



# A facile synthesis of graphite-coated amorphous SiO<sub>2</sub> from biosources as anode material for LIBs

Kydyr Askaruly<sup>a,b,d</sup>, Mukhtar Yeleuov<sup>a,b,d,\*</sup>, Azamat Taurbekov<sup>b,d</sup>, Bibigul Sarsembayeva<sup>a</sup>, Aidos Tolynbekov<sup>b,d,e</sup>, Nurzhamal Zhylybayeva<sup>b</sup>, Seitkhan Azat<sup>a,b</sup>, Alisher Abdissattar<sup>a,b,d</sup>, Chingis Daulbayev<sup>c,e</sup>

<sup>a</sup> Satbayev University, Almaty 050013, Kazakhstan

<sup>b</sup> Institute of Combustion Problems, Almaty 050012, Kazakhstan

<sup>c</sup> National Laboratory Astana, Nazarbayev University, Nur-Sultan 010000, Kazakhstan

<sup>d</sup> Bes Saiman Group, Almaty 050000, Kazakhstan

<sup>e</sup> Institute of Nuclear Physics, Almaty 050032, Kazakhstan

## ARTICLE INFO

### Keywords:

Silicon dioxide

Graphite

LIB

Surfaces

Chemical synthesis

Electrochemical properties

Amorphous materials

## ABSTRACT

The rapid pace of development of the world economy requires the progressive improvement of modern energy storage devices such as lithium-ion batteries (LIBs). The main limiting factor in the specific capacity of LIBs is the anode material, which is traditionally graphite. One possible solution is to use SiO<sub>x</sub>, which has a higher theoretical capacity than commercial carbon. Despite this, SiO<sub>2</sub> has several disadvantages that limit its widespread use as an anode material for LIBs due to low electrical conductivity and short cycling life associated with volume changes during alloying–dealloying of lithium ions during charge–discharge. We have proposed an inexpensive and simple method for obtaining amorphous SiO<sub>2</sub> particles in a carbon shell to solve these shortcomings. SiO<sub>2</sub> was synthesized from biological waste material - rice husks, and the carbon shell was obtained from sucrose, which is also obtained from biomass. Surface morphology, structural analysis, and chemical composition were examined using XRD, thermogravimetric analysis, TEM, SEM, Raman and FTIR. The resulting composite shows a high performance of 450 mAh/g at a current density of 50 mA/g after 50 cycles and high cyclic stability compared to pure SiO<sub>2</sub>, which at 50 cycles showed 295 mAh/g at a current density of 50 mA/g. The proposed inexpensive and easily scalable method for obtaining a SiO<sub>2</sub>/C hybrid composite is a possible solution for creating next-generation LIBs.

## 1. Introduction

LIBs have found wide applications and are an integral part of everyday human life due to their excellent properties such as high energy density, low self-discharge rate, and long service life [1–4]. However, graphite used for the commercial production of LIBs as an active anode material, the theoretical maximum capacity of which is 372 mAh/g, imposes significant limitations in manufacturing high-performance LIBs [5–7]. The development of new or improvement of existing technologies for the production of efficient anode materials with high specific capacitance is a priority task for many research groups [8–12]. One possible solution is to use silicon, which is a promising material for LIBs due to its high theoretical capacity, which is 4200 mAh/g, which is an order of magnitude higher than graphite [13,14].

Despite the high theoretical capacity, it has a number of significant drawbacks that limit its wide application as an anode for LIBs: firstly, the silicon lithiation/delithiation process leads to a sharp change in the anode volume up to 300 %, which leads to mechanical destruction and, consequently, to a decrease in capacitance; secondly, such behavior of silicon anodes negatively affects the service life of LIBs [15,16]. Another problem with using Si-based electrodes is the unstable SEI layer on the electrode surface [17–19]. Due to the increase in the volume of silicon with each cycle, the SEI layer is destroyed and, a new one is formed, which worsens the interaction between the active material and lithium ions due to the increase in the thickness of the SEI layer and cannot provide sufficient protection of the electrode from further interaction with the electrolyte [20–22]. The solution to such problems of silicon-based electrodes is to form a composite material and hold silicon

\* Corresponding author at: Satbayev University, Almaty 050013, Kazakhstan.  
E-mail address: [mukhtar.yu@gmail.com](mailto:mukhtar.yu@gmail.com) (M. Yeleuov).

<https://doi.org/10.1016/j.mtcomm.2022.105136>

Received 4 August 2022; Received in revised form 16 November 2022; Accepted 9 December 2022

Available online 13 December 2022

2352-4928/© 2022 Elsevier Ltd. All rights reserved.

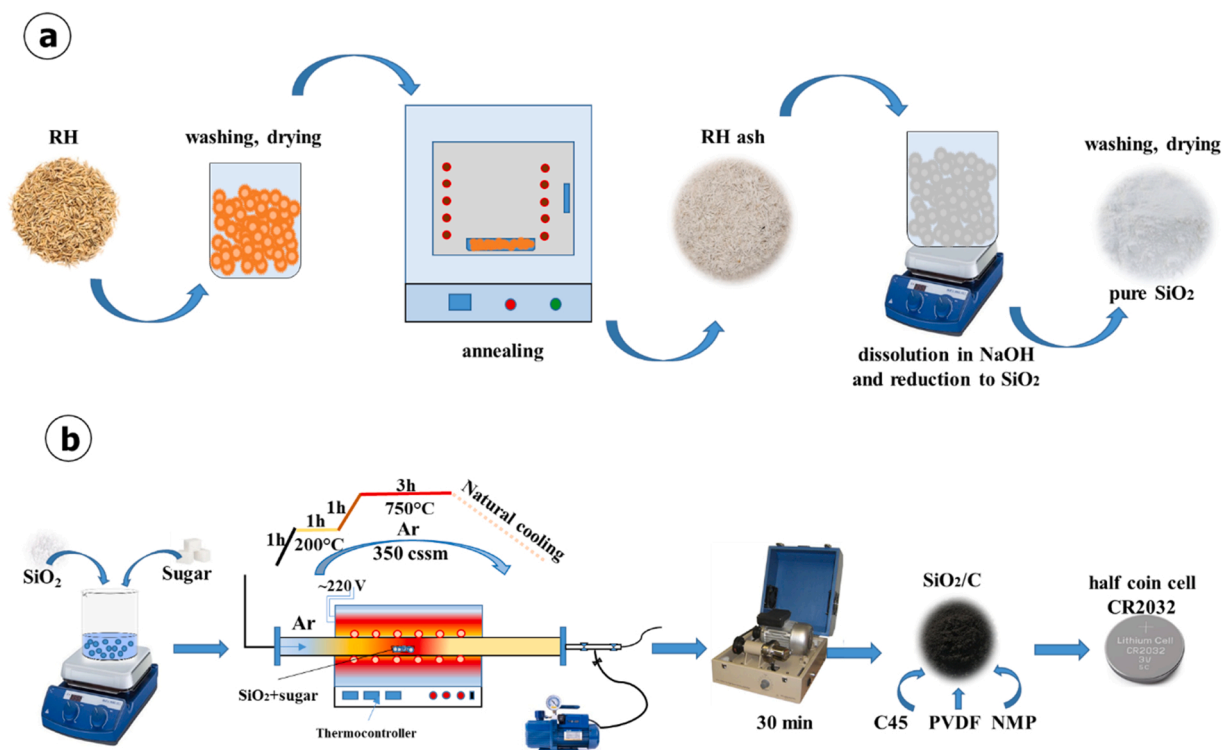


Fig. 1. The scheme of the process for obtaining  $\text{SiO}_2$  in a graphite shell: (a)  $\text{SiO}_2$  and (b)  $\text{SiO}_2/\text{C}$ .

in a carbon shell. These can restrain the expansion of silicon, maintain the structural integrity of the electrode, increase stability by reducing silicon aggregation or electrochemical sintering, and increase the material's conductivity [23–26]. Although these solutions are reasonable in many aspects and show good cyclic stability and capacity performance, the technology of modifications, as well as the production of these materials is complex and currently not suitable for mass production [27–29].

Since 2000, the concept of the conversion reaction into an electrochemically reversible lithium reaction has been developed on some oxide materials such as iron oxide, nickel oxide, silicon oxide, etc., although all materials have their disadvantages and advantages [30–33].

According to a number of experimental works [34–38], the above disadvantages can be eliminated by using silicon oxide, which, in comparison with pure silicon, will improve cycling stability. However, silicon oxide is subject to volume change during lithiation, like Si, while it is characterized by low electrical conductivity ( $\sim 6.7 \times 10^{-4} \text{ S/cm}$ ). The creation of hybrid  $\text{SiO}_x$  composites with the addition of materials with high electrical conductivity and chemical stability in an electrolyte environment, such as carbon (graphene, graphite, CNT, and carbon black), is a possible solution to these problems. Thus, in [38], a simple method for obtaining a  $\text{SiO}_x/\text{C}$ @graphite composite was demonstrated, which has high cyclic stability (842 mAh/g after 300 cycles at 0.5 A/g). This improvement is attributed to the synergistic effect of  $\text{SiO}_x$  nanoparticles derived from biowaste material and the carbon matrix network to improve conductivity and cycle stability. Based on these and many other works [39–42], an assumption was made about the possible use of a  $\text{SiO}_x$  in a graphite shell, which will improve the cycling stability of the hybrid electrode. Graphite, which has unique electrical and mechanical properties, can not only improve the electrical conductivity of the composite, but it will also make it possible to significantly limit the change in the volume of the anode material. The creation of a  $\text{SiO}_x$  hybrid composite in a graphite shell will presumably prevent the surface oxidation of active materials due to the high chemical stability of graphite. Meanwhile, the commercial production of  $\text{SiO}_x/\text{C}$  is a huge problem.  $\text{SiO}_x$  powder produced by PVD and coated with carbon, which

provides a high energy density of about 450 mAh/g (half-cell test), is an expensive material ( $\sim \$1$  per gram, MTI Corporation). A typical method for the synthesis of  $\text{SiO}_x$  powder by reducing  $\text{SiO}_2$  with Si requires a very high temperature of  $1300^\circ\text{C}$ , at which only silicon monoxide (SiO) can be obtained [43]. The above problems associated with a complex production process can be solved by applying an inexpensive and environmentally friendly method from biomass, such as rice husks, sugar beets, sugar cane, walnut shells, cane leaves, and oat husks [44–48].

