



Modification in LiFePO_4 electrode material for lithium-ion battery

Yin Yan

Xiamen University, Xiamen, 361005, China

Abstract: Despite the excellent stability of LiFePO_4 , shortcomings such as poor conductivity and low energy density reduced its comprehensive properties and application range. In this article, I summarized three main practical methods so far. It will briefly introduce the fundamental property of LiFePO_4 , carbon coating, and nanocrystallization, and then describe doping in detail. Comparing the best dopants from research pieces, we can see that the capacity and conductivity will first increase and then decrease, and the proper ions may lie in lanthanide.

Keywords: LiFePO_4 ; electrode material; lithium-ion battery

Introduction

In modern society, our life can not be going on without batteries. From microelectronic products to energy vehicles, and many small objects like a flashlight, batteries exist everywhere. Moreover, the energy problem is always confusing the whole world, and nearly no country is not on the way to finding new energy. Researches show little flexibility in the total use of sustainable energy like wind energy, solar energy, and biomass energy in modern society. We are in the state of lacking fossil fuel as the distance of travel with car extend further and further. Therefore, energy storage is of vital importance, and we are forced to explore the way of improving batteries.

In this article, I will elaborate LiFePO_4 electrode with olivine structure in Lithium-ion batteries. From the former study, we can see these following facts. Compared to other common electrodes like LiCo_2 , LiNi_2 and LiMn_2 , LiFePO_4 owns the characters of high theory specific capacity, excellent thermal stability, stable voltage platform, a wide range of the material source, low cost, environmentally friendly, counted as a new generation of green anode material. Whereas, LiFePO_4 electrode has low electronic conductivity, low ionic diffusion coefficient and low tap density. The poor electronic conductivity is mainly due to the wide original energy gap, and this structure defect could also hinder the one-dimensional diffusion of Li^+ , which limit the application of LiFePO_4 as anode material. Therefore, it is necessary to modify the properties. So far, the main methods of improving its properties include surface coating, ion doping and nanocrystallization of material.

Literature Review

I The basic property of LiFePO_4

Lithium iron phosphate is an ordered peridotite structure, with Fe^{2+} on the Z-chain of octahedron and lithium ions on the linear chain of the alternate plane octahedron. All lithium can be de-intercalated to obtain layered MPO4-type structure, which is the orthogonal space group of Pbnm. The crystal parameter of LiFePO_4 is $a=0.6008$ nm, $b=1.0334$ nm, $c=0.4693$ nm, and the crystal cell volume is 0.2914 nm³. According to the first law, lithium iron phosphate is a

semi-metal, with large electron effective mass and small hole effective mass, but with high anisotropy. After lithium deintercalation, FePO_4 with a similar structure is generated, and its spatial point group is also Pbnm. The crystal parameter of FePO_4 is $a=0.5792\text{nm}$, $b=0.9821\text{nm}$, $c=0.4788\text{nm}$, and the cell volume is 0.2724nm^3 . After the removal of lithium, the cell volume decreases, which is similar to that in spinel manganese oxide. However, oxygen atoms are distributed nearly six square meters in a dense heap, the free volume of lithium-ion movement is small, and the current density should not be high at room temperature. If the current density is high, the capacity decreases, and if the current density is reduced, the capacity returns to its previous level. A two-phase interface $\text{Li}_x\text{FePO}_4/\text{Li}_{1-x}\text{FePO}_4$ is produced when Li^+ is de-escalated, and the interface area decreases with Li^+ removing. When a critical surface area is reached, lithium migration through the interface can no longer support the current, and electrochemical behaviour is controlled by diffusion. After taking off lithium, FePO_4 generated with low electronic and low ionic conductivity, becoming two-phase structure, so we can not make full use of the centre lithium iron phosphate, and especially in large electric current, the actual efficiency is significantly lowered down. After lithium is all removed, iron phosphate, organic solvent and electrolyte differential thermal analysis showed that the obvious exothermic peak is in the range of $250 \sim 360^\circ\text{C}$, the heat release is 147J/g , significantly lower than LiNiO_2 , LiCoO_2 , and LiMn_2O_4 in charging status, and it is with good thermal stability.^[2]

II Carbon coating^[3]

Regarding the drawback of low electronic conductivity, we can address it through coating carbon at the surface of each LiFePO_4 particle. The carbon layer is a kind of excellent conductive material, in which the three-dimensional network in carbon matrix can accelerate the electrons and Li ions and make them faster to reach each particle, hence improving the conductivity.

