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Immobilization of nanosized LiFePO₄ spheres by 3D coralloid carbon structure with large pore volume and thin walls for high power lithium-ion batteries

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HIGHLIGHTS

- Poly(benzoxazine-co-resol) based N-doped porous carbon using silica as template.
- ► Coralloid carbon with large pore volume provides high LiFePO₄ loading.
- ► LiFePO₄ nanospheres from the confinement of carbon lead to fast Li ion diffusion.
- ► Thin interpenetrated walls offer a fast and continuous electron transfer network.
- The obtained LiFePO₄/C exhibit excellent rate and cycling performance.

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ABSTRACT

A novel LiFePO₄/C composite, including 85.4 wt% of spherical LiFePO₄ nanocrystallites with the size of 22 nm is fabricated by using 3D coralloid nitrogen-containing carbon with large pore volume (4.68 cm³ g⁻¹) and thin walls (2–3 nm) as interpenetrating conductive framework. Based on the whole composite, the LiFePO₄/C cathode material exhibits a stable and high reversible capacity of 144.6 mA h g⁻¹ at 0.1 C and 60.4 mA h g⁻¹ at 20 C (based on the weight of LiFePO₄, it can deliver a high capacity of 155.8 mA h g⁻¹ at 0.1 C and 85.3 mA h g⁻¹ at 20 C). The cell retains 96.7% of its initial capacity at 10 C over 1000 cycles with an ultrahigh specific power of 5114 W kg⁻¹ and the coulombic efficiency is >99%. The excellent performance is ascribed to the facile lithium-ion diffusion within the LiFePO₄ nanocrystallites and high conductivity through the 3D continuous network. This coralloid carbon not only provides sufficient space for LiFePO₄ hosting to further assist in energy storage, but also acts as a rigid nano-confinement support that prevents agglomeration of LiFePO₄ during calcinations, which might be extended for the fabrication of other nano-sized electrode materials.

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1. Introduction

In recent years, lithium-ion battery has captured a large share of the rechargeable battery market for its great potential to be used as power sources for electric vehicles (EVs) and hybrid electric vehicles (HEVs) [1]. Lithium iron phosphate (LiFePO₄), is a promising





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cathode material because of its excellent electrochemical properties with a theoretical capacity of 170 mA h g⁻¹, low cost, and low toxicity. However, the low intrinsic electronic conductivity of this material and the slow diffusion of lithium ions across the two phase boundary seriously limit both the utilization and rate capability of the material [2–4]. In order to address these problems, many efforts have been made during the preparation of LiFePO₄-based electrode materials, including doping with isovalent ions [5,6], surface coating or admixing with electronically conductive materials [7–12], and creating porosity [13–17]. Whilst many of these approaches have successfully improved the utilization capacity of LiFePO₄ at low discharge rates, the LiFePO₄ cathode still suffers from a rapid loss in capacity as current density (C-rate) increases [18].

Nano-sized LiFePO₄ as electrode materials for lithium-ion batteries shows high rate performance and have recently attracted much attention because their reduced dimensions enable much higher power [19–21]. According to the diffusion formula $t = L^2/2D$ (where t is the diffusion time, L is the diffusion distance, and D is the diffusion coefficient), reduction of the particle size can significantly shorten the diffusion time of Li in LiFePO₄, resulting in a much enhanced power performance [22]. However, several nano-sized cathode materials synthesized by low-temperature methods are poorly crystalline, which reduces their electrochemical stability. Therefore, its subsequent process should be under high temperature, where larger crystallite sizes are almost inevitable [23]. To restrict the particle size as well as improve the conductivity of LiFePO₄, an effective route is to fabricate carbon coatings around each active and nanosized particles, which is a way to kill two birds with one stone. Approaches based on either thermal decomposition of carbon precursors (e.g. sucrose [24], ascorbic acid [25], and polymers [26,27]) on LiFePO₄ particles or synthesis of LiFePO₄ and carbon composites [22,28] have been widely studied, by which carbon coated LiFePO₄ particles can be produced. Unfortunately, it is often very difficult to achieve ideal, continuous and uniform carbon coating framework.

