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Oxide materials as positive electrodes of lithium-ion batteries

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Abstract. The published data on oxide materials as positive electrodes for lithium-ion batteries are described systematically. The mechanisms of structural changes in cathode materials occurring during the operation of lithium-ion batteries and the problems concerned with their selection are discussed. Modern trends in optimising cathode materials and lithium-ion batteries on the whole are considered. The bibliography includes 167 references.

I. Introduction

Whittingham[1] seems to be the first to demonstrate, by the example of Li_xTiS_2, that the process of electrochemical intercalation of lithium into the positive electrode structure can be utilised in rechargeable cells with lithium anodes. He described the reversible topotactic reaction of lithium insertion into titanium disulfide matrices in the $0 \leqslant x \leqslant 1$ composition range with a plateau at 2 V (with respect to metallic lithium) and a current density in the range 1 – 10 mA cm^{-2}. In the following several years, he and other authors studied a variety of materials with the aim of using them as positive electrodes in secondary lithium cells, *viz*., sulfides MoS_2 and $NiPS_3$, oxides V_2O_5 and MoO_3,[2] oxyhalide FeOCl,[2,3] oxide V_6O_{13},[4] sulfides $Ti_{1+x}S_2$ and TiS_3,[5] layered oxides MO_2 (M = Ti, V, Mn, Mo, W, Nb, Ru, Ir, Os)[6] and lithium cobaltate Li_xCoO_2.[7] Further development of lithium cells was impeded by the difficulties concerned with practical implementation of the reversible operation of negative electrodes made of metallic lithium and the choice of electrolytes. In the early 1980s, several authors[7–9] suggested to apply the principle of lithium electrochemical intercalation for negative electrodes as well. The substitution of reversible lithium intercalation host compounds for metallic lithium gave rise to a new generation of lithium batteries.

The development of a new kind of lithium battery was announced in 1990 by Sony Energetic Incorporated[10] and in 1991 and by Moli Energy Limited[11] and Bell Communications Research.[12] The basis for this was laid by Japanese scientists[13,14] who had discovered that certain carbon forms are capable of reversible lithium intercalation and can be used as materials for negative electrodes.

In these cells, the positive electrodes represented lithiated cobalt oxide (lithium cobaltate) $LiCoO_2$ (Sony), lithiated nickel oxide (lithium nickelate) (Moli) and lithium – manganese spinel $Li_xMn_2O_4$ (Bellcore). At first, these kinds of batteries were named 'rocking-chair' cells, which reflected their ability to transfer lithium from positive to negative electrode (charge) and back (discharge). At present, the conventional name is lithium-ion battery (LIB).

Commercial production of lithium-ion batteries with $LiCoO_2$ cathodes (voltage range 2.5 – 4.2 V, average voltage 3.6 V) was pioneered by Sony in 1991. The batteries had a high voltage level and the highest energy density (with respect to both mass and volume) among secondary cells of that time. Commercialisation of LIB has given powerful impetus to studies in this field, which included the search for new cathode materials. In the past decade, the number of publications on this subject has run into several thousands.[15] The reason for this lies in the fact that, despite all the merits of lithium cobaltate [high average voltage and high energy density, low self-discharge (the capacity fade in the discharged state at open circuit), simplicity of its industrial synthesis, good cyclability], its drawbacks came to light almost immediately. The latter are, first of all, the high cost and toxicity. Taking into account the volume of sales ($40 bln. per year) and the LIB market structure (cellular phones, video cameras, portable computers), these problems are certainly very serious. Moreover, the capacity of lithium cobaltate, even if having a high theoretical value (274 mA h g^{-1}), in practice does not exceed 150 mA h g^{-1}, because the discharge of Li_xCoO_2 involves a phase transition from its tetragonal form to a monoclinic one at $x \approx 0.5$; hence, stable cycling is possible only in the composition range $0.5 < x < 1$. Although lithium cobaltate is still used as the cathode material in the majority of commercial LIB, attempts to improve this material or find another one, cheaper and less toxic, have never stopped. According to the prognoses made by LIBES (Lithium Battery Energy Storage Technology Research Associa-

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tion)[16] and such companies as SAFT,[17] the LIB production will continue to increase; however, the market structure is to change (for instance, according to certain estimates, the cellular phone market, the greatest LIB consumer, is close to saturation) as well as the requirements to LIB. The use of LIB in medicine and space technology (*e.g.*, for satellites) requires much longer service life (at least 15 years in place of the usual 3–5 years of present cells). Their use in military equipment will require not only the increased service life but also the wider rage of operation temperatures (now, it is from −20 to 60 °C) and the possibility of operating at high currents. The use of LIB as reserve power sources of autonomous power-consuming devices (including submarines and planes) and in electrical vehicles and cars with the so-called hybrid power sources (a combination of internal combustion engines with powerful rechargeable batteries) requires both the higher power level and lower costs. The high cost and the capacity fade during operation (the latter should not exceed 20% in 10 years) are the critical parameters in all application fields. All these problems are discussed in numerous publications devoted to materials for positive electrodes of LIB.

In addition to lithium cobaltate, the possible candidates for the cathode materials in LIB with average voltage of 4 V should also involve lithium nickelate $LiNiO_2$ and lithium-manganese spinel $LiMn_2O_4$. An analysis[18] has shown that it is these oxides that have the lithium intercalation potential in the required voltage range. That is why the mentioned compounds and their derivatives were studied most thoroughly. Thus, when analysing the literature data, it is reasonable to consider these three compounds separately while cathode materials based on different compounds united in a special group.

In should be stressed that, in fact, a cathode material represents a composite involving a certain carbon form (as a rule, carbon black) added with the aim of increasing the conductivity together with a binder represented most often by polyvinylidene fluoride. The content of these components in the material, the morphology of the latter, the particle size of the ingredients, and also the methods of cathode manufacturing (chemical method, cold pressing or film formation for polymeric LIB) have a great effect on the electrochemical behaviour of the resulting cathodes; however, these questions deserve special consideration and are beyond the scope of this review.

II. Lithium cobaltate and related materials

Depending on the synthetic method, two forms of $LiCoO_2$ can be obtained. A compound synthesised at high temperatures has a layered structure; that synthesised at low temperatures has the spinel structure. The majority of commercial LIB utilise the high-temperature form of stoichiometric lithium cobaltate, which can be cycled in the voltage range from 2.5 to 4.3 V and the composition range $0.5 < x < 1$ with the reversible capacity of 135–150 mA h g^{-1}. The upper voltage limit ($\sim$ 4.3 V) is chosen for a number of reasons, including safety requirements and the possibility of forming gaseous products. However, first of all, one has to take into account that a phase transition of $LiCoO_2$ from a layered hexagonal structure with rhombohedral symmetry (space group *R*3*m*) to monoclinic structure occurs at $x \approx 0.5$.

The structure of hexagonal $LiCoO_2$ (α-$NaFeO_2$ type, Fig. 1) consists of CoO_2 layers built of interlinked CoO_6 octahedra and separated by lithium-ion layers with octahedral coordination. The cation layers are located in voids of the almost perfect face-centred cubic sublattice of oxygen ions (alternating ABC layers, O3 structure). Other synthetic forms of lithium cobaltate differ in the arrangement of cations (also coordinated in octahedra) in the supercompact oxygen-ion packing. For instance, the low-temperature synthesis results in lithium cobaltate with the spinel structure.