Here, studies are presented on the possible use of a hybrid composite  $\text{SiO}_x$  in a graphite shell derived from biomasses, as an effective anode material for LIBs. At the same time,  $\text{SiO}_2$  was synthesized from biological waste material - rice husk by an inexpensive and straightforward method, and the carbon shell was obtained from sucrose, which is also obtained from biomass. The proposed approach will solve several problems at once related to obtaining pure  $\text{SiO}_2$  and increasing the efficiency of its use in the field of energy storage. The hybrid composite  $\text{SiO}_2$  in a graphite shell ( $\text{SiO}_2/\text{C}$  composite) demonstrates a high reversible capacity with significantly improved cyclic stability.

## 2. Experimental section

### 2.1. Reagents and materials

Rice husk (RH) (Kyzylorda region, Kazakhstan), sulphuric acid ( $\text{H}_2\text{SO}_4$ , 93 %, Labofarm), sodium hydroxide (NaOH, 99 %, Labofarm), hydrochloric acid (HCl, 49 %, Sigma Aldrich), conductive carbon black (TIMICAL SUPER C45, density  $160 \text{ kg/m}^3$ , MTI Corporation), Argon gas (99.993 %, Ikhsan Technogaz LLP), Polyvinylidene Fluoride (PVDF,  $\geq 99.5$  %, Sigma Aldrich), 1-methyl-2-pyrrolidone ( $\text{C}_5\text{H}_9\text{NO}$ , ACS reagent,  $\geq 99.0$  %, Sigma Aldrich), sucrose (Almaty, Kazakhstan), acetone (93 %, Labofarm), Li foil (99.9 %, Shandong AME Energy Co., Ltd., China), electrolyte 1M  $\text{LiPF}_6$  (EC/DMC/DEC=1:1:1 v/v/v) and (Dongguan Gelon Lib Co., Ltd., China), separator Celgard 2500 (Zhengzhou TCH Instrument Co., Ltd, China). All reagents, except for rice hulls, were used without further purification.

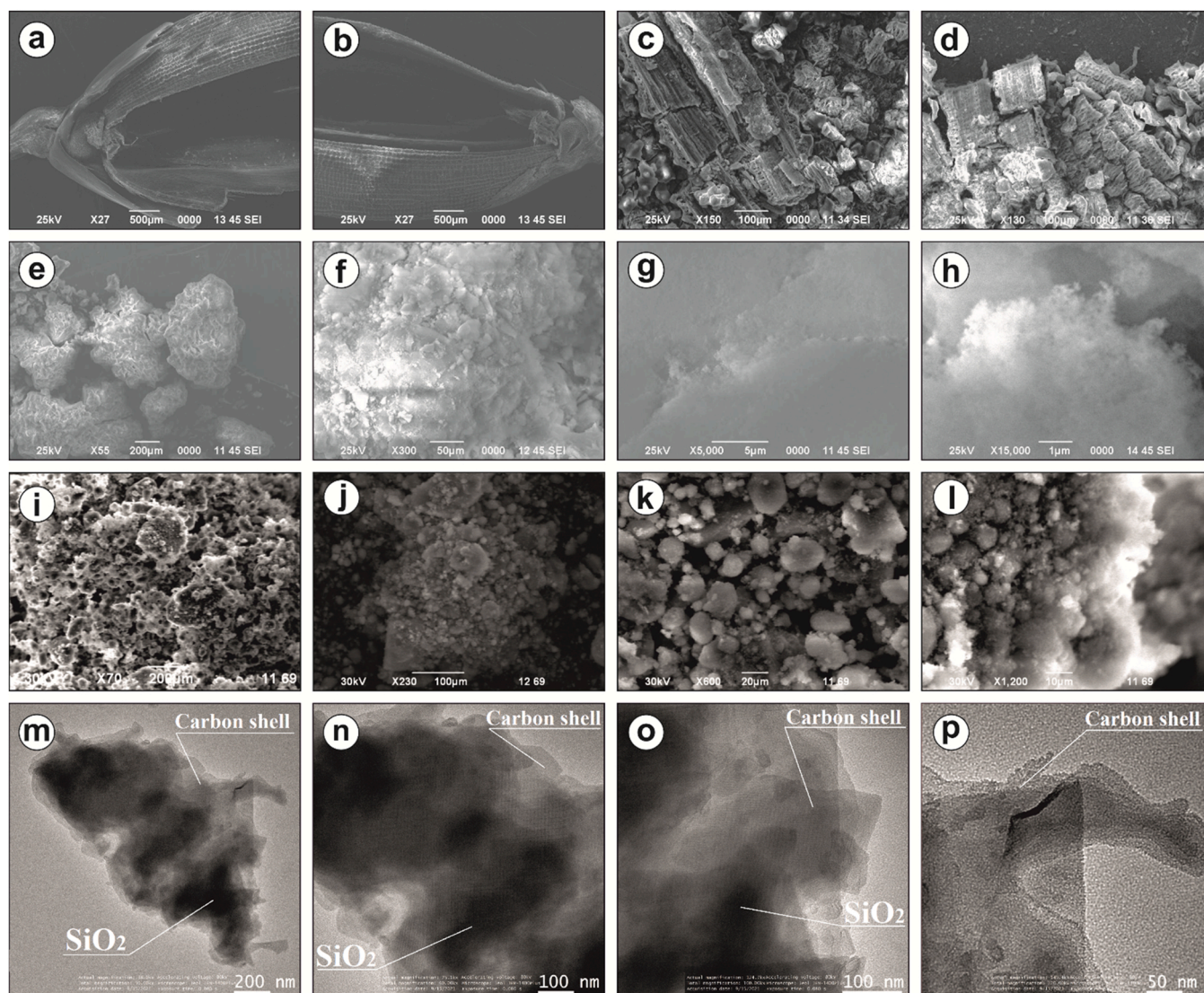


**Fig. 2.** a,b) – SEM images of raw RH; c,d) – SEM images of RH ash after calcination; e,f,g,h) – SEM images of SiO<sub>2</sub> after chemical purification; i,j,k,l) – SEM images of SiO<sub>2</sub> in graphite shell after activation with H<sub>2</sub>SO<sub>4</sub>; m,n,o,p) – TEM images of obtained SiO<sub>2</sub> in graphite shell.

## 2.2. Synthesis of amorphous SiO<sub>2</sub>

The process of synthesis of SiO<sub>2</sub> from RH is carried out in several stages: preliminary cleaning of RH with distilled water to remove dust (1 liter of distilled water was used for 50 g of RH), followed by drying at a temperature of 120 °C for 4 h; a dried 50 g sample of RH was mixed with 500 ml of 2 M HCl and dried again for 2 h at a temperature of 90 °C to accelerate the hydrolysis of cellulose and hemicellulose (2 M HCl can be used multiple times) [49,50]; after the resulting solution is filtered (paper filter 12 µm), washed with distilled water until pH 6 is reached and dried at a temperature of 120 °C (without heating rate control) for 4 h. The resulting powder is then thermally annealed at 600 °C (BS-MF-1200 C/4.5 L, Bes Saiman Group LLP) in the air for 4 h to remove organic elements. After the thermal annealing process, 10 g of the obtained white powder with black spots (black spots indicate that the sample still contains other elements, since ash contains not only SiO<sub>2</sub> but also other elements, including carbon) was added with 100 ml of 2 M NaOH, then heated to 90 °C and maintained at this temperature for 2 h with constant stirring (300 rpm). This step is needed to further increase the purity of the SiO<sub>2</sub> powder. SiO<sub>2</sub> is dissolved in NaOH and other impurities are left as solid substances. The resulting solution is filtered (microporous MCE membrane with a diameter of 50 mm, pore size 0.22

µm) to separate insoluble solid substances and 10 ml of HCl is added to the filtered liquid to form SiO<sub>2</sub> from Na<sub>2</sub>SiO<sub>3</sub>, after which washing, filtering, and drying are carried out again. The final product is pure white SiO<sub>2</sub>.

## 2.3. Carbon coated amorphous SiO<sub>2</sub>

To obtain a carbon shell on the surface of a SiO<sub>2</sub> particle, 0.5 g of sucrose was dissolved in 50 ml of distilled water with constant stirring, followed by adding of 5 g of the synthesized SiO<sub>2</sub>. For the uniform formation of the sugar layer, the resulting mixture was stirred in a magnetic stirrer (500 rpm) at a temperature of 100 °C until the water evaporated. ~5 g of the resulting powder coated with 0.5 g of sucrose was placed in a quartz crucible and heated in an inert atmosphere (Argon, 99.993 %), in several stages: a) from room temperature to 200 °C for 1 h; b) holding at 200 °C for 1 h to carbonize the sugar; c) from 200° to 750 °C for 1 h; d) holding at a temperature of 750 °C for 3 h to ensure complete carbonized sucrose graphitization. All process parameters were selected experimentally. After cooling, a dark gray SiO<sub>2</sub>/C composite material was obtained, which was subjected to mechanical grinding (3D ball milling: 3 times for 10 min with a break of 5 min, ceramic ball sizes 2 and 5 mm) to de-agglomerate. For activation, 5 g of SiO<sub>2</sub>/C was added to 10 ml of

