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Effects of carbonaceous materials on the physical and electrochemical performance of a $LiFePO_4$ cathode for lithium-ion batteries

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Abstract: The effects of carbonaceous materials on the physical and electrochemical performance of $LiFePO_4$/C hybrids are reviewed. The major role, advantages and disadvantages of carbon-based materials in $LiFePO_4$/carbon hybrids are discussed. The introduction of an *in situ* grown carbon coating would be beneficial to limiting the $LiFePO_4$ particle growth and increasing the electric conductivity. The structure and precursors of the *in situ* grown carbons have a great influence in the rate performance of the hybrids, which can be related to an improved electron and ion transfer rate. Deposition of $LiFePO_4$ into a carbonaceous matrix such as a templated membrane can increase the contact area between the active materials and the electrolyte, which favors a fast ion transport. The addition of conductive carbon and graphene would only effectively increase the electrical conductivity. In order to achieve an excellent electrochemical performance of $LiFePO_4$, it is necessary to take advantage of and to combine these approaches to optimize electron and ion transfer rates. Also, it is most important to minimize the carbon content in $LiFePO_4$/carbon hybrids to increase volumetric energy density and tap density when practical applications in electric vehicles are targeted.

Keywords: Lithium iron phosphate; Carbon coating; Carbonaceous matrix; Conductive carbon; Carbon nanotube; Graphene

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1 Introduction

With the rapid development of the automobile industry and the sustainable growth of the global economy, the outputs and ownerships of automotives all over the world will be sharply increased every year. Then the energy consumption and the environmental pollution aroused by the internal combustion engine of vehicles will become more and more serious. In this dilemma, the development of electric vehicle (EV) industry is considered to be an optimal solution to these problems in the transport sector. As a result, the power system supplied to drive EVs becomes one of hot research areas. In the light of the outstanding commercial success of the lithium-ion batteries in portable devices, a great international interest has been focused on applying the lithium-ion battery technology to EVs. As a paramount component of lithium-ion cell, electrode materials, especially cathode materials, are attracting vast attention from science and industry.

In recent years, lithium iron phosphate ($LiFePO_4$) with an olivine structure has been selected as one of the promising cathode materials for EVs and has become a focal point of extensive investigation. This cathode material possesses several particular features, such as potential low cost, environmental compatibility, non-toxicity and exceptional thermal stability even at a full charged state[1-2], which perfectly satisfy the requirements to replace the commercial $LiCoO_2$. However, the major drawbacks of this electrode material lie in its intrinsically poor electric conductivity (about 10^{-9} ~ 10^{-10} $S \cdot cm^{-1}$) and low Li^+ transport velocity (approximately 10^{-14} $cm^2 \cdot s^{-1}$)[2-3]. For this reason, $LiFePO_4$ can only deliver relatively high specific capacity at an extremely small current density, which is difficult to meet the practical demands for the high rate and pulse-power applications.

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Therefore, recent studies of $LiFePO_4$-derived cathode materials were primarily oriented towards how to efficiently increase the electrical conductivity and facilitate the lithium-ion transfer. Only in this way, excellent rate capability and cycling stability could be achieved. Correspondingly, a large number of strategies have been proposed, such as tailoring the particle size (down to the submicron level, even nanometer), optimizing the morphology, decorating the surface with conductive agents, forming $LiFePO_4$/carbon hybrids[4-7] and doping the host framework with alien ions on the Li-ion site (M1-site) or/and the Fe-ion site (M2-site)[8-18] via various synthesis methods[19-24]. However, whatever strategy is taken, making a composite with carbon material is regarded as at least an effortful way and the most important technique to enhance the specific capacity, rate capability and the cycling stability of $LiFePO_4$.

There have been some excellent reviews on the physicochemical and electrochemical performance of $LiFePO_4$ cathodes in terms of synthesis procedures, mechanisms of lithiation/delithiation, solid solution behavior, doping and surface modifications targeting at its practical applications[25-27]. Nevertheless, little attention has been paid to the categories of the available carbon materials, the composite manner with carbon materials and their effects on the performance. Therefore, we tried to summarize this part of research work, hoping that it would be of use to understand comprehensively the important role of the carbon materials in the $LiFePO_4$/C composite and to distinguish clearly the differences among the effects of various composite manners on the performance of $LiFePO_4$. In this article, the effects of various carbon materials and composite manners on the physical and electrochemical performance of $LiFePO_4$/carbon-based hybrids are reviewed.

2 Decorating the surface with carbon

Carbon coating is one of the most common approaches to enhancing the electrochemical performance of $LiFePO_4$. The major role of the carbon coating is not only to dramatically increase inter-granular electric conductivity, but also to efficiently hinder particle growth, reduce grain size and even optimize the microstructure. The increase in the electric conductivity would be beneficial to raising the utilization of the active materials at useful rates. The refined particle size would be favorable for shortening the diffusion distance of lithium ions and thus the lithium-ion diffusion velocity would be improved. Moreover, a porous and loose microstructure would be advantageous to achieving unhindered contact of electrolyte with particle exterior[19]. All these are key factors to determine the electrochemical performances of $LiFePO_4$. $LiFePO_4$ and $LiFePO_4$/C composite materials were synthesized via an inorganic-based sol-gel method, proposed by us, using $FeCl_2 \cdot 4H_2O$, Li_2CO_3 and H_3PO_4 as the raw materials and citric acid as the carbon source. It was found that the bulk electric conductivity for $LiFePO_4$ was about 5.29×10^{-8} S·cm^{-1}. After carbon coating, the electric conductivity is dramatically increased. When the residual carbon was about 2.3% by mass fraction, the bulk electric conductivity was increased by 3 orders of magnitude, approximately 4.14×10^{-5} S·cm^{-1}. And with the continued increase in the residual carbon content, the electric conductivity was increased up to about 2.82×10^{-4} and 1.44×10^{-3} S·cm^{-1} for the remaining carbon of 4.5 and 15% by mass fraction, respectively. The results are similar to those reported by Bewaly et al.[30]. At the same time, the carbon coating also led to evident reduction of the particle size because of a steric hindrance effect. The particle size was reduced from 1 μm to 92 nm, 71 nm and 44 nm upon the residual carbon contents of 2.3, 4.5 and 15% by mass fraction, respectively (as shown in Fig. 1). Correspondingly, the rate capability and cyclic stability were greatly enhanced after amorphous carbon coating (as shown in Fig. 2a and 2b). At 0.1 C, $LiFePO_4$ only delivered a capacity of about 18 mAh·g^{-1} and the capacity fading rate was remarkably high. Meanwhile, $LiFePO_4$ with a residual carbon of 4.5% exhibited a high specific capacity of about 162.7 mAh·g^{-1} and excellent cycling stability. In addition, it is worth mentioning that the pre-existing carbon materials or organic precursors might act as potential reducing agents and thus could efficiently prevent the oxidation of Fe^{2+} to Fe^{3+} during the course of sintering[28-29]. However, the disadvantages of the carbon coating are that cost was inevitably up and its tap density was greatly down, which would directly lead to a low volumetric energy density[25]. In addition, a thick carbon coating would not lead to a further improvement of the lithium-ion diffusion and would be detrimental to electrode electrochemical performance[25]. In our experiment, as shown in Fig. 2c, it was found that $LiFePO_4$ with a carbon coating of 4.5 nm (a residual carbon of 15% by mass fraction) showed a poor rate capability, compared with that of a carbon coating of 3.3 nm (a residual carbon of 4.5% by mass fraction). Therefore, it is of paramount importance to optimize the amount of carbon coated on the surface of $LiFePO_4$ to meet practical requirements for EV applications in terms of the cost and the electrochemical performance. Now, there is a research trend targeted at minimizing the carbon content while maximizing conductivity for practical applications.

