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# Electrode nanomaterials for lithium-ion batteries

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The state-of-the-art in the field of cathode and anode nanomaterials for lithium-ion batteries is considered. The use of these nanomaterials provides higher charge and discharge rates, reduces the adverse effect of degradation processes caused by volume variations in electrode materials upon lithium intercalation and deintercalation and enhances the power and working capacity of lithium-ion batteries. In discussing the cathode materials, attention is focused on double phosphates and silicates of lithium and transition metals and also on vanadium oxides. The anode materials based on nanodispersions of carbon, silicon, certain metals, oxides and on nanocomposites are also described.
The bibliography includes 714 references.

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## I. Introduction

The first rechargeable lithium-ion batteries (LIBs) were developed not very long ago but their use grows at unprecedented pace, so that today the annual world production of LIBs amounts to several billion items and their sales reach a value of several tens of billion US dollars. The fact that they have received so wide recognition in a relatively short time is explained by their high energy density and reliability.[1,2] It is the use of small and handy rechargeable batteries that triggered the development of portable and mobile electronic devices such as various communication facilities, laptops, digital photo and video cameras, wireless tools, *etc*. Yet another important factor is the aggravation of environmental problems all over the world, largely due to emissions of combustion gases (carbon, nitrogen and sulfur oxides) from cars and fuel-burning power stations. To reduce these emissions, the renewable energy came into use, *i.e*., the energy of Sun, wind and sea tides. However, all these sources are cyclic;[3] hence, to be used efficiently, their energy should be accumulated. Most promising among such systems are fuel cells, more accurately, in combination with electrolyzers, and also LIBs. In particular, the latter can serve as energy sources for electric and hybrid cars, submarines and several other vehicles; they are already actively used in numerous electronic devices and tools. All this provides grounds for considering LIBs to be the most promising high-technology products.[4,5] In 2010, the LIB market approached ~12 billion US dollars and, according to specialists, by 2015 their sales should increase more than 2.5-fold.[6]

The energy density of a modern LIB is 150–190 W h $kg^{-1}$ (according to information provided by certain companies, it can reach 240 W h $kg^{-1}$). As regards this parameter, LIBs surpass other accumulating devices,[7,8] which is largely caused by the properties of lithium, the most light-weight metal with the highest negative electrochemical potential. These properties of lithium determined its active use as the electrode material for a long time. The theoretical capacity of the anode material made of graphite is 372 mA h $g^{-1}$, while this value for the cathode material of lithium cobaltate is 274 mA h $g^{-1}$. However, for several reasons, the opportunities provided by these materials

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cannot be used in full measure and, in practice, their capacity does not exceed 320 and 140 mA h $g^{-1}$, respectively.[6] Considering the full assembly of a rechargeable cell, it can be stated that for the potential difference of 3–4 V, the currently achieved energy densities of LIB are close to the limit attainable for traditional electrochemical systems.[2] Nonetheless, the considerable progress in the LIB technology in the past decade is obvious. For instance, the development of methods for enhancing the working power and charge–discharge rates of rechargeable cells is currently quite topical.

The technology of magnesium-ion batteries can also be considered as very promising. The concept of such batteries based on the Mg/S system was recently put forward by Toyota. These batteries are bound to be cheaper and their theoretical volumetric energy density may be almost double that of LIBs.[9] The electrolyte for magnesium-ion batteries has already been developed based on $Mg(BH_4)$,[10] as well as materials for their cathodes[11] and anodes.[12,13] In recent years, keen attention has been paid to sodium-ion batteries.[14,15] However, these technologies can be considered feasible only in the very long run, their working characteristics being much lower as compared with LIBs; hence, the attention is focused on the latter.

A distinctive feature of current studies is the active use of nanomaterials. These materials now occupy the niches that recently fully belonged to amorphous and crystalline materials.[16–20] The idea that nanomaterials can be used in LIBs is not new.[21] Indeed, for several reasons, the use of such materials should be much more fruitful.

Recently, attention was focused on materials for alternative power production. In particular, these were considered in several reviews.[22–28] Reviews surveying the achievements in the field of LIB development were also published[29,30] as well those describing electrode materials for these LIBs.[6,8,31–38] However, the majority of publications either concentrate the attention on a relatively narrow range of materials or present too little information on the specific features of using nanomaterials.

The present review gives a survey of the state-of-the-art research in the field of electrode nanomaterials for LIBs. To provide understanding of this field, we considered it pertinent to cover briefly certain other types of materials, particularly, cathode materials based on transition metal oxides.

## II. General information

### II.1. Operation of lithium-ion batteries

The design of lithium-ion batteries is rather simple (Fig. 1): a separator impregnated with an electrolyte is arranged between the cathode and the anode;[21,29,30] the whole structure is enclosed in a sealed casing that protects the materials from the harsh components of the environment (primarily, oxygen and water vapour).

During the discharge, under the effect of the chemical potential gradient, the lithium ions diffuse through electrolyte from anode to cathode. As this takes place, the cathode acquires the positive charge due to accumulation of excessive cations, while the excess of electrons left at the anode makes it negatively charged. When the circuit is closed, the electrons move between the electrodes *via* the external circuit thus performing useful work. During charging, due to the applied potential difference, lithium ions are deintercalated from the cathode material. The energy density of a battery is determined by the potential difference between the intercalation and deintercalation processes at the cathode and the anode and also by the electrochemical capacity of electrodes.[29] At the same time, the capacity of electrode materials is not used to the full extent due to stability problems. Thus, the most widely used cathode material $LiCoO_2$ is usually charged by less than 50% due to self-degradation (the useful capacity is 140 mA h $g^{-1}$). Moreover, increasing the working potential difference, which is necessary for further charging, brings about problems associated with the use of conventional solvents involved in the electrolyte.[39]

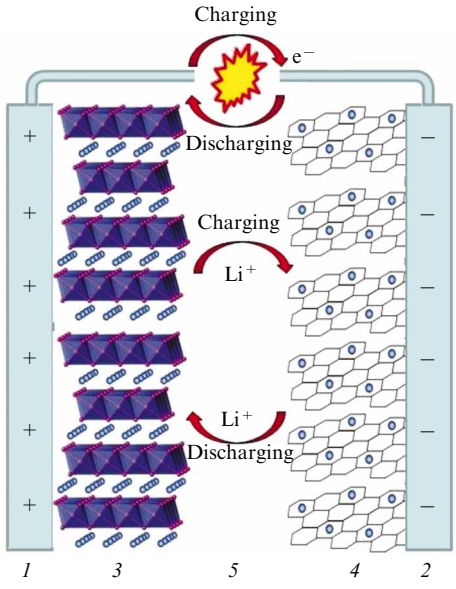



**Figure 1.** Basic diagram of LIB.
(*1*) Cathode collector, (*2*) anode collector, (*3*) cathode material, (*4*) anode material, (*5*) separator with the electrolyte.

In the predecessors of LIBs, lithium cells, metal lithium served as the anode material and several oxidants [$CuF_2$, $CuCl_2$, CuS, $NiF_2$, $Ni_3S_2$, $CdF_2$, $Ag_2CrO_4$, $(CF)_n$, *etc.*] were used as the cathode materials.[40] In the 1970s, manganese and cobalt oxides came to active use as the cathode materials.[36,41] The operation of these devices is based on the concept of topochemical reactions.[42] In the modern LIBs, materials capable of reversibly intercalating and deintercalating lithium at substantially different potentials usually serve as the cathode and anode materials. As a rule, the anode is made of graphite or some other carbon material. The active substance of the cathode represents, most often, lithiated cobalt oxide ($LiCoO_2$) and, more rarely, lithiated nickel oxide ($LiNiO_2$), lithium manganese spinels ($LiMn_2O_4$) or mixed lithiated oxides (*e.g.*, $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$, $LiNi_xCo_{1-x}O_2$, $LiNi_{1-x-y}Co_xAl_yO_2$, *etc.*). Recently, considerable attention has been paid to lithium iron phosphate ($LiFePO_4$).

### II.2. Key advantages of using nanomaterials for electrodes of lithium ion batteries

The liquid and gel electrolytes used in LIBs are characterized by fairly high conductivity;[43] hence, the electrode charging and discharging rates are largely determined by

the rate of simultaneous diffusion of lithium ions and electrons in the solid phase. According to Fick's law, the time of complete charging (or discharging) of a cell should be proportional to the squared thickness of the diffusion zone. The diffusion in the intergrain space is usually substantially faster as compared with crystals;[44,45] hence, for solid electrolytes with not too high conductivity, which dominate among electrode materials for LIBs, the rate of electrochemical processes is determined by the particle size. Thus, the smaller the crystals of electrode materials, the higher the rate of the battery charge and discharge.

Meanwhile, the diffusion of atoms and ions in the surface layers of solids proceeds much faster than in their bulk. This effect was discussed in several reviews.[46–50] Among the factors responsible for this phenomenon, large free volume and the presence of dangling bonds are often considered as the chief factors. Moreover, near the surface, the concentration of defects is always higher.[51] Due to the small size of nanoparticles, this effect can extend to a considerable part of the whole material.

It deserves mention that lithium intercalation and deintercalation can proceed by two different mechanisms. According to one mechanism, a continuous series of solid solutions are formed and the lithium concentration changes in the material bulk (Fig. 2 *a*). For instance, this mechanism operates in the most widely used LIBs with a lithium cobaltate-based cathode and a graphite anode.

In some materials, the mutual solubility of the lithiated and delithiated phases turns out to be extremely low, so that virtually throughout the whole range of charging degrees, two phases coexist during the process (see Fig. 2 *b*). This mechanism is typical of charging and discharging processes in the cathode materials based on lihtium iron phosphate and the anode materials based on lithium titanate.[52]

This seemingly small difference leads to substantial deviation in the character of charging and discharging processes. First of all, note that in terms of the solid solution model, the system potential during the cell charging steadily shifts toward lower potentials with an increase in the lithium content in the cathode material (Fig. 3, curve *1*), which corresponds to the decrease in the LIB power. However, when two phases coexist, the potential remains virtually constant for any degree of lithiation with the exception of small regions in the very beginning and at the end of the process (see Fig. 3, curve *2*). The potential is unambiguously determined by the difference between the energy levels of lithium ions in the two phases of constant composition.[45] The fast potential variation in the initial and final stages of discharging or charging is associated with the limited mutual solubility of the phases, resulting in some change in the phase compositions in these regions. Furthermore, the kinetics of these processes is described by different equations.[52]

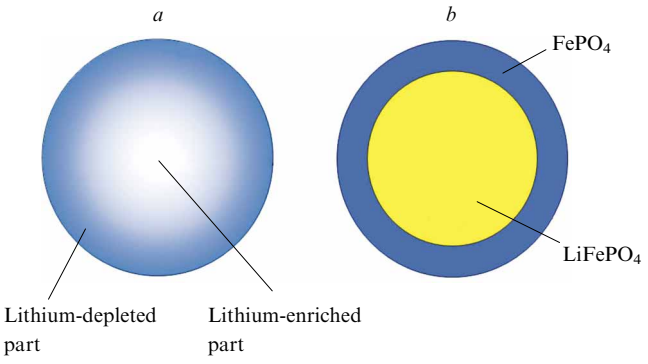



**Figure 2.** Distribution of lithium ion concentration during charging of cathode materials based on $LiCoO_2$ (*a*) and $LiFePO_4$ (*b*).

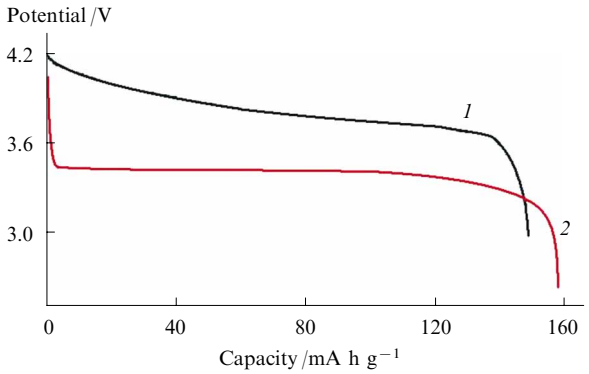



**Figure 3.** Potential variation during the discharge of cathode materials based on $LiCoO_2$ (*1*) and $LiFePO_4$ (*2*).

