STRUCTURAL, CONDUCTIVE, AND ELECTROCHEMICAL PROPERTIES OF CARBON-BASED BIO-COMPOSITES FORMED BY MECHANO-SYNTHESIS

Andrii Hrubiak[1*], Asfaw Beyene[2], Yurii Yavorskyi[3], Bogdan Ostafiychuk[1]

[1]G.V. Kurdyumova Institute of Metal Physics of National Academy of Sciences of Ukraine, 03142 Kyiv, Ukraine

[2]San Diego State University, Department of Mechanical Engineering, 5500 Campanile Drive, CA 92182, San Diego, USA

[3]National Technical University of Ukraine "Igor Sikorsky Kiev Polytechnic Institute", 03056 Kyiv, Ukraine

*Corresponding Author: hrubiak0andrii@gmail.com

ABSTRACT

The electrochemical property in KOH electrolyte of nanostructured mechanocomposites based on thermally expanded graphite (TEG) and carbon nanotubes (CNTs) and amino acids, like aspartate (As) and glycine (Gl) were studied. It was determined that the type of carbon template and the structural organization of the bio-composite play major roles in the electrochemical activity of the prototype material. Compaction of the nanotube structure during mechanical processing of biocomposites leads to partial encapsulation of amino acids, while in the case of graphite encapsulation is not observed and surface-localized aggregates of amino acids are placed heterogeneously and in large clusters. The mechanism of electrochemical activity of mechano-composites is related to the fact that the main role in the processes of capacitive accumulation is played by reactions with the participation of amino acids, and the carbon template mainly plays the role of a conducting agent with the participation of which bridges of electronic conductivity of the bio-composite are formed. This can be observed for CNT-based bio-composites, where the electrochemical activity achieved by pseudocapacitance is due to its structural organization, namely, the uniform wrapping of nanotube aggregates with amino acid particles. The specific discharge capacity during 100 cycles decreases from 18 to 15 F/g, while the Coulombic efficiency decreases from 96% for the 1st cycle to 91% for the 100th cycle. Significant dispersion of the template is observed in bio-composites based on TEG, which leads to the formation of a mixture of carbon and amino acid particles that do not have stable conductive bridges. The best electrochemical activity is demonstrated by the As-TEG bio-composite, for which, when discharged with a specific current of 30mA/g to -1.2V, the discharge capacity was registered as 32F/g remaining constant for 100 cycles.

1 INTRODUCTION

Organic materials derived from proteins are increasingly finding direct applications in technologies aimed at enhancing the performance of electrochemical energy storage and conversion systems (Wang *et al*., 2020; Nguyen *et al*., 2021; Ju *et al*., 2022; Nie *et al*., 2019; Moklyak *et al*., 2021). This trend is attributed to the unique properties of protein molecules, enabling its use as fundamental building block for the development of novel materials that can modify electrodes, electrolytes, and other components within batteries (Wu *et al*., 2023). These materials have exhibited intriguing characteristics in addressing diverse engineering challenges across various battery types, including electronic/ionic conductivity (Zhang *et al*., 2018; Fu *et al*., 2016; Zhao *et al*., 2020), antioxidation capability (Zhang *et al*., 2022), affinity to electrodes (Wu *et al*., 2019), and self-assembly behavior (Hu *et al*., 2018a; Hu *et al*., 2019).

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Currently, organic materials derived from proteins represent one of the most promising classes of organic template structures for crafting 3D hierarchical nanostructures (Rosenman *et al*., 2011; Bhattacharya *et al*., 2014). However, the investigation into the electrochemical activity of organic materials, specifically bio-composites, remains an open question, especially for direct application in electrochemical systems such as supercapacitors and power sources. Additionally, there is a scarcity of information regarding the electrochemical activity of the biopolymer compounds themselves. Despite their notable and distinctive properties, the potential attractiveness of these materials as active components for electrochemical energy converters is not fully understood (Nguyen *et al*., 2021; Liu *et al*., 2021; Sarmadi *et al*., 2022). Only a limited number of works in this direction are known (Nguyen *et al*., 2021; Moklyak *et al*., 2021; Jungki *et al*., 2009; Wang *et al*., 2020), and the conclusions drawn from these works regarding the electrochemical activity of amino acids and it composites are ambiguous. The primary challenges faced by scientists by necessity revolve around increasing the electrical conductivity of electrochemically active biopolymers and preventing their dissolution in electrolytes (Wu *et al*., 2023).

We attempt to address the lags in understanding properties of these interesting materials by employing bio-composite materials based on electrochemically active organic polymers and carbon structures with various modifications. The inherent mechanism of self-assembly and self-organization found in the formation of bio-composite systems containing organic components is key to understanding their unique properties which results in the creation of a new class of materials known as bio-inspired materials (Rosenman *et al*., 2011; Hu *et al*., 2018b). The utilization of carbon nanostructures (thermo-expanded graphite, nanotubes, nonporous carbon) has enhanced electrical conductivity likely by making the presence of localization centers (molecular orbitals which are concentrated in a limited spatial region of a molecule) for organic components possible. This facilitates effective distribution of the nanostructures within the composite. This enhances the overall hierarchical architecture of the composite due to its porosity (Wu *et al*., 2023). Furthermore, the multitude of localized centers of organic components creates conditions for the formation of stable polymer structures, thereby reducing the processes of dissolution of the active material by the electrolyte (Wu *et al*., 2021).

The objective of this work is to investigate the patterns governing the formation of bio-composites based on various forms of carbon nanostructures and amino acids as model compounds of protein biopolymers. Such work has not been done before. Additionally, we aim at establishing cause-and-effect relationships between the structural and morphological characteristics and the state of the surface, conductive, and electrochemical properties of the formed bio-composites. We seek to determine the influence of structural organization of the bio-composite and conductive properties on electrochemical activity. Furthermore, we intend to explore the impact of the type of carbon template on the manifestation of electrochemical activities. Finally, we endeavor to investigate the mechanisms of redox reactions and the processes involved in the formation of the electric double layer (EDL) at the electrolyte/electrode interface for carbon-containing bio-composites.

