



## Review

# A review of recent developments in the synthesis procedures of lithium iron phosphate powders

Dragana Jugović\*, Dragan Uskoković

*Institute of Technical Sciences of the Serbian Academy of Sciences and Arts, Knez Mihailova 35/IV, 11 000 Belgrade, Serbia*

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## ABSTRACT

Olivine structure LiFePO<sub>4</sub> attracted much attention as a promising cathode material for lithium-ion batteries. The overwhelming advantage of iron-based compounds is that, in addition to being inexpensive and naturally abundant, they are less toxic than Co, Ni, and Mn. Its commercial use has already started and there are several companies that base their business on lithium phosphate technology. Still, there is a need for a manufacturing process that produces electrochemically active LiFePO<sub>4</sub> at a low cost. Therefore the interest in developing new approaches to the synthesis of LiFePO<sub>4</sub> did not fade. Here is presented a review of the synthesis procedures used for the production of LiFePO<sub>4</sub> powders along with the highlights of doped and coated derivatives. Apart from already established conventional routes of preparation, numerous alternative procedures are mentioned.

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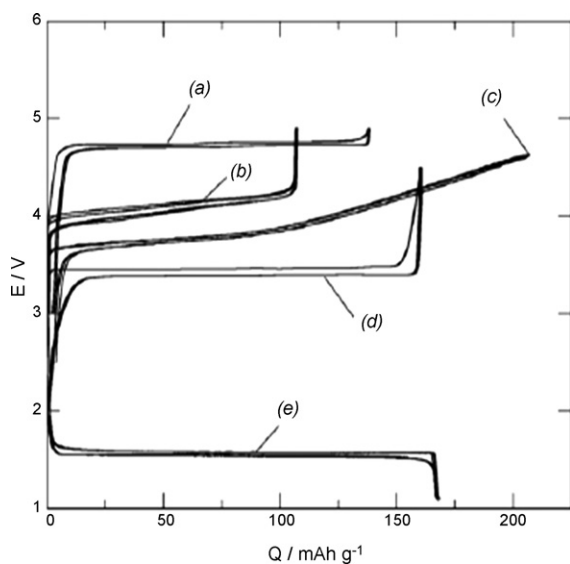
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## 1. Introduction

Lithium is a very attractive material for high energy density batteries due to its low equivalent weight and high standard potential. Lithium battery research began in the 1950s when it was noticed that Li-metal was stable in a number of nonaqueous electrolytes, such as fused salts, liquid SO<sub>2</sub>, or organic electrolytes, such as LiClO<sub>4</sub>

in propylene carbonate [1]. However, the development of rechargeable batteries was much slower [2]. The concept of lithium-ion batteries was first introduced into the market by Sony in 1992. Most of the research and commercial cathode materials for rechargeable lithium-ion batteries are lithium insertion compounds with layered, spinel, or olivine structure [3]. Fig. 1 shows charge and discharge curves of the selected lithium insertion materials examined for advanced lithium-ion batteries [2]. A new class of material with an olivine structure, in particular LiFePO<sub>4</sub>, attracted much attention as a promising cathode material for lithium-ion batteries due to its potentially low cost, environmental benignity, and the belief

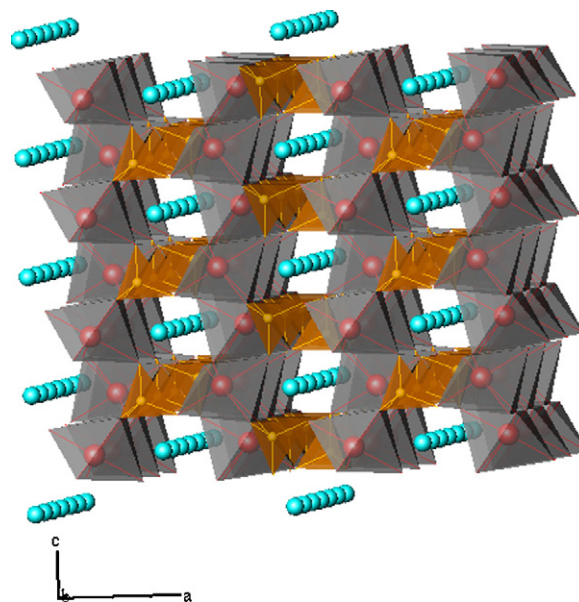
\* Corresponding author. Tel.: +381 641177549; fax: +381 112185263.  
 E-mail address: [djugovic@vinca.rs](mailto:djugovic@vinca.rs) (D. Jugović).



