ABSTRACT

Of dissertation for the doctor of philosophy degree (PhD)

specialty 6D72000 - "Chemical technology of inorganic substances"

Rakhimova Ainura

Microwave synthesis, the study of the structure and electrochemical characteristics of LiFePO4 as a highly efficient cathode material for lithium-ion batteries

The dissertation is devoted to the preparation of the cathode material $LiFePO_4$ by the microwave method. The conditions for obtaining $LiFePO_4$ by the microwave method were optimized and the effect of solid and liquid absorbers on the synthesis of the cathode material was studied. All research within the framework of the dissertation was conducted for the first time, the results are presented in the form of articles, including in a peer-reviewed journal, and abstracts of reports of international conferences.

Relevance of the research topic. In recent years, research has focused on finding new efficient energy storage devices, some of which are lithium energy sources. In rechargeable lithium-ion batteries, one of the key components is the cathode material, which mainly determines the electrochemical characteristics of the battery. A promising cathode material is $LiFePO_4$, which has high stability during cycling, a sufficiently high theoretical capacity (170 mAh / g) and environmental safety. However, this material has low ionic and electronic conductivity. Many studies are aimed at solving this problem and simplifying the synthesis process.

Today, $LiFePO_4$ is a commercially available product, and there are various methods of synthesis, however, these methods are complex in hardware design, often time-consuming and difficult to control the morphology of the samples obtained with this. One promising method is microwave synthesis. It is fast, with its help it is possible to obtain nanosized powders of $LiFePO_4$ coated with carbon through the use of microwave absorbers. The main bias is made for consideration of the microwave synthesis method and combined methods associated with microwave exposure. The effect of water on the microwave synthesis of $LiFePO_4$ was determined and its use as an alternative to a carbon absorber was revealed.

The traditional method of synthesizing $LiFePO_4$ / C via a solid-phase path consists of two heating stages, each of which can take from 5 to 24 hours. The first of them is a synthesis stage and is carried out at a temperature close to 350 ° C, as a result of which the reagents form $LiFePO_4$ / C. Then the second stage (sintering) is performed at a temperature of about 800 ° C, and here $LiFePO_4$ / C forms an ordered crystalline structure, with agglomerating particles and increases in size. During this time, the reactor must operate in an inert (or reducing) atmosphere, for example, in an atmosphere of argon or argon / hydrogen.

For cost reasons, it is also important to make this procedure cheaper as well as faster in order to be practical for its industrial application. However, the synthesis of $LiFePO_4$ is not easy to perform due to the oxidation state of iron, so it is usually controlled by heating the furnace with a flow of reducing or inert gas for several hours, which is not only an expensive procedure (in terms of the energy involved and because of the need to use an inert atmosphere), but also difficult to apply on an industrial scale. One of the possible ways to overcome this problem is microwave processing, which is used in the preparation of many materials and is used to successfully synthesize $LiFePO_4$ compounds of solid-phase reactions, since the substances are heated uniformly at the molecular level, which leads to a steep temperature gradient in contrast to conventional heating, where the samples heated from the outside.

The idea of using microwave synthesis here is to make iron atoms act like a microwave absorber so that they can quickly heat up the precursor and activated carbon and form a reducing atmosphere. Thus, $LiFePO_4$ can be obtained by microwave heating in just a few minutes, thereby avoiding the oxidation of iron. In addition to improving the synthesis of $LiFePO_4$, it is still necessary to optimize the concentration of carbon formed in the composite to improve electronic and ionic conductivity, and therefore maximize specific capacitance and productivity.

There are various methods for the synthesis of lithium iron phosphate, however, the need for repeated calcination steps and subsequent synthesis adjustments to improve the uniformity of the final products entails a long processing time and significant energy consumption. This problem can be solved using the microwave method for the synthesis of $LiFePO_4$.

Microwave synthesis is a process of self-heating; direct absorption of the electromagnetic energy of materials provides fast and uniform heating.

In this context, the aim of this work is to propose an alternative synthesis route for $LiFePO_4$ with reduced processing time and cost.

Microwave synthesis is able to provide fast and uniform heating of components due to the self-heating process based on direct absorption of microwave radiation. Microwave synthesis allows you to synthesize LiFePO4 in a shorter time with less energy consumption relative to temperature synthesis methods. The limiting factor in this synthesis is the choice of precursors capable of absorbing microwave radiation.

Recent studies have shown that using the microwave method as a method of synthesizing $LiFePO_4$ using the following precursors Li3PO4, Fe3 (PO4) 2 • 8H2O and carbon can be a promising low-cost industrial method for its preparation. The synthesized material has a high value of working capacity (95% of theoretical) with excellent cyclability.

The microwave preparation of LiFePO4 from phosphate precursors proceeds very easily, and with a small amount of by-products, in particular, only water is released.

$$Li_3PO_4 + Fe_3 (PO4)_2 \cdot 8H_2O + C \rightarrow LiFePO_4 / C + 8H_2O$$

To obtain the cathode material LiFePO4, there are a diverse number of synthesis methods that can be used to control particle size, morphology, and

ordering of the crystal structure, which significantly affect the electrochemical parameters. The main difficulty lies in combining all of these factors when choosing a synthesis method. Using some methods, it is already possible to synthesize this material with practically specific electrochemical characteristics, however, there is a need for new synthesis methods that can reduce energy consumption, reduce the number of operations and their time, and, accordingly, reduce the cost of the final product. As an alternative to commercialized high-temperature synthesis methods, microwave synthesis and its combination with hydrothermal and mechanochemical methods can be used. These methods do not use high-temperature exposure, and the microwave irradiation time can be up to 5 minutes, in contrast to solid-state methods, where the heat treatment time varies from 5 to 24 hours. However, the optimization and improvement of existing microwave synthesis methods is required for their introduction into large-scale production.