2 MATERIALS AND METHODS

2.1 Materials

In preparation for the lab test, carbon nanostructures, thermally expanded graphite (TEG) and carbon nanotubes (CNTs), along with amino acids aspartate (As) (Sigma-Aldrich) and glycine (Gl) (Sigma-Aldrich), served as initial materials for the preparation of bio-composites. TEG was obtained through the thermal decomposition of naturally oxidized graphite (Ostafiychuk *et al*., 2013). The multilayer carbon nanotubes were synthesized by chemical deposition from the gas phase in a rotating reactor, using the oxide composition Al_2O_3-MoO_3-Fe_2O_3 as a catalyst (Revo *et al*., 2014). Propylene, obtained by dehydrating isopropyl alcohol, served as the carbon source.

To create carbon-containing composites with different forms of carbon nanostructures and amino acids, an effective mechano-synthesis method was employed (Yavorsky *et al*., 2019). The template and amino acid were mechanically mixed in an agate mortar for 2 hours without the addition of a

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solvent. The mass ratio of template to amino acid was maintained at 1:10, a choice based on a synthesis of literature data on the formation of carbon-containing composites (Pantea *et al*., 2001; Kieush *et al*., 2023). For CNT, the mass ratio of composite components was set at CNT: amino acid = 3:100 to preserve the volume proportion. Four mechanical composites, namely As-TEG, Gl-TEG, As-CNT, and Gl-CNT, were formed and dried in air at 60°C for 10 hours.

2.2 Methods and research

The electroconductivity of bio-composites, along with the initial templates and amino acids, were determined using the AUTOLAB PGSTAT12 impedance spectrometer with the FRA2 module (scanning frequency range 10^{-2} – 10^{5} Hz) (Uhorchuk *et al*., 2015). The morphology of the samples was examined using scanning electron microscopy with a PEM-106 operating at 20 kV.

The electrochemical properties of the materials were investigated using cyclic voltammetry (CVA) and galvanostatic mode, employing the charge/discharge system TIONiT P2.00-xx. CVA was measured at different rates of potential change (1-50 mV/s) and cycling capacity during 100 charge/discharge cycles at a rate of 3 mV/s. Galvanostatic studies were conducted during 100 charge/discharge cycles at a specific discharge current of 30 mA/g. A three-electrode cell was utilized for testing. The working electrode was prepared by pressing into the nickel mesh a mixture of cathode composition based on test material/acetylene carbon black (Super P)/polyvinylidene fluoride (ethanol solution) in a mass ratio of 75:20:5 (%). The components were mixed in an agate mortar with the addition of ethanol solution to the formation of a homogeneous mixtures and applied to the electrode made of a nickel grid with an area of 2 cm^2, which served as a collector. After drying at a temperature of 45C^{o}, the electrode was pressed with a hydraulic press at a pressure of 150 bar. After pressing and drying, the mass of the cathode composition on the electrode was 20±1mg. The counter electrode was platinum, and the reference electrode was chlorine-silver. A 3.5M aqueous solution of KOH was used as electrolyte.

3 RESULTS AND DISCUSSION

3.1 Electrically conductive properties of formed bio-composites

Initially, tests were conducted to determine the electrochemical activity of the carbon templates and the proposed bio-composites, based on impedance studies. This allowed to determine the frequency dependence of effective component conductivity and also to estimate the carbon-organic interactions in the composite. **Figure 1** shows the frequency dependence of calculated electrical conductivities of the bio-composites. In all cases, an increase in the electrical conductivity of the bio-composites was observed relative to the electrical conductivity of Gl and As. Amino acids conductance values are shown in Hrubiak *et al*. (2022). The result obtained above indicated a significant contribution of the carbon template component. However, considering the different morphology and degree of packing of carbon packets, depending on the type of template, we have a different contribution of carbon to the electrical conductivity of the corresponding composites. In addition, electrical conductivity depends on the number of direct contacts of material grains, which will also be different if different templates are used.

The highest values of electrical conductivity are demonstrated by bio-composites formed on TEG (**Fig. 1a**). The general appearance of the frequency dependences of the electrical conductivities of these composites, as well as for pure TEG, reflects the electronic conduction mechanism. For the case of the As-TEG bio-composite, it reaches a value of 100 S/m. In the frequency range $\omega = 10^{-2}$–10^{4} Hz, the value of electrical conductivity of bio-composites based on TEG is constant and does not depend on the frequency. The actual parts of the conductivity are several orders of magnitude greater than the value of the imaginary parts, so they can be neglected (Zhu *et al*., 2005; Popovych *et al*., 2021).

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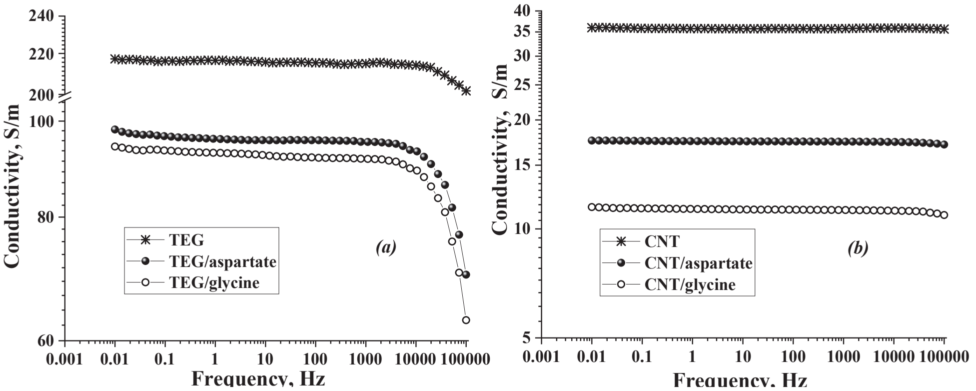

Figure 1: Frequency dependence of electrical conductivities of bio-composites and carbon templates

In the case of bio-composites of amino acids from CNT, the same trend is maintained as for bio-composites from TEG – the contribution of the conductivity of the carbon template is dominant (**Figure 1b**). At the same time, the frequency dependence of the conductivity of bio-composites with CNTs reflects the electronic mechanism of conductivity more clearly than in the case of pure CNTs. The reason for this is possibly related to the partial structuring and arrangement of CNTs in bio-composites (Canobre *et al*., 2015). In the case of pure CNTs, the absence of a clear frequency-dependent component of conductivity related to the spatial arrangement of CNTs and the isotropy of contacts. This interferes with the orderly transport of charge carriers as the frequency increases (Moulaee and Neri, 2021). The presence of amino acids in the molecules structures the orientation of CNTs, since the attachment of molecules mainly occurs at the free ends of the carbon channels of the tubes, rather than at their side surfaces (Mykhaylova *et al*., 2020). In this way, the anisotropy of the CNT orientation is formed, which, when the frequency of the external electric field increases, causes the manifestation of the skin effect and a decrease in electrical conductivity in the region $\omega > 10^4$ Hz.

