Research Progress in Improving the Rate Performance of LiFePO$_4$ Cathode Materials

Sixu Deng[1], Hao Wang[1,*], Hao Liu[2], Jingbing Liu[1], Hui Yan[1]

Abstract: Olivine lithium iron phosphate (LiFePO$_4$) is considered as a promising cathode material for high power-density lithium ion battery due to its high capacity, long cycle life, environmental friendly, low cost, and safety consideration. The theoretical capacity of LiFePO$_4$ based on one electron reaction is 170 mAh g^{-1} at the stable voltage plateau of 3.5 V vs. Li/Li$^+$. However, the instinct drawbacks of olivine structure induce a poor rate performance, resulting from the low lithium ion diffusion rate and low electronic conductivity. In this review, we summarize the methods for enhancing the rate performance of LiFePO$_4$ cathode materials, including carbon coating, elements doping, preparation of nanosized materials, porous materials and composites, etc. Meanwhile, the advantages and disadvantages of above methods are also discussed.

Keywords: LiFePO$_4$; Lithium ion battery; Rate performance

Introduction

In recent years, one of the greatest challenges is to make use of renewable energies to deal with the limited oil storage and global warming threats [1]. The development of electric vehicles (EVs) and plug-in hybrid electric vehicles (PHEVs) is imperative. Currently, challenges remain in designing and manufacturing high safety, high performance and low cost rechargeable batteries for vehicle applications. The large scale lithium-ion batteries (LIBs) have become the prime candidate for the next generation of EVs and PHEVs because of its high operative voltage and energy density [2, 3]. For LIBs, the cathode material has significantly impact on battery capacity, cycle life, safety and cost, on which a lot of attentions are drawn. Since the olivine LiFePO$_4$ was reported by Goodenough and coworkers in 1997 [4], it has been considered as the most promising cathode candidate for the next generation large-scale LIBs used in PHEVs or EVs, because of its in-herent merits including low toxicity, low material cost, flat voltage profile, long cycle ability and high safety compared to other cathode materials including LiCoO$_2$, LiMn$_2$O$_4$, and Li(NiCoMn)O$_2$ etc. [5-7]. Meanwhile, the olivine LiFePO$_4$ exhibits reversible electrochemical lithium insertion/extraction reactions at about 3.5 V (vs. Li/Li$^+$) with a theoretical capacity of 170 mAh g^{-1} [8]. However, with the deepening of the study, researchers find that the pristine LiFePO$_4$ exhibits poor rate capacities. The low intrinsic electronic conductivity and low Li$^+$ diffusion coefficient of LiFePO$_4$ are the main shortcomings that limits its electrochemical performance and commercial applications of LiFePO$_4$ [9]. At room temperature, bare LiFePO$_4$ is an insulating with an electrical conductivity of about 10^{-9} to 10^{-10} S cm^{-1}, which is much lower than that of LiCoO$_2$ (about 10^{-3} S cm^{-1}) and LiMn$_2$O$_4$ (2×10^{-5} to 5×10^{-5} S cm^{-1}) [10-12]. Meanwhile, the intrinsic ionic diffusion coefficient is found to be as low as 10^{-13} (LiFePO$_4$) to 10^{-16} (FePO$_4$) cm^2 s^{-1} depend-

[1]The College of Materials Science and Engineering, Beijing University of Technology, Beijing 100124, China
[2]Chengdu Green Energy and Green Manufacturing Technology R&D Centre, Chengdu 610207, China
*Corresponding author: E-mail: haowang@bjut.edu.cn

ing on the Li^+ concentration and the characterization method such as the electrochemical impedance spectrometry. It should be noted that the diffusion coefficient calculated is related to the state of charge and on the composition of Li_xFePO_4 [13]. Obviously, such a diffusion coefficient is also lower than that of $LiCoO_2$ (about 5×10^{-9} cm^2 s^{-1}) [14]. Hence, how to overcome these drawbacks has become an important factor of study.

Structure of pristine LiFePO₄

The olivine structure of $LiFePO_4$ belongs to the family of lithium ortho-phosphates which is shown in Fig. 1. Its space group is Pnma. The lattice parameters are a = 10.33 Å, b = 6.01 Å, c = 4.69 Å and V = 291.2 $Å^3$. The O atoms occupy a slightly distorted, hexagonal-close-packed arrangement. The P atoms are located in tetrahedral sites; and the Fe and Li atoms are located in octahedral 4a and 4c sites, respectively. A corner-shared FeO_6 octahedron shares edges with two edge-shared LiO_6 octahedrons and a PO_4 tetrahedron. It is notable that the delithiated phase $FePO_4$ has essentially the same structure as $LiFePO_4$. This structural similarity not only avoids capacity degradation resulting from severe volumetric changes during the charge-discharge process, but also effectively compensates the volume changes of the carbon anode during lithiation and delithiation. This explains the excellent electrochemical cyclability of the system to some extent [15]. However, in this structure, there is only one-dimensional tunnel formed by the edge shared Li octahedra, where the Li^+ are mobile in this tunnel. These one-dimensional channels are easily blocked by defects and impurities, which may hinder the ion diffusion rate of Li^+, resulting in the poor ion conductivity of $LiFePO_4$. Meanwhile, such structure cannot form a continuous FeO_6 network, leading to low intrinsic electronic conductivity [16].

Obviously, the low electronic and ionic conductivities seriously restrict the rate performance of $LiFePO_4$. In recent years, various methods have been proposed to solve these problems in order to improve its performance.

Approaches to improve the rate performance of LiFePO₄

Carbon coating

Carbon coating on the $LiFePO_4$ particles is one of the most important techniques to improve its electrochemical performance with respect to the specific capacity, rate performance, and cycling life [18-22]. The main role of carbon coating is to increase the electronic conductivity on the surface of $LiFePO_4$ particles [23]. Meanwhile, carbon coating reduces the particle size and alleviates to aggregation of $LiFePO_4$ particles by inhibiting particle growth [24-27]. In addition, carbon can play the role of a reducing agent, avoiding the oxidation of Fe^{2+} to Fe^{3+} during sintering and thus simplify the atmosphere requirement during synthesis [28, 29]. The beneficial effect of carbon coating has been observed varying depending on the structure, precursor, uniformity, loading and thickness of the coating [30-32]. Different carbon sources have different effects on the electrochemical properties of $LiFePO_4$.

The conventional synthesis route, in which the carbon source materials are simply mixed together with $LiFePO_4$ precursor, yields a non-uniform distribution of carbon in the final $LiFePO_4$/C products. Recently the chemical synthesis routes are widely adopted to achieve homogeneous carbon coating around the surface of

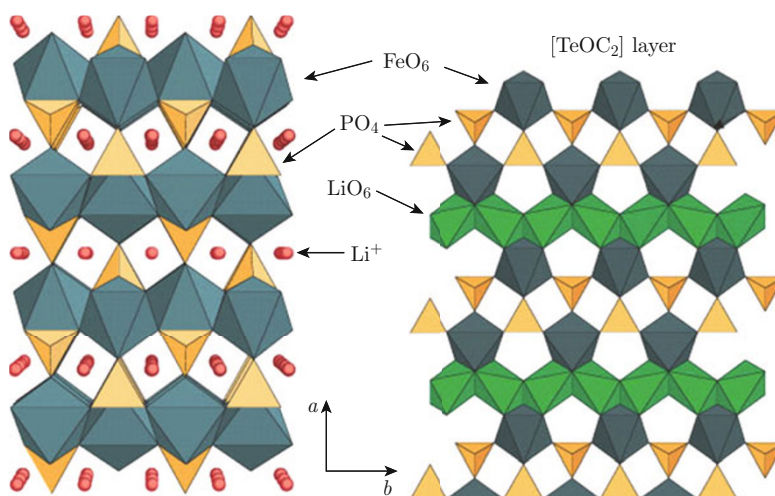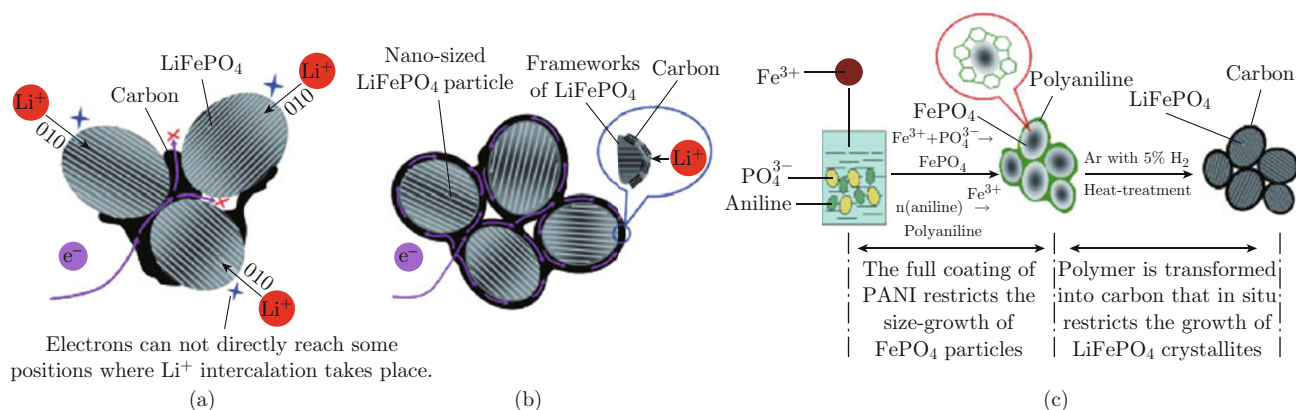Fig. 1   The crystal structure of olivine $LiFePO_4$ in projection along [001] [17].

Fig. 2 (a) Electron-transfer pathway for LiFePO$_4$ particles partially coated with carbon. (b) Designed ideal structure for LiFePO$_4$ particles with typical nano-size and a complete carbon coating. (c) Preparation process for the LiFePO$_4$/carbon composite including an *in situ* polymerization reaction and two typical restriction processes [35].

LiFePO$_4$ particles. Nazar *et al.* [33] prepared LiFePO$_4$-conductive carbon by polymerization of resorcinol-formaldehyde and then heated at 700℃ for 10 h under flowing N$_2$. The discharge capacity reached about 120 mAh g^{-1} at 5 C. Zhao *et al.* [34] synthesized core-shell LiFePO$_4$/C composites from FePO$_4$/C precursor. They used a chemical vapor deposition (CVD) assisted solid-state route with polyvinyl alcohol (PVA) and benzene vapor as the reducing agent and carbon source. The LiFePO$_4$ particles were encapsulated within thin graphite shell with a thickness of 3 nm, which prevented the agglomeration of the LiFePO$_4$ and improved the conductivity of the whole electrode materials. The composites exhibited a high specific capacity of 115 mAh g^{-1} at discharge rate of 5 C. However, generally the polymers are difficult to be dissolved and dispersed, which will lead to inhomogeneity in the process of carbon coating. In order to solve these problems, Wang *et al.* [35] prepared a LiFePO$_4$/C composite by an *in situ* polymerization restriction method, formed from a highly crystalline LiFePO$_4$ core with a size of about 20-40 nm and a uniform semi-graphitic carbon shell with a thickness of about 1-2 nm (Fig. 2). Aniline was polymerized *in situ* on the outer surface of the newly generated FePO$_4$ precipitate to form a green polyaniline shell that can effectively restrict the growth of the FePO$_4$ particles. The unique structure combined with its full coating of conductive carbon, effectively enhanced the electrochemical performance of LiFePO$_4$. The as-prepared LiFePO$_4$/C composite delivered a capacity of 90 mAh g^{-1} at the rate of about 60 C.

