

Mechanical Activation for Rechargeable Lithium Batteries

NINA V. KOSOVA¹, EUGENIA T. DEVIATKINA², VLADIMIR F. ANUFRIENKO², NIKOLAY T. VASENIN¹, SERGEY V. VOSEL^{1,3} and TATIANA V. LARINA²

¹*Institute of Solid State Chemistry and Mechanochemistry, Siberian Branch of the Russian Academy of Sciences, Ul. Kutateladze 18, Novosibirsk 630128 (Russia)*

E-mail: kosova@solid.nsk.su

²*G. K. Boreskov Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences, Pr. Akademika Lavrentyeva 5, Novosibirsk 630090 (Russia)*

³*Institute of Mineralogy and Petrography, Siberian Branch of the Russian Academy of Sciences, Pr. Akademika Koptiyuga 3, Novosibirsk 630090 (Russia)*

Abstract

Mechanical activation (MA) in high-energy planetary activators is used to prepare disperse and disordered cathode (LiMn_2O_4 , LiCoO_2 and $\text{Li}_{1+x}\text{V}_3\text{O}_8$) and anode ($\text{Li}_4\text{Ti}_5\text{O}_{12}$) materials, as well as solid oxide electrolytes ($\text{La}_{0.67-x}\text{Li}_{3x}\text{TiO}_3$) for rechargeable lithium batteries. The effect of various factors including mechanical and structural properties of initial reagents, oxidation state of transition metal ions, etc. on mechanochemical synthesis is investigated. The features of the crystal and electronic structure of the synthesized compounds are studied using different methods in comparison with the materials obtained by the conventional ceramic method. Keywords: mechanical activation, rechargeable lithium batteries, cathode materials, anode materials, solid oxide electrolytes

INTRODUCTION

Long-life, environmentally friendly, low-cost and reliable batteries are urgently requested nowadays to satisfy crucial demands of our modern society for a large variety of portable consumer electronic devices and modern electric vehicles. Rechargeable lithium-ionic batteries based on the combination of anode made of lithium metal or lithiated carbon and a lithium intercalation cathode (e. g., lithium – transition metal oxides) are rapidly replacing bulkier and less energetic nickel-cadmium and nickel-metal hydride batteries in cellular phones and portable computers. They are also scaled-up in view of their use in electric vehicles.

Although being commercially realized, lithium-ion batteries are still the subject of intense study aimed of further improvement of their electrochemical characteristics. Electrochemical performance of lithium – transition metal oxides strongly depends on the method of synthesis. Last years, much attention has

been paid to obtaining these compounds with unusual ordering (structural, magnetic, charge) and electronic state of transition metal ions. The structure of these compounds is expected to be more stable towards intercalation-deintercalation of lithium ions upon discharge-charge processes due to prevention of the appearance of new phases with more efficient electronic structure, which leads to the destruction of electrode material and degradation of cycleability. The reason of the positive effect of disordering in lithium – transition metal oxides on their electrochemical properties is better stability of defect structures towards intercalation-deintercalation of lithium ions. On the other hand, the decrease of particle size is also important, since high specific surface ensures the proceeding of heterogeneous intercalation-deintercalation reaction in kinetic mode, which allows using this material in fast discharged cells.

Mechanical activation (MA) is one of the methods to prepare finely dispersed materials

with disordered structure. In the present work we report the results of investigations of the mechanochemical synthesis of some cathode (LiMn_2O_4 , LiCoO_2 , $\text{Li}_{1+x}\text{V}_3\text{O}_8$, *etc.*), anode ($\text{Li}_4\text{Ti}_5\text{O}_{12}$) materials, and solid oxide electrolytes ($\text{La}_{0.67-x}\text{Li}_{3x}\text{TiO}_3$). Some features of their crystal and electronic structure are reported.

EXPERIMENTAL

Mechanical activation was performed in a planetary activator AGO-2 with steel containers and balls (8 mm, 660 rpm), and water cooling.