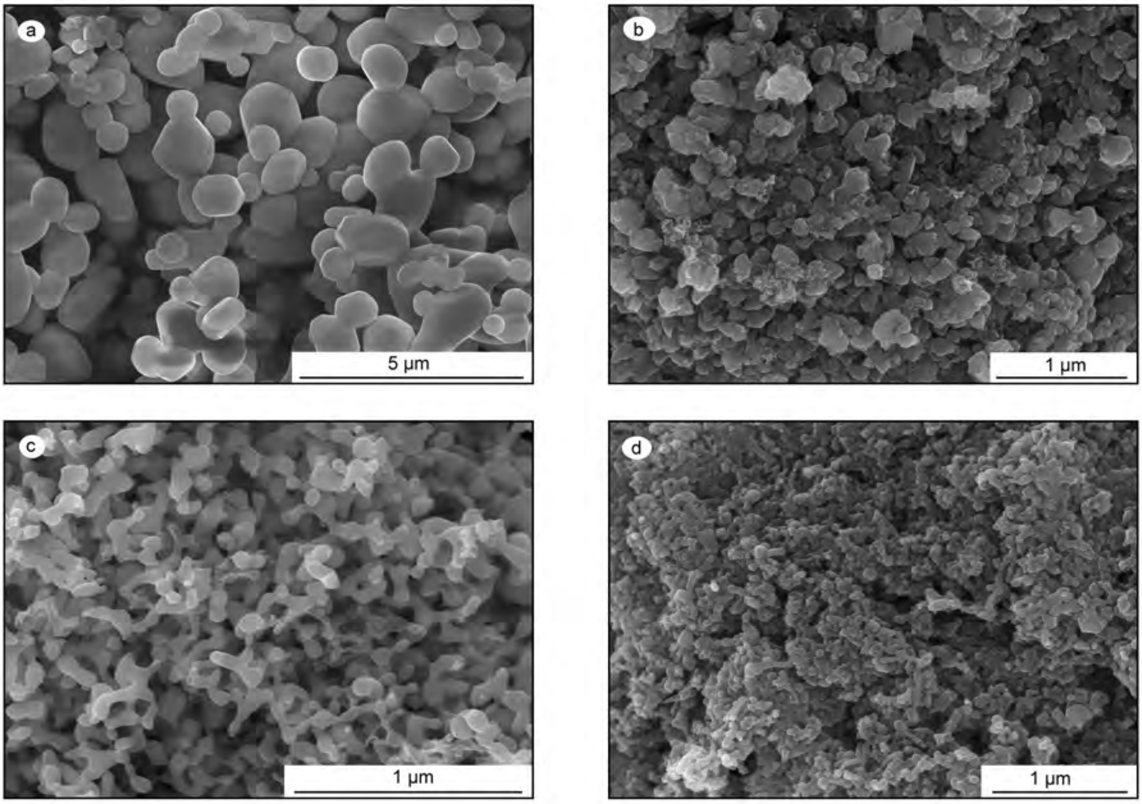

Fig. 1 FESEM photographs of the $LiFePO_4/C$ composites with different mass fraction of carbon
(a) 0% carbon; (b) 2.3% carbon; (c) 4.5% carbon; (d) 15% carbon

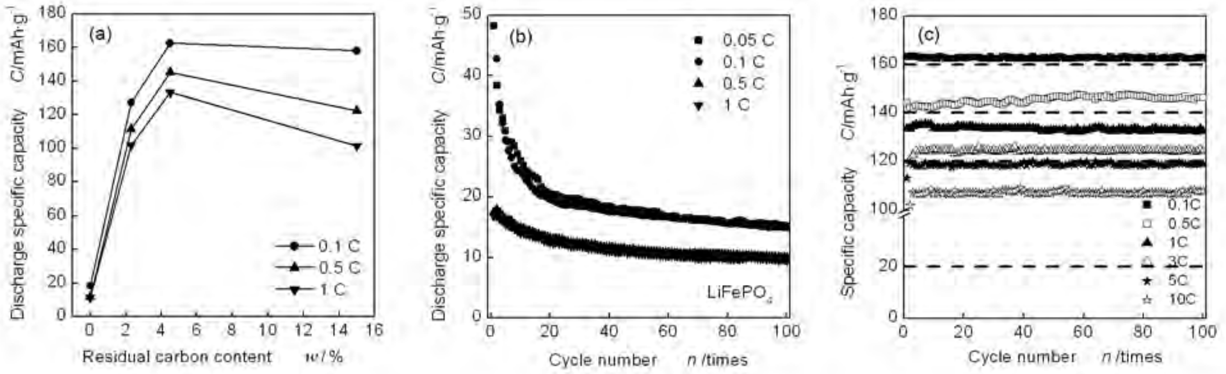

Fig. 2 (a) The relationship between specific capacity and discharge rate of the $LiFePO_4/C$ composites; (b) The discharge specific capacity retention vs. the cycle number for the $LiFePO_4$; (c) The discharge specific capacity retention vs. the cycle number for the $LiFePO_4/C$ composite

