Int. J. Electrochem. Sci., 15 **(2020)** 12041 – 12067, doi: 10.20964/2020.12.71

International Journal of
ELECTROCHEMICAL
SCIENCE
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Review

A review of the Doping Modification of $LiFePO_4$ as a Cathode Material for Lithium Ion Batteries

Huanhuan Zhang, Zhengguang Zou, Shuchao Zhang, Jie Liu, Shenglin Zhong*

College of Materials Science and Engineering, Guilin University of Technology, Guilin, China.
*E-mail: zouzgglut@163.com

Received: 8 September 2020 / *Accepted:* 18 October 2020 / *Published:* 31 October 2020

In the today that energy crisis and the rapid development of electronic equipment, lithium-ion batteries, as a kind of energy storage device with high energy density, safe and cheap, have become a hotspot of research. Lithium iron phosphate ($LiFePO_4$) has attracted wide attention in the field of large-capacity power lithium-ion batteries for its advantages of good stability, low raw material cost and environmental friendliness, and is considered to be one of the most potential lithium-ion battery cathode materials. However, the low intrinsic conductivity and lithium ion diffusion coefficient limit its development and application in the further. For a long time, various methods have been studied to improve its performance. This article will systematically describe the effects of doping of metal element, doping of non-metallic element and doping of metallic simple substance or metal oxide on the electrochemical performance of $LiFePO_4$, and summarize the latest research progress in the modification of doping of $LiFePO_4$ in recent years. Different doped particles have different effects on the performance of $LiFePO_4$ cathode materials. An appropriate amount of doping can often improve the performance of $LiFePO_4$ cathode materials to a certain extent. Multi-element co-doping of $LiFePO_4$ is expected to be an important way to effectively improve its electrochemical performance.

Keywords: lithium ion battery; $LiFePO_4$; Doping modification

1. INTRODUCTION

Recently, with the rapid development of new energy and electronic equipment, energy conversion and energy storage have become a major issue that people need to solve urgently. At present, the commonly used energy storage methods include battery energy storage, inductor energy storage and capacitor energy storage. Among them, lithium-ion batteries have received widespread attention due to their high working voltage, high energy density and environmental friendliness. They are regarded as a kind of energy storage devices with excellent performance, and continue to replace lead-acid batteries, nickel-cadmium batteries and nickel-oxygen batteries in various fields, and further develop in the direction of light, small and thin [1]. In recent years, electric vehicles (EVS) and plug-in the hybrid electric vehicles (PHEVs) has greatly increased the demand for high-power and large-capacity lithium-ion batteries. As one of the polyanionic cathode materials, $LiFePO_4$ attracts the attention of researchers due to its stable discharge platform (3.4 V), high discharge capacity (170 mAh/g), good cycle stability, thermal stability, especially low raw material cost and environmental friendliness. It is considered to be one of the most appropriate cathode materials for power batteries [2,3], and has become a hot research topic.

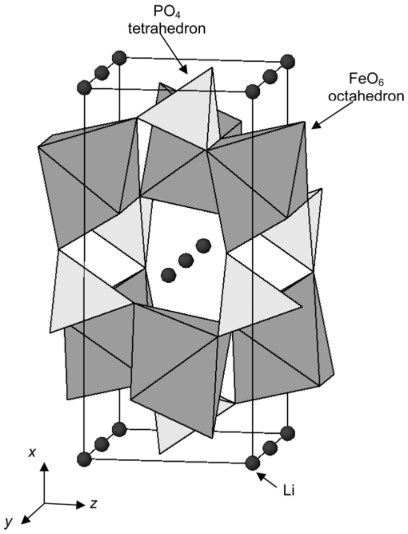

Figure 1. The crystal structure of $LiFePO_4$ [4]

As shown in Figure 1, $LiFePO_4$ belongs to the olivine type structure. In its structure, phosphorus oxide tetrahedral (PO_4), lithium oxygen octahedron (LiO_6) and ferrite octahedron (FeO_6) are formed with P, Li and Fe as the center.. Since the P and O in the PO_4 tetrahedron are connected to each other by a strong covalent bond, the oxygen atom is prevented from being oxidized, so that the oxygen atom is always in a stable state during the charge and discharge process, which makes $LiFePO_4$ far superior to other cathode materials in terms of safety performance and cycle performance. However, the extremely low electronic conductivity (10^{-9}~10^{-10} S/cm) and diffusion coefficient ($D_{Li+}<10^{-14}$ cm^2/S) of $LiFePO_4$ make it inferior to other cathode materials in terms of rate performance [5,6]. This is also one of the reasons that limit the large-scale application of lithium iron phosphate in the field of power batteries.

During the charging and discharging process of $LiFePO_4$, 1 mol of $LiFePO_4$ can be inserted into 1 mol of Li^+, corresponding to 1 mol of electrons, so its theoretical capacity is about 170 mAh/g. With the Fe^{2+} and Fe^{3+} in the cathode electrodes undergo a corresponding oxidation-reduction reaction, the extraction and insertion of Li^+ between the cathode and anode materials, forming a rocking chair cycle [7]. In this process, the $LiFePO_4$ crystal structure hardly undergoes rearrangement, showing good structural stability, as shown in Figure 2 [8].

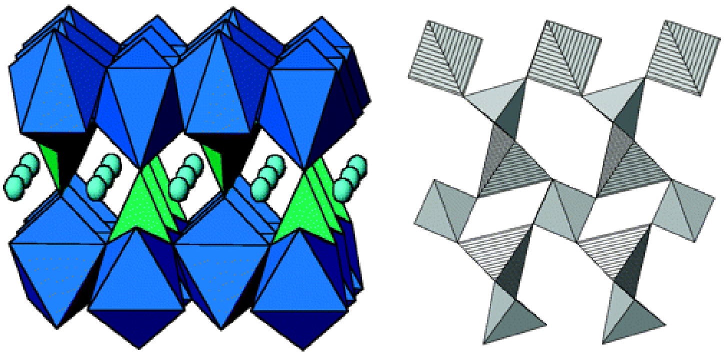

Figure 2. Structures of orthorhombic $LiFePO_4$ and trigonal quartz-like $FePO_4$ [8]

In recent years, the related research on $LiFePO_4$ has mostly focused on its performance improvement, especially for its shortcomings such as low electronic conductivity and low diffusion coefficient. Many measures have been taken, such as surface modification [9-11], nanocrystallization of particles [12,13], doping [14-16], etc. Among them, doping has obvious effects on improving the electronic conductivity of $LiFePO_4$ and the diffusion coefficient of Li^+. A large number of studies [17-20] have proved that reasonable doping modification has a significant improvement effect on the rate performance and cycle stability of $LiFePO_4$.

This article reviews some important researches on the doping modification of $LiFePO_4$ cathode materials, including doping of metal element, doping of non-metallic element and doping of metal simple substance or metal oxide. The latest research progress on the modification effects of different doped particles on the electrochemical performance of $LiFePO_4$ is introduced.

2. DOPING OF LI AND FE

The doping of metal element can increase the lattice defects of $LiFePO_4$, which helps to improve the diffusion rate of lithium ions and the internal conductivity of the particles, fundamentally reconcile the problem of poor conductivity, and improve its electrochemical performance. Taking into account the different doping positions, the choice of doping element will also be different. Generally speaking, the closer the radius of the two ions, the easier it is to replace each other. In addition, the higher the valence state of the doping ions, the better conducive to the formation of more holes in the crystal lattice after doping, which has a very important role in promoting the conductivity of the material and the diffusion rate of lithium ions in the material.

Chung [21] found through experiments that $Li_{1-x}M_xFePO_4$ doped with high-valence metal ions (Nb^{5+}, Mg^{2+}, Al^{3+}, Ti^{4+}, W^{6+}, etc.) will produce positive ion defects, which makes Fe^{3+}/Fe^{2+} appear in $LiFePO_4$. The mixed valence state promote the formation of P-type semiconductors, thereby increasing the conductivity of $LiFePO_4$ to 10^{-2} S/cm, which is a great improvement compared with the pure phase $LiFePO_4$. At present, according to the different doping positions, doping of metal element is mainly divided into doping of metal element in Li site, doping of metal element in Fe site and co-doping in Li site and Fe site. Its influence on the electrochemical performance of lithium iron phosphate is also different.

2.1 Doping in Li site

When doping $LiFePO_4$ with metal element at the Li-site, high-valent metal ions with a smaller radius are often used, such as Nb^{5+}, A1^{3+}, Ti^{4+}, K^+, Na^+, etc. According to first-principles studies, it is found that the doping of high-valent metal ions with a smaller radius in the lithium site can increase the hole mobility in lithium iron phosphate, making it complete the transition from intrinsic N-type semiconductor to extrinsic P-type semiconductor, thereby realizing the improvement of conductivity, which has a positive effect on the improvement of electrochemical performance [22].

Li [23] once reported that when the doping amount of Nb is 2%, the charge transfer resistance of the synthesized $Li_{0.98}Nb_{0.02}FePO_4/C$ is small. The first discharge capacity is 164.9 mAh/g and 118.8 mAh/g at 0.1 C and 10 C, respectively. After 200 cycles at 10 C, the capacity retention rate can still reach to 96.2%. The doping of Nb with a small amount can shorten the b axis in the $LiFePO_4$ unit cell, shorten the diffusion path of lithium ion, and increase the distance between the crystal planes parallel to the [010] direction in $LiFePO_4$, and widen the lithium ion along the [010] direction one-dimensional diffusion channel to promote lithium ion diffusion[24]. In addition, due to the different valence states, it is easy to produce N-type doping, which improves the electronic conductivity of the material and effectively improves its performance [25]. Later, Johnson's related research has also fully confirmed that Nb doping is beneficial to improve the electrochemical performance of $LiFePO_4$ [26].