When nanomaterials are used, due to the structural disorder of a substantial part of material located in the surface layers, the mutual solubility of phases increases [53] and the potential variation during the charge and discharge processes may become more pronounced.

It should also be noted that, as the diffusion layer becomes thicker, the resistance to the transfer processes increases; hence, the complete charge (or discharge) of coarse particles usually requires substantially larger voltage. Due to the necessity of providing safe operation of the battery, the voltage is usually limited, which results in incomplete charging of electrode materials.

In a review [6] devoted to oxide anode materials, it was noted that an ideal anode should meet the following requirements:

— contain elements with relatively low atomic mass capable of intercalating large amounts of lithium (lithium should be reversibly intercalated into the structure);

— have a working potential as close as possible to the working potential of lithium metal;

— be insoluble in and inert toward the solvent and salt components of the electrolyte.

A cathode material should meet virtually the same requirements with one exception: its working potential should, in contrast, be as high as possible. However, if the working potential is too high, the cathode might start to oxidize the solvents traditionally involved in the electrolyte.

A topical problem is to enhance the power density of batteries, which implies the possibility of their fast discharging (charging) and, correspondingly, higher rates of lithium intercalation and deintercalation. However, due to nonequilibrium modes of battery operation and the limited diffusion rates of lithium ions and electrons (or the presence of considerable resistance to their diffusion) at high charge and discharge rates, the LIB capacity is not used to the full extent, which, for understandable reasons, does not satisfy consumers. The loss in capacity at the high cycling rates can

be minimized by using nanomaterials for the manufacture of cathodes and anodes.

Finally, it is noteworthy that cycling also brings about problems of stability of electrode (more often, anode) materials due to substantial changes in their volume on lithiation and delithiation. This is a significant reason for the use of nanoparticles in place of bulk materials. In the presence of a considerable number of interfaces, voids in the packing of particles and also disorder on the particle surfaces, the adverse effects that might lead to destruction of electrodes and the loss of their capacity are largely eliminated. Certain features of the aforementioned processes are discussed below for particular electrode materials.

## III. Anode materials

### III.1. Carbon nanomaterials

The common choice for the LIB anode material is graphite, which provides both high rates of charging and discharging processes and a relatively high energy density due to reversible lithium intercalation into its interlayer spaces.[54] Its working potential is only 0.15–0.25 V, which is close to ideal parameters. However, changes in the structure and volume during these processes lead to fast degradation of graphite anodes; this is why attempts were undertaken to use carbon nanomaterials. Carbon nanotubes (CNT) appeared almost simultaneously with LIB.[55] It was assumed that CNT may provide a higher intercalation capacity as compared with graphite.[56, 57] However, it turned out that insertion of lithium through the cylindrical side surface is hampered,[58] so that lithium is incorporated through the end surfaces and has to diffuse along the nanotube. In this case, the diffusion zone thickness is sufficiently large and the capacity of the material turns out to be low: for single-walled and multi-walled CNT, it does not exceed 400 mA h $g^{-1}$. However, despite the lack of prospects of using CNT as the anode materials for LIBs, the studies along this line are still continued.[59–67]

The other carbon nanomaterials such as nanofibres, graphene particles and heat-expanded graphite also proved to be unsuitable for lithium intercalation.[68–80] The high diffusion rate they provide is not accompanied by strong binding of a large amount of lithium; hence, the enhanced intercalation capacity is possible for these materials only when they are charged up to very high potentials (usually from 0 to 3 V). For nanomaterials, the electrode potentials of lithium intercalaction and deintercalation vary continuously over wide limits and substantially differ (Fig. 4), the energy consumed in the charging process being much higher than that obtained upon discharging. Furthermore, in the potential range of interest for LIBs, the capacity of carbon nanomaterials is much lower than that of graphite (see Fig. 4).

A substantial drawback of carbon materials for LIB anodes is the presence of a high irreversible capacity in the first charge–discharge cycle.[81–85]

At the same time, carbon nanomaterials are widely used for developing composite electrodes, both cathodes and anodes. These materials are characterized by high conductivity and the possibility of fast transport of lithium over the surface; their addition increases the transfer rates in intergrain spaces providing lithium delivery to the surface of all particles. Moreover, in such composites, carbon nanomaterials ensure binding between the nano-sized particles of

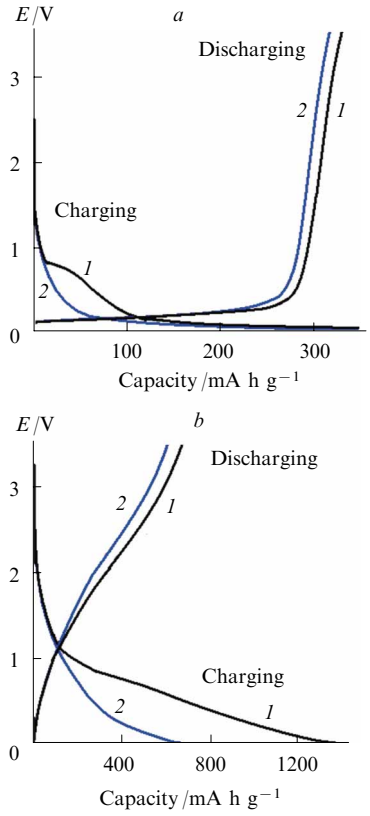



**Figure 4.** Charge and discharge curves of the first (*1*) and third (*2*) cycles for electrodes made of artificial graphite (*a*) and graphene nanosheets (*b*).[56]

other materials with a high lithium intercalation capacity and thus stabilize the material.

Both nano-sized carbon coatings (amorphous carbon) and carbon nanomaterials are used. In 2004, successful use of carbon nanotubes intercalated with tin was reported.[86] Lithiation of tin contained in a nanotube induced strong internal stress, which, however, does not destroy the nanotube. A composite consisting of tin nanoparticles distributed in the network of carbon nanotubes was described.[87] Several other composites of tin and carbon nanotubes were used (*e.g.*, see publications[88–92]); however, they failed to demonstrate any advantages over the materials containing fine graphite dispersions. Somewhat higher characteristics were obtained for composites formed by carbon nanomaterials and tin alloys with other metals, among which the systems Sn–Co–C were most interesting.[93–97] Composites of $SnO_2$ with carbon nanotubes[98, 99] and $TiO_2$ and CuO composites with carbon nanotubes[100, 101] were reported.

Graphene was supposed to find wide use as the material for LIB anodes. For instance, a graphene composite with carbon nanotubes was described.[102] However, in a review,[30] the use of graphene only in composites is discribed.

At present, graphite is still the most widely accepted anode material; however, it has several drawbacks of which mention should be made of its relatively low capacity and fast degradation. Numerous attempts to overcome these drawbacks by using carbon nanomaterials have not yet produced any positive results.

### III.2. Nanomaterials based on silicon

The keen attention paid by scientists to silicon anodes is associated with the fact that silicon-based intermetallic compounds can contain up to 81.5% of lithium. This is why silicon demonstrates the record-breaking lithium intercalation capacity (4200 mA h $g^{-1}$). However, its practical use is hindered by the extremely high ($\sim$4-fold) increase in its specific volume during this process,[103–105] which violates its adhesion to the support and leads to destruction of this material.[8] Moreover, the capacity of such anode material was shown to decrease[106] from 3260 to 200 mA h $g^{-1}$ as soon as after the first ten cycles.

This problem can be solved by using thin-film electrodes of amorphous silicon,[106–122] which is free to expand in the direction normal to the film; moreover, such films allow one to clearly observe the size effect, because their cyclability decreases with increasing thickness. Thus, for 50 nm-thick films, the capacity of amorphous silicon stayed at a level of 3500 mA h $g^{-1}$ for 100 cycles and became 3000 mA h $g^{-1}$ after 1000 cycles. For a 77 nm thick film, the capacity decreased to 1500 mA h $g^{-1}$ after $>1000$ cycles; for 150-nm and 340-nm films, the capacity decreased to 2500 and 2000 mA h $g^{-1}$, respectively, after much fewer numbers of cycles.[106, 110, 113, 114] Among the most widely accepted methods for synthesizing such films of amorphous silicon are magnetron sputtering, laser-induced evaporation and silane decomposition.[8]

However, based on thin-film electrodes, it is impossible to obtain rechargeable cells with a high overall capacity or their design is substantially complicated. From this standpoint, certain advantage is gained by nanoparticle-based materials, which considerably damp down the effect of volume variation. Thus, anodes made of nanosized silicon demonstrated the reversible capacity of 1700 mA h $g^{-1}$ in 15 cycles.[123] With the use of certain surfactants, the nanoparticles measuring 5 nm with the capacity of up to 2500 mA h $g^{-1}$ for the number of cycles $>40$ were synthesized.[124] Highly porous silicon, which is usually synthesized by a chemical reduction of its oxide or by selective etching of silicon plates, was also used.[125–132]

Of considerable interest are nanostructured silicon electrodes.[129, 130, 132, 133] In connection with this, the studies devoted to the possible use of silicon whiskers in the LIB anode (Fig. 5) deserve mention.[134–142] Unfortunately, the achieved results are far from being impressive; however, the active research along this line goes on. Yet another line of research is the development of core–shell structures.[138, 143]

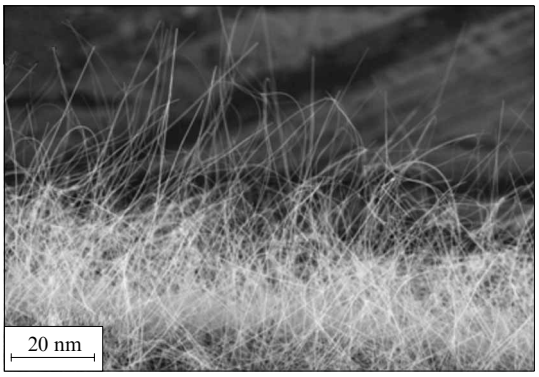



**Figure 5.** Electron microscopic image of silicon whiskers on a stainless steel support.[140]

The formation of silicon composites with carbon proved to be more beneficial.[104, 144–150] The pyrolytic decomposition of solid or gaseous silicon-containing compounds seems to be the most attractive method.[151–156] In such systems, carbon damps down the considerable changes in the silicon volume and provides contact between the particles. In the recent years, several composites were synthesized based on silicon nanoparticles with carbon,[156] which included such carbon allotropes as graphene,[157, 158] nanograins[159] and nanofibres.[160, 161] Anode composite materials based on carbon and silicon were shown[162] to have capacity varying from 1040 to 790 mA h $g^{-1}$ in the first 20 cycles. A still higher value (1950 mA h $g^{-1}$) was observed for highly porous silicon composites,[163] where the specific capacity of silicon nanoparticles approached its theoretical value. Thus, at the $1C$† cycling rate, the composite capacity did not decrease below 1500 mA h $g^{-1}$ during the first 100 cycles. It can be assumed that porous composites eliminate the volume variations most efficiently.

Composites based on silicon nanoparticles with graphene retained the capacity of $>1500$ mA h $g^{-1}$ after 200 cycles.[164] By means of capillary-driven assembly of aerosol droplets,[165] composites in the form of graphene-encapsulated silicon nanoparticles were synthesized and their capacity was shown to reach 1200 mA h $g^{-1}$. Meanwhile, composites based on nanosized silicon particles and carbon nanotubes, despite being very popular, failed to provide a silicon capacity $>50\%$ of the theoretical value.[166–170]

In view of the advances in the use of nano-sized silicon films, the most efficient way seems to be the synthesis of layered silicon composites with carbon. Such composites with the layer thickness from several nanometres to several tens of nanometres (Fig. 6) were synthesized by layer-by-layer magnetron sputtering.[171–174] It is evident that silicon is their key electroactive component. The charge–discharge curves of the layered composites resemble very much those

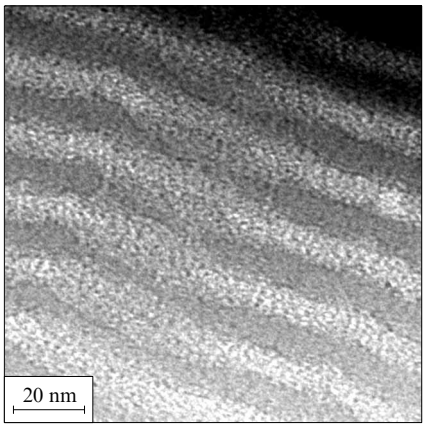



**Figure 6.** Microimage of the cross-section of a silicon–carbon composite sample.[174]
Light strips are carbon and dark strips are silicon.

