POTENTIAL USE OF CARBON ELECTRODE MATERIALS DERIVED FROM VEGETABLE BIOMASS FOR SUPERCAPACITORS

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Introduction

Activated carbons are versatile materials used in a broad range of applications. In the last decade, activated carbons gained a significant amount of interest as the electrodes of electric doublelayer capacitors, often called supercapacitors [12]. This is due to their high surface areas, possibility of tailoring their structure for particular application, good polarization, high chemical stability and favorable price [13, 14]. Vegetable raw materials, based on agriculture wastes are rapidly renewable source for active carbon production. Also it has essential porosity structure, low content of mineral compounds and they are environmental friendly products.

Experimental

Different activated carbons were produced from vegetable raw materials, e.g.: rice husk, apricot stones and walnut shells, by means of chemical activation using phosphoric acid. 70% H3PO4 (p =1.54 g/cm^3) was admixed to appropriate amount of rice husk or 1-2 mm fraction of walnut shells and apricot stones to make H_3PO_4/precursor (wt/wt) impregnation ratio of up to 2:1. The mixtures were first precarbonized in an oven at 200 °C for 12 hours, and then activated in self-generated atmosphere at 500 °C for rice husk and apricot stones, and at various temperatures within range of 400-800 °C for walnut shells. In the case of rice husk, upon carbonization, an additional method of desilication with 0.5M NaOH solution was applied.

To analyze the textural characteristics of carbonized materials at low-temperature (77 ^{o}K) nitrogen adsorption-desorption isotherms were recorded using «ASAP-2400» Analyzer (Micromeritics Instrument Corp., Norcross, GA, USA), upon preliminary training of the samples at 150 ^{o}C & residual pressure of 0.001 mm Hg. The measurements for isotherms were conducted at 77 ^{o}K within range of relative pressures from 0.005 to 0.991.

Analyses of mineral part of the sample were performed using X-ray fluorescent spectroscopy on VRA-30 analyzer with Cr-anode X-ray tube. Carbon and hydrogen contents were determined by use of elemental analyzer «VARIO ELEMENTAR III». 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.

For SEM imaging AC beads and crushed particles (to view internal structure) were mounted onto a sample holder and coated with 4 nm platinum using a Zeiss Sigma field emission gun SEM (Zeiss NTS) at an accelerating voltage of 5 kV.

The electrochemical investigations were conducted by using the VMP-3 «BioLogic». The obtained carbons were used for preparation of composite electrodes with addition of 10 % polyvinylidene fluoride binder (PVdF) and 5 % commercial carbon black. Two-electrode capacitors were assembled by using the Teflon Swagelok® system. Electrodes were prepared by pressing (appr. 100 kg/cm^2) in the form of pellets (5–8 mg/pc) with a geometric surface area of appr. 0,785 cm^2 per electrode. Electrochemical investigations were performed with 1M Li_2SO_4 aqueous solution. A cellulosic fibrous material played the role of the separator Electrochemical characterization of porous carbons in supercapacitor cell assemblies was fulfilled using the methods of cycling voltametry at voltage scan rates from 1 to 100mVs^{-1}, galvanostatic cycling with potential limitation (50–25,000 mAg^{-1}), and by potentio electrochemical impedance spectroscopy (0,1-100 Hz) using the «VMP-3» BioLogic.

Results and discussion

It's well established that phosphoric acid and zinc chloride are used for the activation of lignocellulosic materials that have not been carbonized previously; whereas metal compounds such as KOH are commonly used for the activation of coal precursors or chars [11]. From different literature sources [9, 11] it is known that the process of activation of lignocellulose materials with ortho-phosphoric acid includes two important stages during the process of activation. During the first stage between temperatures of 170–215 ◦C, the cellulosic material along with other components are degraded and a plastic mass. During this stage phosphoric acid loses water molecule and converts into pyrophosphoric acid [10]. During the second stage, carbon particles covered with large amounts of pyrophosphoric acid are exposed to different temperatures.

The contents of carbon, hydrogen, nitrogen and oxygen for various samples are shown in the **Table 1**. It shown, that the activated walnut shell had the biggest carbon content.

