



Short communication

Effects of carbon coating and iron phosphides on the electrochemical properties of LiFePO₄/C

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ARTICLE INFO

Article history:

Received 27 December 2007

Received in revised form 29 February 2008

Accepted 18 March 2008

Available online 22 March 2008

Keywords:

LiFePO₄

Sol–gel method

Rate capability

Carbon coating

Iron phosphides

Specific surface area

ABSTRACT

Carbon coated LiFePO₄ (LiFePO₄/C) with different contents of high electron conductive iron phosphide phase was synthesized by an aqueous sol–gel method in a reductive sintering atmosphere. Different synthesis parameters were used for adjusting the microstructure and phase compositions of the products. The effects of the carbon coating and iron phosphides on the electrochemical properties of the LiFePO₄/C electrodes were studied by means of testing the discharge capacities at rates of 0.1–5C (1C = 170 mAh g⁻¹) and analyzing the CV curves. The results show that carbon coating in a content of 1.5 wt.% derived from the carbon source of ethylene glycol greatly decreases the particle size of LiFePO₄ in one order in the specific surface area, and significantly improves the rate capability of LiFePO₄. The effect of the content of FeP on the capacity of the carbon coated LiFePO₄ was different at different discharge rates. Increasing the content of FeP from 1.2 to 3.7 wt.% slightly decreases the capacity of LiFePO₄/C at low discharge rate (0.1C and 1C), but obviously increases the capacity of LiFePO₄/C when the discharge rate is increased to 5C. For the carbon free sample, even it also has 1.8 wt.% FeP, it still possesses poor capacity due to the large particle size of LiFePO₄ and the lack of conductivity. And too much iron phosphides lowers the discharge capacity of the electrode since they are inert for the deinsertion/insertion of lithium ion.

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1. Introduction

Olivine structured lithium iron phosphate, LiFePO₄, is a promising alternative cathode material for lithium ion battery due to its advantages of low cost, nontoxic properties and safety, etc. Deinsertion/insertion of lithium ion (Li⁺) of LiFePO₄ occurs at a potential value of ca. 3.45 V versus Li⁺/Li, possessing a high theoretical specific capacity of 170 mAh g⁻¹. Unfortunately, the low intrinsic electronic conductivity of LiFePO₄ has been an obstacle for its practical applications. Effective approaches have been introduced to improve the poor rate performance of LiFePO₄, including creating conductive carbon coatings on the particles [1], minimizing the particle size [2,3] and doping with supervalent cations [4].

Yang and Xu [5] synthesized LiFePO₄/C composite of particle size of 200–300 nm by a sol–gel method, and the LiFePO₄ particles were coated with carbon formed in situ in a content of 1–4 wt.%. The composite demonstrated specific capacities of around 150 mAh g⁻¹ at discharge rates of either C/5 or 2C (1C = 170 mAh g⁻¹). A LiFePO₄/C composite prepared via a solid-state route with specific surface area of 24.1 m² g⁻¹ was reported delivering a reversible capacity of 115 mAh g⁻¹ at 5C [6]. Carbon free LiFePO₄ with particle size

centered on ca. 140 nm prepared by a method of direct precipitation of LiFePO₄ under atmospheric pressure was also reported showing a specific capacity high as 147 mAh g⁻¹ at 5C [2]. Carbon coating of the LiFePO₄ particle can possess an increase of the conductive connection, and the decrease of the LiFePO₄ particles can shorten the diffusion path of Li⁺, which can all promote the rate performance.

It was found that the iron phosphides could improve the rate performance of LiFePO₄ in the study of doping Li with Zr, Nb, Mg, Ti [4], nano-network of metallic compounds such as Fe₂P formed during the doping process led to an increase in the conductivity of the bulk composite at seven orders of magnitude. Additionally, it was reported that iron phosphides were prone to form at high sintering temperatures [7,8] and reductive sintering atmospheres [9].

In this work, carbon coated LiFePO₄ was prepared by an aqueous sol–gel method. Reductive sintering atmosphere (N₂ containing 5 vol.% H₂) was used in order to avoid the oxidization of Fe²⁺ and generate iron phosphides. Different synthesis parameters, including the addition of carbon source, the content of iron precursor and sintering times, were applied to optimize the microstructures of the LiFePO₄ products. The effects of the carbon coating and the iron phosphides on the electrochemical properties of LiFePO₄ were investigated, and the mechanism of the effects was also discussed.