† The cycling rate $nC$ means that the battery is completely charged or discharged in a time of $1/n$ h.

of amorphous silicon. The extraction of the major amount of lithium from these composites proceeds in the potential range of 0.3–0.7 V, whereas lithium extraction from graphite occurs predominantly in the range of 0.05–0.3 V.

Attempts have been undertaken to use other composites, for instance, Si–Ge–Mo,[175] Si–$TiO_2$,[176] Si–Ge,[177] Si–Y,[178] Si–Ni,[179] Si–Ti,[180] Si–Cu.[181] The silicon composites with aluminium were found to be most efficient.[182–187] Considerable attention was drawn to systems containing silicon oxide apart from elemental silicon, particularly, to the ternary composites Si–SiO–C.[188–197] A new trend is the development of nanosilicon composites with conducting polymers, *e.g.*, polyaniline.[198]

Silicon is probably one of the most promising anode materials. However, the considerable increase in its volume during lithiation of bulk samples leads to fast degradation. The most impressive progress was achieved for thin-film samples, first of all, those made of amorphous silicon and also for nanomaterials including nanocomposites.

### III.3. Metallic nanomaterials

Certain metals (tin, aluminium) can incorporate large amounts of lithium; moreover, in this characteristics, they even surpass carbon. The tin intermetallic compound with the highest content of lithium has the composition $Li_{4.4}$ Sn. However, due to the large atomic mass, the tin capacity is substantially lower (990 mA h $g^{-1}$; according to some other data, it can reach only 960 mA h $g^{-1}$).[199,200] However, as in the case of silicon, the intercalation of lithium into tin is accompanied by a very large (2.85–3.60-fold) increase in its volume.[28] As a result, the battery anode is destroyed during its first charging. Stabilization of the material is possible by using nanosized particles.[201,202]

There are published data only on electrodes based on tin nanowhiskers[203] with the capacity of 400 mA h $g^{-1}$ and sufficiently good cyclability. Anodes of thin tin foil were described[204] the capacity of which remained at 600 mA h $g^{-1}$ during 15 cycles but substantially decreased on further cycling, which was accompanied by an increase in their electric resistance. Adequate results were obtained also for films consisting of tin and aluminium.[205] Finally, the attempts to use tin coatings on nanowhiskers of copper (Fig. 7) and titanium dioxide proved to be successful. Encouraging results were obtained for thin tin coatings on highly porous nanostructured copper.[207] Indeed, the prospects for the practical use of such systems are vague due not only to their exotic nature but rather to the low overall capacity. However, even the attempt to stabilize tin materials is noteworthy.

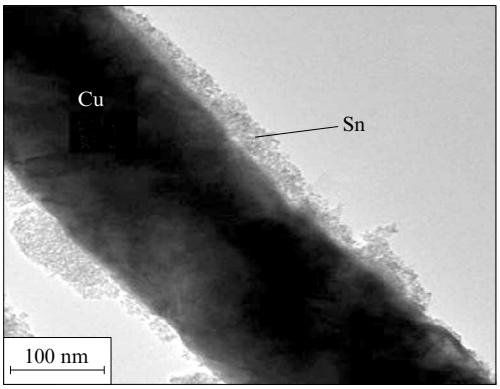



**Figure 7.** TEM image of a copper nanowhisker coated with tin.[206]

Tin alloys or composites with certain metals proved to be much more stable. For instance, nickel and iron alloys with tin demonstrated the following capacity:

| Alloy | $Ni_3Sn_4$ | $FeSn_2$ | $FeSn_5$ |
|---|---|---|---|
| Capacity /mA h $g^{-1}$ | 100–30 | 500 | 750 |
| Ref. | 8 | 208 | 209 |

The $Cu_6Sn_5$ intermetallic can reversibly absorb up to 13 lithium atoms per formula unit and has the theoretical capacity of 358 mA h $g^{-1}$; the tin alloy with antimony has the theoretical capacity of up to 600 mA h $g^{-1}$ (Refs 202 and 210). The use of other tin alloys was reported. Presumably, in certain systems, phase decomposition takes place to form intermetallic compounds. Based on certain alloys, thin-film electrodes were synthesized. Thus, for the film of the Sn/$Cu_6Sn_5$ composite, the capacity of $>400$ mA h $g^{-1}$ was obtained;[211] for $Cu_6$ $Sn_5$ deposited on a porous copper support, the capacity was found to be 400–490 mA h $g^{-1}$ (Ref. 212); on thin films of the Ni–Sn alloy containing 62 at.% tin, the capacity was 650 mA h $g^{-1}$ (Ref. 213). However, it was shown[214] that the capacity of such films also quickly decreases to reach 500 and 350 mA h $g^{-1}$ after 10 and 50 charge–discharge cycles, respectively. A better cyclability was observed when this alloy was deposited on copper nanowhiskers: the capacity was 500 mA h $g^{-1}$ after 200 cycles.[215] However, the anodic deintercalation of lithium in such systems usually proceeds at higher potentials, which leads to a decrease in the LIB efficiency. Thus, for thin-film electrodes made of the Sn/$Cu_6Sn_5$ composite, this process takes place at 0.5–0.7 V, while intercalation occurs at 0.1–0.3 V.[211] One cannot rule out that this is a consequence of phase decomposition.

Considerable attention is given to the development of tin composites with carbon materials. For instance, such a composite[216] demonstrated the capacity of 480 mA h $g^{-1}$ during 30 cycles. The transition to nanocomposites made it possible to reach the capacity of 500 mA h $g^{-1}$ in 200 cycles.[215] The capacity of a nanocomposite containing tin nanoparticles covered with carbon was found to be 760 mA h $g^{-1}$ in 10 cycles.[217] The $\sim 600$ mA h $g^{-1}$ capacity during 200 cycles was demonstrated by a composite based on carbon and a tin alloy with iron.[218] Keen attention was also paid to synthesizing tin composites with carbon nanotubes.[219–222]

The advantages and drawbacks of silicon and tin as anode materials are very similar. However, tin is to a certain extent inferior to silicon, namely, it demonstrates lower capacity due to its higher atomic mass. As for silicon, its capacity can be increased by switching to nanomaterials; however, even for nanomaterials, the reported stability is often limited to small numbers of cycles, probably due to the higher plasticity of such structures and their tendency to restructuring. More encouraging results were obtained in testing tin-based alloys.

### III.4. Metal oxides

Oxide systems are often used as cathode materials. However, numerous recent studies report testing of oxides as anode materials and in some cases, fairly good parameters were achieved. Oxide-based anode materials can be divided

into three classes according to electrochemical reactions occurring in them. In the materials of the first class, only the oxidation state of the transition metal changes during the lithium intercalation

$$Li_x(M^{n+})_yO_z + p\,Li^+ + p\,e = Li_{x+p}(M^{(n-p/y)+})_yO_z \quad (1)$$

Typical examples of such systems are titanium oxide and lithium titanate.

In materials of the second class, the oxide is reduced to the metal and simultaneously lithium oxide is formed

$$(M^{2z/y+})_yO_z + 2z\,Li^+ + 2z\,e = z\,Li_2O + y\,M \quad (2)$$

In complex oxides, one element can be reduced to the elemental metal, while the second one can form its individual oxide phase

$$A_x(M^{n+})_yO_z + ny\,Li^+ + ny\,e = \quad (3)$$
$$= A_xO_{(z-ny/2)} + M + (ny/2)\,Li_2O$$

This group includes certain oxides of transition metals (manganese, lead, cobalt, *etc.*) and also mixed oxides of the same metals with more active metals.

In materials of the third class, the electrochemical process includes two stages: in the first stage, the oxide is reduced to the metal [see Eqn (2)] and, in the second stage, an intermetallic compound is formed

$$M + p\,Li^+ + p\,e \rightleftharpoons Li_pM \quad (4)$$

It should be noted that only reaction (4) is reversible and the original oxides are not recovered on delithiation, *i.e.*, process (2) is irreversible in such systems. Hence, the question arises of what is the use of oxides if they are known to be substantially inferior to metals as regards the specific capacity and require additional amounts of lithium for their reduction in the first stage. Actually, they are used only to prevent the destruction of anode materials during lithium intercalation–deintercalation caused by wide variations in their volume.

For this purpose, oxides of bi- or tetravalent tin were often employed. In the first stage, such oxide is reduced to form metal nanoparticles which later intercalate lithium.[223–226] It is due to their small size that the particles are not destroyed. Moreover, the reversible capacity determined only by the lithium intercalation–deintercalation processes is approximately equal to the irreversible capacity. A close-to-theoretical capacity on the electrodes of nanosized tin oxides was achieved back in the beginning of the 21st century.[227,228] However, in the majority of cases, the capacity of such electrodes turns out to be lower than its theoretical value (300–600 mA h $g^{-1}$) and it is almost halved after the first 10–30 cycles. Such degradation is explained by the gradual recrystallization and coarsening of tin particles.[224,225]

The studies using tetravalent tin oxide are more popular. Comparing the data for commercial $SnO_2$ samples with the particle size of 40 nm with the data for nanoparticles synthesized by various procedures and measuring 5.8 and 4.5 nm have shown[229] that their primary capacities are comparable, *i.e.*, 510, 520 and 525 mA h $g^{-1}$, respectively. However, after 50 cycles, the capacity of the commercial sample was reduced by 80%, while the capacities of smaller nanoparticles decreased only by 50% and 40%, respectively. Later, it was reported[230] that tin-oxide-based nanocrystalline materials with the particle size of 3, 4 and 8 nm synthesized by the hydrothermal method demonstrated capacities of 740, 636 and 554 mA h $g^{-1}$, respectively. Moreover, whereas the capacity of small particles was retained for 60 cycles, it decreased ~30-fold for the large particles. According to scanning electron microscopy, it is the large particles that exhibited the trend towards aggregation when cycling. The results of other studies of $SnO_2$ nanoparticles as cathode materials were also published. The majority of authors reported the initial capacity of about 600–800 mA h $g^{-1}$, which was, on average, halved after 50 cycles.[230–235] The synthesis of hollow nanospheres based on $SnO_2$ the capacity of which reached 930 and 1140 mA h $g^{-1}$ but was more than halved as soon as after 30 cycles was reported.[233,236] Nanomaterials with higher initial capacity (1300 mA h $g^{-1}$) were also synthesized.[237]

Hollow nanocubes of tin oxide with 200 to 800 nm edges were prepared by etching sacrificial materials based on $Cu_2O$ nanoparticles covered with $SnO_2$ (Fig. 8). Their capacity decreased from 1040 to 570 mA h $g^{-1}$ after the first 20 cycles. However, it deserves mention that a substantial part of this capacity was realized in the potential range of 1–2 V, which makes such structure less attractive.

It was reported[238,239] that the use of $SnO_2$ nanotubes may prove to be very advantageous. Such nanotubes accommodate free space sufficient for damping down the volume variations, providing fast lithium transport and preventing aggregation. A template-assisted method of synthesizing $SnO_2$ nanotubes was developed.[240] The resulting materials demonstrated the initial capacity of 940 mA h $g^{-1}$, which decreased to 525 mA h $g^{-1}$ after 80 cycles. Nanowires with relatively low initial capacities of 420 and 750 mA h $g^{-1}$ were synthesized;[241,242] the former lost a little more than 20% after 30 cycles and the latter lost 30% after 10 cycles. Nanotubes and nanowires with the unexpectedly high capacity of 1380 and 1130 mA h $g^{-1}$ were synthesized.[243] However, only 22% and 26% of their initial capacity were retained after 50 cycles. Three-dimensional hierarchical structures of $SnO_2$ nanosheets[244] demonstrated the specific capacity of 400 mA h $g^{-1}$ during 30 cycles at high charge and discharge rates. This may be attributed to the short diffusion path of lithium ions. Structures shaped as flowers assembled of $SnO_2$ nanosheets demonstrated the capacity of >450 mA h $g^{-1}$ during >50 cycles.[245] It was noted that a thin-film tin oxide

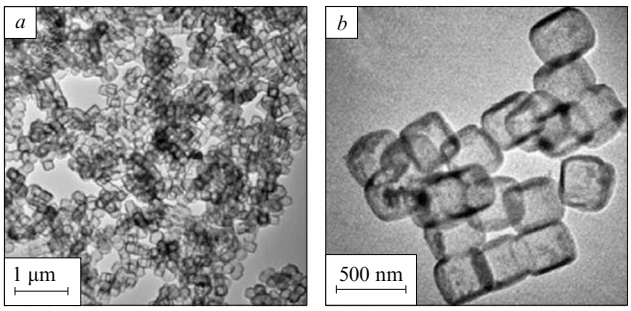



**Figure 8.** TEM images of hollow $SnO_2$ nanocubes with the edge of 200–250 nm.[238]

electrodes exhibited much higher stability. For instance, the films with the initial capacity of 500 mA h $g^{-1}$ used to lose only 2% of this value after 100 cycles.[246,247] Adequate results were also obtained[233] for nanosheets with the thickness of ~5 nm, the capacity of which decreased from 936 to 534 mA h $g^{-1}$ after 50 cycles.

