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Optimized synthesis technology of $LiFePO_4$ for Li-ion battery①

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Abstract: The influence of factors of the carbon black content, sintering temperature, sintering time, molar ratio of Li to Fe, as well as the electrochemical properties of $LiFePO_4$ for lithium ion battery were studied. The only technology was obtained by using range analysis through Latin orthogonal experiment of $L_4^4(16)$. The results show that the optimization synthesis technology of $LiFePO_4$ is content of 5% doping carbon, sintering temperature of 700 ℃, molar ratio of Li to Fe of 1.03∶1 and sintering time of 16 h. The optimized cathode synthesis techniques can make $LiFePO_4$ have good electrochemical properties.

Key words: lithium ion battery; cathode material; $LiFePO_4$; orthogonal test
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1 INTRODUCTION

The interest in lithium rechargeable batteries in electric vehicles has been significantly increased in recent years[1, 2]. The important factors for their application are low price, long cycle life, environmental safety and high specific capacity.

Among typical Li secondary battery cathode materials, such as $LiCoO_2$, $LiMn_2O_4$ and $LiFePO_4$, $LiFePO_4$ proposed by Padhi et al[3, 4] has attracted particular attention due to its low cost, environmental benignity, cycling stability and high temperature capability. Its main problems are low electronic conductivity and low lithium diffusivity[5]. Many research groups have tried to improve the performance of $LiFePO_4$. The conductivity problems have been studied by optimization of particles . Yamada et al[6] identified the undesired particle growth over 600 ℃ and the presence of a residual Fe^{3+} phase below 500 ℃ as two extrinsic obstacles for achieving optimum charge/discharge performance. Other methods include metal doping[7, 8](adding Ag or Cu), coating with the electronically conductive materials like carbon[9-12], metal oxide[13, 14] and low temperature liquid phase synthesis[15].

Of all the methods, synthesis of $LiFePO_4$ doping carbon black by solid-state reaction is a simple and effective way. Some research group only explored isolated factors, such as content of carbon black[11] or sintering temperature[16] that contributed to the electrochemical properties of $LiFePO_4$. And the combined effect of sintering temperature, sintering time, content of carbon black and ratio of Li to Fe in solid-state synthesis $LiFePO_4$ has not been reported yet.

In this paper, the influence of these four factors was studied, the electrochemical properties of $LiFePO_4$ for lithium ion battery in solid-state reaction were tested and the optimized technology was found.

2 EXPERIMENTAL

2.1 Synthesis

$LiFePO_4$ was prepared by solid-state reaction of $FeC_2O_4 \cdot 2H_2O$(AR), $(NH_4)_2HPO_4$(AR) and Li_2CO_3(AR). A stoichiometric mixture of the raw materials and the measured amount of carbon black was dispersed into acetone and then thoroughly mixed and reground. After evaporating the acetone, the olivine phase $LiFePO_4$ was synthesized in a purified Ar gas flow to prevent the formation of Fe^{3+} compounds as impurities; the mixture was first decomposed at 350 ℃ for 8 h to expel the gases and reground, then sintered under a given temperature schedule.

2.2 Characterization

The X-ray diffraction(XRD) with Cu $K\alpha$ radiation was used to identify the phases. Scanning electron microscope(SEM) images were observed using the JSM-5800.

2.3 Electrochemical test

The performance of $LiFePO_4$ as cathode was

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evaluated using an experimental cell with a lithium metal anode. The cathode was a mixture of $LiFePO_4$/acetylene black /polyvinylidene fluoride (PVDF) with mass ratio 70∶20∶10; a microporous polypropylene film (Celgard 2400) was used as a separator and the electrolyte was a 1 mol/L $LiPF_6$-propylene carbonate/dimethy carbonate (PC/DMC) solution. All cells were assembled inside a glove box filled with purified argon. The galvanostatic charge-discharge experiment was performed between 2.6 V and 4.1 V, at the rate of C/10, using a Dc-5computer-controlled galvanostat and potentiostat.