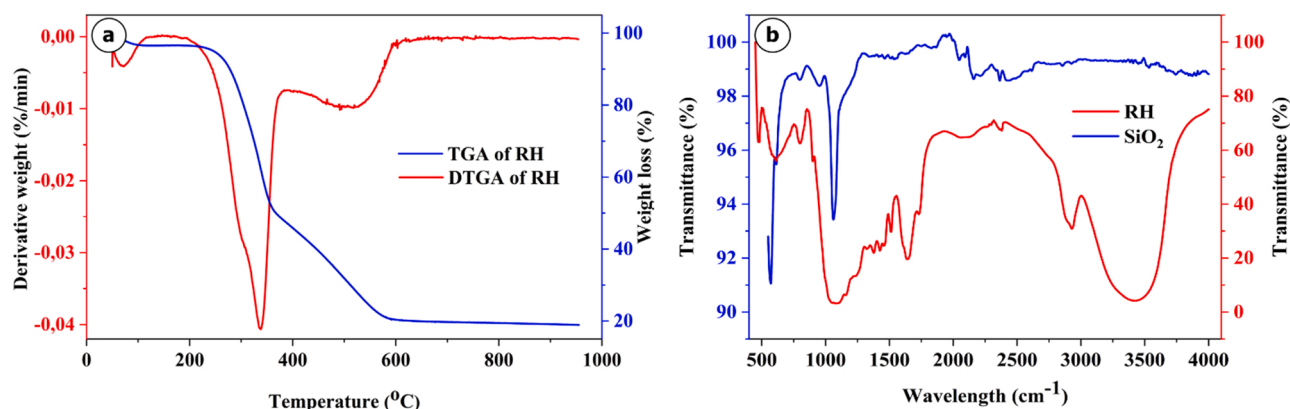


Fig. 3. a) TGA and DTGA of RH. b) FTIR of RH and SiO<sub>2</sub>.

H<sub>2</sub>SO<sub>4</sub> and kept at ambient temperature for 30 min followed by drying at 120 °C. The scheme of the process for obtaining SiO<sub>2</sub> in a graphite shell from rice husk and sucrose is shown in Fig. 1.

#### 2.4. Electrochemical measurements

Electrochemical measurements were carried out using a coin cell (CR2032) assembled in a vacuum glove box filled with high-purity Ar (99.999 %). Lithium chips with a diameter of 16 mm were used as the counter-electrode, the separator was a monolayer polypropylene film (Celgard 2400), and 1 mol/l LiPF<sub>6</sub> dissolved in a mixture of ethylene carbonate, dimethyl carbonate, and diethyl carbonate (EC:DMC:DEC 1:1:1 v/v/v) used as an electrolyte. The working electrode was made of active materials (SiO<sub>2</sub> in a graphite shell), carbon black (TIMICAL SUPER C45, Sigma-Aldrich), and PVDF (arkema HSV900, Sigma-Aldrich), in a weight ratio of 70:20:10 in an NMP solution (N-Methyl-2-pyrrolidone, Sigma-Aldrich). The mixed substance was stirred for 2 h at ambient temperature; it was then applied to Cu foil (16 μm thick) with an automatic film applicator (100 μm layer thickness). Next, copper foil with a wet applied electrode layer was dried at 120 °C under vacuum for 240 min. The prepared electrode is subjected to calendaring using a hot roller press at a temperature of 100 °C, then it is cut into disks with a diameter of 16 mm, and the active mass of the substance on the disk area is calculated. The electrochemical properties of the assembled half-cells were studied using CV in the voltage range of 0.01 V open circuit potential (OCP) to 3 V concerning Li<sup>+</sup>/Li with a scan rate of 0.1 mV s<sup>-1</sup>. Electrochemical impedance spectroscopy (EIS) measurements were carried out at a frequency range from 0.01 Hz to 100 kHz with a 5 mV sinusoidal signal amplitude at the OCP on an electrochemical work station (Potentiostat - Galvanostat P-40x). Galvanostatic charge-discharge cycling tests were performed on a multi-channel battery analyzer (Battery Testing System CT-4008 T-5V10mA-164). All parameters were studied at room temperature.

#### 2.5. Characterization of obtained samples

Raman spectra of the obtained samples were acquired on the Raman spectrometer (NT-MDT Spectrum Instruments) where the light source is a blue laser with a wavelength of 473 nm. Fourier transform infrared (FT-IR) spectra were collected using a specially molded tablets consisting of KBr and analyte. Measurements were taken in the range of 4000–450 cm<sup>-1</sup> at ambient temperature on the device "Spectrum 65" (Perkin Elmer). Nanostructural images of materials were obtained using a transmission electron microscope (JEM-2100, JEOL company, Japan). The surface microstructure images and chemical composition of the obtained materials were analyzed by scanning electron microscope (Quanta 3D 200i, FEI company, USA) equipped with Energy Dispersive X-ray Spectroscopy (Oxford instrument). XRD patterns were obtained

using a multifunctional X-ray diffractometer (DRONE-8, LOMO), using Cu-K (k = 0.15418 nm). The change in the mass of RH depending on temperature was studied on a thermogravimetric analyzer (Simultaneous Thermal Analyzer (STA) 6000).

### 3. Results and discussion

#### 3.1. Characterization of samples

##### 3.1.1. SEM and TEM characterization

The resulting samples were examined using scanning electron microscopy and transmission electron microscopy (SEM and TEM) (Fig. 2). SEM images of RH before and after annealing are presented in Fig. 2a-d, showing that RH samples have a clean, uniform corrugated structure (Fig. 2a,b). After the annealing process, the structure is presented in the form of uniform, clearly defined layers of loose flakes (Fig. 2c,d). At the same time, the entire corrugated structure of the RH was destroyed, which indicates the validity of the choice of parameters of the thermal annealing process, which was also confirmed by the data of thermogravimetric analysis (Fig. 3a). SEM images of pure SiO<sub>2</sub> after treatment with 2 M sodium hydroxide show the presence of small, inhomogeneous agglomerates ranging in size from 200 to 500 μm, while, upon magnification, smaller nanosized particles with a relatively uniform morphology can be seen (Fig. 2e-h). After annealing SiO<sub>2</sub> with sucrose at 750 °C, the particles turn into a more round-shaped powder with different diameters (Fig. 2i-l). The presented TEM images (Fig. 2m-p) for the composite SiO<sub>2</sub> in a graphite shell indicate the presence of a carbon shell around the dark dots, which are SiO<sub>2</sub> nanoparticles. Although the particles inside the shell are unevenly distributed, they are tightly bound in the structure of the carbon matrix, which presumably will reduce the volume effect of SiO<sub>2</sub> nanoparticles.

##### 3.1.2. Thermogravimetric analysis and FTIR of samples

The thermogravimetric analysis data for RH calcination are presented in Fig. 3a, which can be divided into three stages. The first stage, from room temperature to 120 °C, which is associated with the evaporation of residual moisture from the RH. The second stage, from 230° to 400 °C, which is characterized by the decomposition and carbonization of hemicellulose, lignin and other organic substances in the RH structure and the weight loss is 69 %. The third stage, from 400° to 600 °C, where the processes of combustion of carbonized materials take place, after which, as a result, 19 % of the total mass remains, which mainly contains SiO<sub>2</sub>. For the additional study of the obtained samples, an analysis was carried out using infrared Fourier spectroscopy (FTIR) using the total reflection mode (Fig. 3b). Analysis of the data obtained indicates the presence of peaks at 3200–3600 cm<sup>-1</sup>, which corresponds to the stretching vibration of the OH group, and a peak at 1724 cm<sup>-1</sup> corresponding to C—O—C bonds, which indicates the formation of

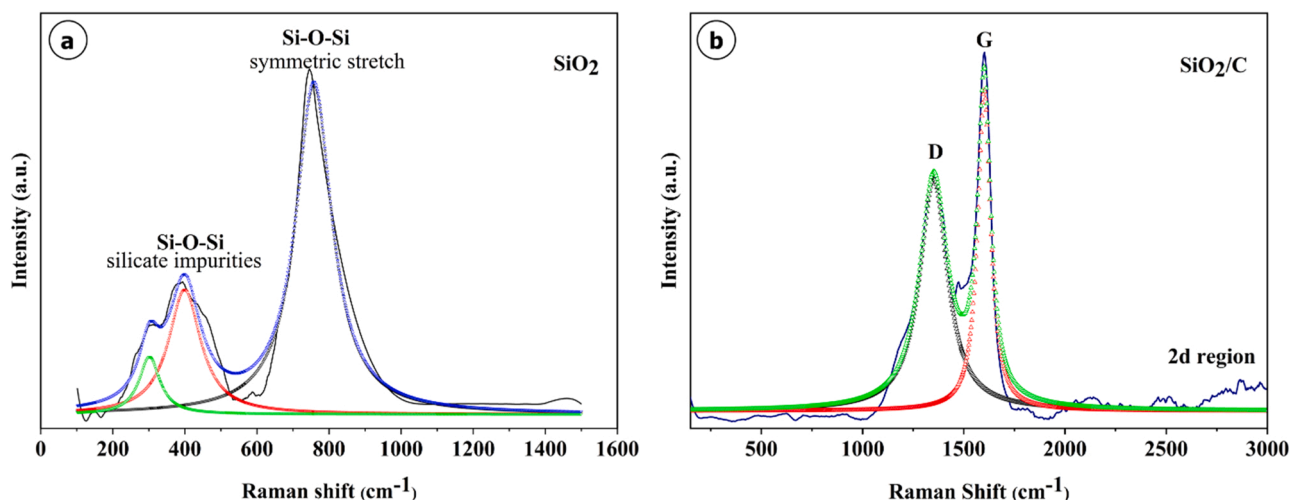


Fig. 4. a) Raman shift of the pure  $\text{SiO}_2$  powder and b)  $\text{SiO}_2$  in a graphite shell.