Phase composition, crystal and electronic structure of as prepared compounds were studied using X-ray powder diffraction (DRON-3, CuK_α radiation), FTIR spectroscopy (Specord-75, pellets with CsI), EPR spectroscopy (Bruker EPR spectrometer, $l = 3$ cm, 77–293 K), electronic diffuse reflectance spectroscopy (EDRS) (UV-VIS 4501 Shimadzu spectrophotometer, $11000\text{--}55000\text{ cm}^{-1}$).

RESULTS AND DISCUSSION

Some aspects of the mechanism of mechanochemical synthesis of the lithium – transition metal oxides

The mechanochemical synthesis of the lithium – transition metal oxides depends on both thermodynamics and kinetics. It was demonstrated that only thermodynamically feasible reactions occur for which $\Delta G < 0$. At the same time, the kinetics of reactions is determined by structural and mechanical properties of initial reagents, redox processes, conditions of MA, *etc.* [1, 2].

For example, when preparing LiMn_2O_4 , mechanochemical synthesis was performed starting from different lithium-containing compounds (Li_2CO_3 and LiOH) and manganese oxides with different manganese ion oxidation state (MnO_2 , Mn_2O_3 , MnO). After MA for 10 min, mixtures with MnO_2 exhibited the reflections of LiMn_2O_4 ; their broadening is connected with the residual strains (Fig. 1). On the contrary, no noticeable interaction was observed in mixtures with Mn_2O_3 and MnO un-

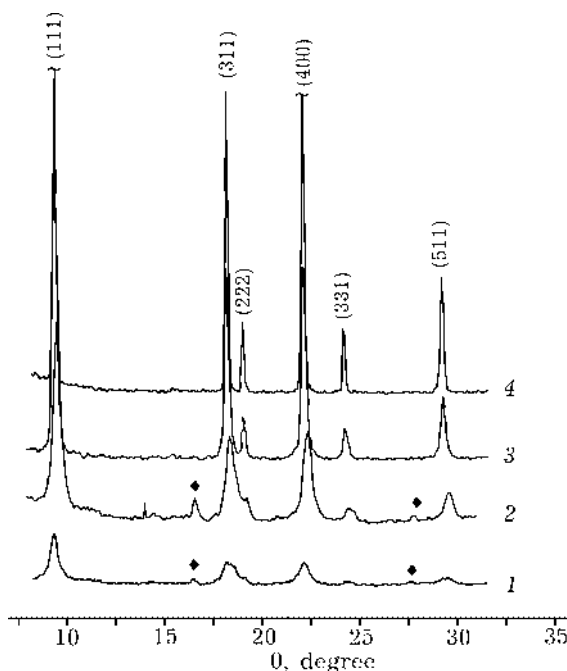


Fig. 1. X-ray diffraction patterns of the $\text{LiOH} + \text{MnO}_2$ mixture activated for 10 min (1) and heated at different temperatures (2–4). * Mn_2O_3 . Indexed reflections relate to LiMn_2O_4 phase.

der the same conditions. Note that the conventional ceramic method of LiMn_2O_4 synthesis includes multi-stage heating of the initial mixture at $800\text{--}850^\circ\text{C}$ for tens hours with intermediate grinding.

The acceleration of the solid state reaction during MA is promoted by the formation of molecular-dense mechanocomposites [3]. It was shown that depending on structural and mechanical properties of lithium reagents, two kinds of mechanocomposites are obtained. When plastic LiOH with layered structure is used, it gets amorphous very quickly and coats the surface of more firm manganese oxide particles. Adhesion forces at the contacts between LiOH and MnO_2 particles exceed the cohesion forces inside MnO_2 particles. A thin film of the amorphous LiOH acts as a surfactant accelerating MnO_2 particle dispersing. A tight contact between the reagents leads to the formation of numerous nuclei of the new product phase. Formation of a large number of nuclei helps forming finely dispersed final product. In the case of less plastic Li_2CO_3 possessing ionic structure, brittle grinding of both components is observed. The growth of the nuclei of new product phase occurs during subsequent heat-