Through coating carbon, we could gain the following advantages:

- Control the growing of LiFePO_4 grain, increasing the specific surface area.
- Improving the conductivity of surface electrons and between particles, decreasing the possibility of battery polarization.
- Work as reductant, avoiding the formation of Fe and improving product purity.
- Serve as a nuclear agent, smaller the size of particles.
- Adsorb the electrolyte and keep the electrolyte stable, avoiding its action with the electrode.

III Nanocrystallization

The rate capability of LiFePO_4 is mainly up to its given specific surface area, because of which we could improve the rate capability of LiFePO_4 material effectively by reducing the grain radius and augmenting specific surface area.

It has been studied how to measure the parameters of the diffraction peak lattice of different samples. Furthermore, the grain size is calculated according to the full width at half maximum by using Scherrer formula: $D=k\lambda/\beta\cos\theta$. The effect of grain size on the properties of lithium iron phosphate is studied. Figure 1 shows SEM images of the powder. When the average particle size of the lithium iron phosphate sample decreases, the specific surface area increases. From cyclic voltammetry in Figure 2, we can determine the performance of different samples under certain conditions. As shown in the figure, the closer the two peaks are, the smaller the difference value between charging voltage and discharging voltage will be. In the study on the effect of grain size on electrode performance, the reason for the proximity of the two peaks is that the smaller the grain size is, the larger the specific surface area is. Moreover, the larger the film area is, the better the reversibility of lithium-ion implantation and reimplantation will be.

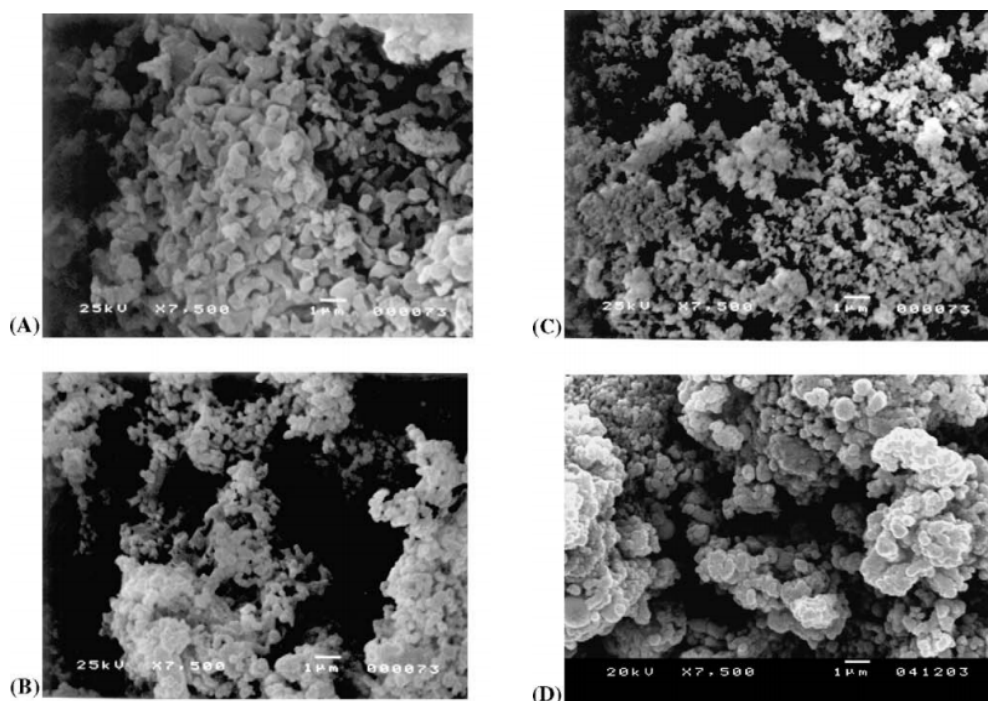


Fig 1. The SEM images of the powder

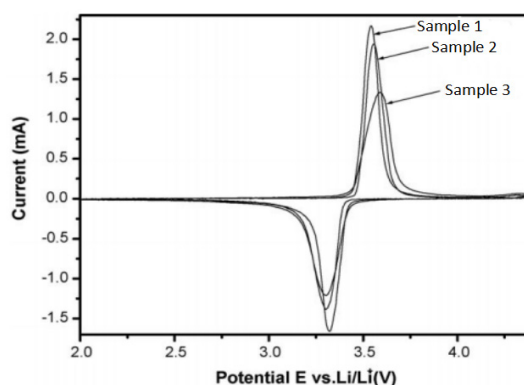


Fig 2. The CV curves of three samples

Through nanocrystallization, we could gain the following advantages:

- a. The large surface area of nano-material expands the reaction interface and provide more diffusion pathways.
- b. Nano-material has more flaws, more micro holes, and higher theory storage capacity of Li.
- c. The little size effect of nano particle shortened Li^+ intercalation and deintercalation depth and distance of travel.
- d. The gap of gathered nano grains reduced the stress during the intercalation and deintercalation of Li^+ , bringing longer cycle life.
- e. The superplasticity and creep properties of nano-material make itself better at bearing the volume change and decrease the vitrification transforming temperature of polymer electrolyte.