In addition to using polymer, various sugar and organic carboxylic acids are also adopted as the carbon precursor. A LiFePO$_4$/C composite synthesized by adding sugar before the heating steps was reported by Dahn *et al.* [36]. The particles of LiFePO$_4$/C were of uniform size and well coated by carbon. These characteristics apparently assured LiFePO$_4$/C of a good rate capability. The capacity of LiFePO$_4$/C showed 125 mAh g^{-1} even at 5 C discharge rate. Zhang *et al.* [37] reported a LiFePO$_4$/C composite cathode synthesized via a mechanochemical activation/sintering process by adopting citric acid as the carbon source. The formation of carbon consisted of two processes *i.e.* pyrolysis of carbon precursor to CH$_x$ and subsequent formation of carbon. Compared with different carbon contents, the cathode with 6.0 wt% citric acid showed the highest initial rate discharge capacities of 92 mAh g^{-1} at 20 C. Manthiram *et al.* [38] synthesized highly crystalline LiFePO$_4$ nanorods via a rapid microwave-assisted solvothermal approach employing tetraethyleneglycol as the solvent. Then they adopted an ex situ coating of carbon by heating the nanostructured LiFePO$_4$ with sucrose in 2% H$_2$-98% Ar at 700℃ for 1 h. The as-prepared LiFePO$_4$/C possessed excellent rate capability of 110 mAh g^{-1} at discharge rate of 10 C, which could be attributed to the formation of highly crystallized sp^2 carbon. Manthiram's group also presented a one-pot microwave-assisted hydrothermal method to synthesize carbon-coated LiFePO$_4$ with a more uniform particle size (220-225 nm). The carbon coating was uniform and found to be 5-12 nm in thickness, which uniformly cover the surface of LiFePO$_4$ (Fig. 3). The composite exhibited high capacity with excellent cyclability and rate capability, which reached at 110 mAh g^{-1} at discharge rate of 10 C [39].

Other carbon sources are also studied. Sides *et al.* [40] reported a new type of template-prepared nanostructured LiFePO$_4$ electrode. This electrode consisted of uniformly dispersed nanofibers of the LiFePO$_4$ electrode material mixed in an electronically conductive carbon matrix. Because of this unique nanocomposite morphology, these electrodes delivered high capacity of 150 mA h g^{-1} at a rate of 5 C. Meanwhile, even at rates exceeding 50 C, these electrodes still maintained a substantial fraction of the theoretical capacity. Due to the conductive carbon matrix, this new nanocomposite electrode solved the problem of the inherently poor

electronic conductivity of LiFePO$_4$.

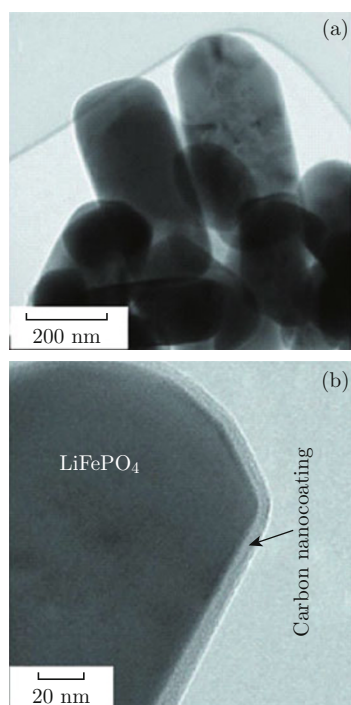Fig. 3 TEM image of LiMPO$_4$/C nanocomposites obtained by the MW-HT process after heat-treatment at 700℃ for 1 h: (a) TEM image of LiFePO$_4$/C, (b) HRTEM image of LiFePO$_4$/C [39].

So far, the application of carbon coating on the LiFePO$_4$ particle surface by various strategies is the most effective way to increase the conductivity of LiFePO$_4$. However, some authors find that carbon coating still have some disadvantages, including reduced tap density and high production costs, which may cause low energy density and high energy cost of the battery [41]. Meanwhile, the high rate capacity and cycling stability of LiFePO$_4$/C materials are still dissatisfactory [42].

Doping

Carbon coating is an efficient way to enhance the conductivity between particles [33, 36, 43]. However, this method obviously has little effect on the chemical diffusion coefficient or lattice electronic conductivity of lithium within the LiFePO$_4$ crystal [44]. The doping of heterogeneous ions, at either cation (Li$^+$ and Fe^{2+}) or anion (O^{2-}) sites of LiFePO$_4$, can greatly improve the intrinsic electronic conductivity of materials in terms of capacity delivery, cycle life, and rate capability [45-48].

Li site doping

Many studies have demonstrated that Li-site doping can cause LiFePO$_4$ lattice defects, which is conducive to the proliferation of Li-ion [9]. The Li-site doping with

supervalent cations was inspired by Chung et al. [10]. They prepared Li$_{1-x}$M$_x$FePO$_4$ samples by the solid-state reaction, with the dopant (M = Mg^{2+}, Al^{3+}, Ti^{4+}, Zr^{4+}, Nb^{5+} or W^{6+}) being added as a metal alkoxide. It suggested that, using supervalent cations to replace the Li-site, lead to the co-existence of Fe^{2+}/Fe^{3+} mixed valent phases. LiFePO$_4$ was charged and discharged in structure between p-type phase and n-type phase according to the variation of Fe^{2+}/Fe^{3+} proportion. Li$_{0.99}$M$_{0.01}$FePO$_4$ showed electrical conductivity at room temperature that was a factor of $\sim$10^8 greater than undoped LiFePO$_4$, and absolute values >10^{-3} S cm^{-1} over the temperature range of –20℃ to +150℃, which was shown in Fig. 4. As shown in Fig. 4, the doped electrode materials exhibited well rate performance, with discharge capacities over 60 mAh g^{-1} at 21.5 C rate.
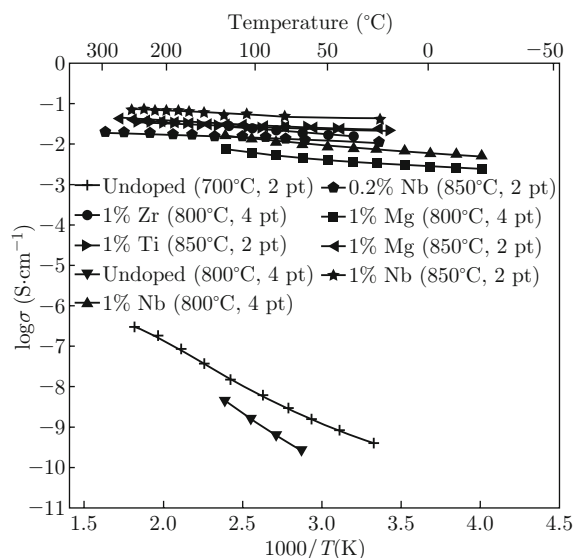

Fig. 4 The electrical conductivity of doped olivines of stoichiometry Li$_{1-x}$M$_x$FePO$_4$ at room temperature [10].

However, the mechanism and effect of supervalent cation doping on electronic conductivity reported so far are still in controversy. Herle et al. [49] examined the Li$_x$Zr$_{0.01}$FePO$_4$ (x = 0.87 to 0.99) and found that percolating "nano-networks" of metal-rich phosphides within the grain boundaries of LiFePO$_4$ crystallites were responsible for the enhanced electronic conductivity. Delacourt et al. [50] were unsuccessful in Nb doping of LiFePO$_4$, instead, they formed crystalline β-NbOPO$_4$ and/or an amorphous (Nb, Fe, C, O, P) 'cobweb' around LiFePO$_4$ particles, which was responsible for superior electrochemical activity. The electronic conductivity of pure LiFePO$_4$ and LiFePO$_4$/β-NbPO$_4$ composites is $\sim$10^{-9} S cm^{-1} while that of Nb- and/or C-containing LiFePO$_4$ composites increase up to 1.6×10^{-1} S cm^{-1}. The first principle calculations by Ouyang et al. [51] showed that Li diffusion in olivine LiFePO$_4$ was one dimensional, thus even though the

Li-site doping could enhance the electronic conductivity, it did not improve the electrochemical performance for LiFePO$_4$ as cathode material. As the high valence heavy metal ions in the Li sites will block the one-dimensional diffusion pathways, the ionic conductivity is decreased, which is certainly harmful to the battery performance. An atomic-scale simulation by Islam *et al.* [16] suggested that, low favorable energies were found only for divalent dopants on the Fe site (such as Mg and Mn), and on energetic grounds, LiFePO$_4$ was not tolerant to aliovalent doping (*e.g.*, Al, Ga, Zr, Ti, Nb, Ta) on either Li or Fe sites.

Fe site doping

Similar to Li-site doping, Fe-site doping can also improve the electrochemical performance of LiFePO$_4$ by causing lattice defects [52, 53]. Wang *et al.* [54] reported Fe-site doped LiFe$_{0.9}$M$_{0.1}$PO$_4$ (M = Ni, Co, Mg) cathode materials with good rate performance and cyclic stability by solid-state reactions. The capacities of LiFe$_{0.9}$M$_{0.1}$PO$_4$ (M = Ni, Co, Mg) maintained at 81.7, 90.4 and 88.7 mAh g^{-1} under 10 C rate, respectively, in comparison with 53.7 mAh g^{-1} and 54.8 mAh g^{-1} for non-doped and carbon-coated LiFePO$_4$, respectively. Such a significant improvement in electrochemical performance should be partially related to the enhanced electronic conductivities (from 2.2×10^{-9} to $< 2.5 \times 10^{-7}$ S cm^{-1}) and Li$^+$ ions mobility in the doped samples. The Cr-doped LiFePO$_4$/C was synthesized by a mechanochemical process with the employment of planetary ball milling followed by a one-step heat treatment [55]. The LiFe$_{0.97}$Cr$_{0.03}$PO$_4$/C showed excellent rate performance, delivering a discharge capacity up to 120 mAh g^{-1} at 10 C. The synchrotron-based *in situ* X-ray diffraction (XRD) analysis indicated that Cr doping facilitated the phase transformation between triphylite and heterosite during cycling and thus improved the rate performances of LiFePO$_4$/C. Sun *et al.* [56] reported V-doped LiFePO$_4$/C cathode materials using a carbothermal reduction route. The V-doped LiFePO$_4$/C showed a high discharge capacity of $\sim$70 mAh g^{-1} at the rate of 20 C. This was attributed to the optimization of the morphology and the crystal microstructure by V-doping, which facilitates the Li$^+$ ion diffusion.

O site doping

Besides cation doping, anion doping is also expected as an effective way to enhance the electronic conductivity of LiFePO$_4$. Some researches select Cl$^-$ and F$^-$ as the substitution for O^{2-} anion [57]. Lu *et al.* [58] reported the F-doped LiFePO$_4$/C nanoparticles synthesized through a low-temperature hydrothermal reaction followed by a high-temperature treatment. The discharge capacities at different rates were 120.4 (5

C), 101.3 (10 C) and 90.5 (15 C) mAh g^{-1}, respectively. The cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were used to investigate the influence of F doping on the electronic conductivity of LiFePO$_4$ as shown in Fig. 5.
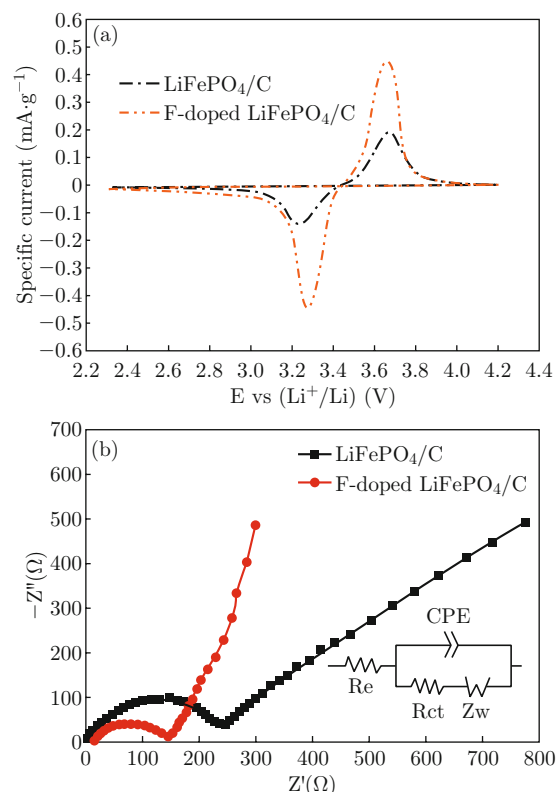

Fig. 5   The CV curves (a) and EIS (b) of un-doped and F-doped LiFePO$_4$/C samples [58].

