Preparation and electrochemical properties of LiFePO₄/C composite with network structure for lithium ion batteries

CHEN Han(陈 晗), YU Wen-zhi(于文志), HAN Shao-chang(韩绍昌), XU Zhong-yu(徐仲榆)

College of Materials Science and Engineering, Hunan University, Changsha 410082, China

Abstract: The bare LiFePO₄ and LiFePO₄/C composites with network structure were prepared by solid-state reaction. The crystalline structures, morphologies and specific surface areas of the materials were investigated by X-ray diffractometry(XRD), scanning electron microscopy(SEM) and multi-point brunauer emmett and teller(BET) method. The results show that the LiFePO₄/C composite with the best network structure is obtained by adding 10% phenolic resin carbon. Its electronic conductivity increases to 2.86×10^{-2} S/cm. It possesses the highest specific surface area of 115.65 m²/g, which exhibits the highest discharge specific capacity of 164.33 mA·h/g at $C/10$ rate and 149.12 mA·h/g at 1 C rate. The discharge capacity is completely recovered when $C/10$ rate is applied again.

Key words: LiFePO₄/C composite; lithium ion batteries; electrochemical properties; network structure

1 Introduction

LiFePO₄ is an interesting alternative cathode material for lithium ion batteries, due to its cheap starting materials, good environmental compatibility, excellent cycling stability and high temperature performance[1−2]. The main disadvantages are very low electronic conductivity and diffusion coefficient of lithium ion, which lead to its poor rate capability and hinder its commercialization as cathode material for lithium ion batteries[3−4]. Some efforts to increase its conductivity have focused on reducing particle size[5−6], coating carbon[7−8] and doping metal cation[9−10].

Carbon coating can not change the intrinsical conductivity of LiFePO₄, but it is very effective to enhance the capacity and rate capability[11−12]. Carbon black and sugar are used as main carbon resources. The electronic conductivity of LiFePO₄/C composite prepared by BEWLAY et al[13] added with sucrose reached 0.1 S/cm. PROSINI's research[14] showed that the practical capacity and rate capability of LiFePO₄ can be improved by adding 10% carbon black to the starting materials. Carbon can control particles growth and enhance its conductivity. Therefore higher capacity and better rate capability can be obtained. At present, it is necessary to optimize carbon source and prepare LiFePO₄/C composite with excellent electrochemical properties, especially rate capability.

Phenolic resin was used as carbon resource by YANG et al[15], the discharge capacity of LiFePO₄/C composite is only 65 mA·h/g at $C/3$ rate and its structure has not been reported in their research. In this study, LiFePO₄/C composite with porous network structure was prepared using phenolic resin as carbon resource.

2 Experimental

2.1 Materials preparation

LiFePO₄/C composites were prepared by solid-state reaction. Li_2CO_3 (AR, Taishan Chemical Plant), $FeC_2O_4 \cdot 2H_2O$ (AR, Fluka), and $NH_4H_2PO_4$ (AR, Mingfeng Reagent Corporation) were used as the starting materials. Phenolic resin was added with different mass fractions. The starting materials were weighed in stoichio-metric ratio and homogenously mixed by ball grinding in

anhydrous ethanol. The mixture was solidified at 150 ℃ for 5 h. To decompose the oxalate and the phosphate, the mixture was placed in a tubular furnace and treated at 350 ℃ for 5 h in argon flow. The resultant powders were cooled down to room temperature and reground, then returned to the tubular furnace and calcined at 650 ℃ for 18 h in argon flow. The last powders were cooled down to room temperature. Thus the LiFePO$_4$/C composites containing various carbon amount were obtained.

2.2 Materials characterization

The crystalline structure was confirmed by a powder X-ray diffractometer (D5000) with CuK$_\alpha$ radiation. The XRD data were obtained over an angular 2θ range from 15° to 45° with the step size of 0.02° and constant counting time of 0.2 s per step. The crystallite size of samples was calculated by the Scherrer equation $D=K\lambda/(\beta \times \cos\theta)$ from the full width at half maximum (β) of the (131) diffraction peaks, in which K value is 0.89. The morphology of the composites was observed by scanning electron microscopy (JSM−6700F). The specific surface area of the powders was measured by the multi-point Brunauer Emmett and Teller (NOVA−1000) method. Conductivity measurement using four-probe testing instrument (SX1934) was made on disc-shaped pellet by four-point direct current method at room temperature, the measured value was revised for the thickness of pellet.

