

The electrochemical behavior of silica and activated carbon materials derived from the rice husk waste for li-ion cells

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ABSTRACT

In this work, an amorphous silica powders (1-SiO₂ and 2-SiO₂) and activated carbon with few-layer graphene were derived from rice husk using simple and efficient process. Synthesized samples were characterized by means of TGA SEM, XRD, XRF, nitrogen low-temperature adsorption/desorption, Raman, and EDAX. Rice husk calcination yields in 18 and 14 wt% of 1-SiO₂ and 2-SiO₂, correspondingly. Carbonization of rice husk followed by activation yielded about 11 wt% of activated carbon with large specific surface area ($S_{BET} = 3292 \text{ m}^2 \text{ g}^{-1}$). Feasibility of resulting materials as anode materials for Li-ion batteries grounded on a high theoretical capacity of silica and high charge/discharge stability of activated carbon. We present here a 2-SiO₂ material with large specific surface area of $980 \text{ m}^2 \text{ g}^{-1}$, of high purity above 99 %, and large pore volume ($1.20 \text{ cm}^3 \text{ g}^{-1}$), which results in a reversible capacity of about 841 and 442 mAh g⁻¹ (1st and 50th cycle) with coulombic efficiency higher than 95 %. Activated carbon demonstrated the highest initial discharge specific capacity and stable reversible capacity after 50 cycles as 1462 and 477 mAh g⁻¹ (1st and 50th cycle), and coulombic efficiency higher than 90 %.

1. Introduction

With the depletion of coal, oil, natural gas, and other finite energy resources and the increasingly serious environmental pollution, it is extremely urgent to develop clean and renewable energy as well as reliable energy storage. At present, as the most efficient energy storage device, Li-ion batteries (LIBs) have been commercialized and widely used in electric vehicles, energy storage power stations, computers, mobile phones, and other electronic products. In addition, self-discharge of those is less than half of nickel-cadmium, which makes the LIBs well suited for application in modern gadgets and devices [1–5]. Lithium is the lightest of all metals, has the highest electrochemical potential, and provides the highest energy density [6]. Designing new materials to improve the energy density of LIBs remains an important challenge, as

both the cathode and anode affect the capacity of LIB. The most common and easily sourced materials are silica and carbon, meanwhile theoretical capacities for silica and carbon capacities are 4200 and 372 mAh g⁻¹ [7–9]. Both, the activated carbon and SiO₂, received a lot of interest due to their attractive cost and insignificant volume change during cycling [10].

Electrode materials with sustainable and low-cost features are the primary choices for the next-generation high performance. To lessen the processing costs, recycling and reusing of by-products of various industrial sectors, such as rice husk (RH) and wheat straw from agricultural industry is of utmost importance in terms of sustainability development [11–13]. RH is a waste of a rice cultivation and via rice husking the RH yields in ~20 wt% by weight of the rice grain. Given that the annual volume of world rice production is 422 million pounds [14]

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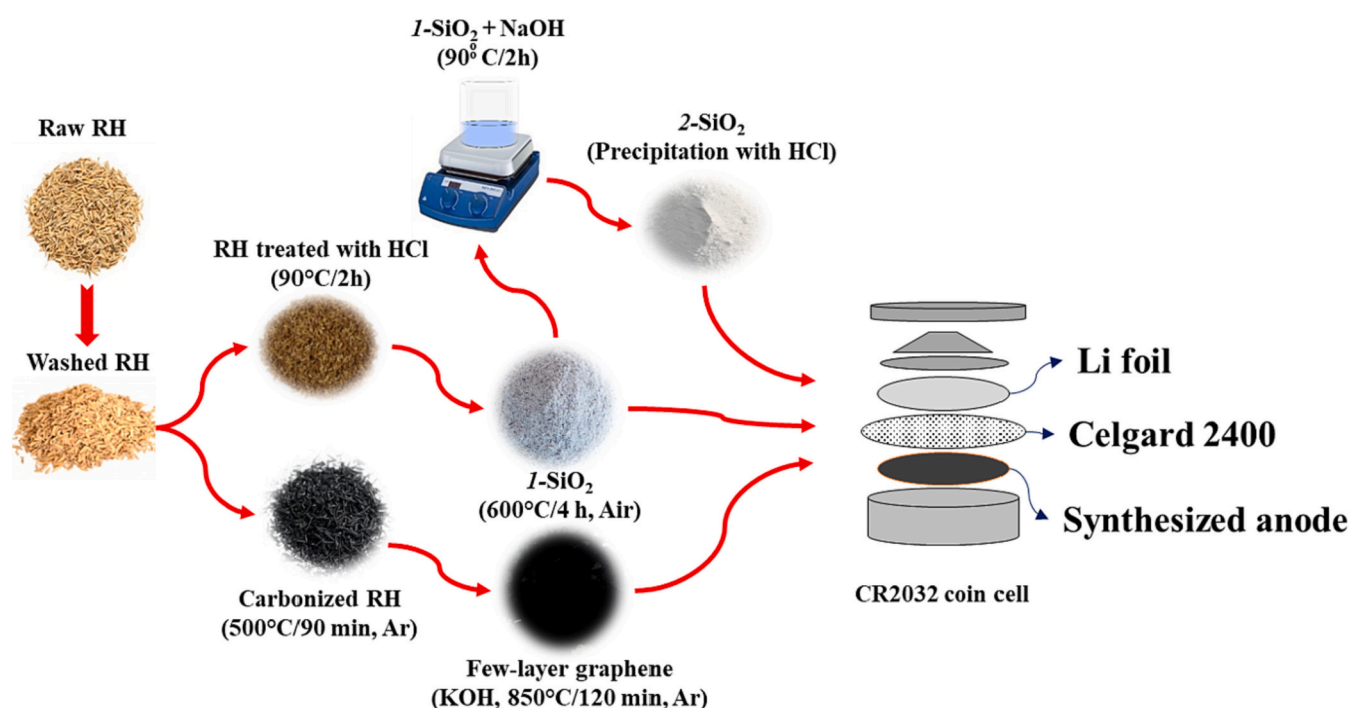


Fig. 1. Scheme of the rice husk conversion into anode materials for LIBs and setup of anode/LIB cell.