The high values of electrical conductivity obtained for mechano-composites of amino acids can be explained by considering the morphology of the carbon template and the method of forming composite systems (Ostafiychuk *et al*., 2013). As a result of the mechano- activation and mixing of the components of the bio-composite, compression occurs within the carbon particles, which is accompanied by elastic-plastic deformation of the elements of its structure. Internal stresses and the density of structural defects increase. The resistance caused by the spaces between particles is practically eliminated, and thus the number and area of contact surfaces of amino acid with carbon increases. Consequently, the increase in electroconductivity of bio-composites is determined by the plastic deformation of grains, because of which the gaps between the composite particles are almost eliminated (Kotsyubynsky *et al*., 2014).

3.2 Structural and morphological characteristics of formed bio-composites

On a second step, the surface of bio-composites was evaluated by direct observation using scanning electron microscopy (SEM) (**Fig. 2**). TEG has a layered, smooth structure formed by graphite scales, while CNTs are characterized by surface porosity. For carbon nanotubes, the developed surface structure contains pores, covers, channels, and structural defects formed by aggregate complexes. The formation of bio-composites leads to structural changes in the templates associated with the destruction of the integrity of the particles and, as a result, dispersion of the material (**Fig. 2, c-d**). In the case of TEG-based bio-composites, cracking of TEG scales and "sticking" of amino acid particles to template surface is observed. The distribution of amino acid particles on the surface of the template is heterogeneous with the formation of areas of amino acid clusters. The graphite-based biocomposite has the appearance of a heterogeneous mechanical mixture for the case of bio-composites based on CNTs, significant dispersion of the template and reduction in the porous structure of CNT aggregates. The cracking of CNT aggregates occurs at the locations of pores and significant morphological irregularities. This effect due to compaction of the template structure and closing of existing pores, channels and covers. This is probably accompanied by blocking in the volume of some part of the amino acids that fall into these inequalities. As a result, it is observed the "encapsulation" on the surface of amino acid aggregates is also observed in the form of individual particles. The dispersion of the template due to mechano-synthesis causes a reduction in the porous structure of CNT aggregates.

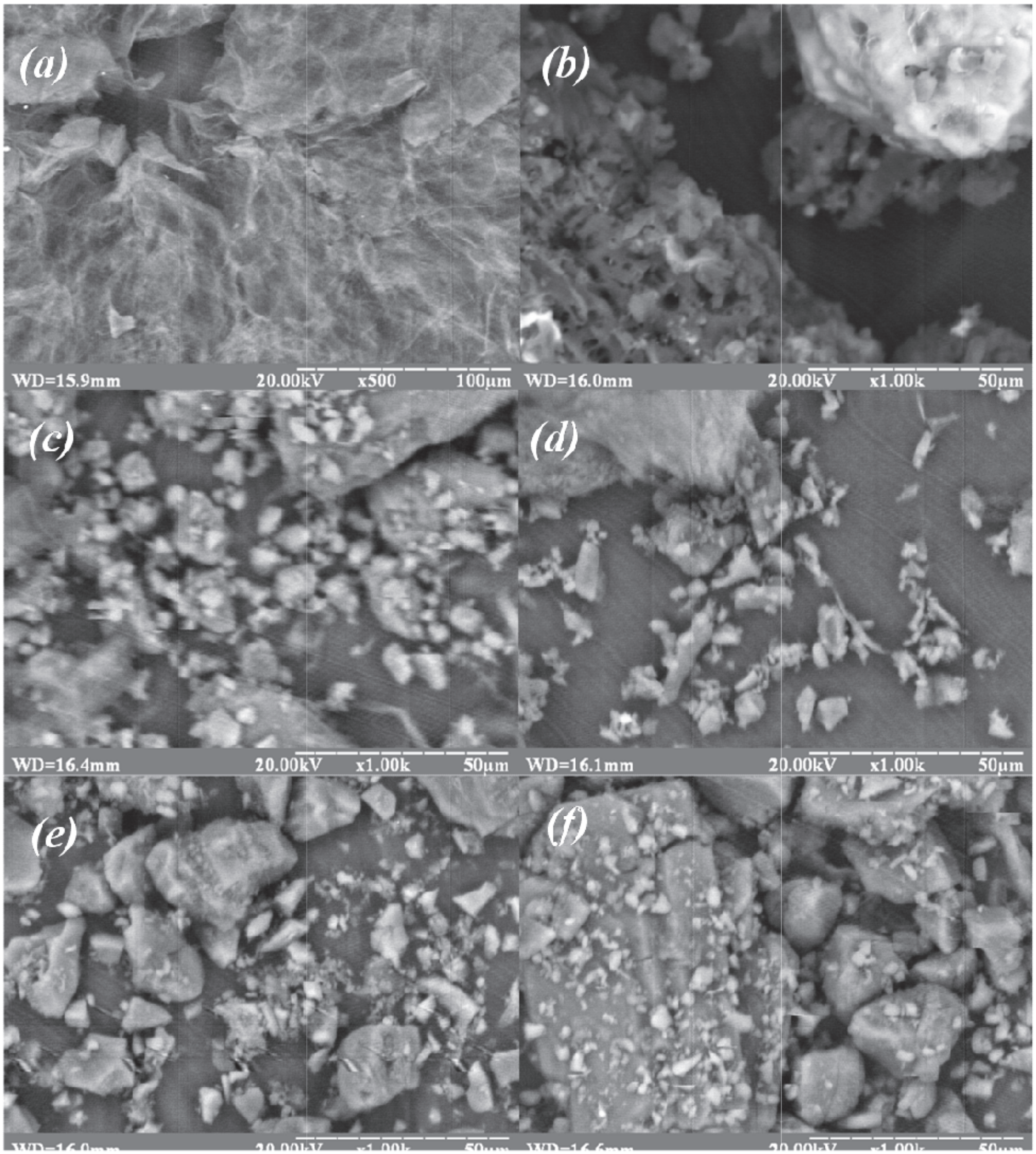

Figure 2: SEM images of: TEG (*a*); CNT (*b*); As-TEG biocomposite (c); Gl-TEG biocomposite (*d*); As-CNTs biocomposite (*e*); Gl-CNTs biocomposite (*f*).

