Academic Journal of Environment & Earth Science
ISSN 2616-5872 Vol.3, Issue 3: 4-8, DOI: 10.25236/AJEE.2021.030302

LiFePO$_4$ cathode material modification and its recycling research based on the development status of lithium-ion batteries

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Abstract: *With the development of industrialization, the problems of environmental pollution and energy shortage are becoming worse. So, the development of sustainable renewable energy, the rational allocation of renewable energy, improve the efficiency of resource utilization, and other issues can't wait.*

Keywords: *LiFePO$_4$, lithium-ion batteries, recycling research*

1. Introduction

Lithium-ion battery has the advantages of high operating voltage, high specific energy and green environmental protection, etc. It is the most promising high-efficiency secondary battery, and has been widely used as the power source of various portable electronic digital products. However, in recent years, the rapid rise of the new energy vehicle industry has put forward higher requirements for the performance of lithium-ion batteries. Energy saving and environmental protection, new energy vehicles and aerospace and other strategic emerging industries, high energy density, higher safety of high-efficiency lithium secondary batteries are in urgent need of development and innovation. Among them, cathode material is the key factor to determine the performance of lithium-ion batteries. As the cathode material for lithium-ion batteries, the following four lithium-containing inorganic salts have been studied: lithium cobaltate, lithium nickelate, lithium manganate and lithium iron phosphate. The olivine-like lithium iron phosphate has outstanding performance compared to these materials (see Table 1).

Table 1: Comparison of four cathode materials [2]

cathode material	$LiCoO_2$	$LiNiO_2$	$LiMn_2O_4$	$LiFePO_4$
Theoretical specific capacity/mAh g^{-1}	273	274	148	170
real specific capacity/mAh g^{-1}	140	160	120	130
working voltage/V	3.6	3.3	3.7	3.4
storage of transition metal/million ton	8.3	99.7	48000	abundant
battery cost	expensive	moderate	cheap	cheap
cyclic stability	good	poor	moderate	good
compatibility with electrolyte	moderate	good	poor	good
electronic conductivity/S cm^{-1}	10^{-2}	10^{-1}	10^{-5}	10^{-10}-10^{-9}
thermal stability	moderate	poor	good	good
safety	poor	poor	good	good
environmental pollution	toxic cobalt	heavy metal(Ni)	good	good

2. Lithium iron phosphate cathode material

It has a high theoretical specific capacity, good thermal stability, stable voltage platform, wide sources of raw materials, lower prices, etc., safety and cost is the key to the implementation of the development of lithium-ion battery applications, is considered a promising new generation of lithium-ion battery cathode materials. In addition, the raw materials for lithium iron phosphate batteries are relatively more accessible and produced in large quantities. [1] It is reported that the use of waste acid, ferrous sulfate, and titanium dioxide production process waste, and then after further processing can be made into lithium iron phosphate. Therefore, in the long term, lithium iron phosphate batteries have little concern about the supply of raw materials. However, its relatively low battery energy density and weak low-temperature charge and discharge performance is still the weakness of lithium iron phosphate batteries can not avoid. At present, the main modification methods include surface coating, ion doping and material nanosizing. This paper reviews the progress of research on the modification of $LiFePO_4$ cathode material and provides personal ideas for its modification development and recycling. The charging and discharging process of $LiFePO_4$ lithium battery is carried out between the two phases of $LiFePO_4$ and $FePO_4$, and during the charging and discharging process, Li^+ is embedded and disembedded back and forth between the two electrodes. Its charge and discharge reaction equation can be tabulated as follows [1].

Charge reaction:

$LiFeO_4 \rightarrow xFePO_4+(1-x)LiFePO_4+xLi^++xe^-$

Discharge reaction:

$FePO_4+xLi^++xe^- \rightarrow xLiFePO_4+(1-x)FePO_4$

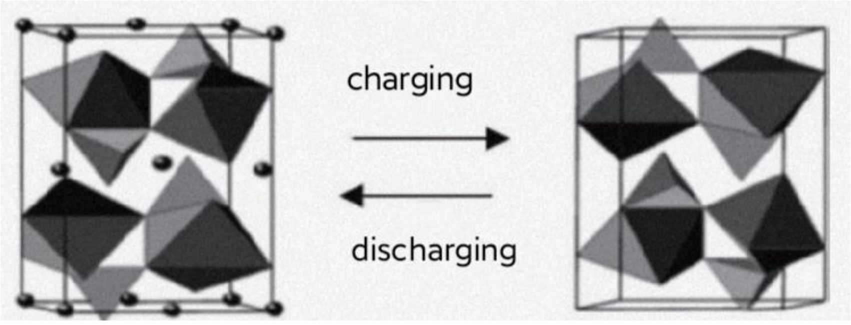


Figure 1: Diagram of charging and discharging principle of $LiFePO_4$[1]