2.3 Electrochemical tests

Active material, conductive additive and polytetrafluorethylene(PTFE) were mixed homogeneously in mass ratio of 75:20:5. The mixture was rolled into a 0.1 mm thin sheet with uniform thickness, from which pellets with 12 mm in diameter were cut. The pellet was used as the cathode and the electrolyte was 1 mol/L LiClO$_4$ in ethylene carbonate and dimethyl carbonate (1:1 in volume). Lithium foil was used for the counter and reference electrodes. The separator was Celgard 2400 microporous membrane. The cell was assembled in an argon glove box. The galvanostalical tests were run by Arbin instrument (BT-2000) between 2.5 V and 4.1 V versus Li/Li$^+$ at various rates.

3 Results and discussions

3.1 XRD analysis

The XRD patterns of LiFePO$_4$/C composites containing various carbon amount and bare LiFePO$_4$ are shown in Fig.1. All peaks of the samples can be indexed as olivine LiFePO$_4$ phase without any observable secondary phase, but the XRD patterns have somewhat difference with the carbon amount increasing. The position of diffraction peaks deviates to lower diffraction angle, which shows that the distance between neighboring crystal planes becomes larger according to the Bragg equation $2d\sin\theta=\lambda$. The intensity of diffraction peaks turns weaker gradually. The practical temperatures of composites are slightly lower than that of bare LiFePO$_4$, because of adsorption of heat during decomposition of phenolic resin[16]. The lattice parameters of the samples are calculated from the Rietveld refinement on the basis of the Pmnb space group and shown in Table 1. The crystallite size of samples is calculated based on the strongest practical peak (131). With the carbon amount increasing, the lattice parameters of the composites become slightly larger. When cell volume increases, the size (D_{131}) decreases gradually. When cell volume is too small, the
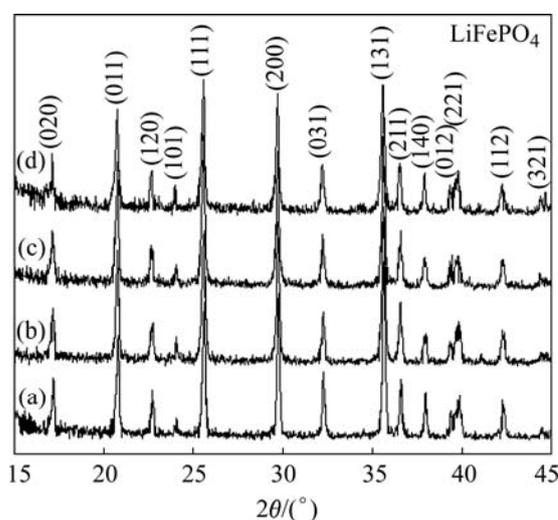

Fig.1 XRD patterns of samples with various carbon amount: (a) 0%; (b) 5%; (c) 10%; (d) 20%

Table 1 Comparison of lattice parameters and crystallite size of samples

Sample	Carbon amount/%	a/nm	b/nm	c/nm	Cell volume/nm^3	D_{131}/nm
a	0	0.600 09	1.031 93	0.468 67	0.290 33	41.28
b	5	0.600 21	1.032 14	0.469 49	0.290 85	38.71
c	10	0.600 81	1.032 87	0.470 01	0.291 66	36.12
d	20	0.601 89	1.034 70	0.470 39	0.292 95	31.75

atoms around lithium ions will hider their diffusion. On the contrary, when the cell volume is too large, the cell will be destroyed due to extraction and insertion of lithium ions. The lithium ions have to diffuse over larger distances between the boundary and center of crystallite grains due to larger crystallite size[17]. Therefore sample c has a good compromise between cell volume and crystallite size.

