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Lithium Iron Phosphate. Synthesis Using Mechanical Activation

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Abstract

A brief overview of works aimed at the investigation of the processes of synthesis of nanosized LiFePO_4 from different precursors using mechanical activation is presented; its structural and electrochemical properties are evaluated. The effect of nanosize on cycling processes including its mechanism is demonstrated. Examples of the influence of carbon component on the morphology of particles and the effect of substitution processes on the cathode properties of LiFePO_4 are described, as well as the data on the thermal stability of LiFePO_4 against heating in the air. The proposed method was accepted as the basis for the industrial technology of obtaining LiFePO_4 at the JSC "Novosibirsk Chemical Concentrates Plant".

Key words: lithium iron phosphate, mechanochecmial synthesis

INTRODUCTION

The number of works dedicated to the investigation of cathode materials with framework structure based on the compounds of lithium and transition metals (Fe, Mn, Co, Ni etc.) with polyanions PO_4^{3-} , SO_4^{2-} and AsO_4^{3-} is increasing during the recent years [1]. Orthophosphates of lithium and *d*-metals having the olivine structure $LiMPO_4$ (M = Fe, Mn, Co, Ni) attracted the attention of researchers due to the high potential of the oxidation-reduction pair $M^{2+}/$ M^{3+} with respect to the pair Li/Li⁺, which exceeds the potential in corresponding oxides by 1.5-2 V. This result is due to the M-O-P "inductive effect" which is in turn determined by the high covalence of the P–O bond in PO_4^{3-} polyanion. The most promising representative of this class of compounds is $LiFePO_4$.

The average voltage of LiFePO_4 discharge, equal to 3.4 V, is optimal for the conservation of high energy density, on the one hand, and prevention of electrolyte decomposition, on the other hand, thus providing longer lifetime of the rechargeable battery. The theoretical capacity is 170 mA · h/g and under definite conditions it may be almost completely realized in practice. Lithium iron phosphate is distinguished by its high chemical stability with respect to moisture, water and the solutions of electrolytes containing no proton groups, even at elevated temperatures. The material possesses high stability to oxygen evolution; no exothermal reactions are observed during its heating, which increases the safety of rechargeable batteries. In addition, $LiFePO_4$ is characterized by the low cost of initial material and low toxicity, so it is very attractive for use in large rechargeable batteries for hybrid transport facilities and electric vehicles in which the price and safety are very important.

Lithium iron phosphate has an ordered olivine structure (orthorhombic system; space group *Pnma*) composed of the tight hexagonal packing of oxygen ions in which Fe^{2+} and Li⁺ ions occupy a half of octahedrons, while P^{5+} ions occupy 1/8 of tetrahedrons. Its structure can be represented as a chain composed of octahedrons along the *c* axis, bound by PO_4^{3-} tetrahedrons and forming a three-dimensional framework. The FeO₆ octahedrons forming zigzag-like chains are connected with each other through vertices but not through faces, which hinders electron transfer. The LiO₆ octahedrons form linear chains along the *b* axis; diffusion of lithium ions occurs along the (010) direction. One lithium ion per the formula unit can participate in changing-discharging processes. Charge compensation is provided due to the oxidation-reduction pair Fe²⁺/Fe³⁺. A two-phase mechanism of insertion-extraction of lithium ions is realized; as a result, a plateau is observed on charge-discharge curves. The formed FePO₄ phase has a similar orthorhombic structure; volume change is 6.81 %.

The major disadvantage of LiFePO₄ is its low electronic conductance ($\sigma \sim 10^{-9}$ S/cm) [2] and lithium ion diffusion ($\sigma \sim 10^{-10}-10^{-11}$ S/cm) [3], and therefore unsatisfactory cycling at high charge-discharge rates. This compound is a semiconductor with the forbidden gap of 0.3 eV, which is determined by its structure. The low electronic conductance of LiFePO₄ is a result of the strong Fe–O bond; the diffusion of lithium ions is limited by the Li–O bond and the presence of uniform-sized diffusion channels. At present, extensive works aimed at the optimization of the conducting properties of LiFe-PO₄ are performed, for the purpose of improving its cathode characteristics.

Several ways to improve the cathode characteristics of $LiFePO_4$ are known:

1. A decrease in particle size, which promotes a decrease in the diffusion distance for lithium ion transport and an increase in the contact area for electron transfer between particles [4].

