

Cathode material for lithium-ion battery based on nanofibers consisting of vanadium oxides phases mixture

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The synthesis methodology of nanofibers consisting of vanadium oxides phases mixture and experimental data analysis on their application as the cathode material basis for lithium-ion battery are presented. Vanadium oxide nanofibers were synthesized by electrospinning method. It was shown that increasing the concentration of V^{4+} ions (obtaining nanofibers consisting of vanadium oxides phases mixture) had a positive effect on the electrochemical properties of the material. The initial specific capacity of the material is comparable with the capacity of the material made of pure vanadium pentoxide nanofibers, but the rate of capacity loss decreases: the material retains 83.1% of the specific capacity after 100 charge-discharge cycles.

Keywords: nanofibers, electrospinning, cathode material, lithium-ion battery, vanadium oxides.

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Nowadays, lithium-ion batteries are the most popular type of batteries. They are used in smartphones, laptops, cameras, electric vehicles, and pacemakers. The main functional parameters of lithium-ion batteries are the battery capacity and its durability (the number of charge-discharge cycles it withstands without a noticeable reduction in capacity). The specified parameters depend largely on the electrode materials.

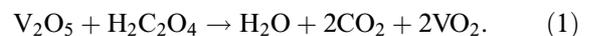
Vanadium pentoxide has attracted considerable research attention, since it is capable of retaining two positively charged lithium ions per lattice site in its crystalline form. Owing to this, the theoretically achievable capacity of vanadium pentoxide is on the order of $300 \text{ mA} \cdot \text{h} \cdot \text{g}^{-1}$. However, a certain fraction of lithium ions remain inside vanadium oxide in the process. In addition, their intercalation alters the configuration of the crystal lattice itself, leading to rapid destruction of the cathode. Research shows that the specific capacity of a nanostructured material is higher than the one of powder samples.

It was proven that vanadium pentoxide nanofibers do indeed have a high initial specific capacity ($330 \text{ mA} \cdot \text{h} \cdot \text{g}^{-1}$) at a current density of $0.068 \text{ A} \cdot \text{g}^{-1}$, but lose it quickly [1]. The specific capacity of the material dropped by 50% within the first 50 cycles and continued to decrease. After 100 cycles, the specific capacity was $110 \text{ mA} \cdot \text{h} \cdot \text{g}^{-1}$, which is 33.3% of the initial value [1].

Obtaining a material consisting of vanadium oxides phases mixture is one of the promising methods to improve electrochemical characteristics. The addition of other vanadium oxide phases (i.e., an increase in concentration of V^{4+} ions) induces the formation of dislocations and vacancies that may facilitate charge transfer, providing a more open structure and additional energy levels.

Vanadium pentoxide nanofibers were produced by the method detailed in [1]. Two-stage annealing was performed to obtain nanofibers consisting of vanadium oxides phases mixture with different ratios of V^{4+}/V^{5+} components. The first stage is needed to evaporate excess water from the material and remove the polymer used in the precursor preparation process. This annealing was carried out in air at a temperature of 400°C (and a heating rate of $10^\circ\text{C}/\text{min}$) for one hour. The second stage is necessary for crystallization of nanofibers. This annealing was carried out in an argon atmosphere at a temperature of 550°C (and a heating rate of $10^\circ\text{C}/\text{min}$) for one hour. Oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$) was used to obtain a phase mixture.

In the course of annealing, oxalic acid decomposes with the release of carbon monoxide (CO), which is a reducer. Vanadium pentoxide gave up an oxygen atom to form vanadium dioxide and carbon dioxide:



The molar ratio between vanadium pentoxide nanofibers and oxalic acid was 1:1.

Elemental analysis of the obtained nanofibers was performed using a Hitachi SU1510 scanning electron microscope fitted with an EDS spectrometer for X-ray fluorescence analysis. The ratio between the numbers of oxygen and vanadium atoms was determined to be 2.05, which is close to the calculated value for vanadium dioxide.