**Fig. 1.** Charge and discharge curves of lithium insertion materials: (a)  $\text{Li}[\text{Ni}_{1/2}\text{Mn}_{3/2}]\text{O}_4$ , (b)  $\text{LiMn}_2\text{O}_4$ -based material of lithium manganese oxide (LAMO), (c)  $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{O}_2$ , (d)  $\text{LiFePO}_4$ , and (e)  $\text{Li}[\text{Li}_{1/3}\text{Ti}_{5/3}]\text{O}_4$  examined in nonaqueous lithium cells [2].

that it could have a major impact in electrochemical energy storage. The use of lithium iron phosphate as a cathode material, instead of expensive  $\text{LiCoO}_2$ , could reduce the cathode cost from 50% to 10% of the battery cost [4]. The olivine structure that typifies  $\text{LiFePO}_4$  has a hexagonally close-packed oxygen array, in which the octahedra share both edges and faces, Fig. 2. The cation arrangement in  $\text{LiFePO}_4$  differs significantly from that in the layered and spinel structures. There is no continuous network of  $\text{FeO}_6$  edge-shared octahedra that might contribute to electronic conductivity; instead, divalent  $\text{Fe}^{2+}$  ions occupy corner-shared octahedra. The phosphorus ions are located in tetrahedral sites, and the lithium ions reside in chains of edge-shared octahedral.  $\text{LiFePO}_4$  initially includes one  $\text{Li}^+$  ion per formula unit that can be extracted and transferred to the anode in the first charge process, compensating for the oxidation of iron ( $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$ ). The theoretical capacity based on this one-electron reaction is  $170 \text{ mAh g}^{-1}$ , but the first attempts to de-insert Li from this material were limited to about  $0.6 e^-$  owing to transport limitations of electrons and ions [5]. The main obstacle in reaching theoretical capacity is its low intrinsic electronic conductivity. Apart from that, lithium motion in the olivine crystal structure occurs through one-dimensional channels, with little possibility of crossing between channels [6]. These one-dimensional paths are particularly susceptible to blockage by defects and impurities [6,7]. Several approaches were explored to solve the conductivity problem [8]. These approaches include the reduction of particle size and homogeneous particle size distribution [9]; coating the particles with carbon [10,11], or co-synthesizing the compounds with carbon to surround each particle with a good electronic conductor [12]; tailoring the morphology and texture of the particle by low temperature synthesis routes [13]; and selective doping with supervalent cations to increase the intrinsic conductivity [14].

There are some excellent reviews on the properties of  $\text{LiFePO}_4$  that deal with its structural, morphological, electrochemical, and other physical properties targeting its cathode application [3,9,15–17]. Nevertheless, little attention has been paid to the synthesis procedures. Therefore, we tried to summarize synthesis routes for obtaining  $\text{LiFePO}_4$  powders, hoping it would be of use to those entering lithium-ion battery research. Since the discovery of the electrochemical properties of the olivine phase by Padhi et al. in 1997 [5], numerous ways of synthesis of the olivine-type  $\text{LiFePO}_4$



**Fig. 2.** The olivine structure of  $\text{LiFePO}_4$ : showing the  $\text{FeO}_6$  octahedra (grey),  $\text{PO}_4$  tetrahedra (brown), and the one-dimensional tunnels in which the lithium ions reside (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article).

were explored. It can be roughly distinguished between the ones starting from solid phase and the ones starting from solutions.

## 2. Solid-state chemistry

### 2.1. Solid-state reaction

Solid-state synthesis is a conventional method for preparing ceramics and includes several successive steps of intimate grinding and annealing of the stoichiometric mixture of starting materials. In general, in the case of  $\text{LiFePO}_4$ , the starting mixture consists of a stoichiometric amount of iron salt ( $\text{Fe(II)}$ -acetate,  $\text{Fe(II)}$ -oxalate), a lithium compound (lithium carbonate or lithium hydroxide), and most commonly ammonium phosphate as a phosphorous source [5,18–24]. The starting mixture firstly decomposes at the temperature of  $300\text{--}400^\circ\text{C}$  to expel the gases, and, after being reground, calcines at a temperatures ranging from  $400$  to  $800^\circ\text{C}$  for  $10\text{--}24$  h. Before the second grinding step, some carbon-containing compound, for example carboxylic acid [25], can be added to the precursor and can be employed as a carbon source in the  $\text{LiFePO}_4/\text{C}$  composite formation. The purity of the material depends on the growth parameters, such as the temperature of calcination, and exposure time [16,26]. During calcination, due to iron oxidation state ( $2+$ ), the use of inert (usually nitrogen or argon) or slightly reductive atmosphere (argon or nitrogen with the addition of hydrogen) is necessary. Still, the presence of the residual  $\text{Fe}^{3+}$  phase is possible and often reported. By calcining above  $800^\circ\text{C}$  both trivalent  $\text{Fe}_2\text{O}_3$  and  $\text{Li}_3\text{Fe}_2(\text{PO}_4)_3$  were formed [20]. Trivalent Fe might be formed by a small amount of oxygen included in inert gas flow and/or residual air trapped in the small pores of the particles [20]. Another disadvantage of the described method is uncontrollable particle growth and agglomeration, so the application potential of large particles is limited by their small surface area [19,20,24].