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Table 1

The proportion of the constituents and the sintering parameters of the LiFePO₄ samples

Samples	Constituents (molar ratio)	Sintering regime
A	Li ⁺ :Fe ²⁺ :PO ₄ ³⁻ = 1:1:1	700 °C × 10 h
B1	Li ⁺ :Fe ²⁺ :PO ₄ ³⁻ :E.G. ^a = 1:1:1:2	700 °C × 10 h
B2	Li ⁺ :Fe ²⁺ :PO ₄ ³⁻ :E.G. = 1:1:1:2	700 °C × 14 h
C	Li ⁺ :Fe ²⁺ :PO ₄ ³⁻ :E.G. = 1:1.1:1:2	700 °C × 10 h

^a E.G. is the abbreviation of ethylene glycol.

2. Experimental

The LiFePO₄ cathode material was prepared by a sol-gel method by using constituents of FeC₂O₄·2H₂O (ferrous oxalate), LiNO₃ (lithium nitrate) and NH₄H₂PO₄ (dihydrogen ammonium phosphate). Ethylene glycol was applied as carbon source. The proportion of the constituents and the sintering parameters used for the synthesis of LiFePO₄ based products were presented in Table 1. Distilled water was used as solvent for sample A and aqueous solution of ethylene glycol was used as solvent for samples B1, B2 and C. The resulting solutions were stirred at 110 °C until they changed to gels. Subsequently, the gels were dried at 120 °C for 24 h and then sintered in a reductive atmosphere of nitrogen containing 5 vol.% of hydrogen at 700 °C for different hours as listed in Table 1. The synthesized products were ground with a mortar and pestle to powders for microstructural characterization and electrochemical property testing.

The phase identification of the synthesized products was carried out by X-ray diffraction (XRD, Thermo ARL X'TRA), using Cu K α radiation ($\lambda = 1.54 \text{ \AA}$). The XRD data were collected by step-scanning method with a step interval of 0.02° and a count time of 1 s per step, a software of MDI Jade 6.0 was used for the analysis of the lattice parameters of LiFePO₄ and the phase abundance of the products. The surface morphologies of the samples were observed by a field emission scanning electron microscope (SEM, Sirion-100, Philips-FEI). The specific surface area of the particles of the products was measured by the BET (Brunauer–Emmett–Teller) method (Autosorb-1-C, Quantachrome). The carbon content of the samples was analyzed by a Flash EA1112 (ThermoFinnigan) element analyzer. The microstructural characteristic of the carbon coating was analyzed by Raman spectra.

Laminated cathode was prepared by spreading the *N*-methyl methyl-pyrrolidone slurry containing 83 wt.% active material (the synthesized product), 5 wt.% Kynar poly vinylidene fluoride (PVDF) binder (Atofina, USA), 6 wt.% synthetic graphite (Super P, Timcal Ltd.) and 6 wt.% acetylene black onto an aluminum foil current collector, and then dried at 120 °C for 16 h. The active materials loaded on the current collector of a surface area of 1.54 cm² was around 3.5 mg. Coin cells of CR2025 type with lithium metal as anode and a solution of 1 M LiPF₆ in 1:1 ethylene carbonate/dimethyl carbonate (EC/DMC) as electrolyte were assembled in an argon-filled glove box.

Cells were cycled galvanostatically at current rates of 0.1C, 1C and 5C (1C is equivalent to 170 mAh g⁻¹), respectively, with a voltage range of 2.5–4.2 versus Li/Li⁺. All phases of the synthesized

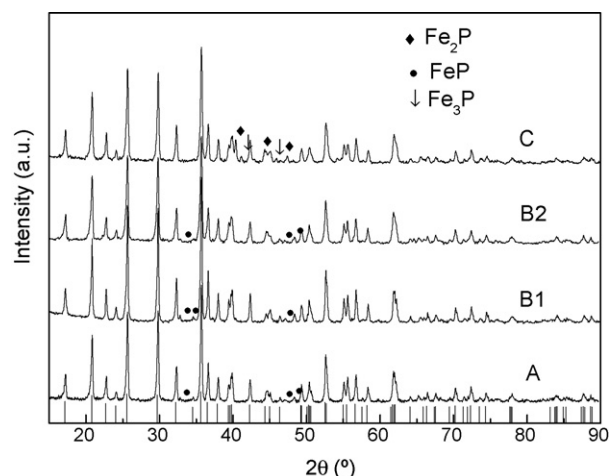


Fig. 1. XRD patterns of LiFePO₄ products prepared from different synthesis conditions.