2.4 Single factor experiment

The first heating step was to decompose the mixture and expel the gases, so we focused on the second heating step. The four single factor experiments are as follows:

1) Sintering time (24 h), sintering temperature (700 ℃) and molar ratio of Li to Fe (1.05∶1) were settled. And content of doping carbon black was fixed at 0%, 1%, 3%, 5%, 7%.

2) The content of doping carbon (5%), sintering time (24 h) and molar ratio of Li to Fe (1.05∶1) were settled. And sintering temperature was fixed at 600, 650, 700, 750 and 800 ℃.

3) The content of doping carbon (5%), sintering temperature (700 ℃), and molar ratio of Li to Fe (1.05∶1) were settled. And sintering time was fixed at 16, 20, 24, 28 and 32 h.

4) The content of doping carbon (5%), sintering time (24 h), and sintering temperature (700 ℃) were settled. And the molar ratio of Li to Fe was fixed at 1∶1, 1.03∶1, 1.05∶1, 1.08∶1 and 1.1∶1.

2.5 Orthogonal test

In order to obtain optimum technological conditions of synthesizing $LiFePO_4$, $L_4^4(16)$ Latin orthogonal test was performed[17] based on single factor experiments. The target was the first discharge capacity. The factors and levels of orthogonal test are shown in Table 1.

3 RESULTS AND DISCUSSIONS

3.1 Single factor experiment

The results of single factor experiments are listed in Table 2.

3.1.1 Effect of content of carbon black on initial rate capacity

The conductivity of $LiFePO_4$ is poor. The addition of carbon during the synthesis of $LiFePO_4$ increases the conductivity, improves the electrochemical performance of the material in terms of practical discharge capacity[18, 19], and reduces the grain size of the active material. The reduction in the grain size can be related to the fact that the carbon particles, uniformly distributed between the starting materials, can interfere with the grains coalescence. The smaller the grain size, the higher current densities it can support. The electronic contact between the grains is enhanced because the conductive filler interacts with the grains during their formation. When the sintering temperature,

Table 1 Factors and levels for orthogonal experiment

Level	Factor			
	Content of doping carbon(*A*)/%	Sintering temperature(*B*)/℃	Sintering time(*C*)/h	Mole ratio of Li to Fe (*D*)
1	1	600	16	1∶1
2	3	650	20	1.03∶1
3	5	700	24	1.05∶1
4	7	750	28	1.08∶1

Table 2 Results of single factor experiment

Content of doping carbon/%	Specific capacity/ (mA·h·g^{-1})	Sintering temperature/℃	Specific capacity/ (mA·h·g^{-1})	Sintering time/h	Specific capacity/ (mA·h·g^{-1})	Molar ratio of Li to Fe	Specific capacity/ (mA·h·g^{-1})
0	107.4	600	88	16	138.6	1∶1	85.2
1	116.8	650	130.2	20	139.3	1∶1.03	137.9
3	125.1	700	140.4	24	140.4	1∶1.05	140.4
5	140.4	750	116.1	28	137.2	1∶1.08	123.5
7	119.6	800	108.5	32	130.3	1∶1.1	119.1

sintering time and the molar ratio of Li to Fe were fixed, the initial discharge capacity stepped up with the increment of carbon black. But when the content of carbon is more than 5%, the reduction of grain size is not notable, the proportion of active material decreases; so the initial rate capacity of $LiFePO_4$ cannot be improved.

3.1.2 Effect of sintering temperature on initial rate capacity

When the content of carbon, sintering time and the molar ratio of Li to Fe were constant, the initial discharge capacity of $LiFePO_4$ reached its peak as samples were prepared at 700 ℃. That is because the crystals grow maturely as the temperature gets up until 700 ℃. When the sintering temperature is over 700 ℃, the particles grow excessively large. This causes less specific area of particles, fewer tunnels for Li ions motion, and less discharge capacity.

3.1.3 Effect of sintering time on initial rate capacity

When the sintering temperature, content of carbon black and molar ratio of Li to Fe were fixed, the initial rate capacity of $LiFePO_4$ didn't seem to change a lot until the sintering time got to 28 h. This illustrates that $LiFePO_4$ grows excessively large after too-long sintering time.