The carbon coating could be easily accomplished by an *in situ* pyrolysis of organic precursors during sintering. For the purpose of the *in situ* carbon coating, various carbonaceous sources were employed, for example, sucrose[18,31-34], glucose[35-36], starch[37], citric acid[12,23,38], lauric acid[19], ascorbic acid[39], adipic acid[40-41], L-ascorbic acid[42-43], pitch carbon[31], polypropylene[44], polypyrrole[45], polyvinyl alcohol[46], polyethylene glycol[47-48], polythiophene[49] and polyacene[50]. It is commonly believed that the electric conductivity and electrochemical performance are strongly influenced by the pyrolysis temperature and the type of the carbon source selected. In general, the sample sintered at higher temperatures (i. e. the upper 973 K) showed a higher electric conductivity than that heat-treated at lower temperatures, as a result of the increase of the graphitization degree (sp^2-coordinated) of the pyrolytic products[25]. However, the high sintering temperature can easily cause an unwanted crystal growth, which would undermine the electrochemical performance of the sample. Therefore, it is necessary to optimize the sintering temperature. In addition, graphitized carbons (sp^2-coordinated) are more conductive than disordered carbons (sp^3-coordinated) and organic precursors with a carbon-string structure are more conductive than the others. Therefore, the selection of carbonaceous precursors is very important, deserving an in-depth investigation for the synthesis of $LiFePO_4/C$ composite cathodes with a high electric conductivity and an excellent electrochemical performance.

Besides, carbon coating could be carried out by mechanical mixing with pre-existing carbon powders as well. The alternative carbon powders are mainly carbon black, acetylene and graphite. However, research revealed that the sample with the *in situ* carbon coating had better electrochemical performance than in the powder mixing method[51]. Liu et al.[16] compared the electrochemical behaviors of $LiFePO_4$ using acetylene and a sugar as carbon sources by the carbothermal reduction method. It was found that the sample using a sugar with a carbon string structure as a carbonaceous additive exhibited better electrochemical performance. At 0.1C, the sample delivered a specific capacity of about 159.3 $mAh \cdot g^{-1}$ and the capacity fading was about 2.2% after 30 cycles.

Lastly, the carbon coating structure is another important factor to influence the electrochemical performance of $LiFePO_4$. Chen et al.[7] synthesized $LiFePO_4/C$ composite with nanometer carbonweb by solid-state reaction using guluronic acid as the carbon source. It was found that the carbonweb on the surface of $LiFePO_4$ particles was formed by carbonization of organic precursor. And the formation of the carbonweb was attributed to the improvement of the electron and lithium-ion transportation (as shown in Fig. 3a). For this reason, the sample exhibited an excellent electrochemical performance. At 1 C and 3 C, the sample delivered specific capacities of about 120 $mAh \cdot g^{-1}$ and 100 $mAh \cdot g^{-1}$, respectively. Recently, Oh et al.[31] reported a double carbon coating of $LiFePO_4$, which was prepared by $Fe(NO_3)_3 \cdot 9H_2O$, Li_2CO_3 and H_3PO_4 as the raw materials, and sucrose and pitch as the carbon sources. The carbonization of the two carbon precursors formed the double carbon coating (as shown in Fig. 3b), which was attributed to an increase in the conductivity, as high as 8.8×10^{-2} $S \cdot cm^{-1}$. The Li/C-$LiFePO_4$ battery exhibited a high charge-discharge reversibility in the temperature range −20 ℃ to 60 ℃, a high tap density and an exceptional rate capability due to this unique morphology.

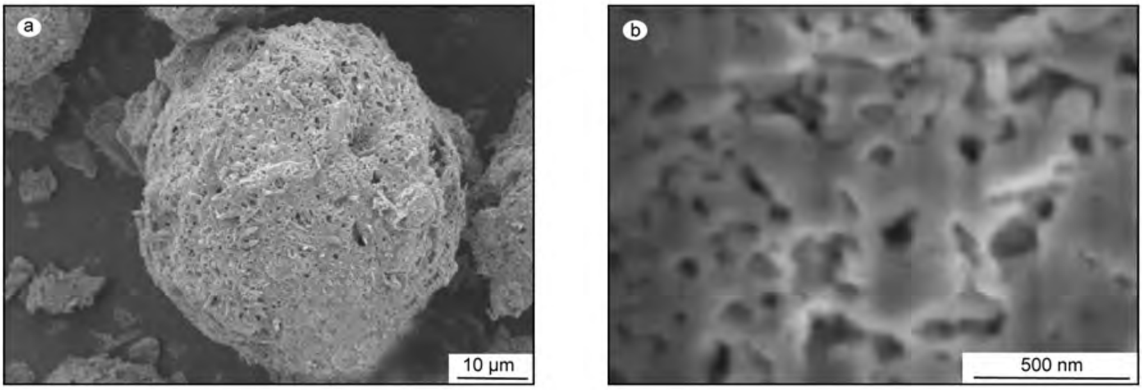

Fig. 3 (a) SEM photograph for $LiFePO_4/C$ with carbon-web[7]; (b) SEM photograph for $LiFePO_4/C$ with the doule carbon coating[31]

With the highquality carbon coatings, the adding amount of conductive carbon during the fabrication of cathode can be greatly reduced[52-53]. An ideal carbon coating needs to be uniform, with a thickness of 2-3 nm and a loading of 1-3% by mass fraction[52, 54].

3 Addition of conductive carbon

Because of low electric conductivity and poor contact between the active materials and the collector, a certain amount of electro-conductive additives (i. e. super P, graphite, Ketjen black or carbon nanotube) were added during the preparation of the cathode. Sometimes, a current collector pre-treated by coating carbon was employed. The major role of the conductive carbon is to greatly improve the electric conductivity and the electrochemical performance. For this purpose, several conductive carbon particles, i. e. acetylene carbon, Ketjen black, carbon nanotubes and graphite, are widely used[44,55-57]. In this case, the adding amount of conductive carbon and the mixing procedure significantly affect the electrochemical performance of the fabricated cells. For an electrochemical battery to deliver energy at high rates, all part of the Li^+ and electron path between cathode and anode active materials have to be capable of sustaining this current density[5]. Therefore, in order to facilitate the electron transfer from the active material and the current collector, a lot of conductive carbon needed to be added. With the adding amount of conductive carbon, the sample would deliver higher capacity and show better rate capability. This way, the true rate capability of electrode material could be achieved. However, it is inappropriate and meaningless for real electrochemical batteries because of the great reduction of energy density. In this respect, the uniform distribution and the mixing procedure of conductive carbon still need further investigations.

