EFFECT OF THE CARBONIZATION TEMPERATURE OF PLANT BIOMASS ON THE STRUCTURE, SURFACE CONDITION AND ELECTRICAL CONDUCTIVE PROPERTIES OF CARBON NANOPOROUS MATERIAL

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In this work, we have obtained a nanoporous carbon material (CM) from walnut shells using the method of thermal carbonization. Moreover, the influence of the carbonization temperature of the raw material on the electrical conductivity of the CM obtained by Raman, infrared (IR), and impedance spectroscopy has been investigated. Consequently, to analyze the evolution of the electrical conductivity of the material with an increase in the carbonization temperature, the theory of percolation has been applied.

Key words: carbon nanoporous material, electrical conductivity, impedance spectroscopy, Raman spectroscopy, IR spectroscopy.

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I. INTRODUCTION

The rapid growth in the consumption of fossil fuels is initiating the search for options for the use of renewable energy sources (wind power and solar energy). However, the critical dependence of the efficiency of renewable energy sources on uncontrollable factors necessitates the development of a new generation of energy storage devices [1]. Promising in this regard is the use of electrochemical capacitor (EC) technology, which is characterized by a high specific power, a fast charge / discharge process and stability during the cycling of EC [2, 3]. However, compared to lithium ion batteries, such systems have low values of specific energy, which significantly limits their use [4]. As a result, a significant amount of research focuses on the development and improvement of electrode materials for electrochemical capacitors to increase their specific capacity and energy [5, 6]. Particular attention is paid to the research on porous carbon materials that have a controlled structure and pore size distribution, a high surface area and technologically low standing. To obtain porous carbon materials, available raw materials of natural plant origin are most often used [7, 8].

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The aim of this research is to optimize the method of obtaining a nanoporous carbon material and to establish the relationship between the carbonization temperature of plant biomass (walnut shells) and the electrophysical properties of the obtained CM.

II. EXPERIMENT

The objects of this research were samples of a CM obtained by thermal carbonization in the temperature range from 400°C to 1000°C with steps of 100°C. The walnut shells were used as a raw material. The nut shells, peeled from the kernels, were poured into an autoclave and placed in a furnace, and were heated to a predetermined temperature. The heating rate was 5° C / min. Conceptually, the applied methodological approach is close to that described in work [8].

Figure 1 shows the scheme of obtaining the CM. The samples were obtained depending on the carbonization temperature, the symbols of which and the values of the bulk density d_0 of the obtained materials are given in Table 1.



Fig. 1. Schematic illustration of the synthesis of a CM from walnut shells

Sample	C1	C2	C3	C4	C5	C6	C7
Carbonization temperature, °C	400	500	600	700	800	900	1000
$d_0,{\rm g/cm^3}$	0.35	0.36	0.39	0.41	0.42	0.43	0.46

Table 1. Parameters of the investigated samples

The Raman spectroscopy was used to identify the different phases of the CM. Spectra were acquired using a Horiba Jobin-Yvon T-64000 triple spectrometer equipped with an Olympus BX41 confocal microscope. The CM samples were irradiated with an Ar^+ / Kr^+ laser (wavelength 488 nm) and recorded at room temperature in the backscattering geometry. The accuracy of determining the frequency position of the phonon line was ≤ 0.15 cm⁻¹.

The method of infrared (IR) spectroscopy was used to obtain information about the state of the surface and the presence of functional groups on the surface of the carbonized CM. The IR spectra were obtained in the transmission mode on a Thermo Nicolet Fourier spectrometer (FTIR method).

The method of impedance spectroscopy was used to establish the regularities of the change in electrical conductivity from the carbonization temperature of the obtained CM. The measurements were carried out using an AUTOLAB PGSTAT100 complex "ECO CHEMIE", (Netherlands). Measurements of the real Z' and imaginary Z'' parts of the complex resistance (Z = Z' - jZ''), where j is the imaginary unit) were carried out in the frequency range $f = 10^{-2} \dots 10^5$ Hz. The resistivity values were calculated according to the equations: $\rho^* = \rho' - j\rho''$, where $\rho' = Z' \cdot A/d$, and $\rho'' = Z'' \cdot A/d$ are the real and imaginary part of the complex resistivity based on the measured geometric parameters of the samples under research (thickness d and surface area A). The complex specific electrical conductivity was calculated according to the equation from the ratio: $\sigma^* =$ $1/\rho^* = \sigma' + j\sigma''$, where $\sigma' = \rho'/M$, $\sigma'' = \rho''/M$ are the real and imaginary parts of the complex specific electrical conductivity by parameter, $M = |Z|^2 \cdot (A/d)$. The ratio according to which the total electrical conductivity of the materials was calculated is as follows $\sigma^* =$ $[(\sigma')^2 + (\sigma'')^2]^{1/2}$ [9].