3.1.4 Effect of molar ratio of Li to Fe on initial rate capacity

When the content of carbon black, sintering time and sintering temperature were fixed, the initial rate capacity went up along with the increase of molar ratio of Li to Fe until it reached 1.05∶1. The main reason is that Li_2O decomposed from Li_2CO_3 is inclined to volatilize, which causes the loss of lithium. But excessive molar ratio of Li to Fe could not meet the stoichiometric proportion of $LiFePO_4$ either. The only ratio of Li to Fe is 1.05∶1.

3.2 Orthogonal test

Table 2 shows the factors and levels of the orthogonal test for synthesizing the cathode material $LiFePO_4$. And Table 3 shows the result and range

Table 3 Result and range analysis of orthogonal test

No.	Level				Specific capacity/ (mA·h·g^{-1})
	Content of doping carbon(*A*)/%	Sintering temperature (*B*)/℃	Sintering time (*C*)/h	Molar ratio of Li to Fe(*D*)	
1	1	1	1	1	92.1
2	1	2	2	2	100.2
3	1	3	3	3	116.7
4	1	4	4	4	102.3
5	2	1	2	3	104.3
6	2	2	1	4	110.6
7	2	3	3	1	103.2
8	2	4	4	2	128.9
9	3	1	3	4	105.2
10	3	2	4	3	132.1
11	3	3	1	2	144.2
12	3	4	2	1	105.7
13	4	1	4	2	106.3
14	4	2	3	1	111.6
15	4	3	2	4	118.5
16	4	4	1	3	125.4
$\overline{K_{1j}}$	102.8	102.7	118.1	103.2	
$\overline{K_{2j}}$	111.8	113.6	107.2	119.9	
$\overline{K_{3j}}$	121.8	120.7	115.6	119.6	
$\overline{K_{4j}}$	115.5	115.6	110.9	109.2	
R	19	18	8.4	16.7	

analysis of the orthogonal test. The figure of R (range) represents the significance of each factor in the experiments. The larger the R (range), the more the factor contributes to the capacity. And the smaller one means that the factor has less weight on the index. According to R(range), the sequence of the weight of these four factors on the initial specific capability is $A \to B \to D \to C$. The content of carbon and sintering temperature are two most important factors . The molar ratio of Li to Fe follows. And sintering time has the least significance. From Fig. 1, as to factor A, if the content of carbon exceeds level 3, the initial discharge capability will not increase according to the single factor experiment. So A_3 is the best choice. As to factor B, if sintering temperature surpasses level 3, the rate capability will not increase according to the single factor experiment as well. So B_3 is chosen. As to factor C, since it has a minimum significance, the influence of sintering time on synthesizing $LiFePO_4$ is least. A sintering time that can satisfy a good crystal development is enough. Considering the result of single factor experiment, C_1 is adopted. As to factor D, the figures of levels 2 and 3 are very similar, which illustrates that there seems to be a platform between 1.03∶1 and 1.05∶1. Considering the cost of the production, D_2 is selected. Judging from the orthogonal test, the optimized technology for synthesizing the cathode material $LiFePO_4$ is $A_3B_3C_1D_2$.

3.3 Confirmation test

Olivine $LiFeO_4$ was synthesized by solid-state reaction. The molar ratio for $FeC_2O_4 \cdot 2H_2O$(AR) ∶ $(NH_4)_2HPO_4$(AR) ∶ Li_2CO_3(AR) was 1∶1∶0.515. The raw materials and carbon black(5%) were dispersed into acetone and then thoroughly mixed and reground. After evaporating the acetone, the mixture was first decomposed at 350 ℃ for 8 h to expel the gases and reground, then sintered at 700 ℃ for 16 h. All the sintering processes were in Ar gas flow.