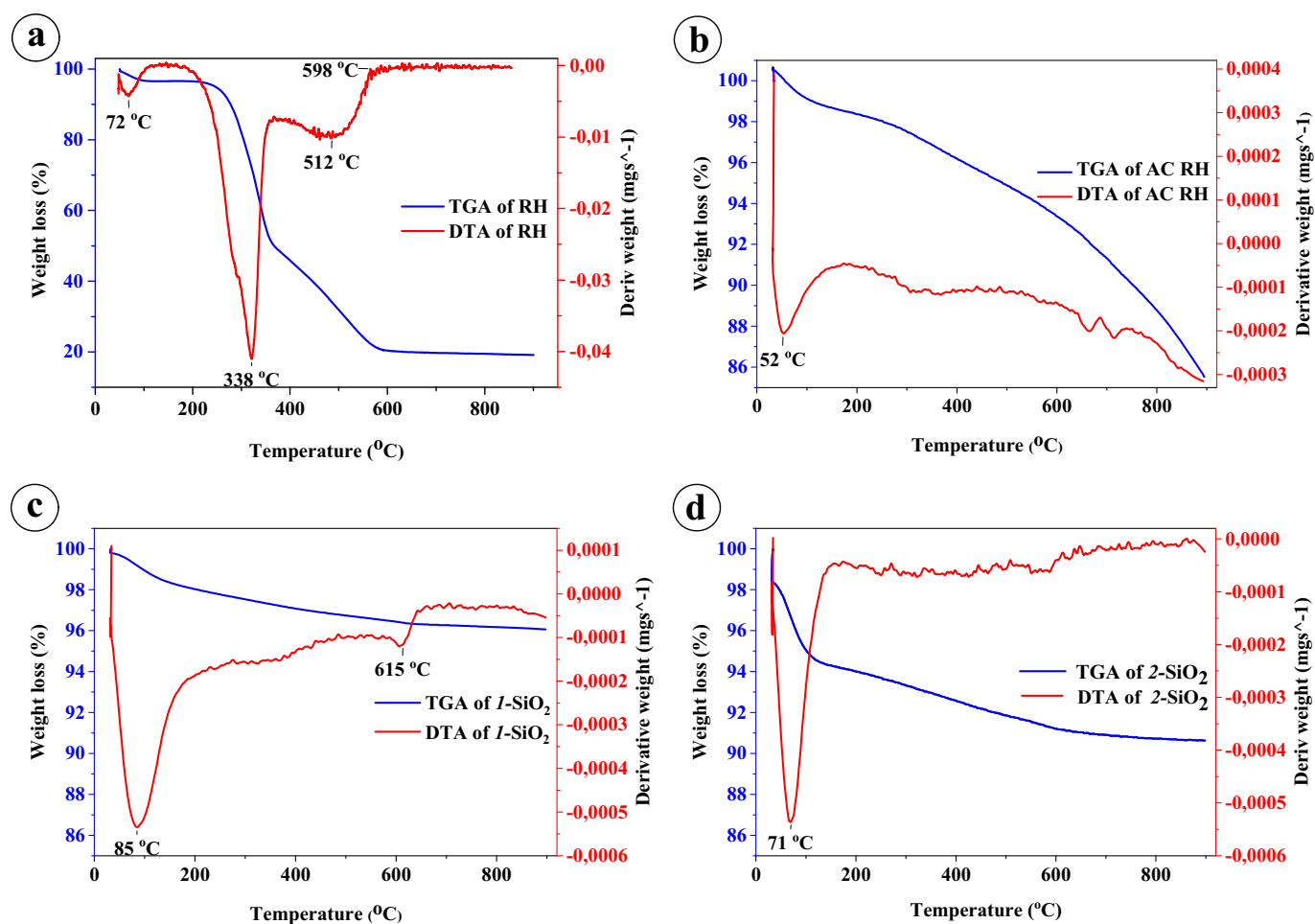


Fig. 2. TGA/DTA curves for RH (a), AC (b), 1-SiO₂ (c) and 2-SiO₂ (d).

Table 1

The main mineral constituent of silica samples according to the XRF analysis, presented as % w/w content of mineral oxides.

Sample	Elemental composition						
	SiO ₂	Cl	MnO	Fe ₂ O ₃	CuO	ZnO	Cr ₂ O ₃
1-SiO ₂	89.64	6.09	0.21	3.73	0.31	–	0.01
2-SiO ₂	99.07	0.79	–	0.02	–	0.12	–

the RHs waste volume reaches enormous scale. RH contains about 80 wt % of organics, about 18 wt% of silica and trace amounts of other elements. High content of organic compounds (mostly lignin) entail production of activated carbon from the RH along with silica. Abundance of RH in the rice growing regions makes it one of the low-cost sources for SiO₂ and carbon materials. The utilization of RH has been an extensive research topic for decades. However, the practical applications of RH products were limited to a narrow range of low-cost agricultural products, such as fertilizer additives, livestock rugs and medicine [15–18]. Current growth in the preparation of RH's silica and AC and their application in environmental and energy functional materials is extensively discussed. Abe [19] synthesized C and SiOx from rice husk via physicochemical route and studied the role of SiOx in the C/SiOx anode; study show the specific capacity for C and SiOx as 375 and 475 mAh g⁻¹. Kim et al. designed and prepared the RH silica/graphite/C composite by the magnesio-milling method followed by carbon coating with the chemical vapor deposition process; whereas different c-SiRH/graphite compositions demonstrated irreversible capacity drops the c-SiRH/graphite (1:9) demonstrated stable reversible capacity of about 494.6 and 432.2 mAh g⁻¹ (1st and 100th cycle) [20]. Authors [21] also synthesized RH-based C/SiO₂ anode focusing on the effect of carbonization temperature on the LIBs performance, they showed that the material synthesized at 700 °C had a specific capacity of about 453 mAh g⁻¹ (40th cycle) at a current density of 100 mAh. Furthermore, activated carbon was extracted from RH via graphitization at 550 °C and after activation at 800 °C with KOH was used as an anode material in LIB, the resulting anode showed capacitance of about 400 mAh g⁻¹ after 60 cycles. Auttawong et al. using the RH silica created a ternary Sn-SiO₂@TiO₂(B) LIB anode which showed stable cycling at a capacity of

500 cycles (81.39 mAh g⁻¹) at a fast charge current of 5000 mA g⁻¹.

