

N.Ya. Ivanichok¹, I.M. Budzuliak¹, M.I. Moiseienko², R.P. Lisovskiy², B.I. Rachiy¹,
A.M. Gamarnyk², L.V. Turovska², S.A. Lisovska²

Electrochemical properties of nanoporous carbon materials obtained from raw materials of plant origin (hemp shives)

¹*Vasyl Stefanyk Precarpathian National University, Ivano-Frankivsk, Ukraine, bogdan_rachiy@ukr.net*

²*Ivano-Frankivsk National Medical University, Ivano-Frankivsk, Ukraine, rlisovsky@ifnmu.edu.ua*

The paper reveals the results of electrochemical studies of activated nanoporous carbon material (NPC) as an electrode material for electrochemical capacitors (EC), the charge of which is accumulated in an electrical double layer (EDL). NPC material has been obtained from raw material of plant origin (hemp shives) by thermochemical activation using phosphoric acid. It has been established that there is an optimal ratio between the amount of acid and precursor based on plant biomass that is equal to 0.75:1. The specific surface area of the obtained NPC was ~ 2000 m²/g, and the maximum specific capacitance of EC models based on them was ~ 113 F/g. At the same time, the contribution of the EDL capacitance to the total capacitance is 60 - 80 %.

Keywords: nanoporous carbon material, thermochemical activation, electrical double layer, electrochemical capacitor, specific capacitance.

Received 26.02.2020; accepted for publication 15.03.2020.

Introduction

NPC material is an important element of human life support, therefore, improving their structure, the search for the cheapest sources of raw materials and new technological solutions is an urgent task of many researches. Currently, study of activated carbon materials obtained from raw materials of plant origin (plant biomass) has gained new prospects in connection with the possibility of obtaining a carbon material with a developed nanoporous structure. Lignocellulosic materials (sawdust, nuts, fruit seeds, rice husks, etc.) are widely used as precursors and make up about 45 % of all raw materials used for the manufacture of activated carbon material with a relatively low cost of production and suitable for use in EC with EDL. The technically widespread implementation of EC is hindered by the high cost of electrode materials, which is an important factor in their demand on world markets. It is promising to use electrodes made of activated carbon material obtained from raw materials of plant origin, given their low cost, environmental safety and chemical inertness to electrolytes [1]. In this regard, important scientific and

applied research tasks are finding the relationship between the structure of the raw material of organic origin and the structural-morphological and electrically conductive properties of activated carbon materials obtained by varying the modes of thermal and chemical activation, and elucidation of the influence of the conditions of their production and morphological characteristics on capacitive parameters of electrochemical systems formed on their basis.

The research purpose is to obtain lignocellulose-based nanoporous carbon materials (from hemp shives) with the use of thermochemical activation and to study the porous structure and electrochemical characteristics of the obtained NPC for use as EC electrodes.

I. Materials and methods of research

Depending on the areas of application of NPC, the choice of raw material (RM) in many cases may be decisive for the sorption properties of the obtained carbon material, which largely depend on the structure and composition of the precursor. Providing activated

carbon with the necessary sorption properties is carried out both in the process of its production and in the process of chemical and thermal activation of the finished material [2-5].

NPC is usually obtained by carbonation of raw materials of natural or synthetic origin, followed by physical or chemical activation. Chemical activation usually occurs at temperatures of (400 - 800) °C using dehydrating agents (phosphoric acid, zinc chloride, potassium hydroxide).

Carbon material based on plant biomass of hemp shives (fraction of 0.25 - 1 mm) was obtained using thermochemical activation with phosphoric acid. Activation was carried out in the temperature range of (450 - 550) °C under an argon atmosphere. The resulting carbon material was washed with hot distilled water until a neutral pH was reached and dried at 80 °C until a constant weight was achieved. The ratio between the amount of acid and the precursor $Y = \frac{m(H_3PO_4)}{m(RM)}$ was 0.25:1; 0.5:1; 0.75:1; 1.00:1; 1.25:1; 1.5:1; 1.75:1; 2.00:1 [6].

The porous structure of the carbon material has been evaluated by nitrogen adsorption/desorption isotherms using sorptometer Quantachrome Autosorb Nova 2200e. The calculations have been performed using the Brunauer-Emmet-Teller (BET) method for specific surface area and the Density Functional Theory (DFT) for pore size distribution.

