CATHODE MATERIALS BASED ON OLIVINE LITHIUM IRON PHOSPHATES FOR LITHIUM-ION BATTERIES

S.A. Novikova and A.B. Yaroslavtsev
Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Leninsky Pr. 31, Moscow, 119991, Russia

Received: March 10, 2016

Abstract. This review addresses the description of the state-of-the-art and recent studies on cathode materials based on olivine lithium-iron phosphates for lithium-ion batteries. Specific features of the crystalline structure of LiFePO$_4$ and principal synthetic methods for the preparation of cathode materials based on LiFePO$_4$ are considered. Electrochemical characteristics of cathode materials such as discharge capacity, charge-discharge rates, and power density of lithium-ion batteries can be substantially improved by the use of nanoscale materials, particles with a special morphology, porous materials with a hierarchical structure, preparation of composite materials containing oxides or ionic conductors, deposition of carbon coatings, and doping with different cations.

1. INTRODUCTION
Lithium-ion batteries (LIBs) are widely used in diverse modern portable devices such as laptops, mobile phones, cameras, videocameras, wireless devices, etc. Moreover, LIBs are considered as energy cells for electrically driven and hybrid cars [1-4]. Cathode materials are the basic components of LIBs [5-7], and their synthesis and characterization present the subject of numerous studies. Modern cathode materials should satisfy various requirements, among which reversibility of high capacity of intercalation of lithium ions, high electropositive potential with respect to the anode based on carbon or silicon are the most important [1]; other requirements also include compatibility with an electrolyte and slight volume variations in the course of intercalation/deintercalation process [1,4,8]. Furthermore, high ionic and electron conductivity is the necessary condition which provides high charge/discharge rates of LIBs because these processes are accompanied by the transfer of lithium cations and electrons within the bulk of the cathode materials.

Olivine phosphates LiMPO$_4$ (M = Fe, Mn, Co, Ni) are acknowledged as promising cathode materials. In this connection, lithium iron phosphates are of special importance due to their low cost, safety, invariable working potential of ~3.4 V, and relatively high capacity which approaches theoretical values (170 mA h/g) at low charge-discharge rates [3,9]. However, these materials have evident drawbacks, and the principal drawback is related to their low conductivity which prevents their successful use in the devices requiring high peak power [10-12]. Phosphates like LiMPO$_4$ (M = Mn, Co, Ni) can be considered as advanced materials for high-voltage cath-
odes. For example, redox potential of Mn$^{2+}$/Mn$^{3+}$, Co$^{2+}$/Co$^{3+}$ and Ni$^{2+}$/Ni$^{3+}$ is equal to 4.1 V, 4.8 V, and 5.2 V (with respect to Li/Li$^+$), respectively [13,14]. However, high operating voltage typical for cobalt and nickel conflicts with liquid electrolytes because, at high voltage, oxidation of solvents traditionally involved in the electrolyte commences. Furthermore, electrical conductivity of LiMPO$_4$ (M = Mn, Co, Ni) is even lower than that of LiFePO$_4$[15-17].

In recent years, marked progress in the development of new approaches to the synthesis and modification of cathode materials based on LiFePO$_4$ and LiFe$_{1-x}$Mn$_x$PO$_4$ (0 < x < 1) has been achieved. This breakthrough makes it possible to overcome the barriers related to the low conductivity of the above materials. At the present time, cathode materials based on LiFePO$_4$ are commercially available, and their market is constantly expanding. This review addresses the state-of-the-art of the studies on cathode materials based on olivine lithium iron phosphates.

2. LITHIUM IRON PHOSPHATE

LiFePO$_4$ AS A CATHODE MATERIAL FOR LIBS

Electrochemical activity of olivine LiFePO$_4$ was discovered in 1997 by Googenough et al. [9]. Their studies revealed the intercalation of 0.6 lithium ions per LiFePO$_4$ formula unit which corresponds to a capacity of ~110 mAh/g. Lithiated (LiFe$^{II+}$PO$_4$) and delithiated (Fe$^{III+}$PO$_4$) forms are stable and slightly soluble in each other. Hence, according to the phase rule, the operating voltage varies slightly upon charge/discharge cycles and equal to ~3.4 V (Fig. 1), and charge/discharge proceeds via the heterogeneous grain model [9,12].

According to the recent publication [18], capacity of these materials can approach the theoretical limit (170 mAh/g) [18]. LiFePO$_4$ offers substantial advantages over existing cathode materials for LIBs such as its relatively low cost, high chemical stability, safety and high theoretical capacity [2]. However, this theoretical level is attained upon cycling with C/20-C/2 rates [18-21] (In this case, cycling rate C/x means that charge or discharge of the battery is accomplished within x hours). As current density increases, discharge capacity decreases dramatically. This plummeting of capacity with increasing current density is reversible and provided by kinetic factors [12].

