ABSTRACT

of the dissertation for the degree of "Doctor of Philosophy" (PhD) in the specialty 6D072300 - "Technical Physics"

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SYNTHESIS AND INVESTIGATION OF POROUS CARBON AND TRANSITION-METAL-OXIDES FOR ELECTROCHEMICAL ENERGY STORAGE APPLICATIONS

General characteristics of the work. The dissertation is devoted to the development and investigation of electrode materials based on graphene-like porous carbon and nanostructured transition metal oxides to enhance the specific capacitance, energy, and power characteristics of supercapacitors and hybrid energy storage devices.

Relevance of the research topic. The global energy storage industry faces serious challenges due to the growing demand for high-performance and environmentally sustainable materials. The accelerated transition to renewable energy sources, widespread adoption of electric transportation, and the proliferation of portable electronics require the development of new, more efficient energy storage technologies.

Among various electrochemical storage systems, supercapacitors have drawn particular attention due to their high power density and long cycle life. However, despite these advantages, supercapacitors are still limited by their relatively low energy density and high production cost. A significant limiting factor is the insufficient technological development of processes for producing active electrode materials with the desired electrochemical characteristics.

The relevance of this research lies in the need to develop new, sustainable, and environmentally friendly materials for electrochemical energy storage, particularly graphene-like porous carbon with high specific surface area, obtained through the processing of biomass waste. Furthermore, the creation of hybrid electrodes for supercapacitors based on nanostructured transition metal oxides deposited on graphene coatings integrated with a novel three-dimensional (3D) porous metallic architecture is of particular interest.

This multicomponent structure provides a synergistic effect, combining the high electrochemical activity of metal oxides, the excellent conductivity of graphene, and the mechanical stability of a 3D nickel framework. As a result, it contributes to a significant increase in specific capacitance, improved cycling stability, and enhanced energy characteristics of storage devices, making this direction highly promising for the development of modern electrochemical energy technologies.

The aim of the research is to develop reproducible and scalable methods for the synthesis and modification of graphene-like porous carbon and nanostructured transition metal oxides for supercapacitor electrodes; to substantiate the choice of synthesis and modification parameters of electrode materials that ensure an increase in specific capacitance and improvement of durability; to establish cause-

and-effect relationships between synthesis parameters, structural–morphological features, and their combined influence on the electrochemical performance of the cells; and to identify optimal electrode compositions and architectures suitable for technological implementation in electrochemical energy storage devices.

Research objectives

- to systematize and analyze modern approaches to the synthesis of porous carbons from biomass and to the integration of transition metal oxides into supercapacitor electrode materials;
- to develop and justify a reproducible method for synthesizing graphene-like porous carbon (GLPC) from various types of biomass using thermochemical activation on a specially designed setup;
- to investigate the structure, texture, and surface chemistry of the obtained GLPC and verify its suitability as an electrode material through comprehensive testing (CV, GCD, EIS), including determination of specific capacitance, charge-transfer resistance, ion-diffusion behavior, and cycling stability;
- to justify and implement the modification of GLPC with nickel hydroxide to enhance the pseudocapacitive contribution, and to analyze the effect of the $Ni(OH)_2$ content and spatial distribution on the morphological features and electrochemical behavior of the material;
- to develop a three-dimensional porous metal current collector (3D current collector) with a hierarchical open structure; justify the choice of composition, formation method and heat treatment modes in order to reduce ohmic losses and increase mechanical stability;
- to modify the 3D porous metallic current collector by applying a graphene coating via chemical vapor deposition (CVD) and forming an active layer of nanostructured manganese dioxide (MnO_2) on its surface by electrodeposition to create hybrid electrodes;
- to evaluate the effect of the multicomponent architecture of hybrid electrodes on the specific capacitance, energy characteristics, and stability of supercapacitors.

The objects of the study are the electrodes of electrochemical energy storage devices based on graphene-like porous carbon derived from biomass and transition metal oxides integrated with a three-dimensional porous metallic current collector.

The subject of the study is the physicochemical and electrochemical properties of electrode materials based on graphene-like porous carbon and transition metal oxides**.**

Research methods. The following methods were employed during the course of this dissertation:

*Synthesis and modification of materials**:*** thermochemical activation; chemical deposition (precipitation); chemical vapor deposition (CVD); electrodeposition.

*Physicochemical characterization**:*** scanning electron microscopy (SEM); transmission electron microscopy (TEM); energy-dispersive X-ray spectroscopy (EDX); X-ray diffraction analysis (XRD); Raman spectroscopy; Brunauer–Emmett–Teller (BET) surface area analysis.

Electrochemical methods: cyclic voltammetry (CV); galvanostatic charge–discharge (GCD); electrochemical impedance spectroscopy (EIS).