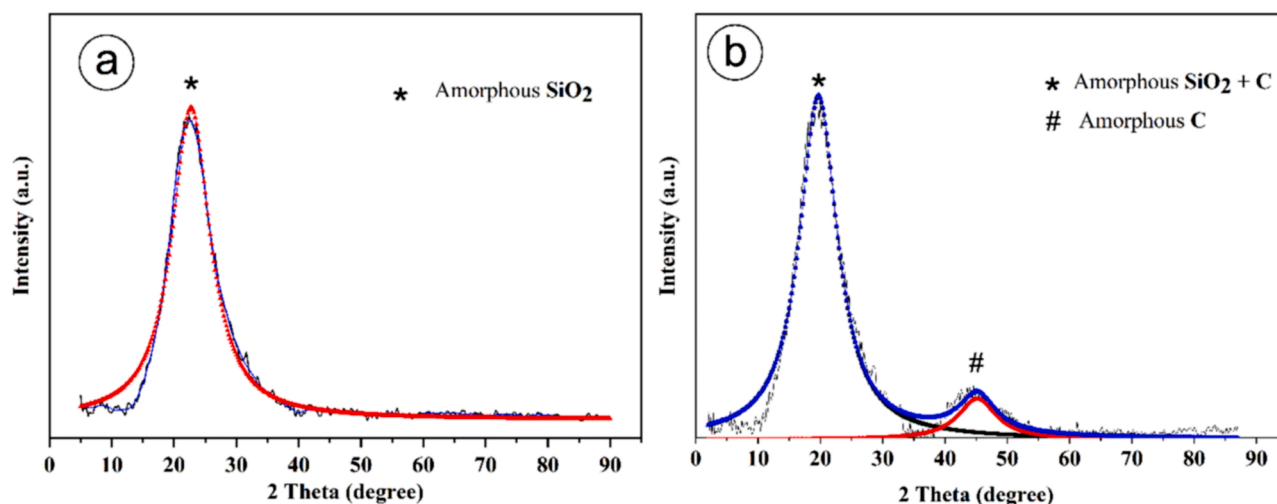


Fig. 5. XRD patterns of the pure  $\text{SiO}_2$  (a) and  $\text{SiO}_2$  in a graphite shell (b).

hemicellulose, while a characteristic peak at  $1514\text{ cm}^{-1}$  corresponds to carbon double bonds indicating lignin formations. For the  $\text{SiO}_2$  sample, the spectra indicate the presence of a peak in the region of  $1020\text{--}1110\text{ cm}^{-1}$ , which is attributed to the asymmetric stretching vibration of Si-O-Si, and a peak at  $566\text{ cm}^{-1}$  indicates the asymmetric bending and stretching vibration of SiO.

### 3.1.3. Raman analysis of samples

Raman spectroscopy analysis for pure  $\text{SiO}_2$  and  $\text{SiO}_2$  in a graphite shell was carried out (Fig. 4a, b). The Raman spectra for  $\text{SiO}_2$  were appropriately normalized to the amplitude of the band at 300, 380,  $800\text{ cm}^{-1}$  associated with the natural vibrational modes of silica O-Si-O [51]. The well-known G peak is observed in all  $\text{sp}^2$  systems near  $1600\text{ cm}^{-1}$  and the Raman peak D indeed indicates the presence of six-fold aromatic rings as well as  $\text{sp}^2$  bonds. The D-peak in Raman spectra is induced by defects or disorders and increases linearly with decreasing graphite crystallite size [52]. In our case, as shown in Fig. 4b, the Raman spectra of  $\text{SiO}_2$  in a graphite shell has two peaks at  $1349\text{ cm}^{-1}$  and  $1602\text{ cm}^{-1}$ , corresponding to the D and G bands corresponding to typical graphite sheet with defects. The Raman spectrum is a characteristic feature of carbon-based materials, and the intensity ratio of the D and G bands ( $I_D/I_G$ ) can also be used to estimate the degree of graphitization in carbon-based materials. The  $I_D/I_G$  ratio is inversely

proportional to the degree of graphitization. A lower  $I_D/I_G$  ratio means a higher degree of graphitization of the carbon component in the composites, while the  $I_D/I_G$  value for the composite  $\text{SiO}_2$  in a graphite shell was  $\sim 0.84$ .

### 3.1.4. XRD analysis of samples

The obtained samples were also examined using XRD analysis, the data of which are presented in Fig. 5. Silicon dioxide powder before modifications with sucrose is amorphous, which is confirmed by X-ray diffraction patterns (Fig. 5a). After calcination of RH at  $600^\circ\text{C}$  and chemical treatment, pure  $\text{SiO}_2$  was obtained. A broad peak between  $18^\circ$  and  $30^\circ$  centered at  $24^\circ$  characterizes the amorphous state of  $\text{SiO}_2$ . The successful modification of  $\text{SiO}_2$  (creation of a carbon shell around silicon dioxide particles) is evidenced by a broad weak peak at about  $44^\circ$  corresponding to diffusion scattering of the carbon coating, while a broad diffraction peak between  $18^\circ$  and  $30^\circ$  is associated with amorphous  $\text{SiO}_2$ . The diffraction peak at around  $26^\circ$ , which belongs to graphitic carbon, is not seen because of the broad peak of amorphous  $\text{SiO}_2$ . Graphitic carbon is the result of the pyrolysis and chemical activation of sucrose. The X-ray diffraction pattern (XRD) of the  $\text{SiO}_2/\text{C}$  composite shows a clear shift of the amorphous  $\text{SiO}_2$  peak from  $24^\circ$  to  $22^\circ$ . There are no Si or SiC peaks in the XRD pattern of the  $\text{SiO}_2/\text{C}$  composite, which indicates successful modification without the formation of these phases.

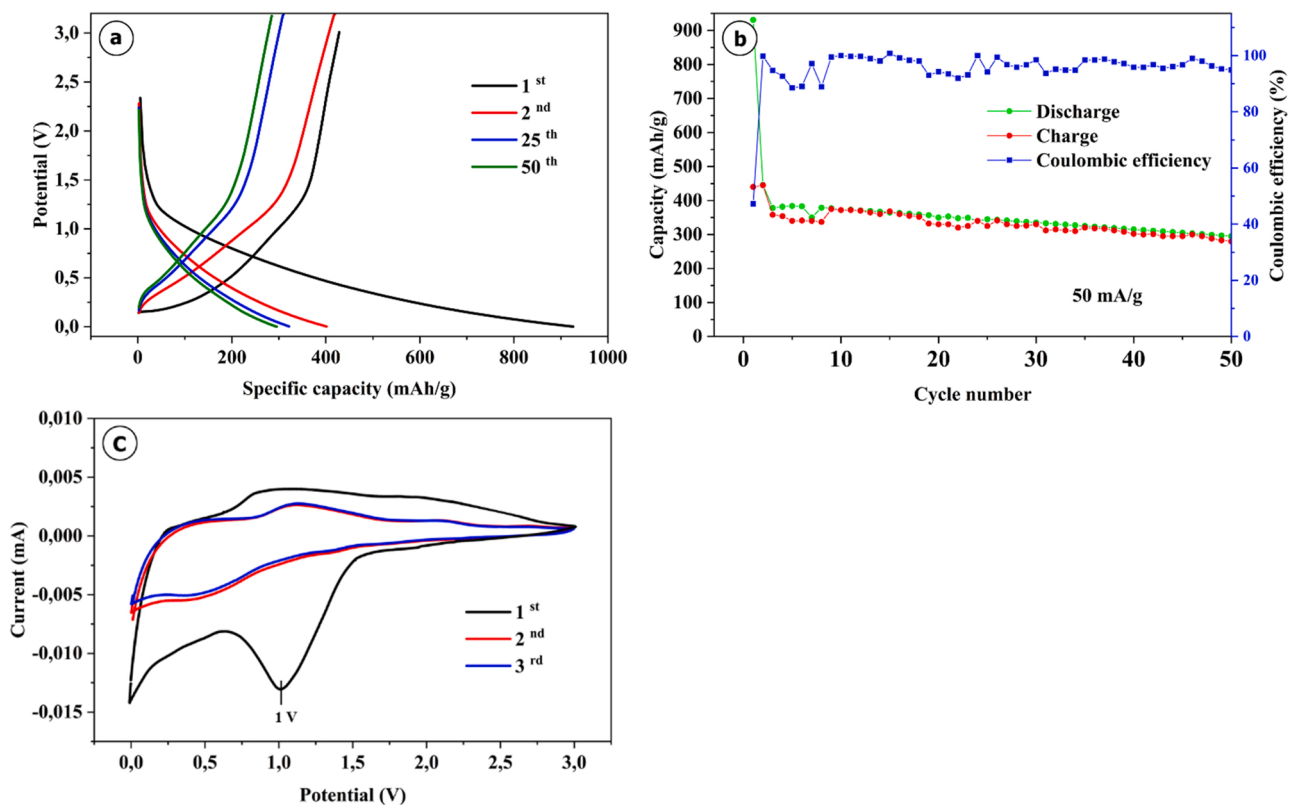


Fig. 6. a) Galvanostatic voltage profiles for SiO<sub>2</sub> at 50 mA/g. b) Charge-discharge capacities versus cycle number. c) CV curves of SiO<sub>2</sub> at a scan rate of 0.1 mVs<sup>-1</sup>.

