Well-dispersed multi-doped LiFePO₄/C composite with excellent electrochemical properties for lithium-ion batteries

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Multi-doped LiFePO₄/C composites are synthesized from FeC₂O₄, Li₂CO₃ and electroless nickel plating wastewater. Scanning electron microscopy in combination with laser particle size analysis, reveals that the material prepared at 700 °C for 10 h consists of narrow-distribution well-dispersed submicron particles. The XRD refinement corroborates that Ni, Co and Mn have been successfully embedded into LiFePO₄. The electrochemical measurements show that the sample gives the first discharge specific capacities of 167.5, 152.3 and 116.8 mAh·g⁻¹, with the capacity retentions of 99.1%, 98.5% and 97.9% after 300 cycles at 25, 0 and -20 °C, respectively.

Keywords: Lithium-ion battery; Lithium iron phosphate; Multi-doping; Low-temperature electrochemical properties

1. INTRODUCTION

In recent years lithium iron phosphate (LiFePO₄) used for lithium-ion batteries (LIBs) displays exuberant vitality owing to its desirable discharge capacity, outstanding cycling performance, little environmental pollution, low cost and good safety [1-3]. Although LiFePO₄ is notorious for its poor electronic conductivity and low lithium-ion diffusivity, it seems that these problems can be satisfactorily solved through doping with alien ions [4-9], coating conductive carbon [10-13], decreasing particle size and optimizing particle morphology and dispersity [14-19]. Among these above-mentioned strategies, carbon coating has been demonstrated to be efficacious for enhancing the surface electronic conductivity, reducing particle size and suppressing the oxidation of Fe²⁺ to Fe³⁺ during high-temperature calcination. And it is generally recognized that carbon layers generated in situ implement much better than preexisting carbons [20]. In addition, the electrochemical properties of cathode materials are tremendously affected by their morphology, particle size and distribution[21-25]. Especially, the spherical or sphericallike materials show superior electrochemical performance to irregular powders owing to their better fluidity characteristics and higher volumetric energy density [26]. Hence, the spherical or spherical-like LiFePO₄with good dispersity gets increasing attention.

From the perspective of circular economy, we previously developed an electroless nickel plating solution characterized by zero-emission, which is composed of Ni(H₂PO₂)₂, H₃PO₂, CH₃COOLi, citric acid (C₆H₈O₇) and maleic acid (C₄H₄O₄) [27]. Ni-Co-Mn doped LiFePO₄/C composites with excellent electrochemical properties were synthesized by using the spent plating bath as all sorts of element sources including P, C, Ni, Co and Mn, Fe₂O₃ [28-29] or iron powder [30] as the iron source. Here, we extended our research on the preparation process optimization and performance characterization of multi-doped LiFePO₄/C using the spent plating bath, ferrous oxalate and lithium carbonate as raw materials. The as-prepared optimum sample is comprised of narrow-distribution well-dispersed grape-like submicron particles and displays outstanding low-temperature electrochemical properties.

2. EXPERIMENTAL

2.1 Sample preparation

As we reported in the previous studies [27-28], the electroless nickel plating wastewater consists of 5.4349 mol·L⁻¹ phosphorus, 1.6977 mol·L⁻¹ carbon, 0.4200 mol·L⁻¹ lithium, 0.0880 mol·L⁻¹ nickel, 0.0126 mol·L⁻¹ iron, 0.0008 mol·L⁻¹ cobalt and 0.0006 mol·L⁻¹ manganese. According to a molar ratio of 1.05 : 1 : 1 for Li : M (Σ Fe, Ni, Co and Mn) : P, the stoichiometric amounts of Li₂CO₃ and FeC₂O₄·2H₂O were added into 0.1 L waste solution. The precursor was obtained through ball-milling the mixture at 500 rpm for 5 h. The Ni-Co-Mn doped LiFePO₄/C composites were yielded through calcinating the precursor in nitrogen atmosphere under different process conditions.