3.2 SEM micrographs analysis

The SEM micrographs of the composites are shown in Fig.2. The porous network structure can be clearly observed in Figs.2(b) and (d). When phenolic resin is solidified, lots of polymeric webs form. Since the starting materials with phenolic resin are uniformly dispersed in anhydrous ethanol during solidification, the starting materials are trapped into the polymeric network. During the heat treatment, phenolic resin carbonizes, the porous network structure forms, and $LiFePO_4$ covers on the carbon framework. This kind of structure characterized in detail in other paper is entirely different from carbon coating. The coexisted network structural composite and $LiFePO_4$ grains can be clearly observed in Figs.2(a) and (b), which is due to inadequate phenolic resin portion to the starting materials of $LiFePO_4$. As shown in Fig.2(c), the perfect network structure without any $LiFePO_4$ grains because of the enough carbon framework adhering $LiFePO_4$ grains is observed. As shown in Figs.2(e) and (f), it is obvious that the porous network structure disappears and the smooth grains pile
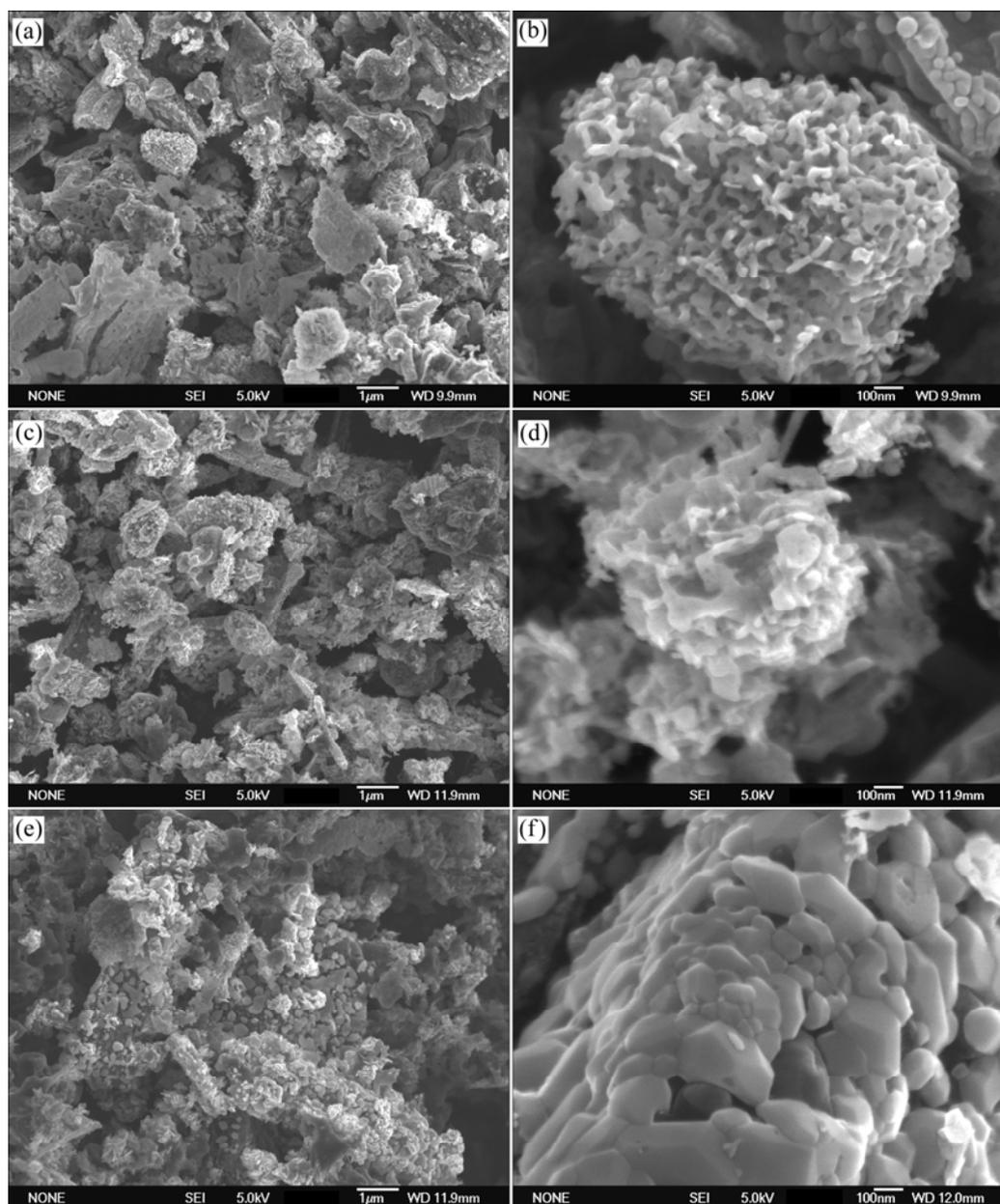

Fig.2 SEM micrographs of composites with various carbon amount: (a), (b) 5%; (c), (d) 10%; (e), (f) 20%

together because the neighboring network incorporates one another during the teat treatment, when the 20% carbon is applied.