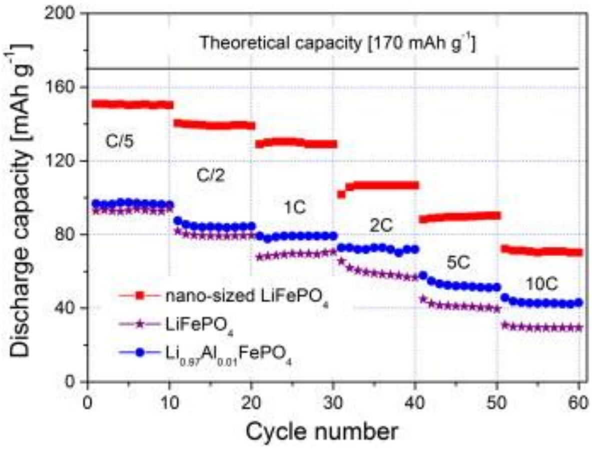

Figure 3. Discharge capacity for investigated Li/Li^+/phospholivine type cells as a function of current density and cycle number [27]

In addition, Kulka [27] conducted Al-doped experiments on $LiFePO_4$, and the results of neutron diffraction experiments confirmed that the intercalation sites of Al^{3+} in $LiFePO_4$ were Li sites. The replacement of Li^+ by Al^{3+} leads to the appearance of Li vacancies, thereby improving the conductivity of the material [28]. According to the charge balance rule, the appearance of Li vacancies caused by the substitution of Al^{3+} to Li^+ improves the conductivity of the material. It was found that, compared with the pure phase of $LiFePO_4$, a small amount of Al doping has a certain adverse effect on the increase of the initial capacity of $LiFePO_4$, but it has achieved better cycle stability, as shown in Figure 3. The result fully verified the constructive modification effect of Al doping on the rate performance and cycle performance of $LiFePO_4$.

Li [29] prepared a pure olive phase $Li_{0\cdot95}Na_{0\cdot05}FePO_4$ with a spherical morphology, as shown in the figure 4. The doped material has better electrochemical performance than the pure phase $LiFePO_4$. As shown in Figure 5, the results show that the charge transfer resistance of the Na-doped material is reduced, and the depth of lithium insertion is reduced, thereby improving the conductivity and the reversibility of Li^+ deintercalation, alleviating the distortion of the internal crystal structure of the $LiFePO_4$ particles, and improving the cycle performance of the material.

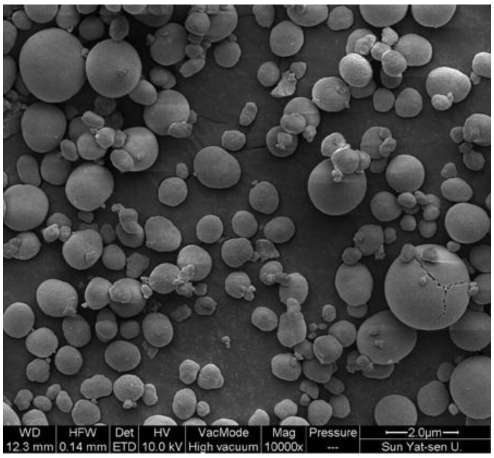

Figure 4. SEM images of $Li_{0\cdot95}Na_{0\cdot05}FePO_4$ [29]

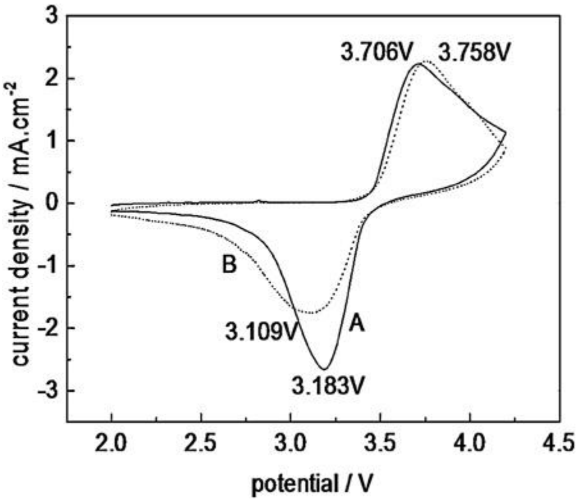

Figure 5. Cyclic voltammogram of $Li_{0\cdot95}Na_{0\cdot05}FePO_4$ [29]

The experiment of Yin [30] also verified the positive effect of Na doping at the Li site of $LiFePO_4$. When they tested the synthesized $Li_{0.97}Na_{0.03}FePO_4/C$ at a current density of 0.1 C, the first discharge capacity reach to 158 mAh/g, and maintained good cycle stability. They believe that the doping of Na with an appropriate amount shortens the length of the b-axis and increases the diffusion rate of Li^+. Wang [31] prepared an appropriate amount of Na-doped nano-porous bowl-shaped material $LiFePO_4/C$ by the sodium salt method. The capacity retention rate can reach to 60.3% after 3000 cycles at a current density of 10 C. At high rates of 20 C and 40 C, there is still a high initial charge and discharge capacity. This nano-porous structure can greatly shorten the diffusion path of Li^+ and help the deintercalation movement of Li^+, while the doping of Na^+ essentially changes the electron and ion transfer characteristics of $LiFePO_4$. This is of great benefit to the improvement of material rate performance.

Li [32] successfully doped $LiFePO_4$ with Ti^{4+} at the Li site, forming a mixed valence state of Fe^{3+}/Fe^{2+}, which proves that the substitution of Li^+ by Ti^{4+} effectively improves the electronic conductivity of the material. The related experiments conducted by Zhang [33] also fully verified the improvement of Ti^{4+} doping in Li site on the cycle performance and rate performance of $LiFePO_4$ cathode material. Therefore, doping of Ti with a proper amount will make the arrangement of the $LiFePO_4$ lattice more compact and the diameter is smaller. The smaller particle size is beneficial to shorten the deintercalation distance of Li^+ and improve its electrochemical performance [34].

Regrettably, the Li-site doping for $LiFePO_4$ does not always achieve good results. Ouyang [35] found that when $LiFePO_4$ was doped with Cr, the substitution of Li^+ by Cr^{3+} improved the electrical conductivity of the material, but it did not improve the rate performance. The main reason is that Cr^{3+} cannot perform diffusion motion on the Li site, and can only vibrate at the equilibrium position. Therefore, the fact that Cr^{3+} occupying the Li^+ site becomes an obstacle to the one-dimensional diffusion of Li^+ along the b axis, which offsets the effect of the increase in conductivity on the increase in rate performance of the material.

In order to further understand the modification mechanism of of Li site doping of $LiFePO_4$, Madram [36] also tried the experiment of multiple-doping modification at the Li site.also tried the experiment of multiple-doping modification at the lithium site. They synthesized $Li_{0.97}Na_{0.02}K_{0.01}FePO_4/C$ composite by solid-phase reaction method. The co-doping of Na and K increased the inherent conductivity of $LiFePO_4/C$ and improved the reversibility of the electrode reaction. The initial discharge specific capacity of the material can reach 159 mAh/g (0.1 C), 150 mAh/g (0.5 C), 146 mAh/g (1 C), 138 mAh/g (3 C) and 100 mAh/g (5 C) at different current densities, while maintaining good cycle performance. Appropriate doping element and doping amount are important factors to improve the performance of $LiFePO_4$ through the doping at Li site.

2.2 Doping in Fe site

Compared with the doping at the Li site, people are more enthusiastic about doping in the Fe site, and many good results have been obtained [37-41]. Studies [42,43] have shown that the weakening effect of Fe site doping on the Li-O bond will increase the lattice volume and obtain higher ion mobility and diffusion coefficient. It can also reduce the distortion of the $LiFePO_4$ lattice and the surface energy of the crystal, and correspondingly reduce the size of the particles, thereby improving the electrochemical performance of $LiFePO_4$.

When $LiFePO_4$ is modified by doping at the Fe site, the choice of doping element is more extensive, and the common ones are Nb, Mo, Co, V, Mn, Ni, Zn, Cu, Mg and Cr and so on. The doping of metal element at the Fe site helps the diffusion of Li^+ in one-dimensional paths, which is very conductive to the improvement of the electronic conductivity and ionic conductivity of the $LiFePO_4$ cathode material. According to the first principles, Zhang [44] calculated and found that the doping of Mn, Nb, Mo and Co is stable for the system, and the doping of Co can inhibit the generation of micro cracks, reduce the capacity attenuation, and then improve the performance of material. Pignanelli [45] reported that although the microstructure of cobalt-doped $LiFePO_4/C$ has not changed, it has a significant impact on the formation of lithium ion channels in $LiFePO_4$. The prepared $LiFe_{0.99}Co_{0.01}PO_4/C$ cathode material has better capacity and diffusion constant than the pure phase. They believe that this change may be related to the amount of doping. In addition, in the experiment of doping with Mo by Oh [46], the charge transfer resistance of $LiFePO_4$ was significantly reduced after doping, showing better rate performance and cycle stability.