2.2 Characterization

The thermal decomposition behavior of the as-prepared precursor was measured using thermogravimetric and differential scanning calorimeter (TG-DSC, NETZSCH STA 449C) with a heating speed of 10 $^{\circ}C \cdot min^{-1}$ between 25 and 850 $^{\circ}C$ in flowing nitrogen. Mastersizer 2000 particle size analyzer, scanning electron microscopy (SEM, JEOL JSM-6360LV) and energy dispersive X-ray spectroscopy (EDS) were used to observe the particle size distribution, morphology and elemental composition of the sample, respectively. The structure of the sample was examined by X-ray diffraction (XRD, D/max-r A type Cu K α) and XRD result was refined with Rietveld method using Rietan-2000 program. The carbon content and other element amounts of the sample were detected by HF infrared C-S analyzer (HIR 944), inductively coupled plasma atomic emission spectroscopy (ICP-AES, Optima 4300DV), separately.

After a positive electrode was made from 80 wt.% as-synthesized composite, 10 wt.% PVDF binder and 10 wt.% acetylene black on aluminium foil, a lithium foil, a polyethylene film (Celgard 2400) and a solution of 1 mol·L⁻¹ LiPF₆ dissolved in EC-DMC-EMC (1:1:1, volume ratio) were chosen as a

counter electrode, a separator and an electrolyte, respectively. These components were assembled into coin-type cells (CR2025) in a glove box full of argon. Then, charge-discharge tests were carried out within the potential range of 2.5-4.1 V (vs. Li/Li⁺) at 0.2 *C* at different temperature on a battery test system (LAND CT2001A). Cyclic voltammetry (CV) measurements were performed at a scan rate of 0.1 mV·s⁻¹ between 2.5 and 4.2 V (vs. Li/Li⁺) by using an electrochemical workstation (AUTOLAB PGSTAT302N).

3. RESULTS AND DISCUSSION

3.1 Thermal analysis

Fig. 1 displays TG/DSC curves of the precursor, which is similar to those of the precursors obtained from the electroless nickel plating wastewater, lithium carbonate and ferric oxide [29] or iron powder [30]. The biggest difference lies in the last stage between 350 °C and 530 °C where the TG profile exhibited consecutive weight loss, accompanying with the endothermic peak at 355.38 °C and the exothermic peak at 433.96 °C in the DSC curve. This may be caused by the decomposition of ferrous oxalate and the formation of lithium iron phosphate, separately [31]. The main plausible equations may be concluded as follows.

 $FeC_2O_4 \rightarrow FeO+CO+CO_2(1)$

 $2FeO + 2H_3PO_4 + Li_2CO_3 \rightarrow 2LiFePO_4 + 3H_2O (gas) + CO_2(2)$

 $Li_2H_2P_2O_7 + 2FeO \rightarrow 2LiFePO_4 + H_2O(gas)(3)$

After 530 $^{\circ}$ C, no weight loss and endothermic/exothermic peaks can be found, indicating the completion of the whole reaction.



Figure 1. TG/DSC curves of the precursor obtained through ball-milling the mixture of electroless nickel plating wastewater, Li₂CO₃ and FeC₂O₄ at 500 rpm for 5 h.

3.2 SEM studies

Fig. 2 shows SEM images of powders sintered at 600-750 °C for 10 h. When the precursor was calcined at 600 °C, the obtained powders possess mono-dispersed grape-like morphology, accompanying with scaly appearance. As the temperature rose to 700 °C, the material is comprised of well-dispersed grape-like particles with the size of 200-400 nm. With the continuous increase of the temperature, partial particles combine with one another to form rocky granules with larger size. The SEM images of samples sintered at 700 °C for 5-12.5 h are compared in Fig. 3. As the calcination time is less than 7.5 h, the morphology of the sample is irregular with the simultaneous emergence of grape-like and scaly particles. The powders prepared for 10 h own high dispersity, uniform size and smooth grape-like morphology. Prolonging further the calcination time leads to increasing tendency of the particle size and the destruction of uniformity. The formation of the mono-dispersed grape-like submicron particles may be contributed to the effects of steric hindrance between citric acid molecules and lattice distortion resulting from the occupation of nickel, cobalt and manganese in the site of iron [28, 32].



Figure 2. SEM images of Ni-Co-Mn doped LiFePO₄/C composites calcined at 600-750 °C for 10 h.



Figure 3. SEM images of Ni-Co-Mn doped LiFePO₄/C composites calcined at 700 °C for 5-12.5 h.