III. RESULTS AND DISCUSSION

In order to predict the prospects of using the obtained CMs as electrodes of electrochemical energy storage systems, much attention is paid to the study of structural and morphological changes that a carbon material undergoes in the process of its production, activation, or modification. A simple and accurate Raman spectroscopy (RS) method was used to identify the various phases of CM. Due to its sensitivity to changes in transsimetry, RS allows the separation of several types of carbon, such as diamond, graphite, diamond type of carbon, and carbon nitride. The Raman spectra of

nanocrystalline and amorphous carbon are dominated by peaks D (D for disordered carbon) and G (G for graphite) with different intensities, positions, and bandwidths [10-12]. The G band at about $1540 - 1600 \text{ cm}^{-1}$ corresponds to the symmetric E_{2q} mode in graphite type materials, while the D band at 1350 cm^{-1} arises from limitations in the size of the graphite domain caused by grain boundaries or defects such as N-substituted atoms sp^3 carbon or impurities. The peak D is absent from an ideal crystal graphite and appears only in the presence of a disordered structure. Thus, the G and D peaks are due only to the sp^2 positions for visible excitation. The sp^2 sites have a large cross section, so they dominate the spectra $(sp^3 \text{ are }$ imperceptible), and the resulting RS corresponds only to the configuration or content of the sp^2 site. Consequently, the spectra for amorphous carbon depend on the clustering of the sp^2 phase, the bond length, the disordering of the bond angle, the presence of an sp^2 ring or chain, and the sp^2/sp^3 ratio. The spectra directly depend on the quality or configuration of the sp^2 phase and partly on the amount of the sp^2 phase. Most often, the sp^2 configuration changes sequentially with the sp^2 fraction [13]–[15]. Figure 2 shows the RS of the CM obtained at different carbonization temperatures.



Fig. 2. The Raman spectra of the carbonated CM

The spectra are dominated by the relatively intense phonon G and D modes of the first order located at about 1350 cm^{-1} and 1600 cm^{-1} , and are characteristic of CM. A typical linear schedule of the output spectrum for the two bands (G and D) is shown in Fig. 3.

The maximum intensity of the G and D bands changes significantly with an increase in the carbonization temperature of the feedstock. Analysis of the integrated intensities of the D and G modes allows one to estimate the average size of graphite fragments along the basal plane (002) of graphite [16] as L(nm) = $(2.4 \cdot 10^{-10}) \cdot \lambda^4 \cdot (I_G/I_D)$, where $\lambda = 488$ nm is the wavelength of the laser radiation. The RS were approximated by two Lorentzians to determine the integral intensities of the D and G modes (Fig. 3). The dependence of the average size of graphite fragments on the carbonization temperature (Fig. 4) demonstrates a decrease in the average transverse particle size of graphite fragments from 9.86 nm to 8 nm during carbonization in the temperature range 400–800°C. An increase in the carbonization temperature (900°C and 1000°C) leads to the growth of graphite particles and can be explained by the process of the material sintering.



Fig. 3. Raman spectrum of the CM cut off at the temperature of carbonization of $700^{\circ}C$



Fig. 4. Dependence of the average size of graphite fragments on the carbonization temperature of the CM

The RSs obtained for the researched CMs are visually similar; therefore, their study was carried out in more detail. The RS was approximated using the Origin 6.1 program by five Lorentz contours (G, D1, D2, D3, D4) (Fig. 5), which are suitable for first-order spectra and give exact characteristics of the CM.