3. Li-ion cathode material modification

3.1 Coating

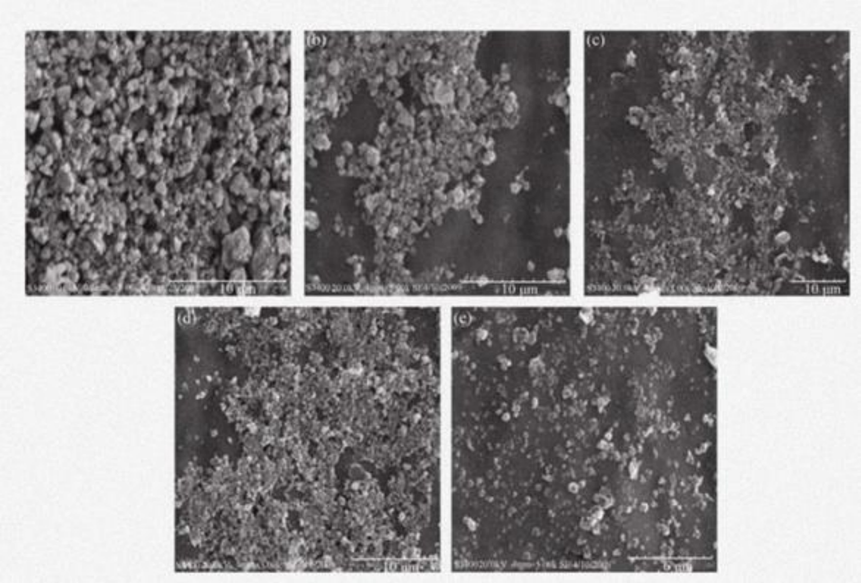
The coating of $LiFePO_4$ particles with a layer of material that has excellent electrical conductivity and remains stable during charging and discharging to improve the electron conduction between the particles. A lot of research has been done on coating from the selection and preparation of raw materials, environmental conditions to synthesis methods to improve the capacity and multiplicity performance of $LiFePO_4$.At present, the research on cladding is broadly divided into two aspects: metal-based and carbon cladding. Among them, carbon cladding is widely concerned by researchers because of its low cost.

3.1.1 Carbon cladding

The selection of different carbon sources for cladding often changes the properties of the material. Hongming Yu [2, 3] et al. used polypropylene and glucose as carbon sources and ferrocene as catalyst precursors to synthesize $LiFePO_4/C$ composites by in situ solid phase method and analyzed their microstructure and morphology, carbon structure and content, and electrochemical properties. The authors showed that the high graphitization of the carbon cladding layer formed by the polypropylene pyrolysis could improve the high rate discharge performance of the material. The addition of ferrocene helps to optimize the carbon structure of the cladding layer. The prepared $LiFePO_4/C$ composites exhibited excellent high-magnification electrochemical performance with a specific discharge capacity of 145 mAh $\cdot g^{-1}$ at 10 C (1 C=170 mA $\cdot g^{-1}$). Lin jing Chen [2, 3] investigated the role of citric acid ($C_6H_8O_7 \cdot H_2O$) in the preparation of carbon-coated $LiFePO_4$ materials by bio-sol-gel method. $C_6H_8O_7 \cdot H_2O$ was added at different times in the formulation of precursors to improve the performance of $LiFePO_4$ cathode materials. The authors showed that the addition of $C_6H_8O_7 \cdot H_2O$ at the initial stage of biomineralization was the most favorable for yeast biomineralization, and the surface of the prepared cathode material was enriched with a conductive network, which was conducive to both improved conductivity and electrolyte penetration. The discharge specific capacity was 156.4 mAh $\cdot g^{-1}$ at 0.1 C multiplicity with low charge transfer impedance. The structure and morphology of the carbon cladding layer have a strong influence on the electronic conductivity of the $LiFePO_4$ cathode material, and the amount of carbon cladding improves the performance differently when the preparation method and environment are the same. In order to investigate the effect of carbon cladding on the structure of $LiFePO_4$, Dongyun Zhang [4] et al. prepared $LiFePO_4/C$ composite cathode materials with different carbon cladding amounts by mechanical activation-high temperature solid phase method using citric acid as the carbon source (see Tables 2), and obtained the following by studying the structure, morphology and electrical properties of $LiFePO_4$ with different carbon cladding amounts Conclusions: 1) The high temperature decomposition of citric acid generated amorphous carbon amorphous material on the surface of the material to form a network structure, the addition of carbon did not change the olivine structure of $LiFePO_4$, but inhibited the growth of crystal particles. 2) The carbon coating affected the growth direction and microstructure of the crystal, thus affecting and improving its electrochemical properties. 3) The diffusion coefficient of lithium ions was significantly increased after coating, and the impedance values were reduced. The material properties were improved.