The charging consists of the removal of lithium from the lithium cobaltate lattice by the reaction

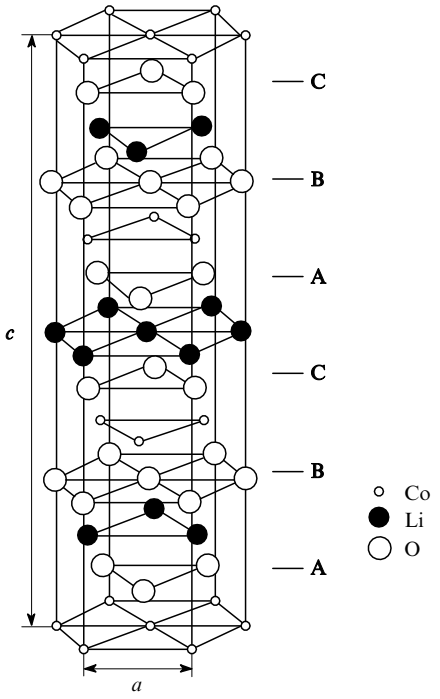


Figure 1. Crystal structure of lithium cobaltate with alternating ABC layers.

$$LiCoO_2 - (1-x)Li^+ - (1-x)e^- \longrightarrow Li_xCoO_2 .$$

As a result, the electrostatic repulsion of CoO_2 layers should become greater and the distance between the layers (the lattice parameter *c*) should increase. The discharge represents a reverse reaction. For a sufficiently long time, it was assumed that reversible cycling to voltages higher than 4.3 V, *i.e.*, up to the complete delithiation leading to CoO_2 is impossible, because removal of lithium should increase the repulsion between the CoO_2 layers and result in the structure failure (the hexagonal form O3 of cobalt oxide is unstable). Later, Amatucci *et al.*[19] have shown that the complete electrochemical delithiation can be achieved upon charging up to 5.2 V. Using a special cell designed for *in situ* XRD experiments, it was shown that upon complete delithiation a transition to a more organised truly hexagonal O1 structure isostructural to CdI_2 occurs rather than the expected decomposition of the original rhombohedral structure. Intercalation of lithium results immediately in the reverse phase transition.

As a whole, changes occurring in a single charge–discharge cycle of stoichiometric lithium cobaltate are sufficiently well studied (see Refs 19–21). In the *x* range from 1 (0.9, according to Ref. 19†) to $\sim$ 0.75–0.78, two hexagonal phases coexist (a wide plateau at 3.9 V in the charge–discharge curve). For *x* from 0.8 to 0.22–0.25, again a single hexagonal phase is present. In a very narrow interval, $x = 0.44–0.49$ (see Refs 20 and 21) (0.46–0.51, according to Ref. 19), the lattice symmetry changes to the monoclinic one; the appearance of this phase is associated with the ordering of ions in lithium layers. Phase transitions to the monoclinic structure and back to the hexagonal phase give rise to two small plateaux at approximately 4.08 and 4.15 V. Substantial changes occur upon reaching 4.2 V. At this voltage, the parameter *c* abruptly decreases indicating the gradual transition to the monoclinic symmetry at 4.5 V and $x = 0.22–0.25$.[19,20] The formation of this second monoclinic phase is explained by the Jahn–Teller effect due to the appearance of low-spin cobalt ions (d^5). Further deintercalation of lithium ions manifests itself, at

† According to data by Amatucci *et al.*,[19] in the *x* range from 1 to $\sim$0.9 the initial hexagonal phase is conserved.

first, by the co-existence of hexagonal and monoclinic phases. After a number of phase transitions,[19] the process is finished at 5.2 V with the formation of the well-crystallised hexagonal phase mentioned above. It should be noted that 95% of initial lithium can be intercalated back into the structure of electrochemically synthesised cobalt oxide.[19]

A relatively small number of studies deal with the changes in the $LiCoO_2$ crystal structure caused by long-term electrochemical cycling. X-ray diffraction, electron diffraction and transmission electron spectroscopy studies[22,23] have shown that after many charge–discharge cycles (~ 300) in the 3.0–4.3 V interval the layered structure of lithium cobaltate gradually gives way to the spinel structure (space group *Fd*3*m*). The lower electrochemical activity of the latter is partially responsible for the capacity fade upon prolonged cycling. Yet another reason for the cycling-induced capacity fade of lithium cobaltate is the change in the surface area of particles, which can reduce the cathode volume and break the electric contact with the active-substance particles. The above-mentioned phase transition at $x = 0.5$ makes the greatest contribution to the capacity fade during cycling in the 2.5–4.3 V range. Lithium cobaltate is very sensitive to overcharge. There are no theoretical limitations to the further polarisation of negative electrodes upon reaching the lithium electrode potential. As a result, a layer of metallic lithium which is highly reactive with respect to the electrolyte can deposit on the carbon surface.[24] This is also favoured by the low thermal stability of lithium cobaltate.[25] Hence, LIB based on lithiated cobalt oxide are equipped with electronic guarding devices, which impairs their specific characteristics and increases the cost of the finished articles.

The self-discharge of LIB with cathodes of lithiated cobalt oxide can be due to different processes, the main one being apparently the interaction of the electrode material with the solvent. However, despite the relatively high (~ 4.2 V) open circuit voltage (OCV) of LIB, their self-discharge is very low. The film formation on the negative electrode was shown to play an important role in the self-discharge process.[26] As was demonstrated[27] by using a method which allows separate determination of cathode and anode contributions,[28] the capacity fade may also be due to the phase transition from the hexagonal structure to spinel, which occurs on the surface of grains under the effect of increasing internal stresses.

In most publications, attempts were made to relate structural and electrochemical characteristics of the cathode material to the method of its preparation.[20,21,29–35] As was noted above, commercial LIB largely utilise the high-temperature (HT) form of $LiCoO_2$. As a rule, the latter is obtained by solid-state synthesis, *i.e.*, high-temperature annealing (700–850 °C) of cobalt carbonate or oxide with lithium oxide or hydroxide in air or in oxygen. This method has a number of drawbacks including the long time of synthesis, high energy consumption and the loss of lithium (it is evaporated in the course of long-term synthesis). As an alternative, sol–gel technologies were developed for the synthesis of lithium cobaltate.[29,30,33]. This method provides better homogeneity of the starting compounds and hence better uniformity of the resulting oxide, minimises the heat treatment time and requires much lower temperatures to produce the same HT form of $LiCoO_2$. As a rule, salts of lower carboxylic acids are used, and the synthesis is carried out in the presence of a chelating agent (citric, oxalic, malonic and other acids) and alcohol (*e.g.*, ethylene glycol). Annealing of the resulting gel at ~ 550 °C affords the high-quality final product.[29,33] According to the literature data, the HT form of $LiCoO_2$ obtained at lower temperatures by the sol–gel method exhibits somewhat better electrochemical characteristics: at the discharge to 2.8 V, its capacity reaches 150 mA h g^{-1}; moreover, the charge–discharge voltage is slightly lower, which is important in view of preventing the electrolyte decomposition.[30]

Among other methods for synthesising lithium cobaltate, mention should be made of a method with mechanochemical treatment, which allows the lower temperatures of final annealing,[31,32] a method employing cryochemical crystallisation,[34] a method of spraying[33] and synthesis in a microwave oven.[36] The mechanochemical synthesis of crystalline $LiCoO_2$ is complicated by its instability with respect to mechanochemical treatment and by redox processes which involve the gas phase.[31] It was shown that the formation of the HT-modification of $LiCoO_2$ can occur at 400 °C.[31] The important features of the resulting cathodic material are the uniform composition, morphology, particle size, texture, all of which strongly affect the electrochemical characteristics of fabricated positive electrodes. All the listed methods provide greater (as compared with the solid-state synthesis) homogeneity upon blending the initial substances and better uniformity of the final product with respect to both composition and particle size (including submicron particles), which defines the enhanced capacity, improves the cycling process and increases the possibilities of cycling at higher charge–discharge rates.[29–31,32–34] The advantages of the microwave synthesis include considerably reduced time of synthesis and, as a consequence, a decrease in lithium losses during this process.[36]