IV Doping

4.1 Mechanism

The structure and electrochemistry analysis proving that doping can shrink the miscibility gap of Li, increase the transformation kinetics during the cycling process and expand Li^+ diffusion pathway in the structure.

When doped by mental ions, crystal flaws formed in LiFePO_4 , increasing Li^+ transfer rate between particles, reducing the impedance between particles, increasing the exchange current density. The diffusion rate is effectively increased and conductivity is largely improved. What's more, it will decrease the possibility of battery polarization, enhance batteries properties of discharging and cycling, especially the charge and discharge performance in large electricity. High mental ions doping may cause defects of Li and Fe in the LiFePO_4 grains, thus forming a mix valence state structure in which exist both Fe^{2+} and Fe^{3+} , effectively improving its conductivity and actual specific capacity. Moreover, a small portion of mental ions doping almost dose not influence the actual density of materials.

4.2 The effect of ion size (discuss from two opposite sides)

On the one side, the diffusion of Li ions may be hindered by doping positive ions. The larger the ion's diameter is, the slower the Li^+ will move. On the other side, when the original ion position is replaced by the bigger one, the pathway of Li^+ would be propped up, the migration of Li^+ thus becomes much easier. And this speciality corresponds to higher diffusion of Li^+ and better conductivity in macroscopic.

When Li^+ travel through the $\text{Li}_x\text{FePO}_4 / \text{Li}_{1-x}\text{FePO}_4$ interface, the interface area become smaller. But it's known that we need a larger critical interface area to satisfy the larger current density. Doping relatively bigger ion is good for maintaining the structure of the interface, improving the reversibility and the stability of LiFePO_4 olivine material at high current density, which comes to the main reason of lower charge transfer resistance of bigger ion doping sample after long-term cycling at high current density.

Generally speaking, after synthesizing those specialties, suitable big ion doping is an effective way to improve the charge and discharge performance of LiFePO_4 material.

4.3 The number of ion species

4.3.1 Single ion doping

sample	a(Å)	b(Å)	c(Å)	V(Å ³)
LFP	10.2546	6.0012	4.6616	286.8744
LFP-Na 01	10.2560	5.9797	4.6926	287.7868
LFP-Na 05	10.2346	5.9807	4.6604	285.2634

Table 1. Lattice parameters of the LFP, LFP-Na 01 and LFP-Na 05 samples.

Element	Fe	P	Zn	Ca	Mn
PS	66.478	17.077	14.932	1.358	0.155
APPS	79.261	18.848	1.795	0.096	—

Table 2. the relative content of each element in purified phosphating slag

If the ion replaces the position of Li or Fe, it can improve the conductivity of the material and reduce the charge transfer resistance. When the radius of the doping metal ion is smaller than Fe^{2+} , the crystal grain become smaller, a distortion appeared, and the structure flaws increased, Li^+ diffusion becoming easier, thus improving the rate ability. When the ion replaces the ion in LiFePO_4 in different valence state, it will also form flaws, and the moving of electrons and holes promotes the conductivity.

If the ion replaces the position of O, it could improve the stability and cycling property of the crystal.

4.3.2 Double ion doping

When we dope two kinds of ions, the two doped ions should have a synergistic effect on the charge and discharge property of LiFePO_4 . For instance, when Mg and Co co-doped in Li FePO_4 structure, Mg doping mainly leads to lattice defects of LiFePO_4 , while Co doping can weaken Li-O bond and improve the mobility and diffusion coefficient of ions so that Mg and Co co-doped energy can co-cooperate to improve its rate property.

4.3.3 Multiple ions doping

Multiple ions doping can decrease the resistance of charge transfer and increase the reaction of charge transfer. But others argue that because of the process of multiple ions doping is complicated, it is not practical to apply it to industrial production. Concluding from those researches, we could dope a kind of compound including several proper ions without other substance liable to react with the electrodes or electrolyte, which may come from nature or some waste chemistry

materials from our production and living, simplifying the production process. The only thing we need to do is just purifying the dopant and doping several ions together.