X-ray phase analysis, which was carried out using a DRON-6 diffractometer in $\text{CuK}\alpha$ ($\lambda = 1.5418 \text{ \AA}$) radiation, revealed that the material is a mixture of vanadium oxides phases (VO_2 , V_2O_5 , V_6O_{13} , V_4O_9). The nominal concentrations were as follows: approximately 23.0% — vanadium pentoxide, 37.5% — vanadium dioxide and phases with a

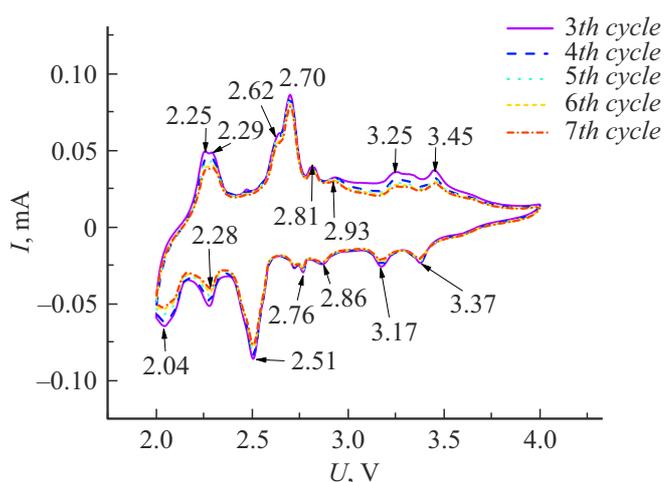


Figure 1. Voltamperograms of nanofibers consisting of vanadium oxides phases mixture within the potential range of 2.0–4.0 V at a scan rate of $0.1 \text{ mV} \cdot \text{s}^{-1}$.

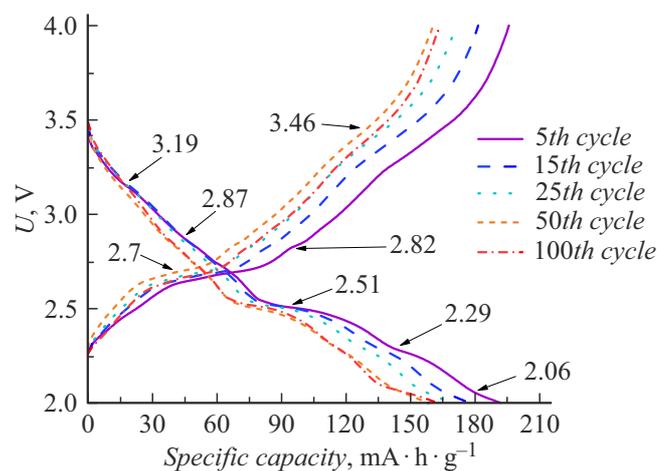


Figure 2. Charge–discharge curves of nanofibers consisting of vanadium oxides phases mixture within the potential range of 2.0–4.0 V at a current density of $0.2 \text{ A} \cdot \text{g}^{-1}$.

close O:V ratio (V_6O_{13}), and 39.5% — intermediate phase V_4O_9 .

The electrode material consisted of vanadium oxides nanofibers, conductive carbon black, and a binder (PVDF) in a ratio of 60:30:10. The components were ground and mixed in a mortar. The resulting mixture was applied to aluminum foil using the doctor blade method (the coating thickness was $150 \mu\text{m}$). The samples were dried in an oven at a temperature of 100°C for 24 hours. Following this, the samples were rolled on rollers to improve the coating–substrate contact, and electrodes were stamped out. Lithium-ion battery models were assembled in a glove box in an argon atmosphere. The anode was lithium foil, and polypropylene film Celgard 2400 soaked with an electrolyte (1M LiPF_6 in a EC:DEC mixture in a ratio of 1:1) served as the separator.

Voltamperograms were recorded using an Elins P20X-8 potentiostat/galvanostat. The voltamperograms of nanofibers consisting of vanadium oxides phases mixture are shown in Fig. 1. A significant number of peaks were observed within the 2.0–4.0 V range that is standard for the material. Some of them correspond to vanadium dioxide and vanadium pentoxide, and the remaining peaks belong to other modifications of vanadium oxides [2–5]. The peaks of vanadium dioxide (2.70 and 2.51 V) are more pronounced than the peaks of vanadium pentoxide (3.45, 3.37, 3.25, 3.17, 2.28, and 2.62 V), which is consistent with the phase composition (vanadium dioxide is predominant in the material).