Fig. 5. Typical Raman spectrum and the result of its modeling for the CM obtained at a carbonization temperature of 700° C

The following bands were identified from the analysis of the obtained spectra; G ($\sim 1589 \text{ cm}^{-1}$) corresponds to an ideal graphite lattice (E2g symmetry) [17, 18]; D1 (D) $(\sim 1350 \text{ cm}^{-1})$ is a disordered graphite lattice (edges of the graphene layer, A1g symmetry) [17, 18]; D2 (~ 1605 cm^{-1}) is a disordered crystal lattice of graphite (surface layers of graphene, E2g symmetry), observed as a wing of the G mode [18]; D3 ($\sim 1500 \text{ cm}^{-1}$) is amorphous carbon [19, 20]; D4 (\sim 1200 cm⁻¹) corresponds to a disordered graphite lattice (A1g symmetry) [21], polyenes [19], ion impurities [20], etc. Using the data from the approximation of the RS, the full line width at half maximum (FWHM) and the relative and integral intensities of all curves were determined (Fig. 6). The degree of CM disordering is displayed by the width of the D and G bands at half their height. A decrease in the width of the D3 and D4 bands (Fig. 6a) indicates a decrease in the degree of disordering, which is observed for the CM carbonized in the range of 400-800°C. Therefore, carbonization at 900° C and 1000° C leads to an increase in the amount of amorphous carbon and an increase in the degree of disordering of the graphite lattice. The relationship between the half-width of the intensity curves D1 and G and the ratio of their integrated intensities I_{D1}/I_{G} indicates a decrease in both parameters. An increase in the I_{D1}/I_G value (Fig. 6b) for C1–C5 CMs probably indicates an increase in the amorphous component due to an increase in the porous structure of the CM. The decrease in the I_{D1}/I_G ratio for samples C6 and C7 is probably the result of an intense graphitization process, which is logical for higher temperatures of the carbonization process. Analyzing the data obtained, it is possible to describe the evolution of the electrophysical properties of a carbon material within the framework of the following model. Thus, the CM can be thought of as a heterophase system in which graphitized particles with relatively high conductivity are dispersed in a matrix formed by porous amorphous carbon and residues of lignin and cellulose, which are characterized by much lower conductivity values.

An increase in the carbonization temperature initiates both the burnout of a part of the amorphous component, reflected by an increase in the bulk density (Table 1), and the graphitization of the material. According to the Raman spectroscopy data, at temperatures below 1000°C, a decrease in the average size of graphite crystallites is observed. This result can be explained based on the position, in the range of 400°–900°C, the nucleation and growth of a large number of small graphite crystallites occurs throughout the entire volume of the system the material is graphitized. In this case, the dispersion of the existing crystallites cannot be expected; however, the average size value decreases. A sharp jump in linear dimensions at 1000°C corresponds to the phase of the graphitization process, in which the nucleation of new crystallites no longer occurs, but the growth of existing ones continues.



Fig. 6. The value of the full line width at half maximum FWHM (a) and the ratio of integral intensities (b) for the carbonized CM

The method of FTIR spectroscopy was used for a more detailed research on the surface state of the obtained CM, identification of functional groups present on the carbon surface. Information about the carbon groups available on the CM surface will make it possible to establish the causes of changes in the physicochemical properties of the CM. The middle infrared spectrum $(4000-400 \text{ cm}^{-1})$ can be conditionally divided into four regions: the XH stretch region $(4000-2500 \text{ cm}^{-1})$, the triple bond region $(2500-2000 \text{ cm}^{-1})$, the double bond region (2000-1500) cm^{-1}) and the area of "fingerprints" (1500-600 cm⁻¹), which is characterized by the spectrum of the molecule and can have a hundred or more absorption bands [22]. Analyzing the IR spectra for samples of carbonized CM (Fig. 7), it was determined that aromatic C-H bending peaks are observed for all samples in the range 900– 600 cm^{-1} .

For samples C1 and C3, a noticeable peak at 870 cm⁻¹ is usually associated with the symmetric deformation of the CO₃ group [23]. The presence of a peak at 1590 cm⁻¹ in the spectra (C1 and C3) is due to the stretching mode of C=C (sp^2) bonds of aromatic rings and indicates the presence of alkenes, which is accordance with the characteristic of stretching vibrations of C–H bonds in CH₂/CH₃ groups [23]. The IR spectra for samples C4 and C7 (Fig. 7) show an absorption band at 1989 cm⁻¹, which is associated with the Raman vibrational modes in the carbon structure. The bands at 2100 cm⁻¹ are due to the stretching of the C=C and C=O bonds. Stretching carbonyl is one of the simplest absorptions that can be recognized in the infrared spectrum. Usually this is an intense band in the spectrum and depending on the type of C=O bond [22].