### 2.2. Mechanochemical activation

A method to overcome this is to include mechanochemical activation in the process. While solid-phase reactions bind the interaction rate with the diffusion of one of the components, at

first over the surface of another component, and then in the bulk through product layer, mechanical activation of a mixture involves continuous renewal of contact surfaces. During mechanochemical activation, particles of the powder undergo repeated welding, fracturing and rewelding in a dry high-energy, ball-milling vessel. This results in pulverization, intimate powder mixing, and then solid-state reaction to a new phase. Accordingly, when mechanochemical activation is applied to the synthesis of  $\text{LiFePO}_4$ , an improvement in electronic conductivity can be expected due to very small size of the particles and their large specific surface area [19,27,28]. However, no literature data have shown that single-phase lithium iron phosphate can be obtained by the mechanical alloying process alone without additional calcination at moderate temperatures. Nevertheless, it has been confirmed that it still provides an effective means in terms of homogeneity and particle size. It is also suitable for the preparation of  $\text{LiFePO}_4/\text{C}$  composites [10,29–32], or composites  $\text{LiFePO}_4$  with  $\text{Fe}_2\text{P}$  [12,33], as well as for obtaining doped  $\text{LiFePO}_4$  samples [14,34]. The duration of both milling and annealing varies: from short milling time with long thermal treatment [28,35,36] to long milling time with short thermal treatment [19,10], and all the cases in-between [12,14,27,32].

### 2.3. Carbothermal reduction

By adding a stoichiometric amount of carbon to the precursor mixture it is possible to use, beside Fe(II) salts, Fe(III) compounds such as cheap  $\text{Fe}_2\text{O}_3$  [12,29,37] or  $\text{FePO}_4$  [38–40]. In this manner, by thermal treatment at  $900^\circ\text{C}$ , conditions for carbothermal reduction are accomplished and single-phase  $\text{LiFePO}_4/\text{C}$  composite can be obtained. Special care must be taken when choosing carbon proportion having in mind that with carbon content higher than the stoichiometric value second phase  $\text{Fe}_2\text{P}$  is observed [12,29]. Total  $\text{Fe}^{3+}$  reduction can also occur at lower temperatures, but only with a polymer as a carbon source [38–44]. This time  $\text{Fe}^{3+}$  reduction occurs through the action of a reductive atmosphere created by the pyrolytic degradation of the organic carbon additive, not via carbothermal reaction [38]. However, the term “carbothermal reduction” is regularly used by the authors to describe both phenomena.

Concerning Patent Applications we can conclude that solid-state synthesis is adopted for the commercial scaled-up production of lithium iron phosphate powders [45,46]. A123 Systems Inc. uses  $\text{Li}_2\text{CO}_3$ , iron(II) oxalate, and ammonium phosphate as reactants [45]. The dry components were weighed and mixed with a sufficient quantity of high-purity acetone to create a free-flowing suspension, and the mixture was roller-milled in a sealed polypropylene jar using zirconia milling media for 24 h, which resulted in a homogeneous and finely divided precursor suspension. The precursor was thoroughly dried and then heat treated in a tube furnace under flowing argon gas, first at  $350^\circ\text{C}$  for 10 h and then at  $600^\circ\text{C}$  for 20 h. Through the use of high-purity acetone as the solvent and extended mixing to allow the starting components to undergo a gas-evolving mechanochemical reaction, resulted in a precursor which upon firing yields low-carbon nanoscale phosphate with very high specific surface area [45]. Valence Technology Inc. prepares  $\text{LiFePO}_4$  using carbothermal reduction via milling in a carbonaceous vessel of an iron(III) oxide containing precursor, followed by heating in inert atmosphere to achieve the reduction of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  without direct addition of a reducing agent to the reactants [46,47]. Sony's original synthetic route for  $\text{LiMPO}_4$ -type cathode composites involves high-energy ball milling of a precursor that contains metal phosphates and disordered conductive carbon [31].

