Fabrication and Electrochemical Characteristics of $LiFePO_4$ Powders for Lithium-Ion Batteries†

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Abstract

Novel powder fabrication technologies provide opportunities to develop high-performance, low-cost cathode materials for rechargeable lithium-ion batteries. Among various energy storage technologies, rechargeable lithium-ion batteries have been considered as effective solution to the increasing need for high-energy density electrochemical power sources. Rechargeable lithium-ion batteries offer energy densities 2 - 3 times and power densities 5 - 6 times higher than conventional Ni-Cd and Ni-MH batteries, and as a result, they weigh less and take less space for a given energy delivery. However, the use of lithium-ion batteries in many large applications such as electric vehicles and storage devices for future power grids is hindered by the poor thermal stability, relatively high toxicity, and high cost of lithium cobalt oxide ($LiCoO_2$) powders, which are currently used as the cathode material in commercial lithium-ion batteries. Recently, lithium iron phosphate ($LiFePO_4$) powders have become a favorable cathode material for lithium-ion batteries because of their low cost, high discharge potential (around 3.4 V versus Li/Li^+), large specific capacity (170 mAh/g), good thermal stability, and high abundance with the environmentally benign and safe nature. As a result, there is a huge demand for the production of high-performance $LiFePO_4$ powders. However, $LiFePO_4$ also has its own limitation such as low conductivity (~10^{-9} S/cm), which results in poor rate capability. This can be addressed by modifying the powder structure using novel fabrication technologies. This paper presents an overview of recent advances in the fabrication of high-performance $LiFePO_4$ powders for lithium-ion batteries. The $LiFePO_4$ powder fabrication methods covered include: solid-state synthesis, mechanochemical activation, carbothermal reduction, microwave heating, hydrothermal synthesis, sol-gel synthesis, spray pyrolysis, co-precipitation, microemulsion drying, and others. The impacts of these fabrication methods on the structure and performance of $LiFePO_4$ powders are discussed. In addition, the improvement of the conductivity of $LiFePO_4$ powders through novel powder technologies is addressed.

Keywords: powder fabrication, $LiFePO_4$ powder, cathode, lithium-ion battery, energy storage

1. Introduction

Lithium is an alkali metal with silver-white appearance, soft handle, low density (0.534 g/cm^3), large specific capacity (3860 Ah/kg), high electrochemical potential, high electro-negativity, and high energy density[1, 2]. As an alkali metal, lithium is highly reactive, and hence it is found in nature as compounds that can be used for different applications, such as pharmacology, aerospace, construction, and energy storage.

Rechargeable lithium-ion batteries, which are based on lithium chemistry and were first commercialized by Sony in 1992[3], are of importance as new generation power sources because they are lighter and have higher energy density, lower self discharge, no memory effect, prolonged service-life, larger number of charge/discharge cycles, better environmental friendliness, and higher safety when compared to

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many other battery systems. Hence, lithium-ion batteries are being widely used for portable electronics from digital cameras to notebooks and music players to cell phones. They are also potential systems for large-scale applications, such as electric vehicles and storage devices for future power grids, if they can be produced with lower cost, smaller sizes, lighter weights, and higher energy storage capacities.

A standard lithium-ion battery consists of anode, cathode and electrolyte, as shown in **Fig. 1**. When the battery is charged, lithium ions deintercalate from the cathode and intercalate into the anode through the electrolyte; while on the discharging process, lithium ions deintercalate from the anode and intercalate into the cathode. During charge/discharge cycles, electrons flow between the anode and the cathode, enabling the conversion of chemical energy and also the storage of electrochemical energy within the battery. Therefore, the performance of rechargeable lithium-ion batteries strongly depends on the active materials employed in both anodes and cathodes for lithium storage.

The common materials for anodes are carbon, lithium-alloying metals, graphite varieties (such as modified natural graphite or kish graphite), and carbon nanotubes/nanofibers. The most used cathode material is $LiCoO_2$, which is currently being used in commercial lithium-ion batteries found in portable electronic devices such as laptops and cell phones. However, the high cost, poor thermal stability at elevated temperatures and high toxicity of $LiCoO_2$ make it an unsuitable material for larger-scale applications. Therefore, battery manufacturers have turned to find other alternative materials to replace $LiCoO_2$, and examples of such materials include layered lithium nickel oxide ($LiNiO_2$), lithium manganese spinels ($LiMn_2O_4$), vanadium oxides (LiV_3O_8), and olivines ($LiMPO_4$, M = Fe, Co, Mn or Ni)[4].

Among various alternative cathode materials, lithium iron phosphate ($LiFePO_4$), which was discovered by Goodenough in 1997[5], is gaining significant attention because of its relatively low cost, high discharge potential (very flat voltage curve around 3.4 V versus Li/Li^+), large specific capacity (170 mAh/g), good thermal stability, excellent cycling performance, and high abundance with the environmentally benign and safe nature. However, $LiFePO_4$ also has its own limitation such as low conductivity ($\sim 10^{-9}$ S/cm), which leads to high impedance and low rate capability for batteries using that material[5]. Approaches to solve that problem include but not limited to: doping $LiFePO_4$ with supervalent cations that enhance the material conductivity at the crystal level[6, 7], coating $LiFePO_4$ with conductive materials such as carbons from organic precursors[8, 9], and decreasing the particle size of $LiFePO_4$ in order to make the diffusion path of lithium shorter[10, 11]. These approaches can be realized by using novel fabrication technologies.

This paper presents an overview of recent advances in the fabrication of high-performance $LiFePO_4$ powders for lithium-ion batteries. The $LiFePO_4$ powder fabrication methods covered include: solid-state synthesis, mechanochemical activation, carbothermal reduction, microwave heating, hydrothermal synthesis, sol-gel synthesis, spray pyrolysis, co-precipitation, microemulsion drying, and others. The impacts of these fabrication methods on the structure and performance of $LiFePO_4$ powders are discussed. In addition, the improvement of the conductivity of $LiFePO_4$ powders through novel powder technologies is addressed.

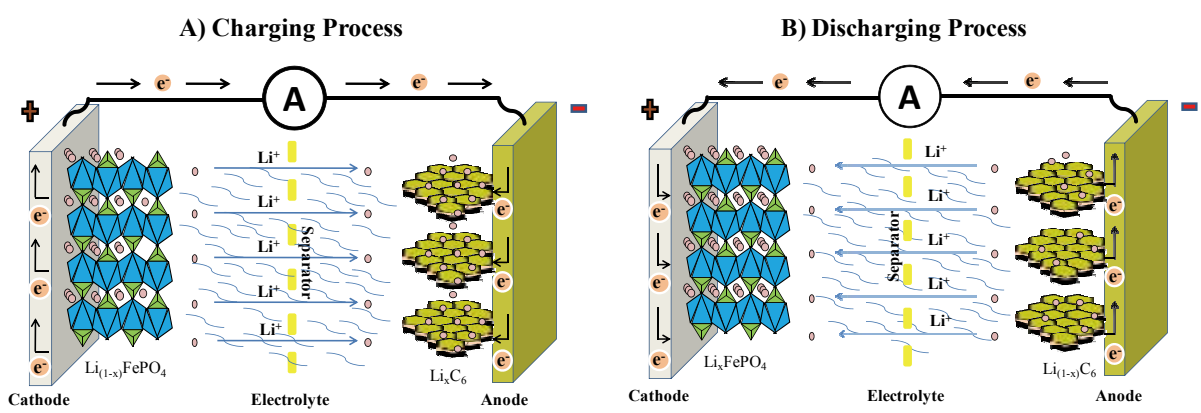

Fig. 1 Charging (A) and discharging (B) processes of a typical lithium-ion battery.

2. Crystalline Structure of $LiFePO_4$

$LiFePO_4$ has an ordered olivine structure with a Pnma space group, in which P atoms (PO_4) reside within tetrahedral 4c sites, and Fe and Li cations (FeO_6 and LiO_6) reside within octahedral 4c and 4a sites, respectively, as shown in **Fig. 2**. Oxygen atoms show slightly distorted hexagonal close packed arrangement[3, 5]. FeO_6 is a corner shared octahedron and PO_4 is an edge-shared tetrahedron, and they form the zigzag skeleton by sharing oxygen and Li ions locate in the octahedral channels. The FeO_6 octahedra are connected through the corners in the bc plane and LiO_6 grows as a linear chain along the b axis and a PO_4 tetrahedral shares the edges with one FeO_6 and two LiO_6. The PO_4 tetrahedral structure is the reason for the good phase stability during lithium deintercalation[3, 5, 12-15].

$LiFePO_4$ powders can be prepared by both solid-state and solution-based methods. Solid-state techniques are carried out at high temperatures without any solvent addition. On the other hand, solution-based methods are based on reactions that take place with the presence of appropriate solvent systems.

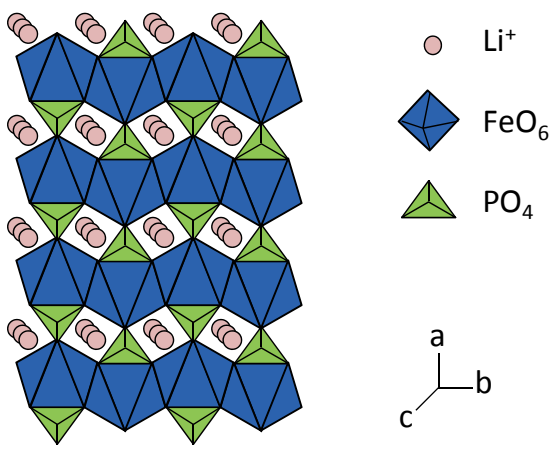

Fig. 2 Crystal structure of $LiFePO_4$.

3. Solid-State Methods for $LiFePO_4$ Powders

Solid-state synthesis, mechanochemical activation, carbothermal reduction and microwave heating are based on solid-state chemistry and are the most common solid-state methods for preparing $LiFePO_4$ powders. **Fig. 3** shows typical routes used in these solid-state methods. Solid state methods are of importance in terms of obtaining ordered crystal structure in a simple way at elevated temperatures.

3.1. Solid-State synthesis

Solid-state synthesis is a technique used to produce chemical structures by reactions carried out at extreme conditions, such as high temperature and pressure, without any solvent. This method is generally used for the mass production of unique, advanced structures, such as special ceramics, scintillation crystals, and piezoelectrics. $LiFePO_4$ powders can be fabricated using the solid-state synthesis method and **Table 1** shows typical precursors used in this method and the particle size and discharge capacity of the resultant $LiFePO_4$ powders. The most commonly used precursors are Li_2CO_3 or $LiOH \cdot H_2O$ for Li, $FeC_2O_4 \cdot 2H_2O$ or $Fe(C_2O_4)_2$ for Fe, and $NH_4H_2PO_4$ for P, respectively[16-20]. However, other precursors can also be used. For example, Wang *et al.*[21] used LiF to replace $LiOH \cdot H_2O$ and Li_2CO_3 and obtained $LiFePO_4$ powders with an average particle diameter of around 500 nm. These $LiFePO_4$ powders have good electrochemical performance, but the release of HF gas, a

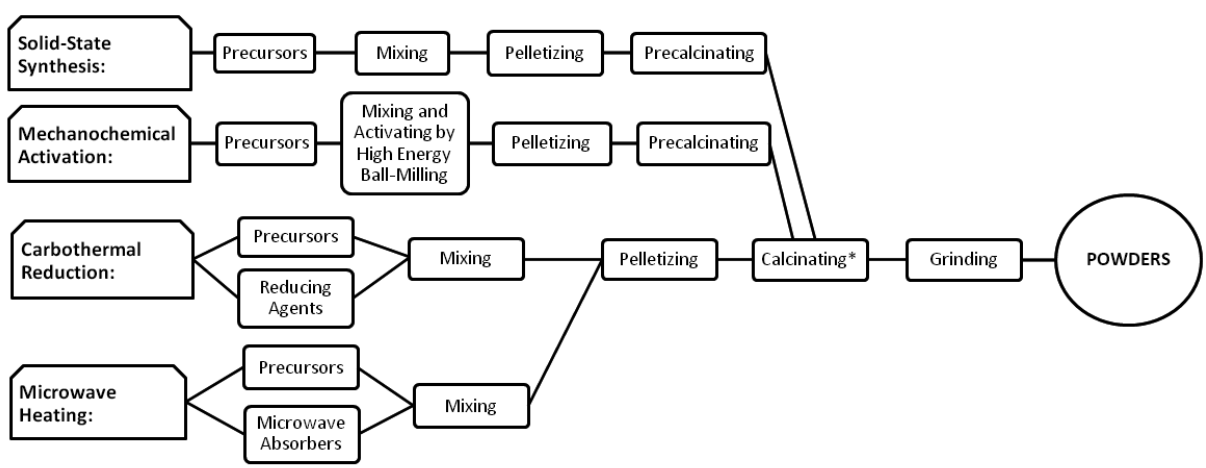

Fig. 3 Typical routes for producing $LiFePO_4$ powders using solid-state methods.