XRD, X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR) analyses indicated that F-doping did not alter the crystal structure of LiFePO$_4$ phase. F-doping could improve the electric conductivity of LiFePO$_4$ cathode materials, which is considered beneficial to the Li$^+$ diffusion between LiFePO$_4$ phase and FePO$_4$ phase. The improved Li$^+$ ion diffusion could be attributed to the weakening of Li-O bonds resulting from introduction of F$^-$ into the lattice of olivine structure. Cl-doped LiFePO$_4$/C cathode materials were synthesized via a carbothermal reduction route by Sun *et al.* [59]. The Cl-doped LiFePO$_4$/C cathode materials presented a high discharge capacity of $\sim$90 mAh g^{-1} at the rate of 20 C. The results indicated that the optimized electrochemical reaction and Li$^+$ diffusion in the bulk of LiFePO$_4$ due to Cl-doping. The improved Li$^+$ diffusion capability was attributed to the microstructure modification of LiFePO$_4$ via Cl-doping.

Preparation of nanosized materials

Carbon coating and elements doping are efficient way to increase the electronic conductivity of $LiFePO_4$ electrode materials [60-62]. However, both carbon coating and doping do not solve the problem of the low intrinsic ionic conductivity of $LiFePO_4$ which could be addressed by downsizing the particles. Obviously, decreasing the particle size, which leads to a decrease in solid state transport length and increase in surface reactivity, has been the main method to solve above problem [17]. In addition, Lee *et al.* [63] studied the lithiation/delithiation mechanism for the general case of nanoparticles with a heterogeneous particle size distribution (Fig. 6). They proofed that ionic transport occurs between nano and bulk particles in a cell at equilibrium, due to their electrochemical potential difference that originates from their different thermodynamic properties and surface energies. Based on the careful analysis of the results reported by different research groups, Gaberscek *et al.* [64] showed the relationship between the average particle size and the electrochemical performance of $LiFePO_4$-based electrodes. They pointed out that the electrical resistance of electrode materials depended solely on the mean particle size, as shown in the Fig. 7(a). Meanwhile, the discharge capacity of $LiFePO_4$-based electrodes dropped approximately linearly with average particle size, regardless of the presence/absence of a native carbon coating, which was shown in Fig. 7(b).
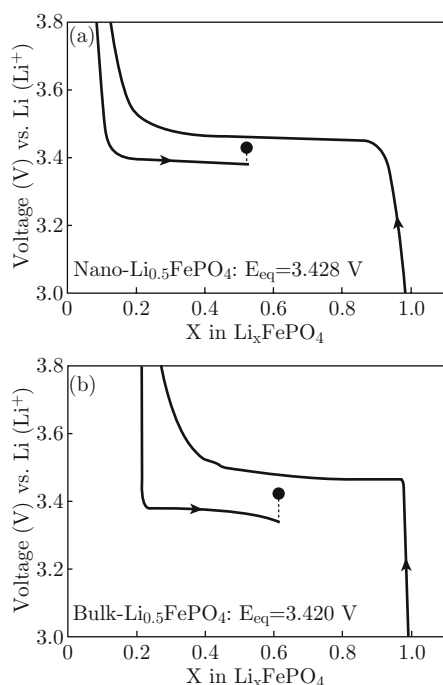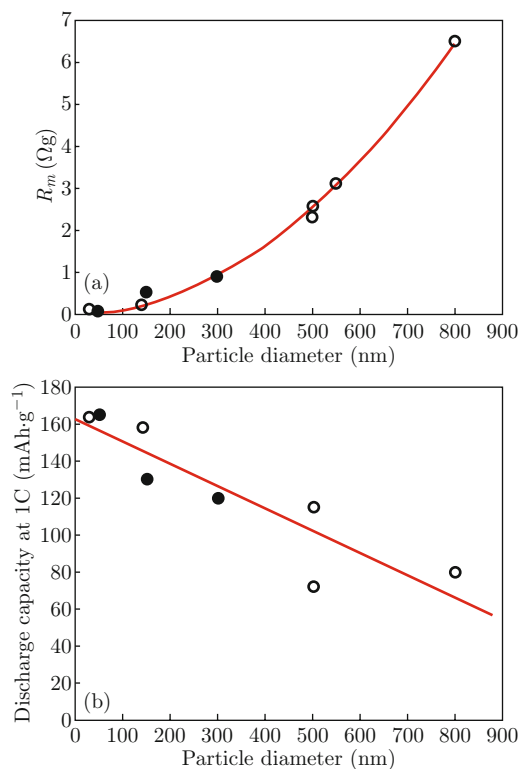

Fig. 7 The relationship between average particle diameter and electrode resistance per unit mass (a); discharge capacity (b) [64].

Delacourt *et al.* [65] prepared carbon-free $LiFePO_4$ crystalline powders by a direct precipitation method. The particle size distribution is very narrow, centered on about 140 nm. A soft thermal treatment, typically at 500℃ for 3 h under slight reducing conditions (N_2/H_2 gas flow) was shown to be necessary to obtain satisfactory electrochemical Li^+ deinsertion/insertion properties. This thermal treatment does not lead to grain growth or sintering of the particles, and does not alter the surface of the particles. The powders exhibited excellent electrochemical performances of about 147 mAh g^{-1} at a rate of 5 C. Gibot *et al.* [66] reported a single phase carbon-free $LiFePO_4$ nanoparticles by a low-temperature precipitation process. They reported the feasibility to drive the well-established two-phase room-temperature insertion process in $LiFePO_4$ electrodes into a single-phase one by modifying the material's particle size and ion ordering. Electrodes made of $LiFePO_4$ nanoparticles (40 nm) exhibited excellent reversible performance and the capacity sustained near 100% after 60 cycles both at 0.1 C and 1 C, which were shown in Fig. 8. Lim *et al.* [67] synthesized nanowires and hollow carbon-free $LiFePO_4$ cathodes using the hard templates SBA-15 and KIT-6, respectively. The nanowires had a diameter of about 7 nm, and the hollow $LiFePO_4$ had a pore size of 5.6 nm. Both the nanowires and hollow $LiFePO_4$ cathodes exhibited excellent rate capability even at 10 C, with over 89%

Fig. 6 The relationship between thermodynamics and particle size: (a) Nano-$LiFePO_4$; (b) Bulk-$LiFePO_4$ [63].

capacity retention of the initial capacity. The rate capability of the hollow cathode was higher than that of the nanowire cathode due to its higher surface area.

Of course, we recognized that the morphology and crystal orientation of LiFePO$_4$ related to the ionic kinetics is also significantly affecting its electrochemical performance in the nanosized electrode materials [68, 69]. Wang's group [70] synthesized

3D hierarchical LiFePO$_4$ particles networked with electronically conducting multi-walled carbon nanotubes (MWCNT) including particle-like nanoparticles, shuttle-like nanoparticles and disk-like nanoparticles by a hydrothermal approach. The particle morphology, crystal orientation, and electrochemical reactivity of the prepared LiFePO$_4$/MWCNT particles could be tailored by varying the P source. Among the as-prepared
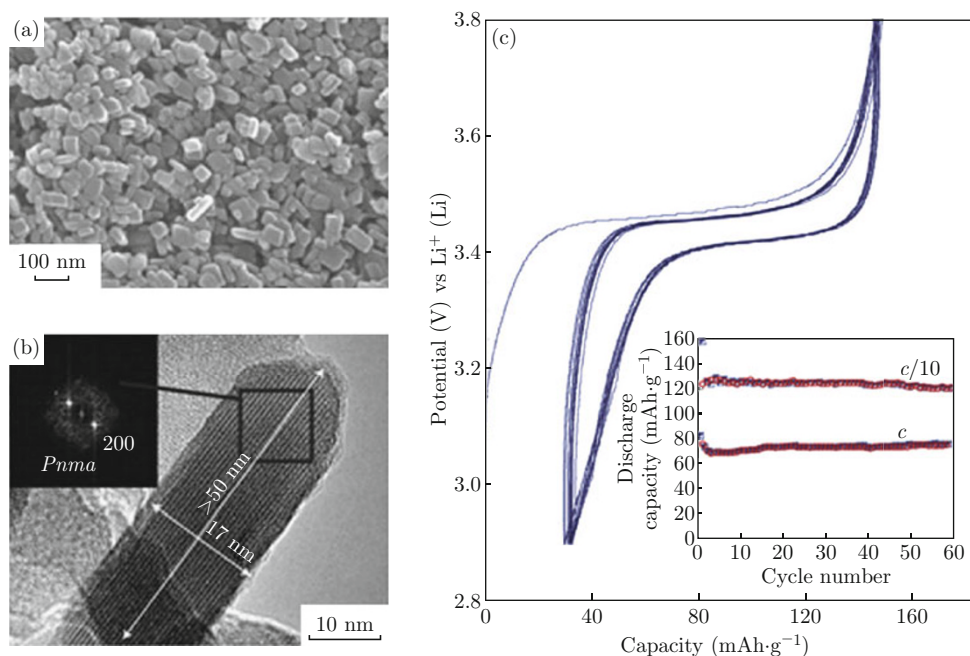
Fig. 8 (a-b) SEM image and HRTEM image combined with the Fourier transform of the selected area showing the orientation of the crystallite of the 40 nm nanosized LiFePO$_4$; (c) Charge/discharge galvanostatic curves at 0.1 C and 1 C for a Li/carbon-free 40 nm LiFePO$_4$ cell cycled between 2.5 and 4 V, together with its capacity retention over 60 cycles [66].
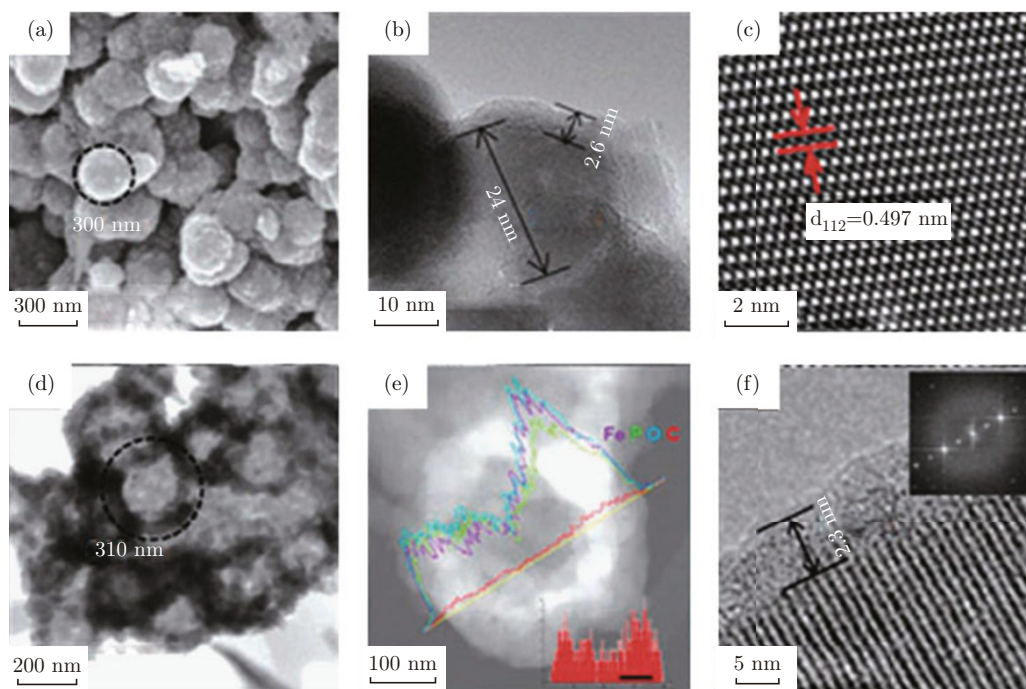

Fig. 9 Electron microscopy images of the hollow sphere secondary structure of nanoparticles [72].