products were taken as active materials in the calculation of the specific discharge capacity of the LiFePO₄ samples. Cyclic voltammograms (CV) of the cells were measured on a Solartron 1287 potentiostat at a scan rate of 0.1 mV s⁻¹. All of the electrochemical tests were performed at room temperature.

3. Results and discussion

The XRD patterns of the products prepared by different synthesis parameters are displayed in Fig. 1. LiFePO₄ (JCPDS83-2092) is the main phase formed in the products, besides, illegible iron phosphides peaks appear in the diffraction patterns. The phase abundances, the carbon content and the specific surface area of the products are listed in Table 2. The generation of iron phosphides can be ascribed to the reduction of phosphate and iron during the sintering process by the reductive atmosphere used (N₂ + 5% H₂). As can be known from Tables 1 and 2, increase in sintering time (from 10 to 14 h) slightly increases the content of FeP (from 1.2 to 3.7 wt.%) when stoichiometric iron to lithium for LiFePO₄ was used, further, the specific surface area is slightly decreased. Iron rich iron phosphides, Fe₂P and Fe₃P, formed when superstoichiometric iron for LiFePO₄ was used (sample C). The lattice constants and the cell volume of LiFePO₄ prepared by different synthesis parameters are listed in Table 3, the goodness of fitting (χ^2) is around 3.0–3.4. Table 3 shows that the lattice constants of LiFePO₄ prepared by the different synthesis parameters are approximately similar, indicating that the addition of ethylene glycol as carbon source, the contents of iron precursor and sintering times in the present range had no obvious effect on the crystal structure of LiFePO₄ itself.

SEM images of the LiFePO₄ samples are shown in Fig. 2(a)–(d). Combining Table 2 and Fig. 2, it can be clearly known that the particle size of the carbon free LiFePO₄ prepared from gel without ethylene glycol is much larger than that of the carbon coated LiFePO₄ particles. The specific surface areas of the carbon coated

Table 2

The microstructural characteristics of the LiFePO₄ products

Samples	Phase abundance of the products (wt.%)				Carbon content (wt.%)	Surface area (m ² g ⁻¹)
	FeP	Fe ₂ P	Fe ₃ P	LiFePO ₄		
A	1.8			98.2	0	0.4
B1	1.2			97.4	1.4	9.7
B2	3.7			94.8	1.6	8.4
C		8.9	6.0	83.5	1.6	11.8