Compared to the surface coating strategy, using porous carbon to synthesize LiFePO₄ cathodes with open structure has been proven to be an effective way to prepare high rate materials with higher specific surface area, faster ion diffusion and better electronic connectivity, because of the continuous carbon network and unique porosity. Furthermore, the morphology and dimension of LiFePO₄ particles can be tailored fine through varying the structures of porous carbon supports. Doherty et al. produced 50 wt% loading of LiFePO₄ inside hierarchically porous carbon synthesized from a porous silica hard template and delivered a specific capacity of 140 mA h g^{-1} at 0.1 C and 100 mA h g^{-1} at a discharge rate of 5 C based on the mass of LiFePO₄ only [29]. Yang et al. achieved 36 wt% and 52 wt% loading of LiFePO₄ by using microporous and mesoporous carbon as support. The synthesized composite using microporous carbon showed capacities of 97 mA h g^{-1} at 0.2 C and 66 mA h g^{-1} at 50 C based on the mass of the entire LiFePO₄/C composite [30]. Wang et al. prepared LiFePO₄/C composite with 87 wt% LiFePO₄ loading using mesoporous carbon CMK-3 as the support, which showed an ultrahigh capacity of 118 mA h g^{-1} at 10 C and capacity retention of 91% after 1000 cycles [31]. Hill et al. made high surface area LiFePO₄ cathode material using mesoporous carbon templated from cubic KIT-6 silica, showing a high power and rate capacity of 128 mA h g^{-1} at 23 C [18]. However, the loading of LiFePO₄ is low, only 34.4 wt%, which certainly leads to low tap density.

Inspired from these previous studies, an ideal structure for highperformance LiFePO₄ should contain high loading of this active materials, nanosized particles coated with connected thin-wall carbon, thus allowing high tap density, easy penetration of lithium ions [32]. Moreover, nitrogen-containing carbon framework is practically more desirable in applications of electrochemistry [33,34]. In our previous work, we have successfully synthesized advanced nitrogen-doped porous carbon materials based on poly(benzoxazine-co-resol) system [35–37], which offers a high degree of flexibility in the molecular design of monomers using amines as both the catalyst and nitrogen source. Considering that the highly interconnected and hierarchical pore structure in the synthesized carbon framework is good for rapid lithium-ion transport, we design a synthesis of coralloid carbon materials based on this system adding colloidal silica nanospheres as hard templates. The obtained carbons show a 3D nitrogen-doped conductive framework, high mesopore volume, uniform mesopore sizes, and thin carbon walls. Using this carbon as the support, LiFePO₄ precursors can be easily infiltrated. The particle sizes of the prepared LiFePO₄ cathode are small and uniform due to the confinement effect of mesopores. Hence, the lithium-ion diffusion kinetic is faster. In addition, less polarization and improved rate performance are expected.

2. Experimental section

2.1. Samples preparation

Chemicals. Resorcinol (99.5%) was purchased from Tianjin Kermel Chemical Reagent Co., Ltd. Ludox AS-40 was purchased from Sigma—Aldrich. Formaldehyde (37 wt%), 1,6-diaminohexane (DAH, 99.0%), phosphoric acid (85%), iron (III) nitrate nonahydrate (98.5%) and lithium acetate dehydrate (99%) were supplied by Sinopharm Chemical Reagent Co., Ltd. All chemicals were used as received.

Synthesis of 3D coralloid carbon structures. The commercially available, aqueous suspension of silica colloids (Ludox AS-40), containing 40 wt% silica and with an average colloid size of 24 nm, were used directly in synthesis. Typically, 2 mmol resorcinol was first dissolved in deionized water with vigorous stirring at the temperature of 24 °C and then 4 mmol formaldehyde (37 wt%) were added to form a clear solution. Subsequently, a certain amount of Ludox AS-40 was added into the clear solution. After addition of 0.5 mmol DAH, the clear solution turns white immediately. The resultant solution was further heated to 80 °C accompanied with vigorous stirring for 42 h. The precipitated compounds were obtained by filtration and then purified with water and ethanol. The as-prepared Si/polymer compounds were pyrolyzed at 800 °C for 2 h under nitrogen atmosphere. The pyrolyzed product was treated with aqueous NaOH solution (2.5 M) to remove the silica and further recovered by filtration, washed with water and ethanol. The molar ratio of SiO₂ and resorcinol vary from 2:1, 3.5:1 to 5:1, the obtained carbon materials were accordingly denoted as C-1, C-2, and C-3.