The LIBs technology has major advantages in the field of energy storage, benefiting from high energy density, long cycle performance, no memory effect, etc. However, the limited lithium content in the earth's crust and volume expansion of LIBs obviously restricts the huge market and long-term development. Therefore, the adjustment of LIBs to overcome those limitations is also under constant research. The properties of the anode materials are one of the main factors influencing the above battery challenges, while nanomaterials and conductive materials greatly affect their electrochemical performance. Silicon (Si) based anodes had been widely studied for new generation LIBs due to ultra-high theoretical specific capacity. Moreover, Si is not only the earth's reserve element it can be extracted from the by-products of various industrial sectors too, so the utilization of it is very affordable and beneficial for environment. Several critical reviews have been published previously, which summarize the Si applications in the LIB technology and up to now most of Si anode research is focused on the overcome the capacity degradation of the Si electrode. Nanoscale silica-based anodes can reduce the damage of cracks on the electrode by reducing the stress/strain and in turns improve reversible capacity. Up to now, there were relatively few reports focusing materials, methods, and questions on synthesis of high-quality LIB anode fabricated from by-product's or waste materials. In this paper we demonstrate a reliable and sustainable method for synthesis of anode materials from the rice husk. The synthetic approach proposed in this paper benefits LIBs technology in a way that from one source material two types of anodes can be obtained – nano-silica and graphene by simple tuning a synthetic method. Since the disadvantages of Si anode can be overcome via nanosizing, the proposed synthetic approach based on the dissolution-precipitation mechanism will help to tune the final properties in silica-based anode and therefore overcome capacity degradation effect via tuning a particle size.

Herein, we present an application pathway of amorphous silica and activated carbon obtained from the RH. When studied as an anode material for LIBs, these materials, AC and silica with developed specific surface area, show excellent electrochemical performance with a high specific capacitance, good cycling performance and excellent rate capability.

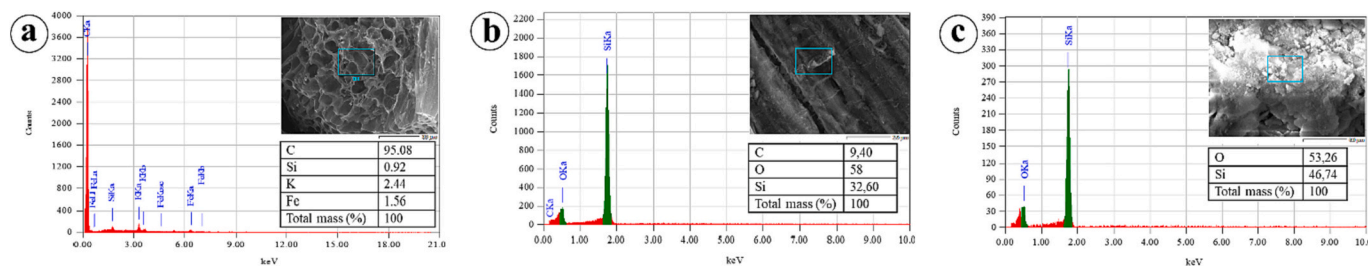


Fig. 3. SEM/EDX of samples AC (a), 1-SiO₂ (b) and 2-SiO₂ (c).

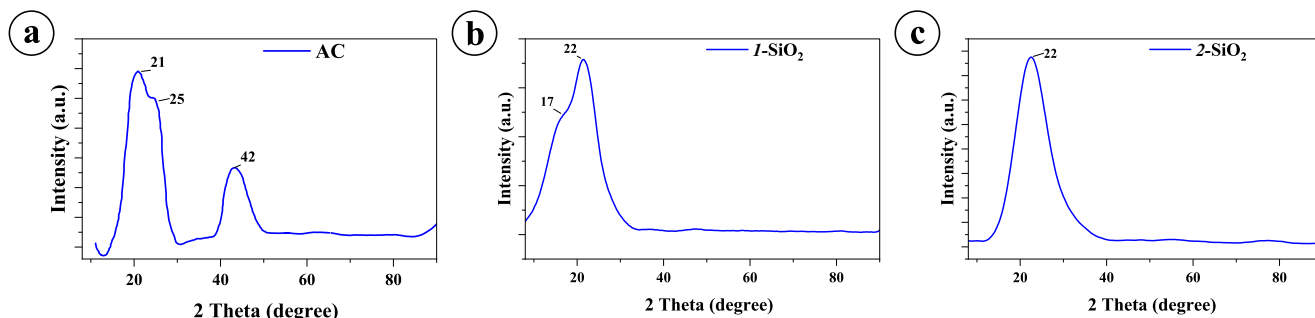


Fig. 4. X-ray diffraction patterns of AC (a), 1-SiO₂ (b) and 2-SiO₂ (c).