2. Deposition of highly conductive carbon coating. The choice of an optimal carbon-containing precursor is made among various carbon types (carbon black, graphite *etc.*) or organic compounds (carbohydrates, carboxylic acids, polymers *etc.*) [5]. In the latter case, it is important that the precursor is characterized by not high temperature of pyrolysis during which a uniform layer of nanometer-sized carbon with high electronic conductance is formed on the surface of LiFePO₄ particles. It is economically efficient to perform the synthesis of LiFePO₄ and its surface modification in one stage.

3. Doping LiFePO₄ (substitution in Li and Fe positions) with heterovalent ions M (M = Nb,

Zr, Mg, Ti *etc.*) leads to obtaining black-coloured semiconductors of p type with the conductivity about 10^{-2} S/cm at room temperature [2]. However, in many cases the positive effect is connected not with the formation of solid solutions but with the modification of the surface of LiFePO₄ particles by highly conducting compounds containing the given dopants. The simultaneous introduction of a dopant and carbon-containing compound (including the use of organometallic compounds) is under investigation.

4. The formation of surface conducting phases of iron phosphides, carbides, nitrides (Fe₂P, Fe₃P, Fe₃C, Fe₂N). As a result of the interaction of $LiFePO_4$ with carbon at elevated temperature (above 850 °C) the neighbouring Fe and P ions in the lattice get reduced with the formation of iron phosphides Fe_2P and/or Fe_3P ; these compounds possess high electronic conductance [6]. Initial iron oxalate may serve as the source of carbon. Heating in the atmosphere of nitrogen leads to the formation of Fe₂N, which also promotes an increase in conductivity. These compounds are most easily formed under soft reductive synthesis conditions when a mixture of inert gas with hydrogen is used. However, the layer of extrinsic conducting phase should be as thin as possible.

5. Coating with metal particles (for example, Ag, Ag/C *etc.*). Conducting nanometer-sized metal particles on the surface of LiFePO₄ or LiFePO₄/C improve the cycling properties at high rates [7].

6. Coating with amorphous compounds possessing high lithium ion conductivity. In the case of low Fe/P content on the surface of synthesized LiFePO₄ particles, amorphous phases composed of lithium phosphates or pyrophosphates are formed; they possess high lithium ion conductivity [8]. Due to the amorphous nature of these coatings, it becomes possible to eliminate the anisotropy of the surface properties of LiFePO₄ and to accelerate the delivery of lithium ions to the face at which its introduction into the lattice occurs.

Iron ions are present in $LiFePO_4$ in the oxidation degree 2+, so it is preferable to use the compounds of Fe^{2+} (in particular ferrous oxalate dihydrate) in mixtures with various lithium compounds and ammonium phosphate as the initial reagents for its solid-phase synthe-

sis. At the same time, the cost of Fe^{2+} compounds is higher than that of Fe^{3+} compounds. In addition, a large amount of gaseous products is formed, which hinders the use of Fe^{2+} compounds for the mass production of LiFePO₄. An alternative to their use has become recently proposed method of solid-phase synthesis of LiFePO₄ on the basis of carbothermal reduction of Fe³⁺ compounds using various carboncontaining precursors [9]. Ferric oxide Fe_2O_3 is the cheapest and the most available reagent possessing the high mass product/reagents ratio (76.7 %). In addition, contaminating gases are not formed when this compound is used. The presence of carbon in the mixture under activation helps slowing down the growth of LiFePO₄ particles during annealing. In the case if the amount of carbon is above the stoichiometry, it remains on the surface of LiFePO₄ particles forming a tight contact with the surface and playing the part of the surface electron-conducting nanometer-sized coating. As a result, the electronic conductance of $LiFePO_4$ increases by 5-6 orders of magnitude. So, the synthesis and surface modification processes take place in one stage.

To obtain nanometer-sized LiFePO₄, the mechanochemical approach was developed at the ISSCM of the SB RAS. This approach is distinguished by the fact that the reactions are conducted in the solid phase, by simplicity, short time, energy- and ecological efficiency.

EXPERIMENTAL

The synthesis of LiFePO₄ and substituted compounds based on it was carried out using the compounds of Fe²⁺ (FeC₂O₄ · 2H₂O) and Fe³⁺ (Fe₂O₃) in mixture with lithium carbonate or hydroxide, and ammonium phosphates. Preliminary mechanical activation (MA) of the mixture of initial reagents was carried out in a planetary activator AGO-2 with water cooling using steel cylinders and balls. Activated mixtures were annealed in the furnace at a temperature of 450–800 °C in the inert gas flow.

