Low temperature preparation of nanosized LiFePO$_4$ by molten salt reactions

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Molten salt reactions between dittmarite-type NH$_4$FePO$_4$.H$_2$O and different lithium eutectic compositions are systematically investigated in order to obtain at low temperature olivine-type LiFePO$_4$ which is valuable electrode material for lithium-ion batteries. Nanosized LiFePO$_4$ powder is successfully prepared by topotactic reactions using LiCl-LiOH eutectic compositions at 277–325 ºC for short reaction time of 60−90 min. It is well crystallized with a preferred crystallite orientation along *a*-crystallographic axis. The prepared LiFePO$_4$ is characterized by a plate-like morphology inherited from the iron precursor. The micrometer LiFePO$_4$ plates are composed of nanosized spherical particles with dimensions about 50 nm which is favorable for further electrochemical performance.

Keywords: LiFePO$_4$, Phospho-olivine, Molten salts reactions, Lithium-ion batteries

INTRODUCTION

The iron-based compounds are very desirable as electrode materials in alkaline-ion batteries since they meet in largest extend the increasing environmental and economic requirements for usage of low-cost nontoxic metals. Among the iron-based polyanion compounds, LiFePO$_4$ is the most attractive electrode material already found application in high-power batteries for hybrid electric vehicles [1,2]. It belongs to phospho-olivine family, LiMPO$_4$ (M^{2+} = Fe, Mn, Co, Ni) that is characterized by a stable crystal structure based on three-dimensional phosphate framework. The phospho-olivine structure presents one-dimensional edge-sharing LiO$_6$ octahedra which define an energetically favorable pathway for Li$^+$ intercalation. LiFePO$_4$ exhibits remarkable electrochemical storage properties in terms of excellent safety due to the intrinsic lattice and thermal stability in both lithiated and delithiated states, long cycle life and reasonable energy density [1,2].

One of the electrochemical characteristics of LiFePO$_4$ electrodes needed to be improved is the low rate capability owing to low electron and ion conductivity. One of the prerequisites for overcoming the problem is that phospho-olivines have to be prepared as nanosized materials [3,4]. In this regard "soft chemistry" routes are particularly recommended [3]. More recently, we have demonstrated that manganese compounds MMnPO$_4$.H$_2$O (M$^+$ = K, NH$_4$) having a dittmarite-type structure can be effectively used as structure-directed precursors for low temperature synthesis (200-270 ºC) of both lithium and sodium manganese phospho-olivines [5-8]. Due to the same topology of M^{2+}–PO$_4{}^{3-}$ layers in the dittmarite structure (along *b*-axis) and olivine structure (along *a*-axis) [9,10], the transformation of dittmarite- into olivine-type structure follows a topotactic pathway by direct ion exchange of K$^+$ or NH$_4{}^+$ for Li$^+$ (accordingly Na$^+$). In present paper we have extended our studies on the preparation of LiFePO$_4$ by ion exchange in molten lithium salts using dittmarite-type NH$_4$FePO$_4$.H$_2$O. This precursor is cheap, easily obtained, remains stable and retains the Fe^{2+} state for long time.

There are only few reports on successful use of NH$_4$FePO$_4$.H$_2$O as a reagent for the preparation of LiFePO$_4$. Ellis *et al.* [11] have obtained LiFePO$_4$ with a unique tablet-shaped morphology at hydrothermal conditions using NH$_4$FePO$_4$.H$_2$O and LiOH. Solid state reaction between NH$_4$FePO$_4$.H$_2$O and Li$_2$CO$_3$ in the presence of sugar at temperatures between 600 and 850 °C for 12h also yields LiFePO$_4$ [12].

EXPERIMENTAL

Precursor preparation

The precursor NH$_4$FePO$_4$.H$_2$O is prepared by a precipitation reaction between aqueous solutions of (NH$_4$)$_2$Fe(SO$_4$)$_2$ (120 ml 0.65M solution) and (NH$_4$)$_2$HPO$_4$ (200 ml 2M

solution). To prevent the oxidation of the Fe^{2+} sulphate were added to the iron solution. The precipitation was performed at temperature higher than 70 °C in order to avoid the crystallization of $NH_4FePO_4.6H_2O$ having a struvite-type structure. So that, both solutions were preliminary heated to about 75 °C before mixing. The precipitate is left in the mother solution for 3-4h to achieve a better crystallinity of $NH_4FePO_4.H_2O$. Then, it is filtered, washed and dried at room temperature.