Indium-doped tin oxide nanoparticles with the initial capacity of 603 mA h $g^{-1}$ were shown to lose no more than 5% of its value in the first 20 cycles.[231] The capacity of nanomaterials containing ~56% graphene, which was initially 900 mA h $g^{-1}$, fell down to 720 mA h $g^{-1}$ after 50 cycles.[248] Adequate results were obtained for composites and sandwich structures of $SnO_2$ nanosheets and graphene the initial capacity of which was 1000 or 970 mA h $g^{-1}$ and decreased by ~25% after 50 cycles.[249,250]

Thin films of mixed nanostructured tin (90%) and titanium (10%) oxides formed by globules with the size of 10–20 nm, which in turn were build of blocks measuring 6–8 nm, were reported.[251–255] They were based on a $(Sn,Ti)O_2$ solid solution with the cassiterite structure in the amorphous $SnO_2$ matrix. There structures could reversibly intercalate lithium virtually without loss in capacity. Based on the analysis of the lithium reaction products with the electrode material and their electrochemical properties, it was shown that the mechanism of charge–discharge processes in these electrodes is characterized by the involvement of oxygen in the reversible reactions of lithium intercalation. The addition of $TiO_2$ stabilized the oxide structures. Titanium dioxide is not reduced by lithium and favours the formation of the oxygen environment for the neighbouring tin atoms even after their reduction by lithium. The cathodic polarization of such material yields tin metal and $Li_xSn$ intermetallics. During the subsequent anodic polarization some of tin atoms are again oxidized, which is stoichiometrically equivalent to the reversible incorporation of lithium into the oxide phase. Thin films containing titanium(IV) and tin(II) oxides were prepared[256] and demonstrated a relatively low initial capacity (162 mA h $g^{-1}$), which was, however, retained almost in full measure after 50 cycles. Somewhat better results were demonstrated by nanocomposites based on divalent tin and trivalent vanadium oxide with the particle size of 20–30 nm. However, their capacity decreased by 13%–20% during the same 50 cycles but the initial values were much higher (435–565 mA h $g^{-1}$).[257]

Although the capacity of tin(II) oxide-based materials should somewhat exceed that of $SnO_2$ samples, it actually turns out to be markedly lower so that these materials attract less attention. Nonetheless, in this case too, switching to nanoparticles tends to increase the capacity. Thus, the maximum initial capacity of 850 and 950 mA h $g^{-1}$ could be achieved for anode materials based on SnO nanoparticles with the average size of ~ 20 nm.[258,259] However, the capacity substantially decreased on cycling. At the same time, the cycling behaviour was shown to be much better in other cases for nanoparticles of almost the same size but with somewhat lower initial capacity.[259,260]

The electrode properties of other tin-containing oxide materials were reported in the literature, for instance, for lithium and some divalent metal stannates.[261–266] However, all of them were obviously inferior to tin oxide.

The electrochemical charge processes for antimony and tin oxides are similar. In the first stage, antimony oxides are irreversibly reduced to the metal by the reaction analogous to reaction (2) and then the $Li_3Sb$ intermetallic is formed. As the oxidation state of antimony increases, the capacity of these materials decreases. Moreover, the oxide of pentavalent antimony was reported to be unsuitable as the anode material.[267] In connection with this, attention was focused on the oxide of trivalent antimony with the reversible capacity of ~ 500 mA h $g^{-1}$ in the first cycle decreasing by 40% in the first ten cycles.[268] A substantially better cyclability was exhibited by thin films of antimony oxide[269] and its nanocomposites with antimony metal,[270–272] where stabilization was precisely due to the presence of nanosized antimony particles.

The amazingly high capacity (up to 1700 mA h $g^{-1}$) was achieved for nanofilms and nanodisks of indium oxide.[273–275] Insofar as the above value far exceeded the theoretical capacity of the formation of $Li_3In$ intermetallic (578 mA h $g^{-1}$), it was assumed that here both processes are reversible [see Eqns (2) and (4)]. However, in all experiments, the capacity rapidly decreased down to 500–580 mA h $g^{-1}$ on cycling.

In anode materials based on the oxides of iron, cobalt, nickel, copper and some other metals, lithium is intercalated reversibly upon the reduction of the metal but without alloy formation [see Eq. (2)], the transition metal oxide being recovered in the anodic process. The reversible capacity of such structures can be 600–700 mA h $g^{-1}$; however, good reversibility of electrochemical processes is typical only of nanostructured materials.[276] Moreover, according to some data,[277] the reduction may produce a composite of still finer particles of lithium oxide and the transition metal within the original nanoparticles in the matrix of the remaining oxide. However, the very high potential of the anodic process (~2 V) restricts the applicability of such materials.

A comparison of the properties of anode materials based on oxides of divalent iron, cobalt and nickel with the rock salt structure has shown[278] that all these systems demonstrate similar initial capacities of about 600–700 mA h $g^{-1}$. However, after 50 cycles, the capacity of systems based on iron and nickel decreased to 200–250 mA h $g^{-1}$ and only for cobalt oxide the capacity variation on cycling was moderate. Better results could be achieved for $Co_3O_4$ the capacity of which remained stably high at a level of 900–1000 mA h $g^{-1}$. For mesoporous nanodisks of cobalt(II) oxide with the thickness of 10 nm, the capacity of 965 mA h $g^{-1}$ was observed and remained virtually unchanged after 100 cycles.[279]

Other oxides of divalent metals were somewhat inferior to cobalt oxide but also provided sufficiently high capacity values when nanosized materials were used. Thus, 40 nm thick nickel oxide plates exhibited capacity of 685 mA h $g^{-1}$, which remained almost unchanged on cycling.[280] The high values of reversible capacity were obtained for porous NiO nanoflakes with the thickness of 20 nm and also for hollow nanospheres: 830 and 880 mA h $g^{-1}$, respectively.[281,282] However, these materials demonstrated much lower stability and were found to lose 20% and 45% of their initial capacity after 50 cycles, respectively. Nanodispersed FeO samples exhibited the initial capacity of ~700 mA h $g^{-1}$; however, the data on their cyclability are very controversial. For the best samples, the capacity decreased by merely 20% after more than 100 cycles.[278]

The formation of composites helps in some cases to ensure the stability of nanostructures and reversibility of reaction (1). Thus, mention should be made of the anode

materials made of composites based on transition metal oxides with graphene,[283, 284] carbon nanotubes[285, 286] and nanospheres.[287–289] Probably, the most interesting results were obtained for nanostructured cobalt oxides.[284, 286, 289–307] For example, CoO nanocomposites with graphene demonstrated the capacity of up to 980 mA h $g^{-1}$ (Ref. 308), which remained virtually unchanged after 50 cycles. An interesting material in the form of needles with the diameter of 15–25 nm based on carbon nanotubes encapsulated in cobalt oxide shells was described.[309] Its initial capacity reached 1080 mA h $g^{-1}$ and decreased by less than 10% after 100 cycles. Composite samples of nanosized nickel oxide with graphene exhibited the capacity of 900 and 750 mA h $g^{-1}$; moreover, the capacity of the latter sample decreased by only 7% after 100 cycles.[310, 311] The nanocomposites of CuO with graphene,[312, 313] MnO with graphene[314, 315] and CuO with carbon nanotubes[316] were described. In the majority of cases, these results were less impressive than those for cobalt oxide but the capacity of the MnO–graphene composite equal to 790 mA h $g^{-1}$ remained virtually unchanged for 90 cycles.[316]

Considerable attention of scientists is focused on iron and cobalt oxides with the spinel structure in which the metal is in the mixed bi- and trivalent state. The chief reason for this is probably their higher stability as compared with oxides of divalent metals. For instance, electrodes of spherical $Fe_3O_4$ particles measuring 100–200 nm demonstrated the capacity of 1050 mA h $g^{-1}$, which decreased only by 20% after 40 cycles.[6] Hollow spheres with the external diameter of 400 and 500 nm had capacities of 900 and 1100 mA h $g^{-1}$ (Refs 317 and 318), which decreased by 6% and 20%, respectively, after 50 cycles. The initial capacity of >900 mA h $g^{-1}$ of one-dimensional nanowires with the diameter of 20–50 nm was halved[319] after 50 cycles. Nanostructured $Fe_3O_4$ films demonstrated a lower initial capacity of 755 mA h $g^{-1}$, which, however, remained virtually unchanged after 280 cycles.[320] The research into the nanocomposites of iron oxide with carbon[321] and graphene[322] has shown that the capacity of the latter material remained at 900 mA h $g^{-1}$ for 30 cycles.

Considerable attention was drawn to $Co_3O_4$ nanoparticles[278, 323–325] with sufficiently high capacity (850–1000 mA h $g^{-1}$) but moderate cyclability. Similar results were obtained for one-dimensional structures[291, 323, 324, 326] and hollow nanospheres[327] including those shaped as dandelions.[293] Mention should be made of the good results for thin $Co_3O_4$ films,[295] the capacity of which decreased after 70 cycles from 1050 to 850 mA h $g^{-1}$, and also for nanoporous materials,[292, 326, 328–330] the capacity of which was in the majority of cases much lower but decreased less than by 20% in 50 cycles. For lamellar microcrystals of $Co_3O_4$, the capacity of ~800 mA h $g^{-1}$ was observed for 30 cycles.[290] The high capacity and good cyclability were demonstrated by $Co_3O_4$ films with the thickness of 40 nm,[296] although they can hardly be used in practice. Noteworthy is the plasma deposition of $Co_3O_4$ nanoparticles, which provides the manufacture of flexible electrodes without addition of any binding and conducting substances into the active mass.[300] More acceptable cyclability was demonstrated by composites of $Co_3O_4$ (see Refs 299, 331 and 332) and CuO with carbon.[333] Mention should be made of rather good results obtained for composites of nanosized filamentous $Mn_3O_4$ with graphene,[334] the capacity of which decreased from 850 to 740 mA h $g^{-1}$ after 100 cycles, but much worse results were demonstrated by carbon-covered nanowires.[335] The capacity of composites of $Co_3O_4$ nanorods with graphene[284] exceeded 1000 mA h $g^{-1}$ for >50 cycles.

Substantial advantages can be provided by using nanomaterials based on oxides of trivalent transition metals. For example, the initial capacity of anode materials based on $Fe_2O_3$ was 700 mA h $g^{-1}$ for particles measuring 5 nm and 1000 mA h $g^{-1}$ for 25-nm particles.[336] After 100 cycles the capacity of the former sample decreased to 410 mA h $g^{-1}$, while that of the latter sample remained virtually unchanged. Fairly good results were obtained for $Fe_2O_3$ nanocubes[337] and nanowires.[338, 339] The electrode properties of $Fe_2O_3$ nanocomposites with carbon materials were extensively studied.[340–346] Some of these studies achieved very high initial capacities of such composites; however, there is no question of them being substantially superior over individual nanosized oxides. More modest parameters were obtained for nanosized oxides of chromium[347, 348] and manganese.[349–351]

For nanomaterials based on mixed oxides with the spinel structure of the $A^{2+}B_2^{3+}O_4$ type (where A = Mg, Mn, Fe, Co, Ni, Cu; B = Co, Fe), the initial capacity of 700–900 mA h $g^{-1}$ was reported; after 50 cycles, it decreased by 30%–50% (Refs 333, 349, 352–358) but for certain samples, the capacity loss did not exceed 6%.[359] The initial capacity of ~960 mA h $g^{-1}$, which decreased by 10%–20% after 50 cycles, was observed for nanocomposites of mixed oxides with various forms of carbon.[360, 361]

The use of biological systems as the templates is a new actively developing trend for stabilization of oxide nanomaterials.[362, 363] This approach was initiated in the Massachusetts Institute of Technology (USA) for producing functional nanowires based on cobalt oxide and M13 filamentous bacteriophage. The use of such nanowires allowed the prototypes of lithium-ion batteries with sufficiently high characteristics to be obtained. A material comprising $Co_3O_4$ nanoparticles attached to the genetically modified filaments of halophilic archaeon *H. Salinarum* was described.[364] Electrodes of this material demonstrated the reversible capacity of lithium intercalation higher than 470 mA h $g^{-1}$.

