

New Approach to Chemical Activation of Plant Biomass for Producing Activated Carbons with High Surface Area and Capacitance Performance

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Abstract: The production of high-quality activated carbons from lignocellulosic biomass for application in advanced energy storage systems in particular the electrochemical capacitors is of great commercial interest because of their high specific surface area, electrical conductivity, electrochemical stability and notably low cost. During this presentation the synthesis and application of microporous carbons derived by improved chemical activation of walnut shells impregnated with phosphoric acid will be presented. The carbons derived from the rice husk are characterized by high specific surface area of $2400 \text{ m}^2 \text{ g}^{-1}$ (calculated by the method of Brunauer–Emmett–Teller) and total pore volume of $1.5 \text{ cm}^3 \text{ g}^{-1}$. Activated carbons were implemented as the active materials for symmetric composite electrodes of electrical double layer capacitors in $1 \text{ mol L}^{-1} \text{ Li}_2\text{SO}_4$. Electrochemical investigations performed by cyclic voltammetry, galvanostatic charge-discharge with potential limitations and impedance spectroscopy revealed high performance of carbon materials derived through modified chemical activation procedure especially under aging tests during floating voltage of 1.6 V. In particular the resulting carbons possess a much higher capacitance of $190\text{--}200 \text{ F g}^{-1}$ (at 0.2 A g^{-1}) that is much higher than most of available commercial blends of activated carbons e.g., the Norit DLC Supra 30 which in similar conditions possessed 108 F g^{-1} .

Key-Words: Carbonization, chemical activation, plant biomass, activated carbon, electrochemical capacitor, impedance spectroscopy

1 Introduction

Activated carbons are universal materials applied as effective adsorbents [1], catalyst carriers [2,3], and for preparing electrodes for electrical double-layer capacitors (EDLCs) [4,5]. The main raw materials for production of ACs are fossil coals, bitumen, petroleum pitch and plant biomass, the latter being a renewable source. It is expedient to use quite dense and strong materials as an initial biomass, among which hard breeds of wood, nut shells and fruit stones are usually chosen. In this regard, the production of activated carbons from vegetable wastes is an affordable alternative to the use of fossil fuels.

There are numerous methods described in the literature for obtaining high surface area activated carbons from natural precursors. They conditionally may be divided into physical activation where gaseous oxidants are used [6], and chemical activation for which various chemical reagents are used [7]. When the carbonaceous precursor, such as tobacco stems, contains a high amount of alkali derivatives, activated carbons can be produced by simultaneous carbonization and self-activation [8].

2 Problem Formulation

The application of recently developed methods for the processing of lignocellulosic biomass with the aim to produce the advanced types activated carbons characterized by the outstanding features of the porous structure include the use of microwave induced activation and are referred to be promising [9, 11]. However, such methods may have serious disadvantages, as which a high energy consumption, difficulties in the large scale manufacturing, and other overhead costs associated with the use of high pressures, high energy sources and hazardous chemicals probably are allocated.

Among the huge number of methods described in the literature which are devoted to a preparation of activated carbons, the extensive practical implementation received only the economically viable, low-waste methods, such as steam-gas activation of coconut shells.

In this regard, the appropriate modification and further development of the traditional methods of chemical activation of carbonaceous precursors is still one of the most attractive directions for the production of carbonaceous materials possessing the highly developed values of specific surface

area, with the volumes and sizes of micro- and mesopores tailored to a certain extent.

Meanwhile the one-step method of chemical activation of lignocellulosic biomass impregnated with phosphoric acid has its undoubted advantages, which include a low processing temperature, higher yield of final products, lower toxicity and corrosivity.

The application of phosphoric acid for preparing AC is also an effective, high yield method. Phosphoric acid treatment promotes dehydrogenation of the precursors impregnated with phosphoric acid, they undergo accelerated carbonization and changing of porous structure at moderate high temperature treatment (HTT) [12], which may be too low when other reagents such as potassium hydroxide is used. Activation of plant wood biomass impregnated with phosphoric acid carried out in the range of 350-450 °C contributes to the formation of microporous AC with a high specific surface area of approximately 1900 m² g⁻¹.

The walnut shells can serve as a carbonaceous precursor suitable for the production of high quality activated carbons in a large industrial scale. For instance, China and Central Asian countries have the biggest plantations of walnut trees; meanwhile annual volume of waste production reaches hundreds thousands of tons. This creates preconditions for the partial replacement of coconut shell as the main carbonaceous precursor with the aim of localized production of activated carbons.

