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**ФІЗИКА І ХІМІЯ ТВЕРДОГО ТІЛА
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Electroconductive Properties of Carbon Biocomposites Formed by the Precipitation Method

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Methods for obtaining biocomposite systems for precipitation on carbon templates of various forms of amino acids of a given composition in reaction media with subsequent drying in air have been tested. In this case, it is recorded that the morphological characteristics of biocomposites are due to the manifestation of adsorption of organic components on the surface structure of carbon templates. In particular, a decrease in the value of the specific surface area of biocomposites compared to the original templates due to the adsorbtion of the developed surface and the existing pores with aminoxylot molecules. The temperature-frequency dependences of the electrical conductivity for biocomposite systems formed by the precipitation method are obtained and the influence of the carbon template type on the changes of the electrical conductivity properties is traced.

Keywords: carbon-containing biocomposites, electrical conductivity, templates, activation energy, functional groups.

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Introduction

The use of biocomposite systems based on amino acids (aspartate, glycine, lysine) as model compounds of biopolymers of the protein series and various forms of carbon structures (nanoporous carbon, thermally expanded graphite, carbon nanotubes, graphene) opens new opportunities for improving energy performance of electrochemical systems of generation of energy [1-3.]. First of all, amino acid compounds have a set of features (biocompatibility with inorganic compounds, chemical versatility and structural diversity, selective adsorption capacity, availability of free positions for adsorption of electrolyte ions) characteristic of efficient cathode components of lithium and lithium-ion power sources [4]. Since one of the key positions of the lithium power source is the diffusion of charges into the cathode structure during charge / discharge processes, the use of such biocomposite systems based on carbon nanostructures will provide high electron-ion transport and the ability to increase specific energy. Therefore, the question of establishing the conductive characteristics of such materials is of key importance for their further use.

Literary research in this direction showed some fragmentary data, which relate mainly to the use of biocomposites in electrochemical systems, in which the role of the organic component is reduced to a template matrix, based on which the formation of 3D hierarchical structures with subsequent removal or mineralization of the template [5; 6]. In this case, the problem of aggregation and degradation of the cathode structure during charge / discharge cycling, which is characteristic of inorganic compounds, is solved [7]. Due to the biocompatibility of such composites, the controlled synthesis of ordered 3D biopolymers with the possibility of including electrochemically inorganic components is realized [4, 8]. Another promising option for the use of amino acid compounds in the biocomposite is to ensure efficient electron-ion transport during discharge through the formation of amino acid bridges of conductivity between the active component and the conductive agent [9].

On the other hand, elements of energy storage, such as supercapacitors and hybrid capacitors are based on the use of carbon materials, for which the most acute issues are structural and morphological adaptation of the material and increase the wettability of its surface by electrolyte [10, 11]. In this case, purposeful chemical modification of the surface of the material by functionalizing its surface of the active groups significantly increases the wettability and provides an increase in the amount of accumulated charge on its surface, as indicated by the authors [12, 13]. In the work [14] was showed that the modification of the carbon electrode by peptide nanotubes increases the capacitance of the supercapacitor by more than an order of magnitude.

This paper investigates the patterns of formation of biocomposites based on various forms of carbon nanostructures and amino acids as model compounds of biopolymers and establishes causal relationships between structural and morphological characteristics and surface condition and conductive properties of formed biocomposites.

I. Materials and methods

1.1. Materials

To obtain carbon-containing biocomposites on the basis of different forms of carbon nanostructures (thermo exfoliated graphite (TEG), carbon nanotubes (CNT)) and amino acids (aspartate and glycine), the method of formation of biocomposites of supercomposites was tested [1]. Experimental results demonstrate that composite systems of such type based on biopolymers and carbon structures show increased electrochemical activity when applied in electrochemical processes. Emphasis was placed on the formation of biocomposites of amino acids from TEG, as these mechanocomposites demonstrate the highest values of electrical conductivity, which is due to their electrical conductivity of TEG. The following are options for the formation of biocomposites by the method of deposition.

- to an aqueous (100 ml) solution of aspartate (1.0 g) with continuous stirring with the help of a magnetic stirrer was added TEG (0.1 g) at a temperature of 50 °C. The resulting mixture was dried in air at 50 °C until the solvent was removed and a dry residue was formed. As a result, the TEG / aspartate (precipitate) composite was obtained in a mass ratio of 1:10, respectively.

- to distilled water (100 ml) with continuous stirring with the help of a magnetic stirrer was added TEG (0.1 g) at a temperature of 50 °C for 8 hours. The resulting solution was air-dried at 50 °C until the solvent was removed and a dry residue was formed. As a result, a dispersed TEG (dispersed) was obtained.

- to an aqueous (100 ml) solution of aspartate (1.0 g) with continuous stirring with the help of a magnetic stirrer was added CNT (0.03 g) at a temperature of 8 °C. The resulting mixture was dried in air at 50 °C until the solvent was removed and a dry residue was formed. As a result, CNT / aspartate (precipitate)composite was obtained in a mass ratio of 3:100, respectively. On the basis of the comparison of structural-morphological and electrically conductive properties of the formed biocomposites, the influence of the role of the template on the manifestations of the soil was determined.

- to an aqueous (100 ml) solution of glycine (1.0 g) with continuous stirring with the help of a magnetic stirrer was added TEG (0.1 g) at a temperature of 8 °C. The resulting mixture was dried in air at 50 °C until the solvent was removed and a dry residue was formed. As a result, TEG/glycine composite was obtained in a mass ratio of 1:10, respectively (precipitate). Comparing the impedance dependences of the composition of the actual part of the electrical conductivity and the corresponding temperature dependences of the conductivity of the samples TEG/glycine (precipitate) and TEG/aspartate (precipitate), the estimation of the samples is estimated.