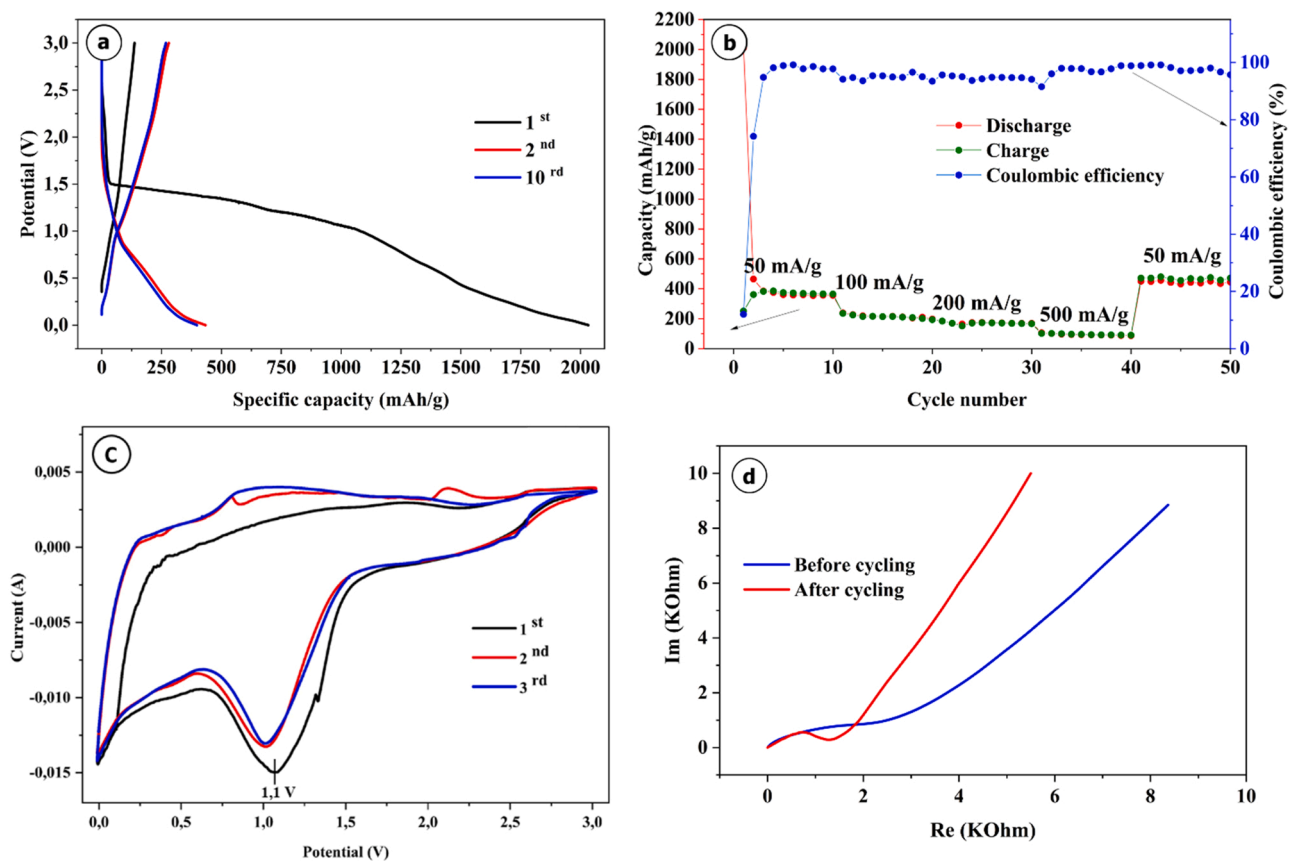


Fig. 7. a) Galvanostatic voltage profiles for SiO<sub>2</sub>/C at 50 mA/g. b) Charge-discharge capacities versus cycle number. c) CV of SiO<sub>2</sub>/C using a scan rate of 0.1 mV/s. d) The Nyquist plots of SiO<sub>2</sub>/C before and after cycling.

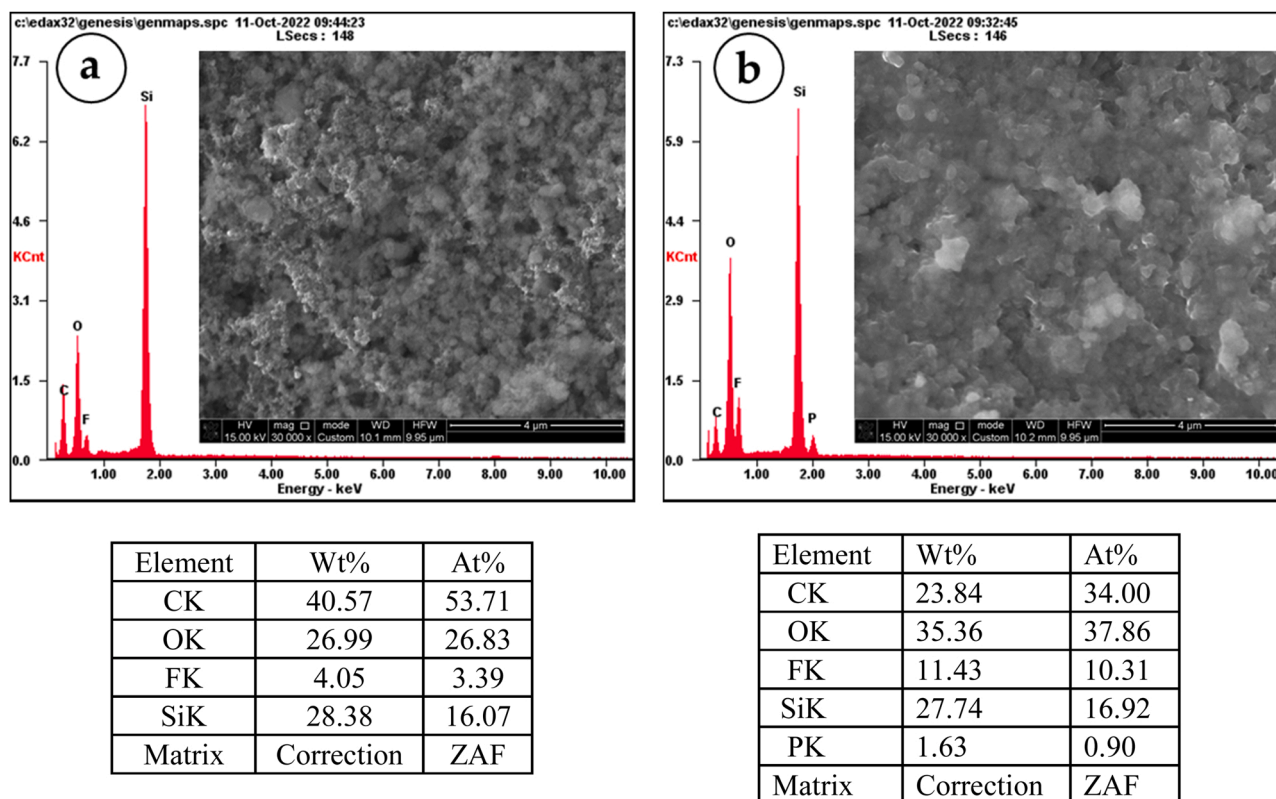


Fig. 8. SEM and EDX analysis of SiO<sub>2</sub>/C a) before cycles b) after 50 cycles.

### 3.2. Electrochemical performance

Cyclic voltammetry and the charge-discharge curve are used to explain the charge and discharge mechanism of batteries. However, unfortunately, the mechanism of electrochemical lithiation of SiO<sub>2</sub> and composites based on it is not completely clear. In this work, electrochemical measurements were carried out using half coin cells (type CR2032) assembled using anodes based on pure SiO<sub>2</sub> and SiO<sub>2</sub>/C composite to understand the effect of the graphite shell on the electrochemical properties of the LIB anode. Half coin cells were assembled from pure SiO<sub>2</sub> and the SiO<sub>2</sub>/C composite, as described in Section 2.4. For pure SiO<sub>2</sub>, CV peaks around 1 V and below 0.2 V, which are associated with irreversible electrochemical reactions between SiO<sub>2</sub> and Li, disappearing in subsequent cycles (Fig. 6.). The first cycle showed a charging capacity of 423 mAh/g at 50 mA/g, while a discharge capacity of 922 mAh/g, at a Coulomb efficiency value of 45 %. This behavior may be related to the formation of a solid electrolyte interphase (SEI) layer on the electrode surface. One can clearly distinguish the decrease in specific capacity in subsequent cycles and reaches a value of 295 mAh/g at cycle 50, which is directly related to the destruction of the active materials.

Galvanostatic charge-discharge measurements were carried out to understand the effect of the graphite shell on the electrochemical properties of the SiO<sub>2</sub>/C composite (Fig. 7). The initial sharp decrease in charge capacity during the first cycles, observed in Fig. 7(b), can be explained by the formation of a solid electrolyte interphase SEI layer on the electrode surface and the decomposition of the electrolyte. The very thin SiO<sub>2</sub> walls allow a higher percentage of active material to be lithiated and thus provide a noticeably higher capacitance. In the first cycle, the SiO<sub>2</sub>/C composite demonstrates a high specific discharge capacity of 2018 mAh/g and a specific charging capacity of 240 mAh/g, while the Coulomb efficiency remains low and is 12 % at a current of 50 mA/g. From the third to the tenth cycle, the specific capacity remains constant and has a value of about 365 mAh/g with a Coulomb efficiency of about 96 %. To further explore the role of graphite, the cyclic

performance of the resulting composite was also tested at various current densities. So, at current values of 100 mA/g, the specific capacity of the batteries decreases to 215 mAh/g, at the same time, at 200 mA/g, the specific capacity of the batteries is 165 mAh/g, while at 500 mA/g, the specific capacity decreases to 88 mAh/g. It should be noted that, starting from the 40th cycle, the capacity increases sharply in comparison with the first 10 cycles and amounts to 450 mAh/g at a current density of 50 mA/g. This behavior is also observed in similar studies [51, 53,54] and may be due to the fact that the carbon shell provides good conductivity and keeps the electrode from expansion/destruction. It is explained that in the initial cycles, the active material in the electrode are not completely used. Still, after a certain number of cycles, more parts of the active material start to react with lithium. It is associated with an improvement in the kinetics of diffusion of lithium ions, as well as with the activation and stabilization of materials during cycling as in some works [55,56]. In addition, the decrease in the first 10 cycles is due to the volumetric expansion of silicon during the cycling process, which leads to partial destruction of the SEI layers. At the same time, the observed stability from cycle 40 indicates a high rate of reactivation, which allows efficient restructuring of porous microstructures and optimization of a stable SEI. According to a number of studies [2,38,57], such a stable capacitance value with high values of the Coulomb efficiency is maintained up to 300 cycles.

