

Nanocarbon Materials of Plant Origin for Supercapacitors

V.B. Boledzyuk, Z.D. Kovalyuk, I.V. Mintianskyi, S.P. Yurtsenyuk, V.V. Shevchyk

*Frantsevich Institute for Materials Science, National Academy of Sciences of Ukraine, Chernivtsi Department,
5, I. Vilde St., 58001 Chernivtsi, Ukraine*

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For the development of supercapacitors, electrode materials with an enlarged active surface are required. This report deals with the technology for obtaining porous carbon materials (PCMs) from various types of organic matter of plant origin. The parameters of PCM depending on the modes of carbonization and activation, and the effect of the chemical modification of the source precursor were studied. Carbonization was carried out by the pyrolysis from the "pure" and pre-modified raw materials, and activation was carried out by thermo-chemical methods in various activators. The dependence of the characteristics on the pyrolysis temperature and the time of heating has been found. Modification of the raw material in the acid medium promotes the growth of the PCM capacity, and the best activator is potassium hydroxide. The porosity of PCM has been studied using nitrogen sorption. The value of the specific surface of the pores, the total volume and their high homogeneity are at the level of the best world analogues. The average pore radius is of 0.7-2.2 nm. On the basis of the obtained nanocarbon, a disk supercapacitor "2325" with an aqueous alkaline solution (30 % KOH) was developed. Material of the electrodes was made by pyrolysis of corn rutile and chemically activated in the medium of KOH. The capacity of 11-15 F, internal resistance of 0.3-0.7 Ohm, Coulomb efficiency of 98-99.5 %, initial power up to 3.5 W and energy up to 5.5 J were obtained at 1 V voltage in the element.

Keywords: Porous carbon materials, Carbonization, Plant raw materials, Supercapacitor, KOH.

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1. INTRODUCTION

Among the most important developments in capacitor design over the past decades is the promotion of the supercapacitors (SCs) almost to industrial output and their relatively wide use in technical devices [1-3]. This is, first of all, due to the creation of new technical devices, in which the use of the SCs has no alternatives [4, 5]. This leads to the intensive research in this field, although the principle of charge storage in the SCs remains the same as in the traditional capacitors – the calculation of capacity is carried out according to the known formula of a flat condenser.

In modern electrical engineering, a new type of the energy-intensive SCs – electrochemical devices, the "plates" of which are a double electric layer at the electrode electrolyte interface – finds more and more applications [6]. They have a number of valuable features, in particular, high reversibility of charge-discharge processes (cycling reaches hundreds of thousands of cycles), ability to give high power in the range of 2-20 kW/kg over short intervals of time, ability to work in a wide temperature range (– 50 ... + 60 °C), tightness, environmental friendliness, long service life, etc. The main electrode material for them is the carbon conductive materials, which actual inner surface of the pores reaches hundreds, and sometimes thousands of m²/g. Such materials are also referred to as porous carbon materials (PCMs).

The main focus of the researchers nowadays is on the superconductor electrode material and an increase in its active inner surface. Different materials are used as the electrodes, but the most common at the present time is PCM [7-9]. It is a "construction" built of the carbon atoms, forming a graphite-like structure. The difference from graphite is a considerable disorder of

atoms, both between layers and in the structure of the layer. Due to this, the carbon material has a porous structure. The volume and pore size of such a structure are determined by the size of the primary crystals, the way in which they are packaged and their mutual orientation [10]. PCMs are widely used, their industrial output reaches hundreds of thousands of tons and continuously increases due to expanding of traditional and emerging of new fields of applications. SCs have recently become such a new field of the use of PCM.

Modern methods of PCM synthesis are based on the use of the organic raw materials of natural origin, in particular, the plant raw materials and waste products of their processing, as replacement of the carbon-hydrogen raw materials for the SC electrodes. Successful attempts have been made to use the PCM electrode materials derived from fruit tree stones [11], corn groats [12], bamboo [13], bark of trees [16].

PCMs for the SC electrodes are obtained in various ways [15, 16]. In the production of activated carbon from the organic raw materials of plant origin, two stages of processing of the carbonaceous raw materials are mainly used – the stage of carbonization (pyrolysis) of the source precursor, and the stage of activation of carbonate with the oxidizing agents. These processes, as well as the natural structure of the initial components, provide the formation of the necessary structural and physicochemical properties of the final product. With the right choice of technological modes and the use of the appropriate raw material base, it is possible to obtain PCM with the required characteristics.