The study of the electrochemical properties of NPC materials has been carried out by the methods of galvanostatic and potentiodynamic cycling. The measurements have been performed on AUTOLAB PGSTAT12 system of ECO CHEMIE company (Netherlands) equipped with GPES program.

II. Results and discussion

Based on the sorption isotherms, the values of specific surface area (S_{BET}), specific surface area of micropores (S_{micro}) and mesopores (S_{meso}), total pore volume (V_{Σ}) and micropore volume (V_{micro}), as well as pore size distribution have been calculated [6]. Before measurements, the samples were degassed at 180 °C for 18 h. Nitrogen adsorption/desorption isotherms for the studied carbon materials obtained at a ratio of $Y = 1.00:1$ for various thermochemical carbonization temperatures are shown in Fig. 1. The curves refer to isotherms that are characteristic of multilayer adsorption in micro- and mesopores of materials of organic origin. In isotherms, a H4 type hysteresis loop (according to the IUPAC classification) is observed, which is associated with sorption processes in narrow pores. A similar picture is observed for the nitrogen adsorption isotherms for all NPC samples; however, in this case (Fig. 1), it can be said about the increase in the relative number of mesopores, which follows from the expansion of the hysteresis loop [6].

The dependence of the specific surface area S_{BET} on the ratio between the amount of acid and the precursor Y for NPC obtained under different modes of thermochemical carbonization is shown in Fig. 2. An

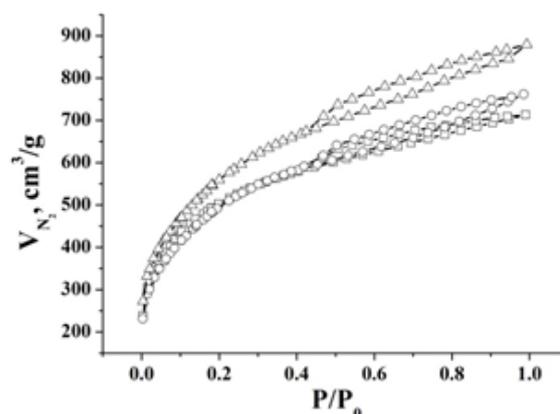


Fig. 1. Isotherms of adsorption for samples BK-100-450 (□), BK-100-500 (○), BK-100-550 (Δ) [6]

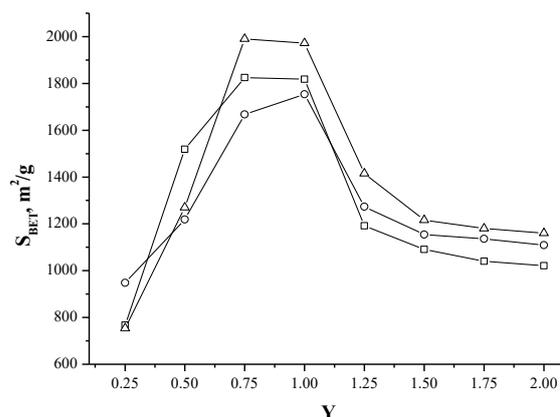


Fig. 2. The dependence of the specific surface area S_{BET} on the acid/precursor amount ratio Y for NPC materials obtained at a temperature of 450 °C (□), 500 °C (○), 550 °C (Δ).

