# ANNOTATION

of dissertation work,
submitted for the degree of Doctor of Philosophy (PhD) in the specialty
6D072300 – «Engineering physics»

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## «Obtaining and study of silicon dioxide-based materials for use as an anode lithium-ion battery»

**General description of the paper**

The dissertation is devoted to obtaining of silicon dioxide based materials from rice husks (RH) for use as an anode material in lithium-ion batteries, as well as to the study of the material obtained.

The composition of $SiO_2$, surface area, thermogravmetric analysis and X-ray structure obtained from RH were studied. By burning RH at different temperatures, it was found the yield of $SiO_2$ in percentage terms. In order to improve the purity of $SiO_2$, purification methods have been studied by chemical treatment of ash before and after heat treatment. The obtained $SiO_2$ were investigated as an anode material in LIB. The influence of the purity of the material on the efficiency of the battery as an anode has been studied. The synthesized $SiO_2$ was modified by incorporation into a carbon matrix.

**Relevance of the research**

Lithium (Li) based batteries are currently the most important storage systems available on the market. However, at the same time they are still under active development. Recently, serious development efforts have been devoted to LIBs for vehicle propulsion as well as for stationary applications. Encouraging results have been achieved in both applications. At present, high-capacity lithium-ion batteries are only available in prototype form. Battery efficiency, performance and weight are by far the most important factors. LIB has a high energy density, is one of the most attractive energy storage devices and plays an important role in modern society, are used in mobile phones, laptops, digital cameras, as well as portable electronics, since the practically achievable specific energy density of about 102 $Wh*kg^{-1}$ is sufficient to meet the basic requirements of this the market. They have also been identified as power supplies for electric vehicles and stationary energy harvesting, however current LIBs cannot meet the needs of electric vehicles and a wide range of energy savings. Because the theoretical capacity of graphite, often used in commercial anodes in LIB, is 372 $mA*h*g^{-1}$, which is not enough for the next generation LIB. One of the main problems of graphite anodes in LIB is the limited speed, especially for the lithium process, i.e. the charge of the full cell, and the associated risk of a metallic lithium coating on the electrode surface, which can lead to a short circuit or rapid aging and accelerated cell withering.

Recently, more and more efforts have been made to solve the above problems and encourage anode materials based on silicon oxide to be applied in practical applications in LIB, since it has a high content in the earth's crust, a low discharge potential and a high initial irreversible capacity and a reversible capacity of 1961 $mA*h*g^{-1}$. Some commercial LIBs have silicon oxides with graphite (usually less than 10%) added to increase capacitance .

Many scientific articles based on $SiO_2$ have been published and described in the form of anodes, including nanostructured materials, thin films and carbon nanoparticles. Also paid attention to non-stoichiometric silicon oxides (SiOx, where $0 < x < 2$) to increase the molar ratio of silicon to oxygen, in which a low oxygen content ensures high productivity due to the cycle.

Thus, the development of new cheap anode materials for LIB is of current interest.

**Purpose of the thesis research**. The purpose of this dissertation is to obtain and study materials based on $SiO_2$ for use as an anode material in LIB.

**Tasks of the work.** To achieve this goal, the following tasks were set:

- Determination of the method and optimal modes for obtaining nano-sized pure $SiO_2$ from RH from different regions.
- Determination of the physicochemical and electrochemical characteristics of the $SiO_2$-based materials to select the most suitable one as an anode material in LIB.
- Study $SiO_2$ by introducing it into a carbon shell using a thermal method to improve the electrochemical characteristics of LIB.
- Assembly CR2032 half-cell from the obtained materials and study of electrochemical properties (capacitance at various current densities, stability, Coulomb efficiency, internal resistance).

**Subjects of the research -** $SiO_2$ powder obtained from RH containing nanoparticles and composites based on it as an active anode material in LIB and its electrochemical analysis.

