Abstract of the dissertation for the degree of Doctor of Philosophy (PhD) in the specialty "6D072000 - Chemical technology of inorganic substances"
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«New composite materials for lithium-sulfur batteries with improved energy capacity characteristics»

General description of the work

The dissertation work includes the synthesis of a graphene-like carbon material obtained from biomass and its use as a sulfur-storing agent for the cathode, as well as the synthesis of GPC-NiO composites for separator modification, the study of their physicochemical properties and the use of the GPC@S cathode and the GPC-NiO composite-modified separator for Li-S batteries and the study of the effective electrochemical characteristics and performance of the battery. Graphene-like porous carbon (GPC) with a high surface area was optimally synthesized from inexpensive and abundant rice husk waste by stepwise carbonization and thermochemical activation. The melt-diffusion method was used to deposit sulfur on the synthesized graphene-like porous carbon. GPC-NiO-based composites were synthesized with different GPC and $Ni(NO_3)_2$ ratios, and the effective composition was determined. The study results showed that the cell consisting of a GPC@S cathode and a GPC-NiO-20 modified separator accelerates the redox reactions of lithium polysulfide (LiPS) and suppresses the shuttle effect. The prepared graphene-like porous carbon (GPC) showed high efficiency as a sulfur-retaining matrix due to its significant specific surface area and pronounced mesoporosity. In addition, technological calculations were performed and designed.

Relevance of the work

Lithium-sulfur batteries are considered a promising energy storage system due to their high theoretical energy capacity (1675 mAh g^{-1}) and theoretical energy density (2600 W h kg^{-1}). However, there are some drawbacks that limit their practical application, such as the low electrical conductivity of sulfur (5×10^{-30} C/cm) and the shuttle effect caused by the dissolution of lithium polysulfides in the electrolyte, which is formed from its reduction products. The subsequent diffusion of dissolved polysulfides to the anode side, the volume expansion caused by the difference in the density of the products formed during sulfur reduction (sulfur 1.66 g cm^{-3} and Li_2S_2.03 g cm^{-3}), all of which cause side reactions, irreversible loss of active material and anode degradation, resulting in a rapid decrease in cell capacity stability. The relevance of the work lies in solving the main problems encountered in lithium-sulfur batteries: the shuttle effect of lithium polysulfide and volume expansion during long cycles. The use of biowaste for the production of materials such as activated carbon and graphene is of great scientific, economic and environmental importance. These nanostructured carbons have great potential for various applications, especially in the field of energy storage. In addition, the use of rice husk to produce graphene-like porous carbon is considered an effective and efficient solution. This is because waste rice husk is a low biodegradable material and has high thermal stability. Therefore, the effective use of biowaste is a new, environmentally friendly solution. By developing a highly efficient sulfur cathode

carbon matrix and separator modifier through carbonization and thermochemical activation of rice husk waste, this study presents solutions that can significantly improve electrochemical performance. It was shown that a cell consisting of a GPC@S cathode and a GPC-NiO-20 modified separator suppresses the shuttle effect. NiO provides strong chemical interactions with lithium polysulfides, which effectively suppresses the shuttle effect. However, NiO has insufficient electrical conductivity, which makes researchers need to create its composites with various carbon materials.

The purpose of the research work:

Synthesis of an effective graphene-like carbon sulfur-storing cathode material from waste biomass rice husk for lithium-sulfur batteries and composite materials for modifying the separator consisting of graphene-like carbon and nickel oxide

The tasks set to achieve the research objectives:

1. Synthesis of graphene-like carbon-GPC material from rice husk, which is considered a bio-waste, and characterization of its properties.
2. Preparation and characterization of a GPC@S cathode consisting of graphene-like carbon and sulfur synthesized from rice husk for Li-S batteries.
3. Synthesis and characterization of a GPC/NiO composite consisting of graphene-like carbon and nickel oxide as a separator modification agent.
4. Study of electrochemical performance of a lithium-sulfur battery consisting of a GPC@S cathode and a GPC-NiO modified separator.
5. Presentation of a technological scheme and calculations for the manufacture of a lithium-sulfur battery consisting of a GPC@S cathode and a modified GPC-NiO-20 separator.