4 $LiFePO_4$ deposited in carbonaceous matrix

Another useful and promising strategy to enhance lithium-ion diffusion kinetics is to boost the ability of lithium ions to travel across the interface between the active materials and the electrolyte, which is crucial for ultrafast diffusion. It can be achieved by creating large interfacial contact between the active material and the surrounding electrolyte[5,58]. The existence of the carbonaceous matrix can significantly restrict the growth of $LiFePO_4$, which would be beneficial to shortening the diffusion path for lithium ions. On the other hand, the carbon network can link embedded $LiFePO_4$ nanoparticles together to improve the charge transfer rate, and most importantly, the sufficient porosity of carbon materials can increase the immersion of electrolyte and thus ensure the facile diffusion of lithium ions for high-rate applications[58]. At the same time, the carbon skeleton can also release the strain induced by phase transition during the course of insertion and extraction of lithium ions. Therefore, it is a very promising and appealing method for high energy and power densities although the higher content of the versatile carbon framework was inevitably increasing cost. These versatile carbon materials can be roughly classified into two kinds, hard carbon and soft carbon, i.e. carbon monolith[59], colloidal crystal[60], triblock co-polymer[59,61], citric acid, glucose[58] and so on. However, the disadvantages of this method are mainly the higher cost and the more complicated synthesis route.

Sides et al.[62] synthesized $LiFePO_4/C$ composites with high rate capability by a template method. The template membrane used was commercially available polycarbonate filters. A sol-gel method developed by Croce et al.[63] was used to deposit the $LiFePO_4$ nanofibers within the pores of this template. After sintered, the polycarbonate was pyrolyzed into amorphous carbon with a low graphitization degree. The $LiFePO_4/C$ composite showed carbon particles dispersed through this matrix and the $LiFePO_4$ nanofibers were coated with thin carbon films (as shown in Fig.4a). This unique structure was suitable for high-rate applications, even at extreme rates, because the diffusion distance of lithium-ion was restricted to the radius of nanofibers and the carbon matrix provided a good electric conductivity. Thus, the sample exhibited an excellent rate capability. At 3 C, the sample delivered a capacity of $165\,mAh\cdot g^{-1}$ and at 65 C, the electrodes still retained 36% of its theoretical capacity. Recently, Yang et al.[64] employed the porous carbon as support to synthesize $LiFePO_4/C$ composite and investigated the effects of the disordered microporous carbon AC-K5 and ordered mesoporous carbon CMK-3 on the electrochemical performance of $LiFePO_4$ in detail. As shown in Fig.4b, sphere-like $LiFePO_4$ nanoparticles uniformly dispersed on the carbon support. The carbon support formed a framework to bind $LiFePO_4$ particles together and provided a hindrance for the growth and aggregation of $LiFePO_4$, which was beneficial to improving the transport rate for the lithium-ions and the electrons. Therefore, the composite with microporous carbon demonstrated a high rate performance with a discharge capacity of $60\,mAh\cdot g^{-1}$ at 50C. Zhao et al.[58] synthesized a novel structure in which the nanospherical $LiFePO_4$ was lodged in a 3D porous carbon framework using glucose as carbon source by solid-state reaction (shown in Fig.4c). The sample possessed a considerably enhanced electric conductivity of $\sim 10^{-2}\,S\cdot cm^{-1}$ and an amazing high surface area of $200.5\,m^2\cdot g^{-1}$. Owing to this unique structure, the sample exhibited $69.5\,mAh\cdot g^{-1}$ at 20C. Dimesso et al.[65] investigated the performance of 3D carbon foam/$LiFePO_4$ composite as a function of the annealing time under inert atmosphere using the commercial carbon foams. As shown in Fig.4d, crystalline $LiFePO_4$ was synthesized in the sponge architecture. The presence of the carbon layer improved the electronic conduction and high inter-particle surface led to a low polarization overpotential. Therefore, the sample showed good electrochemical performance delivering a specific capacity of $105\,mAh\cdot g^{-1}$ at C/25 after sintering for 5 h.

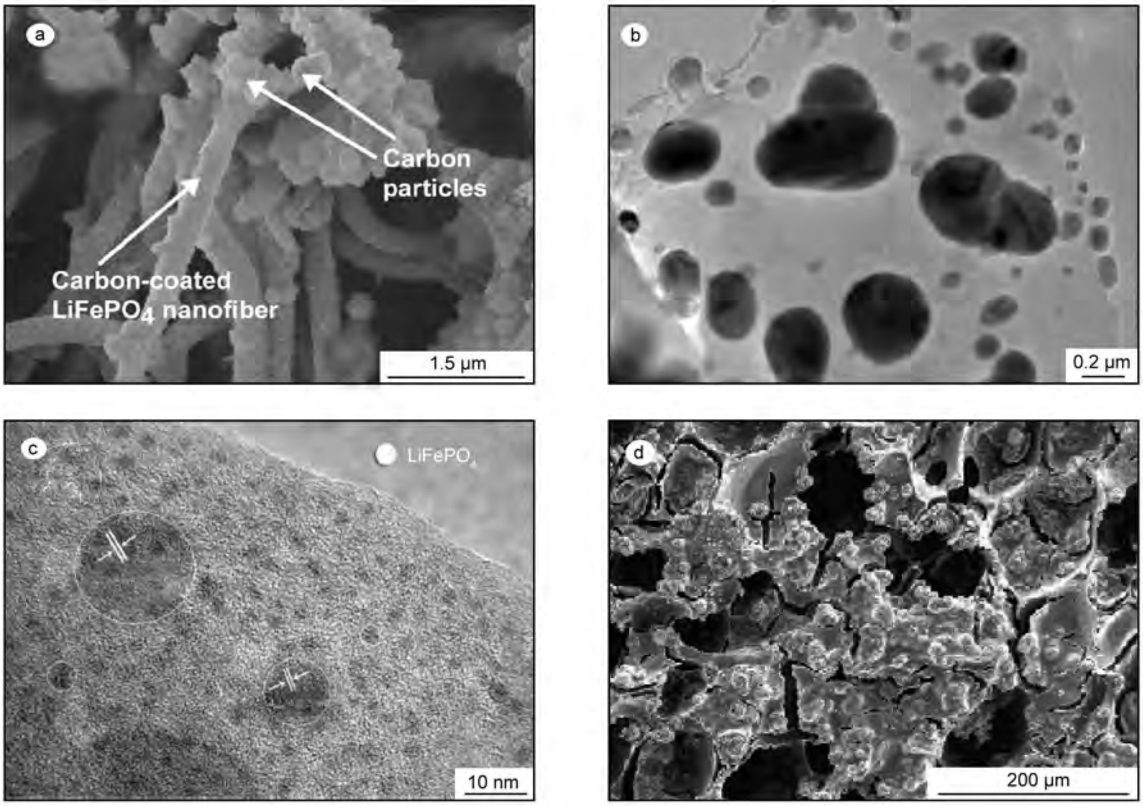

Fig. 4 （a）TEM image for $LiFePO_4$/C nanocomposite synthesized by template dissolution method[61]; （b）HR-TEM image for $LiFePO_4$/C composite[64]; （c）TEM observation of nanometer $LiFePO_4$ dispersed in the continuous porous carbon matrix[58]; （d）HREM image of carbon foam-$LiFePO_4$ composite[65]