**Scope of the research** is the physicochemical, electrochemical properties of $SiO_2$ and composites based on it.

**Research methods.** When solving the tasks necessary to achieve this goal, the following research methods were used: thermogravimetric analysis (TGA), elemental analysis, X-ray phase analysis (XRF), scanning electron microscopy (SEM), method for determining the specific surface area, determination of electrochemical characteristics of the obtained materials, transmission electron microscope (TEM), galvanostatic and potentiostatic method of analysis, cyclic voltammetry (CV).

**Scientific novelty of the research.** The following results were obtained for the first time in the research work:

- The parameters and conditions for obtaining nanoporous amorphous $SiO_2$ from RH with a purity of 99.7%, a specific surface area of 980 $m^2*g^{-1}$ and an average pore size of 0.9 nm were obtained and showed that the $SiO_2$ as an active anode material reaches an average capacity of 400 $mA*h*g^{-1}$ at a current density of 50 $mA*g^{-1}$.

- Using the methods of carbonization and graphitization of $SiO_2$ derived from rice husk and sucrose, a composite material $SiO_2$/C was synthesized for the first time, demonstrating a high capacity (450 mA*h/g) at a current density of 50 mA/g when employed as an anode for lithium-ion batteries.

-The resulting $SiO_2$/C composite material was found to stabilize over 40 charge/discharge cycles and reach a maximum capacity of 450 mAh*$g^{-1}$ on average.

**Defended provisions:**

1. Nanoporous silica obtained from rice husk as an anode of a lithium-ion battery cell has a Coulombic efficiency of 97% and an electrical capacity of 400 mA*h*$g^{-1}$ for 50 cycles at a current density of 50 mA*$g^{-1}$.

2. To improve the electrical properties of half the cell, the $SiO_2$/C composite obtained by integration nanoporous silicon dioxide into carbon by a thermal method reduced the internal resistance of the cell from ~6 kOhm to ~2 kOhm.

3. $SiO_2$/C composite material increased the lithium ion cell capacity to 450 mA*h*$g^{-1}$ by restructuring the active material at a current density of 50 mA*$g^{-1}$, for 40 charge/discharge cycles, which is 17% higher capacity traditionally used graphite.

**Theoretical significance.**

This work will expand the understanding in the field of synthesis and research of the properties of materials from bio-waste and their application in various fields of science.

The creation of new anode materials for LIB is one of the most relevant topics of modern science. The experimental data obtained are of interest for obtaining stable and energy-intensive anode materials for LIB.

**Practical significance.**

Optimal parameters and conditions for the synthesis of $SiO_2$ with a specific surface area of 980 $m^2$*$g^{-1}$ with a porosity of 0.9 nm have been developed, which can be used in the chemical and metallurgical industries. The possibility of synthesizing $SiO_2$/C from cheap raw materials for use as a stable active anode material in lithium–ion batteries is shown.

**Communication with research work and government programs.**

The work was carried out within the framework of the scientific project «Technology for obtaining anodes of lithium–ion batteries with high capacity», funded under the program-targeted funding grants «Development of new composite and structural materials for the development of the innovation industry of the Republic of Kazakhstan» OR11465430/PTF out of competition of the Ministry of Science and Higher Education of the Republic of Kazakhstan (2021-2022).

Competition for grant funding of research of young scientists under the project «Zhas Galym» for 2022-2024 «AP14972926 Obtaining and research of lithium–doped materials with a highly porous structure for use as an anode of lithium– ion batteries».

**Approval of the conducted researches.** The materials of the dissertation work were reported and discussed at various international, republican conferences and symposiums:

- International Conference of Students and Young Scientists « FARABI ALEMI» p. 79. 2022. 6-8 April. ISBN 978-601-04-5945-8 (Almaty, Kazakhstan)

- The 8th International Conference on Nanomaterials and Advanced Energy Storage Systems; Nazarbayev University; National Laboratory Astana; Institute of Batteries, p. 38, 6 August, 2020 | (Nur-Sultan, Kazakhstan)

- XI International Symposium «COMBUSTION and PLASMOCHEMISTRY» November 20-22, 2019, pp. 13-16. (Almaty, Kazakhstan)

**The author's individual contribution** consists in direct participation in conducting experiments and setting tasks, generalizing and interpreting the results obtained, writing articles and reports and preparing an application for an innovative patent of the Republic of Kazakhstan.