3.3 XRD studies

Fig. 4(a) presents the XRD patterns of powders prepared at 600-750 °C for 10 h. Obviously, these samples fit well with an ordered orthorhombic structure (the space group *Pnma*), without any trace for the appearance of impurity phase or amorphous carbon. However, the diffraction peaks of the sample calcined at 600 °C are broader than those of other samples, suggesting the crystallization is imperfect at 600 °C. With the increase of the temperature, all characteristic peaks become sharper and stronger, indicating the enhanced crystallinity of the samples. The XRD patterns of samples synthesized at 700 °C for 5-12.5 h are displayed in Fig. 4(b). All dominant diffraction lines of these samples can be indexed as an olivine phase, and no evidence for impurity phase or amorphous carbon can be found. The crystallinity of the samples becomes increasingly better with the extension of the calcination time, characterized by the increasing sharpness of the diffraction peaks of the samples.



Figure 4. XRD patterns of Ni-Co-Mn doped LiFePO₄/C composites calcined at 600-750 °C for 10 h (a) and at 700 °C for 5-12.5 h (b).

3.4 Charge-discharge analyses

Fig. 5(a) and (b) depict initial charge-discharge curves of samples sintered at various temperatures for 10 h and at 700 °C for different time, seperately. The first discharge specific capacities data obtained from Fig. 5 are listed in Table 1. All of the curves include a charge platform (~3.5 V) and a discharge plateau (~3.4 V), corresponding to the lithium-ion deintercalation and intercalation reactions, respectively, which are the typical characteristic of lithium iron phosphate. Among all of the samples, the material yielded at 700 °C for 10 h delivers the highest initial discharge capacity of 167.5 mAh·g⁻¹ at a rate of 0.2 *C* and the best cyclic performance with the capacity retention of 99.7% after 50 cycles (Fig. 5(c)-(d) and Table 1). These results coincide with the XRD data and the SEM analyses, indicating that perfect crystallinity, uniform size and well-dispersed grape-like morphology of the submicron particles are beneficial to the optimization of electrochemical properties.





Figure 5. The first charge-discharge profiles of Ni-Co-Mn doped LiFePO₄/C composites prepared at 600-750 °C for 10 h (a) and at 700 °C for 5-12.5 h (b) tested at 0.2 *C* at 25 °C. Cycle performance of Ni-Co-Mn doped LiFePO₄/C composites prepared at 600-750 °C for 10 h (c) and at 700 °C for 5-12.5 h (d) tested at 0.2 *C* at 25 °C.

Table 1. The first discharge specific capacities and capacity retentions of Ni-Co-Mn doped LiFePO₄/C composites prepared under different conditions.

Reaction condition	Discharge specific capacity / $(mAh \cdot g^{-1})$	Capacity retention / %
600 °C, 10 h	153.9	90.7
650 °C, 10 h	162.1	94.3
700 °C, 10 h	167.5	99.7
750 °C, 10 h	163.7	96.7
700 °C, 5 h	154.4	97.6
700 °C, 7.5 h	165.4	99.0
700 °C, 10 h	167.5	99.7
700 °C, 12.5 h	162.6	98.6

3.5 Characterization of the optimum sample

From the above analyses of XRD patterns, SEM images and charge-discharge properties, it can be concluded that the material synthesized at 700 °C for 10 h shows the best comprehensive performance. Thus, the following characterization is concerned with the optimum sample. The EDS measurement in Fig. 6(a) illustrates the existence of C, O, P, Fe, Mn, Co and Ni. ICP-AES results demonstrate the molar ratio for Li : Fe : Ni : Co : Mn : P is 1.0092 : 0.9701 : 0.0294 : 0.0003 : 0.0003 : 1.0001, close to the chemical formula LiFe_{0.97}(Ni_{0.98}Co_{0.01}Mn_{0.01})_{0.03}PO₄. The content of the residual carbon is around 2.36 wt.% measured by the C-S analyzer, which mainly originates from the thermal decomposition of citric acid in the spent electroless nickel plating bath. The laser particle size analysis in Fig. 6(b) shows that the particle size distribution is concentrated in 1-20 µm and the average size is 4.987 µm.

Fig. 6(c) gives more information about the lattice parameters of the optimum sample through refining the XRD pattern. The observed pattern matches well with the calculated pattern, with the satisfactory reliability factors of $R_{wp} = 7.33\%$ and $R_p = 5.69\%$. Structural parameters listed in Table 2

indicate that the fitting result is desirable when nickel, cobalt and manganese were supposed to occupy iron site. The doping amounts of occupancy fitted by the quantitative analysis of refinement are consistent with the ICP-AES results.