Additionally, TEG / aspartate (ultrasonic dispersion) biocomposite was formed by ultrasonic dispersion in an aqueous solution of the respective components.

- to an aqueous (100 ml) solution of aspartate (1.0 g) was added TEG (0.1 g) and mixed by ultrasonic disperser for 0.5 h. The resulting mixture was dried in air at 50 °C until the solvent was removed and a dry residue was formed. As a result, the TEG/aspartate composite was obtained in a mass ratio of 1:10, respectively. In this case, the method of activation during the formation of the corresponding composites and the manifestation of their electrically conductive properties was evaluated.

1.2. Metods

The morphology of the samples was studied by scanning electron microscopy (SEM) JSM- 6490 LV JEOL operated at 30 kV.

Electrical conductivity σ as a function of frequency was measured by the method of impedance spectroscopy in the frequency range of 0.01 - 100 kHz (Autolab PG-STAT 12/FRA-2 analyser); all samples were made in pellet form with the diameter of $17\cdot10^{-3}$ m and thickness of $0.1\cdot10^{-3}$ m under pressure about 33 - 35 MPa and the room temperature. The measurement of the real Z' and the imaginary Z'' of the parts of the complex resistance ($Z=Z'-jZ''$) was carried out in the frequency range $10^{-2} \div 10^{5}$ Hz. The values of the specific values of conductivity were determined from the equation:

$$\sigma = \sigma' - \sigma'', \qquad (1)$$

where $\sigma' = \frac{l}{z's}$= and $\sigma'' = \frac{l}{z''s}$ – the real and imaginary part of the complex resistivity, l i S – the thickness and surface area of the sample, respectively. The values of the total specific electrical conductivity of materials were calculated according to the formula:

$$|\sigma| = \sqrt{(\sigma')^2 + (\sigma'')^2}\,. \tag{2}$$

When calculating measurement errors, we used the scheme of calculation of errors of indirect measurements, which is given in [15].

IR spectroscopy studies were performed on a Nicolet iS10 spectrometer. Spectral range – from 4000 cm^{-1} to 650 cm^{-1} with MCT detector. Spectral resolution is 0.4 cm^{-1}.

II. Results

Fig. 1 show curves of frequency dependences of conductivity for glycine and aspartic acid. The frequency dependences of the conductivity $\sigma(\omega)$ for glycine and aspartic acid have the "classical" form of the frequency curves of the conductivity of semiconductors and superconductors [16].

The Jonesher equation is used to approximate $\sigma(\omega)$:

$$\sigma(\omega) = \sigma_{dc}\cdot[1+(\omega/\omega_h)^s], \tag{3}$$

where σ_{dc} is the conductivity in the mode of direct current, ω_h is the frequency of jumps of charge carriers, s is the exponent that characterizes the deviation of the system from the properties provided by the model ($0< s <1$).

For glycine, the frequency-independent component is $\approx 10^{-7}$ $Ohm^{-1} \cdot m^{-1}$, starting from 10^3 Hz, the conductivity is characterized by a significant dependence on frequency. In the case of aspartic acid, the value of the frequency-independent region in several orders of magnitude is poverty and corresponds to the conductivity $\approx 5\cdot 10^{-10}$ $Ohm^{-1}\cdot m^{-1}$. In this case, the frequency-dependent section of the curve $\sigma(\omega)$ starts with a frequency of 0.1 Hz. The reason for the lower conductivity for aspartic acid is probably related to the larger size of its molecule. Because the molar mass of aspartic acid is almost twice as high (M = 133.10 g/mol) as that of glycine (M = 75.07 g/mol) and in the presence of the same "active" group of NH_2 is more likely to perform percolation jumps, which leads to a decrease in the frequency of activation [17, 18].

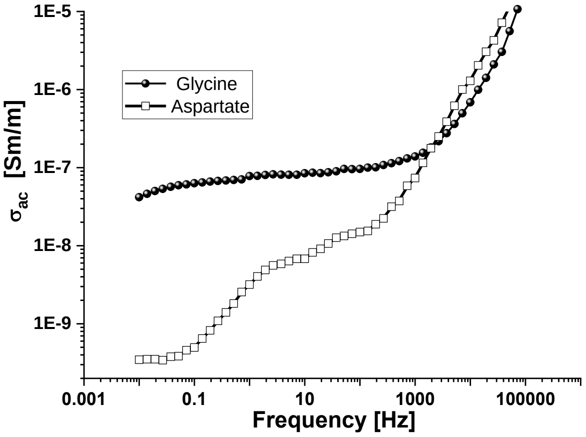

Fig. 1. Frequency dependences of conductivity $\sigma(\omega)$ for model aminoxylotes.

Fig. 2 show the frequency dependences of the conductivity of carbon templates used for the formation of biocomposites. The inserts show the frequency dependences of the imaginary component conductivities for each template.