Key provisions submitted for defense

1. A specially designed laboratory apparatus for the thermochemical activation of biomass and other carbonaceous precursors has been developed and implemented, enabling the controlled synthesis of graphene-like porous carbon (GLPC) of electrode quality from biowaste (in particular, walnut shell) at a KOH-to-carbon mass ratio of 4:1 and an activation temperature of 850 °C, resulting in a material with a specific surface area of up to 2800 $m^2\ g^{-1}$, a specific capacitance of 263 F g^{-1}, and a coulombic efficiency of 99.4 % at a current density of 1000 mA g^{-1}.

2. A nickel hydroxide–modified graphene-like porous carbon ($Ni(OH)_2$–GLPC) has been developed, demonstrating a substantial enhancement of the pseudocapacitive contribution. The 9 wt.% $Ni(OH)_2$ modification increases the specific capacitance of the electrode material from 236 F g^{-1} to 300 F g^{-1} at a current density of 50 mA g^{-1}. The base GLPC, synthesized from rice husk by pyrolysis and alkaline thermochemical activation (KOH:carbon = 4:1) at 850 °C in an argon atmosphere, exhibits a specific surface area of 3292 $m^2\ g^{-1}$ and a well-developed porous structure.

3. A three-dimensional porous current collector, fabricated by applying a nickel-based slurry containing pore-forming agents onto a metallic foil followed by heat treatment at 800 °C in an Ar/H_2 (95:5) atmosphere, and subsequently modified with a CVD-grown graphene coating and an electrodeposited layer of nanostructured MnO_2, exhibits a specific capacitance of 297 F g^{-1} at a current density of 250 mA g^{-1}, while retaining 98 % of its initial capacitance after 5000 charge–discharge cycles.

Main results of the research. The study is aimed at developing scientifically and technologically grounded approaches to the synthesis and modification of porous carbon materials and nanostructured transition metal oxides, as well as at employing three-dimensional porous metallic current collectors as a base for fabricating electrodes based on transition metal oxides. The obtained materials are intended for application in electrochemical energy storage systems, particularly in supercapacitors. The research focuses on creating functional electrode structures with high specific capacitance, long-term cycling stability, and potential for scalable technological implementation.

At the first stage, a specially designed laboratory apparatus for the thermochemical activation of biomass and other carbonaceous precursors was developed and implemented, enabling the controlled synthesis of graphene-like porous carbon (GLPC) of electrode quality. Using this setup, GLPC was obtained from biowaste (in particular, walnut shell and rice husk) at a KOH-to-carbon mass ratio of 4:1 and an activation temperature of 850 °C. The resulting material exhibited a specific surface area of up to 2800 $m^2\ g^{-1}$, a specific capacitance of 263 F g^{-1}, and a coulombic efficiency of 99.4 % at a current density of 1000 mA g^{-1}. The specially engineered unit with a dual-cylinder reactor made of stainless steels (AISI 304L, AISI 316L, AISI 321) ensures high process purity, minimizes

contamination, and improves reproducibility. The developed method is universal and adaptable to various types of biomass and other carbon-containing materials, providing high-quality carbon products with controlled structural and electrochemical characteristics, which makes them promising for use in energy storage systems.

In the second part of the work, the modification of graphene-like porous carbon by chemical deposition of nickel hydroxide was investigated to improve its functional properties. The modification was shown to result in a significant increase in specific capacitance — from 236 F g^{-1} to 300 F g^{-1} at a current density of 50 mA g^{-1} — as well as improved stability under cyclic operation. Morphological and electrochemical studies confirmed the uniform distribution of the active phase, sufficient conductivity of the composite, and its suitability for use in hybrid energy storage devices.

The third research direction focused on the development of three-dimensional current collectors with a hierarchical open porous structure, fabricated by applying a nickel-based slurry with pore-forming additives onto a metallic substrate followed by heat treatment. Surface modification via chemical vapor deposition (CVD) enabled the formation of a uniform graphene layer, after which an active pseudocapacitive layer of nanostructured MnO_2 was electrodeposited. Such an architecture provides high electrical conductivity, a developed active surface, and efficient ion transport, resulting in a significant increase in specific capacitance, improved energy characteristics, and enhanced cycling stability.

Thus, the dissertation research covers the entire technological cycle — from the production of carbon materials from biowaste to the creation of multicomponent hybrid electrodes with high specific capacitance and durability. The obtained scientific and practical results form the foundation for scalable production of advanced materials for modern energy storage systems and contribute to the development of environmentally oriented technologies.

