known that metal balls work in very difficult conditions: shock and dynamic, under static loads and increased wear. This is especially true for the grinding balls of metallurgical mills, the cost of replacing which in some cases is equal to the cost of electricity.

The space between the cathode and the anode is filled with a porous separator, which serves to prevent a short circuit between the electrodes.

The separator also provides the electrolyte reserve required for high ionic conductivity [1]. As the lithium ions (Li) move from the anode through the electrolyte to the cathode, an electric current is generated. The energy consumption of LIB is determined by the number of lithium ions.

The most promising material in this area is silicon (Si). The theoretical electrical capacity of porous Si reaches 4 140 mAh/g, while the capacity of the used graphite is less than 10 times (372 mAh/g) [2]. The disadvantage of using Si as an anode in LIB is the change in its volume during lithiation and delithiation.

One of the ways to increase the resistance of Si in the production of LIB and reduce the charge time is to reduce the thickness of the Si anode to nanoscale and/or to create composite materials [1].

Long-term operation of silicon anodes is possible due to the transition to nanostructured materials: thin silicon films, silicon nanowires, nanoparticles, grown nanotubes, and porous structures based on silicon, as well as the creation of composite materials based on various carbon nanostructures [3 - 8].

A large silicon particle (μm) can reduce the surface area. Also, the tapping density of micrometer particles is usually higher than that of nanoparticles due to the reduced interparticle space. Higher tap density can reduce electrode thickness and shorten the electron path for the same mass load.

EXPERIMENTAL PART

In this article, an analysis of Si products of TauKenTemir LLP (Karaganda, Republic of Kazakhstan) was carried out and the possibility of its further use as an anode material. (Figure 1).

Si sample (Figure 1) looks like a dark gray powder, the size of each particle of Si powder varies from 2 to 75 μm (Figure 2).

The Si-based composite powder was obtained from technical Si, subjected to a crushing process. In the process of crushing technical Si in a jaw crusher, fine dust is formed, which is captured in bag filters. At the moment, the captured silica dust is of limited use. The purpose of this research is to study the possibility of using Si composite powder for the manufacture of thin-film Si anodes for LIB.

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Figure 1 Samples of Si powder

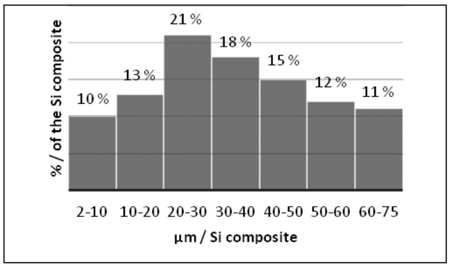


Figure 2 The percentage of particles of different sizes

An anode based on Si composite was fabricated by laser printing. The copper foil was used as a substrate. It is assumed that lithiated cobalt oxide LiCoO2 impregnated with polyaniline was used as the cathode material, and finely dispersed polypropylene powder was used as the material for the separator.

One of the main anode materials on the market is graphite, the capacity of which is low and amounts to 372 mAh / g [9]. Therefore, research in the field of replacing graphite anodes with more promising materials is an urgent task.

As an alternative material, silicon has sufficient capacity and electrical conductivity, but the disadvantage is that it changes in size during the lithiation process.

Below are the methods for obtaining silicon for its further use as an anode material.

A standard LIB consists of an anode and a cathode on two separate current collectors. The electrolyte allows lithium ions to move between the electrodes, and the separator protects the anode and cathode from direct contact [10].

The known LIB designs have a high material consumption and require a long time for charging. Each pair of prismatic plates - cathode and anode is equipped with its own down conductors and housing. This increases the cost and weight of the unit.

To increase the efficiency of using chemically accumulated electricity, laser printing of an anode for LIB is proposed. Composite silicon powder is used as a material for the anode. The material for the cathode is lithium cobaltate LiCoO2. Fine polypropylene powder is used as a material for the separator.

Printing is done in layers. The number of layer printing cycles depends on the required battery capacity.

General printing formula:

Σ(nSiMx+(0,2nSiMx+0,8C)+0,2nSiMx+0,15C+0,65N)+(0,2nSiMx+0,6C+0,2N)+ +(0,65nSiMx+0,15C+0,2N)+(0,2nSiMx+0,6C+0,2N)),

where: nSiM – silicon composite, corresponds to 1st layer of printing; C – separator; N – cathode; 0,2nSiMx+C – 2nd printing layer; 0,2nSiMx+0,6C+0,2N+ – 3d layer printing; 0,2nSiMx+0,15C+0,65N – 4th printing layer; 0,65nSiMx+0,15C+0,2N – 5th layer printing; 0,2nSiMx+0,6C+0,2N – 6th layer printing.

The cathode and anode current leads are glued using a polymer electrolyte solution or soldered to the corresponding collectors of the cathode and anode block. The resulting block with current leads is placed in an electrically insulating housing, filled with lithium-containing electrolyte and hermetically sealed.