The drawbacks of LiFePO$_4$ are concerned with their low electron and, primarily, ionic conductivity which markedly prevents the practical use of the related batteries for the devices operating at high on-peak voltage [11,12,22-24]. At ambient temperature, electron conductivity of this material, by its order, corresponds to $10^{-9}$ Ohm$^{-1}$*cm$^{-1}$; according to the data obtained by different authors using diverse experimental methods such as impedance spectroscopy, cyclic voltammetry, and galvanostatic intermittent titration, the diffusion coefficient of lithium ions is equal to $~10^{-14}$-$10^{-16}$ cm$^2$/s [11,25-28].

Low level of ionic conductivity of LiFePO$_4$ is provided by the specific features of its crystalline structure. LiFePO$_4$ crystallizes in orthorhombic modification. The resultant crystalline structure is a three-dimensional framework composed of distorted octahedrons of FeO$_6$ and tetrahedrons of PO$_4$ (Fig. 2). Each octahedron is connected to one tetrahedron by the edge along the b-axis and by two angles in the ab plane. Lithium ions are accommodated in one-dimensional channels where their transfer takes place [9]. In other words, in olivine materials, diffu-

![Fig. 1. Charge/discharge curves for LiFePO$_4$/C at C/8.](image1)

![Fig. 2. The olivine structure of LiFePO$_4$; showing the FeO$_6$ octahedra (dark grey), PO$_4$ tetrahedra (light grey), and the one-dimensional tunnels in which the lithium ions.](image2)
3. METHODS OF PREPARATION

In literature, numerous methods for the preparation of olivine lithium iron phosphates are described. The principal methods are listed below:

- **Solid-state synthesis** can be described as follows: reagents taken in strictly stoichiometric ratios are subjected to a stepwise thermal treatment in an inert atmosphere [31,32]; [31,32];

- **Microwave synthesis** involves heating of the mixture of precursors by electromagnetic microwave irradiation, thus reducing duration and temperature of synthesis [33];

- **Solvothermal synthesis** is based on the ability of water or some other solvents, for example, ethyleneglycol, to dissolve virtually insoluble substances at high pressures and temperatures. The reaction is performed in an argon-filled autoclave. Once the reaction mixture is cooled down to room temperature, the product is filtered, rinsed, and dried [34,35];

- In the case of co-precipitation synthesis, solutions containing initial reagents in required ratios are mixed, and the formed precipitate is filtered, rinsed with water, dried in vacuo, and annealed in an inert atmosphere [36]. One option of this approach is concerned with the following procedure: at the first stage, insoluble compound of the transition metals, for example, iron-manganese oxalate, are precipitated; then, this compound is sintered with lithium salt or hydroxide [37];

- **Sol-gel method** is based on the dissolution of stoichiometric amounts of initial reagents, often with chelating agents, and subsequent variations in the reaction conditions leading to the formation of an amorphous gel. The as-prepared gel is dried and annealed at high temperatures in an inert atmosphere (argon) [38,39];

- **Template synthesis** is performed under specific factors of spatial constraints which make it possible to control structure and morphology of the formed phase via the use of a given template. The templates for the synthesis of the LiFePO₄-based materials are the following: inorganic matrices, which are later removed by dissolution, for example, nanostructured silicon oxide [40], or hollow microspheres of Li₂PO₄, which later interact with the transition metal cations under hydrothermal conditions [41,42].

All the above-listed methods can be divided into two basic groups depending on the case whether the reagents are mixed in a solid or in a liquid state. The benefits of the solid-state synthesis are concerned with its simplicity and no troubles related to the processing of liquid reagents. However, this method requires the use of relatively high annealing temperatures. The advantages of liquid-phase methods are related to mixing of reagents at the molecular level in the solutions. Hence, this process takes place at lower annealing temperatures and allows development of small-sized particles. In some works, synthesis is performed in the presence of surfactants, for example, oleic acid [43,44] or cetyltrimethylammonium bromide (CTAB) [45], and this approach, similar to template methods, makes it possible to produce particles with a desired morphology.

Another tendency of modern chemistry is related to the use of biological molecules and organisms in the course of synthesis [46]. This tendency is highlighted in the works on synthesis of electrode materials with the use of proteins, viruses, DNA, peptides [47-50] or spirulina [51] as templates for the preparation of the materials with a desired morphology.