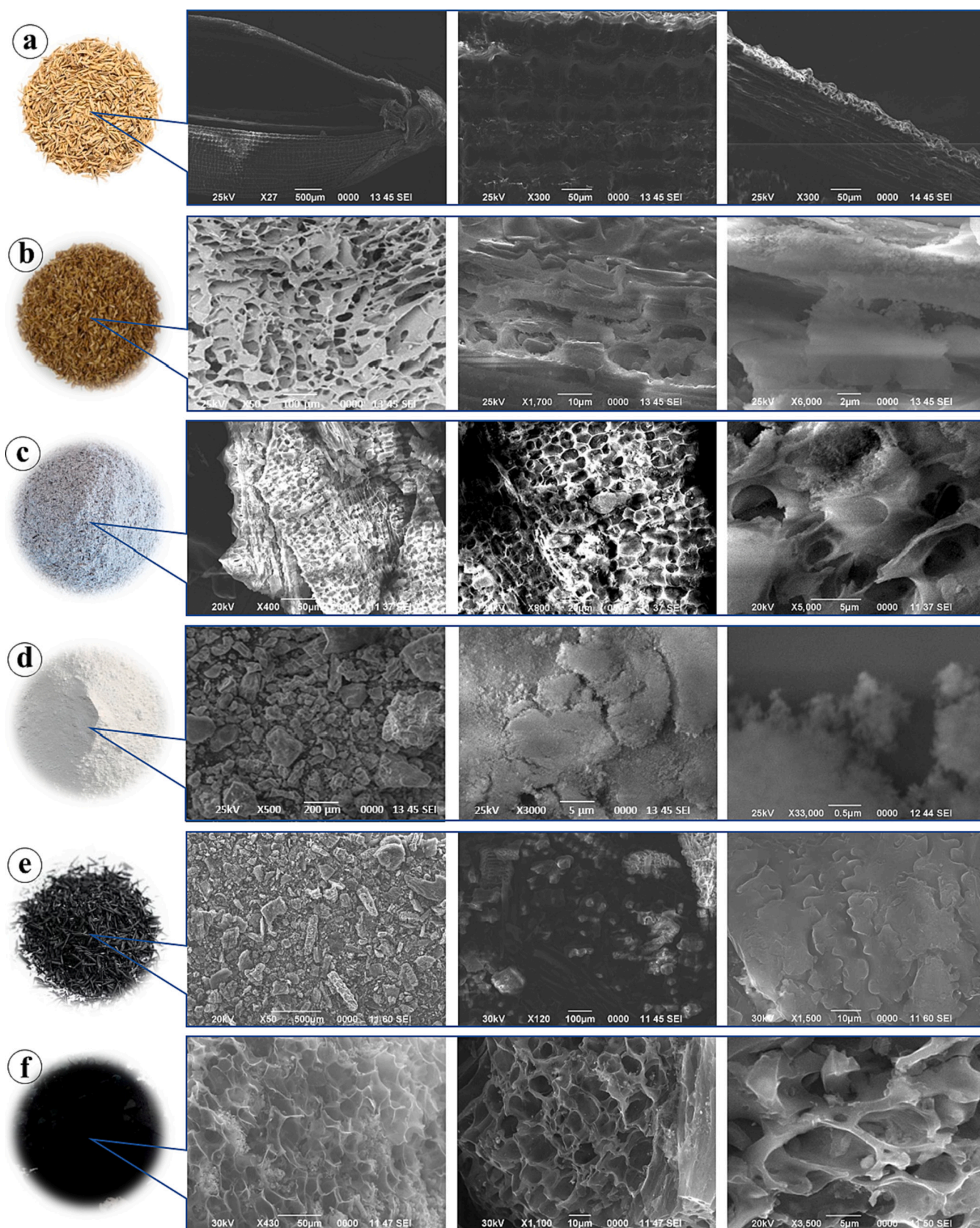


Fig. 5. SEM images (at different magnifications) of RH, its derivatives, and intermediates according to the scheme of the rice husk conversion into anode materials (Fig. 1). Untreated RH (a), acid treated RH (b), silicas: 1-SiO₂ (c) and 2-SiO₂ (d); carbonaceous samples after carbonization (e) and KOH activation (f). Each line contains the optical photography insert of corresponding sample.

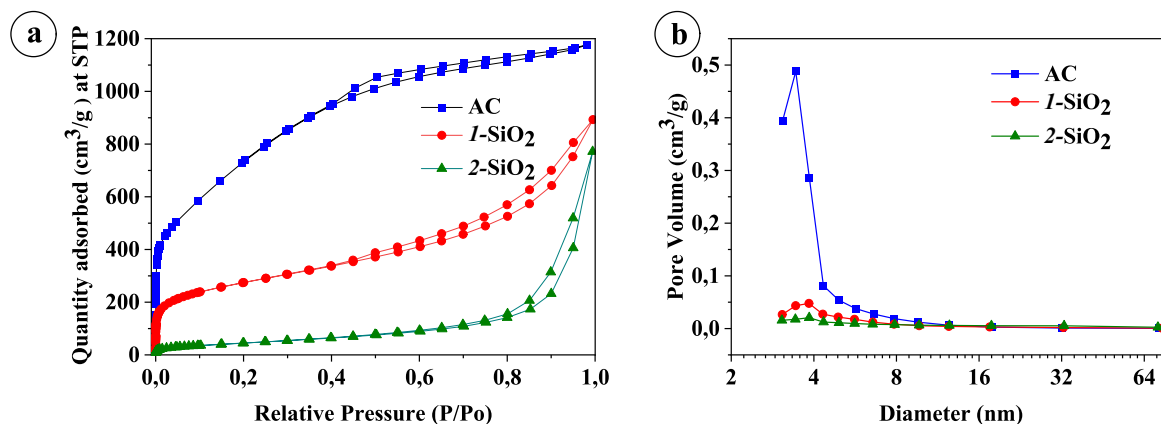


Fig. 6. Experimental nitrogen adsorption-desorption isotherms for of the 1-SiO₂, 2-SiO₂ and AC samples as adsorbed quantity vs P/P_0 (a) and pore-size distribution plot calculated from corresponding isotherms (b).

Table 2

Texture properties of the 1-SiO₂, 2-SiO₂ and AC samples.

Sample	$S_{sp}/m^2\ g^{-1}$ (BET)	Specific pore volume, $cm^3\ g^{-1}$ (DFT)	d_{pore} , nm (DFT)
1-SiO ₂	150	0.75	18.4
2-SiO ₂	980	1.20	0.98
AC	3292	1.41	1.71

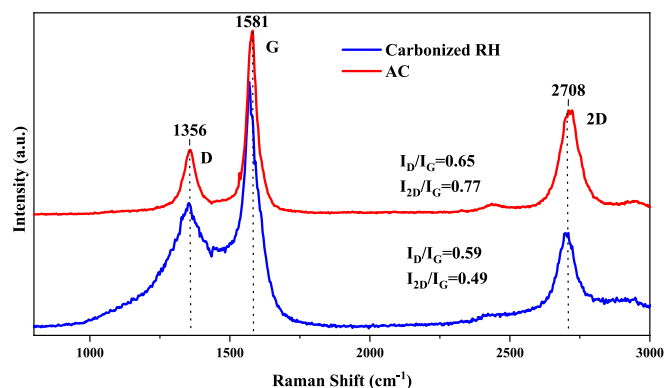


Fig. 7. Raman spectra of carbonized RH and AC.

2. Experimental section

2.1. Chemicals and materials

The RH were received from the rice farm of the Kyzylorda region of Kazakhstan. Hydrochloric acid (HCl) reagent grade (mass fraction 36.6 %) from JSC «ACOS-1», sodium hydroxide (NaOH) reagent grade (mass fraction 98.5 %) and potassium hydroxide (KOH) reagent grade (mass fraction 88 %) from LABORPHARMA «LLP».