Summarizing it can be assumed that in the process of mechano-synthesis the role of structural anisotropy of carbon templates is not a determining factor affecting the course of the bio-composite formation process. As in the case of graphite and nanotubes, mechanical deformations lead to cracking of the layers and particles of the templates with subsequent strengthening and a decrease in porosity. At the same time, the agglomerative stability of both organic components in the form of particles and templates is preserved, in the case of using carbon nanotubes. A similar character in the

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formation of bio-composites determines the manifestation of their conductive properties, where the conductivity of the template comes to the fore. Although the bio-composites' porous structure decreases due to structural deformation, this however becomes the dominant reason for the enhanced electrical conductivity (Hrubiak *et al.*, 2022).

3.3 Electrochemical properties of formed bio-composites in protonic electrolyte

The study of the electrochemical properties of the synthesized materials and the possibility of using them as the electrode material of hybrid capacitors was carried out using the methods of cyclic CVA and galvanostatic charge/discharge. The CVA scanning curves of the electrode based on the As-TEG bio-composite in a proton electrolyte at a speed of 3 mV/s in the range of 0.3 to -1.0V are presented in **Fig. 3a.** The curve has a symmetrical rectangular shape without pronounced redox maxima, which indicates the predominance of capacitive accumulation of charge due to the formation of EDL. Polarization of the electrodes on the anodic and cathodic branches is observed in the vicinity of the final potentials of the scanning range (Bazaluk *et al.*, 2021). Scanning at different speeds showed that capacitive charge accumulation is dominant. Thus, the role of the carbon template comes to the fore in capacity formation.

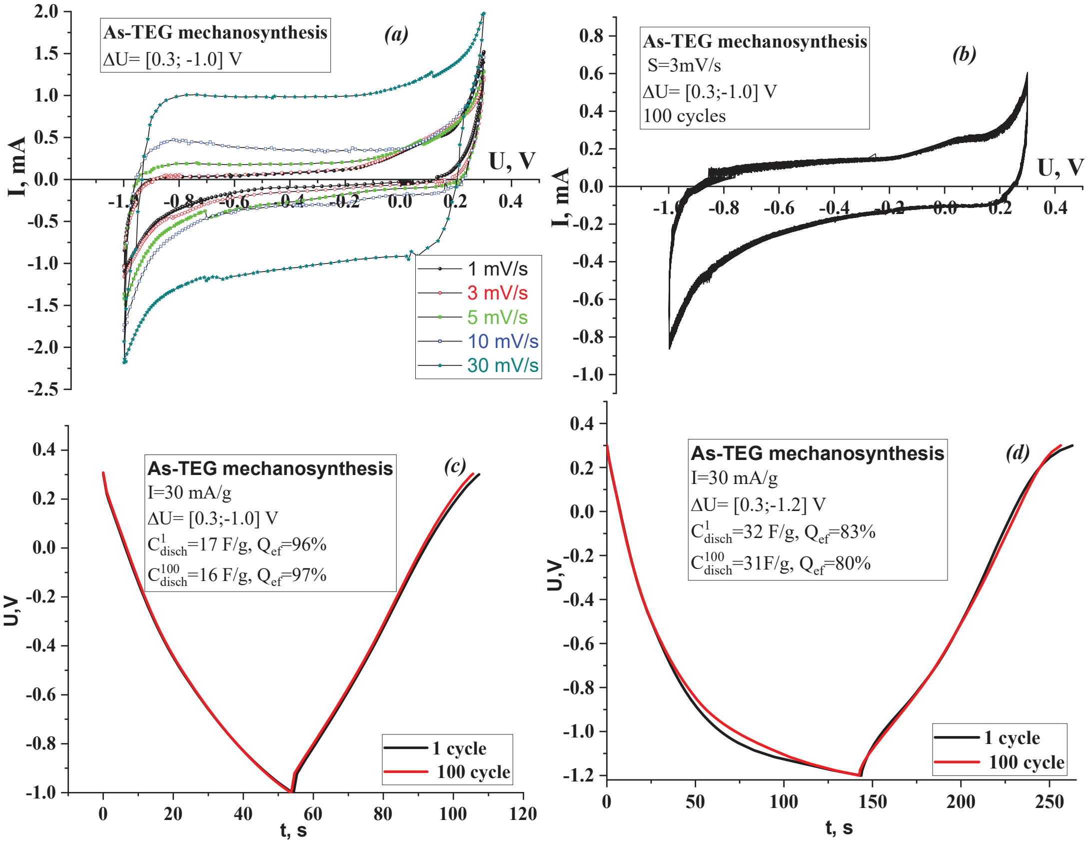

Figure 3. CVA curves of electrochemical systems based on As-TEG bio-composite in the voltage scanning range of 0.3 to -1.0V (*a*); CVA profiles at the 3mV/s during 100 cycles (*b*); 1st and 100nd charge/discharge galvanostatic cycles at the current 30mA/g in the range of 0.3 to -1.0V (*c*) and 0.3 to -1.2V (*d*).

The cycling ability of the As-TEG bio-composite was tested for 100 cycles in the potentiometric mode (**Fig. 3b**). The values of discharge and charge specific capacities and Coulomb efficiency over 100 cycles were calculated. It was found that the capacitive attenuation of the 1st and 100th cycle does not exceed 5%. The specific capacity of the discharge during the entire scan remains constant at the level of 4.5F/g. At the same time, the Coulomb efficiency remains around 70%. Galvanostatic testing

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was also carried out at a specific current of 30mA/g (**Fig. 3c**). In this case, stable cycled discharge capacity at the level of 17-16 F/g is observed for 100 cycles and high Coulomb efficiency values of 97-95% are observed. Thus, the As-TEG bio-composite demonstrates electrochemical activity and stable operation in the charge/discharge mode.