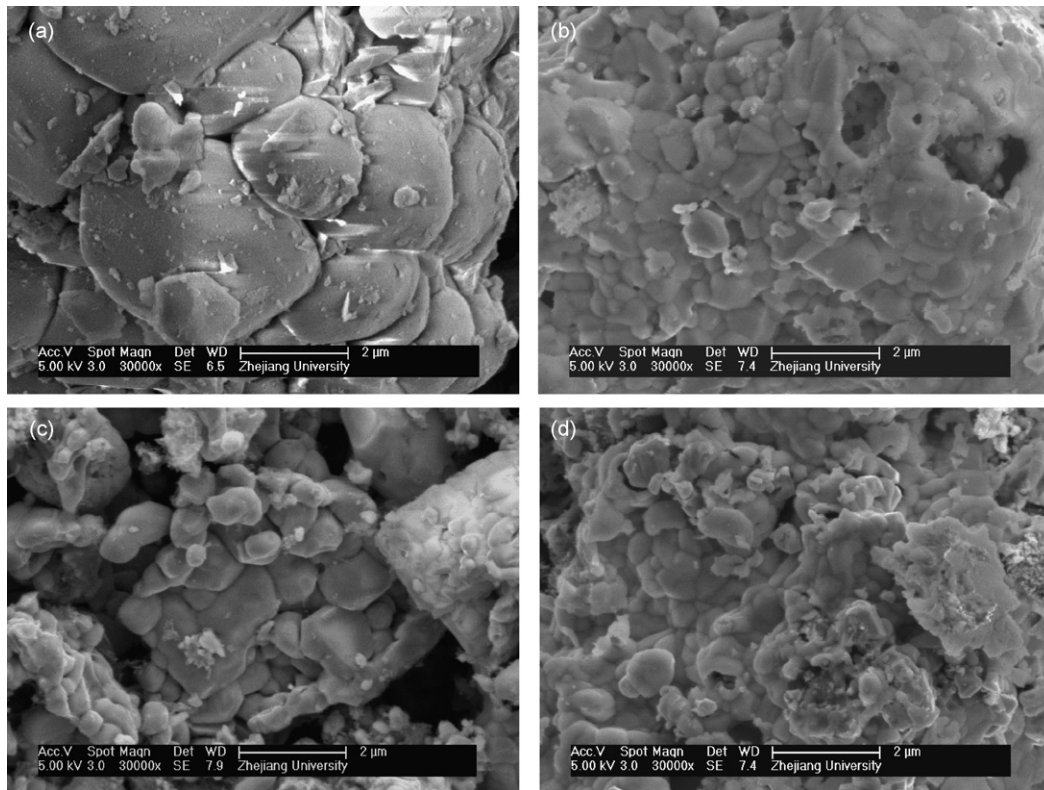


Fig. 2. SEM images of the LiFePO_4 products: (a) sample A, carbon free; (b) sample B1, with carbon coating, 10 h of sintering, stoichiometric iron ion for LiFePO_4 ; (c) sample B2, with carbon coating, 14 h of sintering, stoichiometric iron ion for LiFePO_4 ; (d) sample C, with carbon coating, 10 h of sintering, superstoichiometric iron ion for LiFePO_4 .

Table 3
Lattice parameters of LiFePO_4 prepared from different synthesis parameters

Samples	Lattice parameters (Å)			Cell volume (Å ³)
	<i>a</i>	<i>b</i>	<i>c</i>	
A	10.322	6.004	4.693	290.9
B1	10.319	6.004	4.692	290.7
B2	10.323	6.006	4.693	291.0
C	10.322	6.005	4.695	291.0

LiFePO_4 particles (ca. $10 \text{ m}^2 \text{ g}^{-1}$) are more than one order larger than that of the carbon free LiFePO_4 particles (ca. $0.4 \text{ m}^2 \text{ g}^{-1}$), even the carbon coating just has a content of 1.5 wt.%. The specific surface area of the sample C also slightly increased compared with that

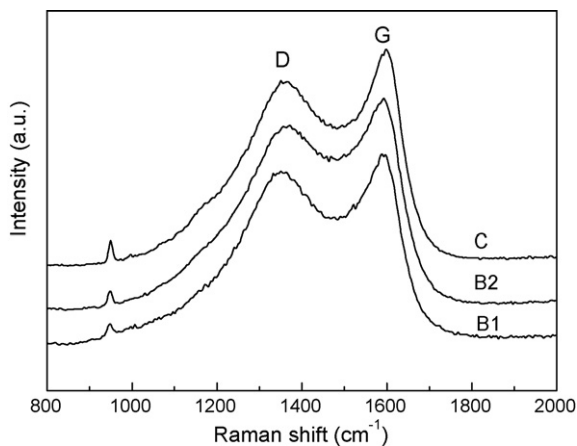


Fig. 3. Raman spectra of the carbon coated LiFePO_4 products. D and G represent the disordered carbon and graphene. The band at 942 cm^{-1} corresponds to the symmetric vibration of the PO_4 group in LiFePO_4 .

of the samples (samples B1 and B2) prepared from stoichiometric iron source addition for LiFePO_4 .