LiFePO₄ preparation

The reactions between $NH_4FePO_4.H_2O$ and molten lithium salts are examined following, in general, the synthetic procedure already developed in the case of manganese dittmarites [5-8]. $NH_4FePO_4.H_2O$ and lithium salts are thoroughly ground, the reaction mixture is rapidly heated in an argon flow to the given reaction temperature (in the case melting point of the lithium salts). After definite reaction time, the product is cooled to room temperature, washed thoroughly with water and ethyl alcohol (96 %) to remove the biproducts and unreacted salts, filtered and dried in air for about 5–6 h. We have performed experiments with three different lithium eutectic compositions having low melting points between 270 and 325 ºC. Based on our previous experience [5,8] we have used small excess of the lithium salts for very short reaction times of 60 and 90 min. The detailed description of the experimental conditions and sample labeling are given in Table 1. Thus prepared samples are additionally annealed at 500 ºC for 10 h in argon flow and these samples are briefly designated as LFP2-500, LFP3-500, LFP4-500 and LFP5-500 (the numbers 2, 3, 4 and 5 correspond to the synthesis parameters according to Table1). All reagents used are of analytical grade.

Methods of characterization

The XRD patterns are recorded on a Bruker Advance 8 diffractometer using CuKα radiation. The lattice parameters are calculated by WinPlotr programme. The TG-DTA analysis of $NH_4FePO_4.H_2O$ is performed using LABSYS^{TM} Evo apparatus (SETARAM) in an argon flow at a heating rate of 5 °C/min up to

ions, several milligrams of hydrazine 700 °C. The infrared (IR) spectra are measured on a Fourier transform Nicolet Avatar-320 instrument using KBr pellets (resolution < 2 cm^{-1}). The SEM images of the precursor and LiFePO₄ powders are obtained by JEOL (JSM-5510) scanning electron microscope.
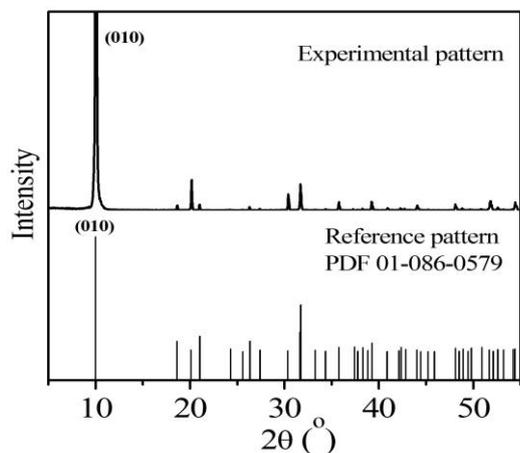
RESULTS AND DISCUSSION
Precursor characterization

The prepared $NH_4FePO_4.H_2O$ is well-crystallized and free of impurities as revealed by its XRD pattern (Fig. 1) where all diffraction peaks match completely these in the reference pattern. Moreover, the XRD pattern shows a preferred crystallites orientation along *b*-crystallographic axis which is evident by the much higher intensity of the (010) diffraction peak than that in the reference pattern. This is a result of the plate-like morphology of the salt (see further) which is consistent with the layered dittmarite-type structure [9]. The calculated unit cell parameters are: *a* = 5.6605(3) Å, *b* = 8.8178(3) Å, *c*= 4.8254(2) Å (space group *Pmn2₁*) and they coincide very well with the reported values from neutron diffraction data [9].

In accordance with our previous findings [5-8] the topotactic transformation of $NH_4FePO_4.H_2O$ into LiFePO₄ should include a direct ion exchange of NH_4^+ from the precursor with Li^+ from the molten salts in the framework of the dittmarite structure, followed by fast release of water of crystallization. For a successful synthesis this mechanism suggests that the dehydration of the precursor would be better to take place with a maximum rate at temperatures close to the reaction temperature. In this regard we have examined the thermal behaviour of $NH_4FePO_4.H_2O$ in Fig. 2.

