A Review of the Application of Nitrogen Doping in $LiFePO_4$ Cathode Materials for Lithium-Ion Batteries

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Keywords: Nitrogen Doping, Lithium Iron Phosphate, Synthesis Method, Nitrogen and Sulfur Dualdoped Carbon.

Abstract: Lithium phosphate is a commonly used material for lithium battery-positive electrode materials, with high energy density, high stability, and long service life. Still, it also has disadvantages such as poor conductivity and heavy weight. Discussion based on the structure and electrochemical properties of lithium iron phosphate, this review focuses on the modification methods of carbon-coated, nitrogen doping, and nitrogen-sulfur co-doping. It analyzes the electrochemical properties after doping through impedance tests, EIS, SEM, and other methods. It can be found that these methods can effectively reduce the charge transfer resistance and increase initial discharge capacity, making the battery have a higher and more stable capacity. This review also discusses the synthesis method of doped lithium iron phosphate. Two methods are introduced: using sucrose and melamine as carbon sources and using polydopamine as a precursor. Also shows the synthetic advantages and improvement principles. Both methods can indicate good electrochemical performance of lithium iron phosphate doped with nitrogen.

1 INTRODUCTION

Lithium batteries are the most popular type of batteries used nowadays. It can be utilized for storing energy using natural resources (such as integrated lithium-ion battery power source, marginal website lithium-ion battery power source), etc. Among them, lithium iron phosphate which is used as a common material has attracted much attention. Lithium iron phosphate ($LiFePO_4$) has an alternating layer structure of octahedral-coordinated iron and octahedral-coordinated lithium mixed with phosphate tetrahedrons (Malik et al, 2013). Compared to $LiMO_2$, lithium cobalt oxide ($LiCoO_2$, LCO) other traditional lithium-ion batteries, $LiFePO_4$ has advantages in energy density, working cycles, stronger durability, and excellent safety and environmental protection (Li et al, 2016). Furthermore, $LiFePO_4$ has many excellent electrochemical properties. Such as high cycle stability, safety, platform potential, and good high-temperature performance.

However, $LiFePO_4$ still has some disadvantages, such as heavy weight, low energy density, poor conductivity, and easy mixing between Li-Fe sites. To overcome these problems, a common approach is to nanosize $LiFePO_4$ to reduce the risk of blockage (Yang et al, 2016). In addition, scientists have proposed a series of improvement methods, including doping, nitrogen-doped carbon layers, high conductivity coatings, morphology optimization, and nanosize (Li et al, 2016), (Cech et al, 2013, Chen et al, 2023, Zhang et al, 2013). This article will review nitrogen-doped carbon layers, focusing on improvement strategies for nitrogen-doped carbon layers and specific methods for the electrical characteristics of the electrolyte $LiFePO_4$.

2 THE CHARACTERISTICS AND STRUCTURE OF $LiFePO_4$

2.1 The Structure of $LiFePO_4$

$LiFePO_4$ is commonly used in lithium-ion batteries. Its crystal structure has a unique alternating layer of octahedral-coordinated iron and octahedral-coordinated lithium mixed with phosphate tetrahedrons. This unique structure gives $LiFePO_4$ material stable chemical properties (Yang et al, 2016),(Eftekhari, 2017). During the electrochemical reaction of $LiFePO_4$ materials, as lithium ions are inserted and removed, their crystal structure will undergo certain changes. The conversion from

Chang, W.
A Review of the Application of Nitrogen Doping in LiFePO4 Cathode Materials for Lithium-Ion Batteries.
DOI: 10.5220/0013935600004914

In *Proceedings of the 2nd International Conference on Renewable Energy and Ecosystem (ICREE 2024)*, pages 314-318
ISBN: 978-989-758-776-4

$LiFePO_4$ to $FePO_4$ is a minor phase transition that corresponds to different lattice parameters. In the phase transition of this decay process, we can see that $LiFePO_4$ has limited electronic and ionic conductivity relative to lithium ions.

