ANNOTATION

of the dissertation for the degree of the Doctor of Philosophy (PhD)
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New cathode materials for lithium accumulators

The relevance of the topic of the dissertation research.

There is a wide variety of cathode materials, but each of them has shortcomings that limit their wide application. To eliminate these shortcomings, numerous studies have been carried out in the field of modification of cathode materials with faster ion transport inside the particles or the synthesis of active materials in nanostructured form. However, to date, little attention has been paid to the problem of transport inside the cathode surface, without optimizing which there may be a significant loss in the specific energy and/or power of the devices. Improving the transport of lithium ions inside the agglomerates of the active material is possible by optimizing the microstructure of the cathode surface.

One of the ways to optimize the cathode surface is to control the thickness and microstructure of the cathode surface using the Doctor blade coating technology and the electrospinning technique.

In this context, the purpose of the thesis was to optimize the performance of cathode surface based on the lithium iron-phosphate ($LiFePO_4$) active material with the olivine structure. The main shortcoming of this material is its low electronic conductivity (10^{-9}-10^{-10} $S{\cdot}cm^{-1}$). The selection of parameters and conditions for the application of lithium iron-phosphate by the coating technology and by the electrospinning technique is an alternative solution to this problem for cathodes. The polymer binder polyvinylidene fluoride was used for the first time as a carbon source to form these electrode surface.

The degree of elaboration of the problem. The efforts to increase the electrical conductivity of the lithium iron-phosphate active material is carried out by many electrochemical laboratories, since it is the optimal material for cathodes for lithium-ion batteries due to its good physical and chemical properties, and the iron contained in it is a cheap and easily accessible element.

A review of the literature data has shown, that although some attempts have been made in this direction, the influence of the cathode surface architecture on the performance of this material and its interaction with conductive additives in the structure of the electrode layer have not been properly studied. Therefore, the search and development of new effective ways to improve the electronic conductivity of lithium iron-phosphate remain relevant.

The purpose of the study is to improve the electrochemical properties of lithium iron-phosphate by optimizing the microstructure and thickness of the cathode surface based on it by the Doctor blade coating technology and the electrospinning technique, and to study the possibility of using polyvinylidene fluoride as a polymer binder and a carbon source in the manufacture of these surfaces.

In order to accomplish the set objective point **the following tasks** were defined:

– to determine the possibility of obtaining electrospun polyvinylidene fluoride film and the conditions of its thermal conversion;

– to study the morphology of the lithium iron-phosphate-based electrode surfaces by the Doctor blade technology and by electrospinning;

– to determine the possibility of application of polyvinylidene fluoride as a source of conductive additives in cathode surfaces for lithium-ion batteries;

- to study the effect of 1, 3 and 5% commercial carbon black on the electrical conductivity of cathodes based on lithium iron-phosphate;

- to study the effect of carbon nanotubes on the electrical conductivity of lithium iron-phosphate-based cathodes;

- to determine the effect of using of both commercial conductive additives on the electrical conductivity of lithium iron-phosphate-based cathodes;

- to determine the electrochemical properties of electrospun calendered electrode surface with 5% carbon black;

- to establish the electrochemical properties of calendered electrospun surfaces with the addition of carbon black and carbon nanotubes;

- to investigate the effect of the thickness of the Doctor blade-coated cathode surfaces on the performance of lithium-ion batteries.

Research methods. In the course of the research, the following physicochemical and electrochemical methods of analysis were used: optical and scanning electron microscopy, IR spectroscopy and galvanostatic testing.

The subject of this study is iron-lithium phosphate for the performance of lithium-ion batteries at high current densities.

The scientific novelty of the work is determined by the fact that for the first time:

– a comparative analysis of cathode surfaces obtained by the Doctor blade technology and by electrospinning;

– the annealing of electrospun polyvinylidene fluoride membranes from 250 to 490°C;

– morphological and chemical changes of the polyvinylidene fluoride-based polymer films while the heat treatment process;

– the investigation of polyvinylidene fluoride use as a source of carbon in the cathodes of lithium-ion batteries;

– a qualitative determination of the composition of annealed electrospun electrode surfaces based on lithium iron-phosphate was carried out;

– the effect of carbon black and carbon nanotubes on the electrical conductivity of lithium iron-phosphate was studied;

– the effect of the thickness of electrospun and Doctor blade-coated cathode surfaces based on lithium iron-phosphate on the electrochemical parameters of the battery was studied.

The scientific and practical significance of the study consists in ways to optimize and improve the performance of the cathode surface by changing its microstructure by electrospinning and using commercial conductive additives and polyvinylidene fluoride as a carbon source by annealing it in cathodes.

The obtained results are of theoretical and practical interest and make a significant contribution to solving the actual problem of improving the power characteristics of lithium-ion batteries.

Conclusions based on the results of the research:

1. Studies on a electrospun polyvinylidene fluoride-based polymer film have been carried out. The polymer film made of a 10% solution of polyvinylidene fluoride has a fibrous porous structure. Heat treatment affects the morphology of the film, and the most optimal temperatures are 300 and 400°C, since at these temperatures its active decomposition begins.

2. The electrospun surface with the addition of lithium iron-phosphate has a fibrous and porous structure, with inlaid and elongated active material particles along the polymer filaments. The Doctor blade-coated surface has an unsmoothly located granular structure with large and small agglomerates of active material. The specific capacity of the electrospun cathode is extremely small (32 mAh/g) and is not comparable with the Doctor-blade coated electrode (133 mAh/g).