The experimental frequency dependences of the conductivity $\sigma(\omega)$ for all types of carbon temperatures demonstrate the electronic mechanism of conductivity. For all studied carbon materials in the low-frequency range, the specific electrical conductivity practically does not change. In this frequency range, the change in resistivity may correspond to the peculiarities of the distribution of jumping barriers between the leading areas. The absence of the frequency dependence of the electrical conductivity in the range of 10^{-2} - 10^3 Hz can be explained by the formation of electrically conductive grids by carbon particles [19]. For all samples, the specific electrical conductivity decreases with increasing frequency. Such a frequency dependence is insufficiently studied. Several explanations for such behavior are possible. The occurrence of the dispersion of electrical conductivity in the region $\leq 10^5$ Hz is possible due to the dependence of the depth of penetration of the field into the sample (skin effect). Another common cause of impedance variance is

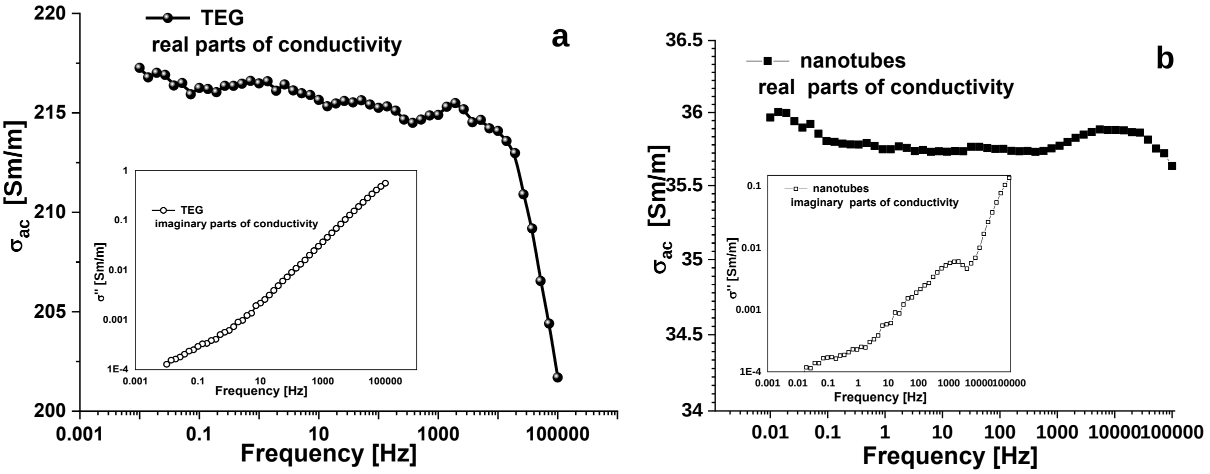

Fig. 2. Frequency dependences of conductivity $\sigma(\omega)$ for carbon templates.

the fulfillment of the condition $\omega \sim 1 / \tau$, where τ is the relaxation time. This dependence is more and more characteristic for semiconductors, for which τ can take a rather wide range of values. The high-frequency change in electrical conductivity is possible due to the occurrence of collective excitations of the wave-type charge density in fine-grained systems. In addition, the porous structure of carbon leads to the delocalization of charge carriers.

As can be seen from Fig. 2 imaginary components of conductivity for each template make an insignificant contribution to the general conductivity of the material. Basically, the conductivity of templates is determined by the contribution of the real component conductivity $\sigma_{ac}(\omega)$. Therefore, in the future, only the actual composition of conductivity will be considered for the analysis of the frequency dependences of the conductivity of biocomposites. The numerical value of the real component electrical conductivity of templates is determined by extrapolation of the frequency-independent section of the curve to its intersection with the σ' axis (at $w \rightarrow 0$ we have an output on a direct current), on the dependence of electrical conductivity on the frequency in semi-arithmetic coordinates. The highest value of frequency-independent electrical conductivity demonstrates the TEG at the level of 215.0 $\text{Ohm}^{-1} \cdot \text{m}^{-1}$. For carbon nanotubes (CNT) it is about 36.0 $\text{Ohm}^{-1} \cdot \text{m}^{-1}$. The high value of the electrical conductivity of the TEG in comparison with other carbon templates is due to the structure of the material and its activation during thermal expansion.

The difference in the values of the actual compositional electrical conductivity of the selected carbon templates is related to the morphology, chemical activity of the surface and topology. The morphology determines the contribution to the electrical resistance of the boundaries between the particles in the direction of compression and contacts with the particles of neighboring agglomerations and, consequently, electrical conductivity. The reliability of the contact depends on the surface roughness of the agglomerations. In addition, the electrical resistance is significantly affected by the porosity of the material, as the presence of pores increases the electrical resistance. Compression of the material can lead to the convergence of the opposite walls of the pores and blocking them with other particles. Finally, as already noted, in addition to the orientation of the particles and their morphology, the size of the electrically conductive particles also affects the electrical characteristics of the material.

Thermally expanded graphite, which is chemically inert, has a sufficiently high specific electrical conductivity and a good compressive ability without the use of binders. The large particle size of the TEG contributes to better electrical conductivity, since the probability of contact between graphite grains is much higher than between the particles of HB and VNT. Thus, electrical conductivity is determined by the texture of the particles, the boundaries of the division between them, their orientation to the direction of measurement, the internal resistance, and so on. The formation of conductive channels takes place mainly at the expense of closely spaced particles, mainly grains of TEG.

Thermo exfoliated graphite, which is chemically inert, has a sufficiently high specific electrical conductivity and a good compressive ability without the use of binders. The large particle size of the TEG contributes to better electrical conductivity, since the probability of contact between graphite grains is much higher than between the particles of CNT. Thus, electrical conductivity is determined by the texture of the particles, the boundaries of the division between them, their orientation to the direction of measurement, the internal resistance. The formation of conductive channels takes place mainly at the expense of closely spaced particles, mainly grains of TEG.