To prepare anode materials, various titanium oxide polymorphs were used; among them, anatase proved to be most active toward lithium intercalation–deintercalation.[365] The reversible intercalation of lithium yielded phases with the $Li_x(Ti^{3+})_x(Ti^{4+})_{1-x}O_2$ composition. According to certain data,[366–369] the intercalation of lithium in anatase leads to spontaneous decomposition to two phases, namely, the lithium-enriched phase and a phase containing almost no lithium, which are approximately described as $Li_{0.55}TiO_2$ and $Li_{0.01}TiO_2$. Hence, the intercalation and deintercalation of lithium into anatase should proceed at almost the same potential, which is 1.72–1.75 V for lithium intercalation and 1.8–1.9 V for its extraction. It is noteworthy that the volume variations on the transition from anatase to the lithium-enriched phase were only 4%, although the structure changed from tetragonal with the unit cell parameters $a = 3.784$ and $c = 9.546$ Å to orthorhombic with parameters $a = 3.814$, $b = 4.084$ and $c = 9.066$ Å.[370–372]

The lithium incorporation into rutile also occurs at coexistence of two phases. The phase enriched with lithium has approximately the $Li_{0.5}TiO_2$ composition and struc-

tural transformations are more significant, namely, the tetragonal structure with unit cell parameters $a = 4.593$ and $c = 2.96$ Å changes to the cubic structure with $a = 4.140$ Å.[365, 373]

Due to the low electrical conductivity of titanium dioxide polymorphs, they were used preferentially in the form of nanomaterials, composites with carbon, or thin films.[8] Mention should be made of the effect of particle size, structure and diffusion processes on the electrochemical activity of titanium dioxide.[368, 374] For instance, it was shown that as the particle size decreases, it becomes possible for anatase to be reduced electrochemically to $LiTiO_2$. However, in the majority of studies dealing with nanoparticles of different morphology, the experimentally reached capacities did not exceed 200–230 mA h $g^{-1}$ even in the initial stage,[375–389] which corresponded to the formation of a product with the substantial fraction of $Ti^{4+}$ ions. At the same time, in the presence of nanomaterials, the capacity more often decreased by 10%–20% after 50 cycles, although in one publication[390] the capacity decreased by only 5% after 100 cycles. Successful experiments on the use of electrode materials based on anatase composites with carbon nanotubes,[391] graphene[392] and polyaniline[393] were performed. A very high initial capacity (335 mA h $g^{-1}$) was attained for amorphous $TiO_2$, although after 50 cycles, it virtually levelled off with the capacities of other samples.[394]

Similar data were published for nanosized titanium dioxide in the form of rutile[387, 395–401] and its composites with carbon.[401] For whiskers of this material the initial capacity was 380 mA h $g^{-1}$.[402] Analogous results were obtained for titanium dioxide-based bronzes,[403–410] although the conductivity of these samples was much higher.

The interest of scientists in the titanium-dioxide-based anode materials somewhat diminishes due to the high potential of lithium intercalation. Much more attention is atracted by lithium titanate $Li_4Ti_5O_{12}$, which has a slightly lower (by 0.2–0.4 V) potential. Not quite clear stoichiometric composition of this compound can be represented for the sake of convenience as $Li[Li_{1/3}Ti_{5/3}]O_4$, which shows that a part of lithium is accommodated in the titanium positions and lithium itself occupies both octahedral and tetrahedral voids. Furthermore, this materials can take up one more lithium ion per formula unit $Li_2[Li_{1/3}Ti_{5/3}]O_4$ ($Li_7Ti_5O_{12}$), which corresponds to the electrochemical capacity of 175 mA h $g^{-1}$ (Refs 365, 411–417).

$$Li_4Ti_5O_{12} + 3e + 3Li^+ = Li_7Ti_5O_{12} \quad (5)$$

The lithiated (limiting composition $Li_{6.93}Ti_5O_{12}$) and delithiated (limiting composition $Li_{4.03}Ti_5O_{12}$) forms are characterized by a very low mutual solubility. It is these phases that coexist in partly charged or discharged samples; hence, their charging and discharging proceed according to the model of heterogeneous grains at virtually the same potential equal to 1.55 V. At the same time, on going from the charged to discharged state, the cubic lattice parameter for this compound remains virtually unchanged (changes by less than one tenth of percent, from 8.3595 to 8.3538 Å).[418] This explains the high stability of this material during cycling.

The main drawback of lithium titanate is the low values of its electronic ($10^{-12}$–$10^{-13}$ S $cm^{-1}$) and, to a lesser degree, ionic ($3 \times 10^{-10}$ S $cm^{-1}$) conductivities.[365, 417, 419, 420] This is why this substance is often used in the form of nanomaterials. Thus, various nanostructured materials were synthesized including thin films, nanowires, mesoporous materials and even nanoflowers with the initial capacity of up to 165 mA h $g^{-1}$ and very good cyclability (as high as 99% after 100 cycles).[421–437]

Considerable effort is directed to the development of doped materials, composites with conductive additives or coatings. To increase the conductivity of $Li_4Ti_5O_{12}$, it was doped by different-valence cations ($V^{5+}$, $Nb^{5+}$, $Sn^{4+}$, $Zr^{4+}$, $Al^{3+}$, $Cr^{3+}$, $Mg^{2+}$, $Sn^{2+}$, $Ru^{4+}$, *etc.*) into both titanium and lithium positions.[419, 438–449] In several cases, the conductivity of doped materials increased. However, this was most often accompanied by a substantial decrease in their capacity. One has to bear in mind that this approach should not lead to a substantial increase in the electronic conductivity, which limits the electrochemical activity of the material itself. In connection with this, an approach was used in which a phase with the high electronic conductivity was added to the composites, in particular, by deposition of carbon materials (including graphene) and metals onto the titanate surface.[450–481] In several cases, this improved the electrochemical parameters of the anode. The studies on the development of hierarchical porous electrode materials aimed at increasing the fraction of highly conductive interfaces in the electrode are also of interest.[431, 482, 483] However, this approach fails to provide any increase in the electronic and ionic conductivity of $Li_4Ti_5O_{12}$ itself.

The above data point to good prospects of using certain oxides as the anode materials, despite their higher atomic mass as compared with metals. The maximum efficiency and stability on cycling can be reached only for nanomaterials and also for their composites. At the same time, it should be noted that many of systems discussed above incorporate lithium in a wide range of potentials, which substantially lowers the working voltage of the rechargeable cell and its efficiency. For tin and titanium oxides, this drawback can be minimized; this is why the scientists focus their attention of these substances.

## IV. Cathode materials

At present, the most widely used and popular cathode material is lithium cobaltate $LiCoO_2$ characterized by the high transfer rates of electrons and lithium ions. The high ionic conductivity is associated with the layered structure of $LiCoO_2$ with a two-dimensional network of bulk channels (Fig. 9); the $LiCoO_2$ cathode demonstrates sufficiently high values of working potential (3.6–4 V, see Fig. 3) and theoretical capacity. However, cobalt dioxide, which should be formed during charging, is unstable; this is why the lithium cobaltate-based cathode materials usually utilize only a half of their theoretical capacity (140 mA h $g^{-1}$). Furthermore, if the battery is charged sufficiently quickly at a large potential difference, the formation of irreversible phases on the surface of particles of the cathode material may result in self-ignition; hence, such a battery is not safe enough. For the utilized capacity of 130–140 mA h $g^{-1}$, a phase transition in $Li_xCoO_2$ occurs being accompanied by a change in the electrochemical potential, this being the signal for finishing the process.[484] It should be noted that cobalt is rather expensive and its disposal is associated with certain environmental problems.[34]

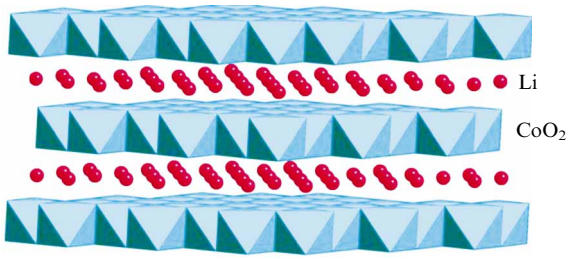



**Figure 9.** Structure of $LiCoO_2$.[34]

The foregoing stimulated the search for alternative materials. High hopes were pinned on the lithium–manganese and nickel–manganese oxides and the lithium–cobalt–nickel and lithium–manganese–nickel triple oxides.[485–491] Thus, $LiNi_{1/2}Mn_{1/2}O_2$ with the capacity of 200 mA h $g^{-1}$ was described;[491] however, its capacity decreased rather quickly on cycling.[492, 493]

The next step was the use of complex oxides $LiCo_xNi_yMn_{1-x-y}O_2$ as the cathode materials. The charge–discharge characteristics of $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ are similar to those of $LiNi_{1/2}Mn_{1/2}O_2$, but the cyclability is much better and the voltage varies in the range of 3.6–4.7 V.[494–498] According to authors of numerous publications,[493, 494, 499–504] this is explained by the fact that cobalt hinders the mutual disordering in the positions of lithium and nickel ions. Presumably, the charge of transition metal ions changes in the following sequence:

$$Ni^{2+} \longrightarrow Ni^{3+} \longrightarrow Ni^{4+}$$

$$Co^{3+} \longrightarrow Co^{4+}$$

Cycling of these materials has been described (for example,[500, 503–506]) and their properties were shown to be maintained during 200 cycles.[495]

Other triple oxides were tested as well as materials of the $LiMn_2O_4$ composition with the spinel structure, including those with partial substitution of nickel for manganese, the capacity of which at low cycling rates ($C/7$) remained sufficiently stable at a level of 140 mA h $g^{-1}$. At the same time, as the cycling rate increased to $3C$, their capacity quickly decreased.[507] These materials exhibit good electrochemical characteristics, but the problems associated with toxicity of cobalt compounds are still unsolved as well as the thermal instability of $LiNiO_2$. While developing these systems, the researchers assumed that they would be charged sequentially utilizing the capacity of different transition metals. However, in fact, the metal oxidation states changed only partly and the capacity of these materials turned out to be comparable with the working capacity of lithium cobaltate.[42]

The information on the use of nanosized $LiNi_{0.5}Mn_{1.5}O_4$ and $LiCo_xNi_yMn_{1-x-y}O_2$ is scarce.[508–510] Nonetheless, it was reported that by decreasing the diffusion paths of lithium ions and electrons, the charge and discharge rates for $LiNi_{0.5}Mn_{1.5}O_4$ could be enhanced.[510, 511]

Despite the wide use of oxide cathode materials (their share in the market is >90% of the total amount of cathode materials), they are not of interest for the present publication because their electronic and ionic conductivities are relatively high. This is why scientists pay insufficient attention to synthesizing nanosized materials based on these oxides and testing their properties. Below, we consider only the properties of lithium iron phosphate and several related materials with the olivine structure and also of vanadium oxides. The synthesis of nanomaterials based on these compounds proved to be more topical.