The need for repeated recalcination and subsequent regrinding in order to improve the homogeneity of the final products in the solid-state reaction makes the procedure both time and energy consuming, and therefore commercially unsustainable. There is a need

for new synthesis methods that reduce energy consumption, cost, and processing time.

### 2.4. Microwave processing

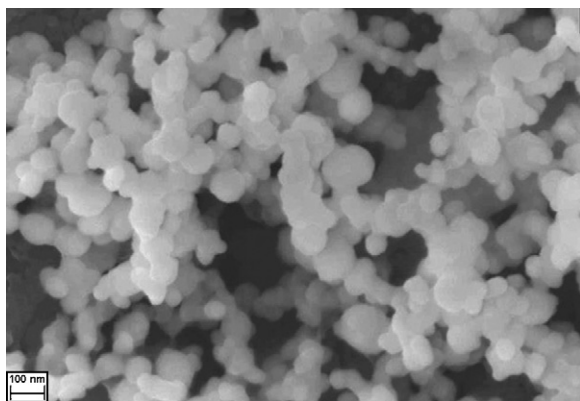
Microwave heating can ensure very fast and uniform heating through a self-heating process based on direct microwave energy absorption by the materials. Furthermore, microwave heating makes it possible to synthesize the target materials at temperatures lower than those required for furnace heating within a short period of time [48]. The limiting step in microwave processing is the adoption of starting reactants that have to be microwave susceptors. Higuchi et al. [48] were the first to apply microwave heating in the preparation of  $\text{LiFePO}_4$ . They prepared precursors by solid-state mixing and calcined it in a domestic microwave oven under inert atmosphere. Starting from lithium carbonate and ammonium phosphate as lithium and phosphorus source respectively, and by varying both iron source (iron lactate or iron acetate) and irradiation time, it was shown that the iron precursor acts as a microwave absorber [48]. Even after prolonged irradiation of the starting mixture with Fe(II) lactate as an iron source the reaction failed. However, after the addition of a small amount of iron metal powder, the reaction occurred. It means that the choice of the precursor iron compound is limited. The papers that followed [11,49,50] have shown that instead of an iron compound acting as a microwave susceptor it is possible to use activated carbon as both microwave absorber and a reducing agent. Carbon provides rapid heating and its partial oxidation to  $\text{CO}_2$  produces a reductive atmosphere which preserves the iron(II) in its oxidation state, thereby enabling synthesis in air. More recently, Song et al. [11] irradiated in a domestic microwave oven a mixture of  $\text{Li}_3\text{PO}_4$ ,  $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$  and carbon, previously ground in a high energy ball-mill, to obtain fine particles of  $\text{LiFePO}_4$ . Wang et al. [50] prepared  $\text{LiFePO}_4$  by microwave irradiation of  $\text{NH}_4\text{H}_2\text{PO}_4$ ,  $\text{CH}_3\text{COOLi}$  and  $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  mixed with different amounts of citric acid in a self-assembly carbon seal reactor. Most recent researches see microwave-assisted synthesis as a promising approach to mass  $\text{LiFePO}_4$  production at low-energy cost for HEV application [51], starting from a solid mixture of  $\text{Li}_3\text{PO}_4$ ,  $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ , carbon, and glucose. A novel microwave-solvothermal approach to obtaining well-defined nanoparticles of  $\text{LiFePO}_4$  with high crystallinity and controlled size in a short time ( $\sim 5$  min) in a non-aqueous solvent medium at temperatures as low as  $300^\circ\text{C}$ , eliminating the need for an inert atmosphere or post-annealing at elevated temperatures in reducing gas atmospheres, was recently presented. Subsequent ambient-temperature coating of the nanosize  $\text{LiFePO}_4$  with a mixed conducting polymer to form a nanohybrid offers 95% of theoretical capacity with excellent cyclability and rate capability [52].

## 3. Solution chemistry

Wet chemical preparation routes, such as hydrothermal/solvothermal, sol-gel, or co-precipitation methods, have an indisputable advantage over solid-state reactions in achieving better homogeneity and mixing of the starting compounds on molecular level.