Figure 3 show the frequency dependences of electrical conductivity at room temperature for samples of biocomposites of TEG / aspartate (precipitate) and CNT / aspartate (precipitate). For the frequency dependences of the electrical conductivity of the TEG / aspartate, several nonlinear regions of the change of conductivity can be distinguished, which indicates the complex course of the process. There are three characteristic regions of frequency-dependent changes in conductivity. For the low-frequency range (up to 0.1 Hz) there is a sharp increase in the conductivity of the frequency, which is characteristic of the predominance of intergranular migration of the population. In the region of medium frequencies (0.1–100 Hz) there is a weakly frequency-dependent conductivity, which can be set in accordance with the electronic mechanism of intermittent charge transfer. As the frequency increases (above 10^3 Hz), there is a tendency to decrease the value of conductivity, which is characteristic of the manifestation of the skin effect. At the same time, the decrease in the relative value of conductivity in the whole frequency range for TEG / aspartate (precipitate) testifies to the increase in the contribution of the conductivity of amine ammonia. Deposition of amino acids from solution involves better adsorption of molecules to the surface with the possibility of forming stable molecular bonds. At the same time, during the drying of the biocomposite, additional deposition of amino acids from the solution takes place, which causes additional encapsulation of the surface of individual parts of the TEG and changes.

In addition, we should not reject the structural changes that occur with TEG during dispersion with the help of a magnetic stirrer in solution, which affect the manifestation of electrostatic precipitates. As can be seen for TEG (dispersed) (Fig. 3, b), a significant decrease in the value of conductivity is observed in the whole frequency range than for the original TEG. The reason for this may be related to the dispersion of TEG in the solution and the increase in the number of contacts between the individual particles, which creates additional barriers to the transfer of power. In addition, the free path of the electron is reduced in the volume of the particles. For the CNT / aspartate (precipitate) sample (Fig. 3, c), the frequency dependence of the conductivity also has a complex character due to the dominance of different mechanisms of charge transfer.

In addition, for the samples of TEG/aspartate (precipitate) and CNT/aspartate (precipitate), temperature impedance measurements were performed in the temperature range 25 – 175 °C, which allowed to determine the activation energies of charge carriers during the processes of their transport in different frequency

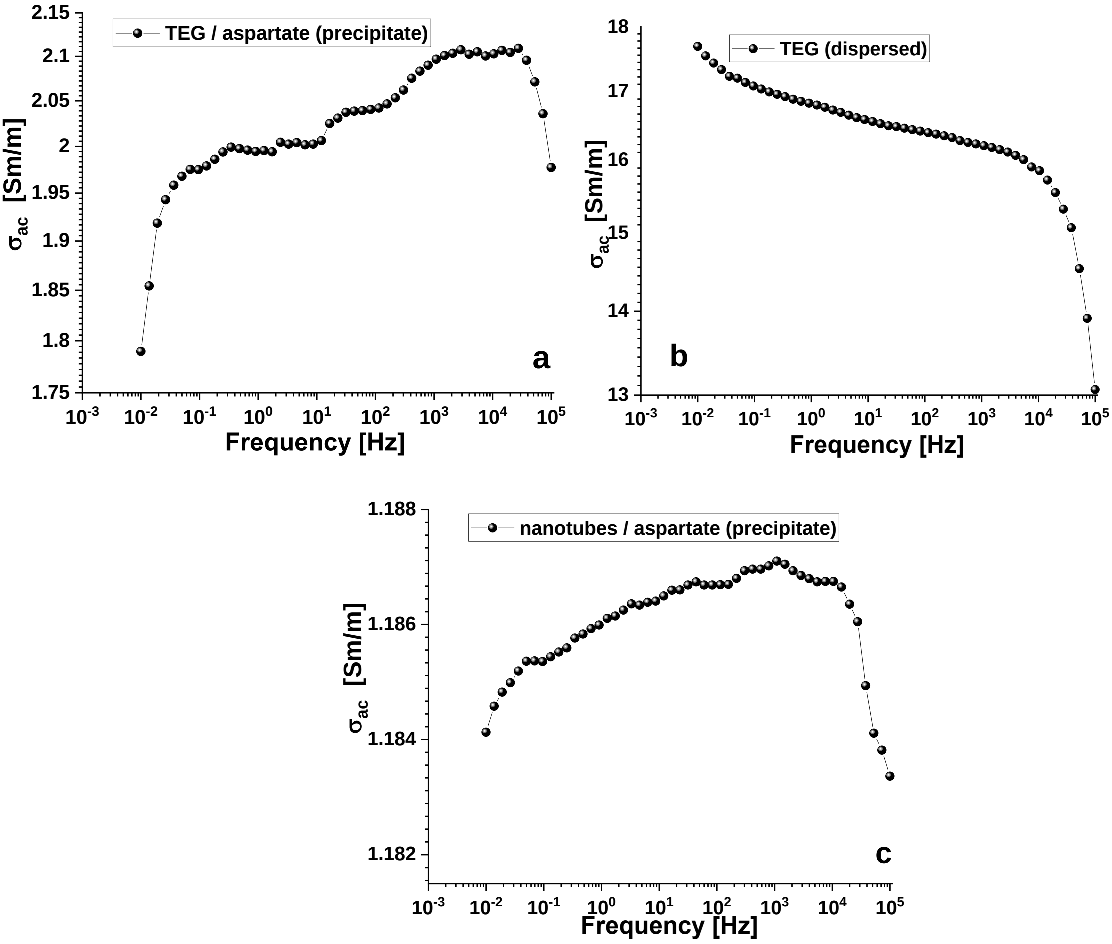

Fig. 3. Frequency dependences of conductivity σ(ω) for carbon biocomposites TEG / aspartate (precipitate) and CNT / aspartate (precipitate) and TEG (dispersed) formed by the method of application.

intervals. The corresponding temperature dependences of the electrical conductivity on the frequency in the coordinates lg σ(T) for the samples are presented in Fig. 4 a, b respectively.