Figure 6. EDS (a), particle size distribution curve (b) and Rietveld refinement of XRD pattern (c) for the Ni-Co-Mn doped LiFePO₄/C composite synthesized at 700 °C for 10 h.

The unit cell parameters from the refinement are a = 1.0315(1) nm, b = 0.6002(7) nm, c = 0.4702(3) nm, V = 0.2911(6) nm³. This cell volume in 0.2900-0.2914 nm³ is regarded as decent degree of perfect cation order in lithium iron phosphate [33-34]. Therefore, the refinement result confirms that theses elements including nickel, cobalt and manganese have been successfully embedded into lithium iron phosphate. The multi-doping into LiFePO₄ may induce cation-deficient which can make a contribution to enhancing the electrochemical properties of the material [4].

Table 2. Cell parameters gained from Rietveld refinement of XRD pattern for the Ni-Co-Mn doped LiFePO₄/C composite synthesized at 700 °C for 10 h. Space group: *Pnma*. Lattice constant: a = 1.0315(1) nm, b = 0.6002(7) nm, c = 0.4702(3) nm, V = 0.2911(6) nm³.

Atom	Site	X	Y	Ζ	Occupancy
Li	4a	0	0	0	1.0041(4)
Fe	4c	0.2828(4)	0.2504(0)	0.9728(7)	0.9702(1)
Ni	4c	0.2828(4)	0.2504(0)	0.9728(7)	0.0297(8)
Co	4c	0.2828(4)	0.2504(0)	0.9728(7)	0.0003(5)
Mn	4c	0.2828(4)	0.2504(0)	0.9728(7)	0.0003(1)
Р	4c	0.0945(9)	0.2500(0)	0.4179(9)	1
01	4c	0.0959(1)	0.2504(1)	0.7523(5)	1
O2	4c	0.4568(3)	0.2504(1)	0.2082(2)	1
O3	8d	0.1658(1)	0.0455(8)	0.2790(1)	1

Fig. 7(a) and (b) compare the initial charge-discharge profiles and cycle performance of the optimum sample at the rate of 0.2 *C* at 25, 0 and -20 $^{\circ}$ C, respectively. It can be obviously discovered that the electrochemical polarization enlarges with the decrease of the temperature. The charge and discharge specific capacities decline with lowering the temperature. The initial discharge specific capacities of the optimum sample are 167.5, 152.3 and 116.8 mAh·g⁻¹, with the capacity retentions of 99.1%, 98.5% and 97.9% after 300 cycles at the temperatures of 25, 0 and -20 $^{\circ}$ C, separately. As shown in Table 3, the Ni-Co-Mn doped LiFePO₄/C composite synthesized at 700 $^{\circ}$ C for 10 h apparently shows superior electrochemical properties to other similar cathode materials for lithium ion batteries. This may be contributed to the synergistic effect of Ni-Co-Mn co-doping, in-situ carbon coating, submicron dispersion and special morphology.



Figure 7. Initial charge-discharge curves (a) and cycling performance (b) of the Ni-Co-Mn doped LiFePO₄/C composite synthesized at 700 °C for 10 h at 25, 0 and -20 °C.

Table 3. Comparison of electrochemical properties of the Ni-Co-Mn doped LiFePO₄/C composite synthesized at 700 °C for 10 h with other similar cathode materials for lithium ion batteries.