3 Problem Solution

In this study, we present a highly efficient method for high-temperature treatment of plant biomass represented by the walnut shells with the aim of obtaining micro- and mesoporous AC possessing a developed specific surface area in combination with a high volume of mesopores. To determine the possibility of using the resulting ACs in energy storage systems, particularly EDLC, we have attempted to establish the influence of the processing conditions on the electrochemical properties of the materials. For this purpose, the synthesized activated carbons were implemented as electrode materials in aqueous electrolyte based electric double layer capacitors.

3.1 Experimental Part

Cleaned walnut shells from local farms were dried to constant mass and subjected to crushing. The fraction with a diameter of less than 2 mm was selected by sieving. Carbonization and physical

activation was carried out in a horizontal furnace, whereas the chemical activation was performed in a shaft furnace with similar construction (60x50x80cm). The temperature was increased at 10 °C min⁻¹ and the argon flow rate was 100 mL min⁻¹.

For chemical activation, the cleaned and crushed walnut shells were impregnated with 85 wt.% phosphoric acid solution and the mixture was left to dry in an oven at 200 °C for 10 hours. The resulting mixture was placed in a ceramic crucible and subjected to activation in an argon atmosphere inside a shaft furnace for 60 minutes at temperatures from 350 °C to 800 °C. After activation, the mixture was washed with hot distilled water until the pH was close to neutrality. Carbonization and physical activation was carried out in a horizontal furnace, whereas the chemical activation was performed in a shaft furnace with similar construction (60x50x80cm) presented in Figure 1.

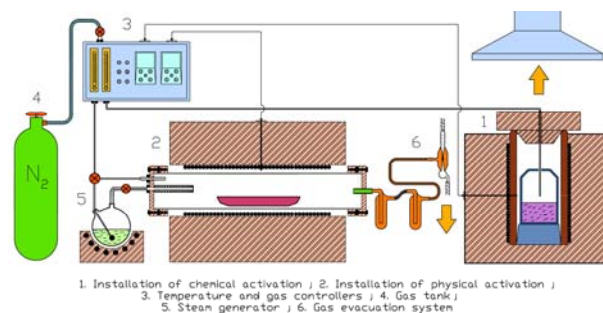


Fig. 1 – Experimental setup for physical and chemical activation

Further in the text, the walnut shell carbons are named according to their processing method which was divided into carbonization, steam-gas activation and activation with phosphoric acid. Numeric index in the name of samples corresponds to the temperature of isothermal holding during their HTT. Activation conditions and reagent to precursor ratio are listed in Table 1.

Table 1. Conditions for high temperature treatment (HTT) procedures

Index	Activation agent	Time, [min]
C-900	Carbonization	900
S-900	Steam gas mixture (IR=10:1)	180
P-450	40 wt.% solution of H ₃ PO ₄ (IR=3:1)	60

For nitrogen adsorption analysis, the carbons were degassed at 200 °C for 3 hours before the

analysis was carried out. The nitrogen adsorption isotherms were determined with an Autosorb-1 (Quantachrome instruments, UK) in the range of relative pressures from 0.005 to 0.991. The data were analyzed with the Quantachrome software using the NLDFT equilibrium pore model. The morphology of activated carbons was studied by scanning electron microscopy (SEM) using a QUANTA 3D 200i microscope (FEI, USA) with accelerating voltage of 15 kV.

For evaluating the electrochemical performance of walnut based ACs in supercapacitors, composite electrodes were used. The electrodes were prepared in the form of pellets with a geometric surface area of 0.785 cm² (5–8 mg/pc) by mixing 90 wt.% of walnut shell based AC, 5 wt.% of polytetrafluoroethylene (PTFE) used as 60 wt.% aqueous suspension (Sigma-Aldrich) and 5 wt.% of carbon black (C-65, Imerys). Symmetric two-electrode cells were realized in teflon Swagelok® vessel using 1 mol L⁻¹ Li₂SO₄ aqueous electrolyte, with glass fiber separator (Whatman GF/A, thickness 260 μm) and stainless steel current collectors (SS 316L). The electrochemical investigations were carried out by using a VMP-3 multichannel potentiostat/galvanostat, BioLogic Instruments, France. The gravimetric capacitance (F g⁻¹) has been calculated from the galvanostatic discharge characteristics of two-electrode cells using the formula:

$$C = (2)I/[(dU/dt)m_{am}] \quad (1)$$

where I is current (A), dU/dt - the slope of the discharge curve (V s⁻¹), and m_{am} - the average mass of activated carbon in one electrode (g).