CV of the original SiO<sub>2</sub>/C composites were investigated in half-cell batteries for 3 consecutive cycles from 3.0 V to 0.01 V at a scan rate of 0.1 mV/s. An intact SiO<sub>2</sub> electrode exhibits cathodic peaks above 1.0 V, corresponding to irreversible electrochemical reactions between SiO<sub>2</sub> and lithium, which disappear in subsequent cycles. The cathode peak below 0.2 V can be attributed to the Si lithiation process. Electrochemical equations can be expressed as follows [58]:

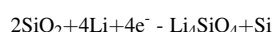
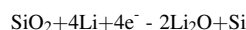
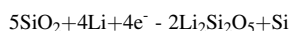


**Table 1**

Performance comparison of Si and C electrodes for LIBs.

| N  | Product                                | Discharge capacities (mAh/g) | Current density mA/g | CE ( %)    | Ref.      |
|----|----------------------------------------|------------------------------|----------------------|------------|-----------|
| 1  | Si/SiO <sub>2</sub> @AL <sub>2</sub> C | ~1000                        | 1 C                  | 74.3 %     | [59]      |
| 2  | Si/C                                   | 965                          | 200                  | –          | [60]      |
| 3  | SiO <sub>2</sub> /C                    | 915                          | 100                  | 93.3 %     | [15]      |
| 4  | SiO <sub>2</sub> /C                    | 800                          | 50                   | above 97 % | [61]      |
| 5  | C/SiO <sub>2</sub> -0.085 M            | 714.3                        | 1 C                  | 98.9 %     | [62]      |
| 6  | SiO <sub>2</sub> @C                    | 653.4                        | –                    | over 97 %  | [63]      |
| 7  | SiO <sub>2</sub> /C                    | 586                          | 0.1 C                | 87 %       | [64]      |
| 8  | SiO <sub>2</sub> @C                    | 557                          | 100                  | ~100 %     | [65]      |
| 9  | Carbon-coated silica macroparticles    | 500                          | –                    | above 97 % | [66]      |
| 10 | Si/SiO <sub>2</sub> @C                 | 482                          | 50                   | above 97 % | [67]      |
| 11 | Activated carbon                       | 448                          | 0.2 C                | ~99 %      | [68]      |
| 12 | SiO <sub>2</sub> aerogel               | 125                          | 100                  | 97 %       | [69]      |
| 13 | SiO <sub>2</sub> /NGA2                 | 418                          | 100                  | 97 %       |           |
| 14 | Activated carbon                       | 400                          | 0.2                  | 99 %       | [70]      |
| 15 | CFCA-850                               | 285.78                       | 0.25 C               | ~100 %     | [71]      |
| 16 | SiO <sub>2</sub> /C                    | 450                          | 50                   | above 97 % | This work |



A less distinct peak occurs at 1.40 V, which may be due to the reaction between the electrolyte and the electrode and the onset of SEI formation. Both of these peaks become inconspicuous in the 2nd cycle, suggesting that the formation of SEI occurs mainly during the first cycle and that these initial reactions are irreversible. Electrochemical impedance spectroscopy (EIS) before and after battery cycling was used to study in detail the kinetics of electrochemical reactions occurring in the battery. Nyquist plots are shown in Fig. 7. Nyquist plots consist of an indented semicircle at high frequencies and a straight line at low frequencies. Before cycling, the ion transfer resistance in a battery with SiO<sub>2</sub>/C – LiPF<sub>6</sub> as active material – electrolyte, corresponding to lithium-ion migration between the electrode and the electrolyte interface, is more than 2 kΩ. After 50 cycles, the cell resistance decreases, and is slightly more than 1 kΩ.

SEM and elemental analysis of the surface of the SiO<sub>2</sub>/C electrode before and after cycling is shown in Fig. 8. In the SEM image before cycling (Fig. 8 a), it is clearly seen that the surface is rough and small particles are associated with each other. Elemental analysis showed that the main elements are C, O, Si and, in small amounts, F. The appearance of F before cycling is associated with the addition of the binder material PVDF. After cycling, the SEM image clearly shows the formation of a hazy SEI layer on the electrode surface (Fig. 8b). Elemental analysis showed the appearance of element P and an increase in the intensity of F. Table 1.

#### 4. Conclusion

The simple and cost-effective method for the synthesis of a composite in the form of SiO<sub>2</sub> in a graphite shell obtained entirely from biosources can be easily adapted for mass production and used as an efficient active anode material for LIBs. The use of the resulting composite as an active anode material for LIB made it possible to achieve a specific capacity of 450 mA h/g at a current density of 50 mA/g in 50 cycles. Cycle stability of the SiO<sub>2</sub>/C composite is due to less volume change of amorphous SiO<sub>2</sub> compared to pure crystalline SiO<sub>2</sub> and as well as the presence of a protective graphite shell. A significant improvement in the electrochemical characteristics of the SiO<sub>2</sub> composite in a graphite shell compared to pure SiO<sub>2</sub> is associated with the positive effect of the carbon matrix, which makes it possible to reduce the eclectic and thermal

resistance and the effect of volume increase. At the same time, a simple method for obtaining a SiO<sub>2</sub> composite in a graphite shell using renewable biomass is a promising direction for creating next-generation LIBs.

#### CRediT authorship contribution statement

**Kydyr Askaruly:** (First Author): Experiment, Original draft preparation, Mukhtar Yeleuov: Idea, Writing – review & editing, **Azamat Taurbekov:** Experiment, **Bibigul Sarsembayeva:** Experiment, **Aidos Tolynbekov:** Calculation. **Zhylybayeva Nurzhamal:** Supervision, **Seitkhan Azat:** Writing – review & editing, **Alisher Abdisattar:** Calculation. **Chingis Daulbayev:** Writing – review & editing.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Data Availability

Data will be made available on request.

#### Acknowledgments

This research was funded by the Science Committee of the Ministry of Education and Science of the Republic of Kazakhstan (Grant No. OR11465430).

#### Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mtcomm.2022.105136.

#### References

- [1] W.-S. Chang, C.-M. Park, J.-H. Kim, Y.-U. Kim, G. Jeong, H.-J. Sohn, Quartz (SiO<sub>2</sub>): a new energy storage anode material for Li-ion batteries, *Energy Environ. Sci.* 5 (2012) 6895, <https://doi.org/10.1039/c2ee00003b>.
- [2] H. Zhang, H. Zhao, M.A. Khan, W. Zou, J. Xu, L. Zhang, J. Zhang, Recent progress in advanced electrode materials, separators and electrolytes for lithium batteries, *J. Mater. Chem. A* 6 (2018) 20564–20620, <https://doi.org/10.1039/C8TA05336G>.
- [3] J. Xie, Y.-C. Lu, A retrospective on lithium-ion batteries, *Nat. Commun.* 11 (2020) 2499, <https://doi.org/10.1038/s41467-020-16259-9>.
- [4] A. Abdisattar, M. Yeleuov, C. Daulbayev, K. Askaruly, A. Tolynbekov, A. Taurbekov, N. Prikhodko, Recent advances and challenges of current collectors for supercapacitors, *Electrochem. Commun.* 142 (2022), 107373, <https://doi.org/10.1016/j.elecom.2022.107373>.
- [5] M. Schnabel, S.P. Harvey, E. Arca, C. Stetson, G. Teeter, C. Ban, P. Stradins, Surface SiO<sub>2</sub> thickness controls uniform-to-localized transition in lithiation of silicon anodes for lithium-ion batteries, *ACS Appl. Mater. Interfaces* 12 (2020) 27017–27028, <https://doi.org/10.1021/acsami.0c03158>.
- [6] Y. Zhang, Y. Li, Z. Wang, K. Zhao, Lithiation of SiO<sub>2</sub> in Li-Ion batteries: in situ transmission electron microscopy experiments and theoretical studies, *Nano Lett.* 14 (2014) 7161–7170, <https://doi.org/10.1021/nl503776u>.
- [7] F. Duffner, N. Kronmeyer, J. Tübke, J. Leker, M. Winter, R. Schmuch, Post-lithium-ion battery cell production and its compatibility with lithium-ion cell production infrastructure, *Nat. Energy* 6 (2021) 123–134, <https://doi.org/10.1038/s41560-020-00748-8>.
- [8] N. Hamzelui, G.G. Eshetu, E. Figgemeier, Customizing active materials and polymeric binders: stern requirements to realize silicon-graphite anode based lithium-ion batteries, *J. Energy Storage* 35 (2021), 102098, <https://doi.org/10.1016/j.est.2020.102098>.
- [9] Y. Wang, H. Li, Z. Wang, C. Lian, Z. Xie, Factors affecting stress in anode particles during charging process of lithium ion battery, *J. Energy Storage* 43 (2021), 103214, <https://doi.org/10.1016/j.est.2021.103214>.
- [10] B. Ghanbarzadeh, A. Khatibi, A. Asadi, B. Shokri, Regulating lithium-ion flux in the solid electrolyte interphase layer to prevent lithium dendrite growth on lithium metal anode, *J. Energy Storage* 47 (2022), 103668, <https://doi.org/10.1016/j.est.2021.103668>.
- [11] Y. Inui, S. Hirayama, T. Tanaka, Temperature dependence of impedance spectrum of charge-transfer processes in lithium-ion batteries with nickel-manganese-cobalt

