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 with high energy density for lithium-sulfur batteries"

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)

Instrumentation

Potentiostat/galvanostat Bio-Logic SP300 and VSP300, 120 kV, scanning electron microscope (SEM) Crossbeam 540 equipped with energy-dispersive spectroscopy (EDS), transmission electron microscopy (TEM) (JEOL JEM - 1400 Plus, 120 kV) Raman spectroscopy study (LabRAM, Horiba), XRD analysis using CuKα radiation (k = 0.15418 nm) was carried out on an X-ray diffraction system - SmartLab (Rigaku). Chemical bonds and interactions were studied using X-ray photoelectron spectroscopy (XPS, NEXSA, Thermo Scientific) and a monochromatic low-power Al Ka X-ray source with an energy of 1486.6 eV. Thermogravimetric analysis (TGA) was used to determine the sulfur content in the composite GPC@S matrix, and a Neware battery analyzer was used to study the electrochemical performance

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. Graphene-like porous carbon material (GPC) obtained from rice husk biomass thermochemically activated with KOH at 800°C has an average specific surface area of 2105m^2/g, which is a highly effective host for sulfur. The sulfur content incorporated into the GPC structure by the molten diffusion method is 60 wt.%.
2. NiO nanoparticles synthesized on the GPC surface at 400°C in the ratio of GPC:$Ni(NO_3)_2$ = 80:20 increase the specific surface area of the composite from 2105m^2/g to 2432m^2/g, which improves the chemical interaction with LiPSs. The use of GPC-NiO-20 composite as a separator effectively suppresses the shuttle effect of lithium polysulfides, which was proven by the following methods: discoloration of the Li_2S_6 solution within 5 minutes, formation of polythionates (XPS), high Li_2S nucleation capacity (129.2 mA h/g) and reduced charge transfer resistance (Rct = 54Ω, EIS).
3. The cell modified with the GPC@S cathode and the GPC-NiO-20 modified separator showed an initial discharge capacity of 1498 mA h/g (0.2C) and retained 928 mA h/g after 60 cycles, with a coulomb efficiency of about 98%. At high current load (1C), the cell operated with an initial capacity of 1142 mA h/g and retained 629 mA h/g after 200 cycles. The capacity loss per cycle is 0.091%, and it works stably for 400 cycles.

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 found by BET BJH method that most of the pores on the GPC surface have a developed structure in the range of 1-4 nm.
3. The graphitization degree of the activated GPC was estimated to be about 29.13%. The measured average specific surface area of GPC was 2105 m^2/g.
4. Graphene-like porous carbon (GPC) was used to fabricate a sulfur cathode for the first time by the melt diffusion method.
5. GPC composites modified with NiO nanoparticles with different compositions and ratios of GPC to $Ni(NO_3)_2$ were synthesized and shown to be effective as separator modifiers.
6. It was found that by incorporating NiO nanoparticles into the GPC structure, the specific surface area of the composite was significantly increased, reaching 2432 m^2/g.
7. It was shown that the GPC@S cathode and the GPC-NiO-20 modified separator accelerated the redox reactions of lithium polysulfides and reduced the shuttle effect. In particular, the GPC@S/GPC-NiO-20 element demonstrated high initial discharge

capacity (1519 mAh/g at 0.2 C), long cycle stability (0.091% capacity loss at 1 C over 400 cycles), and high current density performance (568 mAh/g at 2 C).
8. For the first time, a principle technological scheme for the production of composite materials for the manufacture of a lithium-sulfur battery with a GPC@S cathode and a modified GPC-NiO-20 separator was developed.

Justification of the novelty and significance of the obtained results

This work presents the first successful development of sulfur and NiO-decorated graphene-like porous carbon (GPC) composites for use as cathode and separator materials in lithium-sulphur batteries. Synthesis of GPC from rice husk biomass via carbonization and thermochemical activation is 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, resulting in improved sulfur cathode performance.

In addition, the work proposes the use of GPC-NiO composites as separator modifiers in lithium-sulfur batteries, a novel concept that can help reduce the shuttle effect of lithium polysulfides. The composite separator of GPC with NiO nanoparticles is designed to enhance the oxidation-reduction reaction of lithium polysulfides. can effectively interact and catalyze with the products of the reaction, resulting in improved cyclic stability and electrochemical performance of the batteries. Among the GPC@S/GPC-NiO composites developed in this study, the composition-optimized GPC@S/GPC-NiO-20% cell showed excellent long-term cyclic performance, excellent discharge capacity and rate capability. The combination of GPC-based sulfur cathodes and GPC-NiO modified separators is an innovative approach to improve battery performance.

The significance of this study lies not only in the novelty of the new materials and methods, but also in the environmental efficiency of using 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 provide one of the effective methods in the development of 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 conclusions and results of the dissertation were orally presented and discussed at the following International and Republican conferences:

"10th International Conference on Nanomaterials and Modern Energy Storage Systems (INESS–2023)." Held from July 17 to 21, 2023, at Mugla University, Akyaka, Turkey. The conference was jointly organized with mESC-IS 2023.

International Scientific and Technical Conference "Modern Electrochemical Technologies and Equipment – 2023" (METE–2023), held from May 15 to 19, 2023, in Minsk, Belarus.

"11th International Conference on Nanomaterials and Modern Energy Storage Systems (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 sections, conclusions and a list of 165 references. The work consists of 122 pages, includes 30 figures, 14 tables and 165 bibliographical references.