ANNOTATION

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of

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Synthesis and application of nanoporous carbon electrode materials based on vegetable fibers

The general description of work. The dissertation is devoted to experimental studies of the synthesis of nanostructured carbon materials and their use in three directions: creation and application of capacitors with an electric double layer (supercapacitors), capacitive deionization of aqueous solutions, and electrochemical deposition of gold (III) ions.

The relevance of the research topic. Carbon materials with a high specific surface area are widely used in industry, medicine, and various sectors of the national economy. Activated carbon can be obtained from almost any carbon-containing material (walnut shell (WS), rice husk (RH), apricot kernel, grape seed, etc.), by physical or chemical activation methods. In particular, it is promising to use them as electrode materials for capacitors with an electric double layer, capacitive deionization of aqueous solutions, as well as the electrochemical extraction of gold from leaching solutions.

First, the relevance of research in the field of capacitors with DEL lies in the importance of their practical application. Today, energy consumption is growing at a high rate and the development of alternative energy sources, as well as devices for its accumulation and storage, is of current and paramount importance. Nevertheless, the modern world market is represented by fully justified devices for generating and storing electricity - fuel cells, batteries, galvanic cells and supercapacitors (SC), but the search for more efficient devices does not stop. Despite a significant number of publications on the creation of a SC, the issue of developing the most efficient SC remains unresolved. This is due to the huge variety of materials used for SC electrodes and various scientific approaches in their creation. However, with a variety of approaches to studying SC, the main attention of scientists is aimed at obtaining new forms of materials with a high specific surface area and a developed nanoporous structure, inexpensive to manufacture, as well as new high-energy electrolytes. Ultimately, electrodes should be obtained that have a sufficiently high electrical capacity, low resistivity, high charge-discharge characteristics, mechanical strength, chemical inertness to electrolyte components and high thermal conductivity to dissipate heat release due to ohmic losses.

Currently, in many regions of Kazakhstan, there is an acute shortage of fresh water in the presence of sources with mineralized and low-mineralized water, the device of capacitive deionization (CDI) will solve the problem of water

desalination with high economic efficiency. The growing problem of water supply directly affects the quality of life and economy of various regions of the Republic of Kazakhstan, especially Mangystau, West Kazakhstan and Kyzylorda regions, although it is not limited to these regions. In these regions, water purification is carried out at a number of enterprises, such as "MAEK" and "Caspian", although their capacities are objectively insufficient, which, together with the underdeveloped associated infrastructure, leaves the issue of water supply unresolved. In this regard, in recent decades, a method of capacitive deionization (desalination) of aqueous solutions has been developed, which is a promising and economical method of water desalination. This method consists in pumping aqueous solutions between two porous electrodes having a highly developed surface area, to which a certain potential difference is applied. When an electric current is applied to the electrodes, a potential difference arises and a double electric layer is formed on the surface of the polarized electrodes. The formation of an electric double layer (EDL) is accompanied, respectively, by the adsorption of anions on the positive electrode and cations on the negative electrode. This process of charging and discharging the plates of the electric double layer is also similar for SC.

The processing of man-made raw materials is currently of great importance, since a huge amount of man-made waste containing non-ferrous and ferrous metals has been accumulated, in this regard, the scientific and technical policy of the Republic of Kazakhstan is aimed at creating energy-saving technologies and devices, which makes it possible to ensure the complexity of the use of raw materials and exclude the formation of harmful emissions and waste. Gold is one of the precious metals that plays an important role in the global economy. Gold is mined from ores by two main methods: gravity (dredges, industrial instruments, trays, etc.) and hydrometallurgical. AC is widely used for the extraction, separation and concentration of gold. The world is constantly looking for precursors for the manufacture of AC at low costs. In this regard, ACs synthesized by carbonization of plant waste are relevant. Particularly noteworthy is the cost-effective and affordable raw material - rice husk, which is a waste in the processing of rice.

When performing a doctoral dissertation, ACs were synthesized from RH and WSh with optimal pore architecture and high specific surface areas. Studies of electrode processes using the obtained nanostructured carbon materials have been carried out. Their use made it possible to increase the capacitive characteristics of electrodes in SC, capacitive deionization.

The purpose of the work. The aim of the dissertation work is to optimize methods for obtaining carbon materials with a high specific surface area and to determine the features of the use of the materials obtained in the processes of energy storage in capacitors with an electric double layer, capacitive deionization, as well as for the extraction of gold (III) ions from aqueous solutions.

The tasks of work. To achieve the goal of the dissertation work, the following tasks were set:

1 To synthesize nanoporous carbon materials by optimized methods of chemical activation, as well as to determine the morphological features of the surface of the obtained carbon materials using physicochemical research methods.

2 To reveal the capacitive characteristics of electrodes obtained from activated carbons in test cells of capacitors with an electric double layer with promising inorganic electrolytes.

3 Determine the electrosorption capacity of the obtained carbon materials in the process of capacitive deionization of aqueous solutions with different concentrations of dissolved salts.

4 Establish the sorption capacity of carbon electrode materials used in the process of electrochemical deposition of gold ions from chloride solutions

The main provisions for the defense:

1 Effective nanoporous structures (ENS), based on WS and RH, including micro- and mesopores and surpassing known analogs by 35-55% in specific surface area, can be obtained by the method of physicochemical activation using H_3PO_4 at 400 °C to obtain ENS based on WS and with KOH at 800 °C for ENS based on RH.

2 Composite nanoporous materials based on carbon (80-85%), acetylene black (5-15%) and polyvinylidene fluoride (5-10%) are characterized by improved electrochemical parameters, such as specific electrical capacity (250-300 F/g), internal resistance (~ 0.3 Ohm), stability of capacitance when cycling more than 5000 charge / discharge, and are promising for creating capacitors with EDL with inorganic electrolytes and electrodes for CDI.