Fig. 7. IR spectra of the CM obtained at different temperatures of carbonization

Total impedance spectroscopy is an effective method for studying the electrophysical characteristics of various materials crystalline and disordered semiconductors, heterogeneous systems and composite structures [24]. Measuring electrical conductivity at alternating current allows one to research electrochemical and electrophysical processes in ion-conducting materials, to research the features of diffusive charge transfer in disordered systems, and to determine the parameters characterizing electronic conductivity. The frequency dependences of the real and imaginary parts of the impedance for porous nanomaterials are determined by the predominant mechanism of electron transport and largely depend on their stoichiometric composition and porous structure [25]. The conductivity of such materials is determined by both the bulk characteristics of carbon nanoparticles grains (deviation from stoichiometry or the presence of dopants), the state of intergrain boundaries, and porosity of the material, and can be considered as the sum of electrical conductivities, which are characterized by different mechanisms of charge transfer [26]. According to the results of impedance spectroscopy, the carbonization temperature of the feedstock significantly affects the electrical conductive properties of the obtained carbon material, as evidenced by the change in the form of the impedance hodograph Z'' = f(Z') (Figs. 8–10) and quantitative changes in the real Z' and imaginary Z'' components of the complex resistance of the system. Consequently, as a result of the research, it was found that thermal carbonization in the temperature range of 400-1000°C leads to a change in the values of both the real and imaginary parts of the resistance.



Fig. 8. The nyquist diagrams of CM obtained at carbonization temperatures of 400–600°C (a) and the dependence of the real Z' and imaginary Z'' parts of the impedance on the frequency f of the alternating current (b)

The analysis of impedance hodographs within the framework of the equivalent circuit method allows one to separate the contributions to the conductivity from the volume of particles and intergrain boundaries. It should be noted that this problem is not simple due to the presence of many factors that can affect the conduction mechanism. Therefore, a quantitative analysis of the frequency dependence of the impedance based on the selected equivalent circuit makes it possible to interpret its elements in accordance with possible physicochemical processes in the samples when an electric current flows through them [26].

The frequency dependences of Z'(f) and Z''(f) (Fig. 8, b) have a similar form for samples C1-C3. However, the values of resistance differ by two orders of magnitude. The obtained Nyquist diagrams can be modeled using the same equivalent electrical circuit (EES) (Fig. 8, a tab). The EES used to approximate the experimental impedance spectra for carbon samples C1-C3 (inset in Fig. 8, a - C1) includes a series of lowfrequency $(R_1-CPE_1 \text{ circuit})$ and high-frequency $(R_2 CPE_2$ circuit) links, in which the resistor R and constant phase element CPE are connected in parallel. Probably the low-frequency R_1 -CPE₁ circuit corresponds to the processes of charge carrier transfer across the grain boundaries: CPE_1 is a capacitive-type constant phase element, \mathbf{R}_1 includes the resistance of the lead wires and contacts between the copper electrodes of the cell and the CM and carbon particles in the bulk of the material. This assumption is confirmed by a decrease in R_1 with an increase in the temperature of the carbonizati-

on process of the feedstock, since in the range of 400-600°C the thermal decomposition of organic feedstock does not occur to the full extent, and the resulting carbon material contains resin residues that prevent good contact between carbon particles. It was determine that probably at low carbonization temperatures ($\leq 600^{\circ}$ C) the formation of a complex carbon framework is not yet complete [27]. The high-frequency circuit R_2 -CPE₂ can correspond to the conductivity of the volume of carbon particles: CPE_2 is a capacitive type constant phase element that takes into account the porous (or fractal) structure of the carbon material, R_2 is the resistance of the carbon matrix [26]. The resistance values can be obtained from the points of intersection of the semicircle with the Z'axis, and the capacitance value from the equation for the maximum frequency value $\omega_{\rm max}\,{\rm RC}\,=\,1.$ The values of the EC parameters for all samples are given in Table 2.