Several authors[37,38] reported on the impossibility of synthesising nonstoichiometric compositions of lithium cobaltate. However, according to other authors,[39–41] such compounds can be obtained. Later, the former authors[37,38] also described nonstoichiometric $LiCoO_2$.[42,43] The limit of the existence of solid solutions with excess lithium corresponds to $x = 1.15$. By iodometric titration, it was found that the valence of cobalt in Li_xCoO_2 remains equal to 3.0 up to $x = 1.15$ and decreases to 2.9 only for higher x. The electroneutrality of compounds with $1 < x < 1.15$ is maintained as a result of the decrease in the cobalt content.[42] It was shown that extra lithium gives rise to both cobalt and oxygen vacancies and affects the electrochemical characteristics of the material.[42,43] A small excess in lithium (up to $x = 1.1$) enhanced the capacity, improved the material cyclability and diminished irreversible losses in the first charge–discharge cycle; for higher x, the capacity was found to fade due to the decrease in the cobalt content.[42] In contrast to stoichiometric $LiCoO_2$, nonstoichiometric samples remained structurally homogenous and demonstrated no transition to the monoclinic phase,[41] so that the steps in the charge–discharge curve at 4.08 and 4.15 V ($x = 0.5$) were observed to disappear.[42,43] The results of these studies[41–43] confirmed the rather unexpected results of calculations[44–48] which derived that oxygen ions play the key role in the redox processes during electrochemical intercalation–deintercalation of lithium, notwithstanding the concepts of classical inorganic chemistry according to which delithiation should involve oxidation of cobalt to the tetravalent state. According to calculations, lithium extraction involves the transfer of electronic density to oxygen ions and changes in the hybridisation of oxygen and cobalt orbitals, while the charge of cobalt remains surprisingly constant. Thus, the so-called 'self-regulated' response is observed, *i.e.*, minimisation of the external impact by rehybridisation. The excess of lithium in Li_xCoO_2 gives rise to new states of oxygen ions and statistically distributed vacancies in cobalt and oxygen layers rather than to oxidation of cobalt.[41]

Using nonempirical calculation methods, the authors of theoretical studies cited above determined the average voltage of lithium intercalation into layered matrices of the same structure MO_2 to give $LiMO_2$ for different metal atoms (M = Co, Ni, Ti, V, Cu) and also for a constant chemical composition with different ordering in cations, which included different structures (lithium cobaltate: rhombohedral layered structure and spinel[47]). A detailed theoretical study was carried out for $LiCoO_2$.[49] The results of this study agree well with the experimental observations discussed above.[19–21]

A large number of studies dealt with properties of lithium cobaltate doped with different metals ($LiCo_{1-y}M_yO_2$) aimed at improving its electrochemical characteristics and simultaneously reducing the cost (see, *e.g.*, Refs 50–52). The use of such dopants as nickel, iron and manganese somewhat improved the cyclability of $LiCoO_2$ by stabilising its structure and lowering the probability

of phase transitions. Such metals as aluminium and magnesium were also tested as the dopants. Based on aforementioned ideas on the significant role of oxygen ions in the redox process, it was predicted and later confirmed experimentally that introduction of aluminium increases the charge–discharge voltage.[53,54] By studying the electrochemical characteristics of $LiCo_{1-y}Al_yO_2$ (y = 0.05–0.25), it was shown that aluminium, even if slightly affecting the theoretical and experimental specific capacity (*ca.* 120 mA h g^{-1} for the optimal composition $LiCo_{0.8}Al_{0.2}O_2$), substantially improves the cycling reversibility due to the formation of single-phase samples (the steps in the charge–discharge curve disappear).[30] The results mentioned above [53,54] on the increase in the average charge—discharge voltage were confirmed. Although high voltage is desirable for providing the high energy density of LIB, voltage above 4.2–4.5 V poses serious complications associated with the choice of electrolytes and the extensive practical application of such batteries. Of the materials considered, only $LiCo_{1-y}Ni_yO_2$ has a small niche in the LIB production.[35]

At present, the efforts of scientists engaged in industrial production of cathode materials based of lithium cobaltate are mainly concentrated on studies of their morphological properties and texture, elucidation of the dependence of their electrochemical characteristics on the particle size and size distribution and optimisation of the compositions and methods for fabrication of the cathode mass.[25] It was shown that smaller sizes of powder particles, more uniform size distributions [29–34,32–34,55] and the formation of small agglomerates of fine spherical particles [55] impart better electrochemical characteristics to cathode materials. As was mentioned above, physical characteristics of crystalline materials strongly depend on the synthetic method, the temperature interval chosen, the time of thermal treatment, starting compounds and sample prehistory.

We deliberately leave the questions associated with polymeric LIB beyond the scope of our survey, because the major relationships and trends found for cathode materials are also valid for compounds used in polymeric batteries. However, it is evident that characteristics of the latter should depend much more strongly on the material morphology, particle size and size distribution. For films, of great importance are the texture, the preferential orientation when films are applied on supports, the application method, *etc*. It should be taken into account that common polymeric electrolytes used in such LIB decompose at 3.8 V, which imposes certain limitations on the cathode materials used. All these problems require special consideration.

III. Lithium nickelate and related materials

Lithium nickelate was suggested as the cathode material almost simultaneously with lithium cobaltate,[11] its cost and toxicity are substantially lower as compared with cobaltate, whereas the experimental specific capacity is apparently among the highest known for this class of lithiated oxides $LiMO_2$ (185 and 210 mA h g^{-1} when charged to 4.1 and 4.2 V, respectively).[25] However, $LiNiO_2$ has not yet found use in commercial LIB. This is due first of all to the difficulties associated with the synthesis of such a compound with a stoichiometric or merely reproducible composition. In practice, the obtained compounds have a composition $Li_{1-x}Ni_{1+z}O_2$ where z depends on the conditions of synthesis and on average varies from 0.05 to 0.20.[56] Optimisation of the process can decrease z but has not yet provided values below 0.01–0.02.[25,56] The decrease in the lithium content in a compound lowers the specific capacity of the sample. Nonstoichiometry appears due to instability of trivalent nickel at high temperatures. 'Extra' nickel ions in the bivalent state occupy lithium positions. XRD data point to the ordered arrangement of lithium and nickel cations in the lithium layers;[56] hence, the more correct formula of lithium nickelate should indicate the occupied positions like $[Li_{1-z}Ni^{2+}_z]_{3a}[Ni^{3+}_{1-z}Ni^{2+}_z]_{3b}[O_2]_{6c}$ (rhombohedral structure $R3m$).[57] The presence of nickel ions in the lithium positions prevents free transport of lithium ions. Moreover, in the course of deintercalation, additional nickel ions were observed to occupy the lithium positions.[58] Electrostatic repulsion between lithium ions and extra nickel ions and reduction of the distance between the layers due to the presence of bi- and trivalent nickel substantially impair the reversibility of the charge–discharge process.[56,59,60] Furthermore, lithium nickelate is less stable with respect to overcharging (due to the greater cycling depth and structural changes).[61]

