

The Progress of Carbon Coating Modification on the Surface of Lithium Iron Phosphate Cathode Materials

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Abstract. Due to the urgent need for sustainable development of human society, new energy materials have become one of the hot topics for major powers in the world. Thereinto, lithium iron phosphate (LiFePO₄) as a battery cathode material owing to its high safety, less pollution, low cost, which has achieved remarkable results. The low electrical conductivity and slow diffusion of lithium ions have led to a number of improvements. Carbon materials are inexpensive, non-toxic, non-polluting, widely available and highly conductive. Contemporarily, carbon cladding modification on the surface of lithium iron phosphate to improve its multiplicative performance and cycle life is currently the most widely used and economically feasible method. This paper first briefly describes the development history, basic structure and principle of lithium-ion batteries. Subsequently, we review three different surface carbon coating synthesis methods and analyse the impact of each method on battery performance, and looks into the future of lithium iron phosphate cathode materials. These results shed light on carbon cladding as a surface modification technique, which can significantly improve the multiplicity and cycling performance of LiFePO₄ when applied to the field.

Keywords: Lithium Ion Battery, Lithium Iron Phosphate, Carbon-coat.

1. Introduction

Energy is the basis and driving force for the existence and development of human society, and mankind is constantly obtaining energy directly or indirectly from nature. As human civilization enters the 21st century, mankind has made a series of brilliant achievements in global economy, technology and society, but the energy problem is becoming more and more serious [1]. While mankind is developing at a rapid pace, there is a strong contradiction between the massive exploitation of energy and the shortage of energy. Traditional fossil energy reserves are dwindling due to long-term over-exploitation, while the usage of fossil fuels is causing serious environmental problems, e.g., global warming and atmospheric pollution. This contradiction is becoming increasingly acute and the survival and development of mankind is being threatened and challenged. If the relationship between energy, environment and development is not properly handled, human society will face a serious development bottleneck and survival crisis. In 1800, Volta invented the first chemical power source the battery, which opened the era of chemical power storage. Since the invention of chemical power sources, scholars have developed and researched new battery materials for energy storage, and new battery materials will greatly promote and accelerate the emergence of higher performance batteries. The successive emergence of lead-acid batteries, nickel-based batteries, lithium-ion batteries and other important energy storage batteries not only epitomizes the development of energy storage batteries, but also represents the direction of development of energy storage batteries: high performance, safety and environmental protection.

To improve the conductivity of LiFePO₄, we use two common methods of carbon cladding: in-situ carbon cladding, where a carbon source is added to the precursor of LiFePO₄ to form a carbon cladding layer in-situ on the surface of the particles while LiFePO₄ is formed; and non-in-situ carbon cladding, where LiFePO₄ is prepared and then carbon clad. In-situ carbon cladding is currently the most effective cladding method. The effect of non-in-situ carbon coating depends on the dispersion

and size of the LiFePO_4 particles, generally speaking, the smaller the particle size and the more uniform the dispersion, the better the carbon coating effect. In this paper, ion doping, surface coating and particle nano-modification are investigated. The surface carbon coating not only enhances the electrical conductivity of LiFePO_4 cathode material, but also inhibits the particle growth and weakens the polarization effect of the electrode, thus improving its multiplicity performance and extending its cycle life. This paper reviews the progress of surface carbon coating modification of LiFePO_4 cathode materials, and summarizes the selection of carbon source, carbonization mechanism and surface chemistry, pointing out the problems of current research and future development prospects. The rest part of the paper is organized as follows. The Sec. 2 will give the basic descriptions of the Li-ion batteries. Afterwards, the Sec. 3 will describe the method of carbon cladding on the surface of cathode materials for lithium-ion batteries. Subsequently, the Sec. 4 will present the effects of different methods of carbon cladding synthesis on battery performance. Then, the future prospect will be demonstrated in Sec. 5. Eventually, a brief summary will be given in Sec. 6.