Doeff et al. [10,11] pointed out that the ratio of the disordered/graphene (D/G) of the in situ carbon coating formed from the carbon-containing precursor strongly affected the electrochemical performance of LiFePO_4 . The carbon coating with lower D/G ratios outperformed those with higher D/G ratios. Fig. 3 compares the Raman spectra of the present carbon coated LiFePO_4 products. All Raman spectra consist of a relatively small band at 946 cm^{-1} corresponding to the symmetric PO_4 stretching vibration of LiFePO_4 and two intense broad bands at 1358 and 1595 cm^{-1} corresponding to the D and G bands of the carbon coating of LiFePO_4 , respectively, indicating the carbon coating consists of both disordered carbon

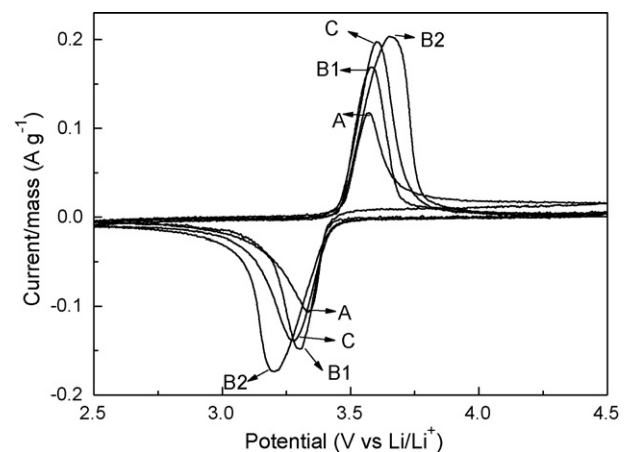


Fig. 4. The CV profiles of the different samples at the scan rate of 0.1 mV s^{-1} .

