ABSTRACT

for the thesis on the topic

«ELECTRODE COMPOSITES FOR SUPERCAPACITORS BASED ON CARBON MATERIALS AND METAL OXIDES»

submitted for the degree of Doctor of Philosophy (PhD) in the educational program 8D07110 - "Materials science and technology of new materials"

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General characterization of the work. The thesis is devoted to the experimental production of composites of carbon materials and metal oxides for the development of electrodes for electrochemical energy storage, as well as the study of the morphology and electrical properties of electrodes based on synthesized and reduced cobalt oxide and a composite consisting of synthesized activated carbon and cobalt oxide.

Relevance of the study.

In order to increase the capacity of supercapacitors, hybrid electrodes are often created using carbon materials (activated carbon, carbon nanotubes, graphene, etc.), which provide a high specific surface area, and nanoparticles of transition metal oxides, which exhibit a pseudo-capacity effect.

Along with other transition metal oxides, the use of cobalt oxide in the manufacture of capacitor electrodes is a common practice and a promising route to achieve high capacitance due to the wide range of redox reactions, high theoretical capacitance, low cost, and availability of electrical conductivity.

However, to our knowledge, there are very few reports of the use of metal nanoparticles coated with a thin layer of oxide grown in anodic oxidation during electrochemical measurements to obtain high capacitance. At the same time, this approach has a number of advantages: the array of metal nanoparticles and the small thickness of the thin oxide provides low serial resistance of the electrode, the small thickness of the oxide-hydroxide contributes to fast kinetics and a wide range of Faraday reactions. Therefore, this work presents studies on the creation of a hybrid capacitor from cobalt metal, obtained by reducing cobalt oxide in a hydrogen atmosphere.

Various techniques, such as the development of zero-dimensional, one-dimensional, two-dimensional and three-dimensional nanostructures, have been implemented to synthesize battery-type electrodes based on Co_3O_4 with high specific capacity and high mass load. However, these electrodes have relatively low electronic conductivity and large volume changes. To achieve high pseudo-capacitive characteristics of Co_3O_4 electrodes, it is necessary to use nanoparticles or thin oxide films with a large specific surface area and pseudo-capacitive properties. Therefore, in this work, cobalt oxide particles are synthesized by various methods, such as pyrolysis of an aerosol from cobalt acetate and a chemical deposition method to obtain electrodes with a high specific capacity.

Analyzing the performance indicators of the researchers' recent work, it became clear that a load of at least 10 mg cm^{-2} is very important for predicting the

characteristics of commercial electrodes of electrochemical capacitors. It is necessary that the active layer of the electrodes has a thickness of at least 100 μm and a load of at least 10 mg cm^{-2}. Such a high load is difficult to achieve by the hydrothermal method or electrodeposition, although these methods provide good electrical and mechanical contact with the conductive substrate. Volumetric specific capacity in the production of supercapacitors is also very important; highly porous materials and aerogels do not satisfy this condition. Our results on electrode formation using active material powder and suitable binder polymer such as PVDF, PTFE are suitable for achieving high load. This method is practically important because of its scalability, so it is developing intensively.

Research that could potentially provide additional cost and performance benefits in the development of supercapacitors is highly relevant. Symmetrical capacitor designs, in which both electrodes are made of the same material and have the same mass and area, have a simplified manufacturing process and require simpler manufacturing processes compared to asymmetric systems. Thus, symmetrical capacitor designs are Interesting from the point of view of efficiency in mass production. However, the capacitance of symmetrical capacitors made of activated carbon (AC), which is the most common material for supercapacitors, cannot be optimized. This is because the potentials of the anode and cathode electrodes of the AC capacitor are not symmetrical. Therefore, the research presented in the dissertation on the creation of a supercapacitor with symmetrical electrodes based on a composite of cobalt nanoparticles and synthetic activated carbon Co@AC is an urgent work.

Objects of study. Carbon materials, Co_3O_4 nanoparticles, Ag nanowires, electrodes for capacitors made of Co_3O_4 and reduced Co_3O_4 and Co@AC composite.

Study subject. The development of methods for producing a composite based on cobalt nanoparticles and synthetic activated carbon Co@AC and the study of their structure and electrochemical properties.

The aim of the thesis research. Research of experimental methods of synthesis of materials for creation of electrodes of supercapacitors, production of prototypes of electrochemical capacitors.

The following tasks were implemented to achieve the assigned aim:

- work out methods for obtaining cobalt oxide nanopowders for the manufacture of supercapacitor electrodes;
- develop a method for the synthesis of activated carbon with cobalt nanoparticles with specified characteristics;
- investigate the characteristics of the obtained materials and to develop methods for achieving high electrochemical parameters of the electrodes;
- study the effect of various technological treatments on their electrochemical properties.