5 $LiFePO_4$/carbon nanotube composite

Carbon nanotubes（CNTs）possess unique structural, electronic, mechanical and optical properties, thus they are actively used as components of devices in a variety of different fields. The importance of constructing CNT-nanoparticle heterostructures is that these composite can take advantage of and combine the unique physicochemical properties of both CNTs and nanoparticles in one discrete structure[66]. Compared with single wall CNTs, multi-walled CNTs are cheap and their electric conductivity is less affected by chemical functionalization. Therefore, multi-walled CNTs are usually employed to form composites with $LiFePO_4$. Now, the effects of multi-walled CNTs on the electrochemical performances of $LiFePO_4$ have been extensively investigated. In this system, the main role of CNTs is to increase the electrical conductivity among the particles and between particles and the current collector. The composites were synthesized by simple mixing[47,67-70], ball-mixing[71-72], hydrothermal synthesis[73] and *in situ* formation from ferrocene[74] and bio-inspired method[75].

Liu et al.[68] investigated the effects of CNTs on the electrochemical performance of C-$LiFePO_4$/graphite batteries. They compared the effects of the two kinds of conductive carbon, CNTs and carbon black. In contrast, the sample with CNTs as additive exhibited better electrochemical performance with a capacity retention of 99.2% after 50 cycles because of smaller polarization voltage. Kavan et al.[76] investigated the electrochemical activation of $LiFePO_4$/multi-walled CNT composite. CNTs were firstly dispersed in water under short sonication. Then $LiFePO_4$ powder was added and stirred overnight. This assembly offers unique electrochemical activation of $LiFePO_4$ called “nanotube wiring”[77-78]. It was found that the functionalization of CNTs by oxidation with HNO_3 is crucial for enhancing the electrochemical activity of the composite. The results indicated that the charge/discharge reversibility was nearly 100% and the cycling stability was unperturbed. In contrast, the composite with pristine nanotubes showed rather low activity, which is even lower than that of the composite with high specific surface area carbon black. Muraliganth et al.[70] synthesized nanoscale networking of $LiFePO_4$ naonrods with CNTs via a microwave-solvothermal route. The acid-treated multi-walled CNT networking increased the electrical conductivity significantly without blocking lithium-ion transfer during cycling. Therefore, the sample showed an increase in the specific capacity with a significant reduction in the polarization loss. Owing to good contact among particles and between particles and the current collector, the sample exhibited excellent capacity retention during cycling.

In addition, Doeff et al.[74] synthesized the $LiFePO_4$/multi-walled CNT composite by sol-gel method or combustion synthesis, in which the multi-walled CNTs were synthesized using pyromellitic acid and graphitization catalysts (iron nitrate or ferrocene) in the final calcination step of $LiFePO_4$. It was found that the increase in the sp^2/sp^3 ratio (graphene content) resulted in an improvement of composite conductivity and electrochemical performances.

6 $LiFePO_4$/graphene composite

Recently, owing to the high conductivity and flexibility, graphene has shown great potential applications in lithium-ion batteries[79-80]. And it is considered to play a very important role in increasing electrical conductivity and improving the rate capability and cycling stability. However, the combination manner of graphene and $LiFePO_4$ seems an important factor to realize the key function of graphene.

Ding et al.[81] investigated the effect of graphene on the electrochemical performance of $LiFePO_4$, which was synthesized by co-precipitation. However, no significant improvement in the electrochemical performance was observed, compared with that by the conventional carbon coating. In this case, $LiFePO_4$ particles were loosely loaded on the graphene sheets (as shown in Fig. 5a). The non-ideal results were possibly related to their composite manner. Later, Zhou et al.[82] created a 3D network of graphene wrapping on the $LiFePO_4$ particles via a hydrothermal method. The graphene sheets were bridged into a 3D conductive network (as shown in Fig. 5b), which supported the maximum fulfillment of its function because electrons could be easily transferred between the particles and graphene. The results indicated that this kind of graphene modification could give rise to an excellent rate performance.

7 Concluding Remarks

The types of the available carbonaceous precursors, the different composite manners and their effects on the physical properties and the electrochemical performance of the $LiFePO_4$/C composite were summarized. The advantages and disadvantages of each composite manner were also discussed. The introduction of the carbon materials with a higher graphitization degree and carbon string structure would be beneficial to dramatically increasing the electric conductivity. For targeting to achieve higher energy and power densities, the *in situ* carbon coating and the $LiFePO_4$ embedding within carbonaceous matrix might be promising strategies because of an increase in specific area and intimate contact. However, they do not have enough conductivity to act as conductive additive. The adding of the conductive carbon and the composite with carbon nanotubes and graphene can just greatly improve the electric conductivity rather than refining particle size. Therefore, combining these two ways, the electric conductivity and the electrochemical performance of $LiFePO_4$/C composites would be dramatically enhanced. However, most importantly, when the practical applications are targeted, strict control of the carbon content on the basis of optimizing the performance is worthy of further investigation.

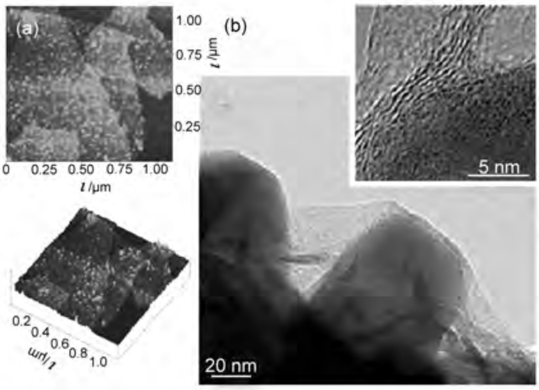

Fig. 5 (a) Morphology of $LiFePO_4$/graphene composite[81]; (b) TEM image of $LiFePO_4$/graphene composite[82] Inset: a high-resolution TEM image illustrates the 3-5 monolayet thickness of the graphene-sheets on the surface of each $LiFePO_4$ nanoparticle

Acknowledgments

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References

[1] Padhi A K, Nanjundaswarmy K S, Goodenough J B. Phospho-olivine as positive-electrode materials for rechargeable lithium batteries [J]. J Electrochem Soc, 1997, 144: 1188-1194.