LiFePO$_4$ materials, the disk-like crystal showed the most excellent performance, with the capacity reaching 121.5 mAh g^{-1} at 30 C. Saravanan *et al.* [71] reported LiFePO$_4$ nanoplates with a uniform amorphous carbon coating of 5 nm surface by the solvothermal method. The thickness of the nanoplates along the b-axis was found to be 30-40 nm. The LiFePO$_4$/C nanoplates delivered the initial discharge capacity of about 165 mAh g^{-1} at 0.1 C and about 50 mAh g^{-1} at 30 C. Lee *et al.* reported on the evolution of a hollow sphere secondary structure of spherical nanoparticles by a solubilization-repreciptation mechanism based on the difference of solubility products (K_{sp}) of two different precipitates [72]. Carbon-coated nanoparticles of olivine structure LiFePO$_4$ served as the primary nano-blocks to build the secondary nano-architecture (Fig. 9). The size of the secondary particles was about 300 nm, which was developed in a shape of hollow sphere with its shell consisting of the primary particles (about 25 nm). The carbon layer wrapping primary particles was clearly shown with the thickness of 3 to 5 nm. By controlling the morphology of the electrode materials, the hollow LiFePO$_4$ spheres showed good rate performances. The high rates charging were achieved 133 mAh g^{-1} at 10 C and 100 mAh g^{-1} at 50 C.

Decreasing the particle size to increase the electrode-electrolyte interface is the most effective method to enhance electrochemical performances of LiFePO$_4$, particularly at high rate charge-discharge. Unfortunately, because of the surface lattice relaxation and self-aggregation, nano-sized LiFePO$_4$ usually exhibit low capacitance retention and low tap density or volumetric energy density. Meanwhile, there are also some problems existed in large-scale production, separation and admixing with carbon black [9].

Preparation of porous materials

In order to introduce fast ionic permeation and high electronic conductivity into the Li-ion battery materials, new concepts of electrode structuring are needed [73]. Recently, the porous LiFePO$_4$ material has attracted comprehensive researchs. In a porous material, the pore-to-pore distance determines the solid-state diffusion of Li$^+$. Apparently, this distance has a similar value as the average diameter of nano-particles in particulate materials [74]. While, porous LiFePO$_4$ particles provide good contact with electrolyte and, in principle, are easier to bind than isolated nano-sized LiFePO$_4$ particles [75]. Meanwhile, such porous structure is more useful if the pores are decorated with an electronic conductor, especially with a thin carbon film [76]. Solid electron-conducting carbon will be homogeneously distributed within the final composite materials [77].

Dominko *et al.* [78] prepared microsized porous LiFePO$_4$/C particles by sol-gel techniques, using Fe(III) citrate as a precursor. The particles internal porosity in the range of 4-200 nm was controlled by appropriate selection of several synthesis parameters. Within this sol-gel technique the increase in heating rate lead to a more interlaced pore system, a smaller mesoporous volume, and a larger number of surface apertures, although the micropore volume did not change significantly. These features resulted in a better electrochemical rate performance of 120 mAh g^{-1} at 5 C rate. Doherty *et al.* [79] used a novel method to prepare nanostructured hierarchically porous LiFePO$_4$ electrode materials. A meso/macroporous carbon monolith with bimodal porosity was nanocasted from a hard silica template, which was used to provide a conductive framework for LiFePO$_4$ and increase the electrode/electrolyte interface. The surface area of the sample detected by Brunauer-Emmet-Teller (BET) was 200 m^2 g^{-1} with a pore volume of 0.3 cm^3 g^{-1}. This type of structure was potentially ideal as electrode materials to improve the rate capability of the batteries. The as-prepared sample displayed a capacity of 100 mAh g^{-1} at discharge rate of 5 C. Drummond *et al.* [80] reported a hierarchically porous LiFePO$_4$ electrode materials via a colloidal crystal templates technique. Beads of polymethylmethacrylate (PMMA) were synthesized with diameters of 100, 140, and 270 nm and used to form colloidal crystal templates to produce LiFePO$_4$, which featured pores spanning from 10 to 100 nm (Fig. 10). The materials with the largest pores, around 100 nm diameters, presented the highest discharge capacities of 160 mAh g^{-1} at 0.1 C and 115 mAh g^{-1} at 5 C. Sinha *et al.* [81] achieved a mesoporous LiFePO$_4$/C composite with dual porosity by a solution-based polymer templating technique. Pluronic acid was used as the templating agent in the presence of a cosurfactant in an emulsion medium. The LiFePO$_4$/C composite prepared at 700℃ contains dual porosity with pore-size distributions spread around 4 and 50 nm, which exhibited a high rate capability and stable capacity retention upon cycling. It delivered 60 mAh g^{-1} reversible capacities even at a current rate of 14.7 C.

Template-free techniques have also been developed to prepare porous LiFePO$_4$ cathode materials. Yu *et al.* [82] prepared porous micro-spherical aggregates of LiFePO$_4$/C nanocomposites via a sol-gel-spray drying method without employing any surfactants or templates. The as-obtained LiFePO$_4$ porous microspheres had an average pore size of 45 nm and gave large specific surface area (20.2 m^2 g^{-1}). The particles could be easy to bring into contact with electrolyte, facilitate the electron and lithium ion diffusion. The as-obtained sample delivered a large reversible discharge capacity of 138 mAh g^{-1} at 0.1 C and a good rate capacity of 54 mAh g^{-1} at 10 C (Fig. 11). Qian *et al.* [83] suggested

that the ideal structure of LiFePO$_4$ with both high volumetric energy density and high rate capability should be a microsphere composed of nanocrystallites tightly compacted to form three-dimensional electronic and ionic channels. They prepared nanoembossed mesoporous LiFePO$_4$ microspheres by a template-free hydrothermal process. The microspheres showed a uniform size distribution of $\sim$3 µm and were composed of many densely aggregated $\sim$100 nm nanoparticles and interconnected nanochannels. This mesoporous structure allowed better irrigation of electrolyte, and therefore provided a huge electrochemically available surface for enhancing the rate capability of the lithium insertion/deinsertion reaction. The discharge capability of LiFePO$_4$ microspheres reached 115 mAh g^{-1} at a high rate of 10 C. Recently, we adopted the supercritical carbon dioxide (scCO$_2$) to modify the size and morphology of hydrothermally synthesized LiFePO$_4$ [84]. After the scCO$_2$ treatment, aggregation was largely reduced, different morphologies were obtained and impurities were almost removed. The effects of the formation of porous LiFePO$_4$ had also been found after the scCO$_2$ treatment. Meanwhile, a possible crystal dissolution formation mechanism was proposed from theoretical models [85]. The electrochemical performance of porous LiFePO$_4$ had been significantly improved. At the
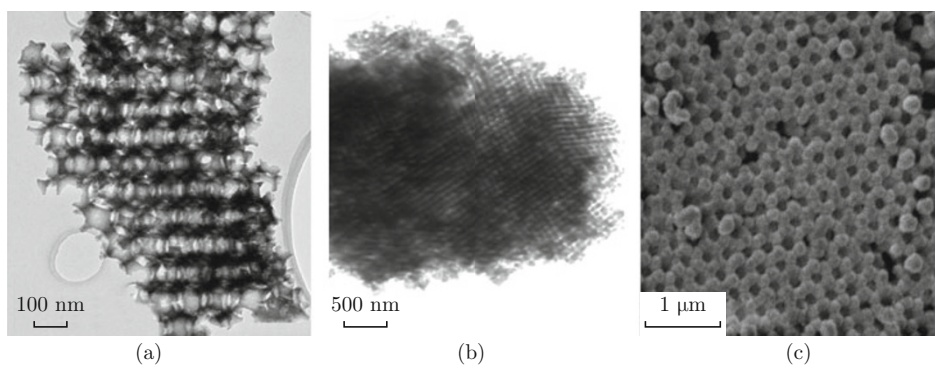
Fig. 10   (a) TEM image of 140 nm bead-templated LiFePO$_4$ calcined at 320℃ and (b) calcined at 600℃. (c) SEM image of 270 nm bead-templated LiFePO$_4$ calcined at 700℃ [80].
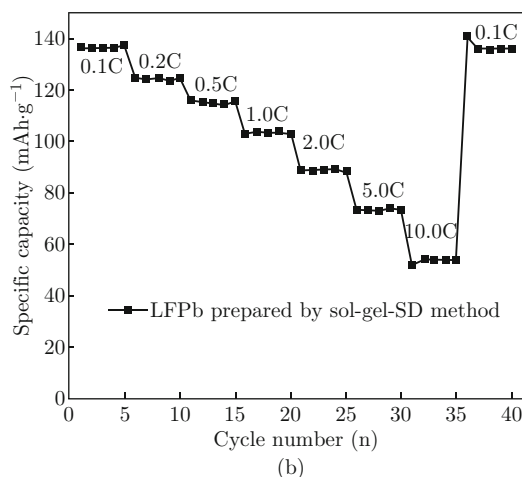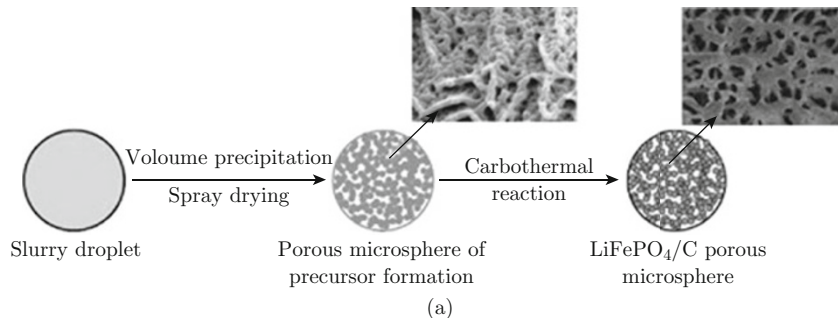
Fig. 11   (a) Description of process from slurry droplet to porous micro-spherical aggregates of LiFePO$_4$/C nanocomposites during spray drying and subsequently carbothermal reaction; (b) the cyclic stability of the as-obtained product LFP with various discharge current rates [82].

217

discharge rate of 5 C, the discharge capacity was 105 mAh g^{-1} [86].

The porous structure could be depicted as an inverse picture of nanoparticles arrangement, where pores serve as paths for Li-ion supply and the distance between the pores determines the materials kinetics [87]. The porous structure is also the critical factor for affecting high power capability of LiFePO$_4$, so optimization of the porous structure by controlling synthesis methods and technological conditions is the key step to improve electrochemical properties of LiFePO$_4$ at high rates [88].

Preparation of composites

As a kind of carbon materials, graphene has attracted attention in increasing the electrochemical performance of LiFePO$_4$ because of its large specific surface area (theoretical value of 2630 m^{2}g^{-1}), flexible structure, superior chemical/thermal stability, and most importantly excellent electric conductivity [89-94]. With the help of graphene, the electrons could be transferred easily between the LiFePO$_4$ particles and current collectors, reducing the internal resistance and enhancing the power density of the batteries [95, 96].