The microwave method is easy in hardware design and the target product can be obtained in one stage in a few minutes and also coated with carbon, which improves the electrochemical properties of the obtained samples.

The purpose of the thesis is to optimize the conditions for obtaining LiFePO4 by the microwave method as a highly efficient cathode material for LIA.

To achieve the goal, the following tasks were set:

1 Development of the method of synthesis of precursors for obtaining LiFePO4 microwave method;

2 Selection of a microwave absorber to ensure efficient synthesis of $LiFePO_4$;

3 The study of the dispersion factor for the synthesis of $LiFePO_4$ microwave method;

4. Electrochemical tests of the obtained $LiFePO_4$.

Objects of study: Cathode material $LiFePO_4$.

Subject of research: Microwave synthesis from phosphate precursors.

Research Methods. Preparative synthesis, gravimetry, potentiometry, pH meter, galvanostatic and potentiostatic analysis method, cyclic voltammetry (CV), intermittent potentiostatic titration method (PITT), galvanostatic intermittent titration method (GITT), X-ray phase analysis (XPA), electron microscopy.

The source base and research materials are 157 sources of literature on methods for producing $LiFePO_4$, as well as on other areas of natural science related to the topic of this study.

Scientific novelty:

- The conditions for obtaining $LiFePO_4$ by the microwave method from phosphate precursors have been optimized;

- the influence of temperature and pH on the formation of $Fe_3 (PO_4)_2 * 8H_2O$ precipitation was established;

- developed a method for determining the temperature of synthesis during microwave synthesis;

- The electrochemical and structural characteristics of the obtained $LiFePO_4$ and the possibility of being used as a highly efficient cathode material for LIB were determined.

The theoretical significance of the study. A new approach to optimizing the microwave method for the synthesis of lithium iron phosphate is proposed. A laboratory setup for synthesis has been developed. The effect of various absorbers on the microwave synthesis of $LiFePO_4$ was studied.

Practical value. The $LiFePO_4$ cathode material with a unique branched morphology was synthesized. The resulting lithium-ion batteries based on the synthesized material have high capacitive characteristics, which undoubtedly makes them competitive products, which are necessary for use in portable equipment

The main provisions to be defended:

1 The obtained precursors of the required dispersion due to changes in pH and temperature of the solution;

2 The use of liquid absorbers and solutions of lithium salts in them to increase the efficiency of the synthesis of $LiFePO_4$ by the microwave method.

3 Establishment of the definition of the effect on the microwave synthesis of the dispersion of the starting reagents and the thoroughness of their homogenization.

4 Preparation of $LiFePO_4$ by microwave synthesis with characteristics corresponding to those close to theoretical capacity.

The main results of the dissertation research are reflected in 8 scientific papers, including:

- in one article published in a periodical indexed by the Web of Science database;
- in three articles published in magazines 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 abstracts of reports at national and foreign international scientific and practical conferences and symposia.

The structure and scope of the dissertation.

The dissertation consists of an introduction, three sections, a conclusion, as well as a list of sources used from 159 items. The work is presented on 104 pages, contains 72 figures and 21 tables.

Based on the results of the dissertation research, the following conclusions are made:

1. Two plants have been created for the synthesis of $Fe_3 (PO_4)_2 * 8H_2O$ precursors and the main product of lithium iron phosphate, including an inert atmosphere synthesis reactor.

2. A method for synthesizing precursors has been developed. The effect of pH and temperature of the solution on the synthesis of $Fe_3 (PO_4)_2 * 8H_2O$ was determined. The optimum pH is 8, the temperature of the solution is 70 ^{0} C. Samples with the required dispersion for synthesis were obtained. The identification of precursors obtained by this synthesis procedure has been carried out. The correspondence of the compositions and structures to theoretical data is proved.

3. A method of microwave synthesis of $LiFePO_4$ in a household microwave oven was developed, which showed the possibility of using iron phosphate (II) and lithium phosphate as effective precursors for the synthesis of cathode material.

4. The effect of solid and liquid absorbers on the synthesis of $LiFePO_4$ was studied and the most optimal water absorber was determined.

5. The resulting cathode material showed a specific discharge capacity of 160 mAh / g, which is 90% of the theoretical value.

6. A schematic diagram of the preparation of $LiFePO_4$ by the microwave method from phosphate precursors has been developed.

Assessment of the completeness of the solutions to the tasks. All the tasks set for solving the purpose of this dissertation are solved in full.

Thus, the objectives of the dissertation research have been achieved — the conditions for obtaining $LiFePO_4$ by the microwave method from phosphate precursors and investigated the effect of solid and liquid absorbers on the synthesis process.

Assessment of technical and economic efficiency of the solutions proposed in the thesis. The solutions proposed as part of this dissertation can form the basis for obtaining commercial $LiFePO_4$ as a highly efficient cathode material for LIA.