Table 1 Precursors used in the solid-state synthesis method, and particle size and electrochemical performance of the resultant $LiFePO_4$ powders

Li Precursor	Fe Precursor	P Precursor	Metal Dopant	Molar Ratio	Carbon Source	Product	Particle Size (nm)	Discharge Capacity (mAh/g)	Ref
Li_2CO_3	$Fe(CH_3CO_2)_2$	$NH_4H_2PO_4$		1:1:1		$LiFePO_4$	<30	162 (C/10)	16
Li_2CO_3	$FeC_2O_4{\cdot}2H_2O$	$NH_4H_2PO_4$		1:1:1		$LiFePO_4$		92	17
Li_2CO_3	$FeC_2O_4{\cdot}2H_2O$	$NH_4H_2PO_4$		1:1:1	Polyvinyl alcohol	$LiFePO_4$/C	200-300	156 (C/10)	18
Li_2CO_3	$FeC_2O_4{\cdot}2H_2O$	$NH_4H_2PO_4$		1.03:1:1	Malonic acid	$LiFePO_4$/C	100-200	149 (C/5)	19
Li_2CO_3	$FePO_4(H_2O)_2$			1:1	Cellulose acetate/sucrose	$LiFePO_4$/C	200-300	160 (C/4)	20
LiF	$FeC_2O_4{\cdot}2H_2O$	$NH_4H_2PO_4$		1:1:1		$LiFePO_4$	500	151 (C/15)	21
Li_2CO_3	$FeC_2O_4{\cdot}2H_2O$	$NH_4H_2PO_4$		1.03:1:1	Malonic acid	$LiFePO_4$/C	188	161 (C/10)	22
Li_2CO_3	FeC_2O_4	$(NH_4)_2HPO_4$				$LiFePO_4$			23
LiF	$FeC_2O_4{\cdot}2H_2O$	$NH_4H_2PO_4$		1:1:1		$LiFePO_4$	300-600	149 (C/5)	24
Li_2CO_3	$FeC_2O_4{\cdot}2H_2O$	$NH_4H_2PO_4$		1:1:1		$LiFePO_4$	1,000	111 (C/8)	25
Li_2CO_3	$Fe(C_2O_4)_2$	$NH_4H_2PO_4$	$MnCO_3$	0.5:y:1:1-y		$LiFe_yMn_{1-y}PO_4$		160 (C/2)	26
Li_2CO_3	$FeC_2O_4{\cdot}2H_2O$	$NH_4H_2PO_4$		1:0.97:1		$LiFePO_4/Fe_2P$			27
Li_2CO_3	$FeC_2O_4{\cdot}2H_2O$	$NH_4H_2PO_4$		1:1:1		$LiFePO_4$			28
Li_2CO_3	$FeC_2O_4{\cdot}2H_2O$	$(NH_4)_2HPO_4$		1:1:1	Chitosan gel	$LiFePO_4$/C		90 (C/5)	29
$LiOH{\cdot}2H_2O$	$FeC_2O_4{\cdot}2H_2O$	$NH_4H_2PO_4$		1:1:1	Glucose, Carbon gel	$LiFePO_4$/C	500	163 (C/10)	30
$LiOH{\cdot}H_2O$	$FePO_4{\cdot}4H_2O$			1:1	Polypropylene	$LiFePO_4$			31
$LiOH{\cdot}H_2O$	$FeC_2O_4{\cdot}2H_2O$	$NH_4H_2PO_4$	Nb_2O_5	0.99:1:1:0.01	Polypropylene	$Li_{0.99}FeNb_{0.01}PO_4$			31
Li_2CO_3	$FeSO_4$	$(NH_4)_2HPO_4$				$LiFePO_4$			32
$LiOH{\cdot}H_2O$	$FeC_2O_4{\cdot}2H_2O$	$(NH_4)_2HPO_4$		3:1:1		$LiFePO_4$		115 (C/2)	33

byproduct of reaction, should be appropriately managed during powder production.

The solid-state synthesis of $LiFePO_4$ powders typically starts with the mixing of precursors by ball-milling or other techniques (**Fig. 3**). For example, Fey *et al.*[22] prepared $LiFePO_4$/C powder by ball milling of mixed precursors for 3, 12 and 18 hours, followed by heat treatment at 600℃. An 18 hour ball-milling time was found to produce $LiFePO_4$ powders that have an average particle size of 188 nm and a good discharge capacity of 161 mAh/g at C/10 with good cycling performance. In addition to ball milling, precursors can also be mixed by generating dispersion in a solvent such as acetone, followed by solvent evaporation[16, 18-20, 23, 24].

Mixed precursors can be pelletized and then calcined using one-step heat treatment. For example, Li *et al.*[25] prepared $LiFePO_4$ powders by one-step heat treatment under vacuum at 700℃ for 10 h. The resultant $LiFePO_4$ powders have a particle size of 1 μm with a few aggregations, and the discharge capacity is around 111 mAh/g. Although one-step heat treatment is convenient[18], prepared mixtures are more often heat treated in two steps. The first step (precalcination) is carried out at 250 − 350℃, which is designed for the decomposition of the precursors and expelling of the gases. The second step is the final calcination of powders, which occur at relatively high temperatures (400 − 800℃). The calcination temperature has an important effect on the structure, particle size (particle growth), and discharge capacity of $LiFePO_4$ powders. For example, Yamada *et al.*[16] synthesized $LiFeO_4$ powders by solid-state synthesis at different temperatures and found that the highest discharge capacity of 162 mAh/g was obtained by calcining the homogeneously mixed precursors at 500 − 600℃. Takahashi *et al.*[33] also fabricated $LiFePO_4$ powders by solid-state synthesis and found that the optimum calcination temperature for achieving the highest discharge capacity was 675℃. In addition to the calcination temperature, it is also important to control the calcination atmosphere for avoiding oxidized byproducts, such as Fe_2O_3 and $Li_0Fe_2(PO_4)_3$[16, 18, 23, 24]. Atmospheres that can be used include inert (Ar), slightly reductive (Ar-H_2), reductive (H_2-N_2 or N_2)[16, 18, 23-28], and vacuum conditions[25].

One limitation of pure $LiFePO_4$ powders is their low electrical conductivity, which results in poor rate capability. In solid-state synthesis, the conductivity of $LiFePO_4$ powders can be improved by introducing conductive carbon, which can be obtained by directly adding a carbon source into the precursors. Yun *et al.*[18] prepared $LiFePO_4$/C powders by solid-state synthesis using polyvinyl alcohol (PVA) as a carbon source. The presence of PVA prevents the particle growth during calcination because the polymer decomposes around the same temperature of $LiFePO_4$ formation. As a result, these $LiFePO_4$/C powders

have small particle sizes ranging from 200 to 300 nm. The maximum capacity achieved in that work was 156 mAh/g, but the cycling performance was poor.

The performance of $LiFePO_4$/C powders can be improved by using other carbon sources to replace PVA. Fey *et al.*[19] used malonic acid as a carbon source, and the resultant $LiFePO_4$/C powders (100 – 200 nm) have a discharge capacity 149 mAh/g at C/5 and a good cycling performance. In addition to malonic acid, other carbon sources that have been studied include but not limited to chitosan, glucose, cellulose acetate, and sucrose[20, 29, 30].

In addition to carbon, metal dopants can be added in solid-state synthesis to adjust the structure and performance of $LiFePO_4$ powders. Mi *et al.*[31] used Nb_2O_5 as a metal dopant to form Nb-doped $Li_{0.99}Nb_{0.01}FePO_4$ powders by solid state synthesis. $MnCO_3$ has also been used as a metal dopant to produce $LiFe_yMn_{1-y}PO_4$ powders with enhanced conductivity.

Solid-state synthesis is of importance in terms of obtaining unique structures; however, reactions take place in a solid phase, which requires high temperature, high energy, long processing time, repeated grinding, and special atmosphere. As a result, the product cost of solid-state synthesis is relatively high.

3.2. Mechanochemical activation

Mechanochemical activation is one of the most common methods for preparing metal and alloy powders, and is mainly based on increasing the chemical reactivity of the mixtures by high-energy ball milling. The main reasons for the enhancement of reactivity can be given as: the formation of free valences on the outermost layer of the material and the increase in the surface area where reactions take place. Mechanochemical activation enables the preparation of powders with relatively low particle size and high surface area. However, mechanochemical activation also has some drawbacks, such as higher impurity stemmed from the milling medium and the rise of temperature during the high-energy milling process[34]. For the synthesis of $LiFePO_4$ powders, the temperature rise during high-energy ball milling may contribute to the decomposition of precursors, but is not sufficient for the formation of $LiFePO_4$ crystalline structure[34-36]. Therefore, mechanochemical activation is generally used as a preparation step prior to the classical solid-state synthesis, and the aim is to have the smallest possible particle size to drive the reactions at lower temperatures. Franger *et al.*[23] compared different synthesis methods and found that $LiFePO_4$ powders prepared by the mechanochemical activation have pure, uniform, and well-crystallized structure, and present higher specific capacity (150 mAh/g at C/5) than those prepared by conventional solid-state synthesis.

Table 2 shows typical precursors used in the mechanochemical activation method and the particle size and electrochemical performance of the resultant $LiFePO_4$ powders. As shown in **Fig. 3**, typical procedure starts with activating mixed precursors using high-energy ball-milling for 3 – 15 hours, depending on the desired particle size, in air[37] or in an inert atmosphere[38]. Mechanochemically activated mixtures are then pelletized and calcined at elevated temperatures at 600 – 900℃ in appropriate atmosphere such as 95% Ar + 5% H_2[37], N_2[38], or vacuum[39] for 0.5 – 10 hours[37-39].

To improve the electrical conductivity of $LiFePO_4$ powders, carbon materials, such as graphite, carbon black, and acetylene black, can be added to the mixtures during high-energy ball milling[37]. As reported by Shin *et al.*[37], among these three carbon materials, graphite gave the highest conductivity with the highest stability and capacity (141 mAh/g at C/10) because of its low charge transfer resistance and low ion migration resistance. The dispersion of carbon in $LiFePO_4$/C composite powders is important. Porcher *et al.*[40] investigated the effect of surfactants on the dispersion of carbon black in the $LiFePO_4$/C powders, which were produced by using mechanochemical activation. In their work, three different types of surfactants (anionic, non-ionic, and cationic) were added during the electrode preparation process. It was found that non-ionic surfactant (Triton X-100) led to more homogeneous carbon dispersion and the resultant $LiFePO_4$/C powders have better electrochemical performance than those prepared using ionic surfactants.