2. Basic description of lithium ion batteries

In the late 1970s, Steele and Armand et al. proposed the concept of lithium ion intercalation compounds, and proposed two solutions to solve the lack of safety of lithium batteries: (1) preparation of all-solid-state lithium metal secondary batteries; (2) using Lithium-ion intercalation/deintercalation materials to replace lithium metal, and developed into lithium-ion secondary batteries that use lithium-ion intercalation materials for both positive and negative electrodes [1]. In 1979, Goodenough et al. first proposed that LiCoO_2 could be used as a positive electrode material for batteries. In 1982, Yazami and Touzain first reported the successful electrochemical intercalation and deintercalation of lithium ions in graphite. This experiment laid the foundation for today's use of graphite as the anode material for lithium-ion batteries. In 1983, Akira Yoshino of Japan successfully developed a new type of lithium-ion battery with LiCoO_2 as the positive electrode and conductive polymer material polyacetylene as the negative electrode. In 1991, the Sony company realized the commercialization of LiCoO_2 lithium-ion battery for the first time [2]. LiCoO_2 cathodes are also widely used due to their high discharge voltage (4V), good stability and safety, and high energy density. In 1997, Goodenough et al. announced that the discovery that olivine-type LiMPO_4 (M: Fe, Mn, Ni, Co) materials can be used as cathode materials for lithium-ion batteries, especially LiFePO_4 shows good capacity and cycleability. In 1994, the Tarascon group of Bellcore (Bell) Company of the United States applied for a patent and took the lead in proposing to use a polymer with lithium ion conductivity as an electrolyte to manufacture a polymer lithium ion battery (PLIB). In 1999, Panasonic launched the polymer lithium-ion battery and realized commercial production.

Lithium-ion battery materials mainly include positive electrodes, negative electrodes, separators, electrolytes, and auxiliary components. The functions and materials of each part are demonstrated as follows. Positive electrode, which has a layered or tunnel structure and can freely deintercalate Li. Usually, a permetal-containing lithium salt with a higher redox potential is selected. There are mainly layered structures of LiCoO_2 , LiMnO_2 , LiNiO_2 and spinel structure of LiCo_2O_4 , LiNi_2O_4 , LiMn_2O_4 and other compounds, as well as regular octahedral olivine structure LiFePO_4 , LiMnPO_4 , LiNiPO_4 , LiCoPO_4 , etc. Lithium ions are held in a lithium battery during charging and released during discharge. The lower the negative electrode potential, the higher the output voltage and the higher the energy density. Therefore, try to choose a substance that can insert and extract lithium ions that is close to the potential of lithium metal, such as lithium titanate, graphite, mesophase carbon microspheres and other carbon layers like materials or transition metal oxides of lithium, nitrides, etc. Diaphragm is a barrier that separates the positive and negative electrodes, which is an insulator with tiny holes. It separates the positive and negative electrodes to prevent internal short circuits and also allows lithium ions to pass through. Generally, it is an insulating polymer material such as polyolefin resin. Commonly used diaphragms include single-layer or multi-layer polypropylene (PP) and polyethylene

(PE) microporous films. Electrolyte is used to separate ion transport from electron transport, like the separator, allowing lithium ions to pass through but not electrons. Generally, it is prepared by mixing organic liquids such as propylene carbonate, ethylene carbonate, diethyl carbonate, dimethylethane, etc. or their mixed liquids as organic fluxes, and lithium salts such as LiClO_4 , LiPF_6 , LiBF_4 as electrolytes, and mixing them in a certain proportion. The scheme of lithium-ion battery is shown in Figure 1.