Synthesis of LiFePO4/C composites. LiFePO4/C composites were fabricated using the synthesized porous carbon as the support. The lithium iron phosphate precursor solution was prepared using water based solution chemistry, and the precursors were chosen so that the solution would not precipitate prior to infiltration. In a typical procedure, 10 mmol of Fe(NO₃)₃·9H₂O, 10 mmol of $C_2H_3O_2Li \cdot 2H_2O_1$, and 10 mmol of H_3PO_4 were dissolved in a minimal amount of water with stirring to ensure the total solution to 5 mL. Then, the transparent solution was added dropwise to 0.1 g of carbon with stirring, followed by drying at 90 °C. The amount of the impregnating solution was calibrated based on the pore volume of the carbon structure. To bring about full utilization of the pores, the same impregnation procedure was repeated once more, followed by drying at 90 °C overnight. Finally, the powder was heated under a flowing atmosphere of H₂ (5 vol%)/N₂ (95 vol%) at 3 °C min⁻¹ to 750 °C and maintained at this temperature for 6 h to yield a black powder. The obtained LiFePO₄/C composites were denoted as LFP/ C-1, LFP/C-2, LFP/C-3, which were prepared by using carbon supports C-1, C-2, and C-3, respectively.

As a contrast, a pure LiFePO₄ sample was synthesized under the same conditions as that of LiFePO₄/C, but only the carbon framework excluded, which was denoted as pure-LFP.

2.2. Characterization

The X-ray diffraction (XRD) measurements were taken on a Rigaku D/Max 2400 diffractometer using Cu-Ka radiation (40 kV, 100 mA, $\lambda = 1.5406$ Å). Scanning electron microscope (SEM) investigations were carried out with a Hitachi S-4800I instrument at 10 kV. Transmission electron microscopy (TEM) images were obtained with a FEI Tecnai F30 or a Hitachi HF2000 transmission electron microscope, equipped with a cold field emission gun. Nitrogen sorption isotherms were measured with a Micromeritics tristar 3000 instrument at liquid nitrogen temperature. Samples were degassed at 200 °C for at least 4 h prior to determination of the isotherms. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas (S_{BET}). Pore size distributions (PSDs) were derived from the adsorption branches of the isotherms using the Barrett-Joyner-Halenda (BJH) model. Thermogravimetric analysis was measured from room temperature to 800 °C in air with a heating rate of 10 °C min⁻¹ using a STA449 F3 Jupiter thermogravimetric analyzer (NETZSCH). The electronic conductivity was measured by 4-Point Probes Resistivity measurement System (RTS-8).

2.3. Electrochemical tests

The electrodes were fabricated using a mixture of active material (80 wt%), conductive carbon black (15 wt%), and polyvinylidene fluoride (PVDF 5 wt% Aldrich) in N-methyl-2-pyrrolidone (NMP) to form a slurry. The slurry was spread onto Al foil and dried in a vacuum oven at 100 °C overnight. The electrode area is 1.13 cm² and the loading of active material is 2.0 ± 0.5 mg cm⁻². Electrochemical experiments were performed via CR2025 cointype test cells assembled in an argon-filled glove box, using Li metal as the negative electrode and Celgard 2400 membrane as the separator. The electrolyte consists of a solution of 1 M LiPF6 in dimethyl carbonate (DMC), ethyl methyl carbonate (EMC) and ethylene carbonate (EC) (1:1:1, v/v/v). The galvanostatic charge and discharge experiment was performed in the range of 2.5–4.2 V at room temperature on a Land CT2001A battery test system. Cyclic voltammetry (CV) measurement was carried out on CHI660D electrochemical workstation. The electrochemical impedance spectroscopy (EIS) was performed by using EG&G model 273 Gal-vanostat/Potentiostat equipped with 5280 two phase lock-in analyzer by superimposing an AC signal of 5 mV amplitude on open circuit potential over a frequency domain from 100 kHz to 10 mHz.