RESULTS AND DISCUSSION

LIB is intended for use as energy storage devices for electric transport, alternative energy, uninterruptible power supplies, energy recovery systems, and equalization of network loads.

Despite the presence of various microstructures in the powder, it is impossible to speak about the unsuitability of this composite powder as an anode material.

The Scanning Electron Microscopy (SEM) image of the Si-based composite powder (Figure 3) shows that the Si powder looks like a thin plate. The limits (2 - 75 μm) should be estimated as follows: 2 μm is the thickness of the plates, and 75 μm is the length and width of the plates. It means that if it turns out to lay the plates flat in one layer, then an anode thickness of 2 μm (2 000 nm) can be achieved. This would be many times less than the currently existing anodes with a thickness of 400 μm.

The Energy Dispersive X (EDX) results of the elementary mapping of the cross-sectional sample and chemical analysis of the silicon powder showed the presence of impurities (Table 1, Figure 4 and 5).

Silicon powders at Tau-KenTemir LLP (Karaganda, Republic of Kazakhstan) are obtained by grinding lump technical crystalline silicon produced in electric arc furnaces by reducing quartz or quartzite with a complex solid reductant, which includes charcoal, petroleum coke, and other carbonaceous materials.

In conventional batteries, the charge is held in electrodes and delivered to energy storage devices as ions

Table 1 **Chemical composition of silicon powder products of LLP «Tau-KenTemir»**

Element	Line	Mass / %	Atom / %
O	K	6,04 ± 0,03	14,89 ± 0,03
Al	K	5,46 ± 0,00	13,38 ± 0,00
Si	K	85,19 ± 0,03	70,26 ± 0,03
Ca	K	0,89 ± 0,03	0,50 ± 0,00
Fe	K	0,79 ± 0,01	0,38 ± 0,00
Cu	K	0,59 ± 0,01	0,24 ± 0,00
Zn	K	0,51 ± 0,01	0,17 ± 0,00
Sn	K	0,53 ± 0,01	0,18 ± 0,00
Total		100,00	100,00

