ABSTRACT

of the PhD thesis in specialty “6D072000- Chemical technology of inorganic substances” of **Kokhmetova Saule Talgatovna**

on the topic “New cathode materials for sodium-ion batteries”

General characteristics of the work

The dissertation is devoted to the synthesis of new substances, the study of their physical-chemical properties and the manufacture of cathodes based on them for a sodium-ion battery. In the course of the work, new materials of the composition $K_{2-x}Na_xMn_2(SO_4)_3$ (x=0; 0,5; 1,0; 1,3; 1,4) and $NaFe(SO_4)_{1,5}A_{0,5}$ (A= SO_4, SeO_4, PO_3F, HPO_4), were synthesized, their physicochemical properties were investigated, and the possibility of their use as cathode materials for a sodium-ion battery was evaluated. In addition, a new method was proposed to increase the conductivity of a cathode mixture based on an active material, a dielectric, taking into account its structural properties and the proposed mechanism of the sodium intercalation process.

Relevance of the research topic

The daily increase in living standards implies an increase in electricity consumption, which requires various universal energy storage devices for large-scale renewable energy processing plants, electric vehicles and portable electronic devices, etc. Based on the latest estimates provided by the U.S. Energy Information Administration, global energy consumption is expected to increase by almost 50% by 2050. In this connection, there is a growing need for energy storage systems, both small-sized (batteries/batteries) used for consumer electronics and electric vehicles, and large-sized energy storage systems used in conjunction with renewable resource processing stations (solar, wind, geothermal energy, tidal energy). In addition, forecasts suggest an almost doubling of electricity production from renewable resources by 2050. Lithium-ion batteries suitable for these purposes, along with their advantages, have a number of disadvantages (flammability, toxicity, high cost and limited lithium resources), can be partially replaced with other metal-ion batteries. In addition, the use of large-sized energy storage systems requires the use of a huge amount of lithium resources, so only common elements should be considered. One of the alternatives to lithium can be sodium, which has no problems with high cost, due to the widespread availability of sodium salt resources around the globe.

Sodium-ion batteries with a similar mechanism of intercalation/deintercalation of ions, as in lithium-ion batteries, have been proposed as promising alternative energy storage systems due to the possibility of using widespread sodium resources, which is an essential criterion for large-sized energy storage systems that impose higher requirements on the cost of materials. Intercalation materials for sodium-ion battery electrodes are quite limited. In addition, they usually show a lower energy density compared to lithium-ion batteries due to the greater atomic mass of sodium.

At the moment, the electrochemical characteristics of sodium-ion batteries are limited by the parameters of the cathode material. The specific volume and mass indicators of anode materials are twice / three times more, not to mention the use of metallic sodium. Therefore, the search for the most suitable cathode materials with acceptable electrochemical parameters is still relevant.

In addition, it is worth noting that most of the developed cathode materials have low conductive properties, which significantly affects their electrochemical and kinetic parameters. There are various universal ways to solve this problem, such as: the introduction of electrically conductive additives, particle size reduction and doping with polyvalent metals – which significantly increase the electrochemical performance of cathode materials. However, cathode materials often have their own individual characteristics that must be taken into account when solving this problem. Thus, the question of achieving the maximum, close to theoretical, capacity is possible only with a detailed analysis of the mechanism of reactions occurring in a certain material during the charge / discharge process.

The purpose of the study

Synthesis of new cathode materials of langbeinite and eldfellite structure and development of an effective method for manufacturing an electrode for sodium-ion batteries based on them.

Research objectives

1) Synthesis of new materials $K_{2-x}Na_xMn_2(SO_4)_3$ (x=0; 0,5; 1,0; 1,3; 1,4) with langbeinite structure and $NaFe(SO_4)_{1,5}A_{0,5}$ (A= SO_4, SeO_4, PO_3F, HPO_4) with eldfellite structure.

2) Study of physical-chemical properties of synthesized materials.

3) Conducting detailed electrochemical studies of synthesized materials, including the study of kinetic parameters of intercalation-deintercalation of sodium.

4) Development of an effective method of manufacturing an electrode based on a cathode material with poorly conductive properties.