Lithium nickelate has the same structure of the α-$NaFeO_2$ type as lithium cobaltate, namely, the ordered rocksalt structure with alternating Li^+ and Ni^{3+} layers which occupy octahedral voids in the supercompact cubic packing of oxygen ions. However, for trivalent nickel (electronic configuration $t^6_{2g}e^1_g$), the Jahn–Teller effect is observed; hence, despite the identical structures, lithium nickelate and cobaltate behave differently. The distortion of NiO_6 octahedra due to the Jahn–Teller effect (different lengths of N—O bonds) was first discovered when analysing the fine structure of X-ray absorption spectra.[62] This distortion is of the local nature and cannot be observed in ordinary XRD spectra. Thus the lowering of the local symmetry from rhombohedral to monoclinic was observed. According to calculations,[63,64] the monoclinic distortion observed in the course of lithium deintercalation is due to the combined action of the Jahn–Teller cooperative effect and the ordering of the Li-ion vacancies. Ultimately, the lattice distortion has the decisive effect on the propensity of lithium nickelate to reversibly intercalate–deintercalate lithium. The phase diagram of Li_xNiO_2 calculated in the aforementioned studies [63,64] is in sufficient agreement with experimental results;[65–68] however, it should be stressed that the sequence of phase transitions in Li_xNiO_2 as a function of intercalation depth is not yet determined as reliably as for lithium cobaltate and certain discrepancies are still observed.[65–69] The number of individual phases detected in the system during the charge–discharge varies from three [67] to eight (according to *ab initio* calculations).[64] According to both experimental results [65–68] and calculations,[63,64] the rhombohedral phase exists in the $0.75 < x < 1$ range, whereas the monoclinic phase occurs at $0.4 < x < 0.75$. Within this range, lithium nickelate exhibits good electrochemical characteristics (the corresponding potential range is from approximately 3.6–3.65 to 3.9–4.0 V). Charging to 4.2 V substantially changes the Li_xNiO_2 structure, which is associated with great changes in its volume and the loss of charge–discharge reversibility.[66,68] The nickel dioxide phase $\square NiO_2$ (see ‡) (space symmetry $R3m$) is unstable in nonaqueous solvents at room temperature.[66] As in the case of cathodes based on lithium cobaltate, the surface of particles also changes, which results in the formation of microcracks and finally in the cathode failure.[70,71] The thermal behaviour of completely or partially charged Li_xNiO_2 was studied by differential scanning calorimetry (DSC).[72] It was shown that exothermal peaks of decomposition of delithiated phases for the samples with $x \leqslant 0.25$ are observed at temperatures above 180 °C, whereas the reaction begins at room temperature.

It was found [50] that doping with cobalt stabilises the lithium nickelate structure and minimises deviation from stoichiometry. The introduction of a 3d metal prevents lithium from ordering over the vacancies and weakens the monoclinic distortion, which results in a more stable structure. The charge–discharge curves for such samples are smoothed out, which points to the smaller number of phase transitions during intercalation–deintercalation. That is why the majority of scientists used this way for improving the electrochemical characteristics of lithiated nickel oxide and for studying the properties of doped lithium nickelates. Manganese,[73–80] cobalt,[50,81–86] iron,[87,88] aluminium,[72,89] titanium,[74,89] copper [89] and magnesium [90] were chosen as the dopants. Multicomponent systems with two dopants, *e.g.*, cobalt and gallium,[58] cobalt and aluminium,[61,91] cobalt and titanium,[92] cobalt and magnesium,[91] manganese and aluminium, manganese

‡ Symbol □ means vacancy.

and cobalt, manganese and magnesium, manganese and titanium,[80] gallium and magnesium,[93] and even systems with three dopants [92] were also studied.

According to the results of *in situ* X-ray spectroscopy with synchrotron emission, $LiNi_{1-y}Co_yO_2$ samples first undergo fast and almost complete oxidation of nickel, whereas cobalt is slowly oxidised at the end of charging.[83] Samples doped with cobalt exhibit higher thermal stability in the completely charged state and, hence, are more resistant towards overcharging.[80] For such systems, heat-induced (in the 50–150 °C range) structural changes were studied as a function of the cobalt content. For equal discharge depths (the same x) in $Li_xNi_{1-y}Co_yO_2$ ($y \leqslant 0.30$) in CD2032 coin cells, the temperature-induced changes in the $c:a$ ratio of the hexagonal lattice parameters (which reflects the degree of trigonal distortion) decrease with the increase in the cobalt content.[86] For cobalt-doped samples $LiNi_{1-y}Co_yO_2$, the smallest cycling-induced changes in the unit cell volume and reversible lithium intercalation–deintercalation at higher cycling rates in the range $0.2 \leqslant y \leqslant 0.4$ were observed.[50,94] At the same time, very good characteristics were reported for $LiNi_{0.5}Co_{0.5}O_2$,[85] $LiNi_{0.8}Co_{0.2}O_2$,[95] $LiNi_{0.85}Co_{0.15}O_2$ (see Ref. 83) and similar compositions. Solid solutions $LiNi_{1-y}Co_yO_2$ demonstrated good electrochemical characteristics for virtually all y values in the range $0.2 \leqslant y \leqslant 0.85$.

XRD and Mössbauer spectroscopy studies have shown that the introduction of Fe prevents the phase transition in solid solutions $Li(Ni_{1-y}Fe_y)O_2$ ($y \leqslant 0.30$) with rhombohedral structure.[87] Deintercalation up to $x = 0.12$ results only in oxidation of Ni^{2+}. As indicated by Mössbauer spectra, further deintercalation increases the oxidation state of iron and simultaneously trivalent nickel is oxidised to the tetravalent state. However, as the amount of introduced iron increases, the capacity is observed to substantially decrease, which can only be attributed to the decrease in the concentration of electrochemically active nickel. Moreover, the charge–discharge voltage of such samples is somewhat higher, which suggests that nickel oxidation in this compound is complicated as compared with pure lithium nickelate.

Kim and Amine [89] studied how the oxidation state of a dopant (bi-, tri- and tetravalent ions, namely, Cu^{2+}, Al^{3+}, Ti^{4+}) added to lithium nickelate affects the characteristics of the resulting material. Introduction of copper not only substantially decreased the specific capacity of samples (because copper is electrochemically inactive in this range), but also noticeably impaired their ability to reversibly intercalate–deintercalate lithium. Moreover, samples containing copper tend to form cubic lattices rather than layered structures. Introduction of aluminium resulted in the formation of stable solid solutions; however, the specific capacity of aluminium-containing substances also decreased with Al concentration, even if to the lesser extent than for copper; and the cycling reversibility was impaired. Finally, a 10%–20% titanium admixture, even if insignificantly (2.5%–5%) lowering the capacity (down to capacities of 187 and 161 mA h g^{-1} for 2.8 and 4.3 V, respectively), substantially improved the reversibility of the charge–discharge process (100 cycles). This can be explained by the fact that both nickel and bivalent copper can reside in the lithium layer, which impairs the electrochemical characteristics of the original nickelate. XRD analysis with Rietveld refinements have shown that in $Li_{1-x}(Ni_{1-y-z}Co_yMg_x)O_2$ bivalent magnesium ions occupy the positions of bivalent nickel in lithium layers.[91] Introduced trivalent aluminium was shown to substitute trivalent nickel ions in nickel layers and, at best, had no effect on the migration of Ni^{2+} ions to the lithium layers. Finally, Ti^{4+} ions compensate both the charge deficiency and the structural instability caused by the presence of Ni^{2+} ions in the lithium layers.

The information on the influence of aluminium added to lithium nickelate on the structural and electrochemical characteristics of the latter is ambiguous. It was shown that, in contrast to lithium nickelate, $Li(Ni_{1-x-y}Co_xAl_y)O_2$ demonstrates no phase transitions during cycling and can be deeply discharged (to voltages below 2.5 V), which increases the specific capacity and ensures its long shelf-life in the discharged state (its characteristics remained virtually unchanged after two years storage at 40 °C).[61] It was also noted that addition of aluminium has a positive effect on the thermal stability during lithium deintercalation.[61,92] However, the results of DSC studies [91] suggest that the thermal stability of multidoped samples $Li(Ni_{0.80}Co_{0.15}Al_{0.05})O_2$ reveals no dependence of the decomposition temperature on the nature and concentration of the second (after cobalt) dopant for equal degrees of lithium extraction. At the same time, the increase in the grain size enhanced the thermal stability regardless of the lithium extraction degree. It was also stated [72] that substitution of a fourth part of Ni atoms [$Li(Ni_{0.75}Al_{0.25})O_2$] suppresses the exothermal reaction of decomposition, making the resulting compound more resistant to overcharge. A cathode made of this material demonstrated a specific capacity up to 150 mA h g^{-1}; however, its characteristics can be improved by optimising the conditions of its synthesis and fabrication of the positive electrode.