4. PREPARATION OF MATERIALS WITH SPECIFIC MORPHOLOGY OF LiFePO₄

Particles size and shape of particles as well as surface area and porosity of cathode materials are among important parameters that control the resultant electrochemical performance. Liquid [52,53] and solid electrolytes [54] used in LIBs are characterized by sufficiently high conductivity. Therefore, charge/discharge rate of lithium ion batteries is primarily governed by the diffusion rate of lithium ions and electrons in a solid phase. As particle size is reduced, the diffusion path length of charge carriers decreases and the rate of diffusion processes is accelerated. Hence, for cathode materials with a comparatively low conductivity, the charge/discharge rate markedly increases with decreasing particles size because charge transfer in the interface proceeds with a higher rate as compared with the bulk [4,55,56]. Moreover, as the particle size decreases, the fraction of near-surface atoms increases. Diffusion of atoms and ions in the surface layers of solids also proceeds with higher rates as compared with the diffusion in bulk due to uncompensated bonds [57,58] and increased concentration of defects [59]. Therefore, for high-performance cathode materials, reduced size of particles seem to be ad-
Fig. 3. SEM images with different magnification (a,b) of the LiFePO$_4$ particles synthesized by solvothermal method.

Fig. 4. High magnification SEM image of an individual LiMn$_{0.5}$Fe$_{0.5}$PO$_4$/C sphere, adapted from [72].

Vantageous as this factor provides higher surface area and a shorter diffusion path. Noteworthy is that this approach proved to be the most efficient for the materials with low conductivity, including olivine materials. In this connection, much effort is focused on the development of new synthetic approaches for the preparation of finely dispersed materials based on LiFePO$_4$ [31-44,60-64]. All basic synthetic approaches to the synthesis of the LiFePO$_4$-based cathode materials were considered in the previous section [31-44].

As the particle size decreases, discharge capacity increases and cycling performance at higher current density is improved [62-64]. According to the published data on nanosized cathode materials based on LiFePO$_4$ and carbon, discharge capacity of the best materials at low charge/discharge rates approaches the theoretical limit. Incorporation of carbon additives, on one hand, increases electrical conductivity of the material and, on the other hand, prevents the occurrence of agglomeration processes. For example, according to [62], discharge capacity is equal to 160 mAh·g$^{-1}$ at the C/5 discharge rate and higher and to 120 mAh·g$^{-1}$ at the 5 C discharge rate. According to [64], discharge capacity of LiFePO$_4$/C is equal to 166.9 mAh·g$^{-1}$ at a current of 0.1 C and to 142.3 mAh·g$^{-1}$ at a current of 10 C.

Therefore, reduced dimensions of particles provide an efficient route how to shorten the diffusion path length and to improve both surface area and diffusion rate of Li$^+$ in the cathode materials. Moreover, porosity of cathode materials is of great importance as this parameter allows one to improve penetration of an electrolyte to the electrode surface [21,42,65-67]. For example, according to [66], discharge capacity of nanoporous LiFePO$_4$ containing micronic particles is higher as compared with the discharge capacity of nanosized LiFePO$_4$.

Materials composed of particles with a specific morphology (nanosheets, nanorods, nanotubes, nanofilaments) and hierarchical structures composed of nanoscale modules offer substantial benefits for the development of high-performance cathode materials. In this case, as compared with bulk material, the diffusion path length of lithium ions decreases, the contact with the electrolyte is improved, and diffusion of lithium ions is facilitated; at the same time, as compared with nanoparticles, the tendency for aggregation is diminished [68].

For the materials with volume anisotropy of diffusion of lithium cations, especially, for one-dimensional diffusion as in the case of LiFePO$_4$, preparation of particles with a given shape and size along certain crystallographic axes provides an effective tool for the improvement of discharge capacity.
and cycling performance. In this case, the necessary condition is concerned with the minimum diffusion path length of Li\(^+\) along diffusion channels [010], where one-dimensional diffusion of lithium cations in the crystal proceeds. The desired morphology can be attained via solvothermal synthesis when ethylene glycol is used as a solvent [35,69-71] or when oleic acid is used as a surfactant [43,44]. Fig. 3 shows the SEM images of LiFePO\(_4\) nanosheets prepared via solvothermal synthesis. Olivine materials based on LiFe\(_{1-x}\)Mn\(_x\)PO\(_4\) (x = 0-1) with [010] facet-oriented nanoplatelets are characterized by improved discharge capacity at high charge/discharge rates [69-71]. Even at high cycling rates, the cathode materials based on LiFePO\(_4\) nanosheets preserve their high performance and their discharge capacity is about 60 mA h/g at 30 C [70].