Objects of research

Materials of composition $K_{2-x}Na_xMn_2(SO_4)_3$ (x=0; 0,5; 1,0; 1,3; 1,4) and $NaFe(SO_4)_{1,5}A_{0,5}$ (A= SO_4, SeO_4, PO_3F, HPO_4).

Subject of research

Electrochemical parameters of synthesized new materials of langbeinite and eldfellite structure. Regularities of intercalation and deintercalation processes occurring in a cathode material with poor conductivity during electrochemical charge/discharge.

Research methods

The main research methods are instrumental methods of analysis in combination with electrochemical research: X-ray phase analysis, neutron diffraction method, Raman spectroscopy, IR-Fourier spectroscopy, laser diffraction method, scanning electron microscopy, cyclic voltammetry, galvanostatic analysis.

The main provisions submitted for protection:

1) Materials of composition $K_{(2-x)}Na_xMn_2(SO_4)_3$ (x = 0; 0,5; 1,0; 1,3) with langbeinite structure do not have electrochemical activity in 1 M $NaClO_4$ electrolyte in a mixture of ethylene carbonate/dimethyl carbonate solvents (1:1).

2) Doping of the material $NaFe(SO_4)_2$ by anions of SeO_4, HPO_4, PO_3F in an amount of 0.5 mol does not violate the original structure of eldfellite.

3) The substitution of SO_4 anions in the $NaFe(SO_4)_2$ material of the eldfellite structure with SeO_4, HPO_4, PO_3F anions in an amount of 0.5 mol leads to a decrease in the specific capacity by more than 29% during the first cycle at a current of 0.1 C in comparison with the original material.

4) The dependence of kinetic parameters of intercalation of the cathode material $NaFe(SO_4)_2$ of the eldfellite structure on the thickness of the conductive coating based on MoS_2 has extreme (maximum) point.

The main results of the study

1) Materials with cationic substitution of the composition $K_{(2-x)}Na_xMn_2(SO_4)_3$ (x = 0; 0,5; 1,0; 1,3; 1,4) with langbeinite structure were synthesized. It was found that the structure of langbeinite is preserved at $x \leq 1.0$, with further substitution of potassium cation for sodium, structural changes occur, leading to a violation of stoichiometry and, as a consequence, the appearance of impurity phases. The electrochemical activity of these materials was not detected.

2) New materials were synthesized with anionic substitution of $NaFe(SO_4)_{1,5}(A)_{0,5}$, where A – SO_4, SeO_4, HPO_4, PO_3F. The identity of the crystal structure of all four types of samples, regardless of the substitutive anion, is shown. According to the analysis data, it is assumed that the PO_3F group was hydrolyzed during synthesis, which led to the formation of the HPO_4 anion. The discharge capacities of the materials $NaFe(SO_4)_{1,5}(A)_{0,5}$, where A – SO_4, SeO_4, HPO_4, PO_3F, were 63, 45, 39, 39 mAh/g, respectively, at current 0.1 C on the first cycle. The diffusion coefficients determined using cyclic voltammetry for $NaFe(SO_4)_{1,5}(A)_{0,5}$, where A – SO_4, SeO_4, HPO_4, PO_3F, were $1,27 \times 10^{-13}$, $4,43 \times 10^{-14}$, $2,81 \times 10^{-14}$, $3,50 \times 10^{-13}$ cm^2/s, respectively.

3) New materials $NaFe(SO_4)_{2-x}(PO_3F)_x$ (x = 0-0,5) were synthesized with varying the concentration of anionic dopant by solid-phase synthesis.

4) The optimal method of applying an electrically conductive layer to the surface of the synthesized cathode material was determined. The influence of the nature of electrically conductive additives on the kinetic and capacitive parameters of the $NaFe(SO_4)_2$ cathode material was studied. It has been found that as the layer thickness increases, the area of the electrochemical process increases, but there is also an increase in the resistance of the transfer of sodium cation from the electrolyte to the surface of the cathode material, which ultimately leads to the fact that this process becomes limiting, leading to a drop in the overall speed of the process.