Table 2: Diagram of charging and discharging principle of $LiFePO_4$ [1] Crystal parameters of $LiFePO_4/C$ coated with different carbon contents [4]

carbon content/wt%	Lattice parameters				Half-width of main diffraction peaks(FWHM/rad)			
	a/nm	b/nm	c/nm	V/nm^3	(101)	(111)	(211)	(311)
0	1.03375	0.60079	0.46905	0.29131	0.148	0.156	0.136	0.145
4	1.03237	0.60007	0.46918	0.29065	0.128	0.179	0.180	0.206
6	1.03189	0.60028	0.46887	0.29043	0.150	0.270	0.210	0.173
8	1.02947	0.59970	0.46950	0.28985	0.168	0.207	0.252	0.205
10	1.02819	0.59787	0.46949	0.28861	0.225	0.312	0.206	0.244



((a)-(e) corresponding to carbon content: 0, 4wt%, 6wt%, 8wt% and 10wt%) [4]

Figure 2: SEM images for $LiFePO_4$ coated with different carbon contents

3.2 Doping

Table 3: Modification analysis of the $LiFePO_4$ doped with different ions

Dopant ions	Synthesis method	Electrochemical properties
V	Gel-Sol Method	The specific capacities of the vanadium ion-doped $LiFe_{1-x}V_xPO_4/C$ materials were 140.2/120.4/105.8/ mAh g^{-1} at 5C/10C/20C multiplicity respectively.[7]
MO^{6+}	Microwave solid state method	The specific capacity of the $LiFe_{0.95}Mo_{0.05}PO_4$ material was 168 mAh g^{-1} after 50 charged/discharged cycle at 0.1C.[8]
Na^+/Ti^{4+}	High temperature solid phase method	The discharge specific capacity of $Li_{0.97}Na_{0.03}Fe_{0.97}Ti_{0.03}PO_4/C$ materials at 1C / 20C were 151.0 / 97.3 mAh g^{-1}[9]
Mg/Al/Zn/Mn	Sustainable wet chemical method	The specific capacities of Li(FeM)PO4/C (M containing Mg/Al/Zn/Mn) were 154/143/127/118 mAh g^{-1} at different current densities of 75/150/300/750 mAh g^{-1} respectively. And the capacity retention after 150 cycles was 97.4%/97.1%/96.1%/96% respectively.[10]

Doping method mainly refers to the cation position in the lithium iron phosphate lattice doped with some metal ions with good conductivity, changing the size of the grain, thus causing lattice defects in the material, and then improve the electronic conductivity and lithium ion diffusion rate within the grain, and thus improve the $LiFePO_4$ material properties. Both the doped ions and their preparation methods have different effects on their material properties, and the analysis of different examples of modification of $LiFePO_4$ doping is shown in Table (3, 4). A large number of studies show that ion doping is an effective way to improve the $LiFePO_4$ material multiplicity performance.

Table 4: Comparison of different synthetic methods [2]

synthetic method	sol-gel method	hydrothermal method	Mechanical activation method	co-precipitation method	Microwave method
Purity	high	high	low	high	moderate
particle size	50-150nm	bigger	40-80nm	100-200nm	40-50nm
Agglomeration	no	no	yes	yes	yes
complication degree of equipment	simple	complicate	simple	simple	complicate
reactive period	long	moderate	moderate	moderate	short
energy consumption	low	low	high	low	low
reaction control	easy	easy	difficult	easy	difficult
Industrialization	difficult	difficult	easy	easy	difficult
performance(discharge capacity and cycle)	good	moderate	moderate	good	moderate