### IV.1. Materials based on double phosphates

The possibility of using lithium iron phosphate $LiFePO_4$ as the cathode material was pointed out by Goodenough and co-workers[512] However, at first, nobody considered seriously its possible commerciallization because it has too low conductivity and fairly low cycling rate. However, $LiFePO_4$ is environmentally safe and cheap . Its discharge potential is ~3.45 V, the theoretical capacity is 170 mA h $g^{-1}$ and it considerably surpasses $LiCoO_2$ as regards the specific capacity.[28]

The lithium deintercalation from $LiFePO_4$ produces $FePO_4$ and the mutual solubility of these phases is only 2% and 4%, respectively.[52] As a consequence, during the charging and discharging processes, it is only the ratio of $LiFePO_4$ and $FePO_4$ phases that changes, while the potential of the process, which, as was noted above (see Fig. 3), corresponds to the equilibrium between these phases, remains virtually constant.[513–517] The lower value of this potential as compared with that of lithium cobaltate is an adverse factor; however, this, together with its insignificant changes during the charging, substantially simplifies the problem of electrolyte oxidative degradation and additionally enhances the safety of these batteries. Furthermore, $LiFePO_4$ is characterized by the high resistance to high temperatures.[518]

It is worth noting that, despite the low mutual solubility, the structures of $LiFePO_4$ and $FePO_4$ are very similar[519] [*e.g.*, their unit cell volumes are 291.3 and 278.6 $Å^3$ (Ref. 520)]. This determines the low deformation of this material during the charge and discharge processes and its good cyclability. For instance, for $4C$ discharge rate, the capacity of lithium iron phosphate-based electrodes decreased from 130 to 110 mA h $g^{-1}$ after 1500 cycles.[521] The 80 mA h $g^{-1}$ capacity after 2400 cycles at $12C$ discharge rate was also reported.[522]

However, the electronic and (especially) ionic conductivities of $LiFePO_4$ are too low,[523–525] which prevents using the whole capacity of this material in the case of large particles. Thus, even for the discharge at the current density of 2 mA $g^{-1}$, the capacity is 100–110 mA h $g^{-1}$ (Ref. 512), which is ~60% of its theoretical value. The situation is dramatized by the fact that the ionic conductivity of $LiFePO_4$ is one-dimensional, being realized along the channels running through the structure along one axis. This determines the low variability of transport processes in this material.

When studying the conductivity of $LiFePO_4$, one should take into account the structural disorder caused by the partial exchange of lithium and iron positions. Since the lithium diffusion proceeds in one-dimensional structure channels, the consequences of their partial plugging by much less mobile iron cations can be dramatic. Thus, according to calculations, the replacement of 0.5% of lithium by iron in the channels should decrease the lithium diffusion coefficient by more than two orders of magnitude.[526] At the same time, in weakly crystallized samples, the concentration of such defects reaches 7%.[527, 528] The

analysis of the defective structure of single-crystalline samples revealed the presence of ~3% iron in the lithium positions for approximately equivalent concentration of vacancies.[529] The presence of iron ions in lithium positions was confirmed by TEM data.[530] Synchrotron X-ray diffraction examination revealed the substitution of iron for ~7% of lithium at room temperature. According to the published data,[531] such imperfection is completely removed by heat treatment at >500 °C.

The possibility of synthesizing defect-free $LiFePO_4$ single crystals by the long-term hydrothermal treatment at 260 °C was reported.[532] However, the conclusion about the necessity of enhancing the degree of ordering in the material by crystal perfection can hardly be considered as an unambiguous recommendation. The increase in the synthetic temperature inevitably leads to intensification of crystallization processes and the increase in the particle size. The analysis of data for samples with different particle sizes made it possible to conclude[533] that the capacity of $LiFePO_4$ samples decreases linearly with increase in the particle size, which could be caused only by shortening of the lithium diffusion path. Furthermore, it was concluded[526] that the decrease in the particle size induces a decrease in the degree of plugging of lithium transfer by antisite defects.

The problem of low conductivity of $LiFePO_4$ is systemic. For charging, it is necessary to deliver lithium ions and electrons to the particles along interfaces and provide their subsequent diffusion inside each particle (Fig. 10).[45] As a rule, the diffusion along interfaces proceeds much faster due to the higher concentration of defects.[46] Nonetheless, this is insufficient. To increase the diffusion rate along interfaces, the $LiFePO_4$ particles are coated with a conducting material, most often, carbon (Fig. 11).[525, 534–542] Furthermore, the carbon coatings prevent crystals from agglomeration. Publications have appeared on the synthesis of $LiFePO_4$ composites containing some nanostructured forms of carbon (graphene, carbon nanotubes, *etc.*).[543–548] It was shown[549] that electrochemical properties of $LiFePO_4$ can be improved by modifying its surface with amorphous lithium phosphate with high ionic conductivity. The electronic conductivity of $LiFePO_4$ somewhat increases on heating in the presence of oxygen as a result of defect formation by the quasichemical reaction[550]

$$2\,Li + \frac{1}{2}O_2 \longrightarrow V'_{Li} + h^* + Li_2O \qquad (6)$$

where $V'_{Li}$ is a vacancy in the lithium position, which is negatively charged with respect to the lattice; h* is the electron hole located most probably on iron ions, which are thus transferred to the trivalent state.

To solve the low conductivity problem for $LiFePO_4$ particles, the following approaches are used:

— decreasing the size of $LiFePO_4$ particles and providing their uniform size distribution;[533, 551, 552]

— developing a special morphology of $LiFePO_4$ particles (Fig. 12);

— doping $LiFePO_4$ with polyvalent cations.[554, 555]

Since the lithium transfer rate is determined, first of all, by the ionic conductivity,[556] this problem can be solved by heterovalent doping. The heterovalent substitution in lithium iron phosphate was studied by many authors.[557–568] It was assumed that cations can be incorporated into the $LiFePO_4$ structure in both lithium and iron positions.

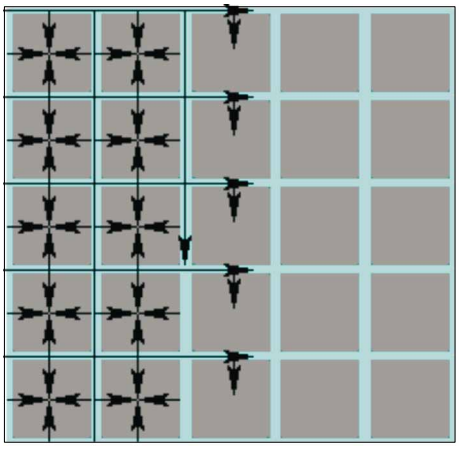


**Figure 10.** Migration paths of lithium ions and electrons in a cathode material.[45]
Long arrows show fast lithium transport through the interface space (in composites, through the highly conducting carbon phase); short arrows mean slower lithium transfer within the particles of the material.

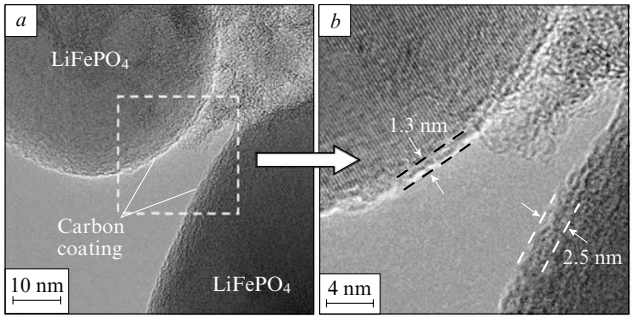



**Figure 11.** TEM images of $LiFePO_4$ particles coated with carbon.[539]

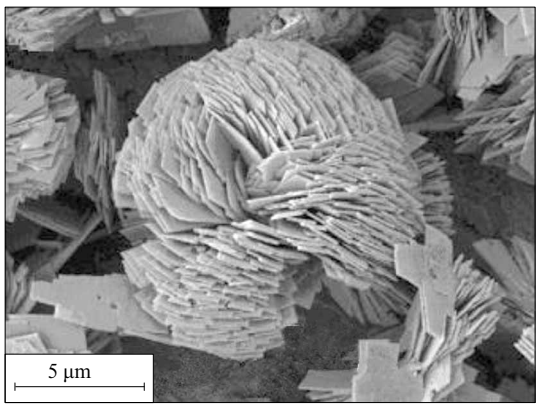



**Figure 12.** Morphology of $LiFePO_4$ samples according to SEM data.[553]

Usually, a part of iron ions is replaced by divalent cations or cations with a higher charge ($Co^{2+}$, $Ni^{2+}$, $Zn^{2+}$, $Ti^{4+}$, $Zr^{4+}$, $V^{5+}$).[557, 558, 561, 568–575] At the same time, different authors have obtained materials in which the positions of iron and lithium were presumably occupied by $Mg^{2+}$, $Cu^{2+}$ ions.[542, 556, 567–582] It deserves mention that these data were not always confirmed. Thus, it was reported [583] that attempts to synthesize samples with partial substitution of niobium for iron always produced two-phase products containing β-$NbOPO_4$.

Several mechanisms were proposed to make up for the excessive positive charge upon incorporation of higher-valence cations into the $LiFePO_4$ structure: the formation of negatively charged vacancies in lithium or iron positions, the introduction of additional electrons to the system; however, most probably, the main mechanism is the formation of vacancies in lithium positions,[556] which can increase the ionic conductivity of $LiFePO_4$.

It was noted [584] that doping imparts the ability to withstand the high currents during fast charge–discharge processes. Such ability of this material is explained by the fact that substitution, for example, of $Mg^{2+}$ for a part of $Fe^{2+}$ weakens the Li—O bonds which, in turn, results in the high mobility of lithium ions and, hence, high diffusion coefficient of lithium. Comparing the mass transfer rates in the doped and undoped lithium iron phosphate demonstrated the increase in the diffusion coefficient from $2.9 \times 10^{-11}$ to $1.86 \times 10^{-10}$ $cm^2\ s^{-1}$ for $LiFe_{1-x}V_xPO_4$ (Ref. 571) and from $5.68 \times 10^{-15}$ to $3.90 \times 10^{-14}$ $cm^2\ s^{-1}$ for $LiFe_{0.9}Mn_{0.1}PO_4/Fe_2P$.[585] Presumably,[571] this is associated with optimization of the doped sample microstructure, equalization of the particle size and also partial distortion of the olivine structure.

It was reported that doping with cobalt may improve the cyclability of $LiFePO_4$.[586, 587] It was shown [588] that the substitution of nickel, magnesium and cobalt for 10% of iron atoms makes it possible to obtain the specific capacity of 70 mA h $g^{-1}$ at 20*C* discharge rate, whereas electrodes of non-substituted iron phosphate demonstrated an equal capacity only for 8*C* discharge rate. As has been noted,[536] this is determined by the ionic conductivity of the material, and the highest increase in the conductivity could be achieved for the cobalt content of 2%–5%. The majority of studies devoted to the effect of doping of $LiFePO_4$ with heterovalent cations indicate considerable improvement of electrochemical characteristics of the cathode material at high current densities, which was explained by the increase in its electronic and(or) ionic conductivity.[556–558, 589] Mössbauer spectroscopy data point to the ordered arrangement of the intercalated cobalt ions in the $LiCo_xFe_{1-x}PO_4$ structure.[536] Presumably,[590] the heterovalent substitution of a small part of iron atoms induces aggregation of antisite defects and less pronounced plugging of conduction channels. A similar assumption on the appearance of antisite disorder upon partial substitution of aluminium, zirconium or niobium for iron was also put forward.[559]

Replacement of iron ions by manganese ions in a wide range of concentrations and replacement of 1% of lithium ions by $Al^{3+}$, $Ti^{4+}$ or $W^{6+}$ ions were reported.[591] According to this publication, for a partly deintercalated sample $Li_{1-x}Mn_{0.55}Fe_{0.45}PO_4$, the diffusion coefficient of lithium increased by more than two orders of magnitude in the range of lithium content of $0.4 < 1-x < 0.7$ and remained virtually unchanged for other $(1-x)$ values. It was shown that substitution of manganese for a part of iron atoms increases the electronic conductivity of the material and also the charge and discharge potentials of manganese oxidation/reduction processes. At the same time, the cyclability of this material was impaired precisely at the potentials characteristic of manganese ions. A slight increase in the ionic and electronic conductivity of samples was achieved upon the substitution of manganese for 55% of iron atoms, and a substantial (by several orders of magnitude) increase in the electronic conductivity was reached by substituting small amounts of $Al^{3+}$, $Ti^{4+}$ and $W^{6+}$ ions into lithium positions.[592] It was shown [593] that substitution of molybdenum for 1% of lithium atoms increases the capacity of $LiFePO_4$.

Lithium iron phosphate is an anisotropic material. Calculations of the migration energy in its structure have identified only one preferential direction.[559] Incorporation of $V^{3+}$ cations into olivine leads to some expansion of the conduction channels along the *a* and *c* axes, which favours the transport of $Li^+$ ions.