The obtained samples were analyzed by means of X-ray phase analysis, IR, Raman, Mössbauer spectroscopy, ^{6,7}Li and ³¹P MAR (magic angle rotation) NMR spectroscopy, scanning and transmission electron microscopy and galvanostatic cycling. Structural studies were carried out with the help of D8 Advance Bruker diffractometer (Cu K_{α} radiation). IT spectra were recorded with a FTIR BOMEM IR spectrometer within the range $4000-200 \text{ cm}^{-1}$ (tablets with CsI); Raman spectra were recorded with a Bruker Raman spectrometer; Mossbauer spectra were recorded with an NZ-640 spectrometer (Hungary) using $Co^{57} \gamma$ radiation; ^{6,7}Li and ³¹P MAR NMR spectra were recorded with a Bruker Avance AV-300 solid-state spectrometer ($H_0 = 7.05$ T, v = 7 kHz), diluted aqueous solutions of LiCl and H₃PO₄ serves as references. Electron microscopic images were taken with a LEO 1430 VP scanning electron microscope and JEM-4000EX transmission electron microscope with the resolution of 0.17 nm. Electrochemical tests were carried out in half cells cathode + C (Super P, Timcal Co.) $/LiPF_6$ + ethylene carbonate + dimethyl carbonate /Li with polypropylene separators at the cycling rate of C/10 - 10C (current density 0.3-30 mA/cm²) and temperature of 20 °C.

RESULTS AND DISCUSSION

Synthesis of nanometer-sized LiFePO₄ using mechanical activation

We carried out a comparative investigation of the synthesis of LiFePO₄ using MA of the mixtures of Li₂CO₃, NH₄H₂PO₄ with FeC₂O · H₂O (three-component system, mixture **1**) and Li₂CO₃, NH₄H₂PO₄ with Fe₂O₃ and C (four-component system, mixture **2**) followed by heating in the inert atmosphere [10]. The diffraction patterns of activated mixtures reveal the formation of the intermediate product Li₃PO₄ according to the reaction $2NH_4H_2PO_4 + 3Li_2CO_3 \rightarrow$

 $2Li_3PO_4 + 2NH_3 + 6H_2O$ (2)

During heating mixture 1, the formation of the final product starts at a temperature of $300 \,^{\circ}$ C (Fig. 1), while in the case of mixture **2** it starts at 700 $^{\circ}$ C. The average size of the particles of LiFePO₄-450 $^{\circ}$ C is 50 nm and increases gradually with an increase in annealing temperature. The Mössbauer spectra of the products are symmetrical doublets with the chemi-



Fig. 1. Diffraction patterns of the activated mixture of Li_2CO_3 , $FeC_2O_4 \cdot 2H_2O$ and $NH_4H_2PO_4$ (1) and the products of its heating at different temperature, °C: 450 (2), 500 (3), 550 (4), 600 (5), 700 (6).



Fig. 2. Mössbauer spectra of activated and annealed mixture of $\rm FeC_2O_4\cdot 2H_2O$ c $\rm Li_2CO_3$ with $\rm NH_4H_2PO_4.$



Fig. 3. Charge-discharge curves for LiFePO_4 obtained at a temperature of 450 (a) and 700 $^{\rm o}{\rm C}$ (b).

cal shift 1.22 mm/s and δ (quadrupole splitting) 2.95 mm/s (Fig. 2). In the spectrum of the product obtained from FeC₂O₄ · 2H₂O, an additional doublet is observed; it is connected with the extrinsic phase containing Fe³⁺ or Fe₂P. The formation of phosphides is not observed during carbothermal reduction at any annealing temperature.

It was established that the shape of chargedischarge curves and the mechanism of the processes of lithium intercalation-deintercalation depend on the size of LiFePO₄ particles. For example, a plateau is observed in the case of Li_xFePO_4 obtained at 700 °C, while the curves for Li_xFePO₄ obtained at 450 °C have a gentle slope within a broad range of x values (Fig. 3). It is known that extraction (insertion) of lithium from (into) the $Li_x FePO_4$ structure proceeds according to the two-phase mechanism with the formation of FePO₄ phase (in each point of the curve, the cathode material is a mixture of two phases: initial LiFePO₄ and final $FePO_4$). This process is accompanied by the appearance of a plateau on the charge-discharge curves. However, within narrow ranges of the x values near 1 and 0 for nanometer-sized samples, the formation of solid solutions was discovered [11]. We established in the in situ synchrotron radiation diffraction studies that low-temperature LiFePO₄ samples are distinguished by broadening of the regions of solid solution formation, that is, the two-phase mechanism is replaced by the single-phase one [12].