- cathode and graphite anode, *J. Energy Storage* 44 (2021), 103390, <https://doi.org/10.1016/j.est.2021.103390>.
- [12] M. Nazhipkyzy, A.B. Maltay, K. Askaruly, D.D. Assylkhanova, A.R. Seitkazinova, Z. A. Mansurov, Biomass-derived porous carbon materials for Li-ion battery, *Nanomaterials* 12 (2022) 3710, <https://doi.org/10.3390/nano12203710>.
  - [13] Z. Favors, W. Wang, H.H. Bay, A. George, M. Ozkan, C.S. Ozkan, Stable cycling of SiO<sub>2</sub> nanotubes as high-performance anodes for lithium-ion batteries, *Sci. Rep.* 4 (2015) 4605, <https://doi.org/10.1038/srep04605>.
  - [14] Y. Zhao, Z. Liu, Y. Zhang, A. Mentbayeva, X. Wang, M.Yu Maximov, B. Liu, Z. Bakenov, F. Yin, Facile synthesis of SiO<sub>2</sub>@C nanoparticles anchored on MWNT as high-performance anode materials for Li-ion batteries, *Nanoscale Res. Lett.* 12 (2017) 459, <https://doi.org/10.1186/s11671-017-2226-2>.
  - [15] L. Cao, J. Huang, Z. Lin, X. Yu, X. Wu, B. Zhang, Y. Zhan, F. Xie, W. Zhang, J. Chen, H. Meng, Amorphous SiO<sub>2</sub>/C composite as anode material for lithium-ion batteries, *J. Mater. Res.* 33 (2018) 1219–1225, <https://doi.org/10.1557/jmr.2017.298>.
  - [16] Z. Liu, Q. Yu, Y. Zhao, R. He, M. Xu, S. Feng, S. Li, L. Zhou, L. Mai, Silicon oxides: a promising family of anode materials for lithium-ion batteries, *Chem. Soc. Rev.* 48 (2019) 285–309, <https://doi.org/10.1039/C8CS00441B>.
  - [17] P. Saha, T.R. Mohanta, A. Kumar, SEI layer and impact on Si-anodes for Li-ion batteries, in: P.N. Kumta, A.F. Hepp, M.K. Datta, O.I. Velikokhatnyi (Eds.), *Silicon Anode Syst. Lithium-Ion Batter*, Elsevier, 2022, pp. 183–263, <https://doi.org/10.1016/B978-0-12-819660-1.00001-3>.
  - [18] G. Yang, S. Frisco, R. Tao, N. Philip, T.H. Bennett, C. Stetson, J.-G. Zhang, S.-D. Han, G. Teeter, S.P. Harvey, Y. Zhang, G.M. Veith, J. Nanda, Robust solid/electrolyte interphase (SEI) formation on Si anodes using glyme-based electrolytes, *ACS Energy Lett.* 6 (2021) 1684–1693, <https://doi.org/10.1021/acsenenerglett.0c02629>.
  - [19] U.S. Vogl, S.F. Lux, E.J. Crumlin, Z. Liu, L. Terborg, M. Winter, R. Kostecki, The mechanism of SEI formation on a single crystal Si(100) electrode, *J. Electrochem. Soc.* 162 (2015) A603–A607, <https://doi.org/10.1149/2.0391504jes>.
  - [20] Y. Sun, K. Liu, Y. Zhu, Recent progress in synthesis and application of low-dimensional silicon based anode material for lithium ion battery, *J. Nanomater.* 2017 (2017) 1–15, <https://doi.org/10.1155/2017/4780905>.
  - [21] C. Xu, F. Lindgren, B. Philippe, M. Gorgoi, F. Björefors, K. Edström, T. Gustafsson, Improved performance of the silicon anode for Li-Ion batteries: understanding the surface modification mechanism of fluoroethylene carbonate as an effective electrolyte additive, *Chem. Mater.* 27 (2015) 2591–2599, <https://doi.org/10.1021/acs.chemmater.5b00339>.
  - [22] U.S. Vogl, S.F. Lux, P. Das, A. Weber, T. Placke, R. Kostecki, M. Winter, The mechanism of SEI formation on single crystal Si(100), Si(110) and Si(111) electrodes, *J. Electrochem. Soc.* 162 (2015) A2281–A2288, <https://doi.org/10.1149/2.0361512jes>.
  - [23] J.R. Szczech, S. Jin, Nanostructured silicon for high capacity lithium battery anodes, *Energy Env. Sci.* 4 (2011) 56–72, <https://doi.org/10.1039/C0EE00281J>.
  - [24] G.X. Wang, J.H. Ahn, J. Yao, S. Bewlay, H.K. Liu, Nanostructured Si-C composite anodes for lithium-ion batteries, *Electrochem. Commun.* 6 (2004) 689–692, <https://doi.org/10.1016/j.elecom.2004.05.010>.
  - [25] J. Hwang, M. Jung, J.-J. Park, E.-K. Kim, G. Lee, K.J. Lee, J.-H. Choi, W.-J. Song, Preparation and electrochemical characterization of Si@C nanoparticles as an anode material for lithium-ion batteries via solvent-assisted wet coating process, *Nanomaterials* 12 (2022) 1649, <https://doi.org/10.3390/nano12101649>.
  - [26] S. You, H. Tan, L. Wei, W. Tan, C. Chao Li, Design strategies of Si/C composite anode for lithium-ion batteries, *Chem. – Eur. J.* 27 (2021) 12237–12256, <https://doi.org/10.1002/chem.202100842>.
  - [27] Q. Shi, J. Zhou, S. Ullah, X. Yang, K. Tokarska, B. Trzebicka, H.Q. Ta, M. H. Rummeli, A review of recent developments in Si/C composite materials for Li-ion batteries, *Energy Storage Mater.* 34 (2021) 735–754, <https://doi.org/10.1016/j.ensm.2020.10.026>.
  - [28] W. Tu, Z. Bai, Z. Deng, H. Zhang, H. Tang, In-situ synthesized Si@C materials for the lithium ion battery: a mini review, *Nanomaterials* 9 (2019) 432, <https://doi.org/10.3390/nano9030432>.
  - [29] M.S. Al Ja'farawy, D.N. Hikmah, U. Riyadi, A. Purwanto, H. Widiyandari, A review: the development of SiO<sub>2</sub>/C anode materials for lithium-ion batteries, *J. Electron. Mater.* 50 (2021) 6667–6687, <https://doi.org/10.1007/s11664-021-09187-x>.
  - [30] W.-C. Shi, Y.-R. Shao, Y. Shen, Z.-F. Li, T.-L. Hu, Facile synthesis of porous iron oxides heterostructural nanosheets as an enhanced anode material for lithium ion battery, *Mater. Lett.* 321 (2022), 132454, <https://doi.org/10.1016/j.matlet.2022.132454>.
  - [31] F. Bu, W. Zhou, Y. Xu, Y. Du, C. Guan, W. Huang, Recent developments of advanced micro-supercapacitors: design, fabrication and applications, *Npj Flex. Electron.* 4 (2020) 1–16, <https://doi.org/10.1038/s41528-020-00093-6>.
  - [32] J.C. Barbosa, R. Gonçalves, C.M. Costa, S. Lanceros-Mendez, Recent advances on materials for lithium-ion batteries, *Energies* 14 (2021) 3145, <https://doi.org/10.3390/en14113145>.
  - [33] C. Floraki, A. Sapountzis, D. Vernardou, APCVD graphene-based composite electrodes for Li-Ion batteries, *Energies* 15 (2022) 926, <https://doi.org/10.3390/en15030926>.
  - [34] Y. Ju, J.A. Tang, K. Zhu, Y. Meng, C. Wang, G. Chen, Y. Wei, Y. Gao, SiOx/C composite from rice husks as an anode material for lithium-ion batteries, *Electrochim. Acta* 191 (2016) 411–416, <https://doi.org/10.1016/j.electacta.2016.01.095>.
  - [35] Q. Xu, J.-K. Sun, Y.-X. Yin, Y.-G. Guo, Facile synthesis of blocky SiO<sub>x</sub>/C with graphite-like structure for high-performance lithium-ion battery anodes, *Adv. Funct. Mater.* 28 (2018) 1705235, <https://doi.org/10.1002/adfm.201705235>.
  - [36] G. Li, J.-Y. Li, F.-S. Yue, Q. Xu, T.-T. Zuo, Y.-X. Yin, Y.-G. Guo, Reducing the volume deformation of high capacity SiOx/G/C anode toward industrial application in high energy density lithium-ion batteries, *Nano Energy* 60 (2019) 485–492, <https://doi.org/10.1016/j.nanoen.2019.03.077>.
  - [37] G. Zheng, Y. Xiang, L. Xu, H. Luo, B. Wang, Y. Liu, X. Han, W. Zhao, S. Chen, H. Chen, Q. Zhang, T. Zhu, Y. Yang, Controlling surface oxides in Si/C nanocomposite anodes for high-performance Li-ion batteries, *Adv. Energy Mater.* 8 (2018) 1801718, <https://doi.org/10.1002/aenm.201801718>.
  - [38] M. Xu, J. Ma, G. Niu, H. Yang, M. Sun, X. Zhao, T. Yang, L. Chen, C. Wang, A low-cost and high-capacity SiO<sub>x</sub>/C@graphite hybrid as an advanced anode for high-power lithium-ion batteries, *ACS Omega* 5 (2020) 16440–16447, <https://doi.org/10.1021/acsomega.0c00686>.
  - [39] G.G. Eshetu, H. Zhang, X. Judez, H. Adenusi, M. Armand, S. Passerini, E. Figgemeier, Production of high-energy Li-ion batteries comprising silicon-containing anodes and insertion-type cathodes, *Nat. Commun.* 12 (2021) 5459, <https://doi.org/10.1038/s41467-021-25334-8>.
  - [40] J. Peng, W. Li, Z. Wu, H. Li, Y. Huang, Y. Ouyang, Y. Wang, X. Guo, G. Chen, X. Wang, Rational design and performance of anode materials based on Si/SiO<sub>x</sub>/C particles anchored on graphene sheets, *ACS Appl. Energy Mater.* 4 (2021) 4966–4975, <https://doi.org/10.1021/acsaem.1c00523>.
  - [41] J. Moon, Tailoring the oxygen content in lithiated silicon oxide for lithium-ion batteries, *Int. J. Energy Res.* 45 (2021) 7315–7325, <https://doi.org/10.1002/er.6314>.
  - [42] S. Azat, R. Busquets, V.V. Pavlenko, A.R. Kerimkulova, R.L.D. Whitby, Z. A. Mansurov, Applications of activated carbon sorbents based on greek walnut: 2013 International Conference on Materials Science and Mechanical Engineering, ICMSME 2013, *Mater. Sci. Mech. Eng.* (2014) 49–51, <https://doi.org/10.4028/www.scientific.net/AMM.467.49>.
  - [43] M. Hoch, H.L. Johnston, Formation, stability and crystal structure of solid silicon monoxide<sub>1,2</sub>, *J. Am. Chem. Soc.* 75 (1953) 5224–5225, <https://doi.org/10.1021/ja01117a023>.
  - [44] J. Liu, P. Kopold, P.A. vanAken, J. Maier, Y. Yu, Energy storage materials from nature through nanotechnology: a sustainable route from Reed plants to a silicon anode for lithium-ion batteries, *Angew. Chem. Int. Ed.* 54 (2015) 9632–9636, <https://doi.org/10.1002/anie.201503150>.
  - [45] C. Daulbayev, F. Sultanov, A.V. Korobeinyk, M. Yeleuov, S. Azat, B. Bakbolat, A. Umirzakov, Z. Mansurov, Bio-waste-derived few-layered graphene/SrTiO<sub>3</sub>/PAN as efficient photocatalytic system for water splitting, *Appl. Surf. Sci.* 549 (2021), 149176, <https://doi.org/10.1016/j.apsusc.2021.149176>.
  - [46] M. Yeleuov, C. Seidl, T. Temirgaliyeva, A. Taurbekov, N. Prikhodko, B. Lesbayev, F. Sultanov, C. Daulbayev, S. Kumekov, Modified activated graphene-based carbon electrodes from rice husk for supercapacitor applications, *Energies* 13 (2020) 4943, <https://doi.org/10.3390/en13184943>.
  - [47] K. Askaruly, S. Azat, Z. Sartova, M. Yeleuov, A. Kerimkulova, K. Bekseitova, Obtaining Charact. AMorphous Silica Rice Husk (2020) 10.
  - [48] S. AZAT, Z. SARTOVA, K. BEKSEITOVA, K. ASKARULY, Extraction of high-purity silica from rice husk via hydrochloric acid leaching treatment, *Turk. J. Chem.* 43 (2019) 1258–1269, <https://doi.org/10.3906/kim-1903-53>.
  - [49] R. Hernández Pérez, A. Olarte Paredes, R. Salgado Delgado, A.M. Salgado Delgado, Rice Husk Var., 'Morelos A-2010' as an eco-friendly alternative for the waste management converting them cellulose and nanocellulose, *Int. J. Environ. Anal. Chem.* 0 (2021) 1–16, <https://doi.org/10.1080/03067319.2021.1972991>.
  - [50] R.A. Bakar, R. Yahya, S.N. Gan, Production of high purity amorphous silica from rice husk, *Procedia Chem.* 19 (2016) 189–195, <https://doi.org/10.1016/j.proche.2016.03.092>.
  - [51] Y. Jiang, J. Wen, Z. Ding, Y. Ren, Z. Liu, X. Chen, X. Zhou, Li+ storage properties of SiO<sub>2</sub>@C core-shell submicrosphere and its hollow counterpart synthesized by molecular self-assembly in wet-chemistry condition as anodes for LIBs, *J. Alloy. Compd.* 861 (2021), 157932, <https://doi.org/10.1016/j.jallcom.2020.157932>.
  - [52] E.I. Biru, H. Iovu, Graphene Nanocomposites Studied by Raman Spectroscopy, in: G.M. do Nascimento (Ed.), *Raman Spectrosc. InTech*, 2018, <https://doi.org/10.5772/intechopen.73487>.
  - [53] I. Sharma, A.D.K. Deshan, H.D. Pham, C. Padwal, W.O.S. Doherty, D. Dubal, Zero-waste: Carbon and SiO<sub>2</sub> composite materials from the solid residue of the hydrothermal liquefaction of anaerobic digestion digestate for Li-ion batteries, *Sustain. Mater. Technol.* 31 (2022), e00364, <https://doi.org/10.1016/j.susmat.2021.e00364>.
  - [54] Q. Chen, L. Tan, S. Wang, B. Liu, Q. Peng, H. Luo, P. Jiang, H. Tang, R. Sun, A facile synthesis of phosphorus doped Si/SiO<sub>2</sub>/C with high coulombic efficiency and good stability as an anode material for lithium ion batteries, *Electrochim. Acta* 385 (2021), 138385, <https://doi.org/10.1016/j.electacta.2021.138385>.
  - [55] M.V. Blanco, V. Renman, J. Zhu, F. Vullum-Bruer, A.M. Svensson, Optimizing carbon coating parameters for obtaining SiO<sub>2</sub>/C anodes with improved electrochemical performance, *J. Solid State Electrochem* 25 (2021) 1339–1351, <https://doi.org/10.1007/s10008-021-04912-2>.
  - [56] Y. Feng, X. Liu, L. Liu, Z. Zhang, Y. Teng, D. Yu, J. Sui, X. Wang, SiO<sub>2</sub>/C composite derived from rice husks with enhanced capacity as anodes for lithium-ion batteries, *ChemistrySelect* 3 (2018) 10338–10344, <https://doi.org/10.1002/slct.201802353>.
  - [57] S. Huang, D. Yang, W. Zhang, X. Qiu, Q. Li, C. Li, Dual-templated synthesis of mesoporous lignin-derived honeycomb-like porous carbon/SiO<sub>2</sub> composites for high-performance Li-ion battery, *Microporous Mesoporous Mater.* 317 (2021), 111004, <https://doi.org/10.1016/j.micromeso.2021.111004>.
  - [58] Y. Han, X. Liu, Z. Lu, Systematic investigation of prelithiated SiO<sub>2</sub> particles for high-performance anodes in lithium-ion battery, *Appl. Sci.* 8 (2018) 1245, <https://doi.org/10.3390/app8081245>.