Fig. 9. The nyquist diagram of the CM obtained at 700°C (a) and the dependence of the real Z' and imaginary Z'' parts of the impedance on the frequency f (b)



Fig. 10. The nyquist diagrams of the CM obtained at 800–1000°C (a) and the dependence of the real Z' and imaginary Z'' parts of the impedance on the frequency f (b)

Param	eter	C1	C2	C3	C4	C5	C6	C7
\mathbf{R}_1		$2.4\mathrm{E8}$	$2.2 \mathrm{E6}$	$4.0\mathrm{E4}$	7.474	0.085	0.075	0.036
R_2		3.8E7	$4.0 \mathrm{E5}$	3.0E3	_	—	-	—
CPE_1	А	6E-13	5E-10	1E-9	$1.35 \mathrm{E6}$	1.30 E6	1.29 E 6	1.50 E6
	n	0.8	0.7	0.73	-0.9	-0.95	-0.98	-0.91
CPE_2	А	4E-7	4E-6	5E-5	15	—	_	—
	n	1	0.6	0.4	0.2	_	_	_

Table 2. The values of parameters of the equivalent circuit elements for C1–C7 samples

The frequency dependences of the real and imaginary parts of the impedance undergo significant changes with an increase in the temperature of the carbonization process from 400 to 700° C (Fig. 8, b and Fig. 9, b). On the one hand, there is a significant decrease in the values of Z' and Z'' (more than $7 \div 9$ orders of magnitude). On the other hand, the dependences Z''(f) exhibit a "plateau" and a region of rapid decline in the value of Z' (Fig. 8, b and Fig. 9, b), which undergo displacements with an increase in the carbonization temperature from 400° C to 700° C (samples C1 and C4). Accordingly, a maximum is observed on the Z''(f) dependences, which also shifts towards high frequencies and passes into the region lying outside the measuring range. There is a transition of the value of the imaginary resistance from the negative half-plane to the positive. For the CM which was obtained at 700–1000°C, we observed the predominance of the inductive component of the system over the capacitive one in the frequency range $10^5 \div 800$ Hz (Fig. 9, b and Fig. 10, b samples C4-C7).



Fig. 11. Frequency dependence of the specific electrical conductivity of CM

The equivalent circuit used to approximate the experimental spectrum of sample C4 (Fig. 9, a tab) includes a series-connected low-frequency element of the DC phase inductive type CPE₁, resistor R_1 and highfrequency CPE₂ capacitive type. For samples C5–C7, the impedance modeling is also reduced to one scheme, but different from the EES obtained for samples C1–C3 and sample C4 (Fig. 10, a — tab). In the EES for samples C5–C7, there is no highfrequency constant phase element of the capacitive type CPE₂. The values of the EEC parameters are given in Table 2. Figure 10 b shows the low-frequency sections where the dependence of both the real and imaginary parts of the impedance on the frequency of the alternating current is not observed for samples C5–C7. An increase in the value of Z', which is accompanied by a decrease in the imaginary part of the impedance Z'', occurs in the high-frequency region $(10^3 \div 10^5 \text{ Hz})$. At the same time, the value of the apparent resistance for materials C5–C7 is unchanged and is equal to about $4.4 \cdot 10^{-5}$ Ohm in the low frequency range (Fig. 10).

The real, imaginary, and full conductivity of the CM were calculated based on the above relations. Figure 11 shows the dependence of the total conductivity σ^* on the frequency. Moreover, the figure shows that for all materials in the frequency range $10^{-3} \div 10^3$ Hz, the value of σ^* is independent of frequency. Thus, the specific conductivity of the CM increases sharply with an increase in frequency at carbonization temperatures below 700°C (Fig. 11). At the same time, its decline occurs in the frequency range $10^3 \div 10^5$ Hz at carbonization temperatures of 700-1000°C. Such frequency dependence is insufficiently studied. There are several explanations in the literature: a possible dispersion of electrical conductivity in the region $f < 10^5$ Hz due to the skin effect or under the condition $\omega \sim 1/\tau$, where τ is the relaxation time; due to the occurrence of collective excitations of the wave type of charge density in fine systems [28].