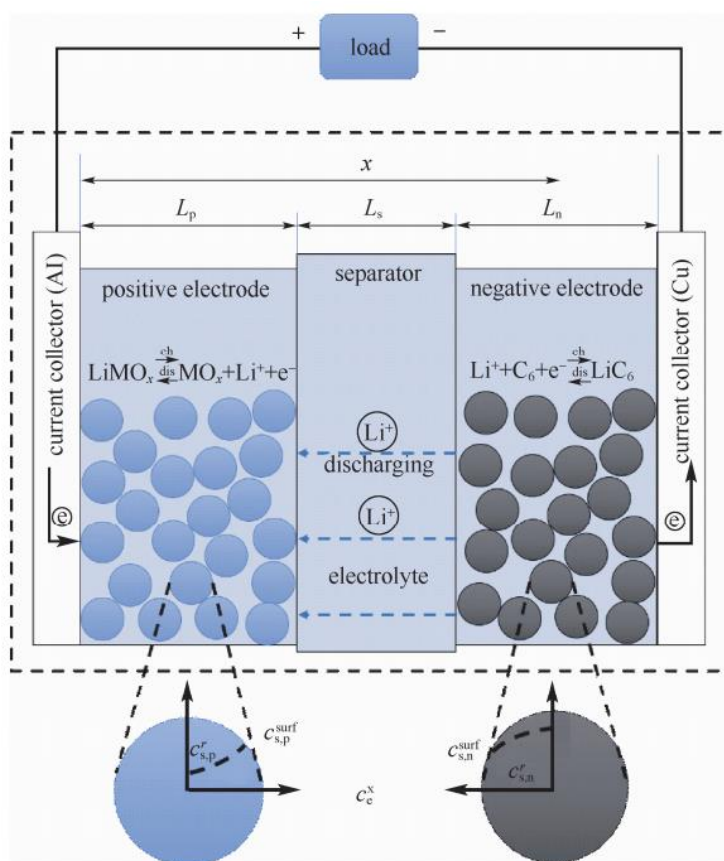


Figure 1. P2D model of lithium ion battery [1]

During charging, the transition metal ions in the positive electrode are oxidized, and the electrons enter the current collector and flow out. After being embedded into the layered structure of the negative electrode material, it is paired with the electrons entering the negative electrode from the external circuit, but it is not reduced. Specifically, when the battery is discharged, the situation is completely opposite, the transition state metal ions in the positive electrode material are reduced, and the lithium ions are removed from the negative electrode. The detachment re-enters the lattice of the cathode material through the electrolyte and separator. The cathode material undergoes a process of delithiation and intercalation, switching between two compounds with and without lithium. The charging and discharging process of the battery is actually the redox process of the positive electrode material. The positive electrode material is also called the active material, which plays a decisive role in the overall performance of the battery.

3. Synthesis and surface carbon coating methods

The performance of LiFePO_4 cathode materials is closely related to the synthesis method. The synthesis process and conditions can affect the structure, morphology, size and other important parameters of the cathode materials, which are directly related to the electrochemical performance of LiFePO_4 cathode materials. The requirements for synthesis methods for next generation Li-ion batteries are simplicity, high feasibility, low cost and good performance of the synthesised material. The selection of a suitable surface coating method is essential to form a homogeneous cladding layer

on the surface of the LiFePO_4 active particles. The commonly used surface carbon cladding methods can be divided into solid phase and liquid phase synthesis methods.

The first LiFePO_4 cathode material was synthesised by Goodenough et al. using a high-temperature solid-phase method [3]. Subsequently, many researchers have continued to investigate the high temperature solid phase method in depth and to improve the performance of the synthesized LiFePO_4 cathode materials. The synthesis of LiFePO_4 by the high temperature solid phase method is a simple process suitable for industrial mass production. The starting materials for the conventional high temperature solid phase method are ferrous acetate or ferrous oxalate, lithium carbonate and ammonium phosphate. The starting materials are weighed in stoichiometric ratios, ball-milled and mixed to obtain the precursor materials. The precursor materials are sintered in an inert atmosphere (or reducing atmosphere). Sintering can be divided into two stages, i.e., pre-sintering (temperature range 300-400) and high temperature sintering (temperature range 400-800). In the low temperature pre-sintering stage, gases (NH_3 , CO_2) are released from the decomposition of the material and the pre-sintering also removes moisture from the material to facilitate the high temperature stage of sintering. Usually, to ensure uniform sintering, the material is naturally cooled after pre-sintering and the material is ground twice. In high temperature sintering, the material undergoes a phase change, with in situ carbon encapsulation of the material and ultimately pure phase LiFePO_4 crystals are obtained. Although the solid phase method is widely used, it is a complex process, sometimes requiring repeated grinding to obtain homogeneous particles, and some steps require high reaction temperatures to suppress the formation of heterogeneous phases. These repeated heat treatments can lead to particle growth and agglomeration, which can affect the performance of LiFePO_4 cathode materials and thus limit their practical application.