Hierarchical structure of LiMn\(_{1/2}\)Fe\(_{0.5}\)PO\(_4\) prepared via the template method presents hollow spheres with dimensions varying from 400 nm to 1 µm. These hollow spheres are composed of aggregated carbon-coated particles with a particle size of 50 nm (Fig. 4). Discharge capacity of this material is equal to 159.3 mA h/g and 80.6 mA h/g at 0.1 C and 20 C rates, respectively [72].

5. FORMATION OF COMPOSITE MATERIALS

One of the promising methods for the improvement of conductivity is the development of composite materials (heterogeneous doping). In this case, depending on the type of a heterogeneous additive, either electron or ionic conductivity increases. For composites, improvement in ionic conductivity can be achieved by the formation of additional point defects at interfaces. Heterogeneous doping by inert oxides (finely dispersed alumina, silica, etc.) are widely used to improve conductivity of solid electrolytes [73], for example for silver iodide [74] and acid sulfates [75-77]. Noteworthy is that the maximum gain in conductivity can be achieved at relatively low concentrations of the oxide phase [77]. At low concentrations of the oxide phase, conductivity increases due to the formation of a highly conducting double electric (Debye) layer on the grain boundary between the salt and oxide. At a certain concentration of the oxide phase (percolation threshold), a continuous contact between doping particles is attained and the resultant conductivity approaches the maximum level. Near the critical concentration, conductivity of the system dramatically decreases due to the blocking effect of oxide particles [78,79].

At the present time, a relatively small number of publications on the deposition of oxides [79-85] or ion-conducting coatings [86-88] onto the surface of LiFePO\(_4\) particles are available. For example, the results on the effect of LiFePO\(_4\) surface coating by silica were reported in [81]. The composite was prepared via hydrolysis of tetraethoxysilane in the presence of LiFePO\(_4\). As a result of this modification, discharge capacity increases, rate capability is improved, and bulk resistance of the battery based on this cathode material decreases. Due to modification of LiFePO\(_4\) by ceria, cycling stability of the material increases and discharge capacity at low temperatures is improved [82]. For the composite based on LiFePO\(_4\) with the CuO-modified surface, discharge capacity increases, in particular, for the charge/discharge runs at high currents (1 C) [83]. The data on improved discharge capacity can be found in [86] for the cathode material based on LiFePO\(_4\) containing lithium-titanium phosphate with the NASICON structure which is characterized by high ionic conductivity.

Most publications on the formation of the LiFePO\(_4\)-based composites address the materials containing electronic conducting additives, including such polymers as polyaniline or polypyrrole [89-92] and different types of carbon (amorphous carbon, graphite, graphene, carbon nanotubes) [93-99]. In addition to high electrical conductivity, the benefits of the carbon-based additives are related to their low cost and availability. The sources of carbon are carbohydrates [100-102], resins [35,103], carboxylic acids [104-107], poly(vinyl alcohol) [108], organophosphonic acids [109], and hydrocarbons [110-112]. Particles of active materials are coated with carbon by deposition of the carbon source onto a precursor of the cathode material followed by further thermal decomposition in an inert medium [100-102,110] or by chemical vapor deposition (CVD) [110-112].

The formation of carbon-containing composites provides an efficient strategy for the improvement in electrical conductivity of the cathode materials. In addition to the advantages related to enhanced electrical conductivity, incorporation of additives prevents sintering of particles upon annealing and assists the formation of a finely dispersed material. A thin carbon layer provides an efficient transport of electrons without blocking access for lithium ions [113]. Fig. 5 shows the TEM images of the carbon-coated LiFePO\(_4\)/C (thickness of the deposited carbon layer is 1.5-2 nm) [114]. Discharge capacity of the as-prepared material approaches the theoretical level.
at low charge/discharge rates (168 mA h/g at 0.6 C), and high discharge capacity is preserved up to high rates (90 mA h/g at 60 C).

For the carbon-containing composites, the optimum content of carbon was estimated. This value depends on microstructure and operating conditions but, as a rule, it equals 4-12% wt.% [21,43,44,115-117].

In some works, sintering of cathode material particles can be additionally prevented by the incorporation of anti-agglomerating additives, for example, polyvinylpyrrolidone [37,44] prior to the heat treatment. As a result, the overall surface area of the material increases, and the contact with electrolytes is improved. Carbon nanotubes can also be used in order to improve electrical conductivity and to reduce the LiFePO$_4$ particle size, thus providing their uniform size distribution [118].