Table 1. Elemental analysis of carbon materials

Sample	C, %	H, %	N, %	O, %
CRH	87,96	1,92	0,26	8,62
SGO 600	90,53	no data	no data	7,75
AS-P-500	88,5	1,68	0,11	8,6

Phosphoric acid appears to function both as an acid catalyst to promote bond cleavage reactions and the formation of crosslinks via processes such as cyclization, and condensation, and to combine with organic species to form phosphate and polyphosphate bridges that connect and crosslink biopolymer fragments [6].

For effective use as electrodes for supercapacitors, the selected materials should meet some requirements such as: 1) a high conductivity for assuring a high power density [1]; 2) an adequate pore size distribution consisting mainly of nanopores with an average pore size smaller than 1 nm enhancing capacitance either in organic or aqueous electrolytes [2, 3] 3) a large amount of surface functionalities that could undergo fast redox reactions in order to enhance the capacitance through pseudo-capacitive processes when working in aqueous electrolytes [4,5].

The SEM images of the carbonized and activated walnut shell displayed in **Figures 1 (a, b)** demonstrate the

porous internal structure in the macropore- and micro-mesopore range of diameters respectively.

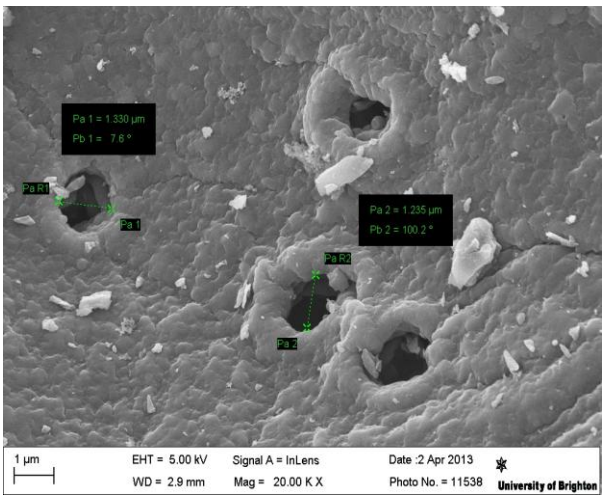

Figure 1a. SEM image of KWS-P-500

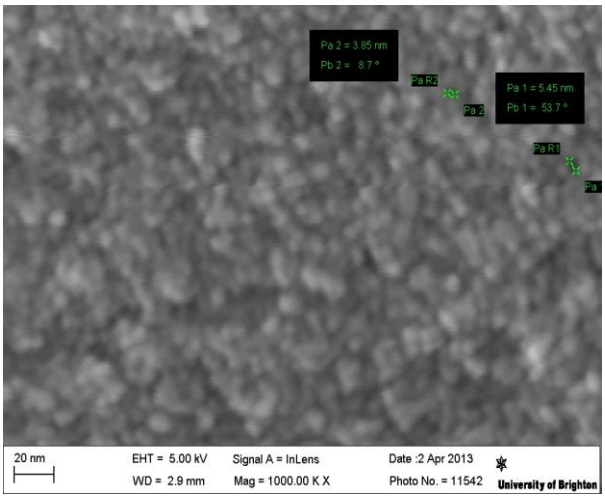

Figure 1b. SEM image of KWS-P-500

By conducting the activation process of rice husk with concentrated phosphoric acid during two hours at 500^{o}C we obtained the micro- mesoporous sample (**Figure 2**).

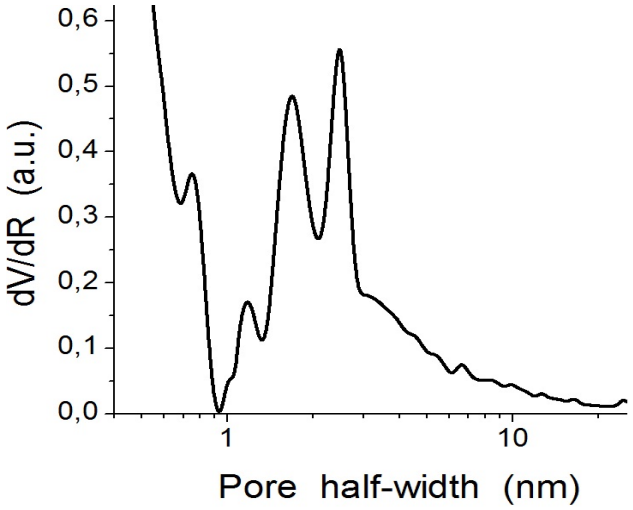

Figure 2. Pore size distribution for CRH using QSDFT

The electrochemical properties of the carbon electrodes obtained from apricot stones (AS-P-500), rice husk (CRH) and walnut stones (KWS-P-500) have been investigated by using two-electrode cells. Figure 3 shows the cyclic voltammograms obtained for some carbonized and chemically activated materials in 1 mol L^{-1} Li_2SO_4 media.