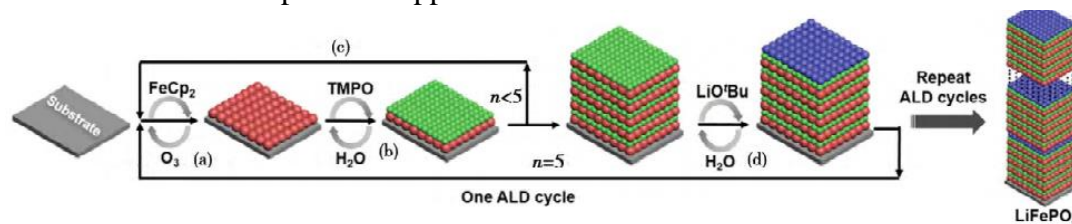


Figure 2. Atomic deposition of amorphous LiFePO_4 using ferrocene (FeCp_2), ozone (O_3), trimethyl phosphate (TMPO), water (H_2O) and lithium butoxide (LiOt Bu) at 300°C . (a) Sequential pulses of FeCp_2 and O_3 lead to the growth of the Fe_2O_3 layer (red); (b) sequential pulses of TMPO and H_2O lead to the POx layer deposition (green); (c) repeating steps (a) and (b) five times; (d) sequential pulses of LiOt Bu and H_2O leading to the formation of the Li_2O layer (blue). An ALD cycle for amorphous LiFePO_4 growth consists of steps (a)-(d) [2]

Precipitation is the formation of insoluble precipitates of starting materials in the liquid phase by means of a precipitating agent, followed by a heat treatment to obtain the desired material. In recent years, atomic layer deposition (ALD) has found considerable application in the engineering of nanostructures [4]. ALD is a film deposition technique based on the sequential use of gas-solid surface reactions, which gives the superior advantage of depositing a uniform film on a substrate by controlling the reactive deposition process, with the flexibility to adjust the size, thickness and composition of the target material at the atomic scale. Liu et al. successfully synthesised $\text{LiFePO}_4/\text{CNT}$ nanocomposites were successfully synthesised and the calcined $\text{LiFePO}_4/\text{CNT}$ showed excellent battery performance as a cathode material, including excellent multiplicity performance, high power density and long lifetime. The formation principle is shown in Fig. 2 [4]. Precipitated LiFePO_4 materials also have the advantages of fine particle size, uniform distribution, relatively easy to control morphology and short synthesis cycle time. However, co-precipitation of LiFePO_4 materials utilises different reaction components in the liquid phase, which makes it difficult to control the reaction parameters and the batch stability of the synthesised cathode material is not good.

The sol-gel method is a highly attractive method for preparing materials, which generally uses soluble salts as starting materials for the reaction. The starting material is homogeneously dispersed at the molecular level in the liquid phase and then subjected to hydrolysis, condensation and

subsequent heat treatment to obtain the desired pure phase [5]. The sol-gel method generally uses citric acid, ethylene glycol (EG) as chelating agents or carbon sources. Sols are formed by dispersing colloids in the liquid phase and are distributed as colloids with diameters between 1 and 100 nm. Gels are porous, sub-micron, interconnected mesh structures. The synthesis of LiFePO_4 cathode materials using the sol-gel method has the advantages of small size and good dispersion in the liquid phase synthesis, but also facilitates the synthesis of porous LiFePO_4 materials. Thus, it ensures the purity of LiFePO_4 and low synthesis temperature, which is conducive to controlling the size and morphology of the particles. In general, the material prepared by the sol-gel method has a porous structure and a large specific surface area, which can increase the contact area between the electrolyte and the electrode material and help to improve the multiplicity performance.

4. Effects of Different Carbon Coating Synthesis Methods on Battery Performance

Nyten et al. synthesized nano- $\text{Li}_2\text{FeSiO}_4/\text{C}$ composites by high-temperature solid-phase method [6], and cycled at C/16 times at 3.1-2.8V, with a specific charge capacity of 165mAh/g. Qiao et al. used material mechanical grinding supplemented by high-temperature solid-phase method to prepare $\text{Li}_2\text{FeSiO}_4/\text{C}$ composites with material crystallinity [7]. The specific capacity of the product was measured at 55°C, 1.5-4.7V, and 0.2c rate.

In the manufacture of spacecraft, the Eastern solid phase method therefore achieves high-precision material requirements, product size and uneven distribution, resulting in the realization of practical calculation problems, size synthesis, development of appearance, structure, and controllability. The chemical problem method is very necessary.