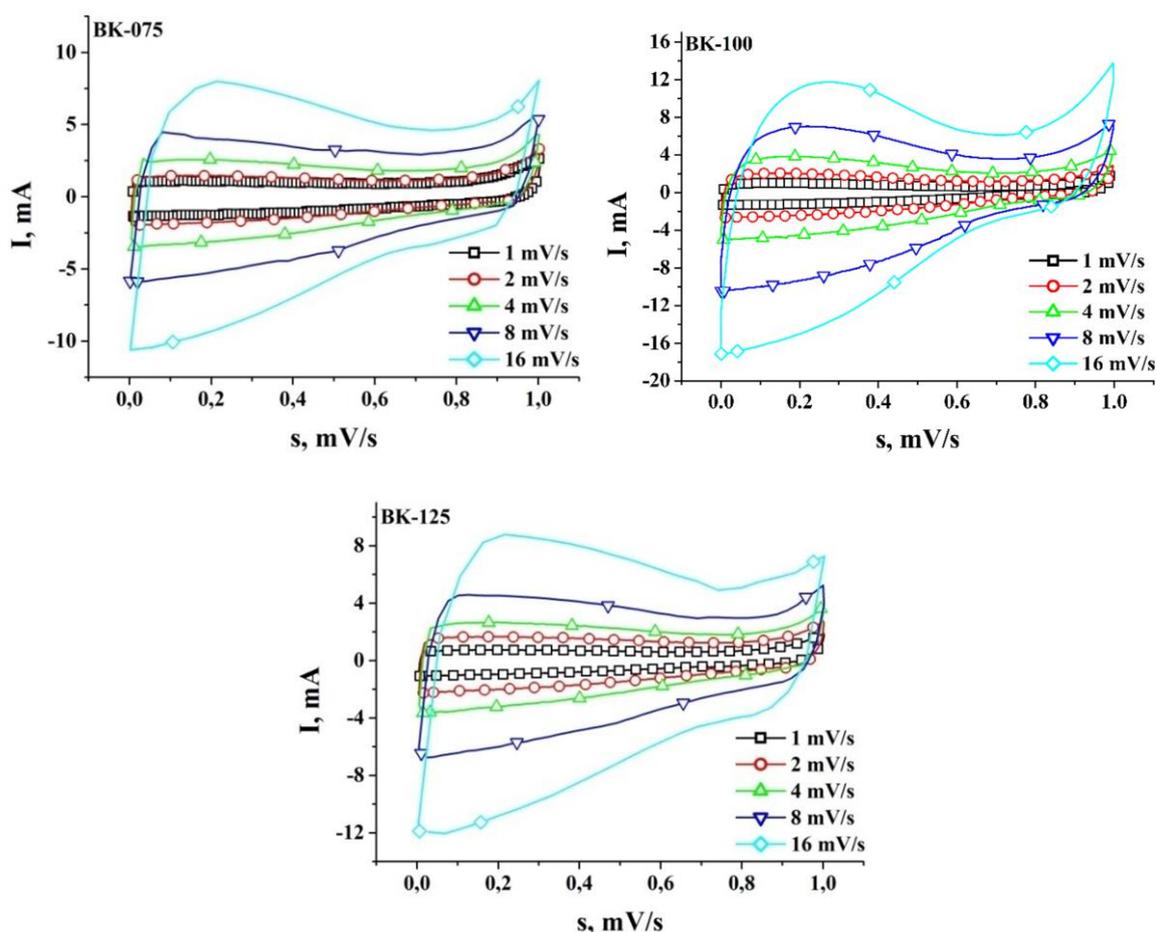
analysis of the presented dependences and the data obtained by authors of [6] suggests that for all thermally modified samples, the main contribution to the total pore volume is made by pores of < 2 nm in size. At low ratios $m(H_3PO_4)/m(RM)$, NPC materials with a microporous structure and a total pore volume of 0.9 - 1.1 cm³/g were obtained, and with a further increase up to 1.75, meso- and macropores are formed, constituting (75 - 90) % of the total pore volume. Summing up the above data, it can be said that a change in the mass ratio of activator (H_3PO_4) and plant biomass (hemp shives) allows to control the value of the specific surface area of the material (in the range of (750 - 2000) m²/g) and the pore size distribution in different percentages of their values. An analysis of the results of studies carried out using low-temperature nitrogen sorption correlates well with the data obtained by scanning electron microscopy, and indicates that at relatively low concentrations of H_3PO_4 , the NPC structure is microporous, and the material has a developed surface area. The surface of carbon particles at high concentrations of acid undergoes significant corrosion, as a result of which the volume of meso- and macropores increases [6].

In order to achieve the objectives of the study and obtain data on the relationship between the specific

Table 1

The parameters of the porous structure of the NPC material

Samples	$Y = \frac{m(H_3PO_4)}{m(BC)}$	Specific surface			V_{Σ} , cm ³ /g	V_{micro} , cm ³ /g	V_{meso} , cm ³ /g	V_{micro}/V_{Σ} , %	V_{meso}/V_{Σ} , %
		S_{BET} , m ² /g	S_{meso} , m ² /g	S_{micro} , m ² /g					
BK-025	0.25:1	754	48	706	0.318	0.294	0.024	0.925	0.076
BK-050	0.50:1	1270	181	1089	0.605	0.463	0.142	0.765	0.235
BK-075	0.75:1	1990	595	1395	1.083	0.632	0.451	0.584	0.416
BK-100	1.00:1	1972	1029	943	1.322	0.435	0.887	0.329	0.671
BK-125	1.25:1	1415	1023	392	1.182	0.187	0.995	0.158	0.842
BK-150	1.50:1	1275	923	352	1.539	0.176	1.363	0.114	0.886
BK-175	1.75:1	1216	952	264	1.602	0.132	1.47	0.082	0.918
BK-200	2.00:1	1061	729	332	1.087	0.162	0.925	0.149	0.851