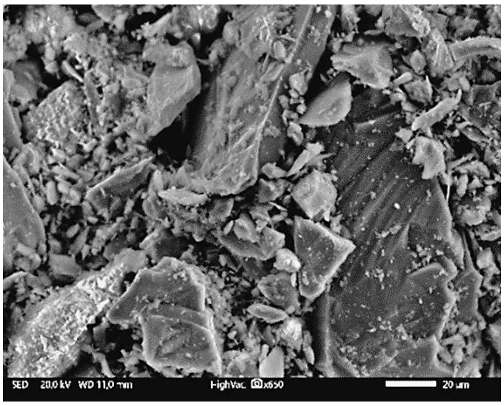


Figure 3 SEM image of Si-based composite powder

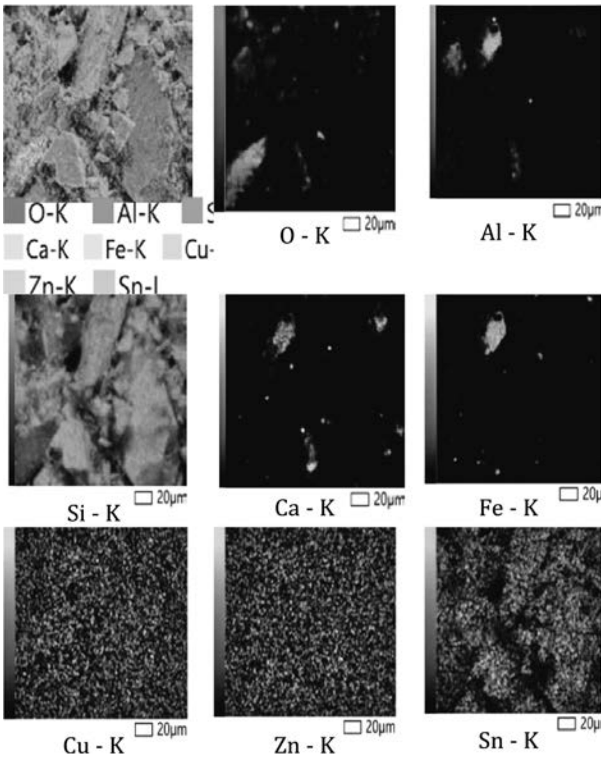


Figure 4 EDX mapping images of silicon-based composite powder

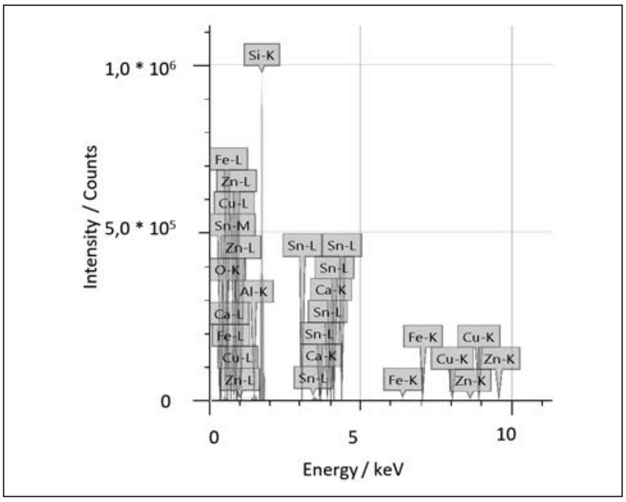


Figure 5 Energy Dispersive Analysis of Silicon Powder

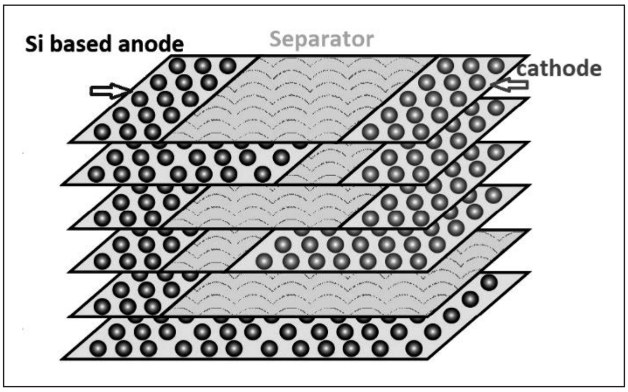
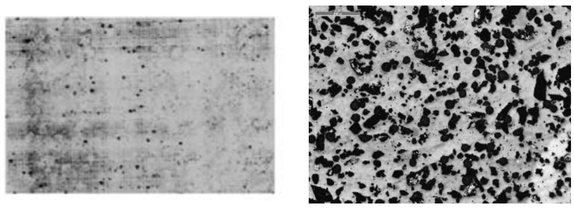


Figure 6 Si composite material printing scheme



a) Formation a film from silicon powder material by laser printing

b) Structure after printing with an optical microscope

Figure 7 The result of the formation of a film from silicon powder material

move from the anode to the cathode. During battery charging, ions return to the anode. Replacing graphite with silicon as the main material in the lithium-ion anode will improve its ion absorption capacity.

This approach will generally increase the efficiency of using chemically stored electricity. Printing is carried out on an insulating substrate. The micro-layer of the Si-based anode is formed by electrostatic spraying. The printing scheme is shown in Figure 6.

Printing is done in layers. Initially, a layer of silicon powder is printed. The next layers are printed according to a cyclic scheme, by the sequential repetition of the layers shown in Figures 6. Each subsequent layer is fixed by heat treatment. The heat treatment power is adjusted in such a way as to ensure the diffusion porosity of the liquid electrolyte separator on the one hand and the impossibility of direct contact between the cathode and the anode as a result of the application of powders during printing, on the other hand. The number of layer printing cycles depends on the required battery capacity. Printing ends at the creation of the layer shown in Figure 6 above. It should be noted that the third and sixth layers in the diagram are identical. The cathode and anode current leads are glued using a polymer electrolyte solution or soldered to the corresponding collectors of the cathode and anode block. The resulting block with current leads is placed in an electrical insulating case, filled with lithium-containing electrolyte and hermetically sealed.

The advantages of the proposed design of the battery block include a decrease in the weight of the block, a decrease in the consumption of current-carrying parts. This will make it possible to more efficiently use the accumulated electricity in electric transport due to the general decrease in the mass of the electric vehicle. It will also be possible to quickly charge the battery pack, which will allow the use of electric transport on long routes with a limited time spent on intermediate stops.

An attempt was made to print a film using Si powder material without using an organic binder. The result is shown in Figure 7.

As can be seen from Figure 7, it is impossible to obtain a uniform anode layer without an organic binder. It turns out that when silicon particles lose their electrical charge, they fall off the substrate. Therefore, it is necessary to impregnate the surface of the silicon powder particles with an organic polymer. Then, when passing through the hot drum, the organic polymer on the surface of the silicon particles will melt and bind the silicon particles together, and also bind the layer of these particles to the substrate surface. But the use of polymer, since it is an inert material, reduces the charging capacity of the anode.

CONCLUSIONS

This silicon-based composite material can be used as an anode material in modern LIBs. The energy consumption of new microstructures is lower than that of bulk pure Si. The proposed microstructures are not pure Si, and therefore the cyclic properties can be improved during the introduction and extraction of Li ions.

The LIB seal will make it possible to more efficiently use the accumulated electricity in electric transport due to the overall reduction in the mass of the electric vehicle.

The size of the proposed Si-based anode reaches 2 000 nm, which is 2 times smaller than the existing analogs.

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