Zhou *et al.* [97] described a graphene-modified LiFePO$_4$ composite for a Li-ion battery cathode material. The composite was prepared with LiFePO$_4$ nanoparticles and the relatively simple availability of graphene oxide nanosheets using spray-drying and annealing processes. The LiFePO$_4$ primary nanoparticles embedded in micro-sized spherical secondary particles with diameters of 2-5 μm were wrapped homogeneously and loosely with a graphene 3D network. The carbon film had a thickness of about 2 nm and consisted of 3-5 layers of graphene, which was shown in Fig. 12. Such structure supported the maximum fulfilment of graphene's functionality, because electrons were easily transferred between the surface of LiFePO$_4$ nanocrystals and graphene, and moved unobstructed over the nanoparticles to attain a high rate capability. The composite delivered a capacity of 70 mAh g^{-1} at 60 C discharge rate and showed a capacity decay rate of < 15% when cycled under 10 C charging and 20 C discharging for 1000 times. Su *et al.* [98] reported a novel LiFePO$_4$/graphene/carbon composite by an *in situ* solvothermal method to synthesize LiFePO$_4$/graphene powders as precursors and then followed by a carbon-coating process. The ethanol adopted in the experiment acted as a reducing agent, which was used to avoid the formation of undesirable ferric impurities in the solvothermal [99]. The results indicated that the co-modification of LiFePO$_4$ with graphene and carbon coating could construct an effective conducting network, which significantly enhanced the electrochemical activity of LiFePO$_4$/carbon based composite. The composite with a low content of graphene exhibited a high initial discharge capacity of 163.7 mAh g^{-1} at 0.1 C and 114 mAh g^{-1} at 5 C, as well as an excellent cycling stability. Ha *et al.* [100] mixed chemically activated graphene (CA-graphene) with LiFePO$_4$ to prepare the composite for lithium ion batteries. CA-graphene in the composite provided abundant porous channels for the diffusion of lithium ions. Moreover, it acted as a conducting network for easy charge transfer and as a divider, preventing the aggregation of LiFePO$_4$ particles. The CA-graphene/LiFePO$_4$ composite exhibited remarkably better rate capability and stable cycling
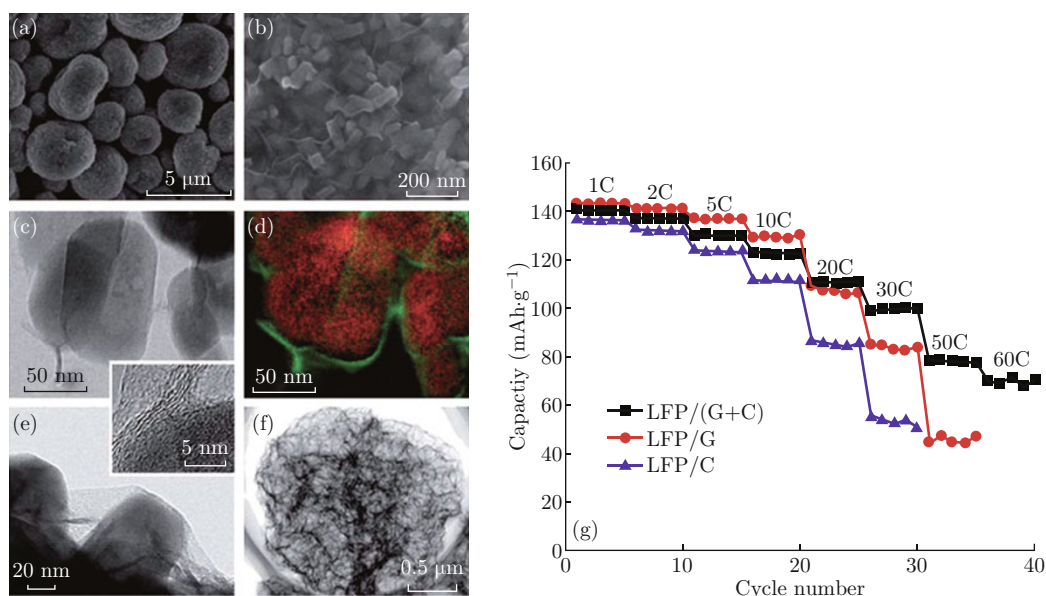

Fig. 12 (a-f) SEM and TEM images of the LFP/G particles; (g) Comparison of rate capability of LFP/G, LFP/C, and LFP/(G + C) [97].
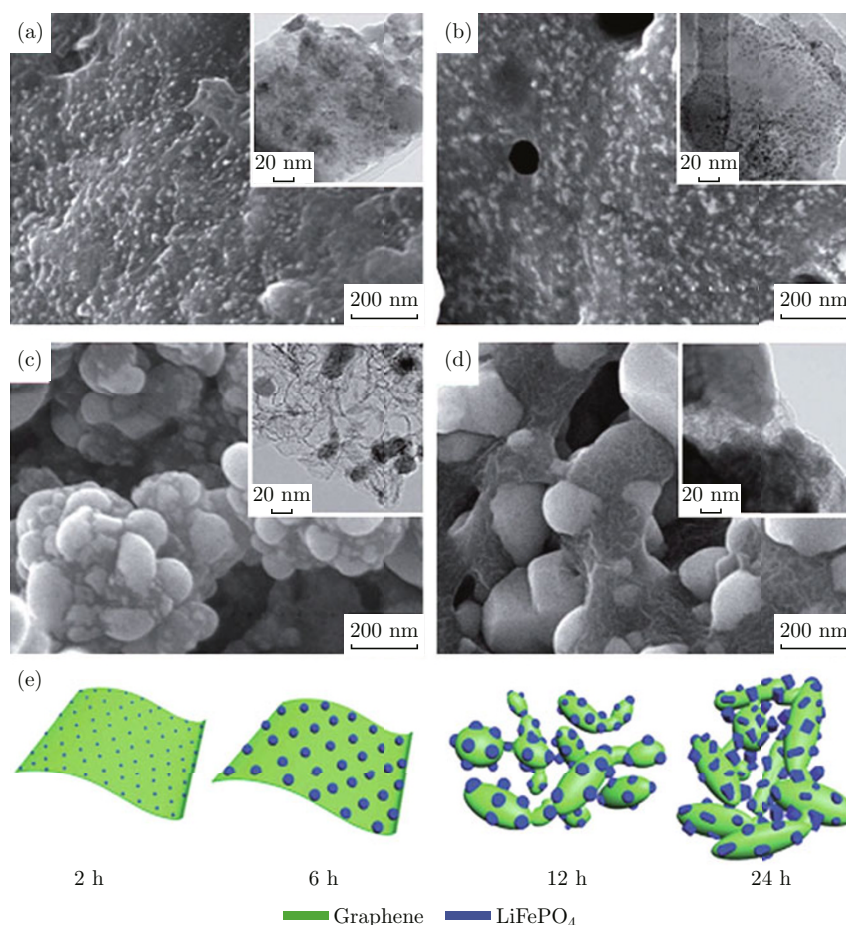
Fig. 13   SEM and TEM (inset) images of LiFePO$_4$-unfolded graphene nanocomposites obtained with different annealing time: (a) 2 h; (b) 6 h; (c) 12 h and (d) 24 h. (e) Schematic image of LiFePO$_4$ growth on the unfolded graphene [105].

performance compared to the conventional graphene/LiFePO$_4$ composite and bare LiFePO$_4$. The as-obtained sample delivered 73 mAh g^{-1} of discharge capacity at 25 C. Shi and co-workers [101] described an advanced microwave-assisted hydrothermal route for preparation of a highly ordered LiFePO$_4$/C/graphene nano-composite. LiFePO$_4$/C nanoparticles were embedded in the conductive and interconnected graphene networks, and exhibited a discharge capacity of 88 mAh g^{-1} at 10 C.

On the other hand, in order to improve the lithium ion diffusion of the electrode materials, the modified graphene with 3D conducting matrix are developed to grow and anchor on the insulating LiFePO$_4$ materials [102, 103]. Sun et al. [104] successfully prepared a three-dimensional porous self-assembled LiFePO$_4$/graphene (LFP/G) composite using a facile template-free sol-gel approach. Graphene nanosheets were dispersed into the porous hierarchical network homogenously, which greatly enhanced the efficient use of the active materials, leading to an outstanding electrochemical performance of the hybrid cathodes. The LFP/G composite had a reversible capacity of 65 mAh g^{-1} at 5 C rate. One year later,

Sun's group [105] reported that the unfolded graphene was used as a three dimensional (3D) conducting network for LiFePO$_4$ nano-particle growth (Fig. 13). The use of unfolded graphene improved the dispersion of LiFePO$_4$ and restricted the LiFePO$_4$ particle size at the nanoscale. Meanwhile, it enabled both Li-ion and electrons to migrate and sufficiently utilized the LiFePO$_4$ active materials. This facile designed composite showed both high specific capacity and rate performances. The discharge capacity of the nanocomposite remained stable at relatively high rate (75 mAh g^{-1} at 10 C and 60 mAh g^{-1} at 15 C, respectively).

Carbon nanotubes, with high electrical conductivity, large surface area and high aspect ratio, are also considered as the promising materials to form high electrical conductivity and enhance the ion transport for LiFePO$_4$ [106, 107]. Sun and his colleagues [108] synthesized 3D nitrogen-doped CNTs modified porous LiFePO$_4$ by a sol-gel method without templates or surfactants. Nitrogen doped CNTs possessed many active defects and hydrophilic properties, which brought to intimate contact with active materials. Meanwhile, in nitrogen doped CNTs, nitrogen atom provided electron carriers for the conduction band, which further

improved the electronic conductivity [109-111]. The as-prepared LiFePO$_4$/nitrogen-doped CNTs exhibited excellent rate performance of 80 mAh g^{-1} at the rate of 5 C. Toprakci *et al.* [112] reported that the LiFePO$_4$/CNT/C composite nanofibers were synthesized via a combination of electrospinning and sol-gel methods, where polyacrylonitrile (PAN) was used as the electrospinning media and carbon source. Electrospinning was an effective way to minimize the aggregation of LiFePO$_4$ particles and promote the formation of a conducting carbonaceous layer. CNTs were found to be well-dispersed in the carbonaceous matrix and increased the electrochemical performance of the composite nanofibers. The average reversible capacities of the above composites were obtained as 134 mAh g^{-1} and 121 mAh g^{-1} at 1 C and 2 C, respectively. Zhou *et al.* [113] prepared the highly-conductive 3D nanotube networks combined with interlaced porous LiFePO$_4$ electrodes by an *in situ* sol-gel technique. This design developed the manifold benefits of CNTs to create a highly-conductive 3D network united with the porous LiFePO$_4$. At high rate of 6 C, the composite material retained a capacity of 110 mAh g^{-1}.

From the above papers we can see that the composites electrode materials are believed to be one of the most promising cathode materials for lithium ion batteries.

Others

During the synthesis process of LiFePO$_4$ material, some conductive impurities and amorphous phases may be produced [114]. These metal impurities play an important role in increasing electronic conductivity and evidently improving the electrochemical performance. Xu *et al.* [115] prepared LiFePO$_4$/C materials by a reformative solid-coordination method. Fe$_2$P phase arised as an impure phase among the LiFePO$_4$/C materials when they were prepared at relatively high annealing temperature of 725℃. The discharge capacity of the above sample was 10% higher than the pristine LiFePO$_4$. Kang and Ceder [116] created a fast ion-conducting surface phase of Li$_4$P$_2$O$_7$ through controlled off-stoichiometry. The as-prepared LiFePO$_4$ exhibited excellent rate performance of 136 mAh g^{-1} and 60 mAh g^{-1} at 50 C and 400 C, respectively. However, Goodenough *et al.* doubted that the announced battery was impossible to reach high recharging rate capability for a Li-ion battery of 9 s, although the authors responded to the unsupported claims of ultrafast charging of Li-ion batteries [117, 118]. This debate is not yet clear.

Conclusions

The olivine LiFePO$_4$ has been considered as the most promising cathode materials for EVs and PHEVs applications due to its inherent merits including low toxicity, low material cost, flat voltage profile, long cycle ability and high safety compared to other cathode materials. However, LiFePO$_4$ has severe disadvantages of low intrinsic electronic conductivity of LiFePO$_4$ and small diffusion coefficient of lithium ion, which are the main demerits that make it difficult to be applied in high-rate battery. In this paper, we have reviewed some of the recent progress and advances in improving the rate performance of LiFePO$_4$ from peer-reviewed journal publications. Carbon coating on the LiFePO$_4$ particle surface is one of the most important techniques used to improve its electronic conductivity between particles. Doping with cations and anions can greatly improves the intrinsic electronic conductivity of materials, although the mechanism and effect of doping on electronic conductivity reported are still in controversy. Both carbon coating and doping do not solve the problem of the low intrinsic ionic conductivity of LiFePO$_4$, which could be addressed by downsizing the particles. In order to introduce fast ionic permeation and high electronic conductivity into the Li-ion battery materials, porous structure and the composites electrode materials are depicted to improve the high rate electrochemical properties of LiFePO$_4$. With regard to the large-scale industrial production, a reliable, low-cost, highly effective synthetic method for preparing LiFePO$_4$ cathode materials with high rate performance is still highly desirable. With comprehensive research, we believe that LiFePO$_4$ will be widely used for the Li-ion battery and practical application of EVs.