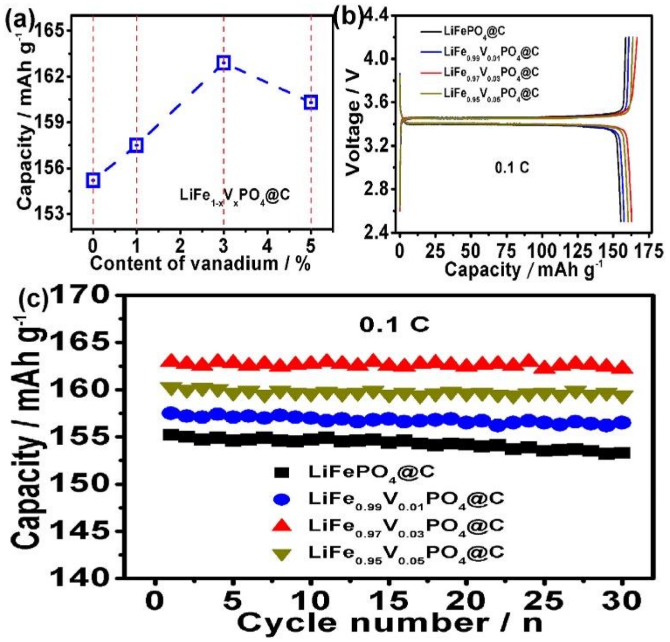

Figure 6. (a) The tendency chart of the first discharge capacities, (b) the initial charge/discharge curves and (c) cyclic properties of the synthesized $LiFe_{1-x}V_xPO_4@C$ ($x = 0$, 0.01, 0.03 and 0.05) electrodes at 0.1 C between 2.5 and 4.2 V [47]

Jiang [47] used a simple sol-gel method to synthesize V-doped $LiFe_{1-x}V_xPO_4@C$(x=0.01, 0.03, 0.05) composite materials with different doping amounts. After a series of electrochemical tests, it can be seen that as the amount of vanadium increases, the specific capacity of the material increases first and then decreases, and the doped samples have better rate performance and cycle stability, as shown in Figure 6. This is attributed to the effect of vanadium on the intrinsic conductivity of $LiFePO_4$ cathode material. The performance of the material $LiFe_{0.97}V_{0.03}PO_4@C$ is the most prominent when the content of vanadium is 3%. Its first discharge capacity can reach to 162.9 mAh/g, and it has excellent rate performance and stability, as shown in Figure 7. Similarly, the research results of Xu [48] and Shao [49] also fully proved that an appropriate amount of vanadium doping in the Fe site has a positive effect on improving the performance of $LiFePO_4$. Johnson [50] used muon spectroscopy (μSR) as a local probe to study the lithium ion diffusion characteristics of V and Nb doped $LiFePO_4$ and pure phase. They selected pure phase and the best-performing $LiFe_{0.99}Nb_{0.01}PO_4$ and $LiFe_{0.95}V_{0.05}PO_4$ for comparative experiments, and found that at room temperature, no quantitative difference was observed in the diffusion coefficients of the pure phase and the doped sample,which indicates that the intrinsic diffusion jump rate of lithium ions at room temperature is not affected by doping. The observed increase in electrochemical performance of doped $LiFePO_4$ may be related to the increase in electronic conductivity caused by doping.

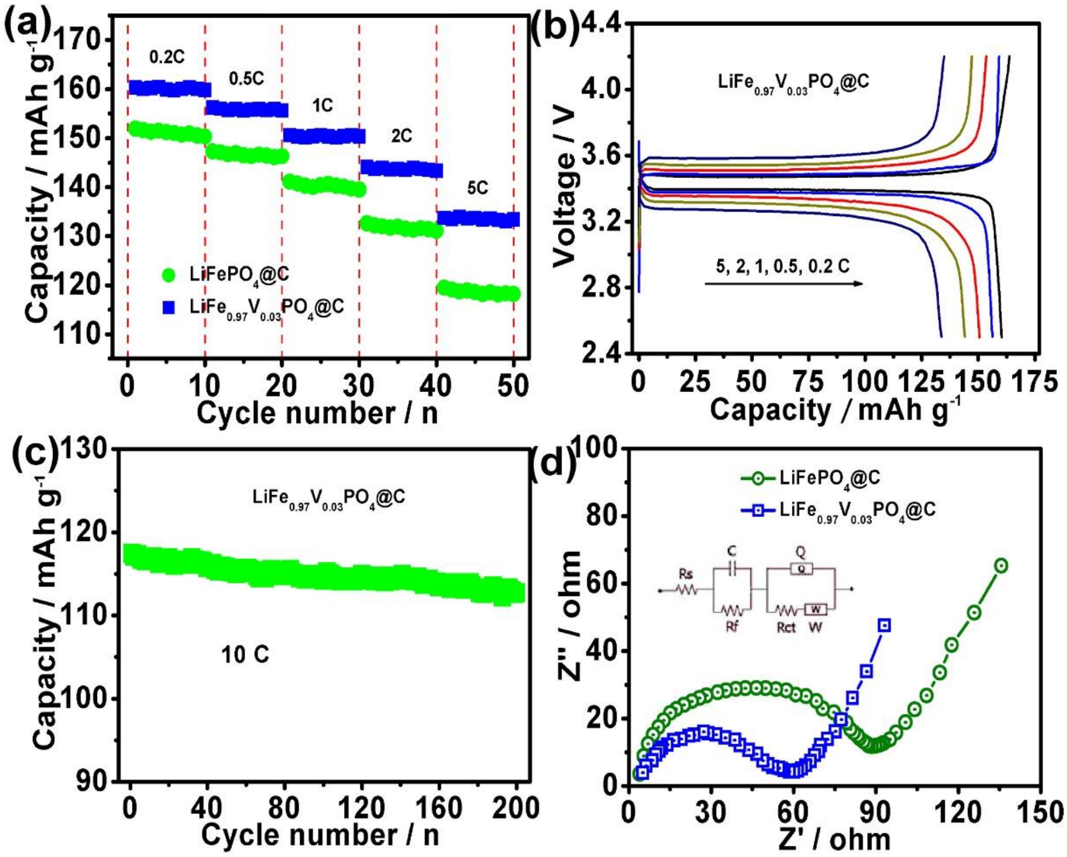

Figure 7. (a) Rate capabilities of $LiFePO_4$@C and $LiFe_{0.97}V_{0.03}PO_4$@C at various current rates; (b) Charge/discharge curves of $LiFe_{0.97}V_{0.03}PO_4$@C; (c) Long-cycle performance of $LiFe_{0.97}V_{0.03}PO_4$@C at 10 C; (d) Nyquist plots of $LiFePO_4$@C and $LiFe_{0.97}V_{0.03}PO_4$@C [47]

Gupta [51] studied the influence of manganese doping on the conductivity of olivine $LiFePO_4$. The experiment found that the conductivity increased with the increase of Mn content in the range of 0%~15%. When the content is 20% , the conductivity is significantly reduced, as shown in Figure 8. The ionic radius of Mn^{2+} is larger than that of Fe^{2+}, so the partial replacement of Fe by Mn will increase the unit cell size of $LiFePO_4$, which is conducive to the movement of Li^+ in the lattice, thereby improving the ionic conductivity of $LiFePO_4$ [52,53]. Research [54] found that although Mn-doped $LiFePO_4$ has better conductivity, its structural stability is relatively poor. With the increase of Mn doping, the formation of high-spin Mn^{3+} will make the structure of the cathode material is distorted, hindering the diffusion of lithium ions and delaying the charge transfer process of $LiFePO_4$ [55]. In addition, as the reaction progresses, the dissolution of Mn^{2+} will change the structure of the cathode material and reduce the discharge capacity [56]. Therefore, with the increase of the amount of doping, the electrochemical performance of the composite material shows a trend of first improving and then decreasing [57].

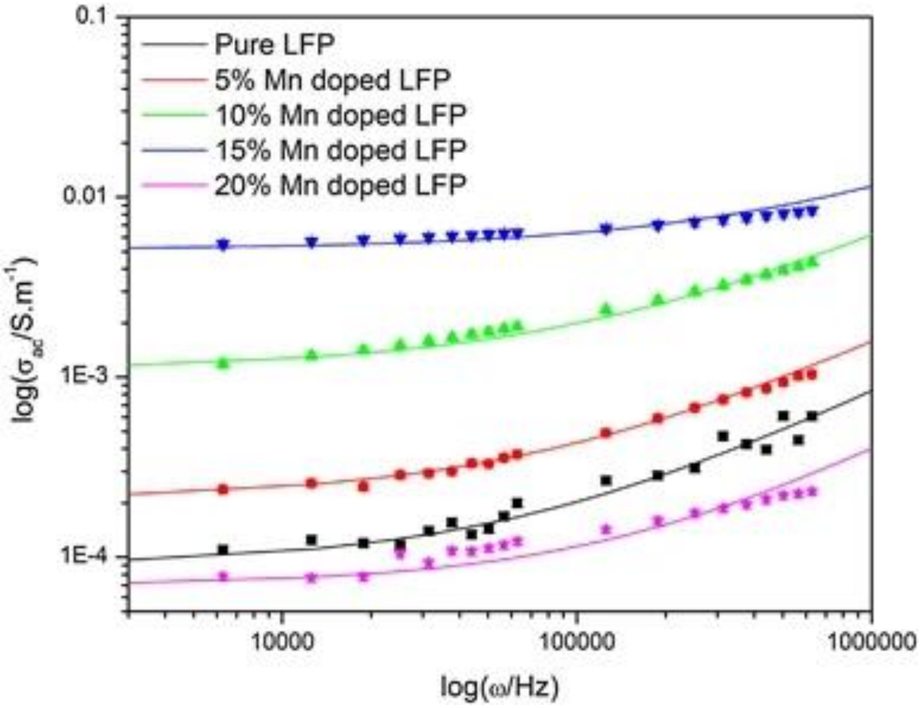

Figure 8. Room temperature variation of conductivity with frequency for pure and doped LFP [51]

Xu [58] synthesized nano-scale $LiFePO_4/C$ and $LiFe_{0.95}M_{0.05}PO_4/C$ (M=Sm, Eu, Yb) by hydrothermal method for the first time, and the first discharge capacity at 0.2 C were 109.4, 153.6, 144.0 and 160.7 mAh/g, respectively. It also showed better performance in the subsequent constant current charge and discharge, electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) tests, as shown in the figure 9 and figure 10. This improvement is mainly attributed to the effect of lattice defects on the electrochemical activity of the material caused by doping. Herrera [59] modified $LiFePO_4$ with doping yttrium ($0.01\% < x < 5\%$ w/w), the structure of the doped material is more stable, and the resistance decreases. When the yttrium doping concentration is 1%, the performance is optimal.