Research methods

Energy-dispersive spectroscopy Scanning electron microscope (SEM), transmission electron microscopy (TEM), Raman spectroscopy, XRD X-ray diffraction (XRD) equipped with (EDS)method, X-ray photoelectron spectroscopy (XPS), thermogravimetric analysis (TGA), cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), chronoamperometry (CA)

Object of the study

Graphene-like carbon synthesized from rice husk - GPC material, GPC/NiO composite, GPC@S cathode, and lithium sulfur cells with GPC@S cathode and modified separators

Research subject

Research subject: Capacity, efficiency, discharge/charge potential, nucleation of product formation, polysulfide adsorption ability of the composite, redox potential

Main principles of the defense

1.The graphene-like porous carbon material synthesized from rice husk biomass demonstrates effectiveness as a host material for sulfur loading into pores due to its high specific surface area (2143.5 m^2/g), pore volume (1.02 cm^3/g) (including micro-, meso-, and macropores), and a graphitization degree of 29.13%. Graphene-like porous carbon material synthesized from rice husk biomass effectively immobilizes sulfur for constructing lithium–sulfur battery cathodes due

to its high specific surface area, large pore volume, and well-developed micro- and mesoporous structure.

2. Incorporation of nickel oxide (NiO) into GPC exerts a catalytic effect by increasing the oxidation and reduction rates of polysulfides in the active material of the Li–S cell. Additionally, GPC acts as a physical barrier against polysulfide dissolution, while nickel oxide serves as a chemical barrier due to its polar nature. Nickel (II) oxide nanoparticles synthesized on the surface of graphene-like porous carbon enhance the oxidation and reduction rates of lithium polysulfides through their catalytic effect.

3.The cell with the GPC@S cathode and the GPC-NiO-20 modified separator exhibits a higher initial capacity (1519 mAh/g at 0.2C for the GPC-NiO-20 separator vs. 1190 mAh/g for the unmodified separator) and improved cycling stability (870 mAh/g after 100 cycles with GPC-NiO-20 separator compared to 589 mAh/g for the unmodified separator).

Main results of the study

1. Graphene-like porous carbon (GPC) with a high specific surface area was efficiently synthesized from rice husk biological waste through carbonization and thermochemical activation processes.

2. It was established that the surface of GPC possesses a highly developed macroporous structure with pore diameters ranging from 15 to 30 μm.

3. The calculated degree of graphitization in the activated GPC was approximately 29.13%. The measured specific surface area of GPC was 2143.5 m^2/g, and the total pore volume was 1.020 cm^3/g.

4. For the first time, graphene-like porous carbon (GPC) was used to fabricate a sulfur cathode via the molten diffusion method.

5. GPC composites modified with NiO nanoparticles were synthesized in various compositions and ratios of GPC to $Ni(NO_3)_2$, which demonstrated effectiveness as separator modifiers.

6. It was found that the specific surface area of the composite significantly increased to 2476.6 m^2/g due to the incorporation of NiO nanoparticles into the GPC structure.

7. It was shown that a cell with a GPC@S cathode and a GPC-NiO-20 modified separator accelerates the redox reactions of lithium polysulfides and reduces the shuttle effect. In particular, the GPC@S/GPC-NiO-20 cell demonstrated a high initial discharge capacity (1519 mAh/g at 0.2 C), long-term cycling performance (capacity fading of 0.091% over 400 cycles at a current rate of 1 C), and high-rate capability (568 mAh/g at 2 C).

8. For the first time, a conceptual technological scheme was developed for the production of composite materials for the fabrication of a lithium-sulfur battery with a GPC@S cathode and a GPC-NiO-20 modified separator.

