**ELECTRODE MATERIALS BASED ON CHEMICALLY ACTIVATED CARBONS FROM VEGETABLE WASTE FOR APPLICATION IN LITHIUM/SULFUR BATTERIES**

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**Introduction**

The aim of this work is to test carbons obtained from renewable materials, e.g.: vegetable wastes such as rice husk (RH) and apricot stones (AS), via H3PO4-activation for suitability of being used for preparation of carbon/sulfur (C/S) composites applied as cathodes in lithium/sulfur (Li/S) batteries. The C/S cathode is considered as one of the most promising candidates due to its low cost, environmental friendliness and large theoretical capacity up to 1672 mAh g-1 [1]. The impregnation of sulfur into conductive highly porous carbon significantly increases electronic conductivity of naturally insulating sulfur. Moreover, excellent adsorption properties of carbon synthesized from vegetable wastes are used to trap the spare discharge products such as polysulfides [2]. Reduction of spare products results in improved electrochemical characteristics of battery such as cyclability and rate capability.

**Experimental**

70% phosphoric acid (ρ ≈ 1.54 g/cm3) was admixed to appropriate amount of RH or 1-2 mm fraction of AS to make Н3РО4/precursor (wt/wt) impregnation ratio of 2:1. The mixtures were transferred into alumina crucibles, precarbonized in an oven at 200 ºС for 12 hours, loosely covered with stoppers and activated at 500 °C during 1 hour (AS) and 2 hours (RH) in a vertical cylindrical furnace equipped with chromel/alumel thermocouple at the temperature ramp rate of ca. 5 ºС / min. Carbonized apricot stones (CAS-P-500) were continuously washed with hot distilled water till neutral pH. To obtain carbonized rice husk (CRH-P-500), the residue underwent additional neutralization to Na2HPO4 with the equivalent amount of concentrated NaOH followed by desilication in 0.5M NaOH and washing with hot distilled water till neutral pH according to the technique [3]. Samples were dried in hot air oven at 110±5 °C. Product yields: 44% for CAS-Р-500 and 30% for CRH-Р-500. To analyze the textural characteristics of carbonized materials low-temperature (77 °K) nitrogen adsorption-desorption isotherms were recorded using “ASAP-2400” Analyzer (Micromerit ics Instrument Corp., Norcross, GA, USA), upon preliminary training of the samples at 150 °С & residual pressure of 0.001 mmHg. The measurements for isotherms were conducted at 77 °K within range of relative pressures from 0.005 to 0.991. The desired concentrations for methylene blue (MB) adsorption studies and calibration solutions for spectrophotometric evaluation were obtained by successive dilution of aqueous MB stock solution (4000 mg/L). Each time a 50 mL glass-stoppered flask with 0.10 g activated carbon and twenty five millilitres of a dye solution added was placed on a magnetic stirrer at room temperature for 20 min. Then the absorbance of supernatant solution was estimated to determine the residual concentration. MB adsorption was calculated from the mass balance equation:

$$q\_{e}=\frac{(C\_{0}-C\_{e})×V}{m}$$

where *C*0 and *C*e are the initial and equilibrium dye concentrations, V is the volume of liquid phase and m- mass of adsorbent. Obtained adsorption isotherm data were plotted in the linear Langmuir-isotherm model [4]:

$$\frac{C\_{e}}{q\_{e}}=\frac{1}{q\_{max}K\_{l}}+\frac{C\_{e}}{q\_{max}}$$

where *qmax* is the monolayer capacity and *Kl* is a constant related to adsorption free energy. Analyses of mineral part of the sample were performed using X-ray fluorescent spectroscopy on VRA-30 analyser with Cr-anode X-ray tube. Carbon and hydrogen contents were determined by an elemental analyser (Vario MicroCube, Elementar). The morphology of activated carbons was studied by scanning electron microscopy (SEM) using a QUANTA 3D 200i microscope (FEI, USA) with accelerating voltage of 30 kV.

The C/S composites were prepared in a planetary ballmilling machine (Planetary Micro Mill PULVERISETTE 7, Fritsch, Germany) using 3 mm zirconia balls and ethanol as a liquid medium in zirconia bowl. The rotation speed was 800 rpm and ball-milling time was ﬁxed at 3 h. The C/S composites with various carbon to sulphur ratios (C:S = 1:1, 2:1, 2:3, 3:7) were prepared. The composition of material after ballmilling was measured by chemical analysis (CHNS, Vario MicroCube, Elementar). Thermal behavior of the S/C composites was studied by means of thermogravimetric analysis (TGA, Q500, TA Instruments) and differential scanning calorimetry (DSC, Q2000, TA Instruments) at a heating rate of 5 oC min-1 in argon atmosphere. The composites conductivities were measured using ac impedance spectroscopy (EIS), and their electrochemical stability were evaluated using cyclic voltammetry (CV) measurements (both VMP-3, BioLogic). For these purposed, the S/C composites were pelletized (pellet’s thickness about 100 μm, diameter 8 mm) using a hydraulic press at the pressure of 10 t. For the EIS measurements, the samples were sandwiched between two blocking stainless steel electrodes. For the CV measurements, the composite samples were sandwiched between lithium metal counter/reference electrode separated with a Safegard separator, and stainless steel working electrode in a Swagelok type cell.