In addition to carbon, Fe_2P can be used to modify the conductivity of $LiFePO_4$ powders. Kim *et al.*[39] produced pure $LiFePO_4$ and $LiFePO_4$/Fe_2P powders by mechanochemical activation, followed by calcination at 900℃ for different time intervals under 10^{-6} Torr pressure. Pure $LiFePO_4$ showed a discharge capacity of 162 mAh/g and good capacity retention. As reported, Fe_2P had an important effect on the conductivity of the powders, especially at higher concentrations; however, lower capacity values were obtained mainly because of the increase in particle size and decrease in surface area. Maximum initial discharge capacity obtained was 113 mAh/g for $LiFePO_4$/Fe_2P powders (Fe_2P : 8 wt. %).

Table 2 Precursors used in the mechanochemical activation method, and particle size and electrochemical performance of the resultant $LiFePO_4$ powders

Li Precursor	Fe Precursor	P Precursor	Carbon Source	Molar Ratio	Product	Particle Size (nm)	Discharge Capacity (mAh/g)	Ref
Li_3PO_4	$Fe_3(PO_4)_2 \cdot 5H_2O$		Sucrose	1:1	$LiFePO_4/C$		150 (C/5)	23
Li_2CO_3	$FeC_2O_4 \cdot 2H_2O$	$(NH_4)_2HPO_4$	Graphite	1:1:1	$LiFePO_4/C$	100-300	141 (C/10)	37
Li_2CO_3	$FeC_2O_4 \cdot 2H_2O$	$(NH_4)_2HPO_4$	Acetylene black	1:1:1	$LiFePO_4/C$	60-115	152 (C/10)	38
Li_2CO_3	$FeC_2O_4 \cdot 2H_2O$	$(NH_4)_2HPO_4$	Acetylene black	1:1:1	$LiFePO_4/C$	65-90	166 (C/10)	38
$LiOH \cdot H_2O$	Fe_2O_3	$(NH_4)_2HPO_4$	Acetylene black	1:0.5:1	$LiFePO_4/Fe_2P$	100-1,000	113-122 (C/5)	39
$LiOH \cdot H_2O$	Fe_2O_3	$(NH_4)_2HPO_4$		1:0.5:1	$LiFePO_4$	100-1,000	162 (C/20)	39
Li_3PO_4	$FeSO_4 \cdot 7H_2O$	Na_3PO_4	Sucrose	1.05:3:2	$LiFePO_4/C$		140 (C/10)	40
Li_3PO_4	$FeSO_4 \cdot 7H_2O$	BPO_4	Sucrose	1:3:2	$LiFePO_4/C$		160 (C/10)	41
$LiOH \cdot H_2O$	$FeC_2O_4 \cdot 2H_2O$	$(NH_4)_2HPO_4$		1:1:1	$LiFePO_4$	100-2,000	115 (C/10)	42
$LiOH \cdot H_2O$	$FeC_2O_4 \cdot 2H_2O$	$(NH_4)_2HPO_4$	Carbon black	1:1:1	$LiFePO_4/C$	100-1,000	140 (C/10)	42
Li_2CO_3	$FeC_2O_4 \cdot 2H_2O$	$NH_4H_2PO_4$		1:1:1	$LiFePO_4$		110-120 (C/10)	43
$LiOH \cdot H_2O$	Fe_2O_3	$(NH_4)_2HPO_4$	Acetylene black	1:0.5:1	$LiFePO_4$	100-2,000	140 (C/20)	44
Li_3PO_4	$FeSO_4 \cdot 7H_2O$	BPO_4	Sucrose	1:1:1	$LiFePO_4/C$		110 (C/10)	45

The particle sizes of $LiFePO_4$ and $LiFePO_4/C$ powders prepared by mechanochemical activation are typically in the range of 60 – 300 nm[37, 38]. In addition to conventional mechanochemical activation, modified methods can be designed to further reduce the particle size. Kim *et al.*[38] prepared $LiFePO_4/C$ powders by mixing the precursors with distilled water for 7 hours, evaporating the water, high-energy ball milling for 15 h under Ar atmosphere, powder pressing in order to obtain pellets, and thermal processing at 600 ℃ for 10 h under N_2 atmosphere. Using this modified mechanochemical activation method, the particle size of the resultant $LiFePO_4/C$ powders reduced from 60 – 115 nm to 65 – 90 nm. As a result, the modified method gave better and more uniform carbon coating, larger specific surface area, and higher electronic conductivity. The discharge capacity for $LiFePO_4/C$ powders obtained by the modified method is 166 mAh/g at C/10 and 154 mAh/g at C/2, respectively.

3.3. Carbothermal reduction

In both conventional solid-state synthesis and mechanochemical activation methods, Fe(II) compounds are used as the Fe precursor for $LiFePO_4$ powders. However, it is often challenging to prevent the oxidation of unstable Fe(II), which tends to form Fe(III) as the impurity during the $LiFePO_4$ formation. Recently, carbothermal reduction is gaining attention because it allows the direct use of Fe(III) compounds as Fe precursor. In general, Fe(III) compounds are relatively cheap, readily available, and chemically stable when compared with Fe(II) compounds.

Carbothermal reduction is a high-temperature reduction reaction, which utilizes a carbon source as the reducing agent. Carbon black, graphite, and pyrolyzed organic chemicals are commonly used reducing agents. Carbothermal reduction is a highly endothermic reaction, and hence the critical energy, which is given to the synthesis environment, must be high enough to drive the reaction. In addition, since solid carbon is used as the reducing agent, it is important to keep all precursors/reactants in good contact with each other throughout the reaction. The mechanism and reaction rate are closely related with the particle sizes of precursors and reducing agents, mixing conditions, diffusion rates, gas concentration, and impurities in the environment[46-48]. Properties of the resultant powders depend on the processing conditions such as temperature, pressure, precursors, and reducing agents.

When used to produce $LiFePO_4$ powders, the carbothermal reduction method is excellent for the reduction of Fe(III), stabilization of Fe(II), control of particle morphology, and enhancement of electrical conductivity by coating $LiFePO_4$ with residual carbon. Studies show that, compared with other solid-state methods, carbothermal reduction is an energy efficient approach to produce $LiFePO_4$ powders with fine, uniform particle morphology and high capacity[3, 48-50]. **Table 3** shows the precursors used in the carbothermal reduction method, and the particle size and discharge capacity of the resultant $LiFePO_4$ powders. Typical procedure includes two major steps: mixing stoichiometric amounts of precursors and reducing agents by ball milling for 2 – 4 hours, and calcining (generally without precalcination) the mixtures at a temperature between 550 and 850℃ for 8 – 10 hours in an inert atmosphere, such as N_2 or Ar (**Fig. 3**). During the calcination process, two main carbon oxidation reactions occur to reduce Fe(III) to Fe(II)[48]

Table 3 Precursors used in the carbothermal reduction method, and particle size and electrochemical performance of the resultant $LiFePO_4$ powders

Li Precursor	Fe Precursor	P Precursor	Metal Dopant	Reducing Agent and Carbon Source	Molar Ratio	Product	Particle Size (nm)	Discharge Capacity (mAh/g)	Ref
LiH_2PO_4	Fe_2O_3		$Mg(OH)_2$	Carbon	1:0.45:0.1	$LiFe_{0.9}Mg_{0.1}PO_4$	100, 000	151 (C/20)	48
Li_2CO_3	$FeSO_4{\cdot}7H_2O$	$NH_4H_2PO_4$		Carbon	1:2:2	$LiFePO_4$/C	100-300	156 (C/10)	49
Li_2CO_3	$FePO_4{\cdot}4H_2O$			Acetylene black	1:2	$LiFePO_4$/C	1,000-3,000	133 (C/10)	51
Li_2CO_3	Fe_2O_3	$NH_4H_2PO_4$		Glucose, Carbon black	1:1:1	$LiFePO_4$/C	300-1,000	159 (C/10)	52
Li_2CO_3	$FePO_4$			Glucose	0.5:1	$LiFePO_4$/C	2,490	151 (C/5)	53
Li_2CO_3	Fe_2O_3	$(NH_4)_2HPO_4$		Ferric citrate	1:1:1	$LiFePO_4$/C		135 (C/10)	54
LiH_2PO_4	Fe_2O_3			Glucose	2:1	$LiFePO_4$/C	1,330	154 (C/5)	55
$LiOH{\cdot}H_2O$	$Fe(NO_3)_3$	$NH_4H_2PO_4$		$C_3H_8O_2$:H_2O, Sucrose	1:1:1	$LiFePO_4$/(C+Fe_2P)	36	157 (C/10)	56
Li_2CO_3	$Fe(NO_3)_3{\cdot}9H_2O$	$NH_4H_2PO_4$		Citric acid	1:1:1	$LiFePO_4$/C		150 (C/10)	57
LiH_2PO_4	$Fe(NO_3)_3{\cdot}9H_2O$			Polycarboxylic acid, Polyhdric alcohol	1:1	$LiFePO_4$/C		134 (C/100)	58

$$C + O_2 \rightarrow CO_2 \quad (T < 650℃) \quad (1)$$

$$2C + O_2 \rightarrow 2CO \quad (T > 650℃) \quad (2)$$

Both the volume and entropy changes in Reaction (1) are negligible and the reaction produces less reductive atmosphere. However, Reaction (2) occurs at temperatures higher than 650℃, which results in a stronger reducing condition than Reaction (1), and the volume and entropy increases are significant[48].

In carbothermal reduction, processing conditions, especially calcination temperature, are of great importance for the morphological and electrochemical performance of the resultant powders. Mi *et al.*[50] synthesized $LiFePO_4$/C powders by using $FePO_4$ as the Fe precursor and polypropylene as the reducing agent and carbon source. Calcination was carried out at 650℃ for 10 h under N_2 atmosphere without any pre-calcination step. The pyrolysis of polypropylene during the calcination ensured the reduction of Fe(III) to Fe(II). The resultant $LiFePO_4$/C powders have homogeneous carbon coating with particle sizes ranging from 100 to 300 nm. Initial discharge capacity was 160 mAh/g (C/10) at 30℃. Liu *et al.*[51] synthesized $LiFePO_4$/C powders by the carbothermal reduction method using different calcination temperatures. The best calcination temperature was reported as 750℃, which produced powders with an initial discharge capacity of 133 mAh/g at C/10 and capacity retention of 96% after 20 cycles. Liu *et al.*[52] used cheap Fe_2O_3 as the Fe source and carbon black and glucose as the reducing agent and carbon source. The effects of calcination temperature on the particle size and electrochemical performance of $LiFePO_4$/C powders were investigated. When the precursors were treated with glucose at 700℃ for 8 h, the best performance was obtained: the capacity was 159 mAh/g at C/10 and the cycling fading was 2.2% at the end of 30 cycles. It was also found that the use of high concentration carbon source not only decreased the particle size but also enhanced the cycle life.