As can be seen from Fig. 4, a frequency dependences of the actual component electrical conductivity at different temperatures vary in the range 1-2 $Ohm^{-1}\cdot m^{-1}$. At that, as well as at higher temperatures, a complex frequency character of the dependence of conductivity with dominance at medium and high frequencies of the electronic charge transfer mechanism is observed. It can be seen that with increasing temperature, the frequency dependence of the electrical conductivity first decreases in the range of 25 - 75 °C with the following sharp increase at a temperature of 100°C and with a subsequent decrease of 125 °C. For the TEG/aspartate (precipitate) biocomposite, the increase in temperature leads to an increase in the actual component resistance of the carbon component with electronic characteristic conductivity. This effect is the reason for the decrease in conductivity

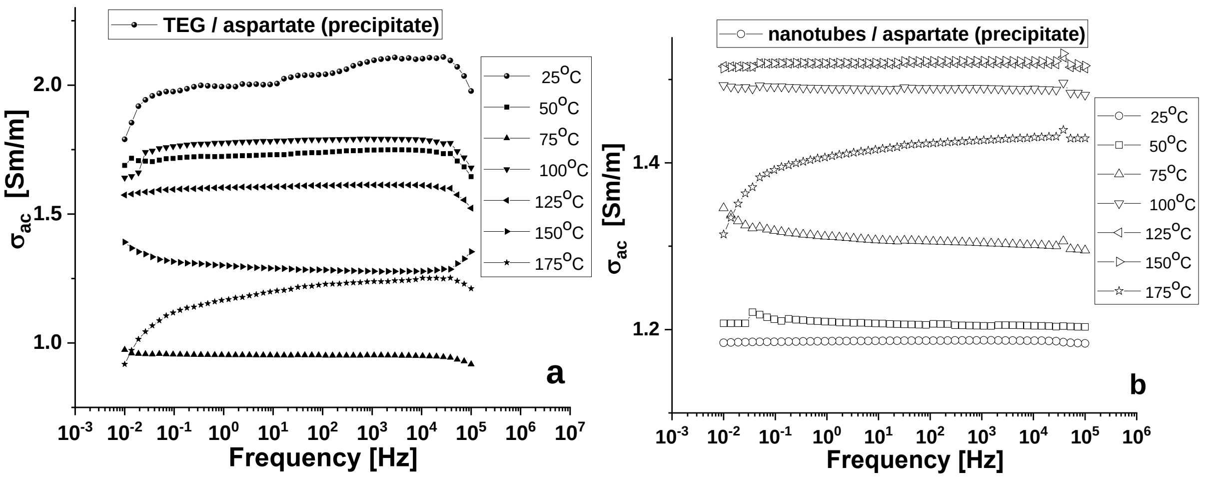

Fig. 4. Temperature dependences of conductivity σ(ω) for carbon biocomposite of TEG/aspartate (precipitate) (a) and CNT / aspartate (precipitate) (b) formed by the deposition method.

with temperature. The local increase in electrical conductivity at a temperature of 100 ºC can be caused by the removal of structurally bound water and restructuring at the expense of this biocomposite with the possibility of forming direct carbon bridges of conductivity and reducing the number of contacts between amino acids and particles of the template.

For CNT/aspartate (precipitate) (Fig. 4,b) the presented frequency dependences of electrical conductivity demonstrate an increase with increasing temperature in the range 25 - 150 ºC.

The temperature dependence of electrical conductivity can be represented by:

$$\sigma = \frac{ne^2d^2\nu}{kT} exp\left[-\frac{E_a}{kT}\right][1+(\omega/\omega_h)^s], \qquad (4)$$

where $\frac{ne^2d^2\nu}{kT}$ is the coefficient of proportionality, which is a function of the frequency of charge jumping from a distance, E_a is the activation energy for jumping conductivity, and , k is the Boltzmann constant, T is absolute temperature.

Based on the experimental data, the activation energy of CNT / aspartate (precipitate) at the level Eg = 0.037 eV was determined. The increase in conductivity with temperature can be explained by an increase in the efficiency of proton conductivity due to the hydrogen bond of sorbed water molecules on the surface of the group of composes (-OH, -COOH, C-O-C). Relatively small values of activation energy (Eg < 0.037 eV) confirm the course of proton conductivity due to the fire bonds of adsorbed water molecules.

Temperature dependences of conductivity were also performed for TEG / glycine (sediment) biocomposite. The corresponding Nyquist curves are presented in Fig. 5.

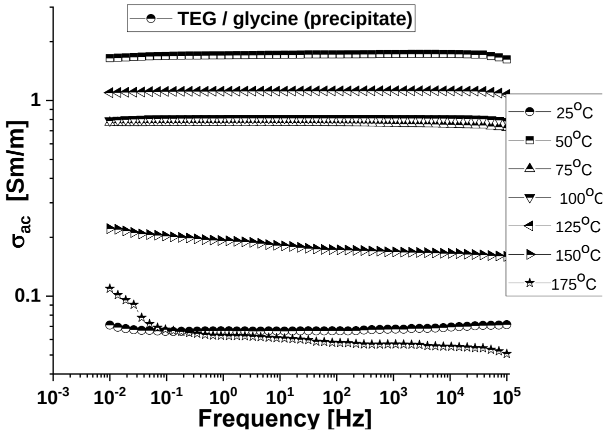

Fig. 5. Temperature dependences of conductivity σ(ω) for carbon biocomposite TEG/glycine (precipitate) formed by the deposition method.

In the case of TEG/glycine (precipitate) biocomposite, a complex character of the dependence of the conductivity on the temperature in the whole range of 25 - 175 ºC is observed, which has a value of 0.1 - 1.0 Ohm^{-1}·m^{-1}. As in the previous case, for the samples of TEG/ spartate (precipitate) and CNT/aspartate (precipitate), the competition of different mechanisms of conductivity inside and above them and on them is observed. The additional factors of influence are the desorption of structurally bound water molecules and the growth of the actual component resistance of carbon particles with increasing temperature.