In recent years, mixed lithiated oxides based on nickel and manganese were actively studied.[73–80] These compounds can be classified among both nickel-based materials ($LiNiO_2$) and manganese-based materials ($LiMnO_2$). At the same time, in contrast to lithium cobaltates and nickelates, lithiated manganese oxide ($LiMnO_2$) has a layered rhombohedral structure (space group *Pmnm*).[95] For a long time, due to different structures of lithium nickelate and lithium manganate, all attempts to obtain solid solutions in the Li–Ni–Mn–O systems with layered rhombohedral structures failed. A large body of data appeared only after Makimura and Ohzuku [73] proposed to synthesise these substances from a binary nickel–manganese hydroxide [$Ni(OH)_2$ and $Mn(OH)_2$ in the 1 : 1 ratio]. Later, the compound $LiNi_{0.5}Mn_{0.5}O_2$ was actively studied both experimentally and theoretically (*ab initio* calculations).[95] In the voltage range from 4.0 to 2.0 V, its specific capacity was 200 mA h g^{-1} with sufficiently good cyclability;[78] moreover, as compared with lithium nickelate, the material proved to be more resistant to heating. Samples of manganese–nickel oxides of other compositions were synthesised and studied.[75–77,79] Different synthetic methods were used, including those based on the sol–gel technology with organic acids as the chelating agents (*e.g.*, see Refs 75, 79). According to the results obtained (including those of nonempirical calculations [95]), $LiNi_{0.5}Mn_{0.5}O_2$ contains bivalent nickel and tetravalent manganese. Intercalation–deintercalation of lithium in the course of charge–discharge in the range between 4.0 and 2.0 V involves a two-electron process of nickel oxidation–reduction. The oxidation state of manganese remains unchanged. The absence of Mn^{3+} and Ni^{3+} ions which cause lattice distortion due to the Jahn–Teller effect and subsequent structural rearrangement makes this compound stable during cycling. It was found [77] that in the voltage range from 2.0 to 1.25 V one more lithium atom per formula unit can be inserted to give $Li_2Ni_{0.5}Mn_{0.5}O_2$ with hexagonal symmetry (space group *P3m*1). This compound has excellent cyclability but is unstable in air. However, the latter problem can be partially solved by synthesising composites based on it [*e.g.*, with Li_2TiO_3 (see Ref. 77)]. Presumably,[77] the form with the higher lithium content can be used for the development of a new kind of LIB in which the Li_2MO_2 phase is introduced to compensate the first-cycle irreversible losses.

Quite recently, an interesting compound, namely, $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ was synthesised and studied.[96] This mixed oxide was obtained from a ternary hydroxide. It possesses very good characteristics: the specific capacity of *ca.* 200 mA h g^{-1} (2.5–4.5 V), insignificant capacity losses during 30 charge–discharge cycles and enhanced thermal stability.

Mention should be made of studies on partial substitution of fluoride or sulfide anions for oxygen anions in the oxygen sublattice of lithium nickelate. This substantially improved the reversibility of the charge–discharge process for layered $LiNiS_yO_{2-y}$ (see Ref. 97), although the sulfide anions added

lowered the specific capacity of the sample (the higher S^{2-} concentration, the lower the capacity). Ohzuku, Ueda and Kouguchi[98] suggested another way of improving cyclability which consists of introducing fluoride anion by adding HF to the original material. Similar results were obtained by other authors.[90] The synthesised samples of $Li_{1-z}Ni_{1+z}F_yO_{2-y}$ ($y = 0.015$, $z = 0.06$) demonstrated better cycling reversibility as compared with those nonsubstituted. The effect of dual doping with cations and anions was studied.[99] The compound $Li_{1.075}Ni_{0.755}Co_{0.17}$ $O_{1.9}F_{0.1}$ obtained by solid-phase synthesis demonstrated the best characteristics: initial capacity 182 mA h g^{-1} with only 2.8% lost during cycling (100 cycles). These results make it possible to assume that both cationic and anionic substitutions can contribute to the improvement of cyclability.

From the foregoing it is evident that for lithium nickelate the synthetic method still plays a greater role than for lithium cobaltate. Studies on the nature of starting materials, the synthesis temperature and the time of thermal treatment have shown that smaller deviations from stoichiometry are observed for more reactive starting materials and relatively low (600–700 °C) temperatures.[56] Under certain conditions,[56, 69] samples withstanding a large number of charge–discharge cycles (more than 50 cycles; capacity loss less than 0.12% per cycle) can be obtained.[69] The electrochemical behaviour of $LiNi_{1-y}Co_yO_2$ samples prepared by solid-phase synthesis was shown to be closely related to their particle size and size distribution.[82] The Coulomb efficiency in the first cycle is higher the smaller the particles, while the specific capacity remains virtually unchanged. As for lithium cobaltate, a comparison of samples obtained by solid-state synthesis and sol–gel methods confirmed that the latter method provides better homogeneity of starting reagents and the smaller particle size. As a rule, the starting compounds in the sol–gel method include aqueous solutions of nickel and metal-dopant salts, nickel hydroxide and a solution of ammonium hydroxide as the complex-forming agent. The ammonia concentration and pH of the solution were shown to be the most important synthetic parameters in view of preparing samples with desired properties.[84] Organic acids can also be used as the complex-forming agents in the sol–gel technology.[75, 79]

To increase the energy density of LIB, one should use materials possessing both high specific capacity and high density. The higher degrees of crystallinity and the greater particle size, the smaller bulk densities of materials, but simultaneously the lower specific capacities of samples. The bulk density is closely related to the morphology of particles, their sizes and size distribution. However, among materials with the same degrees of crystallinity, spherical particles have the highest bulk density. Thus, the characteristics of cathodes for nickel hydride batteries could be substantially improved when using $Ni(OH)_2$ with spherical particles was used.[84] Samples of cobalt-doped lithium nickelate $LiNi_{0.8}Co_{0.2}O_2$ with quasi-spherical particles and a narrow size distribution were synthesised.[84] This allowed the authors to increase the bulk density of $LiNi_{0.8}Co_{0.2}O_2$ up to 3.24 g cm^{-3} as compared with 2.3 g cm^{-3} for common commercial samples of this material. As compared with commercial samples produced by Merck (irregular crystals with a wide size distribution), $LiNi_{0.8}Co_{0.2}O_2$ samples with spherical particles demonstrated not only high bulk weight but also improved electrochemical characteristics when cycled in the range from 3.0 to 4.3 V (217 mA h g^{-1} in the first cycle and a discharge capacity of 172 mA h g^{-1} in further cycles, as compared with 210 and 165 mA h g^{-1}, respectively, for commercial samples).

IV. Lithium–manganese spinel and spinel-based materials

Among cathode materials under consideration, lithiated manganese oxides and their derivatives are the cheapest and most readily available. Their advantages also include a sufficiently high discharge voltage, high thermal stability especially in the discharged state and nontoxicity. That is why, the compounds of this class were the subject of active studies and wide speculations.