The distribution of particle size can also be controlled during the carbothermal reduction. Wang *et al.*[53] synthesized $LiFePO_4$/C powders by using $FePO_4$ as the iron source and glucose as the reducing agent and carbon source. $LiFePO_4$/C powders with uniform particle size distribution were obtained when the precursors were calcined at 650℃ for 9 h. The discharge capacities of these powders are 151 mAh/g at C/5 rate and 144 mAh/g at 1C rate, respectively. Zhong *et al.*[54] prepared high tab-density $LiFePO_4$/C powders by the carbothermal reduction method using Fe_2O_3 and ferric citrate as the Fe (III) source with an equimolar ratio. It was found that the resultant $LiFePO_4$/C powders consisted of nanometer-sized and micrometer-sized particles, and showed trimodal particle size distribution with good discharge capacity (135 mAh/g at C/10). In these powders, the small particles filled the free space between the bigger particles, and led to high tap density (1.4 g/cm^3).

In addition to particle size and its distribution, the processing conditions also influence the crystallization degree of $LiFePO_4$ powders. One important contribution of high crystallization degree is that it can suppress the dissolution of $LiFePO_4$ during cycling and leads to improved cycling behavior[55]. Therefore, in order to obtain good electrochemical performance, it is important to determine the optimum crystallization degree. Zhi *et al.*[55] studied the effect of calcination temperature on the crystallinity degree and electrochemical performance of $LiFePO_4$/C powders obtained by carbothermal reduction. It was found that the powders calcined at lower temperatures have lower degree of crystallization with nano-sized structure, which leads to higher electrochemical ac-

tivity and larger initial discharge capacity. But, they showed unsatisfactory cycling performance because of their metastable structures.

To obtain optimized powder structure and performance, modified carbothermal reduction methods were also developed. Liu *et al.*[56] designed a modified process by introducing amorphous gel precursor into conventional carbothermal reduction, and they obtained $LiFePO_4/(C+Fe_2P)$ and $LiFePO_4/C$ composite powders. While $LiFePO_4/C$ showed a discharge capacity of 146 mAh/g, $LiFePO_4/(C+Fe_2P)$ has a higher capacity of 157 mAh/g, which was attributed to the enhanced conductivity caused by Fe_2P in the structure. Yu *et al.*[57] prepared $LiFePO_4/C$ powders by combining carbothermal reduction with spray drying and used different carbon sources (such as carbon black, sucrose, citric acid and polyethylene glycol (PEG)) as the reducing agents. As reported, the best electrochemical performance was obtained from citric acid-added powders, which were calcined at 539℃. It was also found that 453℃ was the crystallization temperature of $Li_3Fe_2(PO_4)_3$, 539℃ was the transform temperature from $Li_3Fe_2(PO_4)_3$ to $LiFePO_4$, 840℃ was the formation temperature of $LiFePO_4/C$ with an excess of Fe_2P impurity phase, and 938℃ was the decomposition temperature of $LiFePO_4/C$. Recently, Zhu *et al.*[49] synthesized $LiFePO_4$ powders from $FeSO_47H_2O$ and $NH_4H_2PO_4$ by combining the carbothermal reduction and aqueous precipitation methods. The resultant $LiFePO_4/C$ powders showed capacities ranging from 95 – 156 mAh/g at C/10, depending on the processing conditions.

3.4. Microwave heating

Microwave heating is another easy and useful method for producing $LiFePO_4$ powders[59-63]. Unlike other solid-state methods, microwave heating is a molecular level heating process, which allows volumetric heating of the material by the absorption of microwave energy. In microwave heating, the heat is generated directly inside the material and is caused by the change of polarization that is activated by the motion of electric charges. Heating rate is controlled by the power of the microwave and heat dissipation occurs through the surface of the material.

Major advantages of microwave heating include good controllability, uniform and selective heating, short processing time (2 – 20 min), reduced energy consumption, and low cost. In addition, microwave heating is a low temperature process with good repeatability and no reductive gas is required for the synthesis of $LiFePO_4$ powders[59-66]. Higuschi *et al.*[59] used the microwave heating method to obtain $LiFePO_4$ powders with an initial discharge capacity of around 125 mAh/g at 60℃ with low capacity loss. Guo *et al.*[67] compared $LiFePO_4$ powders synthesized by microwave heating and solid-state synthesis methods. It was found that microwave-processed $LiFePO_4$ powders have smaller particle size, more uniform size distribution, smoother surface morphology, and higher discharge capacity.

In microwaving processing, a microwave absorber is often added to ensure effective heat generation (**Fig. 3**). **Table 4** shows typical precursors, microwave absorbers, and processing time used in the microwave heating methods. Carbon is the most used microwave absorber because it is low cost, produces rapid heating, and is capable of forming reductive atmosphere, which protects Fe(II) and prevents Fe(III) based impurities. As a result, when carbon is used as the microwave absorber, the formation of $LiFePO_4$ powders can be directly carried out in air, which significantly lowers the production cost[60, 64]. In addition, the use of carbon can help to reduce the particle size and improves the electrical conductivity of $LiFePO_4$ powders[68]. Wang *et al.*[61] used active carbon as a microwave absorber to synthesize nano-sized $LiFePO_4$ powders, which have a particle size of 40 – 50 nm and discharge capacity of around 112 mAh/g at C/2. Although carbon is the most used microwave absorber, other materials can be used to enhance the heat generation efficiency, such as Fe[59], glucose[69], and yeast cells[69].

The microwave heating time is of importance for controlling the particle size and electrochemical performance of the powders. Typically, longer microwave heating time causes larger particle size, lower Li diffusion coefficient, and consequently more capacity loss[60]. In addition to increased particle size, some impurities such as Fe_2P can be observed with prolonged heating time[70]. It was found that the amount of Fe_2P in $LiFePO_4$ powders is directly proportional to the heating time, and above a critical amount of Fe_2P, $LiFePO_4$ tends to change into an insulating phase, $Li_4P_2O_7$. However, when the heating time is too short, incomplete crystalline structure can form contaminates in the resultant $LiFePO_4$ powders, which in turn decreases the charge and discharge capacities[66]. Park *et al.*[60] synthesized $LiFePO_4$ using the microwave heating method, and found that a heating time of 4 min is sufficient and can produce $LiFePO_4$ powders that have a specific capacity of 151 mAh/g at C/10 with stable cycling behavior.

Like most other methods, $LiFePO_4$ powders pro-

Table 4 Precursors, microwave absorbers, power, and time used in the microwave heating method, and particle size and electrochemical performance of the resultant $LiFePO_4$ powders

Li Precursor	Fe Precursor	P Precursor	Microwave Absorber	Power (W)	Time (min)	Carbon Source	Molar Ratio	Product	Particle Size (nm)	Discharge Capacity (mAh/g)	Ref
Li_2CO_3	$Fe(CH_3COO)_2$	$NH_4H_2PO_4$		500	5-20		1:1:1	$LiFePO_4$		95 (C/11)	59
Li_2CO_3	$Fe(CH_3CHOHCOO)_2{\cdot}2H_2O$	$NH_4H_2PO_4$	Iron Powder	500	5-20		1:1:1	$LiFePO_4$		100 (C/11)	59
LiOH	$(NH_4)_2Fe(SO_4)_2{\cdot}6H_2O$	H_3PO_4	Activated Carbon	650	4	Carbon black	1:1:1	$LiFePO_4$	1,000	151 (C/10)	60
CH_3COOLi	$FeC_2O_4{\cdot}2H_2O$	$NH_4H_2PO_4$	Activated Carbon	850	A few	Citric acid	1:1:1	$LiFePO_4$	40-50	112 (C/2)	61
Li_3PO_4	$FeSO_4{\cdot}7H_2O$	H_3PO_4	Carbon	300	A few	Glucose	1:1:1	$LiFePO_4/C$	100	117 (C/10)	62
LiOH	$Fe(CH_3COO)_2$	H_3PO_4		600	5		1:1:1	$LiFePO_4$	40 ± 6	135 (C/15)	63
LiOH	$Fe(CH_3COO)_2$	H_3PO_4		600	5	Poly(3,4-ethylenedioxy thiophene)	1:1:1	$LiFePO_4/C$	40 ± 6	166 (C/15)	63
$CH_3COOLi{\cdot}2H_2O$	$FeSO_4{\cdot}7H_2O$	H_3PO_4	Carbon Black	400	18	Polyethylene glycol	1:1:1	$LiFePO_4/C$	132 - 465	147 (C/10)	66
$LiOH{\cdot}H_2O$	$FePO_4{\cdot}4H_2O$		Graphite	700	4	Glucose	1:1	$LiFePO_4/C$	160 - 600	150 (C/10)	67
Li_3PO_4	$Fe_3(PO_4)_2{\cdot}8H_2O$		Activated Carbon	750	2-5	Acetylene black	1:1	$LiFePO_4/C$	≤640	161 (C/10)	68
Li_2CO_3	$FePO_4{\cdot}4H_2O$			1000	1.33	Glucose	1:1	$LiFePO_4/C$	50 - 100	162 (C/10)	69
Li_3PO_4	$Fe_3(PO_4)_2{\cdot}8H_2O$			750	2	Acetylene black	1:1	$LiFePO_4/C$		165 (C/50)	70
LiOH	$Fe(CH_3COO)_2$	H_3PO_4		600	5	MWCNT	1:1:1	$LiFePO_4$/MWCNT	40 ± 6	161 (C/10)	71
LiOH	$Fe(CH_3COO)_2$	H_3PO_4		600	5		1:1:1	$LiFePO_4$	40 ± 6	147 (C/10)	71
Li_3PO_4	$C_6H_5FeO_7$	H_3PO_4		300				$LiFePO_4/C$			73
$CH_3COOLi{\cdot}2H_2O$	$FeSO_4{\cdot}7H_2O$	Na_2HPO_4	Activated carbon, Yeast cells	650	A few	Yeast cells	1:1:1	$LiFePO_4/C$	35-100	147 (C/10)	74
Li_2CO_3	$FeSO_4{\cdot}7H_2O$	$(NH_4)_2HPO_4$	Carbon Black	300	10	Carbon black,	0.3:1:1	$LiFePO_4/C$			75

duced by microwave heating typically have spherical shape. However, other unique particle structure can be obtained using the microwave heating method. For example, Muraliganth *et al.*[71] synthesized $LiFePO_4$ nanorods (width: $25-40$ nm; length: $0.1-1$ μm) using microwave heating. These nanorods were mixed with multi-walled carbon nanotubes (MWCNTs) to improve the conductivity, which resulted in a high discharge capacity of around 161 mAh/g at C/10 with good cyclic performance. Zhou *et al.*[74] synthesized mesoporous $LiFePO_4$ powders by using yeast cells as a template for the porous structure. During the formation of $LiFePO_4$, yeast cells not only connected metal ions chemically but also acted as a reducing agent because of their microwave absorbency. These mesoporous $LiFePO_4/C$ powders have specific capacity of 147 mAh/g at C/10 and good cycle performance. Jegal *et al.*[72] also synthesized mesoporous $LiFePO_4$ spheres, which consisted of smaller particles with average thickness of $2-30$ nm. The mesoporous structure gave short lithium diffusion length during charge/discharge.

In most cases, traditional continuous microwaves are used to produce $LiFePO_4$ powders. However, other microwave patterns can also be used. For example, Zou *et al.*[69] used intermittent microwave and obtained $LiFePO_4/C$ powders with small particle size, ranging from 50 to 100 nm. The powders have enhanced conductivity and improved capacity (162 mAh/g at C/10).

