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REVIEW

Recent developments in the doping and surface modification of $LiFePO_4$ as cathode material for power lithium ion battery

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Abstract Lithium ion batteries have become attractive for portable devices due to their higher energy density compared to other systems. With a growing interest to develop rechargeable batteries for electric vehicles, lithium iron phosphate ($LiFePO_4$) is considered to replace the currently used $LiCoO_2$ cathodes in lithium ion cells. $LiFePO_4$ is a technically important cathode material for new-generation power lithium ion battery applications because of its abundance in raw materials, environmental friendliness, perfect cycling performance, and safety characteristics. However, the commercial use of $LiFePO_4$ cathode material has been hindered to date by their low electronic conductivity. This review highlights the recent progress in improving and understanding the electrochemical performance like the rate ability and cycling performance of $LiFePO_4$ cathode. This review sums up some important researches related to $LiFePO_4$ cathode material, including doping and coating on surface. Doping elements with coating conductive film is an effective way to improve its rate ability.

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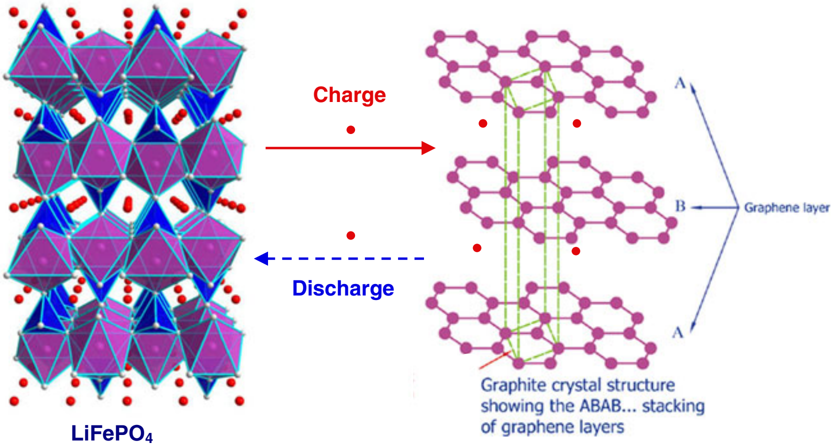
Introduction

One of the greatest challenges at present is how to make use of renewable energies and the replacement of petroleum with electric propulsion as a worldwide imperative. Among the various available storage technologies, the lithium ion battery, which has conquered the portable electronic market, has become the prime candidate to power the next generation of electric vehicles (EVs) and plug-in hybrid electric vehicles (PHEVs) [1]. With regard to large-size applications of lithium ion battery such as in EVs and HEVs, in contrast, lower-cost and safe cathode materials are required. As the demand for powerful and large Li ion batteries grows, $LiFePO_4$ has received much attention as a positive electrode (cathode) material because of its stability, low cost, and environmental friendliness. Figure 1 shows the charge and discharge diagram of $LiFePO_4$/graphite battery [2, 3]. $LiFePO_4$ initially includes one Li^+ ion per formula unit that can be extracted and transferred to the anode in the first charge process, compensating for the oxidation from Fe^{2+} to Fe^{3+} as shown in Fig. 2 [4–6]. The theoretical capacity based on this one electron reaction is 170 mAh g^{-1}, but the poor conductivity, resulting from the low lithium ion diffusion rate and low electronic conductivity in the $LiFePO_4$ phase, has posed a bottleneck for commercial applications. Ever since it was introduced by Radhi et al. [5], many efforts have been made to enhance its low conductance. Improvements in conductivity have been achieved in two ways. One was to dope with certain elements in Li, Fe, or O sites to

Fig. 1 Charge and discharge diagram of $LiFePO_4$/graphite battery obtained reference [2, 3]

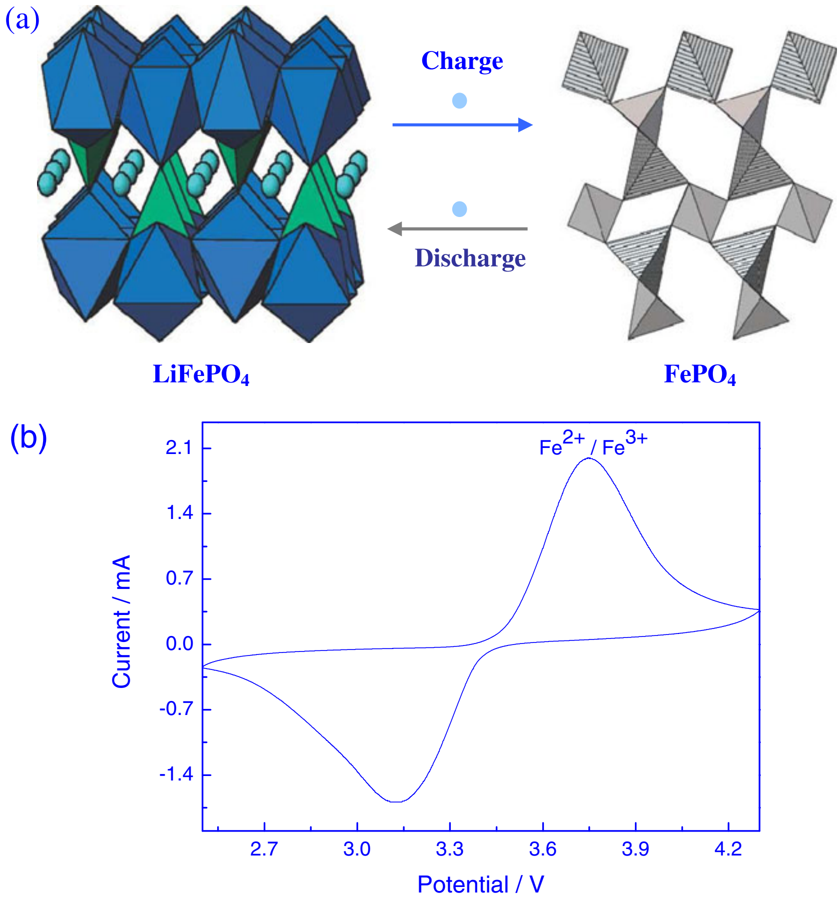


improve the intrinsic conductivity and promote the redox potential. Surface modification of the $LiFePO_4$ is another effective way to improve the conductance and reduce the side reactions. This review sums up some important researches related to $LiFePO_4$ cathode material, including doping and coating on surface. The latest research progresses which improve the electrochemical properties of $LiFePO_4$ such as rate capability and cyclic performance are presented.