**Publications.** The results of the work performed are reflected in 11 scientific papers, including :

1. **Askaruly K**., Azat S., Xintai Su, Zhaksylyk N. Synthesis of pure silica from rice husk ash and its characteristics. Al-Farabi Kazakh National University bulletin Ecology Series. 2019 Almaty, pp. 69-77. ISSN 1563-034X; eissn 2617-7358. Index 75880; 25880

2. **K. Askaruly**, Zh. Sartova, S. Azat, M. Yeleuov, A. Tauyrbekov. Assessment of synthesis methods of $SiO_2$ produced from rice husk and its main physicochemical characteristics. Горение и плазмохимия 16 (2018) 186-194

3. **Askaruly K**., Azat S., Yeleuov M., Azamat T., Sarsembaeva B. The modern anode with high capacity for li-ion batteris. Almaty University of Power Engineering and Telecommunications. No4(6) (43)2018. pp. 7-13.

4. **K. Askaruly**, S. Azat, M. Yeleuov, A.R.Kerimkulova, U.N. Zhantikeev, A.E. Berdikhanov. Obtaining silicon oxide from rice husks by heat treatment. Горение и плазмохимия. Vol. 17. No. 3, p. 178. 2019.

4 articles in the **Scopus** database :

1. **Askaruly K**. et al. The electrochemical behavior of silica and activated carbon materials derived from the rice husk waste for li-ion cells //Diamond and Related Materials. – 2023. – Т. 133. – С. 109759. (**процентиль 78%, IF 3.806, CiteScore 5.2**) https://doi.org/10.1016/j.diamond.2023.109759

2. **Askaruly K**. et al. Obtaining and characterization of amorphous silica from rice husk //Journal of Chemical Technology & Metallurgy. – 2020. – Т. 55. – №. 1. (**процентиль 38%, IF 0.81, CiteScore 1.4)**

3. Kapizov O. Azat, S., **Askaruly, K**., Zhantikeyev, U., Tauanov, Z., Bergeneva, N. S., & Satayeva, A. R. Perspectives of the silicon dioxide production from rice husk in Kazakhstan: an overview //Eurasian Chemico-Technological Journal. – 2020. – Т. 22. – №. 4. – С. 293-285. (**процентиль 31%, IF 1.222, CiteScore 1.3**) https://doi.org/10.18321/ectj993

4. Azat, S., Sartova, Z., Bekseitova, K., & **Askaruly, K**. Extraction of high-purity silica from rice husk via hydrochloric acid leaching treatment //Turkish Journal of

Chemistry. – 2019. – Т. 43. – №. 5. – С. 1258-1269. (**процентиль 38%, IF 1.222, CiteScore 1.7)** https://doi.org/10.3906/kim-1903-53

A patent for utility model No. 5144 of the Republic of Kazakhstan was obtained for «A method for obtaining high-purity amorphous silicon dioxide from rice husks» (published 10.07.2020).

**Reliability and validity of the obtained results**

The reliability of the results of the dissertation work is confirmed by the consistency of the data obtained using a complex of modern physico-chemical research methods.

Research work was carried out in the conditions of the laboratory «Kazakh National Research Technical University named after K.I. Satpaev» and «Institute of Combustion Problems».

**Scope and structure of the dissertation**

The dissertation work consists of 100 pages and contains 55 figures and 9 tables. The work consists of an introduction, a review of the literature, a description of the objects and methods of research, their discussion, a conclusion and a list of references of 152 titles and 7 appendices.