Liu [60] successfully synthesized spherical zinc-doped $LiZn_{0.01}Fe_{0.99}PO_4$ by solid-phase method for the first time. The doping of zinc increased the lattice volume, and the radius remained unchanged during the deintercalation and insertion of lithium ions. This has played a role in stabilizing the crystal lattice and improving the diffusion coefficient of lithium ions, and has a positive effect on the improvement of the discharge specific capacity and rate performance of $LiFePO_4$.

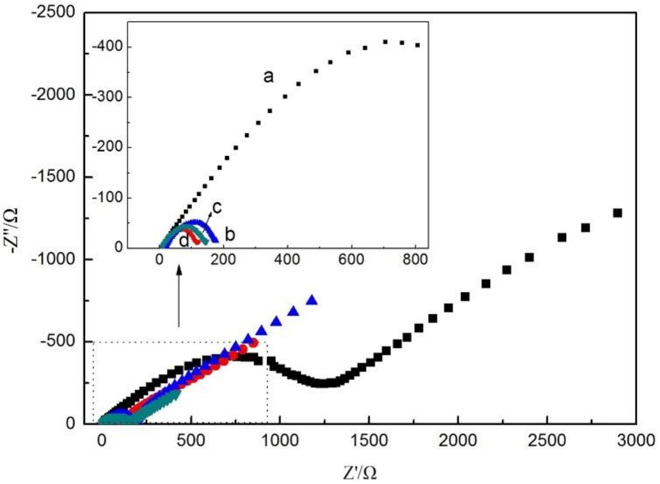

Figure 9. EIS for $LiFePO_4/C$ electrode and $LiFe_{0.95}M_{0.05}PO_4/C$ (M = Sm, Eu, Yb) composite electrode after 5 cycles. a $LiFePO_4/C$ b $LiFe_{0.95}Eu_{0.05}PO_4/C$ c $LiFe_{0.95}Sm_{0.05}PO_4/C$ d $LiFe_{0.95}Yb_{0.05}PO_4/C$ [58]

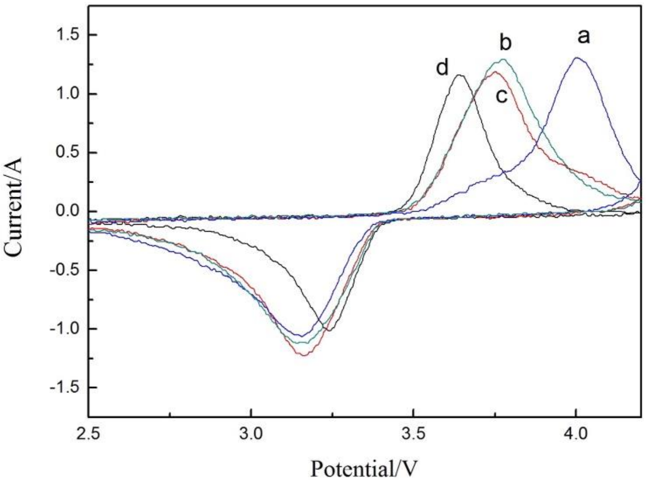

Figure 10. Cyclic voltammograms of $LiFePO_4/C$ and $LiFe_{0.95}M_{0.05}PO_4/C$ (M = Sm, Eu, Yb) at a scanning rate of 0.5 mV/s and the potential span rom 2.3 V to 4.2 V. a $LiFePO_4/C$ b $LiFe_{0.95}Eu_{0.05}PO_4/C$ c $LiFe_{0.95}Sm_{0.05}PO_4/C$ d $LiFe_{0.95}Yb_{0.05}PO_4/C$ [58]

Liu [61] synthesized the Cu-doped $LiFePO_4/C$ composite material by the optimized ethylene glycol co-precipitation method. The discharge capacity doesn't increase significantly at 0.1 C, but when the current density increased to 1 C, the charging and discharging voltage platform and specific capacity of the Cu-doped sample are improved, and they showed better rate performance and cycle performance compared with pure phase. This is due to the fact that the doping of Cu reduces the degree of particle agglomeration, shortens the diffusion path of Li^+, and improves the conductivity. In addition, a study [62] found that copper can increase the interplanar spacing of $LiFePO_4$ crystals parallel to the [010] direction, broaden the diffusion channels of Li^+ along the [010] direction, and improve the lithium ion diffusion coefficient and the lithium storage activity of the material. Compared with $LiFePO_4$/C, the copper ion substituted $LiFePO_4$/C composite material has better electrochemical performance.

Li [63] modified $LiFePO_4$/C with $Fe_3(PO_4)_2·8H_2O$ as the Mg source, and obtained an initial discharge capacity of 153 mAh/g (0.2 C) and better rate performance. Since the ion radius of Mg^{2+} (0.66 Å) is smaller than that of Fe^{2+} (0.78 Å), the unit cell volume of $LiFePO_4$ will be slightly reduced after doping, which will help increase the diffusion rate of lithium ion [64]. When $LiFePO_4$ is modified by by doping equivalent cations (such as Zn^{2+}, Cu^{2+}, Mg^{2+}, Co^{2+}, etc.), it is easy to replace Fe^{2+} and cause lattice distortion, which broadens the space for lithium ion intercalation/delamination, thereby improving the electrochemical performance of the $LiFePO_4$.

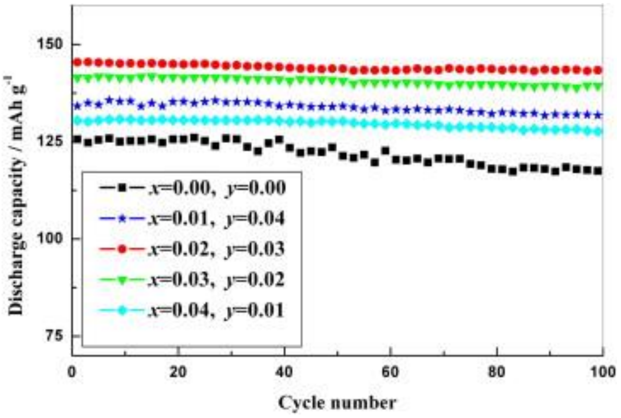

Figure 11. The cycle performance of $LiFePO_4$/C and $LiFe_{1-x-y}Ni_xMn_yPO_4$/C (x =0.01, 0.02, 0.03 and 0.04; y= 0.04, 0.03, 0.02 and 0.01) at 1 C [65]

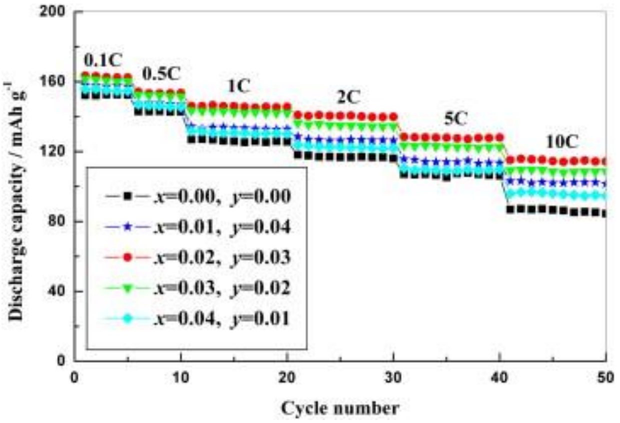

Figure 12. The cycle performance of $LiFePO_4$/C and $LiFe_{1-x-y}Ni_xMn_yPO_4$/C (x =0.01, 0.02, 0.03 and 0.04; y= 0.04, 0.03, 0.02 and 0.01) at different current rates [65]

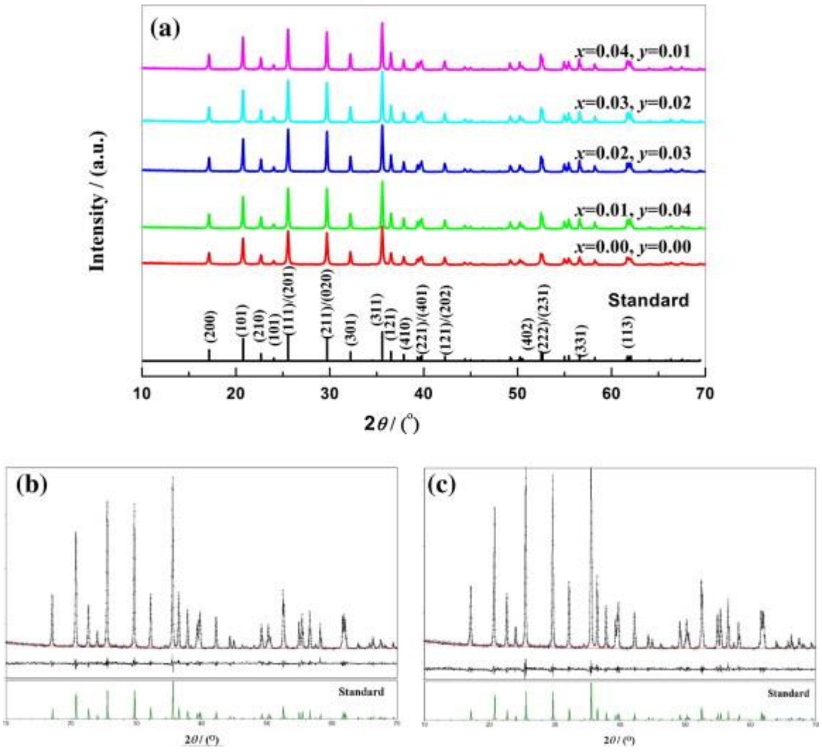

Figure 13. (a) XRD patterns of $LiFe_{1-x-y}Ni_xMn_yPO_4/C$ (x=0.01, 0.02, 0.03 and 0.04;y=0.04, 0.03, 0.02 and 0.01); Rietveld refinements of X-ray diffraction patterns for (b) $LiFePO_4/C$ and (c) $LiFe_{0.95}Ni_{0.02}Mn_{0.03}PO_4/C$ [65]

Table 1. Structural parameters obtained from XRD Rietveld refinement for $LiFePO_4/C$ and $LiFe_{0.95}Ni_{0.02}Mn_{0.03}PO_4/C$ [65]

Samples	$LiFePO_4/C$	$LiFe_{0.95}Ni_{0.02}Mn_{0.03}PO_4/C$
Lattice bond/Å		
Fe-O (1)◊1	2.2086	2.2070
Fe-O (2)◊1	2.1032	2.0890
Fe-O (3)◊2	2.0612	2.0588
Fe-O (3)◊2	2.2592	2.2499
Fe-O average	2.1581	2.1512
P-O (1)◊1	1.4406	1.4019
P-O (2)◊1	1.4941	1.4897
P-O (3)◊2	1.4555	1.4836
P-O average	1.4634	1.4584
Li-O (1)◊2	2.1543	2.1585
Li-O (2)◊2	2.0890	2.0907
Li-O (3)◊2	2.1805	2.1889
Li -O average	2.1413	2.1460
Reliability factors/%		
R_{wp}	7.97	7.76

In addition to the doping of single metal element in the Fe site, researchers have also explored the idea of the doping of multiple metal elements in the Fe site. For the first time, Shu [65] used a simple solid-phase synthesis method to co-doped $LiFePO_4$ with different proportions of Ni and Mn in the Fe site, and obtained $LiFe_{0.95}Ni_{0.02}Mn_{0.03}PO_4/C$ with good cycle performance and rate performance, as shown in Figure 11.