**Fig. 3.** Potentiodynamic curves of electrochemical capacitors taken at different scan rates.

capacitance of NPC material and the values of the specific surface, we have studied the behaviour of the obtained materials in an aqueous KOH electrolyte. Theoretically, the larger the surface area of NPC materials, the higher the specific capacitance of the studied materials is expected. However, in practice, the situation is more complicated, and the measured specific capacitance of the material and the EC models is usually not linearly related to the specific surface area of the electrode material. One of the main reasons for this phenomenon, according to the authors of [7-9], is that the presence of a large number of small diameter nanopores is not sufficient for obtaining high capacitance values,

since they are inaccessible for the formation of EDLs by electrolyte ions with large solvates and large ions of organic electrolytes. Thus, the surface area of these nanopores does not contribute to the total capacitance of the EDL of the electrode material. A sufficient condition for the maximum specific parameters of EC models, according to the authors of [10], is the creation of conditions for the ratios of the sizes of the so-called “working” and “transport” pores.

For further electrochemical studies of the NPC/electrolyte system, we have chosen a series of samples obtained at a temperature of 550 °C, since these carbon materials had almost maximum values of the

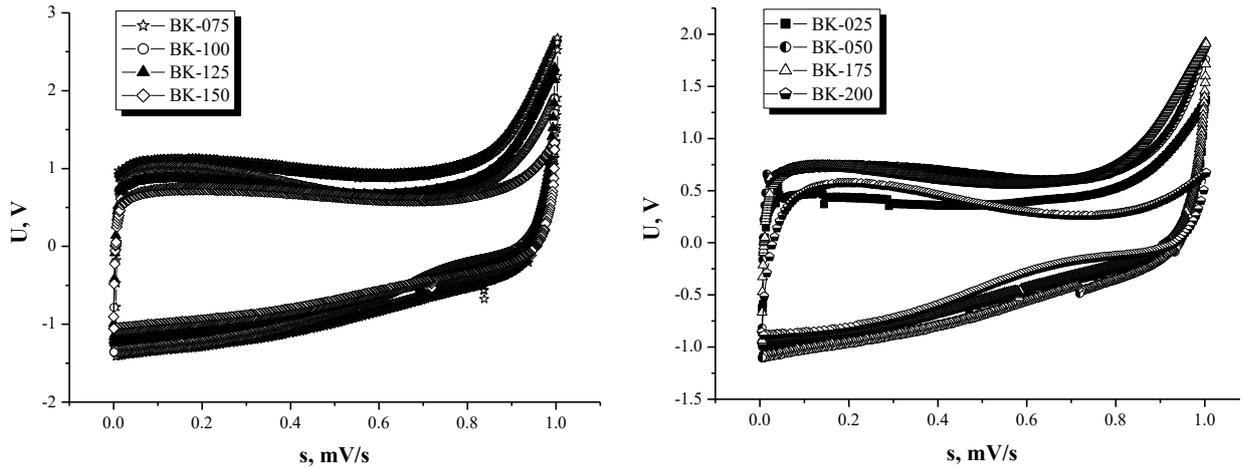


Fig. 4. Potentiodynamic curves of electrochemical capacitors taken at a scan rate of 1 mV/s.

specific surface area (Fig. 2). The parameters of the porous structure of NPC material of this system are given in Table 1. Studies have been conducted using a two-electrode cell. The “button” type electrodes were prepared by pressing into a nickel mesh a mixture of the composition: NPC (75 wt.%), conductive additive (20 wt.%) and a binder (5 wt.%). The formed electrodes were separated and placed in a cell, where they were filled with electrolyte (30 % aqueous KOH solution) and sealed.