The TG curve shows two steps: the first one finishes at 315 °C and the second one is between 315 and 550 °C (Fig. 2). The course of DTA curve is consistent with that of the TG curve exhibiting two endothermic effects with peak temperatures 256 and 448 °C (Fig. 2). As in the case of $NH_4MnPO_4.H_2O$ [8] the first step is due to simultaneous release of H_2O and NH_3 resulting in formation of an intermediate $FeHPO_4$ at 315 ºC (18.64 % mass loss *vs* calculated 18.73 %). Above 315ºC a

dehydration-condensation process takes and $Fe_2P_2O_7$ is a final product at 550 °C (4.52 % mass loss *vs* calculated 5.93 %). The small exothermic effect observed immediately after this process at 546 °C is most probably due to the crystallization of $Fe_2P_2O_7$. From obtained
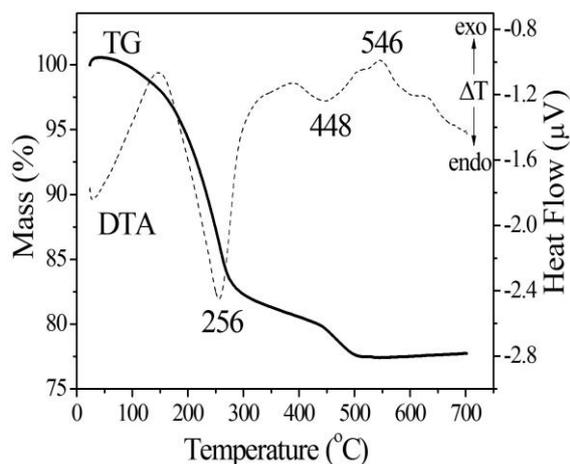
data one can conclude that the water molecule is released from the iron precursor at temperature that will favor the successful transformation of dittmarite- into olivine-type structure.

Fig. 1. Experimental and reference XRD patterns of $NH_4FePO_4.H_2O$. In the plot of the experimental pattern, the scale range of vertical *y* axis is much extended for better view of the diffraction peaks.

Fig. 2. TG and DTA curves for $NH_4FePO_4.H_2O$

Characterization of LiFePO₄

The XRD patterns of the reaction products between $NH_4FePO_4.H_2O$ and three lithium eutectic compositions are presented in Fig. 3. The phase analysis showed that $LiCl:LiNO_3$ eutectic composition (LFP1-270) is not appropriate because of the complete oxidation of Fe^{2+} to Fe^{3+}, although the inert atmosphere, with formation of mixture from $\alpha-Li_3Fe_2(PO_4)_3$ (about 75 wt %) and $\alpha-Fe_2O_3$ (about 25 wt%) (Fig. 3). The replacement of $LiNO_3$ by LiOH in other eutectic compositions (Table 1) gave a positive effect and in all next experiments the major product is the target $LiFePO_4$ (Fig. 3). Thus, in the XRD pattern of the sample obtained in molten LiOH:LiCl at 325 ºC for 90 min (LFP2-325) only a weak peak from admixture Li_3PO_4 can be seen. The annealing at 500 ºC (LFP2-500) improves the crystallinity of all reaction products, and now the presence of biproducts Li_3PO_4 (4.5 wt %) and $\alpha-Fe_2O_3$ (3.5 wt %) becomes visible (Fig. 3). In order to increase the purity of the target olivine phase in the next experiments we have slightly decreased either the excess LiCl-LiOH (LiFP3-325 in Table 1) or the reaction time to 60 min (LFP4-325 in Table 1). The XRD

patterns of LFP3-325 (Fig. 3) and LFP4-325 (XRD pattern not given) are the same and both
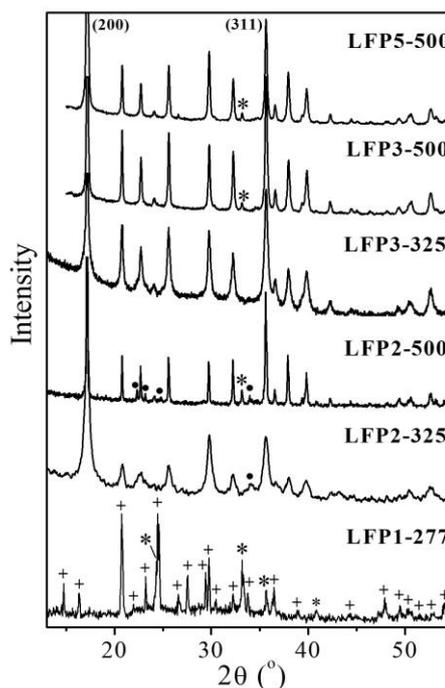

Fig. 3. XRD patterns of: LFP1-270; LFP2-325; LFP2-500; LFP3-325; LFP3-500 and LFP5-500. Symbols: * denotes $\alpha-Fe_2O_3$ (PDF 01-073-0603); + denotes $Li_3Fe_2(PO_4)_3$ (PDF 00-047-0107) and • denotes Li_3PO_4 (PDF 00-15-760). The diffraction peaks without symbols correspond to olivine-type $LiFePO_4$.