The first discharge capacity is 145.4 mAh/g, and the capacity retention rate is 98.6% after 100 cycles at a current density of 1 C. At the same time, it has good rate performance, as shown in Figure 12. As shown in Figure 13 and Table 1, the co-doping of Ni and Mn not only does not destroy the crystal structure of $LiFePO_4$, but also extends the Li-O bond. Doping promotes the diffusion of lithium ions, reduces charge transfer resistance, and improves the electrochemical performance of $LiFePO_4/C$.

Liu [66] used iron powder and electroless nickel plating waste liquid as raw materials to successfully synthesize Ni-Co-Mn doped $LiFePO_4/C$, with an initial discharge specific capacity as high as 165.1 mAh/g. In the subsequent electrochemical performance test, it also shows good rate performance and cycle performance, as shown in Figure 14. After 100 cycles at a current density of 1 C, the capacity of the sample basically did not decrease, and remained at a relatively high level, showing good reversibility, as shown in Figure 15.

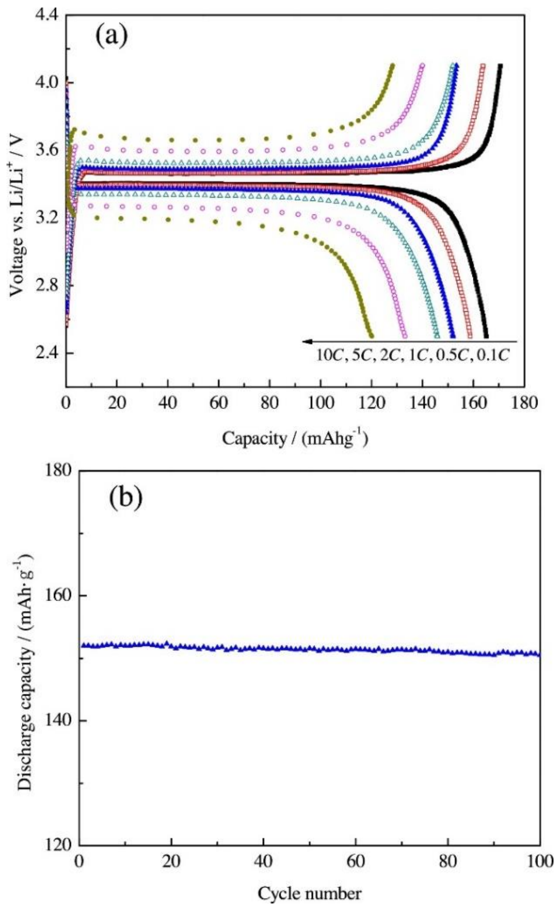

Figure 14. The initial charge/discharge curves at various C-rates (a) and cycle-life curve at 1 C (b) of Ni-Co-Mn doped $LiFePO_4/C$ [66]

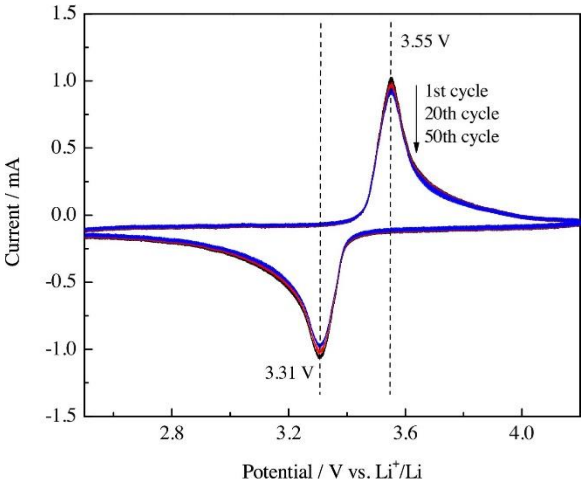

Figure 15. Cyclic voltammogram of Ni-Co-Mn doped $LiFePO_4/C$ [66]

Lv [67] established a correlation function model based on the application of the central composite design (CCD) method to study the comprehensive effect of doping amount on the electrochemical performance of vanadium and titanium co-doped $LiFePO_4/C$. The results show that the charge and discharge capacity increases first and then decreases with the increase of the doping amount of V or Ti, and the optimal doping amounts of V and Ti are 0.07 and 0.03, respectively. This is because when the concentration of doped element is at a low level, they can enter the crystal structure to form a solid solution, and increase the concentration of cation vacancy defects to improve ion mobility and diffusion coefficient [68-70]..

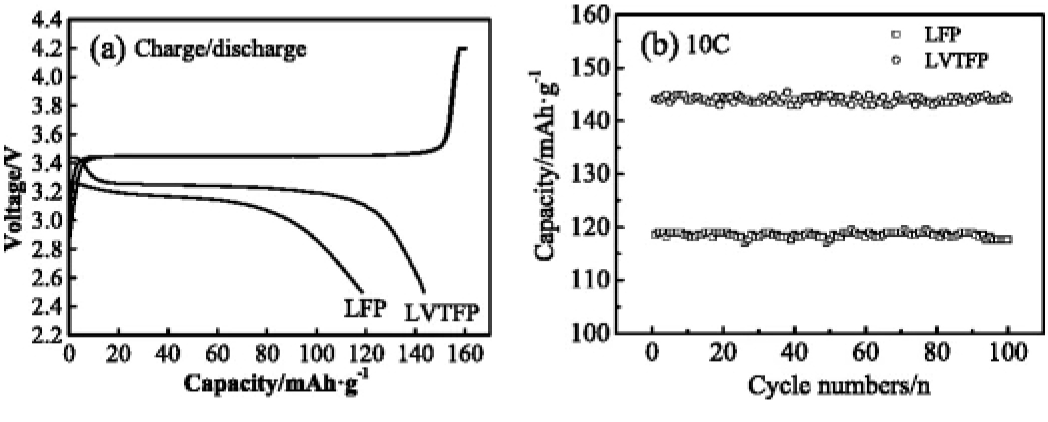

Figure 16. Charge/discharge curves of first cycle (a) and (b) rate performances for $LiFePO_4/C$ (LFP) and $LiV_{0.07}Ti_{0.03}Fe_{0.9}PO_4/C$ (LVTFP) [67]

Correspondingly, the conductivity of the material and the reversibility of the reaction will also be improved. When the doping concentration is too large, impurity phases are easily generated in the material [71,72], resulting in a significant decrease in charge and discharge capacity. After that, the author performed relevant data fitting through experiments to verify the credibility of the conclusion.

The $LiV_{0.07}Ti_{0.03}Fe_{0.9}PO_4/C$ composite prepared by the wet ball milling assisted carbothermic reduction method under optimized conditions has a discharge capacity of 144.1 mAh/g. at 10 C, which is consistent with the predicted value (144.8 mAh/g.). After 100 cycles, no capacity degradation, showing good rate and cycle stability, as shown in Figure 16.

Tu [64] successfully synthesized porous $LiFe_{0.985}Mg_{0.005}Ti_{0.01}PO_4$ microspheres through carbothermic reduction reaction combined with spray drying process. Compared with the pure phase, the electrical conductivity and diffusion coefficient of the porous $LiFe_{0.985}Mg_{0.005}Ti_{0.01}PO_4$ microspheres are greatly improved, and they exhibit excellent high-rate performance, and their discharge capacity at a current density of 8 C is still Up to 131.5 mAh/g.

At present, there are a lot of work on doping with metal element in Fe sites, some of which have achieved some good results, but it is undeniable that there are still some objections to the modification effect of individual metal elements. Choosing appropriate metal element for multi-element co-doping in the Fe site may be an effective method to improve the electrochemical performance of $LiFePO_4$ cathode materials.

2.3 Simultaneous doping of Li and Fe

When $LiFePO_4$ is modified by doping, the results are often different due to the difference in doping element and positions. Therefore, multi-site doping with suitable element has also become another direction that has attracted the attention of scholars.