A notable feature of $LiFePO_4$ is its low electronic and ionic conductivity. This is mainly because the mobile lithium ions are restricted to 1D channels along the b-axis, and their movement is restricted by phosphate ions (Gabrisch et al, 2003). In addition, the strong covalent bond between oxygen and P5 ions forms a stable $(PO_4)^{3-}$ unit, and this structural stability enhances the safety of the material. To improve the conductivity of $LiFePO_4$, a common method is to enhance its electronic conductivity by introducing nitrogen atoms into the carbon structure. This modification measure can improve the properties of $LiFePO_4$ in lithium-ion batteries while maintaining their high stability and safety characteristics.

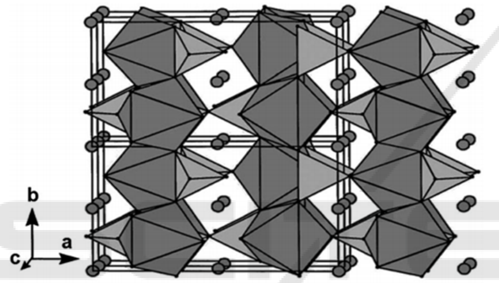

Figure 1. LiFePO4 crystal structure of (Bi et al, 2013).

2.2 Electrochemical Properties

$LiFePO_4$ has many excellent electrochemical properties as the electrode, which provides a good basis for improving the performance and expanding the applications of lithium-ion batteries.

First, the platform potential is relatively flat. The insertion/extraction potential platform of $LiFePO_4$ is relatively flat, which gives it relatively stable discharge voltage and charge voltage, which it is advantageous to the battery's energy density and cycle performance. The long platform of the voltage curve of charging and discharging $LiFePO_4$ is about 3.4 V (0.2 C). When the temperature reaches 5°C, the $LiFePO_4$ discharge capacity decreases from 139.6 mAh/g to 77.6 mAh/g (Kim et al, 2008).

Second is the high cycle stability. Because the oxygen atoms in the $LiFePO_4$ structure are tightly bound to the Fe and P atoms, it performs better at higher temperatures compared to $LiCoO_2$ and other layered electrode materials. The high lattice stability enables $LiFePO_4$ to maintain its structural integrity during long-term cyclic charge and discharge, thereby ensuring the cycle life of the battery.

Third is safety. Golubkov et al showed that, under adiabatic conditions, a heating element placed around an 18650 LFP cell with 100% SOC can provide constant power, the maximum temperature of the cell during TR was between 400° C-450° C (Bugrynice et al, 2008). This shows that compared with other lithium-ion battery-positive electrode materials, $LiFePO_4$ has a lower risk of thermal runaway and explosion, making lithium-ion batteries safer and more reliable.

Fourth is the low self-discharge rate. By using in situ Raman spectroscopy to study the performance of $LiFePO_4$ particles of different sizes and morphologies during charging and self-discharging, it can be found that $LiFePO_4$ has a low self-discharge rate, and the battery suffers less loss during storage and idleness, so it can maintain relatively long battery life.

Finally, there is the good high-temperature performance. $LiFePO_4$ has good stability and cycle performance in high-temperature environments and can remain stable even at 400°C. It makes it suitable for various high-temperature environments, such as electric vehicles.

3 MODIFICATION STRATEGY

Materials with a larger surface area to volume ratio can provide shorter paths for ions to travel, thereby achieving higher power and energy density. However, the increased surface area may also have adverse effects, because the increased electrolyte exposure promotes electrolyte decomposition, the formation of unstable interfaces, and the dissolution of transition metals (Quilty, 2023). Poorly performing binders can negatively impact the cycling performance of lithium batteries. Therefore, structures containing highly π-conjugated polymer chains should be considered when designing and synthesizing polymer binders.

3.1 Carbon-Coated

Carbon coating is a good way to increase the conductivity of the electrode. The addition of N, S, B, P, F and other heteroatoms into the carbon network further enhances the electrochemical activity. Heteroatoms can act as electron donors, increase carbon electron transfer, break down graphite's ordered structure, and promote the diffusion of lithium ions. Simultaneously, a lot of defects will be generated to promote the transmission of lithium in the carbon layer.