3. Results and discussion

The overall fabrication procedure of LiFePO₄/C composite is schematically illustrated in Fig. 1. The coralloid carbon materials were prepared by the polymerization of resorcinol, formaldehyde and DAH to form polybenzoxazine using colloidal silica as the hard template. It is known that the isoelectric point of silica is at pH about 2 [38]. The Ludox AS-40 silica nanospheres are actually stabilized by ammonia solution (pH = 9.1-9.5). Under this condition, the surface of silica is negatively charged, which is then surrounded by NH_4^+ through electrostatic attraction. Our study shows that polybenzoxazine exhibits negatively charged surface under alkaline conditions. Thus, ammonium cations can act as bridges to link the silica surface with polybenzoxazine through such electrostatic attraction, resulting in a successful polymer coating around silica nanospheres. The as-prepared SiO₂/polymer compounds were pyrolyzed at 800 °C under nitrogen atmosphere. And then the pyrolyzed product was treated with aqueous NaOH solution to remove the silica template and bring abundant spherical mesopores. After infiltration and thermal annealing, the open channels of the mesoporous carbon were loaded with LiFePO₄ nanocrystallites. Finally, the coralloid LiFePO4/C composites were successfully obtained by heat treatment at 750 °C for 6 h under N₂/ H₂ atmosphere (see the Experimental section for details).

3.1. Porosity, crystallinity and morphology of 3D mesoporous carbon structure and LiFePO₄/C composite

The nitrogen sorption isotherms were measured to determine the pore structure and the Brunauer–Emmett–Teller (BET) surface areas of both the carbon framework and the LiFePO₄/C composites. As shown in Fig. 2, all isotherms feature hysteresis between the desorption and adsorption branches, indicating the presence of mesopores. The pore size distribution plots specifically confirm that all the samples have a bimodal pore system concentrated at 22 and 2 nm, which are attributed to the diameter of silica nanospheres template and the pores in the carbon walls. With an increase in the



Fig. 1. Synthesis principle for 3D coralloid carbon structures with large pore volume and thin walls for the immobilization of LiFePO₄ nanospheres.



Fig. 2. Nitrogen sorption isotherms of the carbon structures and LiFePO₄/C composites C-1 and LFP/C-1 (a), C-2 and LFP/C-2 (c), C-3 and LFP/C-3 (e). The right is the corresponding pore size distributions (b), (d), (f) calculated using the BJH formula from the adsorption branch.

amounts of the silica template used, the pore volumes of samples from C-1 to C-3 significantly enlarged, indicating that the silica nanospheres are indeed play a role as porogens. As expected, all the LiFePO₄/C composites show reduced surface area and total pore volume after infiltration, revealing that the porous spaces originally corresponding to the silica nanospheres were now occupied by the LiFePO₄ analogous.

Table 1 contains the characteristics of textural parameters for all samples. The developed porosity of the carbon supports is beneficial to promise high LiFePO₄ loading and interface area between the active material and carbon framework. Taking the carbon support C-3 as the example, it has a larger total pore volume (4.68 cm³ g⁻¹) and higher BET surface area (977 m² g⁻¹). After infiltration, a significant reduced surface area (136 m² g⁻¹) and pore volume (0.33 cm³ g⁻¹) are observed. This is an indication that LiFePO₄ filled in most pore spaces of the carbon support C-3. The overall weight percentage of LiFePO₄ in the LFP/C-3 composite is estimated to be

Table 1
Parameters of porous carbon framework and LiFePO ₄ /C composites.

Sample	V _{total} (cm ³ g ⁻¹)	S_{BET} (m ² g ⁻¹)	D _{peak} (nm)	LFP D _{size} (nm)	LFP loading (wt %)
C-1	1.04	563	22	_	_
C-2	3.07	878	22	-	-
C-3	4.68	977	22	_	_
LFP/C-1	0.84	408	21	23.7	54.1
LFP/C-2	0.61	211	21	21.8	77.1
LFP/C-3	0.33	136	18	19.6	85.4

85.4 wt% by a TG analysis (Fig. S1 in the Supporting information). It is noted that all the samples have certain surface area after infiltration, which is ascribed to the retaining of the intrinsical meso-structure of such mesoporous carbon framework.