Gao [73]found through first-principles calculations that when $LiFePO_4$ is doped with Zr in Li site and Co in Fe site at the same time, the band gap of $LiFePO_4$ is reduced and the electrochemical performance of the material is improved. After that, they synthesized $LiFePO_4$ and $Li_{0.99}Zr_{0.0025}Fe_{1-x}Co_xPO_4$ (x=0.005, 0.01, 0.015, 0.02) cathode materials by solid-phase method, and found that the specific capacity and cycle stability of the materials showed a trend of first increasing and then decreasing. When x=0.01, the overall performance of the composite material is optimal, and its discharge capacity at 0.1 C can reach 139.9 mAh/g, and the capacity retention rate is 85% after 50 cycles. This is because the doping of Zr^{4+} forms Li^+ vacancies to expand the lattice of $LiFePO_4$, which offsets the shrinkage of the lattice caused by delithiation to a certain extent, and stabilizes the structure while enhancing conductivity. The doping of a small amount of Co^{2+} weakens the Li-O interaction and improves the ion mobility and diffusion coefficient. At the same time, its columnar effect in the crystal lattice prevents the collapse of the crystal during the Li^+ intercalation and delamination cycle, and further ensures the stability of the structure. In addition, the co-doping of Zr and Co also improves the particle morphology of the material, resulting in a material with a smaller particle size and particle size distribution. It can be seen that the co-doping of Zr and Co the stability of structure and morphology of particle simultaneously, thereby improving the electrochemical performance of the material.

Yang [74] first synthesized nano-scale sodium vanadium co-doped olivine $Li_{1-x}Na_xFe_{1-x}V_xPO_4/C$ cathode material and pure phase $LiFePO_4/C$ by solid-phase reaction method. The study found that simultaneous Na doping at Li site and V doping at Fe site can reduce the charge transfer resistance of the material and increase the conductivity, so that the doped sample exhibits better electrochemical performance than pure phase $LiFePO_4$/C. Among them, the first discharge capacity of $Li_{0.97}Na_{0.03}Fe_{0.97}V_{0.03}PO_4$/C at a rate of 0.1 C can reach 156.5 mAh/g, and the capacity retention rate can still reach 97.6% after 50 cycles. This is because the ion radius of sodium (0.097 nm) is much larger than that of lithium (0.068 nm), so the unit cell volume of the doped material increases, which facilitates the extraction and insertion of lithium ions, thereby improving the diffusion of lithium ions and electrochemical reversibility. In addition, $Li_{0.97}Na_{0.03}Fe_{0.97}V_{0.03}PO_4$/C also showed good performance at the low temperature. It can still reach an initial discharge capacity of 76.7 mAh/g at a low temperature of -20 °C and a rate of 1.0 C. After 100 cycles, there is still a 92% capacity retention rate, and the overall performance is better than the pure phase $LiFePO_4$/C, as shown in Figure 17.

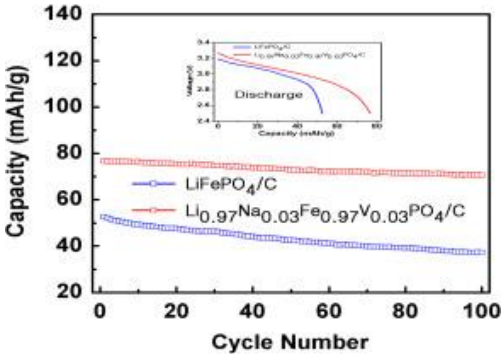

Figure 17. Cycle performance and initial discharge curves (shown in the inset) of $LiFePO_4$/C and $Li_{0.97}Na_{0.03}Fe_{0.97}V_{0.03}PO_4$/C at a charge/discharge rate of 1.0 C at -20 °C [74]

Shu [75] doped $LiFePO_4$/C with a small amount of Na and Ti. They found that the doping of Na and Ti can optimize the microstructure of crystal and the morphology of particle, reduce charge transfer resistance, and improve the conductivity of the material and the diffusion rate of lithium ions, thereby improving the electrochemical performance of $LiFePO_4$/C. The initial discharge capacity of their synthesized $Li_{0.97}Na_{0.03}Fe_{0.97}Ti_{0.03}PO_4$/C can reach 151.0 mAh/g, and the capacity is still 99.3% after 100 cycles at 1 C. Even at a high rate of 20 C, it still shows a high discharge capacity exceeding 97.3 mAh/g and excellent rate performance.

In general, the modification of $LiFePO_4$ by doping with metal element is still the mainstream choice. Table 1 summarizes the aforementioned experiments on improving the electrochemical performance of $LiFePO_4$ by the doping of metal element. It can be seen that the type of metal element, the target doping position in $LiFePO_4$ and the amount of doping have a great influence on the doping effect. Therefore, comprehensive consideration of ion species, target doping position and doping amount is an indispensable step for improving $LiFePO_4$ cathode material through doping. The doping of metal element is of great help to the improvement of the cycle performance of $LiFePO_4$, especially the doping substitution that occurs at the Fe site, which can often increase the initial discharge specific capacity while maintaining a high capacity retention rate.

Table 2. A mini sum up of electrochemical performance of $LiFePO_4$ doped by metal element

Doping ions	Doping sites	The best doping amounts	Electrochemical performance (Initial capacity; Cycle abilities)
Nb [23]	Li-site	$Li_{0.98}Nb_{0.02}FePO_4/C$	164.9 mAh/g (0.1 C), 114.3 mAh/g (10 C);97.3%(0.1 C,200 cycles),96.2%(10 C,200 cycles)
Al [27]	Li-site	$Li_{0.97}Al_{0.01}FePO_4$	95 mAh/g (0.2 C)
Na [29]	Li-site	$Li_{0\cdot95}Na_{0\cdot05}FePO_4$	164.2 mAh/g (0.2 C);97.2%(0.2 C,20 cycles) 130.5 mAh/g, 93.1%(2 C,20 cycles
Ti [32]	Li-site	3% atomic ratio	150.1 , 130 and 120 mAh/g (0.1 C, 1 C and 2C), 102.3% (1 C,100 cycles),96.8%(2 C,100 cycles)
Na&K [36]	Li-site	$Li_{0.97}Na_{0.02}K_{0.01}FePO_4/C$	159, 150,146,138 and 100 mAh/g (0.1 C, 1 C, 3 C and 5 C)
Mo [46]	Fe-site	1% mole ratio	145, 130 and 96 mAh/g (0.1 C,1 C and 7 C), 100% (0.1 C,50 cycles)
V [47]	Fe-site	$LiFe_{0.97}V_{0.03}PO_4/C$	162.9,160.3,156.2,150.6,144.1,133.7 and 117.4 mAh/g (0.1 C, 0.2 C, 0.5 C, 1 C, 2 C, 5 C and 10 C), 96%(10 C,200 cycles)
Mn [57]	Fe-site	$LiFe_{0.98}Mn_{0.02}PO_4/C$	156.0, 110.0 mAh/g (0.1 C, 5 C), 105%(0.2 C, 70 cycles)
Sm, Eu, Yb [58]	Fe-site	$LiFe_{0.95}M_{0.05}PO_4/C$ (M = Sm, Eu, Yb)	153.6, 144.0, 160.7 mAh/g (Sm, Eu, Yb; 0.2 C); 96.2%, 98.1%, 94.9% (0.2 C, 20 cycles)
Cu [61]	Fe-site	$LiFe_{0.99}Cu_{0.01}PO_4/C$	148, 137, 132, 126, 120 and 111 mAh/g (0.1 C, 0.5 C, 1 C, 2 C, 5 C and 10 C), 99.9%(1C, 100 cycles)
Mg [63]	Fe-site	1% mole ratio	153, 150, 147, 141 and 132 mAh/g (0.2 C, 0.5 C, 1 C,2 C and 5 C), 98% (1 C, 100 cycles)
Mg&Ti[64]	Fe-site	$LiFe_{0.985}Mg_{0.005}Ti_{0.01}PO_4$	161.5, 160.3, 156.7, 147.5, 139.8 and 131.5 (0.2 C, 0.5 C, 1 C, 3 C, 5 C and 8 C), 99.6% (0.5 C, 100 cycles), 97.4% (1 C, 100 cycles), 92.9% (5 C, 100 cycles),
Ni&Co&Mn [66]	Fe-site	$LiFe_{0.95}Ni_{0.02}Mn_{0.03}PO_4/C$	165.1, 158.8, 152, 145.8, 133.1 和 120.2 mAh/g (0.1 C , 0.5 C, 1 C,2 C, 5 C and 10 C)
Zr&Co [73]	Zr at Li-site &Co at Fe-site	$Li_{0.99}Zr_{0.0025}Fe_{0.99}Co_{0.01}PO_4$	139.9 mAh/g (0.1 C), 85% (0.1 C , 50 cycles)
Na&V [74]	Na at Li-site	$Li_{0.97}Na_{0.03}Fe_{0.97}V_{0.03}PO_4/C$	156.5, 149.0, 136.3, 125.5, 111.8 mAh/g (0.1 C, 0.5 C, 1 C, 2 C and

	&V at Fe-site		5 C); 97.6% (0.1 C , 50 cycles), 98.2% (5C, 30 cycles), 96.8% (5 C, 30 cycles), 96.1% (5 C, 30 cycles), 93.3% (5 C, 30 cycles)
Na&Ti [75]	Na at Li-site &Ti at Fe-site	$Li_{0.97}Na_{0.03}Fe_{0.97}Ti_{0.03}PO_4$/C	164.0, 160.1, 153.7, 151.5, 144.0, 136, 121.4 mAh/g (0.1 C, 0.2 C, 0.5 C, 1 C, 2 C ,5 Cand 10 C), 99.3%(1 C, 100 cycles)

3. DOPING OF NON-METALLIC ELEMENT

Although there are few researches on the doping of non-metallic element of $LiFePO_4$, some of them have achieved good results. At present, the doping of non-metallic element common includes Cl doping, F doping, N doping, etc. Suitable doping of non-metallic element often stabilizes the internal structure of $LiFePO_4$, which is beneficial to the electrochemical performance of the material. Studies have shown that the appropriate amount of doping with fluoride and chloride ions has a positive effect on the performance of $LiFePO_4$ cathode materials, especially in terms of cycle performance and rate performance [76,77]. Liu [78] reported that Cl doping can ameliorate the microstructure of $LiFePO_4$ to increase its stability, and it can also increase its electrical conductivity and diffusion rate of lithium ion, thereby significantly improving the electrochemical performance of $LiFePO_4$/C cathode materials. The electrochemical impedance spectroscopy (EIS) test found that the charge transfers resistance (Rct) value and Warburg impedance (Zw) of the Cl-doped $LiFePO_4$/C electrode material are much smaller than those of the $LiFePO_4$/C, as shown in the figure 18. It fully shows that Cl doping can improve the diffusion kinetics of $LiFePO_4$/C cathode materials and reduce the impedance.

