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Use of Vegetable Raw Materials as Electrode Materials for Li-Ion Batteries

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Kazakhstan possesses a large scale of cereal crops, bulrush, seeded fruits, grasslands and forests which are significant renewable resources for carbon materials. The agricultural sector, upon processing seeded fruits (e.g. apricots), rice, and others, produces large amounts of high carbon content wastes. It is known that obtaining carbon from these biomasses (wastes) is a cheap way of their utilization/disposal. There are existing technologies to produce so-called activated (porous) carbons mainly using thermolysis. Biomass waste could be considered as a potential material source for the preparation of porous carbons, which may have enhanced electrochemical capacitive performance in capacitors and cycling efficiency in lithium-ion batteries (LIBs).
Biomass derived activated carbon (AC) is a promising solid carrier due to its high adsorption capacity specific surface area, hierarchical porous structure, and can exhibit excellent electrical conductivity.
The main aim of this study was to research the influence of the properties of different vegetable raw materials, such as apricot stone (AS), rice husk (RH), walnut shell (WSh) on their electrochemical properties. The results of the electrochemical investigations showed good cyclic reversibility and stability. The battery with carbon electrode from walnut shells performed the highest capacity of 1000 $mAhg^{-1}$ over 150 cycles.
Keywords: biomass, activated carbon, porous, electrode, lithium-ion battery

1. Introduction

Last several decades, scientific interest was focused on the development of new efficient energy storage devices. Since 1991, lithium-ion batteries (LIBs) are broadly used in portable electronic devices, static energy depository systems, electronic vehicles, and aerospace owing to their high energy density, excellent cyclic stability, high electro-motive force, and extraordinary storage capacity (Xu et all., 2014, Ding et all, 2020).
In order to reduce the cost of lithium-ion batteries, it is necessary to suggest methods and approaches for optimization of the battery manufacturing process, increase cell performance and lifetime.
The capacity, performance, and cycle stability of LIBs depend on the electrode materials. The improvement of the anode materials is more relevant than the cathode materials. Industrial production of anode materials superior to commercial graphite still faces some challenges. Currently, graphite with a theoretical capacity of 372 $mAhg^{-1}$ is broadly used as electrode materials for lithium-ion batteries (Liu et all., 2022). The increasing demand for high-capacity energy sources requests new materials for this. Amorphous carbon (AC) can be obtained by carbonizing a polymeric materials, cellulose, charcoal, petroleum pitch, saccharides, vegetable raw materials and fruit shells (Yu et all., 2015). Pyrolysis of biomasses under low temperature (< 1200 ^{0}C) is a simple method to obtain AC. Amorphous carbons have been the most promising and cost-effective anode materials for LIBs and can achieve the capacity of more than 1000 $mAhg^{-1}$. Up to now, amorphous carbons obtained from biomass sources as coconut shell (Hwang et all, 2008), rice husk (Yu et all., 2018, Wang et all., 2015, Liao et all., 2021, Li et all, 2020), walnut shell (Tao et all., 2017, Fang et all., 2020), apricot stones (Pozio et all., 2022), pomelo peel (Sun et all., 2013), and pinecone shell (Fey et all, 2003), hazelnut shell (Unur et all, 2013) have been studied. Also, biomass source, as cellulose (Liao et all., 2016, Kierzek et all., 2015), lignin (Wyatt et all,

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2014, Du et all, 2018, Culebras et all, 2019), alginate (Liu et all., 2016, Wu et all., 2017), wood sawdust (Jain et all., 2017), reed flowers (Weimin et all., 2020), banana peels (Fernando et all., 2021), and enteromorpha prolifera (Wang et all., 2017) have shown magnificent electrochemical capacity as electrode materials for energy applications. They integrate a high conductivity, chemical, and physical permanency with a tunable pore structure and surface chemistry. These features open the door to create electrodes with tailored properties to maximize the resulting capacitive performance. Biomass as a source of activated carbons provides benefits of economic and natural sustainability (Soltani et all., 2021, Shirvanimoghaddam et all., 2022, Benítez et all., 2022). Batteries with porous electrodes offer high power density in addition to high energy density (Jayaraman et all., 2017, Sennu et all., 2019). In comparison with presented work (Tao et all., 2017, Fang et all., 2020) anod materials based on walnut shells performed the highest capacity of 1000 $mAhg^{-1}$ over 150 cycles. In this paper, we consider the possibility of using activated carbon obtained from rice husk, walnut shell and apricot stone as an anode material for LIB. Electrode materials in Li-ion batteries that are based on biomass-derived carbon may allow not only a technical breakthrough, but also an ethically and socially acceptable product.