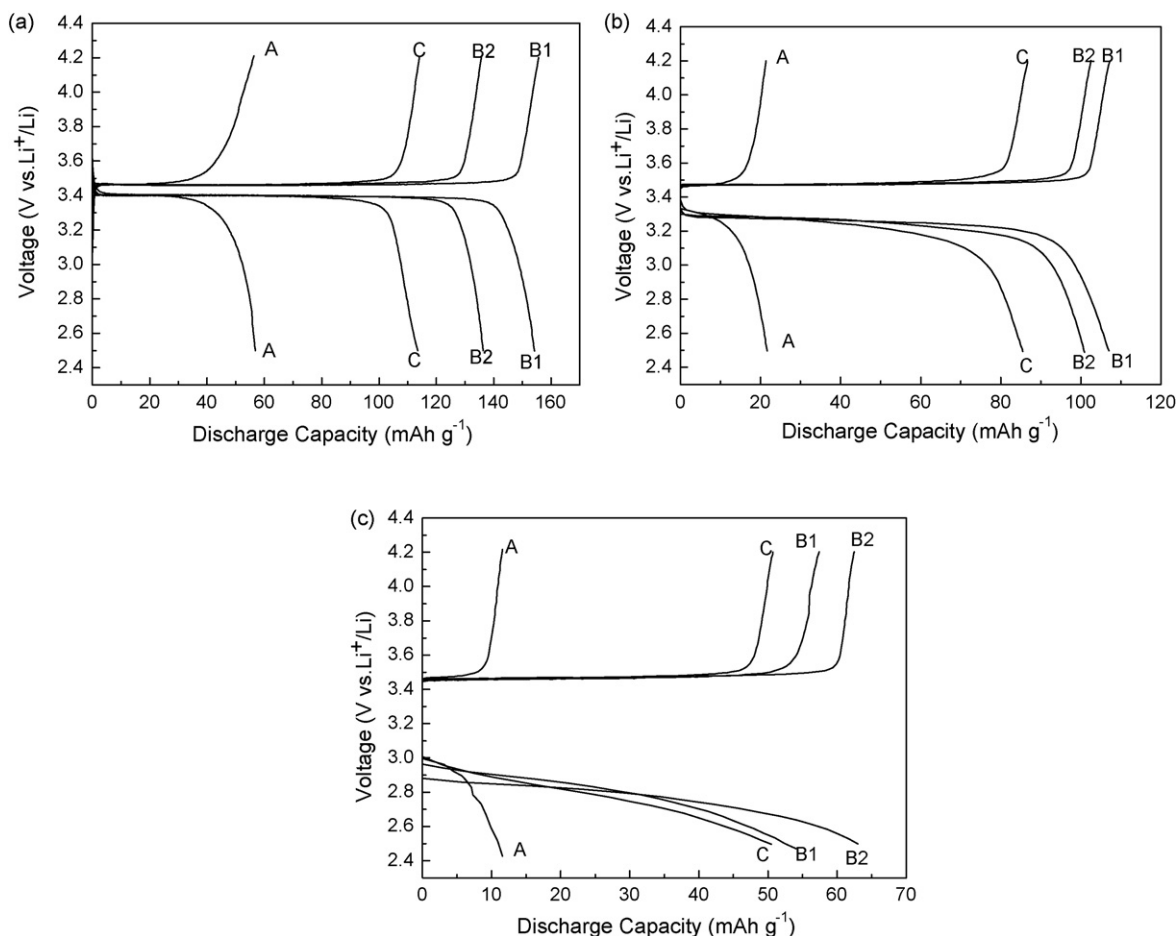


Fig. 5. Charge/discharge profiles of LiFePO₄ samples at discharge rates of (a) 0.1C; (b) 1C; (c) 5C.

and graphene, but the relative intensity of the D and G as well as their shapes do not change much for the different samples. It was reported that the ratio of D/G changed as a function of the sintering temperature [12] and the addition of graphitization catalysts prior to final calcinations also resulted in lower D/G ratios [11]. In our present work, due to the same organic carbon source and sintering temperature applied, the structure of the carbon in the different samples was nearly similar.

Fig. 4 shows the cyclic voltammogram (CV) curves of LiFePO₄ samples at a scan rate of 0.1 mV s⁻¹. Each of the CV curves consists of an oxidation peak and a reduction peak, corresponding to the charge–discharge reaction of the Fe²⁺/Fe³⁺ redox couple. The midpoint between the oxidation and reduction peaks, which corresponds to the open-circuit voltage (OCV) of the LiFePO₄ electrode, is about 3.43 V. In the CV profiles, higher peak current means better electrode reaction kinetics, and consequently, better rate performance of the LiFePO₄ cathode material. Combining Fig. 4 and Table 2, it can be known that though sample A also contained 1.8 wt.% of high electron conductive FeP, however, the large particle size of LiFePO₄ and the lack of conductive carbon coating seriously deteriorated the reaction kinetics. Minimization of particle size of LiFePO₄ and carbon coating significantly improve the reaction kinetics of the LiFePO₄ electrode. Fig. 4 further indicates that suitable increase in the content of FeP from 1.2 wt.% (sample B1) to 3.7 wt.% (sample B2) favors the reaction kinetics of the LiFePO₄/C electrode due to the high electron conductivity of iron phosphides. But too much amount of iron phosphides (16 wt.%) lowers the reac-

tion kinetics of the electrode, due to that iron phosphides are inert for the deinsertion/insertion of lithium ion.

Fig. 5 demonstrates the charge–discharge curves of the samples at different discharge rates. The carbon free sample (sample A) always shows the lowest discharge capacity at any discharge rate. Besides that the carbon coated LiFePO₄ particles are much smaller than the carbon free LiFePO₄ particles, thus having much shorter path for Li ion diffusion during the charge–discharge process, the conductivity of LiFePO₄ was also increased by the carbon coating, therefore, carbon coated LiFePO₄ possess much better electrochemical performance.

As can be seen from Fig. 5, at current densities of 0.1C and 1C (170 mAh g⁻¹), the discharge capacities of the electrodes prepared from carbon coated LiFePO₄ particles with 1.2 wt.% FeP (sample B1) are 155 and 110 mAh g⁻¹, respectively, which are slightly larger than that of the electrode with 3.7 wt.% FeP (sample B2). At the discharge rate of 5C (850 mAh g⁻¹), the electrode prepared from carbon coated LiFePO₄ particles with 3.7 wt.% FeP (sample B2) shows the largest discharge capacity, which is of 63 mAh g⁻¹, while sample B1 and sample C demonstrate discharge capacities of 54 and 50 mAh g⁻¹, respectively. Despite sample B2 having the smallest specific surface area (Table 2), which had the possibility to deteriorate the rate property, it still possesses the largest discharge capacity at high rate among the three carbon containing samples. Therefore, it can be inferred that increasing the iron phosphide from 1.2 to 3.7 wt.% favors the high rate performance of LiFePO₄/C. At rate of 0.1C and 1C, higher discharge capacity of the sample with low

Table 4
The actual discharge capacities and the corresponding actual discharge rates of LiFePO₄ only