Microwave heating can also be combined with other methods to produce $LiFePO_4$ powders with controlled structure and performance. Methods that have been combined with microwave heating include: solid-state synthesis[59, 66], mechanochemical activation[68], sol-gel synthesis[66, 73], hydrothermal synthesis[72], solvothermal[71], and co-precipitation[65, 74]. For example, Song *et al.*[68] combined microwave heating ($2-5$ min) with mechanochemical activation (30 min) to obtain $LiFePO_4/C$ powders. The mechanochemical activation decreased the process temperature and led to a uniform distribution of carbon. The average particle size of the resultant $LiFePO_4/C$ powders was ≤ 0.64 μm and the discharge capacity was 161 mAh/g at C/10 with a stable capacity retention. Li *et al.*[75] synthesized $LiFePO_4/C$ powders by combining microwave heating with the co-precipitation method. During the synthesis, beer yeast, a nontoxic, environmentally-friendly, and low cost biosurfactant, was used as a carbon source to increase the material

conductivity. Li *et al.*[65] also reported the synthesis of $LiFePO_4$ powders by incorporating the solid state synthesis and microwave heating methods, and these powders have a high specific capacity of around 156 mAh/g at C/20. Zhang *et al.*[66] synthesized $LiFePO_4$/C powders by the combination of sol-gel synthesis and microwave heating, and achieved initial specific capacity of 147 mAh/g at C/10 and good cycling performance.

4. Solution-Based Methods for $LiFePO_4$ Powders

Although solid-state methods are simple to use, they are typically time and energy consuming techniques and often lead to large particle size, low purity, and relatively poor electrochemical performance. Therefore, solution-based methods are of increasing importance since they often result in smaller and more uniform particle size, higher purity, more homogeneous carbon coating, and higher electrochemical capacity. Hydrothermal synthesis, sol-gel synthesis, spray pyrolysis, co-precipitation, and microemulsion drying are common solution-based methods used for the preparation of $LiFePO_4$ powders. General production routes are shown schematically in **Fig. 4**.

4.1. Hydrothermal synthesis

Hydrothermal synthesis is a chemical process that occurs in an aqueous solution of mixed precursors above the boiling temperature of water. In hydrothermal synthesis, it is possible to avoid the calcinations step and obtain pure $LiFePO_4$ powders directly from the heated solution. However, if the carbon coating is desired, it is necessary to carry out the calcination step at higher temperatures. During hydrothermal synthesis, heated water accelerates the diffusion of particles and the crystal growth is relatively fast. Hydrothermal synthesis is typically carried out in a closed system called autoclave and there are less environmental concerns than many other powder production technologies. Therefore, hydrothermal synthesis is a simple, clean, and relatively low-cost method that can be used to produce powders with high uniformity and purity[76-78]. Currently, hydrothermal synthesis has been widely used for the synthesis of oxides, silicates, and some specific compounds with unique characteristics.

Hydrothermal synthesis was first used by Yang *et al.*[79,80] to prepare $LiFePO_4$ powders. As shown in **Fig. 4**, standard hydrothermal synthesis starts with the mixing of precursors with the exact stoichiometric ratio in an aqueous solution. After the homogeneous mixing of the precursors, the solution is treated in an autoclave at a temperature above 100℃, generally between 120 − 220℃ for 5 − 10 h. $LiFePO_4$ powders can then be obtained by drying the slurries or participates[7, 79-85]. $LiFePO_4$ powders produced by hydrothermal synthesis are typically low cost, high purity, and have small grain size and large surface area. In addition, the presence of high-temperature water hinders the oxidation of Fe(II) to Fe(III). **Table 5** shows precursors that have been used in the hydrothermal synthesis of $LiFePO_4$ powders.

Like many other methods, carbon sources can be added to the hydrothermally obtained $LiFePO_4$ powders to enhance the conductivity. However, in this case, an additional heat-treatment (or calcination) step should be carried out at elevated temperatures such as 400 − 750℃ for 0.5 − 12 h under N_2 or argon atmosphere in order to carbonize the carbon source[79, 83-86]. Carbon sources used include sugar,

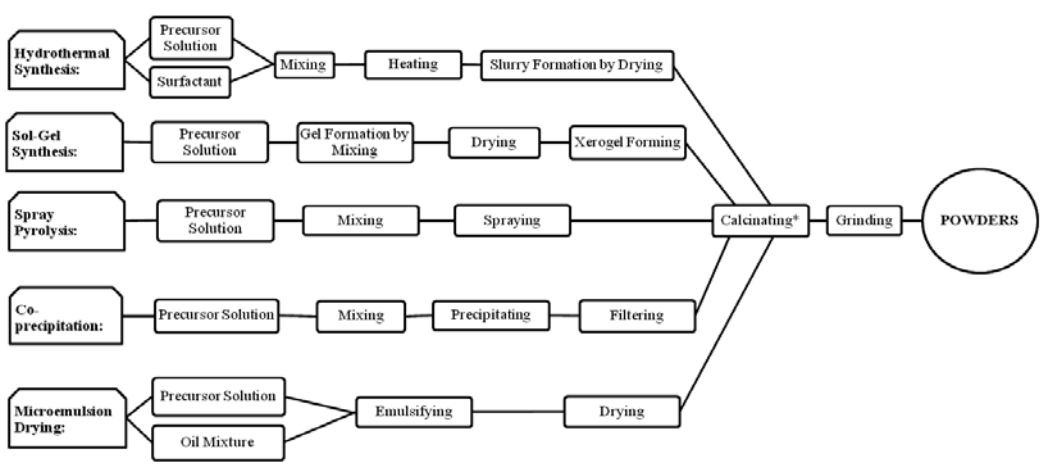

Fig. 4 Typical routes for producing $LiFePO_4$ powders using solution-based methods.

Table 5 Precursors used in the hydrothermal synthesis method, and particle size and electrochemical performance of the resultant $LiFePO_4$ powders

Li Precursor	Fe Precursor	P Precursor	Metal Dopant	Carbon Source	Molar Ratio	Product	Particle Size (nm)	Discharge Capacity (mA/g)	Ref
CH_3COOLi	$FeC_2O_4{\cdot}2H_2O$	$NH_4H_2PO_4$	Iron wire	Sugar	1:1:1	$LiFePO_4/C$		136 (1C)	7
$LiOH{\cdot}H_2O$	$(NH_4)_2Fe(SO_4)_2$	H_3PO_4		Ascorbic acid	3:1:1	$LiFePO_4$		160	17
Li_3PO_4	$Fe_3(PO_4)_2{\cdot}5H_2O$			Sucrose		$LiFePO_4/C$	1,000	140 (C/10)	23
Li_3PO_4	$FeSO_4{\cdot}7H_2O$	Na_3PO_4		Sucrose (5wt.%)	1:1:1	$LiFePO_4/C$		160 (C/20)	45
LiOH	$FeSO_4$	H_3PO_4		Sucrose	3:1:1	$LiFePO_4/C$	3,000	100 (0.14C)	79
CH_3COOLi	$FePO_4{\cdot}2H_2O$			Carbon gel	1.2:1	$LiFePO_4/C$		148 (C/2)	80
LiOH	$FeSO_4{\cdot}7H_2O$	H_3PO_4		Sucrose , Ascorbic acid, CNT	3:1:1	$LiFePO_4/C$	3,000-5,000	145 (0.3C)	81
$LiOH{\cdot}H_2O$	$FeSO_4{\cdot}7H_2O$	H_3PO_4		Ascorbic acid, sugar	3:1:1	$LiFePO_4/C$	1,000-3,000	90 (0.15C)	82
$LiOH{\cdot}H_2O$	$FeSO_4{\cdot}7H_2O$	$(NH_4)_3PO_4{\cdot}3H_2O$		Ascorbic acid	2.5:1:1	$LiFePO_4$	100-200	167 (C/10)	83
LiOH	$FeSO_4{\cdot}7H_2O$	H_3PO_4		CTAB ($C_{19}H_{42}BrN$)	3:1:1	$LiFePO_4/C$	50	135 (C/10)	84
LiOH	$FeSO_4{\cdot}7H_2O$	H_3PO_4		CTAB ($C_{19}H_{42}BrN$)	3:1:1	$LiFePO_4/C$	20-30	145 (C/10)	85
$LiOH{\cdot}H_2O$	$FeSO_4{\cdot}7H_2O$	H_3PO_4	$MgSO_4{\cdot}7H_2O$	Glucose	3:0.98:1:0.02	$LiMg_{0.02}Fe_{0.98}PO_4$	500-1,000	144 (C/5)	86
$LiOH{\cdot}H_2O$	$FeSO_4{\cdot}7H_2O$	H_3PO_4		Ascorbic acid, Carbon black (3, 5, 10w%)	3:1:1	$LiFePO_4/C$	100-200	128 (C/10)	87
$LiOH{\cdot}H_2O$	$FeSO_4{\cdot}7H_2O$	H_3PO_4		Ascorbic acid w/ CNT	3:1:1	$LiFePO_4/C$	3,000-5,000	153 (0.15C)	88
$LiOH{\cdot}H_2O$	$FeSO_4$	H_3PO_4		Hydrazine	3:1:1	$LiFePO_4/C$	3,000-5,000	80 (0.15C)	88
$LiOH{\cdot}H_2O$	$FeSO_4{\cdot}7H_2O$	H_3PO_4		MWCNTs	3:1:1	$LiFePO_4$/MWCNTs		160 (0.3C)	89
$LiOH{\cdot}H_2O$	$FeSO_4{\cdot}7H_2O$	H_3PO_4		Citric acid	3:1:1	$LiFePO_4/C$	200-500		90
LiOH	$FeSO_4{\cdot}7H_2O$	H_3PO_4			3:1:1	$LiFePO_4$			91
LiOH	$FeSO_4{\cdot}7H_2O$	H_3PO_4			3:1:1	$LiFePO_4$	1,000-2,000		92
Li_3PO_4	$FeSO_4{\cdot}7H_2O$	H_3PO_4			1:3:2	$LiFePO_4$	3,000-10,000		93
Li_3PO_4	$FeSO_4{\cdot}7H_2O$			Sucrose	1:1	$LiFePO_4/C$	100	140 (C/10)	93
$LiOH{\cdot}H_2O$	$(NH_4)_2Fe(SO_4)_2{\cdot}6H_2O$	H_3PO_4			3.75:1:1	$LiFePO_4$		90 (C/100)	94

L-ascorbic acid, carbon, MWCNTs, and organic surfactant cetyl trimethyl ammonium bromide (CTAB), which not only increase the conductivity but also act as the reducing agent to prevent the oxidation of Fe(II) during calcination[79, 81-84, 86-88]. Chen *et al.*[82, 88] studied the effect of different carbon sources, such as hydrazine, ascorbic acid, sugar, carbon black, and MWCNTs, and found that ascorbic acid gave $LiFePO_4/C$ powders with the highest discharge capacity of 153 mAh/g at 0.15C. In addition, Xu *et al.*[89] prepared MWCNT-coated $LiFePO_4$ by hydrothermal synthesis, followed by calcination. These $LiFePO_4$-MWCNT (5 wt.%) powders showed an initial discharge capacity of 160 mAh/g at 0.3C, and the capacity fading was only 0.4% after 50 cycles. However, the agglomeration of MWCNT particles was observed at higher MWCNT concentrations. In addition to carbon, metal can be doped into $LiFePO_4$ powders to improve the conductivity. For example, Ou *et al.*[86] synthesized Mg-doped $Li_{0.08}Mg_{0.02}FePO_4$ by hydrothermal synthesis at 180℃ for 6 h, followed by calcination at 750℃ for 6 h.