Table 1. Description of the synthesis parameters and sample labeling.

| Sample labeling	Lithium eutectic compositions	T, ºC	Mole ratio Li-salts:Precursor	Reaction time, min
LFP1-270	LiCl–LiNO₃ (0.12:0.88)	270	2:1	90
LFP2-325	LiCl:LiOH (0.3:0.7)	325	2:1	90
LFP3-325	LiCl:LiOH (0.3:0.7)	325	1.5:1	90
LFP4-325	LiCl:LiOH (0.3:0.7)	325	2:1	60
LFP5-277	LiCl:LiOH (0.35:0.65)	277	1.5:1	90

exhibit diffraction peaks only due to LFePO₄ [10]. The annealed samples at 500 ºC (LFP3-500 and LFP4-500), however, contain a small amount of α-Fe₂O₃ (about 2 wt %) according to the XRD data. As an illustration, Fig. 3 displays the XRD pattern of LFP3-500, while the IR spectrum of LFP4-500 is included in Fig. 4b. We have also probed another LiCl-LiOH eutectic composition having melting point at 277 ºC (LFP5-277 in Table 1). The result obtained is the same as in the two previous experiments which is evident from the XRD pattern of the annealed sample at 500 ºC (LFP5-500 in Fig. 3). In our opinion the formation of small amount of α-Fe₂O₃ during the ion exchange synthesis of LiFePO₄ most probably arises from the presence of residual oxygen in the argon flow. The calculated lattice parameters of LiFePO₄ obtained at 325 ºC are: $a = 10.3271(8)$ Å, $b = 5.9912(8)$ Å, $c = 4.6953$ Å (space group *Pnma*). These values are very close to the reported data for single crystal grown by hydrothermal method [10] as well as for "defectless" LiFePO₄ powders obtained by other methods [13-15]. It should be mentioned that LiFePO₄ crystallites exhibit preferred orientation along the *a*-crystallographic axis which is clearly manifested by the much higher intensity of the (200) diffraction peak than that of (311) peak. In the case of random crystallite orientation the (311) peak is the strongest peak in the XRD pattern of LiFePO₄ [10,13-15]. This crystallite orientation is inherited from the dittmarite precursor (the difference in the space groups of the dittmarite and olivine-type structures switches *a* and *b* axes) [9,10].

The formation of LiFePO₄ by ion exchange reactions is further supported by IR spectroscopy (Fig. 4). All IR spectra are dominated by the strong absorbance related to the fundamental vibrations of the PO₄³⁻ ions: P–O stretching vibrations in the 1137-947 cm⁻¹ region and OPO asymmetric bending vibrations in the 651-546 cm⁻¹ region. The two bands at 500 and 447 cm⁻¹ are mainly related to
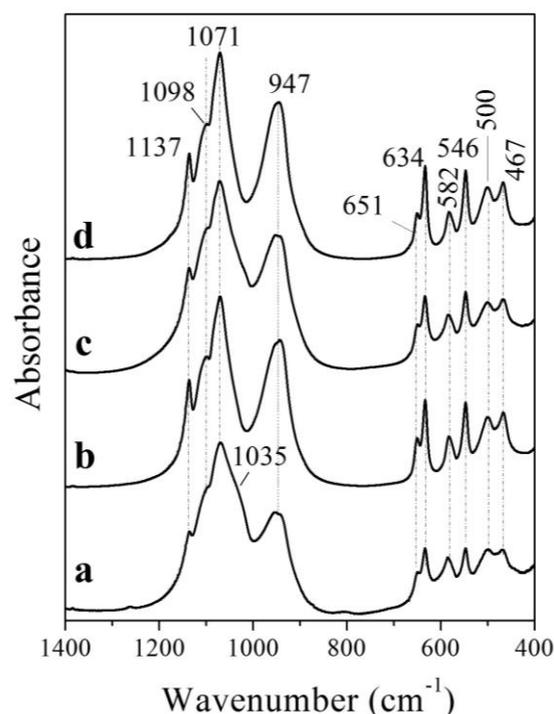
Fig. 4. IR spectra of: (a) LFP2-500; (b) LFP4-500; (c) LFP3-325; (d) LFP3-500