The battery models were cycled within the potential range of 2.0–4.0 V. The charge–discharge curves of nanofibers consisting of vanadium oxides phases mixture are presented in Fig. 2. The obtained results are consistent with the data of cyclic voltammetry (the „plateau“ potentials in the charge–discharge curves match the positions of peaks in the voltamperogram).

The dependence of the specific capacity on the sequential number of a charge–discharge cycle is shown in Fig. 3. This dependence characterizes the stability of the material. The initial specific capacity of the material in the first charge–discharge cycle is $227.9 \text{ mA} \cdot \text{h} \cdot \text{g}^{-1}$, by the second cycle, the capacity drops to $195.6 \text{ mA} \cdot \text{h} \cdot \text{g}^{-1}$ (a 14.2% reduction). A sharp drop in capacity after the first cycle may be attributed to irreversible processes proceeding within the first cycle that inflate the specific capacity. The capacity after 100 charge–discharge cycles is $162.5 \text{ mA} \cdot \text{h} \cdot \text{g}^{-1}$, which corresponds to 71.3% of the capacity in the first cycle and 83.1% of the capacity in the second cycle. The capacity reduction is the most pronounced within the first cycles, and the specific capacity stabilizes after 35–40 cycles. A similar dependence for vanadium pentoxide nanofibers

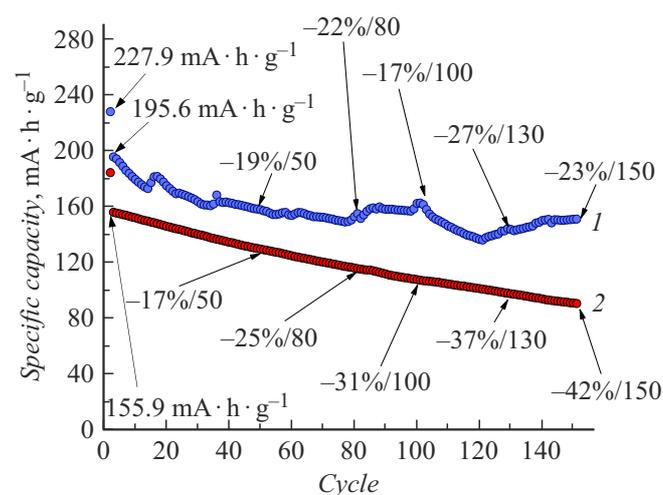


Figure 3. Dependence of the specific capacity of nanofibers consisting of vanadium oxides phases mixture on the sequential number of a charge–discharge cycle within the potential range of 2.0–4.0 V at a current density of $0.2 \text{ A} \cdot \text{g}^{-1}$. 1 — Nanofibers consisting of vanadium oxides phases mixture; 2 — vanadium pentoxide nanofibers.

is shown in Fig. 3 for comparison. The initial specific capacity was $184.3 \text{ mA} \cdot \text{h} \cdot \text{g}^{-1}$. The capacity dropped to $155.9 \text{ mA} \cdot \text{h} \cdot \text{g}^{-1}$ after the first cycle and continued to decrease steadily in subsequent cycles.

Thus, an increase in the concentration of V^{4+} ions (production of nanofibers consisting of vanadium oxides phases mixture) had a positive effect on the electrochemical properties of the material. Its initial specific capacity is comparable to that of pure vanadium pentoxide nanofibers, but the rate of capacity loss has decreased: the material retains 83.1% of the second-cycle capacity after 100 charge–discharge cycles. The change in curve shape is also worth noting: pure vanadium pentoxide nanofibers lose capacity steadily, while the loss of specific capacity in nanofiber consisting of vanadium oxides phases mixture slows down gradually to a virtually zero level after the 40th cycle.

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Conflict of interest

The authors declare that they have no conflict of interest.

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