Polypropylene separator (Celgard 2400, 25 μm , porosity – 39 %) was received from Xiamen Tmax Battery Equipments Ltd. (China) in a roll and cut into discs (d-19 mm). Polyvinylidene fluoride (PVDF, purity ≥ 99.5) and carbon black (C45, density 160 kg/m³) were purchased from MTI Corporation (USA). *N*-methyl 2-pyrrolidone (NMP, Mw 99.13 g/mol), copper foil (30- μm -thick), lithium hexafluorophosphate (LiPF₆, 99.99 %, battery grade) ethylene carbonate (EC, 99.99 %), diethyl carbonate (DEC, 99.99 %) and dimethyl carbonate (DMC, anhydrous, purity ≥ 99 %) were purchased from Sigma-Aldrich. Battery-grade lithium foil sheets (25x100mm, thickness 0.6 mm, as rolled, 99.9 %) were purchased from AME Energy Co. Ltd. (China), and CR2032 coin

cell cases (304ss, including a spring and 0.2 mm spacer) from Xiamen Tob New Energy Technology Co. Ltd. (China). Ar (99.999 %) was purchased from Ikhsan Technogas Ltd. Ultrapure deionized water (DI) was used throughout experiments, unless otherwise noted. All reagents were used without further purification.

2.2. Experimental procedure

As stated above, the high lignin content coexisting with silica within the RH structure makes this waste material versatile and useful in production of both silica and activated carbon. Within this research all tested materials (1-SiO₂, 2-SiO₂ and AC) were synthesized from the same RH batch and synthesis pathway is depicted in Fig. 1. Prior to any manipulations the RH was washed with hot deionized water and dried in a bench oven at 110 °C for 8 h.

2.2.1. Synthesis of 1-SiO₂

Silica extraction from the RH includes 2 stages: acid treatment and calcination. Batch (50 g) of the purified RH was treated with 2 M HCl solution (500 ml) for 2 h to remove heavy metals and to accelerate pyrolysis, then washed with hot distilled water until neutral pH (~ 7.0) and dried at 110 °C for 12 h; and afterwards calcinated at 600 °C for 4 h in a muffle furnace. Resulting white RH ash was denoted as 1-SiO₂ (Fig. 1) (yielding of about ~ 18 wt%).

2.2.2. Preparation synthesis of 2-SiO₂

2-SiO₂ was derived via re-crystallization from as-obtained 1-SiO₂ sample. Firstly, 10 g of 1-SiO₂ was mixed with 100 ml of 2 M NaOH at 90 °C under continuous vigorous stirring for 2 h to transform the solid SiO₂ into the water-soluble sodium silicate through a chemical reaction (1):



Then a sodium silicate solution was filtered through 100 μm ceramic filter to remove insoluble residues and precipitated as insoluble silicic acid with appropriate amount of HCl (conc.) under continuous stirring (2):



Precipitate was filtered and washed continuously with hot DI water to remove by-products and dried in the bench oven at 120 °C for an 8 h, completing the silica formation (3). Obtained white powder was denoted 2-SiO₂ (Fig. 1) (yielding of about ~ 14 wt%).

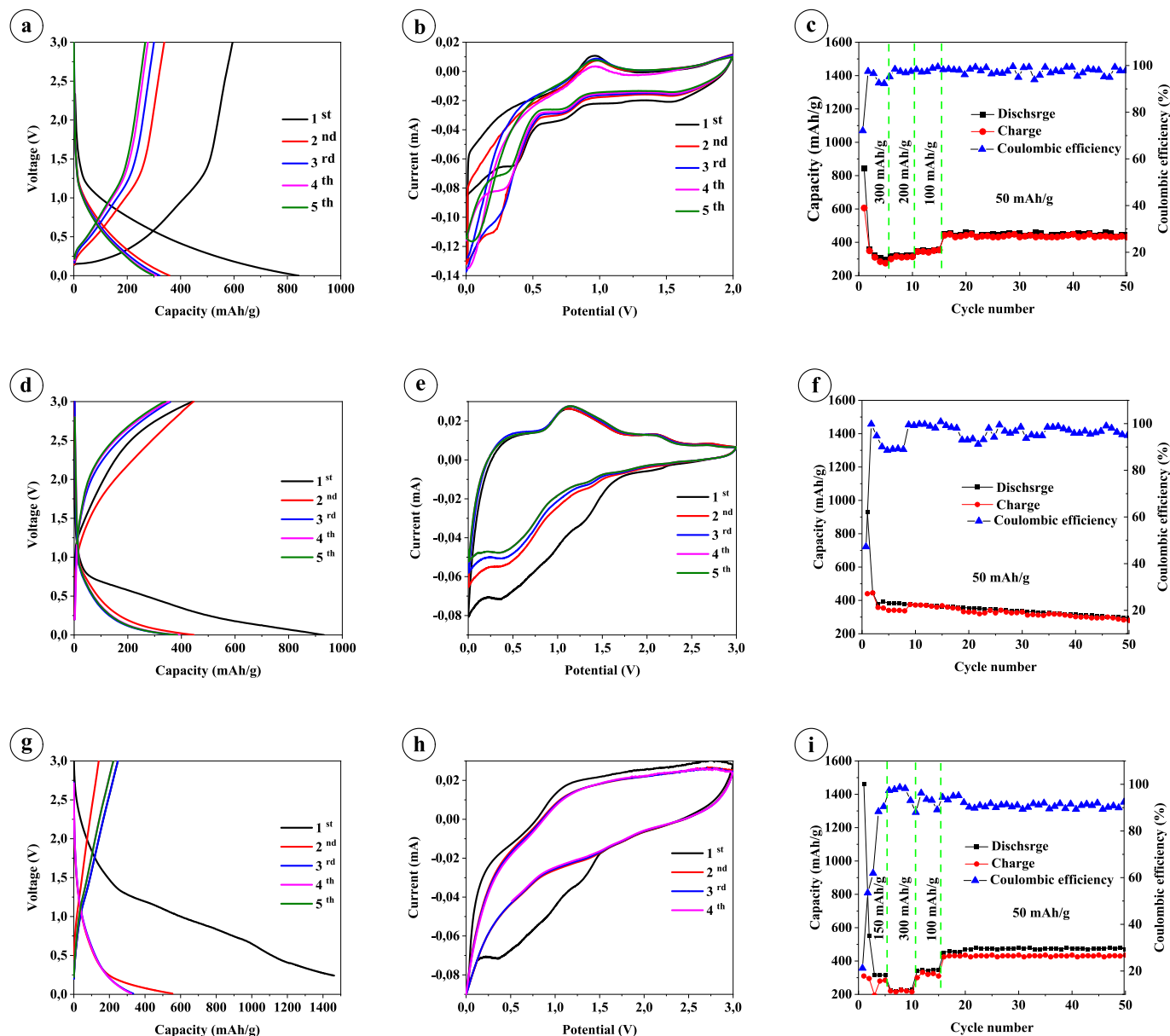
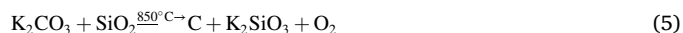
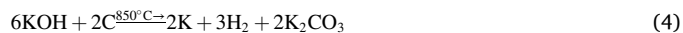


Fig. 8. Charge and discharge curves for the first five cycles: (a) - 2-SiO₂, (d) - 1-SiO₂ and (g) - AC; Cyclic voltammety (CV) curves measured for: (b) - 2-SiO₂, (e) - 1-SiO₂ and (h) - AC; rate performance at various current densities and cyclic performance at current density of 50 mA g⁻¹ to 300 mA g⁻¹: (c) - 2-SiO₂, (f) - 1-SiO₂ and (i) - AC.

