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Optimized synthesis of Cu-doped LiFePO₄/C cathode material by an ethylene glycol assisted co-precipitation method

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ABSTRACT

LiFePO₄/C and cupric ion doped LiFePO₄/C cathode materials were synthesized via an ethylene glycol assisted co-precipitation method. We assessed the influence of different parameters on electrochemical performance including calcination conditions, the amount of cupric ions added, doping ways, and drying methods. The microstructure of the materials was characterized by XRD, SEM, TEM, and EA. The results indicated the optimized Cu-doped LiFePO₄/C shows enhanced electrochemical performance with excellent high-rate capacity and cycle stability compared with LiFePO₄/C. The optimized Cu-doped LiFePO₄/C exhibited a high specific capacity of 148 mA h g^{-1} at 0.1 C. Even at a rate of 10 C, it still achieved a specific capacity of 111 mA h g^{-1} and its capacity retention ratio remained at 99.9% after 100 cycles at 1 C. These enhanced electrochemical properties were mainly due to a lesser extent of particle aggregation and more uniform carbon coating. Importantly, the synthesis process of this study is simple, fast, and economical thus it is promising to apply in industrialization.

1. Introduction

In recent years, lithium ion batteries have been considering as one of the important power sources for energy storage, electric vehicles and hybrid electric vehicles. Among various Li-ion cathode materials, lithium-iron phosphate (LiFePO₄) first reported by Padhi et al. in 1997, is recognized as a suitable cathode material for lithium ion batteries, due to its low toxicity, low cost, good thermal stability, high theoretical specific capacity (170 mA h g^{-1}) and excellent cycle performance [1]. However, the poor electrical conductivity and low lithium-ion transportation lead to poor high rate performance and limit its practical application in powerful lithium ion batteries. To solve above problems, several effective approaches have been proposed including carbon coating [2–4], doping metal ions [5,6] and controlling particle size [7,8] and crystal growth orientations [9].

The carbon coating can considerably enhance the electronic conductivity of LiFePO₄, prevent particle growth, inhibit particle agglomeration and increase the contact area between LiFePO₄ material and electrolyte. These factors are beneficial to the diffusion of lithium-ion. However, higher carbon contact reduces the volumetric energy density of batteries [2]. Moreover, the metal ions doping is an efficient method that can raise the intrinsic electronic conductivity of LiFePO₄, reduce the particle size and improve the Li-ion diffusion in order to enhance the electrochemical performance [10–13].

In this work, cupric ion doped LiFePO₄/C cathode materials were prepared via an ethylene glycol assisted with co-precipitation method. The influence of calcination conditions, Cu doping and drying methods on electrochemical properties, morphology, and microstructure of LiFePO₄/C were investigated. We found that high-rate capacity could be effectively improved by Cu doping. Compared with vacuum drying, the drying method of heating and stirring showed the enhancement of electrochemical performance with increasing specific capacity and capacity retention ratio.

2. Materials and methods

2.1. Synthesis of LiFePO₄/C and Cu-doped LiFePO₄/C composites

In order to synthesize the LiFePO₄/C and Cu-doped LiFePO₄/C composite cathode materials, the co-precipitation method via an ethylene glycol assisted was conducted. For distinctive synthesis, FeSO₄·7H₂O, H₃PO₄ (85%) and CuSO₄·5H₂O were dissolved in de-ionized water. Ethylene glycol was slowly added to the mixed solution under stirring. Then LiOH·H₂O was dropped into the mixed solution under an N₂ environment, leading to a gray-purple precursor. The molar ratio of Li:Fe:P is set to 3:1:1. After 30 min stirring, the mixed solution was heating to 106 °C for two hrs with continuous stirring, and then air cooled to room temperature. The obtained gray-green pre-

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Table 1
Taguchi factors and their levels..

Factors	Level 1	Level 2
Calcination temperature (°C)	600	650
Calcination time (hr)	4	7
Heating rate (°C /min)	1	2

cursor was filtered and washed five times with de-ionized water and dried in a vacuum at 80 °C for 12 h.

In order to achieve carbon coating, the LiFePO$_4$ precursor was mixed with a glucose solution. This solution was irradiated with ultrasonic waves at room temperature for 1 h and then dried by means of method A (vacuum drying at 80 °C for 12 h) or method B (heating to 80 °C and stirring 3 h) to remove the excess water. The mixture was firstly heated to 250 °C for 5 h and then calcined at 650 °C for 4 h under an Ar/H$_2$ (95/5 v%) gas flow with a heating rate of 2 °C min^{-1}. The obtained samples were correspondingly designated by LF$_{1-x}$Cu$_x$P/C (x=0.01 and 0.03) and LFCu$_x$P/C (x=0, 0.01 and 0.03). The LiFePO$_4$ precursor dried using method B was denoted SLFCu$_{0.01}$P/C.