During hydrothermal synthesis, organic surfactants are often used to improve the dispersion of precursors and increase the specific surface area of final products. Meligrana *et al.*[84] prepared $LiFePO_4$ powders by hydrothermal synthesis and investigated the effect of organic surfactants on the morphological and electrochemical properties of $LiFePO_4$ powders. It was found that the pyrolysis of surfactants increased the material conductivity and generated a reductive environment for avoiding the oxidation of Fe(II) to Fe(III). As a result, the cycling performance and discharge capacity increased noticeably after the addition of surfactants. Zhang *et al.*[90] also prepared monodispersed and well-crystallized $LiFePO_4$ powders by the hydrothermal synthesis of Fe(II)-citric acid complex precursors at 180℃ and the application of isopropanol as a surfactant. It was found that the powder morphology was significantly influenced by the volume ratio of isopropanol to water. Monodispersed short rod-like $LiFePO_4$ crystals were obtained when equal volume isopropanol and water were used, and the particle size was in the range of 200 − 500 nm. However, when isopropanol was absent, column-like $LiFePO_4$ particles were obtained, and the particle size was in the range of 800 − 1100 nm.

Water temperature is one of the most important parameters for the hydrothermal synthesis process because reaction rate, ionization degree, particle size and crystalline structure of $LiFePO_4$ powders are all temperature dependent. Chen *et al.*[81] investigated the effect of water temperature on the structure and performance of $LiFePO_4$ powders. It was found that

the water temperature is directly related with the crystal structure and must be above 170℃ to produce correct lattice parameters. With a water temperature of above 170℃, they obtained $LiFePO_4$ powders with a discharge capacity of 145 mAh/g, which did not decay even after 50 cycles. Jin *et al.*[83] also synthesized $LiFePO_4$ powders by hydrothermal synthesis at 150, 170 and 200℃ for 10 h, followed by an additional calcination step. $LiFePO_4$ powders hydrothermally synthesized at 170℃ and calcined at 500℃ have the highest discharge capacity of 167 mAh/g at C/10. This value is one of the highest capacities reported for $LiFePO_4$ powders in the literature. The average particle size of these $LiFePO_4$ powders was in the range of 100 − 200 nm. Although the water temperature is typically above 170℃, there is report on obtaining $LiFePO_4$ powders using a temperature below 170℃. For example, Jin *et al.*[87] synthesized $LiFePO_4$ powders by hydrothermal synthesis at 150℃. These $LiFePO_4$ powders were assembled into cells with solid polymer electrolyte, which showed higher discharge capacity when compared with $LiFePO_4$ cells using liquid electrolyte.

In addition to the water temperature, the flow rate of water and the concentrations of precursors have significant influence on the structure and electrochemical properties of $LiFePO_4$ powders. Xu *et al.*[91] prepared $LiFePO_4$ powders at different water flow rates and precursor concentrations. It was found that high flow rates led to more uniform particles and higher precursor concentrations resulted in larger particle size.

Recently, supercritical hydrothermal synthesis was developed to produce $LiFePO_4$ powders. Lee *et al.*[92] carried out the $LiFePO_4$ synthesis under sub and supercritical water at different temperatures, pH values, and reaction times. It was found that neutral or slightly basic pH was required for the successful synthesis of $LiFePO_4$ powders. Supercritical water gave smaller particle size ranged in the submicron scale and lower reactant concentration led to better particle size distribution. In addition, the heating time should be short in order to prevent the growth and agglomeration of particles. In a similar study, the same authors obtained $LiFePO_4$ powders by supercritical water with a capacity of 140 mAh/g at C/10, which is higher than that achieved by the subcritical approach[93].

So far, most $LiFePO_4$ powders were produced using the batch hydrothermal synthesis approach. However, a continuous hydrothermal synthesis route can be used for the mass production of $LiFePO_4$ powders[91]. Aimable *et al.*[94] prepared $LiFePO_4$ powders by continuous hydrothermal synthesis and investigated the effects of heating temperature and time on the morphological and electrochemical properties of $LiFePO_4$ powders. It was found that, with increase in temperature from subcritical to supercritical water conditions and increase in time from 6 to 12 s, well-crystalline and impurity-free $LiFePO_4$ powders were produced. Although the discharge capacities of these $LiFePO_4$ powders were only 90 mAh/g at C/100 and 75 mAh/g at C/10, it can be improved with a carbon coating.

4.2. Sol-Gel synthesis

Sol-gel synthesis is a low temperature, wet chemical approach, which is often used for the preparation of metal oxides or other specific compositions. Standard sol-gel synthesis involves the formation of a sol, *i.e.*, a stable colloidal suspension of solid particles in a solvent, and the gelation of the sol to form a gel consisting of interconnected rigid skeleton with pores made of colloidal particles. The properties of the gel are determined by the particle size and cross-linking ratio[95-98]. The gel can then be dried to form xerogel, which shows reduced volume[95-98]. To obtain the final powder products, all liquids need to be removed from the surface of pores by a heat treatment carried out at elevated temperatures, which also reduces the number and connectivity of pores, known as densification[97, 98]. Reaction parameters, such as temperature, time, pH, precursor, solvent, concentration, and viscosity, etc., are of importance for the formation and ultimate morphology (particle size and shape, pore size, and porosity) of the obtained powders. In sol-gel synthesis, the surfaces of the powder products are controlled from the beginning of reactions. In addition, sol-gel synthesis is low cost and does not require high processing temperature, and powders produced by this method have the advantages of precise stoichiometry control, high purity, uniform structure, and very small size.

Sol-gel synthesis has become an important means to prepare $LiFePO_4$ powders[99, 100]. Dominko *et al.*[101] compared $LiFePO_4$ powders prepared by sol-gel and solid-state synthesis methods. Powders prepared by sol-gel synthesis have more micropores and higher capacity (150 mAh/g at C/10) than those by solid-state synthesis (130 mAh/g at C/10). Hsu *et al.*[102] also used the sol-gel synthesis method to prepare $Li_{0.99}Al_{0.01}FePO_4$ powders, and they found that the sol-gel synthesis gave powders with higher conductivity when compared with the solid-state route. The resul-

tant specific capacity was about 150 mAh/g at C/40 rate.

As shown in **Fig. 4**, during the sol-gel synthesis of $LiFePO_4$ powders, precursor solutions are mixed to form sols, which are vigorously stirred at 60 – 80℃ for 12 – 24 h in order to obtain wet gel[103, 104]. After the gelation, wet gel is dried in a vacuum or in argon atmosphere at 80℃ for 12 h in order to produce xerogel[103, 104]. Finally, xerogel is calcined either in one or two steps at 500 – 900℃ for 3 – 30 h to produce $LiFePO_4$ powders[102-105]. In general, a slow heating rate during calcination causes rougher and relatively less porous structure. On the other hand, with a high heating rate, more porous structure can be obtained, which also affects the electrochemical properties of $LiFePO_4$ powders[101].

Different precursors and solvents have been used in sol-gel synthesis to produce $LiFePO_4$ powders (**Table 6**). The type of solvent is extremely important for the control of powder structure. Water is the most used solvent, but organic solvent can also be used in sol-gel synthesis[105-106]. For example, Yang *et al.*[105] synthesized $LiFePO_4$ powders by sol-gel synthesis and used ethylene glycol as a solvent. These $LiFePO_4$ powders have a specific capacity of 165 mAh/g at C/100 and 150 mAh/g at both C/5 and 2C, which is the indication of good rate capacity. Li *et al.*[107] used ethanol-based sol-gel synthesis method, which took relatively shorter synthesis time when compared with water-based sol-gel synthesis.

$LiFePO_4$ powders obtained by sol-gel synthesis often have pores in the range of 30 – 200 nm. For example, Dominko *et al.*[103] synthesized porous $LiFePO_4$/C powders, which have pore size between 60 and 90 nm and initial capacities of 160, 140 and 120 mAh/g at C/20, C/2 and 5C, respectively. During the formation of porous $LiFePO_4$ powders, the agglomeration tendency can be reduced noticeably by using surfactants[108]. Choi *et al.*[108] prepared porous $LiFePO_4$ powder with a narrow particle size distribution (100 – 300 nm) by employing lauric acid as a surfactant and achieved discharge capacities of 123, 157 and 170 mAh/g at 10C, 1C and C/10, respectively. The presence of pores not only increases the specific surface area but also shortens the transportation pathway of lithium inside the material. The porous structure is useful especially if the pores are covered by an electrical conductor[102-105, 108].

The most common approach to create an electrically conducting coating on the pore surface is by directly adding a carbon source during sol-gel synthesis[103, 109, 110]. The carbon source not only improves the electrical conductivity of $LiFePO_4$ powders, but also contributes to the formation of the porous structure through the degradation and pyrolysis processes. In addition, the presence of carbon source enhances the uniform growth of $LiFePO_4$ particles with relatively small sizes by decreasing the aggregation tendency[102, 105, 109]. The thickness of the carbon layer can be as low as 1 – 2 nm in the form of amorphous carbon or graphene-rich phase[104, 109, 110]. Sucrose and citric acid are the most commonly used carbon sources for the sol-gel method[103, 104, 110]. Kim *et al.*[104] used sucrose and citric acid as the carbon sources to synthesize porous $LiFePO_4$/C powders, in which the pore surfaces are covered by a graphine-rich carbon layer of 2 – 4 nm thick. It was found that these porous $LiFePO_4$/C powders showed high discharge capacities of 153 and 94 mAh/g at C/10 and 5C, respectively, which are probably caused by the large surface areas of the porous structures. In addition to sucrose and citric acid, other carbon sources can be used. For example, Li *et al.*[107] used PEG and D-fructose as the carbon source and obtained porous $LiFePO_4$/C powders with the highest specific capacities of 130.9 and 157.7 mAh/g at 1C and C/5, respectively. One advantage of the sol-gel synthesis method is the relatively easy control of carbon coating thickness. Dominko *et al.*[110] synthesized $LiFePO_4$/C powders with different carbon layer thicknesses ranging from 1 to 10 nm, which are among the lowest values in the literature. These $LiFePO_4$/C powders have high discharge capacity of 150 mAh/g at C/5.

In addition to carbon coating, metal dopants can also be added to modify the structure and electrochemical performance of $LiFePO_4$ powders. Wang *et al.*[111] doped Mg, Zr, and Ti metals into the crystal structure of $LiFePO_4$ powders and they found that the Ti doping led to the highest discharge capacity, which is around 160 mAh/g at C/8. Lee *et al.*[112] also prepared sulfur-doped $LiFePO_{3.98}S_{0.03}$ powders by sol-gel synthesis in order to enhance the performance of the Li/$LiFePO_4$ cells at high temperatures. They obtained good discharge capacities of around 155 mAh/g at all temperatures because of the improved stability caused by the substitution of O^{2-} with S^{2-}.