2. EXPERIMENTAL

Pyrolysis of all selected raw materials was carried out in the same way. The material was washed with water and dried in a drying chamber at the tempera-

ture of 105 ± 3 °C to constant weight before loading for carbonization. Then the material was loaded into an open type quartz ampoule, pre-setting the mass of the material necessary to determine the mass release factor (carbon output). The ampoule was placed in a quartz retort, which was connected to the backing pump and was pumped out to the residual pressure of 10-20 Pa. After this, the vacuumized retort was placed in a tubular electric heater, preheated to the working temperature (~ 850 °C). The retort was kept in the heater at this temperature and constant pumping for various periods of time.

The studies of the pore surface area, volume and pore size distribution for the obtained PCM samples were carried out using Autosorb Station 1 (Quantachrome Instruments, version 3.0) using adsorption-desorption of nitrogen. The installation allows automatic measurements without any interference by the operator. The calculations were carried out using the computer program NOVA Win 1.2.

3. RESULTS AND DISCUSSION

The specific capacity of the carbonized material at optimal loading of the retort almost reaches the maximum value at holding in the heater for about one hour for all studied types of the plant materials (Fig. 1). Some decrease of the specific capacitance is observed at carbonization during three hours. This is due to an increase in the degree of burning and an increase in the size of a part of the mesopores to the size of the macropores.

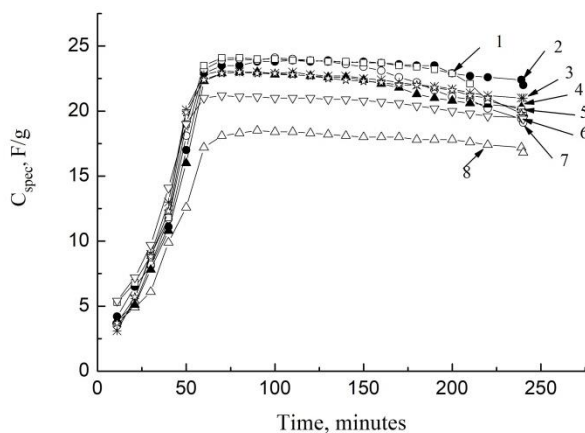


Fig. 1 – Dependence of the specific capacity of the carbonized material on the time of exposure at the working temperature. 1 – corn stigmas (CS); 2 – beech wood (BW); 3 – spruce bark (SB); 4 – flax bonfire (FB); 5 – banana skins (BS); 6 – cherry stones (ChS); 7 – orange peel (OP); 8 – sunflower bark (SfB)

One of the important criteria for the selection of the PCMs for the SC electrodes is their electrical conductivity. Moreover, it is necessary to take into account both the characteristics of the electrode material itself and the finished electrode as a whole, as it is a composition consisting of the different forms of carbon or other additives. Almost all types of carbon obtained from the organic raw materials have a high electrical resistance, which is close to the resistance of dielectrics. This is mainly due to the σ -bonds between the carbon atoms. The electrical conductivity slightly increases with in-

creasing the working temperature up to ~ 900 °C, and it changes slightly with further heating. This is due to the fact that during the carbonization process, the number of the carbon atoms in the sp^2 -hybridized state increases, while the π -bound electrons are delocalized and act as the charge carriers. In addition, the increase of the electrical conductivity can also be caused by an interaction between the microcrystals and their systems during heat treatment that is similar to the formation of a wiring network (conductive frame). The temperature region in which the increase of the electrical conductivity is slowing down coincides with the range in which the solid carbon material loses acid residues with the release of water and carbon dioxide [17].

The data on the specific pore surface area, calculated according to the different methods, for PCMs obtained from different precursors and some of PCMs subjected to further treatment are presented in Table 1. As follows, the type of the source precursor significantly affects the final characteristics of PCM. Thus, the pore surface area by the BET method for different PCM samples differs by almost an order of magnitude. The highest value 2950 m^2/g of the specific surface area by BET was obtained for precursor B (CT) with chemical activation and additional processing, while for the precursor KR (carbonization and activation technology is identical) the corresponding pore specific surface is only 409.2 m^2/g . The data on the specific volume of the pores obtained according to the calculations by different methods are presented in Table 2. The values somewhat differ due to the fact that different methods differently take into account the presence of certain pores and their configuration.

The obtained data on specific values of the surface area of the pores and their volume show a good correlation between these parameters. In Table 3 we present the average values of the pore radius calculated by different methods.