**Results and Discussion**

Phosphoric acid is a known porogen letting the carbonization reactions to occur at much lower temperatures (due to acidic catalysis causing dehydration) compared to simple pyrolysis which is governed mostly by radical mechanisms, causing tar formation due to disproportionation reactions. The use of it thus is to provide both higher yields (less volatiles and tar) and high surface area, as well as to functionalize carbon surface with phosphate groups (C-O-P-bonding) via phosphorylation of cellulose OH-groups.

According to the analysis results, CAS-P-500 and CRH-P-500 have C-content- 88.51% and 87.96%, while H-content- 1.68% and 1.92% respectively. These results are indicative of sufficient carbonization degree. X-ray fluorescent spectroscopy results showed that phosphorus content of CAS-P-500 is near 1 % and the ash elemental content- ca. 0.02 %. For the sample CRH-P-500, elemental content was as follows: P- 0.895%, Si- less than 0.04%, and other ash elements- 0.065%.

The standard calculations for isotherms were performed by Barret-Joyner-Halenda method, with the admission of postulated model for cylindrical pores, the calculation of total pore surface area SƩ and micropore surface area Sµ by BET-method, total pore volume VƩ and micropore volume Vµ; average pore diameter Dpore. According to these results shown in Table 1, the largest portion of pores of both samples CAS-P-500 and CRH-P-500 is accounted for mesopores.

High values of MB-monolayer capacity (Table 1) of CRH-P-500 and CAS-P-500 samples also suggest high mesoporosity, since the MB molecule is accessible to the pores with diameters larger than 1.5 nm [6].

SEM images of the CRH-P-500 and CAS-P-500 are shown on **Figure 1a-d**. It can be observed at a higher resolution (Fig 1b, d) that the morphology of surface CRH-P-500 and CAS-P-500 samples is characterized by porous structure having nanoscale elements (pores).

Table 1. MB-monolayer capacity of activated carbons and their textural properties according to N2 adsorption

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Sample** | **Max. MB-sorption capacity, mg/g** | **SƩ****m2/g** | **VƩ****cm2/g** | **Dpore****nm** |
| CRH-P-500 | 562 | 1690 | 1.95 | 4.4 |
| CAS-P-500 | 893 | 2030 | 1.64 | 3.2 |



Figure 1. SEM images of CRH-P-500 (a,b) and CAS-P-500(c,d) magnification: (a) - x 1 200; (c) - x 600;

(b) and (d) - x 160 000

The TGA analysis data of sulfur/carbon composites based on the CAS sample are presented in Figure 2. It can be seen that the composite weight keeps unchanged up to 180 oC. Upon the further temperature increase, one can observe a drastic weight loss of 40 % of the initial weight, which continuous up to 400 oC. This weight loss could be attributed to the sulfur sublimation, because the total weight loss corresponds exactly to the weight ratio of sulfur initially contained in the sample. Further heating of the sample in argon atmosphere up to 600 oC does not remarkably affect the sample weight.



**Figure 2.** Thermal analysis data of a S/C composite with the weight ratio S:CAS = 3:2; Ar, 5 o/min.



**Figure 3.** XRD patterns of sulfur, a carbon component and the S:CAS = 3:2 composite.

Chemical analysis of the S/C composites have confirmed that the sulfur content in the samples has not changed during ball milling and accompanying increase of temperature. This could be attributed to large specific surface area and porosity of the carbon materials used, providing sulfur absorption and preventing its evaporation (sublimation). **Figure 2** presents the XRD data for the CAS based S/C composite and starting materials. It can be seen that the characteristic peaks of sulfur disappear from the composite XRD patterns. Combined with the chemical analysis data, this allows us to conclude that sulfur has been “trapped” in porosities of the carbon material prepared in this work. It was shown that the composites conductivity increases with the C content. The CV results (not shown) revealed absence of any electrochemical reactions in a voltage region 1.5 – 3 V vs. Li+/Li, except the typical peaks of a sulfur cathode redox reactions in a lithium battery [1], confirming the electrochemical stability of the composites prepared using carbon materials from vegetable waste.

Further investigations on the electrochemical performance of the S/C composite prepared in this work are under development.

**Conclusion**

Highly mesoporous carbons were made by means of chemical activation using phosphoric acid at 500 °С from vegetable row materials, for example rice husk and apricot stones . In the case of RH, upon carbonization, an additional method of desilication with 0.5 M NaOH solution was applied. SEM-investigation together with low-temperature adsorption studies, as well as methylene blue sorption studies revealed both high surface area and mesoporosity of obtained carbons making them suitable to be employed as component of C/S composite cathode material for Li/S batteries. Elemental analyses of the carbons showed sufficient degree of carbonization and functionalization of their surface with phosphate group. Large surface area of the carbon materials prepared in this work allowed for sulfur adsorption and its retention upon ball milling, which was confirmed by the XRD, chemical and thermal analysis data. The S/C composites prepared using the carbons from vegetable waste materials showed suitable electrochemical stability within the operation voltage region, which allows to suggest that the new carbon materials prepared in this work and the S/C composites on their base are promising materials for lithium battery application.

**Acknowledgements**

This research was supported by a grant from the Ministry of Education and Science of Kazakhstan, and partially by the Nazarbayev University Corporate Fund.

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