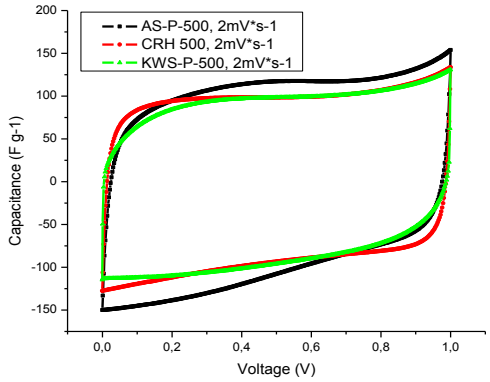

Figure 3. Dependence of the specific capacitance at different potential limits

Figure 4 shows the Nyquist plot for two-electrode capacitors that were assembled with three different carbonized and chemically activated vegetable raw materials in 1 mol L^{-1} Li_2SO_4 aqueous electrolyte. Out of these different plant materials, rice husk has a better square shape of cyclic voltammograms and its characteristics may prove a good charge propagation in this material (**Figure 5**).

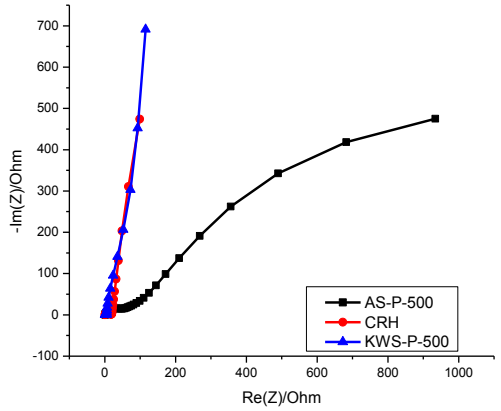

Figure 4. Nyquist plots for different carbon materials

As it can be seen from the **Figure 4** the Warburg impedance region for activated apricot stones sample was associated to Faradaic reactions together with the kinetic leakage processes in the diffusion line, also it had very significant ohmic drop value of 0,3 volts (**Figure 7**). These factors doubtless lead to definetely low general quality of the carbon, which was obtained through carbonization and activation of apricot stones sample despite it's mild specific capacitance of 112 F*g^{-1} (current density 0,2 A*g^{-1}, vertex potential 1V) in the media of 1 mol L^{-1} Li_2SO_4 aqueous electrolyte.

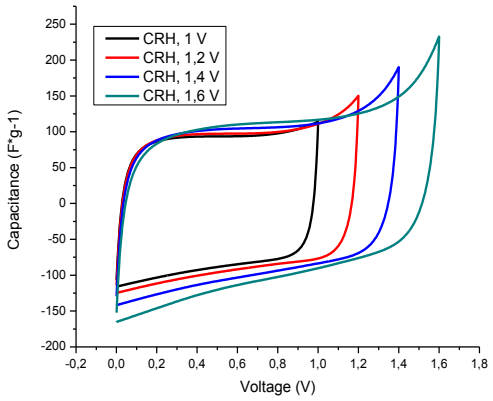

Figure 5. Dependence of the specific capacitance vs different potential

The dependence of capacitance at low frequencies showed the maximum capacitance for activated rice husk (**Figure 6**). The dependence of capacitance at different current loads (**Figure 8**) for a supercapacitor which was assembled with carbonized and activated with phosphoric acid walnut shell in 1 $M*L^{-1}$ Li_2SO_4 media showed the optimal electrochemical performance.