Fig. 2 shows the dependencies of the total specific volume of the pores on their radius for nitrogen adsorption, and Fig. 3 – for nitrogen desorption. The dependencies have clear maxima indicating a narrow range of the pore size distribution. This indicates also the homogeneity of the porous structure of the PCM.

At the process of thermochemical activation, we calculate the parameters of the obtained porous structure and characteristics satisfying the requirements for the SC effective operation. The method of chemical activation of carbonate with the KOH aqueous solution has been selected. In general, the method of activation of the carbon material from the vegetable raw materials is as follows:

- mixing the dried to constant weight carbonate with aqueous KOH solution in appropriate proportions;
- heating in a sealed metal container under vacuum or in a pyrolysis gas environment to the activation temperature. Free outlet of the pyrolysis gases from the container with carbonate or their constant pumping by a vacuum pump are provided during the heating;
- holding at activation temperature for a specified time. The activation temperature was varied within 600-900 °C and the holding time was 30-90 min. At this stage, the porous structure of the carbon material is formed due to the interaction of alkali with carbonate;

Table 1 – Specific pore surface area obtained by different methods (m²/G)

PCM type	Research method								
	BET Multi-point	BJH Adsorption	BJH Desorption	DH Adsorption	DH Desorption	t-met. Ext.	t-met. Micropores	DR Micropores	DFT S pores
CS	409.2	26.89	23.53	27.5	24.07	41.49	367.7	432.2	766.3
CS (MO)	282.5	22.75	13.52	23.23	13.86	54.8	227.7	333.7	354.5
E (OD)	2950.0	644.7	568.3	662.8	584.9	1699.0	1252.0	2664.0	2498.0
E	2270.0	409.1	372.0	420.3	382.1	647.6	1623.0	2102.0	2049.0
SsC	487.1	46.74	65.61	47.67	66.96	66.38	420.7	480.9	607.2
SsC (MO)	826.0	69.00	99.3	70.4	101.6	253.2	572.8	833.4	970.5
Ss (HP)	754.5	21.02	20.91	21.52	21.37	34.33	720.2	804.0	1526.0

CS – corn stigmas; CS (MO) – corn stigmas treated with microwave oven; E (OD) – elderberry treated with oxygen digestion; E – elderberry; SsC – sunflower stem, core; SsC (MO) – sunflower stem, core treated with microwave oven; Ss (HP) – sunflower stem, hard part

Table 2 – Specific volume of the pores (cm³/g)

Research method	PCM type							
	CS	CS (MO)	E (OD)	E	SsC	SsC (MO)	Ss (HP)	
Total volume of the pores with radius less than 1865.07 Å at P/P ₀ = 0.994830	0.2276	0.1674	2.238	1.621	0.3842	0.5663	0.3466	
BJH Adsorption	0.0653	0.0576	0.9991	0.6451	0.1871	0.2261	0.0546	
BJH Desorption	0.04375	0.0304	0.8778	0.5518	0.1887	0.2291	0.0483	
DH Adsorption	0.06383	0.0559	0.9754	0.6296	0.1882	0.2191	0.0533	
DH Desorption	0.0428	0.0296	0.8582	0.5390	0.1842	0.2231	0.0472	
t-met. (Micropores)	0.1540	0.0913	0.6368	0.8584	0.1857	0.2410	0.2845	
DR (Micropores)	0.1543	0.1189	0.9489	0.7487	0.1709	0.2969	0.2857	
HK (Micropores)	0.1647	0.1136	1.1430	0.9163	0.1985	0.3422	0.2924	
SF (Micropores)	0.1478	0.0994	0.7639	0.6440	0.1586	0.2779	0.2737	
DFT (pore volume)	0.2079	0.1492	1.9230	1.3990	0.3113	0.4925	0.3228	

Table 3 – Values of the pore size obtained by different methods (Å)

Research method	PCM type							
	CS	CS (MO)	E (OD)	E	SsC	SsC (MO)	Ss (HP)	
Average radius of the pores	11.12	11.85	15.17	14.28	15.78	13.71	9.188	
BJH Adsorption	15.56	21.95	15.40	15.48	15.57	15.61	15.59	
BJH Desorption	18.76	18.78	16.92	17.01	18.90	18.97	18.69	
DH Adsorption	15.56	21.95	15.40	15.48	15.57	15.61	15.59	
DH Desorption	18.76	18.78	16.92	17.01	18.90	18.97	18.69	
DR half-width of the pores	4.366	7.532	7.804	7.238	5.584	5.857	3.940	
DA	5.900	7.900	7.600	7.900	6.400	6.900	5.300	
HK	1.838	1.838	1.838	1.838	1.838	1.838	1.838	
SF	1.754	2.261	2.261	1.754	2.261	2.261	2.261	
DFT	12.17	12.17	16.02	12.59	12.17	6.392	12.17	

– washing PCM in distilled water to remove residues of chemical reagents and soluble products of chemical reactions;

– thermal vacuum drying of the activated material to remove residual water vapor.