Acknowledgments

References

[1] Y. Wang and G. Cao, "Developments in nanostructured cathode materials for high-performance lithium-ion batteries", Adv. Mater. 20(12), 2251-2269 (2008). http://dx.doi.org/10.1002/adma.200702242

[2] G. Jeong, Y.-U. Kim, H. Kim, Y.-J. Kim and H.-J. Sohn, "Prospective materials and applications for Li secondary batteries", Energ. Environ. Sci. 4(6), 1986-2002 (2011). http://dx.doi.org/10.1039/C0EE00831A

[3] J. Wang and X. Sun, "Understanding and recent development of carbon coating on LiFePO$_4$ cathode materials for lithium-ion batteries", Energ. Environ. Sci. 5(1), 5163-5185 (2012). http://dx.doi.org/10.1039/c1ee01263k

[4] A. K. Padhi, K. S. Nanjundaswamy and J. B. Goodenough, "Phospho-olivines as positive-electrode materials for rechargeable lithium batteries", J. Electrochem. Soc. 144(4), 1188-1194 (1997). http://dx.doi.org/10.1149/1.1837571

[5] A. Ritchie and W. Howard, "Recent developments and likely advances in lithium-ion batteries", J. Power Sources 162(2), 809-812 (2006). http://dx.doi.org/10.1016/j.jpowsour.2005.07.014

[6] T. Ohzuku and R. J. Brodd, "An overview of positive-electrode materials for advanced lithium-ion batteries", J. Power Sources 174(2), 449-456 (2007). http://dx.doi.org/10.1016/j.jpowsour.2007.06.154

[7] D. Jugović and D. Uskoković "A review of recent developments in the synthesis procedures of lithium iron phosphate powders", J. Power Sources 190(2), 538-544 (2009). http://dx.doi.org/10.1016/j.jpowsour.2009.01.074

[8] K. Tang, J. Sun, X. Yu, H. Li and X. Huang, "Electrochemical performance of $LiFePO_4$ thin films with different morphology and crystallinity", Electrochim. Acta. 54(26), 6565-6569 (2009). http://dx.doi.org/10.1016/j.electacta.2009.06.030

[9] Y. Zhang, Q. Y. Huo, P. P. Du, L. Z. Wang, A. Q. Zhang, Y. H. Song, Y. Lv and G. Y. Li, "Advances in new cathode material $LiFePO_4$ for lithium-ion batteries", Synthetic Met. 162(13-14), 1315-1326 (2012). http://dx.doi.org/10.1016/j.synthmet.2012.04.025

[10] S. Y. Chung, J. T. Bloking and Y. M. Chiang, "Electronically conductive phospho-olivines as lithium storage electrodes", Nat. Mater. 1(2), 123-8 (2002). http://dx.doi.org/10.1038/nmat732

[11] J. Molenda, A. Stokłosa and T. Baok, "Modification in the electronic structure of cobalt bronze Li_xCoO_2 and the resulting electrochemical properties", Solid State Ionics 36(1–2), 53-58 (1989). http://dx.doi.org/10.1016/0167-2738(89)90058-1

[12] Y. Shimakawa, T. Numata and J. Tabuchi, "Verwey-type transition and magnetic properties of the $LiMn_2O_4$ spinels", J. Solid State Chem. 131(1), 138-143 (1997). http://dx.doi.org/10.1006/jssc.1997.7366

[13] H. C. Dinh, S. I. Mho and I. H. Yeo, "Electrochemical analysis of conductive polymer-coated $LiFePO_4$ nanocrystalline cathodes with controlled morphology", Electroanal. 23(9), 2079-2086 (2011). http://dx.doi.org/10.1002/elan.201100222

[14] H. Fang, Z. Pan, L. Li, Y. Yang, G. Yan, G. Li and S. Wei, "The possibility of manganese disorder in $LiMnPO_4$ and its effect on the electrochemical activity", Electrochem. Commun. 10(7), 1071-1073 (2008). http://dx.doi.org/10.1016/j.elecom.2008.05.010

[15] L. X. Yuan, Z. H. Wang, W. X. Zhang, X. L. Hu, J. T. Chen, Y. H. Huang and J. B. Goodenough, "Development and challenges of $LiFePO_4$ cathode material for lithium-ion batteries", Energ. Environ. Sci. 4(2), 269 (2011). http://dx.doi.org/10.1039/c0ee00029a

[16] M. S. Islam, D. J. Driscoll, C. A. J. Fisher and P. R. Slater, "Atomic-scale investigation of defects, dopants, and lithium transport in the $LiFePO_4$ olivine-type battery material", Chem. Mater. 17(20), 5085-5092 (2005). http://dx.doi.org/10.1021/cm050999v

[17] J. M. Tarascon and M. Armand, "Issues and challenges facing rechargeable lithium batteries", Nature 414 (6861), 359-367 (2001). http://dx.doi.org/10.1038/35104644

[18] Y. Wang, J. Wang, J. Yang and Y. Nuli, "High-rate $LiFePO_4$ electrode material synthesized by a novel route from $FePO_4 \cdot 4H_2O$", Adv. Funct. Mater. 16(16), 2135-2140 (2006). http://dx.doi.org/10.1002/adfm.200600442

[19] K. Hanai, T. Maruyama, N. Imanishi, A. Hirano, Y. Takeda and O. Yamamoto, "Enhancement of electrochemical performance of lithium dry polymer battery with $LiFePO_4$/carbon composite cathode", J. Power Sources 178(2), 789-794 (2008). http://dx.doi.org/10.1016/j.jpowsour.2007.10.004

[20] M. M. Doeff, J. D. Wilcox, R. Kostecki and G. Lau, "Optimization of carbon coatings on $LiFePO_4$", J. Power Sources 163(1), 180-184 (2006). http://dx.doi.org/10.1016/j.jpowsour.2005.11.075

[21] Y. Kadoma, J.-M. Kim, K. Abiko, K. Ohtsuki, K. Ui and N. Kumagai, "Optimization of electrochemical properties of $LiFePO_4$/C prepared by an aqueous solution method using sucrose", Electrochim. Acta 55(3), 1034-1041 (2010). http://dx.doi.org/10.1016/j.electacta.2009.09.029

[22] S. T. Myung, S. Komaba, N. Hirosaki, H. Yashiro and N. Kumagai, "Emulsion drying synthesis of olivine $LiFePO_4$/C composite and its electrochemical properties as lithium intercalation material", Electrochim. Acta 49(24), 4213-4222 (2004). http://dx.doi.org/10.1016/j.electacta.2004.04.016

[23] M. R. Yang, T. H. Teng and S. H. Wu, "$LiFePO_4$/carbon cathode materials prepared by ultrasonic spray pyrolysis", J. Power Sources 159(1), 307-311 (2006). http://dx.doi.org/10.1016/j.jpowsour.2006.04.113

[24] M. A. E. Sanchez, G. E. S. Brito, M. C. A. Fantini, G. F. Goya and J. R. Matos, "Synthesis and characterization of $LiFePO_4$ prepared by sol–gel technique", Solid State Ionics 177(5–6), 497-500 (2006). http://dx.doi.org/10.1016/j.ssi.2005.11.018

[25] Y. Lin, M. X. Gao, D. Zhu, Y. F. Liu and H. G. Pan, "Effects of carbon coating and iron phosphides on the electrochemical properties of $LiFePO_4$/C", J. Power Sources 184(2), 444-448 (2008). http://dx.doi.org/10.1016/j.jpowsour.2008.03.026

[26] K. Wang, R. Cai, T. Yuan, X. Yu, R. Ran and Z. Shao, "Process investigation, electrochemical characterization and optimization of $LiFePO_4$/C composite from mechanical activation using sucrose as carbon source", Electrochim. Acta 54(10),

2861-2868 (2009). http://dx.doi.org/10.1016/j.electacta.2008.11.012

[27] S. A. Needham, A. Calka, G. X. Wang, A. Mosbah and H. K. Liu, "A new rapid synthesis technique for electrochemically active materials used in energy storage applications", Electrochem. Commun. 8(3), 434-438 (2006). http://dx.doi.org/10.1016/j.elecom.2005.12.011

[28] L. Wang, G. C. Liang, X. Q. Ou, X. K. Zhi, J. P. Zhang and J. Y. Cui, "Effect of synthesis temperature on the properties of $LiFePO_4$/C composites prepared by carbothermal reduction", J. Power Sources 189(1), 423-428 (2009). http://dx.doi.org/10.1016/j.jpowsour.2008.07.032

[29] S. H. Ju and Y. C. Kang, "$LiFePO_4$/C cathode powders prepared by spray pyrolysis from the colloidal spray solution containing nano-sized carbon black", Mater. Chem. Phys. 107(2-3), 328-333 (2008). http://dx.doi.org/10.1016/j.matchemphys.2007.07.025

[30] Y. H. Nien, J. R. Carey and J. S. Chen, "Physical and electrochemical properties of $LiFePO_4$/C composite cathode prepared from various polymer-containing precursors", J. Power Sources 193(2), 822-827 (2009). http://dx.doi.org/10.1016/j.jpowsour.2009.04.013

[31] Y. D. Cho, G. T. K. Fey and H. M. Kao, "The effect of carbon coating thickness on the capacity of $LiFePO_4$/C composite cathodes", J. Power Sources 189(1), 256-262 (2009). http://dx.doi.org/10.1016/j.jpowsour.2008.09.053

[32] R. Dominko, M. Bele, M. Gaberscek, M. Remskar, D. Hanzel, S. Pejovnik and J. Jamnik, "Impact of the carbon coating thickness on the electrochemical performance of $LiFePO_4$/C composites", J. Electrochem. Soc. 152(3), A607-A610 (2005). http://dx.doi.org/10.1149/1.1860492

[33] H. Huang, S. C. Yin and L. F. Nazar, "Approaching theoretical capacity of $LiFePO_4$ at room temperature at high rates", Electrochem. Solid ST. 4(10), A170-A172 (2001). http://dx.doi.org/10.1149/1.1396695

[34] B. Zhao, Y. Jiang, H. Zhang, H. Tao, M. Zhong and Z. Jiao, "Morphology and electrical properties of carbon coated $LiFePO_4$ cathode materials", J. Power Sources 189(1), 462-466 (2009). http://dx.doi.org/10.1016/j.jpowsour.2008.12.069

[35] Y. Wang, Y. Wang, E. Hosono, K. Wang and H. Zhou, "The design of a $LiFePO_4$/carbon nanocomposite with a core-shell structure and its synthesis by an *in situ* polymerization restriction method", Angew. Chem. Int. Ed. Engl. 47(39), 7461-5 (2008). http://dx.doi.org/10.1002/anie.200802539

[36] Z. Chen and J. R. Dahn, "Reducing carbon in $LiFePO_4$/C composite electrodes to maximize specific energy, volumetric energy, and tap density", J. Electrochem. Soc. 149(9), A1184-A1189 (2002). http://dx.doi.org/10.1149/1.1498255

[37] D. Zhang, X. Yu, Y. Wang, R. Cai, Z. Shao, X.-Z. Liao and Z.-F. Ma, "Ballmilling-assisted synthesis and electrochemical performance of $LiFePO_4$/C for lithium-ion battery adopting citric acid as carbon precursor", J. Electrochem. Soc. 156(10), A802-A808 (2009). http://dx.doi.org/10.1149/1.3183880

[38] A. V. Murugan, T. Muraliganth and A. Manthiram, "Comparison of microwave assisted solvothermal and hydrothermal syntheses of $LiFePO_4$/C nanocomposite cathodes for lithium ion batteries", J. Phys. Chem. C 112(37), 14665-14671 (2008). http://dx.doi.org/10.1021/jp8053058

[39] A. Vadivel Murugan, T. Muraliganth and A. Manthiram, "One-pot microwave-hydrothermal synthesis and characterization of carbon-coated $LiMPO_4$ (M=Mn, Fe, and Co) cathodes", J. Electrochem. Soc. 156(2), A79-A83 (2009). http://dx.doi.org/10.1149/1.3028304

[40] C. R. Sides, F. Croce, V. Y. Young, C. R. Martin and B. Scrosati, "A high-rate, nanocomposite $LiFePO_4$/carbon cathode", Electrochem. Solid ST. 8(9), A484 (2005). http://dx.doi.org/10.1149/1.1999916

[41] S. T. Yang, N. H. Zhao, H. Y. Dong, J. X. Yang and H. Y. Yue, "Synthesis and characterization of $LiFePO_4$ cathode material dispersed with nano-structured carbon", Electrochim. Acta. 51(1), 166-171 (2005). http://dx.doi.org/10.1016/j.electacta.2005.04.013