It should be noted that the Li–Mn–O system is much more complex as compared with Li–Co–O and Li–Ni–O systems, because it includes more than ten stable compounds with different structures that contain manganese in various oxidation states and have different degrees of defectiveness.[100] Figure 2 shows an isothermal section of the phase diagram for the Li–Mn–O ternary system (see Ref. 100) and also demonstrates the 'routes' of electrochemical insertion and extraction of lithium (designated by dashed lines with the corresponding average charge–discharge voltages written on the top) and the compounds involved (*T* and *C* designate tetragonal and cubic structures). Lithium intercalation–deintercalation is possible for samples located between λ-MnO_2 ($\square Mn_2O_4$, a stable compound) and $LiMn_2O_4$ (at 4 V), $LiMn_2O_4$ and $LiMnO_2$ ($Li_2Mn_2O_4$) (at 3 V), $Li_4Mn_5O_{12}$ and $Li_7Mn_5O_{12}$ (the latter two compositions can be represented as $LiMn_{1.67}Li_{0.33}O_4$ and $Li_2Mn_{1.67}$ $Li_{0.33}O_4$).

Among the compounds mentioned above, lithium–manganese spinel $LiMn_2O_4$ attracts the keen attention of scientists. Spinel is crystallised in the cubic system (space group *Fd*3*m*). The crystal structure of normal spinel $A[B_2]O_4$ is shown in Fig. 3. Oxygen anions form a supercompact cubic lattice where cations are localised in tetrahedral and octahedral voids. Two limiting positions are possible for cations. In normal spinels, atoms A occupy tetrahedral positions (8*a*), while cations B occupy octahedral positions (16*d*). In inverted spinels, atoms A and a half of atoms B are located in octahedral positions, the remaining atoms B occupy tetrahedral positions. Between these two versions, a continuous series of intermediate structures can be realised. It is a

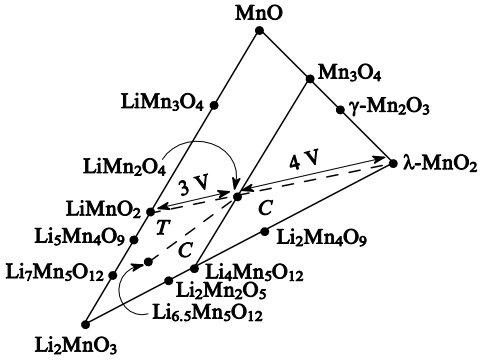


Figure 2. Isothermal section of a phase diagram for a ternary system Li–Mn–O.[100]

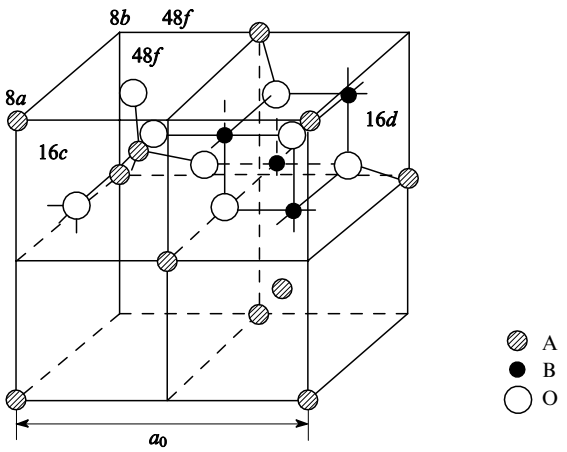


Figure 3. A scheme of $A[B_2]O_4$ spinel structure.

possibility to form different kinds of cationic positions and vacancies (defective structures) that determines the stability of spinel structures with different cations in variable valences. For the same reason, the spinel structure of $LiMn_2O_4$ can host lithium ions in both octahedral and tetrahedral positions.[101] Moreover, there is a 'hierarchy' of voids in the spinel structure, which suggests that discharge characteristics of cathodes based on these structures vary nonmonotonically in the absence of kinetic limitations.[102]

Indeed, electrodes with the working voltage of 4 V are formed when lithium is electrochemically intercalated–deintercalated into tetrahedral positions 8*a* of $Li_x\ Mn_2O_4$ spinel (for normal spinel).[103] For $x > 1$ (according to certain results,[100] at $x > 1.08$), lithium begins to migrate to octahedral positions. The process occurs at 3 V and results in the formation of a layered rhombohedral phase of $LiMnO_2$. In principle, if we consider the overall transition from λ-MnO_2 to $LiMnO_2$ from the theoretical viewpoint, the latter compound could be characterised as an excellent cathodic material with the theoretical capacity of 285 mA h g^{-1}. However, two different electrochemical mechanisms are responsible for the two plateaux at 3 and 4 V, *i.e.*, with a great voltage difference. From the viewpoint of practice, materials with such properties are of no interest.[25] The mentioned phase transition of the first kind was attributed to the increase in Mn^{3+} concentration, which strengthens the co-operative Jahn–Teller effect and gives rise to tetragonal distortions followed by structural changes.

As a whole, the following changes occur during the charge–discharge of a material with the stoichiometric composition $LiMn_2O_4$ in the range from 3.5 to 4.5 V.[104] At $\sim$ 4 V, lithium is electrochemically extracted and inserted in two stages divided by a small step of 0.1 V at $x = 0.45–0.6$ (4.05 and 4.15 V, respectively). The presence of this step is explained by the ordering of the remaining half of lithium ions over tetrahedral positions,[105] which contributes to the gradual specific capacity loss of the spinel. In the x range from 1 to 0.5, two phases coexist. For x below $\sim$ 0.5, also two $Li_xMn_2O_4$ cubic phases coexist, namely, with x equal to 0.15 and 0.4.[104]

Structural and phase transitions that occur during cycling, especially in the high voltage range, are accompanied by great changes in the cathode material bulk and, ultimately, cause irreversible changes in the cathode properties. Among the drawbacks of $Li_xMn_2O_4$ spinel, mention should be made of its relatively low theoretical specific capacity (148 mA h g^{-1}), the capacity loss during storage, especially at high temperatures, and the danger of its dissolution in inorganic solvents in the presence of moisture.

A spinel with nonstoichiometric composition $Li_{1+x}Mn_2O_4$ demonstrates much better cycling reversibility.[106] The disappearance of the step in the cycling curve suggests the homogeneous structure of nonstoichometric spinel. This is explained by the increase in manganese vacancies, which is responsible for certain strengthening of the Mn—O bond, and changes in the surrounding of lithium in tetrahedral positions.

It should be noted that the properties of lithium–manganese spinel strongly depend on the synthetic method.[18, 103, 106–111] Single-phase samples are obtained in the range $0.9 < x < 1.15$.[18] The parameter a of the spinel cubic lattice and the oxygen ion deficiency are shown to increase with an increase in the temperature of synthesis, or (when samples are prepared by quenching) with an increase in the quenching temperature and a decrease in quenching time. The loss of oxygen is responsible for tetragonal distortion of the spinel lattice. As the quenching temperature increases, the phase structure of $LiMnO_2$ spinel undergoes the following changes: first, a two-phase domain appears (840–890 °C), then, a domain of the existence of a single tetragonal phase is observed (895–910 °C) and, finally, above 910 °C, a domain of mixed phases (the main phase is rhombohedral $LiMnO_2$) occurs. The transition from the spinel phase to the tetragonal one is reversible. Spinels synthesised at low temperatures contain higher concentrations of oxygen and lower concentrations of trivalent manganese, which reduces the specific capacity of a sample to a certain extent but enhances its cyclability due to the weaker distortions associated with the Jahn–Teller effect.[107, 108] Moreover, both anionic and cationic kinds of nonstoichiometry were shown to depend not only on the temperature of synthesis but also on the nature of the starting compounds.[109, 110] The anionic nonstoichiometry has the greater effect on the properties of $LiMn_2O_4$, as compared with cationic nonstoichiometry (the Li/Mn ratio).[111] Certain publications[108, 112] reported good cyclability of samples made of disordered defective spinels with the nonstoichiometry Li/Mn < 1 (average cycling capacity of 120 mA h g^{-1}).