Justification of the novelty and significance of the obtained results

This work presents the first successful development of graphene-like porous carbon (GPC) composites decorated with sulfur and NiO for use as cathode and separator materials in lithium–sulfur batteries. The synthesis of GPC from rice husk biomass via carbonization and thermochemical activation represents a novel,

environmentally friendly approach that significantly enhances the electrochemical performance of lithium–sulfur batteries. This method utilizes the high surface area and mesoporosity of GPC to efficiently accommodate sulfur, thereby improving the performance of the sulfur cathode. In addition, the work proposes the use of GPC-NiO composites as separator modifiers in lithium–sulfur batteries, offering a new concept to mitigate the shuttle effect of lithium polysulfides. The significance of this study lies not only in the innovation of new materials and methods, but also in the ecological efficiency of utilizing biomass waste (rice husk) as a resource for advanced battery materials. The results contribute to the development of high-performance, environmentally friendly energy storage solutions and offer one of the effective approaches for advancing lithium–sulfur battery technologies.

Theoretical significance

The theoretical significance of this study lies in the development of a new approach to improve the performance of lithium-sulfur batteries by using biomass-derived graphene-like porous carbon (GPC) as a sulfur-hosting matrix and NiO-decorated GPC as a separator modifier. This work provides insight into how sulfur-based graphene-like materials and metal oxide composites can improve electrochemical performance by addressing key issues such as the shuttle effect and volume expansion in lithium-sulfur batteries. In addition, the study contributes to the theoretical basis for utilizing biomass waste as a sustainable source of high-performance battery materials, providing a new direction for designing efficient energy storage systems.

Practical significance

The practical significance of this study lies in the development of a stable and efficient sulfur host and separator modifier for lithium-sulfur batteries that enhance their electrochemical performance, cycling stability, and rate capability. The use of graphene-like porous carbon (GPC) derived from biomass offers a cost-effective and environmentally friendly alternative to conventional materials, making it a promising approach for the future of high-performance, environmentally friendly energy storage systems.

Compliance with the directions of scientific development or state programs (projects)

The dissertation work was carried out within the framework of the following project: National Laboratory Astana, Center for Science on Energy and New Materials, code: OPFE2021001 "New materials and devices for defense and aerospace applications", budget program 008 "Applied scientific research in the field of space activities and information security", subprogram 102 "Scientific research within the framework of program-targeted financing from the republican budget" 2021-2023.

The author's personal contribution to the study is the preparation and analysis of literature data on the topic of the dissertation, synthesis of GPC@S cathode, conducting experiments on the synthesis of NiO-decorated GPC, cell assembly, summarization and analysis of results

Approbation of the work

The main statements and results of the dissertation were presented and discussed at the following international and national conferences:

10th International Conference (INESS–2023) in collaboration with mESC-IS 2023, July 17–21, 2023, Muğla University, Akyaka, Turkey.

International Scientific and Technical Conference METE–2023, May 15–19, 2023, Minsk, Republic of Belarus.

11th International Conference (INESS–2024), August 7–9, 2024, Nazarbayev University, Astana, Kazakhstan.

Description of the contribution of the doctoral student to the preparation of each publication

1. Fail Sultanov, Nazerke Zhumasheva, Akmaral Dangaliyeva, Azhar Zhaisanova, Nurzhan Baikalov, Batukhan Tatykayev, Mukhtar Yeleuov, Zhumabay Bakenov, Almagul Mentbayeva, “Enhancing lithium-sulfur battery performance with biomass-derived graphene-like porous carbon and NiO nanoparticles composites”-Journal of Power Sources-2024-conducting experiments, writing the original article

2. N. Zhumasheva.,M. Tursynbek, F. Sultanov, A. Mentbayeva, L. Kudreeva, Zh. Bakenov “Porous graphene-like carbon composite based on rice husk with nickel oxide nanoparticles for lithium-sulfur batteries” Izvestiya NAN-RK-2024№4- conducting experiments, writing the original article

Scope and structure of the dissertation

The dissertation consists of an introduction, 4 chapters, a conclusion, 101 pages and includes 25 figures, 10 tables, and 142 bibliographic citations.