For galvanostatic testing in the discharge/charge mode for 100 cycles in the voltage range of 0.3 and -1.2V shown in **Fig. 3d**. In this case, when discharging to -1.2V, the specific capacity of the discharge increases to 32 F/g and remains constant for 100 cycles, a significant increase. Compared to previous studies, a weakly pronounced galvanostatic plateau is formed at a potential of -1.0V, which ensures the achievement of higher values of the discharge capacity. At the same time, the Coulombic efficiency significantly decreases to 83% for the 1st cycle, and 80% for the 100th cycle, which indicates the partial irreversibility of the charge/discharge. We assume that due to the formation of coarsely dispersed components of the biocomposite from TRH, there is a predominance of capacitive charge accumulation processes both from the side of the carbon template and due to amino acid complexes.

For the As-CNT bio-composite the CVA curves at different scanning speeds (**Fig. 4a**) have clearly pronounced symmetrical maxima on the anodic and cathodic branches: -0.4V and 0.1V – for the anodic branch, -0.6V and -0.3B – for the cathode line, respectively. An increase in the scanning speed leads to a decrease in the intensity and displacement of the maxima, which indicates the limiting factor of the rate of potential change on the course of pseudo-capacitive reactions. Also, the lack of a rectangular shape of the CVA curves indicates the predominance of pseudo-capacitive charge accumulation in this system in comparison to the As-TEG bio-composite. We assume that functionalized CNTs by amino acids with redox processes render high pseudo capacitance (Wang *et al*., 2014). The redox process on a bio-composite is associated with a reaction of the addition of cations to the carboxyl group of the peptide link with the release of a hydrogen ion is possible (Moulaee and Neri, 2021):

$$COOH + K^+ \rightarrow COOK + H^+ \tag{1}$$

The course of such a reaction is most possible because the deprotonation of the carboxyl group or weakly bound side H atoms occur in the entire range of energies, starting from ≈0 eB (Muftahov and Schukin, 2018). Along with this, the mechanism of attachment of potassium ions to double-bonded oxygen on the side branches of peptide chains is implemented (Seebach, 1988):

$$carbonyl(N - C = O) + K^+ \rightarrow (N = C - OK) \tag{2}$$

When potassium is attached to oxygen, the C=O double bond is broken and the C=N double bond is formed with the release of a hydrogen atom, as in the case of lithium joining the carboxyl group of a peptide link. This mechanism of reactions does not contradict the above and allows to increase the load of lithium on the formula unit of the peptide link (Goodman and Peggion, 1981).

The CVA cycling over 100 charge/discharge cycles (**Fig. 4b**) indicates a partial degradation of pseudo-capacitive reactions: there is a fading of the maxima of cathodic and anodic reactions. At the same time, the shape of the CVA curve after 100 cycles becomes more rectangular, which indicates the growth of capacitive processes. The specific discharge capacities calculated based on CVA curves are about 5.5F/g. As the pseudo capacitance contribution decreases, the Coulomb efficiency also decreases from 85% for the 1st cycle to 79% for the 100th cycle. Galvanostatic studies (**Fig. 4c**) demonstrate a similar tendency to decrease the contribution of pseudo capacitance to the electrochemical activity of the As-CNT during cycling. Galvanostatic discharge profiles have a linear shape without a pronounced plateau. The specific discharge capacity during 100 cycles decreases from 18 to 15 F/g, while the Coulombic efficiency decreases from 96% for the 1st cycle to 91% for the 100th cycle.

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For bio-composites formed by the mechano-synthesis method based on TEG and CNT templates and Gl, also study of their electrochemical activity in proton electrolytes was carried out using a three-electrode cell. For bio-composites Gl-TEG CVA curves at different scanning speeds in the voltage range of 0.3 to -1.0V, there is a predominance of the capacitive mechanism of charge accumulation, which is reflected in the rectangular shape of the curves (**Fig. 4d**). As mentioned earlier, for TEG and the Gl the current-generating reactions in the proton electrolyte are related to the processes of the formation of EDL on the surface, which is reflected by a similar trend for their composite.

The CVA cycling shows a significant degradation of the specific capacity of the charge for the first 20 cycles, followed by reaching saturation at the level of 4 F/g (**Fig. 4e**). Coulombic efficiency after 100 charge/discharge cycles remains at about 95%. The CVA curves show slightly broadened maxima on the cathodic and anodic branches, which indicates the presence of pseudo-capacitive charge accumulation at low scanning speeds (3 mV/s). However, with an increase in the cycling order, the intensity of redox peaks decreases. This indicates the irreversible degradation of current-generating pseudo-capacitive reactions on the Gl-TEG electrode. Galvanostatic testing during 100 cycles (**Fig. 4f**), shows good Coulombic efficiency and discharge stability: Coulombic efficiency after 100 cycles is 94%, and specific discharge capacity during the entire cycle is 7-8 F/g.