Samples	Actual rate of LiFePO ₄ only corresponding to nominal rate of 1C and 5C (1C = 170 mAh g ⁻¹)	Actual discharge capacity of LiFePO ₄ only (mAh g ⁻¹)
A	1.02C	22.1
	5.09C	11.8
B1	1.03C	109.9
	5.13C	55.5
B2	1.05C	106.4
	5.27C	66.5
C	1.2C	102.4
	5.99C	60.5

content of FeP (1.2 wt.%, sample B1) should also be affected by the slight smaller particle size (Table 2, the larger specific surface area). The result consists with the reaction kinetic property of the electrodes from the CV study, again indicating that suitable increase in the iron phosphide and minimization of the particle size of LiFePO₄ favor the high rate performance of LiFePO₄/C. But too much content of iron phosphide (16 wt.%) lowers the rate performance of the electrode.

Iron phosphide Fe₂P is reported to play an important role in the improvement of the bulk conductivity of LiFePO₄ [4,8,13]. Here, FeP and Fe₃P should also improve the bulk conductivity of LiFePO₄ samples due to their high electron conductivity similar as Fe₂P, then improve the rate performance of LiFePO₄. Since the measurement of the specific discharge capacity of the electrode of Fig. 5(a)–(c), as discussed above, includes the content of all the phases in the LiFePO₄ products, and iron phosphides are inert for the deinsertion/insertion of lithium ion, thus, too much content of iron phosphides (16 wt.%) greatly lowered the discharge capacity of the electrode (sample C). In order to better understand the effect of the iron phosphides on the rate performance of LiFePO₄ only, the values of the discharge capacities of the synthesized products at different discharge rates were converted to that of LiFePO₄ only. The actual discharge capacities and their corresponding actual discharge rates for LiFePO₄ only of the samples are listed in Table 4. The content of LiFePO₄ used for the conversion was from Table 2. Table 4 gives obvious evidence that suitable increase of the content of iron phosphides can effectively increase the high rate performance of LiFePO₄/C. Increasing FeP from 1.2 to 3.7 wt.% increases the capacity of LiFePO₄ by almost 20% (from sample B1 and sample B2) at an actual current density of about 5.1C. And the rate performance of LiFePO₄ only in sample C (16 wt.% iron phosphides) retained similar to that of sample B2 (3.7 wt.% iron phosphide) at rate around 5–6C. Combining the discharge capacity of the electrode, too much iron phosphides is unnecessary, it lowers the capacity of the electrode. It can be known that the design of suitable amount of high electron conductive iron phosphides is important to get a satisfying rate performance of LiFePO₄/C electrode.

4. Conclusions

LiFePO₄ with in situ formed carbon coating and iron phosphides was prepared from an aqueous sol–gel method by using ethylene

glycol as carbon source in a sintering atmosphere of N₂ + 5 vol.% H₂. The content of the carbon coating was about 1.5 wt.%, but it greatly suppressed the growth of LiFePO₄ particles, leading to an increase of more than one order in the specific surface area compared with the carbon free LiFePO₄ particles. The content of FeP increased from 1.2 to 3.7 wt.% with increasing the sintering time from 10 to 14 h at sintering temperature of 700 °C when stoichiometric iron ion to lithium ion for LiFePO₄ was used. The iron phosphides increased to 16 wt.% when 10 mol.% more iron ion for stoichiometric LiFePO₄ was used. At rate of 0.1C and 1C (170 mAh g⁻¹), the carbon coated LiFePO₄ sample with 1.2 wt.% FeP showed discharge capacities of 155 and 110 mAh g⁻¹, respectively, which were slightly larger than that with 3.7 wt.% FeP. But with increasing the discharge rate to 5C, the electrode with 3.7 wt.% FeP showed larger discharge capacity than that with 1.2 wt.% FeP, despite the former having smaller specific surface area. Carbon coating and thus the reduction of the particle size of LiFePO₄ and suitable increase in the content of iron phosphides can obviously increase the reaction kinetics and thus the rate performance of LiFePO₄/C. But too high content of iron phosphides lowered the rate capacity of the electrode due to that they are inert for the deinsertion/insertion of lithium ion. The capacity of the carbon free LiFePO₄ with large particle size was extremely low even though it also had 1.8 wt.% FeP.

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