[2] Andersson A S, Kalska B, Haggstrom L, et al. Lithium extraction/insertion in $LiFePO_4$: an X-ray diffraction and Mossbauer spectroscopy study [J]. Solid State Ionics, 2000, 130: 41-52.

[3] Prosini P P，Lisi M，Zane D，et al. Determination of the chemical diffusion coefficient of lithium in $LiFePO_4$［J］．Solid State Ionics，2002，148：45-51.

[4] Choi D，Kumta P N. Surfactant based sol-gel approach to nanostructured $LiFePO_4$ for high rate Li-ion batteries［J］．J Power Sources，2007，163：1064-1069.

[5] Kang B，Ceder G. Battery materials for ultrafast charging and disaharging［J］．Nature，2009，458：190-193.

[6] Park K S，Benayad A，Park M S，et al. Tailoring the electrochemical properties of composite electrodes by introducing surface redox-active oxide film：VO_x-impregnated $LiFePO_4$ electrode［J］．Chem Comm，2010，46：2572-2574.

[7] Chen J M，Hsu C H，Lin Y R，et al. High-power LiFePO4 cathode materials with a continuous nanocarbon network for lithium batteries［J］．J Power Sources，2008，184：498-502.

[8] Yamada A，Kudo Y，Liu K Y. Phase diagram of Lix(MnxFe1-x)PO4（0≤x，y≤1）［J］．J Electrochem Soc，2001，148：A1153-A1158.

[9] Eills B，Subramanya H P，Rho Y H，et al. Nanostructured materials for lithium-ion batteries：surface conductivity vs. bulk ion/electron transport［J］．Faraday Symposia of the Chemical Soc，2007，34：119-141.

[10] Chung S Y，Bloking J，Chiang Y M. Electronically conductive phosphor-olivines as lithium storage electrode［J］．Nature Mater，2001 1：123-128.

[11] Yin X，Huang K，Liu S，et al. Prepartion and characterization of Na-doped $LiFePO_4$/C composites as cathode materials for lithium-ion batteries［J］．J Power Sources，2010，195：4308-4312.

[12] Yang M R，Ke W H. The doping effect on the electrochemical properties of $LiFe_{0.95}M_{0.05}PO_4$（$M = Mg^{2+}$，Ni^{2+}，Al^{3+}，or V^{3+}）as cathode materials for lithium-ion cells［J］．J Electrochem Soc，2008，155：A729-A732.

[13] Sun C S，Zhou Z，Xu Z G，et al. Improved high-rate charge-discharge performance of $LiFePO_4$/C via V-doping［J］．J Power Sources，2009，193：841-845.

[14] Arumugam D，Kalaignan G P，Manisanker P. Synthesis and electrochemical characerizations of nano-crystalline $LiFePO_4$ and Mg-$LiFePO_4$ cathode materials for rechargeable lithium-ion batteries［J］．J Solid State Electrochem，2009，13：301-307.

[15] Li L J，Li X H，Wang Z X，et al. Stable cycly-life properties of Ti-doped LiFePO4 compounds synthesized by co-precipitation and normal temperature reduction method［J］．J Phys Chem Solid，2009，1：238-242.

[16] Liu H，Cao Q，Fu L J，et al. Doping effects of zinc on $LiFePO_4$ cathode materials for lithium ion batteries［J］．Electrochem Comm，2006，8：1553-1557.

[17] Chu Y Y. Preparation and property study of cathode material of lithium-ion battery［D］．Hsinchum，Taiwan：National Tsinghua University，2006.

[18] Jayaprakash N，Kalaiselvi N，Periasamy P. Synthesis and characterization of $LiM_xFe_{1-x}PO_4$（M=Cu，Sn，x=0.02）cathode-A study on the effect of cation substitution on $LiFePO_4$ materials［J］．Int J Electrochem Sci，2008，3：476-488.

[19] Gómez L S，Meatza I D，Martín M I，et al. Morphological，structual and elelctrochemical properties of lithium iron phosphates synthesized by spray pyrolysis［J］．Electrochim Acta，2010，55：2805-2809.

[20] Mestre A F，Hamelet S，Mascquerlier C，et al. High temperautre electrochemical performance of nanosized $LiFePO_4$［J］．J Power Sources，2010，195：6897-6901.

[21] Liu H. P，Wang Z. X，Li X. H，et al. Synthesis and electrochemical properties of olivine $LiFePO_4$ prepared by a carbonthermal reduction method［J］．J Power Sources，2008，184：469-472.

[22] Zhecheva E，Mladenov M，Zlatilova P，et al. Particle size distribution and electrochemical properties of $LiFePO_4$ prepared by a freeze-drying method［J］．J Physics Chemistry Solid，2010，71：848-853.

[23] Kuwahara A，Suzuki S，Miyayama M. Hydrothermal synthesis of $LiFePO_4$ with small particle size and its electrochemical properties［J］．J Electroceram，2010，24：69-75.

[24] Kim J-K，Choi J-W，Chauhan G S，et al. Enhancement of elelctrochemical performance of lithium iron phosphate by controlled sol-gel synthesis［J］．Electrochim Acta，2008，53：8258-8264.

[25] Ellis B L，Lee K T，Nazar L F. Positive electrode materials for Li-ion and Li-batteries［J］．Chem Mater，2010，22：691-714.

[26] Jugovic D，Uskokovic D. A review of recent development in the synthesis procedures of lithium iron phosphate powders［J］．J Power Sources，2009，190：538-544.

[27] Zhang W J. Structure and performance of $LiFePO_4$ cathode materials：A review［J］．J Power Sources，2011，196：2962-2970.

[28] Bewlay S L，Konstsntinov K，Wang G X，et al. MW-assisted synthesis of $LiFePO_4$ for high power applications［J］．J Power Sources，2008，180：875-879.

[29] Wang K，Cai R，Yuan T，et al. Process investigation，electrochemical characterization and optimization of $LiFePO_4$/C composite from mechanical activation using sucrose as carbon source［J］．Electrochem Acta，2009，54：2861-2868.