The working models of the SC were made in a collapsible cell with a visible surface of each electrode of 2.7 cm² and the PCM weight of 0.02 g. The electrodes were made using the bulk method directly in a cell with mechanical distribution over the surface of the nickel current collector to a possibly acceptable uniformity. Two layers of BAHIT-48 material (about 48 μm thick asbestos paper for chemical current sources) were used as a separator. The characteristics of the SC were stud-

ied in the direct current charge/discharge process at the SERIES 2000 BATTERY TEST SYSTEM setting by MACCOR (USA). Determination of the discharge capacity of the SC at the discharge by direct current was carried out according to the NESSCAP methodology that is, using the discharge curve section from 0.8 U_{max} to 0.4 U_{max}, where, U_{max} is the maximum operating voltage to which SC is charged. In the case of an aqueous solution of alkaline electrolyte U_{max} = 1 V.

According to the measurements of the frequency dependence of the SC impedance by the ZSimpWin program, an equivalent circuit of a single SC element is determined (Fig. 4).

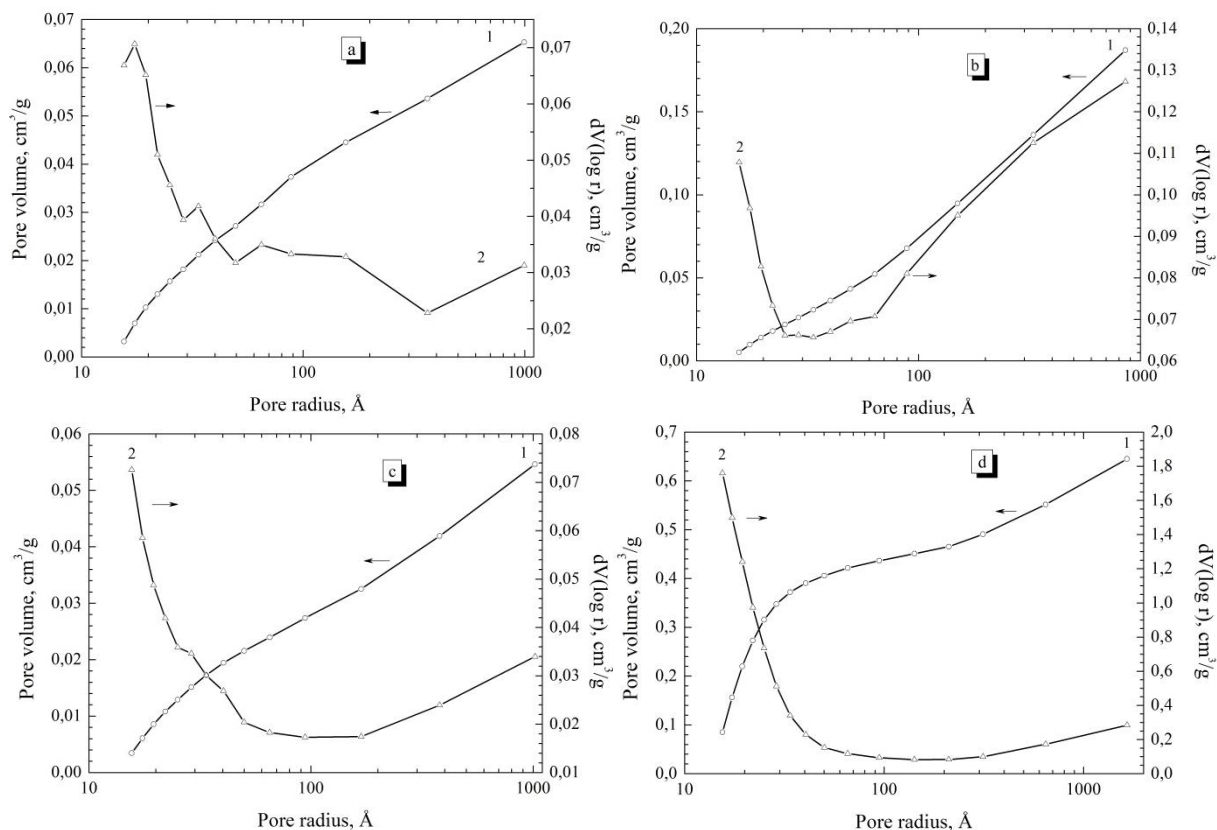


Fig. 2 – Total specific volume of the pores as a function of their radius during nitrogen adsorption for PCM obtained from different precursors (a – CS, b – SsC, c – Ss (HP), d – E)

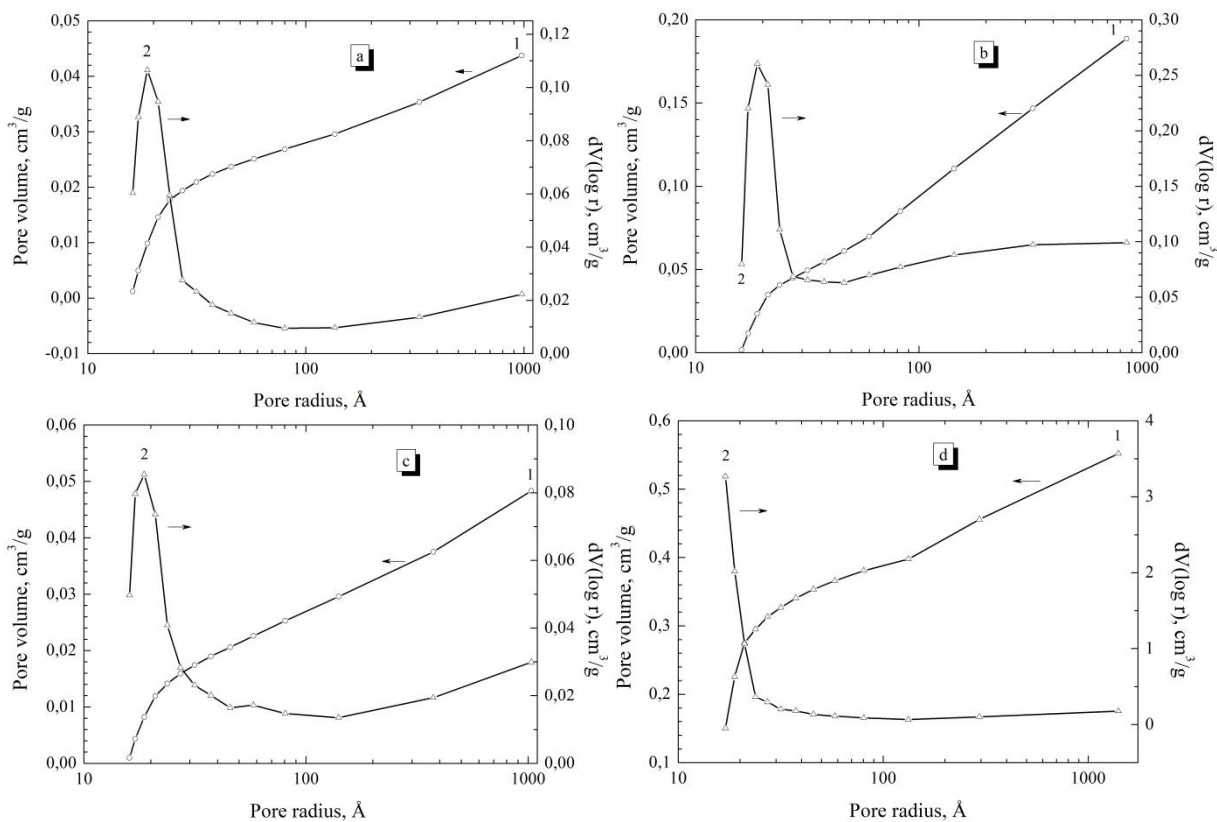


Fig. 3 – Total specific volume of the pores as a function of their radius during nitrogen desorption for PCM obtained from different precursors (a – CS, b – SsC, c – Ss (HP), d – E)