For the case of formation of TEG/aspartate biocomposites by the method of ultrasonic dispersion (Fig. 6), the frequency dependences of conductivity have the form characteristic of materials. However, when considering the temperature dependences of conductivity, a clear increase in the value of conductivity with temperature is observed, which was not observed for the TEG/ aspartate (precipitate) sample.

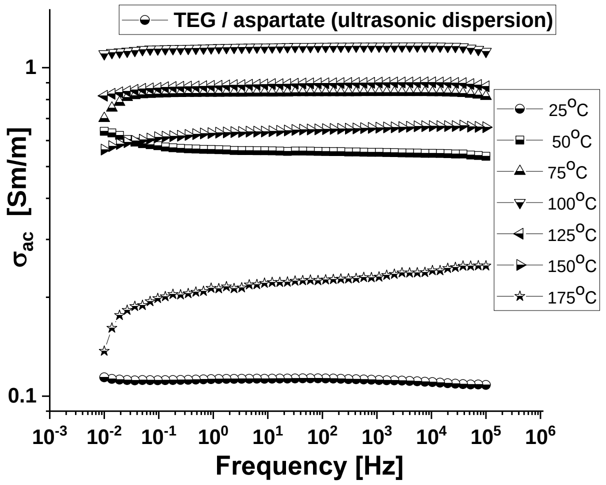

Fig. 6. Temperature dependences of conductivity σ(ω) for carbon biocomposite TEG/aspartate (ultrasonic dispersion).

For TEG/aspartate biocomposites, the components obtained by ultrasonic dispersion in an aqueous medium the nature of the frequency dependences of the electrical conductivity reflects the combination of the input in the material of two component components with different types of conductivity mechanism. Namely: electronic for the carbon temperature and semiconductor for the organic component. Moreover, the temperature dependences of conductivity are of a complex nature - at low temperatures (25-100ºC) there is a decrease in electrical conductivity in the entire frequency range. Further increase in temperature (125 - 175 ºC) leads to an increase in frequencies. This type of dependence at lower temperatures is due to the desorption of water molecules from the surface, through which the charge is transferred by the migration of the proton to the hydroxyl groups. The next increase in temperature causes the activation of electrons and their contribution to the electrical conductivity of the biocomposite. The calculated value of activation energy for the TEG/aspartate (dispersed) biocomposite is 0.170 eV.

For all biocomposites obtained by the deposition method, relatively lower values of conductivity are observed than for the case of the templates themselves. Since the conductivity of carbon templates is the dominant component of the conductivity of biocomposites. It can be assumed that in the case of deposition there is a partial elimination of percolation charge transfer between the boundaries of carbon grains due to the deposition of amino acid molecules. An additional factor may be a decrease in the size of the grains themselves, and as a result of the dissociation of the temperature in the solution, which is observed for TEG dispersed in water, and as a result, as a result.

To confirm the fact of "clogging" of the surface of the carbon template during the deposition of amino acids, structural-morphological and IR-spectroscopic studies of the formations were performed. The adsorption/desorption isotherms of the corresponding biocomposites (Fig. 7) have H4-type hysteresis according to the IUPAC classification [20].

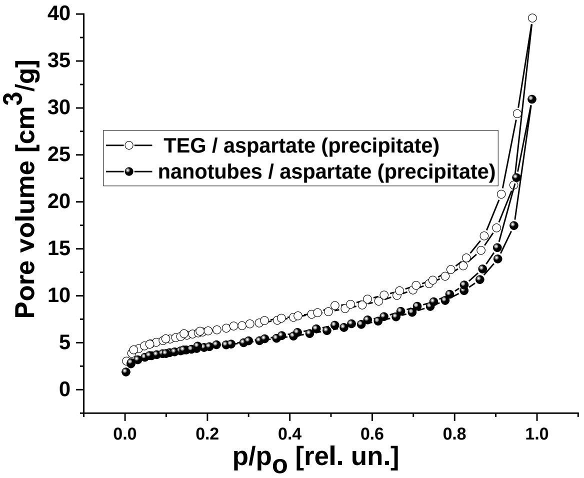

Fig. 7. Adsorption/ desorption curves for formed by the method of deposition of biocomposites TEG/aspartate and CNT/aspartate.

Characteristic of isotherms is the presence of high-pressure hysteresis, which is manifested in the divergence of adsorption and desorption branches in the region of high relative pressures. The reason for the formation of this hysteresis is related to the phenomenon of polymolecular condensation in the pores. It was established that the synthesized samples are weakly used materials. In the Table 1 presents the porosity parameters for the studied biocomposites TEG/aspartate (precipitate) and CNT/aspartate (precipitate).

Table 1

Porosity parameters for the studied samples of TEG/aspartate (sediment) and CNT/aspartate (sediment) biocomposites.

Sample	S, m^2/g	S$_{micro}$, m^2/g	V$_{micro}$, sm^3/g	d$_{pores}$, *nm*
TEG	26.0	19.3	0.103	1.90
TEG/aspartate (sediment)	18.0	16.1	0.072	1.18
CNT	145.0	100.9	0.171	3.55
CNT/aspartate (sediment)	35.0	31.7	0.090	1.11

As can be seen, the values of the specific surface areas for both composites are comparatively smaller than for the initial temperatures of TEG (30 m^2) and CNT (200 m^2), which is a confirmation of the assumption of the assumption of the space pro- There is also a significant reduction in the size and volume of existing micropores due to the adsorption of amino acid molecules on their surface.