As further confirmation, Fig. 3 compares the X-ray diffraction (XRD) patterns of pure LiFePO₄ versus the LiFePO₄/C composites. Both patterns can be indexed to the orthorhombic LiFePO₄ (JCPDS



Fig. 3. Powder X-ray diffraction patterns of the LiFePO₄/C composites and pure LiFePO₄.

No. 81-1173). Using Scherer's formula, the crystalline size of sample LFP/C-1, LFP/C-2 and LFP/C-3 are calculated to be 23.7, 21.8 and 19.6, respectively. Thus, the particle sizes are in line with the sizes of mesopores. The similar dimension (\sim 22 nm) of LiFePO₄ crystallites in sample LFP/C-1, LFP/C-2 and LFP/C-3 means LiFePO₄ nanocrystallites grew within the mesopores of the carbon framework, agreeing with the N₂ sorption measurements. However, the peaks occurred in the sample pure-LFP are much narrow. This demonstrates that the narrowing of the peaks in the pure sample is corresponding to the free grew large LiFePO₄ crystallite in the absence of the confinement effect from the mesoporous carbon framework. The SEM observation (Fig. S2 in the Supporting information) further confirmed that pure-LFP agglomerates into larger particles, that agrees the XRD result.

The morphology features of the carbon framework and LiFePO₄/ C composite were observed by SEM. As shown in Fig. 4a, c, e, the carbon framework consists of many branches, which interpenetrate to form a 3D open porous structure with a coral-like morphology. The thin carbon walls and open mesopores (\sim 22 nm) that derived from silica template can be clearly seen from Fig. 4e. The large pore volume of this sample implies that such open mesopore system is the unique feature of this sample as a whole. Fig. 4b, d, f shows that the LiFePO₄/C composites inherit the morphology of the carbon framework, which further confirms that LiFePO₄ crystallites nucleated and grew within the mesopores without affecting the external morphology of the carbon support. The SEM observation is well in agreement with the findings by N₂ sorption measurements and XRD analysis.

To throw further light on the structure and detection of the carbon surrounding walls on the LiFePO₄ particles, the synthesized LFP/C-3 powders were examined by TEM. As shown in Fig. 5a, the particles exhibit a spherical shape with a similar size of the



Fig. 4. SEM images of the carbon structures C-1 (a), C-2 (c), C-3 (e), and their corresponding LiFePO₄/C composites LFP/C-1 (b), LFP/C-2 (d), LFP/C-3 (f).



Fig. 5. TEM image (a) and HRTEM image (b) of LFP/C-3 composite, the inset is the image of LiFePO₄; SEM image of a representative region of sample LFP/C-3 (c); EDX chemical maps depicting X-ray K-shell peaks for: (d) iron, Fe; (e) potassium, P; (f) oxygen, O; (g) carbon, C; (h) nitrogen, N.

mesopores (\sim 22 nm) of the carbon structures, indicating that most of the pores within the carbons are filled with LiFePO₄ nanospheres. This shape control is derived from the confinement effect from the spherical mesopores. Each unit in the carbon framework shows elongated leguminous shape with a number of connected LiFePO₄ nanospheres embedded in it, which is consistent with the SEM observation. Fig. 5b shows the high resolution TEM (HRTEM) image of the LFP/C-3 composite. The dark spheres are the LiFePO₄ crystals. It can be seen that the LiFePO₄ crystals have close contact with the carbon surrounding walls. The inset image shows that the dspacing values of the adjacent lattice planes are about $2.52 \cdot$, which corresponds to (311) planes of orthorhombic phase LiFePO₄. Additionally, we can clearly see the smooth and uniform carbon walls with thickness of 2-3 nm on the surface of LiFePO₄ nanocrystallines. The thin carbon walls connect each of the active particles together to form a highly 3D conductive framework. Closer observation confirms that the thin carbon walls contain micropores, agreeing with the N₂ sorption measurements. This ideal structure allows electrons effectively supply into the LiFePO₄ cores through the continuous thin carbon walls during an operation. Meanwhile, Lithium ions can readily diffuse into and out of the composite, due to the 3D open structure with small LiFePO₄ cores and continuous thin carbon walls.