The reversible capacity of carbon-coated $LiFePO_4$ at 0.2C is about 140 $mAhg^{-1}$. After the cycle, it can maintain its capacity. And the capacity is much greater than naked $LiFePO_4$. By studying the capacity of carbon covering $LiFePO_4$ of different materials, it can be found that compared with other carbon sources, graphite-covered $LiFePO_4$ has better power chemical performance. After the impedance measurement for different materials, the $LiFePO_4$ covered with graphite has a lower lithium-ion migration resistance, and it also has a lower charge transfer resistance. From this, we can conclude that the addition of carbon will significantly reduce the size of $LiFePO_4$ particles. The reduction of grain size of $LiFePO_4$ and the enhancement of carbon electrical contact will significantly improve the electrochemical performance (Shin et al, 2006).

Bai N et al. (2016) studied Hierarchical porous $LiFePO_4/C$. Not only is the synthetic vegetable protein pollution-free and easy to extract, but it also has a circulation capacity of up to 166.8 $mAhg^{-1}$. $LiFePO_4/C$ has a high capacity at different rates. At high rates, the discharge capacity of carbon-coated $LiFePO_4$ is twice that of the original $LiFePO_4$, and the capacity retention rate also is high.

Xiao Q.C et al. (2014) studied $Li_{1\cdot2}(Mn_{0.54}Co_{0.13}Ni_{0.13})O_2@AlF_3/C$ (LMSAC) which is prepared by AlF_3 and the carbon hybrid layer of LMSS. The LMSS coated with AlF_3/C has an initial coulombic efficiency of more than 85%. Therefore, carbon-coated improves the rate performance and cycle performance. Impedance experiments show that the electrode has a lower R_{ct} and better conductivity after carbon-coated.

3.2 Nitrogen Doping

The particle size of LFP/C-N ($LiFePO_4$/N doped C) materials prepared by nitrogen doping technique is about 143 nm, in which LiFePO4 contains N. The specific capacity of the material is 160.7 $mAhg^{-1}$ (0.1 C). It was demonstrated that the capacity of the $LiFePO_4/C$ cathode did not decay after a long period of operation, while the core-shell structure improved its cycling performance.

Through the SEM image of LFP/C-N, it can be found that the N element is distributed in the $LiFePO_4$ particles and surface carbon membranes. In addition, it can be found from the structure of N doped that the N doped in the carbon coating can expand the gap, effectively increase the density of the carrier, and increase the conductivity. When measuring 0.1C, the charging and discharge voltage of each material can obtain the conclusion that the discharge capacity gradually increases with the increasing carbon covering and N doped. After performing impedance experiments, it can be found that materials with a nuclear shell structure have lower charge transfer resistance, and the N doped can further reduce the transfer resistance. This also illustrates that the nuclear shell structure and N-doped have a synergy effect (Zhang et al, 2022).

Wang p et al. (2016) uses polybenzoxazine to make $LiFePO_4$ nitrogen-doped material. Nitrogen doping can provide a fast transport path for Li^+. The insertion process of Li^+ has a flat platform potential, indicating that the battery is stable. It can maintain 75.8% of the initial discharge capacity, and through continuous charge and discharge tests, it can be found that it has stable cycle performance and excellent recyclability.

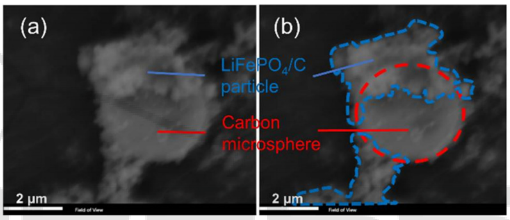

Figure 2. (a) SEM image of LFP/CN. (b) LiFePO4 granules (Bai et al, 2016)

3.3 Nitrogen and Sulfur Dualdoped Carbon

Double-doped carbon materials are carbon-doped with nitrogen and sulfur. Compared with single-doped materials, double-doped carbon materials have better electrochemical properties. The heteroatom is an electron donor, which can enhance the electron transfer, and destruction of C, and facilitate the diffusion of lithium ions. Moreover, doping with NSC can create more defects, which can be used as the active site. The cathode discharge capacity of LFP doping by NSC was 155 $mAhg^{-1}$ and showed no significant decay with cycling, which was significantly higher than that of LFP. Furthermore, NSC@LFP has 126 mAh·g-1 in the first period of 1 C. Heteroatom-doped carbon layer is an effective method to modify the electrode (Xiao et al, 2014).