$LiFePO_4$ doped by ions

In order to improve the conductance of $LiFePO_4$, much effort has been paid. Coating by carbon is an efficient way to increase the electrochemical performance of these materials [7–9]. Unfortunately, the carbon coating method obviously helps nothing in the lattice electronic conductivity or chemical diffusion coefficient of lithium within the crystal [10]. Substitution of a small quantity of Li^+, Fe^{2+}, or O^{2-} by

Fig. 2 **a** Structure transformation of orthorhombic $LiFePO_4$ and trigonal quartz-like $FePO_4$ during charge and discharge obtained from [6]. **b** Cyclic voltammograms of $LiFePO_4$ at a scan rate of 0.1 mV s^{-1} between 2.5 and 4.3 V (vs. Li/Li^+) obtained from our experimental data



other ions greatly improves the kinetics of materials in terms of capacity delivery, cycle life, and rate capability. The first-principles investigation also reveals that $LiFePO_4$ is most affected by F ion doping at O site with the narrowest band gap, followed by Mn ion doping at Fe site and Na ion doping at Li site, indicating that appropriate ion doping in $LiFePO_4$ could improve its electronic conductivity [11].

Doping in the Li site

Chung et al. [12] have reported that the controlled cation doping with metal ions supervalent to Li^+ increased the electronic conductivity of $LiFePO_4$ by a factor of $\sim 10^8$. Although there is much controversy in this report, there is no dispute that doping can increase the conductivity of $LiFePO_4$ in the Li site. The first-principles calculations show that the electronic conductive properties and ionic transport feature of $LiFePO_4$ can be improved by Na doping in the Li site and favorable for high-rate performance [13]. Yin et al. [14] reported the single-phase $Li_{1-x}Na_xFePO_4/C$ (x=0, 0.01, 0.03, 0.05) samples synthesized by in situ polymerization restriction–carbon thermal reduction method. The doped Na ion does not destroy the lattice structure of $LiFePO_4$, and the discharge capability and cycle performance are improved by an appropriate amount of Na doping as plotted in Fig. 3a. This can be attributed to its smaller charge transfer resistance than that of $LiFePO_4/C$. Yang et al. [15] reported the stoichiometric Cu-doped lithium iron phosphates synthesized via improved co-precipitation, followed by sintering at high temperature for crystallization. The particle size of the $Li_{0.98}Cu_{0.01}FePO_4$ with pure single phase was drastically fine with 100–200 nm, and the reversible capacity, cycle number, and charge–discharge characteristics exhibited better than those of $LiFePO_4$ as shown in Fig. 3b. Ying et al. [16] reported the spherical olivine $Li_{0.97}Cr_{0.01}FePO_4/C$ powders synthesized by carbothermal reduction process, and the spherical olivine $Li_{0.97}Cr_{0.01}FePO_4/C$ powder has a higher tap density (1.8 gcm^{-3}) than that of the non-spherical $LiFePO_4$ powders and then shows excellent cycling performance as given in Fig. 3c. Li et al. [17] reported submicron-sized Ti-doped $LiFePO_4$ cathode materials synthesized by a reformative co-precipitation and normal-temperature reduction method. The result shows that higher Ti ions' doping levels are conducive to the electrochemical performance of $LiFePO_4$, and the sample doped with 3 at.% Ti shows the most impressive cycling performance among all samples, even after 100 cycles at 1-C rate (see Fig. 3d). Zhang et al. [18] reported the Nd-doped $LiFePO_4/C$ cathode synthesized by a novel solid-state reaction method at 750 °C without using inert gas. The results indicate that Nd^{3+} and carbon modification do not affect the structure, and the particle size is around 200 nm. The $Li_{0.99}Nd_{0.01}FePO_4/C$ powder exhibited a higher discharge capacity than that of pure $LiFePO_4/C$ at different rates as shown in Fig. 3e. Zhang et al. [19] reported the $Li_{0.99}Mo_{0.01}FePO_4/C$ cathode materials prepared by an easy solution method followed by heat treatment at various temperatures. The results indicate that doping does not affect the olivine structure but considerably improves its capacity delivery and cycling performance as shown in Fig. 3f. It can be ascribed to the enhancement of the electronic conductivity by ion doping and carbon coating. In addition, it has been reported that the controlled cation doping with Mg^{2+} [20], La^{3+}[21], and Y^{3+}[22] ions to Li^+ also increased the electronic conductivity of $LiFePO_4$ and then showed a higher electrochemical performance than that of pure $LiFePO_4$.

Doping in the Fe site

According to the report mentioned above, many researchers proposed that the dopants occupied the Li site due to their small ionic radii. Similarly, Fe site doping by small amounts of Na, Cu, Zn, Mg, Ni, Al, Co, Cr, Mn, Ru, Ti, or V also resulted in improved electrochemical properties mainly by enhancing the electronic conductivity. In addition, it has been reported that Fe site doping weakens the Li–O interaction, resulting in high ionic mobility and diffusion coefficiency [23–25]. First-principle calculation shows that doping at Fe site with alkali metal ions facilitates the diffusion of Li^+ ions along the 1D pathway, which can increase both the electronic and ionic conductivity [26]. Wang et al. [27] reported Na^+ and Cl^- co-doped $LiFePO_4/C$ composites prepared via a simple solid-state reaction. The specific capacities of Na^+/Cl^--doped $LiFePO_4/C$ material are 157 mAh g^{-1} at 0.2 C, 115 mAh g−1 at 10 C, and 98 mAh g^{-1} at 20 C, respectively, as shown in Fig. 4a. The improvement can be ascribed to the enhanced electronic conductivity and electrode kinetics due to the micro-structural modification promoted by co-doping.

Chang et al. [28] reported Cu-doped $LiFe_{1-x}Cu_xPO_4/C$ (x=0, 0.01, 0.015, 0.02, 0.025) cathode materials with a high tap density synthesized by a solid-state reaction in an inert atmosphere. $LiFe_{0.98}Cu_{0.02}PO_4/C$ exhibits excellent charge/discharge capacities of about 150 $mAhg^{-1}$ (297 mAh cm^{-3}) at a rate of 0.1 C and more than 127.3 mAh g^{-1} (252.1 mAh cm^{-3}) at a rate of 2 C.