3.3 BET tests

Fig.3 shows the specific surface areas of the samples with various carbon amount. As shown in Fig.3, the specific areas of materials increase rapidly with increasing the carbon amount. When 10% carbon is applied, the sample exhibits the highest specific surface area of 115.65 m^2/g, nearly twenty times greater than that of bare LiFePO$_4$. The high specific surface area is mainly attributed to porous network structure. When 20% carbon is applied, the specific surface area decreases abruptly because of the disappearance of porous network structure and the formation of smooth grains.
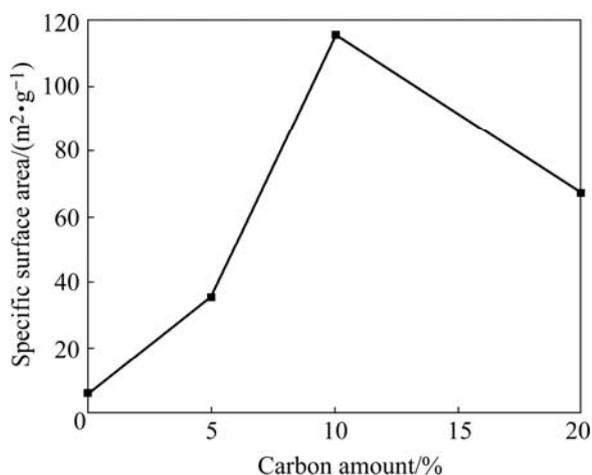

Fig.3 Specific surface areas of samples with various carbon amount

3.4 Conductivity measurement

The electronic conductivity of LiFePO$_4$/C composites compared with bare LiFePO$_4$ is shown in Table 2. Phenolic resin carbon plays a significantly important role to enhance electronic conductivity. The electronic conductivities of LiFePO$_4$/C composites are much higher than that of bare LiFePO$_4$. They increase with increasing carbon amount. The lowest limit of conductivity testing instrument (SX1934) is 10^{-6} S/cm,

Table 2 Electronic conductivity of samples with various carbon amount

Sample	Carbon amount/%	Electronic conductivity/ (S·cm^{-1})
a	0	1.5×10^{-8}[18]
b	5	1.72×10^{-4}
c	15	2.86×10^{-2}
d	20	3.47×10^{-1}

and the electronic conductivity of bare LiFePO$_4$ is cited to compare with that of LiFePO$_4$/C composite.

3.5 Electrochemical properties analysis

Fig.4 shows the charge and discharge curves of LiFePO$_4$/C composites and bare LiFePO$_4$ at C/10 rate. The calculation of specific capacity of LiFePO$_4$/C composites is based on LiFePO$_4$. The potential difference between the charge and discharge plateau of LiFePO$_4$/C composites is only 0.05 V, which shows the weaker potential hystereresis compared with that of bare LiFePO$_4$ because of the formation of porous network structure. The initial discharge specific capacity of LiFePO$_4$/C composites is much larger than that of the bare LiFePO$_4$. Especially, the LiFePO$_4$/C composite containing 10% carbon has the largest initial discharge specific capacity (164.33 mA·h/g). The perfect porous network structure increases the contact area between carbon and LiFePO$_4$, providing multi-dimension channels for diffusion of lithium ions.
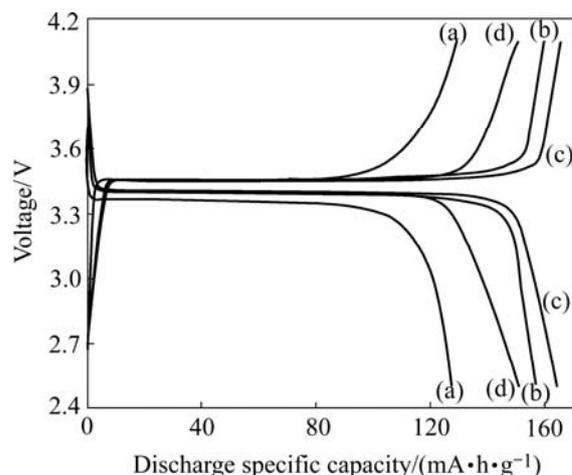

Fig.4 Charge and discharge curves of samples with various carbon amount: (a) 0%; (b) 5%; (c) 10%; (d) 20%