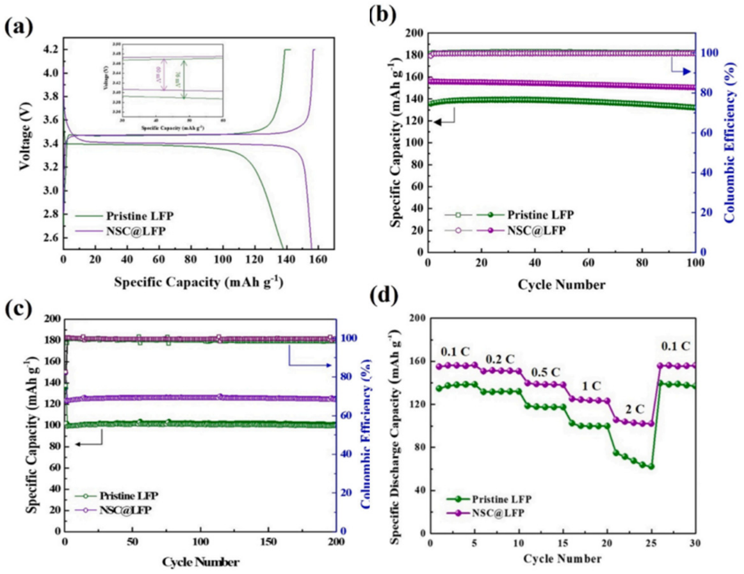

Figure 3. (a) the potential profile, (b) cycle efficiency, (c) cycle performance (d) the ability of pure LFP to NSC@LFP (Xiao et al, 2014).

4 THE SYNTHESIS METHOD OF LiFePO$_4$

4.1 Synthesis of Nitrogen-Doped LFB-C with Sucrose and Melamine as Carbon Sources

Nitrogen-doped LFB-C can be synthesized using sucrose and melamine as the carbon source. The addition of melamine helps in the appearance of active surfaces. The effect of nitrogen content on particle size was not significant due to the low nitrogen content. The coating was formed uniformly on the lithium iron phosphate surface. The nitrogen-doped carbon layer and lithium iron phosphate formed a "core-shell" conductive network, which would greatly facilitate electron transfer and thus improve electrochemical performance.

After measuring the EIS, the EIS is composed of a straight line in the low-frequency area and a half in the high-frequency area. The Warburg impedance is used to measure the linear relationship in the low-frequency range, and it can reflect the diffusion ability of the lithium-ion in iron phosphate/lithium iron phosphate. The half-circle diameter of the modified sample was smaller than that of the modified one. The reason for this is that nitrogen provides a lot of conductive carriers for the carbon layer particles in the LFP/C, so the LFP/C resistance is reduced, and the slope of the inclined portion of the nitrogen-modified sample is higher than that of the untreated sample, which indicates that the Warburg impedance is decreased, and the doping of LiFePO$_4$ is advantageous to the improvement of the electrochemical property.

4.2 Synthesis of Nitrogen-Doped LiFePO4 by Microwave Heating with Polydopamine as Precursor Carbon-Nitrogen

LiFePO4 and Tris buffer were mixed with dopamine and stirred for 2 h. The weight ratio of dopamine/LiFePO4 was 1:9, and then nitrogen-doped lithium iron phosphate was synthesized by microwave heating. Generally speaking, the particle size of the electrode material has a great influence on its electrochemical properties, but the microwave heating method makes the product particles homogeneous and small in size, so the influence is small. The LiFePO4/CN synthesized by this method has better cycling and electrochemical properties, as shown in Figure 3 (Zhang et al, 2022).