### 3.1. Hydrothermal processing

Hydrothermal synthesis is quick, easy to perform, low-cost, energy-saving and easily scalable method to prepare fine particles. Yang et al. [53] originally showed that lithium iron phosphate could be synthesized hydrothermally, starting from  $\text{FeSO}_4$ ,  $\text{H}_3\text{PO}_4$  and  $\text{LiOH}$  mixed in molar ratio 1:1:3.  $\text{FeSO}_4$  and  $\text{H}_3\text{PO}_4$  solution were mixed first to avoid the formation of  $\text{Fe}(\text{OH})_2$  because it easily



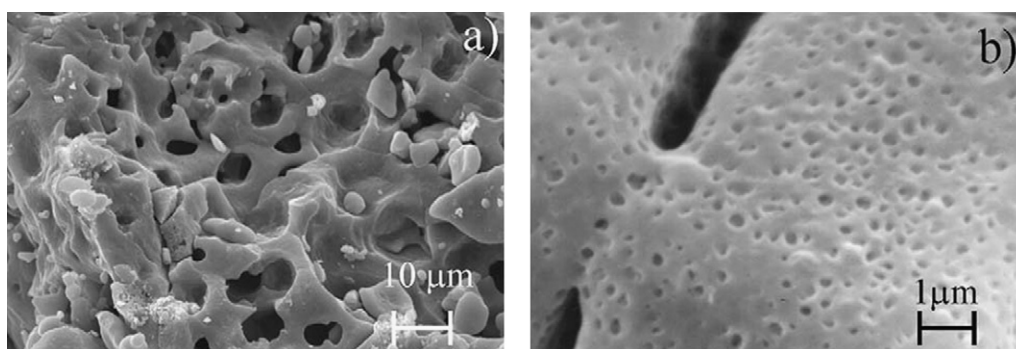
**Fig. 3.** SEM micrograph of lithium iron phosphate powder synthesized in continuous hydrothermal synthesis at 573 K [62].

oxidizes to  $\text{FeO}(\text{OH})$ , then  $\text{LiOH}$  solution was added to the mixture, which was then hydrothermally processed at  $120^\circ\text{C}$  for up to 5 h. However, the capacity of the resulting lithium iron phosphate phase was not high, which was due to some lithium/iron disorder with around 7% iron on the lithium sites, as later shown by the same group of authors [54]. As the structure has one-dimensional tunnels, any iron in lithium tunnels would severely limit lithium insertion and removal. It is therefore essential to ensure complete ordering of lithium and iron atoms. The firing of the hydrothermal material at  $700^\circ\text{C}$  with carbonaceous materials resolved the disorder [55]. In the time of the study (2003), the authors concluded that “for lithium iron phosphate hydrothermal synthesis is not a viable approach” [55], but later on, by modifying the synthesis conditions, came to optimal hydrothermal parameters for obtaining electrochemically active  $\text{LiFePO}_4$  [56,57]. It was found that the temperature of synthesis must exceed  $175^\circ\text{C}$  to minimize iron disorder and obtain a material with correct lattice parameters and volume. Furthermore, reductants, such as ascorbic acid or sugar, prevent the formation of surface ferric films [58,59]. Hydrothermal synthesis leads to well-crystalline material with particle size generally in the micron size, and with a thickness of a few hundred nanometers; fortunately the short dimension is the diffusion direction [59]. Apart from the above-mentioned hydrothermal synthesis in subcritical water, there are studies dealing with the synthesis of  $\text{LiFePO}_4$  in supercritical water with the same reactants [60]. It was shown that  $\text{LiFePO}_4$  could only be obtained over a narrow range of pH at neutral or slightly basic conditions, while pH had little effect on particle size or shape [60]. Smaller and more uniform particles were obtained when the synthesis reaction was carried out in supercritical water rather than subcritical water [61]. Along with batch hydrothermal synthesis, the continuous hydrothermal technique was also applied

to synthesize pure lithium iron phosphate nanoparticles, Fig. 3 [62]. It was found that the flow rate of water has a significant effect on particle morphology. A comparison with results of batch synthesis shows that smaller and more uniform particles are obtained in continuous hydrothermal synthesis than in batch hydrothermal synthesis [62]. Hydrothermal synthesis in the presence of an organic surfactant compound such as CTAB (hexadecyltrimethylammonium bromide) allowed the preparation of high surface area lithium iron phosphate powders with improved electrochemical performances [63]. CTAB pyrolysis enabled both the formation of a reductive atmosphere that prevents  $\text{Fe}^{2+}$  oxidation and *in situ* formation of carbon layer over the particle surface. Hydrothermal synthesis is also suitable for the preparation of metal-doped lithium iron phosphates [64].