Liu et al. [29] first reported the spherical zinc-doped $LiZn_{0.01}Fe_{0.99}PO_4$ synthesized by the solid-state route. Zn doping favors the formation of the crystal structure, expands the lattice volume, and then provides more space for lithium ion intercalation/de-intercalation. Shenouda et al. [30] reported the ZnO-doped $LiFePO_4$ by a solid-state route. The 2.5-% ZnO-doped $LiFePO_4$ demonstrates higher conductivity than the 1.5-% ZnO and 5-% ZnO-doped $LiFePO_4$ or the un-doped sample. The 2.5-% ZnO-doped $LiFePO_4$

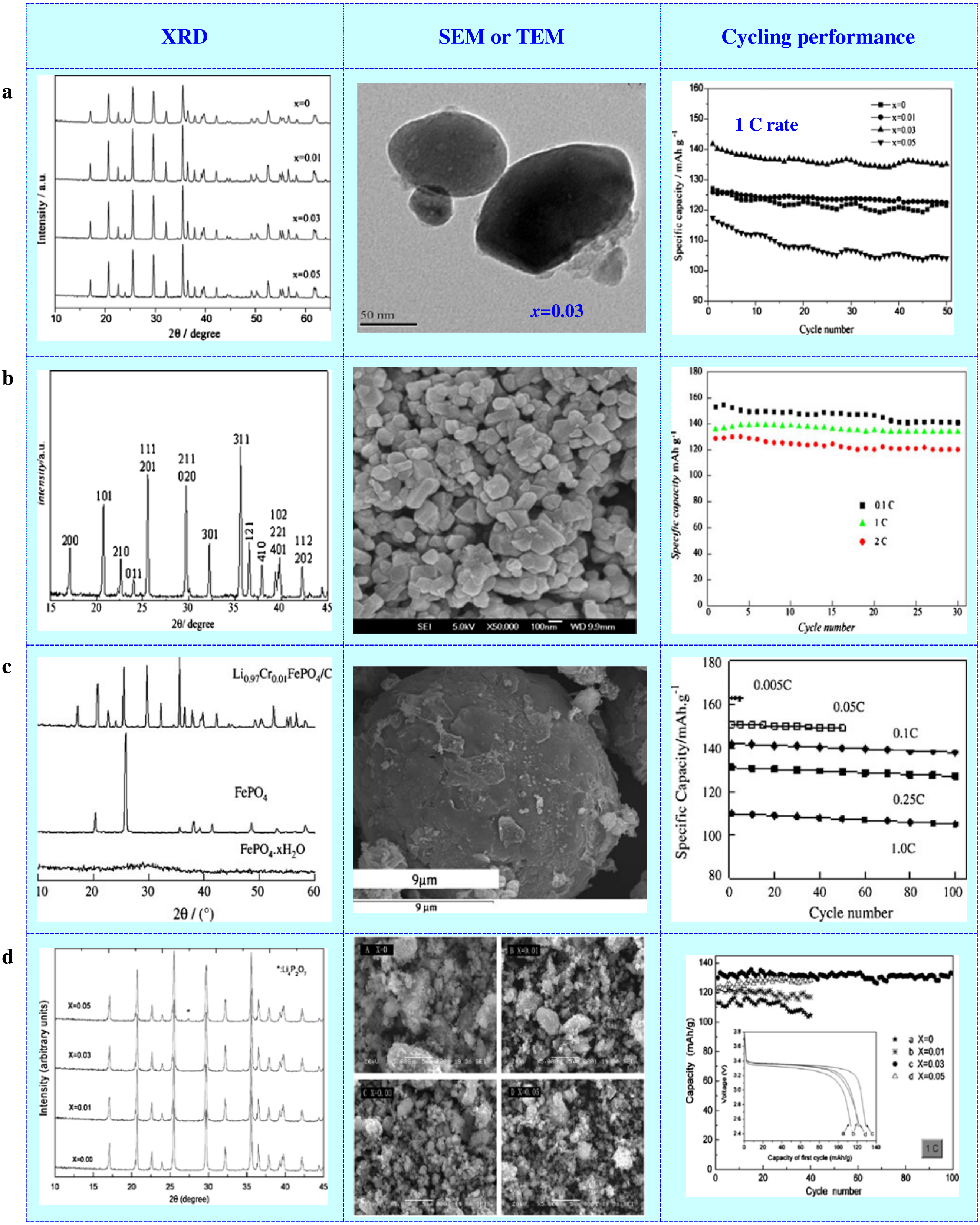


Fig. 3 Effect of metal ions doping in the Li vacancy on the morphology and performance of the synthesized $LiFePO_4$ powders as deduced from XRD, SEM, and cycling performance measurements. **a** $Li_{1-x}Na_xFePO_4/C$ (x=0, 0.01, 0.03, 0.05), **b** $Li_{0.98}Cu_{0.01}FePO_4$, **c** $Li_{0.97}Cr_{0.01}FePO_4/C$, **d** $Li_{1-x}Ti_xFePO_4$ (x=0, 0.01, 0.03, 0.05), **e** $Li_{0.99}Nd_{0.01}FePO_4/C$, and **f** $Li_{0.99}Mo_{0.01}FePO_4/C$ from [14–19]

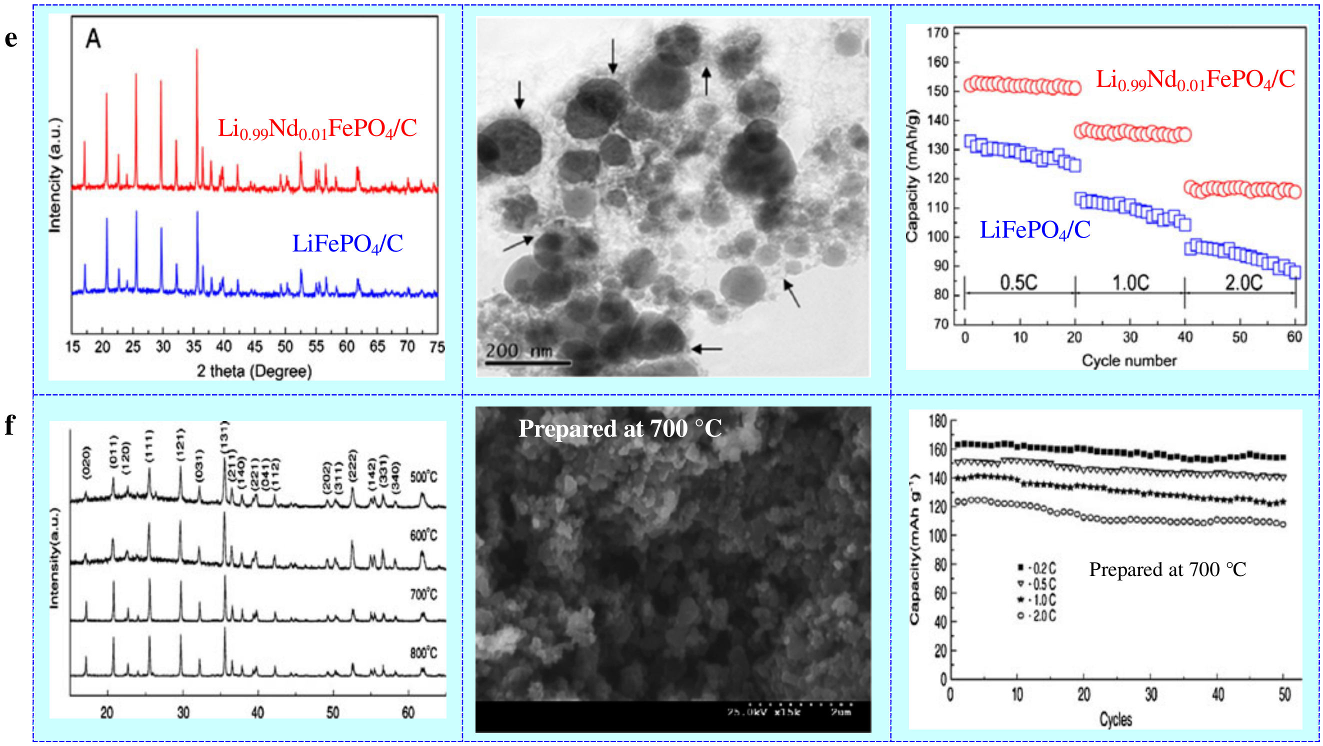


Fig. 3 (continued)