Samula	Electrochemical propert	Deference		
Sample	Initial discharge capacity / $(mAh \cdot g^{-1})$ Capacity retention		Kelerence	
Well-dispersed grape-like 200-	167.5 (0.2 <i>C</i> , 2.5-4.1 V, 25 °C)	99.1% (300 times)		
400 nm Ni-Co-Mn doped	152.3 (0.2 <i>C</i> , 2.5-4.1 V, 0 ℃)	98.5% (300 times)	This paper	
LiFePO ₄ /C	116.8 (0.2 <i>C</i> , 2.5-4.1 V, −20 °C)	97.9% (300 times)		
	165.1 (0.1 <i>C</i> ,2.5-4.1 V, 25 ℃)	No data		
0 1 200 500 N' C M	158.8 (0.5 <i>C</i> ,2.5-4.1 V, 25 °C)	No data	o data 100 times) [30] o data	
donad LiFePO//C	152.0 (1.0 <i>C</i> ,2.5-4.1 V, 25 °C)	98.9% (100 times)		
doped Ell'el 04/C	145.8 (2.0 <i>C</i> ,2.5-4.1 V, 25 °C)	No data		
	133.1 (5.0 <i>C</i> ,2.5-4.1 V, 25 °C)	No data		
	170.0 (0.2 <i>C</i> , 2.0-4.2 V, 40 °C)	No data		
Blocky 100-200 nm	166.4 (0.2 <i>C</i> , 2.0-4.2 V, 20 °C)	No data	[25]	
LiFePO ₄ /C	144.2 (0.2 <i>C</i> , 2.0-4.2 V, 0 °C)	No data	[33]	
	100.5 (0.2 <i>C</i> , 2.0-4.2 V, -20 °C)	No data		
	115.5 (0.1 <i>C</i> , 2.5-4.3 V, 25 °C)	26.1% (40 times)		
Spherical 100-300 nm LiFePO ₄	77.5 (0.1 <i>C</i> , 2.5-4.3 V, 0 °C)	45.2% (40 times)	[36]	
	69.8 (0.1 <i>C</i> , 2.5-4.3 V, -20 °C)	64.5% (40 times)		
Irregular Ni-Mn doped	165.2 (0.1 <i>C</i> , 2.3-4.2V, 25 °C)	98.4% (100 times)		
LiFePO ₄ /C	146.5 (1 <i>C</i> , 2.3-4.2V, 25 °C)	No data		
Image and a Ni day and LiFaDO /C	162.2 (0.1 <i>C</i> , 2.3-4.2V, 25 °C)	96.0% (100 times)	[37]	
Irregular Ni doped LiFePO ₄ /C	143.1 (1 <i>C</i> , 2.3-4.2V, 25 °C) No data			
Imperator Mandamed I E-DO /C	162.4 (0.1 <i>C</i> , 2.3-4.2V, 25 °C)	93.6% (100 times)		
Integular Min doped LIFePO ₄ /C	144.7 (1 <i>C</i> , 2.3-4.2V, 25 °C)	No data		
	155.3 (0.1 <i>C</i> , 2.5-4.2V, 25 °C)	99.5% (20 times)		
	147.8 (0.2 C, 2.5-4.2V, 25 °C) 99.1% (20 tim		[20]	
Irregular Co doped LIFePO4/C	137.6 (1.0 <i>C</i> , 2.5-4.2V, 25 °C)	98.8% (20 times)	[38]	
	127.3 (3.0 <i>C</i> , 2.5-4.2V, 25 °C)	98.8% (20 times)		

To further elucidate the charge-discharge behavior of Ni, Co and Mn co-doped LiFePO₄/C, CV measurements for the optimum sample were carried out. Fig. 8(a) demonstrates the 1st CV curves at 25, 0 and -20 $^{\circ}$ C. There exist an oxidation peak at about 3.53 V and a reduction peak at around 3.32 V at all temperatures, corresponding to the extraction and insertion of lithium-ions from/into the

LiFePO₄/FePO₄, respectively. Both the oxidation and reduction peak intensities display a decrease with lowering the temperature, implying the decline of the specific capacity on account of low electrolyte conductivity at low temperature [39]. The 1st, 50th and 100th CV curves at 25 °C in Fig. 8(b) corroborate the excellent cyclic performance of the optimum sample by the perfect symmetry and minimal peak potential difference of 0.21 V, as well as slight decrease of peak current with the increasing scanning cycles.



Figure 8. The 1st CV curves at 25, 0 and -20 °C (a) and the 1st, 50th and 100th CV curves at 25 °C (b) of the Ni-Co-Mn doped LiFePO₄/C composite synthesized at 700 °C for 10 h.

4. CONCLUSIONS

Ni-Co-Mn doped LiFePO₄/C composites have been successfully synthesized from FeC₂O₄, Li₂CO₃ and electroless nickel plating wastewater. The material synthesized at 700 °C for 10 h shows excellent electrochemical performance. At 25, 0 and -20 °C, the material delivers first discharge specific capacities of 167.5, 152.3 and 116.8 mAh·g⁻¹, with the capacity retentions of 99.1%, 98.5% and 97.9% after 300 cycles, respectively. The outstanding room-temperature and low-temperature electrochemical properties of the material may be attributed to its ion doping, in-situ carbon coating, well-dispersed grape-like submicron particles.

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