All in all, morphological and structural investigations were applied to the resulting activated carbons via Scanning electron microscope (SEM), Energy Dispersive X-ray analysis (EDAX), Brunauer-Emmett-Teller (BET) analysis. Electrochemical measurements were performed by cyclic voltammetry (CV) and galvanostatic charge/discharge test with the rate capability performances.

2. Materials and Methods

Obtaining activated carbons. All samples (AS, RH 1, RH 2, WSh) were washed and dried to a constant mass with ensuing grinding in a ball mill to a fine powdery substance (particle size no more than 100 µm) as it was well explained in (Li et all., 2021). In the production of activated carbons by thermal oxidative modification of lignocellulosic materials of plant origin, two stages of processing carbon-containing raw materials are mainly used, which are: the stage of carbonization of the initial precursors, as well as the activation of the carbon matrices obtained in the previous stage with oxidizing agents.

The rice husk (RH) was obtained from local farms of Almaty region (Kazakhstan), and subjected for cleaning and drying to constant mass with subsequent grinding in a ball mill to a fine powder (particle size less than 100 µm). The preparation of porous carbons from the powdered rice husk was carried out by means of chemical activation using two different methods. Carbon samples for this work were obtained as described elsewhere (Li et all., 2021). According to the first method the powder of RH was carbonized in a muffle furnace by heating to 500 °C at a heating rate of 10 ºC/min and maintained at the final temperature for 1 h before cooling under a nitrogen flow rate of 100 cm^3/min. Carbonized RH was mixed with preliminary grinded potassium hydroxide (with a 1:2 ratio). The mixture was placed in a muffle furnace and heated at 10 ºC /min up to 800 ºC and kept at this temperature for 1 hour a under nitrogen flow rate of 100 cm^3/min. Resulting material was washed with hot distilled water until reaching a neutral pH, and then dried at 100 ºC overnight.

The second method was as follows: the powder of RH was preliminary treated with 2 mol/L sodium hydroxide solution by constant stirring in order to remove the silica. Resulting mixture was filtered and washed till neutral pH, followed by drying to constant mass. Subsequently, the pretreated RH was soaked with solution of zinc chloride using a ratio of activator to precursor equal to 3:1 and placed for drying at 150 ºC for about 24 hours. The resulting dried mixture consisted of pretreated RH with zinc chloride was placed in a muffle furnace and heated at 10 ºC /min up to 850 ºC and kept at this temperature for 1 hour under nitrogen flow rate of 100 cm^3/min. Resulting material was washed with hot distilled water until reaching a neutral pH, and then dried at 100 ºC overnight. AS and WSh was carbonized in a muffle furnace by heating to 850 °C at a heating rate of 10 ºC/min and maintained at the final temperature for 1 h before cooling under argon flow rate of 100 cm^3/min. Carbonized samples was mixed with H_3PO_4 orthophosphoric acid 70% (with 1:3 ratio). The mixture was placed in a muffle furnace and heated to 115 ºC and kept at this temperature for 12 hours. Resulting material was washed with distilled water until reaching a neutral pH, and then dried at 100 ºC overnight. Scanning electron microscope (Quanta 200i 3D", FEI Company, USA) with an Energy Dispersive X-ray analysis AMETEC detector provides detailed morphological characteristics samples. Brunauer-Emmett-Teller was carried out on device Sorbtometer-M in order to identify a specific surface area of samples. *Battery assembling.* Obtained carbon materials were tested as anode in a half-cell battery with lithium foil. The active material, electro conductive component acetylene black, and polyvinylidene fluoride (PVDF) were blended with N-methyl-2-pyrrolidone (NMP) (weight ratio 80:10:10). Then the slurry was casted on the surface of the copper foil, dried in a vacuum oven for 4 hours at 60 °C. The coin cell type batteries CR2032 were assembled in an argon filled glove box (Ar 99.999%, LAB master Pro Glovebox, <0.1 ppm H_2O and O_2, MBraun, Germany). The electrolyte solution consisted of 1 M $LiPF_6$ in ethylene carbonate, diethyl carbonate and dimethyl carbonate (EC/DEC/DMC=1:1:1 v/v). Celgard 2400 polypropylene was used as a separator. Metallic lithium foil was used as both reference and counter electrodes. Figure 1 shows the scheme of coin cell formation.