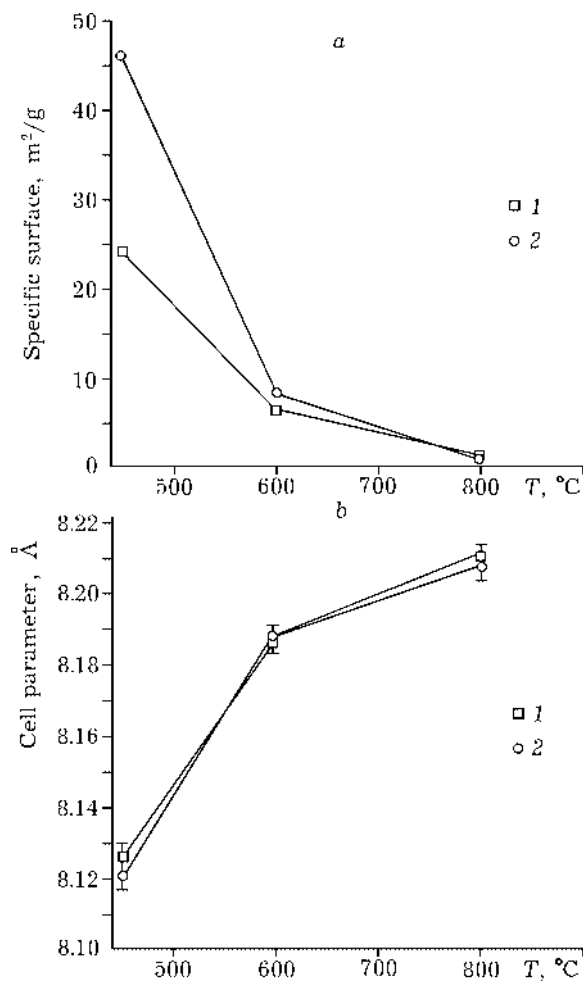
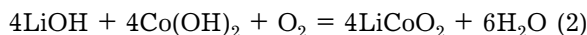


Fig. 2. Changes of specific surface (a) and cell parameter (b) of LiMn_2O_4 obtained using the $\text{LiOH} + \text{MnO}_2$ mixture vs. MA time and heating temperature. MA time, min: 1 (1) and 10 (2).

ing. The larger is the amount of nuclei, the finer dispersed should be final crystal product. Indeed, specific surface of LiMn_2O_4 samples obtained from a mixture with LiOH is larger than that of the samples obtained from a mixture with Li_2CO_3 and reaches $\sim 50 \text{ m}^2/\text{g}$ (Fig. 2, a).

LiCoO_2 was synthesized by MA of a mixture of lithium and cobalt hydroxides (LiOH , $\text{Co}(\text{OH})_2$ or CoOOH). According to [4], hydroxides display higher reactivity in mechanochemical reactions because their hydroxyl groups participate in proton and electron transfer and in the formation of new bonds. This type of acid-base interactions was called soft mechanochemical synthesis [4]. Cobalt hydroxides exhibit their amphoteric properties in mixtures with LiOH . An increased reactivity of these compounds in the synthesis of LiCoO_2 , com-

pared to Co_3O_4 , is also connected with the similarity of their structure and larger specific surface area. It was demonstrated that only the beginning of the formation of LiCoO_2 phase is observed during MA of these mixtures under the chosen conditions. The process goes more intensively in mixture with CoOOH because in this case Co^{3+} ions do not change their oxidation state, therefore, redox processes are absent. On the contrary, in the case of $\text{Co}(\text{OH})_2$, the synthesis is accompanied by the oxidation of Co^{2+} ions. Free oxygen is necessary for this process:



It was demonstrated that the main reason of low product yield is instability of LiCoO_2 towards MA [5]. Single-phase high-temperature (HT) LiCoO_2 is formed as a result of subsequent thermal treatment of the activated mixture at 400 $^\circ\text{C}$ for 4 h. When non-activated mixture is heated under the same conditions, the reaction does not completed; the low-temperature (LT) modification of LiCoO_2 is formed (Fig. 3).