2.2. Physical characterization

The crystalline phases of the prepared samples were analyzed by powder X-ray diffraction (XRD, Bruker AXS, Germany) using Cu Kα radiation (λ=1.5406 Å) over a scanning range of 10–70° at 2°min^{-1}. The morphology of the powders was observed by scanning electron microscopy (SEM, JEOL JSM-6701F, Japan). The microstructure of carbon layer was observed by transmission electron microscope (TEM, *FEI Tecnai G^{2}20 S-Twin, USA*). The residual carbon amount, measured by elemental analyzer (EA, Vario EL III, Germany), was about 4 wt%.

2.3. Electrochemical measurements

The electrochemical performance of samples was measured by using CR2032 coin cells. The cathode was prepared by mixing the active materials, conductive carbon (Super P) and poly-vinylidene fluoride (PVDF) as binder agent in a weight ratio of 80:10:10 in n-methyl-2-pyrrolidone (NMP) solvent, to form black slurry. The slurry was coated onto a thin Al foil (15 μm), and dried in a vacuum at 110 °C for 12 h. The active materials loaded on the single circular electrode (13 mm in diameter) were around 3–3.7 mg. The electrolyte was 1 M LiPF6/EC+DEC+EMC (1:1:1, v/v/v). Lithium metal and Celgard 2400 film were used as the anode and separator, respectively. The cells were assembled in an argon-filled glove box. The galvanostatic charge/discharge measurement of the assembled cells was carried out on a battery testing system (LAND CT2001A, China) at different current densities (1 C=170 mA h g^{-1}) between 2.5 V and 4.2 V at room temperature. The cyclic voltammetry (CV) curves were conducted using an electrochemical workstation (CHI-611D, China) in the range of 2.4–4.2 V at 0.1 mV s^{-1} scan rate.
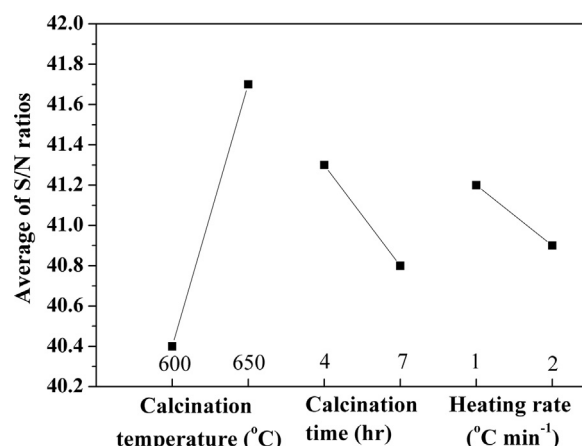
Table 3
Response of S/N ratios and contribution of each factor.

Factors	Level 1	Level 2	SS$_F$	ρ$_F$ (%)
Calcination temperature (°C)	40.4	41.7	1.54	80.2
Calcination time (hr)	41.3	40.8	0.31	16.1
Heating rate (°C min^{-1})	41.2	40.9	0.07	3.7
Sum			1.92	100

Fig. 1. Response of every factor at each level.

2.4. Taguchi method

In this study, we used the Taguchi method to efficiently find out the suitable calcination conditions. The influence of calcination conditions on the specific capacity of LiFePO$_4$ was studied by using the L4 Taguchi orthogonal array. Calcination temperature, calcination time, and heating rate, were selected as controllable factors and each factor had two levels. The levels of the selected factors are shown in Table 1. With Taguchi's method, the analysis can reveal one of the following three conditions: larger-the-better, smaller-the-better, or nominal-the-best. In this study, the specific capacity of LiFePO$_4$ is the larger-the-better. Therefore, the signal-to-noise (S/N ratio) is given by Eq. (1)

$$S/N = -10 \log \left[\frac{1}{n} \sum_{i-1}^{n} \frac{1}{yi^2} \right] \tag{1}$$

where yi is the specific capacity of each sample at 0.5 C and n is the number of reiterations under the same calcination conditions.

Analysis of variance (ANOVA) was used to determine the contribution of each factor on the specific capacity, ρ_F, as given by Eq. (2)

$$\rho_F = (SSF/SST) \times 100\% \tag{2}$$

where SS$_T$ signifies the total sum of SS$_F$. The factorial sum of squares (SS$_F$) is given by Eq. (3)

$$SS_F = 2 \times [(A_1 - \overline{S})^2 + (A_2 - \overline{S})^2] \tag{3}$$

Table 2
The experimental parameters, specific capacity and corresponding S/N ratios of samples.

Test	Samples	Factors			Specific capacity (m Ah g^{-1})				S/N
		T	t	H	0.1 C	0.5 C	1 C		
Test 1	LFP/C-600-4-1	600	4	1	133	110	96		40.8
Test 2	LFP/C-600-7-2	600	7	2	122	100	80		40.0
Test 3	LFP/C-650-4-2	650	4	2	133	123	113		41.8
Test 4	LFP/C-650-7-1	650	7	1	132	119	100		41.5
								Mean	41.0

H: Heating rate; T: Calcination temperature; t: Calcination time.