the Li⁺ translations but a mixing with the OPO symmetric bending mode was also supposed [16,17]. The positions of the IR vibrational bands agree with these previously reported for well-crystallized olivine phase LiFePO₄ [16,17]. In the IR spectrum of LFP2-500 (Fig. 4a), however, additional shoulder at 1035 cm⁻¹ appears and it most probably originates from Li₃PO₄ present in this sample according to its XRD pattern (Fig. 3c). In the IR spectrum of Li₃PO₄ the band at 1040 cm⁻¹ due to P–O stretching vibrations is the strongest one [16]. It is important that the IR spectrum of LiFePO₄ obtained at 325 ºC for 90 min is identical to that after annealing at 500 ºC for 10h (Fig. 4 c and d). This is an additional evidence that our method ensures well-crystallized olivine phase LiFePO₄ which remains stable upon further annealing, although the low synthesis temperature and very short reaction time of 60-90 min.

Moreover, the absence of any pyrophosphate phases gives further support that the ion exchange between NH_4^+ and Li^+ occurs very quickly in the framework of the dittmarite structure before the precursor decomposition. This ion exchange process is immediately followed by the H_2O release, so that the dittmarite structure is easily transformed in the olivine structure by a topotactic pathway.
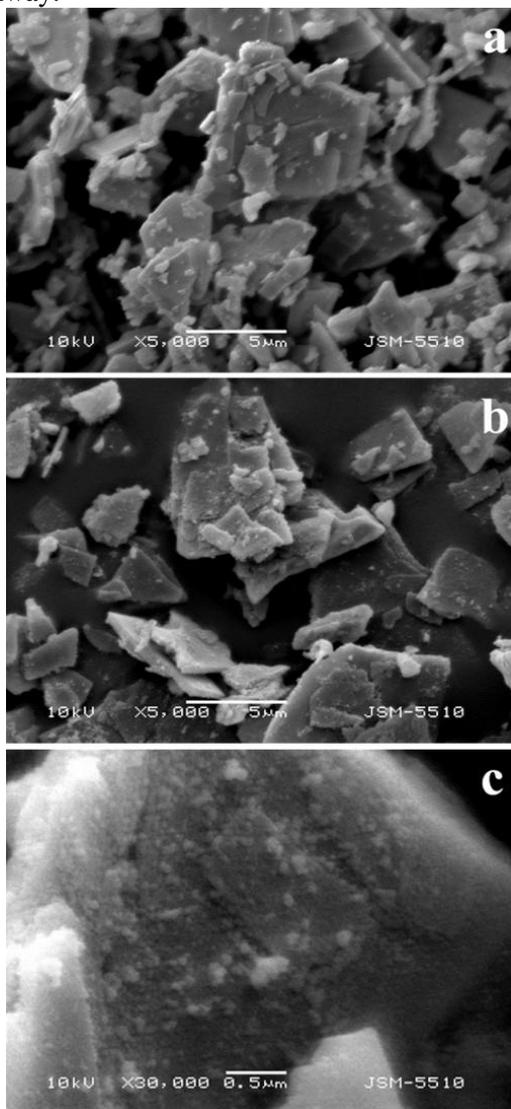
Fig. 5. SEM images: (a) $NH_4FePO_4.H_2O$; (b, c) LiFePO₄ obtained at 325 °C.

The topotactic transformation is manifested by the SEM images of $NH_4FePO_4.H_2O$ and obtained LiFePO₄ (Fig. 5). Evidently, the plate-like morphology of the precursor is preserved in the reaction product. In both SEM images (Fig. 5a, b) plates with basal dimensions of 2−7 μm are clearly visible. At higher magnification (Fig. 5c) one can see that micrometer plates of LiFePO₄ are composed of spherical particles with sizes about 50 nm. The SEM particle dimensions are slightly larger as compared to the crystallite dimensions (30

nm) determined by Scherrer equation from XRD line broadening. This fact again evidences for the good crystallinity of as-prepared LiFePO₄ powder although the rapid low-temperature synthesis.