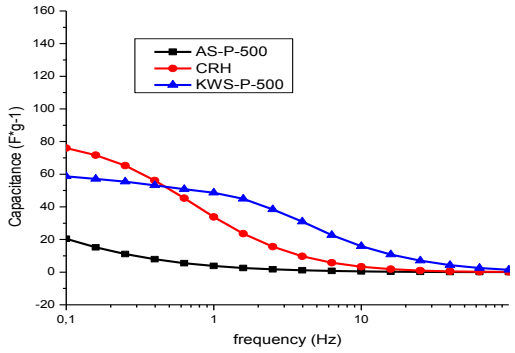

Figure 6. The capacitance at different frequencies

Upon the results of a series of experiments on carbonization and activation of different plant materials in inert atmosphere and at mild temperatures (500-600^{o}C) the walnut shell was selected as main precursor for the further testing under various conditions. In particular we had chosen a one-step process (carbonization+activation) in carbon dioxide atmosphere at temperature range from 500 to 800 ^{o}C.

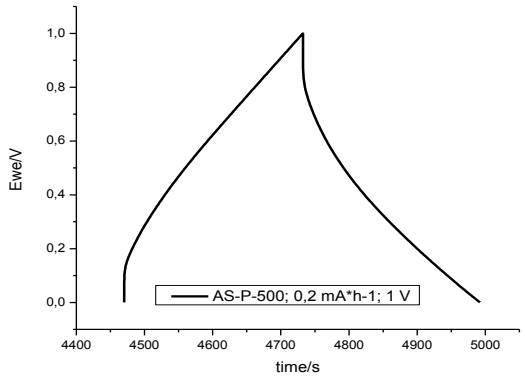

Figure 7. Galvanostatic characteristic of supercapacitor built from carbonized and activated apricot stones

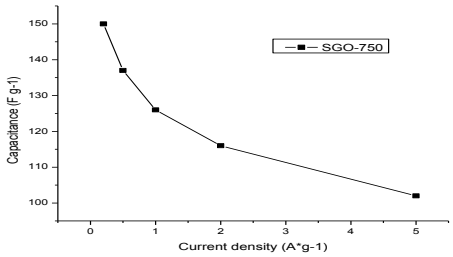

Figure 8. Dependance of capacitance vs current density

In their works Jagtoyen and Derbyshire found out that treatment with phosphoric acid promotes an expansion of the lignocellulose structure over the temperature range 250-450 ^{o}C corresponding directly to the development of porosity, especially for mesopores, which maximum volume development (0,55 cm^3/g) evolved at 500 ^{o}C [6]. Therefore with subsequent growth of temperature it would be expected the reduction in specific surface area and as a consequence - the decrease of the capacitance values. This statement is in good agreement with the data of specific surface area which was obtained by adsorption of argon molecules (**Table 2**).

Table 2. Properties of carbonized and activated walnut shell

The name of sample	Temperature of carbonization + activation, ^{o}C	Specific surface area (BET N_2-desorption), m^2/g	Specific capacitance (calculated from GCPL-data), F*g-1
CRH	500	1690	109
AS-P-500	500	2030	112
KWS-P-500	500	1062	82
SGO 600	600	1380	135
SGO 700	700	1241	140
SGO 750	750	1152	150
SGO 800	800	1050	160

From the **Figure 9** it can be seen the increase of the specific capacitance for the sample «SGO 800» (appr. 160 F*g-1) it may be due to the influence of the pseudocapacitance. This fact can be associated with some irreversible reactions occurred on electrode surface leading to increased low reversible capacitance of this material.

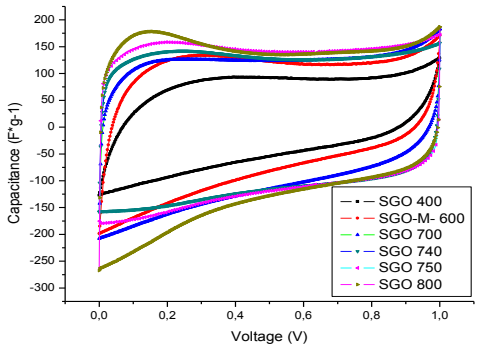

Figure 9. Capacitance vs. Voltage for walnut stones activated at different temperatures

Conclusions

Different active carbons were obtained from vegetable raw materials by carbonization and activation with phosphoric acid; they were characterized in terms of their

morphology, structure and other physical and chemical properties.

Using these active carbons, the electrode materials were made; they were tested as electrodes for supercapacitor cells.

Electrochemical investigations of the assembled cells were conducted. Perspective of using these materials is shown.

The maximal capacitance was obtained for activated walnut shells of 160 $F*g^{-1}$ (in the media of 1M Li_2SO_4) which was synthesized at 800 ^oC .

References

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