3.2 Results and Discussion

Fig. 2 shows SEM images of the ACs based on WS impregnated with H₃PO₄ with followed activation at various temperatures (Fig. 2a,b,c) and carbonized WS further activated by steam-gas mixture (Fig. 2d). It is noted that the samples based on H₃PO₄-impregnated WS activated at 600 °C possesses most clearly expressed porous structure with openwork texture characterized by large numbers of cracks and crevices. Porous texture characterized by a large number of fissures and cavities, according to their appearance, they resemble the loose cellular structure. General view of these carbons has the similar features typical for carbonized and physically activated walnut shell including the high inherent porosity, represented by system of cavities interconnected to each other by channel holes of different sizes and depths and

narrow pores. It can be concluded that porous structure was formed since the most of the organic volatiles were evolved, leaving behind the ruptured surface of activated carbon.

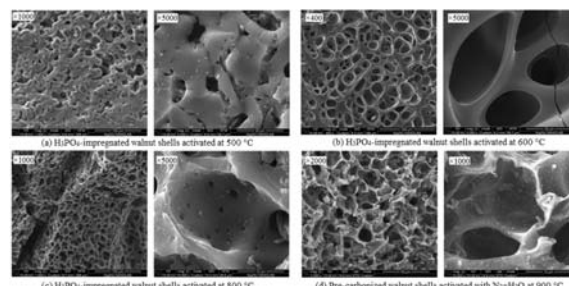


Fig. 2 – SEM images of walnut shell based carbons activated at various temperatures

Walnut shell (WS) is the typical lignocellulose biomass with composition of cellulose 25%, hemicelluloses 21% and lignin 53% [10]. From the published data it's known that the ash content of WS samples varies from 0.7 to 2.1 wt.%, and depends on the specific grade of walnuts and its growth conditions. As can be seen from Table 3, the process of carbonization leads to increase of carbon content and reduced oxygen content therefore is a result of removing most of the volatile components of the WS. Meanwhile, the growth of burn-off results to the higher mass fraction of mineral part, to the instance the iron content in the samples of C-900 and S-900 reaches more than 1.5 wt.%. It is noted that the transition metals in composition of carbon electrodes are capable to catalyze self-discharge processes, i.e. the increased leakage currents caused by some impurities are extremely undesirable for practical application in EDLCs [11].

Fig. 3 shows the nitrogen adsorption isotherms of carbons derived on a basis of WS, meanwhile the Fig. 4 represents their pore size distribution (PSDs) determined using the (2D-NLDFT) model assuming energetical heterogeneity of carbon pores. Compare to physical activation of pre-carbonized WS, the porous structure of resulting carbons became much more developed when the WS precursor was exposed to chemical activation with phosphoric acid.

Due to the fact that 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 also to combine with organic species to form phosphate and polyphosphate bridges that connect and crosslink biopolymer fragments [13], the accelerated carbonization of WS and the development of carbons porosity at low

temperatures was observed. As an appropriate evidence, the P-350 possesses highly developed specific surface area which value was equal to $1960 \text{ m}^2 \cdot \text{g}^{-1}$.

The maximal values of specific surface area and pore volume have been experimentally identified and correspond to the activation temperature of 400°C . The BET specific surface area of chemically activated carbons gradually declines with increase in the temperature of HTT from 400°C to 700°C , accompanied by the shrinkage and reducing of the average micropores size as it shown in Table 2. Downtrend trend changes dramatically at 800°C , since at high HTT the phosphorus species could react with carbon and release gaseous elemental phosphorus while also creating porosity. It is known that this process is thermodynamically favorable at a temperatures above 700°C , and the most probable reaction of H_3PO_4 with carbon atoms proceeds as: $4\text{H}_3\text{PO}_4 + 10\text{C} \rightarrow \text{P}_4 + 10\text{CO} + 6\text{H}_2\text{O}$ [14]. As a result, the P-800 is characterized by relatively high values of specific surface area and increased volume of micropore.