### 3.2. Sol–gel processing

The motivation for sol–gel processing primarily lies in the fact that it ensures a potentially higher purity and homogeneity and lower processing temperatures than traditional ceramic powder methods [65]. Sol–gel processing enables the control of the structure of a material on a nanometer scale from the earliest stages of processing. Sols are dispersions of colloidal particles in a liquid. Colloids are solid particles with diameters of 1–100 nm. A gel is an interconnected, rigid network with pores of submicrometer dimensions and polymeric chains whose average length is greater than a micrometer. The term “gel” embraces a diversity of combinations of substances that can be classified in four categories: (1) well-ordered lamellar structures; (2) covalent polymeric networks, completely disordered; (3) polymer networks formed through physical aggregation, predominantly disordered; (4) particular disordered structures [6]. For the purposes of sol–gel synthesis of  $\text{LiFePO}_4$  various solvents were used: *N,N*-dimethylformamide [16,66,67], water with ascorbic acid [67], or citric acid [22,68–71] as chelating agent, ethylene glycol [72,73], and ethanol [74]. Lithium acetate and iron (II) acetate [66,67,72], lithium phosphate and iron (III) citrate with phosphoric acid [22,69,75], lithium oxalate and iron (II) oxalate [73], lithium carbonate and iron (II) oxalate [71] are examples of some combination of lithium and iron sources, respectively. Thus obtained sols were dried until the solvent evaporated, which was followed by calcination at temperatures from 500 to  $700^\circ\text{C}$  in inert (argon or nitrogen) [72,73,75], or slightly reductive atmosphere (argon/nitrogen containing 5–10% of hydrogen) [66,74,76]. Apart from homogeneous mixing of precursors at the molecular level, another significant advantage of sol–gel method is that surface carbon can be generated *in situ* when organic solvent [72,76] or some carbon included compound (acetates, citrates, oxalates, etc.) [71] are used. Along with the *in situ* formed carbon coating, iron phosphides can be generated, for instance when gel precursor made of iron(III) nitrate, 2-methoxyethanol, and sucrose



**Fig. 4.** SEM micrographs of  $\text{LiFePO}_4/\text{C}$  composite powder synthesized by sol–gel method showing (a) porous “chess-like” structure with (b) numerous apertures in the sub-micron range [69].

followed by carbothermal reduction reaction of xerogel precursor with Li, P resources is used [77]. Composites with carbon and iron phosphides can also be generated from an aqueous sol–gel method by using ethylene glycol as carbon source in a calcination atmosphere of  $N_2 + 5 \text{ vol.}\% H_2$  [76]. The use of citrate in the preparation of the gel enables the formation of hierarchically organized pores in the meso and macro range, Fig. 4 [69,75]. These pores are decorated with conductive carbon, another citrate–degradation product, within micrometer-sized  $LiFePO_4$  single crystals. In this way intertwined 3-D networks of ionic and electronic conductors are formed [75].

### 3.3. Precipitation method

The solution-based methods offer the advantages of optimum particle size, also ensuring phase purity. Phase pure, homogeneous, and well-crystallized lithium iron phosphate was synthesized by aqueous co-precipitation of an Fe(II) precursor material and subsequent heat treatment in nitrogen [78]. Heating the solution containing  $Li^+$ ,  $Fe^{2+}$ , and  $P^{5+}$  ions above  $105^\circ C$  with the pH value adjusted between 6 and 10 facilitates the formation of  $LiFePO_4$  rather than the formation of  $Li_3PO_4$  and  $Fe_3(PO_4)_2$ . The solution should also contain water-miscible boiling point elevation additive such as: ethylene glycol, diethylene glycol, N-methyl formamide, dimethyl formamide, particularly dimethyl sulfoxide [79]. After the temperature of the solution is increased to the solvent's boiling point,  $LiFePO_4$  begins to precipitate. Afterward, the obtained precipitate is calcined at  $500^\circ C$  at a slightly reducing atmosphere [79]. As the crystalline  $LiFePO_4$  phase is already formed during the precipitation step, the temperature and the dwell time of the thermal treatment are significantly reduced compared to ceramic synthesis process.  $LiFePO_4$  was also prepared by aqueous precipitation of  $FePO_4 \cdot H_2O$  from  $FeSO_4 \cdot 7H_2O$  and  $NH_4H_2PO_4$  with hydrogen peroxide as the oxidizing agent, followed by carbothermal reduction of a mixture made of precipitator iron(III) phosphate and lithium carbonate with carbon as the reducer [39]. Modifying the latter approach in the second stage of the synthesis where amorphous  $LiFePO_4$  was firstly obtained at room temperature through lithiation of  $FePO_4 \cdot xH_2O$  using oxalic acid as a novel reducing agent, and then amorphous  $LiFePO_4$  was calcined at  $500^\circ C$ , nanocrystalline  $LiFePO_4$  with enhanced electrochemical performance was formed [80].