An increase in the unit cell volume of olivine was reported for zinc-substituted $LiFePO_4$. Zinc prevents compression of the host material upon the removal of lithium, *i.e.*, the so-called 'pillar' effect.[573] This favours the increase in the migration space for $Li^+$ ions and, hence, the increase in its mobility and diffusion coefficient. The best performance characteristics for $LiFePO_4$ were observed upon the introduction of ZnO in the amount of 2.5%: the discharge capacity was 177 mA h $g^{-1}$ in the first cycle and 167 mA h $g^{-1}$ after 150 cycles.[573]

Note that many authors offer no solid arguments for the statement that the dopant cation is incorporated precisely in a given position. In the majority of cases, this statement is based only on the stoichiometry of precursors and the absence of considerable changes in the diffraction patterns as compared with the single-phase product; however, this is not quite correct for the degree of lithium displacement of ~1%. For instance, the composition of such material was written as $Li_{0.99}Mo_{0.01}FePO_4$,[593] which probably implies the divalent state of molybdenum. In the majority of cases, the authors succeeded in enhancing the electrochemical capacity and(or) cyclability of materials; however, unfortunately, their data are sometimes poorly reproducible.

Above, it was noted that the electrochemical parameters of lithium iron phosphate depend on the degree of dispersion and homogeneity; and, hence, the characteristics of this material can be substantially improved by changing the synthetic method.[594] Moreover, when the other aforementioned approaches were used, the adequate results were obtained only for structured samples. In a review,[595] the different methods for the $LiFePO_4$ synthesis were compared. Solid-phase synthesis was used most often.[513] This method produces rather large particles; hence, the capacity of these cathode materials is not used in full measure. The minimum size of $LiFePO_4$ particles can be achieved by using spray pyrolysis (~50 nm) [596] and the sol–gel technology (~40–45 nm).[597] An interesting version of nanomaterials with dumbbell-like particles synthesized by the solvothermal method was described.[598]

Recently, the use of thin-film electrodes based on lithium iron phosphate with even finer particles was reported;[599–601] this served for more effective use of the cathode material capacity.

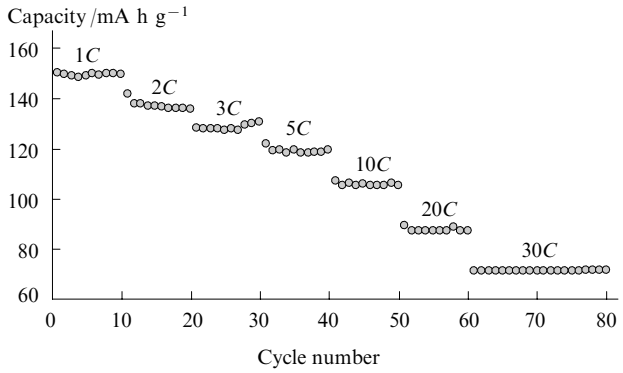



**Figure 13.** Data on the discharge capacity of electrodes made of a material based on lithium iron phosphate at high *C*-rates.[539]

The best electrodes made of $LiFePO_4$/C composites exhibited the capacity close to theoretical one. For example, the capacities of 160 mA h g$^{-1}$ for *C*/5 discharge rate and $>120$ mA h g$^{-1}$ for 5*C* discharge rate, which are close to theoretical values, were reported.[602] A capacity of 80 mA h g$^{-1}$ at 20*C* discharge rate was observed.[603] The information on the behaviour of lithium iron phosphate electrodes in 30*C* discharge mode is available.[539] As the discharge rate increases, the utilized capacity of the cathode material considerably decreases (Fig. 13). The data on the discharge of electrodes based on lithium iron phosphate at 200*C* rate were obtained.[604]

The discharge potential of the manganese compound $LiMnPO_4$ isostructural to lithium iron phosphate approached 4.1 V.[512, 605] Taking into account their close molecular masses and, hence, capacities, this value implies a more than 10% increase in the specific energy of $LiMnPO_4$ cathodes. However, the conductivity of $LiMnPO_4$ is lower, which determines the lower demands for these cathodes. As for lithium iron phosphate, a number approaches were used to solve this problem, including synthesis of nanomaterials, deposition of carbon coatings and heterovalent substitution for manganese atoms.[606, 607] Samples of nanocomposites based of $LiMnPO_4$ and coated with carbon were synthesized; their capacity was 155 and 162 mA h g$^{-1}$ and only slightly decreased after 50 cycles.[608, 609]

Cathode materials based on $LiCoPO_4$ and $LiNiPO_4$ demonstrated the potential values even higher as compared with $LiMnPO_4$ (4.8 and 5.1 V, respectively).[610, 611] However, the major part of electrolytes cannot steadily operate at such potentials due to side reactions at the electrode/electrolyte interface. This explains the smaller number of publications devoted to these materials. Their conductivity is also very low; hence, they can serve as the LIB cathodes only in the nanostructured state.[612, 613] Nanocomposites based on carbon-coated $LiCoPO_4$ exhibited the initial capacity of 131 and 145 mA h g$^{-1}$ when cycled at a low rate (*C*/10), but after 50 cycles their capacity decreased to 100–110 mA h g$^{-1}$ (Refs 614 and 615).

It was noted[616] that the $LiCo_{1/3}Mn_{1/3}Fe_{1/3}PO_4$ phosphate has certain advantages over the common lithium iron phosphate. This compound is in fact a solid solution of $LiCoPO_4$, $LiMnPO_4$ and $LiFePO_4$. The electrode made of this ternary phosphate demonstrated the capacity of 159 mA h g$^{-1}$ at 5*C* rate of discharge, but withstood also 20*C*. However, it deserves mention that in the discharge curves recorded at low rates ($<1C$), one can clearly distinguish three regions corresponding to individual phosphates at potentials of 4.7, 4.2 and 3.6 V.

The fluorine-containing materials described as $Li_2MPO_4F$ have a structure close to that of $LiMPO_4$ and their properties are also much similar. Lithium ions in the lattice are surrounded with $MO_4F_2$ transition-metal octahedra and $PO_4$ tetrahedra.[617] The introduction of an additional fluoride ion increases the dimension of lithium-ion migration paths[618, 619] and the capacity somewhat decreases. Table 1 shows the capacity of certain $Li_2MPO_4F$ materials. Lithium iron phosphate doped with 2% fluorine was reported.[622] This material had the capacity of $\sim$160 mA h g$^{-1}$ at cycling rate of 0.1*C* and $\sim$90 mA h g$^{-1}$ at 5*C*. According to some data,[623] the $LiFe(PO4)_{0.97}Cl_{0.06}$/C composite showed the capacity of 138 mA h g$^{-1}$ at cycling rate 1*C* and 90 mA h g$^{-1}$ at 15*C*. Due to their sufficiently high conductivity, the synthesis of these materials in the nanosized state does not seem reasonable.

**Table 1**. Capacity of certain materials based on $Li_2MPO_4F$ (M = V, Fe, Co).

| Material | Capacity /mA h g$^{-1}$ | Ref. |
|---|---|---|
| $Li_2VPO_4F$ | 140 | 617 |
| $Li_2FePO_4F$ | $\sim$150 | 618 |
| $LiFe(PO_4)_{0.9}F_{0.3}$/C | 110 | 620 |
| $Li_2CoPO_4F$ | 113 | 621 |

The proposed use of oxyfluorides as the active material for LIB positive electrodes deserves mention. Electrodes of a material based on FeOF with the theoretical capacity of 885 mA h g$^{-1}$ were described.[624] With an adequate choice of cycling potentials, the electrodes demonstrated the capacity of $\sim$500 mA h g$^{-1}$ but considerably degraded.

Thus, the cathode materials based on phosphates (first of all, iron phosphate) are considered among the most promising materials for LIBs and are already produced commercially. However, taking into account the low electronic and, the more so, ionic conductivity, good cycling results can be achieved only for their nanocomposites (mainly, with carbon). Certain additional advantages were demonstrated for samples with substitution of other metal ions for a part of iron ions.

## IV.2. Materials based on orthosilicates

The orthosilicates $Li_2MSiO_4$ (M = Fe, Mn, Co) have rather recently attracted attention as a new class of cathode materials for LIBs. Their layered structure based on transition metal octahedra and $SiO_4$ tetrahedra enables two-dimensional diffusion.[625] Their main drawback is probably the low conductivity ($5\times10^{-16}$ S cm$^{-1}$ for $Li_2MnSiO_4$ and $6\times10^{-14}$ S cm[71] for $Li_2FeSiO_4$), which turns out to be several orders of magnitude lower than the conductivity of $LiFePO_4$.[626] In the course of testing at *C*/16 cycling rate, $Li_2FeSiO_4$ demonstrated the capacity of 165 mA h g$^{-1}$, which corresponds to deintercalation of one lithium ion per formula unit. However, after several cycles, the capacity

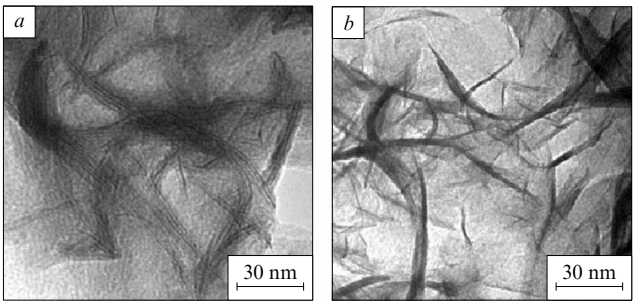



**Figure 14.** TEM images of nanosheets of $Li_2FeSiO_4$ (*a*) and $Li_2MnSiO_4$ (*b*).[635]

dropped down to 140 mA h $g^{-1}$ at the potential of ~2.9 V.[627]

The key approaches to overcome the low conductivity of $Li_2MSiO_4$ also include decrease in the particle size and covering them with carbon. For instance, $Li_2MnSiO_4$-based materials with carbon coating and particles measuring ~100 nm demonstrated a capacity close to theoretical values; however, it was < 100 mA h $g^{-1}$ after 15 cycles.[628] Similar results were obtained in later studies.[629, 630] Materials based on $Li_2FeSiO_4$ particles measuring 40–80 nm which were synthesized by the sol–gel technology and then covered with carbon[631] demonstrated the discharge capacity of ~160 mA h $g^{-1}$ for *C*/16 cycling rate and 125 mA h $g^{-1}$ when cycled at 2*C* rate. Somewhat lower results were obtained for elongated ('shuttle') $Li_2FeSiO_4$ nanoparticles (160 and 70 mA h $g^{-1}$ for cycling rates of *C*/10 and 2*C*, respectively).[632] Coating the $Li_2FeSiO_4$ nanoparticles with carbon also failed to provide any advantage.[633]

The reason for the fast decrease in the $Li_2MnSiO_4$ capacity on cycling is presumably the degradation of its structure upon lithium deintercalation.[634] Electrodes of materials based on $Li_2FeSiO_4$ and $Li_2MnSiO_4$ nanosheets (Fig. 14) demonstrated a high capacity of 160 and 220 mA h $g^{-1}$, respectively, for 15–20 cycles.[635, 636] Other authors also obtained these values for $Li_2MnSiO_4$-based materials; however, their capacity was high and irreversible in the first cycle and rapidly decreased to 140 mA h $g^{-1}$ on further cycling.[636, 637] Of certain interest are composites based on $Li_2CoSiO_4$ coated with carbon; however, they are characterized by the high irreversible capacity in the first cycle.[638, 639] Among the tested silicate materials, good results on cycling within LIB were achieved only for nanocomposites based on $Li_2FeSiO_4$. Nonetheless, once their conductivity and stability are improved, the silicate materials would have good prospects as the cathodes.