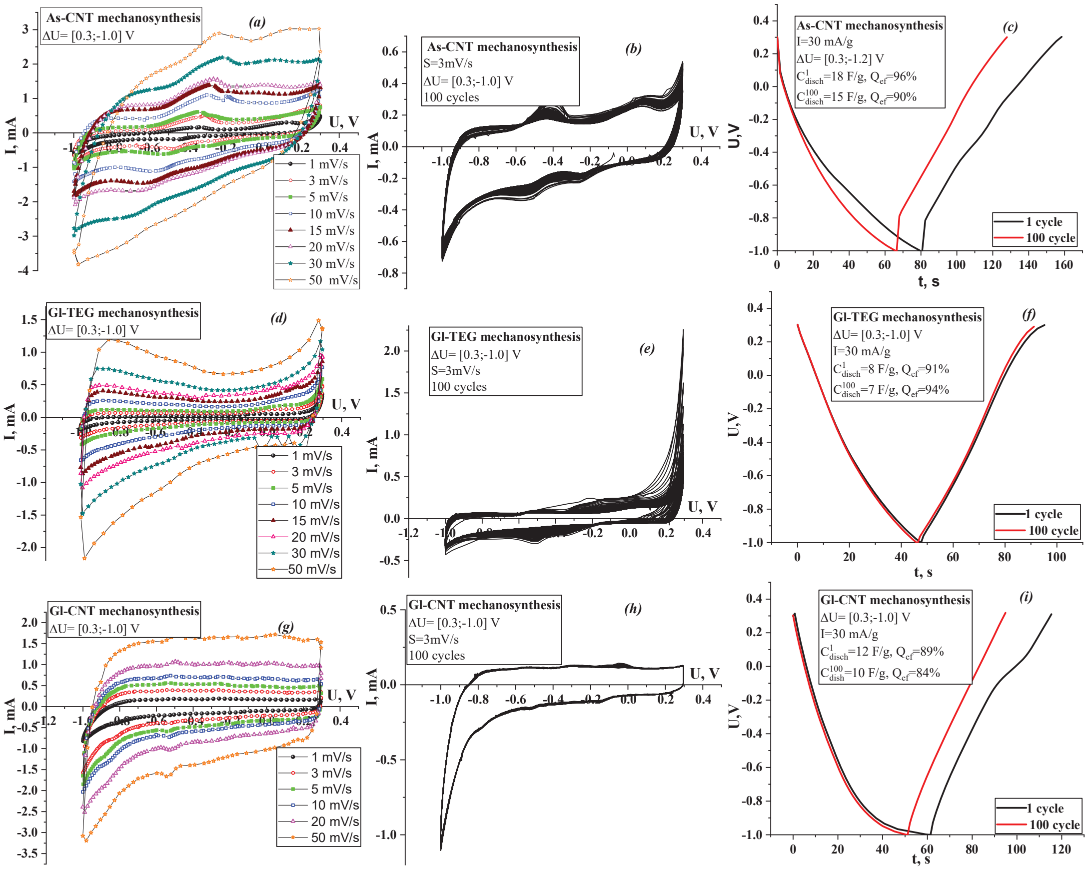

Figure 4: CVA curves of electrochemical systems based on As-CNT, Gl-TEG, Gl-CNT bio-composites in the range [0.3 to -1.0]V (*a, d, g*), CVA profiles at the 3mV/s during 100 cycles for As-CNT (*b*), Gl-TEG (*e*), Gl-CNT (*h*) bio-composites; 1st and 100nd charge/discharge galvanostatic cycles at the current 30mA/g in the range [0.3 to -1.0]V for As-CNT (*c*), Gl-TEG (*f*), Gl-CNT (*i*) bio-composites.

In the case of the Gl-CNT bio-composite the CVA curves at different scanning speeds have a rectangular shape, which indicates, as in the case of the Gl-TEG bio-composite, the predominance of

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capacitive charge accumulation processes due to the formation of EDL (**Fig. 4g**). When the lower limit of the potential -1.0V is reached, a significant polarization of the electrode is observed, which is a similar trend as for the Ac-CNT bio-composite. Based on this we can assume about the determining influence of the template (CNT) in the polarization effects at this potential. On the CVA curves at different speeds, there are insignificant redox maxima, but their intensity is insignificant, so their contribution to the formation of the total capacity is not dominant. The cycling of the Gl-CNT bio-composite in the CVA regime demonstrates good reversibility despite significant polarization upon reaching the lower potential limit (**Fig. 4h**). Minor oxidation-reduction maxima are present on the cathodic and anodic branches. The calculated values of charge and discharge-specific capacities are stable throughout the cycle and are about 8.0 and 4.5 F/g, respectively, so the value of the Coulomb efficiency is insignificant at the level of 55%. Comparing the obtained results with the data for the cycling of the As-CNT bio-composite, as already mentioned earlier, we note the dominant contribution of the amino acid to the processes of charge accumulation. For aspartate, pseudo-capacitive redox reactions play a decisive role, while for Gl, the processes of capacitive charge accumulation are dominant. Galvanostatic charge/discharge studies over 100 cycles demonstrate a gradual degradation of the capacitive accumulation, which is reflected by a linear decline of the charge and discharge-specific capacities with increasing cycling (**Fig. 4i**).

Summarizing and comparing the obtained results, it is possible to trace the significant contribution of the template to the manifestation of the electrochemical activity of amino acid compounds. Due to the presence of a conductive template, which ensures efficient transport of charges, the electrochemical activity increases significantly, which is reflected in the increase in the intensity of pseudo-capacitive energy storage and the increase in capacity. In addition, the effective contribution of capacitive storage due to the formation of EDL is also extended. However, as we prove in this case, the formation of EDL is possible both with the participation of the template and organic components, especially for the case of biocomposites based on carbon nanotubes. The influence of the type of amino acids on the performance of the electrochemical activity of biocomposites based on them is also noticeable. This is due to different courses of redox reactions involving different amino acid molecules. A higher cation load as a result of current-generating reactions with the participation of aspartate results in higher values of the test indicators. Finally, the process of mechano-synthesis leads to the destruction of the template structure and the discrete distribution of organic components on the surface of the template parts. This fact shows the lack of influence of structural anisotropy of the carbon template on the process of distribution of organic agglomerates on its surface. Considering the electrochemical activity of amino acids as model compounds of biopolymers, bio-composites with carbon nanostructures formed on their basis will combine two mechanisms of energy storage - electrostatic with the formation of an electric double layer and Faraday, associated with the course of redox reactions, which opens up prospects for their use in hybrid capacitors.

4 CONCLUSIONS

The regularities of the formation of carbon-containing bio-composites formed since various forms of carbon nanostructures and model amino acids by the mechano-synthesis method are presented. The structural organization, electroconductive and electrochemical properties of the bio-composites and the regularities of the manifestation of properties depending on the type of template were revealed.

