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The influence of nanostructured carbon additives to the functional electrode characteristics of lithium-ion batteries

This research is devoted to the study of the effect of nanostructured carbon additives on the functional characteristics of a positive electrode based on vanadium oxide for lithium-ion batteries. It has been shown that the use of carbon nanotubes and graphene oxide instead of traditional carbon black significantly increases the specific characteristics of the electrode. Also the improvement of the specific characteristics of the positive electrode in lithium-ion batteries when using graphene and carbon nanotubes instead of carbon black was proved. This effect is explained by an increase in the speed of movement of lithium ion inside the material, due to the higher conductivity of nanotubes and graphene, and a more compact contact of crystals. It is due to higher electronic conductivity of carbon nanotubes and graphene compared to conventional carbon black. In addition, the intercalation of quasi-one-dimensional (nanotubes) and quasi-two-dimensional (graphene) structures into the electrode makes possible to ensure a more compact contact of active substance particles with a current collector. This helps to reduce the mass fraction of the conductive additive in the electrode structure and increase its specific parameters. It is shown that the use of graphene and carbon nanotubes as conductive additives instead of conventional carbon black may increase significantly the specific characteristics of positive electrodes in lithium-ion batteries.

Keywords: nanostructured carbon additive, electrode, carbon soot, speed of Li-ion, Li-ion battery, carbon nanotubes, graphene oxide, vanadium oxide.

Currently, lithium-ion batteries are the most commonly used chemical energy sources. Considering the evolution of modern electronic devices there are clear trend to minimization and increased functionality. This leads to a significant increase in energy consumption which, in return, requires the creation of more efficient and compact energy sources.

Specific energy lithium-ion battery is determined by specific characteristics of electrode materials and first of all by the cathode material characteristics as it accounts for approximately 40 % of the mass of all active components. In addition, the battery contains inactive components such as current collectors, separators, box, etc., which are necessary for the functioning of the battery.

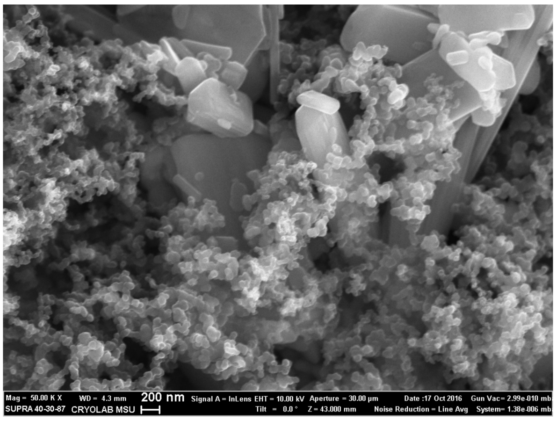
Therefore, the problem of increasing energy efficiency of modern energy storage devices with restrictions imposed on the battery form-factor, on the one hand is related to the problem of obtaining and investigating new active electrode materials. On the other hand, it is important to search for new engineering solutions that allow reducing the mass of inactive components, and thereby contributing to an increase in the specific energy of the battery.

Among the most promising cathode materials the highlight vanadium pentoxide (V_2O_5), of which the specific capacity reaches 400 mAh/g [1], that is 2–2.5 times exceeds the specific values of traditional positive electrode materials ($LiCoO_2$, $LiMn_2O_4$, $LiFePO_4$). Vanadium oxide, like traditional cathode materials, has low electron conductivity. Therefore, when forming a positive electrode, it is necessary to use a conductive additive that would ensure the transport kinetics of lithium ions during the intercalation/deintercalation into vanadium oxide structure. Typically, in commercial batteries, various carbon blacks are used as such an additive (for example, TimcalSuperC45). Publications of recent years indicate that the use of various carbon nanostructures, such as graphene and nanotubes, as conductive additives, can significantly improve the specific parameters of the electrodes of lithium-ion batteries [2–5].

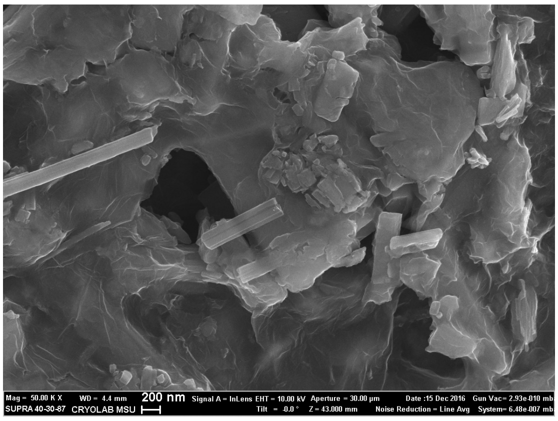
This effect is due to the higher electronic conductivity of carbon nanotubes and graphene compared to conventional soot. In addition, the introduction of quasi-one-dimensional (nanotubes) and quasi-two-dimensional (graphene) structures into the electrode makes it possible to ensure a more intimate contact of active substance particles with a current collector. This helps to reduce the mass fraction of the conductive additive in the electrode structure and increase its specific parameters.