Mechanochemical synthesis of $\text{Li}_{1+x}\text{V}_3\text{O}_8$ is easily carried out in a mixture of V_2O_5 with LiOH both having layered structure [6]. Under shear strain in activator, layered compounds are fragmented along layers, which causes easy layer-by-layer mixing of reagents as a result of plastic deformations. In this case, the diffusion of lithium ions becomes unimportant in solid-state reaction, that allows the process to be carried out at room temperature. It should be noted that the interaction in non-activated mixtures occurs only after lithium compounds get melted.

Mechanochemically prepared $\text{Li}_{1+x}\text{V}_3\text{O}_8$ is characterized by weak crystallinity, presence of microstrains and high specific surface area ($>10 \text{ m}^2/\text{g}$). According to IR spectroscopy data, these samples contain residual H_2O and CO_2 molecules that are present in the interlayer space, thus, increasing it and facilitating the diffusion of lithium ions during intercalation. These admixtures can be easily removed by heating to 100–400 $^\circ\text{C}$.

Features of the crystal structure and electronic states of ions in the synthesized samples

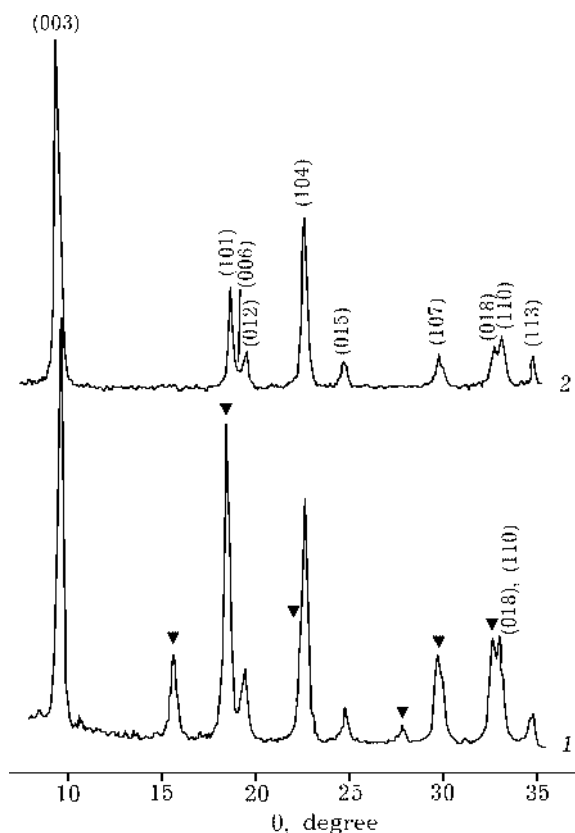


Fig. 3. X-ray diffraction patterns of LiCoO_2 obtained by heating at 400 °C of the initial (1) and activated (2) $\text{LiOH} + \text{Co}(\text{OH})_2$ mixture. ▼ Co_3O_4 . Indexed reflections relate to the high-temperature LiCoO_2 phase.

Since mechanochemical synthesis of the indicated compounds is carried out under non-equilibrium conditions, there are some specific features of crystal structure and the electronic states of ions in the lithium – transition metal oxides as prepared. Some of these features are conserved in the samples even after their thermal treatment.

Mechanochemically synthesized LiMn_2O_4 samples are characterized by very low lattice parameter a (8.13 Å instead of 8.24 Å for ceramic LiMn_2O_4), which increases during subsequent heating (see Fig. 2, b) [1, 2]. First, this points to an increased Mn^{4+} ion content because the radius of Mn^{4+} ion is smaller than that of Mn^{3+} ion. Besides, Mn^{4+} ions are more stable at moderate temperatures. On the other hand, low cell parameter for spinel may be caused by noticeable disordering in cation sublattices, *i. e.* by the presence of cationic vacancies and cation mixing. The presence of the former type of disordering was confirmed by

thermogravimetric analysis: the irreversible evolution of the excess oxygen during heating evidences of the presence of cationic vacancies [2]. On the other hand, the appearance of a new absorption band at 270 cm^{-1} in the IR spectra and an asymmetric line in ^7Li NMR spectra of mechanically activated spinel points to the formation of mixed spinels (a part of lithium ions occupy 16 d octahedral positions) [2].