2.2.3. Preparation of AC with few-layer graphene

The AC with few-layer graphene (graphene with 2–10 layers in a flake) was obtained via two-step approach from RHs (Fig. 1). 100 g of RH was transferred into a cylindrical steel reactor and carbonized in a vertical tube furnace. The final temperature of the carbonization process was 500 °C, with a heating rate of 5.5 °C min⁻¹ and an Ar flow of 160 cm³/min. The final temperature was kept for 90 min and then it was allowed to cool down to room temperature, preserving the Ar circulation flow. Afterwards, the carbonized RH was mixed with a dry powdered KOH in a weight ratio of 1:4 to simultaneously activate the lignin carbonizate and facilitate a further removal of silica. The mixture then was transferred into a stainless steel (AISI 316 l) cylindrical reactor with gas inlet and outlet and heated to 850 °C with a heating rate of 7.0 °C min⁻¹ and activation temperature was held for 120 min. After the holding time samples were cooled down freely. Argon (Ar) with a flow of 160 cm³/min was used as inert gas throughout the whole experiment.

Process is summarized in following chemical reactions:



After cooling down, the intermediate was washed with DI water until the washing water pH reached ~7. Derived carbonaceous sample was dried in two stages: in a bench oven at 120 °C for 10 h (1st stage), and then in the vacuum drying oven at 150 °C for 2 h (2nd stage). Resulting sample was denoted as AC with few-layer graphene (yielding of about 11 wt%).

2.3. Electrochemical measurements

Chosen composition of active material/PVDF/C45 carbon black electrodes contained 68 wt% of active material (1-SiO₂ or 2-SiO₂), 20 wt % of C45 carbon black and 12 wt% of PVDF dissolved in NMP. Slurries were stirred for 1.5 h before casting onto a copper foil by Film Applicator

Table 3Performance comparison of SiO₂ and C electrodes for LIBs.

Materials	Reversible capacity (mAh g ⁻¹)	Initial discharge/charge specific capacity (mAh g ⁻¹)	Current density mA g ⁻¹	Cutoff potential range (V)	Ref.
SiO ₂ @C	557 (40 th)	991/615	100	0.01–2.5	[35]
Si/SiO ₂ /C	550 (30 th)	3356.5/2107	800	0.01–1.5	[38]
SiO ₂ @rGO	490.7 (60 th)	1709/628.9	100	0–3	[36]
Nano-SiO ₂	253.7 (2 nd)	999.6/349.4	100	0–3	
Si@SiO ₂ @C	513.2 (30 th)	1829.4/828.4	200	0–1.5	[37]
SiO ₂ NTs	1247 (100 th)	2404/1040	4C	0–3	[39]
AC	477 (50 th)	1462/310	50	0.01–3	This work
2-SiO ₂	442 (50 th)	841/606	50	0.01–3	This work
1-SiO ₂	295 (50 th)	937/440	50	0.01–3	This work

(MSK-AFA-I, MTI Corporation, USA) with a thickness of 100 μm and dried in a vacuum oven for 4 h at 120 °C. Afterwards the electrode was cut out in the form of a disk with a diameter of 15 mm by Compact Precision Disc Cutter (MSK-T-07, Zhengzhou CY Scientific Instrument Co Ltd., China), and the presentative (68 wt%) of the substance active mass was confirmed. The AC anode was prepared by the same manner, but at a mass ratio of 75:15:10 (AC:PVPF:C45). The CR2032 coin-type half cells were assembled by Coin Cell Sealing Machine (TMAX-JK-KF20-TC, TMAX, China) in an argon-filled glove box using electrode prepared under investigation. Lithium foil was used both as a reference electrode and as a counter electrode.

The experimental electrolyte was 1.0 M LiPF₆ solution in 1:1:1 (v/v/v) mixture of EC, DEC and DMC, the electrolyte was mixed and stored in a glove box under argon. Celgard 2400 polypropylene was used as separator. Cyclic voltammetry (CV) and galvanostatic charge/discharge cycling of the assembled batteries were conducted at ambient temperature using BTS CT-4008-5V10mA-164 and Potentiostat-Galvanostat p-40x. The scan rate for CV was 0.1 mV s⁻¹ with a voltage range of 0.01–2.0 and 0.01–3.0 V. All the electrochemical performance measurement was carried out after the assembled battery was left standing for 12 h.

2.4. Material characterization

The morphologies and elemental distribution of the obtained samples were observed by scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM, JEOL, JSM-6490LA, USA). Major element analysis of synthesized RH derivatives were obtained with a PANalytical Axios 1 kW Wavelength Dispersive X-ray Fluorescence (XRF) spectrometer using the PANalytical's WROXI software. X-ray diffraction patterns were recorded using the Rigaku powder diffractometer at a scanning speed of 0.02 2 θ /min, using nickel-filtered CuK α radiation in the angular range from 10 to 90 of 2 θ . Thermal Gravimetric Analysis (TGA) was performed using simultaneous thermal analyzer STA 6000 (PerkinElmer, Inc.) in temperature range from 50 to 900 °C under constant nitrogen flow (heating rate - 10 °C min⁻¹). Raman spectra were captured with a multi-purpose analytical instrument NTEGRA Spectra (NT-MDT, with excitation laser at λ = 473 nm, and a pixel size of 80 nm). Specific surface area and pore size of materials under investigation were calculated from their isotherms of N₂ adsorptions obtained with the ASAP 2400 (Micromeritics Instrument Corp., USA). Brunauer-Emmet-Teller (BET) analysis was used to calculate values of specific surface area (S_{sp}); cumulative pore volume (V_{p}) and their diameter (D_{p}) were calculated by non-linear DFT (NLDFT) methods

using the slit-pore equilibrium model and pore-size distribution (PSD) graphs were plotted using BJH model. Cyclic voltammetry (CV) and galvanostatic charge/discharge cycling of the assembled batteries were conducted at ambient temperature using Potentiostat/Galvanostat P-40x ("Electrochemical Instruments") and BTS CT-4008-5V10mA-164.