shows excellent cycling performance at a discharge current intensity of 20 mA cm^{-2}. The initial specific discharge capacity is about 177 mAhg^{-1}, and the capacity reaches 167 mAhg^{-1} after 150 cycles as shown in Fig. 4b.

Zhang et al. [31] reported the spherical Ni-doped $\mathrm{LiFePO_4/C}$ synthesized by the conventional solid-state reaction method. The EIS results reveal that Ni doping can decrease the resistance of $\mathrm{LiFePO_4/C}$ composite electrode drastically and improve its reversibility. Hence, Ni-doped spherical $\mathrm{LiFePO_4/C}$ composite exhibits better electrochemical performances compared to an un-doped one as shown in Fig. 4c. Lu et al. [32] reported the $\mathrm{LiFe_{1-\mathit{x}}Ni_\mathit{x}PO_4/C}$ (x=0, 0.02, 0.04, and 0.06) composites prepared by a solid-state reaction. $\mathrm{LiFe_{0.98}Ni_{0.02}PO_4/C}$ delivers the highest initial discharge capacity (121 mAh g^{-1}) and the best cycling performance (108 mAh g^{-1} in the 50th cycle) at the 2-C rate (2.5–4.2 V) among all samples because nickel doping enhances the P–O bond, stabilizes the structure, and then decreases the charge transfer resistance.

Several authors reported that $\mathrm{Mn^{2+}}$-doped $\mathrm{LiFe_{1-\mathit{x}}Mn_\mathit{x}PO_4}$ solid solution could significantly improve the kinetic properties of $\mathrm{LiFePO_4}$ in the region of $0 \leq x \leq 0.75$ [33–35]. It can be concluded that Mn doping may be an effective way to enhance the electrochemical performances of $\mathrm{LiFePO_4}$. Li et al. [36] reported the $\mathrm{LiFe_{1-\mathit{x}}Mn_\mathit{x}PO_4/C}$ (x= 0, 0.05, 0.1) prepared by chelation-assisted mechanochemical activation method using $\mathrm{C_2H_2O_4}$ as the chelating reagent. The results indicate that $\mathrm{Mn^{2+}}$ doping can effectively enhance the electrochemical performance especially at high charge/discharge rate. However, Chen et al. [37] reported that the substituted metal $\mathrm{Mn^{2+}}$ does not work completely at a higher discharge rate due to the poor electrical conductivity and a serious Jahn–Teller effect by in situ metal K-edge absorption analysis.

Xu et al. [38] reported the $\mathrm{LiAl_\mathit{x}Fe_{1-3\mathit{x}/2}PO_4/C}$ (x=0, 0.01, 0.02, 0.04, 0.06, 0.12) prepared via an easy solution method. The results indicate that $\mathrm{Al^{3+}}$ does not affect the olivine structure but considerably improves its initial capacity and cycle performance as plotted in Fig. 4d. $\mathrm{LiAl_{0.01}Fe_{0.985}PO_4/C}$ shows the best electrochemical performance at a discharge rate of 5 C, and it can be ascribed to the enhancement of the electronic conductivity by $\mathrm{Al^{3+}}$ substitution and carbon coating.

Yoon et al. [39] reported that a cobalt-doped sample was found to have less covalent P–O bonds due to the increased covalence of $\mathrm{Fe^{3+}}$–O bonds via the inductive effect compared to the pristine $\mathrm{LiFePO_4}$. It is likely that cobalt ion doping can stabilize the covalence of P–O bonds in $\mathrm{LiFePO_4}$ and then improve its electrochemical performance. Yang et al. [40] reported Co-doped $\mathrm{LiFePO_4/C}$ materials synthesized by a hydrothermal method. The Co-doped sample shows good electrochemical performance at a discharge rate of 5 C as plotted in Fig. 4e. However, Shanmukaraj et al. [41] reported that cobalt doping does not have a favorable effect on the electrochemical performance of $\mathrm{LiFePO_4}$ cathode materials.