4.3. Spray pyrolysis

Spray pyrolysis is an important method for the preparation of ultrafine powders[119, 120], and it is based on the generation of droplets in a continuous way from a solution containing precursor colloidal particles. Droplets can be generated by using different techniques, such as ultrasonic transduction[121] and

Table 6 Precursors used in the sol-gel synthesis method, and particle size and electrochemical performance of the resultant $LiFePO_4$ powders

Li Precursor	Fe Precursor	P Precursor	Metal Dopant	Solvent	Carbon Source	Molar Ratio	Product	Pore* or Particle Size (nm)	Discharge Capacity (mAh/g)	Ref
$LiOH·H_2O$	$Fe(NO_3)_3·9H_2O$	H_3PO_4		Methanol	Ascorbic acid	1:1:1	$LiFePO_4/C$	100, 000	80 (C/5)	14
Li_3PO_4	$FeC_6H_5O_7·nH_2O$	H_3PO_4		Deionized water		1:3:2	$LiFePO_4$		117	17
Li_3PO_4	$C_6H_5FeO_7$	H_3PO_4		Deionized water		1:3:2	Porous $LiFePO_4/C$	*90	150 (C/10)	101
$LiNO_3$	Iron powder	$NH_4H_2PO_4$	$Al(NO_3)_2·6H_2O$	Deionized water	Citric acid	0.99:1:1:0.01	$Li_{0.99}Al_{0.01}FePO_4/C$	50	150 (C/40)	102
Li_3PO_4	$C_6H_5FeO_7$	H_3PO_4		Deionized water	Citric acid	1:3:2	Porous $LiFePO_4/C$	*60-90	160 (C /20)	103
$LiCO_3$	$FeC_2O_4·2H_2O$	$NH_4H_2PO_4$		Deionized water	Citric acid	1:1:1	Porous $LiFePO_4/C$	*9.1	128 (C/10)	104
$LiCO_3$	$FeC_2O_4·2H_2O$	$NH_4H_2PO_4$		Deionized water	Sucrose	1:1:1	Porous $LiFePO_4/C$	*6.1	153 (C/10)	104
$Li(COOCH_3)·2H_2O$	$Fe(COOCH_3)_2$	H_3PO_4		Ethylene glycol	Ethylene glycol	1:1:1	$LiFePO_4/C$	200-300	165 (C/100)	105
$LiNO_3$	$FeC_2O_4·2H_2O$	$NH_4H_2PO_4$		Deionized water	Ethylene glycol	1:1:1	$LiFePO_4/C$		155 (C/10)	106
$LiCl·H_2O$	$FeCl_2·4H_2O$	H_3PO_4		Ethanol		1:1:1	$LiFePO_4$		116 (C/5)	107
$LiCl·H_2O$	$FeCl_2·4H_2O$	H_3PO_4		Ethanol	PEG, 1-hexadecanol	1:1:1	Porous $LiFePO_4/C$		145 (C/5)	107
$LiCl·H_2O$	$FeCl_2·4H_2O$	H_3PO_4		Ethanol	PEG, D-fructose	1:1:1	Porous $LiFePO_4/C$		157.7 (C/5)	107
$LiCl·H_2O$	$FeCl_2·4H_2O$	H_3PO_4		Ethanol	PEG, Cinnamic acid	1:1:1	Porous $LiFePO_4/C$	100-200	137 (C/5)	107
$Li(COOCH_3)·2H_2O$	$FeCl_2.4H_2O$	P_2O_5		Ethanol	Lauric acid	1:1:1	$LiFePO_4$	100-300	170 (C/10)	108
$Li(COOCH_3)·2H_2O$	$FeCl_2.4H_2O$	P_2O_5		Ethanol		1:1:1	$LiFePO_4$	500-3,000	146 (C/10)	108
Li_3PO_4	$C_6H_5FeO_7$	H_3PO_4		Deionized water		1:3:2	Porous $LiFePO_4/C$	500-20,000	140 (C/2)	109
Li_3PO_4	$C_6H_5FeO_7$	H_3PO_4		Deionized water	Hydroxy ethyl cellulose	1:3:2	Porous $LiFePO_4/C$		150 (C/5)	110
$LiOH·H_2O$	$FeC_2O_4·2H_2O$	$NH_4H_2PO_4$		Deionized water	Polyacrylic acid, Citric acid	1:1:1	$LiFePO_4$		160-165(C/8)	111
$LiOH·H_2O$	$FeC_2O_4·2H_2O$	$NH_4H_2PO_4$	$Mg(CH_3CO_2)_2·4H_2O$	Deionized water	Polyacrylic acid, Citric acid	1:0.99:1:0.01	$LiMg_{0.01}Fe_{0.99}PO_4$		160-165(C/8)	111
$LiOH·H_2O$	$FeC_2O_4·2H_2O$	$NH_4H_2PO_4$	$Zr(OC_2H_5)_4$	Deionized water	Polyacrylic acid, Citric acid	1:0.99:1:0.01	$LiZr_{0.01}Fe_{0.99}PO_4$		160-165(C/8)	111
$LiOH·H_2O$	$FeC_2O_4·2H_2O$	$NH_4H_2PO_4$	$Ti(OCH_3)_4$	Deionized water	Polyacrylic acid, Citric acid	1:0.99:1:0.01	$LiTi_{0.01}Fe_{0.99}PO_4$		160-165(C/8)	111
Li_3PO_4	$C_6H_5FeO_7$	H_3PO_4		Deionized water	Citric acid	1:3:2	Porous $LiFePO_4/C$	*50	120 (1C)	113
$LiCO_3$	$Fe(NO_3)_3·9H_2O$	$NH_4H_2PO_4$		Deionized water	Ascorbic acid	1:1:1	$LiFePO_4$			114
$LiOH·H_2O$	$Fe(NO_3)_3·9H_2O$	H_3PO_4		Deionized water		1:1:1	$LiFePO_4$			114
$Li(COOCH_3)·2H_2O$	$Fe(COOCH_3)_2$	H_3PO_4		DMF		1:1:1	$LiFePO_4$			114
$Li(COOCH_3)·2H_2O$	$Fe(COOCH_3)_2$	H_3PO_4		DMF		1.05:1:1	$LiFePO_4$	5,000	145 (C/2)	115
$Li(COOCH_3)·2H_2O$	$Fe(COOCH_3)_2$	H_3PO_4		Ethylene glycol	Functionalized CNF by HNO_3	1:1:1	$LiFePO_4$/CNF	200	120 (C/2)	116
$Li(COOCH_3)·2H_2O$	$Fe(COOCH_3)_2$	H_3PO_4		Ethylene glycol		1:1:1	$LiFePO_4/C$	500-1,000	110 (C/2)	116
$LiOH·H_2O$	$Fe(NO_3)_3·9H_2O$	H_3PO_4		Deionized water	Ascorbic acid	1:1:1	$LiFePO_4/C$	350	165 (3C)	117
$LiOH·H_2O$	$Fe(NO_3)_3·9H_2O$	H_3PO_4		Deionized water	Ascorbic acid	1:1:1	$LiFePO_4/C$		110 (C/5)	118
$LiOH·H_2O$	$Fe(NO_3)_3·9H_2O$	H_3PO_4	Metal powder (Co, Ag)	Deionized water	Ascorbic acid	1:1:1	$LiFePO_4/C$		140 (C/5)	118

peristaltic pump[122]. In spray pyrolysis, the generation of droplets is a key step because the droplets act as the nucleation centers and eventually evolve to well-crystallized, dense, and pure particles. Powders produced by this method have small particle size (< 1 μm), narrow size distribution (1 − 2 μm), large surface area, and high purity[121-126, 128, 129]. All these properties are desirable for achieving high electrochemical performance for $LiFePO_4$ powders, and hence spray pyrolysis method is becoming an important alternative approach for producing $LiFePO_4$ powders[122-124]. **Table 7** shows the precursors used in the spray

Table 7 Pecursors used in the spray pyrolysis method, and particle size and electrochemical performance of the resultant $LiFePO_4$ powders

Li Precursor	Fe Precursor	P Precursor	Metal Dopant	Solvent	Carbon Source	Molar Ratio	Product	Particle Size (nm)	Discharge Capacity (mAh/g)	Ref
$LiNO_3$	$FeSO_4$	H_3PO_4		Deionized water	Sucrose		$LiFePO_4$/C			32
$LiNO_3$	$Fe(NO_3)_3{\cdot}9H_2O$	H_3PO_4	$Mg(NO_3)_2{\cdot}6H_2O$	Deionized water	White sugar 40 wt%	1:0.9:1:0.1	$LiFe_{0.9}Mg_{0.1}PO_4$/C	1,000-2,000	132 (C/10)	121
Li_2CO_3	$FeC_2O_4{\cdot}2H_2O$	$NH_4H_2PO_4$	$Mg(C_2H_3O_2)_2{\cdot}4H_2O$	Deionized water		1-x:1:1:x	$Li_{1-x}FeMg_xPO_4$	1,000-2,000		122
$LiNO_3$	$Fe(NO_3)_3{\cdot}9H_2O$	H_3PO_4		Deionized water	Ascorbic acid, white sugar	1:1:1	$LiFePO_4$/C	1,000-2,000	124 (C/10)	124
$LiCO_3$	$FeC_2O_4{\cdot}2H_2O$	$NH_4H_2PO_4$		Deionized water (HNO_3)	Sucrose ($C_{12}H_{22}O_{11}$)		$LiFePO_4$/C	300		125
$Li(HCOO){\cdot}H_2O$	$FeCl_2{\cdot}4H_2O$	H_3PO_4		Deionized water (HCl)		1:1:1	$LiFePO_4$		100 (C/10)	126
$Li(HCOO){\cdot}H_2O$	$FeCl_2{\cdot}4H_2O$	H_3PO_4		Deionized water (HCl)	Citric acid	1:1:1	$LiFePO_4$/C	1,000-3,000	140 (C/10)	126
$Li(HCOO){\cdot}H_2O$	$FeCl_2{\cdot}4H_2O$	H_3PO_4		Deionized water (HCl)	Acetylene black	1:1:1	$LiFePO_4$/C	58	163 (C/10)	128
$Li(HCOO){\cdot}H_2O$	$FeCl_2{\cdot}4H_2O$	H_3PO_4		Deionized water (HCl)	Acetylene black	1:1:1	$LiFePO_4$/C	300-1,000	158 (C/10)	129

pyrolysis method and the particle size and discharge capacity of the resultant $LiFePO_4$ powders.

The spray pyrolysis of $LiFePO_4$ powders typically starts with the pumping (or spraying) of a solution of mixed precursors into a pyrolysis furnace (around 400 − 600℃) in the droplet form by a carrier gas (**Fig. 4**)[122-125]. Collected precursor powders are then calcined at temperatures around 700 − 800℃. Jugovic *et al.*[32] compared $LiFePO_4$ powders prepared by solid state synthesis and spray pyrolysis, and found that $LiFePO_4$ powders by spray pyrolysis have smaller particle size and present spherical morphology without agglomeration. However, powders by solid-state synthesis are formed of larger and nonspherical particles with apparent agglomeration. In addition, powders prepared by solid-state synthesis show well crystallized structure as single-phase phospho-olivines, whereas those prepared by spray pyrolysis have olivine phase with small portion of other phases such as lithium carbon and iron carbon, which lead to higher electrical conductivity.

Like many other methods, carbon sources can be added during spray pyrolysis, and the resultant $LiFePO_4$/C powders not only have higher electrical conductivity, but also have smaller particle size, which increases the specific surface area of the powders[124, 126]. Bewlay *et al.*[125] used sucrose as a carbon source to prepare $LiFePO_4$/C powders, which had an average diameter of 300 nm and showed a conductivity from 10^{-7} to 10^{-1} S/cm, depending on the amount of the carbon source added in the precursor solution. Konarova *et al.*[126] also prepared $LiFePO_4$ and $LiFePO_4$/C powders by the spray pyrolysis method. While $LiFePO_4$ powders had low discharge capacity of around 100 mAh/g at C/10, $LiFePO_4$/C powders showed 140 mAh/g at C/10 and 84 mAh/g at 5C, respectively, with small capacity fading during cycling. Ju *et al.*[123] also reported fine, spherical $LiFePO_4$/C powders with charge capacities between 108 − 136 mAh/g, depending on the size and amount of the carbon. Capacities and cycling performance of $LiFePO_4$/C powders are reported to be improved by preparing nano-sized particles. It must be noted that, when a carbon source is added, the carbon content in the final $LiFePO_4$/C product needs to be carefully controlled because, if the carbon content is too high, the discharge capacity may decrease due to either reduced $LiFePO_4$ content[127] or dominant barrier behavior of the thick carbon layer[126, 110]. Yang *et al.*[124] prepared non-agglomerated, smooth $LiFePO_4$/C powders with carbon evenly distributed. When the carbon content is 15 %, the $LiFePO_4$/C powders have the highest discharge capacity of 124 mAh/g at C/10.