The crystal phase of the sample was identified to be $LiFePO_4$ phase with ordered olivine structure indexed by orthorhombic Pnmb (as shown in Fig. 2). Fig. 3 shows SEM image of the sample

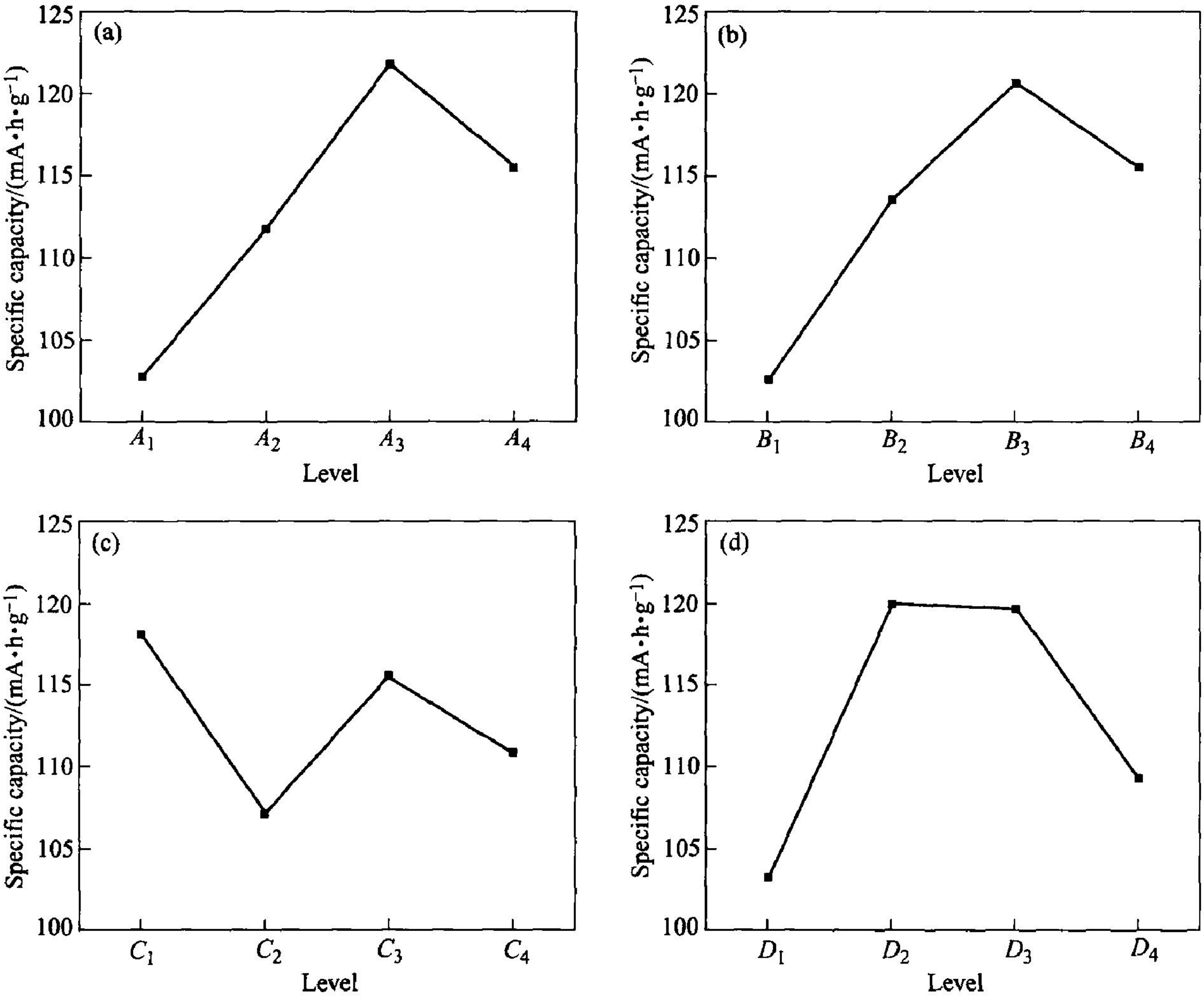

Fig. 1 Relationships between factors and target in orthogonal test
(a) —Factor A(content of doping carbon) vs specific capacity;
(b) —Factor B(sintering temperature) vs specific capacity;
(c) —Factor C(sintering time) vs specific capacity;
(d) —Factor D(ratio for Li to Fe) vs specific capacity

of $LiFePO_4$ prepared in optimized technology. To test its electrochemical performance, experimental batteries were assembled by using the method of section 2. 3. The result of electrochemical test shows that initial discharge capacity reaches 143. 5 mA • h/ g(Fig. 4) , which matches the result of the orthogonal test.