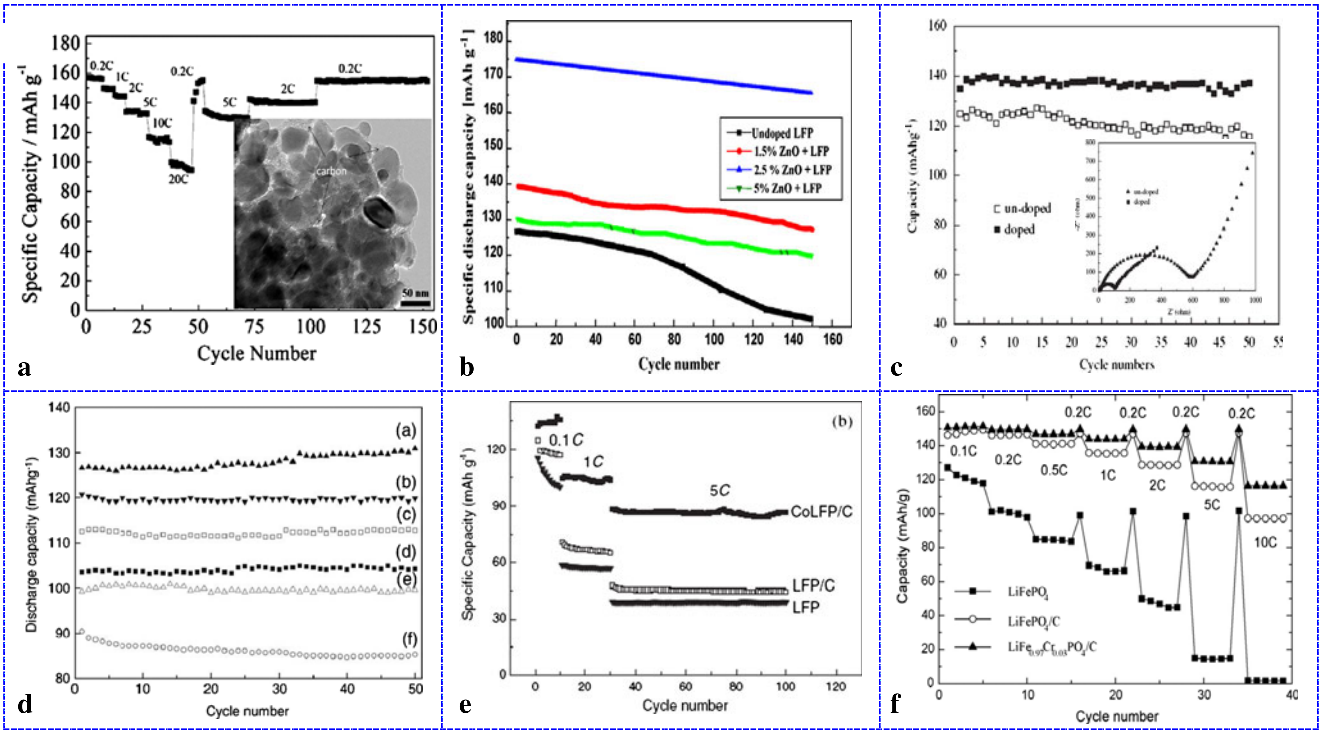


Fig. 4 Cycling performance of metal ion-doped LiFePO$_4$ cathode materials. **a** Na$^+$, Cl$^-$ co-doped LiFePO$_4$ from [27]; **b** 0, 1.5, 2.5, and 5 % ZnO-doped LiFePO$_4$ at a discharge current intensity of 20 mA cm^{-2} from [30]; **c** Ni-doped LiFePO$_4$/C at 0.5-C rate from [31]; **d** Cycling performance of LiAl$_x$Fe$_{1-3x/2}$PO$_4$/C at 5-C rate (*a*) x=0.01, (*b*) x=0.02, (*c*) x=0.04, (*d*) x=0.06, (*e*) x=0.12, (*f*) x=0 from [38]; **e** rate performances of Co-doped LiFePO$_4$/C from [40]; **f** rate performances of LiFePO$_4$, LiFePO$_4$/C, and LiFe$_{0.97}$Cr$_{0.03}$PO$_4$/C discharged at various C rates from [42]

Shin et al. [42] reported the Cr-doped LiFePO$_4$/C synthesized by a mechanochemical process followed by a one-step heat treatment. LiFe$_{0.97}$Cr$_{0.03}$PO$_4$/C shows the best/excellent rate performance among all samples, delivering the discharge capacity up to 120 mAh g^{-1} at 10-C rate as given in Fig. 4f. Chromium doping facilitates the phase transformation between triphylite and heterosite during cycling. Recently, it was reported that Ru-doped material could offer quick Li permeation in addition to high electronic conductivity [43–45]. Yang et al. [46] reported the Ru-doped LiFePO$_4$/C cathode material synthesized by RPR (rheological phase reaction) method, and the doped Ru enhances the conductivity and diffusion coefficient of Li$^+$ and then improves the charge–discharge performance. The RPR preparation process is as follows: The starting materials (CH$_3$COOLi, FeC$_2$O$_4$·2H$_2$O, NH$_4$H$_2$PO$_4$ and polyethylene glycol) were mixed by grinding for 10 min and then added in deionized water to get a rheological body. The mixture was calcinated in a tube furnace at 350 °C for 10 h with flowing nitrogen gas, then it was sintered at 750 °C for a few hours.

In addition, the positive effect of doping by Ti^{4+}, Zr^{4+} [47], and V^{5+} [48, 49] in the Fe site on the rate capacity and cyclic stability of LiFePO$_4$ also has been reported in a group of studies. Wang et al. [47] reported that the Zr- or Ti-doped LiFePO$_4$ demonstrated a stable discharge capacity of 160–165 mAh g^{-1}, almost approaching the theoretical capacity. The good electronic conductivity and nanocrystalline could contribute to the unique performance of LiFePO$_4$ electrodes. Sun et al. [48] reported V-doped LiFePO$_4$/C cathode materials prepared through a carbothermal reduction route. V-doped LiFePO$_4$/C shows a high discharge capacity of ~70 mAh g^{-1} at 20 C. Bilecka et al. [50] reported a microwave-assisted liquid-phase synthesis route to LiFePO$_4$ doped with divalent (Mn, Ni, Zn), trivalent (Al), and tetravalent (Ti) metal ions in varying concentrations. The result shows that Ni- and Zn-doped LiFePO$_4$ with nominal dopant concentrations of 7 and 2 mol%, respectively, outperformed all the other samples. They offer initial specific charge of about 168 Ah kg^{-1} and excellent capacity retention of 97 % after 300 full cycles. A discharge rate of 8 C still results in 152 Ah kg^{-1} after 50 cycles. From the discussion mentioned above, it can be concluded that it will be promising if proper cation doping can be used in LiFePO$_4$ to further improve its electrical conductivity, favoring fast charge and discharge rate.

Doping in the O site

Besides cation doping, there are some researches relative to the substitution of the small amount of Cl$^-$ and F$^-$ for