Metal dopants have also been used in the spray pyrolysis method to improve the performance of $LiFePO_4$ powders. For example, Teng *et al.*[121, 124] synthesized Mg-doped $LiFePO_4$/C powders, which have an average particle size between 1 and 2 μm and a conductivity 10^4 times greater than that of pure $LiFePO_4$. These powders have a capacity of 132 mAh/g at C/10 and exhibit lower capacity decay when compared with undoped $LiFePO_4$/C powders. Wang *et al.*[122] also prepared Mg-doped $LiFePO_4$ powders using spray pyrolysis and achieved 10^4 times higher

conductivity than pure $LiFePO_4$ powders.

The spray pyrolysis method can also be combined with wet or dry ball-milling techniques in order to increase the specific surface area and discharge capacity of the resultant $LiFePO_4$ powders[128, 129]. Konarova *et al.*[128] produced $LiFePO_4$ powders with average diameter less than 100 nm by the combination of spray pyrolysis and wet ball-milling. These powders have discharge capacities of 163 mAh/g at C/10 and 100 mAh/g at 10C, respectively. The same authors also reported the preparation of $LiFePO_4$/C powders with diameters ranging from 300 to 1000 nm by the combination of spray pyrolysis and planetary ball-milling, and achieved a discharge capacity of 158 mAh/g at C/10[129].

4.4. Co-Precipitation

Co-precipitation is another solution-based method, which is easy to control and can lead to well-crystallized powders with high purity and small particle size. In that method, lithium and phosphate compounds in mixed precursor solutions are co-precipitated by controlling the pH values. The co-precipitated slurries are then filtered, washed, and dried under N_2 atmosphere. During that process, dried precursors may form amorphous $LiFePO_4$. Crystalline $LiFePO_4$ powders are obtained by carrying out the calcination at 500 – 800℃ for 12h under N_2 or argon flow[130, 131]. The typical synthesis route for the co-precipitation method is shown in **Fig. 4** and precursors used in this method are shown in **Table 8.** Depending on the precursors and other processing conditions, the particle sizes of the synthesized $LiFePO_4$ powders can range from 100 nm to several microns[130-133]. For example, Zheng *et al.*[131] prepared pure crystalline $LiFePO_4$ powders by calcining an amorphous co-precipitated $LiFePO_4$ at 500℃. These powders have a homogenously distributed particle size ranging from 100 and 200 nm, and their discharge capacity is 166 mAh/g at C/10. In addition to particle size, the particle morphology can also be controlled using the co-precipitation method. Arnold *et al.*[130] prepared flat, rhombus-shaped $LiFePO_4$ powders in the submicron range by an aqueous co-precipitation method. These pure and well-crystallized $LiFePO_4$ powders have a high discharge capacity of 160 mAh/g at C/20.

The structure and performance of $LiFePO_4$ powders can be improved by introducing carbon source or metal dopant into the co-precipitation process. For example, Ding *et al.*[132] prepared $LiFePO_4$/graphene composite powders by directly adding graphene during co-precipitation, and observed the restacking of graphene sheets because the van der Waals forces during synthesis caused a decrease in surface area of graphene. The resultant $LiFePO_4$/graphene powders have an average particle size of around 100 nm and a discharge capacity of 160 mAh/g at C/5 rate. Li *et al.*[133] prepared spherical shaped, sub-micron sized Ti-doped $LiFePO_4$ powders by the co-precipitation method. $Ti(SO_4)_2$ was used as the titanium dopant. It was found that 3%-Ti-doped powders exhibited a good discharge capacity of 150 mAh/g at C/10 with good cycling performance.

Co-precipitation can also be combined with other methods to produced $LiFePO_4$ powders with controlled structures and performance. Chang *et al.*[134] prepared high-density $LiFePO_4$/C powders by the solid-state synthesis of $FePO_4$ (1.56 g/cm^3), which was obtained by using the co-precipitation method supported with high-pressure filtering and two-step drying at 80℃. The tap-density of the obtained $LiFePO_4$/C powders was 1.80 g/cm^3 when the carbon content was 7 wt.%. The initial volumetric and gravimetric discharge capacities were 300.6 mAh/cm^3 and 167 mAh/g, respectively, at C/10.

4.5. Microemulsion drying

$LiFePO_4$ powders can also be prepared by the drying of microemulsion solutions[135-137], which are thermodyamically stable liquid mixtures consisting of water, oil, and emulsifying agent that stabilizes the microemulsions[135-138]. During the microemulsion drying process, microemulsions act as microreactors for the synthesis of $LiFePO_4$ powders. The type and property of the microemulsions are depended on the amount of oil and water, type and amount of emulsifying agent, and process temperature, etc[139-142]. As shown in **Fig. 4**, the microemulsion drying process of $LiFePO_4$ powders starts with the preperation of aqueous precursor solutions based on the stoichiometric ratios. The aqueous phase is mixed intensively with an oily phase consisting of hydrocarbons such as Kerosene[135-138]. The obtained microemulsions are dried between 300 and 400℃, during which extensive weight loss can be observed due to the evaporation of water and pyrolysis of organic hydrocarbons. It was reported that little amount of crystalline olivine $LiFePO_4$ starts to form during drying. However, in most cases, dried microemulsions need to be calcined at 650 – 850℃ under argon flow for 12 h. The optimum calcination temperature is reported to be around 750 ℃[136, 137]. Higher calcination temperature might result in increased particle size[136]. The microemulsion drying process is of importance for $LiFePO_4$ synthesis

Table 8 Precursors used in the co-precipitation and microemulsion drying methods, and particle size and electrochemical performance of the resultant $LiFePO_4$ powders

Method	Li Precursor	Fe Precursor	P Precursor	Solvent	Carbon Source	Molar Ratio	Product	Particle Size (nm)	Discharge Capacity (mAh/g)	Ref
Co-precipitation	LiOH	Ferrous ions	H_3PO_4	Deionized water			$LiFePO_4$			23
Co-precipitation	Li_3PO_4	$Fe_3(PO_4)_2{\cdot}5H_2O$		Deionized water		1:1	$LiFePO_4$	<1,000	160 (C/20)	130
Co-precipitation	Li_2CO_3	$FeSO_4{\cdot}7H_2O$	H_3PO_4	Deionized water	$C_2O_4H_2{\cdot}2H_2O$	1:1:1	$LiFePO_4$	100-200	166 (C/10)	131
Co-precipitation	LiOH	$(NH_4)_2Fe(SO_4)_2{\cdot}6H_2O$	$NH_4H_2PO_4$	Deionized water	Natural graphite		$LiFePO_4$/graphene	100	160 (C/5)	132
Co-precipitation	Li_2CO_3	$Fe(NO_3)_3{\cdot}9H_2O$	H_3PO_4	Deionized water	Glucose	1:1:1	$LiFePO_4$/C	2,000-4,000	167 (C/10)	134
Emulsion-Drying	$LiNO_3$	$Fe(NO_3)_3{\cdot}9H_2O$	$(NH_4)_2HPO_4$	Deionized water	Carbon Bl (40%)	1:1:1	$LiFePO_4$/C	1,000	133 (C/8.5)	136
Emulsion-Drying	$LiNO_3$	$Fe(NO_3)_3{\cdot}9H_2O$	$(NH_4)_2HPO_4$	Deionized water		1:1:1	$LiFePO_4$	1,000	121 (C/8.5)	136
Emulsion-Drying	$LiNO_3$	$Fe(NO_3)_3{\cdot}9H_2O$	$(NH_4)_2HPO_4$	Deionized water	Karosene:Twee n85	1:1:1	$LiFePO_4$/C	<1,000	125(C/8.5)	137
Emulsion-Drying	LiOH	$(NH_4)_2Fe(SO_4)_2$	H_3PO_4	Octane, Butyl alcohol	Sugar	3:1:1	$LiFePO_4$/C	90	163 (C/10)	143

because the formation of pure, fine powders is facilitated by the atomic scale, homogeneous distrubution of reactants in microemulsions from the beginning[135-137].

During microemulsion drying, the partcile growth is directly restricted by the size of the droplets in the emulsions. As a result, the particle size and morphology are affected by many factors such as solution concentration, droplet size, stirring power, and surfactant. Particle sizes and discharge capcities of $LiFePO_4$ powders produced by microemulsion drying are shown in **Table 8**. Myung *et al.*[137] used the microemulsion drying method (drying at 300℃ and calcination at 750℃) to prepare $LiFePO_4$/C powders, which have an average particle size of 1 μm. Good discharge capacity (around 125 mAh/g at C/8.5 and 25℃) and good electrical conductivity (10^{-4} S/cm) were obtained for the $LiFePO_4$/C powders due to the atomic level mixing of precursors and carbon source. Smaller particle size can be obtained using the microemulsion drying method. For example, Xu *et al.*[143] prepared $LiFePO_4$/C powders by using CTAB and PEG in emulsions to control the particle size and using sugar as the carbon source. $LiFePO_4$/C powders calcined at 600℃ exhibited 90 nm average particle size and very good discharge capacity of 163 mAh/g at C/10. Cho *et al.*[136] prepared pristine $LiFePO_4$ and $LiFePO_4$/C powders using the same method. Discharge capacities of 121 and 133 mAh/g at C/8.5 with excellent cycle stability were obtained for $LiFePO_4$ and $LiFePO_4$/C powders, respectively.

5. Other Methods

There are other methods that can be used to produce $LiFePO_4$ powders in addition to the previously mentioned approaches. Among these methods, template synthesis[117], polyol process[11], in-situ polymerization restriction method[144] and solid-state synthesis with controlled off-stoichiometry[145] stand out because they lead to $LiFePO_4$ powders with desired structure and fast charge/discharge behavior. In addition, a molten salt synthesis method was used to accelerate the crystallization process and help form spherical powders with increased tap density[146]. Other methods that have been used to produce $LiFePO_4$ powders include ceramic granulation[148], freeze-drying[148], sonochemical synthesis[135, 32], and rheological synthesis[149].

Recently, a few research groups are working on synthesizing $LiFePO_4$ films that have comparable electrochemical performance to powders. For example, LiFePO4[150-153] thin films with different thicknesses, such as 35 nm[152], 50 nm[150], and 300 nm[151, 153], have been produced by using pulsed laser deposition method. Another method to produce $LiFePO_4$ thin films is radio frequency magnetron sputtering, which can be used to obtain submicron size film thickness[154].

6. Conclusion

A good cathode material for lithium-ion batteries should have large capacity, good cycling performance, high stability, low toxicity, and high purity, and it should be easily produced and affordable. In order to obtain these features, small particle size, narrow size distribution, uniform morphology, optimum crystallinity degree, high specific surface area, minimum defects and agglomeration, and homogeneous carbon coating or metal doping are required for the practical application of $LiFePO_4$ powders in lithium-ion batteries. Methods described in this review were designed to obtain $LiFePO_4$ powders with desirable structures and high electrochemical performance. However, it is often challenging to obtain all the desired properties. Typically, solid state

methods are of importance in terms of obtaining ordered crystal structure, but they require higher treatment temperature and longer process time, which may lead to larger particle size and lower electrochemical capacity. On the other hand, solution-based methods give high purity, small particle size, uniform size distribution, and hence relatively higher electrochemical capacity, but additional solvent cost and environmental issues are major disadvantages of these methods. Many solid-state and solution-based methods are good candidates for the mass production of $LiFePO_4$ powders at industrial scale; however, the cost, productivity, reproducibility and complexity of these methods should be taken into consideration.

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