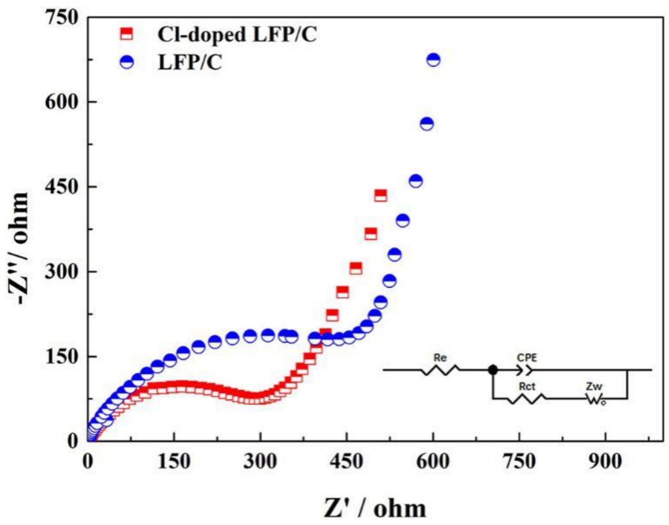

Figure 18. The EIS curves of LFP/C and Cl-doped LFP/C [78]

Liu [79] predicted the effect of N doping on $LiFePO_4$ based on first-principles calculations, and the results show that N doping can reduce the activation energy of Li diffusion in $LiFePO_4$ and increase the diffusion coefficient of lithium ions Afterwards, Chiu [80] conducted related experiments and obtained results consistent with previous studies. Nitrogen doping can significantly improve the electrochemical performance of $LiFePO_4$.

Later, Lu [81] reported that F doping can improve the diffusion of lithium ions in $LiFePO_4$, which has a positive effect on the improvement of material conductivity. The first discharge capacity of $LiFePO_{4-x}F_x/C$ (x=0.05, 0.1, 0.15, 0.25) synthesized by Gao [82] by co-precipitation method at 0.1 C is 159.9, 163.2, 165.7 and 162.8 mAh/g, respectively. These are better than the 150.0 mAh/g of the $LiFePO_4/C$, while showing stable cycle performance and excellent rate performance, as shown in Figure 15 (a, c and d). Figure 15(b) shows the transition process of $LiFePO_4/C$ and $LiFePO_{4–x}F_x/C$ (x = 0.15) from the single-phase solid solution in the slope area to the two-phase miscible area in the plateau area as the initial discharge progresses.

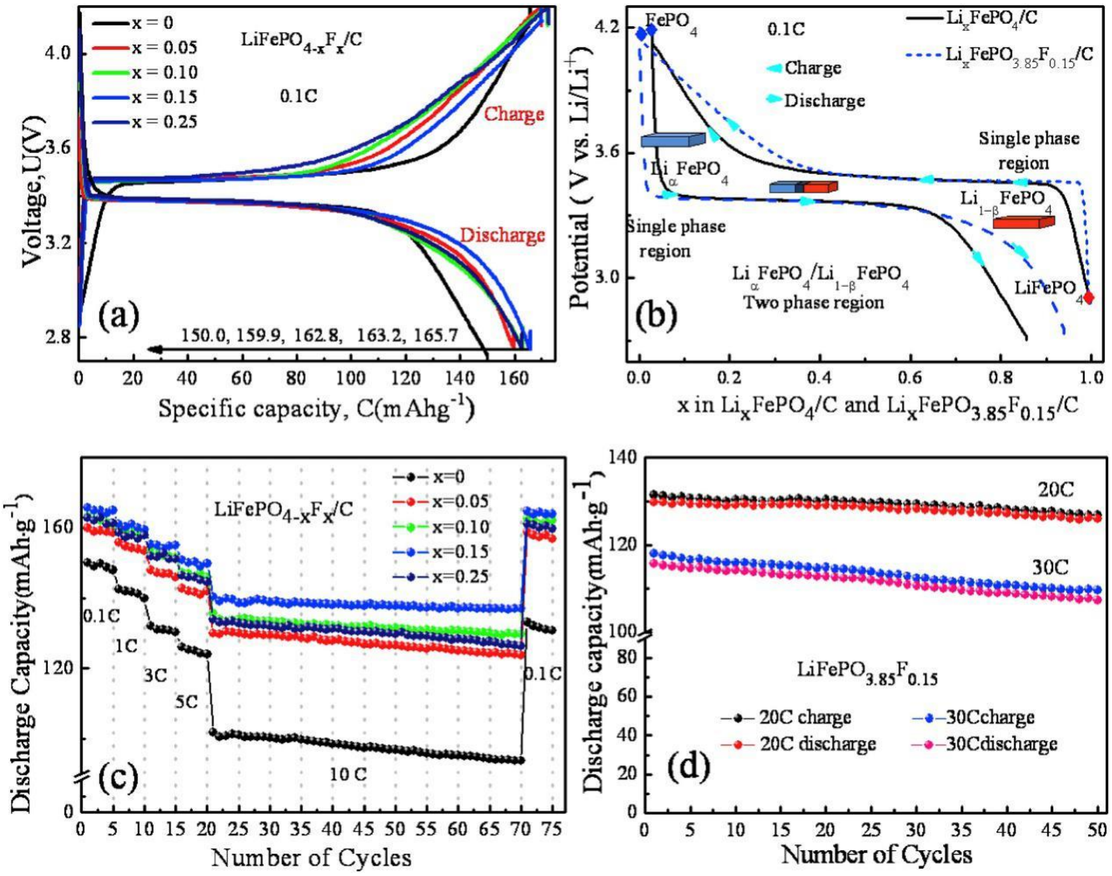

Figure 19. (a) The initial charge/discharge curves of undoped and F-doped $LiFePO_4/C$ samples at 0.1 C rate, (b) The initial charge/discharge curves of $LiFePO_4/C$ and $LiFePO_{4–x}F_x/C$ (x = 0.15) samples at 0.1 C rate, (c) rate and cycle performances of undoped and F-doped $LiFePO_4/C$ samples, (d) cycle performances of $LiFePO_{4–x}F_x/C$ (x = 0.15) sample at high-rate 20 C, 30 C [82]

Among them, the overall electrochemical performance of $LiFePO_{3.85}F_{0.15}/C$ is the best, even at high rates of 20 C and 30 C, it still has good cycle stability, as shown in Figure 15(d). This is because the doping of F enhances the P-O interaction, which is conducive to the structural stability of Li during the intercalation and delamination process.

F doping can increase the lattice volume of $LiFePO_4$, which is conducive to the deintercalation of lithium ions, and at the same time, the electronegativity of F is greater than that of O, so the substitution of F for O helps to narrow the band gap and increase the concentration of electrons and holes, thereby improving the electronic conductivity of the material and improving the stability of structural [83,84]. Dragana [85] found through experiments that a small amount of fluorine doping can reduce the anti-site defects of $LiFePO_4$ cathode material, making it have better crystallinity and larger lithium diffusion channel volume. At the same time, F-doping can also greatly increase the electrical conductivity of the material to significantly improve the electrochemical performance. Liao [86] prepared F-doped $LiFePO_4$/C material by ball milling and also got good results.

In addition to the doping of a single non-metallic element, the composite doping of metal element and non-metallic element has also attracted the attention of many scholars in the industry. Ban [87] used a solid-phase method to dope $LiFePO_4$ with Si at the P site and F at the O site at the same time. The results show that the conductivity of the doped material is greatly improved, and it shows more excellent electrochemical performance. Zhan [88] reported that co-doping of V and F can improve the structural stability of $LiFePO_4$/C cathode material and reduce its charge transfer resistance. At the same time, the electronic conductivity and the diffusion rate of lithium ion are increased, so that $LiFePO_4$/C obtains excellent electrochemical performance. Afterwards, Li [89] doped with V and F in the Fe site and PO_3 site of $LiFePO_4$ to obtain uniformly distributed spherical LFP-VF samples, as shown in Fig 20. The initial specific capacity of the LFP-VF can reach up to 165.7 mAh/g, and it has good rate performance and cycle performance.

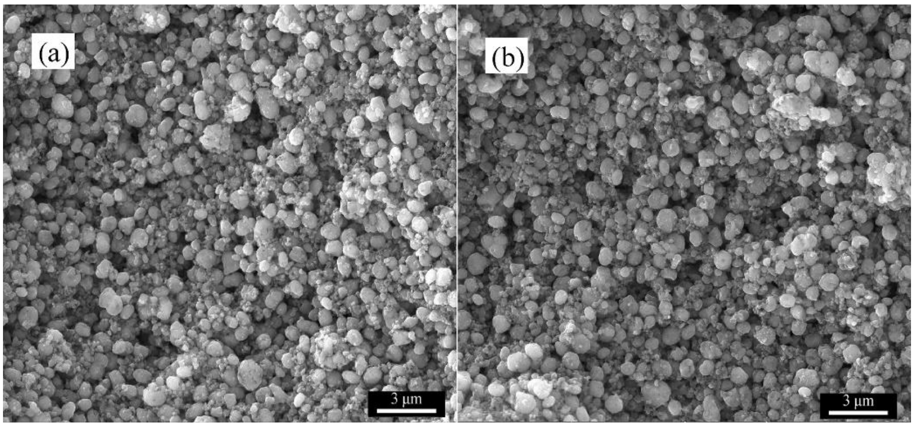

Figure 20. SEM images of (a) LFP and (b) LFP-VF, respectively [89]

Table 3 summarizes the modification effects of the above-mentioned different non-metallic element doping on $LiFePO_4$. It is not difficult to find that the doping of non-metallic element can not only effectively improve the charge and discharge performance of $LiFePO_4$ cathode material, but also can obtain better rate performance. Among them, the performance of co-doped $LiFePO_4$ with V and F is the best, the initial discharge specific capacity is the highest, and with the increase of current density, it can still maintain good cycle performance and rate performance. Even after 500 cycles at a current density of 10 C, a capacity retention rate of 90.9% can be maintained.