Scientific novelty of the research. In the course of the dissertation research, the following scientific results were obtained:

- a reproducible method for the synthesis of graphene-like porous carbon from biomass (walnut shell and rice husk) was developed using a specially designed apparatus equipped with stainless steel reactors (AISI 304L, AISI 316L, and AISI 321), ensuring high process purity and reproducibility of the results;
- the feasibility of using biomass-derived GLPC as an efficient electrode material for supercapacitors was experimentally confirmed. The synthesized GLPC is characterized by a high specific surface area (2800–3292 m^2 g^{-1}), a well-developed micro- and mesoporous structure, and the presence of graphene-like domains that enhance the electrochemical performance. Electrochemical tests showed that electrodes based on GLPC demonstrate a specific capacitance of 263 F g^{-1} and a coulombic efficiency of 99.4 % at a current density of 1000 mA g^{-1}, maintaining high stability after 5000 charge–discharge cycles, which confirms their effectiveness in energy storage systems;
- a method for modifying GLPC by chemical deposition of nickel hydroxide was proposed, which significantly improved the specific capacitance and cycling stability of the material;

- a technology for fabricating three-dimensional porous nickel current collectors with a hierarchical open interconnected pore structure was developed by applying a nickel-based slurry with pore-forming additives onto a metallic substrate followed by heat treatment;
- for the first time, integration of a CVD-grown graphene coating onto the surface of a three-dimensional porous current collector was realized, ensuring uniform distribution of the graphene layer and improved electrical conductivity;
- hybrid electrodes based on nanostructured MnO_2, deposited electrolytically onto the CVD-graphene-coated three-dimensional current collector, were obtained and demonstrated a high specific capacitance of up to 297 F g^{-1} at a current density of 250 mA g^{-1}, retaining 98 % of their capacitance after 5000 charge–discharge cycles.

Practical significance of the obtained results. The practical significance of the dissertation research lies in the development and implementation of technological solutions for the creation of high-performance electrode materials intended for use in supercapacitors and other energy storage systems.

During the course of the study, the following technical and instrumental solutions were designed and realized: - an apparatus for the thermochemical activation of carbon-containing materials (biomass); - a system and technology for producing three-dimensional porous current collectors and graphene deposition via chemical vapor deposition (CVD); - a technology for forming nanostructured manganese dioxide (MnO_2) on the surface of CVD-modified current collectors.

The developed technologies and equipment contribute to the creation of environmentally safe and economically efficient materials for energy storage systems, in accordance with the principles of sustainable development. The research results can be implemented in industrial production and utilized in the scientific and educational process for training specialists in materials science and engineering physics (technical physics).

Reliability and validity of the obtained results. The reliability of the results of the dissertation research is confirmed by the consistency of data obtained through a comprehensive set of modern physicochemical characterization methods. The research work was carried out in leading scientific institutions, including the laboratories of Satbayev University (KazNITU), Bes Saiman Groupp LLP, Al-Farabi Kazakh National University (KazNU), the Institute of Combustion Problems, and the University of Houston (USA).

Relevance to Scientific Priorities and State Programs. The dissertation research corresponds to the priority areas of development in materials science and energy and has been carried out within the framework of research projects and state programs, with the indication of their IRN codes and implementation periods:

1) AP05133792 – «Development and fabrication of supercapacitors based on nanoporous carbon materials derived from plant-based waste». Institute for Combustion Problems. (2018-2020);

2) NATO project – Valorization of biomass waste into high efficient materials for CBRN protection (reference G5636) (2020-2021);

3) AP05132875 – «Theoretical and experimental study of radiative processes in nanostructured carbon-based objects». Satbayev University. (2018-2020);

4) AP08856683 – «Development of hybrid supercapacitor electrodes based on nanostructured transition metal oxides/graphene/3D-porous metal» Institute for Combustion Problems. (2020-2022)

5) AP14869581 – «Development of a Cost-Effective and Scalable Method for Synthesizing Graphene-Like Structures from Biomass Waste for Electrochemical Energy Storage Devices» Institute for Combustion Problems. (2022-2024)

Personal Contribution of the Doctoral Candidate to Each Publication. Within the framework of the dissertation research, 11 scientific works were prepared and published, including 3 articles in journals recommended by the Committee for Quality Assurance in Science and Higher Education (CQASHE) of the Ministry of Science and Higher Education of the Republic of Kazakhstan for obtaining the PhD degree, 5 articles in international journals indexed in Web of Science and Scopus, and 3 patents. For each publication, the personal contribution of the doctoral candidate is clearly defined and includes: initiation of the research, development of methodology and experimental setups, synthesis and modification of materials, physicochemical and electrochemical characterization, data analysis, visualization, manuscript preparation and responses to reviewers, and patenting of the obtained results.