So, MA results in fine mixing of the multicomponent initial mixture of indicated reagents, accompanied by amorphization and initial interaction processes. This causes a decrease in the temperature of synthesis and crystallization of the final product LiFePO_4 , which is essential from the viewpoint of the synthesis of the material in the fine dispersed state.

Composite materials LiFePO₄/C with carbon coating

The role of carbon coating is not only in dramatic increase in the intergrain electron conductivity of LiFePO₄ (by 5–6 orders of magnitude) but also in efficient braking of particle growth and even optimization of its microstructure. Shortcomings of carbon coating include an increase in the bulk density of the product, which causes a decrease in the volumetric energy density. For example, with an increase in carbon content from 0 to 15 %, the volumetric density of LiFePO₄ decreases by 22 %, while the gravimetric density decreases by 15 %. It is necessary to optimize the concentration of carbon additive, thickness and structure of the coating.

The choice of carbon-containing precursor becomes critical for obtaining the cathode material based on LiFePO₄ with high conductivity and good cycling ability. It is generally believed that the electric conductance and electrochemical properties of LiFePO₄ depend on pyrolysis temperature and the type of carbon-containing compound. Graphitized carbon coatings have higher conductivity in comparison with disordered coatings. Using carbothermal reduction of Fe³⁺ compounds, it becomes possible to perform synthesis and surface modification of LiFePO₄ with carbon simultaneously.

We carried out a comparative investigation of the effect of carbon material nature and content (amorphous carbon black and crystal graphite) on the synthesis of LiFePO₄ from Fe_2O_3 with the formation of composite materials LiFePO₄/C. It was shown that MA of the mixture of reagents with graphite is accompanied by its dispersing and structural disordering [13]. After MA for 10 min, graphite becomes X-ray amorphous. According to the data of Raman spectroscopy, the spectrum of initial graphite is characterized by one band (G) at 1575 cm^{-1} , corresponding to the presence of sp^2 bonds. The second band (D) appears at 1355 cm⁻¹ in the spectra of mixtures activated with graphite; this band corresponds to the formation of sp^3 bonds (Fig. 4). It was established by means of electron scanning microscopy that the nature of carbon material has a substantial effect on the morphology of the particles of final product LiFePO₄/C. For example, for the content of carbon black in the composite equal to 25 %, spherical particles are formed, while in the case of the same graphite content the particles are lamellar (Fig. 5). The electrochemical properties of LiFePO₄/C improve with an increase in graphite content and MA time.

Solid solutions in the system LiFePO₄-LiMnPO₄

Coating of LiFePO₄ with conducting materials does not have any effect on the structural parameters or intrinsic volume conductance. To improve volume conductance, LiFePO₄ doping with heterovalent cations and anions at different positions is carried out: Li (M1), Fe (M2) and O. According to the data of quantum chemical calculations [14], it is preferable to substitute Fe²⁺ ions only by bivalent ions such as Mg²⁺ and Mn²⁺. The absence of LiFePO₄ tolerance to aliovalent substitution was noted.



Fig. 4. Raman spectra of activated mixtures with graphite depending on MA time, min: 1 (1), 2.5 (2), 5 (3), 10 (4).

In the present work we carried out the synthesis of the solid solutions $\text{LiFe}_{1-y}\text{Mn}_y\text{PO}_4$ through carbothermal reduction of Fe_2O_3 and MnO_2 using preliminary MA and studied their crystal local structure and electrochemical properties [15].

The changes of the parameters of orthorhombic cell in $\text{LiFe}_{1-y}\text{Mn}_{y}\text{PO}_{4}$ within the entire concentration range corresponds to Vegard rule (Fig. 6). The MAR NMR spectra of ⁷Li and ³¹P have a broad asymmetric envelope (half-width is about 150 kHz). The isotropic chemical shift depends on sample composition and on temperature; this dependence is much stronger expressed on phosphorus nuclei than on lithium nuclei (Fig. 7). The shift of the signals of ^{6,7}Li and ³¹P is determined by the contact hyperfine interaction of the resonant nucleus with the paramagnetic atom through the oxygen atom, which depends on the nature of the paramagnetic atom and the ionicity of M–O



Fig. 5. SEM images of mechanocomposites $LiFePO_4/C$ with graphite (a) and carbon black (b).