The purpose of this work was to study the effect of various nanostructured carbon additives on the specific characteristics of a positive electrode based on vanadium oxide for lithium-ion batteries.

The procedure for preparing the electrode included several stages. At first stage, a cathode paste consisting of a hydrothermally synthesized vanadium oxide powder [1], a conductive additive and a polymer binder, was needed. As conductive additives, carbon nanotubes (Oxal, RF), reduced graphene oxide obtained by the modified Hammers method, or carbon black TimcalSuper C45 were used. Polyvinylidene fluoride, hsv-900 (kynar), was used as a polymer binder. Dry components were added with N-methylpyrrolidone, and then the solution was mechanically stirred for 6 hours at 60 ºC. The portion of dry substances in the solution was 60–80 mg/ml. The mass loading of each of their dry components was determined by the ratio of 88.5 % (vanadium oxide powder): 1.5 % (conductive carbonaceous additive): 10 % (polymer binder).



a



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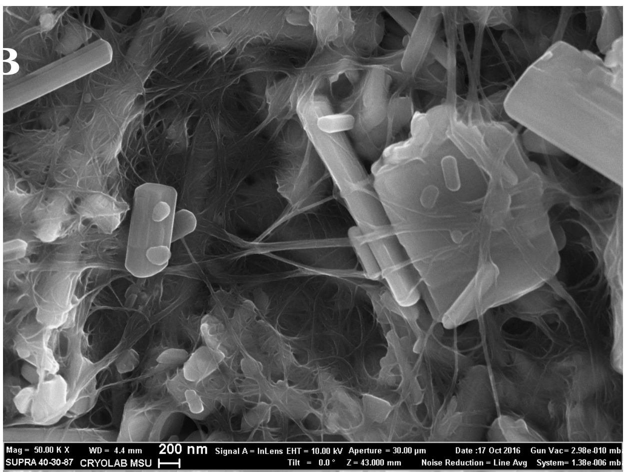

c

Figure 1. Micrographs of vanadium oxide electrodes with the addition of carbon black C45 (*a*), reduced graphene oxide (*b*) and carbon nanotubes (*c*)

After stirring, the solution was applied using an airbrush onto aluminum foil 20 μm thick. Further, the sample was dried and electrodes with a diameter of 1.5 mm were formed from it. Electrochemical testing of the electrodes was carried out in standard 2032 cells. Metallic lithium was used as a negative electrode. The cells were assembled in a glove box in an argon medium with a moisture/oxygen level of not more than 0.1/1 ppm.

As a separator, polypropylene film Celgard 2500 was used. As an electrolyte, 1M $LiClO_4$ solution was used in a mixture of propylene carbonate with 1, 2-dimethoxyethane (PC:DME) with a ratio of 7:3 by volume. Galvan static cell cycling was performed on an 8-channel MTI-BST8-MA power supply analyzer in a voltage range of 2–4 V. The charge/discharge current of the cell was set at a rate of 10 mA per gram of cathode coating.

Figure 1 presents microphotographs of the surface of electrodes with different carbon additives. It can be seen that the particles of all carbon additives are uniformly distributed over the surface of the electrodes. In this case, if the soot particles form separate agglomerates (Fig. 1*a*), the flakes of the reduced graphene oxide (Fig. 1*b*) and the carbon nanotubes evenly cover the vanadium oxide crystals. Presumably, due to the morphology and large surface area, the two-dimensional flexible graphene sheet like particles and the long fibers formed by the nanotubes should have a larger contact area with the active substance particles as opposed to the spherical soot particles, thereby providing the best electronic transport in the cathode material. In addition, in view of the ability of the reduced graphite oxide and carbon nanotubes to form good coatings, an increase in the adhesion of the paste to the aluminum foil is contemplated.

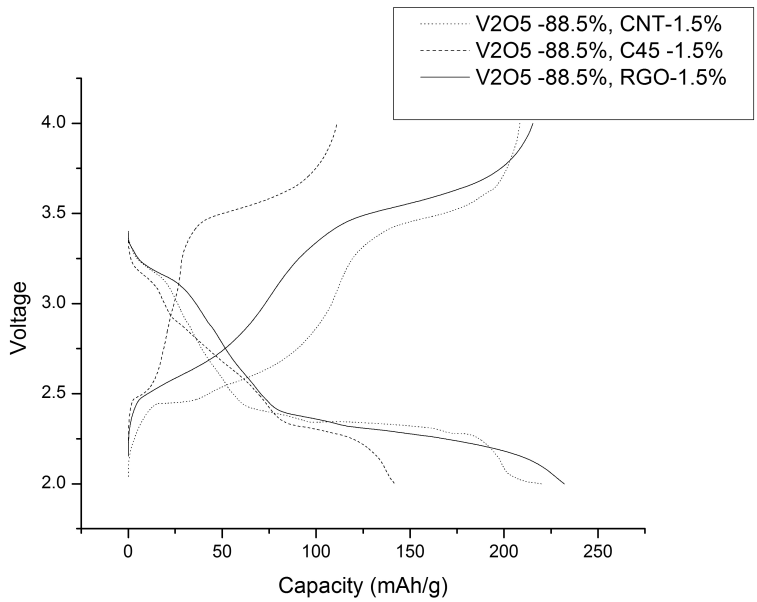

Figure 2. Galvan static Discharges/Charging Curves of Cells with a Positive Electrode
Based on Vanadium Oxide and Various Conducting Additives (1.5 wt.%):
Carbon nanotubes, reduced graphene oxide, and commercial TimcalSuper C45. The current is 10 mA/g