$LiFePO_4/C$  composite can also be successfully synthesized combining sonochemical precipitation and calcination [81]. Sonochemical reaction is a chemical reaction that is induced and/or catalysed by the application of powerful ultrasound radiation (20 kHz–10 MHz). The starting mixture, consisting of  $Li_3PO_4$  and  $FeSO_4$  in polyvinyl alcohol (PVA) aqueous solution, was sonochemically treated, which was followed by the calcination of the as-prepared powder at moderate temperature of  $600^\circ C$  [81]. In this way both calcination time and synthesis time were shortened. The obtained powder, consisting of  $LiFePO_4$  particles coated with carbon, showed appreciable discharge capacity with excellent retention [81]. On the thin particle edges (Fig. 5) carbon film with a typical thickness of several nanometers can be observed.

### 3.4. Emulsion-drying method

Emulsion-drying method was also used for the preparation of  $LiFePO_4/C$  composite powder [82–84]. Stoichiometric amounts of  $LiNO_3$ ,  $Fe(NO_3)_3 \cdot 9H_2O$ , and  $(NH_4)_2HPO_4$  were dissolved in water, and the obtained solution was vigorously mixed with an oily phase to prepare a homogeneous water-in-oil emulsion [82,83]. The oily phase was a mixture made of emulsifying agent named Tween 85 (Polyoxyethylene Sorbitan Trioleate) and kerosene [82,83]. The precursor powders were obtained by dropping the emulsion into

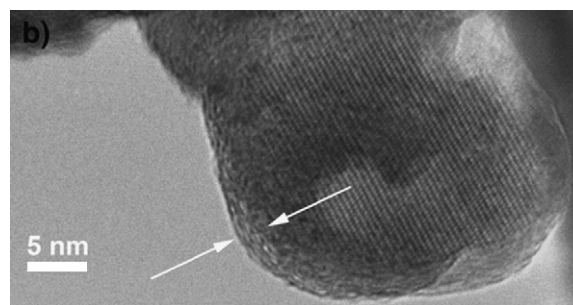


Fig. 5. TEM image of  $LiFePO_4/C$  composite obtained by sonochemical reaction. Arrows point out 2–3 nm thick layer of amorphous carbon [81].

hot kerosene ( $170\text{--}180^\circ C$ ). Water and kerosene contained in the emulsion were distilled through a spiral-type condenser and the resultant powder sank to the bottom of the reaction vessel. The latter powder contained kerosene and Tween 85 and was heated at  $300^\circ C$  or  $400^\circ C$  for a specific time in an air-limited box furnace. The dried emulsion precursor was calcined at different temperatures, and  $750^\circ C$  was found to be the optimal calcination temperature [82].  $LiFePO_4/C$  composite with nanometric dimensions and uniform size distribution was also prepared by *n*-octane/*n*-butyl/cetyltrimethyl ammonium bromide microemulsion system [84]. The main advantage of this synthesis route is that the reactants are mixed on more homogeneous level and that grains are effectively inhibited from coalescence during the synthetic process.

### 3.5. Spray pyrolysis

Another solution-based approach in the synthesis of olivine type  $LiFePO_4$  and  $LiFePO_4/C$  powders is spray pyrolysis, an effective technique for obtaining cathode powders with fine size and regular morphology. The starting solutions can be sprayed ultrasonically [85–87] or peristaltically [88] into the high-temperature reactor at temperatures from  $450$  to  $650^\circ C$  by a carrier gas. The precursor solution can be made by dissolving stoichiometric amounts of lithium carbonate, iron(II) oxalate and ammonium dihydrogen phosphate in nitric acid with the addition of sucrose. In that case sucrose serves as a carbon source and enables the formation of reductive atmosphere so that air can act as a carrier gas [88].  $LiFePO_4$ /carbon composite powder was also synthesized starting from  $Fe^{3+}$  precursor, for example by dissolving metal nitrates, phosphoric acid, ascorbic acid and table sugar in water [85,89], or by a combination of spray pyrolysis with a planetary high-energy ball-milling followed by heat treatment [90]. In addition, ultrasonic spray pyrolysis can be a suitable method for obtaining metal-doped samples of  $LiFePO_4$ /carbon composite powders [89]. The as-sprayed fine powders are spherical in shape but with low crystallinity, so post-annealing process at temperatures ranging from  $600$  to  $900^\circ C$  in inert or slightly reductive atmosphere is necessary. However, during calcination spherical morphology was changed [86].