The potentiodynamic technique (voltammetry method) is one of the classical dynamic methods for studying electrode processes in electrochemistry. This method determines the dependence of the current on the applied potential that periodically linearly varies over a certain time at a rate $s = \pm \frac{dU}{dt}$. The corresponding current of a capacitor with electric capacitance C is supplied as $I = C \frac{dU}{dt} = C \cdot s$. At low scan rates, the EC capacitance is determined by $C = I \cdot s^{-1}$ [11]. Since, as a rule, along with the EDL capacitance in the EC, there is a faraday pseudocapacitance, and the capacitance C is a function of the voltage U of the element during the charge or discharge cycle, that is, $C(U) = f(U)$ [12]. In our opinion, it is interesting to divide the total capacitance of the obtained carbon materials into the EDL capacitance and diffusion-controlled redox capacitance due to faraday reverse redox reactions, according to the methodology of the authors of [13].

The shape of the potentiodynamic curves (Fig. 3) for s obtained in the range of (1 ÷ 16) mV/s confirms the capacitive charge accumulation for the NPC/electrolyte system. We note that the potentiodynamic curves have a symmetrical shape, which indicates that the EDL charge/discharge process is quasi-reversible. In the voltammograms obtained in the voltage range of (0 - 1) V, there are no redox peaks that would indicate the absence of a pseudocapacitive accumulation of electric charge. This form of potentiodynamic curves is typical for ECs that operate on the principle of a charge/discharge of EDL.

At a scan rate of $s = 1$ mV/s (Fig. 4), the curves have a symmetrical, almost rectangular shape. This indicates

that the contribution of redox reactions to the capacitance of NPC material is insignificant, and the high specific capacitance is provided by the EDL charge [14]. The insignificant peak that is observed for all samples at potential of ≈ 1 V may indicate a possible process for OH-groups to enter the pores of the electrode material, since in this region (≈ 1 V) the material capacitance is provided mainly by negative electrolyte ions, i.e., OH-groups. The rectangular shape of the potentiodynamic curves is observed up to $s = 4$ mV/s. With a further increase in scan rate, the curves deviate from a rectangular shape.

Obtaining cyclic voltammograms (Figs. 3-4) made it possible to calculate the specific capacitance (C , F/g) of the studied carbon materials depending on the rate of change of the applied potential (s , mV/s) (Fig. 5). As can be seen from the figure, the specific capacitance of NPC material monotonically decreases with increasing scan rate. This dependence can be explained by insufficient ion mobility within certain pores. This is especially true for the surface of micro- and submicropores, which is partially accessible for electrolyte ions, and becomes less accessible with increasing scan rate ($s \geq 8$ mV/s). Accordingly, EDL within the indicated pores is not able to fully form at relatively high charge/discharge scan rates. In addition, the number of these inaccessible pores increases with increasing scan rates and, accordingly, a monotonic decrease in specific capacitance is observed.

Fig. 5 also reveals that a decrease in the specific capacitance with an increase in the scan rate is insignificant for the NCM-125-NCM-200 samples. This is probably due to the optimal ratio of micropores and transport pores, which makes free access of electrolyte ions to them and allows the use of a large specific surface area for the formation of EDL.

The data obtained by the potentiodynamic technique (Fig. 3) allowed us to calculate the total capacitance of NPC material as the sum of the capacitance of an electric double layer (C_{EDL}) and the diffusion-controlled redox capacitance due to faraday reverse redox reactions (C_F): $C = C_{EDL} + C_F$, using the method described by the authors of [13]. In the kinetic model [13], it is assumed that the scan rate affects the total specific electrochemical capacitance of the system, since the diffuse component of

the capacitance (C_F) is a function of the reaction time. Therefore, the scan rate can be considered inverse to the time of diffusion. Thus, in the case of a semi-infinite linear diffusion, the total capacitance is related to the

scan rate by the following equation: $C = C_{s \rightarrow \infty} + a \frac{1}{\sqrt{s}}$, where a is a constant value and $C_{EDL} = C_{s \rightarrow \infty}$. As follows from Fig. 6, the specific capacitance of the carbon material linearly depends on $s^{-1/2}$. Extrapolation of the