Considering that the largest pore volume of the carbon framework will bring maximum LiFePO₄ loading to promise high tap density, we made EDX chemical maps of sample LFP/C-3 for the region imaged by wide range SEM in Fig. 5c. As shown in Fig. 5d-h, X-ray K-shell peaks for iron (Fe), phosphorus (P), oxygen (O), carbon (C) and nitrogen (N) can be unambiguously identified, indicating that LiFePO₄ nanocrystallines are uniformly dispersed within the carbon support. Meanwhile, due to the use of amines in the synthesis, such LiFePO₄/C composite contains intrinsic nitrogen-containing groups. The nitrogen content in the composite LFP/C-3 is directly detected by EDX pattern to be 1.26 wt% (Fig. S3 in the Supporting information), which is beneficial to the improvement of electrochemical performance [33,34,39,40].

3.2. Electrochemical performance of LiFePO₄/C composite as cathode in LIBs

The electrochemical properties of LiFePO₄/C composites were tested in CR-2025 coin half-cells at 298 K. The galvanostatic charge—discharge curves of various LiFePO₄/C versus Li cell, cycled between the voltage window of 2.5–4.2 V at 0.1 C are shown in Fig. 6a. It is obvious that the pure LiFePO₄ shows a lower initial discharge capacity of 70.4 mA h g⁻¹ with a substantial drop in the plateau potential compared with LiFePO₄/C composites. After encapsulating LiFePO₄ inside the carbon framework, the polarization between the charge and discharge plateaux is reduced to 60 from 140 mV of the sample without carbon. This strongly confirmed that the kinetics of the LiFePO₄/C are indeed improved. Samples LFP/C-1 and LFP/C-2 deliver the initial discharge capacities of 68.1 and 106.5 mA h g⁻¹ (based on the weight of composite, the same below except special claimed), respectively. While, sample LFP/C-3 gives the largest initial discharge capacity of 144.6 mA h g⁻¹ with much flatter and longer discharge plateaus.



Fig. 6. Electrochemical tests of the LiFePO₄/C composites and the pure LiFePO₄: (a) the first charge–discharge profiles at 0.1 C (0.1 C corresponds to 17 mA g⁻¹); (b) rate performance at current rates from 0.1 C to 10 C, and back to 0.1 C for 5 cycles and cycling performance at 1 C for cycles 40–90; (c) cyclic voltammograms at a scanning rate of 0.2 mV s⁻¹; (d) AC impedance spectroscopy of the batteries placed 12 h after assembled. The specific capacity is based on the entire weight of a LiFePO₄/C composite.

This difference is likely due to the larger pore volume and thinner walls of C-3 carbon, leading to a high LiFePO₄ loading of 85.4 wt% (see Table 2) and also increased interface areas between the carbon and the LiFePO₄ active electrode material. This probably facilitates current collection from the particles and ultimately alleviates electrode polarization.

The rate performance and the cycling stability during the lithium-ion insertion/extraction processes are key factors for successful industrial production of cathode electrodes. Fig. 6b reveals that the cycling stabilities are almost the same for all of the LiFePO₄/C composites, while the rate performance and the overall storage capacity vary, as shown in Table 2. Although the specific capacity gradually decreases as the current rate increased, sample LFP/C-3 shows the best electrochemical performance of 128.4 mA h g^{-1} at 1 C followed by LFP/C-2 (102.3 mA h g^{-1}), and LFP/C-1 (50.3 mA h g^{-1}) with nearly 100% capacity retention over 50 cycles. Even at a high current rate of 10 C, a capacity of 83 mA h g^{-1} is still obtained, demonstrating that our carbon-coated composite can endure high rate charge and discharge. In contrast, the pure LiFePO₄ only delivers a capacity of 39.1 mA h g^{-1} at 1 C with obvious capacity fading over 50 cycles and shows inferior rate performance. This is due to the slow Li-ion transportation within large particles and low electronic conductivity. After infiltration,

Table 2

Capacity summary of LiFePO₄/C composites and pure LiFePO₄ used in this study.