For the preparation of carbon-containing composites, the type of carbon modification also plays an important role because, for example, graphite ($sp^2$-hybridization) is usually characterized by a higher conductivity. Therefore, carbon coatings based on graphite seem to be advantageous [35,119-121].

6. ISOVALENT AND HETEROVALENT DOPING

Doping with different metal cations is a well-known approach how to improve bulk conductivity of the materials. This approach is based on the formation of additional point defects in the bulk of solid electrolytes as, in these systems, ion transfer proceeds via migration of defects [122]. In this case, the preferred case involves incorporation of doping cations into iron sites within LiFePO$_4$, because occupation of lithium sites suppresses ion transport processes [123,124]. With respect to the cathode materials, this approach appears to be efficient and, in some cases, rate capability is improved with high capacity maintaining [31,123,125-141].

Doping with divalent cations (isovalent doping) proved to be best-studied and most efficient option of this approach [126-141]. When a dopant is not electrochemically active, optimum characteristics are attained at a low dopant content (2-10%). For example, for LiFe$_{1-x}$Mg$_x$PO$_4$/C ($x = 0.00, 0.02, 0.04, 0.06$, and $0.08$), the best composition was shown to contain 4% of Mg [139].

In some cases, partial substitution of iron sites makes it possible to increase the working potential due to electrochemical activity of doping metals and, as a result, the power density of the cathode material increases. At the same time, the total capacity is comparable with that of undoped sample? For example, the manganese-doped samples show an additional step at ~4.1 V [37,42-44]. Fig. 6 presents the charge/discharge curves of the LiFe$_{0.7}$Mn$_{0.3}$PO$_4$/C sample [141].

Incorporation into LiFePO$_4$ of other than divalent cations (heterovalent doping) is less studied [22,142-149]. In some publications, heterovalent doping was shown to improve electrochemical characteristics of LiFePO$_4$ [142,145,147-149].

The published data on the available sites within the LiFePO$_4$ structure for the incorporation of doping cations seem to be contradictory. Doping cations can be incorporated either at lithium or iron sites [147-157]. According to [22,146], substitution of some lithium sites in LiFePO$_4$ by cations with
higher than unity valence leads to an increase in electrical conductivity. While, according to [147,151,152] incorporation of trivalent cations proceeds into Fe site and results in the ionic conductivity increase. Compensation of excessive positive charge due to incorporation of cations with a higher valence into the structure of LiFePO$_4$ was explained by different models - from the formation of negatively charged vacancies at lithium or iron sites to the incorporation of additional electrons. The most probable reason of this substitution is the formation of vacancies at lithium sites [147], which provide the increase in ionic conductivity of LiFePO$_4$. At the same time, some information on the incorporation of doping ions into lithium or iron sites seems to be poorly justified. In many cases, the conclusions are based only on the data on the initial loading of the components.

Doping was also shown to improve the operation of the materials at high currents at high charge/discharge rates [158]. The comparison of mass transfer rates in the doped and nonsubstituted lithium-iron phosphate was reported in [148,159]. This analysis shows that the diffusion coefficient increases from $2.9 \times 10^{-11}$ to $1.86 \times 10^{-10}$ cm$^2$/s for LiFe$_{1-x}$V$_x$PO$_4$ and from $5.68 \times 10^{-15}$ to $3.90 \times 10^{-14}$ cm$^2$/s for LiFe$_{0.9}$Mn$_{0.1}$PO$_4$/Fe$_5$P.

In many cases, interpretation of doping effects can be challenged by the effect of doping on microstructure and morphology because variations in the composition can induce changes in the microstructure of the material. For example, upon doping of LiFePO$_4$ with cobalt and manganese cations, conductivity was shown to increase and this increase has a positive effect on the electrochemical characteristics. At the same time, a tendency of particles for agglomeration is observed that has a negative effect on the electrochemical performance of the materials [130,141].

7. CONCLUSIONS

The data presented in this review highlight the keen interest of researchers to the materials based on lithium iron phosphates with olivine structure. These materials are gradually invading the domain of cathode materials for lithium ion batteries. The advantages of lithium iron phosphates are primarily related to their low cost, safety, stability, and relatively high capacity. Numerous methods of their modification offer diverse routes leading to the improvement in their performance and, especially, providing high discharge capacity at high charge/discharge currents. In the nearest future, progress in this direction will extend the boundaries of their practical application.

ACKNOWLEDGEMENTS

This work is supported by the Russian Foundation for Basic Research, project no. 14-08-31599.

REFERENCES


Cathode materials based on olivine lithium iron phosphates for lithium-ion batteries