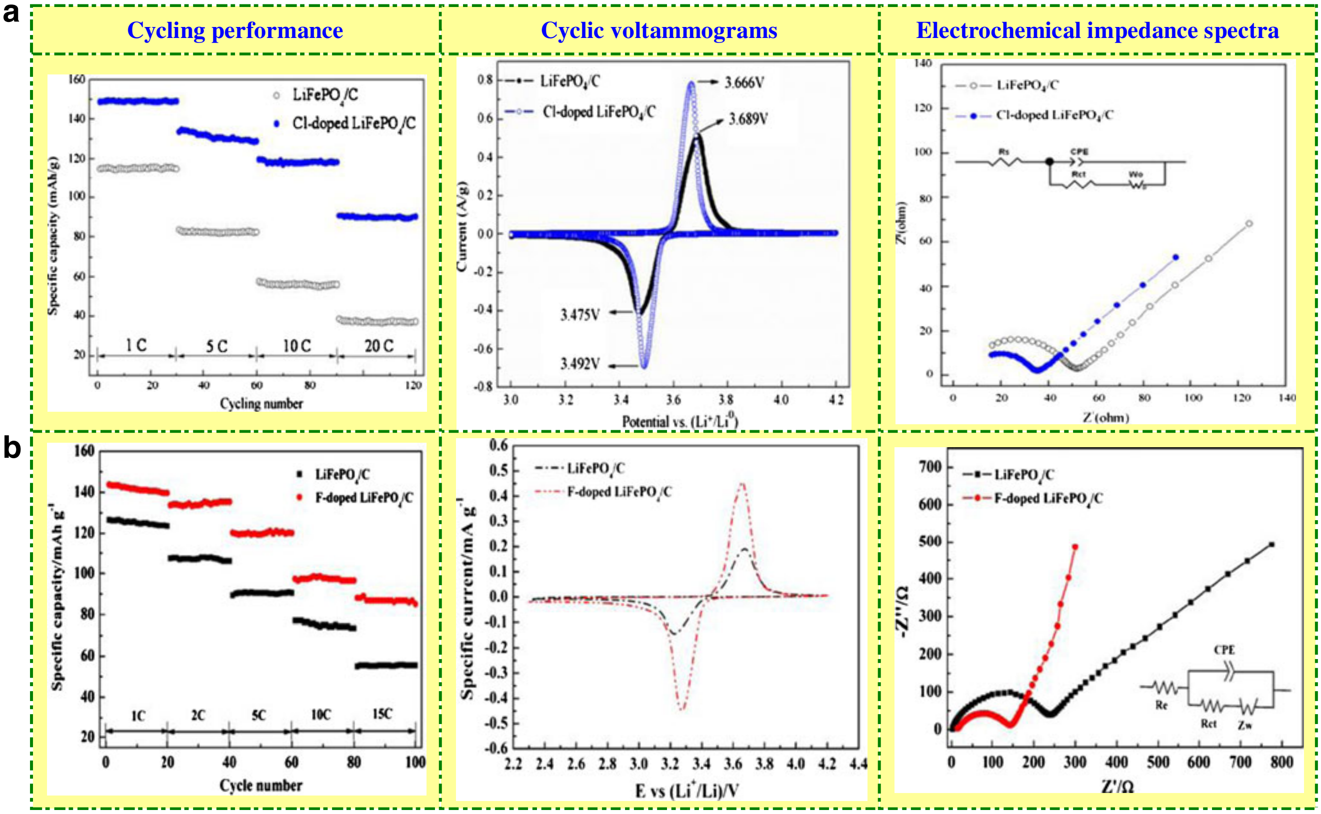


Fig. 5 Electrochemical performance of un-doped and doped $LiFePO_4/C$ samples with different rates from [58, 60]: **a** Cl-doped $LiFePO_4/C$ and **b** F-doped $LiFePO_4/C$

O^{2-} anion. Cl doping has been found to be effective in enhancing the electrochemical performance of cathodes such as $LiNi_{0.7}Co_{0.3}O_2$ [51]. It also has been reported that oxygen substitution with anion such as F^- is effective to acquire high-rate capability and cycle stability for layered structure $LiNiO_2$ [52], $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ [53] cathode materials, and spinel $LiMn_2O_4$ [54, 55] and $LiMn_{1.5}Ni_{0.5}O_4$ [56, 57] material. Sun et al. [58] reported Cl-doped $LiFePO_4/C$ cathode materials synthesized through a carbothermal reduction route, and it presented a high discharge capacity of ~90 mAh g^{-1} at a rate of 20 C at room temperature as given in Fig. 5a. EIS and CV indicate that the improved Li^+ diffusion capability is attributed to the microstructure modification of $LiFePO_4$ via Cl doping. Yang et al. [59] also reported the electrochemical performances of Cl-doped $LiFePO_4/C$ at 15 C at a high Cl doping level, which presented a capacity of ~90

Materials	Electronic Conductivity S cm^{-1}	Carbon Content wt.%	Carbon Thickness nm
(a) $LiFePO_4$	5.88×10^{-8}	0.02	0
(b) Product-0	6.42×10^{-4}	1.25	2-6
(c) Product-1	6.99×10^{-4}	1.67	2-15
(d) Product-2	7.11×10^{-4}	2.28	4-8
(e) Product-3	8.76×10^{-4}	2.54	10-25

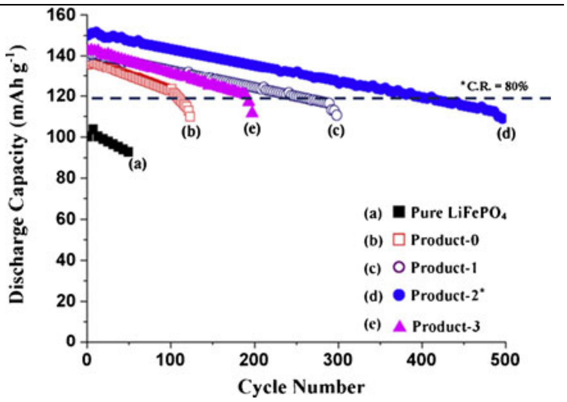


Fig. 6 Discharge capacity versus cycle number for various $LiFePO_4$ electrodes at 0.2-C rate from [66]

Table 1 Synthesis methods and the electrochemical performance of $LiFePO_4$ coated by other non-carbon compounds