Figure 1. The schematic diagram for the creation of coin cell

Electrochemical tests were carried out in the range of potentials from 0.01 to 3.0 V and a rate of 50 mA/g on a multichannel tester (Neware Technology Ltd., China).

3. Results and Discussion

SEM images of the prepared samples from AS, RH 1, RH 2, WSh presented in Figure 2. demonstrate the presence of a porous structure, with a predominant micro-mesoporous pore distribution.

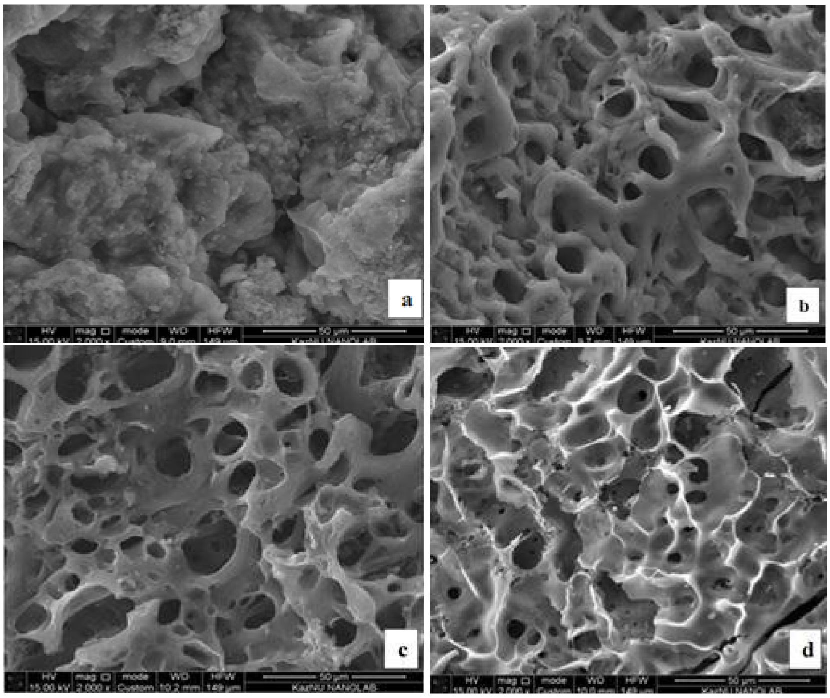

Figure 2. SEM analyses of samples: (a) apricot stones; (b) rice husk 1; (c) rice husk 2; (d) walnut shell

The presence of a large number of macropores on the surface of the sample can serve as a good electrical conductivity. Carbon materials based on RH, AS has lowest specific capacity in comparison with WSh. The reason for this is, most likely, the presence of a large amount of mineral components in the original precursor, which prevents the formation of a highly developed porous structure during the process of steam-gas activation. This fact indicates the need to apply the chemical activation method to this material with the subsequent leaching of the mineral part. An analysis of the experimental results showed that the most developed polymodal porous structure is possessed by samples of walnut shells.Table 1 represents the results of the BET analysis of samples.

Table 1. The results of measurement of a specific surface by the BET method

№	Sample's name	Specific surface area, m^2/g	Specific capacity of battery, mAh/g
1	Apricot stone	1615	700
2	Rice husk 1	2063,3	300
3	Rice husk 2	2507,9	320
4	Walnut shell	2552	1000

BET analysis shows that with an increase in the specific surface area of samples, the specific capacity of batteries increased. It can be seen from Energy Dispersive X-ray analysis results that data of the elemental composition of apricot stones sample, which presented in the Table 2 show that the material consists 88% carbon and 8% oxygen, indicating a high concentration of its carbon component, also a small amount of activating agents' metals as potassium and phosphorus. It should be noted that phosphorus impurity availability in element structure is caused by a technique of carbonization and chemical activation of WSh and AS. The element structure of a sample of rice husk 1 and rice husk 2 presented in the Table 2 has shown that activated carbons for 92% and 86% consists of carbon and for 7% and 11% from oxygen and also minor amount of chlorine, potassium, calcium. The data of the elemental composition of the carbonized walnut shell presented in Table 2 show that the material contains 90% carbon and 8% oxygen.

Table 2. EDAX analyses of samples

№	Sample's name	C (wt%)	O (wt%)	P (wt%)	K (wt%)	Cl (wt%)	Ca (wt%)
1	Apricot stone	88,56	8,00	2,36	1,07	-	-
2	Rice husk 1	92,08	7,49	-	-	0,43	-
3	Rice husk 2	86,59	11,84	-	0,70	-	0,87
4	Walnut shell	90,94	8,35	0,71	-	-	-

The galvanostatic charge–discharge capacity of the 1st, 2nd, 10th cycles of the half cells with prepared carbon electrodes are depicted in Figure 3.