Fig. 6. Parameters of the orthorhombic lattice of synthesized $\text{LiFe}_{1-u}\text{Mn}_u\text{PO}_4$ samples.

bond [16]. Two regions are observed on the chargedischarge curves, corresponding to oxidation-reduction pairs $\text{Fe}^{3+}/\text{Fe}^{2+}$ (3.4 V) and $\text{Mn}^{3+}/\text{Mn}^{2+}$ (4.1 V) (Fig. 8). With an increase in manganese content, the potentials of both pairs increase by 0.1 V. For compositions with $y \ge 0.5$, the electrochemical capacity decreases. The major drop is observed within the region of $\text{Mn}^{3+}/\text{Mn}^{2+}$.



Fig. 7. Chemical shift of NMR ⁷Li and ³¹P signals depending on the composition of the sample $\text{LiFe}_{1-y}\text{Mn}_{y}\text{PO}_{4}$: 1 - literature data, 2 - our data.



Fig. 8. Charge-discharge curves of synthesized $\text{LiFe}_{1-u}Mn_uPO_4$ samples.

Composite cathode materials LiFePO₄-Li₃V₂(PO₄)₃

 $Li_3V_2(PO_4)_3$ is a new cathode material with monoclinic structure. Under charging up to 5 V, three lithium ions can be extracted from its structure, which is accompanied by the oxidation of V³⁺ ions to V⁵⁺ [17]. It was discovered recently that the addition of $Li_3V_2(PO_4)_3$ to $LiFePO_4$ causes an increase in the electron conductance of the cathode material [18].

In the present work, the synthesis of initial LiFePO₄ and Li₃V₂(PO₄)₃ samples was carried out through carbothermal reduction of Fe₂O₃ and V₂O₅. The synthesis of LiFePO₄–Li₃V₂(PO₄)₃ composites was carried out using MA. According to the XPA data, for any component ratio, the diffraction patterns are superpositions of initial compounds [19]. The charge-discharge curves exhibit two regions corresponding to the oxidation-reduction pairs Fe³⁺/Fe²⁺ (3.4 V) and V³⁺/V⁴⁺ (above 3.4 V) (Fig. 9).

Thermal stability of LiFePO₄

According to the published data [20], during long-term exposure of $LiFePO_4$ in the air and during heating it in the air, partial deinter-



Fig. 9. Charge-discharge curves of initial LiFePO_4 and $\rm Li_3V_2(PO_4)_3$ samples and their mechanocomposites.



Fig. 10. Mössbauer spectrum of $\rm LiFePO_4$ annealed at different temperatures.



Fig. 11. Charge-discharge curves of LiFePO₄ annealed at a temperature of 300 (*a*) and 500 $\,^{\circ}\text{C}$ (*b*).

calation of lithium from olivine structure occurs, with the formation of defect-bearing oxidized compositions $Li_r Fe_u PO_4$ and new surface phases. In this situation, the degree of process propagation depends on the size of LiFePO₄ particles. We studied thermal stability of nanometer-sized LiFePO₄ samples obtained using MA from Fe_2O_3 (carbothermal reduction) and from FeC₂O₄ [21]. Anisotropic change of lattice parameters during heating LiFePO₄ samples was discovered: parameters a and b at first insignificantly increase (to 250 °C), then sharply decrease; quite contrary, parameter c increases gradually with temperature rise. The sample obtained from FeC₂O₄ differs by lower thermal stability due to smaller particles. According to Mossbauer data, Fe^{3+} ions (~3%) appear in the samples heated to 120 °C, while after heating to 300 °C the spectrum is a superposition of three phases: LiFePO₄, Fe₂O₃ and Li₃Fe₂(PO₄)₃ (Fig. 10). After heating to 500 °C, the spectrum of LiFePO₄ disappears. The cycling curves of samples heated to 300 °C contain a plateau at 3.4 V within the region 2.0-4.2 V, which is characteristic of LiFePO₄, and a sloping region characteristic of Li₃Fe₂(PO₄)₃ (Fig. 11). During cycling the sample heated to 500 °C, the plateau disappears completely; the shape of chargedischarge curve corresponds to Li₃Fe₂(PO₄)₃ compound.

CONCLUSION

On the basis of studies performed at the ISSCM of the SB RAS, an energy-efficient and ecologically safe method was developed for the synthesis of nanometer-sized cathode material LiFePO_4/C using mechanical activation. The developed method was the basis for the industrial technology of LiFePO_4 production which is under introduction at the Novosibirsk Chemical Concentrates Plant.

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