It was found that the type of carbon template and the structural organization of the bio-composite play a major role in the electrochemical activity of the formed systems. In particular, the type of template will determine the predominant contribution of capacitive processes due to the formation of PES or pseudo-capacitive charge accumulation in the formation of the total capacity of bio-composites obtained by mechano-synthesis. It was found that the predominance of pseudo-capacitive redox reactions for the CNT-based bio-composite is caused by the structural organization, which consists in wrapping the aggregates of nanotubes with amino acid particles. In contrast, significant dispersion of the template is observed in bio-composites based on TEG, which leads to the formation of a mixture of carbon and amino acid particles that do not have stable conduction bridges between them and the

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capacitive accumulation of charge due to the formation of EDL. Another mechanism is the carbon template mainly plays the role of a conducting agent with the participation of which bridges of electronic conductivity of the bio-composite. The best electrochemical activity is demonstrated by the As-TEG bio-composite, for which, when discharged with a specific current of 30mA/g to -1.2V, the discharge capacity is 32F/g and remains constant for 100 cycles.

NOMENCLATURE

The nomenclature should be located at the end of the text using the following format:

AS	Aspartate
CNT	Carbon nanotube
CVA	Cyclic voltammetry
EDL	Electrical double layer
Gl	Glycine
TEG	Thermally expanded graphite

REFERENCES

Bazaluk O., Hrubiak A., Moklyak V., Moklyak M., Kieush L., Rachiy B., Fedorov S., 2021, Structurally Dependent Electrochemical Properties of Ultrafine Superparamagnetic ‘Core/Shell’γ-Fe_2O_3/Defective α-Fe_2O_3 Composites in Hybrid Supercapacitors, *Material*s, vol. 14, no. 6977: p. 1-20.

Bhattacharya, P., Du, D., Lin, Y., 2014, Bioinspired nanoscale materials for biomedical and energy applications, *Journal of the Royal Society interface*, vol. 11, no. 95: p. 20131067.

Canobre, S. C., Xavier, F. F. S., Fagundes, W. S., Freitas, A. D., Amaral, F. A., 2015, Performance of the chemical and electrochemical composites of PPy/CNT as electrodes in type I supercapacitors, *Journal of Nanomaterials*, vol. 16, no. 1: p. 1-13.

Fu, X., Jewel, Y., Wang, Y., Liu, J., Zhong, W., 2016, Decoupled Ion Transport in a Protein-Based Solid Ion Conductor, *Phys. Chem. Lett*., vol.7, no. 21: p. 4304–4310

Goodman, M., Peggion, E., 1981, α-amino acid N-carboxyanhydride polymerizations-a mechanistic analysis, *Pure and Applied Chemistry*, vol. 53, no. 3: p. 699-714.

Hrubiak, A., Moklyak, V., Yavorsky, Y., Onuskiv, B., Chelyadyn, V., Karpets, M., Ilnitsky, N., 2022, Electroconductive properties of carbon biocomposites formed by the deposition method, *Physics and Chemistry of Solid State*, vol. 23, no. 2: p. 302-310.

Hu K., Jiang Y., Xiong W., Li H., Zhang P., Yin F., Zhang Q., Geng H., Jiang F., Li Z., Wang X., Li Z., 2018a, Tuning peptide self-assembly by an in-tether chiral center, *Sci. Adv*., vol. 4, no. 5: p. eaar5907.

Hu, K., Yin, F., Zhou, Z., Lian, C., Liu, Y., Sun, C., Li, W., Zhang, J., Li, Z., 2019, Directional assembly of a stapled α-helical peptide, *Chem. Commun*., vol. 55 p. 10484-10487.

Hu, K., Zheng, C., An, M., Ma, X., Wang, L., 2018b, A peptide-based supercapacitor and its performance improvement via TiO_2 coating, *Journal of Materials Chemistry A*, vol. 6, no. 17: p. 8047-8052.

Ju, Z., Lu, G., Sheng, O., Yuan, H., Zhou, S., Liu, T., Liu, Y., Wang, Y., Nai, J., Zhang, W., Tao, X., 2022, Soybean protein fiber enabled controllable Li deposition and a LiF-nanocrystal-enriched interface for stable Li metal batteries, *Nano Lett*., vol. 22, no. 3: p. 1374-1381.

Kieush, L., Schenk, J., Koveria, A., Rantitsch, G., Hrubiak, A., Hopfinger, H., 2023, Utilization of Renewable Carbon in Electric Arc Furnace-Based Steel Production: Comparative Evaluation of Properties of Conventional and Non-Conventional Carbon-Bearing Sources, *Metals*, vol. 13, no. 4: p. 1-16.

Kotsyubynsky, V. O., Grubiak, A. B., Moklyak, V. V., Pylypiv, V. M., Lisovsky, R. P., 2014, Structural, morphological, and magnetic properties of the mesoporous maghemite synthesized by a citrate method, *Metallofiz. Noveishie Tekhnol*., vol. 36: p. 1497–1512.

Liu, L., Solin, N., Inganäs, O., 2021, Bio based batteries, *Advanced Energy Materials*, vol. 11, no. 43: p. 2003713.

Moklyak V., Hrubiak A., Gogitidze Z., Yavorskyi Y., 2021, Biopolimer Peptide Batteries—A New Concept for Environmentally Friendly and Safer Energy Storage, Batteries, vol. 7, no.50: p. 1-5.

Moulaee, K., & Neri, G., 2021, Electrochemical amino acid sensing: A review on challenges and achievements, *Biosensors*, vol. 11, no. 12: p. 502.

Muftahov, M. V., Schukin, P. V., 2018, Razrushenie peptidov i nukleozidov v reaktsiyah s elektronami nizkih energiy, *Zhurnal tehnicheskoy fiziki*, vol. 88: p. 770-781.

Mykhaylova, H. Y., Len, E. G., Galstyan, I. Y., Tsapko, E. A., Gerasymov, O. Y., Patoka, V. I., Yakymchuk, M. M., 2020, Electrical and mechanical properties of composites Ti–carbon nanotubes, *Metallofiz. Noveishie Tekhnol*., vol. 42: p. 575-593.

Nguyen, T., Easley, A., Kang, N., Khan, S., Lim, S., Rezenom, Y., 2021, Polypeptide organic radical batteries, *Nature*, vol. 593: p. 61-66.

Nie, L., Li, Y., Chen, S., Li, K., Huang, Y., Zhu, Y., Sun, Z., Zhang, J., He, Y., Cui, M., Wei, S., Qiu, F., Zhong, C., Liu, W., 2019, Biofilm nanofiber-coated separators for dendrite-free lithium metal anode and ultrahigh-rate lithium batteries, *ACS Appl. Mater. Interfaces*., vol. 11, no. 35: p. 32373-32380.