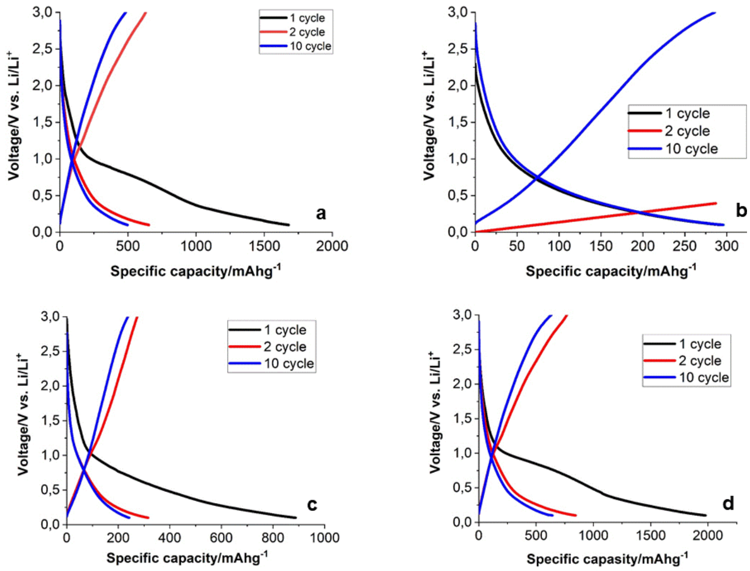

Figure 3. Charge-discharge profiles of batteries with carbon electrodes: (a) apricot stones; (b) rice husk 1; (c) rice husk 2; (d) walnut shell

The average discharge capacity at 2nd cycle of 300, 320, 700, 850 were obtained for batteries with carbon electrodes from apricot stone, rice husk 1, rice husk 2, walnut shell.
The cycling performance of electrodes are presented in Figure 4.

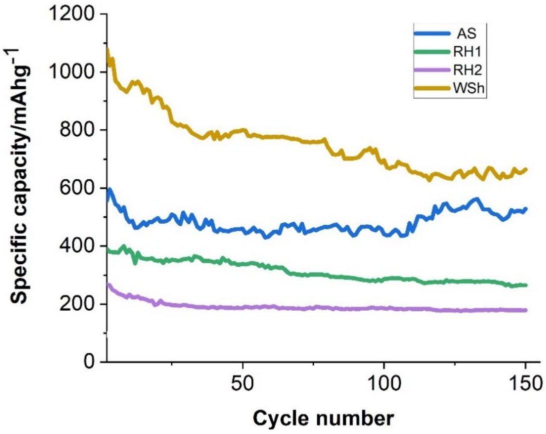

Figure 4. The cycling performance of batteries with obtained carbon electrodes

As seen in Figure 4. capacities of carbon electrodes from rice husk (sample 2 and 3) are higher and show slow degradation by cycling. The cell with electrode from apricot stone (sample 1) performs a stable capacity of 500 mAhg^{-1} over 150 cycles. However, the battery with electrode from walnut shell (sample 4) shows the highest capacity among all tested. Capacity value remains 1000 mAhg^{-1} over 150 cycles. In comparison with carbon electrodes from rice husk, electrodes based on apricot stone and walnut shell show good results.
As it is seen from table 1 the specific capacity of tested batteries agrees well with BET analysis. The capacity of batteries increased in accordance with the surface area of obtained carbon materials.

4. Conclusions

Activated carbon were obtained based on waste from the agricultural industry as apricot stone, rice husk and walnut shell. The obtained samples were examined by Energy Dispersive, X-ray analysis, Brunauer-Emmett-Teller analysis. Lithium-ion batteries are the best solution to the problems of the environmental situation in the world, combined with ease of use, energy efficiency and affordable price. Therefore, obtained carbon materials were used as electrodes for lithium-ion batteries.
The battery with carbon electrode from walnut shells performed the highest capacity of 1000 mAhg^{-1} over 150 cycles. The number of balancing cycles affects the performance of a lithium-ion storage device. With an increase in the number of balancing cycles, the level of the minimum voltage among all cells increases and, consequently, the discharge time of a multi-cell battery increases, but at the same time, the storage charge time also increases.

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