Different methods were used for the synthesis of lithium–manganese spinels, *viz.*, various versions of solid-phase synthesis,[103, 106, 109, 111] including those using the mechanical processing,[113–115] microwave synthesis,[116] sol–gel syntheses with different starting substances and chelating agents (*e.g.*, citric, polyacrylic and stearic acids),[107, 110, 117, 118] a method using the starting reagent in the form of an oil emulsion.[119] The development of synthetic methods is largely focused on the preparation of spinel phases nonstoichiometric in lithium and oxygen and more uniform with respect to composition and particle size.

The drawbacks of lithium–manganese spinels mentioned above can be eliminated by modifying their compositions (doping with cations and anions as in the case of lithium cobaltate and lithium nickelate) and surface as well as by using nonstoichiometric compositions.

Surface is modified in order to form a protective film preventing dissolution of the cathodic material in the electrolyte, *e.g.*, by encapsulating surface particles of $LiMn_2O_4$ in lithium borate. Another goal is to directly affect the active centres on the surface of lithium–manganese spinels, *e.g.*, by treating the surface with acetylacetone.[120] Moreover, the $LiMn_2O_4$ surface is often modified to compensate the losses in the first charge–discharged cycle. Thus by coating the $LiMn_2O_4$ surface with lithium cobaltate in the form of microemulsion, it is possible to reduce the specific capacity losses from 12% to 5% in 100 cycles.[121] To compensate the first-cycle losses, it was proposed[122] to add (to the bulk) Li_2CuO_2 which has an irreversible yet high specific capacity (320—340 mA h g^{-1}).

Numerous studies were devoted to modification of lithium–manganese spinels by doping. The following dopants were studied: Co,[108, 123–127] Ni,[81, 123, 124, 127–130] Cr,[124, 127, 129, 131–136] Fe,[123, 137] Al,[137, 138] Mg,[137, 139], Cu (see Ref. 137), *etc*. Simultaneous doping with two elements was also suggested.[137, 139, 140] These studies were carried out by various techniques: X-ray diffraction, X-ray photoelectron spectroscopy (XPS), ESR, Fourier-transform IR spectroscopy (FTIRS), EXAF spectroscopy, electron microscopy, neutron diffractometry, DSC and cyclic voltammetry. Electrochemical tests were also carried out.

In these publications, the effect of a metal M in $Li[Mn_{2-y}M_y]O_4$ was studied in the domains of existence of single-phase products with the spinel structure over the entire concentration range. In the majority it was shown that partial substitution for manganese in 16*d* positions weakens the distortion due to the Jahn–Teller effect, thus stabilising the spinel structure, and also reduces the specific capacity losses at high voltage (> 4 V). Moreover, as a rule, a step in the charge–discharge curve at $x \approx 0.5$ is 'smoothed', which apparently can be explained in the same way as for the case of nonstoichiometric spinel samples (the latter can be considered as lithium-doped), *i.e.*, by changes in the Mn—O bond strength and in the surrounding of lithium ions in tetrahedral positions. At high concentrations of an introduced substituent, the dopant ions can partly occupy the 8*a* positions of lithium [123, 137] (partially inversed spinel). The increase in the degree of substitution into 8*a* positions with an increase in the dopant concentration was shown to impede the migration of lithium ions and reduce the specific capacity of the cathode material.[137]

Doping (*e.g.*, with chromium) also increases the diffusion coefficient of lithium,[136] which allows one to increase the current density of the charge–discharge process. It should be noted that, in the voltage range from 2.5 to 4.5 V, oxidation–reduction of manganese occurs. In this case, doping is ineffective; hence, when improving the reversibility of electrochemical intercalation–deintercalation of lithium, it should be borne in mind that the lower capacities of materials the higher dopant concentrations (see, *e.g.*, Refs 125, 126, 134, 136).

Simultaneous introduction of anionic (S^{2-}) and cationic (Mg^{2+}) substituents is beneficial as regards reversibility but substantially reduces (up to 85 mA h g^{-1}) specific capacities of samples.[139]

Yet another feature of lithium–manganese spinel which has not been touched upon above, namely, the low-temperature transition to the other rhombic phase at 280–285 K deserves mention.[140, 141] Multidoping (with cobalt and nickel) makes it possible to suppress this phase transition,[141] because the latter is also caused by distortions due to the Jahn–Teller effect; this will allow using LIB at low temperatures.

Since the advent of electrolytes stable at high voltages, it has been found that cycling of doped samples up to 5.1–5.2 V gives rise to the second wide plateau (at $\sim$4.7–4.8 V) in the cycling curve.[81, 123, 127, 137] Its appearance is associated with redox transformations of the dopant metal,[123, 127] as was demonstrated by several techniques including the analysis of the fine structure of X-ray absorption spectra.[127] The reversibility of this process at $\sim$4.7–4.8 V strongly depends on the degree of crystallinity and the morphology of particles and takes the maximum value for quasispherical particles.

The role of the morphology of cathode-material particles, their sizes and size-distribution has been discussed in the previous Sections devoted to lithium cobaltate and lithium nickelate. Yet another study in which these problems are discussed in detail deserves mention.[142] It was shown that at high cycling rates of lithium–manganese spinel, it is the morphology of particles that plays the key role rather than their sizes. Hence, larger but porous particles with big surface areas exhibit better electrochemical characteristics, do not crack when cycled and do not affect greatly the cathode volume.

V. Miscellaneous materials with average voltage of 4 V

Although the main objective of this survey is to discuss cathode materials based on lithium cobaltate, lithium nickelate and lithium–manganese spinel, *i.e.*, compounds which are recognised to date as the main candidates for lithium-ion batteries,[143] a small group of different LIB materials with the voltage of 4 V also deserve discussion.

It should be noted that the efforts to apply materials based on layered manganese compounds never stop. These materials are often synthesised (for example, by ion exchange) in such a way as to make their structure as close to the structures of lithium cobaltate and lithium nickelate with good cyclability as possible.[73–80, 144–148] All of them, as a rule, are stabilised by introducing different dopants, *e.g.*, aluminium,[145] iron, manganese, cobalt,[146] chromium [147, 148] and, most often, nickel.[73–80] Properties of such materials are discussed in detail in section III using the example of nickel compounds.

Attempts were undertaken to develop cathodes based on the orthorhombic phase of $LiFeO_2$. However, the charge–discharge process in these compounds is irreversible due to the instability of Fe^{4+} in Li_xFeO_2 with respect to electrolyte.[25]

Recently, there was reported [149] a new cathode material in the Li–Co–Ti–O system. The resulting layered material has a structure resembling those of Li_2MnO_3 and Li_2TiO_3 and represents a solid solution of Li_2TiO_3 and Li_2CrO_2 with the general composition of Li_3CrTiO_5 ($Li[Li_{0.2}Cr_{0.4}Ti_{0.4}]O_2$). The samples were identified in the monoclinic system (space group $C2/m$). It was shown that this compound undergoes a redox process involving chromium (Cr^{3+}/Cr^{6+}) with a very good cycling reversibility in the voltage range from 2.0 to 4.8 V. Similar results (with electrochemically active chromium) were obtained for $LiMn_xCr_{1-x}O_2$.[148]

Recent publications discussed the prospects of using $LiFePO_4$.[150–153] This material is cheap, safe, has a high energy density and is sufficiently attractive as regards the working voltage (3.5 V); however, it has an extremely low electronic conductivity. Nevertheless, the introduction of a small amount (no more than 1%) of a dopant metal (Zn, Nb or Mg) was shown to increase the electronic conductivity by eight orders of magnitude.[151]