Publications.

Articles published in journals indexed in the international scientific databases Web of Science and Scopus:

1. **Yeleuov, M.**, Daulbayev, C., Taurbekov, A., Abdisattar, A., Ebrahim, R., Kumekov, S., ... & Batyrzhan, K. (2021). Synthesis of graphene-like porous carbon from biomass for electrochemical energy storage applications. *Diamond and Related Materials*, *119*, 108560. DOI:10.1016/j.diamond.2021.108560. (CiteScore: 6, Q2, Impact Factor: 4.3).

2. **M. Yeleuov**, C. Seidl, T. Temirgaliyeva, A. Taurbekov, N. Prikhodko, B. Lesbayev, F. Sultanov, C. Daulbayev, and S. Kumekov . Modified Activated Graphene-Based Carbon Electrodes from Rice Husk for Supercapacitor Applications // Energies 2020, 13, 4943, P. 1–10.; DOI:10.3390/en13184943, (CiteScore: 3.86, Q3, Impact Factor: 3).

3. Abdisattar, A., **Yeleuov, M.**, Daulbayev, C., Askaruly, K., Tolynbekov, A., Taurbekov, A., & Prikhodko, N. (2022). Recent advances and challenges of current collectors for supercapacitors. *Electrochemistry Communications*, 107373. DOI:10.1016/j.elecom.2022.107373 (Web of Science: IF 4.7, Q1, и Scopus: Cite Score – 8.5, 86-й процентиль).

4. Prikhodko, N., **Yeleuov, M.**, Abdisattar, A., Askaruly, K., Taurbekov, A., Tolynbekov, A., ... & Daulbayev, C. (2023). Enhancing supercapacitor performance through graphene flame synthesis on nickel current collectors and active carbon material from plant biomass. Journal of Energy Storage, 73, 108853. DOI: 10.1016/j.est.2023.108853 (Q1 Web of Science, Impact Factor (2023): 9.4).

5. Sultanov, F., Zhumasheva, N., Dangaliyeva, A., Zhaisanova, A., Baikalov, N., Tatykayev, B., **Yeleuov M.**, ... & Mentbayeva, A. (2024). Enhancing lithium-

sulfur battery performance with biomass-derived graphene-like porous carbon and NiO nanoparticles composites. Journal of Power Sources, 593, 233959. DOI:10.1016/j.jpowsour.2023.233959 (Q1 Web of Science, Impact Factor (2023): 8.41).

Articles Published in Journals Recommended by the Committee for Quality Assurance in the Field of Science and Higher Education of the Ministry of Science and Higher Education of the Republic of Kazakhstan

1. **Елеуов, М.А.**, Сейтжанова, Д.И. Ченчик, А.Т. Таурбеков, Ж.К. Елемесова, Ж.А. Супиева, З.А. Мансуров. Получение многослойных графенов из рисовой шелухи и скорлупы грецкого ореха. М.А. // Горение и плазмохимия. – 2018. – Т. 16. – №. 1. – С. 8-14.

2. Атаманова Т.С., **Елеуов М.**, Таурбеков А., Атаманов М.К. Разработка гибких электродов без применения полимерных связующих на основе активированных углей и углеродных нанотрубок // Горение и плазмохимия. – 20. – (2022). – 239-246.

3. Приходько Н.Г., **Елеуов М.А.**, Аскарулы К., Толынбеков А.Б., Таурбеков А.Т., Әбдісаттар Ә.Ә., Атаманов М.К. Исследование исходной растительной биомассы для объемного получения графеноподобных структур // Горение и плазмохимия. – 20. – (2022). – 221-231.

Patents obtained:

1. USA patent. Ebrahim, Rabi, **Mukhtar Yeleuov**, and Alex Ignatiev. Porous solid oxide fuel cell anode with nanoporous surface and process for fabrication. Application No. 16/709,016. Date of Patent : Jan. 28 , 2020;

2. Патент № 6564 РК. Способ изготовления пористого токосъемника для гибридных суперконденсаторов / **Елеуов М.А.** Әбдісаттар Ә.Ә., Приходько Н.Г., Таурбеков А.ЬТ., Толынбеков А.Б. Ақаруұлы Қ. // – Опубл. 22.10.2021.

3. Патент № 5404 РК. Способ получения графена и устройство для его осуществления / **Елеуов М.А.,** Мансуров З.А., Таурбеков А.Т., Лесбаев Б.Т., Смагулова Г.Т., Приходько Н.Г. // – Опубл. 02.10.2020.

Approval and Presentation of the Research

The results of the dissertation research were presented and discussed at international and national scientific forums, as well as during specialized seminars and meetings of departments and research institutes.