Ostafiychuk, B.K., Revo, S.L., Kuzyshyn, M.M., Budzulyak, I.M., Rachiy, B.I., 2013, Influence of Degree of Compression on the Electrical Conductivity of the Composite Material, *Physics and Chemistry of Solid State*, vol. 14: p. 734-740.

Pantea, D., Darmstadt, H., Kaliaguine, S., Sümmchen, L., Roy, C., 2001, Electrical conductivity of thermal carbon blacks: Influence of surface chemistry, *Carbon*, vol. 39, no.8: p. 1147-1158.

Popovych, O. M., Budzulyak, I. M., Popovych, O. V., Rachiy, B. I., Ilnytskyi, R. V., Yablon, L. S., Morushko, O. V., 2021, Synthesis and electrochemical properties of nanocrystalline nickel molybdate, *Physics and Chemistry of Solid State*, vol. 22, no. 1: p. 123-131.

Revo, S., Alekseev, A., Ivanenko, E., Labii, T., Boubertakh, A., Hamamda, S., 2014, Structure, tribotechnical, and thermophysical characteristics of the fluoroplastic carbonnanotubes material, *Nanoscale Research Letters*, vol. 9: p. 1-4.

Rosenman, G., Beker, P., Koren, I., Yevnin, M., Bank-Srour, B., Mishina, E., Semin, S., 2011, Bioinspired peptide nanotubes: deposition technology, basic physics and nanotechnology applications, *Journal of Peptide Science*, vol. 17, no. 2: p. 75-87.

Ryu, J., Kim, S. W., Kang, K., Park, C. B., 2010, Synthesis of diphenylalanine/cobalt oxide hybrid nanowires and their application to energy storage, *ACS nano*, vol. 4, no. 1: p. 159-164.

Sarmadi, A., Msoudpanah, S. M., Alamolhoda, S., 2022, Amino Acid-Assisted Solvothermal Synthesis of $LiFePO_4$ Cathode Materials, *Journal of Ultrafine Grained and Nanostructured Materials*, vol. 55, no. 1: p. 37-44.

Seebach, D., 1988, Structure and reactivity of lithium enolates. from pinacolone to selective C-alkylations of peptides. difficulties and opportunities afforded by complex structures, *Angewandte Chemie International Edition in English*, vol. 27, no. 12: p. 1624-1654.

Uhorchuk, O. M., Uhorchuk, V. V., Karpets, M. V., Kaykan, L. S., Deputat, B. J., Boychuk, A. M., Hasyuk, M. I., 2015, Lithium Ferrite as the Cathode of the Electrochemical Power Sources: the Perspectives of Sol-gel Synthesis Method, *Journal of Nano-& Electronic Physics*, vol. *7, no.* 2: p. 1-10

Wang, L.-L., Xing, R.-G., Zhang, B.-W., Hou, Y., 2014, Preparation and Electrochemical Properties of Functionalized Graphene/Polyaniline Composite Electrode Materials, *Acta Phys. -Chim. Sin*., vol. 30: p. 1597-1604.

Wang, S., Park, A. M. G., Flouda, P., Easley, A. D., Li, F., Ma, T., Lutkenhaus J., 2020, Solution processable thermally crosslinked organic radical polymer battery cathodes, *Chem. Sus. Chem*., vol. 13, no. 9: p. 2371-2378.

Wang, T. Li, Y., Zhang, J., Yan, K., Jaumaux, P., Yang, J., Wang, C., Shanmukaraj, D. , Sun, B., Armand, M., Cui, Y., Wang, G., 2020, Immunizing lithium metal anodes against dendrite growth using protein molecules to achieve high energy batteries, *Nat. Commun.,* vol. 11, no. 5429: p. 1-9.

Wu, C., Hu, M., Yan, X., Shan, G., Liu, J., Yang, J., 2021, Azo-linked covalent triazine-based framework as organic cathodes for ultrastable capacitor-type lithium-ion batteries, *Energy Storage Materials*, vol. 36: p. 347-354.

https://doi.org/10.52202/077185-0176

Wu, H., Wu, Q., Chu, F., Hu, J., Cui, Y., Yin, C., Li, C., 2019, Sericin protein as a conformal protective layer to enable air-endurable Li metal anodes and high-rate Li-S batteries, *Power Sources*, vol. 419: p. 72-81.

Wu, Y., Li, H., Liu, T., Xu, M., 2023, Versatile Protein and Its Subunit Biomolecules for Advanced Rechargeable Batteries, *Adv. Mat.*, vol. 35,no. 48: p. 1-25.

Zhang, L., Deng, H., Fu, Q., 2018, Recent progress on thermal conductive and electrical insulating polymer composites, *Compos. Commun*., vol. 8: p. 74-82.

Zhang, S., Qi, M., Guo, S., Sun, Y., Tan, X., Ma, P., Li, J., Yuan, R., Cao, A., Wan, L., 2022, Advancing to 4.6 V Review and Prospect in Developing High-Energy-Density $LiCoO_2$ Cathode for Lithium-Ion Batteries. *Small Methods*., vol. 6, no. 5: p. 2200148.

Zhao, Q., Stalin, S., Zhao, C., Archer, L., 2020, Designing solid-state electrolytes for safe, energy-dense batteries, *Nat. Rev. Mater*., vol. 5: p. 229-252.

Zhu, Z. H., Hatori, H., Wang, S. B., Lu, G. Q., 2005, Insights into hydrogen atom adsorption on and the electrochemical properties of nitrogen-substituted carbon materials, *The Journal of Physical Chemistry B*, vol. 109, no. 35: p. 16744-16749.

Yavorsky, Y. V., Zaulichny, Y. V., Gunko, V. M., Karpets, M. V., Mokliak, V. V., Hrubiak, A. B., 2019, The Dependence between the Structural-morphological Features of SiO_2/TiO_2 Mixesand Discharge Capacities of Lithium Power Sources, *Journal Of Nano-And Electronic Physics*, vol. 11, no. 6: p. 1-8.

https://doi.org/10.52202/077185-0176