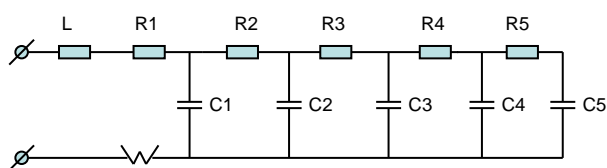


Fig. 4 – Equivalent SC circuit. Here $R_1 = 0.0053$ Ohm, $R_2 = 0.0037$ Ohm, $R_3 = 0.0012$ Ohm, $R_4 = 0.0036$ Ohm, and $R_5 = 0.5768$ Ohm are distributed equivalent resistances; $C_1 = 0.28$ F, $C_2 = 1.68$ F, $C_3 = 6.02$ F, $C_4 = 4.62$ F, $C_5 = 1.4$ F are distributed capacities; $L = 4.2 \cdot 10^{-8}$ N is SC inductance; W is the Warburg component caused by diffusion processes

4. CONCLUSIONS

The dependencies of specific characteristics of the carbon materials on the temperature of pyrolysis and time of isothermal heating are studied. Optimal values of the temperatures, time of isothermal holding at carbonization and activation are determined.

The porosity parameters of some PCM, namely specific pore surface area, specific pore volume, and pore size distribution were studied using the standard methods of nitrogen sorption. The specific surface area of the pores ($2950 \text{ m}^2/\text{g}$) and the total pore volume ($2.238 \text{ cm}^3/\text{g}$) were obtained at high pore homogeneity. It is found that the porosity of the obtained PCM is homogeneous, and

the average pore radius is $0.7\text{-}2.1 \text{ nm}$ and the majority of pores have the radius in a very narrow range.

It is found that the increase in the specific capacity of the carbon material is not proportional to the increase in the surface area of the pores determined by the BET method for adsorption of gases, in particular nitrogen. In this method, the nitrogen atoms penetrate into the smallest micropores, and the solvated ions of the electrolyte, due to its size, wettability and solvation energy do not reach the micropores surface, whose diameter is less than some critical value for a particular ion. It means that technological developments should be focused at both increase in the surface area of the pores and increase in the percentage contribution of the mesopores.

The SC with the aqueous electrolyte solution was developed using the carbon materials obtained by pyrolysis from the organic raw materials of vegetable origin. The developed SC is of symmetric type, the electrode material is nanoporous carbon obtained by pyrolysis of the vegetable raw materials and activated by chemical activation in an alkaline medium. The aqueous solution of alkali (30 % KOH) was used as the electrolyte. The studies show that chemically activated nanoporous carbon obtained by pyrolysis from various types of the vegetable raw materials can be successfully used as a highly efficient electrode material for the SC with an aqueous electrolyte solution.

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Нановуглецеві матеріали рослинного походження для суперконденсаторів

В.Б. Боледзюк, З.Д. Ковалюк, І.В. Мінтянський, С.П. Юрценюк, В.В. Шевчик

Чернівецьке відділення інституту проблем матеріалознавства імені І.М. Францевича, НАН України, вул. Ірини Вільде, 5, 58001 Чернівці, Україна

Для розробки суперконденсаторів потрібні електродні матеріали зі збільшеною активною поверхнею. Цей звіт стосується технології отримання пористих вуглецевих матеріалів (ПВМ) з різних видів органічних речовин рослинного походження. Досліджено параметри ПВМ залежно від режимів карбонізації та активації, а також вплив хімічної модифікації вихідного матеріалу. Карбонізацію здійснювали піролізом із «чистої» та попередньо модифікованої сировини, а активацію здійснювали термохімічними методами в різних активаторах. Виявлено залежність характеристик від температури піролізу та часу нагрівання. Модифікація сировини в лужному середовищі сприяє зростанню ємності ПВМ, а найкращим активатором є гідроксид калію. Пористість ПВМ вивчали за допомогою сорбції

азоту. Значення питомої поверхні пор, загальний об'єм та їх висока однорідність знаходяться на рівні кращих світових аналогів. Середній радіус пор складає 0,7-2,2 нм. На основі отриманого нановуглецю було розроблено дисковий суперконденсатор типорозміру «2325» з водним лужним розчином (30 % KOH). Матеріал електродів отримано піролізом кукурудзяного рутилу та хімічною активацією у середовищі KOH. Ємність 11-15 F, внутрішній опір 0,3-0,7 Ом, кулонівська ефективність 98-99,5 %, початкова потужність до 3,5 Вт і енергія до 5,5 Дж були отримані при напрузі 1 В на елементі.

Ключові слова: Пористий вуглецевий матеріал, Карбонізація, Рослинна сировина, Суперконденсатор, KOH.