3. Partial pyrolysis of polyvinylidene fluoride polymer fibers containing lithium iron-phosphate particles leads to the formation of amorphous carbon. It is found that with an increase of the annealing temperature, the specific capacity increases proportionally. Nevertheless, the electrochemical characteristics of annealed electrospun surface are extremely low for this active material and the annealing of cathode surface cannot be used in practice.

4. The possibility of the electrospun coatings formation with the addition of commercial conductive additives in the form of 1%, 3% and 5% carbon black is shown. The specific capacities of the electrodes with 1% and 3% carbon black are low for lithium-ion batteries. The addition of 5% carbon black has advantages in battery performance at high current densities compared to blade-coated cathode surfaces. The specific capacity of the electrospun cathode of 105, 84 and 68 mAh/g at current strengths of 125, 250 and 500 mA/g differs slightly from those for electrodes obtained by the Doctor blade method with a 10% carbon black content of 113, 90 and 75 mAh/g and with a 15% carbon black content of 115, 100 and 80 mAh/g at similar current densities. Thus, surface with 5% carbon black obtained by electrospinning can be considered as a promising solution for high-power batteries.

5. It was established that even with a small percentage of carbon nanotubes (0.6%), the capacity of the electrospun structure has approximately the same electrochemical parameters as that of the Doctor blade-coated electrode. The architecture of the electrospun surface with carbon nanotubes has a clear advantage over the blade-coated surface.

6. It was found that the addition of both conductive additives to the composite does not improve the electrochemical performance of the electrospun coating. The nominal capacities of a such electrode are 110, 90 and 67 mAh/g at current densities of 125, 250 and 500 mA/g. The performance of the Doctor-blade electrodes at

similar current strengths is 120, 100 and 85 mAh/g. The large proportion of carbon nanotubes in the composition of the blade-coated electrodes explains their performance, which emphasizes the advantage of carbon nanotubes.

7. It was established that changing the thickness of electrospun cathode surfaces without conductive additives by 10% does not improve their performance. Nevertheless, the calendering of the electrospun electrode with 5% carbon black has a positive effect on the electrochemical parameters. With an increase in the current strength of the calendered electrode, in contrast to the uncalendered one, there is no sharp difference in the capacitances, and the capacitance remains constant during cycling.

8. Electrospun calendered coating with the addition of carbon black and carbon nanotubes has advantages over uncalendered similar coating in discharges at high current strengths. Thus, when the current is increased to 500 mA/g, the calendered electrode produces a noticeably larger capacity – 57 mAh/g compared to 50 mAh/g for the uncalendered one. The fact that the electrochemical cells work better after calendering essentially contributes to the further use of this process for lithium-ion batteries production.

9. The dependence of the discharge capacity of Doctor blade-coated electrode surfaces on their thickness is studied. It is shown that the cathodes with a wet surface thickness of 200 and 600 microns are inferior to the cathode with a wet surface thickness of 400 microns in this indicator. A film with a thickness of less than 200 microns is assumed to have a low energy consumption, while a film thickness of more than 360 microns has diffusion limitations that affect the energy consumption of the electrode. The optimal thickness of the Doctor blade-coated cathode surface is approximately 300 microns. The obtained data supplement and expand the understanding of the influence of the design parameters of the cathode on the performance of lithium-ion batteries.

The obtained results can be used for the production of small-sized high-power lithium-ion batteries with high current output and long service life.

The main provisions for the defense:

- a microstructure of the Doctor blade-coated and electrospun cathode surfaces;
- the use of polyvinylidene fluoride as a source of electrically conductive additive for cathodes based on lithium iron-phosphate;
- the results of electrochemical testing of the Doctor blade-coated and electrospun lithium iron-phosphate with carbon black;
- the results of electrochemical testing of the Doctor blade-coated and electrospun lithium iron-phosphate with carbon nanotubes;
- the results of electrochemical testing of the Doctor blade-coated and electrospun lithium iron-phosphate with two electrically conductive additives;
- the effect of the thickness of the cathode surfaces on their diffusion properties.

Interrelation of the work with the plan of state scientific programs. Dissertation work was carried out in the framework of research work conducted at the Department of Chemistry of ENU named after L. N. Gumilyov and at the

Department of Chemistry, New Technologies and Materials of the State University «Dubna» (Dubna).

The doctoral student's contribution for the preparation of each publication. The author's personal contribution consists in direct participation in conducting experiments at all stages of the work; discussing the obtained results and writing each publication.

Approbation of work. The main results of the dissertation work were published in the journals «Rasayan Journal of Chemistry», «Energy Technology», «Bulletin of ENU named after L. N. Gumilyov»; are reported at international scientific and practical conferences: Abstracts 3rd International conference of young scientists «Topical problems of modern electrochemistry and electrochemical materials science» (Moscow, 2018), 14th International Conference «Physical and Chemical Problems of Renewable Energy» (Chernogolovka, 2018), International Scientific Conference of Students, Postgraduates and Young Scientists «Lomonosov-2019» (Moscow, 2019), All-Russian Conference with international participation «Physical and Analytical Chemistry of Natural Resources and Technogenic Systems, new Technologies and Materials» (Dubna, 2019), XIV International Scientific Conference «Science and Education-2019» (Nur-Sultan, 2019).

Volume and structure of the dissertation.

The dissertation is presented on 92 pages of computer text, including 41 figures and 5 tables. The dissertation consists of an introduction, a literary review, an experimental part, the results of the discussion of experimental data, a conclusion, a list of used sources from 168 items.