3. Results and discussion

RH and obtained samples were examined by TGA/DTG analysis to determine mass loss rate of samples under heating cycle (Fig. 2) to identify thermal stability and ash yield. Thermal analysis of RH provides correct temperature values for the organic content carbonization step. TGA/DTG curves recorded for untreated RH (Fig. 2 a) contain three mass loss steps with maximums at about 72, 338 and 512 °C. First stage of thermal decomposition is associate with the moisture removal and crop about 4.0 wt%, two following stages are associated with decomposition of organic compounds in the RH structure [22,23]. No significant mass loss was observed above 600 °C, and residual mass for RH is about 18.0 wt%. TGA/DTG of AC (Fig. 2 b) have only one maximum of mass loss at 52 °C associated with the moisture content; a subsequent mass loss had a monotonous character related to depletion of the oxygen-containing group from the carbonaceous sample surface and yields 85.5 wt% at 900 °C. TGA/DTG profiles for 1-SiO₂ and 2-SiO₂ samples (Fig. 2 c and d) also have a significant moisture content (2.0 and 5.6 wt%, correspondingly), but major difference is in the presence of organic impurities in 1-SiO₂ structure, which reflect in mass loss with the maximum at 615 °C (Fig. 2 c).

The XRF analysis in this study was run to quantify the chemical composition of silicas samples. As shown in Tables 1, 1-SiO₂ and 2-SiO₂ samples are compares by XRF analysis. Their main difference is in significant reduction of metal content. Removing of undesired metallic compounds in 2-SiO₂ is led to producing a fine silica with a purity of 99.07 % (Table 1) from RH.

Elemental analysis of the end-products obtained from RH, i.e. - AC, 1-SiO₂ and 2-SiO₂ was performed using an EDX analyzed embedded into the SEM instrument. It was found that the constituent of the AC is predominantly of carbon (95.08 wt%, Fig. 2.a). As for silica samples: 1-SiO₂ contains 9.40 wt% of carbon (Fig. 3 (b)) and 2-SiO₂ can be considered as pure silica (Fig. 3 (c)), which confirms results of XRF analysis (Table 1).

The activated carbon with few-layer graphene produced from the RH was characterized by means of X-ray diffraction (Fig. 4 a). Overall, a peak broadening in a range of 12–29° (002) indicates the rupture of interplanar C bonds and the formation of graphene structures. Observed (002) peak depletion with two maximums at 21° and 25° may arise from the formation of residual oxygen functionalities in graphene-like sheets [24–26]. The calculated interlayer distance d of low-layer graphenes is 0.344 nm for diffraction peak at 25° (2 θ), the strongest diffraction peak appearing at 21° (2 θ) corresponds to d -spacing of 0.415 nm; which is higher as that of graphite (0.3395 nm, JCPDS No. 75–1621); this indicates the introduction of functional groups (carboxylic, carbonyl, hydroxyl and epoxy) into the basal and edge planes of obtained graphene. This increase in d -spacing proved the oxidation of graphene flakes, since the degree of oxidation is proportional to the interlayer spacing [27]. The broad C (101) diffraction peak (2 θ = 42°) is due to the α axis of the graphite structure.

XRD patterns of silica samples - 1-SiO₂ and 2-SiO₂ are displayed in Fig. 4 (b,c). Both obtained SiO₂ powders have in their XRD spectra one diffuse peak at ~22°, attributed to amorphous structure of the silica (JCPDS 29-0085). Appearance of shoulder at 17° in XRD spectra of 1-SiO₂ can be attributed to (101) plane of cellulose I (ICDD # 00-003-0226), partially entrapped in the silica structure; this assumption was confirmed using SEM (Fig. 5 c). The observed broad halo (Fig. 4 c) with maximum of intensity at 22°, corresponds to the d -spacing value of 0.36 nm and confirms an amorphous structure of the obtained SiO₂ [28,29].

Fig. 5(a-f) shows SEM images of the RH and it's derivatives synthesized accordingly to scheme of the rice husk conversion (Fig. 1). Surface

morphology of untreated RH (Fig. 5a) had regular, and somehow “glossy” surface texture formed by lignin fibers in a husk structure. As a result of hydrolysis reaction caused by concentrated HCl the fiber surface of acid treated RH (Fig. 5b) became rough and nonuniform. The morphology of 1-SiO₂ and 2-SiO₂ silicas prepared from pretreated RH is shown in Fig. 5c and d. It is clearly seen in SEMs of 1-SiO₂ (Fig. 5c) that sample still contain residual honeycomb structure of lignin, while SEM images of 2-SiO₂ (Fig. 5d) exhibits complete transformation of rice husk into silica particles. Carbonization and activation stages of rice husk transformation into carbonaceous material are presented in Fig. 5e and f. The microstructure of the outer surfaces of carbonized RH (Fig. 5e) resembles the creased structures of acid-treated RH (Fig. 5b). The KOH activation (Fig. 5f) results in formation of open porous structure composed of large pores (an average pore diameter measured with SEM is about 10 μm), and formation of extensive mesoporous internal structure within the AC sample (confirmed with the low temperature nitrogen adsorption-desorption, Fig. 6 b).

The texture properties of samples prepared from RH were studied using BET analysis of N₂ adsorption-desorption isotherms (Fig. 6(a)). The quantity of adsorbed is measured in cm³ g⁻¹ STP units corresponding to the volume of gas adsorbed per unit of mass (V/m) at standard temperature and pressure conditions (STP). The steep growth of adsorbed-desorbed amount of N₂ at low pressures ($P/P_0 < 0.001$) in isotherms of 1-SiO₂ and AC samples can be attributed to existence of microporosity in both samples. Isotherm of AC belongs to Type-I (IUPAC) referred to co-existence of micropores with wider distribution of pores; presence of hysteresis loop indicates narrow mesopores. Isotherms of silica samples (1-SiO₂ and 2-SiO₂) are attributed to Type-II and Type-III, correspondingly. Differences in isotherms between 1-SiO₂ and 2-SiO₂ were noteworthy, as shown in a Fig. 6(a). The cumulative volume of N₂ adsorbed was higher for 1-SiO₂ with wider hysteresis loop, compared to the 2-SiO₂ counterpart. Both silica samples contain Type-H3 hysteresis loops in their isotherms, which have no adsorption limitation in at high P/P_0 and are generally attributed to slit-like mesopores. Hysteresis loops in all analyzed isotherms starts at the latter half part (P/P_0 is 0.5–1.0) indicating contribution of mesopores into porous structure of samples. Fig. 6(b) illustrates the curves for pore size distribution (PSD) for tested samples build on the Barrett-Joyner-Halenda (BJH) model. The distribution of pore sizes was observed within the micro-mesoporous range of pores i.e., diameters (1–50 nm) for all materials, however plot of PSD for AC has the largest pore volume among the analyzed samples.