4.4 The grain size change caused by doping

One study mixed 1% and 5% NaNO_3 with LiFePO_4 .

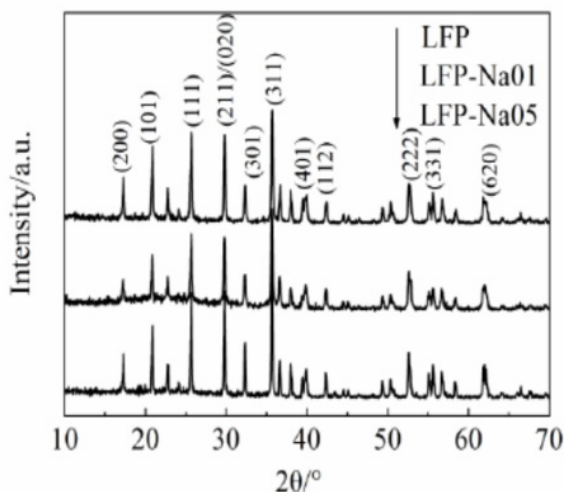


Fig.3 XRD patterns of the LFP, LFP-Na 01 and LFP-Na 05 samples

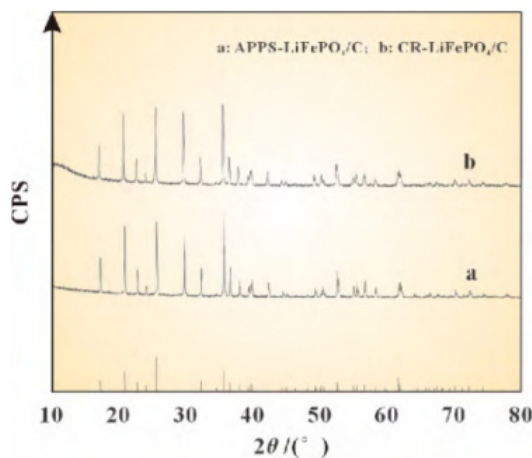


Fig.4 XRD patterns of CR-LiFePO₄ and APPS-LiFePO₄

Fig.3 shows XRD patterns of the LFP, LFP-Na 01 and LFP-Na 05 samples, it indicates the general grain structure of the electrode is not changed. As can be seen from Table.1 , with the increase of Na^+ content, the values of a , c and volume of LFP, LFP-Na 01 and LFP-Na 05 first increased and then decreased. This is because the effective radius of Na^+ is larger than that of Li^+ . When a small amount of Na^+ is doped into LiFePO_4 , the grain size of the original sample will change slightly. However, as the doping ratio increases, the structure of LiFePO_4 formed is greatly changed, and at this time, the structure of the original sample may collapse. The values of a , c and volume of LFP-Na 01 are the largest among the three samples, indicating that this sample has the widest Li^+ channel, which is convenient for Li^+ de-intercalation. At the same time, a smaller b value also means that the path of Li^+ de-intercalation is shorter, which also increases the rate of Li^+ de-intercalation.

Another study doped several elements by phosphating slag and studied the properties of the electrodes.

Table.2 shows the relative content of each element in purified phosphating slag. Fig.4 is the XRD pattern of two materials. Both materials have sharp diffraction peaks, and the positions and intensity of the diffraction peaks are basically consistent with the LiFePO_4 standard card, belonging to Pnma spatial group, indicates that the prepared material has an olivine-shaped structure of LiFePO_4 . No impurity peak was found in the XRD pattern, indicating that doping of Zn, Ca and other elements did not change the crystal structure of LiFePO_4 material. At the same time, carbon source

added to LiFePO_4 material exists in the form of amorphous carbon.

Table.3 is the crystal cell parameters of the two materials, compared with CR materials, APPS-crystal cell parameters are larger, this may be partly because elements such as zinc and calcium succeed in replacing Fe into the LiFePO_4 crystal structure, formed a homogeneous solid solution. Besides, the increase of cell volume can provide more space for the takeoff and embedded of Li^+ . And the APPS material also showed good cycle stability, this could be due to the doping of zinc and calcium making the prepared LiFePO_4/C particles smaller in size, shorting the transfer path of Li^+ in the process of de-intercalation, and effectively reducing the limitation of electrode reaction kinetics.

Results & Discussion

Figure.5 is a synthesis of the data of different doping. The graph shows the specific capacities of first discharge when doped by Al, Na and the other two kinds of multiple doping. Fe-P-Zn-Ca represents the material are doped by Fe, P, Zn, Ca. The per cent of the dopant proportion is $\text{Fe}_{0.79261} \text{P}_{0.18848} \text{Zn}_{0.01795} \text{Ca}_{0.096}$, and the abscissa axis is the radius of the corresponding elements under the figures.