Sample	Rate capacity (mA h g ⁻¹)								
	0.1 C	0.2 C	0.5 C	1 C	2 C	5 C	10 C	20 C	
LFP/C-1	68.1	59.9	53.8	50.3	43.9	33.5	23.1	_	
LFP/C-2	106.5	105.8	102.2	102.3	95.9	78.4	54.8	_	
LFP/C-3 ^a	144.6	139.3	134.3	128.4	118.2	99.3	83	60.4	
LFP/C-3 ^b	155.8	154.5	149.1	146.6	139.1	129.6	115.7	85.3	
Pure-LFP	70	58.7	46.8	39.1	31.2	-	-	_	

^a The discharge capacity of LFP/C-3 based on the weight of LiFePO₄/C.

^b The discharge capacity of LFP/C-3 based on the weight of LiFePO₄.

the electronic conductivity of LiFePO₄/C composites is measured, without any additive by a 4-point probes method, to be 2.3×10^{-5} S cm⁻¹ at room temperature. This value has been greatly enhanced by four orders of magnitude versus pure LiFePO₄ (10^{-9} S cm⁻¹). The intimate interaction between the nitrogendoped carbon C-3 and LiFePO₄ nanocrystallites ensures LiFePO₄ electrochemically active because the charge carriers can be effectively and rapidly conducted back and forth between the nanospheres and the current collector through the 3D continuous highly conducting carbon network.

To further understand the superior electrode performance of the composite, we carried out electrochemical cyclic voltammetry of LiFePO₄/C composite electrode. As seen in Fig. 6c, at a scanning rate of 0.2 mV s⁻¹, all samples display a couple of redox peaks between 3.2 and 3.66 V (vs. Li/Li⁺) in the cyclic voltammetry which should be attributed to the Fe²⁺/Fe³⁺ redox couple reaction, corresponding to lithium-ion extraction and insertion in LiFePO₄ crystal structure. In comparison, composite LFP/C-3 shows the best defined sharp redox peaks with reduced potential interval 0.24 V, which highlights the improved reversibility and reactivity of this composite.

The trend is confirmed with the AC impedance spectroscopy results, as shown in Fig. 6d. The diameter of the semicircle corresponds to the charge transfer resistance (Rct), which is related to the electrochemical reaction at the electrode—electrolyte interface and particle—particle contact [41]. A smallest diameter semicircle in composite LFP/C-3 reflects the lowest charge transfer impedance compared with pure-LFP, because the thin carbon walls around the spherical LiFePO₄ nanocrystallites can boost electron transfer and facilitate lithium-ion exchange across the interfaces. LiFePO₄ nanocrystallites are connected directly to the thin-wall carbon, forming a superior conducting network that allows efficient charge transport and enhancement of the electronic conductivity of the composite. By improving the carbon coating of the LiFePO₄ particles, the charge transfer resistance between them may improve [29]. However, with a reduction of the pore volume of the carbon



Fig. 7. Variations and fittings between Zre and reciprocal square root of the angular frequency at low frequency region of pure LiFePO4 and LiFePO4/C composites.

support and an increase in the carbon content, the semicircle in the LiFePO₄/C composites become larger, confirming that the thicker carbon walls in sample LFP/C-1 and LFP/C-2 may restrict the efficient Li ion transfer [42]. This result indicates that the optimal thickness of carbon walls is a significant factor, which determines the charge transfer impedance.