The flow of electric current in such a system can be adequately described within the framework of the percolation theory. Thus, each point of the material with a probability ψ , which will be determined by the carbonization temperature, corresponds to the conductivity of the graphite component σ_{g} , and with a probability $1-\psi$ is the conductivity of the amorphous component of $\sigma_{\rm am}$. The current flow threshold in this case will be determined by the statistical spatial distribution of the graphite component $\sigma_{\rm g}$. At small values of p, graphite clusters are isolated from each other. Therefore, due to an increase in the carbonization temperature, the probability of contact between graphite clusters increases, and at the threshold temperature $t_{\rm cr}$, the conductivity of the system sharply increases. The concept of the proposed model is close solving the problem of determining the dependence of the conductivity of the composite "carbon structures in a polymer matrix" on the concentration of the leading component [29].

In general, the conductivity of such a system is related to the percolation threshold $\theta_{\rm cr}$ (the value of the concentration of the leading component at which an infinite cluster with a conductivity is formed in the system, which is much higher than the conductivity of the matrix) and the concentration of the leading component according to the power law $\sigma = \sigma_{\rm g} (\theta - \theta_{\rm cr})^p$, where p is the critical index depending on the dimension of the system [30]. In our case, the value of θ is proportional to the carbonization temperature t, therefore, the equation is rewritten in the form $\sigma = A\sigma_{\rm g} (t - t_{\rm cr})^p$, where $t_{\rm cr}$ is the carbonization temperature at which an infinite leading cluster is formed in the system, and A is a constant. To determine the parameters of the percolation threshold and the critical index p, the procedure for constructing and linearizing the dependence is typically used $\ln(\sigma) = f(\ln[\theta - \theta_{cr}])$, which provides for the selection of the value of θ_{cr} and allows finding the parameter p as the slope of the obtained function. We propose a scheme for finding t_{cr} as the inflection point of the functional dependence of the conductivity of the carbon material on the carbonization temperature. It should be noted that the introduction of percolation conductivity in the case under study will depend not only on the carbonization temperature, but also on the frequency of the electric field applied to the material carbonized at a certain temperature. Thus, we analyzed the dependences of the total conductivity of the material on the carbonization temperature at eight selected frequencies in the range $0.01-10^5$ Hz (Fig. 12, a).



Fig. 12. Dependences of the CM conductivity (a) and the dependence of the first derivative of conductivity (b) on the carbonization temperature at the selected frequencies



Fig. 13. Frequency dependences of percolation threshold $t_{\rm cr}$ and critical index p for the CM

The inflection point was found from the position of the maximum of the dependence of the first derivative $d\sigma/dt$ as a function of the carbonization temperature with the application to this dependence of the approximation by Gaussian functions (Fig. 12, b). According to the results obtained, the value of the percolation threshold $t_{\rm cr}$ lies in the range 800–817 °C, and an increase in the frequency of the electric field causes a decrease in $t_{\rm cr}$ (Fig. 13). This dependence is expected, since the probability of electron tunneling between the particles of the leading carbon component, as one of the components of the percolation conductivity mechanism, increases with an increase in the frequency of the external field [31].

The frequency dependence of the critical index was determined based on the statement about the existence of a linear relationship between $\ln(\sigma)$ and $\ln[t - t_{\rm cr}]$ (Fig. 13). It was determined that the value of the exponent p in the investigated frequency range is close to 0.415 (only at a frequency of 0.01 Hz there is a sharp drop to 0.404). The obtained result is somewhat unexpected, since in most cases the value of p is greater than 1, but the good reproducibility of the value obtained at different frequencies allows confirming the reliability of the experimental data obtained. At the same time, according to [32], for the case of composites based on carbon nanotubes, the values of the critical index were close to 0.7.

IV. CONCLUSIONS

On the one hand, the temperature in the process of carbonization of the raw material makes an impact on the structure and condition of the surface of the obtained carbon material. On the other hand, it leads to a change in its conductive properties. It was found that in the Raman spectra for all investigated samples of CM phonon D and G bands are observed, which correspond to A1g and E2g oscillatory modes of carbon atoms with a sp^2 type of chemical bond, respectively. It was determined that the ratio of the integrated intensities I_{D1}/I_G of CM which was obtained at a temperature of \leq 700°C is two to three times lower than for the samples, whose carbonization temperature is 800–1000°C, which is also indicated by the increase in the electrical conductivity of the C5 and C7 samples. The presence of additional D3 and D4 bands in all samples of the carbon material indicates the presence of amorphous carbon and disordered graphite layers.