### IV.3. Materials based on vanadium oxides

In contrast to many other transition metals, vanadium can relatively easily change the oxidation state from 2+ to 5+. Vanadium pentoxide can incorporate up to six lithium atoms, which corresponds to the discharge capacity of 883.5 mA h $g^{-1}$ and is even higher than five times the capacity of other cathode materials utilized in commercial LIBs. However, as for anode materials described above, the incorporation of lithium gives rise to substantial changes typical of structures with weak interaction between layers. At the same time, this factor determines the easy diffusion of lithium through such structures.[640] Furthermore, the potential of cathode materials based on vanadium oxide substantially changes during the discharge. Thus, incorporation of the first lithium atom into $V_2O_5$ occurs in the potential range from 3.5 to 2.5 V, whereas insertion of three atoms decreases the potential to 1.5 V,[8] and the structural changes become irreversible.[641] It deserves mention that the interval of working potentials for electrodes based on vanadium oxides substantially depends on their structure.[642]

The situation with reversibility of operation of cathode materials based on vanadium oxides radically changes when they are used in the form of very thin films or nanostructures. Thin-film electrodes based on vanadium oxides are synthesized by various methods such as chemical deposition, metal oxidation and also rf-magnetron sputtering and vacuum, pulsed laser or ion-beam deposition.[642–652] For these electrodes, fairly high capacity values and good cyclability can be achieved. For example, decreasing the thickness of $V_2O_5$ films to 200 nm allowed the capacity of the corresponding cathode material to be maintained at a level of not lower than 450 mA h $g^{-1}$ for 100 cycles.[647] To improve the properties of $V_2O_5$, the experiments with its porous films were carried out, which lefelled off the change in the volume.[652]

Good results can be achieved by using $V_2O_5$ nanoparticles as the cathode materials. There are publications on the methods of preparation of $V_2O_5$ nanorods,[653] nanofibres,[654–656] nanotubes,[657–659] nanowires,[660] nanoribbons,[554, 661, 662] hollow nanospheres[663] and other nanostructures.[555, 664–673] Thus, cathodes based on $V_2O_5$ nanofibres demonstrated the capacity of ~300 mA h $g^{-1}$ (Refs 654 and 655). One-dimensional $V_2O_5$ nanostructures had the capacity of up to 300 mA h $g^{-1}$.[674] Good (albeit somewhat controversial) data were obtained for xerogels and aerogels of vanadium oxides (Fig. 15).[650, 667–672] Some of these studies[667, 670] described electrodes with the capacity of 270 and 410 mA h $g^{-1}$, respectively.

The use of nanostructured materials makes it possible to avoid complications associated with the changes in the vanadium oxide structure upon incorporation of lithium ions; however, these materials have low electronic conductivity, which is usually increased by heterovalent doping of the oxide or by using vanadium oxide composites with carbon.[8, 675] For example, composites of $V_2O_5$ with carbon exhibited the capacity of 280 mA h $g^{-1}$ (Refs 676 and 677),

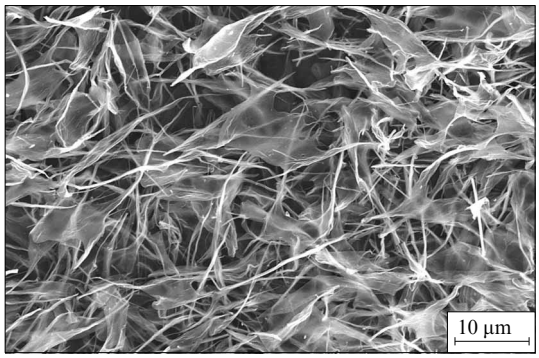



**Figure 15.** Microimage of $V_2O_5$ xerogel prepared by freeze drying.[671]

while the materials based of vanadium oxide xerogels and carbon nanotubes demonstrated the capacity of $>350$ mA h $g^{-1}$ and fairly good cyclability.[678] However, more recent publications report more modest results for $V_2O_5$ composites with carbon nanotubes.[679] A composite of vanadium oxide with reduced graphene oxide shaped as 30 nm thick, 200 nm wide and 1 mm long plates, which was synthesized by the hydrothermal method, was described.[680] This composite was used to manufacture electrodes without conventional supports, which demonstrated the initial capacity of 160 mA h $g^{-1}$ that decreased to 133 mA h $g^{-1}$ after 200 cycles.

A promising method for improving the properties of vanadium oxide is the synthesis of composite materials and the intercalation products of polymers with the high electronic conductivity (polyaniline, polypyrrole, polythiophene, polyethylene glycol, polyvinylpyrrolidone, *etc.*) into the interlayer space. For instance, it was shown[681] that the intercalation product of polyaniline into vanadium pentoxide remains stable on long-term cycling. Mention should be made of the synthesis of nanorods with nickel cores encapsulted in vanadium pentoxide shells, which were grown on viral templates.[682]

Lithium trivanadate $LiV_3O_8$ is also used as the cathode material. Its layered structure can theoretically incorporate up to 4.5 lithium ions per formula unit, which would correspond to the specific capacity of 419 mA h $g^{-1}$. However, in practice, substantially lower capacities can be attained; furthermore, the amorphous material has a higher stability during cycling. Thus, prepared samples[683] retained the capacity of $\sim 200$ mA h $g^{-1}$ for 100 cycles. Substantial advantage was achieved by using $LiV_3O_8$ in the form of thin films[684, 685] or nanostructured materials.[686–697] Cathodes of composites formed by lithium trivanadate and vanadium pentoxide with the $0.8\,LiV_3O_8 \cdot 0.2\,V_2O_5$ composition exhibited the capacity of 365 mA h $g^{-1}$, which decreased to 305 mA h $g^{-1}$ after 20 cycles.[695] The reversible capacity of $\sim 500$ mA h $g^{-1}$, which is the record-breaking value for these materials, at good cyclability was achieved for 10–15 nm-thick nanoribbons of lithium–vanadium bronze.[661]

It was shown[698] that hollow nanospheres of the copper vanadate $Cu_{0.95}V_2O_5$ can exhibit the capacity of 300 mA h $g^{-1}$ as a result of combination of redox processes involving copper and vanadium atoms. In this case, the charge and discharge curves demonstrated two steps.

A material in the form of $LiV_3O_8$ nanoflakes synthesized by the sol–gel technology was described.[699] Electrodes of this material could be steadily cycled to produce the capacity of $>250$ mA h $g^{-1}$ at $C/6$ rate and $>100$ mA h $g^{-1}$ at $3C$ rate. This material demonstrated the record-breaking reversible capacity; however, the prospects for its practical use are largely limited by its low working potential, which is especially low for materials with the high capacity. Furthermore, despite the obvious achievements, the problems with cyclability are not yet solved for this material.

Recently, the attention of researchers has been attracted by double lithium vanadium phosphate $Li_3V_2(PO_4)_3$.[700–704] Its monoclinic structure consists of slightly distorted $VO_6$ octahedra and $PO_4$ tetrahedra, which form a three-dimensional network[705] with channels more suitable for lithium ion diffusion as compared with lithium iron phosphate, which makes them stable on cycling. The charge–discharge curves of this material demonstrated four plateaus at the potentials of 3.62, 3.68, 4.08 and 4.55 V. The potential range of 3.0–4.3 V corresponds to the reaction of the $V^{3+}/V^{4+}$ redox pair involving the transfer of two lithium ions per formula unit. As the potential shifts to 4.8 V, the extraction of three lithium ions takes place, Unfortunately, $Li_3V_2(PO_4)_3$ has a low electronic conductivity. To improve the properties of $Li_3V_2(PO_4)_3$, the latter was doped with cerium and surface-coated with carbon.[706] The resulting $Li_3V_{1.98}Ce_{0.02}(PO_4)_3/C$ composites demonstrated the capacity of $>170$ mA h $g^{-1}$ at $1C$ cycling rate for 100 cycles virtually without any degradation. For cycling rate of $10C$, the capacity was $\sim 120$ mA h $g^{-1}$. Similar characteristics were demonstrated by the $Li_3V_2(PO_4)_3$ composite with reduced graphene oxide.[707] After 50 cycles, the electrodes of the $0.6\,(LiMnPO_4) \cdot 0.4\,(Li_3V_2(PO_4)_3)/C$ composite demonstrated the capacity of $\sim 150$ mA h $g^{-1}$ for cycling rate of $C/20$ and 95 mA h $g^{-1}$ for $C/2$.[708] A procedure of the sol–gel synthesis which provided $Li_3V_2(PO_4)_3$ nanoparticles measuring 30 to 100 nm and covered with $\sim 1$ nm thick carbon coating was described.[709] Electrodes of such composite could be steadily cycled at $5C$ rate with the capacity of $\sim 120$ mA h $g^{-1}$ and at $50C$ rate with the capacity of $>100$ mA h $g^{-1}$. For the $Li_3V_2(PO_4)/C$ composite, the capacity values of 190 mA h $g^{-1}$ for the cycling rate of $C/10$ and 130 mA h $g^{-1}$ for $20C$ were reported.[710]

Vanadyl phosphate was used as the active material for the positive electrode in several studies.[711–714] The two-phase nanocomposite $\beta$-$VOPO_4$/e-$VOPO_4$ exhibited the capacity of $\sim 200$ mA h $g^{-1}$ (for its theoretical value of $\sim 300$ mA h $g^{-1}$).

Vanadium attracted attention of scientists first of all due to its ability to easily change the oxidation state in a wide range (from 5+ to 2+); however, upon intercalation of lithium ions, the transitions between these states occur at substantially different potentials. The reversibility of these transitions can be attained only by using nanomaterials. The wide diversity of nanomaterials based on vanadium oxide compounds deserves mention; however, they were not yet used in practice.

## V. Conclusion

In conclusion, it is noteworthy that the development of LIBs is a very promising field of research, which widely applies nanotechnologies. In the next decades, one can expect substantial extension of the use of LIB in portable and mobile devices and also in various vehicles and aerospace industry. Thus, at present, LIB are used together with fuel cells in environmentally clean electric and hybrid cars.

It should be noted that it is the development of nanotechnologies that contributies to increasing reliability, efficiency, and capacity of LIB. Thus, in the years ahead, the anode materials based on tin and silicon could replace graphite, because they exhibit high charge and discharge rates and high density of lithium accumulation. However, their reliable work and high capacity can be reached only with the decrease in the particle size, the use of porous nanostructures or thin amorphous films. It is the transition to nanomaterials that will provide solution to a key problem associated with the use of anodes based of silicon and tin, namely, the degradation of these materials due to consid-

erable variations in their volume during lithium intercalation, thus achieving the high electrochemical characteristics on cycling. The materials based on nanostructured systems with the capacity of $>500$ mA h $g^{-1}$ which remain stable for $>200$ cycles, are already used. The high capacity values were obtained for oxides of transition metals. However, the good cyclability has been reached only for nanodisperse samples or nanocomposites. It is typical that intercalation products of lithium into such systems represent composites of lithium oxide with nanoparticles of metals or intermetallics with even smaller size. For yet another promising material, lithium titanate, the transition to nanosized particles makes it possible to solve the problem of low electronic conductivity. The wide use of certain oxide nanomaterials as the anodes is hindered by the high value of their working potential, which, however, is the same as the potential of common materials.

The solution of the problem of increasing the energy density and power of LIBs is complicated by the much lower capacity of cathode materials, which for the best samples does not exceed one third of the capacity for tin-based anodes. Studies along this line are probably even more important. At present, the main problem is associated with the replacement of cathode materials based on lithium cobaltate. In view of this, cathodes based on transition element phosphates and vanadium oxides appear to be very attractive. It is for the latter that the maximum values of specific capacity were reached. However, even more close attention is attracted by lithium iron phosphate. It is noteworthy that its high capacity at high charge and discharge rates can be achieved only for nanomaterials and, particularly, nanocomposites. This is accompanied by an increase in the rates of lithium intercalation–deintercalation throughout the whole bulk of this material due to acceleration of transfer processes along grain boundaries and the sharp decrease in the diffusion layer thickness inside the particles, thus providing the good cyclability of the cathode material.

Special mention should be made of double phosphates and silicates of lithium with transition metals. They can also serve as examples of materials for which the nanosize is the key factor determining the high quality of LIB electrodes, which first of all makes it possible to solve the problem of low rate of lithium ion diffusion. In addition, a problem of increasing the ionic component of conductivity for several electrode materials used in LIBs is being successfully solved by preparing composite materials and forming very thin (about several nanometres thick) highly conductive layers on the surface of nanoparticles.

The use of nanomaterials will provide the dynamic development of LIBs is the near future, which includes increasing their specific capacity, reliability, cyclability and providing high charge–discharge rates. Due to this, the LIBs will undeniably continue to play the key role in supplying energy for portable electronic devices and in other fields of modern industry. In turn, everything mentioned above is associated with the increasing role of the alternative and renewable power production, which, according to many scientists, is the essential prerequisite for the development of favourable environmental situation on our planet.

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