Substantiation of the novelty and importance of the results obtained

New materials of the composition $NaFe(SO_4)_{1,5}(A)_{0,5}$ (A = SO_4, SeO_4, HPO_4, PO_3F) and $NaFe(SO_4)_{2-x}(PO_3F)_x$ (x=0-0,5), have been synthesized, their physical-chemical properties were investigated and the possibility of their use as cathode materials for sodium-ion batteries was evaluated.

A method for increasing the electrical conductivity of a cathode mixture based on $NaFe(SO_4)_2$ has been developed by creating a flat contact with particles with mixed conductivity, which made it possible to increase the diffusion coefficient of both intercalation and deintercalation of sodium by 1.5 times.

The mechanism of sodium intercalation into the particles of the cathode material $NaFe(SO_4)_2$ coated with a thin layer of MoS_2 and highly conductive soot is proposed.

Validity and reliability of the data obtained

Validity and reliability of the results is ensured by basing on standardized and correctly used methods, as well as metrological processing of the results of experimental studies. All the results were processed using special licensed computer programs.

Theoretical significance of the results

The results of cationic and anionic doping of sulfate materials of the langbeinite and eldfellite structures will be useful in the creation of new substances with the desired properties.

The proposed mechanism of sodium intercalation into the cathode material of the eldfellite structure with the direct participation of electrically conductive additives will allow to reveal the nature of this process more deeply, as well as to create conditions under which the maximum electrochemical parameters of cathode materials will be realized.

Practical significance of the results

The results of the study on fluorophosphate doping will make it possible to create a cathode material with improved charge-discharge speed characteristics. While the optimization of the conditions for the preparation of the cathode material and the developed method for creating a flat contact in order to increase the conductivity of the cathode mixture based on eldfellite will allow in the future to create an efficient cathode with high power indicators for the manufacture of sodium-ion batteries in the field of large-sized energy storage obtained from renewable energy sources.

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

The work was carried out within the framework of the state grant financing of the project AP05131849 "New intercalation materials for sodium-ion batteries" 2018-2020.

Publications

The results of the work performed are reflected in seven scientific papers, including:

- in two articles in peer-reviewed scientific publications in the scientific direction of the dissertation, indexed in the Science Citation Index Expanded of the Web of Science database (second quartile) and having a CiteScore percentile in the Scopus database of at least fifty;

- in two articles published in journals recommended by the Committee for Control in the Field of Education and Science of the Ministry of Education and Science of the Republic of Kazakhstan;

- in three materials and abstracts of international scientific symposia and conferences;

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

In the article "Synthesis, structure and electrochemical performance of Eldfellite, NaFe(SO4)2, doped with SeO4, HPO4 and PO3F" (doi: 10.1016/j.jssc.2020.121395), the author of the dissertation performed work on section 3.7 Electrochemical research. The entire experimental part, the primary analysis, the discussion of the results and the writing of the first version of the text of the article were carried out directly by the author of the dissertation.

In the article "Effect of the MoS2 surface layer on the kinetics of intercalation processes in the NaFe(SO4)2/C composite" (doi: 10.1016/j.mtcomm.2021.102723), S.T.Kohmetova is the first author. The author participated in all the experiments and interpretation of the results and prepared the first versions of articles describing the introduction, methodology, results, conclusions and design of schedules. In addition, the author designed the article in accordance with the requirements of the journal and in improving the article after each stage of reviewing.

In the articles "Study of charge transfer in lithium corrosive films formed in LiClO4 solutions in a PC/DME mixture" and "Development of a cathode material with a langbeinite structure for sodium-ion batteries", the author of the thesis participated in the experimental work, discussion of the results, as well as in the design of articles in accordance with the requirements of the journal.

The abstracts of the international conferences «Efficient way to create conductive coatings based on various carbon materials», «Comparison of various dehydrating agents for organic battery electrolytes», «The problem of the determining of kinetic parameters of the deintercalation-intercalation process» were prepared based on the results of experiments performed by the author of the dissertation. The first two of the presented ones were written personally by the author of the dissertation.

Structure and scope of the dissertation

The dissertation is presented on 117 pages (excluding appendices) and consists of an introduction, 7 main sections, a conclusion, a list of used sources from 205 titles, two appendices and includes 12 tables, 54 figures.