In this study, BET, BJH, and DFT were used to compute SSA, pore volume, and pore size, as presented in Table 2. The data shows that a significant variation in BET surface area and pore volume/diameter can be expected within tested samples.

Values of pore diameters calculated with DFT method for samples (Table 2, d_{pore}) corresponds well with their adsorption isotherms. The micropore S_{sp} of AC is highest out of all samples under investigation (3292 m² g⁻¹). For silica samples, the values of S_{sp} are much lower than that of AC, and significantly lower (150 m² g⁻¹) when adsorption is predominantly associated with mesopores (1-SiO₂), illustrating that the micropores have a greater contribution to S_{sp} than mesopores; thus, micropores determine the adsorption capacity to larger extend.

Raman spectra of carbonized RH and AC (Fig. 7) both contains sp^2 characteristic in-plane vibration band of graphene lattice (G band) at 1581 cm⁻¹, the disorder-induced ([30]) D band at 1365 cm⁻¹ and the 2D band at 2708 cm⁻¹, confirming that both samples contain graphene. Spectra of carbonized RH have much pronounced D band then that of AC confirming that activation partially removes defected graphene layers in carbonized structure. Analysis of Raman spectra of the carbonized RH and AC indicated the presence of few-layer graphene structure. To confirm a multi-layer structure the intensity ratios of the 2D and G peaks in Raman spectra were calculated (shown in Fig. 7), those ratios are equal to 0.49 and 0.77, which confirms few-layer graphene structure of both samples. Calculated I_D/I_G ratios (shown in Fig. 7) verifies that

activation with KOH led to “graphitization” (increase of sp^2 content) of the structure as the ratio does increase from 0.56 to 0.65.

Fig. 8 (c), (f) shows the discharge and charge curves from the 1st to 50th cycle of the 1-SiO₂ and 2-SiO₂ under a current density of 300 and 50 mA g⁻¹ in a voltage range of 0.01–3.2 V. Fig. 8 (a), (d) is the cyclic voltammograms of the 2-SiO₂ and 1-SiO₂ particles at a scanning rate of 0.1 mV s⁻¹. The CV plot is shown to 2.2 V to emphasize the noteworthy reactions taking place at lower voltages. Decomposition of the electrolyte and formation of the SEI films on the surface of the active particles occurs at the broad peak of 0.43 V [31–33].

The 2-SiO₂ anode presents the 1st discharge and charge capacities of 841 and 606 mAh g⁻¹ and 1-SiO₂ 937 and 440 mAh g⁻¹, respectively. Compared with the 2-SiO₂ and 1-SiO₂ discharge (Fig. 8c, f) and charge curves, 2-SiO₂ is more stable than 1-SiO₂. The excellent cyclic stability of the 2-SiO₂ electrode can be attributed to the nanoparticle size. Nanosized particles in 2-SiO₂ provide pathways for electrolyte/Li⁺ penetration and allow to compensate for the expansion of the active mass of the anode during cycling [3,34,35].

Fig. 8(g) shows the discharge and charge curves from the 1st to 5th cycle of the AC anode under a current density of 150 mA g⁻¹ in a voltage range of 0.01–3 V. The AC anode presents the 1st discharge and charge capacities of 1462 and 310 mAh g⁻¹, respectively. The primary coulombic efficiency of AC anode is about 21.2 %. The irreversible capacity loss could be attributed to the formation of SEI, the irreversible Li-ion intercalation on the new-formed surfaces, and even disordered carbon binder [36,37]. In the first discharge curve, a plateau is found at about 0.45 V and then disappears in the subsequent discharge curves. This phenomenon is also in line with the CV result. Compared with the 20th and 50th discharge Fig. 8(i) and charge curves, they almost overlap with each other, showing an outstanding cycling stability. Table 3 shows a comparison of anode materials based on silicon dioxide.

CV curves Fig. 8(h) towards the AC anode were measured at a scan rate of 0.1 mV s⁻¹ in the voltage range of 0.01–3 V. A broad reduction peak is found in the first cycle, suggesting the formation of the solid electrolyte interface (SEI) film on the AC electrode surface [37]. An obvious cathodic peak between 0.2 and 1.5 V can be found, corresponding to reversible insertion of lithium into the carbon layers and nanopores [39]. The intensity of the above cathodic peak in the first loop is much higher than that of the rest, which may be due to the formation of the SEI, the electrolyte decomposition, and the irreversible insertion of Li⁺ into special sites of carbon material.

4. Conclusion

In summary, formation of carbonaceous and silica anode materials for LIBs from the agricultural waste via step-by-step carbonization, precipitation and activation procedure is proposed. The 1-SiO₂, 2-SiO₂ and AC samples were synthesized and assessed as active materials in high-performance anodes for LIBs. Microporous structure of pure silica sample (2-SiO₂) contributes into anode's reversible capacity of over 442 mAh g⁻¹ retained at the current of 50 mA g⁻¹ after 50 cycles, and the better performance is due to the high specific surface area (980 m² g⁻¹) and larger specific pore volume. In similar tests 1-SiO₂ exhibit poor performance (295 mAh g⁻¹), which presumably attributed to impurities in the structure and therefore low conductivity. Among the tested materials, a sample of activated carbon with few-layer graphene expresses highest reversible capacity of 477 mAh g⁻¹, indicating excellent cyclic stability and favorable structural integrity maintenance. This work provides convenient methods for preparing anode material for LIB from the agricultural waste.

Author statement

The submission of the manuscript has been approved by all co-authors.

CRediT authorship contribution statement

K. Askaruly: Experiment, writing - original draft, Writing – review. **A.V. Korobeinyk:** Writing - review & editing, methodology. **S. Azat:** Supervision. **M. Yeleuov:** Investigation, Original draft preparation. **A. Taurbekov:** Data processing, experiment. **K. Toshtay:** Data processing. **Zh. Tauanov:** Editing. **X. Su:** Conceptualization, 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.

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