The calculated cell parameters for LiCoO_2 samples obtained by preliminary MA followed by thermal treatment at 400, 600 and 800 °C, along with $c/a = 4.99$ and the presence of splitting in the 006 and 012, 018 and 110 reflections, point to the formation of a single-phase HT- LiCoO_2 [5]. According to the EDRS data, the basic electronic state of cobalt ions in the samples as prepared is a low-spin state $[\text{Co}^{3+}]_{\text{Oh}}$ ($28\,000\text{ cm}^{-1}$) (Fig. 4). However, the spectra of the first two samples contain additional absorption bands with maxima at $18\,000$ – $22\,000$ and $15\,000$ – $17\,000\text{ cm}^{-1}$ that correspond to high-spin ions $[\text{Co}^{2+}]_{\text{Oh}}$ and $[\text{Co}^{2+}]_{\text{Td}}$, respectively (see Fig. 4). The latter band indicates the presence of Co_3O_4 impurity in the samples. This d – d transition is characterized by large extinction, which allows distinguishing this state from other cobalt states even in the case when it is present in tiny amount. The spectrum of LiCoO_2 (800 °C) exhibits no indications of the presence of $[\text{Co}^{2+}]_{\text{Oh}}$ ions. It should be noted that in the spectrum of ceramic LiCoO_2 , the band of $[\text{Co}^{3+}]_{\text{Oh}}$ ion adsorption is observed in higher

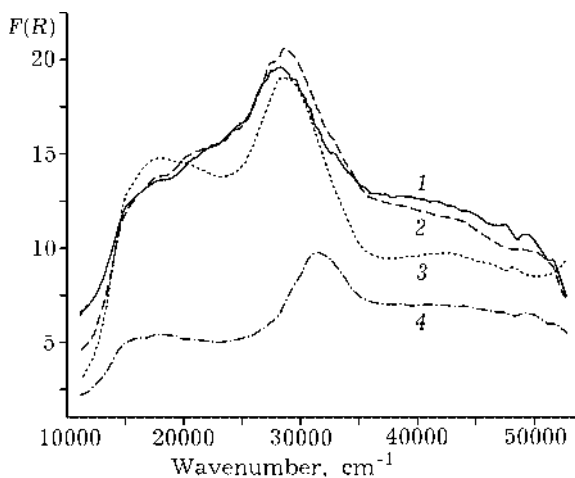


Fig. 4. EDRS spectra of LiCoO_2 obtained by heating activated $\text{LiOH} + \text{Co}(\text{OH})_2$ mixture at 400 (1), 600 (2), 800 °C (3), and of ceramic LiCoO_2 (4).

frequency region ($32\,000\text{ cm}^{-1}$). This indicates that mechanochemically activated LiCoO_2 is distinguished by weaker crystal field, *i. e.* by the formation of less perfect Co^{3+}O_6 octahedrons in comparison with the ceramic LiCoO_2 .