The model of the structure evolution with an increase in the carbonization temperature was created based on the application of the theory of percolation to the analysis of the frequency dependences of the conductivity of the obtained carbon materials. It was determined that the investigated carbon nanomaterials can be described as systems in which graphitized particles are dispersed in a dielectric matrix. At the same time, the formation of graphitization centers in the heat treatment temperature range of 400–900°C is observed by Raman spectroscopy as a decrease in the relative sizes of graphite crystallites. In this case, the percolation threshold corresponds to the carbonization temperature at which an infinite leading cluster is formed in the material, formed by contacting graphitized carbon particles. Thus, an increase in the frequency of the electric field in the range of 0.01 to 10^5 Hz causes a shift in the percolation threshold from 817 to 800°C, which suggests the presence of a mechanism for electron tunneling between graphitized particles. The calculated values of the critical percolation index are weakly dependent on frequency and lie in the range from 0.404 to 0.415.

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ВПЛИВ ТЕМПЕРАТУРИ КАРБОНІЗАЦІЇ РОСЛИННОЇ БІОМАСИ НА СТРУКТУРУ, СТАН ПОВЕРХНІ Й ЕЛЕКТРОПРОВІДНІ ВЛАСТИВОСТІ ВУГЛЕЦЕВОГО НАНОПОРИСТОГО МАТЕРІАЛУ

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Щоб спрогнозувати перспективи застосування нанопористих вуглецевих матеріалів як електродів електрохімічних систем накопичення енергії, вивчено структурно-морфологічні зміни, яких зазнає вуглецевий матеріал під час його отримання. Описано простий метод термічної карбонізації для одержання вуглецевого нанопористого матеріалу (BHM) зі шкаралупи волоських горіхів. Наведено результати дослідження впливу температури карбонізації вихідної сировини на електропровідні властивості отриманих вуглецевих матеріалів. Показано, що температура процесу карбонізації впливає не тільки на структуру та стан поверхні цього вуглецевого матеріалу, але й спричиняє зміну його електропровідності.

Методом раманівської спектроскопії досліджено фазовий склад отриманих ВНМ. Показано, що на спектрах наявні чіткі фононні D- і G-смуги для всіх зразків ВНМ, які відповідають A1g та E2g коливним модам атомів вуглецю з sp²-типом хімічного зв'язку. Також у всіх одержаних вуглецевих матеріалах наявні додаткові D3- і D4 -смуги, які вказують на наявність розупорядкованих шарів графіту та аморфного вуглецю. Підвищення температури карбонізації вихідної сировини суттєво змінює максимум інтенсивності G- і D-смуг. Аналіз інтеґральних інтенсивностей D- та G- смуг дав змогу оцінити середній розмір графітових фраґментів.

Для вивчення стану поверхні отриманих ВНМ, а саме, для ідентифікації наявних на поверхні вуглецю функціональних груп, застосовано метод інфрачервоної фур'є-спектроскопії. Інформація про наявні на поверхні ВНМ вуглецеві групи дала змогу встановити причини зміни фізико-хімічних властивостей вуглецевого матеріалу.

Досліджували електропровідні властивості ВНМ методом імпедансної спектроскопії в діапазоні частот від 10⁻² до 10⁵ Гц. Для інтерпретації спектрів імпедансу всіх зразків використовували діаграми Найквіста. Проаналізовано зміну електропровідності як функцію температури карбонізації вихідної сировини. У праці розраховано значення питомих опорів, комплексну та повну питому електропровідність матеріалів. Застосування теорії перколяції до аналізу частотних залежностей провідності отриманих вуглецевих матеріалів дозволило побудувати модель еволюції їхньої структури з підвищенням температури карбонізації.

Ключові слова: вуглецевий нанопористий матеріал, питома електропровідність, імпедансна спектроскопія, Раманівська спектроскопія, ІЧ-спектроскопія.