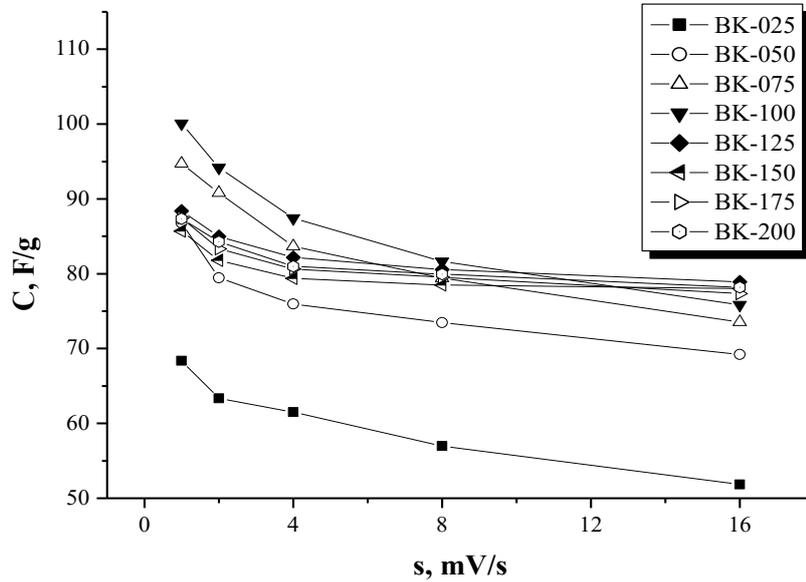


Fig. 5. Dependence of specific capacitance on scan rate for NPC material.

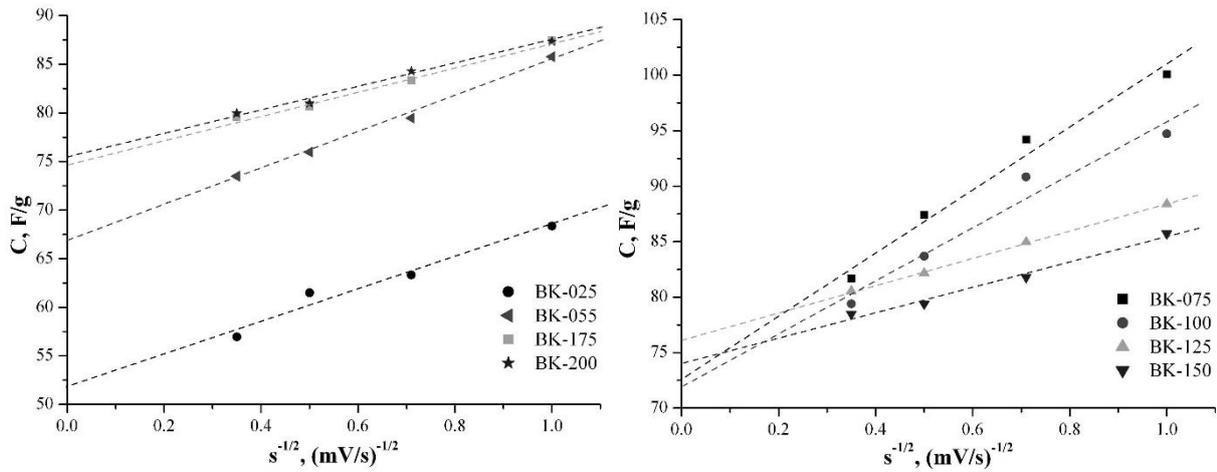


Fig. 6. Dependence of the specific capacitance C on $s^{-1/2}$.