At 77 K, ESR spectra of $\text{Li}_{1.07}\text{V}_3\text{O}_8$ sample obtained by MA and heating at 400°C are characterized by a line with clear axial anisotropy of g factor: $g_{\parallel} = 1.94$ and $g_{\perp} = 1.96$ (Fig. 5). They were attributed to uniform vanadyl ions $\text{V}=\text{O}^{2+}$ (a compressed octahedron) present in the structure of $\text{Li}_{1+x}\text{V}_3\text{O}_8$ [6]. The absence of hyperfine structure points to the magnetic exchange interaction between V^{4+} ions. An unusual feature of the $\text{Li}_{1.07}\text{V}_3\text{O}_8$ spectrum is its sloping shape in the g_{\parallel} region. This can be interpreted as the presence of two types of $\text{V}=\text{O}^{2+}$ ions differing from each other by the directions of the b axis of crystal field. The narrowing of the $\text{Li}_{1.07}\text{V}_3\text{O}_8$ spectrum with measurement temperature decrease (not observed for vanadyl ions) is a result of C-S-C relaxation, where C is paramagnetic ion (vanadyl), S is electron gas (one electron delocalized over several V^{5+} ions). This means that vanadyl ions, present in the $\text{Li}_{1.07}\text{V}_3\text{O}_8$ structure, exchange with each other through the electron gas forming low-dimension fragments with electron delocalization, without the appearance of a new phase and phase separation. The amount of vanadyl ions of various types and the size of these fragments are different for MA $\text{Li}_{1.07}\text{V}_3\text{O}_8$ and $\text{Li}_{1.07}\text{V}_3\text{O}_8$ obtained by means of melting and dissolution. These characteristics are likely to affect the electrochemical behaviour of $\text{Li}_{1+x}\text{V}_3\text{O}_8$ [6].

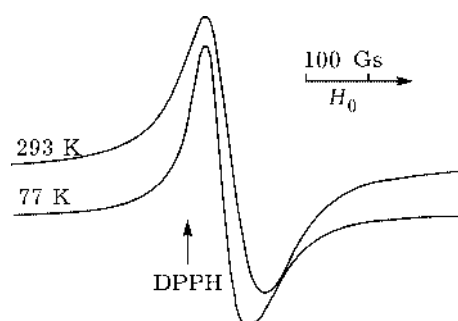


Fig. 5. EPR spectra of $\text{Li}_{1.07}\text{V}_3\text{O}_8$ obtained by MA and heating at 400°C . Measurement temperatures are indicated at the curves.

Electrochemical properties of mechanochemically synthesized cathode materials

Cathode materials obtained by means of MA followed by thermal treatment are distinguished by good stability and low polarization under cycling. Samples obtained directly by MA or after subsequent heat treatment at moderate temperatures (up to 600°C) exhibit higher capacity at the first charging. However, a small loss of the capacity is observed during further cycles. This loss is likely to be due to the high reactivity of disperse materials with respect to liquid electrolyte. This disadvantage may be overcome by passivating particle surface with protective films or by using solid polymer or solid oxide electrolytes.

Mechanical activation for all oxide solid state lithium batteries

The trends of electronics towards the decrease of voltage from 4 to 3 V and in future to lower values may open the chance of alternative materials for lithium batteries. One of the examples is all solid state lithium batteries [7].

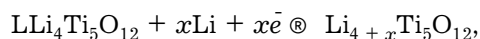
In this case, a suitable anode material is $\text{Li}_4\text{Ti}_5\text{O}_{12}$ [8]. It is distinguished by good reversibility and does not undergo structural changes during charge-discharge processes (zero-dimensional intercalation material). $\text{Li}_4\text{Ti}_5\text{O}_{12}$ has a stable operating potential of ~ 1.5 V with respect to lithium. Hence, this material can be used in couple with 4 V cathodes (LiMn_2O_4 , LiNiO_2 or LiCoO_2) providing cell voltage of ~ 2.5 V, which is twice as large as the value for nickel-cadmium or nickel-metal hydride cells.

The cathode reaction in this cell may be described by the equation:



where $0 \leq x \leq 0.6$;

and the anode reaction:



where $0 \leq x \leq 3$.

Lithium intercalation into $\text{Li}_4\text{Ti}_5\text{O}_{12}$ spinel causes shifts of the tetrahedrally coordinated

lithium ions into octahedral positions giving $\text{Li}_7\text{Ti}_5\text{O}_{12}$ with a rock salt structure. Potential of the cell with the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode may be increased by using 4.5–5 V cathode materials. Well-known high-voltage cathode materials include complex oxides with spinel structure: $\text{Li}_2\text{MM}_3\text{O}_8$ and $\text{LiMM}'\text{O}_4$, where $\text{M} = \text{Co}, \text{Cr}, \text{Fe}, \text{Ni}, \text{etc.}$; $\text{M}' = \text{Mn}, \text{V}, \text{etc.}$ [9].