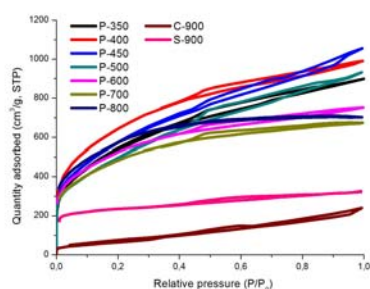


Fig. 3 – Nitrogen adsorption/desorption isotherms realized at -196°C of carbons derived from walnut shells

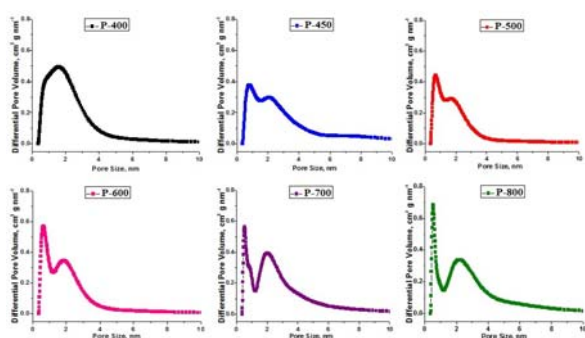


Fig. 4 – Pore size distribution (PSD) of H_3PO_4 -activated carbons activated at various temperatures.

The calculations were made by using the 2D-NLDFT model.

As it can be seen from the Table 2, the maximal values of specific surface area and pore volume have been experimentally identified in the

activation temperature range from 350°C to 450°C . This is due to the fact that acid treatment promotes dehydrogenation and accelerated carbonization at low HTT which was observed for this type of activation.

Table 2. Texture properties of walnut shell (WS) based carbons

Sample	S_{BET} [$\text{m}^2 \text{g}^{-1}$]	V_{total} [$\text{cm}^3 \text{g}^{-1}$]	V_{micro} DR [$\text{cm}^3 \text{g}^{-1}$]	Average micropores size (L_0) [nm]
C-900	246	0.335	0.221	1.41
S-900	757	0.503	0.354	1.64
P-350	1959	1.319	0.858	1.23
P-400	2289	1.460	1.035	1.15
P-450	2095	1.547	0.949	1.05
P-500	1862	1.360	0.817	1.00
P-600	1835	1.164	0.787	0.97
P-700	1697	1.041	0.754	0.94
P-800	1987	1.085	0.896	0.95

Correlation between the values of specific surface area and a specific capacitance of EDLC electrodes based on the AC obtained through carbonization, physical activation and activation of H_3PO_4 -impregnated walnut shell was observed. The carbons obtained by activation at 500°C of H_3PO_4 -impregnated WS demonstrate the presence of highly developed porosity which BET specific surface area has reached of $1860 \text{ m}^2 \text{g}^{-1}$. Owing to the highly developed meso- and microporosity, the cell assembled with P-500 exhibits the quasi perfect box-like shape of CV curve shown in Fig. 4a along with possessing good charging characteristics and nearly straight discharge curve evident from Fig. 4b. This cell displays a high reversible capacitance, which value at 200 mA g^{-1} is equal to 165 F g^{-1} .

Meanwhile, the carbonaceous materials obtained through the activation of H_3PO_4 -impregnated WS at 800°C are characterized by increased volume of micropores. Thereby the cell assembled with P-800 possesses the highest reversible capacitance, which value at 200 mA g^{-1} is equal to 190 F g^{-1} . Although the cell displays some pseudocapacitive contribution and resistive behavior which may have a negative impact on the power characteristics of EDLC, an appropriate thermal post-treatment enable to display typical electric double layer capacitance.

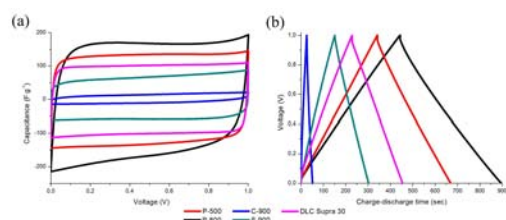


Fig. 4 – Electrochemical properties of two-electrode cells in 1 mol L⁻¹ aqueous Li₂SO₄: (a) Cyclic voltammograms at 5 mV sec⁻¹; (b) Galvanostatic charge-discharge curves at 200 mA g⁻¹ current load.

The average value of the effective series resistance corresponded to the cells assembled with WS-based carbons represented in the Nyquist plots in Fig. 5 is equal to 0.43±13 Ω. Close to similar values are due to the use of same electrolyte and cell assembly. Nyquist plots show a decrease in the relative size of semicircles from the cell with P-500, P-800, C-900 and S-900 respectively. Consequently this fact revealed that the temperature of HTT and its duration have a dominant effect on electrical resistance of carbon materials. The value of charge transfer resistance inherent to the cell assembled with S-900 is equal to less than 0.59 Ω, such value is outstanding for activated carbons, nevertheless it leveled by its moderate capacitance which value is slightly lower than that of Norit DLC Supra 30. The shift in charge transfer resistance from 4.4 to 1.6 Ω for P-500 and P-800, respectively, probably is caused by the reduction of heteroatom containing components represented by oxygenated and phosphorous surface functionalities.