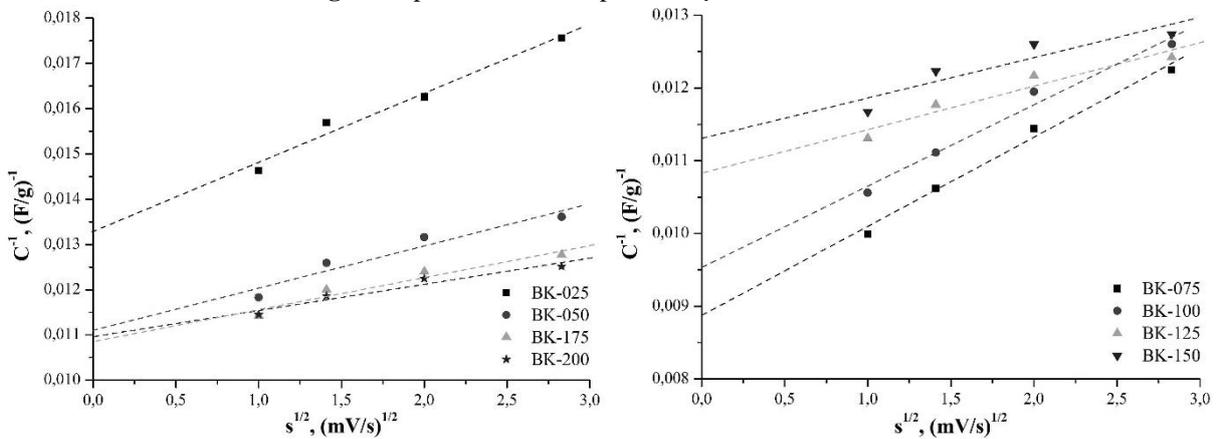


Fig. 7. Dependence of C^{-1} on $s^{1/2}$.

Table 2

Electric double layer capacitance and maximum specific capacitance of NPC material

	Samples							
	BK-025	BK-050	BK-075	BK-100	BK-125	BK-150	BK-175	BK-200
C_{EDL} , F/g	52.0	66.6	72.8	71.8	76.2	74.1	74.8	75.8
C_{max} , F/g	75.2	90.0	113.0	105.0	92.2	88.4	91.9	91.0
C_{EDL}/C_{max}	0.7	0.7	0.6	0.7	0.8	0.8	0.1	0.3

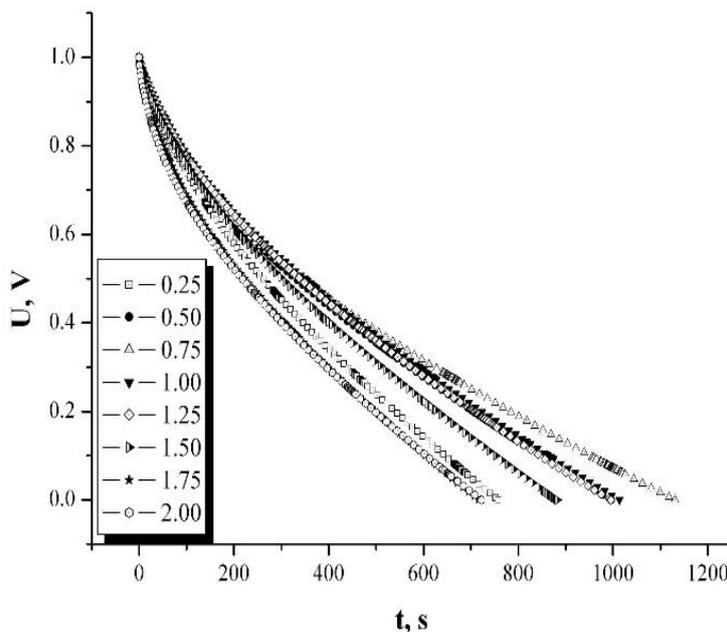


Fig. 8. The bit curves of the EC based on NPC in 33 % aqueous KOH solution and the dependence of the specific capacitance of the NPC material on the ratio between the amount of acid and precursor Y (tab).

dependences of C on $s^{-1/2}$ up to the Y axis (Fig. 6) made it possible to determine the specific capacitance of the EDL of the studied materials (Table 2).

A decrease in the scan rate leads to an increase in the specific capacitance (Fig. 3). Thus, the dependence of the specific capacitance on the scan rate can be extrapolated to the other side to $s \rightarrow 0$ using the functional dependence on s [13]. Since C grows linearly with $s^{-1/2}$, then $1/C$ should decrease linearly with decreasing $s^{1/2}$. Then, $\frac{1}{C} = \frac{1}{C_{s \rightarrow 0}} + b\sqrt{s}$, where $C_{s \rightarrow 0}$ is the maximum specific capacitance that can be reached, b is a constant value (Fig. 7).

As follows from Fig. 6, the inverse value of specific capacitance linearly depends on $s^{1/2}$. The extrapolation of the dependences of C^{-1} on $s^{1/2}$ up to the Y axis (Fig. 7) made it possible to determine the maximum specific capacitance of the studied carbon materials (Table 2).