3.3 Material nanosizing

Compared to the limitations in electrical conductivity, the diffusion of lithium ions in $LiFePO_4$ material is the main and decisive control step for battery discharge. The olivine structure of $LiFePO_4$ determines the diffusion channel of lithium ions is one-dimensional, so the particle size can be reduced to shorten the lithium ion diffusion path, thus achieving the problem of improving the diffusion rate of lithium ions. The main advantages of nanomaterials available for current material nanization are: 1) nanomaterials have high specific surface area, more larger reaction interface, more diffusion channels, more micropores and high theoretical lithium storage capacity; 2) the small size effect of nanoparticles can reduce the lithium ion embedding stroke; 3) the gap of aggregated nanoparticles relieves the stress of lithium ions during de-embedding and improves the cycle life. Huang [6] prepared nanoscale $LiFePO_4$ by the sol-gel method with a capacity of 150 mAh g^{-1} at C/2 magnification discharge and 120 mAh g^{-1} at 5 C high magnification discharge, which decayed by only 8% for 800 cycles. Such a high capacity at high discharge rate shows the outstanding advantages of nanomaterials.

4. Research on the recycling of lithium-ion electrode materials

The development of new energy vehicles has led to the growth of lithium-ion battery production and sales, and because of the limited life of lithium-ion batteries, the retirement of a large number of waste batteries, the number is increasing year by year, if not effectively dealt with in a timely manner will lead to waste of metal resources and pollution of the environment. Lithium-ion battery recycling research is very economic and environmental benefits. Among them, lithium iron phosphate batteries occupy a large market demand, so it is necessary to study the corresponding reasonable recycling measures. At present, the recycling methods are chemical precipitation method, high temperature solid phase repair method, high temperature solid phase regeneration method, etc. Waste $LiFePO_4$ batteries do not contain high-value metals, so the economic efficiency is low.

Compared with the wet method recovery process is long, costly reagents and complicated operation, the high temperature solid phase recovery method has the characteristics of, short process, less costly test solution and easy operation. Liang Libo [5] et al. separated the cathode material and aluminum foil collector from the used $LiFePO_4$ battery by the immersion process of strong alkali solution, and achieved the regeneration of $LiFePO_4$ by heat treatment, grinding and mixing, and high temperature roasting. The results showed that the particles of the regenerated $LiFePO_4$ material were distributed at nanometer scale with uniform particle size distribution and no agglomeration. At 0.1 C and 5 C current densities, the specific discharge capacity of the regenerated $LiFePO_4$ was 165.2 and 101.5 mAh g^{-1}, respectively; after 100 cycles at 1 C multiplicity, the capacity of the material was 150.1 mAh g^{-1} with a retention rate of 97.85%, and the electrochemical performance showed that it had good multiplicity and cycling performance.

5. Prospection

Lithium iron phosphate cathode material for lithium-ion batteries exists in olivine form and has many advantages such as better safety, but also has its own defects that cannot be ignored. Improving the conductivity and electrical conductivity is worthy of being researched and practiced. Since carbon cladding can significantly improve the performance of this material, it can be the primary solution to enhance the electronic conductivity between particles. Since the low density of carbon can reduce the material's vibronic density, which in turn leads to fluctuations in the volumetric specific capacity of $LiFePO_4$, the selection of a suitable carbon source and the appropriate amount of carbon doping are of great importance. Reducing the particle size of the material can improve the electrical conductivity of the material, but also reduce the vibration density, so the method also needs to be improved. If two or more modification means are combined together, seeking reasonable matching ratio and composite method, can make various materials in the performance of each other's strengths and weaknesses, and obtain more stable structure than the raw material, better cycle performance and higher safety performance. There are many physical and chemical properties and analyses of materials, and the selection of suitable analytical methods for the performance of lithium-ion battery cathode materials can help to better show the performance and modification. Given the differences between laboratory conditions and large-scale industrialization needs, there are still corresponding limitations. Therefore, the implementability of industrial modification methods is still an important research need and breakthrough point in the future. In the context of continuous research on new lithium-ion battery materials and the popularity of new energy vehicles, recycling is becoming more and more important, and how to solve the problem of end-of-life lithium-ion battery disposal in the downstream needs to be gradually put on the agenda. The government should also introduce relevant recycling policies to supervise the implementation of waste battery treatment, and relevant enterprises should also vigorously develop recycling projects, develop relevant technologies jointly with universities, and share resources and data to promote technological innovation.

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