Coated non-carbon compounds and references	Synthesis	Electrochemical performances
Ag [79]	$LiFePO_4$ powder prepared using a co-precipitation method was suspended in the solution with vigorous stirring and then added with ascorbic acid to reduce Ag^+ ion and $AgNO_3$ solution. After stirring, the suspended powder was separated by a centrifugal separator. The completion of the Ag^+ reduction was checked by adding 3 M KCl to the separated solution. The silver-coated $LiFePO_4$ was annealed at 500 °C for 30 min in N_2/H_2 (1 vol.%) gas flow	The capacity of the silver-coated $LiFePO_4$ is larger than that of the pure $LiFePO_4$ in all current densities, and the ratio of increase in the capacity by coating is about 10 % in all current densities due to great electronic conductivity
Ag+C [81]	A sol–gel method was developed to synthesize $LiFePO_4$/(Ag+C) composite. Stoichiometric amounts of Fe^{3+} and Ag^+ were dissolved in distilled water and then added with citric acid solution with continuous stirring. To this solution, a solution of ammonium dihydrogen phosphate and a solution of $LiOH{\cdot}H_2O$ were then added. The mixtures were heated gently with continuous stirring for 5 h to remove excess water. The resulting gel precursor was dried in an oven for 4 days at 80 °C and then further calcined in a muffle furnace at 400 °C for 2 h. The calcined precursor mixed with polypropylene was sintered in a tube furnace at 700 °C for 10 h under a N_2 atmosphere	The kinetics of $LiFePO_4$ is improved because of the co-modifying silver and carbon. Discharge capacity is improved from 153.4 mAh g^{-1} of $LiFePO_4$/C to 162.1 mAh g^{-1} for $LiFePO_4$/(Ag+C) cathodes at 0.5-C rate. The discharge capacity of $LiFePO_4$ co-modified with Ag+C is higher than that of $LiFePO_4$ coated with carbon, varying from 0.5 to 1.5 C. EIS measurements show that the Ag+C co-modification decreases the charge transfer resistance of $LiFePO_4$/(Ag+C) cathode
CuO+C [82]	The CuO coating was carried out by chemical precipitation method. $LiFePO_4$/C prepared by sol–gel method was dispersed in ethanol by continuous stirring at room temperature and then two drops of dilute sulfuric acid were added to the suspension to create activated sites on the $LiFePO_4$ surface. A 0.1-M $CuCl_2$ solution was added drop by drop to the suspension with stirring for 2 h, and then added with stoichiometric NaOH to form $Cu(OH)_2$ precipitation with continuous stirring for 8 h. The mixture was filtered and washed three times with distilled water. The precursor was dried at 60 °C for 4 h and then heated to 400 °C for 2 h in N_2/H_2 (5 %)	The Li ion diffusion coefficient is improved due to the CuO coating. The CuO/C–$LiFePO_4$ electrode shows a greater discharge capacity (125 mAh g^{-1}) compared with the C–$LiFePO_4$ cathode material (110 mAh g^{-1}) at a discharge rate of 1 C. The capacity fading of the CuO/C–$LiFePO_4$ electrode is lowered to be 1.6 % after 20 charge–discharge cycles at 1-C rate
SiO_2 [83]	$LiFePO_4$ powder (Aleees Inc.) was mixed with tetraethylorthosilicate in a molar ratio of TEOS/$LiFePO_4$=5:100 in ethanol. The slurry was stirred for 5 h and dried at 70 °C, and then the dried materials were fired at 500 °C for 1 h in a purified Ar gas flow and the SiO_2-coated $LiFePO_4$ was obtained	The discharge capacities are improved from 150 and 140 mAh g^{-1} of $LiFePO_4$ to 160 and 145 mAh g^{-1} for $LiFePO_4/SiO_2$ cathodes at 0.1- and 1-C rate, respectively. The reason is derived from improvement of the structural stability of $LiFePO_4$ grains coated by amorphous SiO_{2-x} layer, increasing the orderliness of Li ion intercalation/ deintercalation
TiO_2 [84]	The $LiFePO_4$ powder (with average particle size of ~5.0 μm) employed has a carbon content of 1.9 % by weight. $Ti(C_3H_7O)_4$ in ethanol was mixed with the $LiFePO_4$ powder in a molar ratio of $Ti(C_3H_7O)_4/LiFePO_4$=0.03:1, and the slurry was heated to about 70 °C in ambient atmosphere until totally dried. The as-prepared powder was then fired in a horizontal oven at 750 °C for 0.5 h under N_2/H_2 (1 %) atmosphere	Coating reduces capacity fading of the $LiFePO_4$/Li cell because it reduces Fe dissolution from the $LiFePO_4$ and hence alleviates the impedance increase associated with the erosion process. However, it imposes a deteriorating effect on the $LiFePO_4$/C cell because the coating itself is eroded upon cycling, and the dissolved Ti ions are subsequently reduced at the anode surface
ZrO_2 [85]	The commercial $LiFePO_4$ materials contain less than 1 % carbon mixed in distilled water with magnetic stirring. Then, one or two drops of dilute sulfuric acid were added to create activated sites on the $LiFePO_4$ surface. A 0.1-M $ZrCl_4$ solution was added in and stirred for 2 h, and then NaOH solution was added to obtain $Zr(OH)_4$ precipitation until the pH value was between 7 and 8. The mixture was filtered and washed with distilled water then it was dried at 50 °C overnight. The powder was sintered at 600 °C for 2 h in inert atmosphere. The nominal ZrO_2 percentage was maintained at 1 wt.%	At 0.1-C rate, the maximum capacity of $LiFePO_4$ is 146 mAh g^{-1}. After 100 cycles, ZrO_2-coated $LiFePO_4$ (143.4 mAh g^{-1}) is higher than that of the uncoated sample (138 mAh g^{-1}). At 1-C rate, the maximum discharge capacity is improved from 90 mAh g^{-1} of $LiFePO_4$ to 97 mAh g^{-1} for $LiFePO_4$/ ZrO_2 cathodes; the capacity is improved from 82 mAh g^{-1} of $LiFePO_4$ to 94 mAh g^{-1} for $LiFePO_4/ZrO_2$ cathodes after 100 cycles
CeO_2 [86]	The calculated amount of $Ce(NO_3)_3{\cdot}6H_2O$ was dissolved in deionized water, then commercial $LiFePO_4$/C powder was added. The mixture was slightly heated at 60 °C to evaporate the solvent. The resulting mixture was heated at 650 °C for 5 h	The CeO_2-coated $LiFePO_4$/C shows high discharge capacities of 138.4 and 128.3 mAh g^{-1} at 1- and 2-C rates, remaining 90.0 % and 83.4 % of the capacity at 0.1 C, while the capacity of the bare one is only 116.6

Table 1 (continued)

Coated non-carbon compounds and references	Synthesis	Electrochemical performances
	under Ar atmosphere. The nominal CeO_2 was about 2 wt.% of the $LiFePO_4$/C powder	and 101.9 mAh g^{-1} at the same rates, respectively. At 253 K, the CeO_2-coated material delivers a discharge capacity of 99.7 mAh g^{-1} at 0.1-C rate and the capacity retention of 98.6 % is obtained after 30 cycles at various charge/discharge rates. The results indicate that the CeO_2 surface treatment is an effective way to improve the comprehensive properties of $LiFePO_4$
NiP [87]	$LiFePO_4$ powders prepared by a solid-state reaction were coated with NiP alloy by electroless plating. The $LiFePO_4$ powders were immersed under stirring in the plating bath containing 0.22 M $NiCl_2·6H_2O$, 0.10 M $NiSO_4·6H_2O$, 0.07 M $NaH_2PO_4·6H_2O$, 0.07 M $Na_2C_6H_5O_7·2H_2O$, and 0.8 M NH_4Cl with 5 ppm KIO_3 as the stabilizer. After plating (25 °C and pH=8–9) for 8 min, the suspension was then filtered and washed using distilled water and ethanol for several times and finally dried at 40 °C in vacuum oven. The amount of the NiP coating was measured as about 2.5 wt.% of the $LiFePO_4$ powders	At 55 °C under 0.1-C charge rate and 1-C discharge rate, the maximum discharge capacity for the uncoated $LiFePO_4$ is 149 mAh g^{-1} and dramatically decreases to 81 mAh g^{-1} after 100 cycles, but the maximum capacity of the NiP-coated $LiFePO_4$ is 151 mAh g^{-1} and is well maintained at 140 mAh g^{-1} after 100 cycles, exhibiting a good capacity retention of 93 % after 100 cycles
PPy/PEG conductive layer [88]	Pyrrole monomer and $LiFePO_4$ prepared by solvothermal method were placed in a 100-mL round-bottom flask. The mixed $FeCl_3$ and HCl (0.1 M) aqueous solution was added to the flask. The mixture was kept at ~4 °C and stirred vigorously for 7 h, and a black precipitate formed progressively. The resulting PPy–$LiFePO_4$ powder was recovered by filtration, washed with water and acetone, and dried in an oven (~70 °C). The preparation of PPy/PEG–$LiFePO_4$ samples with blended polymer coatings was done in the same way, except that polyethylene glycol as an additional component was dissolved in the reaction mixture at the beginning of polymerization (weight ratio PPy/PEG=33:1)	The PPy/PEG coating effectively decreases the charge transfer resistance of the corresponding $LiFePO_4$ cathode. The discharge capacity of PPy–$LiFePO_4$ and PPy/PEG–$LiFePO_4$ are 138 and 146 mAh g^{-1} (at 0.1 C), respectively. The data obtained on the carbon-free $LiFePO_4$ were even slightly better: PPy–$LiFePO_4$ (carbon-free) and PPy/PEG–$LiFePO_4$ (carbon-free) give capacities of 153 and 156 mAh g^{-1}, respectively
Fe_2P [90]	$LiFePO_4$ was synthesized by a previously reported work [91]. $LiFePO_4/Fe_2P$ composites were prepared by ball-milling the starting materials with carbon in stoichiometric excess (1, 3, 5, 7, 10 wt.%, respectively), and subsequent firing at 900 °C for 30 min. Each heating rate was 15 °C min^{-1} and the cooling rate was 4 °C min^{-1}	$LiFePO_4$ shows the highest discharge capacity of 162 mAh g^{-1} at the C/20 rate, and the capacity decreases with increasing amounts of Fe_2P. The discharge capacity of $LiFePO_4/Fe_2P$ composite increased with cycling regardless of the amount of Fe_2P present at 0.2-C rate. Fe_2P-3 sample containing 8 % Fe_2P shows improved electrode performance at high current rate by enhanced electronic conductivity. The initial discharge capacity of Fe_2P-3 is 113 mAh g^{-1}, and the capacity is 122 mAh g^{-1} after 50 cycles