In Fig. 8 shows the IR spectra of the starting amino acids of asparagine, glycine, TEG, as well as biocomposites formed by the method of deposition on their basis and carbon rates. As can be seen from the comparison of the spectra of the original amino acids on the biocomposites formed on their basis by the deposition method, the identity of all absorption maxima is preserved, and the absorption maxima [21].

At the same time, the maxima corresponding to the TEG can be estimated on the spectrum only qualitatively. Therefore, it can be argued that as a result of the deposition of amino acids from the solution on the surface of the carbon temperature, the processes of adsorption and condensation of the corresponding processes take place. As a result, a decrease in the size of the specific surface area of biocomposites obtained by the deposition method is observed. The decrease in the value of the electrical conductivity of the corresponding composites is due to the elimination of percolation charge transfer between the carbon grain boundaries. This is due to the deposition of amino acid molecules and the reduction of the free-charge

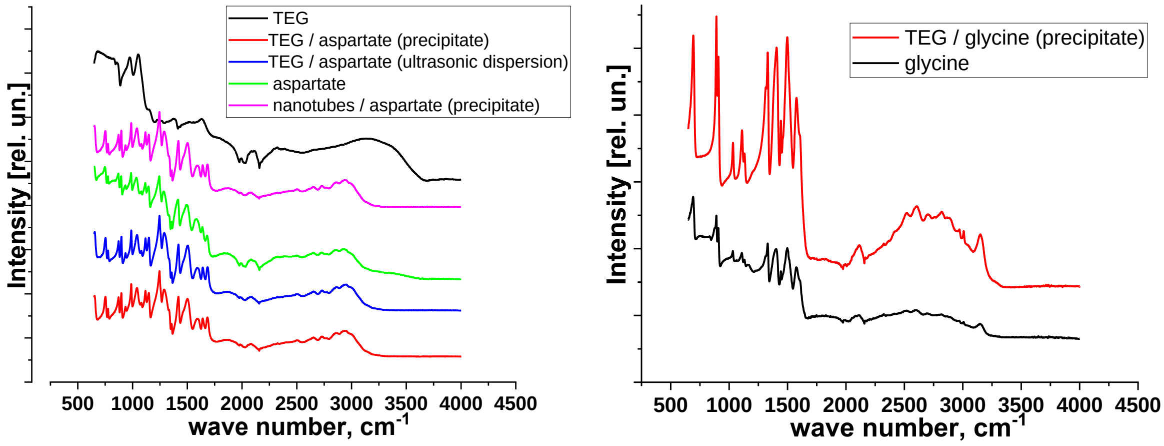

Fig. 8. IR spectra of the starting amino acids of asparagine and glycine, as well as biocomposites formed by the method of deposition on their basis and carbon temperatures.

charge length inside the carbon particles due to the reduction of their sizes.

Conclusions

The formation of carbon-containing biocomposites on the basis of various forms of carbon nanostructures has been carried out: thermo exfoliated graphite (TEG), carbon nanotubes (CNT) and amino acids of aspartate and glycine by the method of deposition on carbon of templates of different forms of amino acids of a given composition in reaction media with the following height. It is fixed that the morphological characteristics of biocomposites are caused by the manifestation of adsorption of organic components on the surface structure of carbon temperatures.

The temperature-frequency dependences of the electrical conductivity for biocomposite formed systems are obtained, and the influence of the carbon temperature type on the changes of the electrically conductive systems is observed.

It has been established that the electrical conductivity at a direct current of 1.2 $Ohm^{-1}\cdot m^{-1}$ is formed for CNT/aspartate biocomposites. Such electrical conductivity is weakly dependent on frequency. The temperature dependence of the conductivity of CNT/aspartate allowed to set the activation energy at the level of $E_g = 0.037$ eV, which indicates the predominant role of the mechanism of translucency.

For biocomposites, TEG / aspartate obtained by ultrasonic dispersion of components in an aqueous medium, the nature of the frequency dependences of the electrical conductivity reflects the combination of the inputs in the material of two component components with different types of mechanisms. Namely: electronic for the carbon temperature and semiconductor for the organic component. This type of dependence at lower temperatures is due to the desorption of water molecules from the surface, through which the charge is transferred by the migration of the proton to the hydroxyl groups. The next increase in temperature causes the activation of electrons and their contribution to the electrical conductivity of the biocomposite. For the TEG / aspartate biocomposite, the calculated value of activation energy will be 0.170 eV.

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[1] V. Moklyak, A. Hrubiak, Z. Gogitidze, Y. Yavorskyi, Biopolimer Peptide Batteries—A New Concept for Environmentally Friendly and Safer Energy Storage, Batteries 7(3), 50 (2021); https://doi.org/10.3390/batteries7030050.

[2] G. Rosenman, P. Beker, I. Koren, M. Yevnin, B. Bank-Srour, E. Mishina, S. Semin, Bioinspired peptide nanotubes: deposition technology, basic physics and nanotechnology applications, J. Pept. Sci. 17, 75 (2010); https://doi.org/10.1002/psc.1326.

[3] J. Bitenc, K. Pirnat, G. Mali, B. Novosel, A.R. Vitanova, R. Dominko, Poly(hydroquinoyl-benzoquinonyl sulfide) as an active material in Mg and Li organic batteries , Electrochem. Commun. 69, 1 (2016); https://doi.org/10.1016/j.elecom.2016.05.009.

[4] J. Ryu, S.-W. Kim, K. Kang, C.B. Park, Synthesis of diphenylalanine/cobalt oxide hybrid nanowires and their application to energy storage, ACS Nano 4, 159 (2009); https://doi.org/10.1021/nn901156w.