CONCLUSIONS

The present study confirms that the dittmarite-type compounds are very effective precursors for fast, low-temperature synthesis of crystalline lithium iron and lithium manganese phospho-olivines, $LiMPO_4$ (M^{2+} = Fe, Mn). In both cases the reactions between dittmarite precursors $NH_4MPO_4.H_2O$ (M^{2+} = Fe, Mn) and lithium salts follow a topotactic pathway. This is manifested by the plate-like morphology and preferred crystallite orientation of prepared $LiMPO_4$ which are inherited from the used dittmarite-type precursors.

REFERENCES

1. Z. Gong, Y. Yang, *Energy Environ. Sci.*, **4,** 3223 (2011).
2. C. Masquelier, L. Croguennec, *Chem. Rev.,* **113**, 6552 (2013).
3. C. Delacourt, P. Poizot, S. Levasseur, C. Masquelier, *Electrochem. Solid-State Lett.,* **9**, A352 (2006).
4. S. Ferrari, R. L. Lavall, D. Capsoni, E. Quartarone, A. Magistris, P. Mustarelli, P. Canton, *J. Phys. Chem. C,* **114**, 12598 (2010).
5. V. Koleva, E. Zhecheva, R. Stoyanova, *Dalton Trans.,* **40**, 7385 (2011).
6. V. Koleva, T. Boyadzhieva, E. Zhecheva, D. Nihtianova, S. Simova, G. Tyuliev, R. Stoyanova, *Cryst. Eng. Comm.,* **15**, 9080 (2013).
7. T. Boyadzhieva, V. Koleva, R. Stoyanova, *Bulg. Chem. Commun.,* **45B,** 208 (2013).
8. V. Koleva, R. Stoyanova, E. Zhecheva, D. Nihtianova, *Cryst. Eng. Comm.,* **16**, 7515 (2014).
9. G. Carling, P. Day, D. Visser, *Inorg. Chem.,* **34,** 3917 (1995).
10. V.A. Streltsov, E.L. Belokoneva, V.G. Tsirelson, N.K. Hansen, *Acta Cryst.,* **B49,** 147 (1993).
11. B. Ellis, W.H. Kan, W.R.M. Makahnouk, L.F. Nazar, *J Mater. Chem.,* **17,** 3248 (2007)
12. N. W. Li, J. Gao, J. Ying, C. Wan, C. Jiang, *J. Electrochem. Soc.,* **153,** F194 (2006).
13. F. Gao, Zh. Tang, J. Xue, *Electrochim. Acta* **53** 1939 (2007).
14. D. Choi, P. N. Kumta, *J. Power Sources* **163**, 1064 (2007).
15. V. Koleva, E. Zhecheva, R. Stoyanova, *J. Alloys Compd.,* **476** 950 (2009).
16. A. A. Salah, P. Jozwiak, K. Zaghib, J. Garbarczyk, F. Gendron, A. Manger, C.M. Julien, *Spectrochim. Acta* **65A,** 1007 (2006).
17. C. M. Burba, R. Frech, *Spectrochim. Acta* **65A,** 44 (2006).

НИСКОТЕМПЕРАТУРНО ПОЛУЧАВАНЕ НА НАНОРАЗМЕРЕН LiFePO₄ ЧРЕЗ РЕАКЦИИ В СТОПИЛКА

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(Резюме)

Реакции в стопилка между дитмаритен-тип $NH_4FePO_4.H_2O$ и различни литиеви евтектични състави са систематично изследвани с цел нискотемпературно получаване на оливинов-тип $LiFePO_4$, който е ценен електроден материал за литиево-йонни батерии. Наноразмерен $LiFePO_4$ е успешно синтезиран чрез топотактични реакции използвайки $LiCl$-$LiOH$ евтектични състави при температури 277–325 ºC за много кратко реакционно време 60–90 мин. Фосфо-оливиновата фаза е добре изкристализирала с предпочитана ориентация на кристалите по *a*-кристалографска ос. Прахообразният $LiFePO_4$ се характеризира с плочковидна морфология, унаследена от железния прекурсор. Микрометърните плочковидни агрегати на $LiFePO_4$ са изградени от наноразмерни сферични частици с размери около 50 нм, което е благоприятен фактор за по-нататъшно електрохимично приложение.