The inclined lines in the low frequency range in Fig. 6d are attributed to Warburg impedance, which is associated with lithiumion diffusion within the LiFePO₄ electrode. The electrodes store and release electrical energy by insertion and extraction of the lithium ions and electrons throughout the electrode material. Hence, rapid ionic diffusion for achieving high rate performance is essential. As can be seen in Fig. 7, lithium-ion diffusion coefficients of samples LFP/C-1, LFP/C-2, LFP/C-3 and pure-LFP were calculated to be 1.31 \times 10 $^{-14}$, 5.74 \times 10 $^{-14}$, 1.38 \times 10 $^{-13}$ and 1.56 \times 10 $^{-15}$ cm 2 s $^{-1}$ accordingly using Zre (see the Supporting information for the specific calculation), which shows a good correlation with the capacity results in Fig. 6b. Lithium-ion diffusion is kinetically hindered in the pure LiFePO₄ electrode, while drastically promoted in LiFePO₄/C samples. This is attributed to that the nanosized LiFePO₄ crystallites confined in the mesoporous carbon significantly shorten the diffusion path for electrons and ions. Among the LiFePO₄/C samples, LFP/C-3 shows the fastest lithium-ion diffusion, which means the thinner carbon walls around the LiFePO₄ nanocrystallites facilitate insertion and extraction of the lithium ions and contribute toward the enhanced kinetics. Combining the nanodimension of LiFePO₄ and the thin carbon walls, the lithium-ion diffusion coefficient in sample LFP/C-3 is drastically improved, which is comparable to the reported values $(1.6 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1} \text{ for doped LiFePO}_4 [43],$ 1.7×10^{-12} cm² s⁻¹ for carbon coated LiFePO₄ [44] and 6.3×10^{-13} cm² s⁻¹ for porous LiFePO₄ with carbon nanotube [15]). This result is consistent with the observed high Li-storage capacity and excellent rate performance.

For HEV or PHEV applications, we cycled LiFePO₄/C electrodes at 10 C (less than 3 min for discharging) and 20 C for 1000 cycles (as shown in Fig. 8a). Surprisingly, the LFP/C-3 cell can retain 96.7% of its initial capacity at a high rate of 10 C over 1000 cycles and the coulombic efficiency is higher than 99%. The average specific discharge capacity of LFP/C-3 in 1000 cycles at 10 C is 83 mA h g⁻¹ based on the whole composite containing both LiFePO₄ and carbon.

Converting to specific power, it delivers an ultrahigh specific power of 5114 W kg⁻¹ during 1000 cycles. Even at a high rate of 20 C, it also shows a discharge capacity of 60.4 mA h g⁻¹. Considering the outstanding rate and cycling performance, the coralloid LFP/C-3 composite is a promising cathode material for high power LIBs and other critical applications.

More interestingly, the specific capacity of LFP/C-3 based only on the weight of LiFePO₄ is 155.8 mA h g⁻¹ at 0.1 C, as shown in Fig. 8b. When the charge—discharge rate increased to 1, 5, 10 and 20 C, LFP/C-3 demonstrates a remarkable reversible capacity of



Fig. 8. (a) Cycling performance and coulombic efficiency of sample LFP/C-3 at 10 C and 20 C over 1000 cycles based on the weight of LiFePO₄/C; (b) cycling performance of sample LFP/C-3 at 10 C over 200 cycles. The inset shows its rate performance from 0.1 C to 20 C based on the weight of LiFePO₄.

146.6, 129.6, 115.7 and 85.3 mA h g⁻¹, respectively. For clarity, the results are listed in Table 2. Over 200 cycles, the discharge capacity is almost no fading at a high rate of 10 C. The superior electrochemical performance of our LiFePO₄/C composites is comparable or even better than those of previously reported LiFePO₄/C composites, such as LiFePO₄ nanoparticles embedded in nanoporous carbon matrix [22], porous monolithic LiFePO₄/C composite [45,46], LiFePO₄ nanospheres in tridimensional porous carbon framework [28], and carbon-coated LiFePO₄ nanoplate microspheres [47].

4. Conclusions

We have developed an effective method to synthesize high LiFePO₄ loading composite with superior cycling and rate performance for lithium-ion batteries by encapsulating LiFePO₄ nanocrystallites inside the coralloid, conductive and interconnected carbon structure. The intimate contact between the carbon framework and LiFePO₄ not only affords a highly conductive matrix but also has a nano-confinement effect during the calcination process. The nanosized LiFePO₄ spheres restrained in the mesoporous carbon support show reduced lithium-ion and electron transport diffusion resistance. The combination of uniform LiFePO₄ nanospheres with continuous nitrogen-doped thin-wall carbon offers an alternative way to achieve ideal electrochemical reaction kinetics with the improved electronic conductivity and facile lithium-ion diffusion. Therefore, this material is of interest as high performance cathode materials for energy storage and high power applications.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jpowsour.2012.12.036.

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