[29] Kim K，Cho Y H，Kam D W，et al. Effects of organic acids as reducing agents in the synthesis of $LiFePO_4$［J］．J Alloys and Compounds，2010，504：166-170.

[31] Oh S W，Myung S T，Oh S M，et al. Double carbon coating of $LiFePO_4$ as high rate electrode for rechargeable lithium batteries［J］．Adv Mater，2010，22：4842-4845.

[32] Guo X F，Zhang Y T，Zhan H，et al. Investigation on the microwave-derived $LiFePO_4$/C cathode materials［J］．Solid State Ionics，2010，181：1757-1763.

[33] Liu A F，Hu Z H，Wen Z B，et al. $LiFePO_4$/C with high capacity synthesized by carbonthermal reduction method［J］．Ionics，2010，16：311-316.

[34] Hong S-A，Kin S J，Kim J，et al. Small capacity decay of lithium iron phosphate（$LiFePO_4$）synthesized continuously in supercritical water：Comparsion with solid-state method［J］．J Supercritical Fluids，2011，55：1027-1037.

[35] Liu Y Y，Cao C B. Enhanced elelctrochemical performance of nano-sized $LiFePO_4$/C synthesized by an ultrasonic-assisted co-precipitation method［J］．Electrochem Acta，2010，55：4694-4699.

[36] Zhao X，Tang X Z，Zhang L，et al. Effecs of neodymium aliovalent substitution on the strucutre and electrochemical performance of $LiFePO_4$［J］．Electrochem Acta，2010，55：5899-5904.

[37] Pan M S，Zhou ZT. Carbon rich surface of $LiFePO_4$ grain en-

hancing its rate capability [J]. Mater Lett, 2011, 65: 1131-1133.

[38] Koltypin M, Aurbach D, Nazar L, et al. More on the preparation of $LiFePO_4$ electrodes - The effect of synthesisi route, solution composition, aging and temperature [J]. J Power Sources, 2007, 174: 1241-1250.

[39] Salah A A, Mauger A, Julien C M, et al. Nano-sized impurity phases in relation to the mode of preparation of $LiFePO_4$ [J]. Mater Sci Eng B, 2006, 129:232-244.

[40] Lim H H, Jang I C, Lee S B, et al. The important role of adipic acid on the synthesis of nanocrystalline lithium iron phosphate with high rate performance [J]. J Alloys Compunds, 2010, 495: 181-184.

[41] Son C G, Yang H M, Lee G W, et al. Manipulation of adipic acid application on the electrochemical propeties of $LiFePO_4$ at high rate performance [J]. J Alloys Compounds, 2011, 509: 1279-1284.

[42] Liu Y Y, Liu D W, Zhang Q F, et al. Lithium iron phosphate/carbon nanocomposite film cathode for high energy lithium batteries [J]. Electrochim Acta, 2011, 56: 2559-2565.

[43] Uchiyama H, Imai H. Preparation of $LiFePO_4$ mesocrystals consisting of nanorods through organic-mediated parallel growth from a precursor phase [J]. Crystal Growth and Design, 2010, 10: 1777-1781.

[44] Boyano I, Blazquez J A, Meatza I D, et al. Preparation of C-$LiFePO_4$/polypyrrole lithium rechargeable cathode by consecutive potential steps electrodeposition [J]. J Power Sources, 2010, 195: 5351-5359.

[45] Huang Y H, Goodenough J B. High-rate $LiFePO_4$ lithium rechargeable battery promoted by electrochemically active polymer [J]. Chem Mater, 2008, 20: 7237-7241.

[46] Jugovic D, Mitric M, Cvjeticanin N, et al. Synthesis and characterization of $LiFePO_4$/C composite obtained by sonochemical method [J]. Solid State Ionics , 2008, 179: 415-419.

[47] Liu H W, Yang H M, Li J L. A novel method for preparing $LiFePO_4$ nanorods as a cathode materials for lithium-ion power batteries [J]. Electrochim Acta, 2010, 55: 1626-1629.

[48] Fey G T-K, Huang K-P, Kao H-M, et al. A polyethylene glycol-assisted carbonthermal reaction method to synthesize $LiFePO_4$ using industrial raw materials [J]. J Power Sources, 2011, 196: 2810-2818.

[49] Bai Y M, Qiu P, Wen Z-L, et al. Improvement of electrochemical performance of $LiFePO_4$ cathode materials by coating of polythiophene [J]. J Alloys Compounds, 2010, 508: 1-4.

[50] Sun L Q, Li M J, Cui R H, et al. The optimum nanomicro structure of $LiFePO_4$/ortho-rich polyacene composite [J]. J Phys Chem C, 2010, 114: 3297-3303.

[51] Liang G, Wang L, Ou X, et al. Lithium iron phosphate with high-rate capacity synthezised through hydrothermal reaction in glucose solution [J]. J Power Sources, 2008, 184: 538-542.

[52] Awarke A, Lauer S, Pischinger S , et al. Percolation-tunneling modeling for the study of the electric conductivity in $LiFePO_4$ based Li-ion battery cathodes [J]. J Power Sources, 2011, 196: 405-411.

[53] Palomares V, Goni A, Muro I G, et al. Conductive additive content balance in Li-ion battery cathodes: Commerical carbon blacks vs. *in situ* carbon from $LiFePO_4$/C composites [J]. J Power Sources, 2010 195: 7661-7668.

[54] Dominko R, Bele M, Gaberscek M, et al. Impact of the carbon coating thickness on the electrochemical performance of $LiFePO_4$/C composites [J]. J Electrochem Soc, 2005 152: A607-A610.

[55] Jin E M, Jin B, Park K-H, et al. Electrochemical characteristics of lithium iron phosphate with multiwalled carbon nanotube for lithium polymer batteries [J]. J Nanosci Nanotech, 2008, 8: 5057-5061.

[56] Kuroda S, Tobori N, Sakuraba M, et al. Charge-discharge properties of a cathode prepared with ketjen black as the electro-conductive additive in lithium ion batteries [J]. J Power Sources, 2003, 119-121: 924-928.

[57] Li X L, Kang F Y, Bai X D, et al. A novel network composite cathode of $LiFePO_4$/multiwalled carbon nanotube with high rate capability for lithium ion batteries [J]. Electrochem Comm, 2007, 9: 663-666.

[58] Zhao J Q, He J P, Zhou J H, et al. Facile synthesis for $LiFePO_4$ nanospheres in tridimensional porous carbon framework for lithium ion batteries [J]. J Phys Chem C, 2011, 115:2888-2894.