Table 3. A mini sum up of electrochemical performance of $LiFePO_4$ doped by non-metallic element

Doping ions	Doping sites	The best doping amounts	Electrochemical performance (Initial capacity; Cycle abilities)
N&B&F [76]	N/A	N/A	161.5, 156.6, 147.9, 141.7, 123.9 and 71.3 mAh/g (0.1 C, 0.3 C, 1 C, 3 C, 5 C and 15 C); 100% (0.1 C,40 cycles)
Cl [78]	N/A	0.047 wt.%	164.1 mAh/g (0.1 C), 91.5%(10 C, 500 cycles)
F [82]	O-site	$LiFePO_{3.85}F_{0.15}/C$	165.7, 161.1, 155.3, 150.8, 140.3, 129.8 and 115.7 mAh/g (0.1 C, 1 C, 3 C, 5 C,10 C, 20 C and 30 C); 97.3% (10 C, 50 cycles)
F [83]	O-site	$LiFePO_{3.938}F_{0.062}$	164.8, 159.2, 148.6, 135.8 and 102.3 mAh/g (0.1 C, 0.5 C, 1 C, 5 C and 10 C); 95.6% (5 C, 500 cycles)
Si&F [83]	Si at P-site &F at O-site	0.05 [Si-F] atoms per formula unit ($LiFePO_4$)	140 mAh/g (C/8); 88% (10 C, 200 cycles)
V&F [88]	V at Fe-site &F at PO_3-site	2% mole ratio of V 6% mole ratio of F	165.7, 154.9, 147.2, 140.2 and 124.9 mAh/g (0.1 C, 1 C, 2 C, 5 C and 10 C); 98.5% (0.1 C, 100 cycles), 95.7% (1 C, 500 cycles), 93.8% (2 C, 500 cycles), 91.2% (5 C, 500 cycles)， 90.9% (10 C, 500 cycles)

4. DOPING OF METALLIC SIMPLE SUBSTANCE OR METAL OXIDE

The main purpose of metallic simple substance or metal oxide doping of $LiFePO_4$ is to improve the conductivity between particles of $LiFePO_4$ without destroying its structure. Common metallic simple substance or metal oxide used for doping are Ag, Cu, NiO and ZnO, etc.

Mahmud [90] found through experiments that a small amount of NiO doped into $LiFePO_4/C$ will form a complete solid solution, which increases the diffusion coefficient of lithium ion and improves the rate performance. When the NiO content is 0.01 mol,, the initial discharge capacity reaches 158.8 mAh/g, and the overall electrochemical performance is the best, as shown in Figure 21.

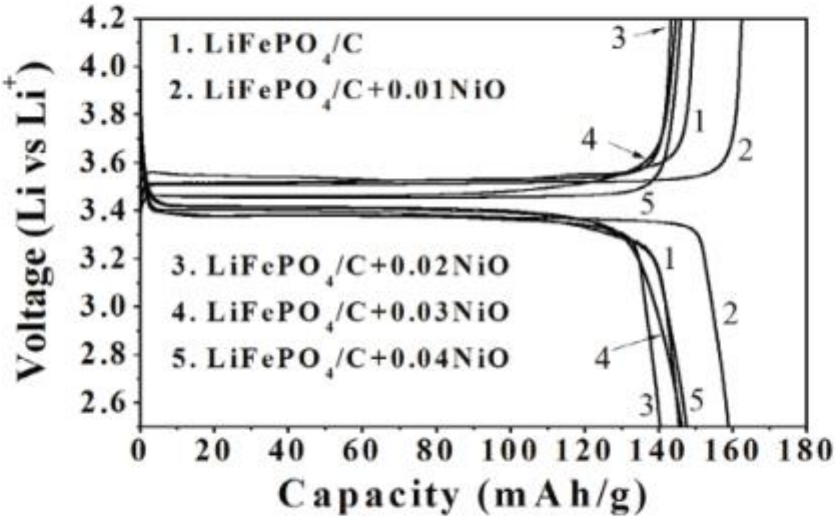

Figure 21. Galvanostatic initial charge/discharge curves of $LiFePO_4$/C with different amounts of NiO [90]

LeÓn [91] used ZnO to dope and encapsulate pure $LiFePO_4$ respectively, and compared its electrochemical performance. The results showed that the cycle stability of $LiFePO_4$-ZnO mixture formed by ZnO doping is poor, but the initial discharge capacity is a bit higher. Hu [92] used a hydrothermal method to modify $LiFePO_4$ by doping with ZnO to prepare nano-scale, uniform particles. The first discharge specific capacity can reach 132.3 mAh/g. After 100 cycles, the discharge specific capacity attenuation rate is only 1.8%. Compared with the attenuation rate of undoped $LiFePO_4$ 47.4%, the cycle performance of the doped material has a great improvement.

Croce [93] used the sol-gel method to synthesize $LiFePO_4$, and added 1% mass fraction of nano-scale metal powder (Cu, Ag) to it during the process. The initial discharge capacity of the synthesized $LiFePO_4$/metal powder composite material reached 145 mAh/g, which exceeded the pure phase 120 mAh/g, and it also has a good cycle performance. The results show that the metal particles dispersed in $LiFePO_4$ act as conductive bridges to enhance the conductivity between particles and reduce the resistance between particles. At the same time, the incorporation of Cu and Ag can also reduce the size of $LiFePO_4$ particles, thereby increasing the reversible lithium insertion capacity of $LiFePO_4$.

Table 4 lists the initial discharge specific capacity and cycle performance of the $LiFePO_4$ composite materials doped with different metallic simple substance or metal oxides mentioned above. Combining Table 2 and Table 3, it can be seen that the improvement of the overall electrochemical performance of $LiFePO_4$ by metallic simple substance or metal oxide doping is very limited, but it still has a certain improvement effect in terms of the charge and discharge performance at low rates.

Table 4. A mini sum up of electrochemical performance of metallic simple substance or metal oxide doped $LiFePO_4$

Doping ions	Doping sites	The best doping amounts	Electrochemical performance (Initial capacity; Cycle abilities)
NiO [89]	N/A	0.01 mol	158.8 mAh/g (0.1 C)
ZnO [91]	N/A	2.5wt%	132.3 mAh/g (0.1 C), 98.2% (0.1 C, 100cycles), 71.2% (0.5 C, 100 cycles), 60.5% (1 C, 100 cycles)
Cu [92]	N/A	1%	145 mAh/g (5 μA),
Ag [92]	N/A	1%	140 mAh/g (0.2 C), 100 mAh/g (1 C),

However, the method of doping conductive materials such as metallic simple substance or metal oxides mainly changes the conductivity between the particles of $LiFePO_4$, but has little effect on the conductivity inside the particles. Therefore, it is still difficult to $LiFePO_4$ by the single physical doping to have high current and high capacity charge and discharge performance.

In summary, doping has an extremely important effect on the improvement of the electrochemical performance of $LiFePO_4$, and the effects of doping particle types, the amounts and positions of doping are also different. The substitution doping of metal element such as Al, Nb, Na, Ti in the Li site, the substitution of such as V, Mn, Yi, Zn in the Fe site, the substitution doping of non-metallic element such as Cl, F, N in the P site or O site and the physica doping of metallic simple substance or metal oxide have improved different aspects of the electrochemical performance of $LiFePO_4$ in the future. At present, the research on the doping of $LiFePO_4$ mainly focuses on the doping of metal element in the Fe site, but it is undeniable that the multi-elements doping of multi-sites such as Na-K [36], Mg-Ti [64], Ni-Co-Mn [66], Na-Ti [75], V-F [89] and so on. has a more significant effect on the overall electricity of $LiFePO_4$. In particular, the V-F co-doped $LiFePO_4$ composite material has excellent performance in terms of initial discharge specific capacity, high-current charge and discharge stability, and capacity retention rate at high rate. This indicates that the synergistic effect under multiple doping tends to have a more positive modification effect than single doping. Therefore, selecting appropriate doped particles to modify $LiFePO_4$ with the multi-elements doping of multi-sites is an important way to efficiently improve its overall electrochemical performance.

4. CONCLUSIONS

$LiFePO_4$ cathode material is considered to be the most potential power lithium-ion battery cathode material due to its low price, good cycle stability, excellent safety performance and good storage performance. However, the shortcomings of low electronic conductivity and low lithium ion diffusion coefficient of $LiFePO_4$ have a negative impact on its electrochemical performance, which seriously hinders its further expansion in the field of power batteries. In order to improve these shortcomings of $LiFePO_4$, scholars in the industry have conducted various research experiments, among which the most commonly used method is doping modification. The doping of metal element can increase the lattice defects to improve the internal conductivity of $LiFePO_4$. It can also increase the diffusion rate of lithium ion, so that its charge-discharge specific capacity and rate performance can be improved. The doping of non-metal element can stabilize the crystal structure of $LiFePO_4$ and improve its cycle stability. The physical doping of metallic simple substance or metal oxide can effectively improve the conductivity between of $LiFePO_4$. The modification effects of different doped particles have their own merits, but there is no doubt that the synergy produced by the appropriate multi-sites has the best modification effect on the overall performance of $LiFePO_4$. It is foreseeable that the multi-elements doping at multi-sites will become an effective way to obtain $LiFePO_4$ cathode materials with better electrochemical performance in the future.

ACKNOWLEDGEMENTS
This work was supported by the National Nature Science Foundation of China (No.51562006)

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