Dai used a high-temperature solid-phase method to prepare lithium ferrous phosphate, and improved the synthesis process [8]. Fe and Ni catalysts were added to the pre-fired lithium ferrous phosphate powder as a carrier, and then by vapor deposition method. Cyclohexane and ethylene were used as carbon sources, carbon nanofibers and carbon nanotubes were grown in situ at 750°C, and $\text{LiFePO}_4/\text{CNF}$, $\text{LiFePO}_4/\text{CNT}$ composite materials were prepared. The incorporation of CNF and CNT can effectively improve the lithium iron phosphate. battery performance. Among them, cyclohexane was used as the carbon source, when the reaction temperature was 750°C, 2 wt.% NiCO_3 catalyst was added, H/Ar mixture was used as the carrier gas, and the carbon source injection rate was 12mL/h. A large number of carbon nanofibers with a diameter of 30 nm were grown on the surface of Fe-Li particles. The discharge capacities of $\text{LiFePO}_4/\text{CNF}$ composites were 125mAh/g, 96mAh/g, 77mAh/g and 60mAh/g at 0.1 C, 0.5 C, 1 C, and 2C, and 8%-10% capacity decay after 30 weeks of cycling. In the $\text{LiFePO}_4/\text{CNF}$ material, CNF grows between the lithium iron phosphate particles, which are connected to each other to form a conductive network, which effectively improves the conductivity of the material, thereby improving the battery performance of lithium iron phosphate.

Compared with the solid-phase method, the sol-gel method can not only achieve uniform mixing of materials at the molecular level in the solution, but also has a lower synthesis temperature, a shorter time-consuming, and easy control of the size and morphology of the particles, so it is favored by researchers. Bazzi et al. prepared C- $\text{Li}_{1+x}\text{FePO}_4$ ($x = 0, 0.05$) olivine phase complexes by sol-gel method using surfactant oleic acid as carbon source [9]. Among them, adding excess Li can not only change the crystal structure of the nanocomposite, but also reduce its particle size. At 1/3C rate, the specific capacity of the composite is 155mAh/g, and its rate performance is effectively improved. Saravanan et al. synthesized nanosheet LiFePO_4/C composites using glucono- δ -lactone as the in-situ carbon-coated carbon source [10]. The layered nanosheets LiFePO_4/C with a thickness of 10-30nm exhibit high stable cycling performance, with a specific capacity of 167mAh/g at 0.1C and after 50 cycles at a high rate of 30C. The capacity can be maintained at 46mAh/g after cycling. The TEM of carbon nanofibers and performances comparison are given in Figs. 3 and 4.

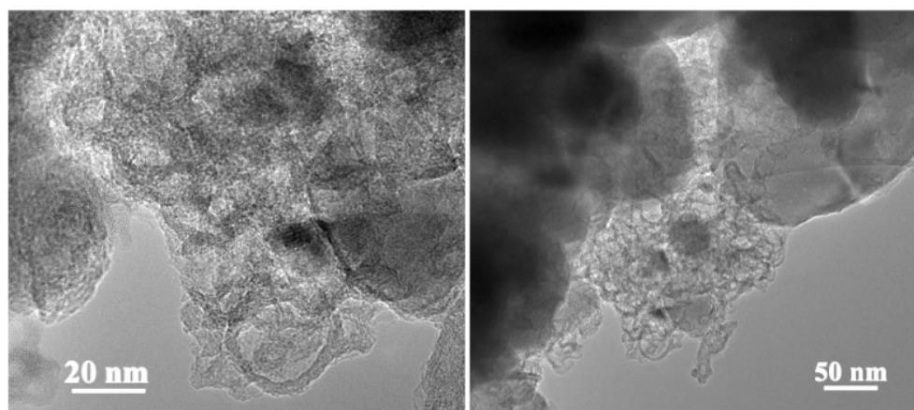


Figure 3. The TEM of carbon nanofibers [4].