VI. The prospects of using metastable superstructures

The analysis of published data shows that most scientists tend to develop positive-electrode materials based on single-phase structures or solid solutions. However, as has already been noted in the previous section (see, *e.g.*, Ref. 77), the prospects of using complex multicomponent systems based on oxides of cobalt, nickel and manganese including multidoped systems are also considered. Thus in studies on the electrochemical behaviour of composites $LiMO_2 \cdot Li_2M'O_3$ (M = Co, Ni, Mn; M′ = Ti, Zr, Mn) [77, 154, 155] it was found that the addition of $Li_2M'O_3$ enhances the stability of the positive-electrode material. It was also shown [156] that the addition of $LiNi_{0.8}Co_{0.2}O_2$ to lithium–manganese spinel $Li_{1+x}Mn_{2-x}O_4$ inhibits spinel dissolution in the electrolyte and reduces capacity losses during storage at elevated temperatures. Mention should be made of several patents in which the materials for positive electrodes of lithium-ion batteries were developed on the basis of lithiated oxides. For instance, a mixture of $Li_xNi_yCo_zM_nO_2$ (M = Al, Ti, W, Cr, Mo, Mg, Ta, Si or their combinations) with lithium–manganese spinel $Li_xMn_{2-r}M'_rO_4$ (M′ = Cr, Ti, V, Ni, Co, Fe, Sn, Zn, Zr, Si or their combinations) was proposed to enhance the cycling stability of capacity characteristics and the stability with respect to overcharging.[157] A Japanese Patent of the Fuji Photo Film Company [158] also suggested using a mixture of two lithiated oxides, *viz.*, lithium cobaltate $Li_{1-y}CoO_2$ ($0.1 \leqslant y \leqslant 1$) and a spinel $Li_{2-x}Mn_2O_4$ ($0 \leqslant x \leqslant 1$). The materials were applied simultaneously on aluminium foil; one layer is expanded during the discharge, while the other is contracted. This material provided high initial capacity and stable cycling characteristics and eliminated the electrolyte leakage. Multiphase systems based on lithium–manganese spinel and lithiated oxides $LiNiO_2$, Li_2NiO_2, $LiNi_2O_4$, $Li_2Ni_2O_4$ and $LiNi_{1-x}M_xO_2$ (M = Co, Mn, Al) were suggested by scientists from the Japanese 'NEC Corporation'[159] with the aim of improving the cyclability, shelf life and safety of lithium-ion batteries. The authors of a patent [160] aimed at the development of LIB with enhanced high-temperature stability during discharge and overcharge and, at the same time, preservation of high energy characteristics suggested the use of a composite of the two following compounds as the positive-electrode material: $Li_xM_yO_4$ ($0 < x < 2$); $0.8 < y < 1.2$; M = Fe or Fe_zMn_{1-z}) and one of the lithiated oxides $LiCoO_2$, $LiNiO_2$ or $LiMn_2O_4$ with the potential of lithium intercalation–deintercalation higher than that of $Li_xM_yPO_4$.

From our viewpoint, along with analysing possible practical approaches to the development of such multiphase systems (and solid solutions), attempts should be made to understand the mechanisms of formation of these compositions and to study the processes that occur during the formation of eutectic compositions and solid solutions. It should be noted that, according to published data, eutectic compositions were never studied as candidates for cathode materials, although, undoubtedly, they are of interest. In recent years, a group that includes the authors of this review accomplished a number of studies aimed at elucidating self-organisation mechanisms for structures like supramolecular ensembles in the series of two-phase systems of oxides and

selenides. In a survey devoted to this problem,[161] we proposed to consider the structure of resulting eutectics and solid solutions as supramolecular structures formed due to self-organisation of incommensurable (which is also true for multiphase compositions of positive-electrode materials under discussion) interacting structures of components. Experimental studies of some eutectic oxide ($PbO-ZnO$, $PbO-Mo_2O_3$, $PbO-Y_2O_3$, $PbO-V_2O_5$)[162] and selenide ($GaSe-Ga_2Se_3$) (see Ref. 163) systems demonstrated that such self-organisation can occur and anomalous phases can form due to interaction of their components. The survey involved a theoretical part, in which the process of formation of supramolecular ensembles was considered within the framework of a static version of the Frenkel–Kontorova model for finite systems.[164–166] In this model, abstract thermodynamic criteria such as surface energy or surface tension are replaced by real parameters of interacting structures, *viz*., incommensurability, rigidity and interaction potential. The results of analytical and numerical simulations in terms of this approach allowed us to make certain very significant conclusions on how the mechanochemical processing affects the interacting substructures, to follow the variation of model parameters with temperature and characterise the excited states of the system, thus linking them with the synthetic conditions. It was shown that under certain conditions such systems demonstrate quite a number of very steady metastable states. Only the case of one-dimensional incommensurability was considered; however, the results obtained can be used for explaining certain phenomena observed for eutectic phases and solid solutions.

From our viewpoint, the presented approach to the problem of the formation of self-organised incommensurable interacting structures of eutectic compositions can be extended to multiphase materials for positive electrodes of lithium-ion batteries. The problem is how to choose a multiphase composition which when cycled would reversibly pass from one metastable structure to another without any substantial kinetic barriers and any significant changes in the crystal lattice volumes of these metastable structures. The understanding of self-organisation mechanisms in such multiphase compositions (including considerations in terms of the Frenkel–Kontorova model) opens up possibilities for optimising the methods of synthesising such structures and selecting their components.

VII. Conclusion

The researches directed at improving the performance of lithium-ion batteries constantly become more active. As mentioned above, the number of publications approaches several thousand.[15] Numerous patents devoted to this subject also deserve mention. Despite the incompleteness of selected information, the analysis carried out allowed us to follow the modern approaches to optimising lithium ion batteries. Optimisation of LIB concerns their reactor part as such and involves the materials for fabricating anodes and cathodes. It is noteworthy that in the past 3–4 years the number of publications devoted to negative-electrode materials became relatively smaller, while the number of studies dealing with cathode materials stayed at approximately the same level during the past 5–7 years.

In the field of cathode materials, the major research direction concerns the development of compounds or compositions that will allow us to change expensive, scarce and carcinogenic lithium cobaltate for cheaper, more available and safer materials. Moreover, the problems of improving the charge–discharge characteristics of the cathode material (capacity and energy), enhancing the reversibility and stability (structural and at elevated temperatures), increasing its charge and discharge rates, advancing the technology of electrode production and making the cell operation safer are posed.

For this purpose, the majority of leading research laboratories and companies tend to make positive-electrode materials more complex. Particularly, many studies were devoted to multidoping, *i.e*., simultaneous introduction of two and more dopants, including their combinations with anionic substituents. First of all, this concerns lithium–manganese spinel, when certain samples of substituted spinels are considered in terms of using them as the cathodes in the voltage region of 5 V. Much attention is paid to nickel–manganese oxides, including those doped with other elements $LiNi_{1-x-y}Mn_xM_yO_2$ (M = Al, Ti, W, Cr, Mo, Mg, Ta, *etc*.), and mixed ternary oxides $LiNi_{1-x-y}Mn_xCo_yO_2$ which are often multidoped as well.

In addition to compositions representing solid solutions, *e.g*., systems $xLi_2M'O_3(1-x)LiMO_2$ (M′ = Mn, Ti, Zr, Ru and M = Mn, Ni, Co), the group of M Thackeray [154, 155, 167] works on multiphase compositions which represent mixtures of different oxides. Finally, many laboratories all over the world actively study $LiFePO_4$,[167] *e.g*., as a component of multiphase systems.

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