Typical discharge curves, which are obtained at a discharge current of 1 mA by the chronoamperometric technique and characterize the capacitive behaviour of ECs formed on the basis of the obtained NPC, are shown in Fig. 8. The specific capacitance of the material under study has been calculated by the formula $C_{spec} = \frac{2 \cdot I \cdot t_{dis}}{(U_{max} - \Delta U) \cdot m}$, where I is the charge/discharge current, t_{dis} is the discharge time, U_{max} is the maximum charge potential, m – mass of the material, ΔU is voltage spike

that is related to the internal resistance, the internal resistance was determined from the voltage spike $\Delta U = 2 \cdot I \cdot R$.

Sample BK-075 shows the maximum value of the specific capacitance of NPC material that is 113 F/g, which has been calculated on the basis of the obtained discharge curves. There is no internal resistance at a charge/discharge current of 1 mA for the obtained electrochemical systems NPC/33 % aqueous KOH solution.

Conclusions

The analysis of the influence of technological conditions and modes on the morphology of carbon material from raw materials of organic origin has been performed, which suggests the prospects for its use in the latest energy-storage devices due to the controllability of the porous structure in their preparation. The relationship between structural-morphological, physicochemical and conductive characteristics of the obtained carbon materials has been found. It has been shown that in the process of obtaining carbon materials, depending on their internal structure and the choice of modification modes, it is possible to control their specific surface area (in the range of (600 - 2000) m^2/g) and pore size distribution.

The contribution of the capacitance of the electric double layer to the total capacitance of electrochemical capacitors created on the basis of the obtained carbon materials in aqueous electrolyte solutions has been divided. It has been shown that the maximum capacitance of the EDL is 83 % of the total capacitance of the models of electrochemical capacitors, and the maximum value of the total capacitance of the devices is ~ 113 F/g.

Ivanichok N.Ya. – Candidate of Physical and Mathematical Sciences, Leading Specialist of Joint Educational and Scientific Laboratory;

Budzuliak I.M. – Doctor of Physical and Mathematical Sciences, Full Professor, Professor at the Department of Material Science and New Technology;

Moiseienko M.I. – Doctor of Biological Sciences, Full Professor, Head of the Department of Medical Informatics, Medical and Biological Physics;

Lisovskiy R.P. – Doctor of Physical and Mathematical Sciences, Associate Professor at the Department of Medical Informatics, Medical and Biological Physics;

Rachiy B.I. – Doctor of Physical and Mathematical Sciences, Professor at the Department of Material Science and New Technology;

Gamarnyk A.M. – Candidate of Physical and Mathematical Sciences, Docent, Associate Professor at the Department of Medical Informatics, Medical and Biological Physics;

Turovska L.V. – Candidate of Chemical Sciences, Docent, Associate Professor at the Department of Medical Informatics, Medical and Biological Physics.

Lisovska S.A. – Lecturer at Medical College;

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Н.Я. Іванічок¹, І.М. Будзуляк¹, М.І. Мойсеєнко², Р.П. Лісовський², Б.І. Рачій¹,
А.М. Гамарник², Л.В. Туровська², С.А. Лісовська²

Електрохімічні властивості нанопористих вуглецевих матеріалів, отриманих із сировини рослинного походження (костри коноплі)

¹Прикарпатський національний університет імені Василя Стефаника, Івано-Франківськ, Україна,
bogdan_rachiy@ukr.net

²Івано-Франківський національний медичний університет, Івано-Франківськ, Україна, rlisovsky@ifnmu.edu.ua

У роботі представлені результати електрохімічних досліджень активованого нанопористого вуглецевого матеріалу (НВМ) як електродного матеріалу для електрохімічних конденсаторів (ЕК), заряд яких накопичується в подвійному електричному шарі (ПЕШ). НВМ отриманий із сировини рослинного походження (костри коноплі) шляхом її термохімічної активації з використанням ортофосфорної кислоти. Встановлено, що існує оптимальне співвідношення між кількістю кислоти та прекурсорю на основі рослинної біомаси, яке рівне 0,75:1. При цьому значення питомої площі поверхні отриманого НВМ становила ~ 2000 м²/г, а максимальна питома ємність макетів ЕК сформованих на їх основі рівна ~ 113 Ф/г. При цьому вклад ємності ПЕШ в загальну ємність становить 60 - 80 %.

Keywords: нанопористий вуглецевий матеріал, термохімічна активація, подвійний електричний шар, електрохімічний конденсатор, питома ємність.