Safety remains the major problem for large-sized lithium-ion batteries, especially when large amounts of liquid electrolyte are used, because the danger of gas evolution and electrolyte decomposition arises. For this reason, it is important that the anode used in these batteries does not increase its volume when in combination with the solid-polymer (SPE) or oxide electrolyte without liquid solvent added.

In order to obtain all oxide solid state battery, it is necessary to make a right choice of lithium-ion oxide conductor. The authors [7] tried to use thin films of silicon-type materials ($\text{Li}_{3.6}\text{Ge}_{0.6}\text{V}_{0.4}\text{O}_4$) with ionic conductivity of 10^{-5} – 10^{-6} S cm^{-1} at room temperature but came across substantial difficulties connected with short circuiting between the cathode and anode in the cells because of discrepancy between thermal expansion coefficients of the electrolyte and electrode materials. Lanthanum lithium titanates with perovskite structure [7] and ionic conductivity of about $1 \cdot 10^{-5}$ S cm^{-1} at room temperature [10, 11] were found to be more suitable for this type of batteries. It is believed that the reason of such a high conductivity of these compounds is the presence of vacancies in A positions and a large number of equivalent positions for the lithium ions to occupy and freely move in the space A-site.

All the components of all oxide solid state lithium batteries were obtained by us with the help of MA. $\text{Li}_4\text{Ti}_5\text{O}_{12}$ was synthesized using preliminary MA of the mixtures of corresponding oxides and hydroxides, followed by brief heating of the mechanochemically prepared precursors at 700–800 °C. At lower temperatures, we observed the formation of Li_2TiO_3 as an intermediate phase.

MA provides advantages for obtaining multicomponent cathode materials and oxide electrolytes. Since the probability of contacts be-

tween three or more particles of different types in solid mixtures under heating is low, solid-phase reactions in multicomponent systems proceed through intermediate stages in which contacting pairs of particles take part. MA is accompanied by plastic flow of solid particles; point contacts turn into contacts along the surface making triple contacts possible. An important feature of this process is that every particle of the multicomponent powder mixture gets in contact not only with one particle as in the case of solid-phase interaction under heating but with other particles from time to time. This leads to the decrease of the number of intermediate stages, acceleration and simplification of the synthesis process, and to the increase of the homogeneity of final product.

The series of LiMn_2O_4 spinels doped with cobalt (5 V cathode materials) described by the general formula $\text{LiCo}_x\text{Mn}_{2-x}\text{O}_4$ was synthesized by brief MA of a mixture of LiOH (or Li_2CO_3) with MnO and Co_3O_4 followed by heating at 600 °C. According to the XRP data, these products were single-phase compounds with cell parameters decreasing from 8.196 Å for $x = 0.13$ to 8.099 Å for $x = 0.66$. It should be noted that a long multistage process is necessary when the conventional ceramic procedure is used.

The synthesis of $\text{La}_{0.67-x}\text{Li}_{3x}\text{TiO}_3$ electrolytes was carried out using mixtures of anhydrous and hydrated oxides of lanthanum, lithium, and titanium. Traces of rutile TiO_2 were present in activated mixtures after heating to 800 °C. Ionic conductivity of the obtained samples was $5 \cdot 10^{-3}$ S cm^{-1} .

CONCLUSIONS

Thus, MA can be successfully used to obtain LiMn_2O_4 , LiCoO_2 and $\text{Li}_{1+x}\text{V}_3\text{O}_8$, as well as other cathode and anode oxide materials and oxide electrolytes for rechargeable lithium batteries. With suitable initial reagents, MA allows one to simplify the synthesis of materials with multicomponent composition (*e. g.*, substituted LiMn_2O_4 spinels, solid solutions La-Li-Ti-O , *etc.*). Compared to conventional solid state process, MA method allows us to accelerate synthesis and make it easier, and also to

decrease energy consumption and the cost of materials.

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