[59] Doherty C M, Caruso R A, Smarsly B M, et al. Collodial crystal templating to produce hierarchically porous $LiFePO_4$ electrode materials for high power lithium ion batteries [J]. Chem Mater, 2009, 21: 2895-2903.

[60] Doherty C M, Caruso R A, Smarsly B M, et al. Hierarchically porous monolithic $LiFePO_4$/carbon electrode materials for high power lithium ion batteries [J]. Chem Mater, 2009, 21: 5300-5306.

[61] Wu X L, Jiang L Y, Cao F F, et al. $LiFePO_4$ nanoparticles embodded in a nanoporous carbon matrix : superior cathode materials for electrochemical energy-storage devices [J]. Adv Mater, 2009, 21: 2710-2714.

[62] Sides C R, Croce F, Yong V Y, et al. A high-rate, nanocomposite $LiFePO_4$/carbon cathode [J]. Electrochem Solid-state Lett, 2005, 8: A484-A487.

[63] Croce F, Epifanio A D, Hassoun J, et al. A novel concept for the synthesis of an improved $LiFePO_4$ lithium batteries cathode [J]. Electrochem Solid-State Lett, 2002, 5: A47-A50.

[64] Yang M, Gao Q M. $LiFePO_4$/C composite cathode material with a continuous porous carbon network for high power lithium-ion battery [J]. J Alloys Compounds, 2011, 509: 3690-3698.

[65] Dimesso L, Jacke S, Spanheimer C, et al. Investigation on 3-dimensional carbon foams/$LiFePO_4$ composites as function of the annealing time under inert atmosphere [J]. J Alloys Compounds, 2011, 509: 3777-3782.

[66] Peng X H, Chen J Y, Misewich J A, et al. Carbon nanotube-nanocrystal heterostructures [J]. Chem Soc Rev, 2008, 38: 1076-1098.

[67] Murugan A V, Muraliganth T, Ferreira P J, et al. Dimensionally modulated, single-crystalline $LiMPO_4$ (M = Mn, Fe, Co and Ni) with nano-thumblike shapes for high-power energy storage[J]. Inorg Chem, 2009, 48: 946-952.

[68] Liu Y, Li X, Guo H, et al. Effect of carbon nanotube on the electrochemical performance of $LiFePO_4$/graphene battery [J]. J Power Sources, 2008, 184: 522-526.

[69] Wang L, Huang Y, Jiang R, et al. Nao-$LiFePO_4$/MWCNT cathode materials prepared by room-temperature solid-state reac-

tion and microwave heating [J]. J Electrochem Soc, 2007, 154: A1015-A1019.

[70] Muraliganth T, Murugan A V and Manthiram A. Nanoscale networking of $LiFePO_4$ nanorods synthesized by a microwave-solvothermal route with carbon nanotubes for lithium ion batteries [J]. J Mater Chem, 2008, 18: 5661-5668.

[71] Jin B, Gu H-B, Zhang W, et al. Effect of different carbon conductive additives on electrochemical properties of $LiFePO_4$-C/Li batteries [J]. J Solid State Electrochem, 2008, 12: 1549-1554.

[72] Jin B, Park K H, Gu H B. Electrochemical properties of $LiFePO_4$-multiwalled carbon nanotubes composite cathode materials for lithium polymer battery [J]. Electrochem Comm, 2008, 10: 1537-1540.

[73] Chen J C, Whittingham M S. Hydrothermal synthesis of lithium iron phosphate [J]. Electrochem Comm, 2006, 8: 855-858.

[74] Doeff M M, Wilcox J D, Yu R, et al. Impact of carbon structure and morphology on the electrochemical performance of $LiFePO_4$/C composites [J]. J Solid State Electrochem, 2008, 12: 995-1001.

[75] Lee Y J, Li H, Kim W J, et al. Fabricating genetically engineered high-power lithium-ion batteries using multiple virus genes [J]. Science, 2009, 324: 1051-1055.

[76] Kavan L, Bacsa R, Tunckol M, et al. Multi-walled carbon nanotubes functionalized by carbonoxylic groups : Acitvation of TiO_2(anatase) and phosphate olivines ($LiMnPO_4$: $LiFePO_4$) for electrochemical Li^+ storage [J]. J Power Source, 2010, 195: 5360-5369.

[77] Kavan L, Exnar I, Cech J, et al. Enhancement of electrochemical activity of $LiFePO_4$(olivine) by amphiphilic Ru-bipyidine complex anchored to a carbon nanotube [J]. Chem Mater, 2007, 19: 4716-4721.

[78] Kavan L, Exnar I, Zakeeruddin S M, et al. Molecular wiring of olivne $LiFePO_4$ by ruthenium(II)-bipyridine complexes and by their assemblies with single-walled carbon nanotubes [J]. J Phys Chem C, 2008, 112: 8708-8714.

[79] Novoselov K S, Geim A K, Morozov S V, et al. Electric field effect in atomically thin carbon films[J]. Science, 2004, 306: 666-669.

[80] Geim A K, Novoselov K S. The rise of grapheme[J]. Nat Mater, 2007, 6: 183-191.

[81] Ding Y, Jiang Y, Xu F, et al. Preparation of nano-structured $LiFePO_4$/graphene composites by co-precipitation method [J]. Electrochem Comm, 2010, 12: 10-13.

[82] Zhou X F, Wang F, Zhu Y M, et al. Graphene modified $LiFePO_4$ cathode materials for high power lithium ion batteries [J]. J Mater Chem, 2011, 21: 3353-3358.

碳质材料对磷酸铁锂正极材料物理和电化学性能的影响

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摘　要： 通过综述碳质材料对磷酸铁锂($LiFePO_4$)电极材料物理和电化学性能的影响，评述了碳质材料在不同 $LiFePO_4$/C 复合电极材料中的作用及其优缺点。指出：炭膜的原位包覆和模板炭的引入，限制了 $LiFePO_4$ 晶粒的生长，进而提高了电极材料的电导率；而导电炭和石墨烯的引入，则是直接提高了电极材料的电导率；有机结合这两种碳质材料的复合方式将会极大改善电极材料的电化学性能。但是，为了提高电极材料的体积能量密度及其振实密度，应该最大限度地降低碳质材料在 $LiFePO_4$/C 复合电极材料中的含量。

关键词： 磷酸铁锂；炭包覆；炭基体；导电炭；碳纳米管；石墨烯

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