Figure 2 shows galvan static discharges/charge curves of electrodes with the same percentage of three different conductive additives and the same amount of vanadium oxide. All curves are represented by a series of plateaus in the 2–4 V regions, which are characteristic for phase transitions inside vanadium oxide crystals during intercalation/deintercalation of lithium ions. This indicates that all the carbon structures used in the experiments provide transport of lithium ions into vanadium oxide crystals. However, specific capacitance of the carbon-based electrode was approximately 150 mAh/g, which is significantly lower than the specific electrode indexes, based on reduced graphene oxide and carbon nanotubes. So the specific capacitance of these electrodes was about 225–240 mAh/g.

Thus, it is clearly shown that the use of graphene and carbon nanotubes as conductive additives instead of traditional soot allows increasing significantly the specific characteristics of positive electrodes in lithium-ion batteries. Such an effect can be explained by an increase in the transport kinetics of lithium ions within the active material due to higher conductivity of nanotubes and graphene and more dense contact with crystals.

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Литий-иондық аккумуляторлардың электродтарының функционалды сипаттамаларына наноқұрылымды көміртегі қоспалардың әсері

Мақала литий-иондық аккумуляторлар үшін ванадий тотығы негізіндегі оң зарядты электродының функционалды сипаттамаларына наноқұрылымды көміртекті қоспалардың әсерін зерттеуге арналған. Көміртекті нанотүтікшелерді және қарапайым көміртек күйесінің орнына тотықсызданған графен тотығын қолдану электродтың меншікті сипаттамаларын жоғарлататыны көрсетілген және графен мен көміртекті нанотүтікшелерді қолдану литий-иондық батареялардағы оң зарядты электродтың ерекше сипаттамаларын жақсартатыны дәлелденген. Бұл эффект материал ішіндегі литий-ионның қозғалу жылдамдығының өсуімен түсіндіріледі, және бұл нанотүтікшелер мен графеннің жоғары өткізгіштігін және кристалдармен тығыз түйісуін қамтамасыз етеді. Осындай эффект дәстүрлі күйенің орнына көміртекті нанотүтікшелер мен графеннің электрондық өткізгіштігінің аса жоғары болуымен жүзеге асырылады. Сонымен қоса электродқа квазибірөлшемді (нанотүтікше) және квазиекіөлшемді (графен) жүйелерді енгізу белсенді зат бөлшектерінің тоқ алғышпен тығыз байланысын қамтамасыз етеді. Бұл электрод жүйесіндегі өткізгіш қоспаның массалық үлесінің төмендеуіне және оның меншікті көрсеткіштерінің артуына әкеледі. Литий-иондық аккумуляторларда қарапайым күйенің орнына графен мен көміртекті нанотүтікшелерді өткізгіштік қоспалар ретінде қолдану оң зарядты электродтардың меншікті сипаттамаларының артуына себеп болады.

Кілт сөздер: наноқұрылымды көміртек қоспасы, электрод, көміртекті күйе, литий-ионның жылдамдығы, литий-иондық батареялар, көміртекті нанотүтікшелер, графен оксиді, ванадий тотығы.

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Влияние наноструктурированных углеродных добавок на функциональные характеристики электродов литий-ионных аккумуляторов

Статья посвящена изучению влияния наноструктурированных углеродных добавок на функциональные характеристики положительного электрода на основе оксида ванадия для литий-ионных аккумуляторов. Было показано, что использование углеродных нанотрубок и восстановленного оксида графена вместо традиционной углеродной сажи значительно повышает удельные характеристики электрода, а также доказано улучшение специфических характеристик положительного электрода в литий-ионных батареях при использовании графена и углеродных нанотрубок вместо обычной сажи. Этот эффект объясняется увеличением скорости передвижения литий-иона внутри материала, обусловленным более высокой проводимостью нанотрубок и графена и более плотным контактом кристаллов. Кроме того, внедрение в электрод квазиодномерных (нанотрубки) и квазидвухмерных (графен) структур позволяет обеспечить более плотный контакт частиц активного вещества с токосъемником. Это способствует снижению массовой доли проводящей добавки в структуре электрода и повышению его удельных показателей. Показано, что использование графена и углеродных нанотрубок в качестве проводящих добавок вместо традиционной сажи позволяет существенно повысить удельные характеристики положительных электродов в литий-ионных аккумуляторах.

Ключевые слова: наноструктурированные углеродные добавки, электрод, углеродная сажа, скорость ионов лития, литий-ионные батареи, углеродные нанотрубки, оксид графена, оксид ванадия.