The extended line of the potential plateau intersects the tangents of discharge curves at points A and B, shown in Fig.5. The capacity between points A and B is defined as plateau capacity. The ratio of the plateau capacity to the full discharge capacity is defined as plateau ratio. The materials with higher plateau capacity and plateau ratio can work longer. The comparison on the plateau performance of bare LiFePO$_4$ and LiFePO$_4$/C composites is listed in Table 3. When 10% carbon is applied, sample c possesses the highest plateau capacity and considerably high plateau ratio. But the plateau capacity of sample d decreases due to the hindrance of excessive carbon to the diffusion of lithium ions and the disappearance of porous network structure.
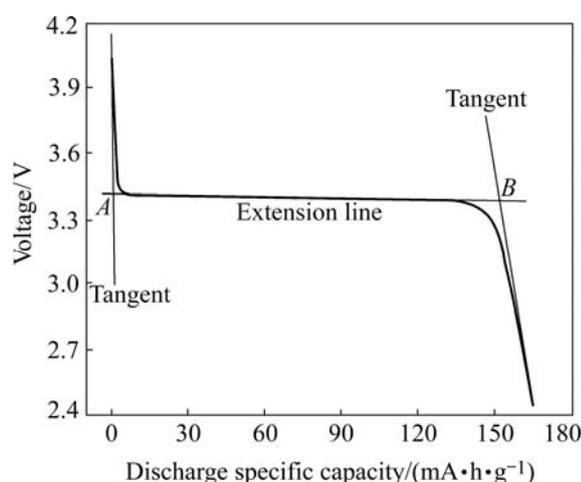
Fig.5 Sketch graph of plateau capacity

Table 3 Plateau capacity and ratio of samples with various carbon amount

Sample	Carbon amount/%	Full capacity/ $(mA·h·g^{-1})$	Plateau capacity/ $(mA·h·g^{-1})$	Plateau ratio/%
a	0	127.49	117.07	91.83
b	5	156.93	146.10	93.01
c	10	164.33	151.65	92.28
d	20	150.90	127.20	84.29

Fig.6 shows the curves of rate and cycling capability of all samples. To investigate the rate capability, various current densities corresponding to C/10, C/2 and 1 C are applied. All of them show excellent cycling stability. The discharge specific capacity of bare $LiFePO_4$ at 1 C rate is only half as much as that at C/10 rate. When the rate increases, the capacity loss of $LiFePO_4$/C composites containing 5% and 20% carbon is much larger than that of the composite containing 10% carbon. The composite containing 5% carbon has fewer network structure and more bare $LiFePO_4$ grains. Likewise, when 20% carbon is applied, the network structure disappears, the smooth grains forms because of incorporation of neighboring network, and the excessive carbon hiders the diffusion of lithium ions, so the discharge specific capacity of $LiFePO_4$/C composite containing 5% and 20% carbon is 100 mA·h/g at 1 C rate. The discharge specific capacity of $LiFePO_4$/C composite containing 10% carbon is 149.12 mA·h/g at 1 C rate, and its capacity loss is only 9.5%. The good rate performance is attributed to perfect porous network structure that provides multi-dimension channels for diffusion of lithium ion and reduces the resistance for diffusion of lithium ion. Moreover, the composite with porous network structure can suck up electrolyte to shorten enormously the diffusive distance of lithium ion.
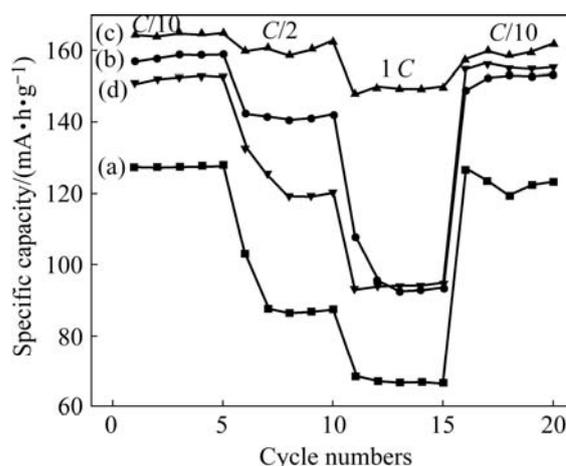

Fig.6 Curves of rate and cyclic capability of samples with various carbon amount: (a): 0%; (b): 5%; (c): 10%; (d) 20%

When C/10 is applied again, the discharge specific capacity of all samples recovers completely, which shows that their structure has not been broken, and the capacity loss is due to stronger polarization at high rate. Therefore the porous network structure plays a significantly important role in improving the rate capability of $LiFePO_4$.

4 Conclusions

1) $LiFePO_4$/C composites containing various amount of carbon have well-crystallized olivine structure.

2) The $LiFePO_4$/C composite with excellent porous network structure and the highest specific surface area is obtained by adding 10% phenolic resin carbon, which exhibits excellent cycling and rate capability.

3) The $LiFePO_4$/C composite with porous network structure is a promising cathode material for lithium ion batteries.

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