It shows that the electrodes doped by sodium or titanium and vanadium are better in Specific capacity of first discharge at 1 C multiplier, and $\text{Li}_{1.02}\text{Fe}_{0.94}\text{V}_{0.03}\text{Ti}_{0.03}\text{PO}_4/\text{C}$ electrode shows the best property. And researches prove that they can maintain more capacity after circle many times. What's more, they also behave well in other aspects.

We can infer from the figure that the radius of the ions that we doped can affect the property. And as the radius expands, the property will first become better and then decrease. Because when the ion radius is properly larger than Li^+ or Fe^{2+} (compare with the one the ion replaced), it can prop up the pathway of Li^+ . But if the radius is too large, it will destroy the original structure of LiFePO_4 , so the specific capacity may decrease.

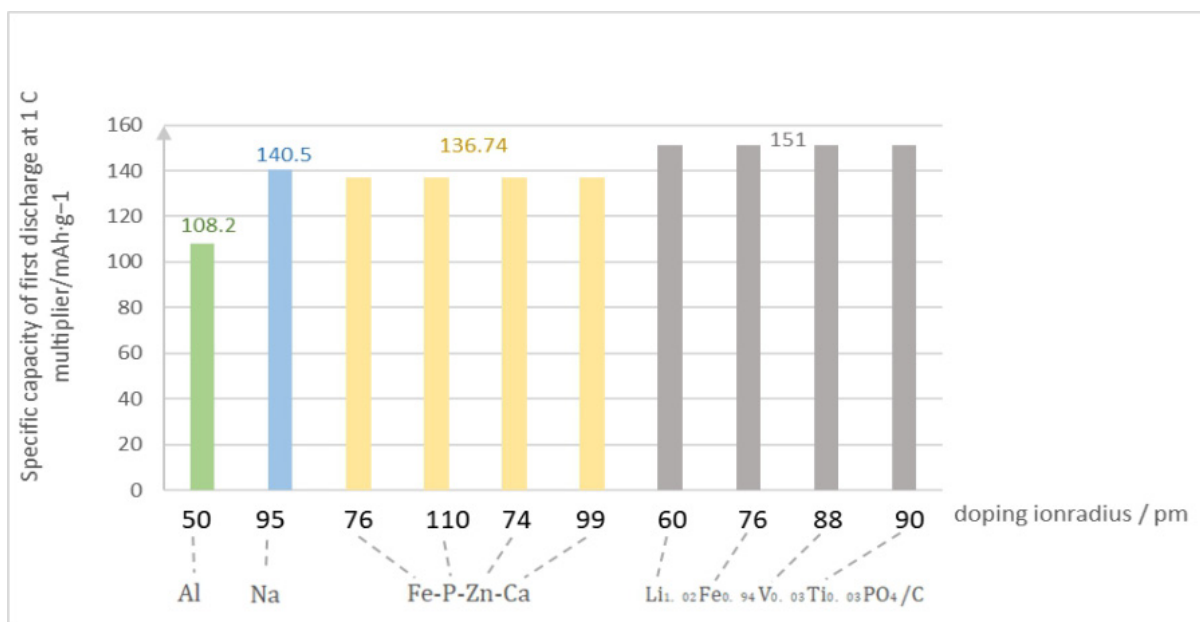


Fig.5 The relation between specific capacity and ion radius

Conclusions & Recommendarions

If there are more available data that can be compared with each other, a more accurate curve can be described and the best radius could be inferred. Then by doping two or three elements, making the average of their radius most close to the best radius, the ideal performance may be reached.

From general data from many researches, ion radius vary from 85 to 95 is excellent. In the Periodic Table of Elements, suitable elements may lie in lanthanide, where the rare-earth metal ions radius vary from Lu 84.8 pm to La 106.1

pm. Because of lanthanide contraction, most rare-earth metal ions are within the scope of the suitable radius. Like Dy and Ho, their radii are respectively 90.8 pm and 89.1 pm, very close to V or Ti ions. It will possibly show satisfied properties when doped into LiFePO_4 electrode.

While searching for the ions, except for the radius, we should also consider other factors. Such as when we doped Na, its conductivity was improved, but its capacity decreased. From the atomic structure, the energy gap will influence the Fermi level, causing different Deintercalated lithium potential and different conductivity. Every dopant has its advantages and disadvantages, we should compare its various properties and weigh their importance, and then it can be effectively and fully used.

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