## 4. Other synthesis routes

Apart from the above-mentioned methods that are already established at various research groups as preparation methods for obtaining well-ordered  $LiFePO_4$  powders with olivine structure, the quest for new alternative methods continues. One of them is the freeze-drying method [91]. A solution containing citric acid, ferrous acetate, lithium hydroxide, and ammonium dihydrogen phosphate is drop-by-drop frozen under liquid nitrogen and subjected to the freeze-drying process. Thus obtained powder is calcined two times, at  $350$  and  $600^\circ C$ , and as a result  $LiFePO_4$ /carbon composite powder is obtained. The amount of carbon in the freeze-dried

sample has been estimated to 16 wt%, and the presence of nitrogen has also been detected. For better utilization of active material it is advisable to reduce the carbon content to a lower value [91]. Highly crystalline  $\text{LiFePO}_4$  material with single olivine phase has been successfully synthesized from amorphous  $\text{FePO}_4 \cdot 4\text{H}_2\text{O}$  using a solid–liquid phase reaction with  $(\text{NH}_4)_2\text{SO}_3$  as a reducing agent and subsequent thermal conversion [92]. Carbon-coated  $\text{LiFePO}_4$  with improved electrochemical performances has been obtained by mixing the above product with sucrose, and by heating the mixture in argon at  $700^\circ\text{C}$  [92]. Spherical micrometer particles of  $\text{LiFePO}_4$  can be obtained by KCl molten salt method [93]. In comparison with the conventional solid-state reaction, the molten salt method shows accelerated reaction rate and controllable particle morphology [93]. The particles synthesized using this method are large, with spherical morphology increasing tap density, but also leading to poor electrochemical performance.  $\text{LiFePO}_4$  nanoparticles with an average size of 300 nm have been synthesized by polyol process without further heating [94]. Iron(II) acetate, ammonium dihydrogen phosphate, and lithium acetate were added to tetraethylene glycol (TEG). The temperature of the solution was kept at  $320^\circ\text{C}$  for 16 h in a round-bottomed flask attached to a refluxing condenser. The resulting particles had various shapes with excellent discharge capacity at a small current rate [94]. Highly homogeneous nanocrystalline  $\text{LiFePO}_4/\text{C}$  composite can be prepared by pyrolyzing the  $\text{Li}^+ - \text{Fe}^{3+} - \text{PO}_4^{3-}$  polyacrylates in reductive atmosphere, which were prepared via *in situ* polymerization of  $\text{Li}^+$ ,  $\text{Fe}^{3+}$  and  $\text{PO}_4^{3-}$  acrylates [95]. A low-cost  $\text{LiFePO}_4/\text{C}$  composite synthesis method uses raw  $\text{Fe}_2\text{O}_3$  and Fe materials through rheological phase reaction under nitrogen atmosphere [96]. Another rapid route to form pure  $\text{LiFePO}_4$  phase is electric discharge assisted mechanical milling (EDAMM) [97]. EDAMM combines the benefits of producing fine, highly reactive particles via mechanical milling, with the accelerated calcination characteristics enabled by the use of electric discharges. However, thus obtained powder has considerably smaller discharge capacity ( $80 \text{ mAh g}^{-1}$ ), but has excellent cyclability.

## 5. Conclusions

Critical to the success of new cathode materials is their preparation, which controls the morphology, particle size and cation order. A major difficulty related to the synthesis of orthophosphate  $\text{LiFePO}_4$  comes from the existence of two oxidation degrees of iron in nature, namely Fe(II) and Fe(III), which makes the preparation of this material with reproducible electrochemical properties difficult. Solid-state chemistry has already established as conventional route for obtaining well-crystallized particles of  $\text{LiFePO}_4$  with ordered structure. Uncontrollable particle growth and agglomeration, associated with solid-state synthesis, can be partially suppressed by using mechanochemical activation. However, there is a need for new synthesis methods that reduce energy consumption, cost, and processing time. Alternatively solution chemistry methods are developing with highlights on hydrothermal synthesis and sol–gel method. It is most probably that hydrothermal synthesis will develop in commercially viable approach to the production of lithium iron phosphate powders.

Depending on the mode of preparation, different impurities can poison this material [67]. It was found that these impurities are often “invisible” for X-ray powder diffraction analyses, either because of their noncrystalline nature, or due to their nanometer size [16]. Mössbauer spectroscopy is more sensitive than the diffraction method to impurities with different valence states of Fe, because it is not based on coherent interaction with the periodic potentials of the lattice but involves direct scrutiny of the electronic states around Fe atoms [98,20]. Magnetic measurements are beneficial for detecting ferric and/or ferrous nano-sized impurities, and

are a sensitive tool to quantify clustering effects [26,67,99]. Another question that arises is: how to detect nonmagnetic impurities, such as  $\text{Li}_3\text{PO}_4$ , when their concentration is too small to be detectable by XRD. Raman or FTIR spectroscopic methods are unavoidable techniques to detect such impurities [16]. Therefore the combination of the above-mentioned techniques is required for both phase purity check and the investigation of the structural properties at any length scale.

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