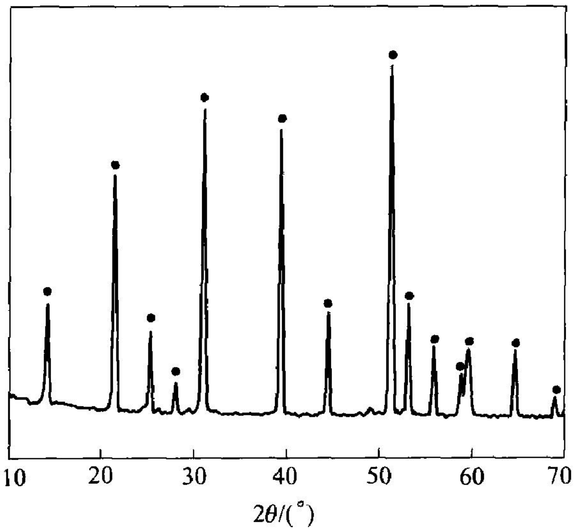

Fig. 2 XRD pattern of $LiFePO_4$ prepared in optimized technology

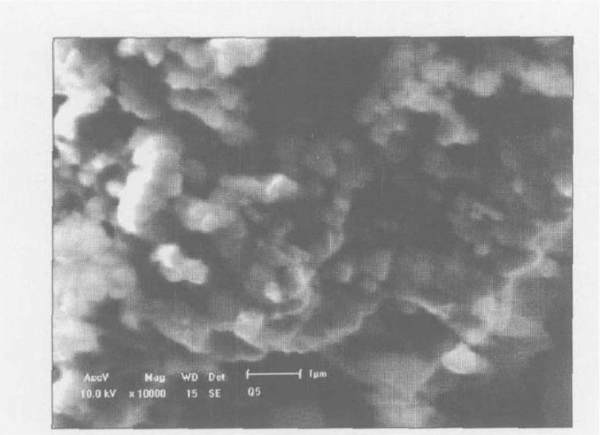

Fig. 3 Morphology of $LiFePO_4$ prepared in optimized technology

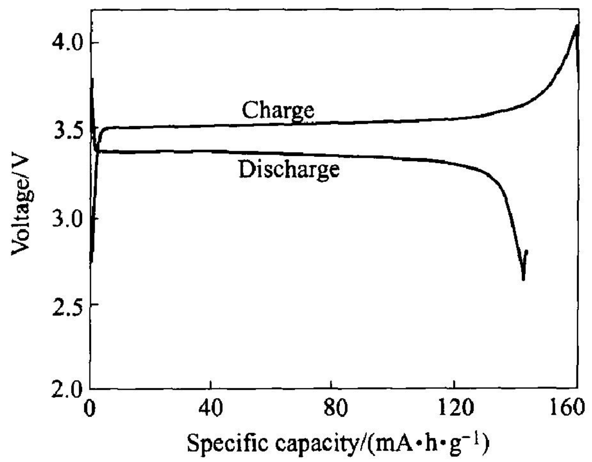

Fig. 4 Charge/ discharge curves of $LiFePO_4$ prepared in optimized technology at room temperature

4 CONCLUSIONS

1) The sequence of factors that can influence the initial rate capacity of $LiFePO_4$ is: content of doping carbon black, sintering temperature, molar ratio for Li to Fe, sintering time. The mass of carbon black and sintering temperature are two most important factors. The molar ratio of Li to Fe follows. And sintering time has the minimum significance. Certain of the only synthesis technology of $LiFePO_4$ is content of 5% doping carbon, sintering temperature of 700 ℃, mole ratio of Li to Fe of 1. 03∶ 1 and sintering time of 16 h.

2) The confirmation tests show that initial discharge capacity reaches 143. 5 mAh/ g, which matches the result of the orthogonal test. The specific capacity of the result is higher than that of the industrialized $LiCoO_2$. $LiFePO_4$ got from optimized synthesis technology has a promising applied future.

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