Research methods: Scanning (SEM) and transmission (TEM) electron microscopy, X-ray diffraction (XRD), Raman spectroscopy, Electrochemical impedance spectroscopy (EIS), Cyclic voltammetry (CV), Galvanostatic charge-discharge method (GCD), X-ray photoelectron spectroscopy (XPS), BET method (gas adsorption/desorption method), Energy dispersive X-ray spectroscopy (EDX)

Scientific novelty of the research:

The novelty and originality of the thesis is that for **the first time** in it:

- Electrochemical activity and specific capacity of Co_3O_4 nanoparticles before and after reduction treatment of the material were studied, a significant improvement in electrochemical parameters was achieved.
- Reduction annealing regimes for the formation of a thin electrochemically active layer responsible for the effect of increasing the specific capacitance of electrodes made of Co_3O_4 nanoparticles have been studied.
- The features of the transformation of the structure of Co_3O_4 nanocrystals into the CoO phase during reduction treatment, and the reverse transition from the CoO structure to the Co_3O_4 structure during oxidation are studied .
- A method for creating a supercapacitor with symmetrical electrodes based on a composite of cobalt nanoparticles and synthetic activated carbon Co@AC has been investigated.

Statements submitted for defense:

1. The electrode capacity enhancement in Co_3O_4 is achieved by subjecting Co_3O_4 powders to reductive treatment in a hydrogen atmosphere at temperatures below 300 °C for a duration not exceeding one hour, followed by controlled mild oxidation.
2. The reductive treatment of electrodes fabricated from Co_3O_4 nanoparticles increases their specific capacity by more than fourfold without compromising their structure, with the Co^{2+}/Co^{3+} transition making a significant contribution to the current response.
3. Surface activation of Co_3O_4 nanoparticles and enhancement of electrode electrochemical activity are achieved through recrystallization, where the transformation of Co_3O_4 nanocrystal structure into the CoO phase and the increase in Co^{2+} state concentration are initiated by reductive treatment.
4. The formation of a composite based on cobalt particles and synthetic activated carbon (Co@AC) for a symmetric supercapacitor enables a ~3-fold increase in the capacity of the positive electrode through Faradaic reactions, while maintaining the capacity of the negative electrode.

Scientific and practical significance of the study:

The scientific and practical significance of this research lies in the development of novel approaches for creating composite materials based on carbon structures and metal oxides, which markedly enhance the performance parameters of electrochemical capacitors. The use of activated carbon and cobalt nanoparticles increases the specific capacitance of electrodes due to the synergistic interaction of

materials, resulting in improved reversible capacity and enhanced stability during cyclic charge-discharge processes. This is particularly crucial for modern supercapacitors intended for energy storage and conversion applications, where high energy density, durability, and resistance to electromechanical stresses are essential.

The synthesis and structural modification of Co_3O_4-based composites using nanoparticles have enabled the improvement of their electrochemical properties by forming a thin active layer with low resistance, capable of sustaining high redox reaction rates. The creation of electrodes with a symmetrical design optimized for high capacitance simplifies manufacturing processes and reduces costs, making these innovations promising for industrial-scale energy storage device production. The findings of this work are of significant importance for enhancing the efficiency and economic feasibility of energy storage systems, meeting both scientific and applied needs.

Compliance with directions of science development or government programs.

The thesis was carried out within the framework of grant-funded research projects AP09058501 "Development of technological foundations for the creation of nanostructured materials promising for energy storage and photoelectrochemical devices" 2021-2023, AP09259253 "Development of carbon compositions for electrochemical energy storage and storage devices" (2021-2023.

The author's personal contribution.

The statement of the purpose and objectives of the thesis was carried out with the scientific supervisor Professor Abdullin Kh.A. All experimental work on the production of Co@AC composites and silver nanofilaments was carried out by the author personally. The author also carried out a set of experimental measurements to study X-ray diffraction and electrochemical characteristics. Experimental studies of the morphology of the surface and measurement of the Raman spectra of synthesized samples were obtained with the assistance of a research group of employees of the National Nanotechnology Laboratory of the Open Type of al-Farabi KazNU and the University of the West of Scotland, Faculty of Engineering, Computer Science and Physical Sciences (Paisley, UK). All the results obtained and presented in the dissertation work were discussed with the scientific supervisor Professor Abdullin Kh.A. The author jointly by the supervisor participated in the writing of scientific articles and testing research results during her participation in major-specific scientific events (conferences, seminars, round tables, etc.).

Approbation of the conducted research.

The results of this work were presented at the following international and foreign conferences: «The 8th International Conference on Nanomaterials and Advanced Energy Storage System INESS-2020», (Astana, 2019); «International Scientific Conference of Students and Young Scientists «Farabi alemi», (Almaty, 2021); XVI conference "Physicochemical problems of renewable energy" (St. Petersburg 2021).

Publications.

According to the results of the dissertation work 9 printed papers have been published, including 3 articles in international peer-reviewed scientific journals included in Q3 quartile, according to Journal Citation Reports of Clarivate Analytics company and/or having Cite Score percentile in Scopus database, 3 articles in journals recommended by the Committee for Control of Higher Education and Science**,** 3 papers in proceedings of scientific and practical international conferences.

Scope and structure of the dissertation.

The dissertation contains a list of notations and abbreviations, an introduction, the main part of 8 sections, a conclusion, a list of used sources and an appendix. The total volume of the thesis is 108 pages with 79 figures, 3 tables and a list of 153 references.