3 In nanoporous composites containing carbon (80-85%), acetylene black (5-15%) and polyvinylidene fluoride (5-10%), a significant increase in the diffusion rate is observed during metal electrodeposition using a solution flow of 10 ml / min gold ions, which makes it possible to significantly increase the concentration of the deposited metal from dilute solutions.

The object of study are nanoporous carbon electrode materials based on WS and RH.

The subject of study are the electrochemical and sorption processes occurring on the obtained carbon nanostructured materials used in capacitors with DEL, desalination of aqueous solutions, as well as in the extraction of gold (III) ions.

The Research Methods. The following research methods were used in the work: scanning electron microscopy, optical microscopy, energy dispersive analysis, X-ray phase analysis, X-ray fluorescence analysis, BET analysis, the method of low-temperature adsorption / desorption of nitrogen, temperature-programmed desorption, Raman spectroscopy, atomic absorption thermal carbonation, chemical activation, cyclic voltammetry, chronoamperometry, galvanostatic cycling with potential limitation, electrochemical impedance spectroscopy, electrochemical quartz microbalance, hydrometallurogic method.

The scientific novelty of the research. In this work, the following results are obtained, which are of scientific novelty:

1 It was established for the first time that in nanoporous structures with a mesopore volume of 0.88 cm^3/g and micropores of 0.97 cm^3/g, a width of less than 2 nm based on WS and RH, a specific surface area can be achieved that exceeds by 35-55% existing commercial world analogues.

2 For the first time, the optimal textural parameters for the synthesis of composite nanoporous materials based on carbon, acetylene black and PVDF have

been revealed, which make it possible to significantly improve the electrochemical characteristics of capacitors with EDL and electrodes for CDI.

3 It is shown that during electrodeposition, the concentration of the extracted metal from dilute solutions is determined by the composition of the nanoporous composite and the rate of the circulating solution flow.

The theoretical significance. Until now, the issues of the optimal macro- and microstructure of the electrode material to reduce the diffusion restrictions on the movement of ions during electrochemical processes remained unresolved. The theoretical significance of the work lies in the fact that it developed ideas about the optimal hierarchical pore structure for the effective operation of electrodes in electrochemical devices.

The practical significance

1 The technology for the synthesis of effective nanoporous CMs based on WS and RH using the method of physicochemical activation has been worked out, which makes it possible to obtain ENS, which surpasses known analogs by 35-55% in specific surface area.

2 Composite nanoporous materials with improved electrochemical parameters reaching 300 F/g in electrical capacity, 0.3 Ohm internal resistance and capacitance stability when cycling more than 5000 charge/discharge, are promising for creating capacitors with EDL and electrodes for CDI.

3 It was found that the use of a nanoporous composite based on carbon in the electrodeposition of gold ions from dilute solutions by means of circulation makes it possible to achieve a gold yield of up to 190 mg per 1 g of carbon.

4 A technological scheme is proposed for the extraction of noble metals from dilute solutions using a nanoporous composite based on carbon in combination with electrical absorption, which makes it possible to significantly increase the yield of pure metal.

Relationship with research and government programs. The dissertation "Synthesis and application of nanoporous carbon electrode materials based on plant fibers" presented for defense was carried out within the framework of the program of applied research, with the support of the Ministry of Education and Science of the Republic of Kazakhstan, on the topics: NoAP05134691 "Development of a method for electrochemical concentration of noble metals using nanoporous electrode materials" and NoAP05133792 "Development and creation of supercapacitors based on nanoporous carbon materials obtained from plant waste" (2018-2020).

The approbation of work. The main provisions and results were reported and tested at the following conferences and symposia: V-VII International Conference on Nanomaterials and Advanced Energy Storage Systems "INESS-2017", "INESS-2018", "INESS-2019" (Astana); X International Symposium on Physics and Chemistry of Carbon and Nanoenergy Materials (Almaty, 2018); XI International Symposium on Combustion and Plasma Chemistry (Almaty, 2019); World Carbon Conference "Carbon 2018" (Spain, Madrid, 2018); World Carbon Conference "Carbon 2019" (USA, Lexington, 2019); Materials of the conference of students and young scientists dedicated to the 30th anniversary of the establishment of the Institute of Combustion Problems (Almaty, 2017); Materials

of the III conference of students and young scientists "Chemical physics and nanomaterials" dedicated to the memory of Batyr Mansurov (Almaty, 2018); Proceedings of the conference of students and young scientists "Problems of technological combustion" dedicated to the memory of associate professor Kazakov Yuri Viktorovich (Almaty, 2018); V International Scientific Conference "Modern Problems of Condensed Matter Physics, Nanotechnologies and Nanomaterials" (Almaty, 2018); XVI International Forum-Competition of Students and Young Researchers "Topical Issues of Rational Use of Natural Resources" (Russia, St. Petersburg, 2020).

The personal contribution of the author consists in setting up and conducting experiments, determining methods of analysis and ways to solve the set practical and theoretical problems, generalizing and interpreting the results obtained, writing articles and reports.

The publications.

The main results of the dissertation work were published in 29 printed works, of which 6 articles are included in the Scopus database, 6 publications are in publications recommended by the Committee for Control in Education and Science of the Republic of Kazakhstan; 15 printed works - in collections of international scientific and practical conferences and symposia, 2 patents for a useful model of the Republic of Kazakhstan were received.

The volume and structure of the work. The dissertation work is presented on 108 pages of typewritten text and includes 57 figures and 13 tables. The work consists of an introduction, a review of the literature, a description of objects and research methods, results and their discussion, a conclusion and a list of used sources of 153 titles.

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