[42] H. Liu, Y. Feng, Z. Wang, K. Wang and J. Xie, "A PVB-based rheological phase approach to nano-$LiFePO_4$/C composite cathodes", Powder Technol. 184(3), 313-317 (2008). http://dx.doi.org/10.1016/j.powtec.2007.09.002

[43] A. F. Liu, Z. H. Hu, Z. B. Wen, L. Lei and J. An, "$LiFePO_4$/C with high capacity synthesized by carbothermal reduction method", Ionics 16(4), 311-316 (2009). http://dx.doi.org/10.1007/s11581-009-0405-6

[44] H. Xie and Z. Zhou, "Physical and electrochemical properties of mix-doped lithium iron phosphate as cathode material for lithium ion battery", Electrochim. Acta 51(10), 2063-2067 (2006). http://dx.doi.org/10.1016/j.electacta.2005.07.014

[45] J. Xu and G. Chen, "Effects of doping on the electronic properties of $LiFePO_4$: A first-principles investigation", Physica B: Condens. Matter 405(3), 803-807 (2010). http://dx.doi.org/10.1016/j.physb.2009.05.035

[46] G. X. Wang, S. L. Bewlay, K. Konstantinov, H. K. Liu, S. X. Dou and J. H. Ahn, "Physical and electrochemical properties of doped lithium iron phosphate electrodes", Electrochim. Acta. 50(2-3), 443-447 (2004). http://dx.doi.org/10.1016/j.electacta.2004.04.047

[47] T. H. Teng, M. R. Yang, S. h. Wu and Y. P. Chiang, "Electrochemical properties of $LiFe_{0.9}Mg_{0.1}PO_4$/carbon cathode materials prepared

by ultrasonic spray pyrolysis", Solid State Commun. 142(7), 389-392 (2007). http://dx.doi.org/10.1016/j.ssc.2007.03.010

[48] X. Z. Liao, Y. S. He, Z. F. Ma, X. M. Zhang and L. Wang, "Effects of fluorine-substitution on the electrochemical behavior of LiFePO$_4$/C cathode materials", J. Power Sources 174(2), 720-725 (2007). http://dx.doi.org/10.1016/j.jpowsour.2007.06.146

[49] P. S. Herle, B. Ellis, N. Coombs and L. F. Nazar, "Nano-network electronic conduction in iron and nickel olivine phosphates", Nat. Mater. 3(3), 147-152 (2004). http://dx.doi.org/10.1038/nmat1063

[50] C. Delacourt, C. Wurm, L. Laffont, J. B. Leriche and C. Masquelier, "Electrochemical and electrical properties of Nb- and/or C-containing LiFePO$_4$ composites", Solid State Ionics 177(3-4), 333-341 (2006). http://dx.doi.org/10.1016/j.ssi.2005.11.003

[51] C. Ouyang, S. Shi, Z. Wang, X. Huang and L. Chen, "First-principles study of Li ion diffusion in LiFePO$_4$", Phys. Rev. B 69(10), 104303 (2004).

[52] M. Abbate, S. M. Lala, L. A. Montoro and J. M. Rosolen, "Ti-, Al-, and Cu-doping induced gap states in LiFePO$_4$", Electrochem. Solid ST. 8(6), A288-A290 (2005). http://dx.doi.org/10.1149/1.1895286

[53] P. P. Prosini, D. Zane and M. Pasquali, "Improved electrochemical performance of a LiFePO$_4$-based composite cathode", Electrochim. Acta. 46(23), 3517-3523 (2001). http://dx.doi.org/10.1016/S0013-4686(01)00631-4

[54] D. Wang, H. Li, S. Shi, X. Huang and L. Chen, "Improving the rate performance of LiFePO$_4$ by Fe-site doping", Electrochim. Acta. 50(14), 2955-2958 (2005). http://dx.doi.org/10.1016/j.electacta.2004.11.045

[55] H. C. Shin, S. B. Park, H. Jang, K. Y. Chung, W. I. Cho, C. S. Kim and B. W. Cho, "Rate performance and structural change of Cr-doped LiFePO$_4$/C during cycling", Electrochim. Acta. 53(27), 7946-7951 (2008). http://dx.doi.org/10.1016/j.electacta.2008.06.005

[56] C. S. Sun, Z. Zhou, Z. G. Xu, D. G. Wang, J. P. Wei, X. K. Bian and J. Yan, "Improved high-rate charge/discharge performances of LiFePO$_4$/C via V-doping", J. Power Sources 193(2), 841-845 (2009). http://dx.doi.org/10.1016/j.jpowsour.2009.03.061

[57] L. Yang, L. Jiao, Y. Miao and H. Yuan, "Improvement of electrochemical properties of LiFePO$_4$/C cathode materials by chlorine doping", J. Solid State Electr. 13(10), 1541-1544 (2008). http://dx.doi.org/10.1007/s10008-008-0721-1

[58] F. Lu, Y. Zhou, J. Liu and Y. Pan, "Enhancement of F-doping on the electrochemical behavior of carbon-coated LiFePO$_4$ nanoparticles prepared by hydrothermal route", Electrochim. Acta 56(24), 8833-8838 (2011). http://dx.doi.org/10.1016/j.electacta.2011.07.079

[59] C. S. Sun, Y. Zhang, X. J. Zhang and Z. Zhou, "Structural and electrochemical properties of Cl-doped LiFePO$_4$/C", J. Power Sources 195(11), 3680-3683 (2010). http://dx.doi.org/10.1016/j.jpowsour.2009.12.074

[60] Z.-H. Wang, L.-X. Yuan, M. Wu, D. Sun and Y.-H. Huang, "Effects of Na+ and Cl- co-doping on electrochemical performance in LiFePO$_4$/C", Electrochim. Acta 56(24), 8477-8483 (2011). http://dx.doi.org/10.1016/j.electacta.2011.07.018

[61] Y. Lu, J. Shi, Z. Guo, Q. Tong, W. Huang and B. Li, "Synthesis of LiFe$_{1-x}$Ni$_x$PO$_4$/C composites and their electrochemical performance", J. Power Sources 194(2), 786-793 (2009). http://dx.doi.org/10.1016/j.jpowsour.2009.05.041

[62] S. Beninati, L. Damen and M. Mastragostino, "Fast sol–gel synthesis of LiFePO$_4$/C for high power lithium-ion batteries for hybrid electric vehicle application", J. Power Sources. 194(2), 1094-1098 (2009). http://dx.doi.org/10.1016/j.jpowsour.2009.06.035

[63] K. T. Lee, W. H. Kan and L. F. Nazar, "Proof of intercrystallite ionic transport in LiMPO$_4$ electrodes (M = Fe, Mn)", J. Am. Chem. Soc. 131(17), 6044-6045 (2009). http://dx.doi.org/10.1021/ja8090559

[64] M. Gaberscek, R. Dominko and J. Jamnik, "Is small particle size more important than carbon coating? An example study on LiFePO$_4$ cathodes", Electrochem. Commun. 9(12), 2778-2783 (2007). http://dx.doi.org/10.1016/j.elecom.2007.09.020

[65] C. Delacourt, P. Poizot, S. Levasseur and C. Masquelier, "Size effects on carbon-free LiFePO$_4$ powders", Electrochem. Solid ST. 9(7), A352-A355 (2006). http://dx.doi.org/10.1149/1.2201987

[66] P. Gibot, M. Casas-Cabanas, L. Laffont, S. Levasseur, P. Carlach, S. Hamelet, J. M. Tarascon and C. Masquelier, "Room-temperature single-phase Li insertion/extraction in nanoscale Li$_x$FePO$_4$", Nat. Mater. 7(9), 741-747 (2008). http://dx.doi.org/10.1038/nmat2245

[67] S. Lim, C. S. Yoon and J. Cho, "Synthesis of nanowire and hollow LiFePO$_4$ cathodes for high-performance lithium batteries", Chem. Mater. 20(14), 4560-4564 (2008). http://dx.doi.org/10.1021/cm8006364

[68] G. Qin, Q. Wu, J. Zhao, Q. Ma and C. Wang, "C/LiFePO$_4$/multi-walled carbon nanotube cathode material with enhanced electrochemical performance for lithium-ion batteries", J. Power Sources 248(15), 588-595 (2014). http://dx.doi.org/10.1016/j.jpowsour.2013.06.070

[69] H. Deng, S. Jin, L. Zhan, W. Qiao and L. Ling, "Nest-like LiFePO$_4$/C architectures for high performance lithium ion batteries", Electrochim. Acta 78(1), 633-637 (2012). http://dx.doi.org/10.1016/j.electacta.2012.06.059

[70] G. Qin, S. Xue, Q. Ma and C. Wang, "The morphology controlled synthesis of 3D networking LiFePO$_4$

with multiwalled-carbon nanotubes for Li-ion batteries", CrystEngComm. 16(2), 260 (2014). http://dx.doi.org/10.1039/c3ce41967c

[71] K. Saravanan, M. V. Reddy, P. Balaya, H. Gong, B. V. R. Chowdari and J. J. Vittal, "Storage performance of LiFePO$_4$ nanoplates", J. Mater. Chem. 19(5), 605-610 (2009). http://dx.doi.org/10.1039/b817242k

[72] M. H. Lee, J. Y. Kim and H. K. Song, "A hollow sphere secondary structure of LiFePO$_4$ nanoparticles", Chem. Commun. (Camb). 46(36), 6795-6797 (2010). http://dx.doi.org/10.1039/c0cc02522d

[73] Y. S. Hu, Y. G. Guo, R. Dominko, M. Gaberscek, J. Jamnik and J. Maier, "Improved electrode performance of porous LiFePO$_4$ using RuO$_2$ as an oxidic nanoscale interconnect", Adv. Mater. 19(15), 1963-1966 (2007). http://dx.doi.org/10.1002/adma.200700697

[74] R. Dominko, M. Bele, M. Gaberscek, M. Remskar, D. Hanzel, J. M. Goupil, S. Pejovnik and J. Jamnik, "Porous olivine composites synthesized by sol–gel technique", J. Power Sources 153(2), 274-280 (2006). http://dx.doi.org/10.1016/j.jpowsour.2005.05.033

[75] F. Yu, J. Zhang, Y. Yang and G. Song, "Preparation and characterization of mesoporous LiFePO$_4$/C microsphere by spray drying assisted template method", J. Power Sources 189(1), 794-797 (2009). http://dx.doi.org/10.1016/j.jpowsour.2008.07.074

[76] G. Qin, Q. Ma and C. Wang, "A porous C/LiFePO$_4$/multiwalled carbon nanotubes cathode material for lithium ion batteries", Electrochim. Acta 115(1), 407-415 (2014). http://dx.doi.org/10.1016/j.electacta.2013.10.177

[77] R. Dominko, M. Bele, J.-M. Goupil, M. Gaberscek, D. Hanzel, I. Arcon and J. Jamnik, "Wired porous cathode materials: A novel concept for synthesis of LiFePO$_4$", Chem. Mater. 19(12), 2960-2969 (2007). http://dx.doi.org/10.1021/cm062843g

[78] R. Dominko, J. M. Goupil, M. Bele, M. Gaberscek, M. Remskar, D. Hanzel and J. Jamnik, "Impact of LiFePO$_4$/C composites porosity on their electrochemical performance", J. Electrochem. Soc. 152(5), A858-A863 (2005). http://dx.doi.org/10.1149/1.1872674

[79] C. M. Doherty, R. A. Caruso, B. M. Smarsly, P. Adelhelm and C. J. Drummond, "Hierarchically porous monolithic LiFePO$_4$/carbon composite electrode materials for high power lithium ion batteries", Chem. Mater. 21(21), 5300-5306 (2009). http://dx.doi.org/10.1021/cm9024167

[80] C. M. Doherty, R. A. Caruso, B. M. Smarsly and C. J. Drummond, "Colloidal crystal templating to produce hierarchically porous LiFePO$_4$ electrode materials for high power lithium ion batteries", Chem. Mater. 21(13), 2895-2903 (2009). http://dx.doi.org/10.1021/cm900698p