[5] Nam Ki Tae, P. Yoo, N. Chungyi Chiang, P. Meethong, Y. Hammond, A. Chiang, Belcher, High rate capabilities Fe3O4-based Cu nano-architectured electrodes for lithium-ion battery applications, Science 312(5775), 885 (2006); https://doi.org/10.1126/science.1122716.

[6] Ryu Jungki, Sung-Wook Kim, Kisuk Kang, Chan Beum Park, Mineralization of self-assembled peptide nanofibers for rechargeable lithium ion batteries, Adv. Mater. 22(48), 5537 (2010); https://doi.org/10.1002/adma.201000669.

[7] V.I. Mandzyuk, N.I. Nagirna, & R.P. Lisovskyy, Morphology and Electrochemical Properties of Thermal Modified Nanoporous Carbon as Electrode of Lithium Power Sources, Journal of Nano-& Electronic Physics 6(1), (2014).

[8] V.O. Kotsyubynsky, A.B., Grubiak, V.V. Moklyak, V.M. Pylypiv, & R.P. Lisovsky, Structural, morphological, and magnetic properties of the mesoporous maghemite synthesized by a citrate method, Metallofiz. Noveishie Tekhnol 36, 1497 (2016).

[9] Lee Yun Jung & Angela M. Belcher, Nanostructure design of amorphous FePO 4 facilitated by a virus for 3 V lithium ion battery cathodes, J. Mater. Chemistry 21(4), 1033 (2011); https://doi.org/10.1039/C0JM02544E.

[10] Koveria, A., Kieush, L., Hrubiak, A. B., Kotsyubynsky, V. O. Properties of Donetsk basin hard coals and the products of their heat treatment revealed via Mossbauer spectroscopy, Petroleum and Coal 61(1), 160 (2019).

[11] Hemiy, O. M., Yablon, L. S., Budzulyak, I. M., Budzulyak, S. I., Morushko, O. V., & Kachmar, A. I., Electrochemical properties of nanocomposite nanoporous carbon / nickel hydroxide, Journal of Nano-& Electronic Physics 8(4), 04074, (2016); https://doi.org/10.21272/jnep.8(4(2)).04074.

[12] P. Beker, I. Koren, N. Amdursky, E. Gazit, & G. Rosenman, Bioinspired peptide nanotubes as supercapacitor electrodes, Journal of Materials Science 45(23), 6374 (2010); https://doi.org/10.1007/s10853-010-4624-z.
[13] V.O. Kotsyubynsky, I.F. Myronyuk, V.L. Chelyadyn, A.B. Hrubiak, V.V. Moklyak, & S.V. Fedorchenko, The effect of sulphate anions on the ultrafine titania nucleation, Nanoscale Research Letters 12(1), 1 (2017); https://doi.org/10.1186/s11671-017-2144-3.
[14] L. Adler-Abramovich, D. Aronov, P. Beker, M. Yevnin, S. Stempler, L. Buzhansky, E. Gazit, Vapor-deposited self-assembled peptide nano-array for energy storage and microfluidics devices, Nature nanotechnology 4(12), 849 (2009); https://doi.org/10.1038/nnano.2009.298.
[15] V.I. Nefedov, V.I. Khakhin, V.K. Bityukov, Metrology and radio measurements: a textbook for universities (Higher school, Moscow, 2003).
[16] A.B. Hrubiak, V.O. Kotsyubynsky, V.V. Moklyak, B.K. Ostafiychuk, P.I. Kolkovsky, S.V. Fedorchenko, & B.I. Rachiy, The electrical conductivity and photocatalytic activity of ultrafine iron hydroxide/oxide systems, Molecular Crystals and Liquid Crystals 670, 97 (2018); https://doi.org/10.1080/15421406.2018.1542070.
[17] M. V. Muftakhov, & P.V. Shchukin, Destruction of peptides and nucleosides in reactions with low energy electrons, Journal of Technical Physics 88(5), 770 (2018); https://doi.org/10.21883/JTF.2018.05.45907.2425.
[18] A.S. Karnup, V.N. Uversky, & N. Medvedkin, Synthetic polyamino acids and polypeptides. N-carboxyanhydride method, Bioorganic Chemistry 22(8), 563 (1996).
[19] M. Lebovka, A. Gohakhakak, Yu. Boyko, L. Lisetsky, G. Puchkvska, T. Gaverlko, M. Drazd, Ryky Crystal. Nanosi, nanotechnology, 2009.
[20] E. Fitzer, K.H. Kochling, H.PBoehm, & H. Marsh, Recommended terminology for the description of carbon as a solid, Pure and Applied Chemistry 67(3), 473 (1995).
[21] G.B. Chernobay, Yu.A. Chesalov, E.B. Burgina, T.N. Drebuschak, E.V. Boldfeva, Temperature effects on the IR spectra of crystalliine amino acids, dipeptides, and polyamino acids. I. Glycine, Journal of Structural Chemistry 48(2), 339 (2007).

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У цій роботі апробовано способи отримання біокомпозитних систем методом осадження на вуглецеві темплати різних форм амінокислот заданого складу в реакційних середовищах з наступним висушуванням на повітрі. Зафіксовано, що морфологічні характеристики біокомпозитів обумовлені проявом адсорбції органічних компонент на поверхневу структуру вуглецевих темплатів. Зокрема, встановлено зменшення величини питомої площі поверхні біокомпозитів, в порівнянні із вихідними темплатами за рахунок заповнення розвиненої поверхні та наявних пор молекулами аміноксилот. Отримано температурно-частотні залежності електропровідності для біокомпозитних систем сформованих методом осадження та простежено вплив типу вуглецевого темплату на зміни електропровідних властивостей.

Ключові слова: вуглецеві біокомпозити, електропровідність, темплат, енергія активації, функціональні групи.