mAhg^{-1}. Lu et al. [60] reported the F-doped $LiFePO_4$/C nanoparticles synthesized via a low-temperature hydrothermal reaction followed by high-temperature treatment. The F-doped sample shows increased initial discharge voltage at various C rates as shown in Fig. 5b because F doping can improve the electrical conductivity of these cathode materials, and the discharge capacities at different rates are 167.3 (0.1 C), 145.2 (1 C), 132.0 (2 C), 120.4 (5 C), 101.3 (10 C), and 90.5 (15 C) mAh g^{-1}, respectively. Liao et al. [61] reported the effects of fluorine substitution on the electrochemical properties of $LiFePO_4$/C cathode materials. They also found that F substitution can improve the rate capability of $LiFePO_4$/C materials, and the $LiFe(PO_4)_{0.9}F_{0.3}$/C sample shows the best high-rate performance among all samples.

$LiFePO_4$ coated by carbon

Carbon coating has been known to be effective not only in enhancing the electrical conductivity of metal oxides but also in increasing their absorbing ability against organic molecules. In addition, a coated carbon layer would protect the metal oxides from chemical corrosion [62–78]. Hence, carbon coating is one of the most important techniques used to improve the specific capacity, rate performance, and cycling life of $LiFePO_4$. Carbon coating also reduces the particle size of $LiFePO_4$ by inhibiting particle growth [63–65, 78] and suppresses the oxidation of Fe^{2+} to Fe^{3+} during sintering act as a reducing agent [65]. However, the analysis of the experimental data suggests that carbon coating has a more significant effect on the rate performance than particle size reduction and doping. The particles of about 300 nm exhibit good rate capability that is comparable to those of the nanosized particles [76]. Huang et al. [8] also reported that both particle size minimization and intimate carbon contact are needed to optimize the rate capability of this material. Cho et al. [66] reported that the carbon coating thickness has a more significant effect on the capacity as given in Fig. 6. Their results indicate that the electrochemical properties of $LiFePO_4$ are correlated to the amount of carbon and its coating thickness and uniformity, and some amounts of graphite-like carbon in the disordered carbon structure can enhance the electronic conductivity of the carbon deposit. The type and morphology of the carbon deposits depend on the source of the carbon. Graphitic carbon generally provides higher conductivity and thus higher rate capacities at large discharge rates, so carbons with large sp^2/sp^3 ratios are generally preferred [77].

$LiFePO_4$ particles with other coated conductive films, such as Ag [78–80], Ag+C [81], CuO+C [82], SiO_2 [83], TiO_2 [84], ZrO_2 [85], CeO_2 [86],NiP [87], PPy/PEG conductive layer [88, 89], and Fe_2P [90], also improve their electrochemical performance. The synthesis methods and the electrochemical performance of $LiFePO_4$ coated by non-carbon compounds are shown in Table 1. The improvement of cycling performance and discharge capacity for $LiFePO_4$ coated by Ag [78–80], Ag+C [81], CuO[82], PPy/PEG [88], and Fe_2P [90] is due to the increase of electronic conductivity and then results in a very significant increase of electro-active zones. The SiO_2 coating increases the order of lithium ion intercalating the outer lattice of the particle and then improves capacity retention significantly [83]. The TiO_2 coating itself is not stable and partially dissolved upon cycling, causing redeposition of Ti at the C anode. Ti deposit can remarkably improve the electrochemical performance at high charge–discharge rate of $LiFePO_4$/Li cell due to the more active Ti [84]. The ZrO_2 coating can remarkably improve the high-rate performance due to the amelioration of the electrochemical dynamics on the $LiFePO_4$ electrode/electrolyte interface resulting from the effects of the ZrO_2 nanolayer coating [85]. The CeO_2 coating decreases the contact resistance and the charge transfer resistance and then improves the electrochemical performance [86]. NiP coating can sustain the structure stability and conductivity of $LiFePO_4$ upon cycling because NiP coating has a good metallic mechanical property [87]. The coated results indicate that the surface treatment should be an effective way to improve the comprehensive properties of the cathode materials for lithium ion batteries.

Conclusions

$LiFePO_4$ has been considered as one of the primary battery materials for EV, HEV, and PHEV applications due to its flat voltage profile, low material cost, abundant material supply, and better environmental compatibility compared to other cathode materials. The improvement of $LiFePO_4$ cathode materials is a big challenge in order to fulfill the requirements of future energy storage. From the discussion earlier, one of the best methods to improve the power performance of $LiFePO_4$ is to improve its electronic conductivity by doping and coating. Coating with carbon or other conductive films can help to modify the total electronic conductivity of $LiFePO_4$ composites, while doping with cations and anions may improve the intrinsic electronic conductivity. It is sure that doping and coating will play, more and more, an important role in improving the electrochemical performance of $LiFePO_4$. Hence, the doped and coated $LiFePO_4$ is one of the promising cathode materials for next-generation power lithium ion batteries since it shows excellent performance such as good safety, cyclability, and rate capability. It can be concluded that the doped and coated $LiFePO_4$ may be the trend of development of power lithium ion battery cathode material in the long term.

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