[81] N. N. Sinha, C. Shivakumara and N. Munichandraiah, "High rate capability of a dual-porosity LiFePO$_4$/C composite", ACS Appl. Mater. Inter. 2(7), 2031-2038 (2010). http://dx.doi.org/10.1021/am100309w

[82] F. Yu, J. Zhang, Y. Yang and G. Song, "Porous micro-spherical aggregates of LiFePO$_4$/C nanocomposites: A novel and simple template-free concept and synthesis via sol–gel-spray drying method", J. Power Sources 195(19), 6873-6878 (2010). http://dx.doi.org/10.1016/j.jpowsour.2010.01.042

[83] J. Qian, M. Zhou, Y. Cao, X. Ai and H. Yang, "Template-free hydrothermal synthesis of nanoembossed mesoporous LiFePO$_4$ microspheres for high-performance lithium-ion batteries", J. Phys. Chem. C 114(8), 3477-3482 (2010). http://dx.doi.org/10.1021/jp912102k

[84] M. Xie, X. Zhang, J. Laakso, H. Wang and E. Lev鋛en, "New method of postmodifying the particle size and morphology of LiFePO$_4$ via supercritical carbon dioxide", Cryst. Growth Des. 12(5), 2166-2168 (2012). http://dx.doi.org/10.1021/cg3003146

[85] M. Xie, X. Zhang, S. Deng, Y. Wang, H. Wang, J. Liu, H. Yan, J. Laakso and E. Lev鋛en, "The effects of supercritical carbon dioxide treatment on the morphology and electrochemical performance of LiFePO$_4$ cathode materials", RSC Adv. 3(31), 12786-12793 (2013). http://dx.doi.org/10.1039/c3ra41133h

[86] M. Xie, X. Zhang, Y. Wang, S. Deng, H. Wang, J. Liu, H. Yan, J. Laakso and E. Levänen, "A template-free method to prepare porous LiFePO$_4$ via supercritical carbon dioxide", Electrochim. Acta 94(1), 16-20 (2013). http://dx.doi.org/10.1016/j.electacta.2013.01.131

[87] M. Gaberscek, R. Dominko, M. Bele, M. Remskar, D. Hanzel and J. Jamnik, "Porous, carbon-decorated LiFePO$_4$ prepared by sol–gel method based on citric acid", Solid State Ionics 176(19-22), 1801-1805 (2005). http://dx.doi.org/10.1016/j.ssi.2005.04.034

[88] R. Dominko, J. M. Goupil, M. Bele, M. Gaberscek, M. Remskar, D. Hanzel and J. Jamnik, "Impact of LiFePO$_4$/C composites porosity on their electrochemical performance", J. Electrochem. Soc. 152(5), A858-A863 (2005). http://dx.doi.org/10.1149/1.1872674

[89] A. Peigney, C. Laurent, E. Flahaut, R. R. Bacsa and A. Rousset, "Specific surface area of carbon nanotubes and bundles of carbon nanotubes", Carbon 39(4), 507-514 (2001). http://dx.doi.org/10.1016/S0008-6223(00)00155-X

[90] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva and A. A. Firsov, "Electric field effect in atomically thin carbon films", Science 306(5696), 666-669 (2004). http://dx.doi.org/10.1126/science.1102896

[91] A. K. Geim and K. S. Novoselov, "The rise of graphene", Nat. Mater. 6(3), 183-191 (2007). http://dx.doi.org/10.1038/nmat1849

[92] Z.-L. Wang, D. Xu, H.-G. Wang, Z. Wu and X.-B. Zhang, "*In situ* fabrication of porous graphene electrodes for high-performance energy storage", ACS Nano 7(3), 2422-2430 (2013). http://dx.doi.org/10.1021/nn3057388

[93] L. P. Biro, P. Nemes-Incze and P. Lambin, "Graphene: nanoscale processing and recent applications", Nanoscale 4(6), 1824-1839 (2012). http://dx.doi.org/10.1039/C1NR11067E

[94] O. A. Vargas C, A. Caballero and J. Morales, "Can the performance of graphene nanosheets for lithium storage in Li-ion batteries be predicted?", Nanoscale 4(6), 2083-2092 (2012). http://dx.doi.org/10.1039/C2NR11936F

[95] F. Y. Su, Y. B. He, B. Li, X. C. Chen, C. H. You, W. Wei, W. Lv, Q. H. Yang and F. Kang, "Could graphene construct an effective conducting network in a high-power lithium ion battery?", Nano Energy 1(3), 429-439 (2012). http://dx.doi.org/10.1016/j.nanoen.2012.02.004

[96] F. Y. Su, C. You, Y. B. He, W. Lv, W. Cui, F. Jin, B. Li, Q. H. Yang and F. Kang, "Flexible and planar graphene conductive additives for lithium-ion batteries", J. Mater. Chem. 20(43), 9644-9650 (2010). http://dx.doi.org/10.1039/C0JM01633K

[97] X. Zhou, F. Wang, Y. Zhu and Z. Liu, "Graphene modified $LiFePO_4$ cathode materials for high power lithium ion batteries", J. Mater. Chem. 21(10), 3353-3358 (2011). http://dx.doi.org/10.1039/c0jm03287e

[98] C. Su, X. Bu, L. Xu, J. Liu and C. Zhang, "A novel $LiFePO_4$/graphene/carbon composite as a performance-improved cathode material for lithium-ion batteries", Electrochim. Acta. 64(1), 190-195 (2012). http://dx.doi.org/10.1016/j.electacta.2012.01.014

[99] J. Popovic, R. Demir-Cakan, J. Tornow, M. Morcrette, D. S. Su, R. Schlögl, M. Antonietti and M. M. Titirici, "$LiFePO_4$ mesocrystals for lithium-ion batteries", Small 7(8), 1127-1135 (2011). http://dx.doi.org/10.1002/smll.201002000

[100] J. Ha, S. K. Park, S. H. Yu, A. Jin, B. Jang, S. Bong, I. Kim, Y. E. Sung and Y. Piao, "A chemically activated graphene-encapsulated $LiFePO_4$ composite for high-performance lithium ion batteries", Nanoscale 5(18), 8647-55 (2013). http://dx.doi.org/10.1039/c3nr02738d

[101] Y. Shi, S.-L. Chou, J.-Z. Wang, D. Wexler, H.-J. Li, H.-K. Liu and Y. Wu, "Graphene wrapped $LiFePO_4$/C composites as cathode materials for Li-ion batteries with enhanced rate capability", J. Mater. Chem. 22(32), 16465-16470 (2012). http://dx.doi.org/10.1039/c2jm32649c

[102] H. Wang, J. T. Robinson, G. Diankov and H. Dai, "Nanocrystal growth on graphene with various degrees of oxidation", J. Am. Chem. Soc. 132(10), 3270-3271 (2010). http://dx.doi.org/10.1021/ja100329d

[103] Y. Zhu, S. Murali, M. D. Stoller, K. J. Ganesh, W. Cai, P. J. Ferreira, A. Pirkle, R. M. Wallace, K. A. Cychosz, M. Thommes, D. Su, E. A. Stach and R. S. Ruoff, "Carbon-based supercapacitors produced by activation of graphene", Science 332(6037), 1537-41 (2011). http://dx.doi.org/10.1126/science.1200770

[104] J. Yang, J. Wang, D. Wang, X. Li, D. Geng, G. Liang, M. Gauthier, R. Li and X. Sun, "3D porous $LiFePO_4$/graphene hybrid cathodes with enhanced performance for Li-ion batteries", J. Power Sources 208(15), 340-344(2012). http://dx.doi.org/10.1016/j.jpowsour.2012.02.032

[105] J. Yang, J. Wang, Y. Tang, D. Wang, X. Li, Y. Hu, R. Li, G. Liang, T.-K. Sham and X. Sun, "$LiFePO_4$-graphene as a superior cathode material for rechargeable lithium batteries: impact of stacked graphene and unfolded graphene", Energ. Environ. Sci. 6(5), 1521-1528 (2013). http://dx.doi.org/10.1039/C3EE24163G

[106] R. H. Baughman, A. A. Zakhidov and W. A. de Heer, "Carbon nanotubes–the route toward applications", Science 297(5582), 787-792 (2002). http://dx.doi.org/10.1126/science.1060928

[107] T. W. Ebbesen, H. J. Lezec, H. Hiura, J. W. Bennett, H. F. Ghaemi and T. Thio, "Electrical conductivity of individual carbon nanotubes", Nature 382(6586), 54-56 (1996). http://dx.doi.org/10.1038/382054a0

[108] J. Yang, J. Wang, X. Li, D. Wang, J. Liu, G. Liang, M. Gauthier, Y. Li, D. Geng, R. Li and X. Sun, "Hierarchically porous $LiFePO_4$/nitrogen-doped carbon nanotubes composite as a cathode for lithium ion batteries", J. Mater. Chem. 22(15), 7537-7543 (2012). http://dx.doi.org/10.1039/c2jm30380a

[109] H. Liu, Y. Zhang, R. Li, X. Sun, S. Désilets, H. Abou-Rachid, M. Jaidann and L.-S. Lussier, "Structural and morphological control of aligned nitrogen-doped carbon nanotubes", Carbon 48(5), 1498-1507 (2010). http://dx.doi.org/10.1016/j.carbon.2009.12.045

[110] Y. T. Lee, N. S. Kim, S. Y. Bae, J. Park, S.-C. Yu, H. Ryu and H. J. Lee, "Growth of vertically aligned nitrogen-doped carbon nanotubes: control of the nitrogen content over the temperature range 900-1100℃", J. Phys. Chem. B 107(47), 12958-12963 (2003). http://dx.doi.org/10.1021/jp0274536

[111] J. Liu, Y. Zhang, M. I. Ionescu, R. Li and X. Sun, "Nitrogen-doped carbon nanotubes with tunable structure and high yield produced by ultrasonic spray pyrolysis", Appl. Surf. Sci. 257(17), 7837-7844 (2011). http://dx.doi.org/10.1016/j.apsusc.2011.04.041

[112] O. Toprakci, H. A. Toprakci, L. Ji, G. Xu, Z. Lin and X. Zhang, "Carbon nanotube-loaded electrospun $LiFePO_4$/carbon composite nanofibers as stable and

binder-free cathodes for rechargeable lithium-ion batteries", ACS Appl. Mater. Interfaces 4(3), 1273-1280 (2012). http://dx.doi.org/10.1021/am201527r

[113] Y. Zhou, J. Wang, Y. Hu, R. O'Hayre and Z. Shao, "A porous LiFePO$_4$ and carbon nanotube composite", Chem. Commun. (Camb). 46(38), 7151-3 (2010). http://dx.doi.org/10.1039/c0cc01721c

[114] G. Arnold, J. Garche, R. Hemmer, S. Ströbele, C. Vogler and M. Wohlfahrt-Mehrens, "Fine-particle lithium iron phosphate LiFePO$_4$ synthesized by a new low-cost aqueous precipitation technique", J. Power Sources 119–121(1), 247-251 (2003). http://dx.doi.org/10.1016/S0378-7753(03)00241-6

[115] Y. Xu, Y. Lu, L. Yan, Z. Yang and R. Yang, "Synthesis and effect of forming Fe2P phase on the physics and electrochemical proper-

ties of LiFePO$_4$/C materials", J. Power Sources 160(1), 570-576 (2006). http://dx.doi.org/10.1016/j.jpowsour.2006.01.042

[116] B. Kang and G. Ceder, "Battery materials for ultrafast charging and discharging", Nature 458(7235), 190-193 (2009). http://dx.doi.org/10.1038/nature07853

[117] K. Zaghib, J. B. Goodenough, A. Mauger and C. Julien, "Unsupported claims of ultrafast charging of LiFePO$_4$ Li-ion batteries", J. Power Sources 194(2), 1021-1023 (2009). http://dx.doi.org/10.1016/j.jpowsour.2009.05.043

[118] G. Ceder and B. Kang, "Response to 'unsupported claims of ultrafast charging of Li-ion batteries' ", J. Power Sources. 194(2), 1024-1028 (2009). http://dx.doi.org/10.1016/j.jpowsour.2009.07.004