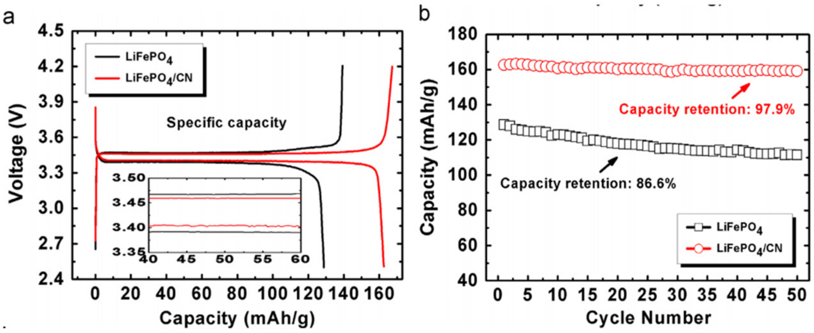

Figure 4. (a) capacity and (b) cycling properties (Zhang et al, 2022).

5 CONCLUSIONS

In summary, doping with C, N, and S can effectively improve the energy properties of the cathode. Moreover, compared with single doping, nitrogen and sulfur dual doping can make lithium iron phosphate have better electrochemical properties. Double doping materials can enhance the electron transfer of carbon, damage the ordered structure of graphite, increase the edge defect, form small pores, and accelerate the diffusion of lithium ions.

In addition, this review also introduces two methods for synthesizing nitrogen-doped $LiFePO_4$: mixing the $LiFePO_4$ sample with sucrose and melamine and synthesizing nitrogen-doped $LiFePO_4$ was carried out by using polydopamine as a precursor of carbon-nitrogen, and by microwave heating.

As a common lithium battery cathode material, LiFePO4 has a longer service life and stronger durability. However, LiFePO4 also has a lower energy density, so how to improve its shortcomings with cheaper materials is an important challenge.

REFERENCES

Bai N et al. 2016 *Mater Technol* **32** 203

Bi Z, Zhang X, He W, Min D and Zhang W 2013 *RSC Adv.* **3** 19744

Bugrynice P.J, Davidson J.N and Brown S.F 2018 *Energy Procedia* **151** 74

Cech O, Thomas J. E, Sedlarikova M, Fedorkova A, Vondrak J, Moreno M. S and Visintin A 2013 *Solid State Sci.* **20** 110

Chen Q, Liu H, Hu J, Wang L, Li Y and Yao Y 2023 Ionics. **29** 4537

Eftekhari A 2017 J. Power *Sources.* **343** 395

Gabrisch H, Yazami R and Fultz B 2003 *J. Power Sources.* **119-121** 674

Han B, Meng X, Ma L and Nan J 2016 *Ceramics International* **42** 2789

Kim H.-S, Kong M, Kim K, Kim I.-J and Gu H.-B 2008 *J. Electroceram.* **23** 219

Li S, Liu X, Liu G, Wan Y and Liu H 2016 *Ionics.* **23** 19

Malik R, Abdellahi A and Ceder G 2013 *J. Electrochem.* Soc. 160 A3179

Quilty C et al. 2023 *Chem Rev* **123** 1327

Shaji N et al. 2023 J. Electrochem. Energy Convers. Storage **72** 108710

Shin H. C, Cho W. I and Jang H 2006 Electrochimica *Acta* **52** 1472

Wang P et al. 2016 *ACS Appl .Mater.*Interfaces **40** 26908

Xiao Q.C et al. 2014 *Mater Technol* **29** A70

Yang Z, Dai Y, Wang S and Yu J, 2016 *J. Mater. Chem. A.* **4** 18210

Zhang B, Wang S, Liu L, Li Y and Yang J 2022 *Materials* **15** 4738

Zhang H, Deng Q, Mou C, Huang Z, Wang Y, Zhou A and Li J 2013 *J. Power Sources.* **239** 538