From the CVs represented above it was stated that increasing of HTT leads to formation of highly capacitive electrode materials corresponded to P-800, which CV curve indicates the Faraday contributions related to the presence of some appropriate functional groups capable to redox transformations. The evidence of changes in physical and chemical composition of the carbon samples as a result of their thermal transformations was the reduction of oxygen and phosphorus, measured by energy dispersive analysis represented in Table 3 which is in Appendix. From other hand the moderate frequency region of the Nyquist plot for the cell assembled with P-500 characterized by notably narrow mass transport region, and consequently due to the most developed micro-mesoporosity, the diffusion inside the pores is more facilitated.

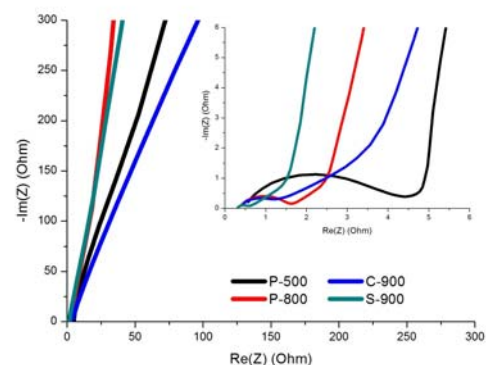


Fig. 5 – Nyquist plot for two-electrode AC/AC cells in 1 mol L⁻¹ aqueous Li₂SO₄

In general, the correlation between the specific surface area, available to nitrogen molecules at -196 °C, and the specific capacitance of two electrode cell, assembled with composite electrodes based on walnut shell activated carbons, was observed. The majority of activated carbons possessing a specific area equal to approximately 1000 m² g⁻¹ demonstrated the specific capacitance of approximately 80 F g⁻¹, estimated by the galvanostatic charge-discharge measurements of the cells assembled with 1 mol L⁻¹ Li₂SO₄ aqueous electrolyte. Under these conditions, carbons which have BET surface area exceeding 1500 m² g⁻¹ display specific capacitance values exceeding 100 F g⁻¹ such as DLC Supra 30 (Norit, S_{BET} = 2066 m² g⁻¹, V_{micro} = 1.04 cm³ g⁻¹, average micropore size L₀ = 1.16 nm) and YP 80F (Kuraray Chemicals Co, S_{BET} = 2270 m² g⁻¹, V_{micro} = 0.99 cm³ g⁻¹, average micropore size L₀ = 1.17 nm). Based on the above discussion, it can be safely stated that the highest specific capacitance values were obtained for the materials having a specific surface area of around 2000 m² g⁻¹.

4 Conclusions

The carbonaceous materials prepared through the facile and efficient processes of carbonization, physical and chemical activation of walnut shells were studied with regard to their morphology, porous structure, composition and performance in electrochemical capacitors. It was shown that the phosphoric acid activation of walnut shells produced carbonaceous materials with highly developed specific surface area and porosity. Activation of H₃PO₄-impregnated WS at 400 °C leads to formation of carbons with highest BET specific surface area equal to approximately 2300 m² g⁻¹. Further increase of the processing temperature in the range up to 700 °C resulted in the decrease of specific surface area, wherein at

800 °C the phenomenon of reformation of porous structure and increasing of microporosity was observed. This effect was accompanied with decreasing the content of heteroatom containing species in particular the reducing mass contents of phosphorus and oxygen. As a result when the carbons obtained at high temperature of HTT were implemented in supercapacitor cell the capacitance and electrical conductivity properties were increased significantly.

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Appendix

Table 3. Elemental composition of carbon materials by the energy dispersive X-ray analysis

Sample	Element composition, wt% (EDS)									
	C	O	P	Na	Mg	Al	Si	K	Ca	Fe
C-900	83.4	13.1	---	0.6	0.1	0.2	0.3	0.3	0.5	1.5
S-900	86.1	10.3	---	0.7	0.1	0.1	0.3	0.2	0.6	1.6
P-400	85.4	14.0	0.6	---	---	---	---	---	---	---
P-500	86.8	11.2	2.0	---	---	---	---	---	---	---
P-600	81.4	15.2	3.4	---	---	---	---	---	---	---
P-700	76.4	21.1	2.5	---	---	---	---	---	---	---
P-800	82.8	15.9	1.3	---	---	---	---	---	---	---