- [59] W. Wu, M. Wang, J. Wang, C. Wang, Y. Deng, Green design of Si/SiO<sub>2</sub>/C composites as high-performance anodes for lithium-ion batteries, *ACS Appl. Energy Mater.* 3 (2020) 3884–3892, <https://doi.org/10.1021/acsaem.0c00300>.
- [60] F. Zhao, M. Zhao, Y. Dong, L. Ma, Y. Zhang, S. Niu, L. Wei, Facile preparation of micron-sized silicon-graphite-carbon composite as anode material for high-performance lithium-ion batteries, *Powder Technol.* 404 (2022), 117455, <https://doi.org/10.1016/j.powtec.2022.117455>.
- [61] V. Renman, M. Blanco, A. Norberg, F. Vullum-Bruer, A. Svensson, Electrochemical activation of a diatom-derived SiO<sub>2</sub>/C composite anode and its implementation in a lithium ion battery, *Solid State Ion.* 371 (2021), 115766, <https://doi.org/10.1016/j.ssi.2021.115766>.
- [62] Carbon-Coated SiO<sub>2</sub> for Li-Ion Batteries, (n.d.). <https://encyclopedia.pub/entry/19090> (accessed October 11, 2022).
- [63] X. Liu, Y. Chen, H. Liu, Z.-Q. Liu, SiO<sub>2</sub>@C hollow sphere anodes for lithium-ion batteries, *J. Mater. Sci. Technol.* 33 (2017) 239–245, <https://doi.org/10.1016/j.jmst.2016.07.021>.
- [64] A. Jumari, C.S. Yudha, H. Widiyandari, A.P. Lestari, R.A. Rosada, S.P. Santosa, A. Purwanto, SiO<sub>2</sub>/C composite as a high capacity anode material of LiNi<sub>0.8</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub> battery derived from coal combustion fly ash, *Appl. Sci.* 10 (2020) 8428, <https://doi.org/10.3390/app10238428>.
- [65] Y. Zhao, Z. Liu, Y. Zhang, A. Mentbayeva, X. Wang, M.Yu Maximov, B. Liu, Z. Bakenov, F. Yin, Facile synthesis of SiO<sub>2</sub>@C nanoparticles anchored on MWNT as high-performance anode materials for Li-ion batteries, *Nanoscale Res. Lett.* 12 (2017) 459, <https://doi.org/10.1186/s11671-017-2226-2>.
- [66] Y.-K. Kim, J.-W. Moon, J.-G. Lee, Y.-K. Baek, S.-H. Hong, Porous carbon-coated silica macroparticles as anode materials for lithium ion batteries: effect of boric acid, *J. Power Sources* 272 (2014) 689–695, <https://doi.org/10.1016/j.jpowsour.2014.08.128>.
- [67] Y. Zhou, Z. Tian, R. Fan, S. Zhao, R. Zhou, H. Guo, Z. Wang, Scalable synthesis of Si/SiO<sub>2</sub>@C composite from micro-silica particles for high performance lithium battery anodes, *Powder Technol.* 284 (2015) 365–370, <https://doi.org/10.1016/j.powtec.2015.07.007>.
- [68] K. Yu, J. Li, H. Qi, C. Liang, High-capacity activated carbon anode material for lithium-ion batteries prepared from rice husk by a facile method, *Diam. Relat. Mater.* 86 (2018) 139–145, <https://doi.org/10.1016/j.diamond.2018.04.019>.
- [69] SiO<sub>2</sub>/N-doped graphene aerogel composite anode for lithium-ion batteries | SpringerLink, (n.d.). (<https://link.springer.com/article/10.1007/s10853-020-04905-y>) (accessed October 11, 2022).
- [70] X. Peng, J. Fu, C. Zhang, J. Tao, L. Sun, P.K. Chu, Rice husk-derived activated carbon for Li ion battery anode, *Nanosci. Nanotechnol. Lett.* 6 (2014) 68–71, <https://doi.org/10.1166/nnl.2014.1714>.
- [71] E. Hastuti, A. Subhan, D. Puspitasari, Synthesis of activated carbon derived from chicken feather for Li-ion batteries through chemical and physical activation process, *Mater. Renew. Sustain. Energy* 10 (2021) 13, <https://doi.org/10.1007/s40243-021-00198-6>.