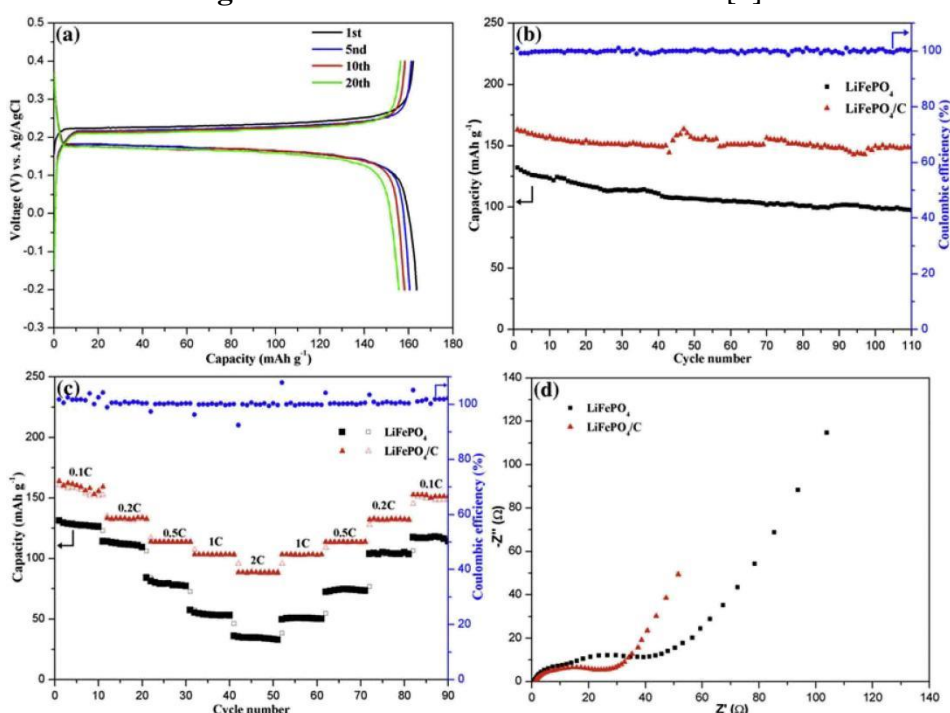


Figure 4. Comparison of coating and uncoating of LiFePO₄ [5]

5. Lithium Battery Outlook

Lithium-ion batteries are the most promising rechargeable secondary batteries, which have many advantages: high energy density, good safety performance, long charge/discharge cycle life, low self-discharge and other characteristics. With the in-depth research of new energy technology, lithium-ion batteries have been improved in all aspects of performance (e.g., safety, cycle life), becoming the first choice for power and energy storage batteries, promoting and facilitating the rapid development of electric vehicles and intelligent energy storage industry.

As the most important component of lithium-ion secondary batteries, the performance of cathode materials directly affects the performance and cost of lithium-ion batteries.

For the entire cost of lithium batteries, cathode materials account for a large proportion of the basic (one-third of the cost of raw materials occupied by the cathode). On this basis, to vigorously promote lithium-ion batteries and expand its application, it is crucial to improve the performance of cathode materials and reduce the cost of materials. Lithium iron phosphate cathode materials possess environmentally friendly, high safety, high temperature, low raw material prices and other advantages. With this in mind, the current battery industry to develop research hotspots, is the most promising power lithium-ion cathode materials, with good prospects for market development.

6. Conclusion

On the basis of summarizing pervious literature and in view of the shortcomings of lithium iron phosphate cathode materials for lithium ion batteries, the basic methods for preparing LiFePO_4/C composites and the electrochemical properties of the prepared materials are systematic summarized. Besides, the surface carbon coating modification methods are described, some of the basic problems that exist in. Carbon coating, as a surface modification technology, can significantly improve its rate and cycle performance when applied in the field of LiFePO_4 . The carbon coating of lithium iron phosphate is divided into in-situ coating and ex-situ coating, and the synthesized LiFePO_4/C composite exhibits excellent reversibility and high-rate performance. Although the carbon coating modification significantly improves the electrochemical performance of lithium iron phosphate, the specific diffusion mechanism of ions in the carbon coating material LiFePO_4 material is not yet clear, and further research is needed. With the rapid development of new energy and new energy vehicles, higher requirements have been placed on the energy, power, price and safety of lithium-ion battery cathode materials. Therefore, the way to further improve the energy and power density of LiFePO_4 cathode material, improve its cycle, low temperature and safety performance, and reduce its cost will be the direction of future research. Overall, these results offer a guideline for urgent needs and correct development direction of LiFePO_4 cathode materials.

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